The Third European Conference on Wood Modification

The Angel Hotel, Cardiff, UK.

15-16th October 2007.

Edited by

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By The Editors

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ISBN 184-220-096-8

Foreword

Welcome to the Third European Conference on Wood Modification.

The proceedings of this conference show case a huge body of work representing the status of wood modification in 2007. Progress in this area has been rapid and we have witnessed many technologies being transferred from the laboratory to become a commercial success. The European Conference on Wood Modification is now firmly established as THE event in this important area. This is illustrated by the large number of abstracts submitted (totalling 95). Many people are presenting previously unreported data in this publication, showing the importance that is attached to this conference as a vehicle for knowledge dissemination.

I wish you a very enjoyable conference.

Prof. Callum Hill
Napier University

Preface

Two years after the Göttingen meeting we will come together now for the 3rd European Conference on Wood Modification ECWM in Cardiff!

Everything started some years ago with the European funded “Thematic Network on Wood Modification”, which was set up to bring together the varying expertises in this relatively new research area. A final conference of this EU project, the 1st ECWM, was very successfully organised in Ghent/ Belgium. Because of the growing interest in wood modification from researchers as well as from industry, the network continued to exist and the 2nd ECWM in Göttingen was jointly organised. More than 250 people from 35 countries attended the conference and after this success it was obvious, that the 2nd should not be the last ECWM!

Now we meet in Cardiff. More than 70 papers and posters will be presented, and again this conference covers a broad range of presentations from fundamental aspects to market related items.

After having attended the last two conferences I am looking forward to an interesting and successful conference. My special thanks to the organisers and the sponsors of this event!

Let’s continue networking!

Prof. Dr. Holger Militz
Georg-August University Göttingen

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Session 1: Commercial Aspects.

The Activities of Finnish ThermoWood Association to Commercialize ThermoWood®

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Keywords: Commercialization, thermally modified timber

ABSTRACT

The Finnish ThermoWood Association (FTWA) was established in 2000 to enhance the use of thermally modified timber. Thermal modification of timber means a method where the composition of the cell wall material and physical properties of wood are modified by exposure to temperatures higher than 160 °C. ThermoWood® is an EU registered trademark owned by the association. The members of the association are either thermally modified wood producers or kiln manufacturers.

Modification methods of wood have been developed at many research institutes for over 70 years. The aim of the research and development projects has been to improve properties of wood. Thermal modification of wood was scientifically studied in the 1930s in Germany and in the 1940s in the United States. More recently, research work has been carried out in the Netherlands, France and Finland in the 1990s.

One industrial scale thermal wood modification process, the ThermoWood® process, was developed in Finland. R&D work was simultaneously carried out at VTT (Technical Research Centre of Finland), YTI (the institute of Environmental Technology in Mikkeli) and Technical University of Tampere. Many research projects were carried out in intensive co-operation between research organizations, wood industry companies and kiln manufacturer companies.

In the early years of the Finnish ThermoWood Association some focused actions were launched to increase the credibility of ThermoWood® in the wood product market. The first activity was to collect all usable research information and report it. The ThermoWood® Handbook was published in 2003. The planing manual and surface coating manual were published after the handbook. The aim of the published manuals was to give information about the product and how it should be processed and coated.

Nowadays, the entirety of focused actions is called ThermoWood® Concept. It consists of many actions like patented process, registered trademark, quality control, life cycle assessment (LCA), certified raw material, standardisation and continuous R&D.

Creation and implementation of the ThermoWood® Concept is a good example of successful co-operation between different companies. Many activities were carried out in co-operation between ThermoWood® producers and kiln manufacturers. The activities are co-ordinated by the Finnish ThermoWood Association. The aim of the implemented concept is to enhance the use of thermally modified timber. The ThermoWood® Concept ensures that the product is a safe choice for authorities, customers and end users.

INTRODUCTION

Thermally modified timber is a relatively new product in the wood product market. New products always meet difficulties during launching. Customers do not have long term experience about the product and in the case of building material the authorities and building sector stipulate standards and certificates.

The purpose of the ThermoWood® Concept is to solve problems that thermally modified wood meets as a new product in the wood product market. The concept consists of following functions:

1. Patented wood modification process

The industry scale ThermoWood® process was developed and patented by VTT Technical Research Centre of Finland (www.vtt.fi). The patent is administrated by a company called Licentia Oy (www.licentia.fi) and it is valid in Belgium, Switzerland, Germany, Denmark, Spain, France, UK, Greece, Ireland, Italy, Holland, Portugal, Sweden, Japan and the USA. The license agreement for exploitation of the patent was signed by the Finnish ThermoWood Association and Licentia Oy.

The valid patents are: EP0695408, JP 3585492, US 5,678,324, CA 2,162,374

2. Registered trademark

ThermoWood® trademark is owned by the Finnish ThermoWood Association. The trademark is now registered in EU, Switzerland and Canada. An additional trademark registered in the EU is ThermoHout®. Only the member companies of the Finnish ThermoWood Association have legal right to use these registered trademarks.

The registered trademarks: ThermoWood® (EU trademark number 000922765), ThermoHout® (EU trademark number 004296331).

The trademark registration process is still unfinished in some countries.

3. Audited quality control system

The quality control of ThermoWood® production was developed in co-operation with Inspecta Oy [www.inspecta.fi]. Inspecta Oy is also the third party auditor of the quality control system and issues the right to use an SFS inspection mark (Fig. 1A). The SFS inspection mark will be replaced by the certification mark (Fig. 1B) at the latest on 31st October, 2008. All member companies that produce thermally modified timber participated in the preparation of quality control. The demands for the developed quality control system were that it has to be simple, reliable, suitable for all producers and usable at production plants.

The quality control of ThermoWood® production consists of the following parts:

1. Receiving and inspection of the quality of the raw material
2. Process parameters of thermal modification process
3. Quality control of wood after modification
4. Instruction for packing and warehousing

The list of ThermoWood® producers that have the right to use the SFS inspection mark / the certification mark can be found at:

[www.sfs-sertifiointi.fi/sfs/sertifikaattihaku/luettelot/rtraport/thermowood.html]

The members that have the right to use the SFS inspection mark / the certification mark with ThermoWood® product have also the right to use the quality stamp of the Finnish ThermoWood Association (Fig. 1C).

(A). SFS inspection mark. (B). Certification mark. (C). Quality stamp of the FTWA.

Figure 1: Inspection, certification and quality stamp marks

Some ThermoWood® producers have the right to use the KOMO certificate of the Dutch testing company SKH.

4. Life cycle assessment (LCA)

LCA of ThermoWood® was carried out by Imperial College London. The approach to LCA was ISO 14040 standards. The framework of the LCA consisted of four main phases: goal and scope definition, inventory analysis, impact assessment and interpretation of results.

The results of the LCA study prove that ThermoWood® has potential of being very ecological building material when considering the production as well as the use and disposal at the end of the life cycle of the material.

5. Certified raw material

The FFCS (Finnish Forest Certification System) was developed for Finnish circumstances and it demonstrates reliably how the Finnish certified forests are managed and used. The certification system includes all the essential components for forest certification: requirements for forest management and use and chain of custody verification as well as the qualification criteria for external auditing. The FFCS was accepted by PEFC (Programme for the Endorsement of Forest Certification schemes) forest certification system. The Finnish Forest Certification Council issues the PEFC logo use rights in Finland on the behalf of the PEFC Council. About 90% of sawn wood that is thermally modified in Finland comes from PEFC certified forests. Information about FFCS and PEFC forest certification systems can be found at:

[www.ffcs-finland.org] and [www.pefc.org]

6. Standardization

ThermoWood® product classification was completed in 2003 when standard treatment classes were introduced. The classes are called Thermo-S and Thermo-D. The classes are introduced in Tables 1 and 2.

Table 1: Treatment classes of pine and spruce

	Thermo-S	Thermo-D
Process parameters - temperature - duration of intensive heat treatment	190 ± 3 °C 2 – 3 h	212 ± 3 °C 2 – 3 h
Changes of properties - durability - dimensional stability - bending strength - colour darkness	+ + no change +	++ ++ - ++
End use recommendations	- building components - wall and ceiling panels in dry conditions - furniture - garden furniture - door and window components - sauna products - fascia boards - cladding - shutters	- cladding - fascia boards - exterior joinery - shutters - sound barriers - sauna and bathroom furnishing - decking - garden furniture - other exterior structures

Table 2: Treatment classes of birch and aspen

	Thermo-S	Thermo-D
Process parameters - temperature - duration of intensive heat treatment	185 ± 3 °C 2 – 3 h	200 ± 3 °C 2 – 3 h
Changes of properties - durability - dimensional stability - bending strength - colour darkness	no change + no change +	+ + - ++
End use recommendations	- wall and ceiling panels - furniture - garden furniture - sauna products - flooring	End uses of hardwood Thermo-D products are same as Thermo-S products. The colour is darker because of higher treatment temperature

Preparation of CEN standard for thermally modified timber is now in process. The CEN standardisation was launched by the Finnish Forest Industries Federation in 2004. The type of the standard will be technical specification and is now proceed to the formal vote stage. The name of the technical specification is "Thermal Modified timber – Definitions and characteristics".

7. Continuous research and development activities

Finnish ThermoWood Association annually allocates resources for topical R&D activities and cooperates with domestic and foreign research institutes (Figures 2 and 3).

Figure 2: Field test areas at VTT in Espoo, Finland

Figure 3: Field test area at BRE in Garston, UK

THERMOWOOD® TODAY

ThermoWood® output

The development of production volume of ThermoWood® is presented in Figure 4 and the share of wood species is presented in Figure 5. The share of the market areas is presented in Figure 6.

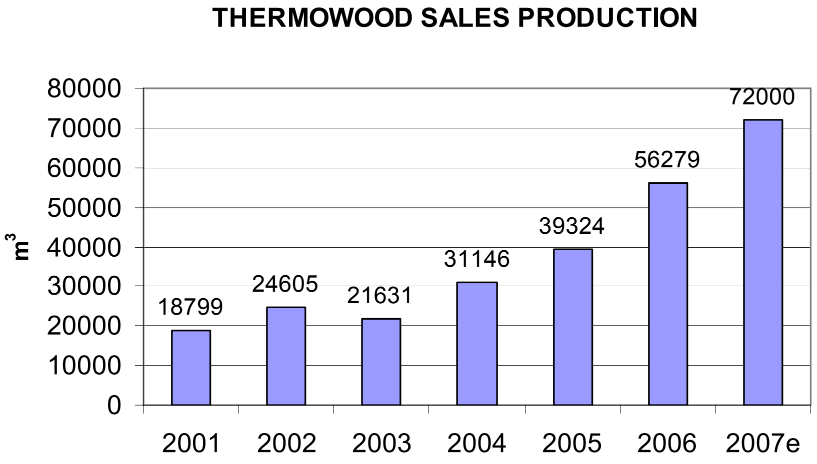

Figure 4: ThermoWood sales production in 2001 – 2006 and estimate for the year 2007

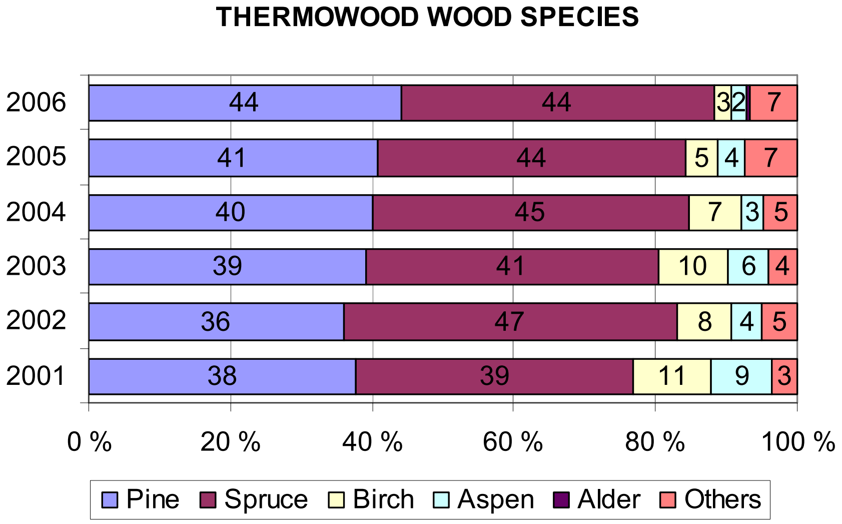

Figure 5: The share of ThermoWood wood species in 2001 – 2006

During the years 2001–2006 18 production kilns and 7 laboratory kilns were delivered to the customers by kiln manufacturer members of the FTWA. The production capacity of delivered production kilns is about 90000 m^3.

Finnish ThermoWood Association

Finnish ThermoWood Association has 13 members (Figure 7). Three of them are kiln manufacturers. The membership of the association is open for all companies that fulfil the conditions.

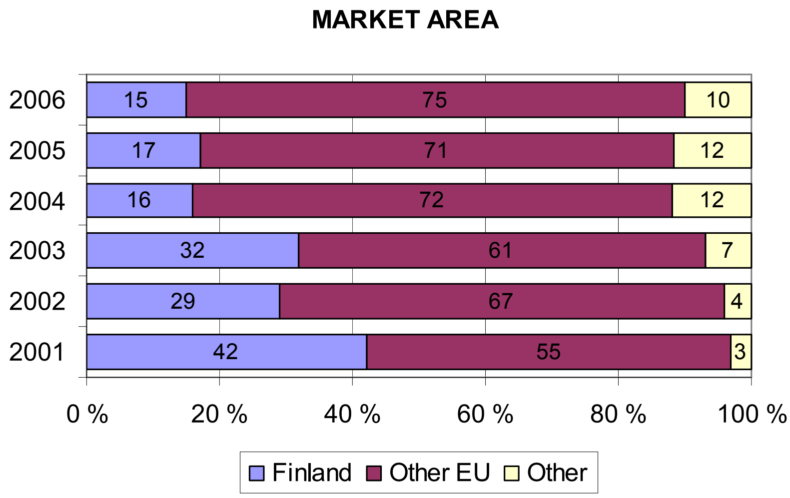

Figure 6: The share of ThermoWood market areas

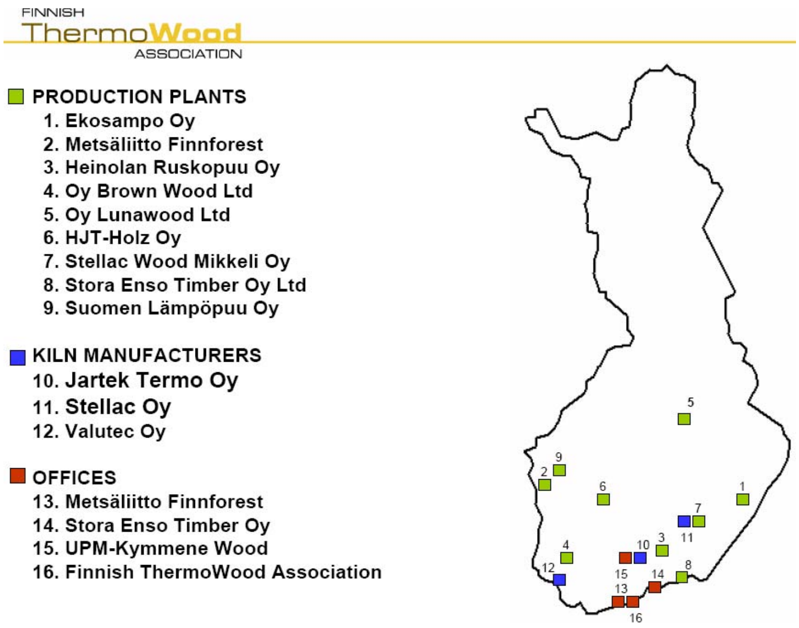

Figure 7: The location of the member companies of the Finnish ThermoWood Association

CONCLUSIONS

Development of The ThermoWood® Concept has been a part of the long term plan of the Finnish ThermoWood Association to enhance use of thermally modified timber. Now the concept creates the entirety that ensures the technical and ecological quality of products sold under the trademark ThermoWood®. All parts of the concept are essential.

The implementation of the concept has been successful. Nowadays ThermoWood® is an established product in the market and the concept ensures that the product is safe choice for customers and end users.

Commercial Development of VisorWood® and Kebony® Furfurylated Wood

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Keywords: Chemical modification, commercialisation, furfurylation, Kebony®, marketing

ABSTRACT

The principles of forming furan polymers from the condensation of furfuryl alcohol have been known for decades. However, only when M. Schneider and M. Westin discovered ways of controlling the polymerisation in dilute systems, using simple organic initiators and stabilisers, did the principle become attractive for modifying wood on a commercial scale.

This paper describes the commercialisation of VisorWood® and Kebony®. Factors like market structure, purchasing criteria, product development and availability in important market segments of durable wood, and the influence of these factors on the positioning of VisorWood® and Kebony® as viable substitute in these segments are discussed.

INTRODUCTION

The principles of forming furan polymers from the condensation of furfuryl alcohol have been known for decades. However, only when M. Schneider (Schneider 1995) and M. Westin (Westin *et al.* 1996) discovered ways of controlling the polymerisation in dilute systems, using simple organic initiators and stabilisers, did the principle become attractive for modifying wood on a commercial scale.

Kebony ASA, formerly Wood Polymer Technologies ASA, started commercial production of furfurylated wood at its Kebony Products DA subsidiary in 2003. The technology is based on inventions by Professor M. Schneider. Two product lines have been developed:

- VisorWood®, which is furfurylated Scots pine. VisorWood consists of both furfurylated sapwood and untreated heartwood, and is sawn and profiled prior to the furfurylation treatment. VisorWood is used for outdoor applications like cladding, decking and roof boards where durability is required.
- Kebony®, which is homogeneously treated sapwood of various pines or temperate hardwoods like beech or ash. Kebony® is marketed as an alternative to tropical hardwoods, and is well suited for floors, interior panels and other applications where an exclusive, tropical appearance, hardness and dimensional stability are important criteria.

Since the start of production in 2003, the demand for VisorWood® and Kebony® has overtaken the current production capacity, and a new state-of-the-art plant is under construction and will be operative by the summer of 2008. The plant will have an annual capacity of 20 000 cubic metres of furfurylated wood.

EXTERNAL MARKET FACTORS

Durable wood / preserved wood in Scandinavia

Market structure

As shown by statistics of the Nordic Wood Protection Council [http://www.ntr-nwpc.com], Sweden is the largest producer of impregnated products in Scandinavia with close to 1000 000m^3 impregnated in 2003. Nearly 50% of this was consumed in Sweden while the rest was exported. Finland and Norway were treating approximately 360 000 m^3 each, while Denmark treated 151 000 m^3 in 2003.

The building supply chains all over Scandinavia have experienced a high degree of consolidation. A clear trend is also the establishment of chains operating across country borders. This consolidation leads to greater purchasing power being placed with the chains – putting greater pressure on prices from the suppliers.

The chains are trying not only to operate in the Do-It-Yourself market – they also sign up frame agreements with construction companies as the “one stop shop” for all construction related supplies. Being able to supply a full range of products directly to the construction site gives the chains an edge compared to “single product” suppliers.

Purchasing criteria

The purchasing criteria for preserved wood will be different from a DIY customer and a construction company (professional customer). The private customer will primarily focus on price and secondly on availability as his purchasing criteria (Nyrud and Rødbotten 2005).

Professional customers are concerned with convenience, streamlined logistics and delivery times in addition to price.

In our home market we see a sharpened focus on maintenance requirements and upholding of buildings in all sectors – private, public and business housing. The extensive use of wood, especially in the private housing market, opens significant opportunities for well functioning wood protection methods. Yet another factor getting increased attention is *climate*. With more extreme and wetter weather there is a need for improved protection of wooden buildings.

Currently there is a trend among architects and in the public to use untreated, exposed wood with the brown - grey appearance coming with its ageing. VisorWood will develop this patina, and is therefore used in an increasing number of projects where such an appearance is wanted.

Furfurylated wood is free of biocides, and this factor is a strength that is important in several segments; especially in private housing projects and public projects; *e.g.* schools, nurseries *etc*.

Availability, quality and costs

Preservative treated wood has often been based on lower quality lumber. The wood that did not have sufficient quality to be sold was impregnated and thereby "upgraded" to a sellable product. Accordingly the price levels for impregnated lumber have also been low. Entering into this scene of competition is challenging, and demands the capability to command premiums based on other product attributes. Furthermore a price jump on pine lumber during 2007 has affected us as well as preservative impregnators.

Opportunities for VisorWood®

VisorWood's strong points are matching the current trends and criteria put down when wood is being considered for use in construction projects. Durability, low maintenance requirements, appearance and an environmentally sound concept – free of biocides - are all features that contribute to generating interest in the product.

Several external factors have also contributed to the opportunities for VisorWood®:

- A generally high building activity in our home market.
- A "fashion trend" towards the use of wood on facades - preferably wood that is not surface coated. The brown - grey appearance of VisorWood® resonates with this trend.
- Since 2002, CCA and Creosote impregnation is restricted to some professional segments. (Norwegian Pollution Control Authority, 2003).
- The need for low-maintenance products.
- Higher consciousness about environmental impact among purchasers.
- Increased awareness about "modified wood" in general. In some European countries the industry of wood modification is gaining momentum. Alternative modification principles are tested and production facilities are established. This start of wood modification as a new industry is helping the promotion of VisorWood®.

Tropical hardwood in Europe

Market structure

European countries have a tradition for using tropical timber with a natural durability. Some countries have even tightened their requirements on durability of wood for various construction purposes (De Lange and Janssen 2005). Other reasons for using tropical timber is appearance, hardness and the image of exclusivity.

Tropical sawn wood consumption in Europe goes to furniture, flooring, windows and doors (both external and internal) staircases and other items of joinery, garden furniture and decking, marine and sea applications and transport, according to FAO (FAO 2001). Table 1 below shows figures from the main consuming countries, from the same FAO reference.

Total tropical hardwood consumption in these countries was 2.3 million m^3 in 2001, whereas total hardwood consumption (tropical + temperate) was almost 12 million

m^3. The main segments are joinery and furniture (48 and 43 % respectively), with flooring at only 3%.

Table 1: Consumption of tropical hardwood in selected European countries (FAO 2001)

Country	**Consumption** Thousand m^3
Belgium	141
France	467
Germany	200
Italy	265
Netherlands	380
Portugal	127
Spain	442
UK	282
Sum	**2304**

From the point of view of users, the availability and price of tropical hardwood are developing negatively, forcing users to look for new sources and species. Due to constraints in the access to tropical hardwood logs, and environmental concerns, combined with reductions in the European furniture manufacturing, the capacity for processing tropical hardwood has actually declined lately in Europe (Oliver *et al.* 2005).

Purchasing criteria

The main criteria when purchasing tropical hardwood on the importer level is quality, availability, delivery time and price. Sustainability is also gaining importance, although the majority of wood imported to Europe still lacks certification, and a large portion may actually be deemed illegal as indicated by GlobalTimber.org.uk. In a survey of environmental criteria perfromed in 1999 (Pajari *et al.* 1999), consumers rated environmental friendliness as a less important criterion than product quality, durability, style, materials used and price in making purchasing decisions for furniture, windows, doors and flooring. On the other hand, de Lange and Janssen's report and others (Oliver *et al.* 2005; [www.GlobalTimber.org.uk]) show that the pressure to ensure sustainability and certification in the trade of tropical timber is increasing in European countries.

Opportunities for Kebony

The deteriorating availability, increasing prices and increasing environmental concern about logging of tropical forests will create opportunities for Kebony® as a viable substitute. The wooden floor industry represents roughly 5% of the European flooring products market, with a volume consumed in 2005 of almost 100 million square metres (FEP, 2005). 55% of this volume was oak, while 16.6% was tropical wood. Replacing only a modest portion of the tropical wood in this market will still represent significant volumes - creating an attractive market opportunity. The joinery and furniture industries are large sectors that will offer opportunities. However, in these sectors the customer (*e.g.* window or door manufacturers) is normally very price sensitive, and a wood supplier easily ends up in the "commodity squeeze", where price becomes the dominant competitive factor. To avoid this, entry at the right level in the value chain is crucial, and the products should be developed and documented to a higher level than sawn lumber.

PRODUCT POSITIONING OF KEBONY AND VISORWOOD

Target segments

Two main segments are targeted:

I. Outdoor applications where durability, appearance and freedom from maintenance are the key features. Products for this sector are decking, claddings, roof boards, piers, jetties *etc*. Materials for external joinery, window frames and doors are also products in this sector.
II. Indoor applications where hardness, dimensional stability and "tropical look" are the main features. Products are floorboards, parquet surface boards, indoor panels, furniture materials *etc*.

These sectors are, as described above, quite different in terms of structure and purchasing criteria. Below is a short description of the marketing approach used in these target segments. The 4 P's approach to marketing - Product, Promotion, Price and Place - is classic textbook marketing theory (McCarthy 1996), and is useful in describing the various aspects of the marketing mix:

The Product - Key product properties

The key product properties that are enhanced by the furfurylation of wood are durability, hardness, equilibrium moisture content - which is considerably lower than for the parent un-treated wood - and dimensional stability. More details on the properties of furfurylated wood are described elsewhere (Lande *et al.* 2004).

The magnitude of each of the enhanced properties depends on the treatment level - most often expressed as the Weight Percent Gain of the wood.

In addition to the tangible product properties, the documentation surrounding the products is important. Thus emphasis is put on obtaining technical approvals, environmental declarations and eco-labels in segments of priority. However, these processes take time and effort.

Currently the Swan Nordic eco-label is obtained, while other technical and environmental approvals are pursued.

Promotion - Communication Strategy

There is no use in having premium products if the potential customer is unaware of their existence. So a critical task is to install the right impression of VisorWood® and Kebony® in the mind of the potential customer. This is the essence of branding and product positioning, - and *communication* is the tool.

The selected strategy has been direct communication with architects and builders about the factual properties of the wood products Kebony® and VisorWood®, *i.e.*

working with the specifying party in building projects. Getting hold of the right projects where the product is positively exposed is crucial. This means that a lot of effort is invested in promoting the product towards architects – a time-consuming exercise with long lead-time. After the start-up of production and marketing in 2003, Kebony ASA are now beginning to harvest what was earlier sown.

Another vital aspect of communication in a development phase is keeping it two-ways. By interacting closely with the users of the products, a lot of learning and improvements may be ploughed back into improving the products and the company's own competence.

This strategy has yielded tangible results on two important counts:

- Awareness of potential strengths that could be exploited in yet more sectors;
- Awareness and correction or improvement of weaknesses that potentially could harm the marketing and the development of the business.

As new production capacity is put into place, a broader communication to the market will be implemented.

Price - capturing cost and value

By nature all modified wood will be more expensive than the parent untreated wood. For the customer, the value of the modified wood should be sufficiently high to at least justify the increased cost. The challenge is then to position the products so a relatively high price can be realised.

This can be done in several ways, but in any case careful considerations of the value chain, and service life or life cycle are crucial. Cost consciousness on all levels of the chain, and a critical look at all its links may significantly save costs at the end user level.

At the upstream end of the value chain, the relations with raw material suppliers cannot be over-rated. The right raw material supplier will ensure quality, regularity and predictability in pricing.

Another strategy for a wood modification company may be further upstream integration; *i.e.* taking some level of control through a partnership or direct investment in saw mills. Bringing more of the raw material processing in-house may also alleviate raw material costs, for example by sawing and splitting of lumber into required dimensions.

In a service life perspective the competitiveness of our "VisorWood® System" - VisorWood® cladding with industrially applied topcoat paint from Jotun - is comparable in cost with primed, painted and maintained similar spruce cladding over a 15 year period.

For modified wood to be competitive with tropical hardwoods, it is imperative that the market is entered at the right point down-stream in the value chain. Thus we have been reluctant to marketing un-machined Kebony® to wood merchants. This strategy may easily lead to a commodity view of Kebony®, and end up in a sharp price competition. Instead we have focused further down the value chain, by offering finished floor products to builders. These finished floorboards of various Kebony® qualities are highly price competitive.

Place – getting the channels right

The last P is "place" – the management of channels for distributing your product. In the first years of Kebony®'s existence all sales went directly from our factory to the builder, mainly professional builders. We have been careful in entering agreements with large distributor or retail chains, as they will confiscate a major portion of margins otherwise going back to Kebony®. However, there are tradeoffs on both directions – managing all distribution yourself – thus accepting the extra workload, or handing it over to a chain – thus sacrificing some of your margins but saving work in distribution management and marketing. Kebony ASA has now come to the point where we are entering into agreements with selected chains.

It is absolutely vital in the product positioning though, that the chain takes care of your product in a manner that is consistent with, and supports, the profile of the brand.

ACHIEVEMENTS AND AMBITIONS

There has been a strong development in demand for VisorWood® and Kebony®, and currently our production capacity is the bottleneck against achieving higher sales.

Since the start of commercial production, considerable work has been done on process development and optimisation, as well as planning and design of new production capacity.

Technology management, involving IPR issues and the proper management of all aspects of production and product know-how has also been an important priority in the development of the business.

In order to boost volumes of both VisorWood® and Kebony®, a new production plant will replace the current production capacity in 2008. This will increase capacity from 3500 cubic metres to 20 000 cubic metres per year in the first phase. The new plant will produce both Kebony® and VisorWood®, with increasing emphasis on the Kebony® range. In order to maximise the profitability of this investment, the plant will also contain with equipment for machining produced material to finished floorboards, panel boards *etc*.

In conclusion, the first years of commercial operation have produced convincing evidence that there are market opportunities for furfurylated wood products.

The properties of the products - as well as external market trends - will ensure a promising future for this line of modified wood.

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The Commercialisation of Wood Acetylation Technology on a Large Scale

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Keywords: Acetylation, product launch, Accoya™

ABSTRACT

For the first time in the world a commercial plant has started to produce acetylated wood on a large scale. This paper explains the experience in marketing acetylated wood. Extensive preparation work is required before the first batches of acetylated wood are sold, This includes testing with the industry and in combination with related products such as coatings, glues and other materials to secure widespread acceptance. Wider availability and production of products by industry follows this pre-commercial development. Guidance and secure procedures are equally important in this second phase. At the same time the marketing and the sales to direct and indirect customers must be organised.

INTRODUCTION

Since 2003 Titan Wood has been working on the commercialisation of acetylated wood. In this period the production processes have been optimised and fine-tuned and the large production operation has been designed and built. A broad market development plan was required for this new product and this marketing plan has run in parallel with the construction programme for the past 3 years. The key words in the preparation of the introduction are differentiation, focus, and control.

The differentiation is needed to distinguish the product quality from the bulk of other products on the same market.

The focus is needed to orientate on the important, mainly technical, issues. First identify all important issues and make certain they all are looked after in the right context. The control is to make certain that there is maximum control on the introduction.

EXPERIMENTAL

In order to introduce a new product into the market it is important to make the new product recognizable, *i.e.* to make it possible to differentiate the new product from other products in the same market. The expressions ‘acetylated wood’ or ‘modified wood’ are not enough to be recognized as something new. Therefore Titan Wood has given the acetylated wood the name of a new ‘wood species’: **Accoya™**. Now the name Accoya™ is created, it is important to create value for the name. A very strong value specific for Accoya™ is the reliability, linked to the high durability, high dimensional stability and high UV resistance. Also a very strong benefit is the possibility to analyse the acetyl percentage formed during the acetylation process.

Measurement of this property for every batch against a strict quality threshold makes the product very reliable.

The method of correctly analysing the acetyl percentage and the correlation between acetyl percentage and quality performances has been developed by Titan Wood to a very precise method. This development is specific for Accoya™ and provides great assurance to Accoya™ customers. A very precise specification for the end product is made. If this specification is achieved, the product is allowed to be named 'Accoya™'. To identify the required acetyl percentage, around 1800 samples have been tested with 5 different types of fungi. The 1800 samples where produced with very low acetyl percentages to very high acetyl percentages. After the test the precise acetyl percentage was identified to reach durability class one on the most aggressive fungi. Knowing the acetyl percentage on which durability class 1 is achieved, Titan Wood is able, together with its developed analysis program, to give solid statements about the quality of the product.

For the dimensional stability hysteresis curves have been made by analysing the moisture content at different relative humidities. Also the swelling and shrinking of Accoya™ has been tested in these different relative humidity conditions. The graphs coming from these results are very clear to express the quality of the Accoya™ in terms of dimensional stability.

Titan Wood has chosen a very close co-operation with the wood industry for the introduction of Accoya™ into the market. Before the commercial introduction Titan Wood has been testing with industry to identify optimal process parameters for Accoya™ in the production processes of, for example, doors and windows, cladding, decking, *etc*.

At the same time, and parallel to the testing with the wood industry, testing with wood related industries was started. Among the most important are the coating and adhesive industries. Together with these and the wood wood-related industries the Accoya™ product has been researched in depth.

The performance of Accoya™ is superior in several ways compared to normal wood. With changing the characteristics, it is sometimes needed to adjust process parameters to optimize results. For the gluing, for example, the process parameters have to be set a little different with water based glue systems as the water uptake is different compared to normal softwood.

As the swelling and shrinking has been reduced enormously, the stresses on the glue line have been reduced significantly which results in good adhesion after accelerated weathering tests. This is just one example of pre-testing before Accoya™ was commercially introduced onto the market.

The testing with different industries has been co-ordinated by Titan Wood and the results have been reported and shared within the group of industrial partners. This widespread assessment of the product in both laboratories and commercial production factories created a broad level of confidence in the product across the industry even prior to its launch.

When the coating industry was convinced of the quality of Accoya™ they have been asked what the possibilities are to extent the coating maintenance cycles on Accoya™ products. Together with a few end-customers, such as housing corporations, a program has been developed where the coating maintenance cycles could be reduced significantly because of the extraordinary dimensional stability of Accoya™ in changing humidity climates.

Before the commercial launch a 'technical committee' has been formed by Titan Wood containing experts from different disciplines in the industry to guide and advise during the introduction. This committee consisted of experts from the wood industry, testing institutes and experts who are involved in inspecting and maintaining wood products in buildings during its lifetime. Before the realisation of the first projects, the critical processes during production of the products, but also during installation of windows, doors and cladding where identified by the different committee members. These processes have been followed precisely during production and installation to reduce risks, including risks not due to the Accoya™ product.

RESULTS AND DISCUSSION

There is considerable risk when introducing any new product, or technology, to the market. Titan Wood has sought to minimise this risk by spending several years with a small group of customers, with whom we have carefully tested and evaluated as many elements affecting the product as were commercially possible to check.

We are, of course, hugely assisted by all the research done on laboratory scale since the 1920's, which when combined with intensive process controls designed to replicate the very best results achieved during acetylation's long history. The Accoya product has been tested over-and-again, first internally and then with industry partners, very much in their real production environments. All of this was carried out before releasing commercial quantities of material, giving our initial group of customers great confidence in the product, such that they are its best ambassadors and referees.

CONCLUSIONS

The basis of quality wood products for external use is the wood itself. The industry partners who have worked with Accoya are convinced about the extraordinary performance and realise the opportunities it creates to differentiate the final product from the 'regular' wood products.

Titan Wood has developed a strong brand to differentiate the product from the bulk of similar products

Because the market introduction has been prepared by a small group of industries the marketing of the Accoya product has been done as a team.

The differentiation is very important and has required co-operation from our customers in industry.

An Accoya™ information guide has been prepared to inform the industry with comprehensive information on the full range of Accoya™ performance and industrial use. This guide covers subjects ranging from storing Accoya in the warehouse up to maintaining the final product and all the steps of production in between.

Accoya has been very well accepted in the market so far, and it was this attention to the quality of the product and the communication with end-customers that has made the launch of this new product a success.

Additional information about Accoya can be found at: [www.Accoya.info] and [www.Titanwood.com]

The Indurite™ Process – a Review from Concept to Business

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Keywords: Enterprise, Indurite™ Process, maltodextrin-melamine co-polymer

ABSTRACT

It is twenty-two years since the Indurite™ Process was initiated in the author's laboratory at the (then) Forest Research Institute (FRI) in Rotorua, New Zealand, as a wood modification project to be applied to plantation-grown radiata pine wood. In 1985, the FRI was approached by the New Zealand Furniture Manufacturer's Federation to seek a solution to the poor appearance performance of radiata pine wood when used for furniture components. During the period 1985 to 1987, every wood modification technology known at the time was applied to radiata pine wood in order to benchmark properties and performance of the modified wood materials. Evaluation of the various processes and the properties of the modified wood materials produced led eventually to the decision to discard all of them as impractical for the New Zealand industry for reasons of cost and risks concerned with monomer chemicals handling and use. There was also a general lack of acceptability of the modified wood materials by users due to colour changes limiting versatility and difficulty in classical wood-working procedures. A new chemistry strategy for wood modification was devised by the author in 1988, in which raw materials were to be biologically-based (biomaterials), and preferably sourced from within NZ. Wood modification formulations were to be restricted to aqueous-based ones, thereby matching the experience and competencies of the New Zealand wood processing sector in handling such chemicals. The outcome of the strategy was a wood modification formulation in which commodity maltodextrins (from hydrolysis of starch, to mimic wood hemicelluloses), commodity melamine resins (aromatic rings with side-chains containing β-ethers, to mimic wood lignin) were combined with commodity radiata pine wood to "pour wood into wood", creating the Indurite™ Process to produce a specialty modified wood product which met the furniture manufacturers' performance expectations. This review will present the science, innovation and entrepreneurship process in developing the Indurite™ wood modification technology from concept to new venture enterprise.

INTRODUCTION

By 1975, much of the timber use in New Zealand had switched from declining endemic species such as rimu (*Dacrydium cumpressinum*) to plantation-grown radiata pine, a pine species introduced from California. This exotic timber tree had been demonstrated to be able to be grown in New Zealand on a sustainable, twenty to forty year crop rotation basis (Kirkland and Berg 1997). Usage of plantation-grown radiata pine wood expanded from traditional applications such as for construction (building framing timber), packaging (boxes and pallets) and pulp and paper to value-added products such as furniture and tongue-and-groove floors. Once in general use, opinions of radiata pine timber began to be expressed regarding the lack of quality and suitability for performance applications, such as furniture (Hitchings 1984).

While there was market perception that radiata pine wood generally had a poor quality image, individual users appeared to be satisfied with it except for two attributes: the large, open grain resulting from fast tree growth, and the rather soft and easily dented or marked surface (Doyle and Walker 1985), both appearance features which were readily apparent to customers.

For furniture makers using radiata pine wood, this raised a problem not only with customer dissatisfaction when the product was in use, but also when furniture items were being delivered, resulting in numerous returns to the factory for repairs to dents and scratches or replacements. Among the approximately four hundred furniture manufacturing companies in New Zealand during the period from the mid 1970's to mid 1980's, many were still using rimu timber (Hitchings 1984), but aware that the resource was becoming scarce and destined to be placed under conservation control.

At a meeting of scientists at the Forest Research Institute, Rotorua, in June 1985, the then president of the New Zealand Furniture Manufacturer's Association expressed these difficulties the furniture manufacturing sector was experiencing in maintaining a good quality finish (and image) for pine furniture from factory to customer. The outcome of that meeting was a simple science and technology brief for a project:

"Make radiata pine wood perform like Formica® on MDF."

This brief was the catalyst for what became known as "the FRI radiata pine wood hardening project" which ran from 1985 to 1998. Timber with density in the vicinity of 600-700 kg/m^3 was considered appropriate for the New Zealand furniture making industries (Doyle and Walker 1985). As there was a demonstrated relationship between wood material density and hardness (Kollman 1968), modified wood material density measurement could be used as a guide for achievement of surface hardness of modified wood material using a range of alternative chemical systems.

Prior to the science from which evolved the Indurite™ Process, radiata pine wood material was modified using a range of experimental techniques. There have been numerous experimental approaches towards wood modification and production of wood-polymer composites described, and a number of these were used in experimental work using radiata pine sapwood as the substrate. Many wood modification approaches were used in order to create a benchmark dataset of processes and modified wood properties, and also to grow the competency of the neophyte chemists and engineers involved with wood hardening and wood modification science and technology. Many of the wood modification methods employed and modified wood material properties have been extensively reviewed (Banks and Gibson 1988, Meyer 1981, Rowell 1983, Schneider 1994, Schneider and Witt 2004). The following wood modification procedures were applied to radiata pine sapwood:

1. Acetylation, and also a number of alternative acid anhydrides were investigated (Dawson *et al.* 1999). Chloroacetic anhydride was also used with scanning electron microscopy and energy dispersive spectroscopy detection in order to locate regions of cell wall acylation when employing various reaction conditions.

2. Vinyl monomers (styrene, methylstyrene, methyl methacrylate, diallyl phthalate, acrylonitrile, acrylamide and N-methylolacrylamide) were used for wood hardening (Beall and Witt 1972, Smith and Sutton 1971), using radical initiator chemicals, such as benzoyl peroxide, azoisobutyronitrile, and hydrogen peroxide, alone and with redox systems, *e.g*. using ascorbic acid.

3. Phenol-formaldehyde resins for the Impreg process (Stamm and Seborg 1955) and furfuryl alcohol (Nguyen and Zavarin 1986) wood modification technologies utilising condensation polymerisation and grafting chemistry.

4. Modified using silica chemistry; using sodium silicate wood treatment followed by carbon dioxide gasification to precipitate silica in lumens and cell walls, using tetraethylsilicate treatment, followed by aqueous ammonia-catalysed hydrolysis, and direct impregnation of wood using colloidal silica with particle sizes less than 7 nm.

5. Modification was attempted using condensation polymerisation of diamines and anhydrides to form polyimides within wood cells, since these polymers had excellent engineering and thermal properties.

6. Wood modifications utilising natural products such as casein and its various acid and enzyme hydrolysates, gelatine and soybean protein hydrolysates were carried out, followed by formalin and glyoxal treatment to condense the proteins into cross-linked polymers.

EXPERIMENTAL

Wood modification using carbohydrate oligomers and cross-linking condensation polymerisation chemistry (Indurite™ Process).

1. Indurite™ formulation preparation. For laboratory-scale research work, enzyme-modified starch (maltodextrin) having a DE value 15 was dissolved in water which had been pre-heated to 50 °C. The solution was agitated using an efficient stirrer while hexamethylmethylolmelamine dissolved in ethanol was added. To the milky dispersion was added an arylsulphonic acid catalyst, biocide (*e.g*., boric acid) and the mixture heated and stirred at 50 °C for periods of 30-60 minutes until the solution became clear, and the solution viscosity had not exceeded 60 cps. The solution was then rapidly cooled to 20 °C by the addition of ice, followed by water (if required) to bring the solids content of the formulation to 37% w/v. The solution was stabilised against spontaneous condensation polymerisation by raising the pH to 8 by the addition of ammonia solution (sp. gr. 0.88). The solid polymer formed from the solution by heating and drying contained 83% carbohydrate and 15% melamine moieties, the balance being preservative chemicals and other proprietary additives. The formulation and the maltodextrin-melamine co-polymer generated were characterised using infrared, ^{1}H and ^{13}C NMR spectroscopies and pyrolysis GCMS.

2. Wood modification. Radiata pine sapwood which had been dried to 12% moisture content was weighed and the wood specimen dimensions recorded. The wood material was placed in a pressure vessel, and secured in place to prevent floating in the Indurite™ formulation. The treatment vessel pressure was lowered to -85 kPa for 10 min, followed by introduction of the Indurite™ formulation kept at ambient

temperature (20 °C) to bring the pressure to atmospheric. The pressure was then increased to 1400 kPa and held for 1 h. At the end of this period, the pressure was released, any un-absorbed formulation recovered, and the treated wood was removed and placed in an oven and heated at 70 °C until constant weight. The Indurite™-modified wood was then cooled, weighed and dimensions determined for calculation of material density.

RESULTS AND DISCUSSION

The learning from the benchmarking stage of the wood hardening project, described in the Introduction above, and understanding the competencies and capabilities of the New Zealand wood processing sector to adopt a wood modification technology, led to a new chemical strategy devised through application of simple constraint theory (Sullivan 2003). Rather than simply focusing on the chemical science as the main driver towards a wood modification technology discovery and development, understanding the opportunities and the constraints which would allow any of the chemical wood modification options which had been explored experimentally to be successfully commercialised became equally important. For these and other reasons (*e.g.*, unacceptable colour of modified wood using furfuryl alcohol polymerisation), most of the known wood modification processes described in the literature and which had been practiced using radiata pine as the substrate were rejected as commercially unworkable in the New Zealand wood processing sector context and not meeting customers' performance expectations. For a wood densification / modification system to be most readily commercialised, it also needed to fit into the existing New Zealand wood processing infrastructure and use existing plant and equipment such as conventional pressure vessels and drying kilns.

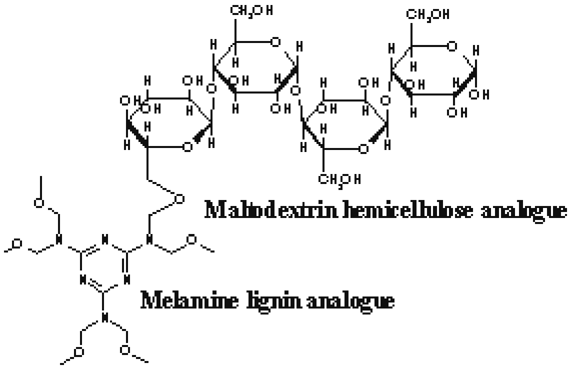

Figure 1: Maltodextrin C6 β-ether of hexamethylmethylolmelamine

In understanding woody cell wall structure and chemistry of plant carbohydrates *e.g.*, starch, cellulose, hemicelluloses (Colvin 1981, Rowell 1984), and lignin-carbohydrate complexes (Koshijima and Watanabe 2003) and their role in imparting the compressive strength to wood cellulose microfibril and lignin-hemicellulose matrix , a creative link was made between acquired wood cell wall chemical knowledge, starch chemistry and the learning from the benchmarking stage of the wood hardening project. The concept generated was to combine maltodextrin (as a chemical analogue for the cell wall hemicellulose component) and methylolmelamine ethers (as a chemical analogue for the lignin cell wall component, *i.e.*, an aromatic ring with side-chain carrying a β-ether) through a condensation polymerisation reaction to create an artificial lignin-hemicellulose composite, in other words, a synthetic wood component material (Figure 1).

This polymer chemistry, produced *in situ* within cell walls and lumens, had potential to augment the natural wood compressive strength and enhance the surface hardness of the composite material. This idea was the genesis of the concept of wood chemical modification by "pouring wood into wood" from which emerged the commercial Indurite™ process for wood hardening.

By combining plantation-grown pine wood, maltodextrin and melamine resin commodities, application of simple water-based formulation chemistry, conventional full-cell wood treatment processing and conventional kiln-drying, "pouring-wood-into-wood" became commercially feasible to manufacture a specialty, modified wood product with density in the range 650-700 kg/m^3, and which had wood-working attributes familiar to re-manufacturing practice. The wood material performance closely approached the furniture manufacturers' original brief. Patents were granted for the process (*e.g.*, US Patent 5,770,319), and the Indurite™ technology promoted to attract commercialisation partners. The Indurite™ process IP rights were assigned in 1994 to a paper company, Wood Hardening Technologies Limited (WHTL), which had a wood preservation chemical supply and wood treatment technology business (Chemicca Limited, Auckland), a wood material supplier and user business (Tasman Forestry Limited, Auckland) and the (then) Forest Research Institute as the science and technology provider as equally-contributing shareholders.

In the event, the initial alliance between the shareholders failed in 1996, through dis-interest from one of the parties and a corporate failure of another, resulting in the Forest Research Institute becoming sole shareholder of WHTL. In a second commercialisation attempt, WHTL granted manufacturing rights in New Zealand to a private equity consortium headed by an entrepreneur who had experience in the construction industry. The outcome of this was the formation in 1996 of Evergreen Industrees Limited (EIL), which built a greenfields factory in Tauranga, NZ. In 2001, after the exit of the founding entrepreneur, EIL changed its name to Pacific Hardwood Limited and Carter Holt Harvey Limited, a major NZ forest owner and wood processing business, assumed a major shareholding and management of the fledgling business.

By 2001, the Forest Research Institute put WHTL on the market, which was acquired by a UK business, Innovative Global Technology Limited (IGT). This in turn sold its shares in the Indurite™ Process business to a new company, Indurite plc. Through this process, the Forest Research Institute divested its shareholding of WHTL and all interest in the Indurite™ Process, with the outcome that the New Zealand manufacturer, PHL, of Indurite™ Process modified radiata pine wood became a licensee to Indurite plc in the UK. Indurite plc in 2004 established a license agreement with Osmose UK to manufacture and sell the Indurite™ formulation.

Concurrently with the above business ownership changes in the UK, Carter Holt Harvey sold its shares in PHL in NZ through a management buyout, resulting in a final business name change from PHL to Fibre7, which has since developed and patented its own wood modification technology, Lignia. The Indurite™ Process is now resident in the UK with Indurite plc and its licensee Osmose UK.

Commercialisation of the Indurite™ technology was not a financial success for the Rotorua Forest Research Institute. There were, though, a number of non-financial benefits arising from the Institute's involvement with the wood modification chemical science, technology innovation and working with the entrepreneurs and businesses involved with the technology commercialisation. There was also the experience gained in running a joint-venture company (the first formed by any Crown Research Institute in New Zealand) and the association with a high-profile development which raised the image of the Forest Research Institute politically, with industry, the general public and internationally. The learning acquired by exposure to the management and decision-making process of the industry partners and acceptance from the partners of the Forest Research Institute competence in the area of technological development, patenting, licensing and commercialisation also lifted staff experience and assurance to continue to deliver leading wood chemistry science and technology into industry.

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Session 2: Chemical Modification.

The Decay Resistance of Anhydride Modified Wood

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Keywords: Acetylation, decay, decay protection threshold

ABSTRACT

Acetylation of wood is now a commercial reality. Acetylation is well known as a means of imparting decay resistance to wood, yet the reason why this happens is not well understood. The decay resistance of acetylated wood has invariably been tested using methods developed for preservative treated wood. There is an urgent need for debate as to the appropriateness of these test methods. This debate must be supported by high quality scientific studies. Although there is considerable potential for variation in results, there is remarkably good agreement when decay protection thresholds are reported in the literature. However, whilst the commercialisation of wood modification technologies has advanced rapidly there is, as yet, no agreed standards by which these modified woods can be evaluated. This paper discusses some of the issues that should be considered when these standards are prepared.

INTRODUCTION

Previous reports to this conference have been concerned with attempting to evaluate the mechanism(s) by which anhydride modification imparts decay resistance to wood (Hill *et al*. 2003, Hill *et al*. 2005a). The decay resistance of acetylated wood has been the subject of a large number of studies in the past 60 years (Hill 2006). Such tests invariably use, or a based upon standards which have been devised to test the efficacy of wood preservatives and may not therefore be appropriate to determining the performance in service of acetylated wood. A common format for laboratory-based studies is to acetylate wood to different weight percentage gains (WPG) and expose the modified wood to a test fungus (pure culture) or in soil burial tests. At the end of the allotted test period the mass loss due to decay is determined and this is plotted against WPG, as shown diagrammatically in Figure 1. The idealised plot such as that illustrated would commonly be observed if the modified wood was exposed to a brown rot fungus (such as *Coniophora puteana*). The dotted line represents that maximum mass loss possible with the remainder being lignin. At some WPG level, zero mass loss is recorded and this is reported as a 'decay protection threshold' or similar.

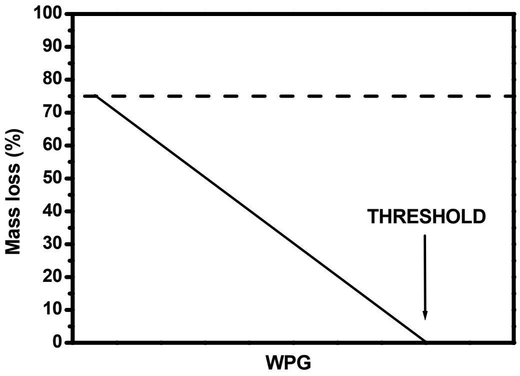

Figure 1: Common format for reporting the decay resistance of acetylated wood

Despite the inherent variability in such tests, the variety of wood species tested, the different fungi and fungal strains, test protocols, *etc.*; a remarkably consistent picture emerges, that with exposure to brown rot fungi there is very little evidence of decay when the WPG reaches 20%. With white rot, a much more complex picture emerges, but this paper will concentrate on brown rot testing. The 'decay protection threshold' value of 20% WPG is commonly viewed as being the value required to prevent decay. However, it is wise to investigate these tests further when consideration is made as to their appropriateness as standards for acetylated wood. One question to be asked is how static is the 20% WPG threshold? Since these tests are for a fixed period in time, they may just represent a 'snapshot' of the true behaviour which may be more like that illustrated in Figure 2.

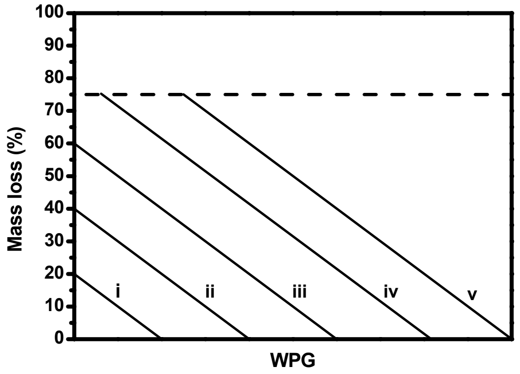

Figure 2: Does the threshold represent a snapshot of the behaviour shown above?

Here, the exposure time in the decay experiment is increased in the order i to v.

Another important point to address is the method of determining mass loss. When wood is acetylated it is increased in weight due to the presence of acetyl. To what extent (if any) is the mass loss data distorted because it is reported on the basis of the wood mass plus the mass of bonded acetyl, whereas control samples are obviously based upon cell wall mass loss only?

Other factors affect the results. The importance of virulence was discussed by Joris Van Acker in the round robin test conducted as an activity within the Thematic Network on Wood Modification (Van Acker 2003). The fungal strain may also affect results, but there has been little reporting of this in the literature (Hill *et al.* 2006).

The decay protection mechanism is not known. A body of results has shown that this can be attributed to the reduction in cell wall moisture content below a threshold value due to space occupied in the cell wall by bonded acetyl. However, there exist results showing that this may not be a generic mechanism. Much work remains to be done here.

The purpose of this paper is to re-examine the data presented in previous papers and suggest some possible ways forward in researching this subject area.

EXPERIMENTAL

All of the decay tests were performed on wood samples of dimension 2.0 x 2.0 x 0.5 cm (R x T x L). Samples were modified with acetic or hexanoic anhydride. Full details have been given in a number of reports (Papadopoulos and Hill 2002, Hill *et al.* 2005a, 2005b, Hill *et al.* 2006).

RESULTS AND DISCUSSION

The results for the exposure of acetylated Corsican pine when exposed to *C. puteana* in a 16 week test are shown in Figure 3.

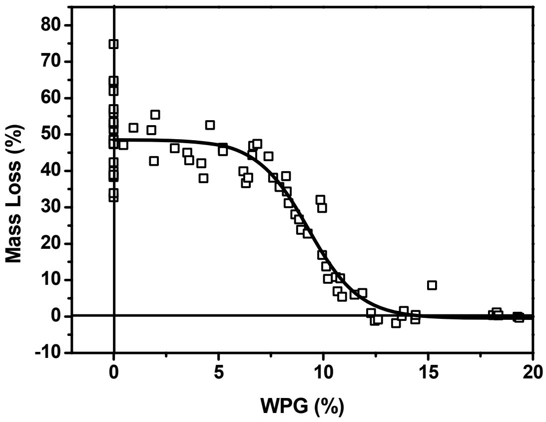

Figure 3: The relationship between mass loss due to decay and weight percentage gain for acetylated Corsican pine exposed to C. puteana for 16 weeks

This plot shows a classic form of behaviour (for this wood species) where there is little change in mass loss at lower WPGs (below about 7%). Above this value there is a significant improvement in decay resistance. It is also significant that the mass loss at low WPG values is around 50%, whereas with unmodified samples, much higher mass losses are possible (up to 75%). Various explanations for this are possible, but this discussion will be postponed until the time series data is presented later. The results from Figure 3 have been re-analysed to shown the effect of different methods of calculating mass loss in Figure 4. The open squares represent the mass loss calculated conventionally (that is as a percentage of the cell wall mass plus the mass of bonded acetyl) (open squares) and the same data based upon the cell wall mass only (filled circles).

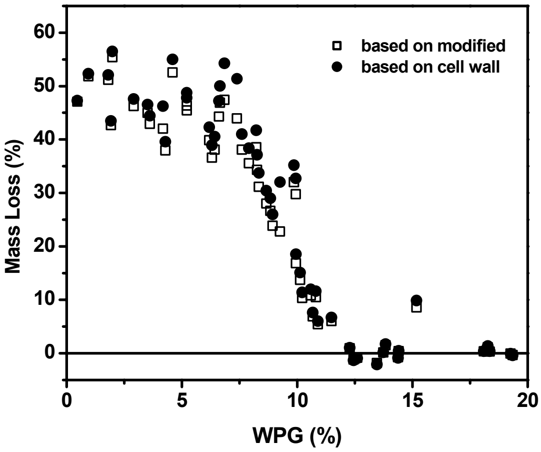

Figure 4: Mass loss based upon weight of the acetylated Corsican pine (open squares) and upon the cell wall mass only (filled circles)

This shows that although there is some difference associated with reporting the mass losses using the two methods, in practice it makes no significant difference and does not justify changing the way all data has been reported to date. The virulence of the fungus can affect the decay threshold and for this reason, the data is often reported as the relative loss of mass compared with a control sample (x-value) from which the decay resistance can be evaluated using a durability scale (Van Acker *et al.* 2003). This is shown in Figure 5, for the same data reported above.

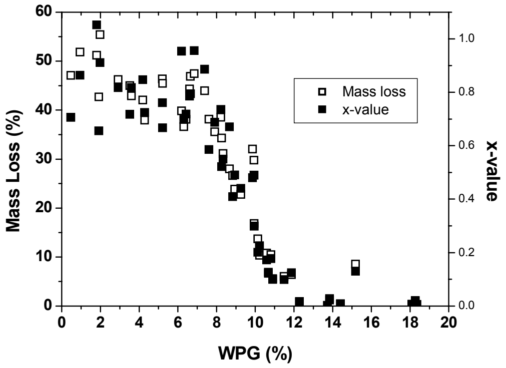

Figure 5: Results from 16 week test for exposure of Corsican pine to C. puteana expressed as mass loss and as x-value

As noted previously, such plots represent the situation at one moment in time (in this case 16 weeks). It is therefore necessary to examine what the effect of changing the exposure period is upon the behaviour (for example is the 'threshold' fixed or not?). This was examined by determining the mass loss of modified and unmodified samples for exposure periods of 12, 16 and 24 weeks (Figure 6). Although there is considerable scatter in the data, it is apparent that for wood modified below 20% WPG, there is an increase in decay mass loss as the exposure period in creases. This was further examined by modifying wood to two WPG levels (8% and 18%) and then exposing the samples for different periods of time up to 24 weeks (Figure 7).

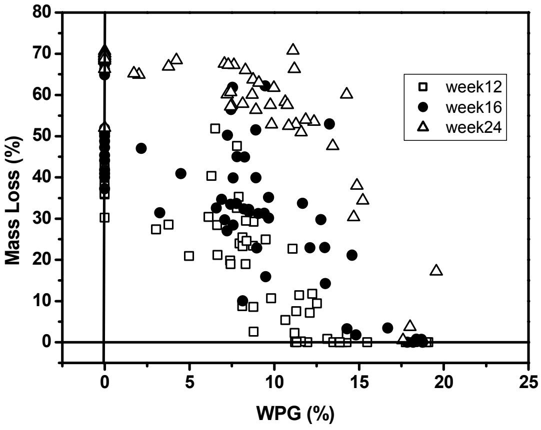

Figure 6: Effect of weight percentage gain upon mass loss due to exposure for varied exposure times

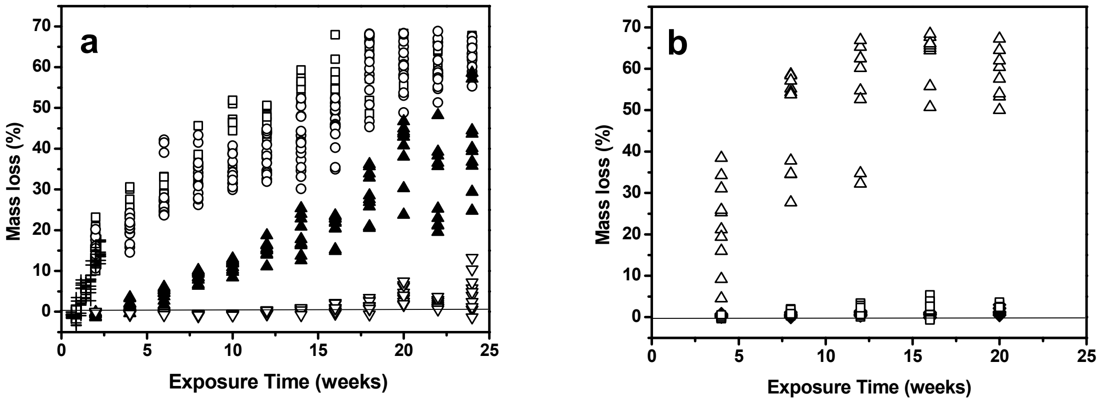

Figure 7: Time series experiment for Corsican pine exposed to FPRL11E strain of C. puteana. Unmodified (open squares), controls (open circles), low WPG (open triangles), high WPG (open inverted triangles), short exposure period (crosses). (b) Time series experiment for Corsican pine exposed to BAM strain of C. puteana. Controls (open triangles), low WPG (open squares), high WPG (filled diamonds). Note that controls are unmodified wood samples which a re located in the same jar as modified wood samples, whereas 'unmodified' refers to unmodified wood samples which are exposed separate from modified wood as a virulence test.

It can be seen in Figure 7a that for unmodified wood exposed to *C. puteana* FPRL 11E strain (crosses, open squares, and open circles) there is a rapid loss of mass for very short exposure times (up to two weeks), with a lower rate of mass loss with a 'ceiling' being reached at 70% mass loss, where the remaining sample is composed only of lignin. With wood acetylated at a WPG of 8%, the rate of mass loss is lower, but reaches levels ranging from 20% to 50% after 24 weeks exposure. When the wood is acetylated to 18% WPG, there is no significant mass loss up to 16 weeks exposure, but mass loss is observed to occur after this time, particularly at 24 weeks exposure. With exposure to the BAM strain the unmodified wood decays as in the previous experiment, but when the acetylated wood is exposed to the fungus, both 8% and 18% WPG provide protection up to 20 weeks' exposure. Thus, significant differences are found when the wood from the same species, acetylated under identical conditions and exposed at the same time is exposed to the same fungal species. It is suggested that there is an urgent need for inter-lab studies to study this effect in greater detail. Thus far, this paper has concentrated upon exposure to brown rot, which has been the subject of most studies. Exposure to white rot fungi has not been exposed to the same scrutiny. Whilst it is generally accepted that 20% WPG represents some kind of 'threshold' to attack by brown rot fungi, this appears to be more variable when acetylated wood is exposed to white rot fungi (Hill 2006). However, the experimental evidence is very limited, with only 12 reported studies on exposure to *Trametes versicolor* one on *Pycnoporus sanguensis* and one on *Phanerochaete chrysosporium* (Hill 2006). The data reported herein represents the most comprehensive simultaneous study of the effect of white rot upon acetylated wood to date. Three wood species were exposed to the white rot fungi *T. versicolor* or *P. chrysosporium*, for 16 weeks. The results of this study are shown in Figure 8. The plots in the LH column are for exposure to *T. versicolor* and in the RH column for exposure to *P. chrysosporium*. Inspection of these graphs show that the decay protection threshold is about 15% WPG in all cases, although there is some variation in the virulence recorded for the unmodified samples, with the softwood species being less susceptible to attack as is commonly reported. The behaviour observed here, does not indicate that there is any reason to invoke a different mechanism to explain resistance to decay by white rot compared to brown rot fungi.

It is not known whether there is a common mechanism protecting acetylated wood from attack by different fungi. It has recently been suggested that there is a generic protection mechanism, where the presence of bonded acetyl in the cell wall occupies space that would normally be available to water. As a result, the cell wall is unable to reach a sufficiently high moisture content to allow decay to occur (Hill *et al*. 2005b). Although a very attractive hypothesis, there has been some evidence to show that this may not be a generic mechanism (Hill *et al*. 2005a). Space precludes reporting the most recent results obtained investigating this phenomenon, but early indications are that the mechanism(s) may well be more varied and complex than hitherto reported. There is still a lot that we do not understand in this respect.

CONCLUSIONS

There have been very rapid developments in the commercialisation of acetylation recently. Whilst there is a reasonable body of laboratory and field data on the decay resistance of acetylated wood, we are very far from having an understanding of the mechanisms by which chemical modification imparts decay resistance. Because there are so many variables that can affect the results obtained, a considerable resource needs to be applied to this problem. In order to understand what the mechanisms for decay resistance are, a comprehensive series of experiments needs to be carried out in a range of laboratories worldwide and the results compared. Although standards specific to acetylated wood are not available, it is most likely that an assessment based upon determining natural durability will be the most appropriate. It is to be expected that significant developments will be reported in this area will be reported to this conference in the future.

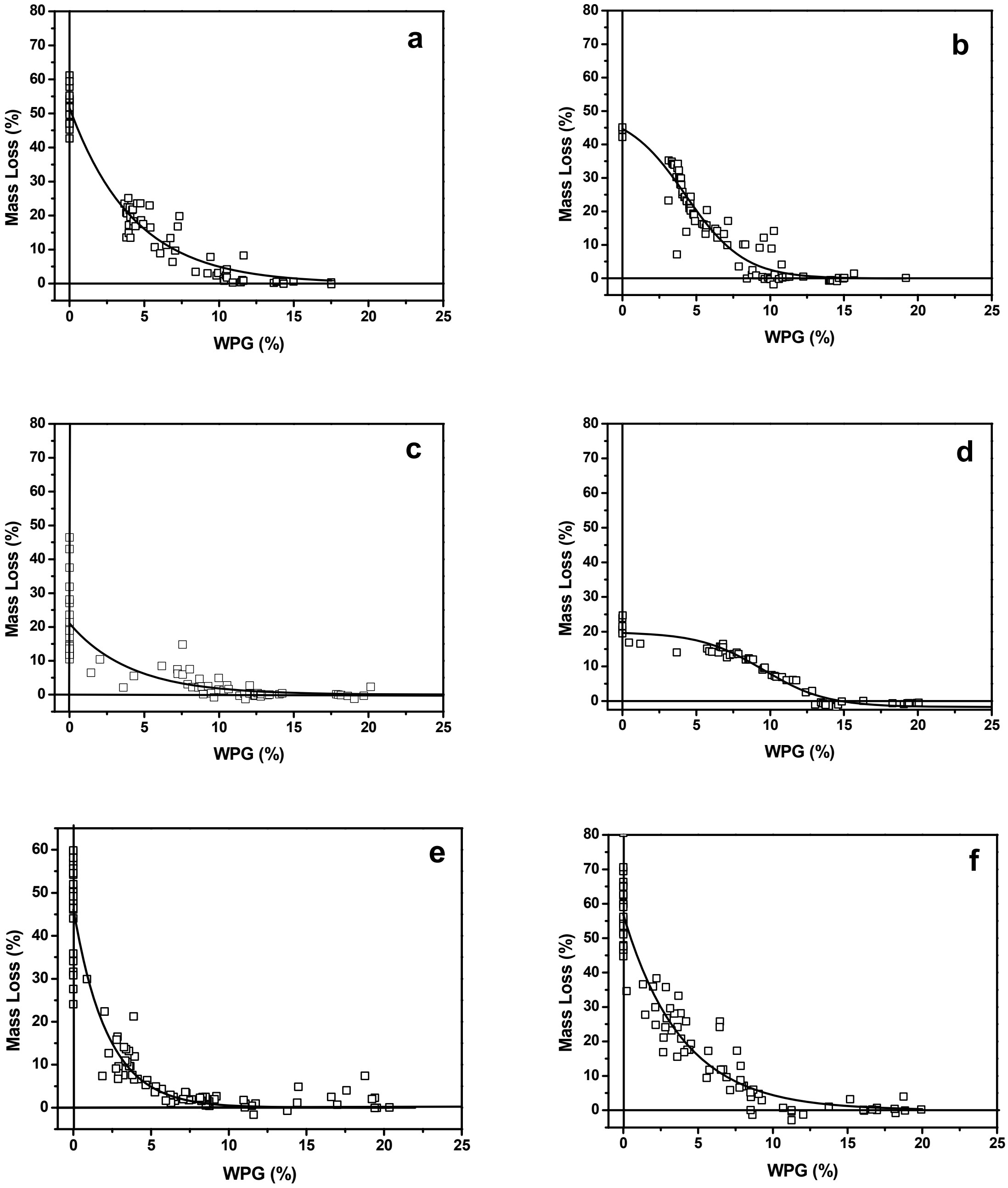

Figure 8: Results obtained for exposure of acetylated wood to white rot fungi, (a) beech T. versicolor, (b) beech P. chrysosporium, (c) Corsican pine T. versicolor, (d) Corsican pine P. chrysosporium, (e) rubberwood T. versicolor, (f) rubberwood P. chrysosporium

ACKNOWLEDGEMENTS

GAO wishes to thank Arch Timber Protection for the funding of a PhD, SRF wishes to thank the Malaysian Government for the funding of a PhD, JHK wishes to thank the Korean Government for the funding of a one year sabbatical.

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^{1}H NMR Demonstration of Chemical Bonds between Lignin-like Model Molecules and Poly(furfuryl alcohol): Relevance to Wood Furfurylation

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Keywords: Chemical modification, wood, furfurylation, furfuryl alcohol, NMR, creosol, lignin

ABSTRACT

The process where wood is impregnated by furfuryl alcohol and catalyst and subsequently heated has previously been proposed to be a chemical modification method. But when furfuryl alcohol polymerizes *in situ* and permanently swells the cell walls, does the reaction indeed generate chemical bonds between the polymer and one or more wood constituents such as lignin, hemicellulose and cellulose? Although indirect observations that support this hypothesis exist, definite proof of such bonding is not yet available. As a first step towards demonstrating the presence of such bonds, we have investigated two liquid model solutions with model compounds (2-methoxy-4-methylphenol and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol) that chemically resemble principal repeating units of lignin. The selected methods are NMR spectroscopic ones. 2D COSY spectroscopy reveals atoms that are connected through covalent bonds. NMR diffusion experiments give translational self-diffusion coefficients, which are identical for chemically bonded entities. We find that a fraction of the model molecules formed covalent bonds with poly(furfuryl alcohol). These results indicate that the furan polymer in furfurylated wood is grafted to the wood lignin.

INTRODUCTION

Chemical modification of wood by furfuryl alcohol has been investigated for a long time, and is referred to as furfurylation of wood. The production and general properties of furfurylated wood, where a wide range of enhanced properties are achieved, have been described earlier (Lande *et al*. 2004a). The most significant modifications are improvements in decay resistance, hardness, and dimensional stability. The altered colour is also a remarkable result of the process.

Although much is known about furfurylated wood, we lack information about the molecular details in the furfurylation process. The basic chemistry of polymerization of furfuryl alcohol has long been discovered, but any chemical reaction between furfuryl alcohol and wood has not been positively identified, only tentatively suggested (Lande *et al*. 2004b). Properties such as bulking of the wood cell wall (permanent swelling) indicate that polymerization has indeed taken place inside the cell wall. The high anti-swell efficiency (ASE) achieved by furfurylation indirectly indicates that chemical bonds are present between poly(furfuryl alcohol) and the wood matrix. Given that poly(furfuryl alcohol) becomes gradually more hydrophobic during polymerization, it is believed that the polymer would migrate out of the cell wall (resulting in lower ASE) if chemical bonds to the wood matrix were absent.

In this paper, we present a study of a liquid-phase system where early stages of the furfuryl polymerization takes place and where bonds to model compounds of wood substituents may form. This examination is the first step in a project where our aim is to demonstrate chemical bonds between wood components and poly(furfuryl alcohol) in genuine wood materials.

The selected wood substituents are two lignin model molecules. The first model compound is creosol, 2-methoxy-4-methylphenol, which is a principal repeating aromatic unit of the lignin macromolecule. The second compound is adlerol, 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol, which is a larger repeating unit in lignin as shown in Figure 1. Note that creosol carries both a hydroxyl and a methoxy group while the equivalents of adlerol are only methoxy substituents.

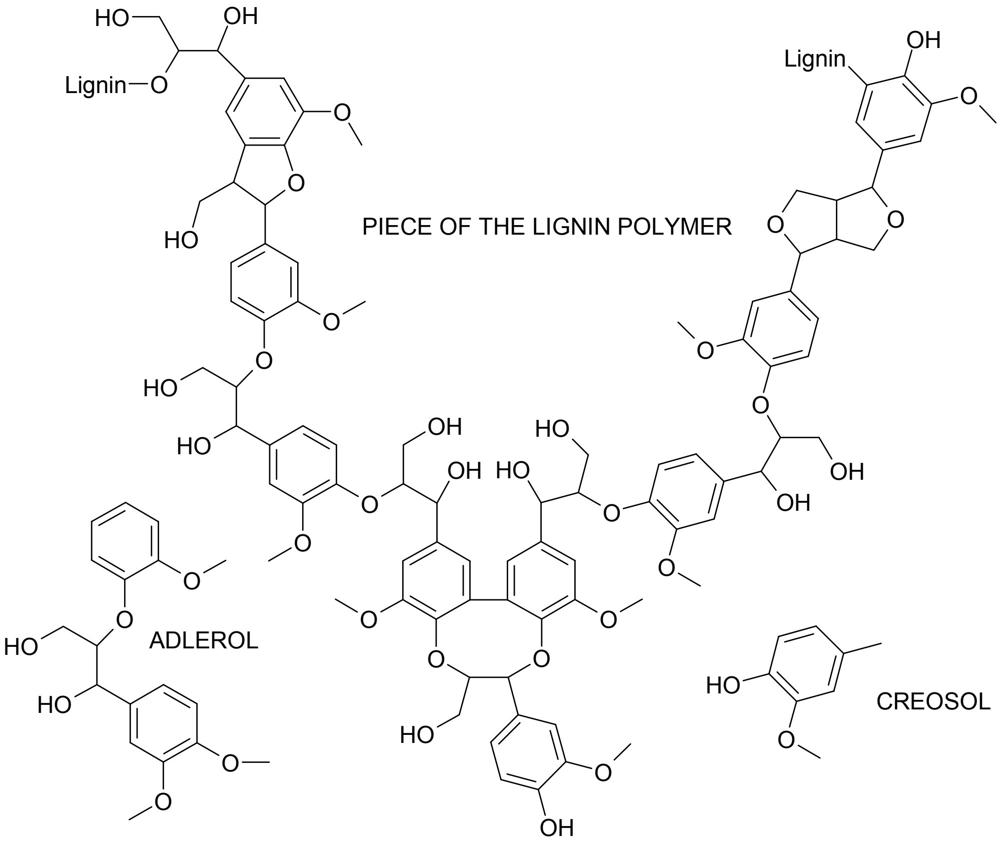

Figure 1: A representative section of lignin with components adlerol and creosol

Furfuryl alcohol polymerizes in the presence of heat and an initiator. The first step of the process is the reaction between the initiator, here maleic anhydride, and furfuryl alcohol, shown in Figure 2.

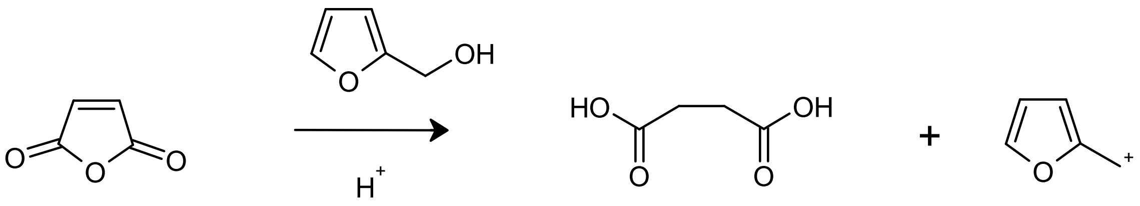

Figure 2: The initial reaction where maleic anhydride forms maleic acid while furfuryl alcohol becomes a cationic and electrophilic methylfuran derivative

The resulting cationic species is very reactive and initiates the polymerization which dominantly proceeds by electrophilic aromatic substitution (González *et al.* 2002) as seen in Figure 3. In reality, the products are not only connected through methyl linkages but also by ether linkages and may even branch (Maciel *et al.* 1982, Chuang *et al.* 1984, González *et al.* 1992, González *et al.* 2002).

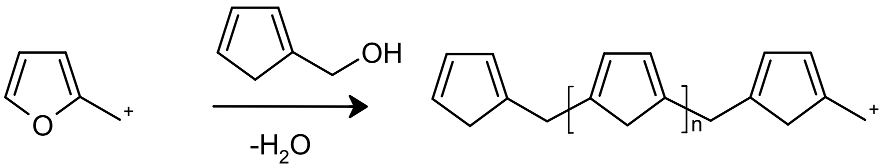

Figure 3: Polymerization of furfuryl alcohol

Creosol is a benzene ring with three substituents. Concerning electrophilic attacks, these attached groups are different in their activating tendency. The hydroxyl group is a strongly activating group, the methoxy group is a moderately activating group, and the methyl group is a weakly activating group. Presumably, the hydroxyl oxygen donates unshared electrons to the π-system directing the electrophilic attack to the ortho-position (Jacobs 1997). This mechanism, illustrated in Figure 4, provides us with a probable structure of the molecule formed when furfuryl alcohol or poly(furfuryl alcohol) binds to creosol.

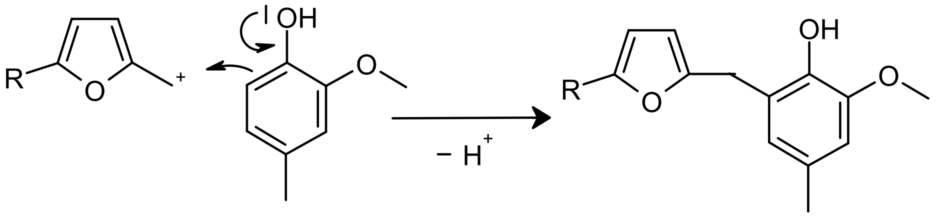

Figure 4: The hypothesized reaction between furfuryl alcohol and creosol. Substituent R is either a poly(furfuryl alcohol) chain or a hydrogen atom

Adlerol consists of two creosol rings connected by a propandiol bridge. Also here, the most likely reaction is an electrophilic attack on the ortho-position but in this case next to a methoxy group since no hydroxyl groups are present.

EXPERIMENTAL

Furfuryl alcohol (Fluka, >98%), maleic anhydride (Fluka, >99%), citric acid (Fluka, >99.5%), sodium carbonate (Fluka, >99.5%), 2-methoxy-4-methylphenol (Fluka, >98%), chloroform-d (Aldrich, 99.8 atom% D), tetramethylsilane (Fluka, >99.5%), and deuterium oxide (Isotec, 99.9 atom% D) were used as received. 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol was generously provided by Prof. Knut Lundqvist. All chemicals added by accurate weights as given in Table 1 were mixed in a closed sample holder. The sample was then kept sealed at 50 °C and was shaken two times a day. An upper aqueous phase and a lower organic phase were formed rather rapidly after shaking. At roughly 7-days intervals from day 3 to day 31, small amounts (~ 0.2 ml) of the organic phase were transferred to 5 mm NMR tubes and diluted with cold $CDCl_3$ containing a small amount of TMS. Those NMR samples were then cooled down and stored at 0 °C. Note that a parallel study of an entirely organic sample (furfuryl alcohol, creosol, and maleic anhydride) yielded results equivalent to those presented below.

Table 1: Chemicals in the furfurylation process

Compound	Function	Mole%
Water	Impregnator	91.5
Furfuryl alcohol	Polymer	6.72
Creosol/Adlerol	Lignin model	1.19
Maleic anhydride	Initiator	0.24
Citric acid	Initiator	0.18
Sodium carbonate	Buffer	0.14

All experiments were based on ^{1}H NMR spectroscopy. First, simple spectra were recorded and the chemical shifts were measured partially for the spectral assignment but also to register chemical changes in the sample. Signal intensities given by spectral integration were used to estimate the degree of polymerization and the amount of reacted lignin model compound. Second, 2D homonuclear correlation spectroscopy (gradient COSY) was used for spectral assignment and for the identification of covalent bonds. Third, self-diffusion of the various molecular components was measured by pulsed-field-gradient stimulated-echo experiments. The NMR measurements were performed on a Bruker 500DRX instrument equipped with a 5mm z-gradient TBI-probe. The experimental temperature was set to 25 °C and the shifts were calibrated to internal TMS at 0 ppm.

RESULTS AND DISCUSSION

Creosol

Initial studies confirmed that no polymerization of furfuryl alcohol takes place in the absence of an initiator. Moreover, no reaction occurs when furfuryl alcohol and creosol are mixed without initiator. There is neither any chemical change of creosol when blended with only initiator. Only the systems containing furfuryl alcohol/initiator or furfuryl alcohol/initiator/creosol are subject to any chemical reactions. With regard to the polymerization process of furfuryl alcohol we observe that longer reaction time and higher temperature increase the degree of polymerization. Based on NMR signal intensities, we can state that ~ 45 % of the furfuryl alcohol has polymerized after 4 days of reaction, ~ 65 % after 7 days, ~ 85 % after 18 days and ~ 89 % after 31 days. Note that these numbers are only accounted for furfuryl alcohol in the organic phase. Polymerization of furfuryl alcohol creates new NMR signals with chemicals shifts in the range as previously reported (Principe *et al*. 2000, González *et al*. 2002). Many new polymer signals were observed and it is apparent that methyl linkages, ether linkages, but also possible branching constitute the poly(furfuryl alcohol) structure. The rather high (in the order of 10^{-10} m^2/s) obtained self-diffusion coefficients indicated that no long polymers but mostly shorter oligomers were formed under the present reaction conditions.

In the presence of creosol, new separate NMR signals also arose at 6.72, 3.78 and 2.21 ppm as shown in Figure 5. There were also two partly overlapping signals at 6.65 and 3.83 ppm. In COSY spectra (not shown here), cross peaks appear between any protons that are connected through 3-5 covalent bonds. H-H pairs that have more than 5 or no chemical bonds in-between typically exhibit no cross peaks. However, even longer-range couplings (6 bonds) may result if an aromatic ring system lies between the protons.

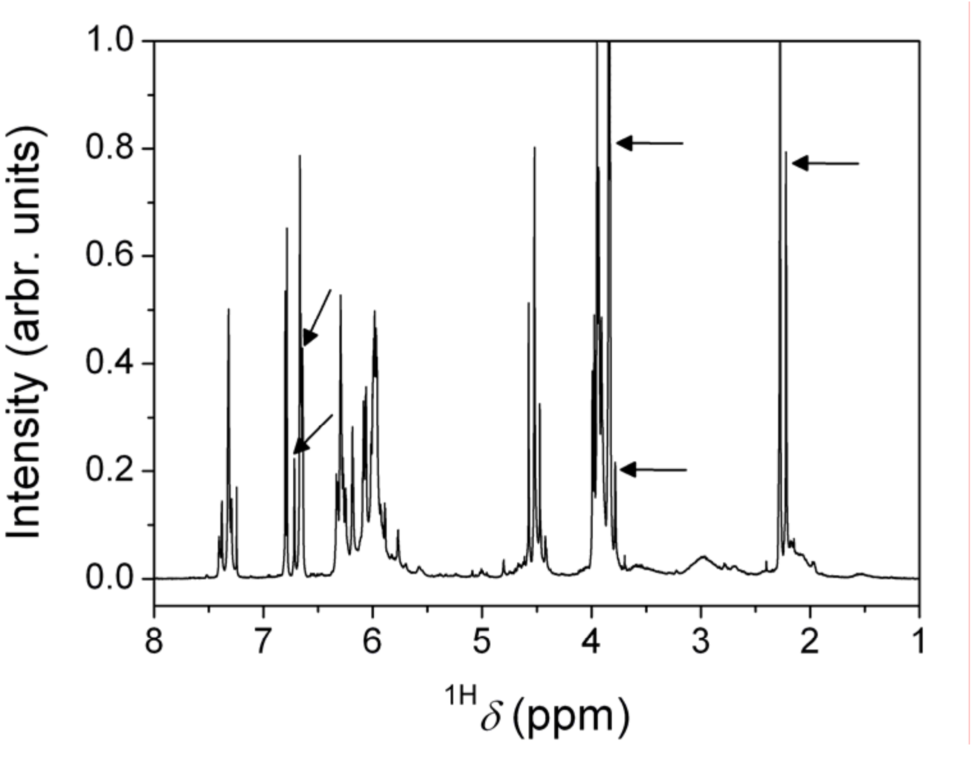

***Figure 5:** The ^1H NMR spectrum after polymerization and reaction with creosol. New signals due to the creosol reaction are marked by arrows*

Significantly, one (3.78 ppm) of the new signals (at 6.72, 6.65, 3.83, 3.78 and 2.21 ppm) displayed COSY cross peaks to atoms assigned to creosol but also to atoms assigned to poly(furfuryl alcohol). The established assignments and connection pattern are shown in Figure 6; clearly, the model in Figure 4 is strongly corroborated by the experimental results. Note that results indicate that the creosol is not connected to a monomeric furan ring but to a polymer or oligomers of at least two rings (note the connection between peaks at 3.78 and 3.93 ppm).

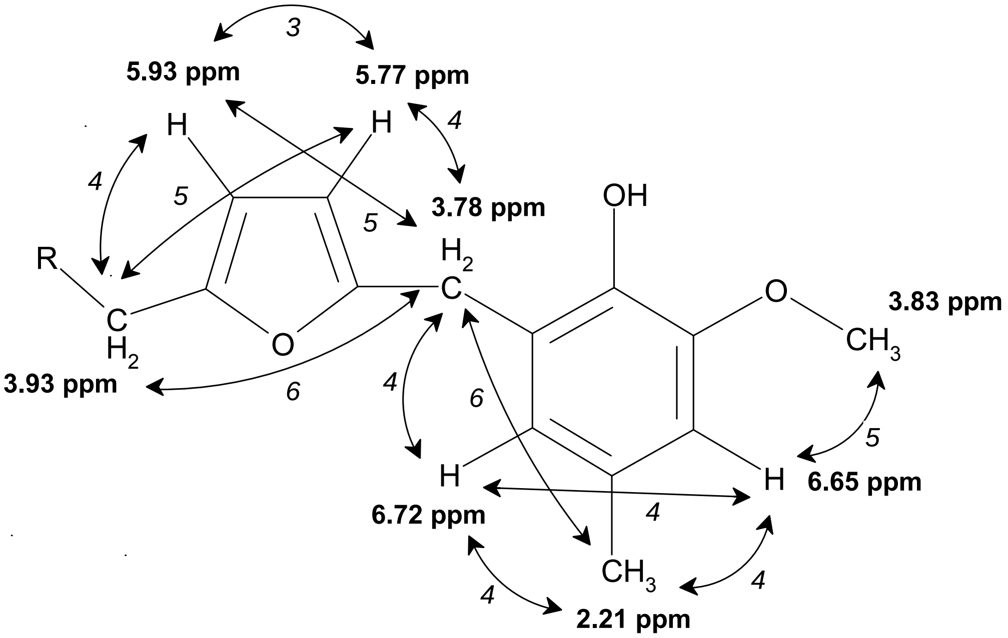

Figure 6: The molecule produced when polymerizing furfuryl alcohol and creosol react. Figures in ppm display chemical shifts. Arrows with figures correspond to COSY cross peaks and the number of bonds between the participating protons. Substituent R is either one or several methylfuran rings

Predicted ^{1}H chemical shifts (ACD/Labs 2007) are very close to the experimental ones. A previous study where the reaction products of benzene-1,3,5-triol with furfuryl alcohol were investigated (Foo and Hemingway 1985) yielded chemical shifts close to the corresponding ones in Figures 5-6.

As an independent argument, the self-diffusion coefficients obtained for the new signals (at 6.72, 3.78 and 2.21 ppm) are identical (within the experimental error of a few percents). That diffusion coefficient is also smaller than that measured for creosol or for furfuryl alcohol. Hence, the new signals arise from a single molecular entity that is larger than either the furfuryl alcohol or the creosol monomer.

To estimate the amount of reacted creosol, NMR signal integral intensities were used. They yield for the amount of reacted creosol: ~ 6 % after 4 days of reaction, ~ 13 % after 7 days, ~ 25 % after 18 days and ~ 29 % after 31 days. Note that these figures only account for creosol in the organic phase.

Adlerol

The working scheme of the adlerol sample followed that of creosol described above. The degree of furfuryl alcohol polymerization was the same as for that in the creosol case. Characteristic chemical shifts indicate linear methylene-linked oligomers and polymers combined with smaller amounts of ether-linked and branched products. Concerning a reaction with adlerol, signal intensities and COSY cross-peaks clearly demonstrate a minor fraction of adlerol binding covalently to poly(furfuryl alcohol) (< 5 % after 25 days, approximately one order of magnitude less than under equivalent conditions for creosol). Clearly, the moderately activating methoxy groups allow less intermolecular bonds to form.

CONCLUSIONS

The studied liquid system of partly polymerized furfuryl alcohol and lignin model compounds creosol and adlerol was subject to different experiments based on ^{1}H NMR spectroscopy. The combined examination of chemical shifts, 2D COSY spectra, signal intensities, and self-diffusion coefficients strongly corroborate the hypothesis that a fraction of the model molecules undergo a chemical reaction during the polymerization of furfuryl alcohol and that the reaction generates covalent bonds between the model compounds and poly(furfuryl alcohol). The strongly activating hydroxyl group on the creosol benzene ring is the dominating cause of this reaction. The similar molecule adlerol that has no hydroxyl groups, but only methoxy groups, and reacts far less extensively with polymerizing furfuryl alcohol under present conditions.

ACKNOWLEDGEMENTS

We thank Prof. Knut Lundqvist for the adlerol sample and Dr. Krister Zetterberg for useful discussions. This study was supported by the EcoBuild Institute Excellence Center established by VINNOVA, KK-stiftelsen and Stiftelsen för Strategisk Forskning (SSF).

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Influence of the Modification with Different Aldehyde-based Agents on the Tensile Strength of Wood

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Keywords: DMDHEU, glutaraldehyde, micro-veneers, N-methylol melamine, tensile strength

ABSTRACT

Pine wood veneers treated with solutions of DMDHEU and a catalyst ($MgCl_2$) showed tensile strength losses of approx. 50%. The strength losses after treatment with solely $MgCl_2$ amounted to more than half of that of DMDHEU and $MgCl_2$ combined. Treatment with DMDHEU solution alone also caused significant WPG and tensile strength losses of approx. 20%. Veneers treated with glutaraldehyde (GA) and $MgCl_2$ displayed comparable strength losses with those treated with DMDHEU and $MgCl_2$. GA treatment without a catalyst did not cause any strength loss and WPG. Difference in the treatment with DMDHEU and GA alone can be attributed to the ability of DMDHEU to react with hydroxyl groups and undergo polycondensation, also in absence of a catalyst. N-methylol melamine (NMM) induced high WPG, but did not cause any tensile strength losses; neither variation in NMM concentration nor in pH had an influence on tensile strength of the treated veneers. These results indicated that hydrolysis of cell wall polysaccharides plays a major role in the strength loss of micro-veneers determined in zero-span mode. The influence of cross-linking of cell wall constituents, however, is also of importance.

INTRODUCTION

Chemical modification is mainly implemented to improve dimensional stability and decay resistance of wood and thereby prolong the service life. The treatment may, however, negatively affect mechanical properties. Wood modification with aldehyde-based chemicals was reported to cause embrittlement of wood. This is observed as a decrease in the tensile strength and in dynamic strength properties such as impact bending strength. Several reasons could be considered as a cause for this phenomenon: (1) hydrolysis of cell wall polysaccharides caused by the modifying agent or/and the catalyst, (2) cross-linking of cell wall polymers by bifunctional agents, which reduces the freedom of movement of these polymers and restricts the possibility of the cell wall matrix to relieve mechanic stress (3) the incorporation of plastic-like substances into the cell wall *e.g.* by polycondensation which press the cell wall polymers into a rigid corset, reduce the freedom of movement among the polysaccharides and, thus, prevents the relief of mechanic stress (Rowell 1998).

Wood modification with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) has been shown to improve the dimensional stability, decay and weathering resistance of wood (Nicholas and Williams 1987, Militz 1993, Yasuda and Minato 1994, Krause *et al.* 2003, Xie *et al.* 2005). The modification requires a Lewis-acid to catalyse the reaction. So far, it is not known if the reaction of N-methylol groups in DMDHEU with hydroxyl groups in wood or the polycondensation of DMDHEU is the predominant reaction. Furthermore, formaldehyde which is released from the N-methylol groups during the reaction could also cause cross-linking in present of a Lewis-acid. Thus, strength losses could be due to all three types of mechanisms mentioned above.

DMDHEU treatment had a deleterious effect on the tensile strength of thin veneer strips, possibly associated with the presence of the magnesium chloride catalyst in the treatment solution (Xie *et al.* 2005). In a very few other studies, the effect of DMDHEU treatment on the mechanical properties of wood is discussed but the authors only refer to reduced bending strength without considering possible reasons for this reduction in any detail (Nicholas and Williams 1987).

Treatment of wood with glutaraldehyde in presence of sulphur dioxide resulted in anti-shrink efficiency (ASE) higher than 60% after treatment of sitka spruce and Japanese cedar (Yasuda and Minato 1994, Yusuf *et al.* 1995). Glutaraldehyde bears two aldehyde groups and is, thus, able to cross-link the cell wall polymers by reacting with four hydroxyl groups. In addition, a high bulking coefficient was obtained which is presumably the main reason for the high ASE (Yusuf *et al.* 1995). Compared to DMDHEU, the reaction of glutaraldehyde also requires a catalyst, but it cannot undergo polycondensation. Static strength properties were affected to a comparable degree as with DMDHEU. Decrease in modulus of rupture (MOR) in the longitudinal reaction was not more than 20%, while the MOR in radial direction decreased up to 40% with sulphur dioxide as catalyst (Yusuf *et al.* 1995).

Aqueous N-methylol melamine stock solutions exhibit high pH values to prevent condensation of the monomers and to guarantee high stability (supplier information). In wood, N-methylol melamine mainly undergoes polycondensation, but a cross-linking of cell wall polymers is still possible. Methylolated melamine caused moderate ASE of approx. 30% at WPG of 10% (Inoue *et al.* 1993). The reactivity of the N-methylol groups increases with decreasing pH; the addition of a Lewis-acid catalyst is not required. Particularly, under neutral and slightly acidic conditions hydrolysis of cell wall polysaccharides plays a minor role. In addition, formaldehyde which is released during the treatment is not likely to react with wood in this pH range.

The main objective of this study is to establish the effect of modification with DMDHEU, glutaraldehyde and N-methylol melamine and of the single constituents of the reaction system (catalyst and reactant) on the tensile strength of thin veneer strips. Hence it tries to elucidate the reasons for embitterment and reduction in impact bending strength of the treated wood.

EXPERIMENTAL

Wood veneers

Wood blocks measuring 100 x 50 x 15 mm^3 (L x T x R) were cut from the sapwood of Scots pine (*Pinus sylvestris L.*) boards as described previously (Evans *et al.* 2000). The blocks were soaked in 10% aqueous ethanol in a vacuum (100 mbar, 30 min) and kept in the solution for 14 days under ambient pressure. Veneers, approx. 100 µm thick, were cut from the radial surface of each block using disposable microtome blades (Reichert-Jung, Nussloch, Germany) as also previously described (Evans and Banks 1988).

Chemicals

The modifying agent was a solution of 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) supplied by BASF AG (Ludwigshafen, Germany). Magnesium chloride hexahydrate ($MgCl_2.6H_2O$) was used as catalyst. The pH of the final treatment solutions was measured at 21 °C using a pH meter (pH 526, Wissenschaftlich-Technische Werkstätten, Weilheim, Germany). Glutaraldehyde (GA) was supplied as aqueous solution (50%) by BASF AG (Ludwigshafen, Germany). N-methylol-melamine (NMM) was Madurit MW 840 supplied by INEOS (Frankfurt a. M., Germany). Both the stock solution of NMM and a typical treatment solution (10%) displayed a pH of approx. 8.4.

Treatment of veneers

Prior to treatment, the veneers were dried in a desiccator (approx. 20 °C) for 3 days and then weighed. Twenty veneers were tested per treatment. Impregnation was performed under vacuum conditions (100 mbar, 30 min) and ambient pressure (10 min). After impregnation, excess treatment solution was blotted off the veneers with filter paper. Subsequently, the specimens were cured at 120 °C (240 min). Both the stock solution of DMDHEU and a typical treatment solution (1.2 mol l^{-1} DMDHEU, 1.5 w/w% $MgCl_2.6H_2O$) displayed a pH of approx. 5.2. The treatment solutions were as follows; all indications w/w or mol l^{-1} (M):

1. 0.5%, 1.5%, and 2.5% $MgCl_2.6H_2O$ (pH approx. 8.0)
2. 0%, 0.5%, 1.5%, 2.5%, and 3.5% $MgCl_2.6H_2O$; pH 5.2 (hydrochloric acid)
3. 1.2 M DMDHEU with 0.5%, 1.5%, 2.5%, and 3.5% $MgCl_2.6H_2O$ (pH approx. 5.2)
4. 0.4 M, 1.2 M, and 2.0 M DMDHEU (pH approx. 5.2)
5. 0.4 M, 1.2 M, and 2.0 M DMDHEU with 1.5% $MgCl_2.6H_2O$ (pH approx. 5.2)
6. 1.5% $MgCl_2.6H_2O$ dissolved in 0.2 M sodium acetate buffer (Stoll and Blanchard 1990), pH 4.0, 4.5, 5.0 and 5.5.

Glutaraldehyde (GA) was applied in an analogue way, but GA and $MgCl_2.6H_2O$ were dissolved 0.2 M acetate buffer (except treatment 4.). Curing was performed in several steps: air drying (4 h), continuous increase from 60 °C to 120 °C over 1 h, maintenance at 120 °C (2 h). The treatment solutions were as follows:

1. 1.5% $MgCl_2.6H_2O$ dissolved in 0.2 M sodium acetate buffer; pH 3.5 - 5.5
2. 1.2 M GA and 1.5% $MgCl_2.6H_2O$ dissolved in 0.2 M sodium acetate buffer, pH 3.5, 4.0, 4.5, 5.0 and 5.5
3. 1.2 M GA with 0.5%, 1.5%, 2.5%, and 3.5% $MgCl_2.6H_2O$ (pH 4.5)
4. 0.4 M, 1.2 M, and 2.0 M GA with 1.5% $MgCl_2.6H_2O$ (pH 4.5, adjusted with NaOH)

The pH of the stock solution of N-methylol-melamine (NMM) amounted to approx. 8.4. The veneers were treated as with DMDHEU and GA, but cured at 80 °C (240 min). The treatment solutions were as follows (all indications w/w):

1. 0.2 M sodium phosphate buffer, pH 6.0, 7.0, 8.0 (Stoll and Blanchard 1990)
2. 5%, 10%, 15% and 20% NMM (pH 8.4)
3. 10% NMM dissolved in 0.2 M sodium phosphate buffer, pH 6.0, 7.0, 8.0

After conditioning (20 °C, 65% r.h.) for 24 h, all the treated specimens were first rinsed with running tap water (approx. 40 °C) for 2 h to remove the unreacted chemicals and subsequently dried in the desiccator (3 days) and weighed. Untreated veneer strips served as control specimens. Prior to further tests, the veneers were conditioned in a climate chamber (20°C, 65% r.h.); their thickness was determined using a dial gauge micrometer (Mitutoyo, Mexico).

Zero-span tensile strength (z-strength)

Zero-span tensile strength losses of the veneers were determined with a Pulmac paper tester (Pulmac International Inc., Middlesex, U.S.A.) as previously described (Evans and Schmalzl 1989). The rate of loading was set to 70 kPa s^{-1}. The initial clamping pressure was set to 0.52MPa for untreated veneers and to 0.45MPa for treated veneers. Tensile strength retention was compared to untreated veneers (controls). For each treatment 20 veneers were used; each of them was cut into two parts which were then measured separately.

RESULTS AND DISCUSSION

Effect of 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU)

Treatment of veneers with 0.4, 1.2 and 2.0 M DMDHEU solution caused WPGs of 8, 26 and 47% after rinsing with water. Veneers which were only treated with acidic magnesium chloride (3.5% $MgCl_2$ concentration) had a weight loss of up to 3% after washing. This was considerably higher than the weight loss of veneers treated only with water (approx. 1%). The former finding is probably a consequence of the hydrolysis of cell wall constituents.

Untreated veneers (controls) displayed a z-strength of 77.6 MPa. Treatment of veneers with a slightly acidic aqueous solution (pH = 5.2) had a minor effect on tensile strength (0% $MgCl_2$ in Figure 1A). At neutral pH (7–8), $MgCl_2$ treatment did not change tensile strength, but under acidic conditions (pH = 5.2) a severe reduction occurred (Figure 1A, C). This strength loss can be attributed to a reduction in the degree of polymerisation of cellulose. $MgCl_2$ is a Lewis acid that does not provide protons *via* hydrolysis; however, it can form a Lewis acid adduct with the free electron pair of the oxygen atom in glucosidic bonds of polysaccharides. Thus, it polarises the bond and makes it susceptible to hydrolytic attack by hydrogenium ions (H_3O^+). Nicholas and Williams (1987) treated wood blocks with DMDHEU (10%) and a two-component catalyst of aluminium chloride (0.5%) and tartaric acid (0.5%) lost 38% of their bending strength (MOR); however, samples treated with the catalysts alone (both 0.5%) displayed the same loss in MOR (38%). Strength losses of cotton fabrics, which initially increased with magnesium chloride concentration, levelled off at 50% strength loss (Yang *et al.* 2000). In this study the tensile strength loss of veneers showed a comparable saturation behaviour pattern when the concentration of magnesium chloride rose above 0.5% (Figure 1A). Treatment with aqueous DMDHEU (without the catalyst) reduced z-strength by up to 20% (Figure 1B, upper line) irrespective of the DMDHEU concentration used. This might be attributed to a hydrolytic effect of DMDHEU or an incorporation of the chemical into the cell wall. The deposition of DMDHEU could make the fibres less elastic and impede any slippage of single micro-fibrils as a result of cross-linking (Zeronian *et al.* 1989).

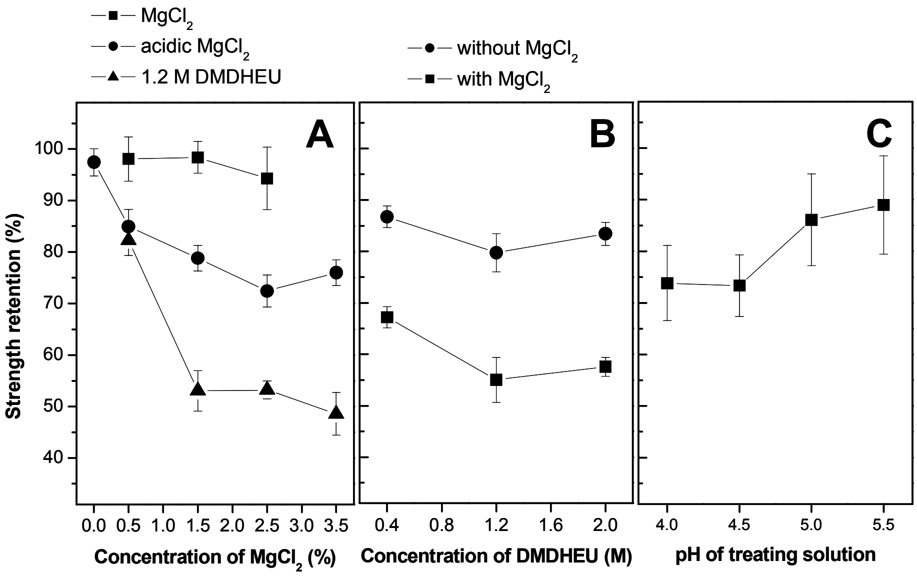

Figure 1: Retention of zero-span tensile strength in veneers treated with (A) $MgCl_2$ (upper line), acidic $MgCl_2$ (middle line), and 1.2 M DMDHEU plus 1.5% $MgCl_2$ (lower line); (B) DMDHEU (upper line) and DMDHEU plus 1.5% $MgCl_2$ (lower line); (C) 1.5% $MgCl_2$ (variation in pH, sodium acetate buffer) the error bars show standard deviation

Veneers treated with DMDHEU and $MgCl_2$ retained only 55-70% of their initial z-strength (Figure 1B, lower line). As reported previously (Xie *et al.* 2005), such strength losses were not significantly related to the concentration of DMDHEU. This type of saturation behaviour was also observed when $MgCl_2$ and DMDHEU were applied alone. Strength losses measured both at zero-span appeared to be the sum of individual strength losses caused by magnesium chloride and DMDHEU alone. Thus, total strength loss is likely to be caused by the hydrolysis of polysaccharides catalysed by acidic magnesium chloride and through the embrittlement of fibres as a result of DMDHEU deposition in the fibre cell wall. Z-strength losses caused by treatment with $MgCl_2$ alone increased with decreasing pH (Figure 1C) and can be attributed to hydrolysis of cell wall polysaccharides. Veneers which were treated with acetate buffer alone (pH 4.0) did not show any strength losses.

Effect of glutaraldehyde (GA)

Treatment of veneers with 0.4, 1.2 and 2.0 M GA solution in presence of $MgCl_2$ caused WPGs of 4, 9 and 11% after rinsing with water. At a fixed GA concentration of 1.2 M $MgCl_2$ concentration of at least 1.5% was required to reach maximum fixation of GA. In contrast to DMDHEU treatment (strength losses of approx. 20%), a reaction and strength loss did not occur when the veneers were solely treated with GA solution at pH 4.5. A reason for this difference could be the ability of DMDHEU to perform polycondensation within the cell wall or to cause low degree of cross-linking without catalyst, while GA can react only with alcohols to form semi and full acetales.

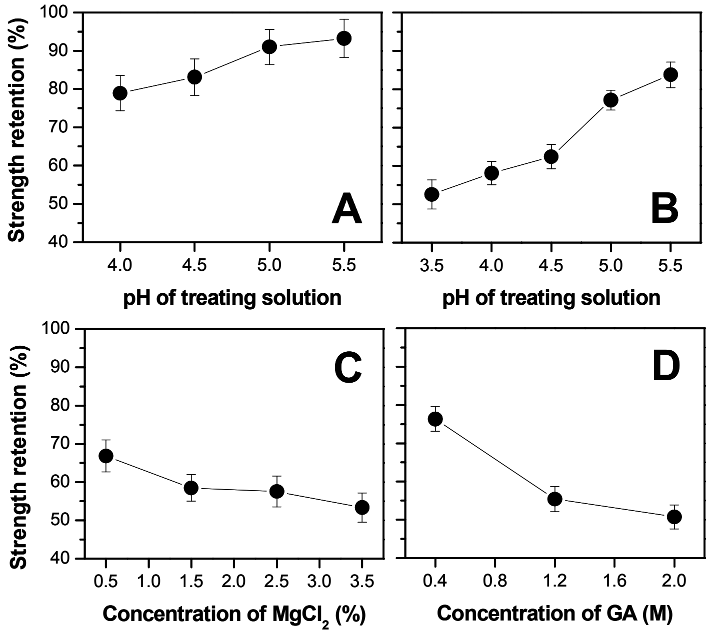

Figure 2: Retention of zero-span tensile strength in veneers treated with (A) 1.5% $MgCl_2$ (variation in pH, sodium acetate buffer); (B) 1.2 M GA plus 1.5% $MgCl_2$; (C) 1.2 M GA plus different concentrations of $MgCl_2$ (acetate buffer, pH 4.5); (D) 1.5% $MgCl_2$ plus different concentrations of GA (acetate buffer, pH 4.5) the error bars show standard deviation

Tensile strength exhibited the same tendency that strength losses increased with increasing concentration of GA and $MgCl_2$. The influence of $MgCl_2$ concentration at fixed concentration of GA, however, was relatively low; the strength reduction between 0.5 and 3.5% $MgCl_2$ amounted to 15% (Figure 2C). Strength retention displayed strong dependence of pH, when the veneers were treated with a fixed concentration of GA (1.2 M) and $MgCl_2$ (1.5%). While at pH 5.5 the loss in tensile strength was only slightly higher than 16%, strength was reduced by 47% at pH 3.5 (Figure 2C). This decrease can be explained with higher degree of hydrolysis of the cell wall polysaccharides and with higher degree of cross-linking through GA. Treatment of veneers with 1.5% $MgCl_2$ caused strength losses of approx. 20%, depending on pH (Figure 2A). Additional loss shown in Figure 2B and C can be attributed to cross-linking of polysaccharides, which impedes slippage of single micro-fibrils and, thus, prevents that the charged fibre can counterbalance the tensile strain. Strength reduction caused by catalysed GA appeared to be a little lower than those induced by catalysed DMDHEU. At the present stage, direct comparison of both treatments is not possible, since catalysed DMDHEU treatment was not performed in acetate buffer. Due to the presence of acidic extractives, pine wood has a pH of about 5.1 (Sandermann and Rothkamm 1959) and acts as a natural buffer. DMDHEU treatment solution (1.2 M) exhibited a pH value of 5.2. Therefore, it can be assumed that the treatment solution in the wood after treatment maintained a pH of approx. 5.1. The effect of lower pH values (4.0-4.5) needs to be further elucidated. Sodium acetate, however, which was used in this study as a buffering agent, could also act as a catalyst for the treatment of textile fibres. Hence, the effect of $MgCl_2$ in presence of DMDHEU cannot be studied individually from the buffering agent. In addition, DMDHEU and GA were applied in equal molar amounts, but DMDHEU treated veneers had a much higher WPG due to the higher molecular mass of DMDHEU.

Effect of N-methylol-melamine (NMM)

Treatment of veneers with 5, 10, and 15% NMM solution at pH 8.4 without catalyst caused WPGs of 6, 15 and 23% after rinsing with water. When the veneers were treated with 10% NMM solution, WPG values increased with decreasing pH; veneers treated at pH 6, 7 and 8 resulted in WPGs of 12, 8 and 7%, respectively. Increase in WPG can be attributed to higher reactivity with decreasing pH.

Table 1: Effect of pH (Na acetate buffer) on tensile strength of veneers treated with NMM (10%)

pH	z-strength retention
6	99.4 ± 4.7
7	97.4 ± 5.7
8	97.1 ± 5.4

NMM treatment did not cause any strength loss compared to untreated veneers; neither variation in pH (Table 1) nor in NMM concentration (not shown) reduced tensile strength. The only way, how NMM can cause strength losses is through cross-linking of cell wall polysaccharides. NMM mainly undergoes polycondensation within the wood, but the N-methylol groups can also react with hydroxyl groups. Hydrolysis of polysaccharides is unlikely to occur, because of the neutral pH and the absence of a Lewis acid catalyst. It can be assumed from these results that the presence of a Lewis acid catalyst under acidic conditions is mainly responsible for the loss in tensile strength rather than cross-linking of the cell wall polymers; however, the penetration of NMM into the cell wall was not established for the treatment. Bulking which is a good indicator for cell wall penetration was reportedly low after NMM treatment (Lukowsky 2002).

CONCLUSIONS

These studies show that Lewis acid catalysts such as $MgCl_2$ at acidic pH significantly contribute to tensile strength loss because of hydrolysis of cell wall polysaccharides. In addition, application of DMDHEU without catalyst induced considerable decrease in strength. Therefore, it can be assumed that incorporation of DMDHEU in the cell wall and cross-linking of cell wall polymers also reduces tensile strength. Strength losses due to treatment with catalysed DMDHEU were regarded as the sum of single strength losses caused by $MgCl_2$ and by DMDHEU alone. In contrast, GA alone did not cause any tensile strength losses, but when GA was combined with $MgCl_2$, the strength reduction was clearly higher than that of $MgCl_2$ alone. In addition, the strength losses tended to increase with increasing WPG, *i.e.* with the degree of cross-linking. Therefore, it can be assumed that cross-linking has high influence on strength loss. The finding, however, that NMM treatment did not cause any strength loss is contradictory to this hypothesis. Further studies are therefore necessary to distinguish the influence of polysaccharide hydrolysis and cross-linking on tensile strength of wood.

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Kinetic Studies on Etherification of some Lignin Model Compounds

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Keywords: Activation energy, etherification, lignin

ABSTRACT

In outdoor applications wood gets discoloured due to exposure to sunlight. Similarly bleached printing papers made of mechanical wood pulps are rapidly yellowed in sunlight. The main cause of such photo induced colour change is the light absorption by phenolic groups in lignin, which initiates photochemical reactions leading to degradation of lignocellulosic materials. Esterification and/or etherification of these free phenolic groups have been found to inhibit such photo-discoloration. The study of kinetics of lignin model compound is very important to get the precise idea of optimum reaction conditions. In this paper, we have investigated the reaction between lignin model compounds (*viz*., phenol and guaiacol) and propylene oxide in aqueous media. The reaction products were characterized using GC-MS. The kinetics of etherification reaction between phenol and propylene oxide was investigated under varying pH conditions in the temperature range 30-60 ^{0}C. The extent of etherification of phenol and rate of chemical reaction was followed by using UV-Visible absorption spectroscopy. The rate constants were determined and the activation energy of the reaction was calculated using the Arrhenius equation.

INTRODUCTION

The etherification of phenolic groups has been found to inhibit photodegradation in lignin rich pulps (Singh 1966, Janson and Forsskahl 1989). The chemically modified wood with proplylene and butylene oxides has been reported to improve dimensional stability and induce resistance against fungi and termites (Rowell and Gutzmer 1975, Rowell and Ellis 1984).

The knowledge of kinetics of chemical reaction is important to find out the optimum reaction conditions and to understand the mechanism of reaction. Kinetic studies on chemical modification reactions of wood components and their model compounds are meager. There are only very few studies which deal with the kinetic aspects of solid wood and lignin model compounds (Hill and Jones 1996, Hill *et al.* 1998, Hill and Papadopoulos 2002,). It is practically difficult to obtain reproducible reaction kinetic parameter with solid wood due to its complex structure and heterogeneous nature. However, kinetic studies on individual wood component and their model compounds can provide useful information about these reactions. In this paper, we present some of our results on the study of the reaction kinetics of lignin model compounds with propylene oxides (PO) under varying pH conditions. This study is being conducted to find out suitable reaction conditions for the selective etherification of phenolic hydroxyl groups in solid wood and wood pulp.

EXPERIMENTAL

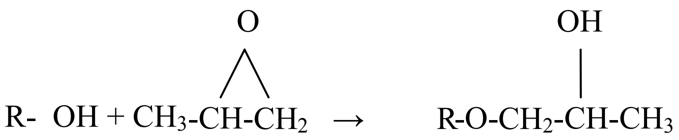
Phenol (Baker Analysed Reagent), guaiacol (Merck) and propylene oxide (Fluka) were used as received. The reaction between phenol and PO was carried out in a closed reaction vessel (25 ml capacity) fitted with magnetic stirrer at 30, 45 and 60 ^{0}C. The aqueous solution of Phenol (0.5M) was prepared under different pH conditions by varying concentrations of sodium hydroxide from 0.05M to 0.5M. The desired amount of propylene oxide (0.5 M) was added to 10 ml of preheated phenol solution in the reaction vessel using a micropipette, the vessel was then sealed and reaction was carried out up to 1h. Changes in pH of the solution during reaction were measured. The reaction was terminated by adding equivalent amount of acetic acid to neutralize the solution. The solution was allowed to cool down and diluted with water and 0.01 M sodium hydroxide solution to measure absorption spectra. Absorption spectra were measured using a UNICAM 5625 UV-VIS spectrometer.

The kinetics of the reaction between phenol and PO was followed by measuring changes in the absorbance of phenol at 312 nm in presence of PO at regular time intervals using a Shimadzu UV-240 UV-visible spectrophotometer. 3 ml of lignin model compound (5mM in 0.01 M NaOH solution) was taken in a quartz cuvette placed in the thermostated sample holder. After the temperature is attained, desired amount of PO (800mM) was added, the cuvette was closed with stopper and the optical density was measured at regular time intervals.

Samples for GC and GC-MS analyses were prepared by taking the desired amount of reacted solution (~ 1mg of the phenol/guaiacol) in a pointed shape flask (10 ml). 0.1 ml of internal standard (0.1 ml sorbitol in 1ml of methanol) was added to the solution and solution was vacuum dried. The dried sample was dissolved in 0.5 ml of pyridine and the solution was trimethyl silylated by adding 0.25 ml of (BSTFA + 5% TMC). GC and GCMS were recorded using a Shimadzu GC-17A Gas Chromatograph and FISONS Instruments GC 8000 Series, respectively.

RESULTS AND DISCUSSION

The reaction scheme for etherification of phenolic compound with PO is as following:



$$\mathrm{R\text{-}\ OH + CH_3\text{-}\overset{O}{CH\text{-}CH_2} \rightarrow R\text{-}O\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}CH_3}$$

The reactivity of the reaction can be enhanced by converting the phenols into ionic form by dissolving in aqueous solution of sodium hydroxide.

$$\mathrm{R\text{-}OH + NaOH \rightarrow R\text{-}O^-Na^+ + H_2O}$$

The reaction between phenol and PO is indicated by increase in pH of the reaction mixture with increasing reaction time. The changes in pH after one hour of reaction at different temperatures are summarized in Table 1. The change in pH increases with increase in the initial pH of the phenol solution.

Table 1: Increase in pH (ΔpH) of the solution after 1h reaction between phenol (0.5M) and PO (0.5M) at different temperatures

[NaOH] [M]	ΔpH		
	$30\ ^0C$	$45\ ^0C$	$60\ ^0C$
0.05	-	0.14	0.19
0.1	0.18	0.22	0.37
0.2	0.20	0.5	1.15
0.5	0.47	0.81	-

Absorption spectra

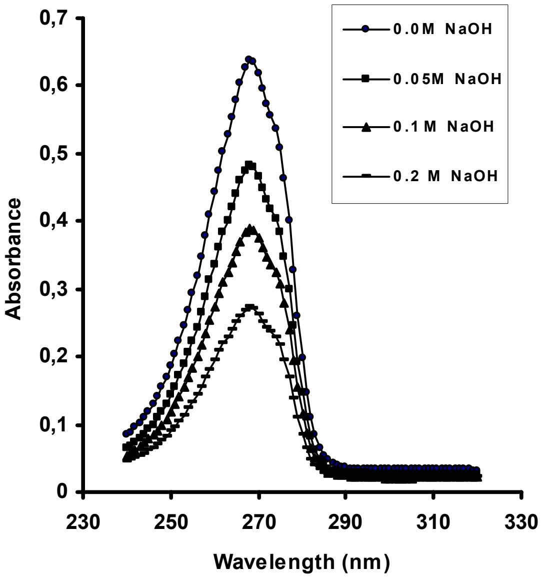


Figure 1a: Absorption spectra of phenol (0.5 M) + PO (0. 5M) after 1 h reaction at different NaOH concentrations at 60 ^0C. The solution was diluted to 5 x 10^{-4} M concentration with water

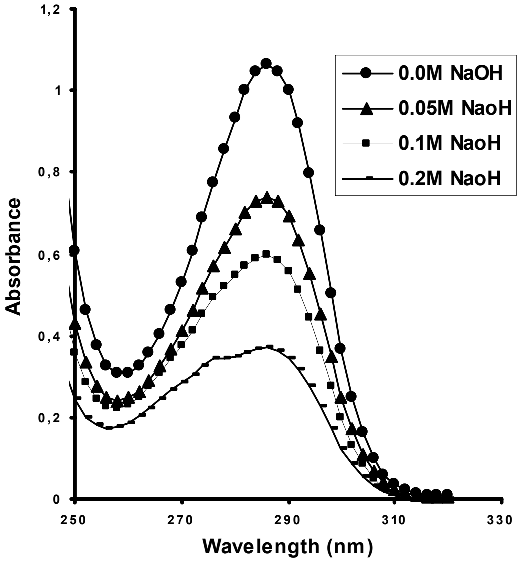


Figure 1b: Absorption spectra of phenol (0.5 M) + PO (0.5 M) after 1 h reaction at different NaOH concentrations at 60 ^0C. The solution was diluted to 5 x 10^{-4} M concentration with 0.01 M NaOH

Figure 1a shows the effect of pH (NaOH concentration) on the reaction between phenol and PO. The decrease in the absorbance of phenol indicates the reduction in the concentration of phenol due to its reaction with PO. Absorption spectra of the reacted solution diluted in 0.01 M NaOH are shown in Figure 1b. The ionization of phenol in NaOH solution results in a red shift in the absorption spectrum. The decrease in the absorption of ionic phenol accompanied by development of absorption peak at shorter wavelength, which corresponds to etherified phenol, provide the evidence for reaction between phenol and PO at higher pH conditions. Similarly, there was a significant decrease in the absorbance accompanied by appearance of absorption band at shorter wavelength (maximum ~ 275nm) corresponding to etherified guaiacol (Figure 2).

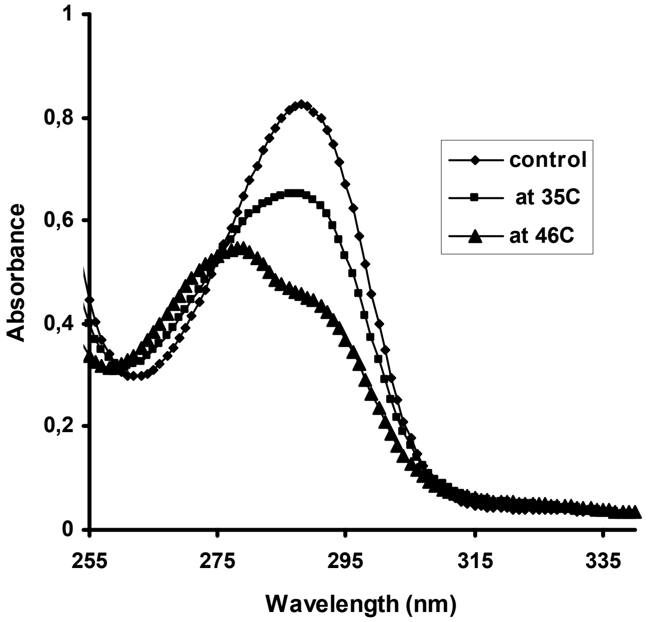


Figure 2: Absorption spectra of guaiacol (5mM) after 1h reaction with PO (1600mM) at different temperatures in 0.01 M NaOH. The solution was diluted to 2 x 10^{-4} M concentration of guaiacol

GCMS

Gas chromatogram of reacted phenol solution shows two products at 11.55 and 28.74 min reaction time (Figure 3). The peak at a retention time of 28.74 min corresponds to sorbitol (internal standard). The peak at a retention time 11.55 min, relative intensity of which increases with increase in NaOH concentration corresponds to etherified phenol. The presence of signal at 11.55 min, which was absent in the GC of unreacted phenol provides evidence for the reaction. GC-MS shows main product having molecular weight 224.2 and fragments at 209.1, 151.1, 135.2, 117.1, 90.9, 77.1 and 73.1. These mass numbers agree with the reaction scheme shown above.

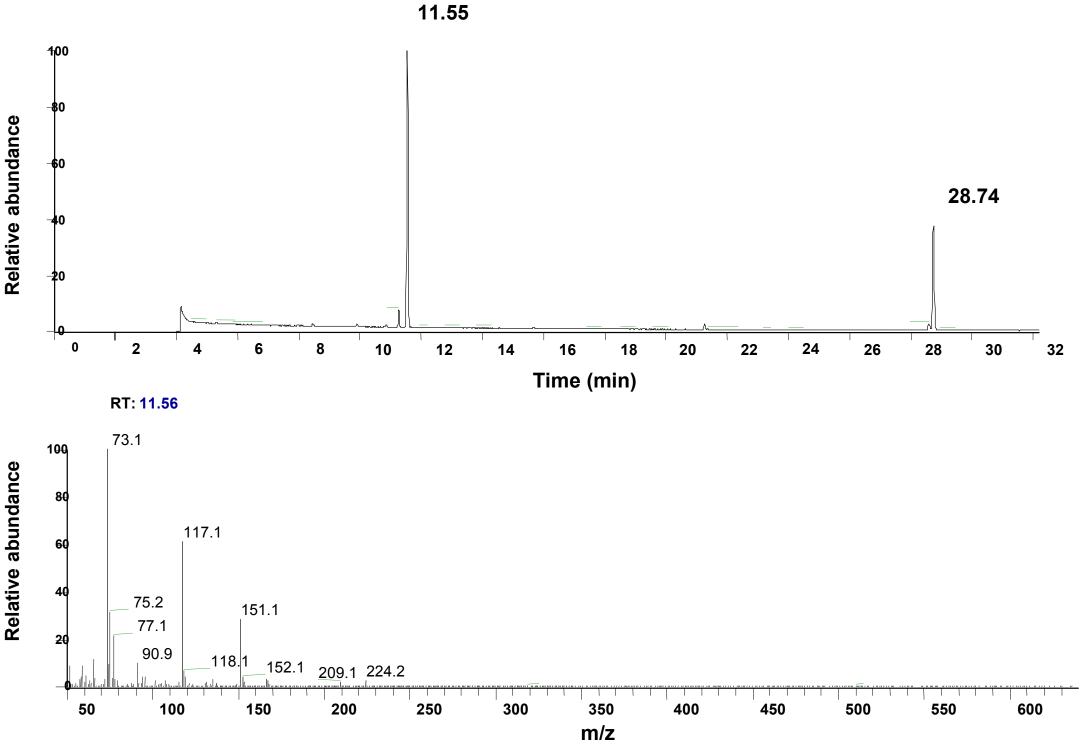


Figure 3: GC-MS of reaction between phenol and PO

The Gas chromatogram of pure guaiacol show peaks at ~ 7.47 min and 28.59 min which correspond to guaiacol and sorbitol (internal standard), respectively. In the GC of reacted guaiacol solution the peak at 7.47 min disappears, whereas a new peak corresponding to etherified guaiacol develops at 16.86 min (Figure 4). The relative intensity of peak at 16.86 min increases with increase in the temperature and concentration of PO. The GC-MS shows main product at a molecular weight of 254.3, which corresponds to etherified guaiacol and fragments at 196.3, 181.2, 166.2, 151.2, 131.2, 124.2, 109.2, 95.2, 77.2 and 75.2. These values agree well with the reaction scheme between guaiacol and PO given by Equation 1.

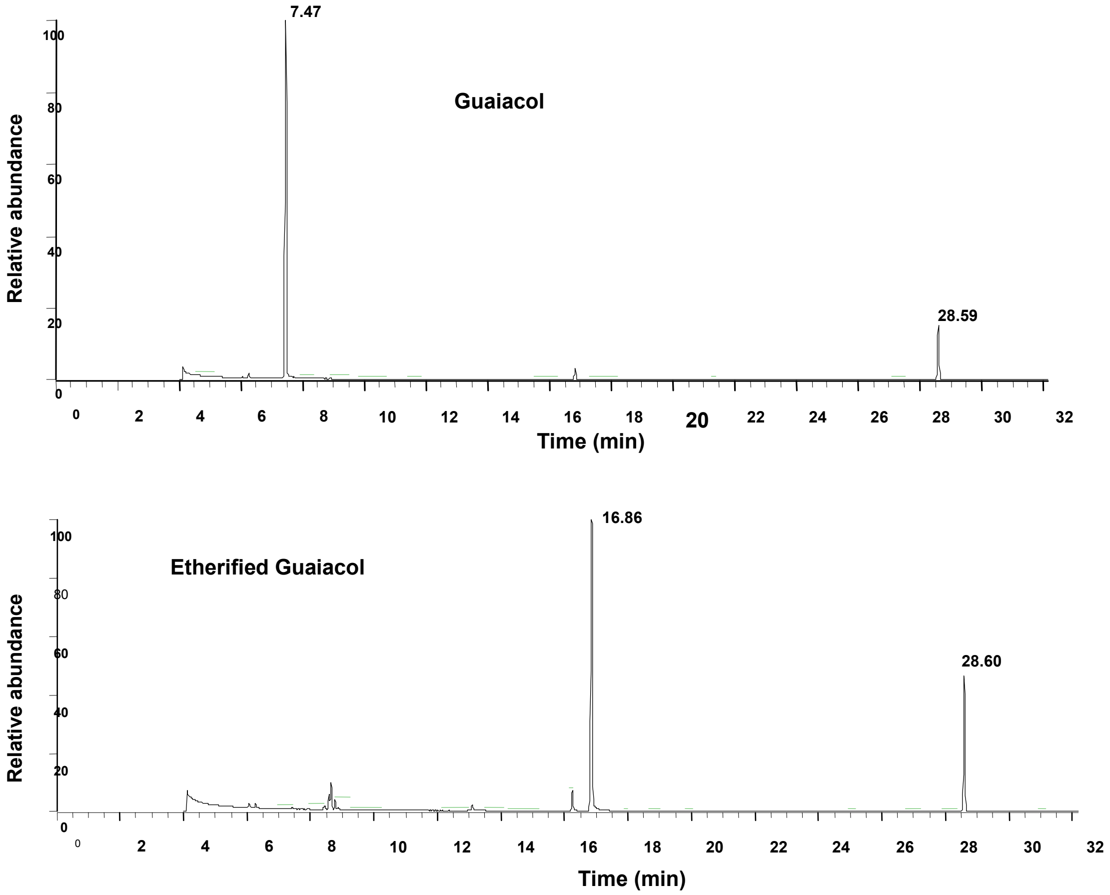


Figure 4: GC-MS of unreacted and etherified guaiacol

Kinetics of reaction

The kinetics of chemical reaction was followed by UV visible spectroscopy according to the procedure described under experimental section. The absorbance decreased linearly with time and reaction followed first order kinetics given by following Equation 1:

$$A = A_0 \, e^{-k[PO]t} \qquad (1)$$

where A_0 is the absorbance of phenol without reaction, k is the rate constant and [PO] is the concentration of propylene oxide. Typical kinetic data of the reaction of phenol with PO are shown in Figure 5. The absorbance decay data were fitted with an exponential function Equation 1 and the rates at the different temperatures were determined. The reaction rate increases with increase in the reaction temperature.

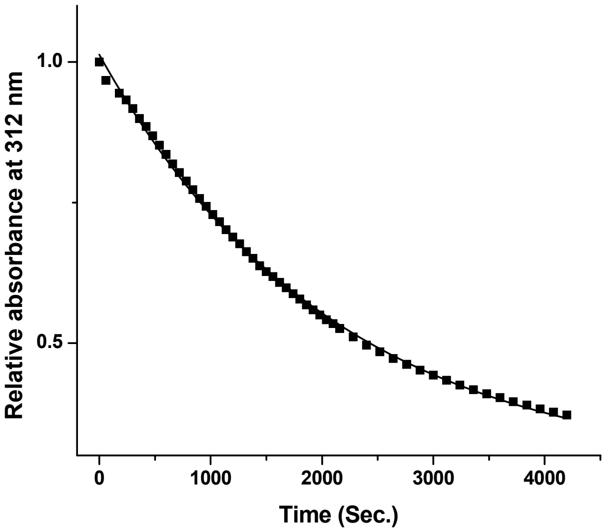


Figure 5: Kinetic profile of reaction between phenol (5mM) and PO (800 mM) at 58 ^{0}C

The value of activation energy (E_a) was calculated from temperature dependence of reaction rate constants by using the well known Arrhenius Equation 2:

$$k = A\ e^{-(Ea/RT)} \qquad (2)$$

where R is the universal gas constant, A is the pre-exponential or collision factor and T is the absolute temperature. The value of activation energy calculated from the gradient of Figure 6 comes out to be 57.2 kJmol^{-1}.

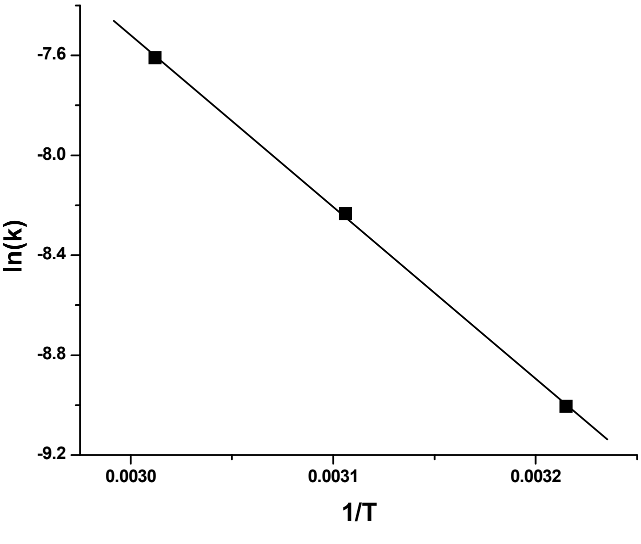


Figure 6: Plot of ln (k) vs 1/T for the reaction between phenol and PO

CONCLUSIONS

The probability of etherification reaction between phenolic compounds and propylene oxide at neutral pH conditions is small. UV visible spectra and GC-MS provide clear evidence of etherification reaction at higher pH. The rate of reaction increases with temperature and concentration of epoxide, reaction following first order kinetics. The activation energy of reaction between phenol and propylene oxide was 57.2 kJmol^{-1}.

ACKNOWLEDGEMENTS

The Finnish Funding Agency for Technology and Innovation (TEKES) as well as Andritz, UPM-Kymmene, Kemira, Metso, and M-real corporations are acknowledged for the financial support. The authors also thank Timo Pääkkönen for his skilful laboratory assistance.

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A Novel Route to Wood Modification by Transesterification with Vinyl Esters

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Keywords: ^{13}C CP-MAS NMR; chemical modification; FTIR; transesterification; vinyl esters; wood

ABSTRACT

A novel route to wood modification by transesterification of vinyl esters is proposed in the current study. The transesterification reaction between varied commercial vinyl esters and the hydroxyl groups of maritime pine sapwood (*Pinus pinaster* Soland) has been investigated, in the presence of potassium carbonate as a catalyst. Preliminary experiments were performed with vinyl acetate as a model reactant: the efficiency of the reaction was found to increase with increasing temperature, reaction time and catalyst amount but a significant WPG was obtained after only 3 h at 90 °C. These conditions were later applied to a selection of commercial vinyl esters bearing varied functionalities and led to esterified wood in high yield. All reactions were confirmed by FTIR and ^{13}C CP-MAS NMR spectroscopy.

INTRODUCTION

The chemical modification of wood has proven to be a very effective means to ameliorate the material properties (Hon 1996, Hill 2006). Among the many reactions envisaged, esterification from acid anhydrides has received the most attention and has been reported to greatly improve a number of wood properties, such as dimensional stability, fungal resistance, photostability or weathering resistance (Hill and Jones 1996, Evans *et al.* 2000, Larsson Brelid *et al.* 2000, Chang and Chang 2001, Papadopoulos and Hill 2002). One of the major drawbacks with this esterification process is that a carboxylic acid is released as a by-product. This compound cannot be totally removed from bulk wood after reaction, leading to a residual smell, strength loss of the material or corrosion of metal fasteners (Simonson and Rowell 2000, Li *et al.* 2000). In this context, a new esterification method based on the transesterification reaction between wood hydroxyl groups and vinyl esters is proposed.

EXPERIMENTAL

Wood treatment

Maritime pine sapwood (*Pinus pinaster* Soland) was ground in a Wiley mill to pass a 0.5 mm screen. Prior to use, the sawdust was extracted in a Soxhlet apparatus with a toluene:ethanol mixture (2:1/v:v) for 8 h then with water for an additional 8 h. Wood was then oven dried at 105 °C for 16 h. All chemical reactions were performed under a standard set of conditions: 1 g of dry extracted sawdust was modified by a 20 ml DMF solution containing 14 mmol vinyl ester. Varied temperatures, reaction times and catalyst concentrations (K_2CO_3) were used. All modified materials were subsequently Soxhlet extracted with water for 2 h to eliminate K_2CO_3, then with a toluene:ethanol:acetone mixture (4:1:1 v/v/v) for 8 h to eliminate all non-bonded chemicals (i.e. unreacted compounds and by-products formed). Samples were finally oven-dried at 105 °C for 16 h and the weight percentage gain after reaction (WPG) was calculated.

Infrared spectroscopy (FTIR)

Infrared absorption spectra of treated and unmodified wood were obtained with the potassium bromide technique (KBr), using a Perkin-Elmer Paragon 1000 PC FTIR spectrometer, at a resolution of 4 cm^{-1} (50 scans). In each case, 3% w/w of dry sawdust was dispersed in a matrix of KBr and pressed to form pellets.

^{13}C CP-MAS NMR spectroscopy

Solid-state ^{13}C CP-MAS NMR spectra of treated and unmodified sawdust were performed at room temperature on a Bruker DPX-400 NMR spectrometer, using MAS rates of 4 to 8 kHz, at a frequency of 100.61 MHz. Samples were packed in MAS 4 mm diameter zirconia rotors. Chemical shifts were relative to tetramethylsilane used as external standard. All the spectra were run for 15 h (25000 scans).

RESULTS AND DISCUSSION

Transesterification is a process where an ester is transformed into another through interchange reaction of the alkoxyl moiety. Since the reaction is an equilibrium, continuous removal of the alcohol produced is indispensable to obtain the desired ester in good yield. But with enol esters, the vinyl alcohol formed during the process tautomerizes to acetaldehyde and the equilibrium is naturally shifted towards the ester formation. The interchange reaction between alkoxyl (or phenoxyl) groups of wood and vinyl ester should therefore lead to the formation of esterified wood with acetaldehyde as a by-product (Figure 1). Unlike carboxylic acids, acetaldehyde is a highly volatile compound (bp_{760} = 21 °C) than can be easily removed from wood after reaction.

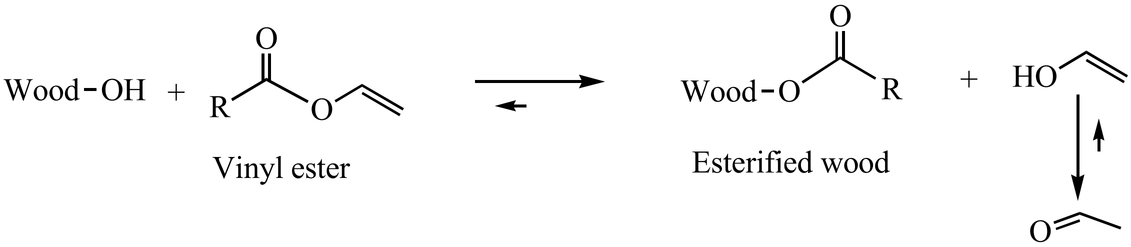

Figure 1: Esterification of wood by transesterification reaction between wood hydroxyl groups and vinyl esters

Acetylation of wood with vinyl acetate

The feasibility of the transesterification reaction was first investigated, with vinyl acetate (VA) as a model vinyl ester (R = CH_3 in Figure 1). The reaction was performed on maritime pine sapwood sawdust (*Pinus pinaster* Soland), with dimethylformamide as a solvent and potassium carbonate as a catalyst. Preliminary reactions were performed in following conditions: 3 hours at 110 °C, with 1.1 mmol of K_2CO_3/g dry wood. Under these conditions, a WPG of 26.2% was measured, indicating that a significant amount of chemicals remained bound in the wood after reaction. The characteristic vibrations of the grafted acetyl groups were easily identified in the FTIR spectra (Figure 2): namely the carbonyl stretching vibration at 1750 cm^{-1} ($\nu_{C=O}$), the C-O stretching vibrations between 1196 and 1298 cm^{-1} ($\nu_{C\text{-}O}$) and the methyl vibrations at 2953 cm^{-1} ($\nu_{C\text{-}H}$), 1375 cm^{-1} ($\delta_{C\text{-}H}$) and 900 cm^{-1} ($\gamma_{C\text{-}H}$). Although the vibration at 600 cm^{-1} has not been clearly identified, it was associated with the presence of acetyl groups in wood.

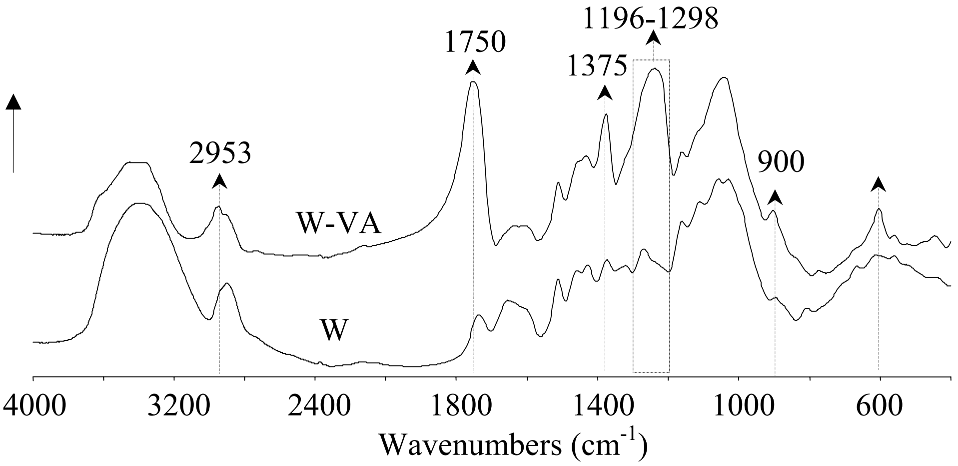

Figure 2: FTIR spectra of unmodified wood (W) and wood acetylated with vinyl acetate (W-VA; WPG = 26.2%)

The ^{13}C CP-MAS NMR spectra are presented in Figure 3. After reaction with VA, the carbons of the grafted acetyl groups appeared clearly at 173 and 23 ppm. A few changes were also observed between 60 and 110 ppm, indicating that the cellulose and/or hemicelluloses were modified. Although not demonstrated yet, the modification of lignin is also very likely (lignin is generally more accessible to chemical reactants than cellulose).

Table 1: Weight percentage gains (WPG) after acetylation of wood by vinyl acetate in varied conditions: impact of the reaction temperature, reaction time and catalyst amount

Reaction temperature (°C)[a]	25	50	90	110	130	150
WPG (%)	0.8	9.5	24.6	26.2	27.2	27.9
Reaction time (min)[b]	10	30	60	180	360	960
WPG (%)	2.8	7.5	22.3	24.6	26.7	25.6
K_2CO_3 amount (mmol/g dry wood)[c]	0	0.05	0.1	1.1	10.7	21
WPG (%)	0	0.052	5.71	24.6	24.8	26.9

[a] Reaction time was 3 h and K_2CO_3 amount was 1.1 mmol/g dry wood
[b] Reaction temperature was 90°C and K_2CO_3 amount was 1.1 mmol/g dry wood
[c] Reaction time was 3 h and reaction temperature was 90°C

The acetylation reaction with VA was further studied as a function of temperature, reaction time and catalyst amount. The WPG's obtained under these different conditions are listed in Table 1. The efficiency of the transesterification reaction with VA was found to increase with increasing temperature, reaction time and catalyst amount. No acetylation occurred without catalyst, emphasizing the importance of the potassium carbonate in the reaction process. The significant WPG obtained after only 1 h indicates that the reaction with VA was rapid. All these modifications were confirmed by FTIR spectroscopy (results not shown).

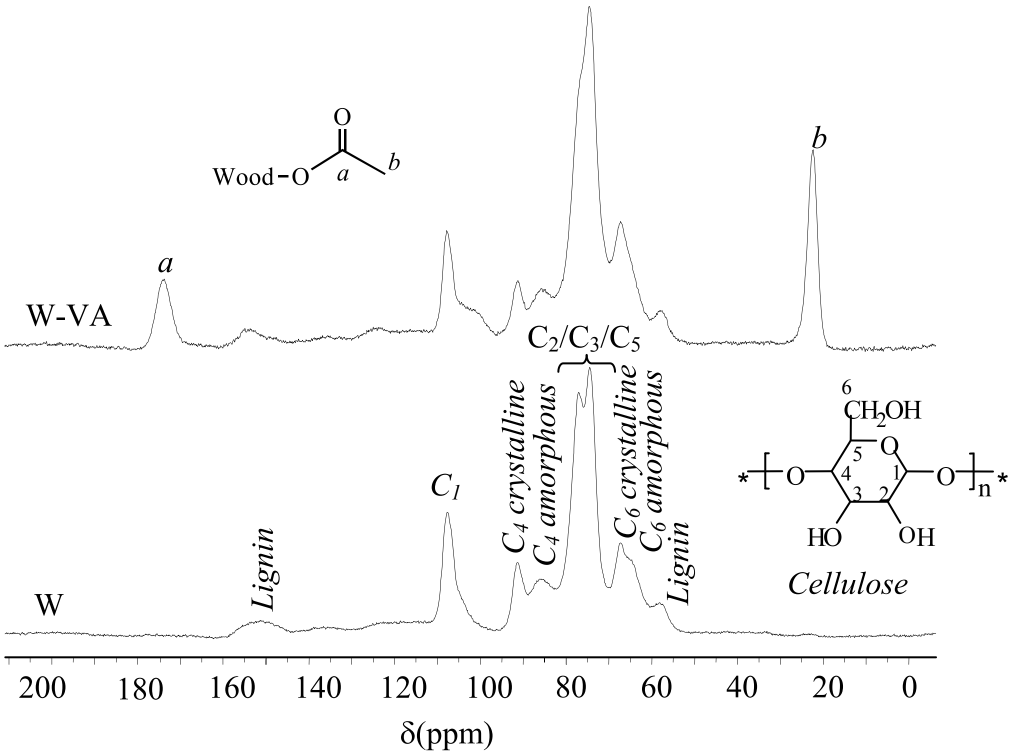

Figure 3: ***^{13}C CP-MAS NMR spectra of unmodified wood (W) and wood acetylated with vinyl acetate (W-VA; WPG = 26.2%)***

Application to other vinyl esters

The transesterification reaction was later applied to a selection of commercial vinyl esters bearing varied functionalities (Table 2). Since the VA-acetylation was nearly complete after only 3 h reaction at 90 °C (with 1.1 mmol K_2CO_3/g of dry wood), these relatively mild conditions were selected for these new investigations.

The significant WPG's obtained after the different reactions indicate that transesterification with vinyl esters is a valuable method to graft varied functionalities in wood, in mild conditions. All reactions have been confirmed by FTIR and ^{13}C CP-MAS NMR spectroscopy (results not shown).

Table 2: Weight percentage gains (WPG) obtained after esterification of wood with varied vinyl esters

Vinyl esters (R-COO-CH=CH$_2$)	R	WPG (%)
Vinyl propionate	$-CH_2-CH_3$	23.6
Vinyl butyrate	$-CH_2-CH_2-CH_3$	30.0
Vinyl pivalate	$-C(CH_3)_3$	15.2
Vinyl décanoate	$-CH_2-(CH_2)_7-CH_3$	49.6
Vinyl stearate	$-CH_2-(CH_2)_{15}-CH_3$	52.2
Vinyl cinnamate	$-CH=CH-C_6H_5$	46.3
Vinyl crotonate	$-CH=CH-CH_3$	16.8
Vinyl methacrylate	$-C(CH_3)=CH_2$	24.8
Vinyl benzoate	$-C_6H_5$	46.5
Vinyl 4-*tert*-butylbenzoate	$-C_6H_4-C(CH_3)_3$	31.8

CONCLUSIONS

A novel method based on the transesterification of vinyl esters has been proposed for the modification of wood. The grafting of the ester moieties in wood has been confirmed by WPG calculations, FTIR spectroscopy and ^{13}C CP-MAS NMR analysis. This transesterification method has a clear advantage compared with the classical esterification route from acid anhydrides: the acetaldehyde produced as a by-product is a non-acidic compound with a low boiling point that do not provoke acidolysis reactions and can be easily removed from wood after reaction. Control experiments performed without solvent or catalyst indicated that the presence of potassium carbonate and DMF was required in the conditions tested. A solvent-free reaction cannot be ruled out at this stage of the study but more investigations are needed to first clarify the reaction mechanism.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Agence Nationale de la Recherche (ANR) that financially supported this work.

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Acetylated Wood – Results from Long-term Field Tests

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Keywords: Acetylation, Scots pine, EN 252, EN 275, durability, coating systems

ABSTRACT

The effectiveness of acetylation as a method to increase the durability of wood has been demonstrated in several studies over the last sixty years, starting with pioneers like Tarkow, Stamm and Goldstein. Nevertheless, as acetylated wood has now reached large scale production, the importance of long term-field test data on the performance of acetylated wood has increased. Firstly, this paper will address a project started in 1991, where acetylated Scots pine is tested in a full EN 252 test. The test is still running in Nordic NWPC test fields, Simlångsdalen in Sweden and in Viikki, Finland. The results show that irrespectively of test field, pine wood test stakes with an acetylation level of about 22% (expressed as acetyl content) were as durable as the CCA treated wood at a high retention level (10.3 kg/m^3) after 15 years in ground contact. Secondly, acetylated wood (acetyl content 22%) is also being evaluated under marine conditions in Kristineberg on the Swedish west coast, according to EN 275 (marine borer resistance). The test has been running since 1999 and the X-ray rating shows a slight attack by marine borers after eight years in test, whereas the untreated controls failed after only one year. If the acetylation (acetyl content 21%) is followed by a post treatment with melamine resin (weight gain 19%) no attack could be observed after eight years. Thirdly, coated acetylated pine panels were exposed on rigs 45º facing south for 13 years, according to an early version of EN 927-3 in Ultuna and Malmö. The results indicate that acetylated wood in combination with a proper coating system, gives a considerably longer service life of the panels as compared to coated unmodified panels.

INTRODUCTION

By far, the most thoroughly studied wood modification method is acetylation with acetic anhydride (Goldstein *et al.* 1961, Rowell *et al.* 1986 a, b). Over the years, several authors have shown that properties of lignocellulosic material can be considerably improved by this modification method, primarily dimensional stability and resistance to biological degradation (Rowell *et al.* 1987, Nilsson *et al*. 1988, Takahashi *et al.* 1989). Like most wood modification methods, acetylation with acetic anhydride involves a reaction with wood hydroxyl groups, forming covalently bonded acetyl groups in the wood material and acetic acid as a by-product. The acetylated wood is non-toxic and has no harmful impact on the environment. Laboratory tests have shown considerably improved protection against attack by white, brown and soft-rot fungi. In this report, results from two test fields with acetylated pine wood, in ground contact for 15 years, are presented.

A few studies have been conducted on the resistance of acetylated wood to marine borers (Tarkow *et al.* 1950, Johnson and Rowell 1988, Larsson 1998, Borges *et al.*

2004). The results are somewhat diverging, but it can be concluded that the level of acetylation needs to be high in order to get a significant effect.

The increased dimensional stability gained by acetylation, also influence the field performance of coated wood panels, since a dimensionally stable wood material does not induce stress on the paint as it gets brittle.

EXPERIMENTAL

Field test according to EN 252

The acetylation was carried out according to Rowell *et al.* (1986 a, b). Scots pine sapwood samples *(Pinus sylvestris* L.), 25 x 50 x 500 mm: r x t x 1, were oven-dried for 12 hours at 80 °C in order to reduce the moisture content to about 4%. The wood samples were separated by small pieces of wood, placed in a reactor, and vacuum/pressure impregnated with acetic anhydride. After the impregnation step, excess chemicals were drained off. The impregnated wood samples were then reacted at 120 °C for 2 to 6 hours, giving different acetylation levels. After reaction, unreacted acetic anhydride and by-product acetic acid were evaporated during 2 hours by applying vacuum while still heating the wood. The wood samples were then oven-dried at 80 °C to constant weight (about 8 days). From each wood sample, wood particles were collected by drilling and used for analysis of acetyl content. The drilled hole was located 100 mm from the upper end of the stake wood sample as placed in the field. The degree of acetylation was determined as wood acetyl content (wt-%) for each wood sample, and was calculated from the amount of acetate liberated from oven-dry wood particles by treatment with 1M sodium hydroxide. The liberated acetate was determined by ion chromatography. The acetylated wood samples were divided into three groups depending on their acetyl content, as shown in Table 1. For each group, 30 stakes were tested in ground contact.

Table 1: The acetyl content range and average value of pine wood stakes in the field test

Group	Acetyl content [%]	Average value in field test [%]
1	14.5-18.1	16.6
2	19.5-20.1	19.8
3	20.8-23.8	22.0

The stakes were set out in Oct. 1991 in Simlångsdalen in the southwest of Sweden and in Viikki, situated near Helsinki in Finland. The soil type at the test site in Simlångsdalen is a sandy soil and the prevailing type of decay is brown-rot and soft-rot. At the test site in Viikki, the soil type is loam, and the prevailing type of decay is soft-rot and brown-rot. The mean daily temperature in Simlångsdalen is 6.4 °C and in Viikki 4.8 °C. The annual mean precipitation is 1053 mm in Simlångsdalen and 700 mm in Viikki. For each group of acetylated stakes and each retention level of the reference preservatives, 20 stakes were set out in Simlångsdalen and 10 in Viikki. The stakes were installed at random at the test sites and buried to half of their length. Inspection of the stakes was carried out in autumn every year. The extent of decay was graded according to the scale in Table 2.

Table 2: The grading of decay used in this study.

Condition	Grading of decay	Index of decay
Sound-no decay	0	0
Slight decay	1	25
Moderate decay	2	50
Severe decay	3	75
Very severe decay (stake rejected)	4	100

By adding the index of decay for the stakes of each group and dividing the sum by the number of stakes, the average index of decay for each preservative and retention level is obtained. When all stakes in a group have failed (average index of decay = l00), the average service life is calculated.

Marine test according to EN 275

The wood material used in this test was sapwood of Scots pine (*Pinus sylvestris* L.). The acetylation was performed in the same way as for the field test (EN 252). Two levels of post treatment of acetylated pine with methylated melamine resin (MMF resin) were also included. As references, wood samples were treated with CCA (Chromated copper arsenate) preservative to two CCA retention levels.

In each marine test samples, a centre hole of 25 mm in diameter was drilled before the installation on the test rigs. The test rigs were placed in the bay outside Kristineberg Marine Research Station, on the west coast of Sweden, and the test was performed according to EN 275. The water temperature varies between 18-22 ºC in the summer and -1.5 ºC in mid-winter. Salinity varies between 26 psu and 34 psu. Borer activity (the characteristics listed are for the actual test site): gribble *Limnoria lignorum* (Rathke) was present but not very active; *Teredo navalis* L. (most occurring mollusc specie) up to 7 cm length during one growth season; *Nototeredo norvagica (Spengler)*, up to 15 cm length during one growth season. There is borer activity all around the year. The most common borer specie, *Teredo navalis*, was active 11 months out of 12. The service life of untreated controls is approx. 1.5 years. Acetylated samples together with unmodified and preservative treated samples were randomly hung on a ladder-like rig and submerged in the seawater. The rig was placed on the sea-bed at a depth of 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. The test was started in 1999. Annually, the rigs were taken out of the water for identification and determination of the extent of fouling. Attack by marine borers was evaluated by X-ray.

Wood coating performance according to EN 927-3

Scots pine panels (*Pinus sylvestris* L.), acetylated in the same way as for the field test (EN 252), were coated with two coating systems. The first was an alkyd system (alkyd primer + alkyd top) and the second was an acrylic system (alkyd primer + acrylic top). The panels were exposed on rigs 45º facing south for 13 years, according to an early version of EN 927-3 in Ultuna and Malmö.

RESULTS AND DISCUSSION

Field test according to EN 252

The wood stakes were examined annually and the extent of decay was expressed as the average index of decay for each treatment group. The use of untreated controls and CCA preservative treated wood samples also indicates the aggressiveness of the individual field. The results obtained show that the acetylation caused a major improvement in decay resistance of wood. The resistance of acetylated wood with an acetyl content of about 22% is in the same range as that of wood impregnated to the higher level of CCA preservative. Results after 15 years in test at the test field in Simlångsdalen are presented in Table 3, and the corresponding results from Viikki are presented in Table 4.

Table 3: Average decay rating after 15 years for acetylated pine wood stakes at the test site in Simlångsdalen, Sweden.

Wood Preservative	**Retention [kg/m^3]**	**Number of stakes**	**Number classified Sound**	**of stakes as Rejected**	**Index of decay 15 years**	**Aver. life [years]**
NWPC Standard[1]	2.0	20	-	20	100	4.7
NWPC Standard[1]	8.8	20	-	3	54	-
EN Ref. CCA[2]	2.0	20	-	20	100	3.3
EN Ref. CCA[2]	10.3	20	-	-	46	-
Wood Modification	**Acetyl Content [%]**					
Untreated	1.8	20	-	20	100	1.6
Acetylated	16.6	20	-	14	88	-
Acetylated	19.8	20	-	4	65	-
Acetylated	22.0	20	-	2	54	-

[1] *CuO*	*19.0 wt-%*	[2] *$CuSO_4 \cdot 5H_2O$ wt-%*
CrO_3	*36.0 wt-%*	*$K_2Cr_2O_7$ wt-%*
As_2O_5	*45.0 wt-%*	*$As_2O_5 \cdot 2\ H_2O$ wt-%*

Table 4: Average decay rating after 15 years for acetylated pine wood stakes at the test site in Viikki, Finland.

Wood Preservative	**Retention [kg/m^3]**	**Number of stakes**	**Number classified Sound**	**of stakes as Rejected**	**Index of decay 15 years**	**Aver. life [years]**
NWPC Standard[1]	2.0	10	-	20	100	9.1
NWPC Standard[1]	8.8	10	-	1	55	-
EN Ref. CCA	2.0	10	-	20	100	8.1
EN Ref. CCA	10.3	10	-	-	60	-
Wood Modification	**Acetyl Content [%]**					
Untreated	1.8	10	-	20	100	2.9
Acetylated	16.6	10	1	3	65	-
Acetylated	19.8	10	4	0	40	-
Acetylated	22.0	10	5	0	20	-

[1], [2] *See Table 3*

The average index of decay after 15 years exposure in Simlångsdalen was in the range of 50 both for the NWPC Standard preservative and the EN Reference CCA preservative. The same index of decay was obtained for acetylated test stakes having an average acetyl content of 22%. Within this group, the acetyl content ranged from 21 to 23%. The comparatively higher index of decay obtained for stakes tested in Simlångsdalen is probably attributable to the higher brown-rot activity in Simlångsdalen than in the test field in Viikki.

Marine test according to EN 275

The acetylated samples were only slightly attacked after eight years (see Table 5), which is better than the performance reported by Larsson (1998), but in line with the results of Johnson and Rowell (1988). However, the acetyl content in the present study was higher than the acetyl content in Larsson's study, which may explain the better performance. Both groups of acetylated wood samples post-treated with MMF resin are still rated sound after 8 years, although the acetyl content was much lower for these (17 instead of 22%) which indicates a synergistic effect. The level of attack on CCA treated samples with high retention of CCA (18 kg/m^3) was very low, which seems is in line with earlier tests at this site, where this reference treatment usually gives a service life of up to 30 years.

The extent of gribble (*Limnoria lignorum)* 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 marine borers (*Teredo navalis* and *Nototeredo norvagica*) on control samples was extensive (see Figure 1), always leading to failure in one year.

Table 5: Condition of pine sapwood samples (25 x 75 x 200 mm) after 8 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, borer attack**	**Overall rating**	**Aver. life**
	WPG	**[kg/m^3]**		**sound**	**attacked**	**rejected**	**(0-4)**		**[years]**
Acetic anhydride (Ac)	22% AC		5	2	3	-	1.4	Slight	-
Ac + MMF	21+ 8		5	3	2	-	0.4	Sound	-
	21+19		5	5	-	-	0.0	Sound	-
CCA(NWPC[a]		4[b]	6	-	-	6	4.0	Failed	3.2
Standard No.1)		18[b]	6	5	1	-	0.5	Sound to slight	-
Untreated pine sap controls[c]	-	-	8+5+5+5+7+5+6+10	-	-	8+5+5+5+7+5+6+10	4.0[c]	Failed[c]	1.0[c]

[a] *Nordic Wood Preservation Council* [b] *CuO (19 wt-%); CrO_3 (36 wt-%); As_2O_5 (45 wt-%)*

[c] *New sets of controls tested each year*

Figure 1: Example of a unmodified control sample after 1 year of exposure

Wood coating performance according to EN 927-3

The coating system consisting of an alkyd primer followed by two layers of acrylic top coat, seems to work the best in combination with acetylated wood. Coated acetylated pine panels, exposed for 13 years, according to an early version of EN 927-3 in Ultuna and Malmö, showed a considerably improved service life when compared to unmodified coated panels (Figure 2).

Figure 2: Performance of acetylated coated panels after 13 years of exposure. The 4 panels on the right hand are aceylated and the others are unmodified controls. Prior to testing the panels were coated with alkyd primer followed by acrylic top coating

The acrylic coated acetylated wood panels were in good condition after 13 years in field, whereas the corresponding control panels from unmodified wood would have needed repainting already after 5 years. In the same trial, an alkyd coating system (alkyd primer + alkyd top) performed slightly poorer on acetylated panels than on the control panels, indicating that the more acidic surface of the acetylated panels increased the aging of the alkyd coating film (making it more brittle).

CONCLUSIONS

The considerably increased biological resistance of acetylated wood obtained in laboratory tests has been further verified in the in-ground field test in both Simlångsdalen and Viikki. The same average index of decay was obtained for acetylated samples with an acetyl content of about 21% as for the higher retention levels of the reference preservatives, after 15 years in ground contact.

Many types of modified wood have poor resistance to marine borers. However, acetylation followed by MMF-treatment seems to provide excellent resistance to marine borer attack even after eight years. The growth of fouling organisms did not seem to differ, when comparing modified and unmodified wood, indicating that the resistance of the modified wood is not a biocidal effect.

Evaluation after 13 years of exposure in the coating performance test showed that acetylated wood panels coated with acrylic top layer performed significantly better than the coated control panels.

ACKNOWLEDGEMENTS

Over the years many people have been involved in the evaluation of the EN 252 samples. Thank you, Östen Bergman, Marie-Louise Edlund, Thomas Nilsson, Nasko Terziev and Antti Nurmi, your help is gratefully acknowledged.

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Session 3: Resin / Surface Treatments.

Renewable Furfuryl Resin Technology for Wood Modification

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Keywords: Furfuryl resin, FA prepolymers, full cell impregnation, kiln technology, modified wood

ABSTRACT

A new resin system has been developed for the production of furfuryl polymer modified wood. This resin system is based on prepolymers of furfuryl alcohol (FA). The use of FA for chemical wood modification has already found its way to the market through the pioneering work of WPT (Norway). With prepolymers of FA (FA-pp) the technology platform of wood furfurylation is expanded. The absence of free furfuryl alcohol in these formulations simplifies the production process. Formulations based on prepolymers are VOC free, storage stable and ready to use waterborne solutions which can be impregnated in wood with a standard vacuum pressure impregnation vessel. After impregnation the wood is dried and cured in a kiln where a rigid polymer network is formed inside the cell wall. The actual modification of the cell wall can be visualized with fluorescence microscopy. Modification with this pre-polymer results in wood with high durability, improved dimensional stability and increased hardness. Non-refractory hardwood and softwood species, treated throughout the cross section can be upgraded to durable new materials. Next to these functional properties the process gives the wood an aesthetic light to dark brown color as is common with furfurylated wood. Adjustment of the amount of resin in the waterborne impregnation mix allows a whole range of modified woods, each specifically prepared to fit its final purpose *e.g.* decking, cladding, waterworks, joinery, flooring, *etc*.

INTRODUCTION

For the past 35 years TransFurans Chemicals has been producing furan chemicals from renewable raw materials. The Geel-based facility was established in 1972 as the European chemicals division of the American food group Quaker Oats. Since 1997 this facility operates under the name of TransFurans Chemicals (TFC). With an annual production capacity in excess of 30 000 tonnes, TFC operates the largest furfuryl alcohol plant.

Furfural, the raw material for furfuryl alcohol, is produced from the hemicellulosic part of agricultural wastes. A controlled high temperature digestion of this pentose based fraction yields furfural. With biomass as the sole raw material, it is a renewable and CO_2-neutral chemical. Technically furfural can be produced from any raw material which contains pentose. On industrial scale the pentosan (hemicellulose) content, price, local availability and cost of collection, transportation and handling of raw materials determine overall profitability. Corncobs and bagasse from sugar cane (Figure 1) are the major industrial feedstock for furfural production.

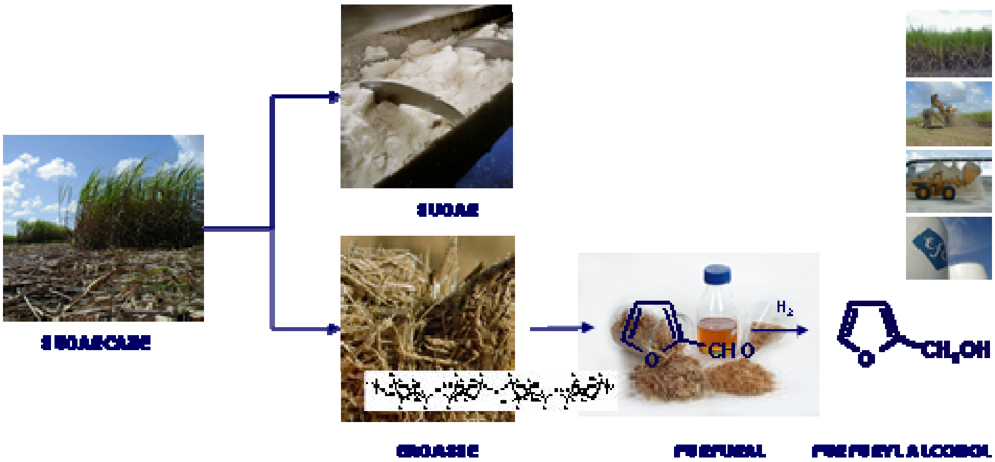

Figure 1: Production route of furfural and furfuryl alcohol from sugarcane

For over thirty years FURAN foundry resins have been extensively used to produce cores and molds for metal casting. Furfuryl alcohol is the major ingredient in FURAN foundry binders. In foundry industry Furan is a generic term of binders containing furfuryl alcohol and either urea and phenol formaldehyde or mixtures of both.

The use of furfuryl alcohol as a base chemical for wood modification was introduced in the 1960’s by Goldstein. The work of Goldstein was picked up in the 1990’s by Schneider and Westin who further developed the catalytic curing system. At the end of the 1990’s it was Wood Polymer Technologies ASA (now Kebony ASA) who introduced furfurylated wood successfully on a commercial scale. Recently Kebony ASA announced an additional furfurylation factory with an annual production capacity of 20 000m^3 modified wood.

Next to the production and supply of FA, TFC has developed a range of prepolymer systems of FA. These FA prepolymers (FA-pp) can be formulated as water-soluble resins which are free of solvents and monomeric furfuryl alcohol. With these new user-friendly chemicals TFC wants to support customers in the growing market of wood modification.

EXPERIMENTAL

Resin

For the modification on wood TFC has developed FA-pp resins under the trade name BioRez. These resins contain no organic solvents and can be diluted with water. Curing of BioRez resins occurs by an internal catalyst/hardener.

BioRez type resins are stored preferentially at 20-25 °C. At these temperatures the resin exhibits long term stability. At 20 to 25 °C the resin stability is about 3 months.

The resins can be mixed with water to any desired dilution. A dilution of 20% to 30% dry resin in water is advised to obtain a weight percent gain (WPG) of 20 to 40%.

Impregnation

(Diluted) resin can be impregnated in wood with a full cell autoclave process. Standard vacuum (-0.9 to -0.8 bar) and pressure cycles (7 to 12 bar) can be maintained. Liquid uptake is dependant on the wood species.

Drying – Curing

After impregnation the wood is dried with a conventional or accelerated drying program in a wood kiln. A conventional drying cycle is sufficient to prevent drying damage to the wood. Drying should be continued until the measured moisture content of the wood is around 15 - 20%. When this moisture content is reached the wood is heated to 130 °C for 16 h to allow curing of the resin. After 16 h temperature can be lowered to ambient. If conditioning of the wood is necessary to increase the moisture content after curing, the cool down period may be performed under high humidity.

RESULTS AND DISCUSSION

Modification of Scots Pine

Samples of Scots Pine sapwood (*Pinus sylvestris, L*) were impregnated with different aqueous concentrations of BioRez resin. After impregnation the samples were dried and cured at 130 °C. The weight percentage gain (WPG) was measured after treatment.

Physical properties

Modification with BioRez FA prepolymer resins results in an increase of dimensional stability of the Scots Pine. As can be seen in Figure 2 there is a relation between the polymer loading in the wood and anti shrink efficiency (ASE). Next to the reduction of swelling and shrinking of the wood, the wood becomes stiffer. The modulus of elasticity (MOE) increases with increasing WPG (Figure 3).

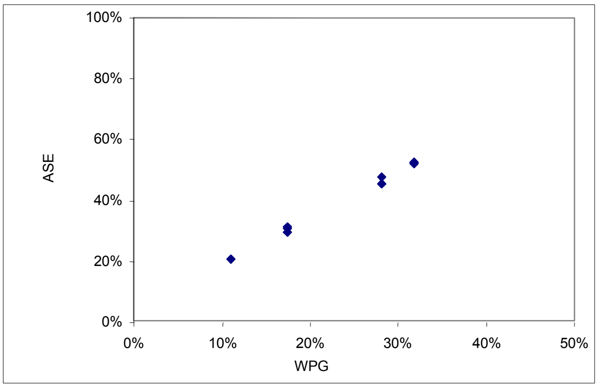

Figure 2: Relation between WPG and ASE of Scots Pine sapwood upon modification with FA-pp

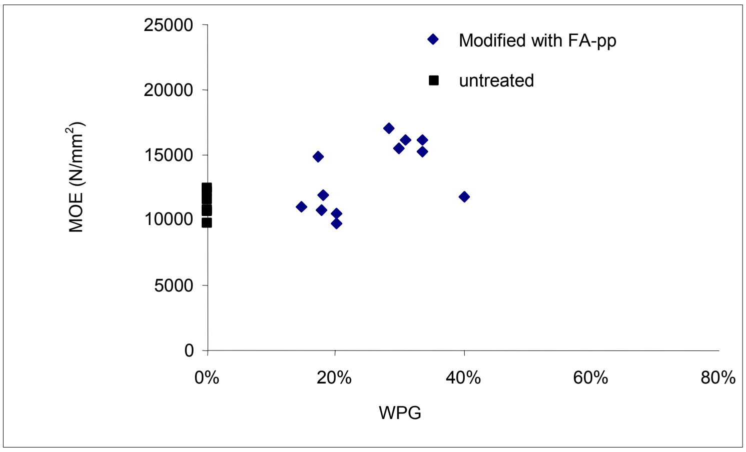

Figure 3: Relation between WPG and MOE of Scots Pine sapwood upon modification with FA-pp

Durability

As with furfuryl alcohol the furfurylated wood becomes more durable after treatment. The durability of pine treated with the furan resin was tested in soil contact (ENV 807) after 72 weeks and in contact with wood rot fungus *Coniphora puteana* (EN 113) after 6 weeks. Results are given in Figure 4 and Table 1.

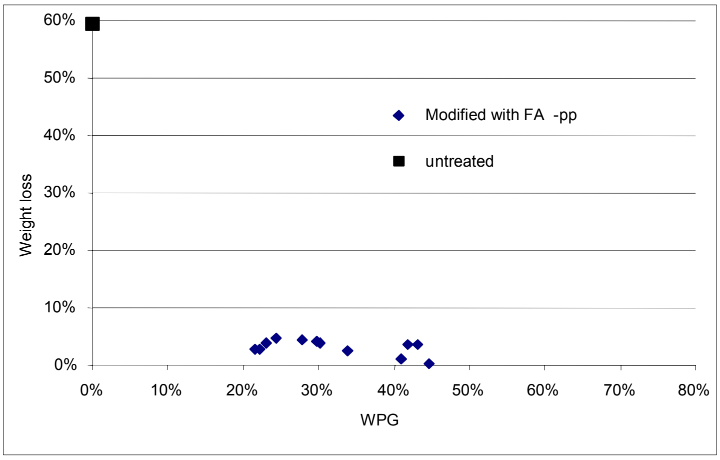

Figure 4: Relation between WPG and durability (ENV807) of Scots Pine sapwood upon modification with FA-pp

Table 1: Durability test (EN113) on Scots Pine sapwood untreated and upon modification with FA-pp

Scots Pine sapwood	WPG	Weight loss after 6 weeks
Untreated	0%	40%
Modified with FA-pp	29%	0.2%
Modified with FA-pp	45%	0%

The values the ENV807 soilbox tests were evaluated according to the EN350 method. According to the EN350 method (durability class determination) the treated wood has an x-factor between 0 and 0.1 which corresponds to a durability class of 1.

Modification of Radiata Pine

Another example of softwood treatment with BioRez is the modification of Radiata Pine. Radiata pine was treated with resin to obtain modified wood with different WPG. The natural durability of Radiata pine does not allow unprotected outdoor use. Table 2 gives an overview of the use of FA-pp modified Radiata Pine at different WPG compared to other wood species in an ENV807 ground contact test. Whereas the unmodified Radiata pine shows a high level of decay, FA-pp modified Radiata Pine has a durability comparable to Azobe even at a WPG level of 20%.

Table 2: Mass loss of modified Radiata Pine compared to reference samples in an ENV807 test

Wood species	WPG (%)	Weight loss after 20 weeks (%)
Reference Beech	/	57.3± 2.4
Reference Azobe	/	4.3± 1.4
Reference Scots Pine (sapwood)	/	26.8± 3.6
Reference Radiata pine	/	17.9± 6.9
Modified Radiata pine	20	3.1± 0.4
Modified Radiata pine	30	3.2± 0.3
Modified Radiata pine	50	3.1± 0.2
Modified Radiata pine	60	3.2± 0.2
Modified Radiata pine	70	4.0± 0.7
Modified Radiata pine	85	3.0± 0.2

Cell wall modification can be visualized with fluorescence microscopy (Figure 5). With an excitation wavelength of 488 or 688 nm polyfurfuryl alcohol can be made fluorescent. Figure 5 indicates that the fluorescent polyfurfuryl alcohol is completely present in the cell wall at a WPG of 20%. At this WPG the lumen does not contain polyfurfuryl alcohol.

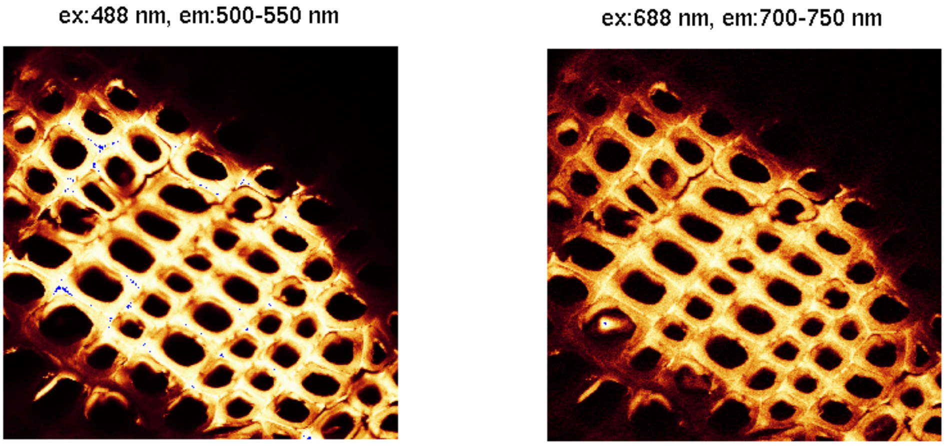

Figure 5: Visualisation of cell wall modification of the cured furan resin on Radiata Pine (WPG 20%) with fluorescence microscopy

CONCLUSIONS

The two case studies are an example of the potential of FA-pp modification of wood with BioRez. The results on Scots Pine and Radiata Pine indicate that these two wood species can be transformed to highly durable material. Furthermore, as with known modification by furfuryl alcohol the wood becomes stiffer and exhibits an improved dimensional stability. Wood modification with FA-pp targets the cell wall of the wood. With FA-pp technology TFC wants to support the emerging technology and market of wood modification. FA-pp technology allows a simplified conversion of wood by the use of traditional equipment of the wood industry and supports the pioneering companies active or interested in wood modification through furfurylation.

ACKNOWLEDGEMENTS

The authors wish to thank Lisbeth Garbrecht Thygesen of Danmarks Tekniske Universitet (BYG•DTU) for the fluorescence microscopy analysis. The authors also wish to thank the European Commission for the financial support in the 6th framework project ECOBINDERS (NMP2-CT-2005-011734).

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Bi-oleothermal© Treatment of Wood at Atmospheric Pressure: Biological Properties, Weatherability and Coatability

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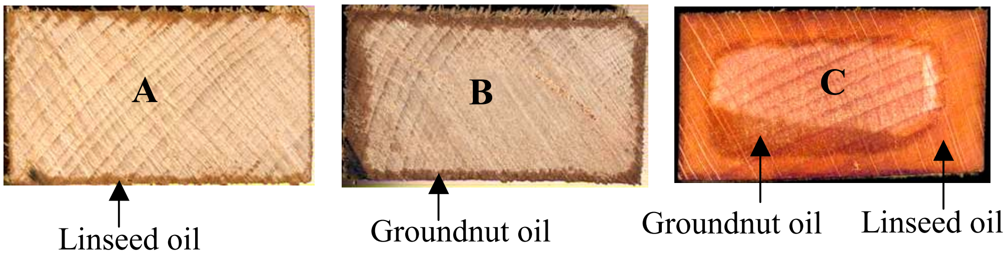
Keywords: Wood modification, oil treatment, fungi, insects, coating, weathering

ABSTRACT

Bi-oleothermal© process is a simple treatment which operates at atmospheric pressure and allows a deep impregnation of wood with hydrophobic products using cheap facilities. The process comprises two stages. The first one is a dipping of wood samples in a hot oil bath (between 110 °C and 200 °C). At the end of the first stage the wood contains a significant volume of vapour. The second one is a dipping in an oil bath but at a lower temperature (20 °C to 80 °C). In this second bath samples cooling leads to water condensation. A vacuum is created inside the samples which enables the oil to impregnate the wood. In this study, this process has been used to impregnate several wood species with different linseed oil compounds with and without addition of biocides. The resistance to wood destroying fungi has been assessed using a method adapted from EN 113. Results show that the linseed oil compounds lead to an increase in the natural durability. The resistance to termites and to house longhorn beetles has been assessed using EN 117 and EN 47 respectively. Wood treated with biocide-free oil is attacked by termites but afterwards the oil induces the death of the insects. The addition of biocide makes the wood completely protected from termite attack. EN 47 results show that 83% of mortality amongst the beetles is obtained with the biocide-free oil and 100% with the oil including biocide. The resistance of the treatment to weather has been studied using artificial weathering test according to EN 927-6. Results show that the coating provided by this process constitutes a low performing product compared to conventional stains. However the compatibility with a solvent-borne or a waterborne stain is shown, leading to good performances after artificial weathering.

INTRODUCTION

Environmental pressures have led to the development of new environmentally friendly methods of wood protection and to an increasing interest in wood modification. Amongst wood modification methods, thermal wood improvements have been developed and optimised for a considerable time. Most heat treatments are carried out at temperatures between 180 °C and 260 °C under low oxygen conditions. This has led to the idea of heating up the wood in hot oils as developed for example in Germany within the company Menz Holz. This treatment is performed in a closed process vessel. Hot oil is pumped from a stock vessel into the process vessel where the hot oil is kept at high temperatures circulating around the wood. Temperatures between 180 °C and 200 °C are used. Typical process duration for a whole treatment cycle is 18 hours (Rapp 2001, Homan and Jorissen 2004). A noticeably lower mass loss was determined for oil-treated specimens than for air-heated treated specimens when tested for resistance to *Coniophora puteana* in accordance with EN 113. A mass loss of less than 2% was found in the case of pine sapwood when oil-heat treatment (linseed oil) was applied at 200 °C (Rapp 2001). Another oil-based treatment usually referred to as “Royal Process” was developed and patented by Häger as a process for drying treated timber. The wet timber is placed in a treatment vessel which is then flooded with an oil heated to 60-90 °C. At the same time a vacuum is applied. Powell (Powell 2003) outlined the “Royale” process and the benefits of incorporating stabilising oil into the surface of timber. Recently there has been increasing interest in this technique and in the curing of wood preservatives by hot oil treatments (Treu *et al.* 2003). Other authors (Sailer *et al.* 2000) have shown that a treatment of spruce and pine in a linseed oil bath (180 °C to 220 °C) resulted in a better resistance against *Coniophora puteana* in a lab test according to EN 113 compared to the treatment in air atmosphere. In France a simple bi-oleothermal© process is currently developed by CIRAD in cooperation with FCBA (formerly CTBA) in order to make wood more stable and less sensitive when used outdoors.This two-stage process operates at atmospheric pressure and uses two oil baths. The first stage consists in dipping the wooden piece in a hot oil bath (between 110 °C and 200 °C) for the duration necessary to reach the moisture content of the targeted end-use. At the end of this first stage the wood contains a significant volume of vapour. Then the sample is quickly moved to the second bath where it is dipped for a few minutes in oil between 20 °C to 80 °C. Since the second bath contains oil at a temperature lower than the boiling temperature of water, the wood sample cools leading to water condensation. A vacuum is created inside the sample causing the oil to deeply impregnate the wood. The process and the influence of the treatment parameters on heat and mass transfer have been reported by Grenier (Grenier *et al.* 2003, Grenier 2006, Grenier *et al.* 2007). The process offers several advantages: it is very simple and operates at atmospheric pressure; it contributes to save money since it allows the use of green wood: a fast drying is performed during the first stage; a deep oil impregnation is achieved; the equipment is cheap and easy to use; it allows the recycling of vegetable oils from the food industry. Figure 1 shows that the process (C) leads to a deeper oil impregnation of beech than a dipping in a cold oil (A) or in hot oil (B).



A) 1 hour dipping in oil at room temperature, initial moisture content : 10-11%

B) 1 hour dipping in oil at 180 °C, initial moisture content : 110-120%

C) 30 minute dipping in groundnut oil at 180 °C then soaking in linseed oil at 20 °C for 30 minutes, initial moisture content : 110-120%

Figure 1: Influence of the treatment on oil penetration of end grain sealed beech samples

The aim of this paper is to report on the biological properties, the weatherability and the coatability of wood samples impregnated with several types of linseed oils.

EXPERIMENTAL

Oils and treatment

The protective effectiveness of oil treatments against wood destroying basidiomycetes was tested using five types of oils: H1 is a drying linseed oil, H2 is a maleated drying linseed oil, H3 is H2 + 0.6% propiconazole + 0.3% permethrin, H4 is H2 + 1% propiconazole +0.3% permethrin, H5 is H3 with a UV absorber. The protective effectiveness of oils treatments against termites and longhorn beetles was tested using two types of oils: H1 (same as above), HB is the same than H1 and includes an insecticide (0.3% permethrin). The weatherability of oils treatments was studied on oak samples using H2 and H5.The impregnation of the samples with the different oils were performed by CIRAD using the bi-oleothermal process. The typical conditions were 10 minutes in the hot oil bath (rape oil @150 °C) and 5-10 minutes in the second bath at 60 °C (with Hn).

Protective effectiveness of oil treatments against wood destroying basidiomycetes

Specimens (50 mm x25 mm x15 mm) of *Pinus sylvestris* sapwood and *Fagus sylvatica* fulfilling the requirements of EN 113 were used. Before treatment and for each wood species and each type of oil, the wood specimens were conditioned at (20±2) °C and (65±5)% RH. They were treated with the different oils using the bi-oleothermal process and conditioned once more at (20±2) °C and (65±5)% RH until constant mass. Since oils can be affected by UV, temperature and water we have considered that the conventional accelerated ageing of treated wood prior to biological testing EN 73 (evaporative ageing procedure) or EN 84 (leaching procedure) were not relevant enough for the ageing of oil treated specimens. That is why two other types of artificial ageing were tested:

- V313 cycle according to EN 321: one cycle lasts for 1 week and is made of: soaking in water at 20°C for 70 hours, freezing (-15°C) for 24 hours, exposure at 70 °C for 70 hours, conditioning at (20±2) °C and (65±5) %RH for 4 hours. Oil-treated samples were exposed to V313 cycle for 6 weeks.

- wheel method (FCBA procedure): in this method samples are held on the wheel as shown in Figure 2. One cycle lasts for 1 h 30 min and consists of: soaking in water at room temperature for 12 min, conditioning at room temperature for 27 min, exposure to six UV/IR lamps for 24 min, conditioning at room temperature for 27 min. Oil-treated samples were exposed to the wheel method for 6 weeks.

After artificial ageing wood specimens were conditioned at (20±2) °C and (65±5)% RH to constant mass. Then samples were exposed for 16 weeks to the following wood destroying basidiomycetes: *Coniophora puteana* (BAM Ebw.15), *Gloeophyllum trabeum* (BAM 68), *Poria placenta* (FPRL 280) for the Scots pine specimens, *Coriolus versicolor* (CTB 863 A) for the beech specimens. After artificial ageing and conditioning some samples were not exposed to fungi but were oven dried and weighed to record the dry mass after oil treatment and ageing. After exposure to fungi samples were dried at (103±2) °C and the final dry mass was recorded. The loss in mass of each treated specimen was calculated using the dry mass after treatment and ageing and the final dry mass and expressed as a percentage of the dry mass after treatment and ageing.

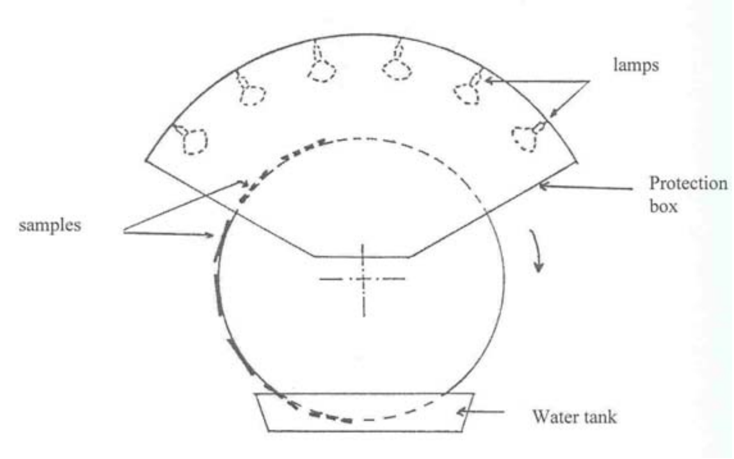


Figure 2: Schematic view of the wheel

Protective effectiveness of oil treatments against insects

The protective effectiveness of oleothermal treatment has been assessed using the house longhorn beetle *Hylotrupes bajulus*, for beetles with wood-boring larvae and the saintonge termite *Reticulitermes santonensis*, for subterranean termites. Tests were performed according to EN 47 and EN 117 respectively. Samples (50 mm x 25 mm x 15 mm) of *Pinus sylvestris* sapwood (P) were tested on both house longhorn beetles and termites. Samples (50 mm x 25 mm x 15 mm) of sapwood (CA) and heartwood (CD) of *Quercus robur* or *Quercus sessiliflora* were only tested on termites. Untreated controls are designated by *Hylotrupes bajulus* larvae (6 larvae per wood block) and the *Reticulitermes santonensis* (250 workers per wood block) from the FCBA-CTBA insect breeding station. For *Hylotrupes bajulus* there are 5 wood blocks with 6 larvae, that is 30 larvae per treatment and per control. After 4 weeks the treated wood blocks were cut up. If a larva was found, the remaining wood blocks in this treatment were kept for a further 8 weeks before the final control. At the end of the test, the dead and live larvae were counted. For *Reticulitermes santonensis* the termite colonies together with one wood block are housed in receptacles of 500 cm^3 and 15 cm high. Damp sand was deposited on the bottom of the receptacle. A glass ring was placed against one of the sides to maintain the wood block at 1 cm above the sand. The groups of termites were introduced into the receptacles which were then closed. After 2 to 4 days of conditioning, the wood blocks were placed on the supports in the recipients which were then conserved in the test room. They were left for a period of 8 weeks. There were 5 recipients per formula and per type of control. At the end of the test, the numbers of live termites were controlled in order to determine the survival rate of workers in each receptacle. A visual examination of each wood block was carried out to characterise an eventual attack by its location, its spread and its depth. The result of this examination is given according to the scale described in standard EN 117. This ranges from 0 (zero attack) to 4 (maximum attack).

Weatherability and coatability

Oak samples (75 mm x 150 mm x 18 mm) were treated with H2 and H5. After conditioning at (20±2) °C and (65±5)% RH till constant mass, some of the samples were coated with two stains: a transparent solvent-borne stain (S) and a transparent waterborne stain (W) both applied by brush in 3 coats. After conditioning, three samples of each set were exposed to artificial weathering in a QUV using the optimised cycle described by Podgorski *et al.* (2003). A non-exposed sample was kept as a control. The cycle lasted 1 week and was repeated during a total period of 12 weeks as recommended in EN 927-6. At the end of these 12 weeks and after conditioning, the general appearance (ISO 4628-1) was recorded for all test specimens. For coated samples the following were also recorded: gloss (ISO 2813), blistering (ISO 4628-2), cracking (ISO 4628-4), flaking (ISO 4628-5), chalking (ISO 4628-6), adhesion (EN ISO 2409, cross-cut test with adhesive tape).

RESULTS AND DISCUSSION

Protective effectiveness of oil treatments against wood destroying basidiomycetes

The weight percent gain (mean and coefficient of variation CV) caused by uptake of oil during the treatment is shown in Table 1 and shows that the oil uptake is slightly higher in pine than in beech.

Table 1: Weight percent gain caused by uptake of oil

	Mean	**CV**
Pine	36%	13%
Beech	30%	15%

The moisture content of the treated samples (mean and coefficient of variation) at the end of exposure to fungi is presented in Table 2 and compared to the moisture content of the untreated samples. This table shows that the oil treatment leads to a considerable decrease in the moisture content at the end of exposure to fungi.

Table 2: Mean and coefficient of variation of the moisture content of the treated and untreated samples

		Mean (%)	**CV (%)**
Pine	Oil treated	23.9	30
	Untreated	57.8	21
Beech	Oil treated	26.0	14
	Untreated	54.9	50

The mean mass loss of specimens treated with the different oil treatments and exposed to fungi were calculated for both weathering methods. For each oil treatment, the maximum of the mean mass loss is presented in Table 3 for accelerated ageing.

Table 3: Maximum of the mean mass loss for both accelerated ageing

	V313		Wheel	
Oil treatment	**Max mass loss (%)**	**Fungus**	**Max mass loss (%)**	**Fungus**
H1	20.8	*Coniophora puteana*	17.6	*Coriolus versicolor*
H2	12.1	*Coniophora puteana*	14.1	*Coriolus versicolor*
H3	8.3	*Coniophora puteana*	8.6	*Coniophora puteana*
H4	3.3	*Gloeophyllum trabeum*	6.0	*Glooephyllum trabeum*
H5	5.9	*Gloeophyllum trabeum*	10.4	*Coniophora puteana*

The efficacy of the different oils to protect wood against basidiomycete fungi can be classified as follows: H4 > H5 = H3 > H2 > H1. The protective efficacy was especially linked to the amount of propiconazole. As expected the lowest efficacy was obtained with the oils without any biocides (H1 and H2). However these oils improved the resistance of wood since they led to a decrease in the mass losses compared to the untreated samples (mean mass loss: 31.5% with *C. puteana*, 34.2% with *C. versicolor*, 31.9% with *G. trabeum*, 33.7% with *P. placenta)*. Compared to natural oil the maleation process significantly improved the resistance against basidiomycete fungi. For the different treatments the mass losses were higher than 3%. Therefore, according to EN 113 and EN 599 specifications, the oil treatments tested were not effective enough to protect wood against basidicomycete fungi. However the mass losses of pine samples can be examined using the method described in the technical specification CEN/TS 15083-1 (2005). The median values for the mass loss of each test specimens have been calculated. The higher median mass loss has been compared (see Table 4 and Table 5) to the provisional durability rating scale provided in Annex D of CEN/TS 15083-1 as follows:

Per cent loss in mass	Durability class
≤ 5	1 = very durable
<5 to ≤ 10	2 = durable
>10 to ≤ 15	3 = moderately durable
>15 to ≤ 30	4 = slightly durable
> 30	5 = not durable

For beech, the same procedure was used (see Table 6) but just with C. versicolor.

Table 4: Pine -Median mass loss (%) after accelerated ageing with the wheel

Oil	*Coniophora puteana*	*Poria placenta*	*Higher median mass loss*	*Durability class*
H1	11.1	11.9	11.9	3
H2	8.7	10.6	10.6	3
H3	9.0	1.3	9.0	2
H4	3.2	1.1	3.2	1
H5	12.3	0.9	12.3	3

Table 5: Pine -Median mass loss (%) after accelerated ageing with the V313 cycle

Oil	*Coniophora puteana*	*Poria placenta*	*Higher median mass loss*	*Durability class*
H1	19.2	12.5	19.2	4
H2	12.0	10.0	12.0	3
H3	9.6	7.4	9.6	2
H4	0.9	2.7	2.7	1
H5	0.8	2.7	2.7	1

Table 6: Beech -Median mass loss (%) after accelerated ageing (wheel or V313 cycle)

	Wheel method		*V313 cycle*	
Oil	*Coriolus versicolor*	*Durability class*	*Coriolus versicolor*	*Durability class*
H1	17.6	4	14.9	3
H2	14.7	3	7.9	2
H3	5.1	2	6.7	2
H4	3.7	1	3.4	1
H5	5.3	2	2.5	1

Table 7 : Median mass loss (%) and durability class of untreated wood

	Pine	*Beech*
Coniophora puteana	31.6	
Poria placenta	33.2	
Coriolus versicolor		34.4
Durability class	5	5

For both species results in Table 4, Table 5, Table 6 show that treatments with biocide-free oils (H1 and H2) increased the durability (durability class 3 or 4) compared to untreated wood (durability class = 5 for pine and beech, see Table 7). A better durability was obtained with the addition of biocides. The artificial ageing according to the V313 cycle seems to be less severe than the ageing with the wheel. The addition of a UV absorber did not increase the performance. The maleated oil displays better results than natural oil.

Protective effectiveness of oil treatments against insects

The weight percent gain (mean and coefficient of variation CV) caused by uptake of oil during the treatment is shown in Table 8.

Table 8: Weight percent gain caused by uptake of oil

	Mean	**CV**
Pine	34.4%	15%
Oak	11.9%	51%

The protective effectiveness of oleothermal treatments against young *Hylotrupes bajulus* larvae is shown in Table 9.

Table 9: Protective effectiveness of oil treatments against Hylotrupes bajulus larvae

		Larvae found		
		Dead		
Assessment	**Oil treatment**	**Without boring**	**With boring**	**Alive**
After 4 weeks	HBP	30	0	0
After 12 weeks	TP	1	0	24
	H1P	4	21	2

The normal behaviour of house longhorn beetle larvae is seen in the untreated pine (TP): they bore and develop inside the wood. When the wood was subjected to an oleothermal treatment, the larvae do not survive. However, the oil alone (H1P) did not prevent them from penetrating the wood. When an appropriate dose of insecticide was added to the oil (HBP), the performance was that of usual preventive wood treatments.

The protective effectiveness of oleothermal treatments against *Reticulitermes santonensis* is shown in Table 10. The control wood blocks (TP and TC) allowed termite survival and to have a maximum attack level. The wood blocks which were treated with biocide-free oil (H1P, H1CA and H1CD) did not allow the termites to survive but the had an attack level which shows that wood treated in this way cannot be considered as protected against termites. It is only the addition of an insecticide to the oil which protects the wood against termites: zero termite survival and an attack level lower than 1.

Table 10: Protective effectiveness of oil treatments against Reticulitermes santonensis

Oil treatement	% of worker survival	Mean degree of attack
TP	55	4
H1P	1	2.4
HBP	0	0.6
TC	11	4
H1CA	0	3
H1CD	6	2.2
HBCA	0	0
HBCD	0	0.2

Weatherability and coatability

After 12 weeks of artificial weathering according to EN927-6, the general appearance of samples treated with H2 and H5 was 5. This means that the coating provided by this oil process constituted a low performing product compared to traditional stains. However, the compatibility with conventional stains is ensured as shown in Table 11. This table shows that both stains S and W are well performing coatings. There was no significant difference in the results with and without oil treatment. The oil treatment did not improve the performance of good performing finishes within the 12 weeks of artificial ageing. Further tests with longer test duration or with low performing coatings should be carried out to see if the oil treatment can improve the performance of finishing products.

Table 11: Results of artificial weathering (EN927-6) for stains S and W on oil treated samples and untreated samples

	Stain W		*Stain S*	
	Untreated	***Oil treated***	***Untreated***	***Oil treated***
General appearance	1.3	1	2	2
Blistering	0	0	0	0
Cracking	1.3	0.3	0	0
Flaking	0	0	0	0
Chalking	0	0	0	0
Adhesion	0.6	1	0	0.6

CONCLUSIONS

Bi-oleothermal processing is a simple treatment which operates at atmospheric pressure and allows a deep impregnation of wood with hydrophobic products using cheap facilities. In this study, this process has been used to impregnate several wood species with several linseed oils with and without biocides. The resistance to wood destroying fungi has been assessed using a method adapted from EN 113. Since oils can be affected by UV, temperature and water, the conventional accelerated ageing of treated wood prior to biological testing EN 73 (evaporative ageing procedure) or EN 84 (leaching procedure) were considered not relevant enough for the ageing of oil treated specimens. Therefore two other accelerated ageing methods were tested: the V313 cycle of EN 321 and the wheel method. The tested oils improved the resistance of wood since they led to a decrease in the mass losses compared to the untreated samples. Results also show that the linseed oils led to an increase in the natural durability of beech and Scots pine. The artificial ageing according to the V313 cycle is less severe than the ageing with the wheel. The wheel method seems to be well suited to compare the performance of oil treated wood specimens. In the future it would be interesting to compare this method with the ageing procedure of EN 927-6 which is more severe than the wheel method (when tested on coatings). Oil treated wood is not completely repellent to the insects tested, house longhorn beetles and termites. These insects are capable of boring the wood, but this material as a unique source of nutrition does not allow their survival. The treatment causes the wood to lose its nutritive qualities or renders it toxic. An insecticide needs to be added to protect the wood effectively. When an appropriate dose of insecticide is added to the oil there is no survival in the test device and no degradation of the wood and the performance is that of usual preventive wood treatments against wood boring insects. In EN 47 and EN 117 tests, untreated wood and treated wood samples are separately tested. In order to better understand the repellent effect of oils it would be interesting to perform extra test where untreated and oil treated samples are tested in the same receptacle. This would give clearer information about the behavior and the choice of the insects facing the oil treated wood.

In the future further research is needed in order to optimize and reduce the biocide amount.The resistance of the treatment to weather has been studied using artificial weathering test according to EN 927-6. Results show that the coating provided by this process constitutes a low performing product compared to conventional stains. However the compatibility with a solvent-borne or a water-borne stain is ensured and leads to good performance after artificial weathering.

ACKNOWLEDGEMENTS

Special thanks to: Hélène Callot, Véronique Georges, Didier Reuling FCBA-CTBA, Nabil Boutahar CIRAD for their technical support; Vandeputte oleochemicals (Belgium) for their support and the oils supply and Cecil SA (France) for the oils formulation; the French Ministry of Agriculture, the French Ministry of Housing and the French Regions Franche-Comté, Bourgogne, Centre, Basse et Haute Normandie, Lorraine, Midi-Pyrénées for funding.

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Use of Di-carboxylic Fatty Acid Based Resins for Oleothermal Treatments

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Keywords: Wood stabilisation, azelaic acid, permeation, wood swelling

ABSTRACT

Wood is too rarely used for outdoor applications on account of its poor natural resistance. In particular, it is very sensitive to moisture. This paper deals with an original "soft" approach that consists in replacing treatments involving hydrophobic resins that react with the wood components (cellulose and lignin polymers) by "hydrogen bonds". For several years, the ARC-Nucléart laboratory has been performing studies to identify molecules that are able to penetrate into the interior of the cell wall in order to establish hydrogen bonds and maintain the wood in a swollen state. The main goal of this work is to replace bound water in the wood by other molecules that cannot be evaporated. The interest of keeping the swollen state (even with dry wood) is to reduce the dimensional instability of the wood; furthermore, the internal moisture content of the wood decreases artificially, also producing better resistance to fungi. Such molecules are already well known and include glycerol or polyethylene glycol 200 or 400. These formulations have already been studied and used to preserve degraded archaeological wood, but they are unsuitable for outdoor applications because they are strongly water-soluble. Since 1999, different molecules that are both water repellent and able to diffuse into the cell walls have been identified. They include polycarbamates (*e.g.* hexane diethylcarbamate), polyalkylene glycols (*e.g.* polytetramethylene glycol or PTMEG 600) and recently, fatty di-acids (azelaic acid or sebacic acid, which give the most promising results without any esterification of the wood). This work aimed to develop a reliable and simple permeation treatment from available, non-toxic, low-cost resins that are free of petroleum products, such as fatty di-acids, that do not produce any chemical reaction between the resin and wood: the treatment is only limited to thermal permeation treatment (< 120 °C). The polarity of carboxylic functions ensures good bonding of the resin with the hydroxyl groups of the wood and the "fatty" nature of the di-carboxylic acid prevents acid from being leached by water as far as possible. It is now possible to propose an optimised treatment of wood using di-acid impregnation. Interesting results have been obtained by this process in terms of stability during successive drying/wetting cycles, giving an ASE of 60-70%.

INTRODUCTION

Wood is used with difficulty for outdoor applications, mainly due to the fact that the common fast-growing European species have little natural resistance to fungi, moisture, thermal ageing and U.V. radiation. Resistant wooden products used in outdoor conditions are made from either exotic species or timber that has undergone reactive treatments involving toxic chemicals (such as acetic anhydride) to perform in situ grafting of the wood (Magne *et al.* 2005, Dawson *et al.* 1999, Vaca-Garcia *et al.* 2003). These practices therefore remain limited from the industrial point of view on account of the cost of the treatment, *i.e.* handling of dangerous chemicals, "heavy" chemical process involving strict compliance with accurate operating parameters, cleaning of the treated wood by removing the excess reactive, post-neutralization of the reactive, high temperature leading to a decrease in mechanical properties, *etc.* ARC-Nucléart is a workshop with more than 35 years' experience in the conservation of cultural heritage artefacts made of wood. The requirement in this domain is reversibility of the preservation treatment applied. Furthermore, observations of the wood at molecular scale show that the chemical skeleton of the wood substance is built upon non-covalent hydrogen bonding to ensure linkage between the cellulosic chains themselves, and cellulose/lignin interfaces. Consequently, since 2000, ARC-Nucléart has naturally studied reversible and "soft" conservation treatments based on hydrogen linkages for archaeological wood and for modern wood in the framework of industrial applications (Chaumat *et al*. 2003). Size stabilisation involves replacing the hydrogen bonds between the wood's hydroxides and water with hydrogen bonds between the wood's hydroxides and the resin's polar functions. Numerous molecules meet these conditions, but most of them are volatile (water, acetone, ethanol, etc.) and/or water soluble (glucose, polyethylene glycol – PEG, etc.). The main difficulty is to identify chemical formulations that are both insoluble in water, but nevertheless able to diffuse inside the cell wall, which is known to be a hydrophilic medium. Several compounds have been studied and assessed with wood samples.

EXPERIMENTAL PROCEDURE

Choice of resin

To ensure its diffusion into the cell wall, the resin has to be chosen with polar functions such as the alcohol function (-OH), urethane function (O-CO-NH) or carboxylic acid function (-COOH). These polar functions are found at the end of the molecular chain, allowing the resin to penetrate and move within the cell wall. The middle of the chain consists of an aliphatic hydrophobic polymethylene group (-(CH2)n- n ≥ 6) to avoid leaching of the resin by water.

Table 1: List of resins used for wood swelling

Name	**Hexane di-carabamate ethyl**	**Polytetramethylene glycol 650**	**Azelaic di-acid**
Formula	H_5C_2-Ur-$(CH_2)_6$-Ur-C_2H_5 with "Ur" = -O-CO-NH-	HO-$[(CH_2)_4$-$O]_{14}$-H	HOOC-$(CH_2)_7$-COOH
Abbreviation	HDCE	PTMEG 650	Azelaic acid
Molar weight	282	650	188
Melting point	76 °C	33 °C	105 °C
Commercially available	No	Yes	Yes

Each of these molecules is unable to diffuse alone in the cell wall. It is necessary to use a sort of co-solvent, referred to in the text as an "active swelling agent". This active swelling agent acts as both a solvent for the resin considered and an efficient swelling agent for the wood. It is used only to impregnate the wood with the resin. After this step, the "active swelling agent" is removed. Three resin families were investigated: di-carbamate, polyalkylene glycol and di-acid carboxylic. The main properties of each resin family are listed in the following table (Table 1).

Operating parameters for the "swelling" treatment

Before presenting the treatment in detail, it is useful to recall the principle of "swelling" treatments. The first step is to swell the wood with an active swelling agent, which is a liquid solution able to swell the wood by itself, *i.e.* to diffuse directly into the cell wall. Usually, the most efficient molecules are polar and small. In our experiments, we used ethanol, water or a mixture of both. These swelling agents must be an effective solvent for the resin considered. As HDCE and PTMEG are not water-soluble, we used an ethanol-based solution. Pure water can be used with azelaic acid, as this product is fairly hydrophobic under 70 °C, in contrast to over 70 °C, where it is water-soluble in any proportion. The amazing behaviour of this fatty acid is very interesting from an industrial point of view for two reasons:

- Using water is far better than using organic solvents from environmental and economic standpoints,
- It is possible to use wet wood, therefore the delicate and costly air-drying step becomes redundent.

Table 2: Parameters used for impregnation treatment

Resin	**HDCE**	**PTMEG 650**	**Azelaic acid**
Associated swelling active agent / solvent	Ethanol + water	Ethanol + water	Water
Concentration of resin in solvent (% weight)	45% resin 45% ethanol 10% H_2O	40% resin 40% ethanol 20% H_2O	90% resin 10% water
Temperature of impregnation treatment (°C)	70 °C	50 °C	105 °C
Duration of impregnation treatment (hours)	24	12	4
Air-drying temperature (°C)	20 °C	20 °C	20 °C
Air-drying duration (hours)	48	48	48

The second stage consists in removing the swelling agent while leaving the resin in the cell wall. This is done *via* an air-drying operation including ventilation of the wood. The wood is dried but it remains swollen, as it is wet. The hydrogen bonds between the wood molecules and the resin block it in the cell wall. Table 2 above summarises the optimised operating conditions with the different resins considered. These values were established on the basis of a major and long R&D programme involving one study year per resin. All the permeation treatments were carried out in a sealed vessel.

Wood sampling and characterisation

The experimental work was carried out using beech wood. This species is known to swell considerably when wet. Moreover, beech wood is easy to impregnate and is consequently highly suited to the swelling treatment. The sample sizes were L (tangential) = 75 mm, l (longitudinal) = 10 mm, w (radial) = 5 mm. Usually, each measured point corresponds to an average value obtained from 5 samples. With regard to characterisation after the swelling treatment, we calculated a "partial anti-swelling efficiency" (ASEp) using only the L (tangential) direction, which is the most sensitive. The ASEp value is assessed between a "wet state" (three days at room temperature immersed in liquid water) and a "dried state" (three days at room temperature in a ventilated room). Owing to the large quantity of results, a simplified presentation is given, showing the tendency.

RESULTS AND DISCUSSION

Size stabilisation efficiency

The main results concerning stabilisation are summarised in the curve of Figure 1.

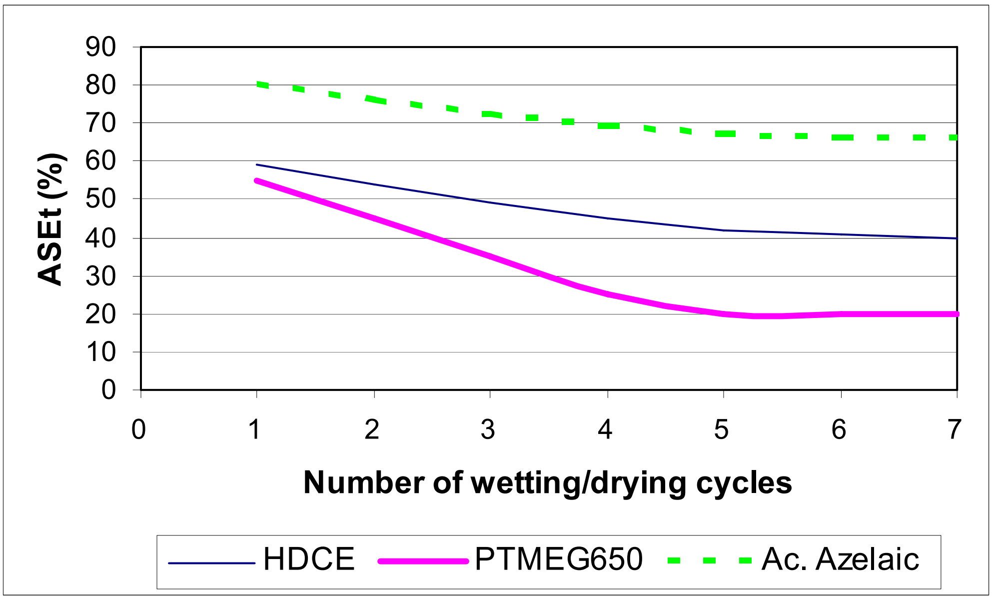

Figure 1: Comparison of size stabilisation efficiency between the resins

Comparison of the results obtained with the three resins considered shows that HDCE and PTMEG650 resins are sensitive to leaching by water. Indeed, though these two compounds are not water-soluble, they can be displaced by water inside the cell wall. This feature may be explained by the level of energy of each "hydrogen" bond type considered. Assuming that a cell wall behaves as a solid alcohol, the "hydrogen" bonds consist of the following linkages: "Wood-C-OH$^{\cdots}$HO-C-PTMEG650" or "Wood-C-OH$^{\cdots}$HN-HDCE". These reversible hydrogen linkages can be replaced by the more energetic "Wood-C-OH$^{\cdots}$H-O-H" hydrogen bond inside the cell wall. The water molecules may get the precipitate outside the cell wall into the natural porosity of the wood.

The second main observation is the good behaviour of azelaic acid with water. The leaching effect still exists, but is nevertheless less sensitive. It is possible to maintain 60% of ASE_t after 7 cycles. A possible reason for this is the better polarity of a carboxylic function with wood constituents and an hydrophobic behaviour more important with fatty acid. Consequently, satisfactory size stabilisation is expected (see

Figure 2). For information, it is useful to note that the average weight percent gain of azelaic acid in wood after swelling treatment is in the range of 40-50% (weight).

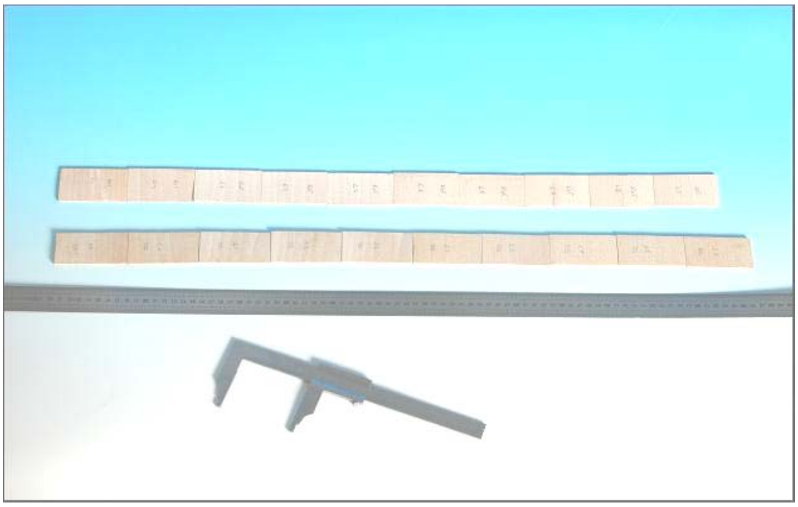

Figure2: Comparison between dried swelled wood (lower) and untreated wood (upper) from the same beech boards.

Biological assessment

In 2004, it was decided to assess the resistance to fungi of swelled wood treated with HDCE resin. An EN 113 test was carried out by the CTBA. *Pinus sylvestris* samples (50x25x15 mm) were used and tested with 3 fungi: *Coniophora puteana*, *Gloeophyllum trabeum* and *Poria placenta*. The results are summarised in Table 3. Each value corresponds to an average obtained from 8 samples.

Table 3: EN 113 results from HDCE swelling treatment

Fungus	**HDCE in wood [WPG%]**	**Weight loss [%]**	**Standard deviation - σ**
C. puteana	27.73	0.41 +/- 0.15	0.30
G. trabeum	27.01	0.43 +/- 0.19	0.38
P. placenta	26.89	0.12 +/- 0.09	0.18

The di-carabamate HDCE does not have any specific biocide properties. These very promising results might be explained by the hydrophobic character of HDCE, which prevents fungus contamination in the wood as there is not enough water in the cell wall for these organisms. Because of the poor results concerning resistance to water leaching, no EN 113 test was performed with PTMEG 650 resin. In return, biological tests were launched for azelaic acid, the results of which will be available in autumn 2007.

CONCLUSIONS

In this work, we succeeded in impregnating the cell wall with hydrophobic resins. After such treatment, the wooden parts remain in a swelled state as a wet wood. Very promising results were achieved for each family of resin studied: ASE_p values of over 60% were obtained easily, even after several leaching cycles. In addition, fungus resistance was assessed with a di-carbamate resin according to the EN 113 standard. A similar test is being performed for carboxylic di-acid. Although a patent has been taken out for each chemical formulation, the most promising approach is azelaic acid, on account of its numerous advantages: cost of the material (7 euros/kg from China), the product is currently used as an active principle for curing skin acne, it is derived from wheat and rye and not from the petrochemicals industry, it is not toxic, colourless, resistant to ageing, and has a high melting point (>100°C). Nevertheless, investigations need to continue with a view to improving properties such as water retention. While the treatment succeeds in stabilising the cell wall, the wood's porosity keeps its capacity to retain liquid water (more than 5%), which is not acceptable in many industrial applications. We are convinced that it is necessary to associate the stabilisation treatment with a second permeation using hydrophobic resins to fill the pores. Some exotic species use the same approach involving natural fatty compounds inside the cell wall to obtain effective resistance to water. It might be very fruitful to launch chemical studies concerning these natural compounds with a view to optimising a suitable formulation that is able to transform a traditional low-resistance wood species into a very water-resistant wood comparable to some exotic species. Such studies dealing with the role of fatty products in wood are beginning to be published (Hernandez 2007). he last point to investigate deals with the mechanical characterisation of the treated wood. Indeed, the "elongation" of wooden fibres due the swelling effect may affect the natural strength of the wood. These data have to be confirmed through a more complete mechanical study. Finally, a further ambitious prospect might be to associate swelling treatment with strengthening treatment through *in-situ* polymerisation of a liquid styrene-polyester. Such a combination will give further mechanical properties to already stabilised wood.

ACKNOWLEDGEMENTS

We wish to thank OSEO ANVAR for financing this research and express our thanks to F. Delorme and I. Lebayon from the Centre Technique du Bois et de l'Ameublement (CTBA) for performing the EN 113 tests.

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Effects of Wood Treatment with Amino-silicone Emulsions on Different Material Properties

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Keywords: Amino-silicones, hydrophobation, penetration, SEM-EDX, basidiomycetes

ABSTRACT

Amino-silicone (AS) emulsions were tested for the impregnation of solid wood. The penetration of silicone into the cell wall was dependent on the particle size of the emulsions. Only a maximum of 14% of the total silicone penetrated the cell wall, when a macro-emulsion (120 nm average particle size) was used for the impregnation. In contrast, 25-35% of the silicone applied as a micro-emulsion (40 nm average particle size) was found in the cell wall and caused significant bulking and dimensional stability. The relatively high degree of cell wall penetration with regard to the micro-emulsion was confirmed through x-ray micro-analysis (SEM-EDX). Mini-blocks treated with high concentrations of AS micro-emulsion (15%) showed high decay resistance against *Trametes versicolor* and *Coniophora puteana* over a long term (12 weeks), while samples treated with low and moderate concentrations underwent considerable mass losses.

INTRODUCTION

Today the application of many conventional wood preservatives is under restriction due to their toxicity and growing customer awareness. In addition, most preservatives only exert a biocidal effect but do not change water related properties such as water uptake and moisture sorption or swelling and shrinkage. This provides a challenge to researchers to find environmentally acceptable solutions for efficient wood protection including dimensional stability and weathering resistance. Water repellents have been shown to reduce the deterioration of wood through weathering (Voulgaridis and Banks 1981). Moisture fluctuation in wood exposed to weather causes repeated swelling and shrinkage giving rise to the formation of checks and cracks and, in extreme cases, twisting, cupping and warping. Two of the main approaches of chemical treatment have been described which are implemented to reduce the moisture content as well as swelling and shrinkage of weathered wooden items. One approach is to bulk the cell wall by incorporating chemical “spacers” or to cross-link the cell wall polymers. The effect of the treatment is expressed as anti-swelling (shrinking)-efficiency (ASE). Most treatments that cause ASE are also able to reduce the equilibrium moisture content (EMC) of wood, *i.e.* the amount of bound water in the cell wall (Rowell 1983). Another approach is to impregnate wood with water repellents, such as oils, paraffins, silanes or silicones (Borgin and Corbett 1970, Mai and Militz 2004). These compounds cause macro-pore blocking by depositing a hydrophobic compounds in the lumens of vessels, of tracheids and of rays cells. Hydrophobic treatment does not generally diminish the EMC of wood since the number of hydroxyl groups and the pore structure of the cell wall are not altered by the treatment. Silicones are important water repellents which impart hydrophobation to wood products (Sell 1977, Jusoh *et al*. 2005, Mai and Militz 2004). The most commonly used silicones are polydimethylsiloxanes which may have various side group functionalities. Depending on the functionality of the silicones, their degrees of hydrophobation can vary. Primary amino groups as part of a side group increase the affinity of silicone molecules to hydrophilic (ligno)cellulosic material; amino silicones are, however, still relatively hydrophobic (Noll 1968). Up to now only little attention has been paid on the decay resistance of wood treated with silicone emulsions. De Vetter and Van Acker (2005) found low efficacy of silicone emulsions and silicone/silane mixtures towards *C. puteana* and *T. versicolor*. The silicones tested in our study were developed for application in the textile industry. They are applied in aqueous systems in the form of macro- or micro-emulsions. These differ significantly with respect to the size of the emulsion particles, thus, giving rise to the expectation that the degree of penetration into the wood matrix can vary (Dawson and Czipri 1991).

EXPERIMENTAL

Chemicals

Two amino-silicone emulsions were tested in the treatment of the pine specimens (*Pinus sylvestris*): HANSA ASE 8130 is a micro-emulsion with an ingredient content of 57% (40% silicone) and HANSA ASE 8730 is a macro-emulsion which contains 60% ingredients (50% silicone). Both formulations contain the same amino-silicone compound bearing primary amino-propyl groups and a nitrogen content of 0.25%. The number of dimethylsiloxane subunits in the silicone molecules amounts to 300-400. In order to adjust the treatment concentration used, the formulations were diluted with water. Both products were supplied by CHT. R. Beitlich GmbH Werk Oyten, Germany.

Water uptake

Scots pine sapwood blocks (25 x 25 x 10 mm^3, R x T x L) were impregnated under vacuum-pressure at 100 mbar (1h) and 12 bar (2h) with aqueous emulsions of HANSA ASE 8730 and HANSA ASE 8130. The ingredient content amounted to 7.5, 15 and 30%. Water impregnated blocks served as controls (blanks). The impregnated samples were dried as described above. Six replicates were used for each treatment. The uptake of silicone was characterised by the weight percent gain (WPG) calculated from the dry mass of the wood specimens before and after treatment. The water repellent characteristics were determined by submersing the samples in water. After given times (0.5, 1, 2, 4, 8, 24, 48, 96 h) the samples were removed from the water, dabbed off with tissue and weighed. The water repellent effectiveness (WRE) was calculated after 30 min of submersion as previously described (Donath *et al*. 2006a).

Dimensional stability

Scots pine sapwood blocks from the water uptake tests were used to determine swelling properties (n = 6). Cell wall bulking (B) caused by the silicone impregnation was established by comparing of the dry sample volumes before and after treatment. The weight percentage gain that causes bulking (WPB) was calculated as follows:

$$WPB\,[\%] = \frac{(V_{treated} - V_{untreated}) \times d_{silicone}}{m_{untreated}} \times 100 \qquad (1)$$

V: volumes of the specimens before and after treatment [cm^3]; $m_{untreated}$: dry mass of the wood specimens before treatment [g]; $d_{silicone}$: density of silicone (0.97 g cm^{-3}). At the end of the water uptake test described above, a vacuum was applied and the specimens were soaked in water for two days to ensure maximum swelling. Anti-swelling efficiency (ASE) of the treated blocks was determined between the dry state and water saturation. It was expressed as the ratio of the volumetric swelling coefficients of the treated and the untreated specimens (Donath *et al.* 2004).

Scanning electron microscopy with energy dispersive x-ray analysis (SEM- EDX)

The scanning electron microscopy studies were conducted using a Hitachi S- 2300 SEM (Krefeld, Germany) equipped with an XFlash detector (Roentec, Berlin, Germany). The instrument was operated at an acceleration voltage of 15kV, 100μA emission current and a working distance of 15mm. The silicon was identified in the EDX spectra at peak positions of K_α1.74 keV and K_β 1.826 keV, and the EDX peak window for silicon was adjusted to 1.710-1.856 keV. The scanning rate for EDX mapping was 3 ms per frame with a resolution of 512 x 384 pixels. The input rate of the detector was about 1000 -1500 cps (counts per second), whereby 150-300 cps were observed for WPGs of 20-30% and 300-450 cps for WPGs of 30-40%. Small pine sapwood blocks (4 x 4 x 4 mm^3) were cut from the centre of the treated specimens used in the water uptake test. The small blocks were water saturated for 48 h at 4 °C in an Eppendorf cup and sections of 4 mm x 4 mm x 10μm (R x T x L) were cut using a freezing microtome Kryostat 2800 Frigocut-N (Reichert-Jung, Cambridge Instruments GmbH, Nussloch, Germany) at -22 °C.

Mini-block decay test

Resistance of wood modified with AS against fungal decay was evaluated using mini-blocks (5 x 10 x 30 mm^3, R x T x L). Treated and untreated beech wood was tested with the white rot fungus *Trametes versicolor* (Linneus) Quélet strain CTB 863 and pine sapwood with the brown rot fungus *Coniophora puteana* (Schumacher ex Fries) Karst. strain BAM Ebw. 15. The wood blocks were vacuum-pressure impregnated at 100 mbar (1h) and 12 bar (2h) with HANSA ASE 8130 of 2, 5 and 15% solute content, respectively. Subsequently, the specimens were cured at 103 °C (16 h) and weighed. All treated specimens were subjected to an accelerated leaching procedure according to the European standard EN 84 and again dried at 103 °C (16 h). The subsequent decay test was performed as described previously (Donath *et al.* 2006b).

RESULTS AND DISCUSSION

Water uptake, bulking and dimensional stability

Impregnation of wood with micro- and macro-emulsions of amino-silicone resulted in almost equal WPG values when the same treatment concentrations were compared. Both amino-silicone formulations caused significant reduction in water uptake in a submersion test (Figure 1). When the water uptake is depicted with respect to the cube root of the submersion time, two phases can be distinguished. Within the first 30 minutes, a fast water uptake occurs, particularly in the control. Most probably the water penetrates into open voids which are not filled with air. In the silicone treated samples the water uptake in this initial phase is significantly reduced compared to the control. The initial WRE of the micro- and the macro-emulsion after 30 minutes immersion was linearly correlated with the WPG (Figure 2); this could be explained with the occlusion of the main voids and penetration paths.

The water uptake in the second phase (30 minutes to 96 h) showed a linear course and proceeded much more slowly. It can be assumed that in this phase the water slowly displaces the air in the wood. It should be noted that the slopes of the treated samples in this phase are actually somewhat higher than those of the control. Thus, the reduction of the water uptake occurs only during the first phase of submersion. This shows that the water repellent efficiency (WRE) of the silicone only plays a role in the initial phase of the submersion test, but not in the second phase.

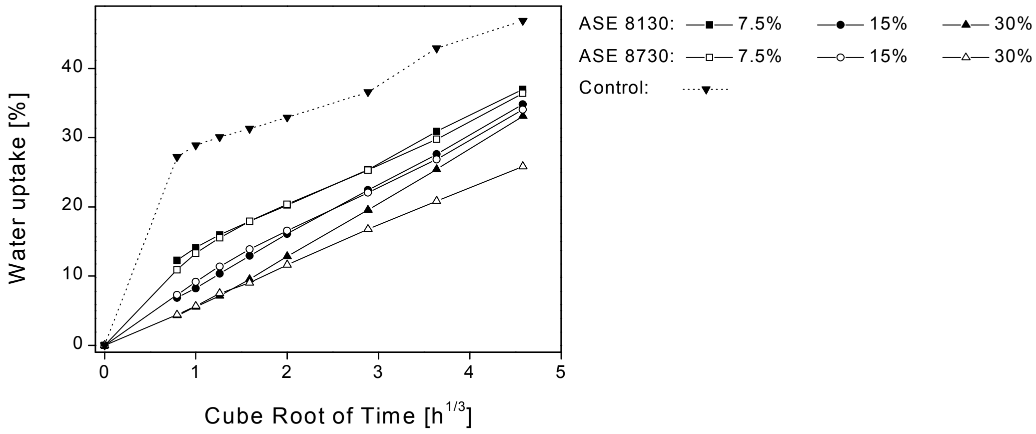

Figure 1: Relative water uptake of pine sapwood blocks treated with the silicone emulsions ASE 8130 and ASE 8730 in a submersion test. Silicone emulsions were applied by vacuum-pressure impregnation

At a concentration of 7.5 and 15%, both micro- and macro-emulsions caused a similar reduction of water uptake; however, at 30% the macro-emulsion was more effective in the hydrophobation than the micro-emulsion. While both emulsions imparted the same degree of hydrophobation within the first 8 h, the macro-emulsion was much more stable after a longer submersion time. This could be explained with the predominant deposition of silicone in the cell lumens (see Figure 4), thus preventing the penetration of water.

The extent of cell wall bulking was dependent on the type of emulsion tested: the micro-emulsion ASE 8130 exhibited significantly more bulking than did the macro-emulsion ASE 8730 (Figure 3A). The pattern of the anti-swelling efficiency (ASE) was similar to the bulking pattern. The highest values for the former were obtained with ASE 8130 amounting to approx. 34% (Figure 3B). Compared to other types of wood modification, the bulking and ASE caused by the treatment were low when the corresponding high WPG is taken into consideration. Thus, the modification of Corsican pine with linear carboxylic acid anhydrides produced bulking values of almost 11% and ASE values of 90% at a WPG of approx. 30% (Hill and Jones 1996). The relatively high average bulking caused by ASE 8130 (5.0 ± 0.5%) shows that in comparison to ASE 8730 a relatively large proportion of silicone penetrated into the cell wall. Still, this proportion was low with regard to the total amount of silicone in the wood specimens, *i.e.*, the WPG.

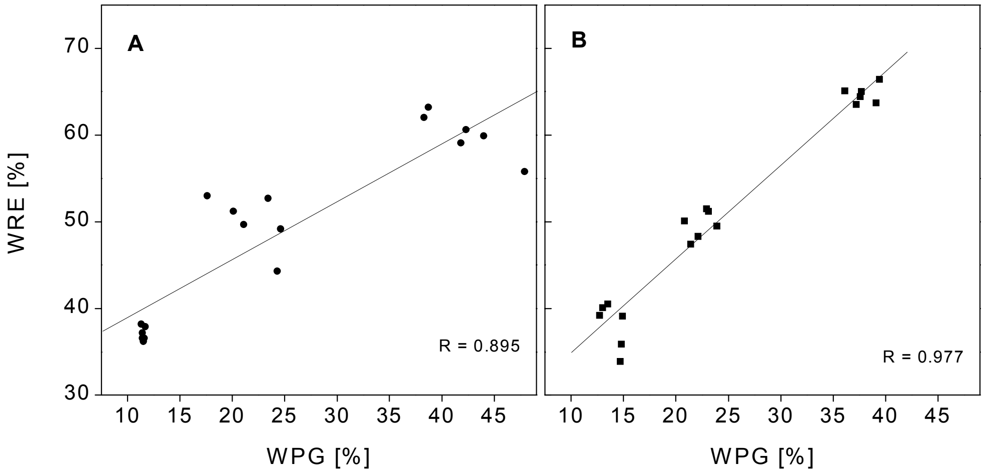

Figure 2: Reduction in water uptake of silicone treated pine sapwood specimens expressed as water repellent efficiency (WRE) within the first 30 min of submersion. This phase corresponds to the first phase of water uptake in Figure 3. (A) ASE 8130; (B) ASE 8730

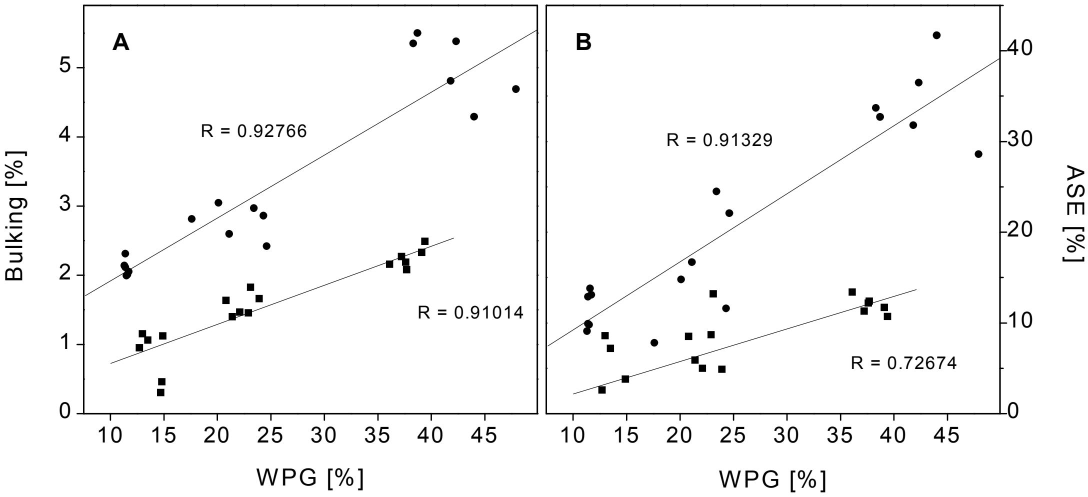

Figure 3: Bulking effect (A) and dimensional stabilisation (B; expressed as anti swelling efficiency, ASE) of pine sap wood due to treatment with silicone emulsions

The highest degree of cell wall bulking (5%) was achieved with the amino-silicone ASE 8130 at a WPG of 42.2%. The mass of silicone which contributes to bulking was calculated by multiplying the bulking volume (Vb) by the density of the silicone (0.97 g cm^3): this was then related to the dry mass of the pine specimens to obtain the weight percentage gain that causes bulking (WPB). According to this calculation, ASE 8130-treated specimens with a WPG of 42.2% display a WPB of only 10.3% at a cell wall bulking of 5.0%. This means that only 24.6% of the total WPG of this sample contributes to bulking (Table 1).

Table 1: The weight percentage gain that causes bulking (WPB) and the ratio between the WPB and the total weight percentage gain (WPG)

	ASE 8130		ASE 8730	
Conc.	WPB [%]	WPB / WPG	WPB [%]	WPB / WPG
7.5%	4.0 (0.2)	34.6 (1.9)	1.6 (0.6)	12.0 (4.9)
15%	5.5 (0.5)	25.1 (2.3)	3.1 (0.3)	14.0 (1.3)
30%	10.3 (0.7)	24.6 (2.9)	4.2 (0.2)	11.2 (0.6)

This calculation assumes that the volume change (V, here called bulking) caused by a chemical modification is solely due to the volume occupied by the chemical (Vi); however, void regions (free-volume, Vf) around the infused chemicals can form as a result of intermolecular repulsion forces (Nakano 1994, Hill and Mallon 1998). This is expressed by the formula:

$$V = k\,(Vi + Vf) \qquad (k = \text{const.}) \qquad (2)$$

If such a void volume (Vf) exists, the amount of silicone which was deposited within the cell wall should be even lower than calculated. The linear relationship between WPG and bulking (Figure 3A) shows that within the tested range of concentration the proportion of silicone which penetrates into the cell wall remains constant. It can be assumed that the distribution of the particle size in the emulsion tested follows a Gaussian curve. Only those particles which do not exceed the diameter of the voids in wood penetrate and, thus, are deposited in the cell wall. Those particles which exceed this critical diameter are deposited on the lumen surface of the cell wall. In the case of ASE 8130, the proportion of the emulsion particles which remains under this critical size ranges from 24.6-34.6% (ratio WPB to WPG). In ASE 8730, this proportion ranges from 11.2-14.0% (Table 1). The deposition of silicone was studied by means of x-ray micro-analysis (SEM-EDX). Tested pine specimens treated with an amino-silicone macro- (ASE 8730) and micro-emulsion (ASE 8130) had a WPG of approximately 18%. In all specimens, silicone was detected in the cell lumens (Figure 4). Ray cells exhibited high amounts of silicone in both micro- and macro-emulsion treated wood; however, the lumens of tracheids of specimens treated with macro-emulsions exhibited higher amounts of silicones than did those of micro-emulsion treated specimens. While the macro-emulsions, in some cases, completely filled the lumens of late wood as well as even early wood tracheids, micro-emulsion silicones only covered the inner lumen surface of tracheids. In contrast, the deposition of silicone compounds in the cell walls of tracheids and in the bordered pits occurred only in specimens treated with micro-emulsions. This confirms the supposition that higher silicone amounts from micro-emulsions penetrated into the cell wall than was the case with macro-emulsions.

Several authors have reported that the diameter of cell wall microvoids in water swollen wood does not exceed 2 nm if the wood was dried (Hill and Papadopoulos 2001). Although the average particle size of the micro-emulsion ASE 8130 is approx. 40 nm (supplier information), a significant proportion penetrated into the cell wall. Even the macro-emulsions which have an average particle size of 120 nm displayed some cell wall penetration.

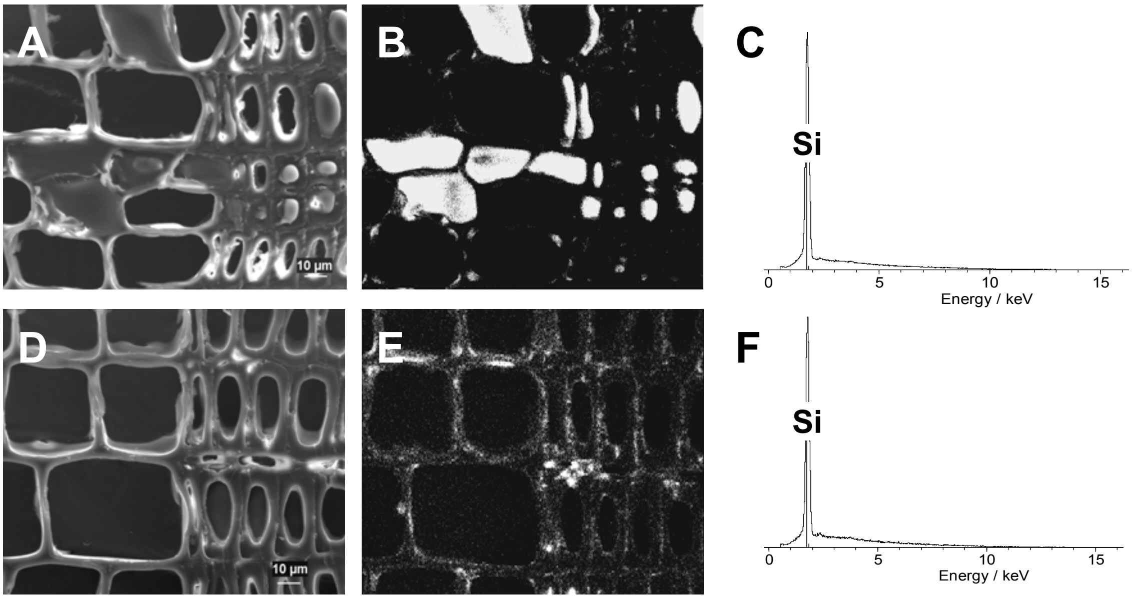

Figure 4: SEM micrograph of Scots pine sap wood treated with the silicon macro-emulsion ASE 8730 (A) and the silicone micro-emulsion ASE 8130 (D). The distribution of reacted Si-product within the cells (B, E: silicon mapping) and the corresponding silicon peak (C, F) in the EDX spectra

Decay resistance against wood degrading basidiomycetes

In order to study the long-term durability of wood treated with amino silicone , beech and pine mini-blocks were impregnated with ASE 8130 emulsions of different concentrations. After the leaching procedure, the beech samples had weight percent gains of 1.7, 4.3 and 12.8% and the pine samples of 1.2, 5.2 and 18.3%. At low treatment concentration (2%) the mass losses of beech caused by *T. versicolor* and of pine caused by *C. puteana* did not significantly differ from those of the controls (Figure 5).

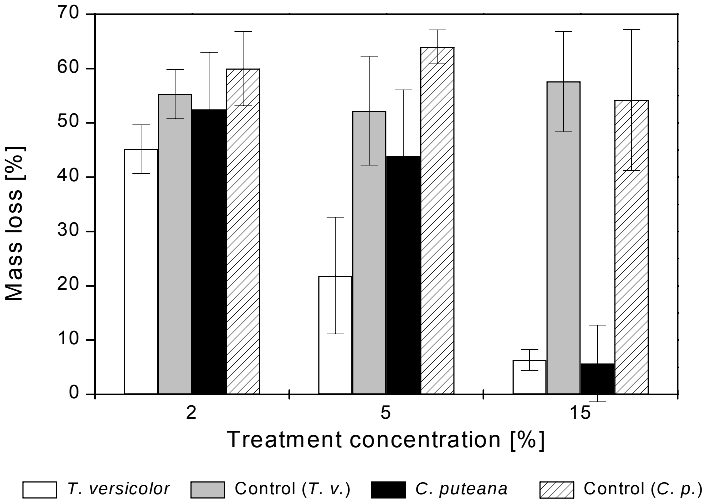

Figure 5: Mass loss of wood treated with silicone micro-emulsion after 12 weeks incubation. Beech wood was tested with T. versicolor and pine sapwood with C. puteana.

At moderate concentration (5%) the mass losses tended to be somewhat lower than in the controls – more pronounced in the beech samples. At high treatment concentration

(15%), however, the mass losses of both treated beech and pine samples were approx. 6%, while those of the controls were above 50%. In this study a mini-block test with a long incubation time was used in order to rule out that the reduction in mass loss was only due to hydrophobation of the wood sample and, thus, due to a prolonged time the fungus needed for colonisation. The time of actual fungal decay in a mini-block test over 12 weeks is clearly longer than in a test according to EN 113, since decay fungi need significantly less time to colonise mini-blocks compared to EN 113 samples. The results of this study show that higher loadings of AS (13% WPG for beech, 18% for pine) can impart high resistance of wood against white and brown rot over long incubation time.

CONCLUSIONS

The aim of this study was to evaluate the suitability of an amino-silicone for the full impregnation of solid wood. A micro-emulsion with an average emulsion particle size of approx. 40 nm and a macro-emulsion with an average particle diameter of 120 nm were tested. The degree of penetration into the cell wall was higher with the micro-emulsion. Although the estimated maximum micro-void diameter is only 2 nm, approx. 25% of the silicone formulation introduced did penetrate into the cell wall. This can result from the polydispersity of the emulsion particles: 25% of the smallest particles within the size distribution should have a critical diameter of less than 2 nm, or the emulsion particles are deformed or break apart under the applied vacuum or pressure and are thus reduced in diameter. In both emulsions (micro- and macro-) most of the silicone appeared to be deposited in the lumens of the cells. Whereas the greater amount of silicone in the cell wall after treatment with the micro-emulsion led to a moderate anti-shrinking- efficiency, the macro-emulsion was somewhat more efficient in reducing the water-uptake during a submersion test. Due to their strong hydrophobation and moderate antifungal effect, amino-silicones constitute an interesting group of preservative chemicals particularly for the application in hazard class III according to EN 335 (outside above ground exposure). Although treated wood was less colonised by decay fungi (particularly at high WPG), the treatment did not appear to affect fungal physiology.

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Wood Fibre Surface Engineering for Use in Wood Plastic Composites

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Keywords: Compatability, compounding, HDPE, wood fibre modification, wood plastic composites

ABSTRACT

Novel wood based materials and composites that have economic and environmental values are sought after for the function of substituting for traditional wood based applications. Wood plastic composites (WPC) proved to be a promising group for the afore mentioned qualities. Most thermoplastics are non-polar substances which are not compatible with polar wood fibres and results in a poor adhesion between the matrix and wood fibre. This study aimed to improve the adhesion properties by chemically modifying the wood fibre surface to enhance its dispersability/miscibility within the plastic matrix. This was achieved by using a reactive diisocyanate (diphenyl-methane-4,4'-diisocyanates, MDI;) linker to couple the micron sized (25 μm) wood fibre with a fatty alcohol (ethanol, octanol, dodecanol, octadecanol) to tentatively form core-shell like structures with weight gains of between 33 and 60%. The reaction products were characterized by FTIR spectroscopy. The effect of differing alkyl group lengths (C_2 to C_{18}) on the modified wood fibre were examined after compounding in a torque rheometer) with high density polyethylene (HDPE). Wood fibre modification was shown to significantly improve the compoundability of WPC systems over controls, as assessed by torque rheometry. In addition, the melt flow index was shown to increase upon modification thus lowering the melt viscosity. Wood modification was shown to increase both the crystallization temperature and extent of crystallization of HDPE in WPC systems as compared to controls.

INTRODUCTION

Novel wood based materials and composites that have economic and environmental values are sought after for the function of substituting for traditional wood based applications. Over the past 10 years the wood plastic composite (WPC) production capacity/market has grown rapidly and dominated by the decking/railing market which is approximately 2/3 of the U.S. $0.9 billion extruded WPC production (Smith and Wolcott 2005). Demand for higher performance products resulted in constant improvement in the processing of WPC. A major apprehension was, most olefinic thermoplastics are non-polar which are not compatible with polar wood fibres (Pickering *et al.* 2003). This results in a poor association between plastic and wood fibre. To alleviate this issue it is necessary to improve the interface between the two substrates. This can be done by three approaches: (i) make the polymer matrix phase more polar by the addition of a coupling agent (such as maleated polyolefins) (Bledski and Faruk 2003), (ii) modify the wood surface to make it more non-polar by chemical modification (Pickering *et al.* 2003), or (iii) increase the wood fibre surface area by reducing fibre size.

Work by various groups on WPCs had shown that by reducing the average wood fibre particle size from 850 to 250 μm resulted in an improvement in mechanical and physical properties (Albano *et al*. 1999). Therefore, going to even smaller wood fibres are likely to give improved WPC attributes. The aims of this study were to enhance the compatability between the wood surface and the matrix by chemical modification of the wood fibre surface and the evaluation of these enhanced WPC materials.

EXPERIMENTAL

Commercial maple wood flour (American wood fibres, 100 mesh, 500 g) was reduced in size by ball milling (7 d). The milled flour (50 g batches) was screened into discrete fractions using 8-inch test sieves (100, 200, 300 and 400 mesh).
Fibre modification approach #1: The alcohols (ethanol (C_2), octanol (C_8), dodecanol (C_{12}), and octadecanol (C_{18})) were stoicheometrically (1:1) reacted with diphenylmethane-4,4'-diisocyanate (MDI) (10 g) in a stirred 1 L glass reactor to a form an alcohol-MDI adduct, leaving an unreacted isocyanate group (Engonga *et al*. 2000). The reaction products were characterized by reverse phase HPLC and electrospray HPLC-MS (Micromass Quattro) as their dibutyl amine (DBA) derivatives (Spanne *et al*. 1996). Chemically modified fibres were prepared by reacting the alcohol-MDI adducts (C_2, C_8, C_{12}, C_{18}) at a 50% w/w loading based on wood content (100 g, 300-400 mesh fraction) in toluene (300 mL) plus catalyst (1%, dibutyl tin laurate), in a stirred 1L glass reactor at 110 ^{o}C for 24-72 h, until the reactant was depleted (reverse phase TLC as DBA derivatives).
Fibre modification approach #2: 100 g extractives free wood fibre (300-400 mesh fraction) was reacted with MDI (50 g, 0.2 mol) in toluene (500 mL) for 48 h at 110 ^{o}C in a 1 L glass reactor with constant stirring. The system was cooled and excess isocyanate solution was removed by filtration. In separate experiments, each of the following alcohols: C_2, C_8, C_{12} or C_{18} (0.2 mol) were added to the reaction mixture together with additional toluene to cover the fibre, dibutyltinlaurate catalyst (1% based on MDI) and the reaction continued for 24 h at 110 ^{o}C. The modified wood flour was recovered by filtration and washed 3 times with warm toluene (500 mL). The modified fibres were initially air dried then vacuum dried (24 h at 75 ^{o}C) and the yield recorded. The fibres were characterized by FTIR spectroscopy (Avatar 370 ThermoNicolet spectrometer) using an attenuated total reflectance probe (Smart Performer with a ZnSe crystal).

Modified fibre and HDPE (Equistar Petrothene Type LB01000) were dried prior to blending and compounding in a bench Haake mixer/torque rheometer at a capacity of 70%. Blends ranging from 30 to 50 % w/w wood were compounded at 163 °C and 35 rpm for 5 min (2). The compounded material was injection-moulded into tensile dog bone specimens on a Dynisco Laboratory Mixing Molder (180 °C, 50 rpm and mould temperature 120 °C). Tensile tests were performed according to ASTM Standard D 1708-02a with a crosshead speed of 1 mm/min using an Instron 5500R test machine and data was analyzed using Bluehill software (v1.0.240, Instron). Strain was measured using an extensometer (Epsilon Technology Corp. Miniature model 3442).

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo FP84HT instrument. Samples (5-8 mg, in duplicate) were equilibrated at 70 °C for 2 min then ramped to 180 °C at 10 °C/min and held isothermally for 3 min, cooled to 70 °C at -10 °C/min and held isothermally for 3 min and the temperature cycle repeated as above. Results were analyzed using Mettler-Toledo FP99A software. Crystallinity was then calculated from the ratio of the melting enthalpy (105-144 °C) of the sample to the melting enthalpy of 100% crystalline HDPE with an enthalpy of 293 J/g (Wunderlich 1973). In addition, the plastic content was taken into account when calculating % crystallinity. Melt flow rate was determined in duplicate of the WPC at 30% wood loading using a CEAST model 7024 melt flow indexer according to ASTMD 1238 method B (10 kg load, barrel temperature 190 °C, 300 s analysis time).

RESULTS AND DISCUSSION

To improve the interfacial bonding between the wood fibre and matrix the wood fibre surface was reduced in size and modified to increase the level of adhesion and dispersion in order to enhance WPC performance. Ball milling of the commercial wood fibre (~250 µm) resulted in fibre size reduction which was screened to obtain a 300-400 mesh fraction with a volume weighted average particle size of 33 µm and the frequency weighted average particle size of 6 µm. Two chemical strategies were employed to then alter the micro-fibre surface, which both used a diisocyanate as a linker between an alcohol (of varying chain length) and the wood surface, which is expected to be tuned for hydrophobicity (Engonga *et al.* 2000).

Approach 1: The following alcohols: C_2, C_8, C_{12}, and C_{18}, were reacted with MDI to form an alcohol-MDI adduct. The alcohol-MDI adducts were characterized by HPLC-MS as their DBA derivatives (data not shown). Modified micro-fibre structures were obtained by reacting the alcohol-MDI adducts (C_2, C_8, C_{12}, C_{18}) with screened wood fibre (to give 37, 51, 29 and 63 % weight gains, respectively).

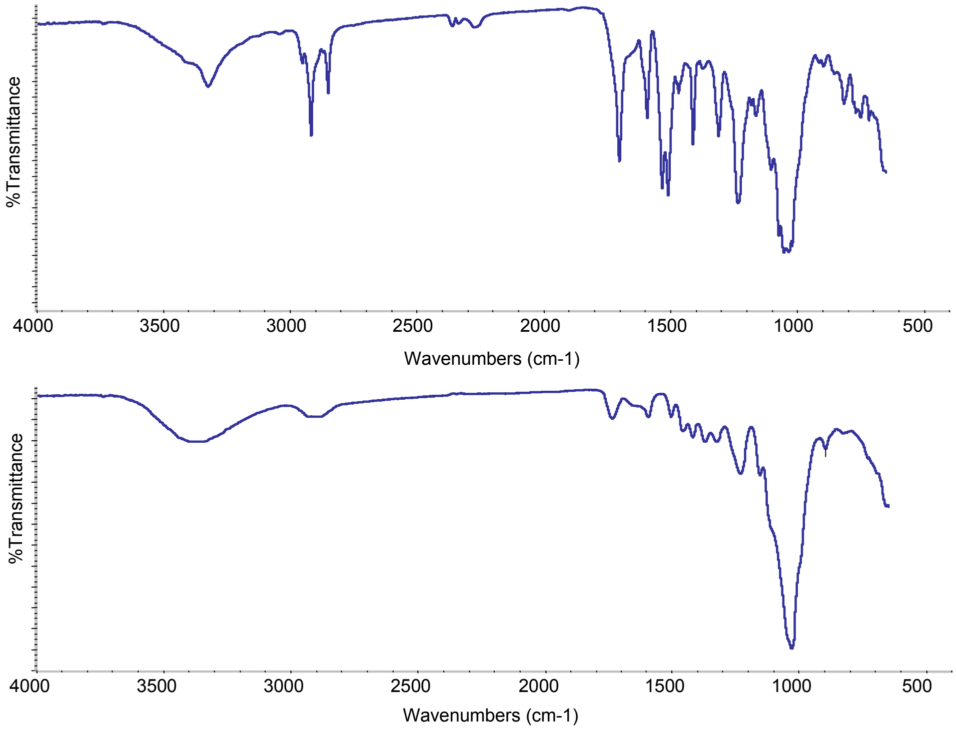

Figure 1: FTIR spectra of the C_2-MDI-adduct modified wood fibre by approach 1 (top) and extractives free wood fibre (bottom)

The presence of the isocyanate modified micro-fibre was supported by the observation of the urethane C=O peak (1720 cm^{-1}), aliphatic -CH$_2$- peaks (2920 and 2850 cm^{-1}), NH stretching band (3340 cm^{-1}) and the disappearance of the isocyanate peak (N=C=O, 2270cm^{-1}) by FTIR spectroscopy (Figure 1) (Engonga *et al.* 2000).

Approach 2: The strategy was to modify the wood surface with MDI and then react the isocyanate activated wood fibre with an aliphatic alcohol (C$_2$, C$_8$, C$_{12}$, C$_{18}$). The modified fibres were exhaustively extracted to yield weight gains for C$_2$, C$_8$, C$_{12}$, C$_{18}$ MDI reacted micro-fibres were 40, 53, 33, and 43%, respectively. The presence of the isocyanate modified wood fibre was supported by the observation of the carbonyl groups of urethane (1700 cm^{-1}) and urea groups (1640 cm^{-1}), aliphatic -CH$_2$- bands (2920 and 2850 cm^{-1}), amide bands (1550 and 1600 cm^{-1}), NH stretching band (3340 cm^{-1}) and the disappearance of the isocyanate band (N=C=O, 2270cm$_{-1}$) by FTIR spectroscopy (Figure 2) (Engonga *et al.* 2000).

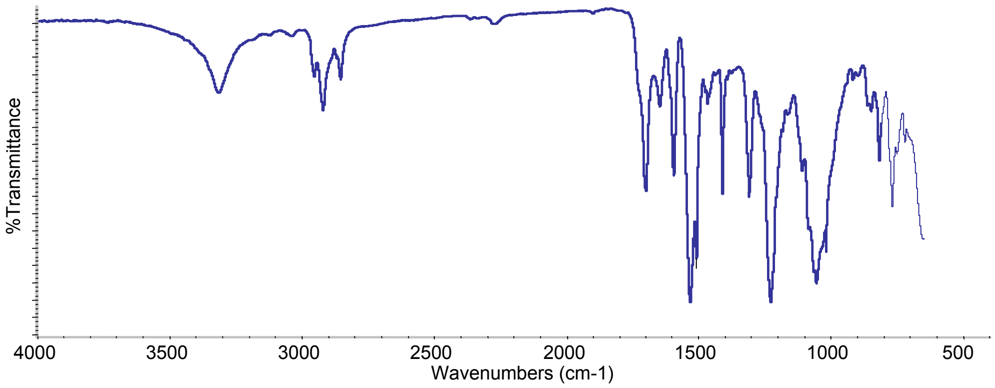

Figure 2: FTIR spectra of the C$_2$-MDI-adduct modified wood fibre by approach 2

To examine the effect of wood fibre modification (approaches 1 and 2) and loading (10, 30 and 50%) on WPC, small batches of micro-fibre and HDPE were compounded using a torque rheometer/mixer. Torque rheometry gave an indication of the compoundability of the modified micro-fibres with HDPE. Figure 3 (top) shows the torque curves of control and modified fibres by approach 1 at 30% wood loading. The C$_2$ modified micro-fibre required a maximum torque of 10 Nm as compared to unmodified "control" wood HDPE blend at 40 Nm. The C$_{18}$, C$_{12}$ and C$_8$ modified micro-fibres required a maximum torque between 25 and 30 Nm. Furthermore, the steady state torque values for the WPC made from control and modified fibres (C$_{12}$ and C$_{18}$) were approximately 10 Nm as compared to WPC made with C$_8$ and C$_2$ modified micro-fibres at 7 and 5 Nm, respectively. Compounding of modified micro-fibres (at 30% loading) by approach 2 showed that the maximum torque required to compound the C$_2$, C$_8$, and C$_{18}$ modified fibres (23-29 Nm) was lower than the control (42 Nm) and the C$_{12}$ modified fibres (Figure 3 bottom). The maximum torque values were comparable to those from the modified wood fibres using approach 1. The steady state torque values for all the compounded WPC control and modified fibres were similar at 12-14 Nm. These data generally show that modification of the wood fibre decreases the load required for blending wood fibre with HDPE and this may be attributable to improved dispersion.

To examine the flow characteristics of these WPC systems during processin the rheological properties, in the molten state, are required (Shenoy 1999). The melt viscosity of the WPC made from modified fibre by approach 2 (30% wood) was assessed by melt flow rate (Table 1). Due to load limitations, melt viscosity measurements at 50% wood loading could not be determined. The results clearly show that the viscosity decreased from 14 to 46% by wood modification as compared to the original fibre. These findings clearly show that the modified micro-fibres were easier to process (*e.g.* moulding and extrusion) than the control fibres.

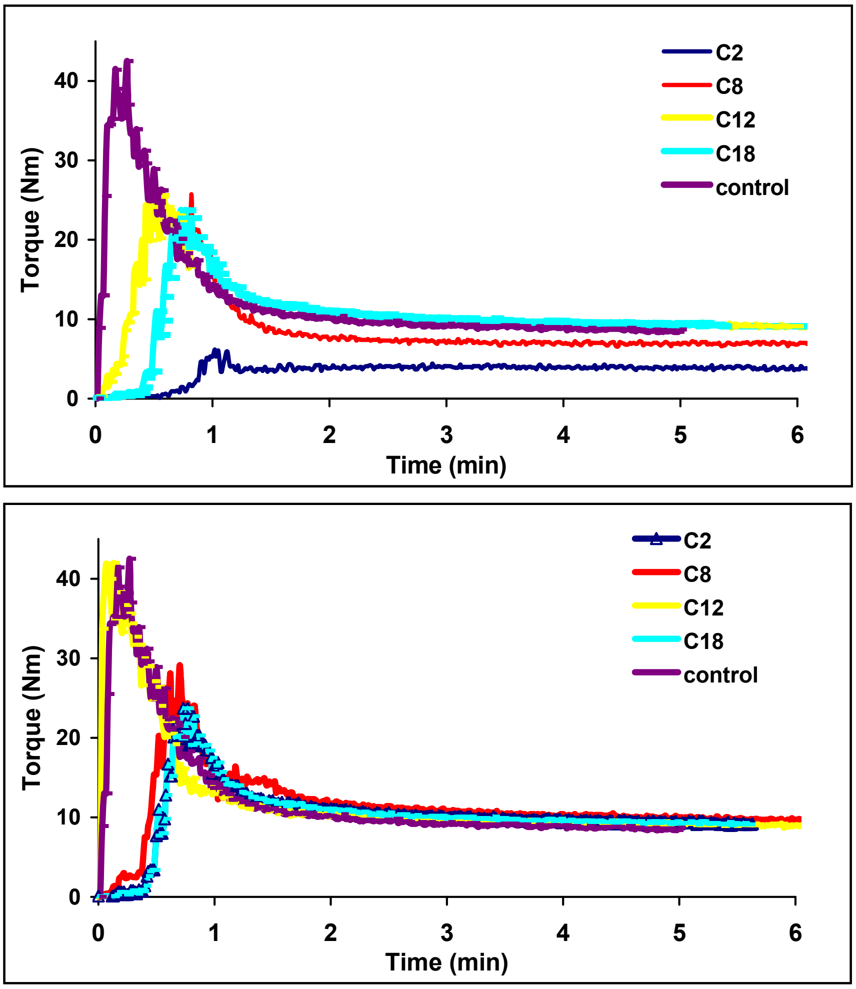

Figure 3: Torque rheometery curves for compounding modified wood (30% loading) by approach 1 (top) and approach 2 (bottom) in HDPE

Table 1: Melt flow rate and viscosity of WPCs made from modified wood by approach 2

Modified fibre (approach 2)	MFR (g/10min)	Viscosity (Pa*s)
Control	2.80	13200
C_2	3.82	9650
C_8	5.15	7170
C_{12}	3.25	11400
C_{18}	3.73	9920

The compounded material was molded into tensile specimens and tested (Table 2). The tensile strength of the modified and control WPCs were similar (20-24 MPa), except for the C_2 modified wood samples which gave higher values at ~23MPa at 50% wood content. There were no real differences in tensile modulus of the WPC between wood modification treatments and approaches (1.5-2.1 GPa at 50% wood loading). On examination of the WPC tensile specimens made from modified wood fibre small air-bubbles (defects) were observed and this may have masked any benefits of improved interfacial bonding.

To help explain why the properties of the WPC made from modified wood fibre (in some instances improved) as compared to the control fibre, DSC was used to investigate the extent of HDPE crystallization in these WPC systems at 30% wood content (Table 3).

Table 2: Tensile strength and modulus of WPC formulations made from modified wood

Modified wood	**10% wood**	**30% wood**	**50% wood**
	Tensile strength (MPa) [%CoV]		
Approach 1: Control	23.0 [3.6]	22.3 [6.1]	17.3 [11]
C_2	24.0 [7.9]	23.0 [12]	23.7 [27]
C_8	24.0 [10]	26.5 [16]	19.2 [3.9]
C_{12}	23.4 [5.7]	21.1 [8.2]	19.0 [8.2]
C_{18}	25.7 [3.9]	25.0 [3.7]	18.1 [24]
Approach 2: Control	23.0 [3.6]	22.3 [6.1]	17.3 [11]
C_2	24.0 [5.2]	23.4 [6.6]	22.6 [19]
C_8	23.2 [9.9]	19.9 [1.7]	13.4 [5.6]
C_{12}	21.5 [1.4]	20.3 [2.1]	17.0 [22]
C_{18}	20.1 [4.2]	21.4 [2.9]	20.6 [5.1]
	Tensile modulus (GPa) [%CoV]		
Approach 1: Control	1.5 [2]	1.7 [5]	1.9 [3]
C_2	1.4 [3]	1.9 [6]	2.1 [2]
C_8	1.3 [8]	1.6 [3]	1.5 [4]
C_{12}	1.4 [2]	1.5 [4]	2.0 [8]
C_{18}	1.4 [1]	1.2 [3]	1.5 [13]
Approach 2: Control	1.5 [2]	1.7 [5]	1.9 [3]
C_2	1.3 [1]	1.9 [3]	1.8 [12]
C_8	1.4 [1]	1.5 [1]	1.6 [18]
C_{12}	1.3 [1]	1.4 [2]	1.8 [11]
C_{18}	1.4 [1]	1.6 [13]	1.8 [1]

Table 3: DSC results for crystallinity and crystallization temperature for WPC made from control and modified fibre at 30% wood loading

Modified fibre	**HDPE crystallinity (%)**	**Crystallization temperature (°C)**
Control	25	119.1
Approach 1: C_2	39	117.3
Approach 1: C_8	38	118.9
Approach 1: C_{12}	44	118.8
Approach 1: C_{18}	39	119.6
Approach 2: C_2	32	118.9
Approach 2: C_8	33	116.4
Approach 2: C_{12}	31	118.6
Approach 2: C_{18}	37	119.3

The melting enthalpy (2nd melt) was used to determine the extent of crystallization. The crystallinity of HDPE in the WPC made from modified wood fibres by approach 1 were significantly higher (37-44%) than the unmodified control fibre (25%), unfortunately no obvious trend was observed. The crystallization temperature of HDPE in the WPC was shown to increase from 117.3 to 119.6 °C with an increase in alkyl chain length (C_2 to C_{18}) of the modified wood fibre. The crystallinity of HDPE in the WPC made from modified wood fibres by approach 2 were higher (31-37%) than the unmodified control fibre (25%). The results showed that as the alcohol chain length increased the degree of crystallinity increased, except for the C_{12} modified fibres. The crystallization temperature of HDPE in the WPC made from the modified wood fibre between 116.4 to 119.3 ^{o}C. These data suggests that the crystallization of HDPE was induced, at a slightly higher temperature, by improving the nucleation at interfacial bond with the wood fibre by having an extended hydrophobic shell (Tang *et al*. 2004).

CONCLUSIONS

Ball milling was shown to be an efficient way to produce micro-fibres at a volume and frequency weighted averages of 25 and 6 µm, respectively. Chemical modification of these micro-fibres was successfully achieved by two approaches to form the alcohol-diisocyanate appendages at the wood surface to tentatively form core-shell type structures. Approach 1 was a 2-step lengthy process to form modified micro-fibre structures. A second approach was devised as a “one-pot” process to activate the wood surface with a diisocyanate and subsequently reacted with a fatty alcohol to form a modified micro-fibre structures. FTIR spectroscopy confirmed that the desired wood modification occurred.

The modified wood fibres (from both approaches) were readily compounded (lower maximum and steady state torque values) into HDPE relative to unmodified wood fibre controls. It is speculated that modifying the wood surface with alkyl chains made the wood fibres more disperable/miscible within the HDPE matrix and therefore required less mechanical energy to compound. Thermal analysis data showed that the WPC made from modified wood fibres had a higher level of HDPE crystallization than WPC made from unmodified fibre controls. These results suggest that nucleation at interfacial region between HDPE and the wood fibre was improved by wood surface modification. The mechanical properties of WPC made from chemically engineered wood fibres gave variable results and show potential for improved performance.

The outcome of this preliminary study has shown that wood fibre modification for use in WPC has potential benefits in improved processability, such as production rate and higher wood loadings.

ACKNOWLEDGEMENTS

This project was supported by the USDA-CSREES-NRI grant number 2003-35103-12902. The FTIR spectrometer was supported by a USDA-CSREES grant #2005-35103-15243. We would like to acknowledge the technical help of Drs. Tieqi Li, Karl Englund, and Michael Wolcott.

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Modification of Wood using a Glow-discharge Plasma Derived from Water

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Keywords: Adhesive, bond, eucalyptus, glue, plasma, strength, wettability

ABSTRACT

Plasma consists of a mixture of atoms, molecules, ions, free radicals, electrons and metastable species. Plasmas generated from inorganic gases modify materials by ion implantation and etching, both of which can increase the energy or wettability of surfaces. This effect of plasmas has led to their widespread use as a means of increasing the adhesive properties of materials such as plastics, which have low surface energy and poor wettability. The surface energy of wood is higher than that of plastics, but some wood species, for example many eucalypts, are difficult to glue because extractives contaminate surfaces and prevent adhesives from wetting the wood and forming strong bonds with sub-surface layers. It was hypothesized here that plasma modification could increase the surface energy of eucalypt wood and improve its adhesive properties. A plasma reactor was built that generated an intense glow-discharge plasma derived from water. This plasma significantly increased the surface wettability of eucalypt wood even at low energy levels, but there was no corresponding increase in the glue-bond strength of the difficult-to-glue species spotted gum. At higher energy levels, however, plasma modification increased the wettability and glue-bond strength of spotted gum and three other eucalypt species. These increases in glue-bond strength appeared to be associated with etching of the wood cell wall and the removal of phenolic rich materials and structures, including vestures that occlude bordered pits in eucalypts. In conclusion, plasma treatment shows promise as a means of modifying wood to improve the adhesive properties of species that are difficult to glue, but further research and scale-up of the treatment is needed before it can be used on an industrial scale.

INTRODUCTION

Plasma is a mixture of atoms, molecules, ions, free radicals, electrons and metastable species (Inagaki 1996). These activated species are capable of modifying the surfaces of materials in a variety of ways depending on the nature of the plasma and the chemical composition of the material (Boenig 1982). Plasmas generated from organic gases are capable of depositing thin films on surfaces. Plasmas generated from inorganic gases, on the other hand, modify materials by ion/atom implantation, oxidation and the etching of low molecular weight materials from surfaces. Both types of plasmas have been used to modify the surface properties of wood. For example, plasma treatments using a range of organic gases or vapours have been used to increase the water repellency of wood surfaces (Podgorski *et al.* 2001). Plasma treatment using inorganic gases has been used to increase the wetting properties and adhesive bond strength of wood (Uehara and Jodai 1987, Sakata *et al.* 1993, Podgorski *et al.* 2000). These studies found that plasma treatment can significantly increase the surface energy of wood and may enhance the capacity of wood to form strong glue-bonds. Many eucalyptus wood species are rich in extractives (Hillis 1984), and these interfere with glue bonding by reducing wettability, preventing adhesives from easily penetrating the wood and interfering with the cross-linking of adhesives (Plomley *et al.* 1976). The high density of many eucalypts also restricts adhesives from penetrating into the wood and forming strong bonds (Brennan and Newby 1993). Hence, many eucalypts are difficult to glue, unless pre-treatments such as chemical modification of wood surfaces or various mechanical treatments are used to remove extractives and increase glue penetration and retention (Gottstein and Plomley 1967, Balfas *et al.* 1993). Plasma can increase the wettability of materials, remove low molecular weight materials from surfaces, and it can also increase the permeability of wood (Chen and Zavarin 1990). Hence, plasma treatment should enhance the capacity of eucalyptus wood to form strong glue-bonds. In this study we test this hypothesis by examining the ability of glow-discharge plasma generated from water to increase the wettability and adhesive bond strength of four eucalypt wood species including the ‘difficult-to-glue’ species blackbutt (*E. pilularis*) and spotted gum (*C. maculata*).

MATERIALS AND METHODS

Experimental designs and statistical analyses

Three designed experiments were carried out. The first experiment examined the effect of four fixed factors: (1), Eucalypt species; (2), Grain angle (parallel and perpendicular to the grain); (3), Plasma power level; (4), Plasma treatment time, on the wetting of wood surfaces. Boards cut from two different trees for each species provided replication at the higher level. Thirteen boards from each tree were obtained for each species. Each board was cross-cut to produce two samples resulting in a total of 52 samples for each species (208 in total). Four samples for each species were randomly allocated to each of the twelve different plasma treatments and the untreated control. A second experiment examined the effect of two fixed factors: (1), Nine plasma treatments (including untreated control); and (2), Adhesive type (six different adhesives) on the dry shear strength of treated *C. maculata* specimens. Boards cut from two different trees provided replication at the higher level. Eighteen boards cut from each tree were selected and cross-cut to produce 3 pairs of samples (strips) each measuring 8 mm (thickness) x 25 mm (width) x 100 mm (length), and these were allocated to the different treatment by glue combinations (54 in total) and used to produce large lap shear specimens, which were each subsequently cross-cut to produce four test specimens. The final and third experiment examined the effects of three fixed factors: (1), Surface treatments including (a) plasma at 50 W/3 mins, (b) plasma at 150 W/3 mins, (c) plasma at 150 W/10 mins, (d) sanded with 80 grit abrasive paper, (e) sanded and plasma treated at 50 W/3 mins, (f) sanded and plasma treated at 150 W/5 mins, (g) untreated; (2) Eucalypt species; (3) Six adhesive types on the dry and wet strength of lap shear specimens. Boards cut from two different trees again provided replication at the higher level. All large shear blocks were cut into four test specimens giving a total of 8 specimens for each treatment/species/adhesive combination. These specimens were allocated to either dry or wet shear tests. All three experiments were essentially randomised block designs that accounted for random variation in wood properties between trees and samples and that occurring as a result of the sequential nature of the experimentation. Analysis of variance was used to examine the effects of fixed and random factors on the wetting properties and shear strength of plasma-modified eucalypt wood.

Wood samples

Air-dry and planed sample boards measuring 100 mm (width) x 8 mm (thickness) and of varying length were obtained from two plantation grown trees for each of the following eucalypt species: blackbutt (*Eucalyptus pilularis* Smith); Gympie messmate (*E. cloeziana* F. Muell); rose gum (*E. grandis* W. Hill ex Maiden) and spotted gum (*Corymbia maculata* Hook. formerly *E. maculata*). Each board was labelled according to its species and tree number (1 or 2) and stored in a conditioned room at 20 °C and 65 % r.h. for 16 weeks. Wood strips measuring 8 mm (thickness) x 25 mm (width) x 100 mm (length) cut from the different boards were treated with plasma. The basic density and extractive content of these wood strips was measured using standard methods (Table 1).

Table 1: Density and extractive content of E. pilularis, E. cloeziana, E. grandis and C. maculata

Species	Basic density [g/cm^3]	Extractive content [%]
E. pilularis	0.664	7.7
E. cloeziana	0.776	7.0
E. grandis	0.553	2.4
C. maculata	0.872	7.6

Plasma and other surface treatments

Wood samples were modified in a small plasma reactor that was designed to treat silicon wafers to produce clean, high energy, surfaces. One or two wood strips were placed in the chamber of the plasma reactor and a vacuum of 0.15 ± 0.01 torr was drawn. A valve was opened to allow water vapour from a glass reservoir into the chamber and the vacuum was redrawn. Radio frequency (R.F.) energy at 135 kHz was transmitted to the treatment chamber. After treatment the chamber was vented to atmosphere. Samples were removed from the chamber, taking care to avoid touching and contaminating their upper surfaces. The effects of plasma treatment on the glue-bond strength of adhesives applied to the four different eucalypt species were compared with that obtained by sanding wood before gluing. The sanding treatment involved manually sanding wood surfaces for 30 seconds with a coarse (80 grit) abrasive paper, as a previous study had shown that this treatment could significantly improve the bond strength of adhesives applied to eucalypt wood (Balfas *et al.* 1993).

Measurement of contact angle and area

Immediately after plasma treatment each individual wood sample was placed on an adjustable platform that was level with a horizontal microscope containing a goniometer eyepiece. A 25 µL droplet of 0.1 M potassium permanganate solution was placed on the surface of the treated sample using a pipette. The contact angle formed by the droplet with the treated wood surface, both parallel and perpendicular to the grain, was measured within 10 seconds of its application. These measurements were repeated on four further droplets of potassium permanganate applied to each sample. Contact angle measurements were also made on duplicate plasma treated (150W/5 minutes) wood samples of each of the 4 eucalypt species after 30 minutes, 1, 2, and 24 hours.

Adhesives and measurement of bond strength

The effects of plasma treatment on glue bond strength of the different eucalypts was assessed using six different adhesives that are recommended for the gluing of furniture, veneer and other secondary wood products (Table 2). A pair of small wood strips, each measuring 8 mm (thickness) x 25 mm (width) x 100 mm (length) from the same board, was selected and an area 100 x 20 mm was marked on the treated surface of each strip. Fresh adhesive was prepared and applied to the marked area using a spatula. A small roller was used to apply an even film of adhesive to the surface or surfaces of the strips. The amount of adhesive applied, glue spread, ratio of hardener to adhesive, and assembly time were in accord with manufacturers' guidelines (Table 2). The two strips were placed together to produce a lap-shear assembly and put in one of 6 small cold presses located in a conditioned room. Each assembly was clamped together using the recommended pressure by screwing the rocker head of the press down using a calibrated torque wrench. The glued assemblies were pressed for the recommended time and they were removed from the presses and conditioned for two weeks. Each assembly was then cut into four shear test specimens, each measuring 25 x 23 x 8 mm. The shear area of each specimen was measured using a digital calliper and their shear strength was determined using a modified ASTMS Method described by Strickler (1968). This involved individually placing each specimen in a shear test jig, which was placed under the loading head of a Shimadzu Universal Testing Machine. Load was applied at a constant strain of 0.5 mm per minute. The force (N) at failure was recorded and shear strength was calculated as described previously (Balfas *et al.* 1993). Shear tests were either performed on conditioned test specimens or specimens that had been immersed in tap water for 24 hours (wet test).

Table 2: Adhesives and gluing parameters used to produce lap-shear specimens from eucalypt wood

Glue Type	Glue-spread [mg/mm^2]	Clamping pressure [Nm]	Pressing time [h]	Adhesive:Catalyst Ratio
PVA dispersion	0.13*	1.5	1	-
Cross-linking PVA	0.265	1.5	1	33:1
Isocyanate/MDI	0.20*	1.6	1	100:15
Polymer isocyanate	0.275	4.3	1	100:15
UF	0.170	3.0	22	10:1
PRF	0.175*	3.0	22	100:25

**Applied to both faces*

RESULTS AND DISCUSSION

Plasma treatment significantly increased the wettability of the four eucalypt wood species (Figures 1-4), in accord with previous studies of the effect of plasma treatments on the wettability of wood. Low energy plasma treatments produced by using low R.F. power (10 W) and/or short treatment times produced large reductions in the contact angles of aqueous droplets applied to modified wood surfaces. These decreases in contact angle were more pronounced in *E. grandis* and *E. cloeziana* than in *E. pilularis* and *C. maculata*. In the former two species some of the low energy treatments were as effective at increasing the surface wettability of wood as the high energy treatments (Figures 2-3). In contrast in *E. pilularis* and *C. maculata*, high energy treatments were required to produce the increases in wettability that low energy treatments produced with *E. grandis* and *E. cloeziana*. The correlation between increases in wettability and treatment power in *E. pilularis* and *C. maculata* may be related to increased hydroxylation and/or greater etching of hydrophobic extractives at higher energy levels.

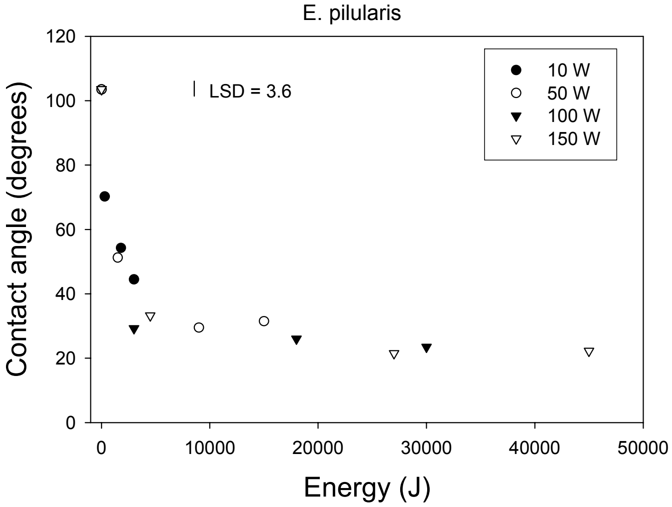

Figure 1: The effect of different plasma treatment energy levels on the wettability of E. pilularis

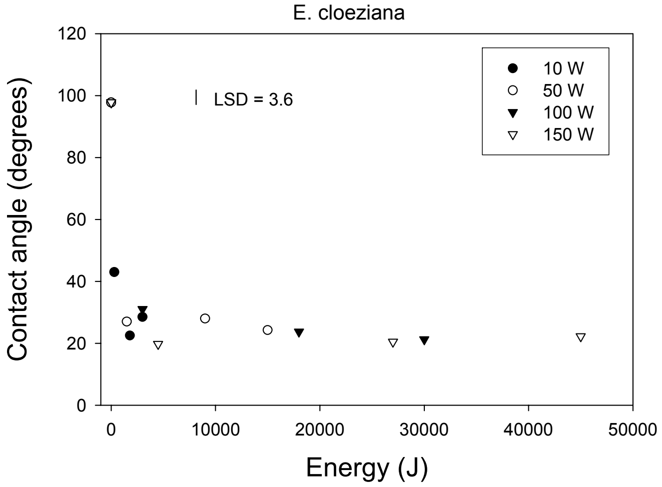

Figure 2: The effect of different plasma treatment energy levels on the wettability of E. cloeziana

Sakata *et al.* (1993) also observed that the wettability of plasma-treated wood surfaces was affected by species. They found that the wettability of species with high extractive contents was lower after a corona discharge plasma treatment than similarly treated wood species with smaller extractive contents. Likewise, the eucalypt species with the highest extractive contents here (*E. pilularis* and *C. maculata*) were generally less wettable after plasma treatment than *E. grandis* and *E. cloeziana*, whose extractive contents were lower (Table 1).

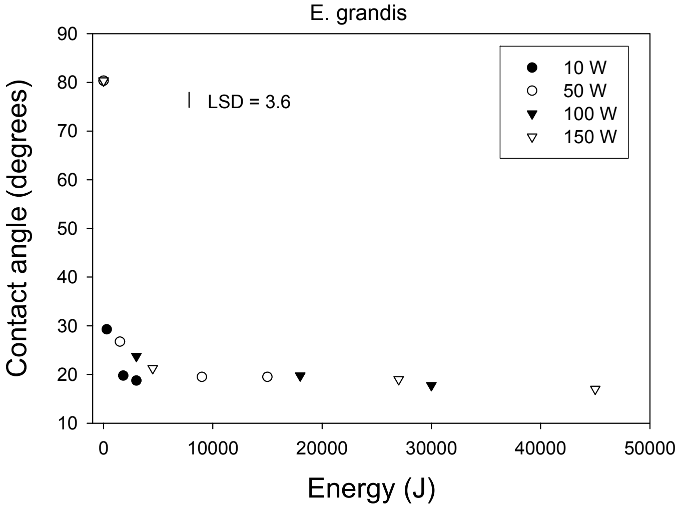

Figure 3: The effect of different plasma treatment energy levels on the wettability of E. grandis

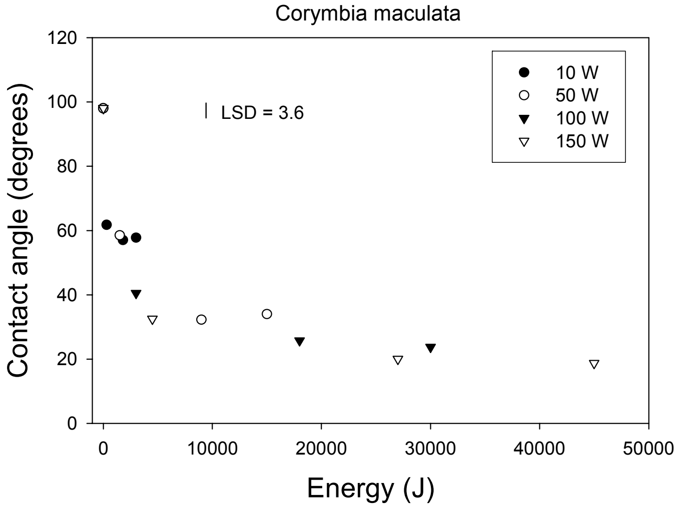

Figure 4: The effect of different plasma treatment energy levels on the wettability of C. maculata

Furthermore, the wettability of *E. pilularis* and *C. maculata* declined quite rapidly after plasma treatment whereas in *E. grandis* and *E. cloeziana* plasma treated surfaces were still significantly more wettable than the untreated controls, 24 hours after plasma treatment (Figure 5). The migration of extractives to wood surfaces is thought to be responsible for reductions in the wettability of wood surfaces as they age (Hse and Kuo 1988), and such an effect may explain why plasma treatment had a transient effect on the wettability of *C. maculata* and to a lesser extent *E. pilularis*. Evidence in support of this suggestion is our finding that the species that showed the smallest (*E. grandis*) reversal in wettability following plasma treatment had the lowest extractive content.

The effect of plasma treatment on the dry lap-shear strength of *C. maculata* specimens glued with a range of adhesives is shown in Table 3. Contrary to expectations most of the plasma treatments generally caused a decrease in the dry adhesive bond strength of *C. maculata* wood specimens.

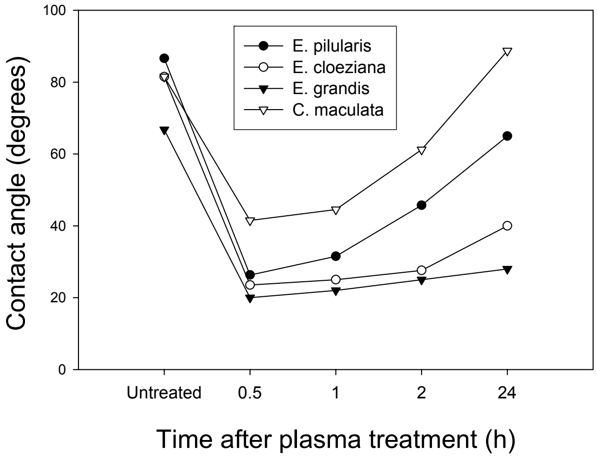

Figure 5: The effect of elapsed time after plasma treatment on the wettability of eucalyptus wood

Table 3: The effect of plasma treatments on the strength (MPa) of C. maculata bonded with different adhesives

Glue	**Plasma Treatment Energy [J]**								
	0	300	1500	1800	3000	9000	18000	27000	45000
PVA dispersion	6.3	4.2	1.8	2.4	3.9	2.3	4.1	4.0	9.3
Cross-linking PVA	5.9	7.0	3.3	3.9	2.2	4.2	3.0	4.0	6.9
Isocyanate/MDI	6.6	5.9	5.4	3.6	6.2	4.6	4.3	4.1	6.6
Polymer isocyanate	5.3	3.1	2.5	1.8	3.2	2.7	2.2	5.8	7.2
UF	6.5	4.0	1.6	2.3	2.3	1.6	6.2	3.6	4.1
PRF	9.6	4.1	5.1	2.9	3.3	3.9	2.0	2.4	8.6
Mean	**6.7**	**4.7**	**3.3**	**2.8**	**3.5**	**3.2**	**3.6**	**4.0**	**7.1**

The only plasma treatment that enhanced the glue bond strength of *C. maculata* was the high energy treatment (45000 J), and therefore subsequent experimentation focussed on similar treatments, and compared their effects on glue bonding with that produced by sanding wood surfaces prior to gluing. Figure 6 shows the effects of high energy plasma treatments, sanding and combination (plasma and sanding) treatments on the glue bond strength of dry and wet lap shear specimens (averaged across adhesives and the four eucalypt species). Plasma treatment significantly increased the dry and wet shear strength of specimens, and the increases in dry strength were comparable to that produced by sanding. The combination of plasma treatment and sanding was particularly effective at increasing the dry shear strength of specimens. In contrast, plasma treatment was less effective than sanding at increasing the wet shear strength of specimens, and there was no significant difference in the wet shear strength of sanded specimens and those treated with a combination of sanding and plasma.

The effectiveness of the plasma treatments at increasing glue bond strength varied with the different eucalypt species. The plasma treatments had no significant effect on the dry shear strength of *E. grandis*, whereas they significantly increased the dry shear strength of the other three eucalypt species (Figure 7). These increases in shear strength were most pronounced for the high energy treatment. This treatment was more or equally effective as sanding at increasing the dry shear strength of *E. pilularis, E. cloeziana* and *C. maculata*. Furthermore, in these species the combination of sanding and plasma treatment produced increases in dry shear strength over and above that produced by sanding alone (Figure 7).

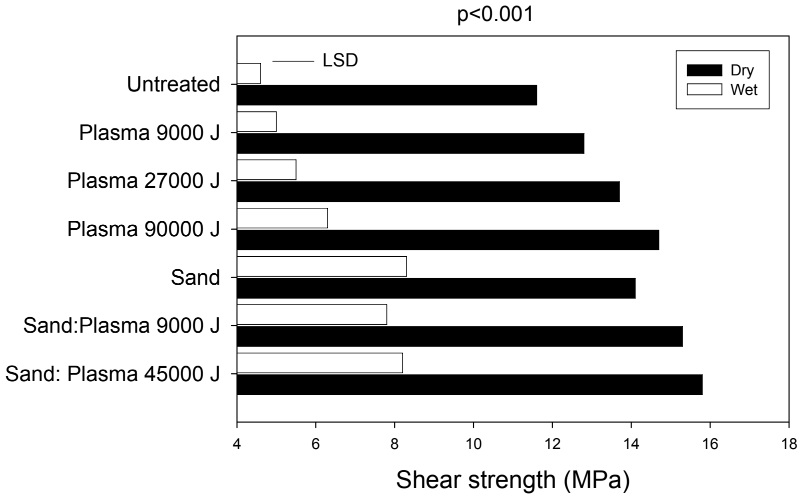

Figure 6: The effect of plasma treatment on the dry and wet shear strength of eucalyptus wood

The plasma treatments were most effective at increasing the dry shear strength of *C. maculata*. They also increased the wet shear strength of *E. pilularis, E. cloeziana* and *C. maculata* (Figure 8), but had no such effect on the wet shear strength of *E. grandis*. However, none of the plasma treatments were as effective as sanding at increasing wet shear strength and the combination of sanding and plasma treatment was only more effective than sanding at increasing wet shear strength of two of the four eucalypt species (Figure 8).

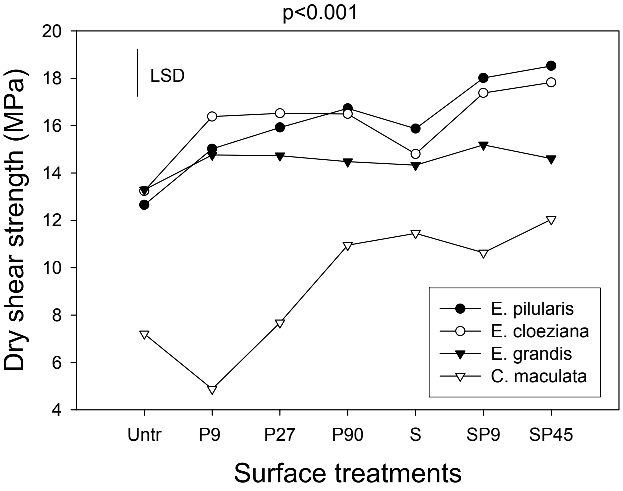

Figure 7: The effect of plasma (P), sanding (S) and combination (SP) treatments on the dry shear strength of four eucalypt species bonded with different adhesives (plasma level x 10^3 J)

Previous studies that have used plasma treatments to increase the bond strength of wood glued with adhesives have obtained mixed results. Both Uehara and Jodai (1987) and Rehn and Vlöl (2003) found that plasma treatments could improve the bond strength of wood glued with formaldehyde-based adhesives. Sakata *et al.* (1993) found that a corona discharge plasma treatment increased the bond strength of the hardwood isunoki (*Distylium* sp.) glued with a mixed UF/PVA adhesive, but it had the opposite effect with purpleheart (*Peltogyne* sp.).

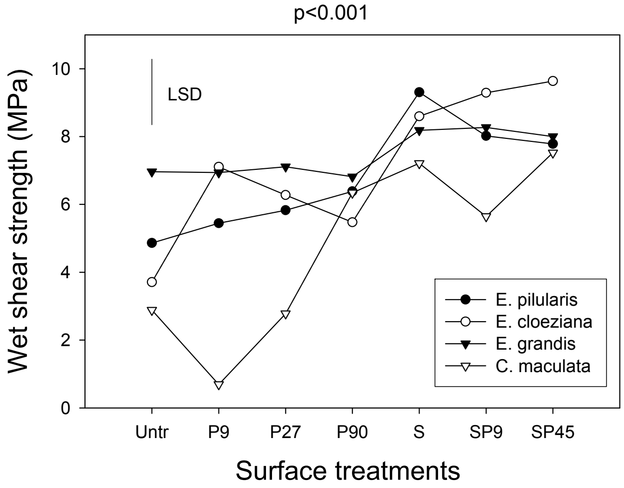

Figure 8. The effect of plasma (P), sanding (S) and combination (SP) treatments on the wet shear strength of four eucalypt species bonded with different adhesives (plasma level x 10^3 J)

More recently, Rehn *et al.* (2003) found that plasma treatment increased glue bond strength of robinia (*Robinia pseudoacacia* L.) and oak (*Quercus* sp.), but it had little effect on the glue bond strength of teak (*Tectona grandis* L.f.). They also found that plasma treatment reduced the susceptibility of robinia and spruce (*Picea* sp.) to delaminate following wetting and fracture testing, but it had no such effect with beech (*Fagus sylvatica* L). In this study, plasma treatment at low energy levels consistently reduced the bond strength of eucalypts wood glued with a range of different adhesives and even at high energy levels it had little effect on the bond strength of *E. grandis*, which is regarded as a species that is not as difficult to glue as the three other eucalyptus species that were tested here. These findings may explain why some previous studies have found that plasma treatments can reduce the bond strength of wood glued with different adhesives. Plasma treatments were most successful at increasing glue bond strength when they were applied at high energy levels to *C. maculata,* which has a reputation as being difficult to glue because of its high density and extractive content (Bootle 1985). These increases in glue-bond strength appeared to be associated with etching of the wood cell wall and the removal of phenolic rich materials, including vestures that occlude bordered pits in eucalypts (Ramos 2001). Overall, our findings suggest that future research on the use of plasma treatments to improve adhesive bonding of wood should focus on their application to dense and extractive-rich species that are difficult to glue.

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Session 4: Poster Session 1

Changes in Cell Wall Volume due to Reaction of Wood with Acetic Anhydride

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Keywords: Acetylation, cell wall volume, helium pycnometry

ABSTRACT

There are many papers in the literature where volume changes due to reaction of wood with acetic anhydride have been interpreted as being representative of cell wall volume changes. This cannot be assumed and requires that the cell wall volume changes are measured directly. However, there is very heavy reliance placed upon the volume changes as determined from external dimensions of the wood samples. From such data, various workers have attempted to correlate theoretical and measured cell wall volume changes, correlation between cell wall bulking and other properties such as dimensional stability. This paper reports upon experiments to determine whether external dimension volume changes and cell wall volume changes can be correlated. Cell wall volume changes were determined using the technique of helium pycnometry, which has been used very little for studies of modified wood. Data is presented on molar volume, and comparisons between volume determination using measurements of external dimensions and using helium pycnometry. It is concluded that cell wall volume changes do not correlate with volume changes determined using external dimensions.

INTRODUCTION

When wood is acetylated it swells, eventually reaching its so called ‘green volume’ (water-saturated volume) at a weight percentage gain (WPG) of the order of 20-25%. This phenomenon has been extensively reported upon in the literature, and there have been many studies where the volume change due to modification has been use to determine the molar volume of the bonded acyl adduct (Hill and Jones 1999), or has been correlated to the volume of adduct added (Rowell and Ellis 1978). Although considerable work has been done in this area, there remains an important issue that all dimensional changes have been determined from the external volumes of samples before and after modification. When attempting to determine changes in the cell wall volume, it is questionable whether evaluation using external dimension measurements is a valid method. This study was undertaken to determine whether there is any correlation between actual cell wall volume changes (as determined using helium pycnometry) and dimensional changes determined using measurement of external dimensions.

EXPERIMENTAL

Two independent experiments were performed to determine reproducibility. Small sample discs of nominal diameter 13 mm and of longitudinal section 0.5 mm were prepared from Corsican pine (*Pinus nigra*) sapwood. The discs were carefully sanded to remove loosely adhering fibres and individually labelled. Samples were treated in batches of seven, which was the number required to ensure an efficient fit into the chamber of the helium pycnometer (Micromeritics accupyc 1330). The wood was modified with acetic anhydride to a variety of WPGs. The dimensions of the individual samples were determined using measurements of external dimensions using a set of callipers and the total volume of the seven discs was found using the helium pycnometer. Full experimental details are given elsewhere (Hill and Ormondroyd 2004, Heon Kwon *et al.* 2007), these data are labelled throughout as (a) and (b) respectively.

RESULTS AND DISCUSSION

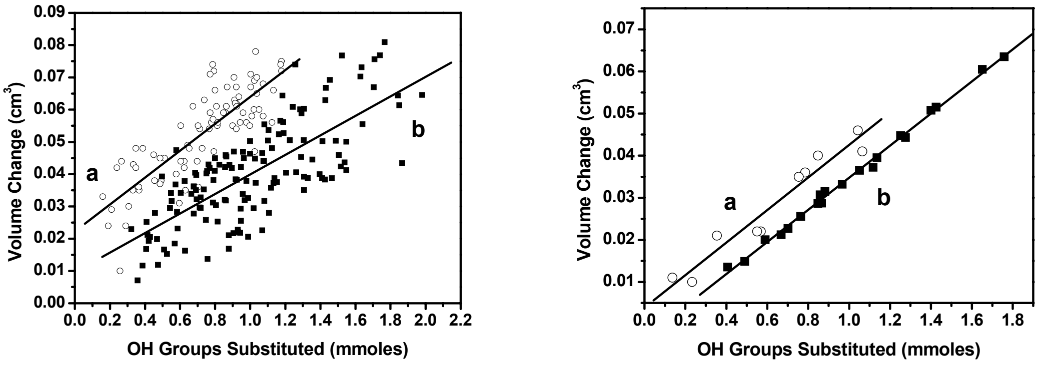

Figure 1: Relationship between volume change and level of OH substitution as determined using external volume measurements (LH graph) and helium pycnometry (RH graph)

The data shown in Figure 1 above shows the change in volume of wood samples from the two experiments as the level of substitution increases, the gradients of the linear fits give the average molar volume for the acetyl group in wood (Table 1) (assuming that external dimensions can be used to determine this value). It should be noted that the total volume change and degree of OH substitution of the seven discs as measured by helium pycnometry have been divided by 7 to make both sets of data comparable.

Table 1: Summary data for molar volume determinations ($cm^3\ mol^{-1}$)

Experiment	External dimensions	He pycnometry
a	41.69 +/- 3.20	38.67 +/- 3.39
b	30.25 +/- 2.30	38.11 +/- 0.58

There is clearly a large discrepancy between the molar volume obtained using external dimensions, whereas the values calculated from helium pycnometry measurements are not significantly different. It is also apparent that there is a considerable amount of scatter in the data when external dimensions are used to determine volume changes. Linear fits are shown for this data, although this should not be assumed to be correct, particularly in view of the fact that neither fit passes through the origin. The above method gives an average molar volume, but it has been reported that this value varies as WPG increases (Hill and Jones 1999, Çetin and Ozmen 2001). In order to check this, molar volumes were calculated for each individual sample at each WPG (for external measurements) and for batches of seven for the helium pycnometry data. The results of this are shown in Figure 2.

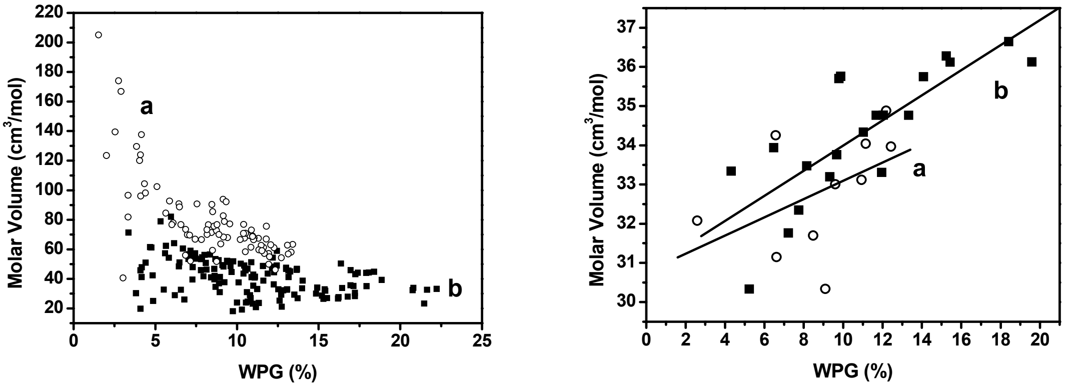

Figure 2: Variation of molar volume with level of reaction as determined from external dimensions (LH) and helium pycnometry (RH)

The LH graph shows that there is an apparent decrease in molar volume as the WPG increases. It is not possible to obtain a definitive molar volume from this data, although the data points converge to a value of the order of 35 cm^3 mol^{-1}. Plots of this type have been taken at face value and falsely interpreted as being due to changes in 'void volume' (Hill and Jones 1999). The true explanation is that the measurement of volume changes does not accurately measure the change in volume of e the cell wall. The RH graph of Figure 2 shows that molar volume data determined from helium pycnometry measurements, with linear fits to the data. The data associated with the linear fits is given in Table 2.

Table 2: Fitting parameters for molar volume determinations using helium pycnometry

Experiment	Intercept	Gradient	R	p
a	30.77 +/- 1.43	0.23 (0.15)	0.48	0.1647
b	30.79 +/- 0.69	0.32 (0.06)	0.79	<0.001

R is the correlation coefficient and p is the p value for the t-test of the slope = 0

Both fits indicate that there is an increase in molar volume as the level of reaction increases (in marked contrast to data obtained from external dimensions), with the data for experiment b being highly significant. Thus, obtaining a definitive molar volume value is problematical. The intercept at WPG = zero provides two values from experiments a and b that are identical (30.8 cm^3 mol^{-1}). Another approach is to assume that there is no change in molar volume as WPG increases and take the average of the data, to obtain the values given in Table 3.

Table 3: Summary data for molar volume determinations (cm^3 mol^{-1})

Experiment	External dimensions	He pycnometry
a	n/a	32.85 +/- 1.49
b	n/a	34.33 +/- 2.32

A t-test of the two means shows that they are significantly different at the 0.05 level. The molar volume for the acetyl group in the cell wall of Corsican pine sapwood, lies in the region from 30 to 38 cm^3 mol^{-1}. The mean molar volume is of the order of 33 cm^3 mol^{-1}. It is likely that with Corsican pine sapwood, the molar volume increases as WPG increases.

CONCLUSIONS

Any determination of cell wall volume changes as a result of modification processes should use a displacement method such as helium pycnometry. Although external dimensions have been used for such purposes in the past, this is not appropriate. Determination of a definitive molar volume for the volume occupied by the bonded acetyl group in the cell wall is problematical. There are clear indications that the molar volume increases with level of substitution for Corsican pine sapwood. The molar volume of the acetyl group in Corsican pine sapwood probably lies in the region 30-38 cm^3 mol^{-1}.

ACKNOWLEDGEMENTS

GAO wishes to thank Arch Timber Protection for provision of a PhD studentship and JHK wishes to thank the Korean government for a visiting scholarship.

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Molecular–mass Distribution of Carboxymethylcellulose in Composition of Carboxymethylated Wood

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Keywords: Molecular-mass distribution, carboxymethylcellulose, wood

ABSTRACT

The possible ranges of use of carboxymethylated wood (CMW) are determined by the molecular-mass characteristics. During the carboxymethylation of wood the uniformity of products increases. The components of CMW do not selectively disssolve in cadoxene, and the study of a molecular–mass distribution (MMD) of cellulose glycolic acid (CMC) in the composition of the modified wood is possible only after its degradation. MMD of carboxymethylated cellulose in wood, studied by a method of turbidimitric titration after its degradation by peracetic acid on the developed procedure. The fractional composition of CMC depends, mainly, on the temperature of alkaline pretreatment and reaction of carboxymethylation. Homogeneous samples of CMC are obtained by carrying out reaction at 60 °C. Samples of CMC were investigated also with the help of a solid-state method of thermomechanical spectroscopy (TMS). The results obtained by us testify to the adequacy of an assessment MMD by methods of fractionating and TMS and show an opportunity of application of TMS for quantitative determination of molecular weights and polydispersity of cellulose and its carboxymethyl ethers.

INTRODUCTION

The modification (including carboxymethylation) of wood and various wastage of its processing without division them on the basic components is a perspective direction in range of chemistry of wood. It allows solving a problem of salvaging lignocellulosic of wastage, to lower environmental and to replace ethers of cellulose on cheaper derivants of wood in some ranges of their application. The possible ranges of use CMW, as well as any other polymeric systems, are determined by the molecular-mass characteristics, including polydisperse of fractional composition. The properties CMW substantially will depend on the molecular-mass characteristics CMC.

RESULTS AND DISCUSSION

Molecular composition of polymers traditionally position by methods of a fractionating of their solutions. The products of carboxymethylated wood have low solubility in cadoxene (up to 67%). The molecular uniformity fraction CMW solvable in cadoxene (contents Cd 5.6%, ethylene diamine – 28%) increases at augmentation of duration of reaction that is established by a method of turbidimitric titration on procedure developed for CMC. The fraction CMW insoluble in cadoxene contains strips of absorption of all components that is established on the data of IR-spectroscopy. It testifies to nonselective dissolution of components of carboxymethylated wood by the cadoxene. The molecular-mass characteristics CMW studied on an example of CMC, discharged of it, since the properties of products of modifying of wood are determined, mainly, transformations of cellulose. The abjection CMC from CMW by traditional methods Kyurshner and with use of peracetic acid (PAA), which is developed for abjection of cellulose from wood, is accompanied practically by complete hydrolysis of the samples containing cellulose. With the purpose of conservation of the molecular-mass characteristics CMC the improvement of methods of abjection CMC from CMW is necessary. On the establishment of the literary data for improvement of conditions of abjection CMC from CMW we choose 15 % peracetic acid (table 1).

Table 1: Property of samples of carboxymethylated pine wood in dependence on duration of processing by peracetic acid (reaction carboxymethylation at 60°C, 70 minutes, pretreatment by alkali in propanol-2 with w_{water}=10 % at 60°C, 2 hours)

Parameter	**Duration of processing, minutes**				
	0 (CMW)	**5**	**10**	**15**	**20**
Yield, %	–	50	29	26	24
Carboxymethyl groups (CG), %	22.4	13.6	9.9	9.6	9.2
Colour of the indicator	dark yellow	yellow	llight yellow	colourless	colourless
Solubility in cadoxene, %	13	100	100	100	100
DP* in solution of cadoxene	780	440	400	360	260
Solubility in NaOH, %	–	76	61	59	56
DP* of a part soluble in 6% NaOH	–	840	380	260	150

w_{water} – mass lobe of water
DP – the conditional degree of polymerization designed from an assumption, that in solution is present only CMC*

The product does not contain lignin after processing CMW by peracetic acid during 15 mins. (negative reaction to phloroglucinol), contents of residual monosaccharides determined by a method of a paper chromatography in system n-butanol : acetone : water, compounds 2.1% (1.3% of glucose and 0.8% of xylose). Molecular uniformity CMW, processed PAA, investigated by a method of turbidimitric titration of its solutions in cadoxene (precipitant – ethanol : n-propanol = 1:1) on procedure developed for CMC. The results of turbidimitric titration are submitted as the curves showing change of absorbency of solution $\Delta D2/\Delta\gamma$ in dependence on volume ratio of the precipitant γ (the above γ, the below DP of solution). The uniformity of molecular composition is increased with augmentation of duration of processing PAA of samples CMW from 5 up to 15 minutes, that follows from the differential curves of a molecular-mass distribution (MMD) (Figure 1). In composition CMC there is a low molecular weight fraction at augmentation of duration of processing up to 20 minutes that testifies to increase of its polydispersity. Thus, for abjection CMC from CMW it is necessary to utilize the 15% peracetic acid, thus the duration of processing should not exceed 15 minutes. Molecular composition of CMC studied on an example of samples CMC, discharged PAA in the conditions, and offered by us, from unpitched pine wood, carboxymethylated in medium aqueous propanol-2 with water content in a reaction mixture w_{water} = 10% and w_{water} = 35%, by the method of turbidimitric titration of cadoxene solutions.

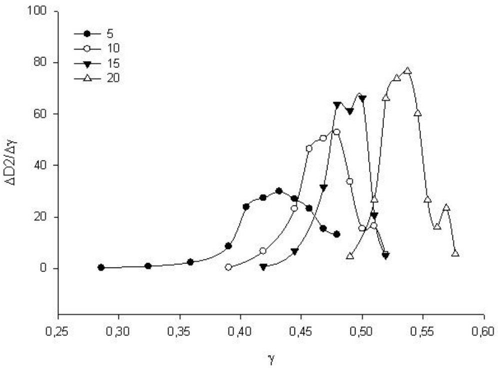

Figure 1: Molecular composition CMW in dependence on duration of processing PAA (5, 10, 15, 20 minutes)

The molecular composition discharged CMC depends, mainly, on temperature of stages alkaline pretreatment and carboxymethylation and practically does not depend from their duration. In Figure 2 the differential curves MMD, characteristic for the investigated series of samples CMC are given. Samples of carboxymethylated cellulose most uniform on composition are received at carrying out of reaction at 60 °C with w_{water} = 10%. Molecular composition of samples CMC investigated also with the help unsolutional method of thermomechanical spectroscopy (TMS), which allows studying MMD both topological frame of polymers and polymeric compositions in a firm state. The method is developed in institute of chemical physics of the Russian academy of sciences in city Chernogolovka of the Moscow range. The comparative analysis has shown that the fractional composition CMC, certain by methods of turbidimitric titration and TMS, has close character of allocation (Figures 2-3).

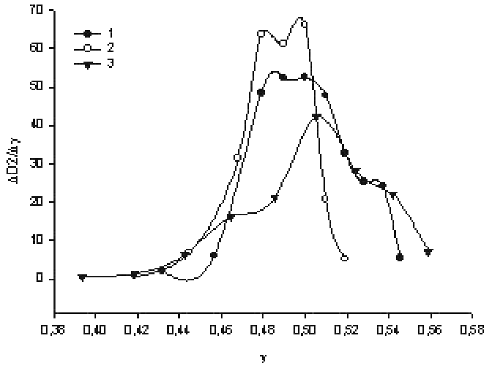

Figure 2: Molecular composition CMC, discharged of CMW with different conditions of synthesis (method of turbidimitric titration)

For samples CMC the comparison of values of molecular weights received by a classical method of viscosimetry and by unsolutional method of thermomechanical spectroscopy (Table 2) is carried out. The accuracy of values of molecular weights determined by traditional methods is insignificant also errors reach 20-30%. The values of molecular weights received by us at research of samples CMC by methods TMS and viscosimetry, differ no more, than on 30%. The results, received by us, testify to adequacy of an assessment of a molecular-mass distribution by methods of a fractionating and of thermomechanical spectroscopy.

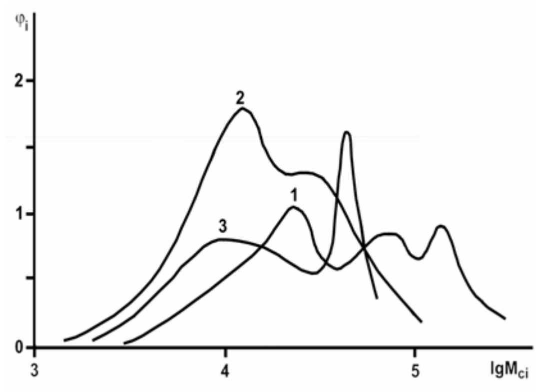

Figure 3: Molecular composition of internodal circuits of the amorphous block CMC discharged of CMW with different conditions of synthesis (method TMS)

Table 2: Molecular Weight CMC, discharged of wood, carboxymethylated in medium aqueous propanol-2, on the data of methods of viscosimetry and TMS (temperature of carboxymethylation 60 °C)

Sample	**Conditions of reception**			**Method of viscosimetry**	**Method TMS**	
	Temperature of alkaline processing,°C	**Duration of carboxymethylation, minutes**	**Water content, %**	**M_η ±5, ×10^3***	**M_w ±5, ×10^3**	**M_n ±5, ×10^3**
1	20	70	10	72	90	56
2	60	50	10	56	31	21
3	20	210	35	61	–	23
* – medium viscosity molecular weight, designed on the contents CG						

CONCLUSIONS

For abjection CMC from CMW it is necessary to utilize the 15% peracetic acid, thus the duration of processing should not exceed 15 minutes. The molecular composition CMC, discharged of carboxymethylated wood, depends, mainly, on temperature of stages alkaline pretreatment and carboxymethylation. The method of thermomechanical spectroscopy for the first time receives the data on molecular composition and values of molecular weights of CMC compared to the data of methods viscosimetry and turbidimitric titration.

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Fixation of Methyltrimethoxysilane in Wood Pre-modified with an Alkoxysilane Coupling Agent

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Keywords: Wood, chemical modification, 3-isocyanatopropyltriethoxysilane, methyltrimethoxysilane, polysiloxane

ABSTRACT

The fixation of methyltrimethoxysilane (MTMS) in wood was envisaged, after prior modification with 3-isocyanatopropyltriethoxysilane (IPTES), an alkoxysilane coupling agent. The modifications were characterized by Fourier-transform infrared spectroscopy (FTIR), solid-state ^{13}C and ^{29}Si NMR spectroscopy (CP-MAS NMR) and Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) analysis. After the carbamoylation reaction between IPTES and wood, the grafted triethoxysilane end groups were transformed into reactive silanol groups by hydrolysis. ^{29}Si CP-MAS NMR spectroscopy indicated that SiOH groups existed mostly in the form of mono- and di-condensed structures in wood. The attachment of MTMS at the remaining silanol sites was subsequently achieved, with ethylamine or dibutyltin dilaurate as catalysts. Results indicated that MTMS was grafted within the wood cell walls, in the form of polysiloxanes.

INTRODUCTION

The chemical modification of wood by organosilicon molecules has received an increasing attention over the last decade and various wood properties such as dimensional stability or durability can be improved after treatment with such compounds (Sèbe and de Jéso 2000; Mai and Militz 2004). Trialkoxysilanes are organosilicon compounds that are reactive towards most inorganic subtrates. They bond well to metal hydroxyl groups, especially if the substrate contains silicon, aluminum or a heavy metal in its structure. The alkoxy groups on silicon hydrolyze to silanols, either through the addition of water or from residual water on the inorganic surface. Then the silanols coordinate with metal hydroxyl groups on the inorganic surface to form an oxane bond and eliminate water. Because lignocellulosic polymers contain a significant amount of hydroxyl groups, condensation reactions between trialkoxysilanes and wood (or plant fibres) can also be envisaged. However, the C-O-Si linkage formed in that case is much more inclined to hydrolysis than the stable oxane bond formed with inorganic substrates. Accordingly, the utilisation of a silane coupling agent was envisaged to durably fix alkoxysilanes in wood (Figure 1). The 3-isocyanatopropyltriethoxysilane (IPTES) was selected as a coupling agent and methyltrimethoxysilane (MTMS) as a model trialkoxysilane.

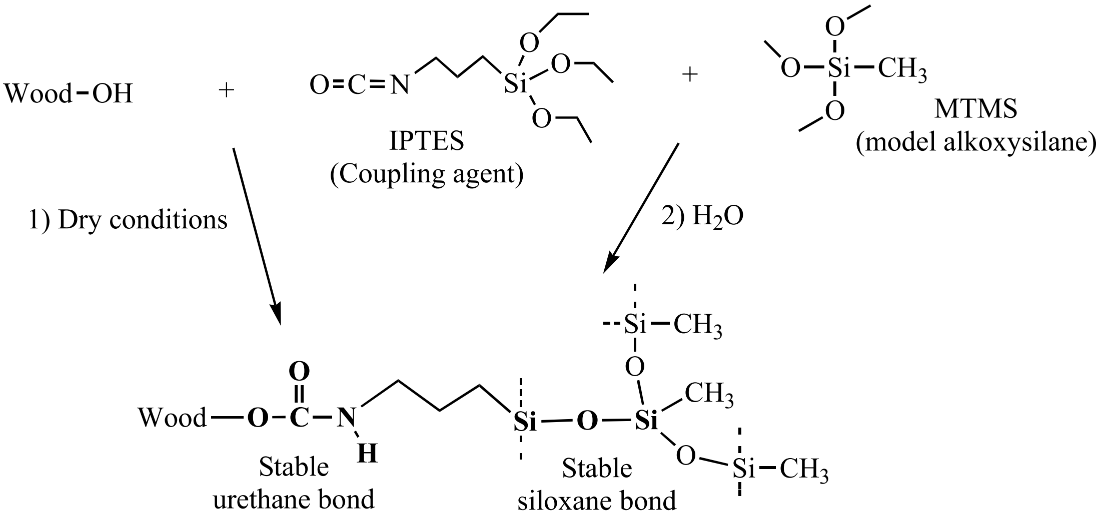

Figure 1: Fixation of MTMS in wood, via IPTES as a coupling agent

EXPERIMENTAL

Wood treatment

20 mm x 20 mm x 2.5 mm (radial x tangential x longitudinal) extractive-free oriented samples of Maritime pine sapwood (*Pinus pinaster* Soland) were used as starting materials. After modification, the weight gain was calculated as a percentage of the dry unmodified material (WPG).

Carbamoylation reactions: DMF solutions consisting of 1 to 12 mmol IPTES/g dry wood and 0.4 mmol DBTDL/g dry wood were used. Reactions were performed at 105 °C, for 6 h. Samples were soxhlet-extracted after reaction (8 h acetone + 4 h dichloromethane), then dried (1 6h, 105 °C).

Hydrolysis of carbamoylated wood: Samples were impregnated with deionised water then immersed in water for 4 days.

Reaction with MTMS: DMF solutions consisting of 14 mmol MTMS /g dry wood and 0.7 mmol ethylamine or DBTD L/g dry wood were used. Samples were soxhlet-extracted after reaction (8 h acetone + 4 h dichloromethane), then dried (16 h, 105 °C).

Analysis

The SEM-EDX studies were conducted using a Hitachi S-2300 SEM equipped with a Roentec-XFlash detector. FTIR spectra of treated and unmodified wood were obtained with the potassium bromide technique (KBr), using a Perkin-Elmer Paragon 1000 PC FT-IR spectrometer at a resolution of 4 cm^{-1} (50 scans). Solid-state ^{13}C and ^{29}Si CP-MAS (Cross Polarisation - Magic Angle Spinning) NMR spectra 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.

RESULTS AND DISCUSSION

In the first stage of the study, the carbamoylation reaction between wood and the coupling agent (IPTES) was investigated. The reaction was performed in dry conditions, with dibutyltin dilaurate (DBTDL) as a catalyst. Samples with varied modification rates were obtained and characterized. The formation of urethane bonds was confirmed by FTIR and ^{13}C CP-MAS NMR spectroscopy (Tingaut *et al.* 2005, Tingaut *et al.* 2006). Infrared vibrations of the carbamate function emerged at 1718 cm^{-1} ($\nu_{C=O}$), 1542 cm^{-1} (δ_{N-H}) and 1210-1310 cm^{-1} (ν_{C-O} and ν_{C-N}). The triethoxysilyl vibrations were observed at 2972 cm^{-1} (ν_{C-H}), 957 cm^{-1} (Si-O-Et) and 830-730 cm^{-1} (ν_{Si-C} and/or ν_{Si-O}). In the ^{13}C NMR spectrum, intense signals associated to the grafted groups emerged at 13 ppm ($\underline{C}H_2$-Si), 21 ppm ($\underline{C}H_3$), 26 ppm (CH_2-$\underline{C}H_2$-CH_2), 46 ppm (NH-$\underline{C}H_2$), and 61 ppm (O-$\underline{C}H_2$) and 160 ppm ($\underline{C}$=O). ^{29}Si CP-MAS NMR spectroscopy indicated that the triethoxysilane moieties remained untouched after reaction. The occurrence of carbamoylation within the wood cell walls was confirmed by SEM-EDX analysis. In a second stage, the reactivity of the grafted triethoxysilane function in IPTES-treated wood was studied. Its hydrolysis was envisaged and the modifications were characterized by FTIR and solid-state NMR spectroscopy (Tingaut *et al.* 2005). After prolonged contact with water, a large band emerged at 914 cm^{-1} and was assigned to Si-OH stretching vibrations formed after hydrolysis of Si-OEt bonds. In the same time, the intensity of the infrared vibrations and ^{13}C chemical shifts associated to the ethoxy group decreased, confirming the cleavage of Si-OEt bonds. ^{29}Si CP-MAS NMR spectroscopy revealed that most of the silicon structures in the samples were in a mono- or di-condensed form after hydrolysis (Figure 2).

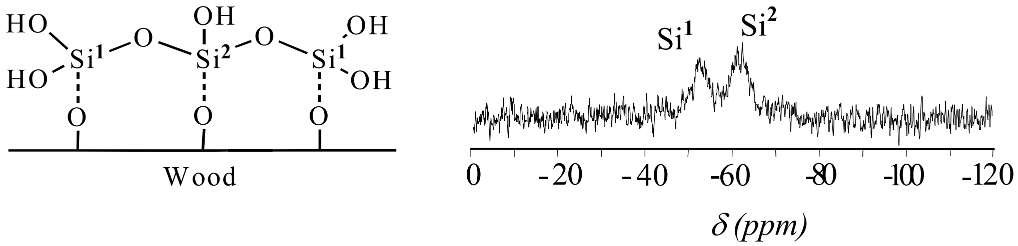

Figure 2: Structure of silicon in IPTES-treated wood after hydrolysis

In the third stage of the study, the chemical coupling between the grafted triethoxysilane functions and MTMS was envisaged (reaction 2 in Figure 1). IPTES-treated samples with moderate WPG's were prepared (11% WPG) and their reaction with MTMS was studied, with ethylamine or DBTDL as catalysts. The presence of MTMS in wood was confirmed by FTIR and ^{13}C CP-MAS NMR spectroscopy, in the form of strong signals at 779 cm^{-1} (ν_{Si-CH_3}) and 0 ppm (Si-$\underline{C}H_3$), respectively (Tingaut *et al.* 2006). The intense signal observed at -71 ppm in the ^{29}Si CP-MAS NMR spectrum, indicated that MTMS was grafted in the form of tri-condensed polysiloxanes (cleavage or the three alkoxy groups of MTMS). These polymers (or oligomers) were highly resistant to water leaching (Tingaut 2006). SEM-EDX analysis revealed that MTMS was grafted within the wood cell walls, at the periphery of the lumen (Figure 3). The condensation of MTMS in unmodified wood (control experiments) was extremely limited, herby proving the importance of IPTES as a coupling agent. It can be noted that, with DBTDL as catalyst, the grafting was significantly increased when MTMS and the grafted triethoxysilane end groups were hydrolysed simultaneously.

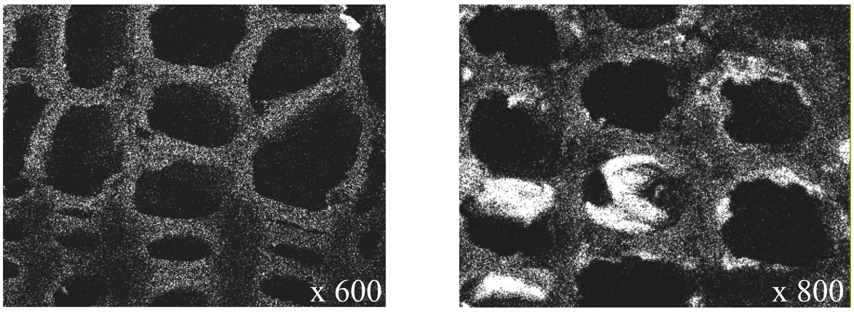

Figure 3: SEM micrographs of IPTES-treated wood before (left) and after (right) reaction with MTMS

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the European Commission for its financial support (HYDROPHOB project).

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Moisture Control in Oil and Bioresin Heat Treated Timber

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Keywords: Oleothermic, moisture content, decay resistance

ABSTRACT

Thermal treatments of timber alter the chemical composition of wood, increasing dimensional stability and resistance to fungal decay. Further improvements are seen when thermal treatment systems are done in oil, or with oil-based resins. A set of decay studies is considered here, and the fluid transfer and water repellency mechanisms at work within these oil heat treated timber systems are discussed. The accessibility of moisture is restricted not only by the modification of the hemicellulose component (reducing hygroscopicity) but also by physical means, both displacing water from the wood bulk and coating the timber with a water resistant or water repellent layer.

INTRODUCTION

The enhanced decay resistance of heat treated wood is often attributed to altered chemical composition and reduced water uptake. The alteration of the composition of both hemicellulose and lignin has been well reported, as has the enhancement of hydrophobicity. The uptake of water can be further reduced by the use of an oleothermal treatment, or the application of resins. A study of the effect of impregnation by linseed oil and other oils (without heat treatment) showed that a good level of water repellency was achieved, with water uptakes of less than 10% in linseed oil treated pine, compared to 30-50% uptake in the untreated control over seven wetting cycles (van Eckeveld *et al.* 2001). In this case, the mechanism of water repellency is purely physical, either by the hydrophobicity of the oil or because the oil occupies available cell lumen space, thus displacing water.

An oil heat treatment system, and a combined treatment with a resin derived from rapeseed oil have been developed (Spear *et al.* 2006). During basidiomycete tests a clear correlation between moisture content and level of decay was seen across the various treatments and temperatures studied. Thus it is proposed that in addition to the principal ideas behind thermal timber preservation systems:

- Chemical changes in the wood due to thermal treatment reduce the digestible hemicellulose to a less palatable form, reducing the susceptibility to decay.
- Chemical changes to the lignin, making it unsuitable for decay.

- Chemical changes in the wood also reduce the hygroscopicity of the wood by substituting and eliminating hydroxyl groups, reducing the equilibrium moisture content and the susceptibility of the wood to decay.

Additional mechanisms act to reduce decay in this oleothermal system:

- The oil further increases the level of water repellence of the wood, by physical means, reducing the ability of microorganisms to colonise and initiate decay.

The use of a bioresin as a coating to further enhance the water repellency is compared with the rapeseed oil treatment. The moisture uptake mechanisms of three species of oil treated wood are reviewed in this presentation. Corsican pine sapwood was selected as a highly permeable timber with low durability requiring treatment, Norway spruce outerwood was selected with low permeability (due to the aspiration of bordered pits) and very low durability. Douglas fir was selected as a moderately durable species with an intermediate level of permeability.

MATERIALS AND METHODS

Blocks of pine and spruce were treated in rapeseed oil at a temperature of 200 °C for three hours. The blocks were subsequently coated with a bio-resin derived from rapeseed oil by ozonisation and reduction (Fowler *et al.* 2004) and cured in an oven at 175 °C. Small sticks (5 x 10 x 100 mm) were treated. These were used for a water soak and leaching experiment (EN84) and a 32 week soil bed test for resistance to soft rot fungi and other microorganisms (ENV807).

OBSERVATIONS

Treated Timber Oil Distribution

Observations of block appearance, weight gain and oil distribution are reported for 15 x 25 x 120mm blocks in Spear *et al.* (2006). Pine blocks had a high weight percent gain and high resin saturation throughout. Spruce had a poor uptake of oil (when treated in the dry state) and Douglas fir had taken up oil slightly deeper into the ends of the blocks than the spruce. The trend for decreasing weight gain from pine to Douglas fir to spruce was repeated when the hot rapeseed oil treatment was followed by a bioresin coating.

Leaching

At the end of a 14 day leaching procedure the moisture content of the rapeseed oil treated pine was very low (24%), due to high oil saturation. The spruce, which had a much lower oil content had taken up 81% moisture. The combined rapeseed oil and bioresin treated spruce sticks had a much lower moisture content of 27%. Thus the bioresin has a significant effect on the permeability of the spruce sticks to water. The mass lost due to leaching was very low. Some rapeseed oil was lost from the rapeseed treated pine, however the bioresin seal on the combined treatments restricted mass loss in all timber species. The tendency for oil to resist mixing with water prevented significant weight loss during the leaching test.

After the period of water immersion, the sticks were re-conditioned to ambient conditions and moisture content monitored. The moisture reduced in an exponential fashion for both the rapeseed treated and the combined treated timbers. Within the first seven days both treatments had reduced to below 10% moisture content and after 21 days they had equilibrated at 6%. The bioresin did not hinder the drying of the treated timber once removed from the water. Drying after wetting is important in reducing the susceptibility of the timber to fungal decay in environments where cycles of wetting and drying occur – *e.g.* garden furniture and decking.

Soil Microorganisms

At the end of test (week 32) the weight loss for the combined treatment was 8% for pine, 8% for spruce and 5% for Douglas fir. The combined treatment performed best overall, and this effect was most clearly seen in pine timber (Figure 1), where the rapeseed oil treatment had a weight loss of 14% and the combined treatment weight loss was 8%. The pine untreated control specimens had a weight loss of 22%. The pine sticks also retained very low moisture contents throughout the eight month exposure period (Figure 2). By comparison the spruce took up a very large amount of water, but this was less for the combined treatment than the rapeseed only treatment, indicating that the bioresin has an additional water repellent effect.

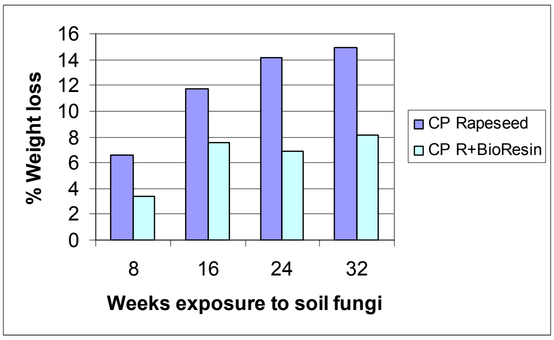


Figure 1: Weight loss for Corsican pine treated with rapeseed oil and with combined treatment

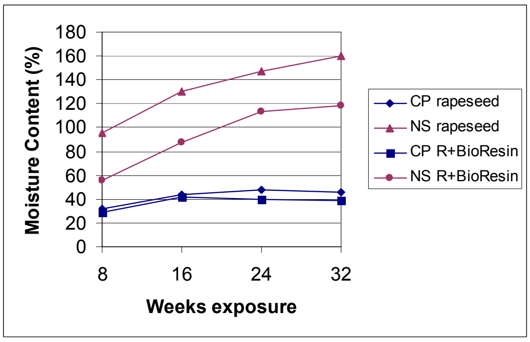


Figure 2: Moisture content during soil bed test for Corsican pine and Norway spruce samples

DISCUSSION

The moisture uptake of the cell wall by thermally modified timber is low, due to alterations in the hemicellulosic component of the cell wall. This reduces the number of hydroxyl groups available and their accessibility as the space between microfibrils contracts during thermal modification. The moisture uptake of timber from an oleo-thermal process is further reduced by the introduction of oil or resin as an additional hydrophobic component. This may act in several ways (a) by increasing the propensity for water to bead and roll off the surface, (b) by physically displacing moisture by its presence within the cell lumena and (c) by forming a polymerised barrier against moisture uptake (in the case of resins). The quantity of oil or resin within the treated wood was calculated by mass balance, using values of 1.460 g/cm^3 and 0.903 g/cm^3 for wood cell wall material and rapeseed oil. These values are presented as percentage of the total block volume in Figure 3. The pine took up more oil, or oil and bioresin, than the Douglas fir and the spruce. The combined treatment has an additional component due to the bioresin, and a slight increase in the block volume due to the coating formation on the surface. The oil filled 81% of the available space in pine, and only 10% of the space in spruce. This difference is due to pit aspiration in the spruce earlywood and other anatomical differences of ray structure. When subjected to water soaking over 14 days, the pine became fully saturated with water in the remaining 19% of the non-wood volume, while the spruce and Douglas fir retained a larger proportion of air, taking up water into 51% of the remaining non-wood volume (Figure 4). In both cases the oil demonstrates a physical displacement effect – in pine the air space was filled and only a very small exchange of oil for water occurred. In spruce many of the major pathways into the refractory species are occupied by oil, thus although some water wicks into the wood displacing air, a significant portion of the volume remains filled with air.

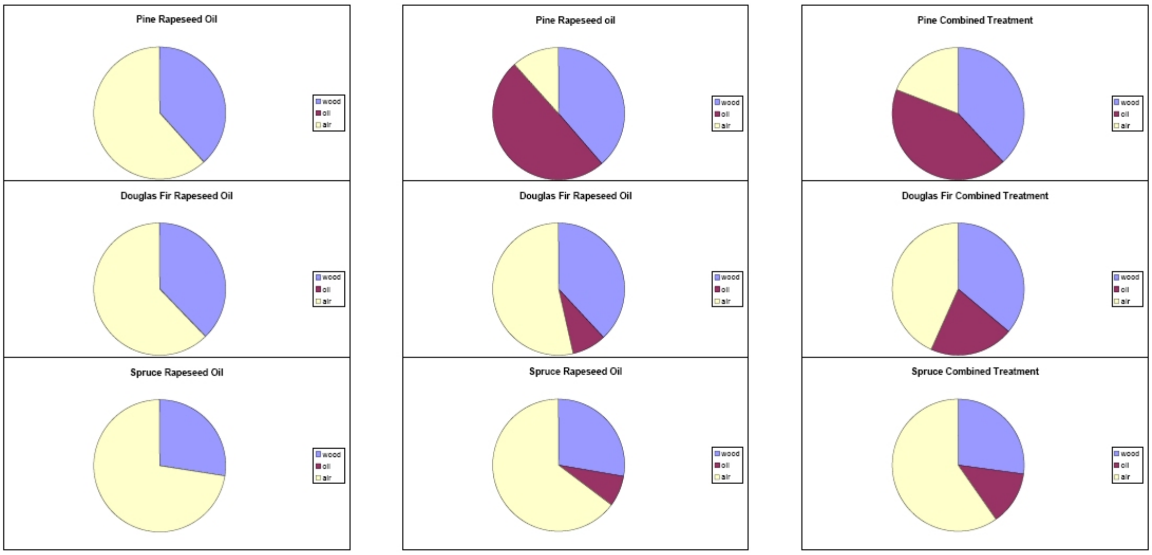
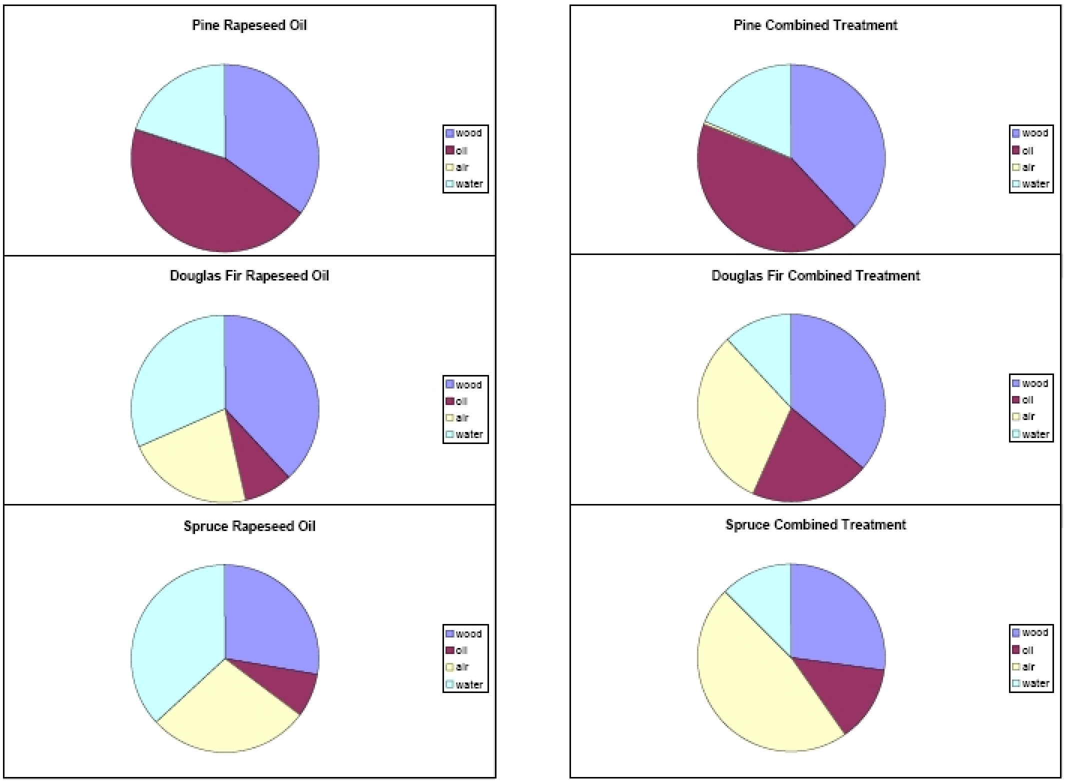


***Figure 3:** Percentage volume of wood wall, oil and air within pine, Douglas fir and rapeseed oil treated sticks. Left to right: untreated, rapeseed treated and with combined rapeseed and bioresin treatment*

The samples from the combined treatment, which had a bioresin coating on their surface performed similarly in the case of pine, but a significant difference in water uptake was seen for Douglas fir and spruce (Figure 4). The proportion of the non-wood volume which was filled with water was only 17% for spruce, and 18% for Douglas fir. Air remained in 65% of the non-wood volume of spruce, and 49% for Douglas fir. The bioresin coating impeded the uptake of water in these species. It is likely that the polymerised resin clogs the remaining channels into the wood more successfully than the oil. This effect was observed during the leaching experiment, as both the spruce and the Douglas fir were buoyant immediately the restraining weight was removed. During ENV807 tests many water transportation methods were available and the moisture content increased steadily during the course of exposure. The uptake of water by pine was limited to 46% for rapeseed treatment, and 39% for combined treatment, at the end of the test. The physical barrier to moisture uptake provided by the oil and the bioresin is still effective after 32 weeks of soil exposure. For spruce the moisture content after exposure was 161% for rapeseed treatment and 119% for combined treatment. These values are higher than the uptake seen after immersion in the leaching experiments (81% for rapeseed oil treated spruce). Here, in addition to biological transportation, the erosion action of the microbes may have re-opened aspirated bordered pits, thus exposing non-impregnated wood from the core of the sample to moisture and allowing water to flow into the vacant air spaces within the wood.


Pine Rapeseed Oil

Pine Combined Treatment

Douglas Fir Rapeseed Oil

Douglas Fir Combined Treatment

Spruce Rapeseed Oil

Spruce Combined Treatment

Figure 4: Percentage volume of wood wall, oil, air and water in sticks after 14 day leaching. Left to right: rapeseed treated, combined treatment

CONCLUSION

The moisture content is a critical factor in determining the extent of fungal decay possible within wood in service. This paper has shown that oil heat treated wood has improved water repellency because of physical water displacement. In addition when the oleothermally treated wood was coated with a resin this further reduced the accessibility of the wood to moisture. The resin also prevented the loss of oil from the pine during leaching. Furthermore, the bioresin coating did not impede the drying of wood after wetting, an important quality for wood in many exterior applications.

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Influence of Wood Modification on Fire Resistance and Hydrophobic Properties

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Keywords: Acetylation, contact angle, critical heat flux, thermal modification, surface energy, wood.

ABSTRACT

Chemical or thermal treatment is used to protect wood against biological deterioration by fungi and wood destroying pests. Such kinds of treatments enhance wood hydrophobic properties and dimensional stability by reduced swelling and shrinkage. Acetylated and heat treated wood can be used as floorings in unfavourable conditions. The objective of this work is the estimation of fire resistance and hydrophobic properties enhancement of wood by acetylation and thermal treatment. Fire is an ever present danger – a threat to life and significant economic losses. Hazards and risks of fire are changing with implementation of new materials with altered chemical composition and structure. A bench scale radiant panel flooring test method was used to measure the critical radiant flux of horizontally-mounted modified wood panels exposed to a flaming ignition source in a graded radiant heat environment. Hydrophobic properties of modified and unmodified samples were estimated with water absorption tests and determination of equilibrium contact angle between the liquid-vapour interface and the solid-liquid interface at the solid-liquid-vapour three phase contact line by sessile drop method.

INTRODUCTION

In spite of many valuable properties, wood swells and shrinks in changing humidity and undergoes deterioration by destroying organisms. Different paints and varnishes are used to protect wood against liquid water and humidity. No paints and varnishes can protect wood for a long period because wood properties are not changed. Water penetrates through varnish film defects that cause wood swelling and additional possibility for destruction of coating. Any wood surface treatment in macro or micro scale can protect wood only in mild conditions. Environmental pollution can cause wood impregnation with harmful for living organisms substances to protect it against biological deterioration. When surface of wood construction frequently is under rain, sharp temperature change or in contact with soil, then it substance chemical alteration is one way to success. Chemical modification of wood cell wall substance had increasing interest world wide in last decades (Kumar 1994, Morozovs *et al*. 2003, Rowell 1983) An overview of different wood modifications was summarized by Callum Hill (Hill 2006).

In the process of selecting new or alternative materials for applications in the built environment a necessary consideration is the fire performance of the material. It is required that the materials selected for use must evaluated in flammability tests to estimate it role in the development and survivability of fires (Panagiotou and Quintiere 2004). The objective of this investigation was to estimate the influence of wood chemical modification with acetic anhydride or by thermal treatment on the wood on fire and hydrophobic properties.

EXPERIMENTAL

Measuring devices

Flammability tests were performed on Flooring Radiant Panel (Fire Testing Technology Ltd, EN ISO 9239 - ASTM E 648 - ASTM E 970 - NFPA 253) Contact angle measuring device OCA20 with dossing unit E-MD (DataPhysics).

Wood modification

Thermal modification of parquet boards was performed: 4 h at 413 K in argon atmosphere, and then 4 h at 468 K in nitrogen atmosphere. Acetylation of parquet boards were prepared by oven dried samples vacuuming for 6 h and impregnation with acetic acid anhydride 10 h at 295 K at room temperature and then 6 h at 390 – 393 K for. Acetylated samples were dried at 376 K for 50 days to evacuate residual acetic acid. Reference parquet boards were stored at 376 K the same period of thermal influence as for acetylated ones. The pine (*Pinus sylvestris*) heartwood samples (50 x 25 x15 mm) corresponding fibre, radial, tangential direction) were acetylated using above mentioned conditions.

Materials

Commercial ash and oak wood parquet boards (200 x 40 x 15 mm); acetic anhydride, pure (Lach-Ner). ethylenglycol G.R. (Lach-Ner), formamide extra pure 99.5% (Acros Organics), diiodomethane 99% stabilized with silver (Acros Organics), water was purified on TKA water purification systems (0,10 μS/cm).

RESULTS AND DISCUSSION

Hydrophobic properties and dimensional stability

To ensure environmentally friendly wood protection and uncomplicated modified wood recycling processes, it is necessary make changes in the biopolymer structure with a method that is not alien for nature to prevent breaking biological cycles. The durability of wood can be considerably improved, when hydrophilic hydroxyl groups of wood components are converted in the larger and more hydrophobic functional groups to provide wood to be in permanently swelled condition that decreases wood's disposition to change dimensions. Customarily acetic anhydride is used to acetylate hydroxyl groups of wood (Hill 2006). Influence of wood hydroxyl group acetylation was evaluated by kinetics of water absorption, wood swelling for pine wood samples. Wood acylation diminished water absorption from 90±8 % for natural wood samples till 44.0±10% for modified samples. Most of the absorption decrease could be explained by a bulking effect, because calculated wood voids fill with water was 44.0±4.2% and 60.0±4.8% for natural and acetylated wood accordingly. Absorbed water swelled natural wood, and less swelled modified wood. Volume antiswelling efficacy of acetylation method was 76.9±2.3%. Absorbed water mostly filled voids in modified wood and swelled cell walls of natural wood. Surface free energy of modified and reference was used to describe hydrophobic properties of acetylated or thermally modified commercial parquet hydrophobic properties and compare them with ones of pine wood. Contact angle of 4 liquids with different surface tension with wood surface were measured immediately after drop formation. Wood samples were sanded with 320 grit sand-paper before contact angle detection to refresh surface. Main wood's substance components lignin, cellulose and hemicelluloses have different reactivity with acetic anhydride and different thermal behaviour that increase wood heterogeneity and wood contact angle with liquid determination uncertainty. Lifshitz-van der Waal forces appear to account for the major of wood surface tension, and the acid-base character comes from the electron donating sites. (Gindl *et al.* 2001). Lifshitz-van der Waals/acid-base (AB) approach was used to determine surface free energy from contact angle measurement results with for liquids: diiodomethane, formamide, ethylenglycol, and water. Contact angle values had great dispersion due to irregular wood grain orientation in commercial parquet boards that caused uncertainty in free energy calculations. Surface energy and those Lifshitz-van der Waal forces component dispersion was near 10% and up to 30 – 40 % for acid and base components that permitted to estimate only trend of wood modified surface properties changes. Both acetylation and thermal treatment decreases surface free energy.

Flammability

Wood acetylation increases the acetyl group content in wood. These groups could be split off by external heat radiation to form acetic acid vapour – the fuel for fire. Contrariwise, wood thermal modification could be considered a pre-charring of solid that covert the solid more difficult to ignite when larger heat fluxes are applied (Babrauskas 2003). For most solids, ignition due to external heating occurs in gas phase of volatiles that are driven off which then ignite and burn in the surrounding atmosphere. Heating by radiation is considered to be the most important in flames and in situations where a non-contiguous hot body provides the heating (Babrauskas 2003). For wood floorings, the flame spread in orientation along the wood grain is more rapid than transverse grain (Ostman and Mikkola 2004). Parquet boards were orientated in specimen assembly (1 x 0.2 m) along the grain on plywood substrate without additional fixation to substrate. The flooring radiant tests were performed according EN ISO 9239-1:2002. Parquet boards were conditioned at 296 K and RH 50% for 45 days. Decrease of critical heat flux at extinguishment (CHF) was established for both acetylated and thermally treated wood and compared with reference of non-modified parquet boards. Decrease of CHF of acetylated wood (MPG 22.04±1.13%) could be explained by acetic acid formation in pyrolysis conditions that was justified by characteristic blue flame of acetic acid. Mass loss by volatile extractives and compounds formed during wood thermal modification didn't increase it resistance in reaction to fire. Wood modification influence index (MII) was calculated according to Equation 1 to evaluate wood modification.

$$MII(\%) = \left(CHF_M - CHF_R\right)/CHF_R \cdot 100 \qquad (1)$$

Where: CHF_M and CHF_R is critical heat flux mean of modified (M) and reference wood (R) accordingly. MII -38.05% of acetylated and -46.7% of thermal modified wood was calculated. These figures must be treated with caution, because acetylation increased wood density, but thermal modification decreased it. It is assumed that wood density enlarges CHF in total for wood, but for each wood species it isn't typical (Babrauskas 2003). The trend of reduction of CHF by increase of density of reference ash parquet board samples was ascertained. Less marked opposite trend was determined with oak wood and acetylated ones. No clear trend in CHF changes with density had been found with thermal modified wood.

CONCLUSIONS

Wood acetylation and thermal modification increase wood dimensional stability by less water uptake in cell wall but reduction of performance in reaction to fire in comparison with non-treated wood. Acetylation decreased critical heat flux at extinguishment by acetic acid split-off in pyrolysis conditions.

ACKNOWLEDGEMENTS

The wood acetylation and surface energy determination presented in this paper were funded by the European Regional Development Fund (ERDF). The flammability tests were carried out on equipment of Forest and Wood Products and Development Institute (FWD). The authors greatly acknowledge financial support from ERDF and FWD for technical support. The authors greatly acknowledge Latvian Council of Science for previous support that made theoretical background.

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Thermogravimetric Analysis of North American Jack Pine

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Keywords: High temperature heat treatment of wood, jack pine, dimensional stability thermogravimetry, mechanical properties,

ABSTRACT

High-temperature wood heat-treatment technologies were developed in Europe for European species. These technologies need to be adapted to the North American species. In this study, North American jack pine was treated at high temperature under different conditions using a thermogravimetric analyser. The effects of the maximum treatment temperature and the heating rate on different properties of the jack pine were studied.

INTRODUCTION

Heat treatment is one of the wood protection methods. This method does not use chemicals harmful to the environment. After heat treatment, wood becomes more resistant to biological attack, its dimensional stability improves, and it has a darker color which is attractive for decorative purposes. However, it might lose some of its elasticity. The change in wood properties are a function of the heat treatment conditions (Mitchell 1988, Vernois 2001). Due to the non-homogeneity of wood species, a specific recipe needs to be developed for each species depending on its intended use. The Research Group on the Thermotransformation of Wood (GRTB – **G**roupe de **R**echerche sur la **T**hermotransformation du **B**ois) at the University of Quebec at Chicoutimi, Quebec, Canada, has established a method for the recipe development and validation using its research infrastructure which is unique in North America. The recipe development starts in the laboratory using a thermogravimetric analyzer. Here, the small wood samples are heat-treated under different conditions, and their properties are measured after the treatment (Poncsak *et al.* 2006). This leads to the identification of promising treatment conditions. Afterwards, these conditions are validated and scaled up to the industrial level by carrying out heat treatment trials first in a prototype furnace and then in an industrial furnace, both of which are owned and operated by the GRTB. In this article, the results of heat treatment experiments which were carried out in the thermogravimetric analyzer for the North American jack pine will be presented. The mechanical properties (MOE, MOR, *etc.*), dimensional stability, and hardness of untreated and treated jack pine will be compared; and the impact of the treatment conditions on these properties will be discussed.

EXPERIMENTAL

The experiments were carried out in the thermogravimetric analyser. This experimental system is composed of a vertical furnace, a balance, a chromatograph, and a data acquisition system. The wood samples (0.035 m x 0.035 m x 0.20 m) are suspended from the balance into a reaction tube in the furnace. The wood samples are heated under a neutral gas atmosphere and desired experimental conditions. In the first group of experiments, the weight change with time is followed. In the second group of experiments, a number of thermocouples are placed in the sample at known positions. The change of temperatures at the thermocouple positions is monitored. Then, the treated wood samples are subjected to different tests in order to measure its properties. ASTM D-143-94 and ASTM D-1324-83 standards are followed for three point static bending test and the penetration hardness test, respectively. Dimensional stability tests are carried out by measuring the swelling in radial direction after 24 hour of soaking in water. The experimental system is explained in more detail elsewhere (Poncsak *et al*. 2006, Kocaefe *et al*. 2007).

RESULTS AND DISCUSSION

Figure 1 shows an example of weight loss vs. time data for the experiment with an average heating rate of 20 ºC/h and a maximum temperature of 230 ºC. The weight loss is given as the percent of the initial sample weight. The temperature history at different thermocouple positions in the wood sample and the gas temperature are presented in Figure 2. As it can be seen, the sample temperature was uniform during the experiment. Initially, the gas temperature was higher than the wood temperature. At later times when the temperature reached about 160 ºC, the wood temperature became higher than the gas temperature. This is due to the exothermic nature of the thermotransformation reactions taking place.

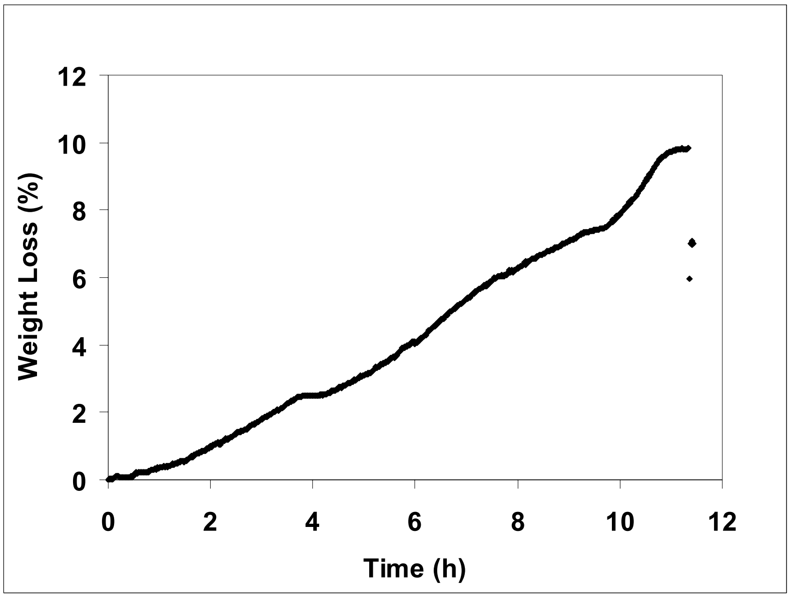

Figure 1: Weight Loss vs. Time Data (Heating Rate = 20 ºC/h, Maximum Treatment Temperature = 230 ºC)

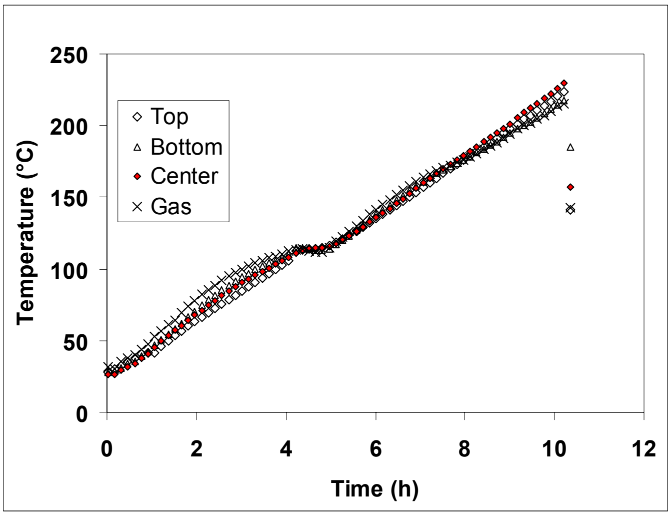

Figure 2: Temperature vs. Time Data at Different Positions (Heating Rate = 20 ºC/h, Maximum Treatment Temperature = 230 ºC)

Table 1 summarizes the percent change in the sample thickness in radial direction where the change was most significant. It can be seen that the change in size decreased with temperature up to 210 ºC showing that the dimensional stability was improved. Above this temperature, the change in size showed a significant increase.

Table 1: Effect of High Temperature Heat Treatment on the Dimensional Stability of Jack Pine

Maximum Temperature [°C]	Heating Rate [°C/h]	Increase in Sample Thickness in Radial Direction [%]
Non treated	-	3.2 ± 0.5
120	20	3.0 ± 0.4
160	20	2.5 ± 0.4
200	20	2.3 ± 0.3
210	20	1.1 ± 0.3
220	10	2.1 ± 0.4
220	20	2.5 ± 0.2
220	30	4.2 ± 0.4
230	20	5.2 ± 0.4

The results of the three point static bending test (MOE, MOR) and the penetration hardness test (in radial and tangential directions) are presented in Table 2. MOR increases with temperature up to 160ºC significantly. Then it decreases until 200 ºC. After this temperature, MOR increases once again up to 220 ºC followed by a decrease at 230 ºC. It seems that the heating rate doesn't have a significant effect on MOR except at 10 ºC/h. This shows that if the heating rate is very slow, wood is exposed to high temperatures for a relatively longer time; and the heating rate can affect the MOR.

There seems to be no effect of the treatment temperature at low values. MOE increased in the vicinity of 160 ºC. At higher temperatures, it stayed relatively constant at a value slightly higher than the initial MOE. Then, it decreased significantly at 230 ºC. MOE decreased when the wood is treated using very a low heating rate (10 ºC/h). At higher heating rates, it reached a stable value which is higher than that of the untreated wood.

The same trend was observed for the radial and tangential hardness; however, the tangential hardness was slightly lower for all the treatment conditions studied. The hardness increased with the treatment temperature and stayed constant between 160 ºC and 200 ºC. Above this temperature, it decreased and stabilized at a value which was almost the same as that of the untreated wood. The heating rate didn't seem to affect the hardness. The radial hardness was slightly higher at 10 ºC/h heating rate, and the tangential hardness was slightly lower at 20 ºC/h heating rate compared to those of the untreated wood.

CONCLUSIONS

Thermogravimetric analysis is a valuable tool which gives a good indication of how the different operating conditions will affect the product properties. With this tool, it is possible to identify the promising treatment condition range depending on the desired wood properties. This reduces the plant trials and, consequently, the cost for industries.

ACKNOWLEDGEMENTS

The authors would like to thank the administration of the University of Quebec at Chicoutimi (UQAC), especially Mr. Sylvain Tremblay, the Foundation of the University (FUQAC), the PCI Industries, especially Mr. Denis Lapointe, and our technicians Mr.Pascal Vandal, Mr. Rénald Delisle, and Mr. Jacques Allaire for their support and contributions.

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Transverse Anisotropy in Thermally Modified Beech and Spruce

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Keywords: Anisotropy, hardness, shear strength parallel to grain, swelling, tensile strength perpendicular to grain, thermal modification

ABSTRACT

The anisotropic characteristic of selected physical and mechanical properties in the transverse plane of beech and spruce after thermal modification was investigated. Anisotropy factors (ratio of tangential to radial property value) were determined for swelling, tensile strength perpendicular to grain, shear strength parallel to grain and hardness and compared to untreated controls. While thermal modification changes properties considerably, thermally modified timber nonetheless retains the distinct anisotropic characteristic of wood. For practical applications of thermally modified timber it has particularly to be taken into account that despite the reduced swelling, the largely unchanged transverse anisotropy may still lead to shape distortions.

INTRODUCTION

Thermally modified timber (TMT) is being increasingly used as an alternative wood based material in applications where an improved dimensional stability and durability are required. However, the thermal modification leads to structural and chemical changes in the wood constituents, which may significantly alter the material properties as compared to untreated solid wood. TMT is therefore regarded in many aspects a 'new' material, whose particular properties have to be known and carefully considered for appropriate and successful applications. Current research has facilitated a considerable knowledge of the physical and mechanical properties of TMT (Hill 2006), but little is known about possible changes regarding special property relationships familiar from solid wood. This is for example the case for the directional dependence of most material properties regarding the three principal axes in the tree trunk (longitudinal, tangential, radial) known as anisotropy or (more precise) orthotropy (Dinwoodie 2000). Usually, anisotropy is most pronounced between properties measured parallel and perpendicular to grain. However, also in the transverse plane (tangential and radial directions) considerable differences may exist (Schniewind 1959). Except when concerning shrinkage and swelling, this topic has received little attention so far regarding TMT. Anisotropy may be changed in TMT, since the thermal modification leads to a partial degradation of the hemicelluloses and therefore to changes in the wood matrix properties (Hill 2006, Bergander and Salmén 2002).

The aim of this paper is to assess the transverse anisotropy of selected physical and mechanical properties of TMT made from hard- and softwoods and discuss possible consequences for practical applications.

EXPERIMENTAL

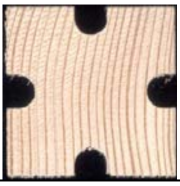
The data used in this analysis has been collected within a larger project to assess the physical and mechanical properties of thermally modified beech (*Fagus sylvatica*) and spruce (*Picea abies*). A commercial thermal modification process (Mitteramskogler 2007) with two treatment levels was used (Table 1).

Table 1: Thermal modifications

Code	Description
T0	untreated controls
T1	'mild' heat treatment, max. temperature 180 °C
T2	'intense' heat treatment, max. temperature 220 °C

For each wood species and thermal modification level (T1 and T2), 4 entire boards were heat treated. Small clear specimens were subsequently cut from the treated boards, with matching control specimens cut from a section of each board left untreated. Care was taken to achieve a parallel/perpendicular orientation of the growth rings within the specimens cross-section. From each board 2 replicate specimens were cut, adding up to 8 and 16 replicates per modification level and untreated controls respectively. Some replicate specimens were discarded because of imperfections.

Table 2: Experimental details

Property	**Swelling coefficient**	**Tensile strength perp. to grain**	**Shear strength parallel to grain**	**Hardness (Brinell)**
Unit	[%/%RH]	[N/mm^2]	[N/mm^2]	[N/mm^2]
Test method	DIN 52184	special	DIN 52187	EN 1534
Specimen shape, size (L x T x R)	disc 10 x 30 x 30 mm^3	notched disc 10 x 30 x 30 mm^3 	block (cube) 40 x 40 x 40 mm^3 (block shear test)	block (cube) 40 x 40 x 40 mm^3
Details	hygroscopic range 35-85% RH	2 axially matched replicates	2 axially matched replicates	beech only, means of 2 indentations
		specimens conditioned at 20 °C / 65% RH		
Parameters	**h_T**: T direction **h_R**: R direction	**TP_T**: load R, fracture T plane **TP_R**: load T, fracture R plane	**SL_T**: load L, fracture T plane **SL_R**: load L, fracture R plane	**HB_T**: T face **HB_R**: R face
Anisotropy factor	**A_h** $= h_T / h_R$	**A_{TP}** $= TP_T / TP_R$	**A_{SL}** $= SL_T / SL_R$	**A_{HB}** $= HB_T / HB_R$

Abbreviations: L: longitudinal, T: tangential, R: radial, RH: relative humidity

Four different material properties to be assessed regarding both radial and tangential growth ring orientation on the same or on axially matched specimens were chosen. Experimental details are given in Table 2. Swelling served as an example of a moisture related physical wood property. Tensile strength perpendicular to grain, shear strength parallel to grain and hardness are examples of different mechanical properties. Tensile strength perpendicular to grain was assessed by a non-standard procedure on notched discs. The other properties were measured according to common tests methods.

RESULTS AND DISCUSSION

The mass loss induced by the thermal modification is reflected in a 3% and 7% decrease in oven-dry density for T1 and T2 respectively. As expected, swelling was improved (reduced) considerably by the thermal modification, while tensile strength perpendicular to grain decreased in the same order of magnitude. Shear strength parallel to grain and hardness were reduced noticeably only at the higher modification level T2. As an example, data for tensile strength perpendicular to grain are shown in Figure 1. While for beech distinct treatment differences and transverse anisotropy are apparent, treatment effects are less pronounced for spruce and hardly any transverse anisotropy is present.

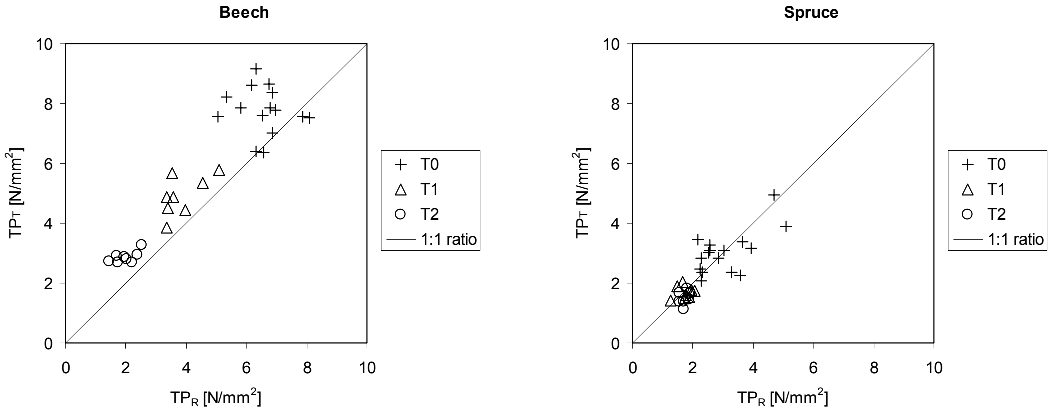


Figure 1: Example of transverse properties: Tensile strength perendicular. to grain for beech and spruce

The calculated anisotropy factors and their changes after thermal modification appear to be highly species and property specific (Figure 2). As expected, transverse anisotropy is much more pronounced for swelling than for the mechanical properties. Anisotropy with swelling is higher for spruce than for beech, while the opposite is the case for the mechanical properties. Overall, the thermal modification has little effect on anisotropy.

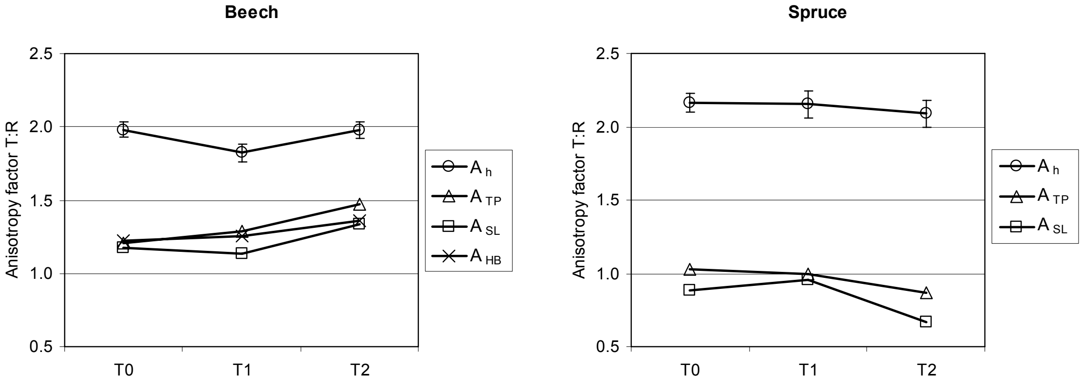


Figure 2: Anisotropy factors (Exemplary error bars for A_h indicate standard error of means)

A statistical evaluation using analysis of variance techniques confirms the observation on the graphed data. All properties show significant transverse anisotropy except tensile strength perpendicular to grain with T0 and T1 and shear strength parallel to grain with T1 for spruce. Multiple comparison tests of anisotropy factors indicate no difference between the treatments regarding swelling, but a slight increase of the anisotropy with the mechanical properties for beech and a slight decrease for spruce with treatment T2 (Table 3). However, changes in anisotropy are too small to be of practical relevance.

Table 3: Results of multiple comparison tests for anisotropy factors in different treatment levels[a]

Modification	**Beech**				**Spruce**		
	A_h	A_{TP}	A_{SL}	A_{HB}	A_h	A_{TP}	A_{SL}
T0	A	A	A	A	A	A	A
T1	A	A B	A	A B	A	A	A
T2	A	B	B	B	A	A	B

[a]Different letters (A, B) indicate significantly different anisotropy factors (5% error level)

CONCLUSIONS

- Despite the considerable changes of the physical and mechanical properties induced by a thermal modification, wood retains its distinct anisotropic characteristic. Obviously, the structural features which are responsible for the transverse anisotropy, remain largely unaffected by the thermal modification.
- Although a thermal modification reduces swelling considerably, shape distortions (*e.g.* cupping) still have to be expected in TMT pieces because of the unchanged transverse anisotropy.
- Regarding the anisotropy of mechanical properties in the transverse plane, a similar behaviour can be expected for untreated solid wood and TMT. However, the general decrease of mechanical properties, the changed equilibrium moisture content and the increased brittleness of TMT have to be considered.

ACKNOWLEDGEMENTS

The presented work was financially supported by the European Commission under contract No. G1ST-CT-2002-50274 (NANOWOOD project). The TMT was provided by Mitteramskogler GmbH, Gaflenz, Austria (St. Schönberger). Specimen preparation and testing was carried out by A. Fischer, D. Heer, W. Risi and K. Weiss (Empa, Wood Laboratory, Dübendorf, Switzerland). Hardness measurements were performed at the Laboratory for Wood Physics, ETH, Zürich, Switzerland (Prof. P. Niemz).

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Reinvestigations of the Wood Polymers Behaviour during Heat Treatment

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Keywords: Char, CP/MAS ^{13}C NMR, heat treatment, holocellulose, lignin, wood

ABSTRACT

Behaviour of wood polymers during heat treatment under inert atmosphere at 240 °C was reinvestigated to explain the decrease of the O/C ratio observed in a previous study using X-ray photoelectron spectroscopy (XPS). Heat treatment was performed on beech sawdust and its lignin and holocellulose fractions obtained after acidic hydrolysis of polysaccharides or delignification with sodium chlorite. ^{13}C CPMAS NMR indicates degradation of hemicelluloses after thermal treatment. However, assignments of the signals appearing in the range of 125 to 135 ppm and 35 ppm attributed up to now to thermoreticulation of lignin and formation of methylene bridges should be reconsidered. Heat treatment of the holocellulose fraction indicates similar signals showing that these latter ones are not due to lignin modification. These new signals have previously been attributed to onset of char formation. Klason lignin and HPLC analyses of the sugars in the hydrolysate indicate the formation of carbonaceous materials during heat treatment of wood by mild pyrolysis.

INTRODUCTION

CP/MAS ^{13}C NMR has been used to characterize wood polymers modification after heat treatment (Tjeerdsma *et al.* 1998) indicating degradation of less ordered carbohydrates (hemicelluloses and amorphous cellulose) while lignin is less affected. Acid degradation catalysed by formation of acetic acid during hemicellulose degradation results in the formation of furfural, aldehydes, *etc.*, as well as some lignin modifications due to β-O-4 ether linkage cleavage and aromatic nuclei demethoxylation followed by formation of methylene bridges. XPS analysis of heat treated wood performed by us recently in our indicates an important decrease of the O/C ratio after heat treatment (Nguila Inari *et al.* 2006) which cannot be explained as outlined above. The aim of the present paper is to reinvestigate chemical modifications occurring during heat treatment using wood.

EXPERIMENTAL

Delignification

After removal of the extractives, dried beech (*Fagus sylvatica* L.) sawdust in distilled water was heated at 75 °C. Acetic acid and 15 % aqueous sodium chlorite were then added each hour for 7 hours. The mixture was filtered, the residue was washed with water and extracted for 2 hours with ethanol and dried at 103 °C to a constant mass.

Hydrolysis of holocellulose

Sawdust was mixed with 72% H_2SO_4 for 4 hours at room temperature. The mixture was then diluted with distilled water, heated under reflux for 4 hours and filtered. The residue was washed with hot water and dried at 103 °C to a constant mass.

Heat treatment

The sample was placed in a reactor under nitrogen and heated at 240 °C in an oven. Weight loss was calculated according to the following formula where m_0 and m_1 are the initial oven dried masses of the sample respectively before and after heat treatment:

$$WL\ (\%) = 100 \times (m_0 - m_1) / m_0 \qquad (1)$$

Solid state (cross-polarisation/magic angle spinning) ^{13}C NMR spectra were recorded on a Bruker MSL 300 spectrometer at 75.47 MHz. Acquisition time was 0.026 s with the number of transients about 12000. All the spectra were run with a relaxation delay of 5 s, CP time of 1 ms and spectral width of 20 000 Hz. Spinning rates were 7 KHz.

For hydrolysis of the carbohydrate fraction, dried extractive free sawdust was stirred with 72 % sulphuric acid at room temperature during 1 h. Distilled water were then added and the mixture heated under reflux for 4 h. The insoluble residue was removed by filtration, washed with distilled water, dried at 103 °C and weighed. The filtrate volume was diluted with distilled water, neutralized to pH = 5 with a saturated $Ba(OH)_2$ solution and centrifuged. The supernatant was evaporated to dryness under vacuum. The residue was re-dissolved in water, filtered through a 0.45 µm filter and analyzed by HPLC. Each hydrolysis was triplicated.

HPLC analyses were performed on a Waters liquid chromatograph equipped with a Waters 2420 Evaporative Light Scattering (ELS) detector (gain = 1, evaporator tube temperature = 60 °C and nebulizer gas pressure = 50 psi) and a Supelco Discovery LC-NH_2 column (250 mm x 4.6 mm i.d,) at 30 °C with a mixture acetonitrile (78%) / water (20%) / methanol (2%) as mobile phase and a flow rate of 1.5 $mL.min^{-1}$. Each sugars hydrolysate was analyzed, each analysis was repeated 3 times and the value averaged. Glucose content (%) was determined on the basis of glucose and cellobiose contents.

RESULTS AND DISCUSSION

Evolution of NMR spectra of heat treated sawdust is in good agreement with observation reported on blocks (Sivonen *et al*. 2002). Deterioration of hemicelluloses is particularly obvious. The shoulder at 102 ppm on the C-1 signal of cellulose at 105 ppm strongly decrease after heat treatment indicating degradations. The signals of the methyl at 20 ppm and carbonyl at 173 ppm of the acetyl groups decreases also after heat treatment.

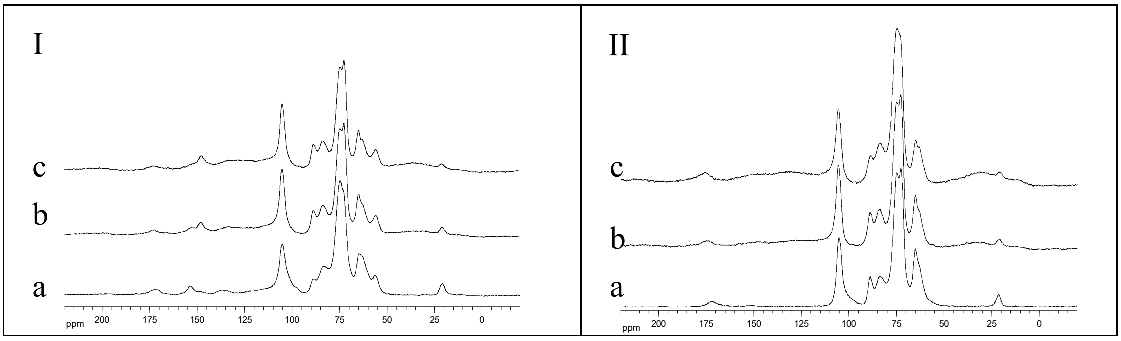

Fig. 1: CP/MAS ^{13}C NMR spectra of untreated (a) and thermally modified (b:5h30, c:21h) beech sawdust (I) and holocellulose fraction (II).

Changes in the lignin signals (not represented here) are less significant indicating its higher stability. NMR spectra of untreated holocellulose fraction indicate characteristic signals of wood polysaccharidic components. Similarly to observations made for thermally modified sawdust, heat treatment of holocellulose fraction results in an important degradation of hemicelluloses characterized by the decrease of the signals at 20, 102 and 173 ppm. More surprisingly, signals previously attributed to lignin thermoreticulation are still obvious on holocellulose fraction. These results clearly showed that new signals appearing between 125 and 135 ppm and 35 ppm on NMR spectra of heat treated wood are not due to lignin modification, but to degradation of holocellulose and probably to a beginning of formation of carbonaceous material within the wood polymers. Indeed, ^{13}C NMR studies reported during cellulose thermal treatment performed in the range of temperature from 300 to 600 °C indicates quite similar observations for samples treated at 300 °C with in a first time the apparition of new signals ascribable to aliphatic carbons (10-50 ppm), aromatic or alkenic carbons (110-160 ppm) and carbonyl groups (205 ppm). At this temperature, cellulose is reported to undergo depolymerization, dehydration reactions and finally char formation. Even if it is well known that chemical composition of Klason lignin obtained after acidic hydrolysis of polysaccharides is different from that of lignin initially present in wood, it is obvious from this study that new signals observed in heat treated wood and attributed up to now to thermoreticulation of lignin are rather due to polysaccharides degradation leading to char formation. These observations corroborate XPS analysis (Nguila Inari *et al.* 2006) indicating an important decrease of the O/C ratio unexplainable by the sole hemicelluloses degradation to volatile by-products. Formation of carbonaceous material is therefore necessary to explain chemical composition evolution of heat treated wood.

Table 1: Klason Lignin, glucose and xylose contents of untreated and heat treated wood (240 °C, 8h)

Sample	Klason Lignin (%)	Glucose (%)	Xylose (%)
Untreated	22.7 ± 0.4	44.0 ± 0.4	14.2 ± 0.3
Heat treated (WL = 21%)	38.0 ± 2.0	35.5 ± 0.6	5.5 ± 0.1

Similar results have also been reported in a study dealing with the contribution of incomplete combustion of vegetation on the carbon content of soil. 13C NMR study of thermally altered red pine wood in a range of temperatures comprised between 70 to 350 °C indicates quite similar observation for samples treated at 200 °C. To confirm these results, wood chemical composition was investigated using classical

Klason lignin determination and HPLC analysis of the sugars present in the hydrolysate. According to literature, beech wood contains approximately 24% lignin, 49% cellulose, 25 % hemicelluloses and 1% extractives. If degradations occurring during heat treatment are mainly associated to hemicelluloses degradation to volatile by-products, it should be possible to calculate *a priori* the theoretical composition of beech wood after treatment. In the case of weight losses comprised between 20 and 25%, composition of thermally modified beech wood should be approximately constituted one third of lignin and two third of cellulose. In all cases (Table 1), Klason lignin determination leads to values higher than expected ones indicating the formation of chars into the wood. Analysis of the sugars in the hydrolysate confirms the higher susceptibility of hemicelluloses to thermal degradation as demonstrated by the lower xylose content detected after treatment. Glucose percentage measured for untreated beech is relatively close from theoretical value (compare 44% to 49%), while that measured after thermal treatment is lower than expected value (compare 35.5% to approximately 66% in the case of degradation of hemicelluloses to volatile by-products). According to these results, it appears that a part of cellulose is degraded during thermal treatment explaining the lower glucose percentage measured after treatment.

CONCLUSIONS

This study shows clearly the formation of carbonaceous materials within the wood structure. CP/MAS ^{13}C NMR spectra indicates a beginning of chars formation rather than to thermoreticulation of lignin and formation of methylene bridges as previously reported in the literature. Determination of Klason lignin content and analysis of sugars present in the hydrolysate indicate that evolution of wood chemical composition during heat treatment can't be explained on the sole degradation of hemicelluloses to volatile by-products. It is postulated that chars formation begins in the range of temperatures comprised between 200 and 240 °C used for wood thermal treatment by mild pyrolysis.

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The Relationship between Mechanical Performance and Chemical Changes in Thermally Modified Wood

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Keywords: Heat-treatment, *Picea abies*, *Pinus sylvestris*, *Fagus sylvatica*, stiffness

INTRODUCTION

The response of wood strength to various combinations of temperatures, heating periods and media of treatment has been the subject of a number of studies in the recent years. While the nature of the heat-induced changes in wood cell wall chemistry has also been examined by a number of authors, little information is available on the relationships between the progressive changes in mechanical properties to the concurrent changes in chemical composition. The purpose of this work was to investigate this relationship.

EXPERIMENTAL

Five residence times (0.33, 1, 4, 8, and 16 h) and four treatment temperatures (190 °C, 210 °C, 230 °C and 245 °C) were used for thermal modification in a N_2 atmosphere. Two softwoods, Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*), and Beech (*Fagus sylvatica*) were modified in matched, small-sized samples (10 × 20 × 150 mm). After conditioning the modified samples for at least six months at 65% RH, 20 °C, six properties were measured to describe its mechanical behaviour, according to BS 373 (BSI 1957) and BS EN ISO 179 (BSI 1997): Janka hardness (H), shear strength (S), Charpy impact strength (I), compression strength parallel and perpendicular to the axis (CA and CE respectively), and bending strength. From the bending test, eight strength parameters were computed, namely: modulus of elasticity (MOE), modulus of rupture (MOR), fibre stress at limit of proportionality (RLP), resilience (R), work to maximum load (MW), total work (TW) and horizontal shear stress at neutral plane at limit of proportionality (SSLP) and at maximum load (SSML). Weight loss (WL) due to the treatment relative to the initial oven-dry weight of the samples was used as the independent variable for the comparisons. Chemical characterisation consisted of the quantitative determination of lignin and polysaccharides, by gravimetric methods.

RESULTS AND DISCUSSION

Properties behaved differently in the rate and magnitude of change at equivalent levels of WL; evidently different mechanisms, polymers or structures are involved in the degree of retention of each property. Relative-to-control changes in each property were generally the same irrespective of the temperature of treatment at equivalent levels of WL in the three species. No major differences were observed in the changing behaviour of most of the properties between the softwoods and Beech in relative-to-control values.

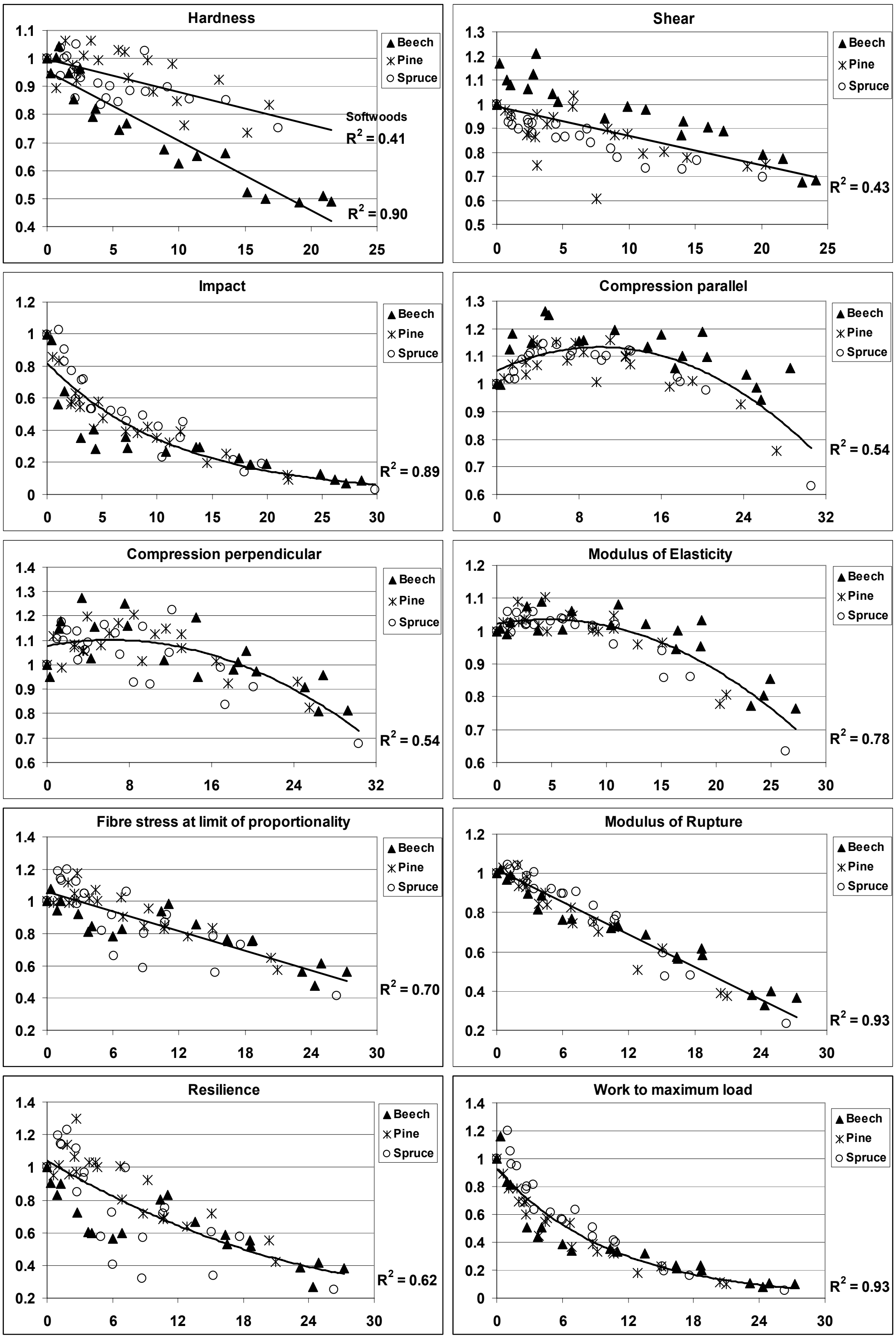

Figure 1: Relative-to-control values (in proportion) versus WL (in %). Each point represents the mean value of n samples. H, n=6; S, n=4; I, n=10; CA, n=8; CE, n=6; E, n=10; RLP, n=10; MOR, n=10; R, n=10; WML, n=10; SSLP, n=10; SSML, n=10. ***Continued over…***

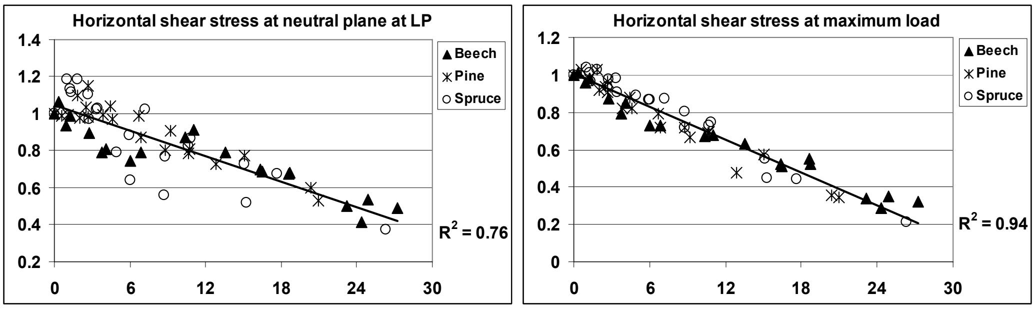

Figure 1: Relative-to-control values (in proportion) versus WL (in %). *Continued…*

MOE remained statistically unchanged up to high levels of modification (WL > 15%); CA was significantly increased to WL of about 5% in Beech and spruce, thereafter remained unchanged and finally significantly reduced at very high levels of modification (WL > 27%). Some properties remained unchanged up to moderate levels of WL, and other properties, mainly those related to energy parameters and impact strength, were significantly reduced at early stages of thermal modification (Figure 1). The fact that the wood MOE is not significantly reduced by thermal treatment up to very high WL is promising, because wood stiffness is of primary value for many applications of TMW, such as flooring, stairs and decking. All parameters could be sufficiently described by a linear relationship between the magnitude of the property and the WL (Figure 1). In all species, resilience was the property that showed the largest variability. Impact strength in Beech was the property most negatively affected by the treatment; most of the strength loss occurring before the WL reached 4% (Figure 1). No differences in the mechanical behaviour were found when comparing the three species at equivalent levels of WL. The magnitude of change in the mechanical properties in each species, expressed as relative-to-control values (in proportion), were in the order: I ≥ MW ≥ TW > R ≥ SSML > MOR > SSLP > RLP > S > H > MOE > CE > CA (Figure 2).

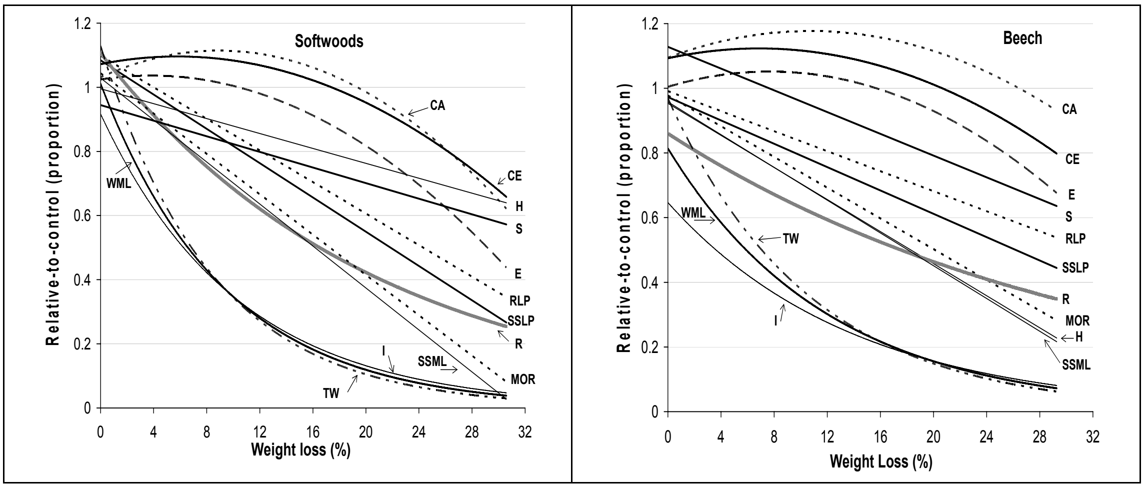

Figure 2: Relative-to-control values (in proportion) versus WL (in %) for the properties plotted together for Softwoods (left) and Beech (right). Data points removed for clarity

The exception was hardness in Beech (in proportion to untreated control), which was significantly different from the behaviour in softwoods. The reduction in bending strength parameters was smaller at the limit of proportionality than the correspondent property at maximum load at equivalent levels of WL (Figure 2). This is an important result, because in practical terms, we normally rely upon the performance of timber not just at maximum load, but in fact well below the proportional limit. Thus, TMW would perform somewhat better in normal situations of service than would be expected from the calculated behaviour based on the ultimate strength values, even for toughness. Our proposal is that a major reason behind the reduction in the ultimate fibre stress in bending (as well as in other strength parameters) is the after-treatment physical state of the cell wall substance in modified wood. The shrinkage of the cell wall leaves the treated material in a permanent state of strain, where the reduction of transversal dimensions concurs with the lengthwise increase in specimen dimensions –the Poisson effect. This reduces the capability of the cell wall for elastic deformation, lowering the limit of proportionality and, thereafter, drastically lowers the ability of the cell wall polymers for plastic flow, leading to failure at lower levels of strain. Strength losses are also thought to occur in chemically degraded wood at low levels of WL because of changes in wood chemical composition. Changes in other properties (MOE, CA, CE), some of them positive, are more related to the minimal changes in wood density due to the treatment and to the reduced moisture content at test than to changes in chemical composition. Degradation of the cell wall chemical constituents followed the order pentoses > hexoses ≥ lignin. Strength properties were positively correlated with pentose and hexose content and negatively correlated with the lignin (Table 1). In Beech, pentoses and lignin were more strongly correlated with the mechanical parameters, whereas in softwoods, the three constituents were strongly correlated with most mechanical properties. It is concluded that most mechanical properties can be predicted from changes in chemical composition or by using WL as predictor. However, as changes in all chemical constituents appear to be significantly related to most changes in mechanical properties, and they are also strongly correlated between themselves, the predictions require the applications of another technique.

Table 1: Correlation of chemical components and strength parameters

	H	S	CA	CE	E	RLP	MOR	SSLP	SSML	Ln (R)	Ln (WML)	Ln (TW)	Ln (I)
Beech													
Lignin	-0.94	-0.94	-0.49	-0.72	-0.80	-0.87	-0.95	-0.90	-0.95	-0.83	-0.94	-0.93	-0.92
Pentoses	0.98	0.90	NS	0.70	0.74	0.85	0.96	0.90	0.97	0.83	0.94	0.91	0.91
Hexoses	0.47	0.70	NS	0.49	0.66	0.56	0.56	0.55	0.53	0.51	0.57	0.64	0.58
Pine													
Lignin	-0.67	-0.55	-0.61	-0.58	-0.81	-0.92	-0.97	-0.94	-0.97	-0.92	-0.98	-0.97	-0.96
Pentoses	0.59	0.46	NS	0.51	0.69	0.81	0.82	0.83	0.82	0.81	0.85	0.84	0.81
Hexoses	0.63	0.54	0.66	0.55	0.79	0.87	0.94	0.89	0.94	0.87	0.93	0.92	0.92
Spruce													
Lignin	-0.66	-0.88	-0.75	-0.76	-0.94	-0.81	-0.98	-0.83	-0.98	-0.77	-0.99	-0.99	-0.97
Pentoses	0.63	0.92	NS	0.58	0.71	0.78	0.91	0.81	0.93	0.74	0.91	0.87	0.86
Hexoses	0.63	0.82	0.82	0.78	0.97	0.78	0.96	0.79	0.95	0.74	0.97	0.99	0.96

All correlations significant at the 0.01 level, but for the shaded combinations, significant at the 0.05 level. NS = not significant

Pentoses include Arabinose and Xylose. Hexoses include Glucose, Galactose, Manose, and Rhamnose. Lignin includes Klason lignin and acid soluble lignin

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Shear and Tensile Strength of Conventionally Dried, Press Dried and Heat Treated Aspen

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Keywords: Aspen, drying, mechanics, modification, *Populus* sp.

ABSTRACT

Shear strength of small clear specimens of European (*Populus tremula* L.) and hybrid aspen (*P. tremula x tremuloides*) was studied in tangential and radial direction. Furthermore, tensile strength was measured both parallel and perpendicular to the grain. The materials were dried using conventional warm air kiln drying, press drying, and heat treatment into class S according to the Thermowood® system. Irrespective of the drying treatment, the tangential shear strength of European aspen specimens was ca. 5% higher than that of hybrid aspens. Similar difference appears between the average wood densities of the aspen species. Heat treated specimens indicated significantly lower average tangential shear strength values (5.7–6.1 MPa) than the conventionally dried ones (6.5–7.0 MPa). Conventionally and press dried specimens, as well as press dried and heat treated specimens did not differ from each other. Conventionally dried specimens showed radial shear strength values of 8.8–9.6 MPa, on average. Heat treated European aspen specimens (8.4 MPa) were significantly weaker than the conventionally dried specimens (9.6 MPa). Other treatment groups did not differ from each other. In case of both aspen species, the longitudinal tensile strengths of heat treated specimens (54–62 MPa) were significantly lower than those of conventionally and press dried specimens (82–103 MPa), which, on the other hand, did not differ from each other. Heat treated specimens had the highest variability among the results. Some of the specimens were very fragile, not fulfilling the requirements for a successful mechanical test. The inherent flaws in aspen wood material, *e.g.*, wetwood and density fluctuations, increases the variability of the properties of heat treated wood. Press drying by the technology used in this study, has only slight effect of the shear and tensile strength of aspen wood.

INTRODUCTION

European aspen (*Populus tremula* L.) is the fifth most common indigenous tree species in Finland. The cross-breeding experiments made between European aspen and North American trembling aspen (*P. tremuloides* Michx.) in the 1950's, resulted in a hybrid (*P. tremula x tremuloides*) that grows exceptionally fast in boreal conditions. Nowadays, there are ca. 1000 hectares of hybrid aspen plantations in Finland (Holm 2004).

Aspen wood is a valued material for interior uses, such as panelling and sauna benches (*e.g.*, Heräjärvi *et al.* 2006), but also used in *e.g.*, ice hockey sticks. From a woodworking point of view, the main problems with aspen are related to drying and quality of dried wood (twisting, non-uniform final moisture content, end-checks). In order to get acceptable kiln-drying results, aspen must be dried very slowly; typical drying times vary from 7 to 30 days. Tangential swelling is very high (10–12%) in sapwood, which causes twisting problems especially in pieces that contain both heartwood and sapwood.

Aspen wood is nowadays commonly heat treated. As a porous species, it is obviously well-suited also to other modification methods, such as compressing. No information has been available on the differences of European and hybrid aspen wood from the viewpoint of woodworking and processing properties. The objective of this study was to detect the between species differences in conventionally dried, press dried and heat treated European and hybrid aspen wood in tensile and shear strength.

EXPERIMENTAL

Prior to the preparing of the actual test specimens, the material was divided into three sub groups, which were subsequently dried in three ways. One third of the material was dried using a conventional warm air kiln drying, one third was press dried using the technology of Arboreo Ltd., and one third was dried into Thermo S class using the Finnish Thermowood® process. The drying schedules and technologies used, as well as detailed descriptions of the material sampling principles have been documented by, *e.g.*, Heräjärvi *et al.* (2006), Junkkonen and Heräjärvi (2006a, b).

All tests were made using small clearwood specimens. Norms presented by Kučera (1992) were followed – these norms are in accordance with the ISO standards 3345 and 3346 (1975), and 3347 (1976). Figures 1 and 2 show the specimen types used in the tests. Numbers of measured specimens in the longitudinal and radial tension tests were 133 and 167, respectively. Shear strength was measured from 143 radial and 147 tangential specimens.

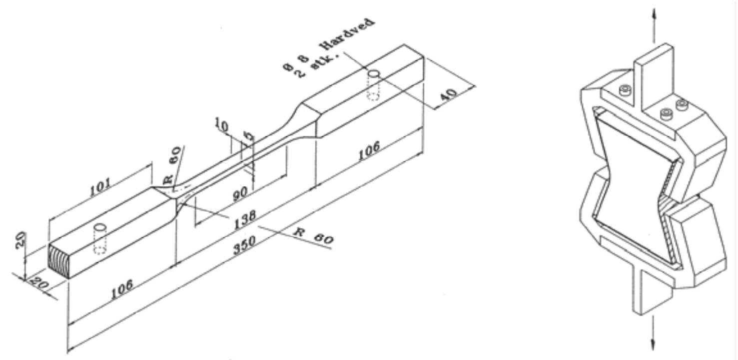

Figure 1: Left: tensile strength test specimen in the parallel to the grain direction. Right: tensile strength test specimen in the radial direction. Original drawings: Kučera (1992).

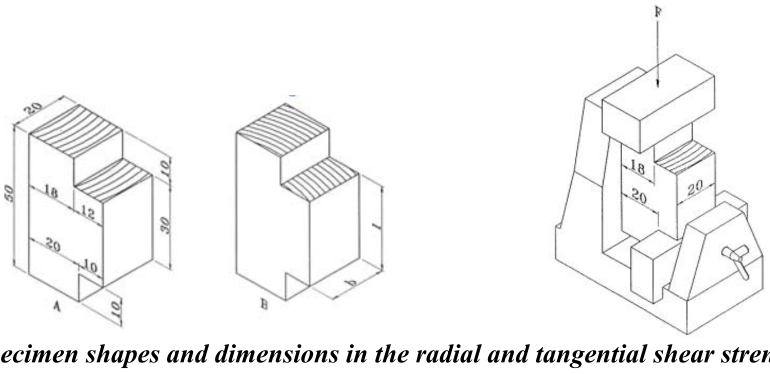

Figure 2: Specimen shapes and dimensions in the radial and tangential shear strength tests (left) and the apparatus to measure the shear strength (right). Original drawings: Kučera (1992).

RESULTS AND DISCUSSION

Figure 3 shows the differences in the tensile strengths between the species and drying methods. Heat treatment clearly reduced longitudinal tensile strength, whereas its effect to the radial tensile strength was smaller. The longitudinal tensile strength of press dried hybrid aspen appeared to be higher than that of European aspen, even though the average density of European aspen wood is slightly higher. This finding is obviously related to the specimen manufacture where some wood was planed away in order to prepare specimens with wanted dimensions. The problem naturally existed in case of all press dried specimens: their surface, the most compressed and, thus, strong part was more or less planed away during the specimen manufacture.

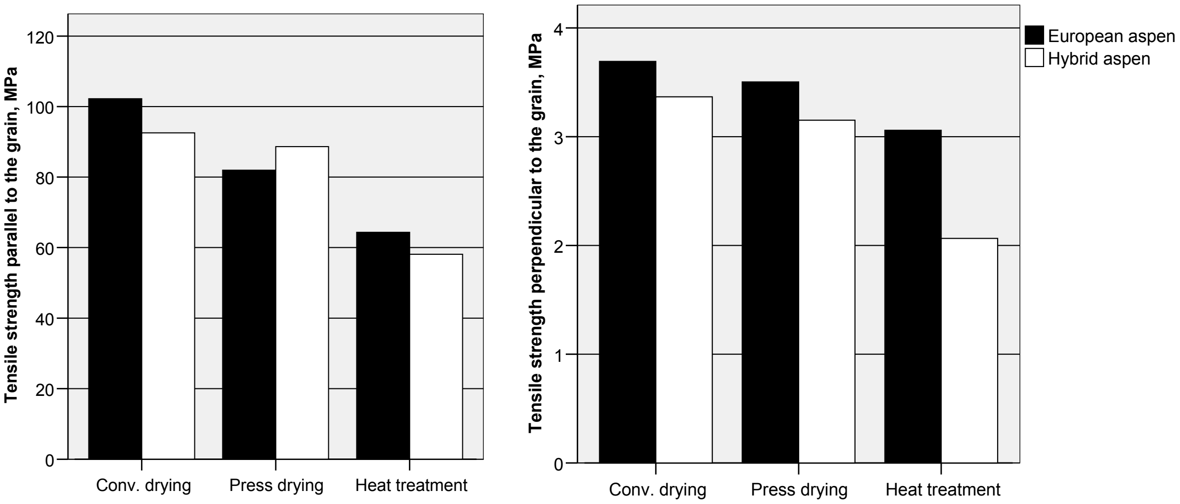

Figure 3: Tensile strength of conventionally dried, press dried and heat treated European and hybrid aspen wood parallel (left) and perpendicular (right) to the grain.

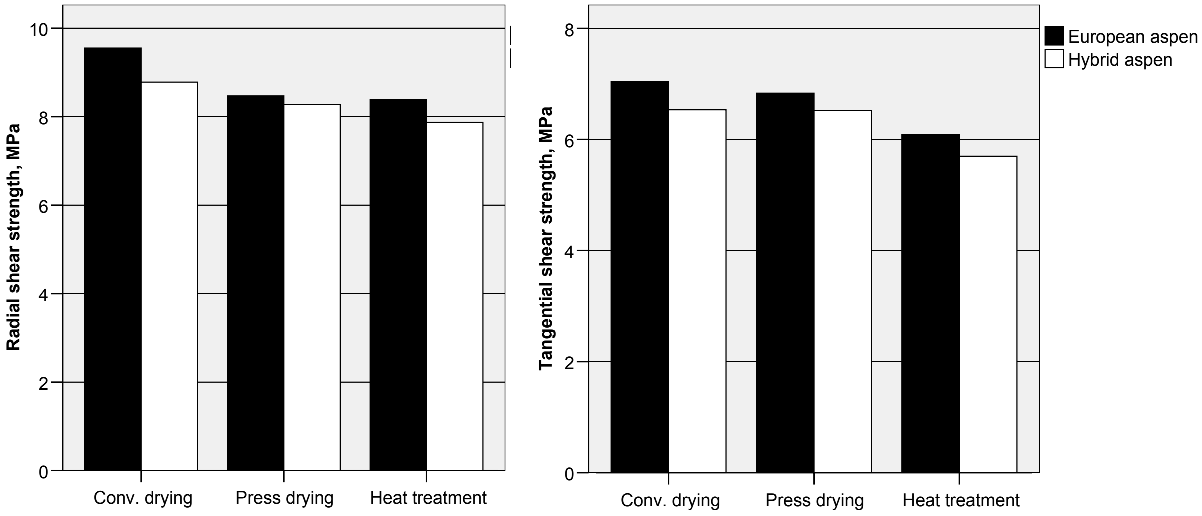

Figure 4: Radial (left) and tangential (right) shear strength of conventionally dried, press dried and heat treated European and hybrid aspen wood.

Figure 4 shows the differences in the radial and tangential shear strength between the species and drying methods. Heat treated specimens showed practically equal values to the press dried ones, the results of both, however, being at lower level in comparison to the conventionally dried specimens.

CONCLUSIONS

Hybrid aspen wood is about 10–20% lighter than European aspen wood. Thus, also its mechanical performance is, in general, poorer. Conventional kiln drying (max. dry bulb temperature ca. 60 ˚C) resulted in the best tensile and shear strength, press dried (*ca*. 150 ˚C) specimens showed slightly poorer performance, and heat treated (ca. 180 ˚C) specimens were most clearly weakened. Hence, the higher the drying temperature, the poorer tensile and shear strength.

Aspen wood has a tendency to check and split in different ways; *e.g.*, loosened grain is a common problem in dried wood. Loss of shear strength, in particular, reduces wood's machining properties (planing, grooving), causing increased risk to various defects, or a need to careful adjustment of machine settings. Thus, products that require good machining properties should not be dried in high temperatures. On the other hand, severe environmental conditions during the service life pronounce the weaknesses in the mechanical performance of a wood product. This study suggests that the use of heat treated aspen, especially hybrid aspen with light wood, should be avoided in structures where the product is exposed to moderate or high shear or tensile stresses.

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Physical-mechanical Properties of Hard- and Softwood Heat Treated in an Autoclave

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Keywords: Heat treatment, sorption, colour, hardwood, softwood, mechanical properties, chemical properties

ABSTRACT

On hard- and softwood, which was industrially heat treated in an autoclave (at varying intensities) the following properties were tested: sorption behaviour, colour modification, swelling, mechanical properties (modulus of elasticity, bending strength, hardness) and selected chemical properties. As consequence of a heat treatment, colour differences of beech with red heartwood and ash with brown heartwood can be equalised and thus an added value can be reached. With increasing treatment intensity (temperature and duration of treatment) the wood becomes darker while the equilibrium moisture and swelling are decreasing to 50% of untreated wood. On the other hand the increasing treatment intensity comes along with a clear decrease in strength and hardness. At the same time the chemical composition of the wood as well as the amount of extractives change clearly, resulting in a decreasing pH-value.

INTRODUCTION

Methods of wood modification gained in acceptation in the last years. Heat treatment is one of these methods. The basic principles of the thermal treatment had been developed several decades ago. First works had been made in the USA by Stamm in 1937. In the seventies again several works had been made, *e.g.* by Burmester (1973, 1975), who developed the FWD (Feuchte-Wärme-Druck-Verfahren) for the dimension stabilisation of particle boards. Further works had been made amongst others by Kollmann und Schneider (1964). The thermal treatment at temperatures between 170 and 200 °C and above leads to a darkening of the colour, a decreased equilibrium moisture and swelling, a decrease of the mechanical properties but increases the resistance against fungal decay.

EXPERIMENTAL

Different species of hard- and softwood were thermally treated on an industrial scale according to Giebler (1981) in an autoclave. Two different levels (2 and 3) of treatment had been chosen, the higher the level the higher the intensity of treatment. The levels of treatment differ in pressure, temperature, time and oxygen content of the atmosphere.

Following tests were made after acclimatisation at 20 °C and 65% RH:

- Density, according to DIN 52182

- Equilibrium moisture according to DIN 52183 and swelling according to DIN 52184
- Water absorption following DIN EN ISO 15148
- Sound velocity / dynamic E-Modulus (at 50kHz). The E-Modulus was calculated using Equation 1.

$$E - Modulus_{Velocity} = v^2 * \rho \qquad (1)$$

where v = sound velocity and ρ = density

- Eigenfrequency / E-modulus out of eigenfrequency. A bending rod supported in its nodal points (at 1/5 of the sample length of both ends of the sample) is brought to oscillation by a hit in the middle of the sample. Using Equation 2 the dynamic E-modulus can be calculated.

$$E - Modulus_{dynamic} = \frac{4\pi^2 * l^4 * f^2 * \rho}{m_n^4 * i^2} * (1 + \frac{i^2}{l^2} * K_1) * 10^{-9} \qquad (2)$$

Where l = length of sample, f = eigenfrequency, ρ = density, m_n^4 = 500.6, i = (height of sample)^2 / 12 and K_1 = 49.48

- Bending E-modulus and bending strength according to DIN 52186
- Brinell hardness: measurements on the radial and tangential surfaces
- pH-Value: measurements according to Roffael und Kossatz (1981)
- Extractives: measurements according to TAPPI-Norm: T 204 cm-97 “Solvent extractives of wood and pulp”, also as the method described by Polyak (1948).

RESULTS AND DISCUSSION

Density and equlibrium moisture

The trend shows a decrease in density with increasing treatment intensity . The intensity of the treatment is also reflected in the equilibrium moisture contents of the samples. Variations may be caused by variable densities of the untreated wood.

E-Moduli and strength

The E-modulus calculated on the base of sound velocity shows a decrease for the hardwoods and partially a slight increase for softwoods. The same tendency can be seen for the E-modulus from eigenfrequency and the E-modulus determined through the bending tests (Figure 1). A much clearer decrease can be seen for the bending strength for all tested wood species (Figure 2).

Brinell-hardness

Slightly higher values were reached for a load in radial direction compared to a load in tangential direction. For both directions there is a decrease of the values with increasing treatment levels.

Sorption and swelling

Clear differences in the behaviour of sorption and swelling can be seen, which are caused by the different levels of treatment. The different groups of treatment levels can be seen clearly. Differences are much more obvious than for the mechanical properties. Wood moisture can be reduced by a thermal treatment up to 50% (as example for pine wood in Figure 3). Swelling in tangential and radial direction can be

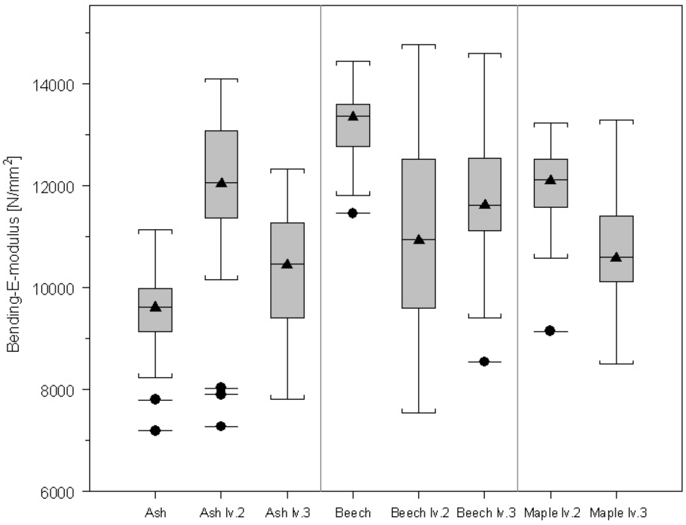

Figure 1: Bending-E-modulus for the tested hardwoods; untreated samples and treated at different levels (lv. 2 and lv. 3)

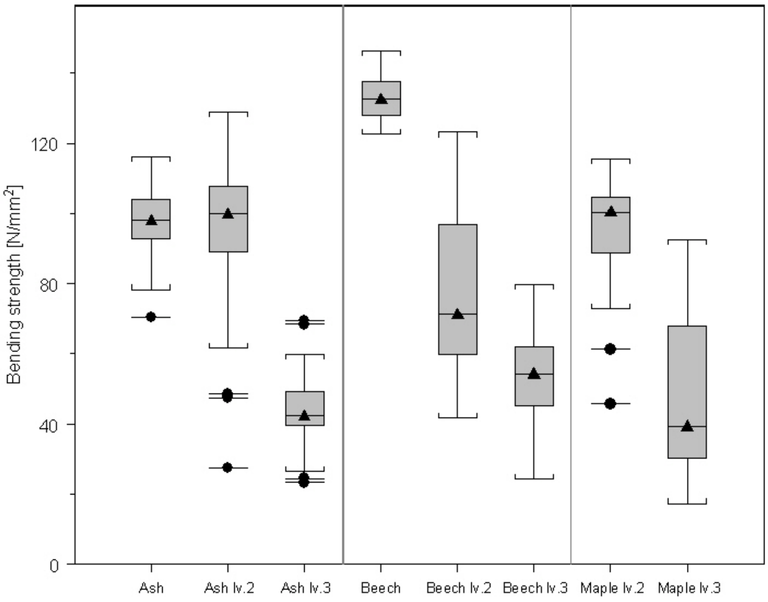

Figure 2: Bending strength for the tested hardwoods; untreated samples and treated at different levels (lv. 2 and lv. 3)

reduced up to 60% of untreated wood. Anisotropy for swelling is still consisting after a thermal treatment.

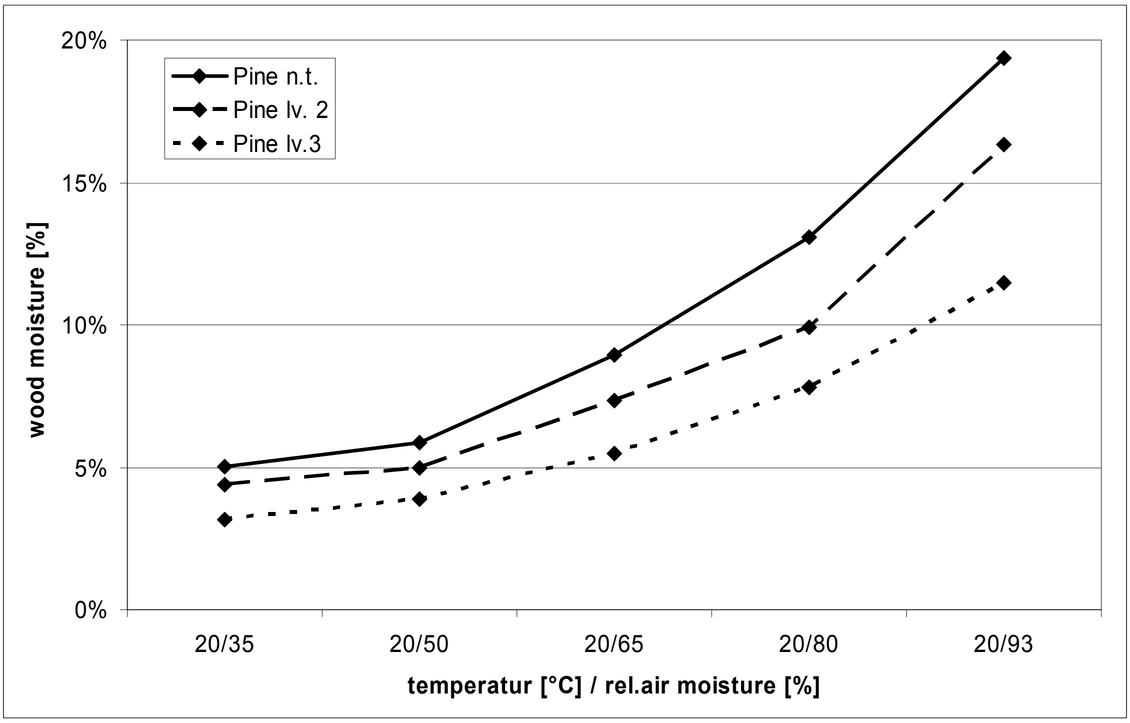

Figure 3: Reduction of wood moisture shown for pine wood. Untreated samples (n.t.) and treated at different levels (lv. 2 and lv. 3).

Chemical properties

pH-value decreases in consequence of the thermal treatment. Nevertheless a clear tendency can not be seen. Table 1 shows the results of the chemical analysis for chosen wood species. The amount of extractives is increasing with increasing treatment level for all tested species, while the amount of hemicelluloses is decreasing (hemicelluloses are essential for the hygroscopic behaviour of wood).

Table 1: Extractives and percentage of hemicelluloses for chosen tested wood species (mean values)

	Beech n.t.	**Beech lv. 2**	**Beech lv. 3**	**Douglas fir n.t.**	**Douglas fir lv. 2**	**Douglas fir lv. 3**
Total of extractives [%]	6.5	15.8	15.9	5.1	13.3	11.9
Percentage of hemicelluloses [%]	13.6	10.4	5.6	17.2	13.3	4.9

Change of colour

The heat treatment causes a colour shift into a darker/blacker colour region. Differences in the colour between radial and tangential sides are minor. Coloured heartwood (for beech or ash; ash can be seen in figure 4) disappears through a thermal treatment. Bright stripes as remarked by Oelhafen, Niemz und Hurst (2006) for a treatment in oxygen atmosphere did not appear in the present research. The change of colour is not stable to UV radiation.

Figure 4: Ash with coloured heartwood; left: not treated, middle: level 2, right: level 3

Nevertheless all of the measured properties showed not always a clear and proper tendency with increasing level of treatment. Due to the process of thermal treatment (industrial scale) an overlay with the wood properties itself may occur (higher density of the treated wood by comparison to the untreated samples).

CONCLUSIONS

Thermally treated wood has its own properties which are not comparable to the ones of untreated wood. Remembering this aspect and using the treated wood in an appropriate way, this novel material opens new applications for wood.

ACKNOWLEDGEMENTS

We thank the fund for the promotion of the research in the field of forest- and wood science (Fonds zur Föderung der Wald- und Holzforschung) and the company Balz AG, Langnau i.E., Switzerland for the material

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Physical Properties of Jack Pine Thermally Modified at Three Temperature Levels

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Keywords: Jack pine, thermal modification

ABSTRACT

Thermally modified wood can be defined as wood heated between 160 and 245 °C within controlled oxygen reduced atmosphere. This treatment results in chemical modification of the wood structure such as degrading the hemicelluloses and lignin components. As a result, physical properties of thermally modified wood are different from those of regular wood. The colour of wood is also modified. Higher temperatures tend to amplify these modifications. For twenty years, many heat treatment processes have been developed in order to be used at an industrial scale 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 in Canada. Since 2002, the eastern laboratory of FPInnovations-Forintek has conducted studies on thermally modified wood. The general objective of the present study is to determine wood properties of thermally modified jack pine vs. natural kiln dried wood. Tests were performed on eastern Canadian jack pine thermally modified using the Finnish ThermoWood process. Wood was modified at three temperature levels including Thermo-S (190 °C) and Thermo-D (212 °C) treatment classes, established by the Finnish ThermoWood Association, and 230 °C. Assessed wood properties were wear resistance, dimensional stability, hardness, resistance to fungal decay, impact and static bending (MOE and MOR). In general, thermally modified wood exhibits enhanced resistance to decay and a significant increase of its dimensional stability. However, the treatment results in a lower MOR, impact and abrasion resistances. The MOE and hardness of thermally modified wood are not significantly affected by the treatment process. Finally, the results highlighted the effect of temperature treatment on the wood properties, including colour.

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 jack pine thermally modified at 190 °C (Thermo-S), 212 °C (Thermo-D) and 230 °C using the Finnish ThermoWood process. Assessed wood properties were wear resistance, dimensional stability, hardness, resistance to fungal decay, impact and static bending (MOE and MOR).

EXPERIMENTAL

Material used for high-temperature treatments were kiln dried jack pine (*Pinus banksiana*) lumber 50 mm x 150 mm x 3.05 m, premium graded. After treatments, wood was conditioned at 20 ^{o}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 based on ASTM D 4060 Standard test method for abrasion resistance of organic coatings by the taber abraser. Mass loss of 10 cm x 10 cm x 2 cm-thick specimens was measured after each 100 cycles of abrasive wheel, up to 500 cycles. Dimensional stability was measured in accordance with ISO 4859 Wood–Determination of radial and tangential swelling and ISO 4469 Wood–Determination of radial and tangential shrinkage. Resistance of wood to fungal decay was determined following the ASTM D 2017-81 Standard test method of accelerated laboratory test of natural decay resistance of woods. Fungi used in these tests were the brown-rots *Gloeophyllum trabeum* and *Postia placenta* and the white-rots *Coriolus versicolor* and *Irpex lacteus*. Results are presented as mass-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 25 mm x 25 mm x 410 mm specimens in order to determine MOE and MOR.

RESULTS AND DISCUSSION

Mass loss of unmodified and thermally modified wood samples of jack pine at 190, 212 and 230 ^{o}C after 500 cycles of the abrasive wheel are shown in Figure 1. Results show that resistance to abrasion of wood is reduced following thermal modification. Also, the resistance to abrasion of thermally modified wood decreases with increment of the treatment temperature. Figure 2 illustrates tangential shrinkage values for unmodified test specimens and specimens modified at 190, 212 and 230 ^{o}C. Maximum shrinkage values were calculated by taking into account the initial dimensions of the test specimens (20 mm cubes) following equilibrium achieved by immersion in water as well as the final dimensions after drying at 103 ^{o}C to an oven-dry state. Shrinkage values at a 12% MC were calculated by taking into account the initial dimensions of the test specimens following the equilibrium achieved by immersion in water as well as the final dimensions after conditioning in an environment at 20 ^{o}C and 65% RH. Results show that tangential shrinkage of thermally modified wood decreases with increment of the treatment temperature. Similar results were obtained based on tangential swelling. From Figure 3, resistance to fungal decay of thermally modified jack pine was improved in close relation with the temperature of treatment, mass loss being negligible at 230 ^{o}C. Unmodified jack pine was mostly affected by brown-rots *Gloeophyllum trabeum* and *Postia placenta*. 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 jack pine samples. Resistance to impact bending of thermally modified wood is lower than unmodified wood. Resistance decreases with treatment temperature increase. MOR values for unmodified and thermally modified jack pine at 190, 212 and 230 ^{o}C are shown in Figure 5. Results show a reduction of the MOR of modified wood ranging from 25 to 44% compared to unmodified jack pine. The values suggest that a rise in treatment temperature results in a reduction of the MOR. However, results obtained demonstrate that the MOE is not adversely affected by the thermal modification process.

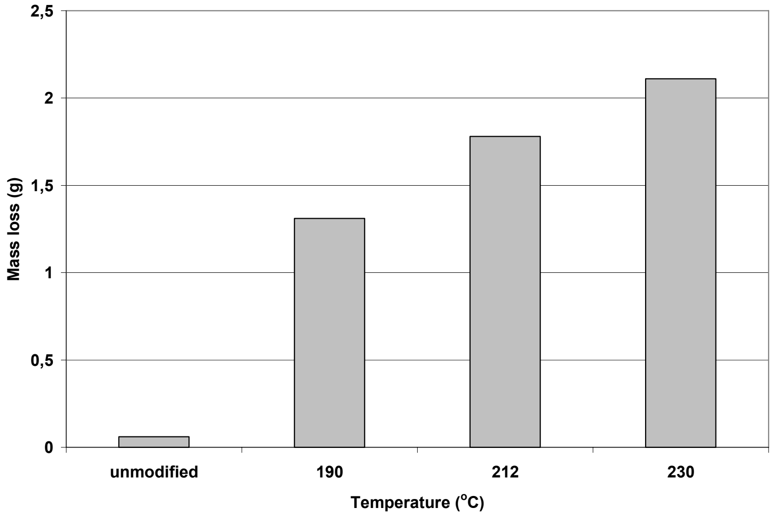

Figure 1: Abrasion Resistance of unmodified and thermally modified jack pine at 190, 212 and 230 °C

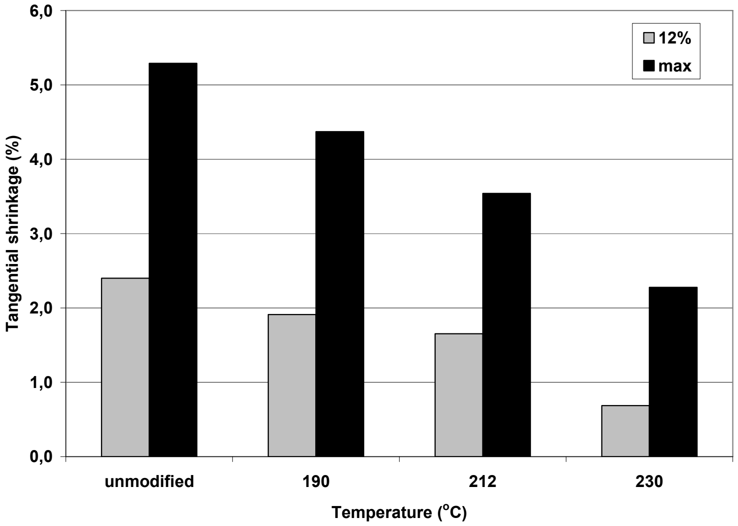

Figure 2: Tangential shrinkage values of unmodified and thermally modified jack pine

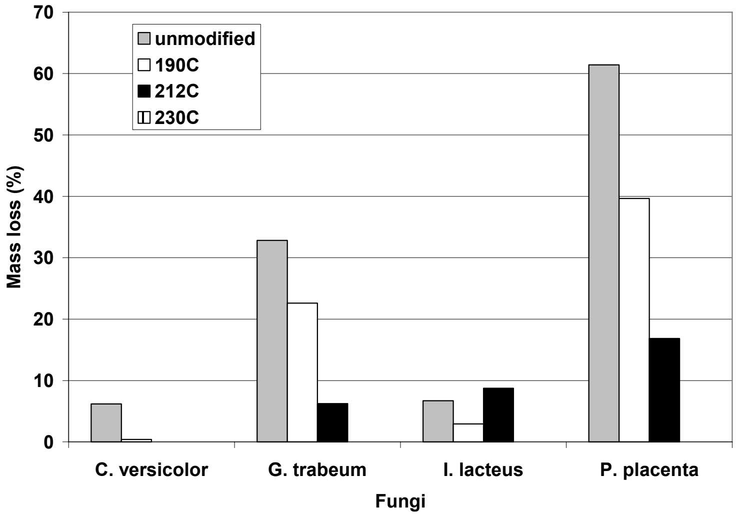

Figure 3: Resistance to fungal decay of unmodified and thermally modified jack pine

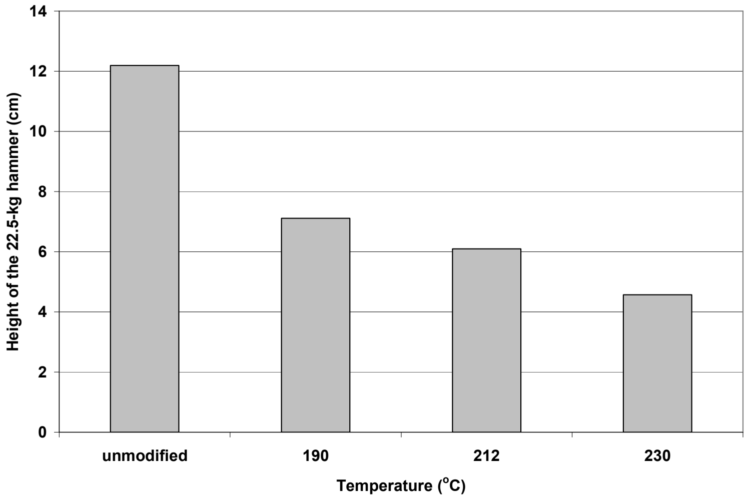

Figure 4: Impact resistance of unmodified and thermally modified jack pine

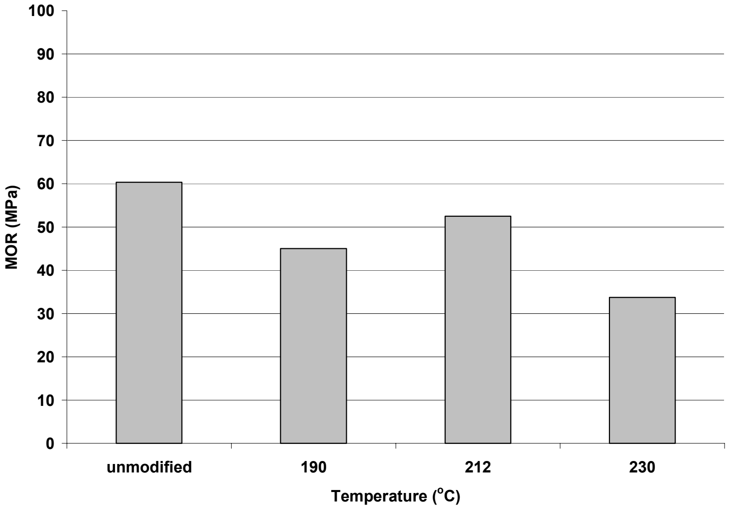

Figure 5: MOR of unmodified and thermally modified jack pine

CONCLUSIONS

Tests results on jack pine show an improvement of dimensional stability and resistance to fungal decay after thermal treatments. However, resistance to abrasion, impact bending and MOR were reduced. Properties are generally related to the temperature used for treatments. Finally, results show that MOE was not affected by treatments.

ACKNOWLEDGEMENTS

Project funded by Natural Resources Canada within the Value to Wood program.

Mechanical Properties of Thermal Treated Hardwood (Beech): Bending and Tension Strength and Stiffness of Boards

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Keywords: Thermally treated timber, beech, bending strength, board, tension strength, modulus of elasticity

ABSTRACT

This paper describes structural tests on boards fabricated from thermally treated timber of beech *fagus sylvatica* (TMTB). In particular bending and tension strength and stiffness were determined. The results were correlated to parameters like density and dynamic modulus of elasticity (MOE) as indicators for the possibility of predicting strength classes by machine grading.

INTRODUCTION

In the past 5 years products made out of thermally treated timber (TMT) are being increasingly used for a wide field of applications. For outdoor its superior durability and dimensional stability makes TMT being a good substitute for tropical hardwoods or impregnated softwoods. For indoor uses the wide range of possible colours of TMT made it becoming a competitor to dark coloured tropical hardwoods. Within the EC-funded FP6 project *Holiwood* the partners intend to widen the field of uses for TMT made out of European hardwoods to structural applications in particular for an outdoor environment. An extensive test program has been set up to determine the strength and stiffness parameters of TMTB. For the determination of respective characteristic values only bending strength and stiffness as well as density have to be tested according to EN 384, all other values can be calculated on base of this. As tests with small dimensions indicated that the relation between several strength/stiffness parameters could differ from respective specifications given in EN 384 the tests will have to cover all parameters that are needed to assign, *e.g.* TMTB to (a) strength class(es) according to EN 338. In the following the results of bending and tension tests on TMTB boards are presented as an example of the still ongoing test program designed to determine the structural behaviour of this material.

EXPERIMENTAL

Material

All tests were executed with TMTB and untreated beech as reference. As cross-sections boards with thicknesses from 28 to 30mm and widths between 120 mm and 150 mm were selected. The boards were free of major defects like knots and bark and also didn't show significant deformations like twist, cup or bow. However, as slope of grain is difficult to determine on beech, this feature could not be verified before testing. All boards were planed. The boards were provided by Mitteramskogler GmbH which is based in Gaflenz, Austria. This company uses the THA thermal treatment process where the respective heating process is executed under a gas atmosphere. According to the desired end-use of the material, the heating temperature can vary between 160 °C and 250 °C with treatment times from 2 h to 16 h (Mitteramskogler 2007). For the tests material that has undergone different heat treatments was used. One series, with untreated beech as reference was treated under 180 °C and treatment times of 4 h, 8 h and 16 h. For all other series TMTB which Mitteramskogler sells under the brand "Buche forte" was used. Detailed data for the respective treatment are not published, however the used fix combination of temperature and treatment time is selected in such a way that durability class 1 can be guaranteed according to the manufacturer. Before testing the boards were stored in standard climate (20 °C/65% r.h.). Moisture content and oven-dry density were determined immediately after testing. An overview of the test material is given in table 1. Each board of series 2 (S2) was divided into a tension and a bending specimen in order to achieve a respective comparison at the best.

Table 1: Test series

Series [-]	**Treatment**	**Temperature** ***T*** **[°C]**	**Time** ***t*** **[h]**	**Number** ***n*** **[-]**	**Density** ρ_0 **[kg/m³]**	**moisture content** ***u*** **[%]**
T0	Beech untreated	-	-	26	580-820	9.7-11.7
T4	TMTB	180	4	26	580-790	6.5-7.3
T5	TMTB	180	8	26	570-800	6.0-6.7
T6	TMTB	180	16	26	580-780	5.3-6.0
S1	TMTB "Buche forte"	nn	nn	57	590 - 750	5.1 – 6.9
S2	TMTB "Buche forte"	nn	nn	38 + 38	570 - 750	5.4 – 7.4

Procedures

Before the tests were executed, the MOE was determined by using two different methods in order to check the possibility for future machine grading of TMT. First an ultrasonic device "Sylva Test" was used to determine the speed of sound v within each specimen. Together with the density ρ measured at the same moment it was possible to calculate a dynamic MOE $E_{\mathrm{dyn},1}$ using the following equation:

$$E_{dyn,1} = \rho \cdot v^2 \tag{1}$$

With the "Grindosonic" equipment another possibility to determine a dynamic MOE $E_{\mathrm{dyn},2}$ was available and used. This determination is based on the measurement of the first eigenfrequency of the board when it is supported as a single beam and can be calculated as follows (Görlacher, 1984):

$$E_{dyn,2} = \frac{4\pi^2 \cdot \ell^4 \cdot f_0^2 \cdot \rho}{m_n^4 \cdot i^2} \cdot \left(1 + \frac{i^2}{\ell^2} \cdot K_1\right) \tag{2}$$

The bending- and tension tests were executed according to EN 408. For the 4-point bending tests the bending strength f_{m} as well as the deformations required to determine the global ($E_{\mathrm{m,g}}$) and local ($E_{\mathrm{m},\ell}$) modulus of elasticity (MOE) were recorded. For the determination of the MOE in tension parallel to grain the deformations were measured on a length of 700mm on both sides of the specimens.

This reference length equals around 6 times the width which is a deviation from EN 408 that requires a reference length of 9 times the width.

RESULTS AND DISCUSSION

Strength and Stiffness

All specimens were tested up to failure. Figure 1 shows the results for the series with different heat treatments. The mean bending strength of the heat treated specimens was around 30% to 40% lower (50% lower at minimum level) compared to the untreated reference specimens but the mean local bending MOE of the TMTB specimens exceeded the respective MOE of the reference by 8% to 10%. However, the variation between the different treatments – here: treatment time – was not significant. Particularly remarkable in regards to its desired use as a structural material are the significantly higher coefficients of variance CV for the bending strengths of the TMTB samples whereas the CV for the MOE's are more or less on an equal level for untreated and heat treated beech.

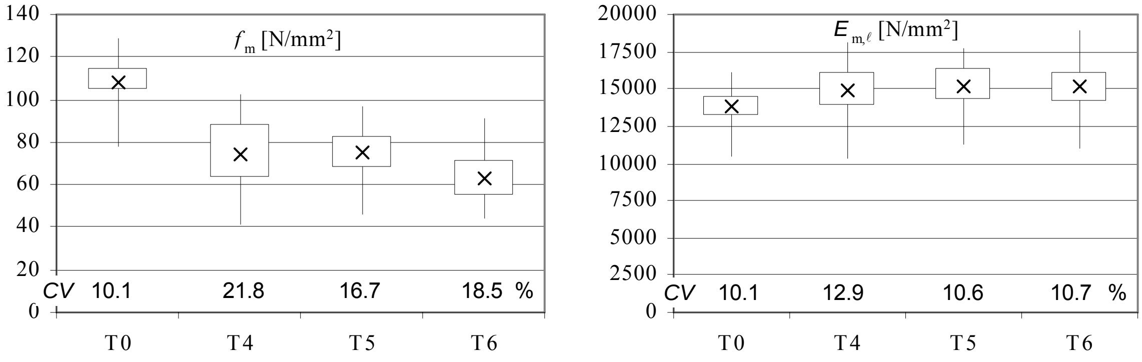

Figure 1: Boxplots including coefficients of variance CV for bending strength and local bending MOE of boards with different heat treatments.

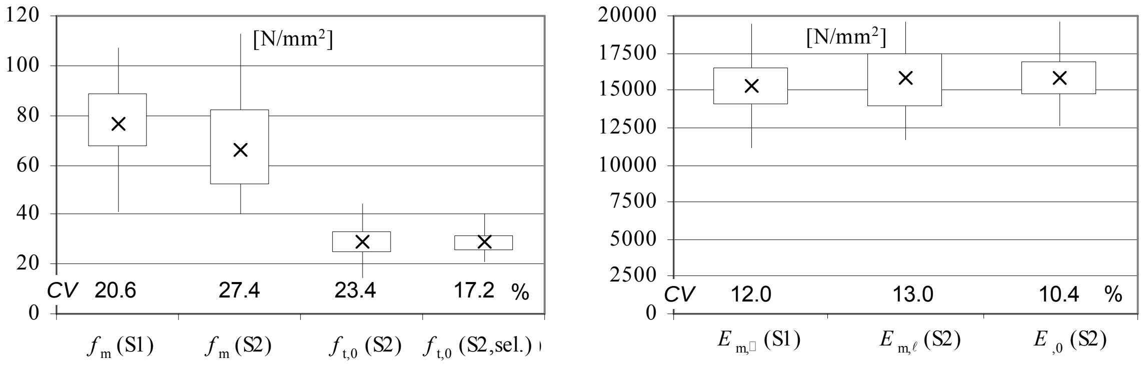

Figure 2: Boxplots including coefficients of variance CV for bending- and tension strength parallel to grain as well as local bending- and tension parallel to grain MOE of boards with treatment "Buche forte".

Figure 2 gives an overview of the results for the series designed to investigate the relation between the behaviour of bending and tension loading of TMTB-boards. In particular series 2 (S2) allows a good comparison, as the bending and tension specimens were taken from one and the same board. After that, the mean tension strength parallel to grain $f_{t,o}$ was about 45% of the mean bending strength f_m and at the minimum level $f_{t,o}$ reached only 35% of f_m . As expected, there was no significant difference between bending and tension MOE. The respective data for series 2 correlated well (R^2 = 0.64). If the tension strength of the specimen that failed completely or partly in the gripping device of the testing machine (40% of the specimens) are sorted out, the tension strength of the remaining specimens (S2,sel) is 50% of the respective bending strength. With this $f_{t,o}$ in any case does not reach 60% of f_m which is given in EN 338 for the respective relation on a characteristic level.

Correlations in regards to machine grading

The obtained strength and stiffness values were correlated to measurements taken in advance to the tests. With this it should be assessed if these data could be taken into account for machine grading of TMTB. The strength values were correlated to respective MOE's and densities as well as to combinations of both (dynamic MOE's). It can be shown that the local bending MOE $E_{m,g}$ correlates well with both dynamic MOE's E_{dyn1} and E_{dyn2} and thus can be predicted with these measurements. The coefficient of determination R^2 within the single series varies between 0.56 and 0.81 with the Grindosonic (E_{dyn2}) measurements prediction being slightly better than the Sylvatest measurements (E_{dyn1}). Prediction of the bending strength on base of MOE however doesn't work well in all cases, with R^2 varying between 0.03 and 0.49. Tension strength and tension MOE within "S2,sel" correlated with an R^2 = 0.41.

CONCLUSIONS

The mean bending strength of defect free boards of TMTB is 30% to 40% lower, mean bending MOE of TMTB is 8% to 10% higher compared to untreated beech. The mean and minimum tension strengths of TMTB boards are 45% to 50% lower than the respective bending strength but tension and bending MOE's are at a same level. Strength values of TMTB-boards vary significantly stronger compared to untreated reference boards. Dynamic MOE based prediction of MOE works well for TMTB but a prediction of strength values is limited.

ACKNOWLEDGEMENTS

The presented work is financially supported by the European Commission under contract No. NMP2-CT-2005-011799 (HOLIWOOD project).

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Characterisation of Wood Chemical Modification by XPS Analysis: Applications to the Study of Heat Treated Wood

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Keywords: XPS; reproducibility; chemical composition; wood; heat treatment

ABSTRACT

The applicability, reliability and reproducibility of XPS analysis has been investigated to characterise chemical composition changes occurring during wood treatments. Our results indicate that XPS could be a valuable method for analysis of wood chemical composition at the condition of using a procedure taking into account the possible contamination of the samples, the presence of contaminants being susceptible to lead to erroneous interpretations. Analysis of a freshly prepared wood chip indicates O/C ratio and carbon atoms distribution in good agreement with literature data on the well known chemical composition of wood. It is reported that wood surface is rapidly contaminated by carbonaceous contaminants during drying, heat treatment or even at room temperature showing the difficulties of its direct analysis without refreshing. After refreshing, the reproducibility of measurements tested on untreated and heat treated samples allowed a safe characterisation of the material. Analysis performed after heat treatment indicated a decrease of the O/C ratio and of the C_2 carbon contribution (carbon atom bounded to a single oxygen) associated with an increase of the C_1 carbon contribution (carbon atoms only bounded to carbon or hydrogen atoms).

INTRODUCTION

Wood is a complex material constituted mainly of three biopolymers: lignin, cellulose and hemicelluloses. In addition to these polymeric components, wood may contain extractives in varying quantities. Well-suited for the study of surface chemistry of complex organic materials, X-ray photoelectron spectroscopy has been widely used for the investigation of the surface chemical composition of numerous lignocellulosic materials especially in the field of pulp and paper, where the surface chemistry is of considerable importance for the properties of the final products (Johansson *et al.* 1999, Koljonen *et al.* 2003, Fardim *et al.* 2005, Li and Reeve, 2004, Johansson and Campbell, 2004, Johannson *et al.*, 2005) Similarly, some studies have been reported on wood to investigate the changes of surface chemistry after different wood transformation processes (Sinn *et al.*, 2001, Sernek *et al.* 2004, Sinn *et al.* 2004, Nzokou and Kamdem *et al.* 2005). However, while most the papers devoted to wood XPS analysis give valuable qualitative results, most of them fail on reliability and reproducibility to allow quantitative analysis. To obtain a deeper insight on the various functional groups, the C_{1s} signal is deconvoluted into four components according to the number of oxygen atoms bonded to C with the C_1 class corresponding to carbon atoms bonded only with only carbon or hydrogen atoms, the C_2 class revealing the carbon atoms bonded with one oxygen atom, the C_3 class corresponding to carbon atoms bonded to a carbonyl or two non carbonyl oxygen atoms and the C_4 class associated to a carboxylic function. In this paper, we are interested in the methodology to obtain reproducible XPS spectra and therefore safe quantitative interpretation of the analysis results after heat treatment of wood and more generally, after any biopolymers modifications. The results will be validate by comparison with other technics (Hakkou *et al.*, 2005, Weiland and Guyonnet, 2003, Sivonen *et al.* 2002, Tjeerdsma *et al.* 1998).

EXPERIMENTAL

Materials

Beech (*Fagus sylvatica*) blocks (10 x 20 x 35 mm in radial, tangential and longitudinal directions respectively) were oven dried at 103 °C for 48 h before determination of their anhydrous mass. Heat treatment was performed at 240 °C for 8 hours under nitrogen atmosphere.

XPS analysis

To reduce contaminations due to handling, samples were prepared just before analysis with a cutter blade, thoroughly cleaned and degreased avoiding all contact with hands and immediately placed in the vacuum chamber of the apparatus. The XPS analysis were carried out with a Kratos Axis Ultra (Kratos Analytical, UK) spectrometer with a hemispherical energy analyser and using a monochromatic AlKα source (1486.6 eV) applying to the X-ray anode a power of 90 W (Work function : BE = 83.96 eV for the Au 4f7/2 line for Au^0 ; dispersion : BE = 932.62 eV for Cu 2p3/2 line for Cu^0). The samples were attached to the sample holder and then evacuated overnight prior to analyses. All spectra were recorded at a 90° take-off angle for an area of about 700 µm. Survey spectra were recorded with 1.0 eV step and 160 eV analyser pass energy and the high resolution regions with 0.05 eV step and 20 eV pass energy.

Effects of surface contamination and reproducibility

To evaluate the influence of carbonaceous contaminants, two locations were analyzed after different storage conditions : the air exposed surface and a freshly prepared surface obtained by removal of a few mm of the sample, after 15 days without any precaution in laboratory conditions, after drying (103 °C) and after heat treatment. To evaluate reproducibility of XPS measurements, different series of analyses were repeated on samples taken just below the surface and in the middle of the block to determine possible differences in chemical composition due to the treatment heterogeneity.

RESULTS AND DISCUSSION

Analysis of the survey spectra of untreated beech wood (Figure1) indicates the presence of carbon, oxygen and small amounts of nitrogen which represent the expected elements in wood. High resolution of XPS spectra of C_{1s} and O_{1s} levels are also presented with their decomposition into 4 and 2 components respectively.

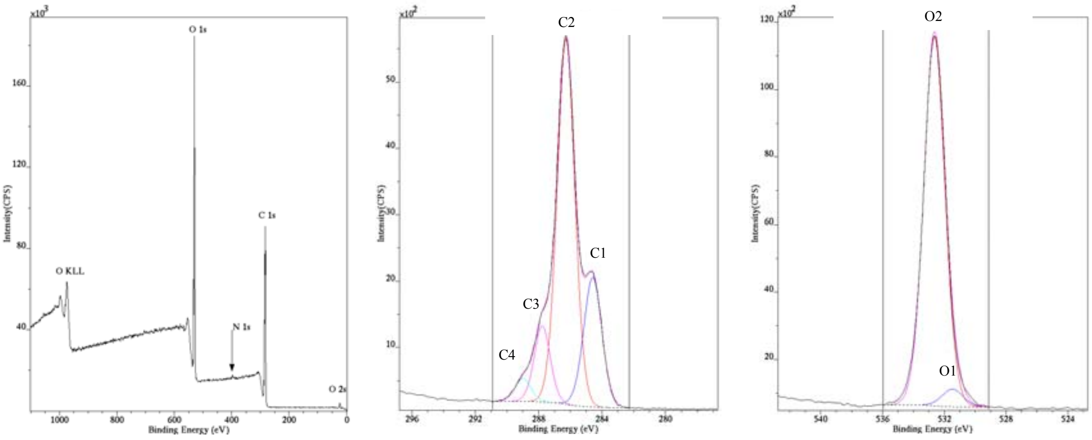

Figure 1: XPS survey C1s and O_{1s} spectra of untreated beech wood

Using the total areas of these peaks and the respective photoemission cross sections, a quantitative determination of the O/C ratio can be calculated. Beech wood contains approximately 24% lignin, 49% cellulose, 25 % hemicelluloses and 1% extractives (Fengel and Wegener 1984). Knowing the chemical composition of each of these components, it is possible to calculate *a priori* the theoretical O/C ratio characteristic of beech wood with an O/C ratios of 0.83, 0.8 and 0.33 for the cellulose, hemicelluloses and lignin respectively. The very small quantities of extractives are negelted. O/C ratio may be estimated from the individual ratio and abundance of each component or from the elemental composition measured in the case of untreated beech wood to be equal to 48.5% of carbon, 6.0% of hydrogen and 45.5% of oxygen. According to these methods, the O/C ratios are found to be of 0.68 and 0.70 respectively, indicating a fairly good agreement between elemental chemical composition estimated from theoretical composition of wood or microanalysis. Measured O/C values are significantly lower than the estimated value determined from chemical composition and elemental analysis (compare 0.55 to previous values), but are in good agreement with value previously reported by Sinn *et al.* (2001). This difference may be attributed to the high vacuum realized during XPS analysis allowing vaporization of residual water contained in the material. Recalculation of O/C ratio on the basis of the presence of 7% of water in the starting material leads to of value of 0.59 in better adequacy with experimental data. XPS analysis of beech wood subjected to different storage conditions or treatments depends strongly on the specific locations from which samples were taken for analysis. Samples taken on the surface presented lower O/C ratio relative to those taken under the surface, clearly indicating significant contamination of the surface by carbonaceous compounds. Contamination was more important for samples subjected to drying or heat treatment with a difference. Analysis of the types of carbon indicates that the C_1 component increases as the O/C ratio decreases. The concentration of non-polar wood components on the wood surface increases with the treatment temperature. Analysis of the samples taken just below the surface indicate O/C ratios closer to the theoretical values of fresh wood. The O/C ratio and distribution of carbon atoms of heat treated samples (O/C= 0.45, C_1: 38.0%, C_2: 53.4%, C_3: 5.8%, C_4: 2.8%) differs considerably from the values obtained for untreated wood (O/C= 0.55, C_1: 23.0%, C_2: 62.6%, C_3: 10.8%, C_4: 3.6%). The C_1 contribution increased while the C_2 contribution decreased, indicating that the content of hydroxyl groups becomes less important. This modification can be partially attributed to an increase of the lignin content due to preferential degradation of hemicellulose. However, the important decrease of the O/C ratio cannot be explained by the sole hemicellulose degradation, but more certainly by the formation of non oxygenated degradation products resulting from dehydration of biopolymers or from formation of new components resulting from degradation by-products. Reproducibility of XPS measurements has also been tested. Measured values for each treatment are very similar showing the reproducibility of the method.

CONCLUSIONS

XPS has been successfully used to analyse wood chemical composition and chemical changes occurring during heat treatment. The reliability and reproducibility of the results have been demonstrated by performing analysis on freshly prepared surfaces to avoid artifacts due to contaminations such as deposition of VOCs. Our results show the difficulties of analysis and interpretation of wood surface modifications which can be affected by carbonaceous contaminants. Changes in chemical composition observed by XPS analysis are in good accordance with results reported in the literature obtained with other spectroscopic methods, indicating applicability and the complementarity of this method. Further studies are currently underway on the application of XPS to wood analysis especially after fungal degradation.

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Sustainable Use of Heat Treated Wood as Façade Material - Preliminary Results of Weathering Tests

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Keywords: Façade material, spruce, heat treated wood, weathering test, sustainable building material

ABSTRACT

The goal of the research project was to investigate the sustainable use of heat treated wood as façade material with the main focus on durability, fixings and discolouration. 16 façade elements have been erected for a long-term outdoor weathering test. The elements differed in horizontal and vertical sheathing, in surface structure (rough, planed and profiled boards), in fixings (*e.g.* nails or self-tapping screws) and in orientation (west and east). During this experiment the following properties and variables were recorded and evaluated: greying and colour changing of wood surface, durability and stability of wood and the fastener and effects of erosion products of heat treated wood on other materials (like plastic or copper). The results showed that heat treated wood changes the colour homogenously faster than untreated wood.

INTRODUCTION

In the last two decades the wood consumption in the construction industry was rising and wood products are often labelled as sustainable building materials. Criteria for sustainable building materials are a sustainable resource extraction, a low life cycle impact, a long life-time and an efficient recyclability. The recyclability of wood depends on the purity of the products, which might be impaired by glues, paints and coatings. For outdoor applications the wood is often treated with chemicals and coatings to achieve a high durability (long economic life-time). To avoid these chemicals it is possible to use wood with a high natural resistance. The alternative to oak, larch or tropical hardwood was the development of heat treated wood (Hill 2006, Patzelt *et al.* 2002).

Heat treated wood has an attractive golden brown up to dark brown appearance and a high dimension stability (preventing cracks and warping) due to a reduced ability to take up water. The goal of the research project was to investigate the sustainable use of heat treated wood. A special task was to analyse fixings, durability and the discolouration of heat treated wood. All natural or modified wood products which are exposed to weathering will start to grey (Dunningham *et al.* 1992, Jämsä *et al.* 2000). The greying and especially the irregular greying are important decision criteria of consumers and often have prevented the application of wood.

EXPERIMENTAL

Materials

Heat treated wood

For this experiment spruce wood was heat treated with the ThermoWood process **(**developed by VTT in Finland) with following parameters (Figure 1):
Phase 1: High-temperature drying
Phase 2: Heat treatment - 3 hours at 215 °C
Phase 3: Cooling and moisture conditioning

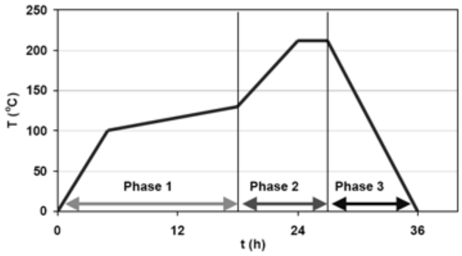
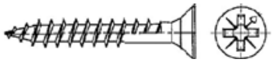
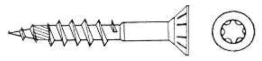


Figure 1: ThermoWood production process

Fixing

For the installation of the façade parts four types of fixings were utilised (Table 1).

Table 1: Four types of fixings

Brad of cool compressed wire	
Clamp or tacker of galvanised steel	
SPAX screw – self-drilling particleboard screw of cool compressed wire tinned after	
Self-drilling screw of stainless steel (V4A) with sliding surface	

Façade elements

16 façade elements with a size of 1 x 1.5 m (Figure 2) were built. The elements differed in surface structure (rough, planed and profiled boards), sheathings (*e.g.* horizontal and vertical sheathing, laths and boards with different widths) and fixings. Untreated spruce wood was used as reference in one element facing eastwards and one facing westwards.

Figure 2: Facade elements

Weathering procedure

All samples were exposed outdoor (Arnold *et al.* 2006, EN 927-3) inclined at an angle of 90° (vertical), facing westwards (main weather direction) and eastwards in

Mödling (near of Vienna), Austria (latitude 48.0667° N; longitude 16.3833°). Over the time of exposure from autumn (1st November) to spring (30th April), the average temperature was 6.6 °C, the average rainfall was 33.4 mm/month and the average radiated power was 29.5 W/m².

Colour measurement

Each board or lath was investigated by one measuring point. A total of 200 measuring points (approx. 12 points per element) were sampled. A Minolta Chroma Meter CR 410 was used to measure colours in L*a*b* (lightness, red-green-axis, yellow-blue-axis) and L*C*h (lightness, chroma, hue) CIE-Lab - colour space coordinates (CIE 1976) at each board on the facade parts. Colour change (ΔE) was calculated for each facade part from the average L*, a* and b* values (Eqn 1).

$$\Delta E^* = \sqrt{((L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2}$$

L_1 … initial value L_2 … continuous value (1)

RESULTS AND DISCUSSION

Colour change

Figure 3 illustrates the medium colour change of the heat treated elements and the untreated reference elements over 24 weeks' exposure. During the first six to eight weeks the changing of all samples was not visible for the naked eye. A ΔE value below 3-4 units is generally not visible (Gierling 2001). However, after this initial time, the greying of treated spruce was increased compared to the untreated wood. After 6 months the medium colour change (ΔE) of westwards oriented heat treated wood was approx. 50 % higher than of the untreated reference. The greying of heat treated wood is very homogenous: The standard deviation of 160 measuring points for ΔE after 6 months was only approx. 1.3 units. Furthermore a significant difference between east- and westward orientated elements has been observed for all colour parameters. After 6 months ΔE was about 40 % higher for elements facing westwards than for eastwards orientation. After six month the lightness has been increased about 12 units and the chroma reduced about six units. The hue levelled off a value of 70. These are typical signs of a visible perceivable greying of wood.

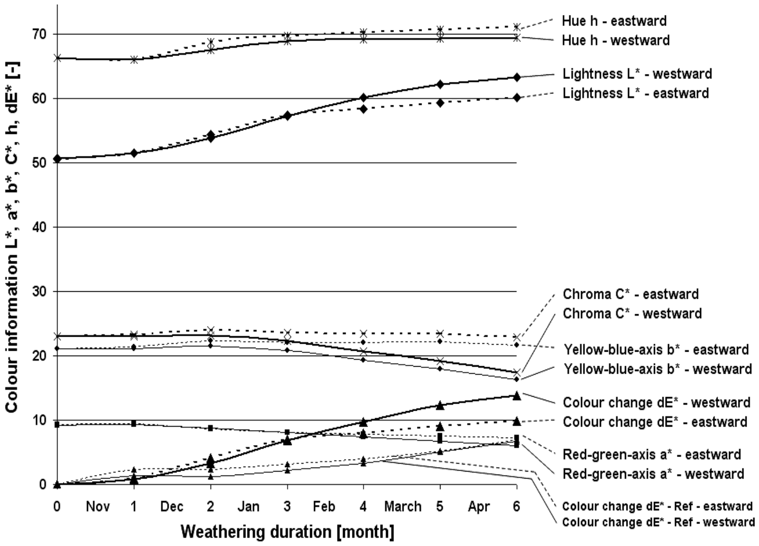


Figure 3: Colour changes of thermal treated and untreated (Ref) spruce

Durability and weathering resistance

During the whole experiment no cracks, twistings or warpings of the various boards were observed. Due to the reduced shrinkage and expansion properties of heat treated wood no joints have been arisen between the boards at the profiled board facade. The durability of heat treated wood was excellent. There was no indication of soft rot, fungal decay or blue stain, also at the precarious areas, like splash water zone or around of the fixings.

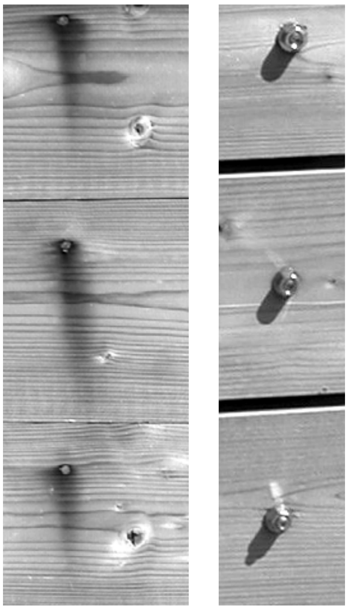


Figure 4: Discolouration of corrosion residues of usual brads (left), no discoloration with screw of stainless steel (right)

Fixing

After six months natural weathering four kinds of fixings (Table 1) have maintained all their strength properties. No board has lost the cohesion to the basic construction. Indispensable is the usage of galvanised or stainless steel – in the other case ugly discolourations of the façade are the result (Figure 4).

Effects of the leaching products on other materials

The leaching products of heat treated spruce have no visible influence on other building materials, like anodised or galvanised steel and aluminium sheets, copper sheets or different kinds of plastic (PE or PP).

CONCLUSIONS

This study showed that heat treated wood is a practicable alternative to native wood species, like Oak, Larch, or to tropical hardwood for outdoor applications. Due to the increased dimensional stability and durability cracking, distortion and fungal decay can be avoided. With regard of edge distance and corrosion of the fastener is it possible to use all fixings. The leaching products of heat treated wood have no influence on other materials. Rainfall and ultraviolet radiation effects a change of the colour and greying respectively on heat treated and untreated wood. The difference of both materials is the velocity - treated wood change the colour faster and homogeneous.

ACKNOWLEDGEMENTS

We gratefully acknowledge the excellent technical assistance of the Upper Secondary School for Technology Mödling – Department of Wood technology. The research project is supported by the Provincial Government of Niederösterreich - Department of Housing Research, the paper, packaging and forest products company Stora Enso

and the Holz Cluster and Ökobau Cluster of Niederösterreich. The study will be continued two more years.

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Performance of Coated Oil-heat-treated Wood Systems before and after Artificially Accelerated Weathering

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Keywords: Adhesion, ASE, contact angle, oil-heat-treatment, permeability, stain, weathering

ABSTRACT

For protection of outdoor wood products, surface finishing is usually used, which has both protective and decorative roles. However, surface finishing does not provide sufficient protection against bio-deterioration and inversely, non-stable substrates cause higher stresses at the wood-coating interface and in the coating film itself which leads to a failure of coated systems. To overcome these two drawbacks, various modifications of wood are nowadays being used. However, pre-treatment of wood may affect some important properties of applied coatings. The aim of our work was to monitor possible influence of the oil-heat-treatment (OHT) of Norway spruce (*Picea abies* [L.] Karst.) wood on the performance of acrylic and alkyd stains before and after artificially accelerated weathering. Our investigation showed that OHT wood is a suitable substrate for finishing with existing commercial coatings. Even, many properties like ASE of substrate, coating penetration and adhesion, water vapour and liquid water permeability *etc.* were improved.

INTRODUCTION

Thermal modification processes have been developed and optimised in various countries for the last few years (Rapp and Sailer 2001a and refs. therein). In Europe, four different heat treatment processes have mainly been recognized: the Finish Thermo wood, the Dutch Plato wood, the French Retification and the German OHT. In all the four treatment processes, the solid wood is subjected to temperature close to or above 200 °C for several hours in an atmosphere with low oxygen content. Though thermal modification processes reduce some mechanical properties, the dimensional stability and the biological durability of wood is increased without any chemicals (biocides) (Rapp and Sailer 2001b). Amongst thermal modifications, the OHT is very effective, since the oil transfers heat to wood equally and it entirely separates wood from oxygen during the thermal modification process. The aim of our research was to study the influence of the OHT on performance of acrylic and alkyd stains on wood. We studied anti-swelling effectiveness of different substrates and some important characteristics, like contact angle, coating penetration, liquid water permeability, water-vapour permeability, adhesion and so called wet adhesion of the wood substrate-coating system. These characteristics were assessed before and after weathering, accelerated artificially.

EXPERIMENTAL

Sampling and Test Systems

For the tests we used Norway spruce (*Picea abies* [L]. Karst), of dimensions (500 × 180 × 20) mm, of planed surfaces with a density of about 450 kg/m^3 at 12 % moisture content. The inclination of the growth rings to the test surface was (45 ± 10)° and their average width was around 2 mm. In order to obtain matched samples, panels were divided into smaller pieces. One half was OHT, and another one was not treated at all. For the OHT, the samples were heated in an oil bath of rapeseed oil in absence of oxygen at 220 °C. The samples were dried at 103 °C for 24 h before the treatment. After heating the oil to the desired temperature of 220 °C, the wood specimens were immersed into it. After obtaining this temperature in the middle of the test samples it was kept for 4 h. Then, the specimens were taken out, wrapped in paper and dried again at 103 °C for 24 h. Left side of each smaller panel was reserved for preparation of samples, on which coating properties before artificial weathering were determined and right one for samples, on which coating properties after artificial weathering were determined. The middle part (10 mm in width) was used for determination of anti-swelling effectiveness. OHT and non-treated panels were then planed and divided to 3 samples of dimensions (70 × 65 × 18) mm. One sample was later coated with the semi-transparent brown pigmented medium build acrylic waterborne stain, another one with the semi-transparent brown pigmented medium build alkyd solvent-borne stain, and the last one was not coated at all. In this way, 12 different test systems were prepared.

Assessment of properties

For assessing of water-vapour permeability we used a procedure in accordance with now redrawn standard EN 927-4 (2000). The only deviation from the standard was dimension of samples ((70 × 65 × 18) mm instead of (150 × 70 × 20) mm). As a result the relative moisture permeability (*RMP*) and the dynamic moisture permeability (*DMP*) were calculated. For assessing of liquid water permeability we used a procedure in accordance with the standard EN 927-5 (2000). The same deviation from the standard as in the case of water-vapour permeability test occurred. Relative water permeability (*RWP*) was calculated. Adhesion of coatings to test substrates was determined following the modified standard pull-off test EN ISO 4624 (2003). A steel faced test cylinder of a diameter of 11.25 mm (instead of 20 mm, as determined by the standard) was used. Determination of wet adhesion was performed similar to the "dry" adhesion. Before measurement of tensile stress, samples with glued test cylinders and roundly cut film of coating were fully immersed in water for 2 h. Coating thicknesses of a dry film were measured according to the EN ISO 2808 (1999) standard with a destructive microscopic method. For determination of coating penetration, the residues of non-treated and pre-treated wood from previous sampling were coated on the side of end grain. Thin strips were then microtomed from radial faces of blocks using a conventional sliding microtome. The nominal thickness of the strips was 25 μm. Static contact angles immediately after application of stain or water, after 0.5 s and 1.5 s were measured as proposed by Scheikl and Dunky (1998). For determination of Anti-Swelling Effectiveness (*ASE*), the samples were dried at 103 °C for 16 h, subsequently submerged in water under vacuum of 5 mbar for 20 min followed by atmospheric pressure (1 bar) for 72 h. The change in dimension was determined by measuring the radial and tangential length of the dried and the water-saturated samples. The well known *ASE* was calculated from the ratio of the percentage radial/tangential length change of OHT specimens in relation to the radial/tangential length change of non-treated wood specimens.

Accelerated weathering

The samples were put into the weathering chamber and subjected to weathering for 500 h with 1 h repeated cycle, which consisted 22 min of artificial rain, 9 min of resting, 27 min of UV (Osram Ultra-Vitalux 300 W sunlamps) and IR irradiation (60 °C), and 2 min of pause.

RESULTS

The OHT led to the reduction of swelling over non-treated control. Consequently, the *ASE* was quite high and there was no difference between tangential and radial *ASE*. The average radial *ASE* of OHT wood was 43.4 % and tangential 43.5 %. As expected, the contact angles decreased rapidly with increase in contact time. The variation of substrates and test liquids used, resulted variation of values of contact angles and the most significant differences were occurred for contact angles after 1.5 s (Table 1).

Table 1: Mean values of contact angles after 0 s, 0.5 s and 1.5 s

Substrate pre-treatment	**Test liquid**	**Contact angle**		
		Initial	**After 0.5 s**	**After 1.5 s**
None	Solventborne alkyd stain	60.8°	37.9°	31.8°
	Waterborne acrylic stain	76.1°	63.9°	54.1°
	Distilled water	75.0°	53.2°	39.5°
OHT	Solventborne alkyd stain	58.5°	35.7°	29.7°
	Waterborne acrylic stain	69.5°	59.8°	52.7°
	Distilled water	81.9°	73.8°	65.6°

The highest values of the coating penetration for all substrates were recorded on the early wood. Though, stains penetrated through the open grain into the longitudinal tracheides, yet no penetration occurred through the pits into the ray cells. The lowest coating penetration was observed in case of waterborne acrylic stain on non-treated wood (1.326 mm). This stain did penetrate significantly deeper on OHT wood (3.703 mm). This might be due to lower density of the OHT wood with increased porosity. As proven in literature (de Meijer *et al.* 2001 and refs. therein), alkyd stain did penetrate deeper than waterborne acrylic stain, on non-treated wood (1.941 mm) and on OHT wood (5.078 mm). From the visual observation of the artificially weathered test systems we noticed that the bending of the sample and extend of cracks on the surface of uncoated substrates is correlated with dimensional stability of the substrate. The lowest extent of cracks and bending occurred in case of OHT wood. The worst result was obtained for non-treated control wood. It was also interesting that colour of OHT wood was not changed markedly as like of non-treated substrate. However, this is not a quantitative evaluation. Properties of the system wooden substrate-dry coating material (Table 2) varied dependently on the type of the substrate and stain, and of course on the use of artificially accelerated weathering. Generally, OHT wood proved to be less problematic substrate as non-treated wood, especially under/after conditions of weathering.

Table 2: Mean values of properties results of tested systems (1st letter: C – non-treated wood, H – OHT wood; 2nd letter: N – not coated, W – waterborne stain, S – solventborne stain; 3rd – letter: N – not weathered, W – artificially weathered)

Test system	**Coat. thick. [µm]**	***RMP* [%]**	***DMP* [%]**	***RWP* [%]**	**Dry adhesion**			**Wet adhesion**		
					σ	**Fracture**		***σ***	**Fracture**	
					[MPa]	**A**	**K**	**[MPa]**	**A**	**K**
CNN	-	-	80.5	-	-	-	-	-	-	-
CNW	-	-	86.0	-	-	-	-	-	-	-
CWN	*54*	50.2	32.6	13.5	7.63	*34*	*66*	1.64	*100*	*0*
CWW	*54*	32.6	6.3	13.0	6.12	*0*	*100*	1.36	*29*	*71*
CSN	*75*	19.7	20.0	4.2	7.57	*75*	*25*	2.22	*56*	*44*
CSW	*75*	27.5	7.9	16.0	5.88	*0*	*100*	1.08	*3*	*97*
HNN	-	34.0	41.7	37.4	-	-	-	-	-	-
HNW	-	40.7	43.7	54.2	-	-	-	-	-	-
HWN	*70*	25.8	34.0	10.0	3.55	*0*	*100*	1.92	*55*	*45*
HWW	*70*	22.2	4.1	5.7	4.63	*0*	*100*	2.55	*17*	*83*
HSN	*79*	12.4	22.4	3.1	5.31	*0*	*100*	2.01	*33*	*67*
HSW	*79*	14.8	14.6	3.5	3.69	*0*	*100*	1.40	*0*	*100*

A – adhesive fracture, K – cohesive fracture of a substrate

CONCLUSIONS

The properties of the wood, of the system wooden substrate-wet coating material and of the system wooden substrate-dry coating material were in case of OHT wood improved. OHT wood exhibited very high ASE, higher contact angle of water and improved penetration of solvent and waterborne stains. Coated systems of OHT wood showed lower water vapour and liquid water permeability; wet adhesion of coatings was higher, and these systems performed the best under conditions of artificially accelerated weathering which altered many properties of the system wooden substrate-dry coating material. This alternation was again in case of OHT wood more suitable, especially in case of waterborne stain: water vapour and liquid water permeability decreased and wet adhesion of coating increased. After these conclusions we can safely say that OHT wood is more than suitable substrate for finishing with the existing commercially available coating formulations.

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Weathering Properties of Wood Modified with Hydrophobation Agents

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Keywords: Hydrophobation, paraffin, silicone, basidiomycetes, blue stain, weathering

ABSTRACT

Three formulations which contain hydrophobing agents from the textile industry were used to improve the resistance of wood against weathering: 1. a dispersion containing paraffin and an aluminium salt (AP), 2. a dispersion containing paraffin and a fatty acid N-methylol compound which was combined with an aluminium salt as catalyst (Al-FNM), 3. an emulsion of an epoxy-functional siloxane (ES). Beech wood (*Fagus sylvatica*) treated to weight percent gains (WPG) of 10% (Al-FNM and AP) resulted in significant decrease in water uptake of 40-50% in a submersion test. Significant dimensional stabilization was only observed with Al-FNM; ASE amounted to 18% at 10% WPG. All formulations imparted high durability towards white- and brown-rot decay in a mini-block test. Al-FNM and AP showed highest efficiency against blue stain in a laboratory test and during 1 year outdoor exposure. Treated pine samples (*Pinus sylvestris*) showed less deformation (cupping) and cracking than untreated samples after 1 year outdoor exposure. These improvements were most pronounced for Al-FNM and ES.

INTRODUCTION

Chemical modification of wood for outdoor exposure requires long-standing weather resistance and environmentally friendly technologies. Non-biocidal treatments aim at changing wood characteristics such as durability and water related properties. Hydrophobic treatment lowers the moisture level of wood in service and, thus, decreases the tendency of crack formation and the risk of biological degradation. This study focuses on the application of hydrophobation agents in order to reduce moisture uptake and, as a consequence, swelling and shrinkage as well as fungal decay during outside exposure.

EXPERIMENTAL

Equilibrium moisture uptake and ASE

Beech wood specimens (*Fagus sylvatica* L.) with a size of 25 x 25 x 10 mm (R x T x L) were impregnated with a dispersion containing paraffin and aluminium salt (AP), a dispersion containing paraffin and a fatty acid N-methylol compound which was combined with an aluminium salt as catalyst (Al-FNM), an emulsion of an epoxy-functional siloxane (ES) as recently described (Nguyen *et al.* 2007). The concentration of the formulations amounted to 30% based on the stock solution of the commercial formulation. Treated and untreated wood specimens were conditioned in a climate chamber at 20 °C and 65% relative humidity and water uptake was determined in a submission test (n = 10; Donath *et al.* 2006a, Nguyen *et al.* 2007). Anti-swelling efficiency (ASE) of the treated blocks was determined between the dry state and water saturation. It was expressed as the ratio of the volumetric swelling coefficients of the treated and the untreated specimens (Donath *et al.* 2004).

Resistance against basidiomycetes

Resistance against fungal decay was evaluated in a mini-block test (Donath 2006b) using the white-rot fungus *Trametes versicolor* (CTB 863 A) with beech wood (*Fagus sylvatica* L.) and the brown-rot fungus *Coniophora puteana* (BAM Ebw. 15) with Scots pine sapwood (*Pinus sylvestris* L.). Nine mini-blocks (10 x 5 x 30 mm^3; R x T x L) were treated as described above (hydrophobation testing). Mass loss of the specimens was evaluated after 8, 16 and 24 weeks of incubation. The wood samples were impregnated with 50% of stock solutions of AP, Al-FNM and ES.

Blue stain

The infection of wood surfaces with a blue stain fungus was studied with pure cultures of *Aureobasidium pullulans* on malt-agar (2% malt, 2.5% agar) in Petri dishes as recently described (Nguyen *et al.* 2007). Scots pine sapwood measuring 40 (longitudinal) x 40 x 5 mm^3 were treated with AP, Al-FNM and ES in concentrations of 30 and 50% based on the stock solution.

Outdoor exposure

Scots spine sapwood with a size of 15 x 75 x 270 mm^3 (R x T x L) was prepared according to EN 927-3. The specimens were impregnated with 30% of the stock solution as described above. After impregnation, the specimens were cured in a steam bag (to prevent pre-cracking) with increasing temperature as: 40 °C (15h), 60 °C (10h), 90 °C (15h), 103 °C (10h) and 120 °C (6h).

RESULTS AND DISCUSSION

Water uptake

Beech specimens treated with Al-FNM, AP and ES reached a WPG of 7 ± 0, 9 ± 1 and 13 ±1 %.

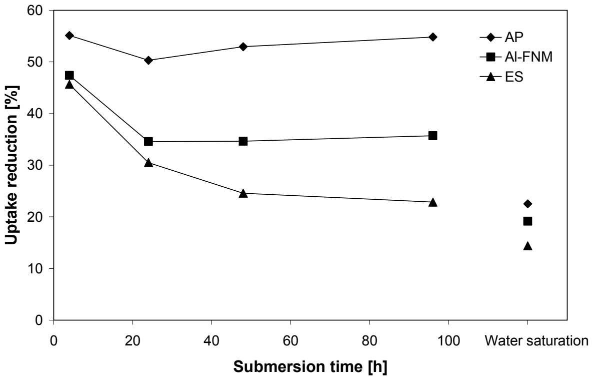

Figure 1: Water uptake reduction of beech wood treated with 10% solution of AP, AL-FNM and ES.

All treatments caused significant water uptake reduction (WUR) in a submersion test (Figure 1). High WUR can be explained with occlusion of the wood lumens particularly of ray cell through the hydrophobation agents. Application of vacuum during submersion (after 96 h) led to a decrease in WUR because the lumens of the cells were filled with water. The WUR was very similar during the first 96 h water submersion for all treatments. Water uptake reduction amounted to 14–23 %, when full water saturation was reached. Anti-shrink efficiency (ASE) of beech specimens treated with 30% solution of Al-FNM (WPG 10%) was 18±1%. AP and ES did not cause significant ASE.

Resistance against basidiomycetes

Mass losses of treated wood after incubation with the white rot fungus *T. versicolor* and the brown rot fungus *C. puteana* were very low after 24 weeks of incubation, particularly for Al-FNM (Table 1). Only AP treated beech (14% WPG) and ES treated pine specimens (26% WPG) display mass losses above 10%. The untreated controls underwent high mass losses which tended to increase with incubation time. The effect appears to be not exclusively due to hydrophobation, since sufficient time was available to establish high moisture content in the treated wood blocks. Decay protection could, however, be due to blocking of colonisation paths such as ray cells. Presence of aluminium in AP and Al-FNM might also have a negative impact on the fungi.

Table 1: Mass loss of Al-FNM, ES and AP treated beech and Scots pine sapwood after 24 weeks exposure to the white-rot fungus T. versicolor and the brown-rot fungus C. puteana

Formulation	**Beech (*T. versicolor*)**		**Pine (*C. puteana*)**	
	WPG (%)	**Mass loss (%)**	**WPG (%)**	**Mass loss (%)**
AP	14 ± 1	16.8 ± 3.5	14 ± 1	9.1 ± 2.2
Al-FNM	15 ± 1	5.5 ± 1.0	21 ± 1	2.4 ± 1.5
ES	22 ± 2	2.9 ± 1.4	26 ± 1	15.3 ± 2.3
Control		80.8 ± 3.6		65.0 ± 6.1

Resistance against blue stain

Table 2: Infection classes (0-4) of Scots pine sapwood after incubation over 8 weeks with pure culture of the blue stain fungus Aureobasidium pullulans

Formulation	**WPG (%)**	**Infection class**
AP	4	1.0 ± 0.0
	6	1.3 ± 0.5
Al-FNM	17	1.9 ± 0.4
	26	0.3 ± 0.5
ES	17	3.6 ± 0.5
	29	2.5 ± 0.5
Control		4.0 ± 0.0

Untreated Scots pine sapwood was heavily infected by the blue stain fungus *A. pullulans* (Table 2). Specimens treated with AP and Al-FNM showed the lowest degree of infection (class 0.3-1.9), but cannot be directly compared, because of different WPG. Reduction of blue stain infection achieved with ES was relatively low, in spite of high WPG.

In the test set-up, wood is infected by mycelium of *A. pullulans* (in contrast to outdoor weathering where wood is mainly infected by fungal spores). Reduction in blue stain infection can be attributed to sealing of the wood surface and to the detrimental effect of aluminium in AP and Al-FNM on fungal physiology.

Outdoor Exposures

The results after 1 year outdoor exposure (Oct. 04 – Oct. 05) showed that blue stain infection was effectively prevented on wood treated with AP and Al-FNM. In most cases, the reverse sides of AP and Al-FNM treated specimens did not exhibit any surface colonisation. All treatments caused a slowdown of photo degradation compared to untreated wood, but were not able to prevent it. Wood treated with Al-FNM and ES effectively diminished cracking.

CONCLUSIONS

The hydrophobing agent used in this study reduced the water uptake during submersion in water. During outdoor weathering, wood treated with Al-FNM and ES developed fewer cracks and showed less deformation. High resistance of Al-FNM and AP treated wood towards wood-decay fungi and staining fungi was achieved. Wood treated with ES was resistant against decay by *T. versicolor*, but less effective against *C. puteana*. This study shows that the Al-FNM, AP and ES formulation are suitable for hydrophobation of outdoor exposed wood in Hazard Class 3 according to the European standard EN 335-1 over a long time period. Al-FNM in particular displayed high potential as a substitute for conventional biocides to protect outdoor exposed wood without soil contact.

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UV-resistance of Ammonia Treated Wood

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Keywords: Anatomy, brightness, CIELAB, colour, radiation, stability

ABSTRACT

In order to change the colour of several wood species across the whole thickness, fumigation with ammonia took place at room temperature for a period of 20 days. The sample set covers 11 diffuse porous, 2 semi-ring porous, 5 ring porous and 2 coniferous wood species. Fumigated and untreated samples were exposed to artificial UV-radiation (765 W/m² underneath 800nm) during 24 hours. Colour was determined as L*a*b* colour space values (CIE 1976 colour system). Measurements show that fumigation with ammonia is an effective way of pre-aging wood resulting in stabilized brightness and colour of wood for some species.

INTRODUCTION

Ammonia treatment as a method to change the colour of wood is known by carpenters as a surface modification (Tinkler 1921, Flocken *et al.* 1975) as well as by industry as a process of modifying whole wood pieces. A lot of chemical reactions between the cell wall substances as well as extractives and ammonia are possible and described in literature (Kalnin´s *et al.* 1967, Bariska 1969, Onisko and Matejak 1971, Parham *et al.* 1971, Amburgey and Johnson 1979). These reactions cause a wide range of colours for ammonia treated wood. The well known colour reaction of ammonia fumigated oak wood was found to be possible only in combination with the availability of atmospheric oxygen (Tinkler 1921). Kalnin´s *et al.* (1969) reported that an ammonia treatment can highlight the texture of inconspicuous hardwoods and has the potential to compete with other species like oak, walnut or mahogany. In general these wide ranges of colours have the potential to substitute tropical wood species as well as thermal modified wood.

Beside the colour itself, colour stability is an important characteristic of wood. Changes of colour due to UV radiation (*e.g.* known for beech) is usually unwanted and often the reason of customer complaints. Due to the spectral composition of UV-radiation, penetration into the wood is different. UV-radiation with longer wavelength is of lower potential energy than shorter wavelengths and covers the mayor dose of global UV-radiation. Whilst short waves get absorbed at the sample surface, longer waves can penetrate into deeper cell rows (Fengel and Wegener 1984). Due to the influence of UV wood colour can turn grey, yellow, red-orange or brown

(Sandermann and Schlumbom 1962). Colour stability is defined as the resistance of colour against UV radiation. Reactions of UV-radiation with wood take place at several functional groups and are described by Fengel and Wegener (1984) for lignin and cellulose.

This study illustrates the differences in brightness and colour stability of various untreated and ammonia fumigated central European wood species.

EXPERIMENTAL

To capture a wide range of optical wood properties, 20 species known for good ammonia gas permeability were selected. All species are growing in central Europe and almost all of them are commonly traded. The species are listed below grouped due to their anatomical structure:

Coniferous trees: Norway spruce (*Picea abies*), silver fir (*Abies alba*);
Ring porous trees: ailanthus (*Ailanthus altissima*), ash (*Fraxinus sp.*), black locust (*Robinia pseudacacia*), elm (*Ulmus sp.*), oak (*Quercus sp.*);
Semi-ring porous trees: cherry (*Prunus avium*), walnut (*Juglans regia*);
Diffuse porous trees: beech (*Fagus sylvatica*), red heart of beech, birch (*Betula sp.*), black alder (*Alnus glutinosa*), hornbeam (*Carpinus betulus*), lime (*Tilia sp.*), maple (*Acer sp.*), pear (*Pyrus pyraster*), plum (*Prunus domestica*), poplar (*Populus sp.*), tulip (*Liriodendron tulipifera*);

As wood quality varies strongly between different individuals, three different boards per species were selected for sample preparation. From each board two samples were prepared by splitting. The final samples showed the dimensions: 70 x 70 x 5 mm. One sample of each pair got fumigated for 20 days using an aqueous ammonia solution (30%) at normal pressure conditions, while the other one was kept as reference. All samples got sanded with 180 grid corundum sanding paper.

All samples were exposed to UV-radiation for 24 hours (Xenon burner, 765 W/m² underneath 800nm) using a Heraeus SUNTEST CPS and conditioned at room temperature for at least two weeks. Colour measurements were carried out prior to and after radiation using a Chroma Meter (Minolta CR-410). Determination of colour was due to L*a*b* colour space values (CIE 1976 colour system, DIN 6174). Colour measurements before UV-radiation were references for calculated brightness distances expressed as ΔL^* and colour distances expressed as ΔE^*_{ab}.

As untreated Oak wood usually shows quite stable optical properties during surface life time, it was selected as a reference for all other wood species.

RESULTS AND DISCUSSION

Brightness and colour stability due to UV-radiation of untreated wood varies strongly between the different species. For example untreated plum shows due to radiation a ΔL^* of more than -15, meaning that wood turns significantly darker, while elm even shows slightly positive values, meaning wood gets brighter.

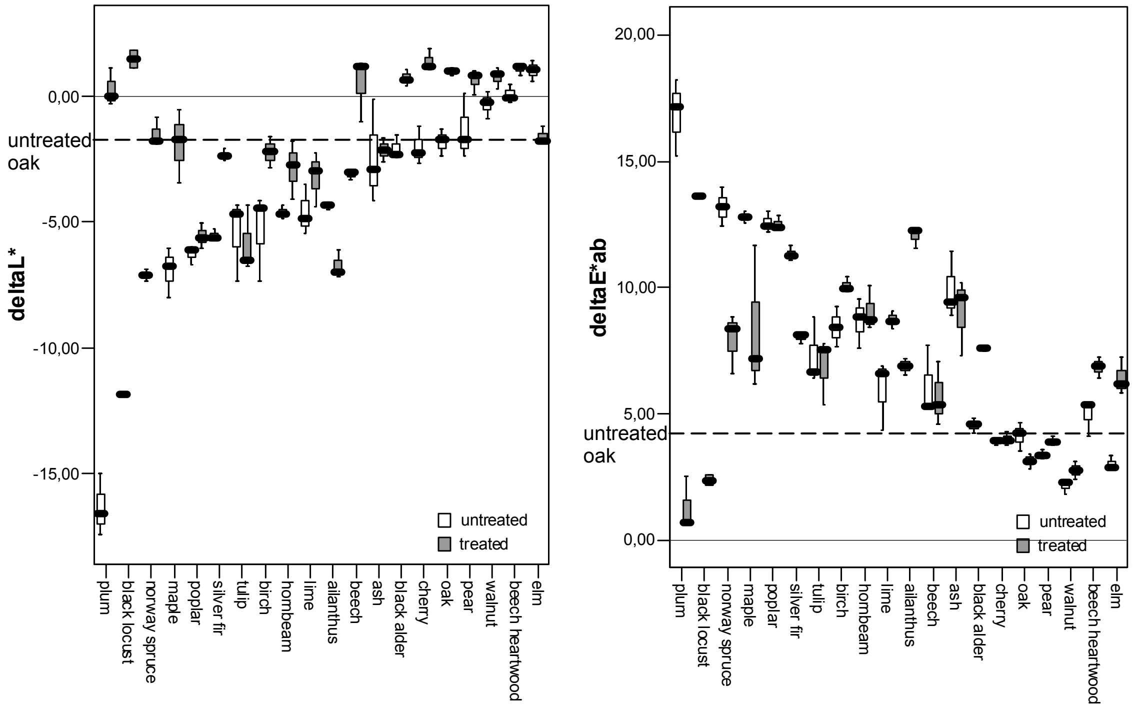

Figure 1 (left) and 2 (right): Comparison of ΔL^* respective ΔE^*_{ab} -values for all 20 species separated into untreated and treated wood. Species are listed in the order of increasing ΔL^*-values for untreated wood.

The highest stability of brightness was found for untreated beech heartwood and fumigated plum (Figure 1). For plum, black locust, Norway spruce, maple, silver fir, birch, hornbeam, beech, black alder, cherry, oak and pear fumigation leads to a distinct stabilisation of brightness. Only tulip, ailanthus and elm show reduced stability of brightness due to fumigation. For birch, ash and pear deviations of colour within the species can be reduced by fumigation.

The reference, untreated oak, showed a mean stability of brightness of $\Delta L^* = -1.80$ (Figure 1). In comparison, fumigated wood of plum, black locust, Norway spruce, maple, beech, black alder, cherry, oak, pear, walnut, beech heartwood and elm showed comparable or increased stability of brightness.

The highest stability of colour (ΔE^*_{ab}) was found for fumigated plum followed by black locust, Norway spruce, maple, silver fir and oak (Figure 2). Untreated wood of birch, lime, ailanthus, black alder, pear, walnut, beech heartwood and elm showed higher stability of colour than the corresponding fumigated samples. For birch, lime, oak and beech heartwood deviations of the colour within the species can be reduced by fumigation.

The mean stability of colour of the reference (untreated oak) is $\Delta E^*_{ab} = 4.13$. The number of species within this range is about half of them found for stable brightness (ΔL^*). Fumigated plum, black locust, cherry, oak, pear and walnut show better stability of colour than the reference.

No significant relationship between the wood anatomy and the colour changes was observed for fumigation as well as for the stability of brightness and colour due to radiation.

CONCLUSIONS

Fumigation with ammonia is an accurate method to change the colour of wood. As some species showed higher stability in brightness and colour after fumigation than untreated wood, this treatment can be described as a pre-aging procedure. Further more, variations of colour within some species can get reduced due to fumigation.

ACKNOWLEDGEMENTS

We are thankful to Juergen Pimingstorfer and Veronika Knoblich for supplying with wood and to Sonja Leder for practical help concerning colour measurements.

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Weathering and Coating Properties of Chemical Modified Wood

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Keywords: Adhesion; chemical modification; coating; cracking; DMDHEU; weathering

ABSTRACT

Scots pine sap wood was modified with methylated 1,3-dimethylol-4,5-dihydroxyethyleneurea (mDMDHEU) to weight gains of 6-42% and coated with commercial water-borne stains and paints. The pre-treatment of the wood substrate with mDMDHEU enhanced the wet adhesion of the coatings. The pre-treatment reduced the crack formation, deformation and discoloration of both coated and uncoated wood panels during 18 months of natural weathering.

INTRODUCTION

Wood used in exterior application is susceptible to weathering and attack by microorganisms. It needs to be protected from these abiotic and biotic impacts in order to prolong its service life and to preserve its pleasant appearance. Coatings pigmented or with added UV absorbers, are the only effective measures available to prevent the deterioration caused by weathering. Coatings, however, have a limited service life on wood due to the photodegradation of the underlying wooden substrate and entry of moisture and liquid water. In addition, the humidification of wood facilitates the growth of microorganisms, which, in turn, affect both the appearance and performance of coatings. An efficient means to improve the performance of coatings is chemical modification of the wood substrate to minimize specific problems such as moisture absorption, swelling and shrinkage, as well as susceptibility to photodegradation and microbial attack. Wood modification with the N-methylol compound 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) was shown to improve the dimensional stability (Militz 1993). DMDHEU-modified veneers have shown better surface performance and lower weight losses during artificial weathering than untreated specimens (Xie *et al.* 2005). The objective of this study is to investigate how the changes in the properties of wood modified with methylated DMDHEU influence the coating and weathering performance of wood compared to the untreated wood substrate.

EXPERIMENTAL

Preparation of wood samples

Scots pine (*Pinus sylvestris*) sapwood was cut into blocks of 170 x 50 x 15 mm^3 (long x rad x tang) and panels of 250 x 15 x 70 mm^3 (long x rad x tang). These wood samples were vacuum-pressure treated with a commercial solution of methylated 1,3-dimethylol-4,5-dihydroxyethyleneurea (mDMDHEU) received from BASF AG.

Magnesium chloride hexahydrate ($MgCl_2.6H_2O$) was used as a catalyst. After impregnation, the samples were dried at 120°C for 24 hours. The treated wood attained weight percent gains of 6%, 23% and 42%, respectively.

Application of coatings

All coating systems were obtained from Akzo Nobel Deco GmbH (Wunstorf, Germany). Three were acrylic-based water-borne systems. Two were translucent brown stains, Cetol WF780 and Cetol WF950; both were applied with Cetol WP 560 primer. The third was a white paint, Cetol WF380, which was applied with Rubbol WP 176 as a primer. In addition, Novatech 006 served as an example of an alkyd-based solvent-borne stain. The wood samples were immersed in the primer for 20 seconds and then were given two topcoats using a brush. The solvent-borne topcoat was applied twice in the same manner, but without precedent primer. The coatings were applied with a brush on one of the radial sides of the wood blocks. The dry thickness of coating films was about 50 µm. To perform the weathering studies, 5 treated (mDMDHEU) and 5 untreated panels were each coated on the sanded surfaces (all other sides were left uncoated) with (1) a water-borne acrylic system including a primer and a stain (WBA), (2) an oil-based coating (OBC), or (3) remained uncoated. For the water-borne coating, the primer was first brushed on the panel surface, followed by one layer of topcoat. The oil-based coating was directly brushed three times on the panel surface without using a primer.

Adhesion test

Wet adhesion of coatings on wood was determined by a modified pull-off method as described in European standard PrENV 927-8. It was measured by means of a self-aligning PosiTest (pull-off adhesion tester) manufactured by DeFelsko Corporation, New York, USA (Xie *et al*. 2006).

Weathering of wood

Outdoor weathering was performed according to the European standard EN 927-3. The weathering test was carried out in Göttingen (central Germany) from May 2003 to November 2004. After 18 months of weathering, the surface performance of weathered wood was evaluated.

RESULTS AND DISCUSSION

Adhesion of coatings on the wood

Modification with mDMDHEU clearly improved the wet adhesion of WF 780 and Novatech 006 on the wood compared to untreated and water-treated samples (Fig. 1A). The wet adhesions of WF 950 and WF 380 on the mDMDHEU-treated samples demonstrated only tendentious improvements which were not significant. For all coatings tested the concentration of mDMDHEU during treatment did not influence wet adhesion; only in the case of WF 780 did the treatment with 10% mDMDHEU cause lower adhesion than with 30% and 50%, respectively. The appearances of the reverse side of the detached finish films showed that the wet adhesion is positively correlated with the amount of wood debris consisting mainly of cells attached to the film (Fig. 1B). Improvements in wet adhesion which were imparted by mDMDHEU modification might be attributed to the following reasons: the incorporation of mDMDHEU into the cell walls and in part into the lumina might increase the presence of hydroxyl groups on the wood surface. These can enhance the interaction of the substrate and the coating *via* different kinds of bonds such as hydrogen and Van-der-Waals bonds. Another positive factor might be that mDMDHEU causes the wood cells to swell and keeps them in a swollen state (cell wall bulking). This enlarges the contact area between the wood and the coatings. In addition, treatment with mDMDHEU is known to improve the dimensional stability of wood, *i.e.* to reduce the swelling under wet conditions (Krause *et al.* 2003) When the wood substrate is wetted during the test, it starts to swell; this exerts stress on the coating film and can lessen its adhesion to the substrate.

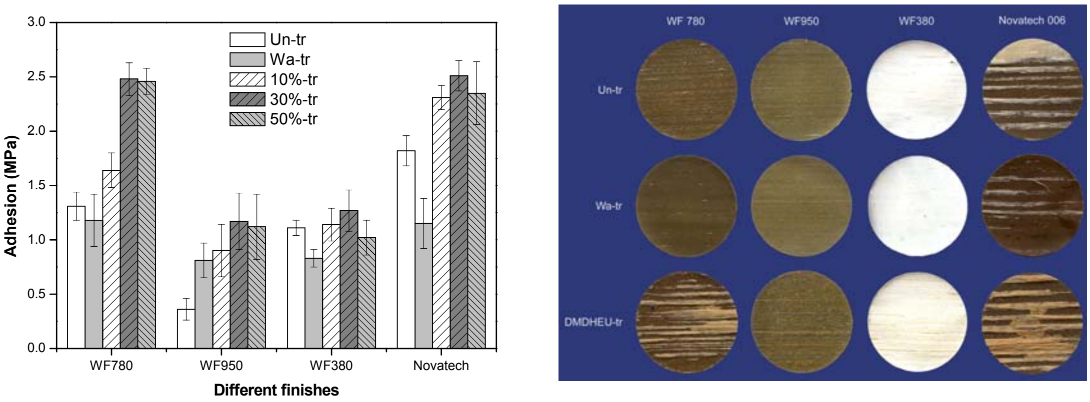
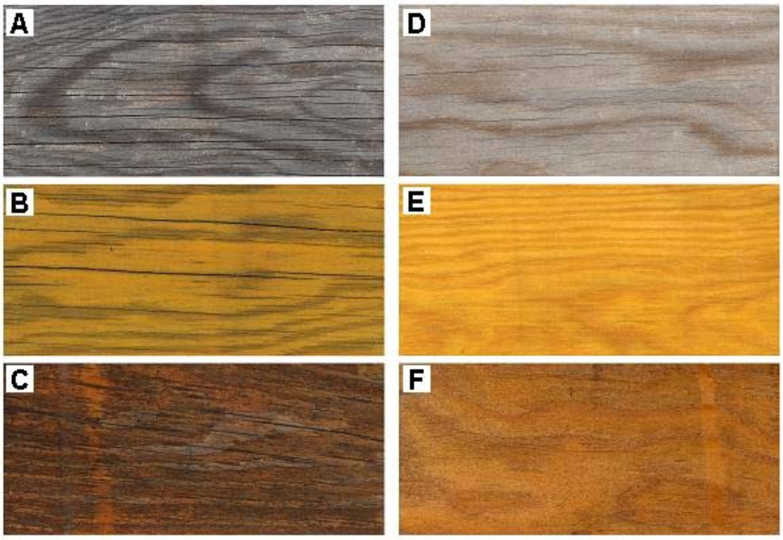


Figure 1: (Left) Wet adhesion of coatings on wood substrates determined by the pull-off method (PrENV 927-8); (Right) Appearances of the detached (reverse side) film after pull-off test

Surface evaluation of weathered panels

Treatment with mDMDHEU reduced the moisture uptake of uncoated wood panels during outdoor exposure (18 month). Submersion tests after appointed intervals revealed that the treated panels took up less water than untreated specimens. This can be explained with reduction in crack formation due to the treatment (data not shown). After weathering, the untreated and uncoated panel surfaces were dark grey and displayed many large cracks (Fig. 2A). The weathered untreated surface exhibited a tangible roughness caused by the cracks and strong erosion of earlywood cells, while the surface of uncoated panels treated with mDMDHEU was only light grey and smooth after weathering (Fig. 2D). Less and smaller cracks were formed on the exposed surface of uncoated treated panels and the earlywood cells did not seem to be as severely eroded as in the untreated panels. In addition, the treated samples were less deformed after weathering. Light microscopic studies showed that the growth of blue stain fungi was reduced through mDMDHEU treatment (not shown). Weathering of coated untreated panels over 18 months caused considerable deterioration of the surfaces accompanied with the occurrence of checks and cracks (Fig. 2B, C). The oil-based coating showed severe flaking on untreated panels (Fig. 2C) and severe deep-brown discoloration, whereas the water-borne acrylic coating did not flake off the untreated panels during weathering. The coatings applied on mDMDHEU treated panels retained their appearance over 18 months weathering (Fig. 2E, F) and displayed only few thin cracks. Almost no discoloration occurred. As observed for the uncoated panels, pre-treatment with mDMDHEU reduced the waviness of coated panels. This indicates that treatment of the wood substrate with mDMDHEU improves the weathering performance of coated panels.



Figure°2: Appearance of uncoated and coated panels after 18 months of weathering: untreated and uncoated (A) or coated with WBA (B) and OBC (C); treated with mDMDHEU to 23% WPG and uncoated (D) or coated with WBA (E) and OBC (F)

CONCLUSIONS

Wood modified with mDMDHEU is compatible with various conventional coating systems and modification does not negatively affect the performance of either water-borne or solvent-borne coatings. Therefore, mDMDHEU-modified wood does not require special development of novel types of coating systems. The wet adhesion of coatings, determined by pull-off testing, depended on the type of coating and on the pre-treatment of the wooden substrate. Modification of wood with mDMDHEU significantly increased the wet adhesion of one of the water-borne acrylic and of the solvent-borne alkyd coating tested. The treatment also improved the weathering performance of wood coated with different coating systems with regard to of cracking, deformation and discoloration.

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Infrared Studies of Weathering in Acetylated Beech Wood

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Keywords: Beech wood, acetylation, artificial weathering, Fourier Transform Infrared

ABSTRACT

In this study Beech wood (*Fagus orientalis*) was acetylated and subjected to a variety of artificial weathering conditions (water only, light only, water and light together) in different times (0, 50, 150, 300 h), then wood surface was analyzed using Fourier Transform Infrared spectroscopy (FTIR). Light and water, acting together (full weathering) cause the greatest damage to the surface polymer structure and greatest chemical changes. The effect of light on the weathering process is quite rapid as monitored by FTIR spectroscopy within a few hours exposure (50 h). Changes observed in the infrared spectra of the surfaces after wood samples were subjected to water- only weathering are minor compared with the effect of light-only and water plus light. Acetylation of wood under mild conditions serves to protect the surface from weathering.

INTRODUCTION

Wood exposed outdoors undergoes photochemical degradation primarily in the lignin component, due to UV light, which gives rise to characteristic colour changes. Because the lignin acts as an adhesive in wood, and holds cellulose fibres together, the wood surface becomes richer in cellulose content as the lignin degrades and fibres are washed off from the surface during a rain, exposing new lignin to continue the degradation reactions (Rowell 1983). The degradation mechanism depends on the type of material, but the cause is a combination of factors found in nature: moisture, sunlight, heat/cold, chemicals, abrasion by windblown materials, and biological agents (Williams 2005). Chemical modification of wood can play a very important role in controlling the natural weathering process. Researching the effects of chemical modification of wood on weatherability and elucidating the mechanism(s) of UV degradation of modified woods have been undertaken (Rowell *et al.* 1981, Feist and Rowell 1982). Among the different possibilities the chemical modification of the cell wall by acetylation, seems to be the best way. In this reaction, hydroxyl groups in the aliphatic and the aromatic part the lignin can be substituted by acetyl groups (Sundell and De Meier 2001). Infrared spectroscopy has been widely employed to provide evidence of the existence and changes of chemical bonds established during the modification of wood with chemical reagents (Chen 1994).

EXPERIMENTAL

Samples of beech wood (*Fagus orientalis* Lipsky) measuring 150 × 75 × 5 mm were prepared, treated with acetic anhydride (approximately 18% weight gain) at the Wood Technology Laboratory in Tehran Azad university, then weathered. The full weathering process comprised of continuous exposure in an Atlas Xenon Test Beta LM Weatherometer to UV radiation (300 nm) and visible light (750 nm) and bombardment by a water spray for 4 h per day (18 min water spray for 102 min radiation), for the allotted time period. The UV light-only samples were subjected to continuous exposure to UV light for the appropriate periods. The water-only samples were continually sprayed with water for specific time periods. For FTIR spectroscopy, dried samples taken from surfaces were milled and passed through a 40 mesh sieve. Then small pellets prepared with KBr and wood powder. Using a Bruker Vectra 22 FTIR spectrometer, all samples were examined at a spectral resolution of 4 cm^{-1}, spectra from 24 scan/min.

RESULTS AND DISCUSSION

Light only weathering of beech

The most significant feature in the spectrum of Beech wood exposed to 50 h of light-only weathering compared with the spectrum of the control is that the carbonyl absorption has increased in intensity at 1742 cm^{-1}. In addition, the 1425 cm^{-1} lignin aromatic skeletal vibration has decreased in intensity and C–H deformation in lignin somewhat has increased in intensity at 1375 cm^{-1}. After the samples have been subjected to 150 h of light only weathering, the FTIR spectrum is very similar with 50 h. After 300 h of light only weathering, compared with the spectra of the control sample, some relative intensity changes can be observed in the infrared spectrum. The carbonyl absorption has increased in intensity at 1727 cm^{-1} and aromatic skeletal vibration and C-H deformation in lignin at 1330, 1420 and 1507 cm^{-1} have increased in intensity. Also C-H deformation in cellulose at 894 cm^{-1} has slight increased.

Full weathering (light plus water)

The most significant feature in the spectrum of Beech wood exposed to 50 h of full weathering compared with the spectrum of the control is that the carbonyl absorption (1741 cm^{-1}) has increased in intensity. In addition, a dramatic decrease in the intensity of the 1510 cm^{-1} and 1460 cm^{-1} peaks are observed. Also the bands at 1600, 1660 cm^{-1} decreased in intensity. After 150 h exposure, the spectral pattern observed is rather similar, except that the 1647 cm^{-1} absorption (absorbed H_2O in cellulose) is a more. 1507 cm^{-1} and 1458 cm^{-1} absorptions are little weaker. Increased exposure to weathering (300 h) results in the virtual disappearance of the aromatic 1510 cm^{-1} absorption and the 1457 cm^{-1} band, together with a decrease in intensity of the 1600 cm^{-1} absorption and a decrease in the relative strength of the carbonyl absorption (Figure 1).

Acetylated wood

A comparison of the spectra of the untreated and acetylated control samples (*i.e.* unweathered) shows some distinct differences. As might be expected, the acetylated sample has a very intense carbonyl absorption band at 1750 cm^{-1} (Figure 2). In addition, absorptions at 1375 and 1238 cm^{-1} appear as strong peaks–obviously attributable to the presence of acetyl groups replacing many of the O-H groups in the wood polymer matrix.

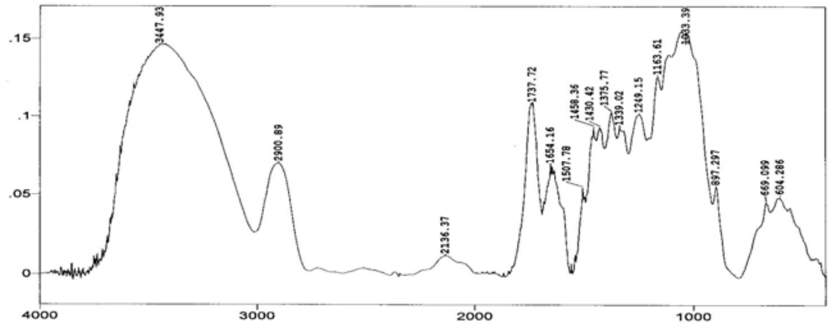

Figure 1: FTIR spectrum, between 4000 and 500 cm^{-1}of Beech wood weathered with light and water (300h)

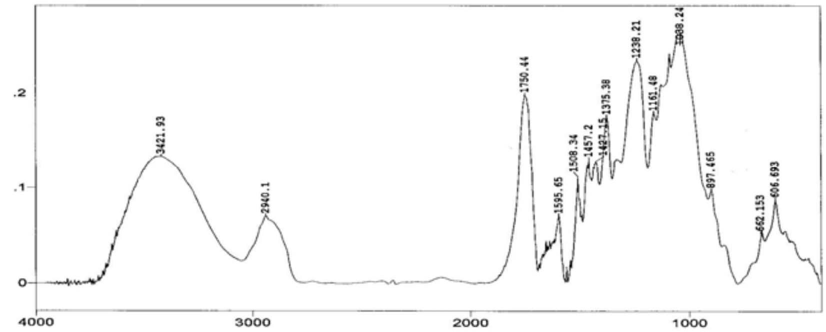

Figure 2: FTIR spectrum, between 4000 and 500 cm^{-1}, of acetylated Beech wood (unweathered)

Light only weathering

Exposure to 150 h of light only, the diminution of the aromatic bands (1510 cm^{-1}) and the 1475 cm^{-1} absorptions can be clearly observed. After 300 h exposure, the O-H stretching band and carbonyl absorption at 1748 cm^{-1}, increasing in intensity. Aromatic bands at 1510, 1460 and 1600 cm^{-1} decreasing in intensity and making the band quite asymmetric.

Full weathering (light plus water)

After 50h of full weathering, the spectral changes can not be observed. After 150h, making the peak at 1641 cm^{-1} have decreased in intensity relative to other absorption. After 300h, the 1641, 1596 and 1507 cm^{-1} peaks are reduced. In addition all trace of the 1600 cm^{-1}absorption has disappeared. Intensity of the absorption in about 1000-1700 cm^{-1} decreased. Any resulting changes in the intensity of the absorptions due to the original carbonyl groups are totally masked by the presence of the intense carbonyl absorptions due to the protecting acetate groups. At the higher wave number region, the O-H stretching band remains similar in size and shape, whereas the C-H doublet has become asymmetric (Figure 3).

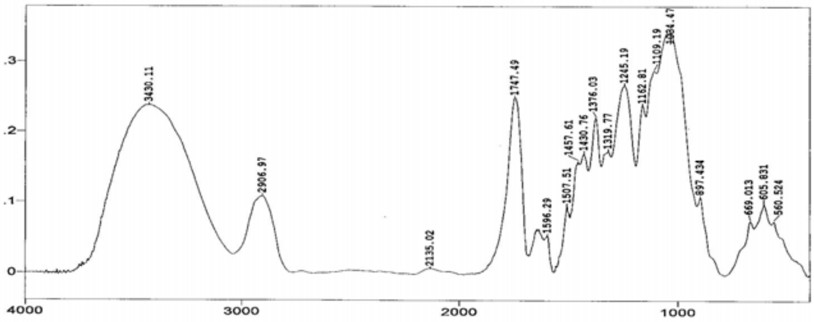

Figure 3: FTIR spectrum, between 4000 and 500 cm^{-1}, of acetylated Beech wood full weathered for (300h)

CONCLUSIONS

It is apparent from the results of this study that weathering has a significant effect on the functional groups found on the surface of wood. It is also apparent from the spectra that full artificial weathering (light and water) affects wood quite differently (the chemical changes are greater) from the effect of either light or water alone. There is general agreement that the process is initiated by UV light, and is primarily a surface phenomenon. The first component of wood to be broken down is lignin (Rowell, 1983) and some possible photochemical reaction schemes have been proposed for what is obviously quite a complex series of chemical changes. The effect of UV light on wood surfaces is quite rapid – noticeable effects are seen and after 50 h of light-only artificial weathering, the whole weathering process cannot be represented by one simple chemical reaction. Acetylation of wood under mild conditions serves to protect the surface from the weathering effects of light and water. The extent of weathering is reduced by approximately 50% (Sundell and De Meier 2001).

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Aspects of Wood Degradation and Effects of Surface Impregnation of Beech and Fir Wood with Reactive Resins Revealed by a Modified L-joint Test

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Keywords: Outdoor exposure, reactive resins, surface impregnation, wood and coatings degradation

ABSTRACT

"Surface impregnation" of wood with reactive resins refers to a simple treating procedure that should lead to the formation of an inner waterproof envelope blocking or limiting to some extent water access into wood. A reduction of water adsorption/absorption and consequent wood swelling and shrinking, as well as reduction of cracking and a delay of biological attack are the expected benefits. The present paper is focussing on the results of a long-term in field evaluation of the efficiency of such a wood improvement procedure, as a starting point in a more complex treating scheme including bio-protection and coating. Fir and beech samples were treated with three different reactive resins, preserved with a biocide primer and coated with a alkyd white paint. The efficiency of these treatments was evaluated employing a modified L-joint test. The main types of biotic and non-biotic degradation phenomena, occurring on unmodified or treated wood, after a period of 27 months exposure, were observed and marked according to standardised and original grading schemes.

INTRODUCTION

Traditional and modern at the same time, wood is continuing to be one of the most important and versatile materials with very different structural or decorative, indoor and outdoor applications. In the context of the modern sustainability concept, both ecological and economical reasons motivate international efforts aiming to improve wood properties and to extend its life and performance in service. Reduction of reversible swelling and shrinking as a consequence of water adsorption/ desorption, and a better biological and weathering resistance have been the main objectives of extensive research approaching classical or alternative wood improvement methods, such as chemical modification, heat treatments and deep impregnation with resins, waxes or oils (Militz and Hill 2005). "Surface impregnation" with reactive resins is a simple technology conceived based on the idea of blocking or limiting to some extent water penetration into wood by a thin waterproof inner envelope. This should be formed inside the treated wood by the curing of a reactive resin penetrating in liquid form into the wood structure (cell lumens and eventually cell walls) to a small depth as a result of a short time immersion treatment in low viscosity resin solutions. A reduction of water adsorption/absorption and consequent wood swelling and shrinking, as well as diminuation of cracking and a delay of biological attack are the expectable benefits. Previous laboratory research in this field as well as some preliminary weathering tests encouraged further in-field testing (Timar *et al.* 2005). The present paper is focussing on the results of a long-term in-field evaluation of the efficiency of such a wood improvement procedure, as a starting point in a more complex treating scheme including bio-protection and coating. For this purpose a modified L-joint test was employed (Timar *et al*. 2002, Timar *et al*. 2005, Van Acker and Stevens 1997).

EXPERIMENTAL

Several series of beech (*Fagus sylvatica*) and fir wood (*Abies alba*) samples (tenon members of the L-joints) were prepared. Three different reactive resins, coded Ra, Rb, Rc (presented in Table 1) were employed for surface impregnation. This was achieved by short time immersion (15 minutes at 20 °C) into fluid resin solutions followed by curing and conditioning at room temperature. The resin treated samples alongside untreated controls represented the series A1. A series A3 of samples was prepared by further coating with alkyd white paint the control and resin treated samples. The series B1 consisted in control and resin treated samples further bio-protected with a biocide alkyd basecoat (Rombai G-coded RG), whilst the series B3 represented samples treated following the most complex treating scheme: surface impregnation with reactive resins, bio-protection and coating.

Table 1: Types and characteristics of resins for surface impregnation

Type of product	Code of product	Aspect	Solids content [%]
Waterborne acrylic-polyurethane lacquer	Ra	Aqueous opalescent, white solution	24.1
Epoxy resin Epikote 1001	Rb	Transparent, colourless solution	43.05
Alkyd-polyurethane lacquer	Rc	Transparent, yellowish-brown liquid	28.22

The test samples were exposed in the conditions of the Hazard Class 3 being examined periodically to observe the aspect changes and occurring degradation phenomena. Special emphasis was put on evaluating the following aspects: wood cracking following swelling and shrinking (rated from 0 to 4), biodegradation consisting up to now only in surface discolouration due to mould and sap stain fungi (rated from 0 to 3 according to *PrCEN/TS 12037:2002*) and coating performance (aspect changes, flaking, exfoliation and adherence on a 0 to 4 scale). Not only the joint area (actual tenon), but also the all the faces of the external exposed part of tenon members were carefully examined.

RESULTS AND DISCUSSION

The exposure of samples for 27 months to the direct action of climatic factors and biological agents active in the conditions of the Hazard Class 3 brought about evident aspect changes and caused different biotic and non biotic degradation phenomena. Wood cracking and discolouration due to moulds and blue stain fungi were characteristic for all the series of samples, whilst colour change to grey due to the combined action of ultraviolet light and water was characteristic, as expected, for the uncoated samples. The coated samples presented some of the degradation phenomena characteristic to the coating films: cracks, bubbling, blisters, adhesion loss and tendency of exfoliation on limited areas. Obviously different degradation was registered for the non-directly exposed parts of the samples (the actual tenon of the joint) and the exposed part of the samples. For the latter one maximum degradation was observed, as expected, on the upper face and only some of these results will be further briefly presented in this paper. The degradation level was obviously related to the treatment applied and influenced very much by the wood species (Figure 1).

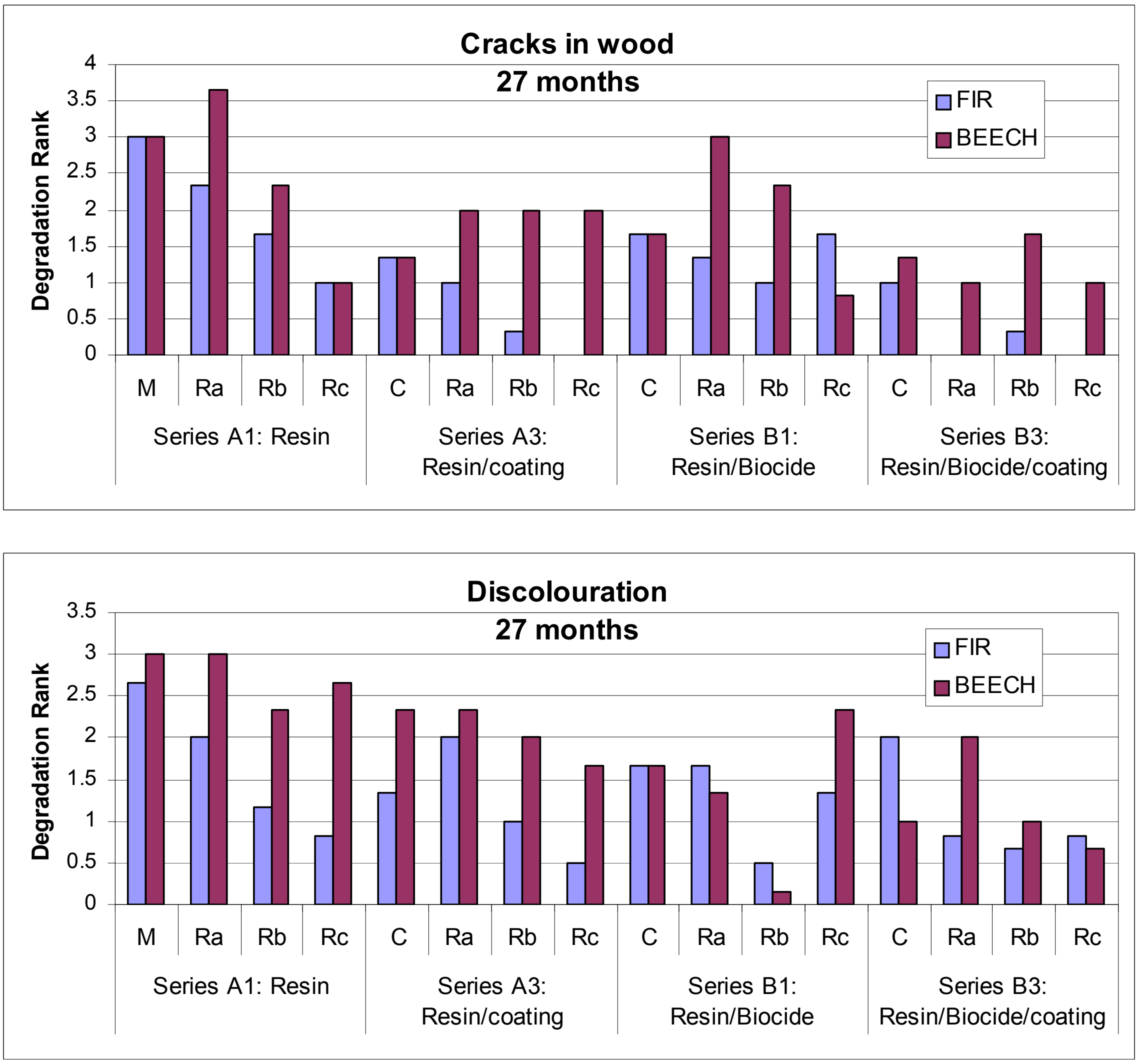

Figure 1: Comparative degradation f fir and beech tenon members (upper face) after 27 months exposure as a function of treatment applied

The experimental results showed that, surface impregnation with certain reactive resins (series A1) reduced to some extent wood cracking. This effect was registered for all the three resins in the case of fir wood, but only for the alkyd-polyurethane resin in the case of beech. This is somehow in accordance to laboratory experiments where the best and lasting stabilisation effects were obtained for this resin. Wood cracking was also reduced to some extend by coating due to the physical barrier against water absorption represented by the coating film (series A3). For the fir samples better results were obtained for the resin treated samples that were further coated, but this was not the case for the beech samples. The biocide basecoat RG had a slight effect of dimensional stabilisation of control wood leading to cracking diminishing. This could be explained by its low content of alkyd resin (7 %). However, this effect could not be observed for the resin impregnated samples where the penetration of this material into the wood was difficult (series B1). Thus cracking of resin treated samples further treated with RG was similar to the cracking of resin treated samples.Wood cracking was further diminished for the series B3 due to the effect of the applied top coating film. This effect was even more effective when applied on resin pre-treated and further bioprotected wood. The best results for both studied wood species were obtained once again for the alkyd-polyurethane resin Rc. The biological resistance of wood was not significantly influenced by the resin treatment, a delay in the mould fungi colonisation being registered only for fir wood (series A1). The treatment with the biocide base coat RG was limited and had different efficiency on control wood and resin impregnated wood (series B1). Generally, wood coating with the alkyd white paint had only a very limited effect on wood biological resistance, as mould fungi developed well under the coating film penetrating finally through it. However, the minimum discolouration and mould growth was registered for some of the samples of series B3. Degradation of the coating films consisted mainly in cracking, spotwise damages, flacking or exfoliation, being quite similar for all the samples, though a lower adherence of the coating film on the resin treated samples was registered.

CONCLUSIONS

These experimental results suggest that surface impregnation with reactive resins could be a useful first step in the surface treatment of wood for outdoors above ground applications. However, the effects of this treatment depend obviously on the resin type, its physical and chemical properties, as well as on its compatibility with the preservation and finishing materials. Moreover, wood species with different structure and initial properties (swelling coefficients, natural durability, treatability), such as fir and beech, respond differently to such an improvement treatment. The best results were obtained in the case of treatment of fir wood with an alkyd-polyurethane resin.

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Session 5: Poster Session 2.

Thermally Modified Wood as Raw Material for Particleboard Manufacture

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Keywords: Thermal treatment, particleboards, properties

ABSTRACT

The possibility of using thermally modified pine and birch wood (*Pinus silvestris* L. and *Betula verrucosa* Ehrh.) as raw material for laboratory made particleboards has been examined. Wood modification was carried out in laboratory conditions. Physical and mechanical properties of wood before and after thermal modification were determined. The modified and unmodified wood was ground and some particleboards were made in laboratory scale using standard technological parameters. Mechanical and physical properties of the boards were tested.

INTRODUCTION

Thermal treatment is one of the possible ways of wood modification. The visual effect of the process is wood darkening which is related with the conditions of the process, as well as improved resistance to moisture occurs. However, the main drawback of the thermal modification is reduced toughness of wood. Finally the properties of the material strongly depend on the parameters of the process.

Nowadays, thermally modified wood is being produced in large amounts on industrial scale (*e.g*. ThermoWood®, TermoDrewno®, Plato®) and its application area constantly extends. But it must be stressed that with increasing production, available amounts of waste modified wood also increases. These quantities may be recycled in particleboard production. A possibility of waste-wood and non-wood materials application in particleboards production is of great interest and seems to be of outstanding significance in pro-ecological research (Borysiuk *et al.* 2006).

This work concerns the effect of thermal modification on the physico-mechanical properties of pine (*Pinus silvestris* L.) and birch (*Betula verrucosa* Ehrh.) wood, as well as modified wood application in one-layer-particleboard preparation in semi-technical scale.

MATERIALS AND METHODS

Pine and birch wood were subjected to overheated steam treatment according to scheme shown in Figure 1. In order to avoid deterioration of wood mechanical parameters, mild processing conditions were applied.

After treatment, the modified wood was – according to relevant PN –EN Standards – characterized by: Modulus of rupture (MOR), modulus of elasticity (MOE), compression strength parallel to grain, swelling.

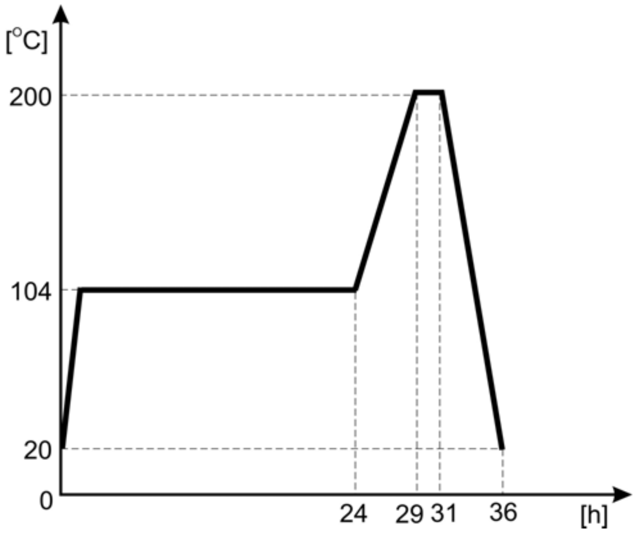

Figure 1: Thermal treatment scheme

Fraction distribution of the particles was made using a laboratory sorter equipped with 6 mm, 4 mm, 2 mm, 1.25 mm, 0.63- mm, 0.35 mm sieve meshes and a dust container. Particles were used in preparation of 16-mm tick one-layer particleboards with density of 700 kg/m^3 under processing parameters as follows:

- Unit pressure – 2.5 MPa,
- Pressing time – 288 s (18 s/mm),
- Pressing temperature – 180 °C,
- Glue content – 10 wt %.

Boards were bonded with UF resin SILEKOL W-1C cured with NH_4Cl (10% aq. solution). MOR, MOE, internal bonding (IB) and swelling after 24 h water soaking were determined both for the test and for the control (unmodified) boards.

RESULTS AND DISCUSSION

It is obvious that treatment conditions strongly affects the properties of modified wood. The conditions applied in the experiments were mild and the final properties of materials are shown below.

Table 1: Effect of thermal treatment on the mechanical properties of pine and birch wood

Species	MOR		MOE		Compression strength	
	[N/mm^2]	z	[N/mm^2]	z	[N/mm^2]	z
pine	99	13	8624	8	51	4
pine mod	106	17	10927	12	69	10
birch	123	10	11652	8	70	5
birch mod	120	14	11246	11	70	6

z – variability coefficient [%]

As Table 1 indicates, thermal treatment did not unequivocally affect mechanical properties of both examined wood species. For birch series, only small statistically insignificant changes in strengths were observed. On the other hand, for pine series, statistically a significant increase in compression strength parallel to grain, MOE and MOR values was observed (95% confidence interval) – MOE 21% and MOR 26% with respect to control series.

The effect of the treatment on swelling was not clear. Depending on the species or anatomic direction, increase or decrease in swelling occurs. Generally, the changes are statistically insignificant at 95% confidence interval. However, influence of the treatment on the moisture content achieved during conditioning in a climate room ($t = 20 - 25\ ^{o}C$, $\varphi = 60 - 65\ \%$) is not explicit. For both pine and birch final moisture content is 32 – 35% lower than that of the respective control series. Although no decrease in swelling values was found, a decrease of equilibrium moisture content was observed.

Since thermal treatment affects mechanical properties of the material, the effects are also visible in particle size distribution after grinding (Figure 2). For pine, increased amounts of 6, 4 and 2 mm fractions as well as decreased amounts of <2 mm fraction were observed. For birch, decreased amount of <1.25 mm fraction was observed. The phenomena can be explained by increased brashness of the modified birch wood when compared to the modified pine.

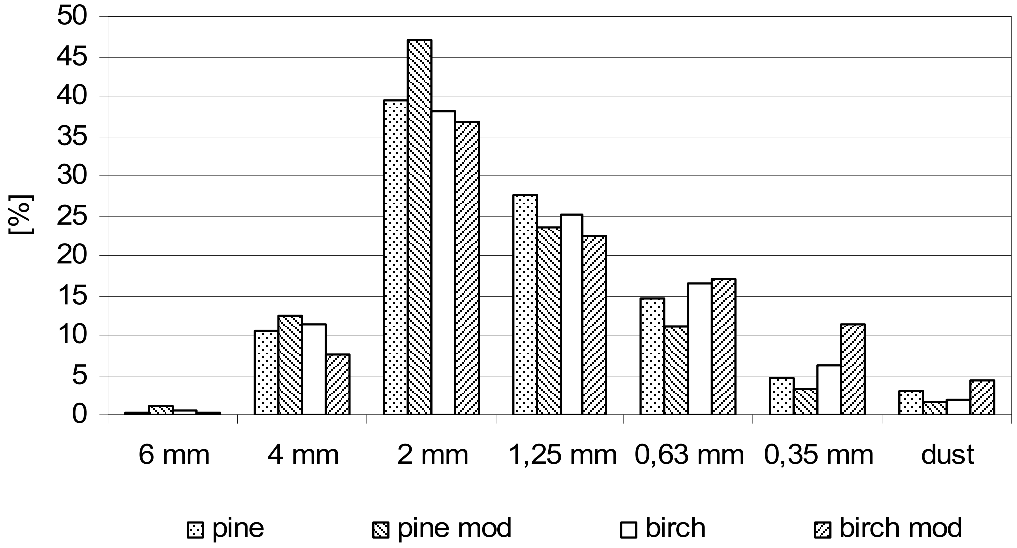

Figure 2: Effect of the treatment on the pine and birch particle size distribution

Mechanical properties of the particleboards obtained from modified pine and birch are shown in Table 2. Just like for the solid wood, the effect of the modification is not explicit. For pine particleboards, the changes are insignificant, but for birch, statistically significant decrease in IB was observed when compared to control series. A 17 % decrease is caused by higher content of <2 mm fraction and, subsequently, increased material specific area which – assuming constant blending level – affected IB between particles.

Table 2: Physico-mechanical properties of the particleboards made of modified pine and birch

Species	MOR		MOE		IB		Swelling	
	[N/mm^2]	**z**	**[N/mm^2]**	**z**	**[N/mm^2]**	**z**	**[%]**	**z**
Pine	12	17	1478	8	1,112	12	16	8
Pine mod	10	21	1320	7	1,107	9	18	5
Birch	13	14	1312	7	1,593	10	25	8
birch mod	12	14	1423	4	1,359	8	19	9

z – variability coefficient [%]

From Table 2, it is worth noting that reduced swelling (-24%) was observed for the modified birch boards. The effect can be explained by higher content of <2 mm fraction and positive influence on dimensional stability of the board during sorption.

CONCLUSIONS

On the basis of the results shown above, it can be concluded that:

- Short-time (2 h) thermal modification of pine and birch wood does not significantly change mechanical properties of the material,
- The modification under the conditions described in this work results in equilibrium moisture content reduced by 35% (t = 20 – 25 °C, φ = 60 – 65%),
- Modified wood can be efficiently applied in particleboard production,
- Statistically significant changes in the properties were observed for the particleboards made of birch wood only. Decrease in IB and swelling values was found.
- The thermal modification described does not affect pine wood properties.

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Glueability and Paintability of Furfurylated wood (Kebony)

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Keywords: Paintability, gluability, furfurylated wood, Kebony Beech, Maple, Southern Yellow Pine, MUF, EPI, coating systems

INTRODUCTION

Recently, different wood modification processes have become available on the market. In the past years the basic properties such as durability, dimensional stability and mechanical properties have been studied extensively. Furfurylation of wood, one of the first and advanced modification techniques on industrial production level, is now in the phase of product improvement and developing new application areas. In order to make its introduction onto the market possible in a wide range of applications other properties like gluability and paintability need to be determined . The interaction of coating and gluing systems with these new types of wooden material need to be tested to assure possibilities in applications where glued, or laminated and/or coated material is essential. The paintability was evaluated by testing the wet and dry adhesion and blistering of three types of Furfurylated wood species with three different coating systems. A comparison with spruce and Meranti was made. The gluability was tested on the same treated wood species using two different gluing systems.

EXPERIMENTAL

Pilot plant Kebony Beech, Maple and Southern Yellow Pine (SYP) was produced by WPT in two treatment classes; 40% WPG (weight percent gain) and 70% WPG. Wood of both treatment levels and untreated material were used for the gluing tests. Dynea EPI glue Prefere 6151 with 6651 hardener and Akzo MUF Casco 1242 with 2542 hardener were used, following the application descriptions of the producers. The sample preparation and determination of the durability of the glue line were performed following the standards EN 204 and EN 205. The initial conditioning sequence (minimal 7 days in standard atmosphere 65% RH, 20 °C; one cycle) and subsequent conditioning sequences (6 hours in boiling water followed by 2 hours in water of 20 °C; 5 cycles) were followed. For each combination, the adhesive strength (N/mm2) and percentage wood failure were determined on 10 samples for the dry shear strength (after initial sequence) and 15 samples for wet shear strength (after multiple conditioning sequences). Kebony 40% WPG samples were used for the paintability tests. Three different coatings were used: white alkyd (Sikkens EPS), white acrylic (Sigma coat) a high solid (Wijzonol) and a transparent acrylic (in house made formulation, based on Joncryl 8383 binder). Wet and dry adhesion were tested following SKH 98-04, Appendix 2, using Pressure Sensitive Tape 8981 of 3M. Blistering of the coating followed the standard ISO 4628/2. Coated samples were put over a 40 °C water bath, the non-coated side towards the water. The loss of adhesion of the coating through the formation of blisters was evaluated after 10 and 14 days. Laminated Kebony SYP window corners were coated with the four tested coatings and exposed at the exposure site at SHR. The wet adhesion was tested after half a year of exposure.

RESULTS AND DISCUSSION

The results of the gluing tests is visually represented in the graphs below (Figures 1-3), where shear strength and percentage wood failure are shown for the three wood species. The graphs show that the dry shear strength in Beech does not change due to the treatment, whereas in SYP an Maple the dry shear strength is reduced. The reduction is mainly due to the reduces wood strength as demonstrated by the percentage wood failure. In wet samples a reduction in shear strength in treated wood compared to untreated wood is mainly due to glue line failure, not to wood failure. In SYP the treatment only slightly influences the glueability. The EN 204 standard states the minimal glue line strength of Beech. The average dry adhesion should be > 10 N/mm2, the wet adhesion > 4 N/mm^2, and that the shear strength can be less if the percentage wood failure is 100%. The results in the tests described in this paper show that these criteria are met for the Beech and Maple combinations, treated or non-treated. For SYP the criteria are also met. Although the shear strength does not reach the required 10 respectively 4 N/mm^2 for all combinations, the wood failure percentage is 100% for those combinations that do not meet the requirements. For both hardwood species however the percentage glue line failure was higher in the treated samples compared to the untreated samples. In Beech a effect of the concentration could be seen. In Maple, the trend was less obvious. In can be concluded that the treatment influenced the gluability although the criteria were still met.

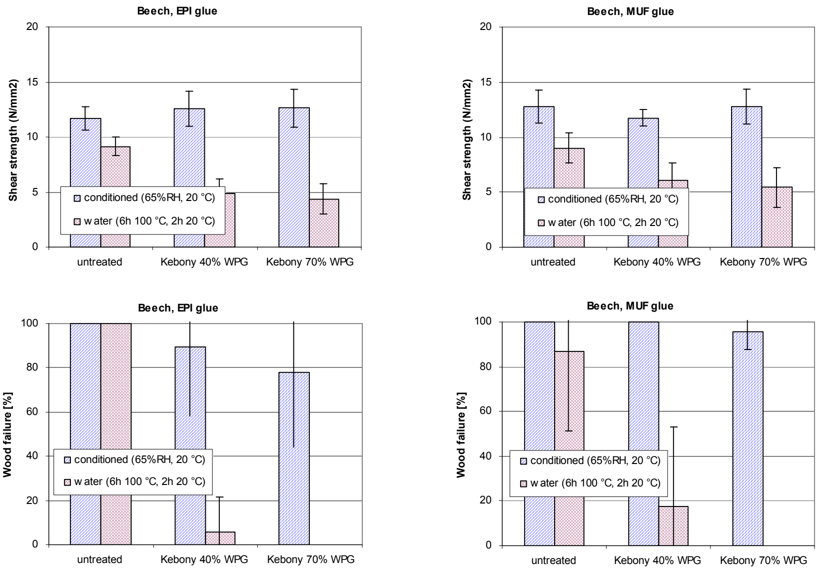

Figure 1: Shear strength and wood failure of furfurylated and untreated Beech.

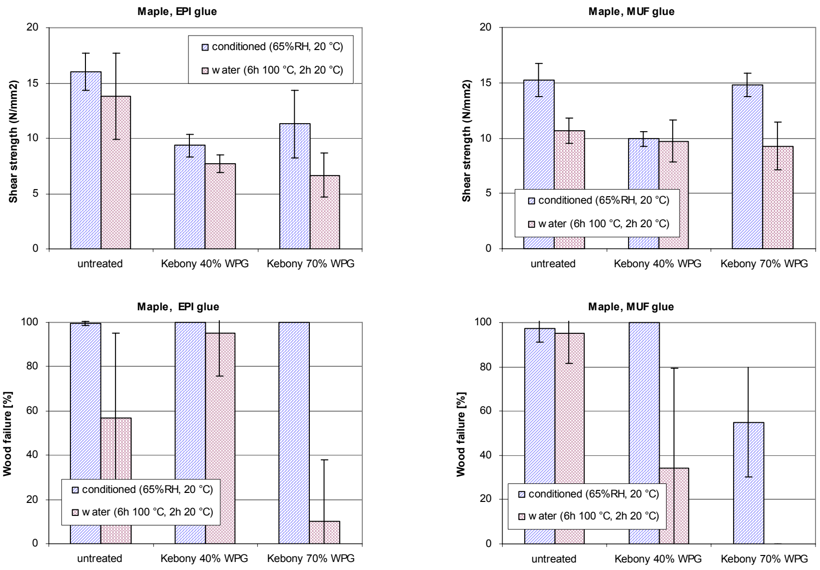

Figure 2: Shear strength and wood failure of furfurylated and untreated Maple.

Paintability is determined by the determination of wet and dry adhesion and blistering. For dry adhesion classification 0 was obtained for all combinations, complete adhesion was found. The results for the wet adhesion results are shown in Table 1. The results show that alkyd and acrylic coating systems maintain complete adhesion after water penetration in the incisions for one hour. The high solid coating system was found to be the least of the tested coating systems.

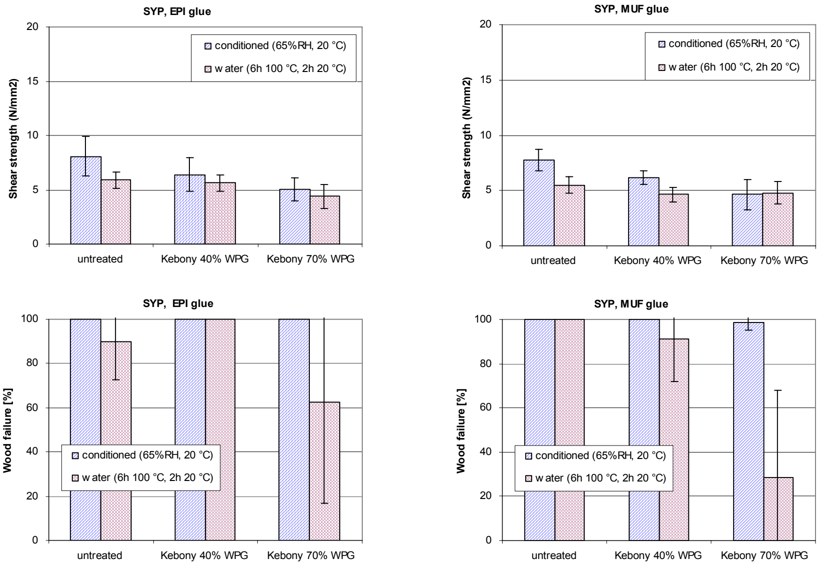

Figure 3: Shear strength and wood failure of furfurylated and untreated Southern Yellow Pine

Blistering by water vapour pressure through the samples did not occur in any of the Kebony wood species, however in spruce blistering did occur on the transparent acrylic coating. As the vapour pressure on the un-coated sides of the samples is high several samples appeared to curve. The Kebony SYP samples and spruce samples did not curve under vapour pressure however all Kebony beech and Kebony maple samples did not remain flat.

Table1: Wet adhesion, 0 = complete adhesion, 5 = complete loss of adhesion. Duplicate experiments were performed if the results of both tests differ, both classifications are given

Type of paint ► **product▼**	**White alkyd**	**White acrylic**	**White high solid**	**Transparent acrylic**
K. Beech	0	0	1/3	0
K. Maple	0	0	1	0
K. SYP	0	0	1/2	0
Meranti	0/1	0	1	0
Spruce	0	3	1/2	5

Irrespective of the coating the curving ranged from 1.4 to 2.4 µm/mm sample width. As a comparison the meranti samples coated with the acrylic coating curved 1.4 µm/mm sample width. The given values for the curving are not exact values, as besides dimensional stability they depend greatly on the annual ring orientation within the samples it shows that differences occur between the treated wood species. The wet adhesion after 6 month outdoor exposure did not change compared to the initial wet adhesion shown in Table 1

CONCLUSIONS

The results presented in this paper show that furfurylated wood can be glued with an EPI or MUF gluing system. The glue line of the treated reacts differently from untreated wood as in wet conditions the percentage glue line failure increases. However, the criteria stated in EN 204 are easily met. Differences between the different wood species were found. In Kebony Beech and Maple the glue line was found to be the weakest link where as in Kebony SYP the glue line was found stronger compared to the wood itself. Acrylic and alkyd coating systems were found to maintain complete adhesion after testing the wet or dry adhesion. The loss of adhesion of the high solid coating was higher compared to both other coating systems. The results are comparable to those of Meranti. These laboratory scale tests show that Kebony Beech, Maple and Southern Yellow Pine have great potential to be used in glued or laminated, coated applications.

ACKNOWLEDGEMENTS

The work described in this paper was performed within the European research project ‘Ecobinders’. The authors which the European Community for their financial support.

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Holiwood – International Research and Development for Innovative Products made out of Thermal Modified Timber

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Keywords: Thermally treated timber, product, noise barrier, ecobuilding

ABSTRACT

The thermal treatment of hard wood is an innovative and environmentally friendly process to improve the wood properties in terms of a higher durability, better resistance against fungi, improved dimensional stability and a decreased tendency towards cracking and enabling the employment of wood in weather exposed applications. Looking at the wide range of possible applications for Thermally Modified Timber (TMT) with all its unique properties, this material could be *e.g.* industrially implemented as new, knowledge based material in the construction sector. TMT could replace commonly used resource intensive materials like concrete, steel, plastics and impregnated wood can be replaced. Due to its potential for the future, the European Commission has funded a project called Holiwood, aiming at further investigating and developing the characteristics of TMT and at realizing prototypical product innovations. The Holiwood project is funded under the 6th Framework Programme in the field of nanotechnologies, nanosciences, knowledge-based multifunctional materials and new production processes and devices. It started in July 2005 and will last until June 2009 with a total budget of €11 million. 19 companies and research institutes from 9 European countries collaborate. The paper presents the project, first results after 24 months regarding the property investigations for TMT and first experiences with the developed prototypes.

INTRODUCTION

The integrated project “Holiwood”, dedicated to SMEs, aims to demonstrate the possibilities for use of thermally modified hardwoods in industrial scale. This is carried out by using a highly interdisciplinary approach for the development of three product lines. The products developed are an eco²building, a massive wooden, adhesive free flooring system and noise protection barriers.

THEMAL MODIFICATION OF HARD WOODS

Thermal modification of wood is an environmentally friendly process to improve the properties of wood in terms of a higher durability (equal to tropical hardwood), better resistance against fungi, improved dimensional stability and a decreased tendency towards cracking and enabling the employment of wood in weather exposed applications (Militz 2000). During the scientific investigations of thermal treatment process of hard woods (beech, ash) the variation of heat treatment parameters (T, t, pre-treatment) will be investigated in terms of the changes to the wood physical parameters, namely dimensional stability, capillary water up-take and hydrophobicity, the mechanical properties namely MOE, MOR, impact bending, hardness for the use in construction and for flooring as well as coloration by UV-Vis measurements and the wood chemical point of view. These investigations are carried out allowing to a correlation of these parameters to the heat treatment parameters. This correlation is carried out by appropriate mathematical methods, *i.e.* artificial neural networks. After the validation of results by experiments the optimum process parameters will be applied in industrial application. In the next technological step, experiments with functional prototypes from assembly-unit development, flooring development and noise protection barrier system design will be tested on their mechanical and functional properties as well as the coating procedures.

ECO² BUILDING

The aim is a modular system based on prefabricated, self supporting wooden wall elements in passive house quality complete with cladding, roof elements and detachable parts under consideration of all cut surfaces including optimised domestic techniques for the construction of eco²buildings – efficient in ecology and economy. Wood has obviously less demand on primary energy than the same construction in steel or reinforced concrete. The energy demand for the equivalent steel profile is 90% higher than wood, reinforced concrete 63% higher. Buildings made of reinforced concrete are difficult and with high energy consumption demountable, because all surface materials are composites and are not recyclable. The aim is to minimize the life span costs as sum of building costs and consequential costs. Only the consideration of the consequential costs in the design and development can lead to optimisation of the complete life cycle. 40% of the energy consumption in the EU account for buildings. Building concepts that do not improve a radical change in the energy consumption are actually not representable. What we build today will use energy for at least 30 years! Using wood, and TMT where appropriate, as substrate with its as brilliant primary energy numbers and being a renewable material, the basis for renewal of buildings for trade and industry (eco^{2}buildings) is set. Developing a constructions system, insulating and surface providing attributes highest building physics qualities will be reached as well as high span widths. Integrating the two basic principles of the passive house dwellings shown below:

- Avoid heat loss by optimisation of thermal attribute of the envelope of the building
- Optimize free heat gain by optimisation of openings for light (heat gain through windows), design of floor plans and usage of internal heat sources (machines) for heating the building.

brings the benefits of the industrial eco^{2}building - ecologically and economically.

The strategy of the development of eco^{2}buildings is that constructive, functional, aesthetical, physical and technical aspects are defined and consolidated in an interactive planning process. Constructive processes are always compared with thermal needs, with calculations audited and optimized. The cut surfaces between constructive elements and detached elements like windows, doors, delivery, window stripes are calculative, constructively and aesthetically accounted, so that superior system correlations make actual balances.

The objectives for the development of the industrial eco^{2}buildings are:

- Improvement of the ecological requirements by reduction of heat energy demand to 60%, reduction of life cycle costs to 20%, reduction of CO_2 to 50%, reduction of primary energy demand to 50%, minimization of the outward heat transfer coefficient by use of ecological insulations with low heat conductivity, high air tightness by careful joint building, choice of ecological materials by evaluation and optimization of various building materials with similar function.
- Development of a 3 D modular system, which makes the optimisation of the insulation thickness and the required degree of equipment individually creatable.

The holistic development of the industrial quality product – the elements of the eco^{2}building – the usage of exclusively ecological materials will be achieved. By this way the primary energy demand is reduced and the building costs will be minimized making the eco^{2}building even more interesting for the customer.

NOISE PROTECTION BARRIER SYSTEM

The problem of high noise levels affecting dwellings, schools, hospitals *etc.* is of increasing concern as witnessed by the recent European Directive by which member states are required to undertake noise mapping exercises (The European Parliament and the Council of the European Union Directive 2002). The use of acoustic barriers represents the only feasible option to reduce noise from sources such as road traffic and hence they are widely employed throughout Europe. Noise screens are made from a number of materials including concrete, plastic, glass and treated timber. Each of these materials presents problems of sustainability.

A feasibility study on Noise Barriers showed the limitations of existing noise barrier systems in Austria (noise on the top edge, reduction of noise absorption due to deformation of the absorbing material, maintenance intensity) and the needs and requirements of “customers” (noise protection, preferred material wood).

The performance of a simple noise barrier will increase with its height, which may cause structural problems as well as being visually intrusive. The limiting factor in the performance of a noise barrier is due to diffraction from the top edge and a considerable amount of research has been undertaken to combat this effect in order that comparable performance to that of a very tall barrier can be achieved with a much lower one (Ekici and Bougdah 2003). Techniques to reduce the level of sound diffracted to the screened region typically involve the use of novel barrier geometries and the addition of acoustic treatment. These novel geometries are impractical for barriers constructed from concrete or glass. In addition, conventional absorbent treatments such as rock wool, used at the top edge to further enhance performance, can lose dimensional stability and hence become less effective when exposed to rain water. Thermally modified wood offers the possibility of developing a noise barrier system which is constructed from sustainable materials, low cost, aesthetically pleasing, easy to erect (preferably pre-fabricated) and capable of being constructed in novel geometric forms to ensure maximum performance in a given location with minimum visual intrusion. A number of natural materials are possible candidates for the role of practical sustainable sound absorbers. The structural properties, surface to volume and surface to weight ratios of reed provide the basis for the development of highly noise absorbing materials. Reeds have a long history of being employed for roofing where they are exposed to the full range of climatic conditions, typically over many years. They maintain their geometric form when wet and shed water efficiently. A comprehensive review of barrier theory in order to identify potential geometric forms, a comprehensive review of sound absorbent mechanisms in order to identify the most promising natural sound absorbers; the development of state of the art computer models for predicting barrier performance; measured data regarding the acoustical properties of natural sound absorber subjected to different environmental conditions; the simulation of barrier configurations incorporating novel geometric forms and natural sound absorbers and validation studies by means of acoustic scale models are carried out. The final outcome will be a specification for the acoustical design of a noise barrier system suitable for construction using thermal wood which will offer a performance in excess of that currently achieved with conventional barrier forms. It will make a valuable contribution to the quality of life of people exposed to high levels of noise arising from road and rail transportation systems, both by reducing noise levels and also by reducing the visual intrusion associated with conventional barriers, and contribute to sustainable development.

SUMMARY

Currently the thermal treatment processes for beech and ash are optimized and more than 15 physical and mechanical properties under investigation within an artificial neural network. The construction system has been designed, the prefabricated elements of the eco²building are designed, specified and prototyping is currently running. The demonstration object is under detail planning will be finished until the end of the project. Reed turned out to be an effective and highly interesting absorber material, especially at low frequencies. The mechanical properties of reed allows investigation to it also as structural material, additionally to TMT. The second series of different full scale prototypes are installed and under long term investigation. Beside these results, two different approaches of coatings – one for indoor use and one for outdoor use are under development with promising results, and the life cycle analyses of TMT is almost finished.

ACKNOWLEDGEMENTS

The presented project is financially supported by the European Commission under contract No. NMP2-CT-2005-011799 (HOLIWOOD project).

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Wood Modification of Portuguese Wood species, Physical Properties. Review

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Keywords: Acetylation, furfurylation, preservative, timber modification, TMT

ABSTRACT

This research project, involving Modified Wood, is being developed in the Oporto Institute of Engineering, Portugal. Three main types of wood Modification have been studied: Thermally modified Timber (TMT), Acetylation (AC) and Furfurylation (FW). A survey of scientific papers on this subject, published essentially by European researchers after the year 1995 have been gathered and studied. The mains results obtained by experimental research have been collected, quantified and compared. The most relevant conclusion has been used to define which method is more convenient to be applied to modify Portuguese wood species, specifically *Pinus Pinaster* and *Eucalyptus globulus*.

INTRODUCTION, MOTIVATION

The Portugese forest represents approximately 35% of the total land area (≅3.4 million ha). Of this area, 75% is private and 90% is in areas smaller than 3ha. The most frequent species with commercial tendency are: *Pinus pinaster* (710,000 ha, 21%) and *Eucalyptus Globulus spp* (646,700 ha, 19%). Portugal has 3 to 4 times less land area and 10 times less forest area than Northern European Countries and is continuously losing forest area to fires each summer (from 2002 to 2005 some 250,000 ha were lost per year; 2006 approximately 75,000 ha). This results in a slightly higher forest area per capita (0.33 ha/inhabitant) than the European average (0.23) but much lower than the northern Europe countries (3 to 4.5). The Portuguese forest generates approximately 9% national employment, 10% of exports and 4% imports. In 1995 it was considered a national "Cluster" in M. Porter report, entitled "*Strategy for economical development of Portugal*". However, forestry continues to be observed with distrust, lessened, forgotten and, considered an "economical poor relative". The necessity to preserve wood, like conifer (smooth, quick growing) and Eucalyptus (hard, quick growing) lead the scientific community to find ways to treat / modify wood. Many authors have reported on the physical properties of modified wood; however few studies have been done with Portuguese species. In this study the author aimed to compare the results of modification process (AC, FW and TMT) applied to species *Fagus sylvatica* and *Pinus sylvestris*. The two type of wood selected, have similar characteristics as the most frequent Portuguese species. The main physical properties were (density with WPG - weight percent gain or WL-weight loss, ASE - anti swelling efficiency and EMC - equilibrium moisture content). The main purpose of this work is to compare the most efficient modification process to apply in the Portuguese wood species.

Material and Methods

Web information was the source used to select the scientific papers from the main researchers on this subject published essentially by European reviews after the year 1995. An extensive bibliographical research on the modification wood subject was accomplished- AC, FW and TMT. The analytical method used was the comparison of rates. This selection of 4 species is to be done because: Beech and Pinus are the most investigated species of wood in Europe, and maritime pine and eucalyptus are the most abundant species at Portugal. They were also considered because of the likeness in some properties, such as strength and density. This result is to be used in a research project on Portuguese wood species.

Table 1: Wood species in analyses, NP EN 350-2:2000 and NP EN 1192:2000

wood species		**γ–kgm^{-3} (12%)**	**Impregnability Heart/sapwood**	**sapwood width**
Fagus sylvatica	D40	720	1-(4) 1	x
Pinus sylvestris	C18 C30 ME-2 ME-1	520	3-(4) 1	p-m
Pinus pinaster	C18C30 E EE	540	4 1	g
Eucalyptus globulus	D40	750	3 1	p

Actually, D40 is not yet fully accepted by the scientific community. For the other features, they have identical impregnability in the sapwood (1-easy to) and almost identical for the heartwood (3-difficult), in the four species. For the “sapwood width”, they have different features, where (x) suggests that it does not have clear distinction, (g) big distinction, > 10 cm, (p) small distinction, 2 to 5 cm. The different treatability of sapwood / heartwood can take some trouble of the content gradients like acetyl group (Homan and Bonger 2004), Furfuryl Alcohol - FA or CCA in the transversal section, specifically in the *Eucalypt*. The most results found in the bibliography were done with sapwood sample.

RESULTS AND DISCUSSION

Weight percent gain - WPG or weight loss - WL

In the traditional treatments, wood take some weight to the samples of control, like CCA in the hazard class 3, 4 and 5 have WPG, in (kgm^{-3}) 4 to 7, 15 and 40, respectively. The variations in the traditional treatments are well known.

The TMT-vapour had 25% WL with high temperature-T 235 ºC, and the TMT-HOT RSO or LSO had 20% WPG. In a wide perspective we can found in the TMT-vapour 25% WL. Is the modification process were the wood density can reduces like no other one, in TMT-vapour. For TMT-HOT WPG was 10 to 60%, in AC can reach 30% it is depending of T and time-t of reaction. For *Pinus sylvestris* with times of treatment t 0.5, 1, 2 and 4 hours were obtained WPG 7.5, 15, 20 and 32%, respectively (Ramsden *et al.* 1997). For FW the WPG depending on FA concentration. Is possible to obtain 125% WPG. To WPG 20% for 20% AF, WPG 50% for 50% FA and WPG 100% for 100% FA (Lande *et al.* 2004a).

Equilibrium moisture content - EMC

For *Pinus sylvestris* it decreases to 50% (Kegel 2006), for *Fagus sylvatica* and *Pinus sylvestris* also reduced 50% (Militz 2002). For *Pinus sylvestris* with TMT-vapor T 190 ºC in relative humidity-RH 90% the EMC was reduced 30% (Epmeier *et al.* 2004). In the TMT-vapor *Pinus pinaster* and *Eucalyptus globulus*, with T 190 ºC for t 8 to 24 h the EMC reduced 50% at environment RH 35 and 65%. The EMC reduced 40% for RH 85% and t 8 to 24 hours. In *pinus* the t is important, because for RH 65% with variation of t from 2 to 24 h the EMC reduced ≅ 25 to 50%, respectively. For the *Eucalypt,* the variation t 2 to 24 h didn´t reduce the EMC, which was ≅50%. The treatment time have significant importance, for RH 85% environment. For RH 35% and 65% the EMC was reduced 40% and 50%, respectively in *pinus* and *Eucalyptus* for t 8 to 24 h (Esteves *et al.* 2006). In AC WPG 20% *Picea sitchensis* and *Pinus sylvestris*, for any HR, the EMC reduced 50%, for WPG 7.5%, any HR, reduced 20% (Minato *et al.* 2003, Homan *et al.* 2003). For *Pinus sylvestris* AC WPG 20% at 90% RH the EMC is 6%, it reduced 70% (Epmeier *et al.* 2004). In *Pinus sylvestris* FW WPG 50% at 90% RH environment the EMC was 7%, reduced 65% (Epmeier *et al.* 2004).

Anti swelling efficiency ASE

In TMT-vapor, to *Pinus pinaster* and *Eucalyptus globulus* the ASE is directly connected with WL. For T 170 º and 180 ºC, WL was 2% and ASE 55% e 75%, respectively. For WL 10 % with T 200 ºC, the ASE was 60% and 90% for *Pinus* and *Eucalyptus*, respectively (Esteves *et al.* 2006). In other words, as high is WL, more stable is the material and bigger is the value of ASE. For *Fagus sylvatica* in TMT-NOW the ASE was the same for T 220 ºC with t 1 h and T 240 ºC with t 5 min (Perré 2003). In TMT-vapor with T 200 ºC and t 10h the ASE 53% and 40% for *Fagus orientalis* and *Picea orientalis*, respectively (Yildiz *et al.* 2003). For *Pinus Sylvestris* with T 220 ºC the ASE to TMT-vapor and TMT-HOT, is similar ≅40%, for differently atmosphere (Rapp and Sailer 2001). They check, the increase of RH environment, or, the increase of T, the ASE was a slightly reduction. n the *Pinus sylvestris* AC WPG 20% the ASE was 70% (Epmeier *et al.* 2004). In the *Fagus sylvatica* AC WPG 20% the ASE was 75% (S1 acceded in 10/2006). For FW WPG 50%, in *Pinus sylvestris* sapwood and heartwood and *Fagus sylvatica*, the ASE was 70%, 55% and 75%, respectively (Epmeier *et al.* 2004). To *Pinus Sylvestris,* in FW WPG 15, 32, 47 and 125% the ASE was ≅37, 57 and 72%, respectively, (Lande *et al.* 2004b). For Portuguese wood species similar values are expected.

CONCLUSIONS

The author found that greater WL or WPG was associated with wood species, it depends on T and t in TMT, FA concentration in FW and t of treatment in AC. In the modified wood is not easy to extract numeric values with isolated variables. In the Portuguese wood species they will be obtained similar values. We can verify that is more dependent of the modification process than properly of the wood species.

We can expect that the EMC reduced by approximately 50%, at 65% RH environment in all type of modification process, at least. The EMC is strongly dependent on RH of the environment. We can expect, also, the same results for maritime pine and eucalyptus. For TMT-vapour, Esteves *et al.* (2006) found values in line with other researchers. For AC and FW we can find better results for high RH.

For ASE, we can verify that as big was WL as well as WPG we can find great values for ASE and more stable is the wood species.For Portuguese wood species we can expect the same values to the *Pinus sylvestris* and *Fagus sylvatica.* In the same way, it is expected the same difficulties, similar internal checking, up-scaling, hardness mainly at Eucalyptus.With this study of mainly physical properties it is possible predict that the appropriate modification process for Portuguese species will be FW or AC, for the reduction of EMC for high RH and high values of ASE.

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TMT-Façade panels; Product Performance and Application

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Keywords: 3-layer boards, coating, durability, hardwood TMT, substructure, wooden façade system

ABSTRACT

As one of the leading producers of heat treated hardwood, our costumers are always interested in new applications for TMT. Some of the main technical advantages of TMT are the rising durability and the reduction of swelling and shrinking. These advantages are very useful in the outdoor use and so we were able to develop a wooden façade-system. One of the main **U**nique **S**elling **P**roposition is a complete solution and so our system is consisting out of four main components:

1. aluminium substructure
2. three-layer board out of TMT (ash forte)
3. UV-lacquer coating (solvent free)
4. installation- and constructional engineering service (CAD-drawings, static)

The substructure is able to settle the differences of walls and is easy to install. It is possible, to install insulation material between the substructure, too. All three layers of the panels are made out of heat treated ash, so the panel is very homogeneous. The UV-lacquer is environmental friendly, without harmful solvent and worked up in an industrial process under well-defined terms. For an easy and fast installation on site, all panels are predrilled at the attachment point, so you have only to fix the hanger.

INTRODUCTION

Mitteramskogler GmbH is an Austrian hard wood sawmill, which was funded in 1954 by Herta Mitteramskogler. In 2000 the development of the heat treatment processes started and in 2002 the first heat treatment chamber was built. Current we have four heat treatment chambers with a treatment capacity of 10,000 m³/a.

At the beginning we have made some basic research on TMT for different wood species. For the different TMT processes it was necessary to establish the physical and chemical properties.

During the process the properties are changed. The new properties are basically:

1. rising durability (partly durability class one)
2. reduced swelling and shrinking
3. darker colour than untreated

Durability

The rising of durability is depending on the used process. In the following table is a short overview about the different classes.

Table 1: Durability classes of Mirako TMT according EN 350-2

Wood species	**Durability class**	
	untreated	heat treated
Beech (forte) / Fagus silvatica	5	**1**
Ash (mezzo exterior) / Fraxinus excelsior	5	**1 - 2**
Larch Heartwood / Larix decidua	3…4	-
Red Meranti / Shorea negrosensis	2…4	-
Teak / Tectona grandis L.f.	1…3	-

Swelling and shrinking

The swelling and shrinking is, depending on the treatment and wood species, reduced up to 50%. If the swelling and shrinking of wood is reduced in such a high dimension new application areas are possible.

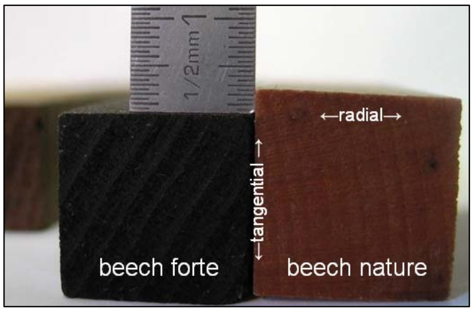

Figure 1: Differences in swelling and shrinking of beech

Darker colour

By increasing thermal treatment the wood colour gets darker. The colour is uniform over the whole width. Figure 2 shows the difference possibilities by varying treatment temperature.

Figure 2: Darker colour with rising treatment, by left birch, ash, beech and poplar

PRODUCT

After we made some basic research on TMT we had the knowledge to start the development of engineered products. In the project Nanowood, which was funded by the European Commission, the first deliverables were presented. Together with strong partners was a façade system, based on TMT was developed. The main parts of the system were the following:

1. Three-layer board out of TMT (ash forte)
2. invisible aluminium substructure
3. UV-lacquer coating (solvent free)
4. installation- and constructional engineering service (CAD-drawings, static)

Three-layer board

For the façade we are using the wood species ash, with the treatment forte. The panel is built-on three layers of TMT. The gluing is according the standard DIN 68705 suited for outdoor use. The panels have a thickness of 21 mm. The gluing of three layer boards is according to the standard EN 13354, Solid wood panels- Bonding quality- Test method, separated into three classes (SWP1, 2, 3). For the outdoor use, the highest class, SWP 3, is necessary. After many tests with different glues we have found a useful MUF-system which fulfilled the requirements.

Figure 3: Three-layer panel out of TMT

Lacquer-system

The surface gives the panel the colour and is a protection against climatic influence like water or solar irradiation. We have tested six different systems from six different manufacturers how well they are working on TMT. In the test, only environmentally friendly, water-based systems were tested. The actual system was painted four times on both sides. The application was done in an industrial process under well defined conditions, so removing influence of weather as on-site. The additional advantage is that the angle has the double lacquer thickness, so the protection is higher at that area.

Substructure

The substructure is invisible, so fixing material like screws does not damage the lacquer-system on the front. The substructure is able to equalize tolerances up to 170 mm. With a maximum distance of 210 mm from the wall to the substructure it is possible to use a thick insulation material.

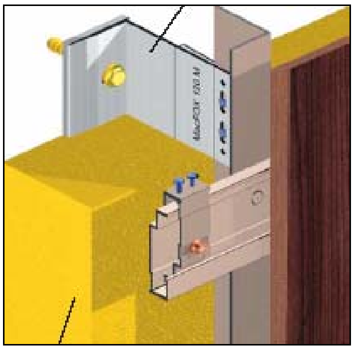

Figure 4: Substructure (Euro Fox)

Fixing material

To fix a panel on a substructure, appropriate fixing material is necessary.
The use of stainless steel screws in the outdoor area is required. On the other hand the screw-in depth must be fourfold panel thickness.

The holding force of mechanical systems like screws were from 0.9 kN – 1.16 kN. The exact value depended on the wood species and the treatment program.

Installation- and constructional engineering service (CAD-drawings, static)

The single panels were predrilled on the backside, so it was very easy to fix the hanger. With an adjusting screw it was possible to level the panels up and down, if they have small tolerances in the high. Our service package includes carrying out structural analysis and drawing up the installation plans. We also provide a comprehensive service for planners as detailed drawings and specification clauses.

Figure 7: Office Façade at Mitteramskogler

Thermal Modification of Beech (*Fagus sylvatica* L.) containing Red Heartwood

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Keywords: *Fagus sylvatica* L., mechanical properties, MIR, NIR, red heartwood, thermal modification, wood colour

ABSTRACT

For the European Beech wood resource the inhomogeneous discoloration of red heartwood is very common. By means of thermal treatment it was possible to align the colours of white and red heartwood but significant differences of mechanical properties of white and red heartwood occurred which are not typical for untreated heartwood types. Infrared analyses provided an indication for a different degree of deacetylation and lignin degradation in red and white heartwood due to thermal treatment.

INTRODUCTION

For the European Beech wood resource the inhomogeneous discoloration of red heartwood is very common. Up to now, red heartwood significantly restricts the log quality of beech stems and end products and therefore leads to severe economic losses. By means of thermal treatment it was possible to align the colours of white and red heartwood (Stingl *et al.* 2006) which could increase the yield of Beech containing red heartwood and products thereof. Whilst it is generally known that the mechanical properties of white and red heartwood do not differ significantly, distinct differences of mechanical properties could be found after thermal treatment (Hansmann and Stingl 2007). In this study an infrared analysis was performed to identify the chemical background of this phenomenon.

EXPERIMENTAL

The basic material was conventionally dried native Beech wood, with a red heartwood portion of 40 % to 60 %. The wood was modified in different treatment grades, at constant high temperature and durations of 4, 8 and 16 hours. After the treatment the modified wood was stored in a standard climate (65 % humidity, 20 °C) for one month until constant weight. Defect free samples were prepared according to the standards for mechanical testing on which also the infrared analyses were performed.

FT-MIR spectra were recorded in DRIFT mode on a Bruker Equinox 55. 32 scans per spectrum were taken with a resolution of 2 cm^{-1}. Each DRIFT spectrum was transformed into an absorption spectrum with the help of the Kubela-Munk theory. The CO_2 band was removed. The baseline was corrected using the rubber band method. A 17 points smoothing filter was applied and the spectra were min-max normalised in the region between 1190 cm^{-1} and 850 cm^{-1}.

FT-NIR spectra were recorded on a Bruker Equinox 55 equipped with a NIR fibre-optic probe measuring the diffuse reflected light from a spot of 4 mm diameter. The spectra were collected in the wavenumber range between 11000 cm^{-1} and 4000 cm^{-1} with a spectral resolution of 4 cm^{-1}.To reduce the background noise 100 scans per spectrum were averaged. Each anatomical direction of the specimens was measured five times and the average spectrum was used for further investigations. For the post spectroscopic data treatment OPUS Quant 6.0 (Bruker Optik GmbH; Ettlingen, Germany) was used. PCA was conducted with the Unscrambler 9.6 (Camo Process AS; Oslo, Norway) software package.

RESULTS AND DISCUSSION

During thermal treatment the wood components are on the one hand partially degraded, on the other hand new linkages are build up. A lot of work has already been done to elucidate the complex reactions occurring during the treatment process (Sandermann and Augustin 1963 & 1964, Weiland and Guyonnet 2003, Yildiz and Gümüskaya 2007).

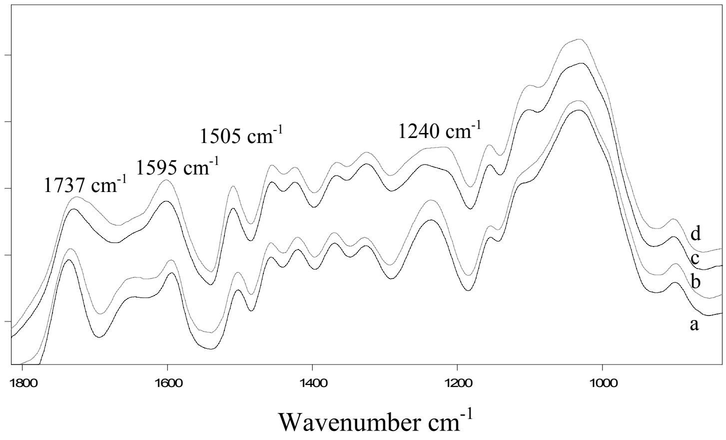

Figure 1: Fingerprint region of the MIR spectra of untreated a) white and b) red and thermal treated (16h) c) white and d) red beech heartwood (no absorbance scale is given because the spectra were shifted parallel to the wavenumber axis)

The comparison of MIR spectra in the fingerprint region between 1800 cm^{-1} and 800 cm^{-1} of untreated white and red heartwood samples with treated ones for 16 hours (Figure 1) showed evident differences which could be assigned to changes in the hemicelluloses and lignin structure. It is well known that the thermal treatment of wood results in the formation of acetic acid originating from the acetyl groups of hemicelluloses (Kollmann and Fengel 1965, Fengel and Wegener 1989). During the heat treatment the band at 1737 cm^{-1} (C=O stretching vibrations in acetic acid esters) decreases and shifts to lower wavenumbers (1727 cm^{-1}) which could be due to the formation of new carbonyl functions (Fengel and Wegener 1989). The deacetylation of the polyoses can also be followed at the band around 1240 cm^{-1} resembling syringylring and C-O stretching vibrations in lignin and xylan respectively (Faix 1991, Pandey and Pitman 2003). At higher temperatures and long treatment times lignin is also going to be degraded and modified (Kollmann and Fengel 1965). The shift of the “lignin” bands at 1505 cm^{-1} and 1595 cm^{-1} is already described in literature (Schwanninger and Hinterstoisser 2002, Schwanninger *et al.*

2003) and is caused by the formation of linkages between the aromatic rings and the increasing percentage of C=C bonds.

Almost no differences in the spectra of untreated white and red heartwood could be observed except a more pronounced shoulder at 1100 cm^{-1} for the white heartwood. After thermal treatment differences between the heartwood specimens around 1737 cm^{-1} and 1240 cm^{-1} could be detected indicating differences in the degradation of hemicelluloses which are mainly responsible for the swelling and shrinking behaviour.

In the NIR spectra a baseline shift to higher wave numbers with the proceeding duration of the thermal treatment corresponding to the darker colour of the samples could be observed (data not shown). The thermal treatment could also be followed in the second derivative mode of the NIR spectra (Figure 2). Most obvious is the decrease of the band at 5800 cm^{-1} (first overtone of CH stretching vibrations) resembling the deacetylation of xylan and the increase of the band around 5950 cm^{-1} (“lignin” band; first overtone of aromatic skeletal CH stretching vibrations).

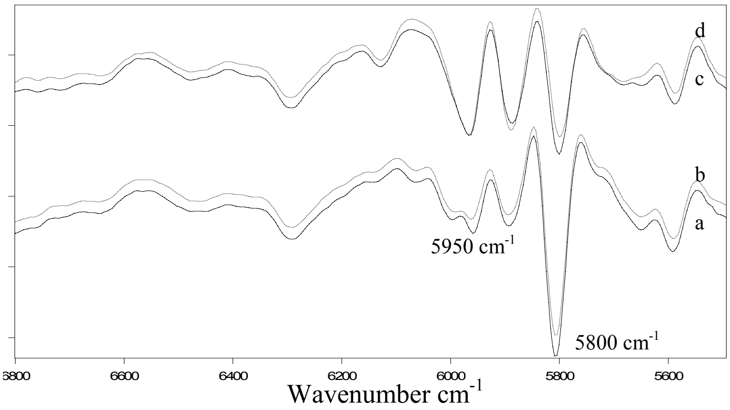

Figure 2: NIR spectra of untreated a) white and b) red and thermal treated (16h) c) white and d) red beech heartwood in the 2nd derivative mode (no absorbance scale is given because the spectra were shifted parallel to the wavenumber axis)

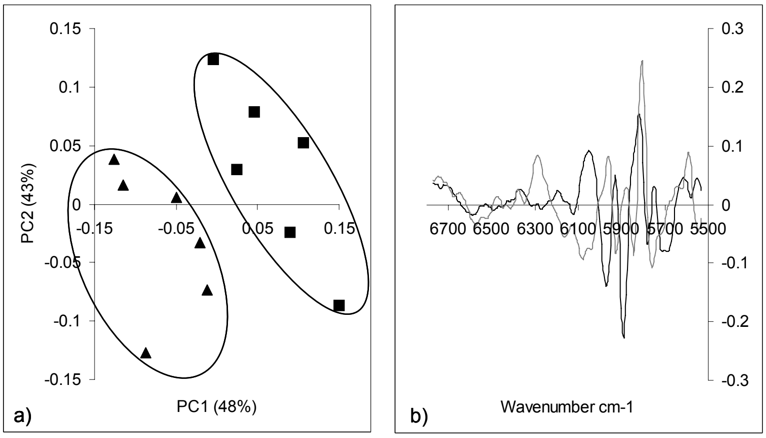

Figure 3: a) Sores plot PC1-PC2 of the NIR spectra (6800cm^{-1}– 5500cm^{-1}) in second derivative mode: red (■) and white (▲) heartwood after thermal treatment; b) The corresponding loadings to the scores plot: ▬ PC1; ▬ PC2

To enhance the differences and find clusters the NIR spectra in the second derivative mode in the range from 6800 cm^{-1} to 5500 cm^{-1} of thermal treated white and red beech heartwood were subjected to a PCA. Figure 3 shows the projection of the first two PCs (91 % of the data variance is modelled by PC1 and PC2). Two very broad clusters could be found demonstrating a high variability within the clusters. Regarding the corresponding score plots PC1 is influenced by the lignin bands and PC2 is affected by the band at 5800 cm^{-1} corresponding to the acetyl group of the hemicelluloses.

CONCLUSIONS

Effects observed in the physical data of thermal treated white and red beech heartwood might be caused by a different degree of deacetylation and lignin degradation. To prove this fact and to find a reason for this behaviour more wet chemical analyses have to be carried out.

ACKNOWLEDGEMENTS

Financial support by Mitteramskolger GmbH (Gaflenz, Austria; http://www.mitteramskogler.at) is gratefully acknowledged.

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Stellac®Technology and Equipment for Thermal Modification of Wood

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Keywords: Process control, technology for thermal modification, quality of thermally modified wood

ABSTRACT

The process for Stellac® modification of wood takes approximately 24 hours depending on dimensions of the timber, initial moisture content and the wood species. Different Stellac®Wood thermal modification levels are achieved depending on temperature in the heat peak, varying from 190 °C to 250 °C. These levels indicate certain durability classes and end use classes according to the EN standards. Stellac equipment for thermal modification of wood are delivered in flexible units. Thermal modification of wood requires heating energy which can be produced with various alternatives. Also water and/or water steam is needed in each phase of modification. A factor resulting into a fluent process of a thermal modification plant is additionally the choice for other equipment, for example traverse rail systems for moving wood loads and sticking and stacking machinery.

INTRODUCTION

The aim of this presentation is to clarify the basics of Stellac® thermal modification technology of wood other issues needed to ensure a controlled process from raw material to high quality heat treated wood.

STELLAC®TECHNOLOGY FOR THERMAL MODIFICATION OF WOOD

Stellac®Process

The Stellac process for thermal modification of wood takes place in high temperatures in a special air tight stainless steel kiln. The wood load is first piled into a package and moved to kiln on rails. The process inside the Stellac® kiln consists of several steps (Figure 1).

At first there is a phase of initial heating where temperature inside the kiln is fast raised to 100 °C. The second phase of the process is pre-conditioning where all the tension in the wood is released, the wood is prepared for the heat peak and the moisture content of wood brought to almost 0%. Raw material can be green or pre-dried when starting the process. The actual Stellac® modification phase takes only 2 - 4 hours when the temperature rises to maximum 250 °C. After-conditioning and cooling adjust the final moisture content of the wood to the desired level and release the tensions caused by the heat peak.

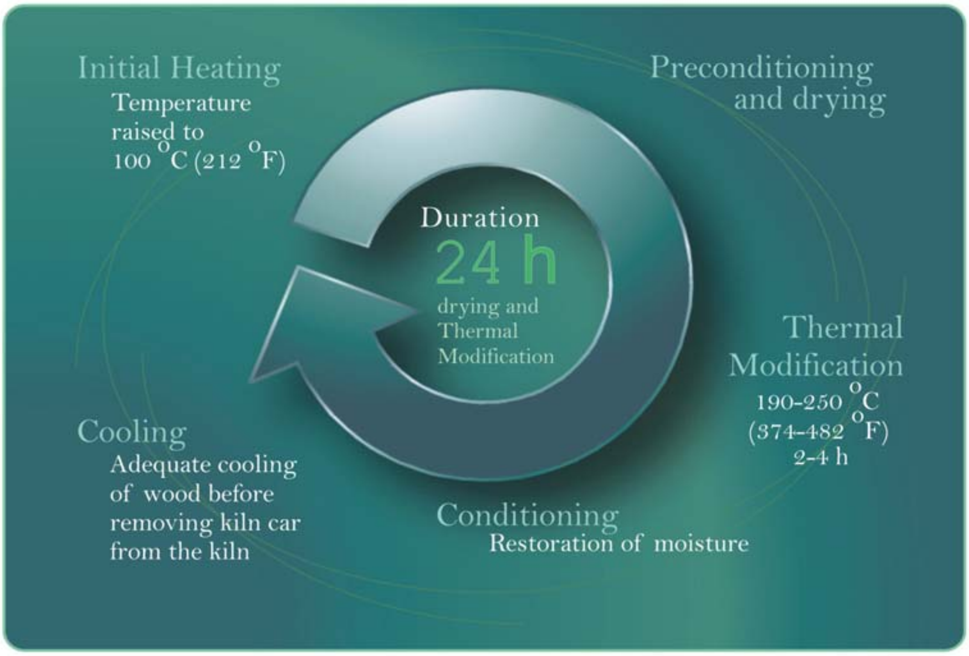

Figure 1: Stellac®Process definition

Highly sophisticated process automation in each phase of the process ensures that the chemical and physical properties of modified wood meet the quality requirements and can be repeated from load to load. One of the most critical issues in the process is air flow. With optimal air flow even the thicker dimensions (> 50 mm) of wood, be it fresh or kiln dried, can be thermally modified in a reasonable time and a high quality of material achieved.

Stellac®Wood Classification and the Quality of Raw Material and Stellac®Wood

Due to the challenging Stellac modification process for each treatment batch only one wood species in equal dimensions and moisture content can be chosen. Moreover different wood species have for example different fibre lengths and are different in annual growth, wood cells, wood pores or the number of chemical components. Raw or kiln dried wood going to a kiln load must be of same thickness, the widths and lengths can vary. Different dimensions from logs to thin parquet layers can be modified. Stellac has tested over 120 wood species in laboratory and each of them has been successfully modified.

In comparison to Finnish Thermowood Association's classification Thermo-S and Thermo-D, Stellac has distinguished the classification a bit further by having 5 treatment levels. Stellac levels of modification are labeled T5, T4, D3, D2 and D1 according to the European Union standards for solid wood durability (EN 350-1) and use in Hazard Classes (EN460). The lower levels of modification are denoted with the letter T (treatment). These levels T5 and T4 only slightly darken the wood and tend to increase surface hardness – these levels are good for indoor usage, for example cabinets, paneling and flooring. Levels D3, D2 and D1 stand for durability (levels of durability against molds, fungi and weather conditions) and are preferable in outdoor usage such as garden furniture, decking or outdoor paneling.

Special quality instructions for raw material and for thermally modified Stellac$^{®}$Wood guide the producers. The quality of raw material has a significant effect on the quality of the thermally modified wood product. In principle, all wood species can be modified. There is no need for additional sorting of the raw material for Stellac modification unless there are some special requirements for the end product. In other words the quality is saw falling (qualities excluding the lowest class and black fully dead knots). With regard to the success of thermal modification, the wood's initial moisture content is an important factor in Stellac process. Practically the treatment can be undertaken with either green or dried wood, but the moisture content has to be equal in the wood load to be treated.

The quality of Stellac thermally modified wood is measured with European Wood Drying Group's recommendation (Table 1). Wood quality is measured in terms of surface and inner cracks, moisture variation and tension. Stellac gives a guarantee value for its customers for annual capacity in the specific quality class, being at least Q (quality). Additionally the colour of thermally modified wood can be measured and guarantee values set.

Table 1: Allowable defects in difference dried lumber quality classes as recommended by the European Drying Group

	E (Excellent)	**Q (Quality)**	**S (Standard)**	**H (Reject)**
Surface cracks Crack length	5%	15%	25%	>25%
Inner cracks Less than 0.5mm	5%	10%	15%	>15%
Inner cracks More than 0.5mm	2.5%	5%	10%	>10%
Tension, mm Width 100 mm	1 mm	2 mm	3 mm	>3 mm
Average MC	±10%	±20%	±30%	>30%
MC gradient ½ - 1/6	20%	30%	40%	>40%

Note: The timber is inspected and the quality class is defined before and after the treatment. To fulfil the requirements of each quality class, 90% of the results must be inside the abovementioned limits.

Stellac Equipment for Thermal Modification

The load space of one Stellac kiln can be 6 - 120 m^3 which equals to 1000 - 20 000 m^3 annual production. A plant can be built up as a flexible entity of several treatment units.

Heating energy is needed for warming up the kiln and for producing steam. Energy can be produced with fuel oil, gas, solid fuels like waste wood or with direct electric heating. The method of producing heating energy can be chosen and designed according to the most economical and convenient way. When a boiler is used for producing the heating energy, the transfer of heat from boiler to the kiln can be done with thermo-oil or steam. Process steam can be produced by an electrically heated steam generator or in a steam generator connected to another heating source like a waste wood boiler.

Figure 2: Installation of a 12 m^3 Stellac Kiln

Other equipment in the wood heat treatment plant are for example traverse rail systems and sticking and stacking machinery to assure fluent logistics of the wood material at the plant. Stellac has solutions for cleaning the process gases evaporating during the heat treatment process.

CONCLUSIONS

Stellac provides all the needed equipment to ensure an optimal process for wood thermal modification. This results in high quality thermally modified timber for the different end uses both indoors and outdoors.

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Moldable Wood Flour by Benzylation

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Keywords: Benzylation, viscous modulus, damping factor, glass transition temperature, moldable wood

ABSTRACT

The effects of chemical modification of wood flour on the moldability of this material were examined. Pine wood fibre was chemically modified with benzyl chloride under alkaline conditions at various mole ratios of benzyl chloride to wood hydroxyl groups (ratio = 1-4) at different reaction time (2-8 h). The extent of benzylation was assessed by weight gain and FTIR spectroscopy. FTIR spectroscopy revealed the reduction of wood hydroxyl group bands, an increase in aromatic bands, a reduction in cellulose crystallinity, and an increase in aryl and alkyl ether bands, which were consistent with etherification. The thermal properties of the benzylated wood fibre were assessed by differential scanning calorimetry (DSC) and dynamic rheometry. The results from DSC were consistent with data from rheometry. Results have also shown that the benzylated wood thermal transition temperature can be manipulated by the extent of benzylation.

INTRODUCTION

In recent years, polymer composite reinforced with natural fibres have attracted considerable interest because of characteristics like low density and light weight, high specific strength and modulus. However, plastic is an expensive and nondegradable material. Therefore, there is an opportunity to develop a natural fibre-based composite material without the use of a resin system. Melt processing of man made materials (metal, plastic, and glass) are commonly used to manufacture products. As the most widely used renewable natural material, wood cannot be melted and molded directly. The lack of thermoplasticity of wood is attributed to three main causes (Shiraishi 1991): (i) cellulose in wood has a 50%~70% crystalline structure, (ii) lignin has a three-dimensional molecular structure with high molecular weight components, and (iii) the main components of wood are linked by chemical bonds. Cellulose has the highest soften temperature among the wood polymeric components, which is about 240 °C (Dwan *et al.* 1987). Cellulose properties are due to its strong inter and intra-chain hydrogen bonds. With substitution of hydroxyl group in cellulose molecule with non-polar groups, thermoplasticity is introduced to cellulose (Sereshti *et al.* 2003). Chemically modified wood can be applied for the preparation of films, sheets and molded products. Furthermore, other materials have been prepared from wood that have been modified with unsaturated substituents to form cured plastic-like wooden boards (Shiraishi 1991). The objective of this project is to generate totally wood-based extrudable and/or moldable composite materials without the need for synthetic resins. In the present work, pine wood fibre was benzylated to produce thermoplastic-like material and the resulting materials characterized.

EXPERIMENTAL

Materials and Methods

Wood fibre (pine, 100 mesh, American Wood Fibres) was dichloromethane extracted prior to use. Extractives free wood fibre (5 g) was pre-treated with 10N NaOH (20 mL) for 1h to aid in swelling. The slurry was then transferred into a flask containing benzyl chloride (6.9-27.6 mL) and the reaction was carried at 110 ºC for 2-8 h with continuous stirring (Hon and Ou 1989) (Figure 1). Different ratios (1 to 4) of benzylchloride to wood fibre hydroxyl groups were examined. The modified wood fibre was collected by filtration and exhaustively washed with water and then with ethanol to remove any residuals. The final product (light yellow in colour) was vacuum dried at 40 °C to determine yields.

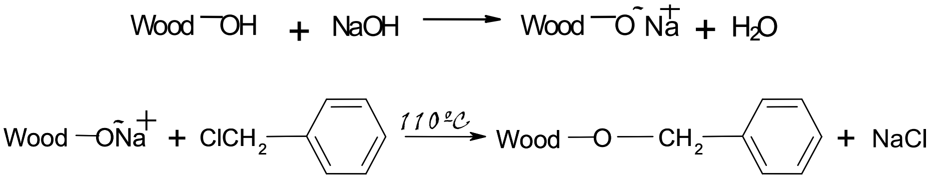

Figure 1.: General reaction scheme for the etherification of wood fibre in a 2-step process

FTIR spectra were obtained on original and benzylated substrates in the attenuated total reflectance (ATR) mode on an Avatar 370 spectrometer (ThermoNicolet). Benzylation was evidenced by changes of functional group and cellulose crystallinity. Differential scanning calorimetry (DSC) was performed to study thermal properties of benzylated wood fibre. The wood fibres were annealed at 100 ˚C for 4 h prior to analysis (TA 2980 DSC, 5mg of sample, 25-300 ˚C at 10 ˚C /min). Dynamic rheometery was performed using Bohlin CVO100 rheometer equipped with an ETC module on molded discs (2mm x 25mm dia.). A negative temperature ramp (250 to 40 ˚C at -2 ˚C /min) was performed at 1 Hz with strain of 0.02%.

RESULTS AND DISCUSSION

Weight gain analysis

The extent of wood fibre or wood constituents benzylation was assessed by weight gain. Reaction time, from 2 to 8 h, was shown to give a 2-fold increase in weight gain with a 1:1 ratio of benzyl chloride to hydroxyl group content (Figure 2). Weight gain of modified wood fibre and wood constituents was shown to increase 4-fold with an increase of the ratio of benzyl chloride to hydroxyl groups from 1 to 4 (Figure 3).

FTIR spectroscopic analysis

FTIR spectra of original wood and benzylated wood are shown in Figure 4. Benzylation of wood was evidenced (Hon and Ou 1989) (Figure 4) by: (i) a reduction in the 3450 cm^{-1} band (OH stretch) and disappearance of 670cm^{-1} peak (C-OH out-of-plane bending); (ii) appearance of bands at 695 cm^{-1} (aromatic C-C angular deformation), 736 cm^{-1} (aromatic C-H out-of-plane bending, mono-substitution);

1592-1612 cm^{-1} and 1496-1454 cm^{-1} (aromatic C-C axial deformations), 1810 cm^{-1} and 1950 cm^{-1} (out of plane deformation vibrations of adjacent hydrogens from mono-substituted aromatic rings), and 3030-3088 cm^{-1}(strong multiplet, aromatic C-H stretch) which are attributable to mono substituted benzyl rings; (iii) a decrease in the bands at 1370cm^{-1} (C-H bending), 895cm^{-1} (deformation of anomeric CH) and 670cm^{-1} (C-OH out-of-plane bending) which are assigned to crystalline cellulose; and (iv) an increase of aryl ether band (-C-O-C- stretching) at 1265cm^{-1} and alkyl ether band at 1150-1060cm^{-1} (C-O stretch from alkyl-substituted ether).

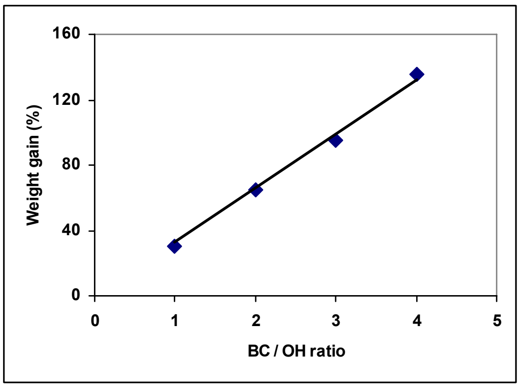

Figure 2: Graph of weight gain versus reaction time at a benzylchloride/hydroxyl group ratio of 1

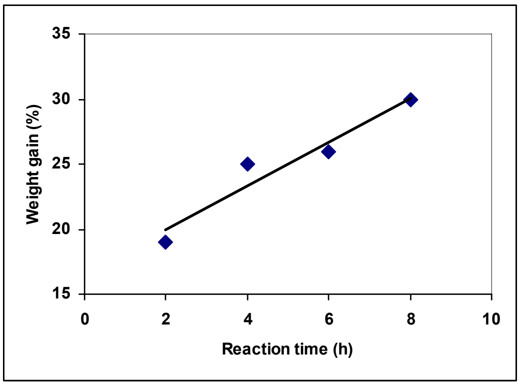

Figure 3: Graph of weight gain versus benzylchloride/hydroxyl group ratio

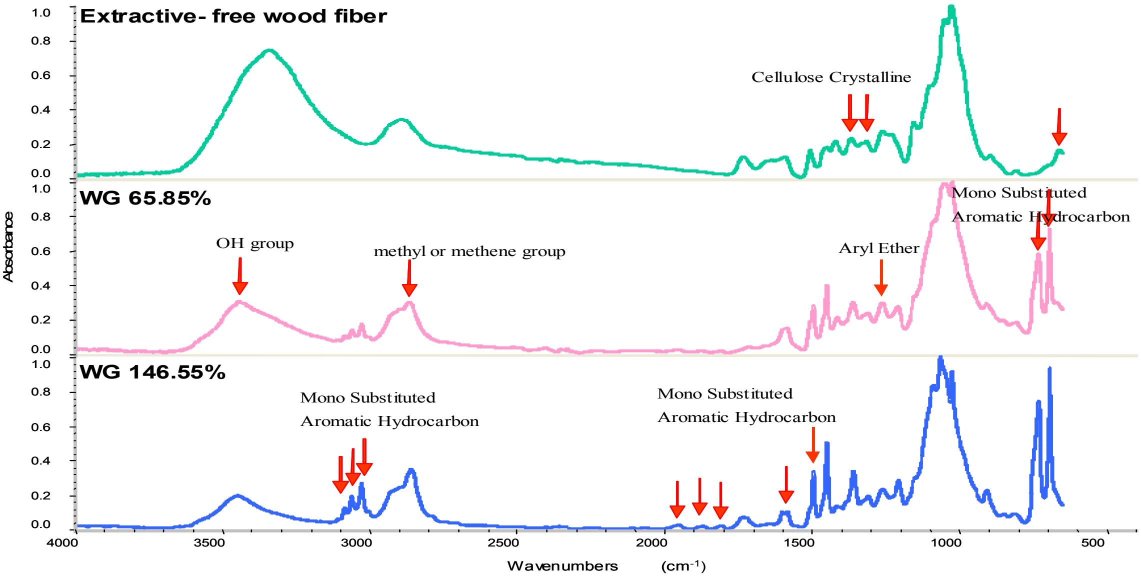

Figure 4: FTIR spectra for unmodified (top) and benzylated wood fibre at 66% WG (middle) and 147% WG (bottom).

Glass transition temperature (T_g)

From rheological data the temperature (assigned to T_g) at the tanδ maximum was shown to decrease from 171 to 90 °C as the extent of wood benzylation increased (29 to 147% WG) (Figure 5). In addition, the viscous modulus (G”) also showed a similar trend to damping factor however, the transition temperature was lower by 10-20 °C (Figure 5). The T_g values determined by DSC were similar to those obtained from the G” curves (Figure 5). The higher the %WG the lower the transition temperature (start of viscous flow based on G”). These findings are consistent with the literature (Hon and Ou 1989).

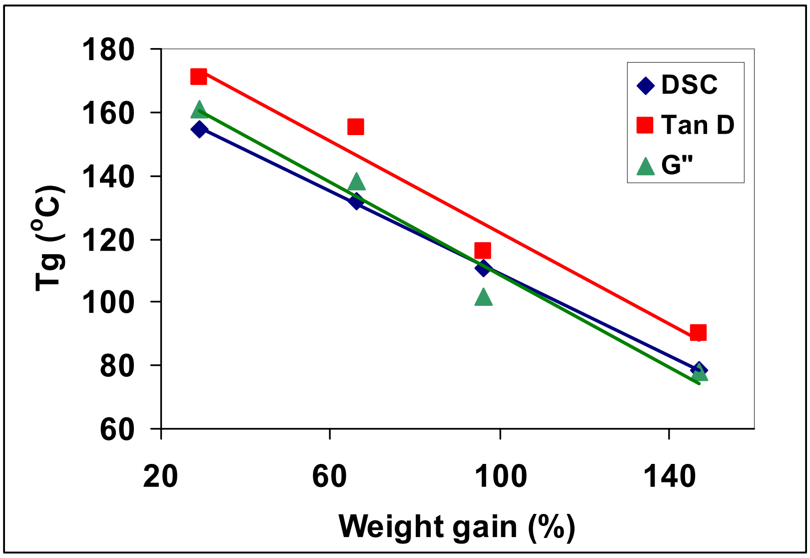

Figure 5: Graph showing the changes in transitions temperatures (Tg) as determined by DSC and rheometry as a function of weight gain.

CONCLUSIONS

Wood fibre was easily benzylated in a 2-step process. Cellulose crystallinity was shown to decrease as substitution increased. The extent of benzylation could be governed by either reaction time or ratio of benzyl chloride to wood hydroxyl content. The thermal properties (T_g and viscous flow transition) could be altered by the extent of benzylation. This process has shown the feasibility of making molded wood composites.

ACKNOWLEDGEMENTS

The project was supported by USDA-CSREES Wood Utilization Research program; Inland-Northwest Forest Products Research Consortium. The FTIR spectrometer was supported by a USDA-CSREES grant number 2005-35103-15243.

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Reduction of Volatile Organic Compounds and Odour Emissions by Enzymatic Modification of Lignin Containing Materials

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Keywords: VOC, Lignin, enzymatic modification, GC-MS, guaiacol

ABSTRACT

Products made from lignocellulosic materials emit volatile organic compounds (VOC). These emissions are caused by the thermal and chemical decomposition of the wood components and consist in particular monoterpenes, sesquiterpenes, phenols (*e.g.* guaiacol) as well as volatile aliphatic alcohols and aldehydes (*e.g.* nonanol and nonanal). Regulations and standards require a reduction of these emissions. The aim of the project was the reduction and/or elimination of VOC emissions and of unfavourable odour emitted from technical lignin or materials containing lignin. To achieve a reduction in VOC emissions a treatment with surfactants and an enzymatic modification using phenoloxidases was carried out. A technical lignin with and without natural fibres was used as raw material. The emission from the material was determined by analyses using gas chromatography combined with mass spectroscopy (GC-MS). The odour characteristics were analysed by test persons. The best results could be achieved by applying a combination of enzymatic modification and surfactant treatment. 60 % of the total emission of volatile compounds were reduced with low mass loss and without a loss in the strength of the products. The modified materials were used as a bio-plastic for the manufacture of musical instruments (*e.g.* flute, harmonica) by an injection moulding process.

INTRODUCTION

A thermoplastic processable natural biomaterial (Naegele *et al.* 1999), consisting of technical lignin and natural fibres, *e.g.* spruce fibres or cellulose, should be examined for its suitability in the music instrument making as substitution material for plastics and/or as replacement for more expensive and rare tropical wood. Technical lignins are produced in large quantities during the production of pulps and paper and are only used thermally at present. The aim was to combine the sound properties of the wood with the advantages of a thermoplastic processable plastic. During the project it became obvious that the odour characteristics of the material are very important for the application in the music instrument making. The main cause for the unfavourable odour characteristics are volatile organic compounds (VOC) of lignin and hemicellulose. Therefore, it was the aim of this investigation to reduce the amount of these substances to meet the limits of VOC emission as well as to improve the odour. Phenols of natural sources, to which lignin belongs, can be degraded or modified by phenol-oxidizing enzymes. Phenoxy radicals are produced, which can lead, depending on the process, to a degradation or a polymerization (Niku Paavola *et al.* 2001). The aim of the investigation was the reduction of VOC emissions and odour loads by the sole application of phenol-oxidizing enzymes or in combination with surfactant treatment. The project resulted in the production and testing of music instruments made form the modified material.

EXPERIMENTAL

As raw material for the investigations powdered pure technical lignin or in mixture with spruce wood fibres (*Picea abies* (L.) Karst.) were used. The substrate was first suspended in water and then the enzyme or a enzyme/surfactant mixture was added. The incubation period was approx. 60 minutes. After the termination of the treatment, low-molecular substances, enzymes and surfactants were separated from the particles by centrifugation. The dried substrate was granulated and converted to test samples by a injection moulding procedure. Odour characteristics, VOC-emission and strength characteristics of the samples were determined. The odour intensity was determined by 5 test persons and estimated within the range of 0 to 4. For the determination of the mass loss the test samples were dried at a temperature of 103°C.

The following treatment procedures were selected:

Treatment with distilled water

A mixture of powdered lignin and spruce fibres was brought in a suspension with distilled water to a 10 % solid content. The suspension was buffered at a pH of 4.5, kept at a temperature of 50 °C. After 60 min incubation time the suspension was drained with a centrifuge and hot-air dried at 60 °C. As reference, an untreated material mixture was processed.

Treatment with Laccase

In a further attempt 2.5 % Laccase (3180 U/ml, enzyme activity measured with ABTS) was added to the suspension. The treatment time was 60 minutes. The subsequent treatments and examinations were carried out as described above.

Treatment with Laccase and Tensid

In a third attempt 2.5 % Laccase and 1 % of a anionic surfactant were added to the suspension. The treatment time was also 60 minutes.

Treatment of a technical lignin with Laccase and Tensid

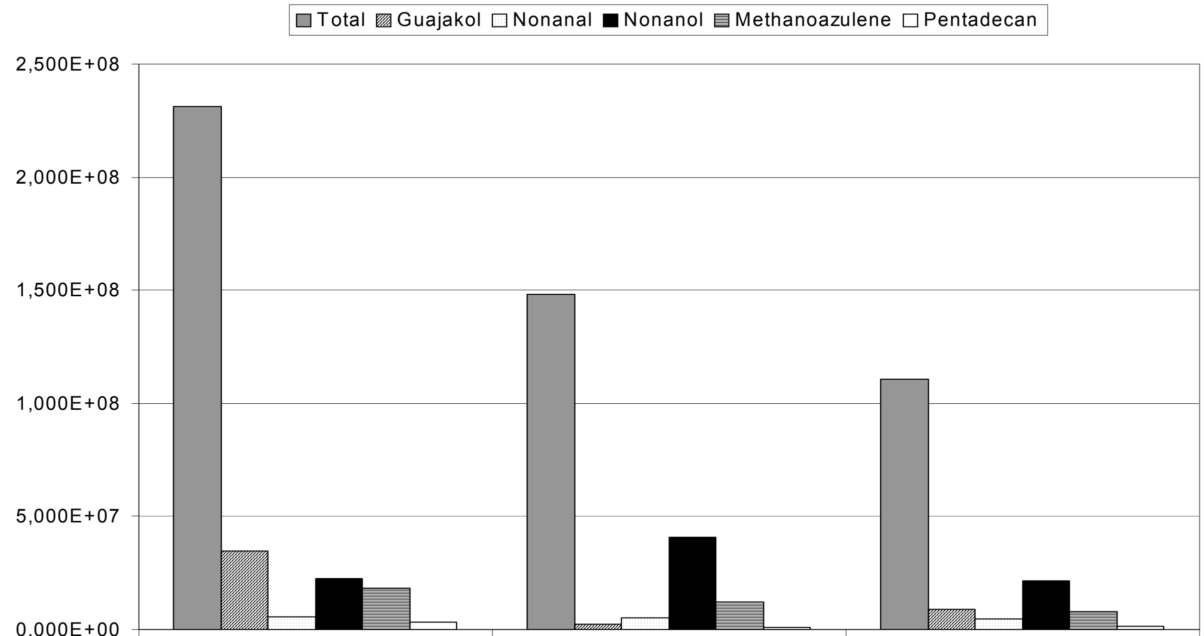
In a further attempt powdered lignin was used separately. A suspension with 14 % solid content was used and treated with 3.5 % Laccase in combination with 1 % surfactant for 60 min. After the drying cellulose fibres were added to the treated lignin powder.

Test of VOC-Emission

Test samples produced by injection moulding of the modified and non-modified materials were stored at -50 °C. Before the VOC analysis, pieces of 0.6 g were cut from those samples and put in glass vials which were gas-tight locked with septa. The samples were stored 14 days at room temperature. For taking the gas-sample, needles provided with special fibres for solid phase adsorption were brought through the septum into the gas area of the vial and remained there for 1 h. Subsequently, the samples were analyzed in a gas-chromatograph (GC) by thermal-desorption. In combination with a mass-specific detector (MSD) the emitted substances could be identified.

RESULTS AND DISCUSSION

The unmodified lignin-spruce fibre mixture mainly emitted four groups of substances which were found as a cause for the odour and VOC-emission: monoterpenes, sesquiterpenes, phenols (*e.g.* guaiacol) as well as aliphatic alcohols and aldehydes (nonanol and nonanal).



	untreated	laccase	laccase + surfactant
■ Total	231468816	148291235	110786358
▨ Guajakol	34767796	2158143	8682771
□ Nonanal	5784681	5010816	4800205
■ Nonanol	22635456	40573333	21782561
▤ Methanoazulene	18415274	12303128	8015952
□ Pentadecan	3323095	1052333	1339209

Figure 1: Emission of selected components depending on treatment of the mixed substrate

After modification, all test persons described a reduction of odour intensity of the treated samples in comparison with the raw material. The strongest odour reduction showed up with the treatment of the substrates with laccase as well as the combined use of laccase and surfactants. Here the mass loss was lower than 5 %. The VOC-analyses showed that by an enzymatic modification of the mixing substrates with laccase in combination with a surfactant treatment a reduction of up to 63 % of the entire emission could be achieved. The emission of the main components guajacol and nonanol were reduced above average. Thus the emission of guajacol decreased by up to 98 % and was for some mixtures below the detection limit. Nonanol was reduced by up to 95 %. Also with the treatment of lignin powder a decrease of the entire emission up to 80 % and the guajacol emission of 88 % was proven. Physical tests showed no negative effect for the strength properties of the test samples.

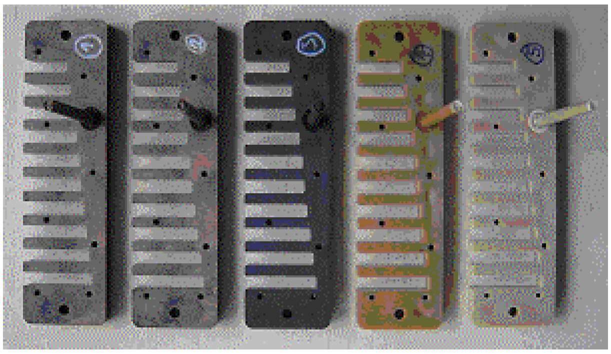


Figure 2: Injection moulded parts for harmonica (source: TecNaro GmbH)

The polymerization and/or the degradation of low-molecular phenols and odour-relevant substances by the enzymatic radical formation and subsequent reactions are regarded as the main cause for the observed effects.

CONCLUSIONS

The presented procedure shows possibilities to reduce VOC- and odour emissions of lignin-containing materials. An emission-reduced natural bio-plastic material is provided, which can be processed to materials, construction elements and products. The emission-reduced characteristics remain after the injection moulding process. The procedure can be used also for other lignocellulose materials such as strands, splinters, chips and shives .

ACKNOWLEDGEMENTS

This publication based on the results of the project Fk-03I4740, which was financially supported by the German Federal Ministry of Education and Research (BMBF).

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Rapid Thermal Modification of Wood by Electroheating

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Keywords: Dimensional stability, electroheating, ponderosa pine, thermal treatment

ABSTRACT

Thermal treatment of wood has been considered an effective method in improving properties like dimensional stability and colour. However, diminishing mechanical properties of thermally treated wood samples is a major problem. Wood colour is a property that can add significant value and increase perceived quality of wood and offers new finishing opportunities. This study was to investigate the effect of a rapid heating procedure coined "electroheating" on flexural properties, dimensional stability, and colour changes of green ponderosa pine and grand fir. Three pressure/temperature regimes (atmospheric pressure at 100 ^{o}C; 276 kPa at 158 ^{o}C; and 552 kPa at 178 ^{o}C) were evaluated. A significant drop in flexural modulus of rupture (MOR) of samples treated at 276 and 522 kPa were observed for grand fir while for ponderosa pine no significant drop in MOR was seen when compared to end-matched controls. A significantly lower tangential shrinkage was observed in grand fir samples treated at atmospheric pressure and 100 ^{o}C, when compared to its matched controls. Treated ponderosa pine showed a higher tangential shrinkage than its controls for 20 mins treatment time. An appreciable colour change throughout the wood sample was noticed on electroheated samples, which may potentially add value to the electroheated wood. It was found that electroheating at 552 kPa for 20 min resulted in average colour changes (ΔE^*_{ab}) of 27 and 35 for grand fir and ponderosa pine, respectively. Furthermore, the results show that electroheating technology can affect wood colour throughout the lumber with as little as 15 mins of treatment time.

INTRODUCTION

Considerable effort has been directed towards developing technologies that add value to enhance wood properties. Recent advancements in heat treatment technologies for wood have been shown to be both technologically and commercially viable processes to improve dimensional stability and enhance biological resistance without adding harmful additives (Hill 2006). Yet, undesirable effects, such as strength loss and increased brittleness, have hindered the widespread commercialization of thermally modified wood for various applications. It has been found that thermal treatment of wood at 180-200 °C can result in up to a 50% reduction in MOR and compression resistance (Giebeler 1983). The permanent intrinsic property change in wood due to extended high temperature treatment is a result of degradation of one or more chemical constituents of the cell wall: namely, cellulose, hemicellulose, and lignin (Fengel and Wegener 1984). However, due to a transitory change in the internal energy level of wood, the strength property will essentially return to its original value if the temperature change is rapid (Green and Evans 2001). Furthermore, these heat treatments are known to change wood colour during treatment, although colour is not a primary reason of these treatments. Electroheating is an innovative technology developed by Raztek Technologies for heating suspended solids by passing an alternating electric current at high voltage through the medium across two electrodes (www.raztek.com). Since current flow through the bulk of material is uniform heating is instantaneous and uniform. Instant heating of wood will bring forth certain advantage in terms of its short process duration and exposure. Hence, this new technology has potential applications to thermally treat wood in the green state with minimal degradation of wood properties. The aim of this study is to evaluate the effects of a mild heating treatment by electroheating on wood properties (colour, flexural and anti-swelling).

EXPERIMENTAL

Three trees each of ponderosa pine and grand fir from the University of Idaho experimental forest were felled and immediately flat sawn into lumber (244 cm x 10 cm x 2.5 cm). Clear wood specimens (40 cm) were planed. Prior to treatment, the samples were cut into 20 cm end matched (control and treated) samples. The electroheater pressure vessel was provided by Raztek, California (Figure 1). The voltage and current were regulated by modulating the A/C current to the desired output needed (typically 1000 V and 0.5-3A) from the power supply for the electroheating process. During electroheating the current, voltage, temperature and pressure inside the chamber were recorded every 2 min. The wood sample was placed in a non-conducting chamber with carbon electrode on both ends and covered with distilled water. An electrically isolated thermocouple was placed into the wood specimen. The experiments were carried out at three different pressures regimes: 0, 276 and 552 kPa. The vessel was pressurized with air. Two treatment times were evaluated (15 and 20 min). For each treatment duplicate experiments were performed. After treatment, the vessel was cooled prior to venting.

Figure 1. Photograph showing the electroheating vessel and set up

Four test specimens (200 x 50 x 13 mm) were cut from each control and treated sample and conditioned (12% MC) and the three point bending properties (MOR) determined according to ASTM D143-83. Length to thickness ratio of test specimens was 15:1. Anti-swelling measurements were performed on control and treated wood samples (50 x 30 x 8 mm). Initial dimensional measurements were done on water soaked samples (60 min vacuum plus for 24 h) and then oven dried to constant weight (104 ^{o}C for 24 h) and the dimensions re-recorded. Colour change (ΔE_{ab})

measurements were determined on control and treated samples using a StellarNet spectrometer (EP2000) with a D65 light source. The data were subjected to statistical analysis using SPSS software.

RESULTS AND DISCUSSION

The electroheating process at pressures 0, 276 and 552 kPa resulted in temperatures of 100, 158 and 178 °C, respectively within 5-8 min. Colour changes were observed upon electroheating for both ponderosa pine and grand fir (Table 1). It was observed that mild treatment (100 °C) of grand fir resulted in a major colour change.

Table 1. Mean colour change (ΔE_{ab}) values for matched sets of grand fir and ponderosa pine samples

Treatment	Grand fir (ΔE_{ab})	Ponderosa pine (ΔE_{ab})
15min, 0 kPa	70	22
20min, 0 kpa	79	19
15min, 552 kPa	24	16
20min, 552 kPa	27	35

The mean MOR for grand fir of treated wood was less than that of the controls and only the higher pressure and longer treatment times resulted in significant differences (Table 2). Thus, electroheating of grand fir had a negative impact with respect to MOR due to wood degradation. However, no statistical differences were observed for mean MOR values for treated ponderosa pine when compared to matched controls (Table 1), except for 100 °C electroheated sample which gave an improvement in MOR. Therefore electroheating of ponderosa pine has no significant impact on its flexural strength properties with respect to MOR. Statistical analysis identified the presence of a highly significant interaction effects on MOR were species, treatment time and pressure.

Table 2. Mean MOR values for matched sets of grand fir and ponderosa pine samples

Treatment	**MOR (MPa) [%CoV]**	
	Grand fir	**Ponderosa pine**
15min, 0 kPa	72.5 [18]	76.4 [13]*
Control	74.0 [22]	67.4 [21]
15min, 276 kPa	67.0 [25]	53.5 [16]
Control	65.4 [12]	57.4 [13]
15min, 552 kPa	53.5 [27]*	62.9 [23]
Control	60.0 [21]	62.7 [23]
20min, 0 kPa	63.7 [22]	65.1 [12]
Control	68.1 [18]	63.3 [13]
20min, 276 kPa	59.4 [25] *	62.0 [22]
Control	67.6 [24]	67.3 [18]
20min, 552 kPa	58.3 [21]*	72.2 [19]
Control	67.1 [13]	66.8 [22]

** pair T-test results are considered statistically significant at 95% confidence interval*

Grand fir showed a tangential shrinkage between 7.2 to 8.3% and ponderosa pine showed shrinkage of 4.7 to 5.3% (Figure 2). A small improvement in dimensional stability of electroheated grand fir samples at 100 °C.

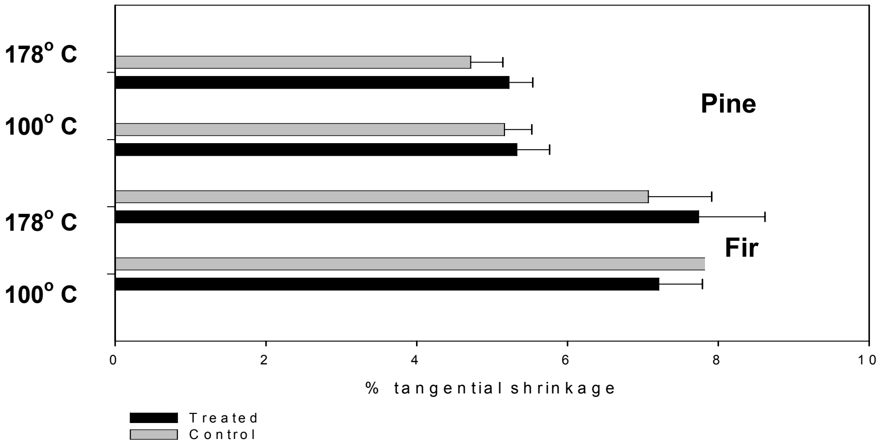

Figure 2: Mean shrinkage values matched sets of grand fir and ponderosa pine samples

CONCLUSIONS

This study shows the potential of this novel thermal process for modifying wood by electroheating. No changes in mean MOR of grand fir samples were shown at low to moderate treatment regimes however; at the higher temperature a reduction in MOR was seen. While for ponderosa pine, no changes in MOR were observed after electroheating. No significant changes in anti-swelling of electroheated grand fir and ponderosa pine were observed. Interaction effect of time, pressure, and species were found to have significant impact on MOR. An appreciable colour change was observed after electroheating wood and this process has the potential to add value to wood as an alternative to staining. This preliminary study shows the potential to enhance wood properties. However, further studies are required to expand the range of processing variables such as time, pressure, temperature, wood species, electrolytes, *etc.* to fully explore the potential of electroheating in wood based products.

ACKNOWLEDGEMENTS

This project was supported by the USDA-CSREES Wood Utilization Research program; Inland-Northwest Forest Products Research Consortium. The electroheater vessel was donated by David Reznik (Raztek Technologies, CA).

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Ponderosa Pine Wood Enhancement by Resin Treatment

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Keywords: Density, dimensional stability, hardness, ponderosa pine, treated wood

ABSTRACT

This study is aimed at adding value to small diameter ponderosa pine by enhancing its properties for several solid wood markets. A series of experiments were carried out to enhance dimensional stability and hardness of lumber by impregnating a low molecular weight urea-formaldehyde (UF) resin system followed by a curing step. The impregnation process included a short vacuum/pressure cycle followed by curing at 110 °C. The yields, density, hardness and anti-swelling properties were determined relative to matched controls. The treated pine samples were shown to have improved anti-swelling and hardness properties relative to controls. The samples were also characterized by colorimetry, FTIR spectroscopy and microscopy. This process shows potential for raising the value and uses of low value ponderosa pine.

INTRODUCTION

Small diameter ponderosa pine is ubiquitous in the western U.S. and is perceived as low value due to its low density and mechanical properties. Therefore, there is a need to transform ponderosa pine into value added products. Over the past 30 years, considerable effort has been given to developing technologies that produce more environmentally benign wood-based products. Many of these technologies add value through the modification and/or enhancement of various wood properties (Hill 2006). Various wood-polymer composite have been investigated to improve the dimensional stability of wood and these have involved either bulking of wood cell walls or filling of lumen by resin impregnation and *in-situ* polymerization. Polymerization occurs *via* thermal curing in the presence of a catalyst. Several researchers (Gsöls *et al.* 2003; Hill 2006) have demonstrated good dimensional stability behaviour on treated wood. Durability and dimensional stability tests also show good performance attributes on treated wood and is mainly dependent on resin loading. This study aims to determine the effects of urea-formaldehyde (UF) resin treatment on ponderosa pine to enhance its properties (density, hardness, anti-swelling, and colour).

EXPERIMENTAL

Ponderosa pine trees (230-300 mm DBH) were felled from the University of Idaho experimental forest and rip sawn into dimensioned lumber (50 mm x 50 mm), kiln dried at 80 °C until a target moisture content of 12%. The dried lumber was planned and cut to 300 mm lengths and further cut in half to obtain end-matched control and sample specimens. Each wood treatment was performed using 5 wood specimens (epoxy-resin end sealed and of known weight and dimensions). The samples were submerged in a UF resin solution (50% solids content; GP-63A16) and subjected to a vacuum cycle (-85 kPa) for 30 min followed by a pressure cycle (860 kPa) for 20, 40, 60 or 120 min in a custom built pressure treatment vessel. Once treated, excess surface resin was removed and the wet weight gain measured. The treated samples were then cured in a forced air oven (110 ^{o}C) for 24 h, cooled and the dry weight and dimensions recorded. Hardness measurements were recorded in accordance with ASTM D143-83 using an Instron universal testing machine (5500R) and Bluehill v2 software package. Anti-swelling measurements were performed on control and treated wood samples (45 mm x 45 mm x 50 mm). Initial dimensional measurements were done on conditioned samples (12% MC), then soaked in water (after a 60 min vacuum cycle) for 24 h and the dimensions re-recorded, and finally the samples were then oven dried to constant weight (104 ^{o}C for 24 h) and the dimensions re-recorded. Colour change (ΔE_{ab}) measurements were determined on control and treated samples using a StellarNet spectrometer (EP2000) with a D65 light source [CIE, 1986]. Chemical changes were monitored by Fourier transform infrared (FTIR) spectroscopy using a Avatar 370 spectrometer in the attenuated total reflectance mode. Microscopy was performed on a confocal Raman microscope (WITec CRM200) with excitation at 785 nm.

RESULTS AND DISCUSSION

The dry weight gains of the UF treated wood samples as a function of pressure cycle time is shown in Figure 1 and range between 43 and 132 %. The result shows that longer pressure cycle times resulted in increased weight gains. A slight colour change, ΔE_{ab} = 6.8, was observed after UF treatment (as compared to controls) and this discoloration is most likely due to exposure to heat. Ponderosa pine had an average density of 366 kg/m^3 and upon treatment had an average density of 700 kg/m^3. Data shows a relationship between weight gain and treated wood density (Figure 1).

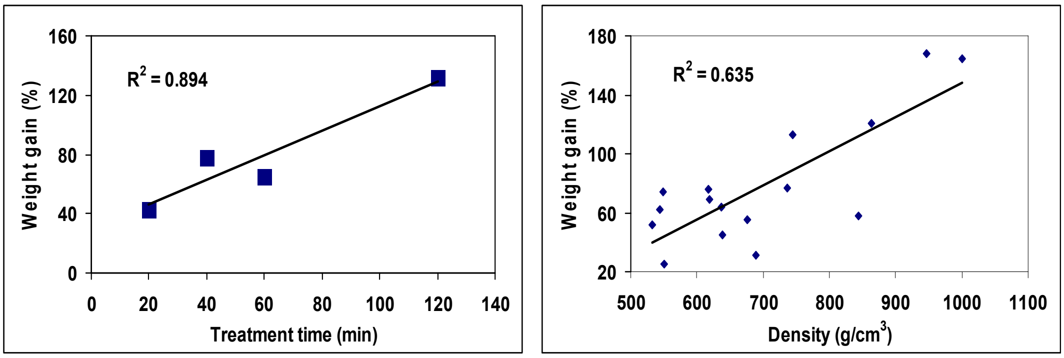

Figure 1: Graphs of weight gains of UF treated pine versus (left) pressure treatment time and (right) treated pine density.

Average hardness values for ponderosa pine and UF treated pine were respectively, 2.4 and 4.2 kN. The aim was to obtain a hardness value of flooring grade white oak at 5.3 kN. Data analysis revealed a relationship between density and hardness values for both treated and control samples (Figure 2). UF treatment of ponderosa pine resulted in a 33% and 23% improvements in the anti-swelling properties relative to controls (4.0% and 3.7%) respectively, in the tangential and radial directions.

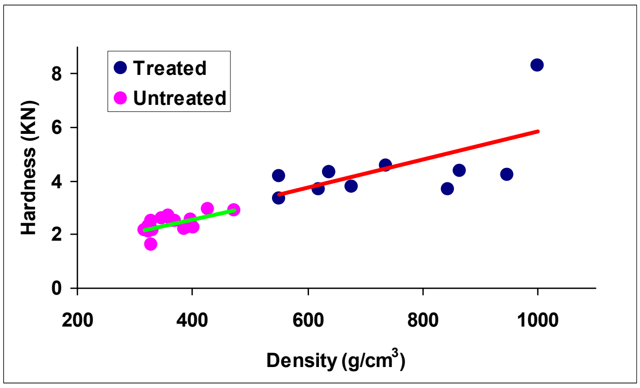

Figure 2: Graph showing hardness versus wood density for ponderosa pine and UF treated pine.

The control pine, UF treated pine, and cured UF resin samples were analyzed by FTIR spectroscopy to monitor functional group changes due to resin treatment (Figure 3). Untreated pine showed characteristic IR bands at 3350 cm^{-1} (O-H band), 1735 (ester carbonyl band), 1507 cm^{-1} (assigned to lignin) and 1050-1015 cm^{-1} (C-O of cellulose/hemicellulose) (Pandey 1998). Cured UF resin showed characteristic IR bands (Park et al. 2003) at 3290 cm^{-1} (N-H stretching of 1° amines), 2926 cm^{-1} (aliphatic amide); 1636 cm^{-1} and 1533cm^{-1} (-NHCONH-); 1379 cm^{-1} (=C-N or-CH-N group); 1240 cm^{-1} (C-N group); and 773 cm^{-1} (C-N_2 group). In the UF treated pine sample, peaks at 1636cm^{-1} and 1539cm^{-1} were clearly associated with the UF resin (amide). Signals at 1050-1015 cm^{-1} and 1508 cm^{-1} were assigned to cellulose/hemicellulose and lignin, respectively. These results show that wood constituents and UF resin are distinguishable by vibrational spectroscopy (FTIR and Raman) and therefore opens the opportunity to chemically image constituents by Raman spectroscopy.

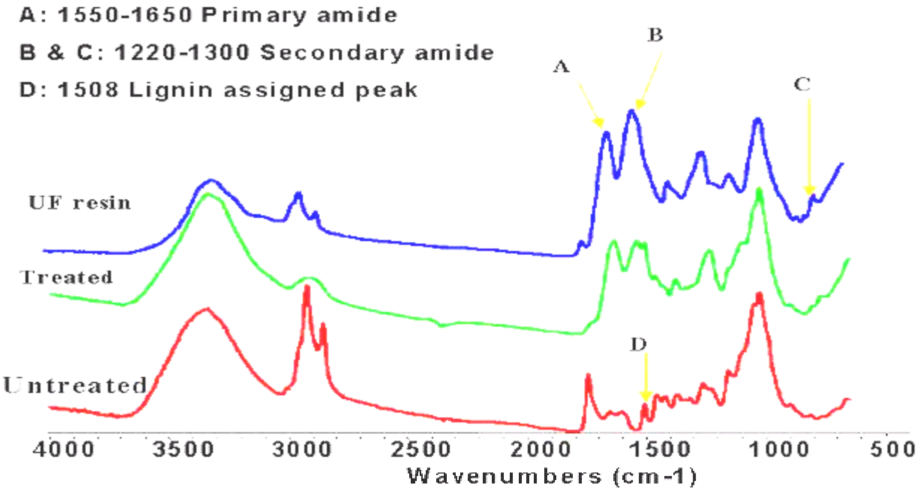

Figure 3: FTIR spectra of UF resin, UF treated pine, and untreated pine.

Figure 4 is a confocal Raman micrograph of a UF treated pine sample. To distinguish between the UF resin and wood a detailed analysis of the spectra was required. Vibrational signals between 1500 and 1700 cm^{-1} were primarily assigned to carbonyl bands in the UF resin (red, Figure 4). While the band between 900 and 1000 cm^{-1} was attributed to wood constituents (green, Figure 4). These results clearly show that the UF resin filled the wood lumens and pits.

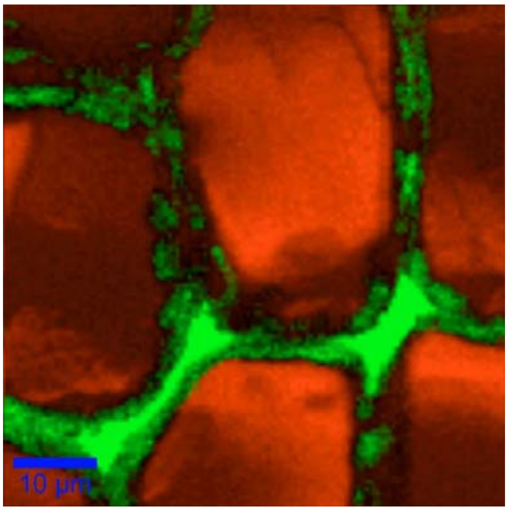

Figure 4: Confocal Raman micrograph of UF treated pine (UF resin shown darker, wood lighter)

CONCLUSIONS

Successfully developed a protocol for impregnating UF resins into ponderosa pine, which resulted in increases in density and hardness together with a reduction in anti-swelling values. A slight color change was observed upon pine treatment. Chemical mapping had revealed that densification was a result of filling the lumens with UF resin. This process offers the potential for a low cost open for wood enhancement.

ACKNOWLEDGEMENTS

This project was supported by the USDA-CSREES Wood Utilization Research program; Inland-Northwest Forest Products Research Consortium. Confocal Raman microscopy was performed by Dr. Matthias Kress at WITec, Germany.

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Wood Modification by Atmospheric Pressure Plasma Treatment

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Keywords: Accelerated curing; dielectric barrier discharge (DBD); fibreboard; particle board; plasma treatment; PVA-glue; water penetration

ABSTRACT

In this study the influence of plasma pre-treatment with a dielectric barrier discharge (DBD) at atmospheric pressure on particleboard and fibreboard is investigated by means of water penetration tests and shear strength tests. The temporal behaviour of water penetration confirmed a faster penetration of the plasma pre-treated specimens in comparison to the untreated specimens. An increase in penetration speed entails a faster curing of PVA glued specimens, which was validated by shear strength tests.

INTRODUCTION

To solve adhesion problems of wood coatings and glues the wood surface often requires certain preparation methods, *e.g.* priming or sanding. In the polymer processing industry plasma treatment has a long tradition (Kogelschatz 2003). By transferring the plasma technique to wood processing, the wood industry can benefit from improved surface characteristics as well (Lukowsky and Hora 2002, Podgorski *et al.* 2002). In this way, increased adhesion, new material combinations, abandonment of primers, reduction of glue amount or shorter drying times and hence increased productivity, performance and cost saving are conceivable. Previous investigations using the contact angle measurement to determine surface characteristics (De Meijer *et al.* 2000, Gindl *et al.* 2004) have shown that wooden materials such as fibreboards and particleboards have almost a non-polar character in the untreated state, but after plasma treatment a distinct increase of surface energy primary the polar part is apparent (Wolkenhauer *et al.* 2005, Wolkenhauer *et al.* 2007). This increased polarity of the surface is assumed to increase wetting and penetration of polar coating systems. In consequence the adhesion of coatings and glues rises and the drying times decreases. In order to prove this assumption penetration tests and shear strength tests were conducted.

EXPERIMENTAL

Plasma Set-Up

The specimens are positioned between two insulated (fused silica, thickness t=2 mm) electrodes and placed onto the lower grounded electrode. An alternating high voltage pulse generator with pulse duration t_p=2 μs, frequency f=17 kHz is connected to the upper electrode. In this unsealed set-up ambient air at room temperature is blown through the discharge gap of d=2 mm between specimen and high voltage electrode at a velocity of v=3 m s^{-1}. During the treatment a burning voltage of u=34 kV (peak) and a power dissipation of P≈60 W was measured. Measured gas temperatures of T<40 °C are likely not to cause thermal damage on heat sensitive wooden surfaces. To minimise thermal influence which could alter the surface characteristics, a treatment duration of t_t=2 s is followed by a break of 2 s. An infrared thermometer measures a mere 6-13 °C specimen surface temperature increase after t_t=60 s (Wolkenhauer *et al.* 2007).

Materials and Methods

In order to investigate decreased drying times and accelerated increase in bonding strength respectively a PVA (Poly-Vinyl-Acetate; Ponal Super 3, Henkel) glue were used. The specimens of particleboard and fibreboard were stored in a climate chamber at T=20°C and rH=50 % and cleaned with oil-free compressed air before plasma pre-treatment. The particleboard and fibreboard specimens were sawn in pieces of (40x40x3) mm³. In order to impede penetration through the sawn sides and to ensure that penetration occurs to the surface only, the sides were sealed with a 2-component-epoxy resin. The plasma treatment duration was 60 s. Before and after submergence into water the specimens were weighed and the percentage increase in weight calculated. The specimens were sawn in pieces of (70x20x3) mm³. To ensure a correct orientation of the specimen in the testing machine auxiliary blocks were glued on the end of the specimens (Figure 1). The specimens were glued with an overlapping of 20 mm so that a glued area of 400 mm² is obtained and pressed with a pressure of approx. 1 N/mm². Two minutes are needed to prepare the shear strength test so that $t_{drying} = t_{press} + 2min$. The test was carried out with a traverse speed of 20 mm/min (ZWICK Z010).

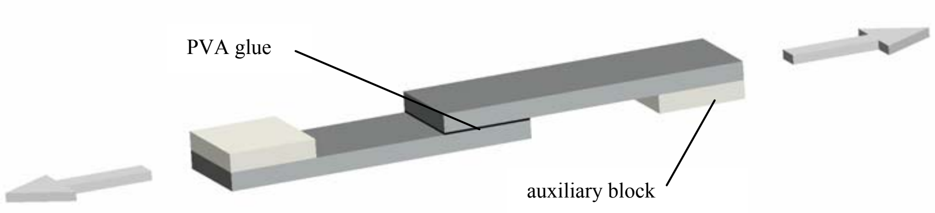

Figure 1: Schematic of specimens used for the shear strength test

RESULTS AND DISCUSSION

Water Penetration Test

In order to provide evidence for an accelerated penetration of water due to the increased surface energy after plasma pre-treatment a penetration test was carried out. The percentage increase of weight of untreated and plasma pre-treated fibreboard and particleboard after different durations submerged into water (T=20 °C) is given in Figure 2. The plasma pre-treated specimens have a faster increase in weight induced by faster water absorption (dashed lines). The grey lines depict the ratio of the percentage increase of plasma pre-treated and untreated specimens. This quotient demonstrates that plasma pre-treatment enhance water penetration in the first 20 min considerably and finally converges towards 1. This characteristic is identical for fibreboard and particleboard. Hence waterborne coatings and glues possibly will dry more rapidly caused by increased extraction rate of the water. In case of gluing this increase will cause a faster hardening and in consequence a faster increase of bonding strength.

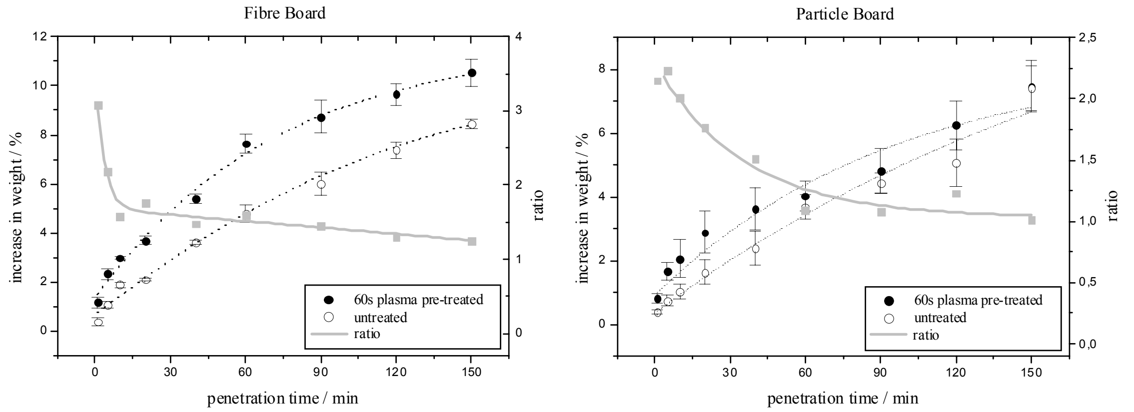

Figure 2: Percentage increase of weight (dashed lines) and the ratio (grey lines) after different submerge durations in water of untreated and 60 s plasma pre-treated fibreboard and particleboard

Shear Strength Test

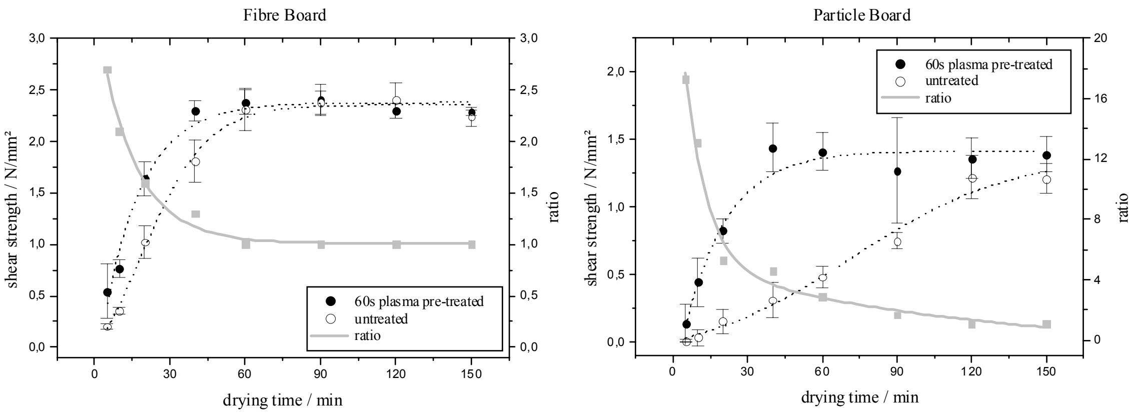

Figure 3: Shear strength (dashed lines) and the ratio (grey lines) of untreated and 60 s plasma pre-treated fibreboard and particleboard against drying time

In order to judge bonding strength a time-dependent shear strength test was carried out. Figure 3 depicts a distinct difference of untreated and plasma pre-treated specimens. Up to 40 min the plasma pre-treated fibreboards possess a higher bonding strength in all cases. At 60 min and more the glue is cured so far that cohesive fracture in the specimens occurs and no further increase in shear strength is detectable.

A similar result is observable for the particleboard where the increase in bonding strength is more pronounced. After 40 min the plasma pre-treated specimens show no further rise in shear strength whereas the untreated specimens approximate these values at 120 min. In order to reveal the differences between plasma pre-treated and untreated specimens the ratios of the shear strengths are depicted with grey lines. These ratios and the ratios of the penetration tests show a similar temporal behaviour.

It means in effect that in early stage of gluing the curing is definitely accelerated due to plasma pre-treatment.

CONCLUSIONS

This study has shown that plasma pre-treatment of fibreboards and particleboards entails faster penetration of water and the curing of PVA is accelerated in early stage of gluing due to faster extraction of water. According to these results advanced curing of water based paints and glues and penetration in impregnation processes are most likely to be expected. By utilisation of this technique increased throughput by reduction of processing times and therefore a gain in productivity in industrial applications is conceivable. Since the plasma treatment increases the surface energy of wood and other wood materials likewise, it is assumed that plasma technique can be utilised in the same way. In this way plasma pre-treatment can be a beneficial supplement for wood engineering. Further researches have to be performed to prove these assumptions.

ACKNOWLEDGEMENTS

The financial support of the German Research Foundation (DFG), contract number VI359/1 is gratefully acknowledged.

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Citric Acid – Promising Agent for Increased Biological Effectiveness of Wood

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Keywords: Chemical modification of wood, Citric acid, FTIR analyses, wood durability, *Gloeophyllum trabeum* (Pers.: Fr.), *Trametes versicolor* (L.: Fr.) Pilat.

ABSTRACT

Obtained results in improving biological durability of pine (Pinus sylvestris L.) sapwood by modification with citric acid (CA) as a representative of polycarboxylic acids are presented in this paper. Modification was performed by impregnation with 7,0 % water dilution of CA and 6,5 % sodium-hypophosphite monohydrate (SHP) followed with curing at 140 °C for 10 hours. The contribution of citric acid ester linkages was monitored with FTIR. In addition, the influence of solely thermal treatment onto durability was investigated. According to EN 113, modified and control specimens were exposed to the fungi *Gloeophyllum trabeum* and *Trametes versicolor*. Results have proved significant improvement of CA modified wood in a case of *G. trabeum*, while thermal treatment didn't have considerable influence on biological effectiveness. Chemical modification with CA showed tendency toward increasing the wood durability and as such offers promising environmentally friendly method.

INTRODUCTION

Chemical modification implicates etherification, esterification or acetylation between some chemical and OH groups of cellulose, hemicelluloses and lignin. Important parameters for successful modification by these chemical are temperature, processing time, type of catalyst and wood species. The 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) combined with an adequate catalyst reacts with cellulose OH groups forming cross-linkages between the cellulose chains. Wood modified by DMDHEU has increased dimensional stability for up to 50-60 %. Pine, Asian cedar and Beech wood modified by DMDHEU have increased durability against several basidiomycetes, although this modification doesn't comply with other nowadays preservatives (Videlov 1989; Ashaari *et al.* 1990; Militz 1993; Yusuf *et al.* 1994). Lignocellulosic materials modified by DMDHEU have a problem of formaldehyde release caused by the hydrolytic destruction of N-methylol groups at higher modification temperatures (Katovic and Soljacic 1988). Because of the formaldehyde problem, scientists are introducing new non-formaldehyde agents, such as polycarboxylic acids (PCA). By application of three-carboxylic acids, first anhydride arises from two neighboring carboxyl groups for first bond creation, and the second anhydride arise from other two neighbouring carboxyl groups. This possibility of bonding the second anhydride with hydroxyl groups of wood ensures cross-linking, bond stability and durability. Katovic *et al.* (2004), Bischof Vukusic et al. (2006) and Sefc (2006) have esterified fir and beech wood with citric acid (CA). Fir and beech wood modified with CA had significantly improved dimensional stability while compression strength parallel to the grain stayed unchanged (Sefc, 2006). Both of these chemical modifications have the same goal – to improve dimensional stability and biological durability with minimally changed mechanical properties. Preliminary results on the weight percentage gain (*WPG*) and biological durability of pine sapwood modified with CA are presented in this article.

MATERIALS AND METHODS

Home-grown pine (*Pinus sylvestris* L.) sapwood was used for this research. Sapwood lattices were sawn from the air-dried and afterwards kiln-dried pine boards. All specimens were cut, successively axially selected and marked from sapwood lattices and prepared according to EN 113 (1996) (R×T×L = 25×15×50 [±0.2 mm]) (Table 1).

Table 1: Distribution and number of specimens

Fungus species	Modification type	No. of specimens
Gloeophyllum trabeum (Pers.: Fr.) (synonym: *Lensites trabea* (Pars.) Fr.)	Modification with CA (CA-G)	8
	Control (CG)	8
	Air heat treatment (AHT-G)	8
	Control (AG)	8
Trametes versicolor (L.: Fr.) Pilat. (synonym: *Coriolus veriscolor* (Fr.) Quel.)	Modification with CA (CA-T)	8
	Control (CT)	8
	Air heat treatment (AHT-T)	8
	Control (AT)	8

Water solution of 7.0 % CA and 6.5 % SHP catalyst was prepared for the modification. Agent's concentration were previously optimized for the modification of cotton cellulose (Katovic and Bischof Vukusic, 2002) and as such applied in this research. Group of specimens was only heated at the thermo-condensation temperature (AHT) and used as a control of possible influence of temperature on biological durability. Oven-dried specimens were weighed, conditioned up to a moisture content of 12 %. The impregnation cycle consisted of a 5-minutes initial vacuum of 2 kPa, followed with impregnation with the CA+SHP solution where the same vacuum conditions were maintained for 3 h and further soaking at atmospheric pressure for 18 h. Specimens modified by CA and AHT specimens were air-dried at standard conditions for 48 h and afterwards cured at 140 °C for 10 h in oven. *WPG* of modified specimens was calculated as a ratio of difference of oven-dried mass after modification (m_2) and oven-dried mass before modification (m_1) and m_1 (1). Determination of biological durability of modified wood against *Gloeophyllum trabeum* and *Trametes versicolor* was done according to EN 113 (1996). Mass loss of specimens caused by fungal nutrition (d*m*) was calculated by dividing the difference of starting mass (m_2) and oven-dried mass of specimens after fungal nutrition (m_3) with starting mass (2).

$$WPG = \frac{m_2 - m_1}{m_1} \times 100[\%] \qquad (1) \qquad\qquad dm = \frac{m_2 - m_3}{m_2} * 100[\%] \qquad (2)$$

PerkinElmer Spectrum GX FT-IR spectrophotometer with Golden Gate attenuated total reflection (ATR) attachment and diamante crystal was used to collect the transmission spectra of grounded wooden samples. Pine sapwood samples, previously impregnated with CA and its catalyst, were treated with 0.1 M NaOH for 2 minutes. In this way ester carbonyl band can be separated from the overlapping carboxyl carbonyl band.

RESULTS AND DISCUSSION

Comparing *WPG* of 12.4 % for pine wood treated with CA with *WPG* of 17.9 % for fir wood (Sefc, 2006), it can be concluded that impregnation procedure can be improved. Pine sapwood is much more permeable than the fir sapwood which is well known on its irregular permeability. AHT specimens lost part of their mass due to the thermal degradation and their *WPG* was (-0.37 %). According to Rapp and Sailer (2001) increase of wood mass losses during oil heat treatment (OHT) increases the biological durability of OHT wood. Results of this study confirmed that there was no significant difference in biological durability between AHT and control specimens. These results indicate that significant increase of biological durability of CA-G specimens against *G. trabeum* was exclusively the result of crosslinking of CA with hydroxyl groups of pine sapwood (Figure 1a). On the contrary, no difference in d*m* against *T. versicolor* between the CA-T and C-T specimens can be determined (Figure 1b).

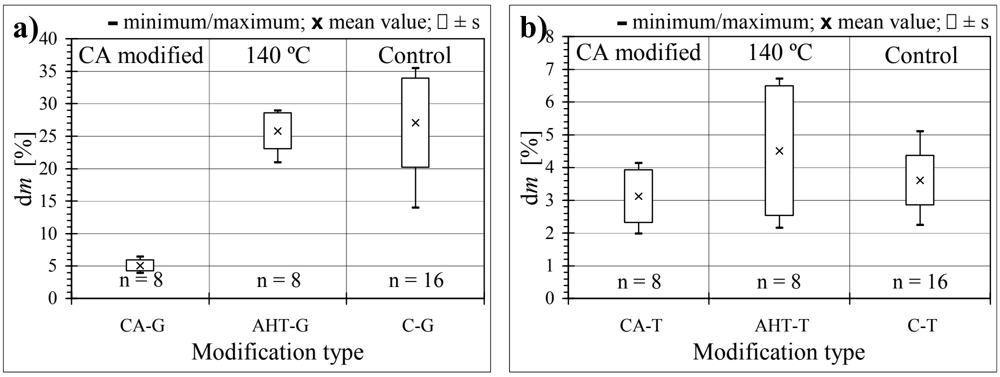

Figure 1:* *Mass loss (*d*m) of specimens after exposure to:* a) *G. trabeum, b*) *T. versicolor

Since *T. versicolor* preferably utilizes lignin, the conclusion is that CA modification did not affect lignin (no difference in d*m* between CA-T and C-T is evident). These results lead to the conclusion that the majority of CA esterifies cellulose hydroxyls. The infrared spectra of CA specimens (a and c) in which the carboxylic-carbonyl band emerges at 1718 cm^{-1} are presented in the Figure 2. CA-G and CA-T specimens showed similar intensity of carboxylic-carbonyl band at 1718 cm^{-1}, which means that both fungi did not have significant influence on ester linkages. Yang and Bakshi, (1996) found that treating cellulose fabrics esterified by a polycarboxylic acid using a 0.1 M NaOH solution converts the free carboxylic acid in the material to a carboxylate anion so that the ester carbonyl band can be measured quantitatively. Peak at 1591 cm^{-1} appears on samples treated with 0.1M NaOH (c and d) representing the unesterified free carboxylic groups.

Results showed the increase of durability against *G. trabeum* of modified pine wood for more than 500 percent in comparison to controls. Durability of CA modified pine wood (cured at 140 °C) against *G. trabeum* seemed to be very similar to the OHT pine wood at the temperatures between 180 and 200 °C (as determined by Rapp and Sailer, 2001). By increasing the *WPG* during the chemical modification biological durability also increases. It is to be expected that *WPG* will increase by optimizing parameters of wood modification with CA. Keeping that in mind, biological durability of CA modified wood could be even more improved.

CONCLUSION

Pine sapwood modified by citric acid showed significant increase of biological durability. Weight percentage gain of 12.4 % resulted with 5.3 times increase of biological durability against brown rot fungus *Gloeophyllum trabeum*. The results presented show that wood modification by CA is a promising method for improvement of wood properties. Research on the optimization of modification parameters is needed for further improvement of biological durability, dimensional stability and mechanical properties of wood.

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Colour and Wetting properties of Wood Modified by Citric Acid

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Keywords: Beech wood, fir wood, wood modification, citric acid, contact angle, colour changes

ABSTRACT

Beech and fir sapwood were modified by citric acid (CA) using sodium hypophosphite (SHP) as catalyst at 180 °C. Influence of thermal and citric acid modification of beech and fir sapwood on wetting, surface free energy and colour changes were investigated. Wetting properties and surface free energy were determined using contact angle obtained by the sessile drop method. Wetting of water on beech wood increased after modification by CA, but on fir wood wetting of water decreased after modification by CA. The total surface energy of wood obtained by the Lifshitz-van der Waals acid-base approach decreased on both wood species after modification by CA.

INTRODUCTION

Citric acid (CA) with SHP as catalyst is ecologically friendly agent for chemical modification, *i.e.* esterification of wood which takes place at temperature above 100 °C. Wood modified by citric acid showed improved dimensional stability and lowered micro tensile strength (Bischof Vukusic *et al.* 2006). The aim of this work was to estimate the influence of curing temperature and applied agent on colour change of wood surface. The exact knowledge of surface properties like wettability and surface free energy is essential for optimising gluing and coating processes. So, another aim of this study was to determine the influence of modification by CA on wettability and surface free energy of investigated woods. To distinguish the changes caused by the heat treatment itself from those caused by chemical modification treatment the wettability and surface free energy were measured also on heat treated bare wood.

EXPERIMENTAL

Wood Samples

The samples were air dried blocks of fir and beech sapwood with dimensions of 20 × 20 × 10 mm^3 (T×R×L). One group of samples were control group, the other was heat treated at 180 °C for 2 h. The third group of samples was vacuum impregnated with 7 % citric acid solutions and 6.5 % SHP as catalyst and cured by the convection method at 180 °C for 2 h.

Colour measurement

The colour of the samples was measured using a portable spectrophotometer Microflash 100 d, Datacolor *(d/8° measuring geometry, 10° standard observer, D65 standard illuminant*) with a measuring diameter of 10 mm. Two measurements were performed on radial surfaces of 10 samples. The CIE L*a*b* colour measuring system was used.

Contact angle measurement

Wettability measurement was performed by the sessile drop technique based on the observation of the profile of a drop deposited on a solid wood surface (Bogner 1991, Liptakova and Kudela 1994, Gindl *et al.* 2001). The measurements were performed only along the wood grain on radial surface of the sample using a *DataPhysics Instruments OCA 20* goniometer (optical microscope coupled to a CCD video camera). The measurements were done at 23 °C by using double distilled water, diiodomethane and formamide as test liquids. Drop volume was 2 µl. The contact angle has been determined 3 s after the pendant drop has touched the surface. The contact angle measurements were performed on control wood samples, on heated bare wood samples (180 °C) and on wood samples treated with CA+SHP solution cured at 180 °C. A total of 8 measurements were done for each wood treatment. From the values of contact angles of used liquids with known surface energies (Mohammed-Ziegler *et al.* 2004), it is possible to analyze the changes in polar-nonpolar and acidic-basic components of the surface free energy of wood using the Lifshitz-van der Waals/acid-base (LW-AB) approach.

Acidity of wood

For the approximate determination of pH-value 2 g of wood meal in 20 ml of distilled water was used. The glass vessel was strongly agitated for 5 minutes. After 2 hours the pH was measured using a combined glass electrode (after 1 minute immersion). This gave an approximate determined pH-value (Sandermann and Rotkamm 1959).

RESULTS AND DISCUSSION

Results of colour measurements are presented in Table 1. The highest discoloration was observed for CA modified fir wood samples. The overall changes in colour (**ΔE***) after heat treatment were large and similar for both wood species. The overall changes in colour (**ΔE***) after modification by CA + SHP at 180 °C were even larger.

Table 1: Results of CIE L*a*b* Color Difference

Sample	**ΔL***	**Δa***	**Δb***	**ΔC***	**ΔH***	**ΔE***
fir 180°C	-6.9	2.6	6.4	6.8	-0.8	9.8
fir 180 °C (CA+SHP)	-19.8	5.9	6.0	7.6	-3.6	21.5
beech 180 °C	-10.1	-0.3	0.9	0.8	0.6	10.2
beech 180 °C (CA+SHP)	-16.0	3.7	5.2	6.2	-1.4	17.2

Contact angles obtained with the different test liquids are presented in Table 2. Wettability of both wood species with water was generally lower after heat treatment. On the other hand, after wood modification by CA+SHP at 180 °C wettability of beech wood with water increased while of fir wood decreased.

Table 2: Contact angles obtained with different test liquids

Sample	Water	Formamide	Diiodomethane
Beech	71.4	44.9	43.4
beech 180 °C	92.8	60.1	46.9
beech 180 °C (CA+SHP)	58.6	60.0	53.9
Fir	55.6	24.2	42.9
fir 180 °C	85.5	66.2	46.5
fir 180 °C (CA+SHP)	70.3	47.6	42.2

The results of total surface free energy and its components according to Lifshitz-van der Walls model are presented in Table 3. The total surface free energies obtained for both wood species decreased after heat treatment and after modification by CA. The Lifshitz-van der Walls components dominated the surface energies for both wood species and the variations of this component between the two species were relatively small and in agreement with data from the literature (De Meijer *et al.* 2000). The Lifshitz-van der Walls components changed only slightly after both treatments, but AB component decreased significantly. The both components (acid - electron acceptor and base - electron donor) were strongly influenced by the treatments. Decrease of base component after heat treatment could be closely related to hemicelluloses degradation (Gerardin *et al.* 2007) and decrease of acid component after heat treatment could be explained by the removal of resinous acids during the thermal treatment (De Meijer *et al.* 2000). The base component of surface energy on CA+SHP modified wood surfaces strongly increased, especially on beech wood samples. At the same time the acid component of surface energy on CA modified wood surfaces strongly decreased.

Table 3: Surface free energy components of different samples

Sample	SE[1]	LW[2]	AB[3]	AC[4]	BC[5]
			mN/m		
beech	43.9	37.9	6.0	1.3	7.3
beech 180 °C	36.8	36.0	0.8	0.7	0.2
beech 180 °C (CA+SHP)	33.3	32.1	1.2	0.0	34.1
fir	51.6	38.1	13.5	3.1	14.4
fir 180 °C	36.2	36.2	0.0	0.0	5.1
fir 180 °C (CA+SHP)	43.5	38.5	5.0	0.7	9.5

[1]*Total surface energy,* [2]*Lifshitz-van der Walls component,* [3]*Acid base component,* [4]*Acid component,* [5]*Base component*

Table 4: Estimated acidity of different samples

Sample	pH-value	
	Beech	Fir
Untreated	5.32	4.65
Treated - 180 °C	4.95	4.69
Treated - 180 °C (CA+SHP)	4.51	4.20

The acidity of beech wood was greater after heat treatment which correlates to data from the literature (Kean Choon and Rofael 1990). After wood modification by CA+SHP acidity was increased even more.

CONCLUSIONS

Wood modified by CA+SHP at 180 °C showed significant colour change compared to untreated bare wood on both wood species. Total surface free energy decreased after modification on both wood species. The Lifshitz-van der Walls components changed only slightly after both treatments. The both components (acid - electron acceptor and base - electron donor) were strongly influenced by the treatments. The results obtained by contact angle measurements could be useful for optimizing adhesives and coatings for CA modified beech and fir wood.

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Acoustic Properties of Hydrothermally Modified Mulberry (*Morus alba* L.) Wood

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Keywords: Hydrothermal modification, Morus alba L., physical properties, specific Young's modulus, modulus of shearing, sound quality factor, swelling

ABSTRACT

This research was carried out to investigate influences of hydrothermal modification on musical properties of mulberry wood. Samples were prepared in sizes of 20×20×360 mm and oven dried to determine their density. Sound properties were determined by using vibration technique. Afterwards, the samples were placed in a water filled stainless steel cylinder and treated at temperatures of 100, 120 and 140 ºC for 1 and 5 hours. Treated samples were oven dried again and the measuring the density and musical properties were repeated for treated samples. Specific Young's modulus, shearing modulus, tangent δ, quality factor (Q) and density were determined before and after the treatment in oven dried samples. Water and moisture absorption and swelling were determined in untreated and treated samples. Results revealed increase in specific Young's modulus and quality factor, No significant effects on tan δ was determined. Water absorption and swelling were reduced due to the hydrothermal treatment. The hydrothermal treatment reduced slightly acoustic converting efficiency (ACE) in treated samples.

INTRODUCTION

Persian traditional instrument producers are considering the application of the heat treated wood in instrument production. They hydrothermally treat thin layers of wood sheet and use it for soundboards or resonance boards in difference instruments; such as Persian xylophone. This paper comprises a study on some physical and musical properties of the hydrothermal treatment of mulberry wood, which is used traditionally for instrument making in Iran.

EXPERIMENTAL

Test materials and treatment.

Wood specimens were cut from three different mulberry (*Morus alba* L.) trees with sizes of 20×20×360mm and air conditioned for few weeks to achieve equal moisture content. Afterwards, a stainless steel cylinder was used for treating the wood. The cylinder was filled with water and heated initially up to 100 °C. Afterwards, the specimens were placed in the reactor and its temperature was elevated according to the tests (100, 120 and 140 °C) for 1 and 5 hours. The treated specimens were oven dried for 24 h to determine density. Sixty replicate specimens were used for each experiment.

Physical properties

Some of the treated specimens were cut into sizes of 20×20×20 mm and weighed to determine the density. Dimensions of the small blocks were initially determined and soaked in water (25 °C). After 2 and 24 hours of the soaking, they were weighed and their dimensions were measured to calculate water absorption and swelling of the wood.

Acoustic properties

Flexural vibration with a free-free end condition was used to determine the specific dynamic Young's modulus (E'/ρ, E', modulus of elasticity and ρ, specific gravity) and internal friction (Q^{-1} or tan δ), shearing modulus and acoustic converting efficiency (ACE). The acoustic properties were measured at the first mode of vibration before and after the hydrothermal treatment in dried specimens with the sizes of 20×20×360 mm. Sound was recorded by a PC and a FFT analyzer software was used to analyze the frequencies. The results were analyzed statically by using a complete randomized factorial design with two factors of treatment temperature and time. Duncan test was used for comparison between the means.

RESULTS AND DISCUSSION

Table 1 shows results of the analysis of variances (ANOVA) in different determined parameters that could be influenced by the hydrothermal treatment in the mulberry wood. ANOVA showed whether the hydrothermal treatment affected a parameter in wood or not and comparison between the means based on Duncan subsets indicated grouping of the means from the smallest to the largest one. ANOVA showed that the water absorption was influenced by the temperature and duration of the treatment as well as their interactions after 2 hours of the soaking. Comparison between the means showed that elevating the temperature and also extending the treatment time reduced the water absorption in the mulberry wood. According to the Duncan subsets, the smallest water absorption determined in the treated wood at 140 °C (subset 1) and then at 120 and 100 °C (subset 2) and finally in control (untreated) wood. Temperature 20 °C was considered for untreated. Based on the treatment time, remaining wood under the noted temperatures for more than one hours had the same effects (subset 1) and reduced the water absorption in treated wood more than the untreated wood (subset 2). Soaking of the specimens for 24 hour showed that the hydrothermal treatment did not affect the water absorption in the wood. All specimens had same water absorption as the untreated wood gained. In other words, the water absorption was reduced by the elevation of the temperature and the treating time. Any increase in the absorption of the water in treated wood after 24h of soaking, might be related to leaching of the formed extractives fro hemicellulose degradation and appearance of micropores in the cell walls due to the removal of those extractives. The water absorption does not significantly indicate the dimensional stability in the wood. Mohebby and Sanaei (2005) reported appearance of small checks during the hydrothermal treatment of oriental beech wood. ANOVA was also applied for the volumetric swelling of the wood. Results showed that only the temperature affected significantly the swelling of wood after 2 hours of soaking in the water; while after 24 hours of soaking, the volumetric swelling was significantly influenced by the main effects of temperature and treatment time with no interactions between. Comparison between the means revealed that the volumetric swelling was reduced by elevation of the temperature as well as the treating time.

Table 1: Analysis of variance for applied treatments Morus alaba L.

Treatments	**ANOVA**			**Duncan Subsets**[1]						
	Temp.	**Time**	**Interaction (Time × Temp.)**	**Temperature (°C)**				**Time (hour)**		
				1	**2**	**3**	**4**	**1**	**2**	**3**
Water absorption-2h	**	**	**	140	120,100	20	-	1,5	0	-
Water absorption-24h	ns	ns	ns	140,100,120,20	-	-	-	5,1	5,0	-
Vol. Swelling-2h	**	ns	ns	140,120,100	120,100,20	-	-	1,5	0	-
Vol. Swelling-24h	**	**	ns	140	120,100	20	-	5	1	0
D_0	ns	*	ns	120,100,140	140,20	-	-	5	1,0	-
ACE	*	*	ns	140,100	100,120	20	-	1	5	0
Tan δ	ns	ns	ns	20	120,100	100,140	-	0	5,1	-
G	ns	ns	ns	100,20,120,140	-	-	-	0,5	5,1	-
Quality factor (Q)	*	ns	ns	140	100,120	20	-	1	5	0
Sp. MOE	ns	*	ns	20	100,120	140	-	0	1,5	-
Dynamic Young's MOE (E)	ns	*	ns	20,100,120	100,120,140	-	-	0,5,1	-	-

*1: Duncan subset is grouped from the smallest to the largest averages; **: Significant at 99%; *: Significant at 95%; ns: Not significant*

ANOVA showed significant effect of the treating time on the oven dry density with no significant effects of the temperature and the interactions between. A Duncan test showed, the smallest density was determined in treated wood for 5 hours (subset 1) and the largest in the treated wood for 1 hour as well as the untreated wood (subset 2). It could be expressed that the period of treatment had great effect on the density loss than the temperature. The Analysis of variance showed no significant influences of the hydrothermal treatment on tan δ. However, Duncan test could find three groups between the means as 20 °C (subset 1) with the lowest amountnt, 120 and 100 °C as the mid (subset 2) and the 100 and 140 °C as the highest amount (subset 3) of tan δ. For the treatment time, two subsets of the untreated (subset 1) as the lowest tan δ and the treated wood for 1 and 5 hours as the highest amount of tan δ (subset 2) were analyzed. In general, Duncan tests showed slight increase in tan δ due to the hydrothermal treatment. ANOVA showed that only the temperature affected quality factor. However, Duncan test determined three temperature groups as 140 °C with the lowest Q (subset 1), 100 and 120 °C as the mid amount of Q (subset 2) and 20 °C with the lowest Q (subset 3). In general it was revealed that Q was reduced by the temperature. Duncan also could determine that the treated wood at both treating time had lower Q than the untreated one. The treated wood had lower Q than the untreated one. Any loss in Q could be related to the loss of density due to the hydrothermolysis of cell wall polymers; especially the hemicelluloses. Q has an inverse relationship with the tan δ and it is also related to loss of the molecular motions in wood. Therefore, any increase in Q indicates lower molecular motions in wood. Analysis of the variance showed only significant effect of the treatment time on specific modulus of elasticity (MOE) and dynamic Young's modulus (E). Duncan test could recognize three groups of the temperatures as untreated (subset 1) for the lowest specific MOE, 100 and 120 °C as mid specific MOE (subset 2) and 140 °C as the highest specific MOE (subset 3). In general it was revealed that the elevation of the temperature could increase the specific MOE and slightly the dynamic Young's modulus (E). For the treatment time, only two groups of untreated (subset 1) and the treated (subset 2) groups were determined for the specific MOE. It was revealed that treating the wood more than 1h could affect specific MOE in wood. ANOVA revealed that the main effects of temperature and treatment time affected the ACE in mulberry wood with no interaction effects between. Concerning the Duncan results, three groups were determined for the main effect of temperature. As it is shown in Table 1, the first group with the lowest ACE was 140 and 100 °C (subset 1) and the second group was 100 and 120 °C (subset 2) as the mid ACE and the group with the highest ACE was 20 °C (subset 3). According to the results of Duncan test it could be conclude that the ACE was reduced due to elevation of the temperature. Duncan test on the main effect of treatment time also showed three groups as 1h (subset 1) with the lowest ACE, 5 h (subset 2) with the mid ACE and the untreated one (subset 3) with the highest ACE. In general it was determined that extending the treatment time reduced the ACE.

CONCLUSIONS

Results showed that the wood became water repellent and dimensionally stable due to the hydrothermal treatment. The density was diminished because of the hydrothermal effects and according to the pervious reports it could be related to depolymerization of the hemicelluloses and formation of soluble extractives and their removal from the cell wall. Consequence of the density loss was the appearance of the micropores in the cell walls and increase of the internal friction. However, the hydrothermal treatment could affects growth of the crystalline part of the cellulose and cross linkings with an improved hydrophobicity. In general, we could conclude that the hydrothermal treatment reduced the density, however due to the improved hydrophobicity and dimensional stability; sound properties became better when the wood is exposed to a humid condition.

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Microwave Modification of *Picea sitchensis* (Sitka spruce).

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Keywords: Microwave processing, permeability, radiata pine, Sitka spruce, *Torgvin, Vintorg*, wood properties, wood treatment

ABSTRACT

The microwave modification of green Sitka spruce (*Picea sitchensis*) wood structure is found to differ significantly from radiata pine (*Pinus radiata* D. Don). Radiata pine is characterised by having soft unlignified ray tissue that is easily ruptured either by pressure steam conditioning or microwave conditioning. The result is an intra-ray modification or internal rupturing of uni-seriate ray tissue. In radiata pine each tracheid is connected to ray tissue through large window pits thus providing very rapid radial pathways for liquid penetration. Microwave modification of sitka spruce is characterised by an inter-ray modification and the induction of micro-voids in the radial-longitudinal direction. This modification results in a substantial improvement in liquid penetration, but with a reduction in strength. Potentially this is a result of the physical disruption and separation of tracheids from ray tissue.

INTRODUCTION

Sitka spruce is a low density, non-durable species with low permeability because of small pit apertures between ray tissue and tracheids. Radiata pine is a medium density species, of low durability. However, it has soft, unlignified, uni-seriate ray tissue and large window pits between ray tissue and tracheids. This structure provides radiata pine sapwood with high permeability. The heartwood of radiata pine has variable permeability depending on the extent of pit aspiration, the degree of lignification of ray tissue, the amount of resin present and the conditioning that the wood has been exposed to prior to measuring permeability. Microwave conditioning, pressure-steam conditioning and high temperature drying improve the permeability of radiata pine heartwood relative to conventional kiln drying (Vinden and Torgovnikov 2000). Microwave conditioning and pressure steam conditioning tends to rupture the soft radial tissue, as well as pit membranes and facilitates the movement of resin. High temperature drying mobilises wood resin from around pit membranes. This tends to improve the flow of liquids.

An indication of the relative permeability of radiata pine heartwood is given by the percentage of cross-sectional area that is impregnated following pressure impregnation. As a rule of thumb, the heartwood of air-dried radiata pine will achieve approximately 30-35% penetration of the cross-section. Conventional kiln drying (*70/60 ^{0}C dry bulb / wet bulb depression*) will often achieve 55-65% penetration; high temperature kiln dried heartwood, (*120/70 ^{0}C dry bulb / wet bulb depression*), approximately 70-78% penetration and pressure steam conditioning (130 ^{0}C.), 80-85 % penetration. Microwave conditioning can achieve between 95-100% penetration of heartwood (Vinden and Torgovnikov 2000).

Microwave conditioning provides substantial control of the wood modification process compared to pressure steaming. However, strength loss is an inevitable consequence of both processes. Pressure steam conditioning results in a strength loss of approximately 18% MOE and 25% MOR in green timber. Strength loss following microwave conditioning varies from being statistically insignificant compared to controls, to up to 60% depending on the level of microwave conditioning applied. Vineyard posts when microwave conditioned for preservative treatment have virtually no strength loss, whereas timber that has been microwave conditioned for cross-section expansion (*Torgvin*) for subsequent *Vintorg* manufacture may lose up to 60% of its strength (Torgovnikov and Vinden 2001). This strength is restored following resin impregnation and curing.

The strength loss associated with pressure steam conditioning is thought to be due to the hydrolysis of cellulose. Pressure steam exposure times can be several hours in duration, whereas microwave conditioning takes minutes or even seconds. The strength loss associated with microwave processing is therefore more likely to arise as a result of mechanical disruption of fibres rather than hydrolysis. Much of the work associated with microwave processing has therefore focussed on characterising the physical modification of wood structure and controlling microwave modification to optimise wood permeability and minimise any associated strength loss.

Directed microwave interaction with wood can be manipulated through the design of the microwave applicator. This interaction is designed so that no hot spots arise in wood (*i.e.* concentrations of microwave energy leading to excessive modification of the wood structure or in extreme cases, charring of the wood). Efforts have also focused on the potential to modify the surfaces of timber to a depth of approximately 10 mm., rather than complete cross-section modification. This acknowledges an industry preference to achieve optimum performance at lowest cost.

The objectives of this program of research are to:

(1). Identify the anatomical changes in Sitka spruce arising from microwave modification and how these compare with the changes observed in radiata pine.

(2). Identify the strength losses associated with the microwave modification of Sitka
spruce.

(3). Identify whether surface modification of spruce can be achieved using microwave technology.

(4). Determine preservative penetration patterns following microwave modification and pressure impregnation using a light organic solvent preservative.

EXPERIMENTAL

Partially green logs of Australian grown Sitka spruce (Picea sitchensis) were sawn and dressed into 75 x 75 mm. boards at a local Victorian sawmill. Green board moisture content was calculated from the weight loss of sample biscuits taken 300 mm from the end of each board. The samples were dried at 103 ^{0}C to constant weight. For microwave modification,two 30 kW microwave generators operating at a frequency of 2.45 GHz supplied microwave energy to the timber. A box microwave applicator measuring 115 x 115 mm with radiator slots measuring 10mm x 86mm was used for the experiments. Power was applied from the top of the box applicator. In the current trials, the timber was passed through the applicator twice. In the initial microwave application the timber was orientated so that face A was exposed to irradiation. In the second pass, face B was exposed to irradiation. The objective was to contain microwave modification to the surfaces of the timber.

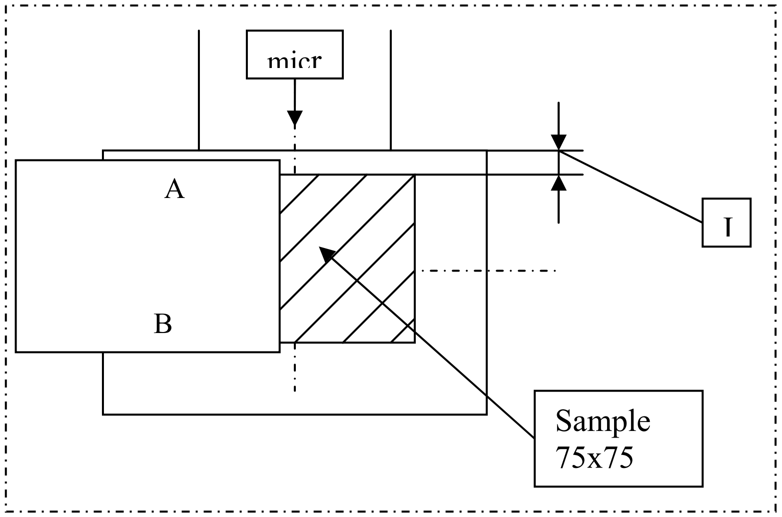

Figure8: Sample location and orientation in the box applicator

I =10mm - distance between radiator and sample surface.

Timber samples passed through the microwave applicator on a conveyor belt at speeds ranging from 10-30 mm/sec. The microwave energy applied to timber was modified according to wood moisture content determination and ranged from 26 kW for lower moisture content samples and to 44 kW for the higher moisture content samples. After microwave irradiation, timber samples measuring 1200 mm in length were end-sealed with PVA glue and then impregnated with a 2% solution of copper naphthenate in light oil. The treatment schedule comprised an initial vacuum of -85 kPa. maintained for 5 minutes followed by flooding and pressure impregnation at 300 kPa. for 10 minutes and then a final vacuum of -85kPa. maintained for 30 minutes. The total cycle time was approximately 45 minutes. Strength testing was carried out on samples measuring 75x75x1200 mm using an *Instron* strength testing machine with a three point bending rig of span 1050 mm (static bending, centre-point loading). Twenty control samples and 20 microwave irradiated and preservative treated samples were conditioned to approximately 12% moisture content prior to testing for MOE and MOR.

RESULTS AND DISCUSSION

Some substantial drying of logs had occurred prior to sawing. Moisture content determination indicated that individual boards ranged from 25 –50% moisture content. Sap-stain was prevalent in the sawn timber. Microscopic examination of Sitka spruce samples after microwave irradiation indicated that micro-void formation was very similar to that found in hardwoods rather than being characteristic of radiata pine. Microwave modification in radiata pine tends to start as an intra-ray modification where the soft radial tissue is ruptured. In Sitka spruce micro-voids tended to form at the tracheid / ray interface. If too much microwave energy was applied there tended to be expansion of the micro-voids to form visible cavities in the radial longitudinal direction. Some distortion of the cross-section was also indicated. Preservative penetration ranged from 60-100% of the total cross-section and there was a 3.5 –5 fold increase in preservative net uptake in microwave-irradiated samples compared to controls. Strength loss (MOE and MOR) was higher than anticipated (approximately 30% strength loss).

CONCLUSIONS

The samples of Sitka spruce used in these trials have probably dried to too low a moisture content to provide any conclusive analysis of the suitability of microwave modification of Sitka spruce for improved permeability. Nonetheless some very useful information has been obtained.

- The microwave modification of Sitka spruce tends to resemble that obtained with refractory hardwoods rather than radiata pine i.e. there is inter-ray modification rather than intra-ray modification.
- High standards of liquid penetration into Sitka spruce are possible following microwave modification, ranging from 60 to 100 %.
- It is possible to achieve surface microwave modification of Sitka spruce. Further work is needed to perfect the microwave applicator design.
- Further work is needed to perfect a process control system for Sitka spruce. Research needs to focus on the combined influence of microwave schedules and preservative treatment schedules on preservative penetration on the one hand and strength loss on the other.
- Strength testing indicates a surprising strength loss in microwave-irradiated samples compared to controls. It should be possible to improve this aspect of microwave processing of Sitka spruce. The strength loss in microwave conditioned samples is almost certainly attributable to excess microwave exposure, perhaps due to the low moisture content of samples prior to irradiation. Most of the wood modification in spruce comprises very fine incising barely visible to the naked eye. The best opportunity for improving the utility of spruce may involve resin impregnation of microwave-irradiated wood.

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Modification of Domestic Timbers by Impregnation Using Supercritical Carbon Dioxide - Preliminary Results

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Keywords: Impregnation, modification, silicon compounds, supercritical carbon dioxide, wood

ABSTRACT

Domestic timbers are often not suited for construction trade applications because of low dimensional stability, low durability or low mechanical strength and are squeezed out of the market by tropical lumbers or other materials (such as plastics or metals). Therefore it is of considerable interest to improve their characteristic properties in order to open new potential markets. One possibility to accomplish this aim is the impregnation of wood with silicon containing substances such as silane based nanosols or silicones. During this process, the silicon compounds are deposited in the lumina and the cell walls causing a change of wood properties. In many important domestic wood species, particularly in spruce wood, conventional procedures using water or organic solvents achieve only superficial penetration with depths of only a few millimetres. Thus a solvent is needed which enables the complete penetration of the wood without damaging its structure. It was previously shown that in a kind of reverse process (extraction), supercritical carbon dioxide (sc-CO_2) was suited to the removal of harmful wood preservatives such as DDT or lindane from the total volume of wooden art treasures without impairing the wood structure (Jelen *et al.*2003). Based on these results and the experience in using scCO_2 as solvent for ordinary wood preservatives, the idea was developed that scCO_2 is also suited to solve and transport silicon containing impregnants. Thus, the objective of the investigations described herein is to verify the suitability of scCO_2 as solvent for the impregnation process and to study the achieved improvement of wood properties. The solubility of various silicones and nanosols were determined in laboratory plants at the Ruhr-University Bochum to specify the conditions for the impregnation experiments in a small technical plant (V= 5 L) at Fraunhofer UMSICHT. The process was designed to have no damage of the wood structure. The resulting impregnated wood specimens were characterized at the University of Goettingen. Preliminary results are: reduced water uptake and verifying the complete penetration of the specimen.

INTRODUCTION

Carbon dioxide becomes a supercritical fluid at a temperature above 32 °C and a pressure exceeding 7.2 MPa (72 bar), a physical state which has the properties of both gas and liquid (Figure 1). Under pressures from 100 to 400 bar) and at temperatures of 35 to 70 °C, supercritical carbon dioxide can be used as a solvent for non-polar substances, and is applied in established processes like the recovery of natural flavours or the decaffeination of coffee and tea. The process temperature does not need to exceed 40 °C. Because of its low surface tension, supercritical CO_2 intrudes deeply into the wood without causing swelling.

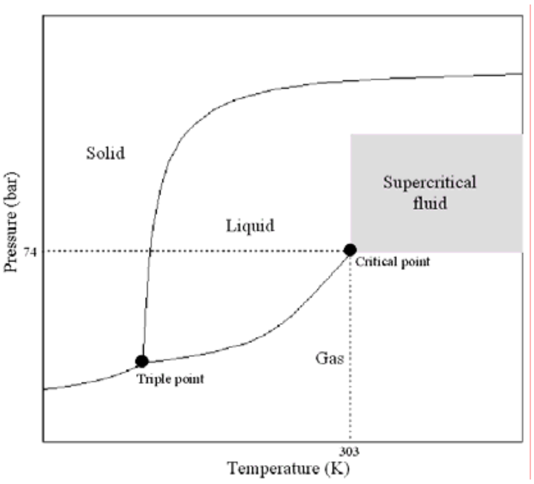

Figure 1: Phase behaviour of carbon dioxide

Any mechanical damage is minimised if care is taken during the pressure build-up and release during the impregnation. Another advantage of supercritical carbon dioxide is that it becomes a gas after pressure release and there is no solvent left in the wood.

EXPERIMENTAL

For impregnation with supercritical carbon dioxide at Fraunhofer UMSICHT the pilot plant station depicted (Figure 2).

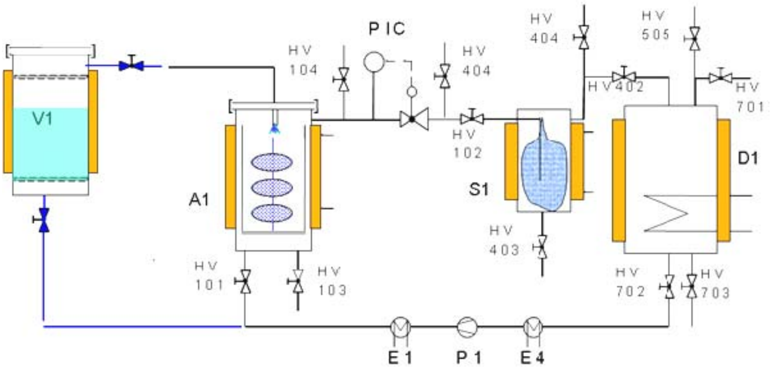

Figure 2: Pilot plant station for the impregnation with supercritical carbon dioxide used at Fraunhofer UMSICHT

First the carbon dioxide from the storage tank was cooled to allow liquefaction (in readiness for pumping through the system). After that the carbon dioxide was heated to up to 40 °C and pressurised up to 15 to 20 MPa. It then flowed through the vessel with the impregnation agent to get into vessel A1. When the impregnation time was over, the pilot plant station was depressurised and the impregnation agent was precipitated on and in the wood.

RESULTS AND DISCUSSION

There are two main results. It could be shown that silica was precipitated in the cell wall of the wood and that the supercritical carbon dioxide completely penetrated through the wood (Figure 3).

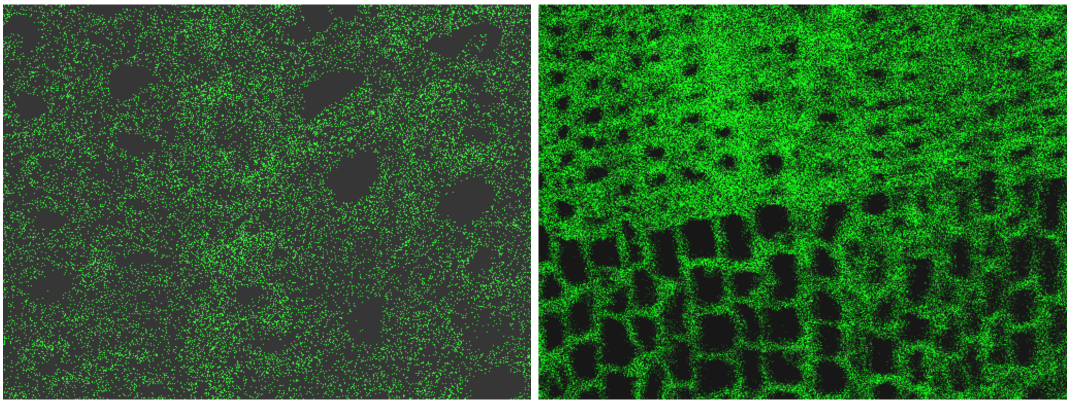
A B

Figure 3: SEM-EDX Si-mapping images:: Silicone oil in Scots pine with SCC treatment (A); Silicone oil M50 in Scots pine with vacuum pressure treatment(B)

In comparison to the vacuum-pressure method the amount of uptake was less. But the intrusion of supercritical carbon dioxide is very good with shorter time of impregnation. As an example of intrusion depth the longitudinal intrusion of a silicone oil in Scots pine is shown (Figure 4).

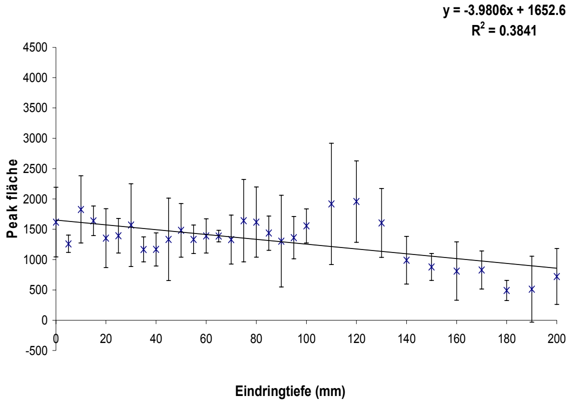

Figure 4: Intrusion depth of silicon oil in scots pine.

The intrusion was measured at University of Goettingen with FT-IR-spectroscopy.

CONCLUSIONS

It could be shown, as preliminary result, that impregnation of wood with supercritical carbon dioxide is suitable. But the impregnation process has to be revised. Further investigations are still running.

ACKNOWLEDGEMENTS

This project was financially supported by the Fachagentur Nachwachsende Rohstoffe, Guelzow, Germany. UHDE High pressure technology made the pilot plant station available.

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Session 6: Modification and Wood Protection

Modifying the Wood Protection Industry

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Keywords: Wood preservation, wood modification

ABSTRACT

During the last two decades, the media's use of pseudoscience has created a social climate in which traditional wood preservation has moved from being seen as a tool in the armoury of the conservationist, to being seen as a potentially dangerous source of pollution. Objectively, such a shift might have been expected to herald a mass movement away from traditional preservation, towards procedures which 'pseudoscientists' perceive as more benign. However, to date the volume of wood modified on a serious industrial, commercial, scale remains inconsequentially small, and is mired in ambivalence as to its fitness for purpose. Is this a reflection of the intrinsic inadequacy of the technology available for wood modification, or is it a failure of our industry to see the real potential for the techniques we have?

IF WE'RE SO GOOD, WHY AREN'T WE RICH?

The exploitation by man, of wood as a structural material must be older than any civilisation on our planet. Utilisation of strategies to enhance wood's performance is equally old and has included Noah coating his ark with tar, and the ancient Romans tenderly rubbing oil of nard onto the multitudinous endowments of wooden carvings of the goddess Diana.

The two enhancements which have been most widely used, and for the longest time, are 'painting' to protect wood from water ingress and UV degradation, and impregnation with fungitoxic and entotoxic chemicals to enhance resistance to degradation by fungi and insects respectively.

Comparatively more recently, and particularly during the last decade, persistent and growing attention has been paid to 'wood modification', in which wood properties are changed without the involvement of chemicals which the man-in-the-street perceives as harmful. To date however, only trivial quantities of wood are modified in this way on an industrial scale.

Why is it that 'wood modification' has, for over a century promised so much and yet has still not resulted in any processes serving significant volume markets?

Perhaps one factor is that every wood-modification researcher seems to have the ambition to be the alchemists of the wood protection world; they have the desire to develop a process which is all things to all men – which makes wood totally resistant to decay whilst remaining biodegradable – which makes wood harder, and yet easier to work – which makes wood fully water repellent whilst remaining over-coatable with 'water-based' paints.

Millions of years of evolution have given us the structural softwood lumber with which we have all grown up since kindergarten. It is unrealistic - even naive – to expect to enhance every property simultaneously, whilst not adversely affecting anything.

A negative effect of this alchemy ambition is that it can lead to reluctance to acknowledge when adverse effects are encountered, and this impacts negatively on credibility of our industry in the eyes of would (not) be consumers. Many end uses would benefit from enhancement of just one property, and are not much affected by moderate alteration of others. For example, in service performance of wooden architraves is enhanced by hardening. Within limits it is not greatly relevant if the hardening process reduces the MOE or MOR as these last two are not critical to the performance of architrave.

In order to bring products to the market, we would do better to focus on a desired enhancement, and be less reticent about any downsides. For instance acetylated timber is stable to moisture but has a persistent odour of acetic acid. To pretend otherwise is disingenuous. Better far to acknowledge this, and to have an open debate with potential users about its implications. Similarly, the strength of heat-treated timber is lower than that of untreated timber, and there are quality control issues. Public confidence in the product will be better won by openly acknowledging these factors, and addressing their implications, than by near denial of their existence.

A third barrier to the forward march of wood modification has sometimes been researchers and product champions being out of tune with their potential customers. A currently available wood hardening system was at one stage offered as a wood densifying process. It is hard to think of any industrial wood user who would view high wood density as a ‘must have’ wood feature. If (s)he were to identify high density as desirable, it is almost certain to be an unconscious association between density and the fact that this property is generally proportional to hardness. However, failure to appreciate the real benefit of a process can lead to its key features not being clearly identified to potential users.

Perhaps the greatest unacknowledged barrier to significant commercialisation of wood modifying technologies lies in the nature of timber itself. At conferences such as this, we sagely consider the relative performance of different systems when tested on straight grained, knot free, permeable, sapwood, paying little regard to the fact that, on an industrial scale, such material is little more than a hypothetical concept. Heartwood-free European redwood, for instance, is almost impossible to obtain in anything but very small dimensions and (impermeable) heartwood is very often much less amenable to modification that the (permeable) sapwood.

One of the objectives of the alchemists was, of course, to turn base metals into gold. The big attraction, and the big drawback, of gold is that it is very expensive. So it is with modified wood. Turning wood into a universal wonder material will also make it prohibitively expensive. Technologies exist which do wonderful things to wood but not as a cost which can be borne by any but the most highly specialised end uses. It is therefore important to maintain a realistic and level-headed balance between the cost of a processing a piece of wood, and the value which the market will attach to it.

Better surely to achieve modest property enhancement at a cost which can be recovered, than to offer the market something which everyone thinks they want but which no one can afford.

If ‘wood modification’ is to establish itself as a significant, profit generating industrial activity which promotes, supports and expands the use of timber as a premium construction material, we need to both fragment and refocus our activities. We must fragment them to the extent that we need to be much more specific about the benefit we are seeking that a process should deliver. Having done that, we need to focus on developing certain processes to maximise hardness, other processes to improve coating performance, others to improve moisture stability and so on. Having ‘fragmented’ and ‘refocused’ our efforts in this way, we should adopt European whitewood and the heartwood of European redwood as our test substrates and seek to take products to market only when they have been optimised for use on the timber which is commercially and locally available in Europe.

Following its millions of years of evolution, wood is an outstanding structural material. To seek to modify it to enhance even one property is a God-like ambition. To hope to enhance all its properties simultaneously, and to adversely affect none, is as naïve as it is arrogant. However, achieving a targeted enhancement, whilst maintaining adverse effects within reasonable bounds, is a much more realistic and affordable goal, adoption of which carries a much higher probability of success.

Bioswitch: a Versatile Release on Command System for Wood Protection

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Keywords: Blue stain fungi, moulds, release on command

ABSTRACT

Wood, as a biological material, is subject to a broad range of breakdown mechanisms. In most applications it is desired to maintain a number of its functions for a long time, usually many years. This can be for structural reasons, but also for aesthetical reasons. In the classical wood preservation, an excess of biocides is brought into the wood to protect it against attack by microorganisms. In modern wood protection systems, such as wood modification, biocides are often excluded. The consequence of this is, that the wood remains vulnerable to growth of *e.g.* algae, moulds or blue stain fungi, even if the wood itself is not decayed. The use of traditional formulations of fungicides to overcome this problem gives raise to problems with the fixation. The chemical groups playing a role in fixation processes are changed by the modification process. Therefore unconventional solutions need to be used. Three years ago, within TNO, a research program was initiated aiming at the development of new delivery concept. The goal was to develop a system which is able to deliver an active ingredient such as biocides only when it is needed: a so-called “release on command”. The technology is nicknamed Bioswitch. The research has lead to a matrix concept constituting biopolymers such as polysaccharides and proteins which are cross linked into a three dimensional network. By giving the matrix specific properties it can be made sensitive to specific breakdown mechanisms. External stimuli such as temperature, pH, humidity or the presence of certain metabolites can cause a reaction of the Bioswitch particles. In this way a true “release on command” system is accomplished. The result of the release on command property is a more efficient use of active ingredients such as biocides and it also prevents premature leakage of biocides. In fact the functionality will only be released when it is needed. The Bioswitch particles are at micrometer level and are therefore expected to act mainly on the woods surface especially in refractory species. Ongoing work is tailoring the Bioswitch to different types of blue stain fungi and moulds.

INTRODUCTION

Wood modification in general is getting a “foot on the ground”. Some of the heat treatments are already on the market for more than 10 years now. Chemical modification processes are also emerging on the market. With the opening of their wood acetylation factory earlier this year, Titan Wood with Accoya® has made a major contribution to this side of the field where WPT with Kebony® and Visorwood® and BASF with Belmadur® were already active with respectively furfurylated and DMDHEU treated wood.

All of the above mentioned modifications fulfil the definition of wood modification that the European Network on Wood Modification formulated several years ago. One of the points in this definition was that the "mode of action" should not be toxicity to wood decaying organisms. This divides wood preservation from wood modification. In general, with wood modification developments, there is a focus on decay and a lack of focus on wood staining organisms.

All of the wood modification processes that are on the market today have their own merits and have found their place on the market because of it. There are many reasons to prefer wood to other materials for use in a specific application. In many cases the aesthetic qualities are extremely important. People like the appearance of wood. Although recognised by market people, this is generally underestimated by the more technology oriented researchers in the field. At the moment the wood is sold, it usually still has a good appearance. However, although the practical experience with modified wood is only limited, already now it has become clear that generally it is much more susceptible to discoloration, in comparison to untreated wood. We give three examples of this.

1. Heat treated wood is turning grey even faster than untreated wood.

Greying of wood is a complex phenomenon consisting of several processes. One of them is UV initiated partial oxidation of the lignin. The formed quinone-type molecules darkenthe wood, which is what is seen in parquet flooring and in furniture. In exterior circumstances the breakdown products are easily washed out of the wood leaving a silvery fibrous surface. At the same time dark coloured hyphae of (blue) staining fungi appear. These give the wood a darker colour. The overall result is greying of the wood (Figure 1). Heat treated wood appears to grey even faster than untreated wood. There are several speculations on the reasons for this. However, that is not the scope of this paper.

Figure 1: Greyed wood on a building in Rhenen, The Netherlands

2. DMDHEU treated wood is susceptible to surface moulds.

The theory behind DMDHEU treatments is that the molecule can react both with cell wall constituents like hemicellulose and lignin and with itself thus forming an extensive network in the wood structure. After a few years of experience with DMDHEU it has become clear that, although the general properties are quite good, the treated wood is susceptible to surface moulds (Figure 2). This was already clear from earlier research at the field site in Wageningen, NL. In 2005 at the 2nd ECWM, all participants were provided with a piece of DMDHEU treated beech. Since a large number of participants of that conference was researchers, many of those samples ended up in field sites or private gardens. Therefore many have been able to witness this problem themselves.

Figure 2: Moulds on DMDHEU treated wood.

3. Acetylated wood is susceptible to blue staining fungi.

Acetylated wood, although very good in many properties, also has a disadvantage: its susceptibility to blue staining fungi. For many years this was believed to be due to remaining acetic acid in the wood. More recently, when better processes for removing the acetic acid were developed, it was seen that even with very low acetic acid contents (*i.e.* lower than 0.5% w/w) the susceptibility to blue staining fungi remains (Figures 3, 4). If the acetylated wood is provided with a paint film (opaque or transparent) this problem is solved. However, if the wish is to apply the wood without coating, this is a serious problem.

These three given cases are just examples of a general problem. It is extremely difficult, perhaps impossible, to reach full protection of the material without the use of biocides. Here a similarity with experiences in a totally different area can be observed: crop protection. In the seventies there was a strong movement away from the use of chemicals in crop protection (*i.e.* biocides). In many different ways other ways of protecting crops were tried. Biological means were the most important. The main strategy was the use of natural enemies to the attacking organisms. Due to all sorts of practical problems the sole use of biological means appeared not to be sufficient in most cases. Sometimes, at specific times in specific quantities and at specific places, biocides are needed. Since this was recognised many systems were developed in which the main protection was non-biocidal but additional protection with biocides was included when needed. This is called IPM (integrated pest management) and is now a wide spread crop protection technique.

Figure 3: Left: Sundial with scale made out of acetylated radiata pine, Arraiolos, Portugal.

Figure 4: Right: Blue stains after one year of use of the sundial.

The same line of thinking could be applied to wood protection. Perhaps the main protection can be done by modification techniques, while additional protection is done by biocides. However, this asks for tailor-made solutions. It is not possible to just take an old fashioned method and just apply it to these new materials. Several industrial attempts have shown that existing formulations of anti-stain or anti-mould products are easily washed out of the modified wood. Their effectiveness is rather limited in time. In many cases a "fixation" mechanism of these biocides is linked to the active chemical groups in the wood constituents. It can easily be speculated that it are these very same groups that are altered by modification and therefore the "anchor" points have disappeared. However, so far there is not much research published that either confirms or falsifies this.

In any case, the problem asks for a different, non conventional, solution. The Bioswitch (Jong *et al.* 2005) could become one of the possible solutions.

BIOSWITCH

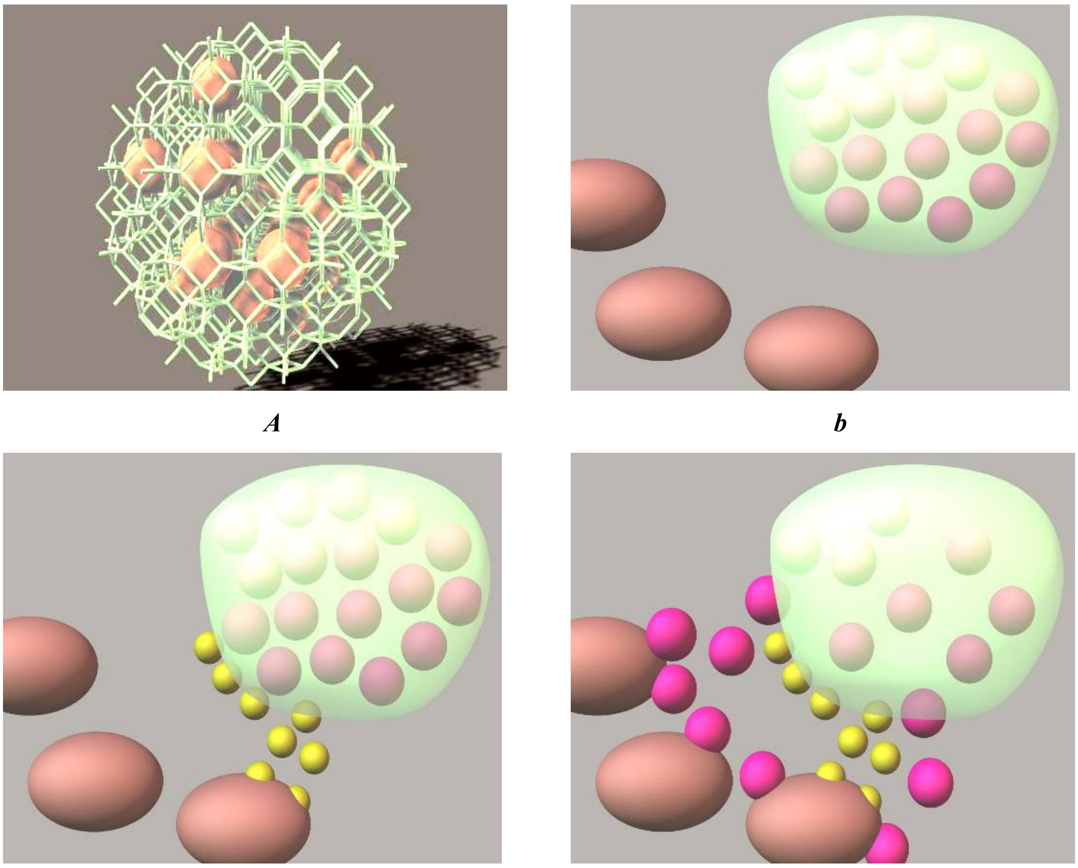
The Bioswitch technology (Jong *et al.* 2005) is based on a carrier system that contains an active component that is only released when it is needed, a so called "release on demand" system. This makes it possible to overcome the disadvantages of the widespread "slow release" systems like leaking out of the active component and a high dose of active component. The Bioswitch "release on demand" system only makes the entrapped active component available when an external stimulus triggers the release. For wood preservation the trigger for release of a preservative could be the presence of initial fungi contamination, thereby preventing further growth of the fungi.

Several release on demand systems have been developed at TNO based on a carrier system of biodegradable micron sized particles. Thereby the active component is released only when a specific enzyme is present that digest the particles made of a specific biopolymer. Amongst the biopolymers used were starch derivatives, cellulose derivatives or proteins. This resulted in carrier particles that were sensitive to the triggers amylase, cellulose or protease, respectively. Amongst the active components were the antimicrobials lysozyme and gentamicin. These charged molecules were entrapped in the Bioswitch particles by electrostatic interactions. This is only an example of a binding and release mechanism. The Bioswitch technology is versatile and can therefore be adapted to many specific applications.

Here an example is presented to illustrate the Bioswitch principle for amylase triggered release of lysozyme. This starts with the preparation of starch based gel particles. These are obtained by crosslinking of partially oxidised starch. The oxidised starch polymer molecules are negatively charged because a part of the primary alcohol groups of starch were converted into carboxylic acids by sodium hypochlorite using TEMPO as a catalyst. These water soluble polymers are dissolved in water and converted into an insoluble three-dimensional network using crosslinkers like epichlorohydrin, sodiumtrimetaphosphate or diepoxides. The obtained gel is than washed, dried and converted in micron sized particles. If these particles are added to water they swell and absorb typically 20 – 200 grams of water by one gram of dry gel. To a suspension of these particles in water an active component like the positively charged lysozyme can be added to the solution. The lysozyme is than absorbed completely in the particles within a few minutes, and will not leak out anymore. The gel can be loaded with more than one gram of lysozyme in one gram of dry gel. The loaded gel particles are than dried on air. The lysozyme will only be relased if amylase is present and degrades the carrier system. This is explained in Figure 5.

In Figure 5, a simplified structure of a Bioswitch particle is depicted. The crosslinked biopolymers form a three-dimensional network, wherein an active component is entrapped. In b microorganisms discover a starch based gel particle and start to produce amylase (lighter spheres) in order to digest the starch. The amylase is released to the environment (c) and starts to degrade the gel particle. Thereby the antimicrobial lysozyme is relased (d). This prevents further growth of the microorganisms of an initial contamination (at low germ count).

To a dispersion of Bioswitch particles in water lysozyme is added stepwise. After each addition the lysozyme concentration in the solution (after sedimentation of the gelparticles) is measured. The amount of lysozyme is depicted as a function of the amount added and is expressed in mass % relative to the amount of dry gel used. Up to 130 m/m % the lysozyme is completely absorbed by the gel. At a higher dose the added lysozyme will remain in the solution (Figure 6).



A *b*

C *d*

Figure 5: Artistic impression of a bioswich particle (a), and its interaction with microorganisms (b) and enzymes (c) and the induced release of the active component (d).

Starch based Bioswitch particles are dispersed in water and after several time steps (in minutes) the released lysozyme is measured in solution after sedimentation of the gel particles (Figure 7). The released lysozyme is expressed in % of the amount loaded in the original Bioswitch particles. After about 1400 minutes the starch degrading enzyme amylase is added. Up to 1400 minutes no significant release of lysozyme is observed. But after the addition of amylase the gelparticles start to digest and the lysozyme is released within a short time.

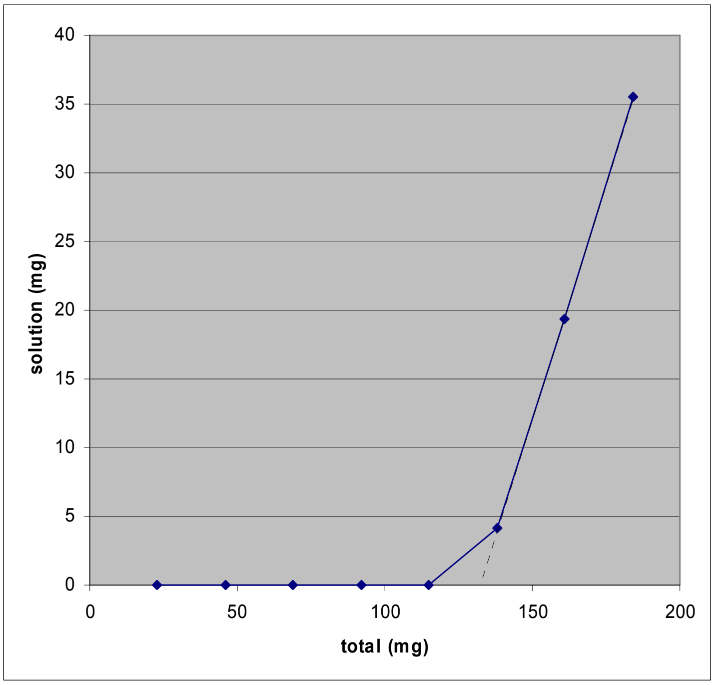


Figure 6: Loading of Bioswitch particles with an active component (lysozyme).

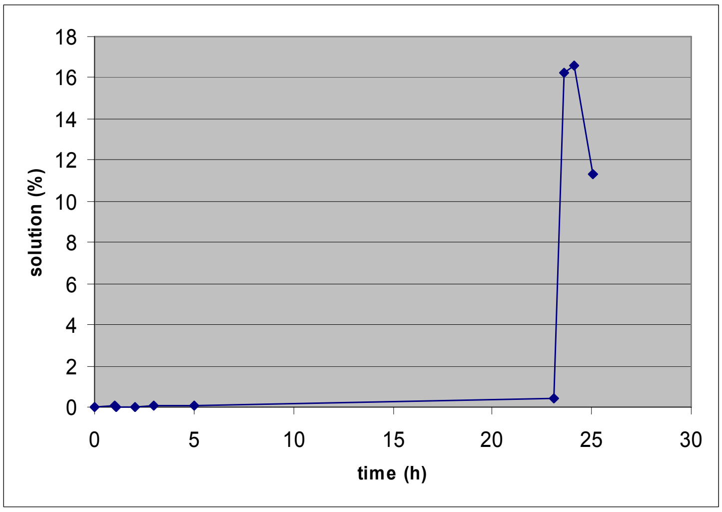


Figure 7: Non-release and release of the active component lysozyme.

CONCLUDING REMARKS

Modified woods are susceptible to growth of moulds and blue stain fungi. Applying biocides in traditionally formulated products can not always be done on modified wood without introducing "fixation" problems. The Bioswitch technology is a proven technique in a number of industrial applications. This versatile system certainly offers opportunities to be used in combination with modified wood. Possible advantages might not only lie in the release on command principle but just as well in solving compatibility problems between biocides and modified wood. Ongoing work will have to deliver the proof of this.

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Durability of Modified Wood in Three Different Soil Types

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Keywords: Decay, soil, terrestrial microcosms (TMC), wood modification

ABSTRACT

The main objective of this study was to evaluate the efficacy of four different wood modification systems (acetylation, furfurylation, ThermoWood and linseed oil) using an expanded version of the ENV 807 test with three different soil types, *i.e.* terrestrial microcosm (TMC) test. The sub-goals were to test: 1) the effect of different soil types, 2) the performance of the different modifications compared to reference treatments, 3) differences in performance after 24 and 40 weeks exposure, 4) the potential differences between the laboratories at SP Trätek and Norwegian Forest and Landscape Institute (NFLI) in duplicate set-ups. Generally compost soil (ENV 807) gave the highest mass loss. In this test the mass loss from the soil from Simlångsdalen test field and the forest soil differed slightly between the labs and between treatments. Even though the different soil types did give differences in degree of decay, the relative performance of the modified wood, compared to each other and compared to the references, was generally the same for all soil types. Both furfurylation, acetylation and ThemoWood D and D+ performed well. Acetylated wood at 23 and 30 WPG gave the best effect. ThermoWood D and D+ perfomed better than ThermoWood S+. Visorwood 25, 37 and 50 WPG had the same performance as ThermoWood D and D+. ThermoWood S+ was approximately in the same range as linseed oil. The modified wood performed at the same level, or better, than the reference CC and CCA preservatives in retentions for UC4 use. An interesting result is the poor performance of the CC preservative in this test. No great variation in relative performance was detected between 24 and 40 weeks of exposure. The duplicate set-ups gave very similar results for all soil types and all wood treatments except for untreated pine sapwood in forest soil, with a higher mass loss in Sweden than in Norway.

INTRODUCTION

Testing of modified wood is facing challenges with regard to the standard methods of evaluation in lab like the EN 113. The mode of action is different from the traditional wood preservatives which the tests were designed for. Hence, the performance of modified wood systems can easily be under (or over) estimated. The TMC method (Edlund 1998a,b) is an expanded version of the European standard ENV 807 using different soil types. This simple test gives a broader basis for evaluation since a broader range of soil inhabitating microorganisms will be included. Furthermore, the test method has proven to be more relevant (than *e.g.* agar-block tests according to EN 113) when testing alternative wood protection methods including modified wood (Westin *et al.* 2004, Westin *et al.* 2007). In order to later (hopefully) be able to verify this, replicate wood materials to the test presented in this paper were also put out in field tests in-ground and above ground in four fields in three countries in 2005.The main objective of this study was to evaluate the efficacy of four different wood modification systems (acetylation, furfurylation, ThermoWood and linseed oil) using an expanded version of the EN 807 test with three different soil types, *i.e.* terrestrial microcosms (TMC) test. The sub-goals were to test:

1) the effect of different soil types
2) the performance of the different modifications compared to reference treatments
3) differences in performance after 24 and 40 weeks exposure
4) the potential differences between the laboratories at SP Trätek and Norwegian Forest and Landscape Institute (NFLI) in duplicate set-ups.

EXPERIMENTAL

The wood modifications, reference treatments and control samples used in this study are given in Table 1. The reference treatments were Kemwood KC73 as CC preservative (where the 1.33% concentration gives the retention level for NWPC Class A) and CT 106 as CCA-preservative (0.6% and 1.3% concentration, corresponding to NWPC Class AB and Class A retention level). 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 ThermoWood spruce S+ and D+.

Table 1: Modification, references and control samples used in this test.

Modified wood material	**Process**
Furfurylated pine (25 WPG)	according to the *VisorWood*^{TM} production process by WPT ASA and Kebony Products AS
Furfurylated pine (37 WPG)	
Furfurylated pine (50 WPG)	
ThermoWood pine D (212 °C peak Temp.)	according to the production process of Finnforest Oy
ThermoWood spruce S+ (200 °C peak T.)	according to a modified version of the production process of Stora Enso Timber
ThermoWood spruce D+ (225°C peak T)*	according to an earlier version of the production process of Stora Enso Timber
Acetylated pine 23 WPG (20% acetyl content)	In a microwave reactor according to Larsson (1998)
Acetylated pine 30 WPG (24% acetyl content)	In a microwave reactor according to Larsson (1998)
Linseed oil** treated pine (150 kg/m³ ret.)	according to the production process of LinoTech AB
Reference	
CC-impregnated pine, 2.5 kg/m³ (0.33%)	Conventional full-cell impregnation
CC-impregnated pine, 5 kg/m³ (0.67%)	Conventional full-cell impregnation
CC-impregnated pine, 10 kg/m³ (1.33 %)	Conventional full-cell impregnation
CCA-impregnated pine, 4 kg/m³ (0.6%)	Conventional full-cell impregnation
CCA-impregnated pine, 9 kg/m³ (1.3%)	Conventional full-cell impregnation
Robinia pseudoaccacia heartwood	Non-treated
Control	
Pinus sylvestris sapwood	Non-treated

* *Only at SP*

*** according to the manufacturer the oil contained compound to induce grafting of the oil to the wood, hence this could be regarded as wood modification.*

The samples had the dimensions specified in ENV 807 (2001), 5 x 10 x 100 mm. The treated samples were leached according to EN 84 before decay testing. The decay study was a 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), garden compost from Sweden and soil from the Swedish test field in Simlångsdalen (Table 2).

The test samples were evaluated at 24 and 40 weeks. Eighteen samples of each treatment were used; six samples were harvested after 24 weeks and oven dried.

Table 2: Soil characteristics of the three test soils; moisture at water holding capacity and pH.

	Conifer forest	Garden compost	Simlångsdalen
pH	4.6	7.4	5.2
Moisture content at WHC % (m/m)	222.9	101.7	19.7

RESULTS AND DISCUSSION

Figure 1 show the mass loss at SP and NFLI after 24 weeks. The mass loss values tend to be higher for the compost soil and the Simlångsdalen soil at NFLI than at SP. Compost soil generally gave the highest mass loss values at both labs. At NFLI, the samples in the Simlångsdalen soil had nearly as much mass loss as the samples in the compost soil, while at SP there was some problems with the virulence of the Simlångsdalen soil.

Scots pine controls had the highest mass loss values, *i.e.* they were most severely decayed. CCA performed better than CC preservative. The mass loss of the CC treated samples was surprisingly high at lower retention levels, approximately in the same range as Robinia heartwood. Acetylated, furfurylated and ThermoWood D and D+ performed well after 24 weeks. ThermoWood S+ and linseed oil had higher mass losses than the other modifications.

After 40 weeks the mass loss had nearly doubled. The compost soil still had the highest mass loss. Simlångsdalen soil at NFLI also gained high mass losses, while the same soil at SP still had low virulence.

The same trend as after 24 weeks was found in decay between the test samples. Scots pine sapwood as control had the highest mass loss. CC at lower retention and Robinia heartwood also gained high mass loss, especially for the compost soil. ThermoWood S+ and linseed oil performed in the same range as CC at high retention and low retention CCA. All the remaining modified wood materials (furfurylated, acetylated and Thermowood D and D+) showed a low mass loss after 40 weeks, whereof acetylated showed the best results.

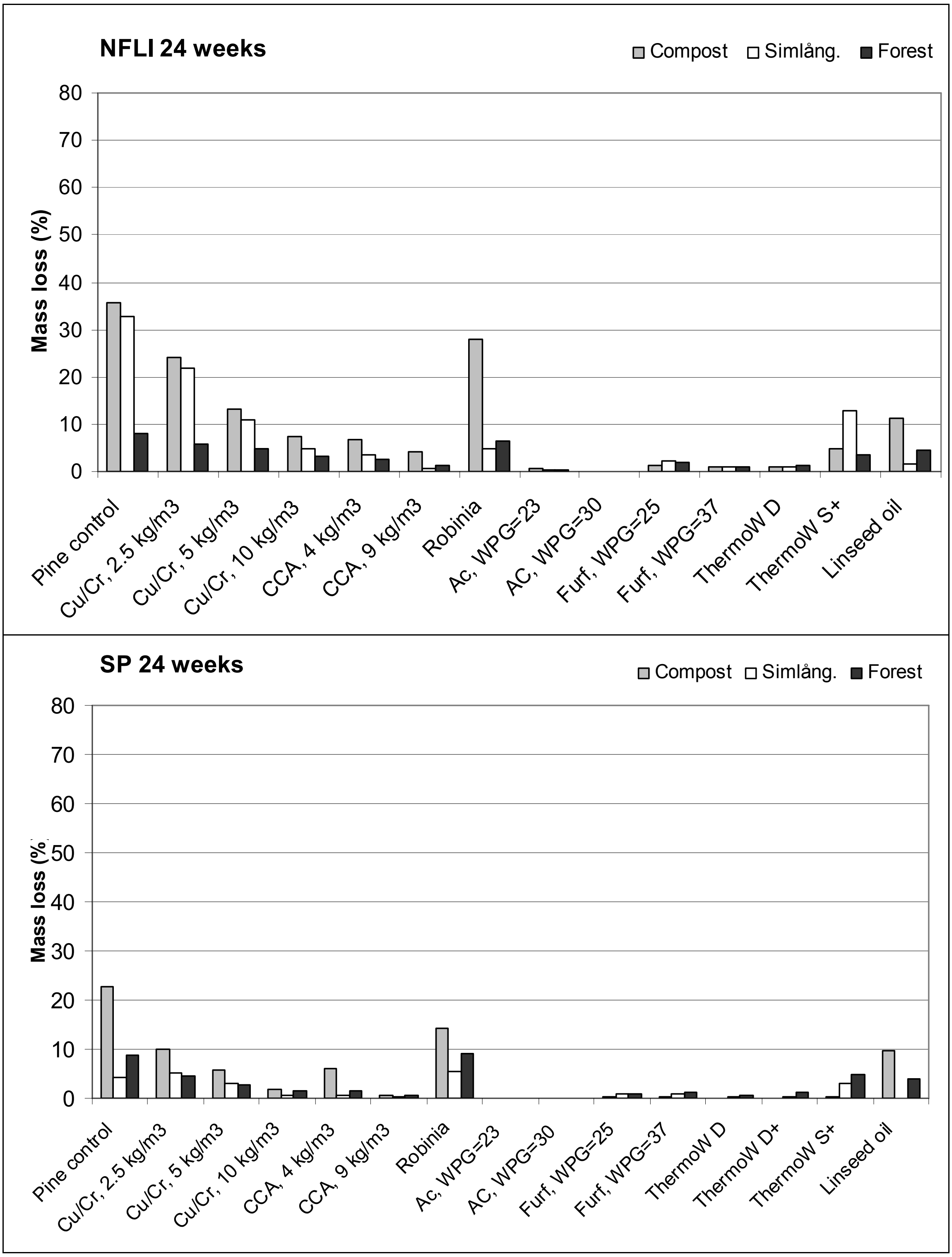

***Figure 1:** Mass loss (in %) after 24 weeks of exposure in three different soil types at SP and NFLI.*

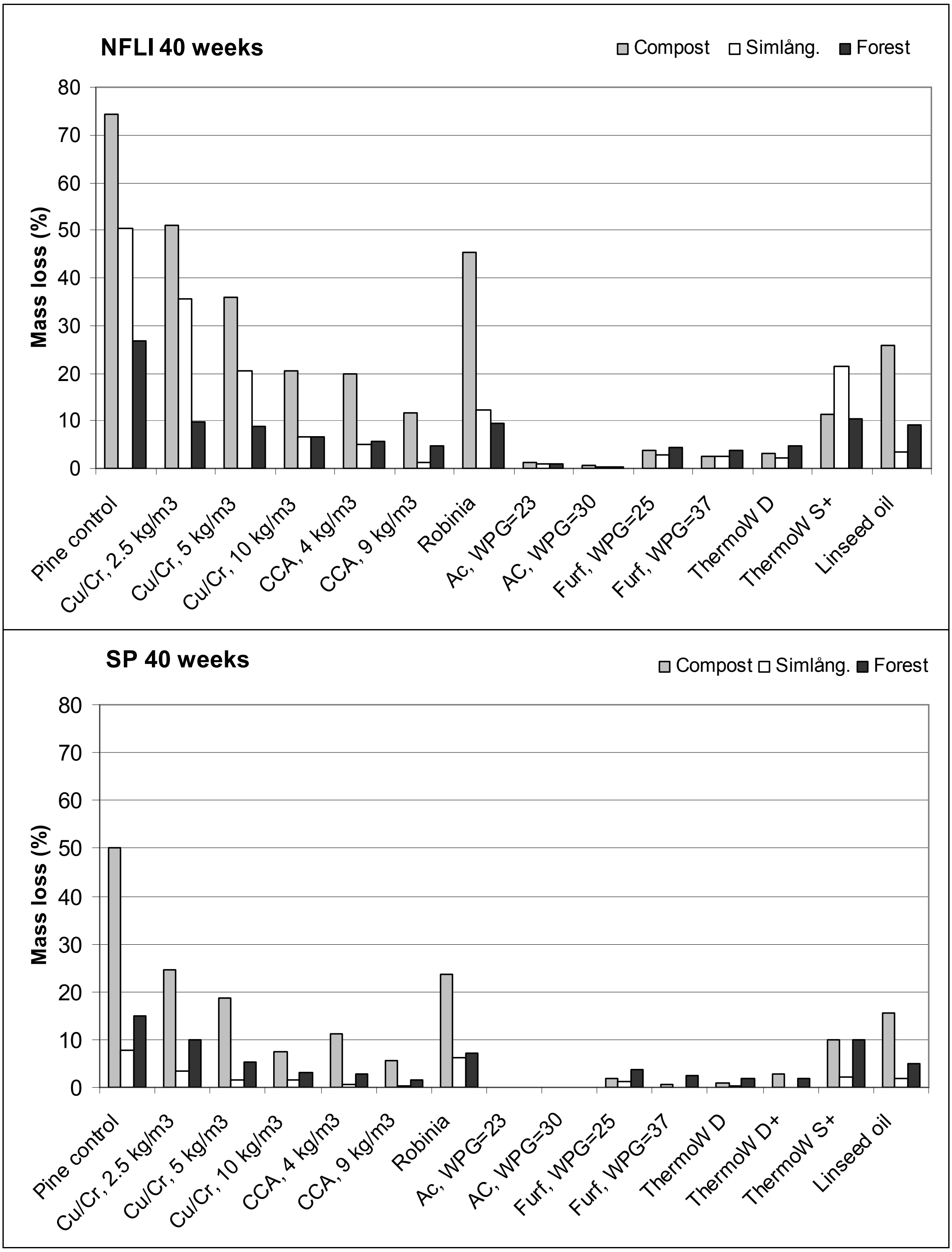

Figure 2: Mass loss (in %) after 40 weeks of exposure in three different soil types at SP and NFLI.

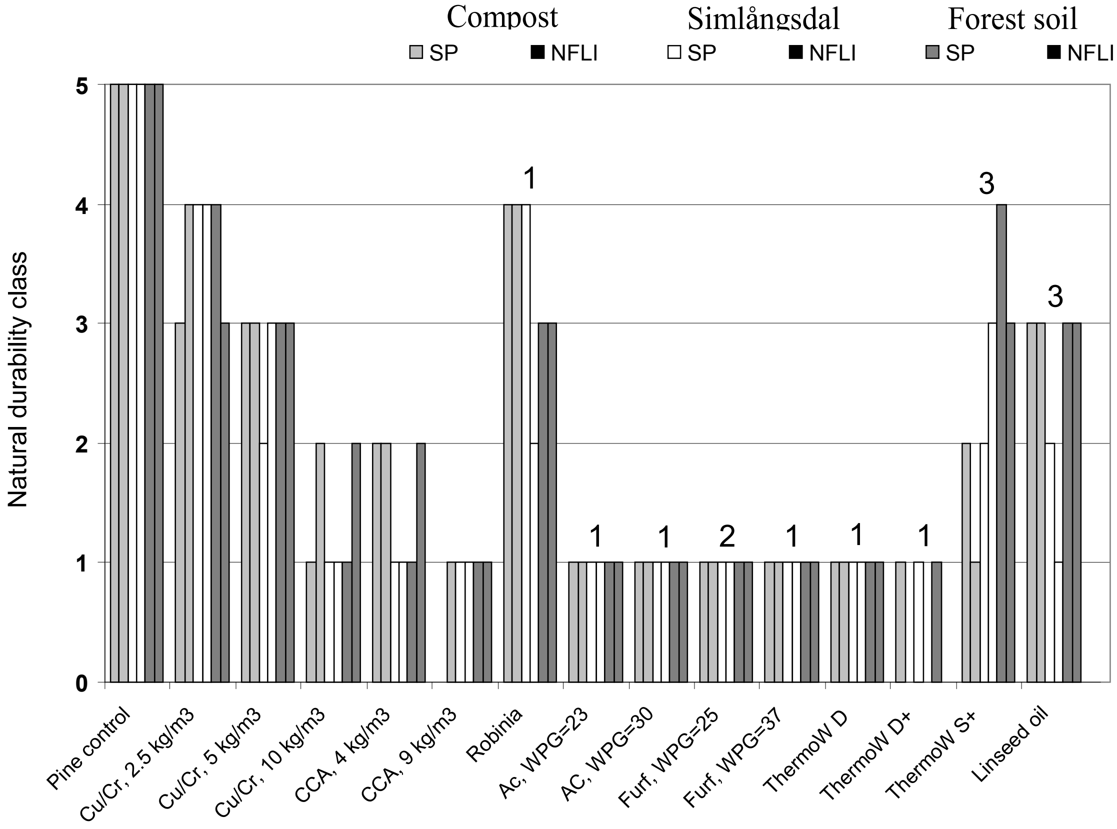

Figure 3: The bars show TMC decay results calculated as natural durability classes, both at NFLI and SP for all three soil types. The value above the bars show natural durability class based on soil-block tests (according to AWPA E10).

CONCLUSIONS

Modification methods

- Furfurylation, acetylation and ThermoWood D gives high decay resistance
- Acetylated wood, both at 23 and 30 WPG, gave the best overall effect
- Visorwood 25 and 37 had approx. the same performance as Thermowood D and D+
- Thermowood D and D+ performed much better than Thermowood S+
- Linseed oil was approximately in the same range as ThermoWood S+
- The modified wood performed at the same level, or better, than the reference CC and CCA preservatives in retentions for Use Class 4.

Soil

- Compost soil gave the highest mass loss
- At NFLI, Simlångsdalen also gave high mass loss, while there were virulence problems at SP. Hence, at SP forest soil gave similar or better decay than Simlångsdalen soil
- Generally the same relative results was found between systems for all soil types

Time

- Higher mass loss was gained after 40 weeks than 24, hence the separation between treatments was higher. But no great variation in performance was detected between 24 and 40 weeks of exposure

Reproducibility

- Higher mass loss at NFLI than at SP, but generally similar trends between the labs for all wood treatments

ACKNOWLEDGEMENTS

Agnieszka Nowięka and Sigrun Kolstad is acknowledged for laboratory support. Finnforest and Stora Enso Timber for supply of ThermoWood, LinoTech AB for linseed oil treatment, WPT ASA for furfurylation and Pia Larsson Brelid for acetylation of wood. Finally we acknowledge funding from Vinnova and the Research Council of Norway.

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Light stabilization of modified wood species

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Keywords: Acetylation, DMDHEU, light stabilizers, artificial exposure

ABSTRACT

Wood modification methods (acetylation, DMDHEU) were regarded concerning their influence on UV protection. Based on the results of artificial weathering studies with fluorescence light according prEN 927-6 and Xenon light according Xe-WOM CAM7 it seems that both modification methods partly protect the lignin from photo-degradation. However there is still a need to protect the modified wood species with a coating that has sufficient UV-VIS light protection with UVA and HALS to prevent the substrate as well as the coating from any damages due to radiation and water. A pre-treatment with a lignin stabilizer can further increase the durability of the.

INTRODUCTION

Despite increased usage of competitive materials such as metals and plastics, wood remains a highly popular material for various indoor and outdoor applications. The popularity of natural wood as a design and construction material for outdoor would be further increased if significant improvements could be achieved in longer durability and hence reduced maintenance work. The coating and wood alteration during service life is the result of phenomena such as photo- and thermo-oxidation due to solar radiation (UV and VIS), water (dew, rain, snow, *etc.*), temperature (night and day, seasons) and oxygen; generally referred to as weathering, as well as bio-degradation caused by fungi, algae and animals.

To understand the unwanted behaviour of wood it is important to understand the wood biology and the related mechanism of photo-oxidation and bio-degradation. Chemically wood is a complex biopolymer composed of structural polysaccharides, essentially cellulose, hemicelluloses and lignin. Cellulose is a long, linear cellobiose based polymer acting as skeleton of wood. Hemicellulose consists of branched polysaccharides surrounding the cellulose fibers. Lignin is an amorphous aromatic polymer and plays an essential role as strength provider (Janes 1969). These wood polymers contains an abundance of hygroscopic hydroxyl (OH) and other oxygen-containing groups, *e.g.* carbonyls (C=O) which adsorb and release water, *i.e.* undergoes dimensional changes and plays an important role in the photo-oxidation of lignin (Janes 1969). Furthermore organisms recognize the OH groups (mainly of hemicellulose) and convert these polymers using enzymes into digestible units. Photo-oxidation of lignin refers to a process where the polymer undergoes chemical modifications such as bond cleavage, and hydrogen abstraction resulting in radical formation, and finally decomposition with the production of coloured and hydrophilic by-products, so called chromophores *e.g.* quinoides, aromatic ketones, aldehydes, *etc.*, due to interaction with light (UV/VIS) in the presence of oxygen. It is generally accepted that 3 main reaction pathways are operating (Leary 1994, Heither 1993): (1) direct excitation or free radical scavenging by phenolic groups to give phenoxyl radicals (the "free phenoxyl radical" pathway); (2) direct excitation of carbonyl groups (the "phenacyl" pathway) both induced mainly by UV light; and (3) formation of ketyl radicals by cleavage of β-O-4-aryl ethers with α-OH groups induced by radicals. Colour change may occur early in the life of indoor applications, as a result of chromophore formation. It is well known that pale wood species tend to colour and darkening whereas coloured or dark wood species first lose initial colour, *i.e.* show bleaching and decolouration effects induced by light up to 500 nm (Schaller *et al.*). Under outdoor conditions the deleterious effect of weathering leads to subsequent photo-degradation and finally graying and erosion of the wood.

To increase the service life of wooden substrates in outdoor applications they are usually coated and preservative treated when (natural) low durable wood species are applied. Traditional methods such as chemical or monomer impregnation (surface modification) are used to improve *e.g.* decay resistance and dimensional stability and do not form covalent bonds with the cell wall. Nowadays wood modifications, which not only improve the biological resistance (durability) but can also strongly enhance other properties like dimensional stability, water repellency, light- and thermal stability and strength properties, are becoming more and more popular. These wood modification methods can be divided into heat treatments and chemical modification methods (*i.e.* acetylation, O-alkylation, furfurylation, silanation) (Hill, 2006). Chemical wood modification is defined as a chemical reaction between some reactive part of a lignocellulosic polymer; *i.e.* OH groups, and a chemical reagent to form covalent bonds. The most research and interest, has been in the reaction of acetic anhydride with cell wall polymer OH groups. Acetylation effectively converts the hydrophilic free OH groups within the wood into hydrophobic acetyl groups. Another alternative is the reaction with cyclic N-methylol compounds and as such 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU). Whereas the acetylation leads to a blocking of OH the treatment with DMDHEU leads to a cross linking by poly condensation. However acetylation has mainly been considered for the reduction of water uptake and therefore improved dimensional stability. Treatment with DMDHEU-based cross linkers causes a permanent swelling of the cell wall leading to reduced swelling and shrinking behaviour. Both technologies offer furthermore an increased decay resistance and durability.

To highlight and preserve the modified wood surface, it is usually coated with various decorative and protective finishes such as transparent stains or film forming varnishes. The key for improving the service lifetime of wood is the optimization of UV and VIS light protection of the wood surface itself in addition to the prevention of the alteration processes of the coating. Today UVA based on 2-(2-hydroxyphenyl)-benzotriazoles (BTZ) chemistry are the most important class for the stabilization of clear coats in a variety of end uses (Valet 1997). Still some limitations of benzotriazole based UVA (Stährfeld and Braig 2002) have pushed the paint industry to adopt a new UVA class based on the 2-hydroxyphenyl-s-triazine (HPT) chemistry (Schaller *et al.* 2006). However the drawback of all organic UVA is the limited absorbance profile with protection from light only < 400 nm. Today it is common practice to combine UVA with hindered amine light stabilizers (HALS) which mainly are derivatives of 2,2,6,6-tetramethylpiperidine and reported to effectively scavenge free radicals at the surface and thus help to prevent surface defects (Gerlock *et al.* 1985). Due to the particular sensitivity of lignin, to UV and also VIS light it became necessary to develop new concepts for optimal protection of wood substrates where clear or low-pigmented coatings are wished or required, which often failed in the past due to insufficient light protection. This was achieved by introducing the lignin stabilizer concept. To stop the effect of unscreened VIS light causing photo-oxidation a lignin stabilizer treatment, based on a special HALS derivative, is used, which provides improved color stability in indoor applications and besides the improved aesthetical aspects long term durability for transparent and semi-transparent wood coatings for outdoor applications (Rogez 2000). According to this new concept an optimized wood protection is achieved, when the lignin stabilizer is applied in an impregnation directly onto wood and associated with selected UVA (indoor) or UVA/HALS (outdoor) in the same treatment or better in a subsequently applied top coat (Hayoz *et al.* 2002, 2003a). Especially for high performance outdoor applications where long lasting coatings are required, *e.g.* wooden window frames, a new UVA based on a substituted tris-resorcinol triazine derivative with excellent photo-permanence was introduced for solvent borne (Hayoz *et al.* 2003b) and in encapsulated form for water borne wood coatings (Peter *et al.* 2005, 2006). A detailed description how to use UVA and HALS in combination with the lignin stabilizer in an efficient and economic way depending on the degree of pigmentation of the used coatings is described elsewhere (Schaller and Rogez 2006).

This paper discusses the weathering performance (service life) of (almost) commercially available modified wood species. Combination of chemical lignin stabilizer impregnation and UV protection as well as wood modification should result in synergistic effects and allow high performance wood construction elements with highest resistance against photo- and bio-degradation as well as dimensional stability. Based on the knowledge of the mechanism of wood modification and degradation processes a guideline for an economic and efficient use of light stabilizers giving optimal performance with increased service life is given.

MATERIAL AND METHODS

Wood

Accoya™ wood was supplied by Titan Wood (www.titanwood.com). Accoya™ wood (www.accoya.info) is based on wood acetylation of Radiata pine (*Pinus radiata*) (AA-Pine-A). DMDHEU modified Scots pine (*Pinus sylvestris*) was supplied by BASF / Belmadure® (www.basf.com) (DMDHEU-Pine-B). As reference (untreated) Radiata pine (Pine-A) and Scots pine (Pine-B) were used.

Finishing

Part of the samples were treated with a lignin stabilizer (LS); a 1% aqueous solution of 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl applied by brush (1 x 80 g/m^2). Further part of the samples were finished with a waterborne self cross linking acrylic dispersion with and without UVA/HALS applied by brush (2 x 100 g/m^2). The UVA and HALS types are: encapsulated 1-isoctyloxycarbonyl ethylated 2,4,6-tris-(2,4-hydroxyphenyl)-1,3,5 triazine derivative (2% active on binder solid); encapsulated HALS: Decanedioic acid, *bis* (2,2,6,6-tetramethyl-1-(octyloxy)-4-piperidinyl) ester (1% active on binder solid).

Artificial weathering

The light source for the artificial weathering study was Xenon light according to the Xe-WOM CAM 7 cycle for exterior applications (outer filter borosilicate / inner filter borosilicate) in accordance with DIN EN ISO 11341 A (0.35 W/m^2 / 340 nm: 102 min light, Black panel temperature (BPT) (60±2) °C, RH (35±5)%; 18 min light and spray, BPT (35±2) °C, relative humidity (RH) (95±5)%) by using an Atlas Weather-Ometer Ci-65 A. Fluorescence light according to prEN927-6 is used; one test cycle (168 h) in the QUV-tester consists of 24 h condensation (BPT (45±3) °C), followed by 48 cycles 2.5 h UV light (BPT (60±3) °C , 0.77 W/m^2 / 340 nm) and 0.5 h dark and spray (BPT (22 ±3) °C). For the artificial weathering studies samples were made of standard sized panels (200 x 68 x 10 mm for Xe-WOM CAM 7 and 305 x 75 x 10 mm for prEN927-6) with back and end grain sealing with an automotive 2K-PUR clear coat.

Methods for sample evaluation during weathering

The discolouration due to accelerated weathering was determined by measure the coloristics at various time intervals with a Minolta CM-3600d device (gloss included). The L*, a*, b*, C*, h and ΔE* were calculated with CGREC software according to DIN 6174 with a standard deviation on wood of ±1 ΔE* units. The gloss evaluation is performed at 60° with a Byk/Gardner Micro-Tri-Gloss equipment according to DIN 67530 with a standard deviation on wood of ±2 gloss units. The cracking and chalking evaluation is performed visually according DIN EN ISO 4628-4.

RESULTS AND DISCUSSION

Artificial weathering

Today increased demands and requirements on the lifetime of most coatings for *e.g.* industrial or automotive applications requests methods to predict the long term performance. Artificial weathering tests are used to manipulate and accelerated reproducibly and repeatedly weathering conditions on demand. Nowadays several light sources are available with its own inherent benefits and pitfalls; *e.g.* there are two main different light sources for artificial exposure of wood: Fluorescence and Xenon light. Tests using fluorescent lamps are widely practiced because of easy handling, low maintenance and the low costs of the device. However these tests are useful for relative ranking comparison and general screening tests, but the comparison to service lifetime performance or correlation to outdoor exposure may not be valid. The most important drawback is the absence of light > 400 nm. The sensitivity of wood to light from 300 to 600 nm depending on the wood species forced the wood coating industry to use Xenon exposure to be able to better predict long term performance of wooden construction elements.

Artificial weathering studies on modified wood

The influence of fluorescence and Xenon light according Xe-WOM CAM 7 on weathering stability of pine modified with acetic acid anhydride (AA-Pine-A) as well as a DMDHEU-based formulation (DMDHEU-Pine-B) with UV protection in the clear top coat (UVA/HALS) and with and without chemical impregnation with the lignin stabilizer (LS) is discussed. Figure 1 shows the color deviation of the used samples after 500 h artificial weathering according Xe-WOM CAM 7 and prEN 927-6.

Based on the results of the artificial weathering it could be stated that both pine wood species behave similar for both prEN 927-6 and Xe-WOM CAM 7 exposure with strong increase in ΔE around 25. As already seen the colour deviation of pale wood species like pine can be reduced to approximately 50% by using a clear non-pigmented paint with the appropriate amount of UVA. Here the use of HALS does not influence the colour retention, *i.e.* HALS are protecting the paint film itself against surface defects like *e.g.* cracking. The additional use of LS further improves the colour stability to retain almost initial color with a reduction of ΔE to around 5. For AA-Pine-A ΔE is obviously reduced to 9.7 (prEN 927-6) and 7.4 (Xe-WOM CAM 7) compared to the non-modified pine what can be seen as clear improvement in weathering stability. The presence of UVA shows further reduction of ΔE to 6 for prEN 927-6 but a strong increase to around 16.5 for Xe-WOM CAM 7 independent of the presence of LS. For DMDHEU-Pine B ΔE behaves similar with reduction to 11.4 (prEN 927-6) and 7.5 (Xe-WOM CAM 7), whereas the use of UVA shows further reduction of ΔE between 2 and 3 for both exposures independent of the presence of LS. A comparison of coloristic data; *i.e.* the lightness L*, chroma C* and hue H* deviation, of radiata pine, AA-Pine-A and DMDHEU-Pine_B after 500 h artificial exposure explain the different behavior in ΔE and is shown in Figure 2.

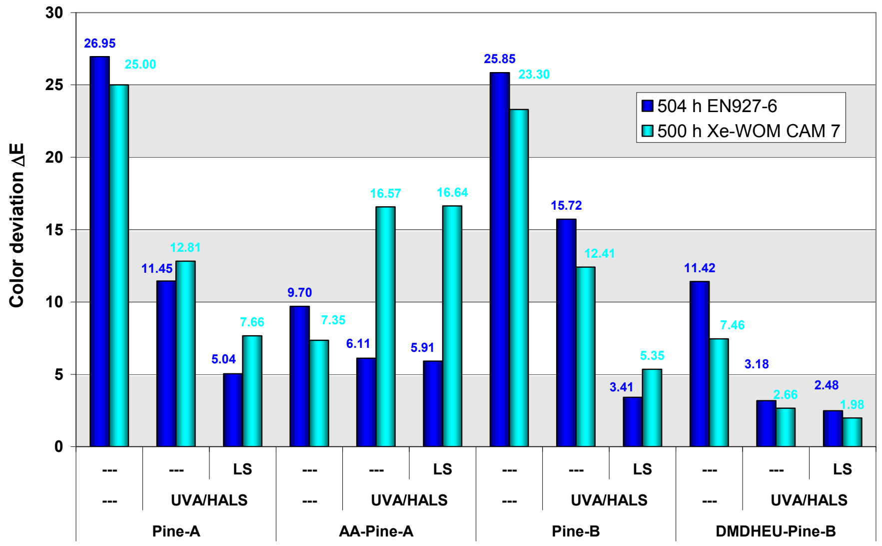


Figure 1: Colour deviation of pine, AA-Pine-A and DMDHEU-Pine-B after 500 h prEN927-6 and Xe-WOM CAM 7

For the non-modified pine the high ΔE is related to a strong increase in color (+ΔC*), *i.e.* yellowing, and darkening (-ΔL*). This can only be partially reduced by the single use of UVA, because of its limited ability of VIS light screening. The use of additional LS can almost completely stop yellowing and darkening due to trapping of radicals built by VIS light in the "Ketyl" pathway. For Xe-WOM CAM 7 even discoloration or bleaching effects can be seen (-ΔC). Here initial wood colour is destroyed by VIS light and due to efficient UV/VIS protection due to LS concept no new chromophores can be built up resulting in a bleaching effect. No significant changes can be seen in the hue (ΔH*) for both cycles. For AA-Pine-A no darkening is found, here in contrast AA-Pine-A seems to be more sensitive to Xenon light; *i.e.* VIS light, because severe brightening (+ΔL*) appears after Xe-WOM CAM 7. Yellowing occurs only during prEN927-6 without UVA, what can be explained by chromophore formation from lignin degradation starting from non-blocked carbonyl structures according the “Phenacyl” pathway. The presence of UVA filters out the damaging light before subsequent reactions with discoloration take place what can be seen by obviously reduced yellowing. The discoloration and brightening (“bleaching”) effects during Xe-WOM CAM 7 seem to be mainly induced by unscreened visible light. An explanation for this brightening can be seen in Figure 3 where pictures of the reference and the exposed wood samples after 500 h artificial weathering are shown.

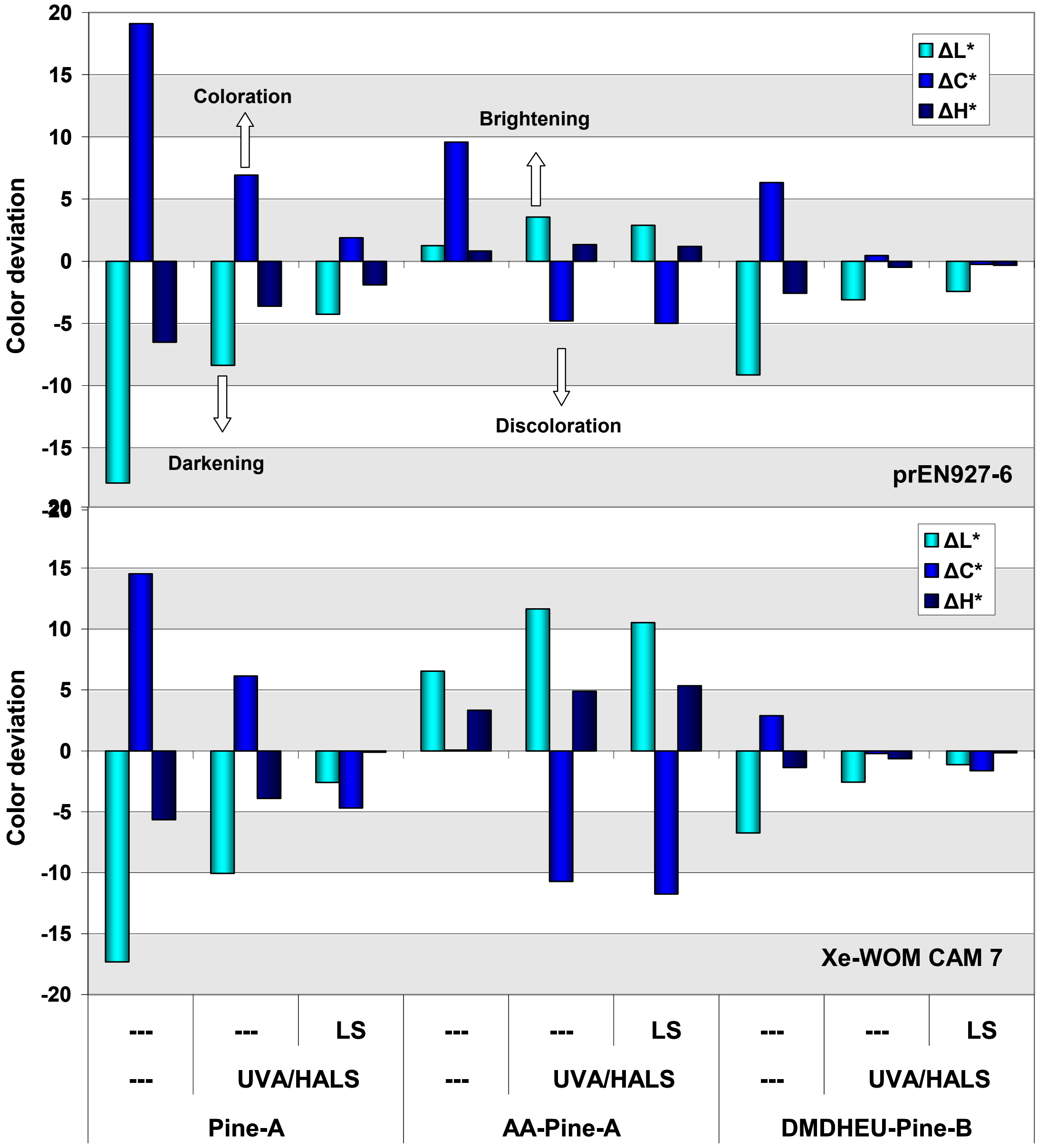
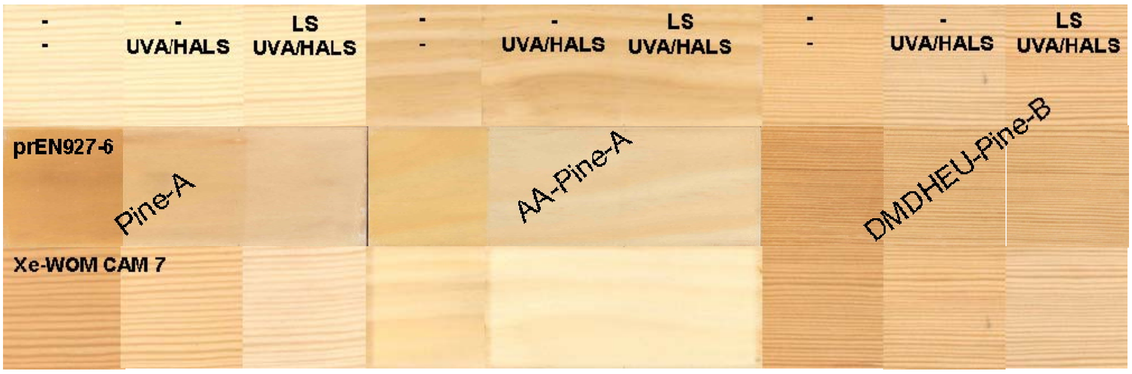


Figure 2: Colourc data ΔL, ΔC* ΔH*, of radiata pine, AA-Pine-A and DMDHEU-Pine-B after 500 h artificial exposure*



Figures 3: Pictures of the wood samples before and after 500 h artificial exposure

Here it is clearly shown that AA-Pine-A exhibits obviously darker initial colour compared to non-modified pine. So the bleaching effects are caused by minor VIS light fastness of chromophores which has been built during the acetylation process. To avoid these bleaching effects combinations of organic UVA with VIS light screeners has to be used. This approach is successfully used for *e.g.* heat treated wood and other coloured or dark wood species with certain VIS light sensitivity (Schaller *et al.* 2007). For DMDHEU-Pine-B as well colouration and darkening of the in initial pine colour due to the modification can be seen. The colour deviation with darkening during exposure behaves similar for both exposure cycles, whereas the changes are slightly more pronounced for prEN927-6. The changes in colouristic of DMDHEU-Pine-B are in the same magnitude compared to non-modified pine stabilized with an UVA. The use of UVA further improves the colour retention and UVA with LS shows the lowest colour deviation of all samples tested. Here almost no bleaching and discoloration effects are visible showing that the coloration due to DMDHEU modification is stable against UV/VIS light. However the reduced colour deviation, indicating reduced lignin degradation (Schaller and Rogez 2007) of acetylated and DMDHEU-modified wood, due to the use of UVA and LS clearly highlight the need of UV protection.

CONCLUSION

Both wood modification methods (acetylation, DMDHEU) seem to partly protect the lignin from UV/VIS degradation. The DMDHEU-modified wood without UV protection shows colour deviation as an “untreated” pine species, although the level is enormously reduced, and almost no change in colour with suitable UV protection. Due to the different nature of the acetylated pine the wood is bleached during exposure. To avoid this bleaching it is recommended to use coatings with VIS light screeners. In conclusion, there is still a need to protect the modified wood species with a coating that has sufficient UV-VIS light protection with UVA and HALS to prevent the substrate as well as the coating from any damages due to radiation and water. A pre-treatment with the lignin stabilizer can further increase the durability of the. The performance of the modified wood species in practice will further depend on quality of the coating system, the quantity and type of light stabilizers, the final application and the local weather conditions.

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Composition and Ecotoxicity of Heat Treated Pine Wood Extractives

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Keywords: Ecotoxicity, extractives, heat treatment, *Pinus pinaster*

ABSTRACT

This work focuses on the extractives produced during thermal treatment but remain present in the wood and might lixiviate when the wood is further processed. Heat treatment of pine (*Pinus pinaster)* wood was made in an autoclave with a mixture of superheated and saturated steam for 2-12 h at 190-210 ºC. A strain of *Bacillus stearothermophilus* was used, as a model, to evaluate the ecotoxicity of the extractable compounds. The first compounds degraded by heat were hemiceluloses. In general, the decrease was higher for arabinose and galactose followed by xylose and mannose. Lignin started to degrade for small losses but at a slower rate than the polysaccharides. Cellulose was significantly affected only for severe treatments. The extractive content increased with heat treatment until about 4% mass loss, decreasing afterwards. The major increase was due to water extractives from 1.2% to 4.9% at 4% mass loss. With heat treatment the original extractives disappear from the wood or are degraded, leading to new compounds mostly anhydrosugars and phenolic compounds. The ecotoxicological assays showed that water extractives of untreated and heat treated pine wood did not affect the bacterial growth. Ethanol extractives increased the length of the lag phase, mainly for heat treated wood, but without significant effects on the specific growth rate and on the cell density reached in the stationary phase. These results suggest that there was no significant increase on ecotoxicity of water and ethanol extracts and that *Bacillus stearothermophilus* may have an efficient molecular mechanism of adaptation to these compounds.

INTRODUCTION

Wood preservation plays an important role on the conservation of forest resources by allowing the increase of the material life time. However the high toxicity of the preservatives that are sometimes released from treated wood can have a significant impact on the ecosystem. Another problem is the destination to give to treated wood with high toxicity compounds at the end of its service life. In the last few years several wood modification processes were developed to correct these problems.

One of the wood modification processes that developed more in the last years was heat treatment. It started with the work of Stamm *et al.* (1946) and has nowadays several commercial processes like Thermowood in Finland, Plato in Holland, Retification and Bois-Perdure in France or OHT in Germany.

Heat treatment is considered an environmentally benign process to improve wood properties like dimensional stability and durability because there is no use of any harmful chemicals. However the heating affects both structural and extractable compounds of wood. In relation to extractives most of the original compounds are degraded or volatilized, disappearing from the wood while at the same time new compounds emerge. Graf *et al.* (2005) analyzed the gaseous emissions of a small industrial unit of thermal treatment of six woods (spruce, fir, larch, oak, ash and robinia) and concluded that about 80% of the products were acetic acid, furfural and some furfuryl derivatives. The emissions of the treated softwoods included several mono-, sesqui- and diterpenes. Manninen *et al.* (2002) reported that the emission of volatile organic compounds of air-dried Scots pine wood was about eight times higher than heat treated wood and consisted of α-pinene, 3-carene and hexanal, and of 2-furacarboxyaldehyde, acetic acid and 2-propanone, respectively. Both 2-furacarboxyaldehyde and monoterpenes are irritating for the respiratory system (Gupta *et al.* 1991, Norbäck *et al.* 1995). However some of the new compounds are not volatilized and remain in treated wood. The nature of these new compounds and their impact on the ecosystem must be evaluated.

EXPERIMENTAL

The heat treatment of pine wood (*Pinus pinaster*) was made in an autoclave with a mixture of superheated and supersaturated steam at temperatures 190-210 ºC for 2 to 12 hours as reported by Esteves *et al.* (2007a). Mass loss of treated samples was determined in relation to dry wood. The samples before chemical analysis were milled in a Retsch SMI mill, followed by a Thomas mill and sifted using a Retsch AS200 basic sifter during 20 min at 50 rpm. The fraction used for the chemical analysis was 40-60 mesh in accordance with Tappi T 264 MAC-88.

Total lignin content was determined by the Klason method (insoluble lignin) followed by absorbance measurement at 205 nm to determine soluble lignin content. The solution was used for the determination of sugar content in accordance to Tappi 249 cm-00. After neutralization the samples were derivatized by acetylation and injected in a gaseous chromatograph HP 5890A with a S2330 column and ionization flame detector as reported by Esteves *et al.* (2007b). The extractive content was determined by successive Soxhlet extraction of about 3 g of each sample using dichloromethane, ethanol and water. Soxhlet extractions were made during 10 hours for dichloromethane and 20 hours for ethanol and water. Half of the solvent containing the extractives was used for chemical analysis and the other half was dried in an oven at 40 ºC overnight, followed by 1 hour at 100 ºC. The percentage of extractives in each solvent was determined gravimetrically in relation to initial dry mass according to Tappi T 204 Mac-88. Extractives composition was determined by GC-MS analysis of trimethylsilylates in a chromatograph HP6890A with a mass detector 5973 Agilent and an Agilent Db-5ms column (Esteves *et al.* 2007b). The autoclave heat treated pine wood samples that were analysed corresponded to treatments at 190 ºC during 2, 6 and 12 hours and at 210 ºC during 12 hours, with mass losses of 0.4%, 3.5%, 3.7% and 6.7%, respectively. For ethanol and water extracts only the samples with 3.5% and 6.7% mass loss were analysed.

For the ecotoxicity tests 2g of dried wood were extracted as referred before. The extracts were concentrated to 50 ml. The strain of *Bacillus stearothermophilus* and the conditions for its maintenance and growth have been described previously (Jurado *et al.* 1987). Liquid cultures were started with an early stationary inoculum and were grown in 300 ml Erlenmeyer flasks containing 50 ml of growth medium (diluted L-Broth), at 65 ºC and shaken at 100 rpm in a GFL 1083 water bath shaker. Water and ethanol pine wood extracts were added to the growth medium in order to obtain the concentrations indicated in the figures. In experiments with ethanol pine wood extracts, control cultures were grown in a medium without pine wood extractives, but with 2% (v/v) ethanol (*e.g.* the maximum amount of solvent used). The bacterial growth was measured by turbidimetry at 610 nm in a Jenway 6505 UV/vis spectrophotometer.

RESULTS AND DISCUSSION

Structural components

Figure 1 presents the summative chemical analysis and sugar composition for untreated and heat treated pine wood as a function of mass loss for the treatment in autoclave.

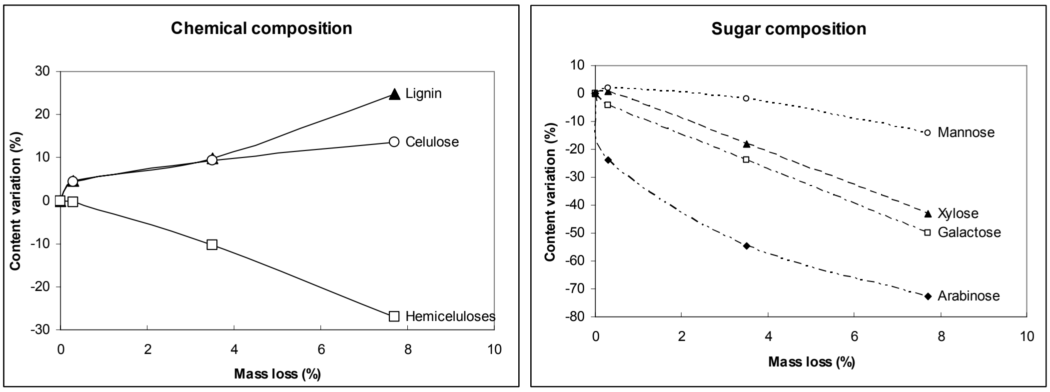

Figure 1: Variation of chemical composition with mass loss of heat treated in relation to untreated pine wood

Wood chemical composition changes along the heat treatment due to the degradation of the most thermally susceptible compounds. Even for small mass losses (0.4%) there was a decrease of hemiceluloses content which further degraded with the increase of treatment severity reaching a 27% decrease for about 8% mass loss (Figure 1). These results are in accordance with those reported by several authors who refer that wood degradation starts by deacetylation of hemiceluloses with the release of acetic acid which further catalyses degradation by depolymerization (Tjeerdsma *et al.* 1998, Sivonen *et al.* 2002). Cellulose content increased with the heat treatment as shown by glucose content which increased about 4.4% and 14.0% for 0.4% and 7.7% mass loss. Lignin content increased even more reaching a 25% increase for 7.7% mass loss (Figure 1). This does not mean that there is an increase on cellulose or lignin absolute amounts but only that there is a higher rate of hemicellulose degradation. According to some authors condensation reactions can also increase the amount of insoluble lignin in treated wood (Tjeerdsma *et al.* 1998, Wikberg and Maunu 2004). The difference in thermal degradation between cellulose and hemicelluloses is often explained by cellulose crystallinity since cellulose degradation is mainly due to the degradation of the amorphous parts leading to an increase of cellulose crystallinity (Bhuiyan and Hirai 2000, Wikberg and Maunu 2004).

The first sugars affected by the heat treatment were arabinose and galactose decreasing 24% and 4% in relation to initial content for 0.4% mass loss (Figure 1). This is probably due to the degradation of pine arabinogalactan and also possibly of arabinan, even though arabinan represents a very small percentage of wood. Increasing the severity of the treatment xylose and mannose content start to decrease, corresponding to the degradation of arabinoglucuronoxylan followed by galactoglucomannan of pine wood. For about 8% mass loss arabinose content decreased 73%, followed by galactose 50%, xylose 43% and mannose 14%. The higher degradation of pine xylan in relation to mannan was also reported by some authors (Alen *et al.* 1995).

Extractive content and composition

The dichloromethane extractives increased with the heat treatment until about 3.5% mass loss reaching about 2% and decreasing after that. Ethanol extractives increased throughout the treatment reaching 2.5% for 7.7% mass loss. The major increase in extractive content was due to water extractives from 1.2% to 4.9% at about 4% mass loss and decreasing afterwards. Total extractives also increased until about 4% mass loss, decreasing after that, since water extractives represent more than half of the extractive content. Despite the increase of the extractive content in all of the solvents, the majority of initial compounds disappeared with the treatment. For example fatty acids are the first compounds to disappear from treated wood decreasing even for 0.4% mass loss and practically disappearing for mass losses higher than 3.5%. Resin acids content also decreased for treated wood but only for mass losses higher than 3.5%, and only a small amount remains for 6.7% mass loss. These results are in accordance with Nuopponen *et al.* (2003) who reported that at 200 ºC resin acids travel from the heartwood to the sapwood and at higher temperatures disappear from wood.

Table 1: Major dichloromethane and ethanol soluble compounds of heat treated pine wood

	Extract (%)							
	Dichloromethane					Ethanol		
Compound	Initial	0.4%	3.5%	3.7%	6.7%	Initial	3.5%	6.7%
Phenolic compounds								
3-Vanilpropanol	-------	1.2	0.5	2.9	6.0	0.2	2.0	1.4
Catechol	-------	1.2	0.6	3.1	2.8	-------	-------	-------
Coniferaldehyde	-------	6.6	3.2	19.3	7.3	-------	4.8	0.3
Vanillic acid	Vest	0.4	0.2	1.0	3.2	-------	-------	-------
Vanillin	-------	1.4	0.6	4.7	17.4	0.1	0.8	0.6
Non--phenolic compounds								
3-Deoxy-D-arabino-hexonic acid	-------	-------	-------	-------	-------	-------	1.8	5.3
3-Deoxy-D-arabino-hexonic acid	-------	-------	-------	-------	-------	-------	3.0	6.3
3-Deoxy-D-erithro-pentoic-γ-	-------	-------	-------	-------	-------	-------	0.2	0.5
3-Deoxy-D-erithro-pentoic-γ-	-------	-------	-------	-------	-------	0.3	0.3	0.4
3-Deoxy-D-ribo-hexonic-lactone	-------	-------	-------	-------	-------	-------	0.9	3.4
C_5 Anhydrosugar	-------	1.5	0.4	3.7	7.4	-------	9.5	7.4
C_5 Anhydrosugar	-------	2.8	0.7	7.1	10.6	-------	6.7	3.3
Galactosan	-------	0.5	0.2	1.6	6.3	0.1	6.4	9.7
Levoglucosan	-------	Vest	0.1	0.4	15.3	0.1	2.2	28.3
Mannosan	-------	-------	-------	0.1	0.9	-------	0.4	1.7

Even for 0.4% mass loss some extractable compounds resulting from the degradation of hemicelluloses appear in the extracts. The major non-phenolic compounds were two C_5 anhydrosugars that appear on the dichloromethane extract, representing 1.5%

and 2.8% and are probably 1-5-anhydroarabinofuranose and 1-5-anhydro-β-D-xylofuranose resulting from arabinose and xylose degradation. Galactosan, possibly resulting from galactose degradation was also found in this extract with 0.5%. With the increase in treatment severity the anhydrosugar content increased representing the C_5 sugars 9.5% and 6.7% and galactosan 6.4% of the ethanol extract. Small amounts of mannosan, possibly from mannose degradation, were found for mass losses higher than 3.5%. These results confirm the decrease in sugar content mentioned earlier (Table 1).

Levoglucosan has been reported as the main product of cellulose thermal degradation (Simoneit *et al.* 1999) so the small amount of levoglucosan found for 0.4% mass loss (vestiges) and 3.5% (0.1% and 2.2% for dichloromethane and ethanol extracts) suggests that cellulose was little affected by heating which confirmed the increase of cellulose content (Figure 1). For 6.7% mass loss cellulose content was still increasing (Figure 1), although a significant amount of levoglucosan was found in the dichloromethane and ethanol extracts (15.3% and 28.3%, respectively). This means that pine wood cellulose was already significantly affected for mass losses of this order of magnitude. Some other anhydrosugars were found in the ethanol extract for 3.5% mass loss, mainly 3-deoxy-D-hexonic acids. In accordance with Luijkx *et al.* (1995) hydrothermolysis of cellulose also leads to the formation of these sugars, namely 3-deoxy-D-ribo-hexonic acid and 3-deoxy-D-arabino-hexonic acid both identified in the ethanol extract of heat treated pine wood and representing 1.8% and 3.0% respectively. These compounds may result from the heat degradation of glucose but also from mannose or fructose. All of these anhydrosugars are generally referred as resulting from the pyrolysis of polysaccharides (Faix *et al.* 1991c, d) and are also frequently found in smoke from forest fires (Nolte *et al.* 2001).

Lignin content increased throughout the treatment however; even for small mass losses (0.4%) several extractable phenolic compounds appear on treated wood extracts like catechol, vanillin, vanillic acid, 3-vanilpropanol and coniferaldehyde. These compounds are generally referred as resulting from lignin pyrolysis (Faix *et al.* 1990a, b) which means that even for small mass losses there is already some lignin degradation. The majority of these compounds can also be identified in the smoke of forest fires and surrounding air (Nolte *et al.* 2001).

The major increase in extractive content was due to water extractives but all of the compounds found on the water extract represented small amounts. This extract was essentially composed of sugars from hemicelluloses in open and close forms and of some disaccharides. However, most of the extract was not derivatized and a residue still remained at the bottom of the vial. The nonderivatized compounds of the water extract are probably some oligosaccharides resulting from the degradation of polysaccharides that could not be volatilized due to their high mass.

Ecotoxicity

The ecotoxic effects of water and ethanol extracts of untreated and heat treated pine wood were evaluated using thermophilic eubacterium *Bacillus stearothermophilus* (Figure 2). Bacteria are routinely used in whole organisms toxicity testing and are considered indicators of relative impacts on the soil and aquatic ecosystems. The eubacterium *Bacillus stearothermophilus* is a model commonly used to investigate the toxic effects of lipophilic compounds, *e.g.* citostatics (Luxo *et al.* 2000), antiarrythmics (Rosa *et al.* 2000) and pesticides (Donato, 1997; Monteiro *et al.* 2005). Figure 2 represents the effects of the increasing concentrations of water (A, B) and ethanol (C, D) extracts of untreated (A, C) and heat treated pine wood (B, D) on the optical density (O.D.) of the liquid cultures of *B. stearothermophilus*, as a function of time. The optical density is proportional to the cell density in the liquid cultures and represents the bacterial growth.

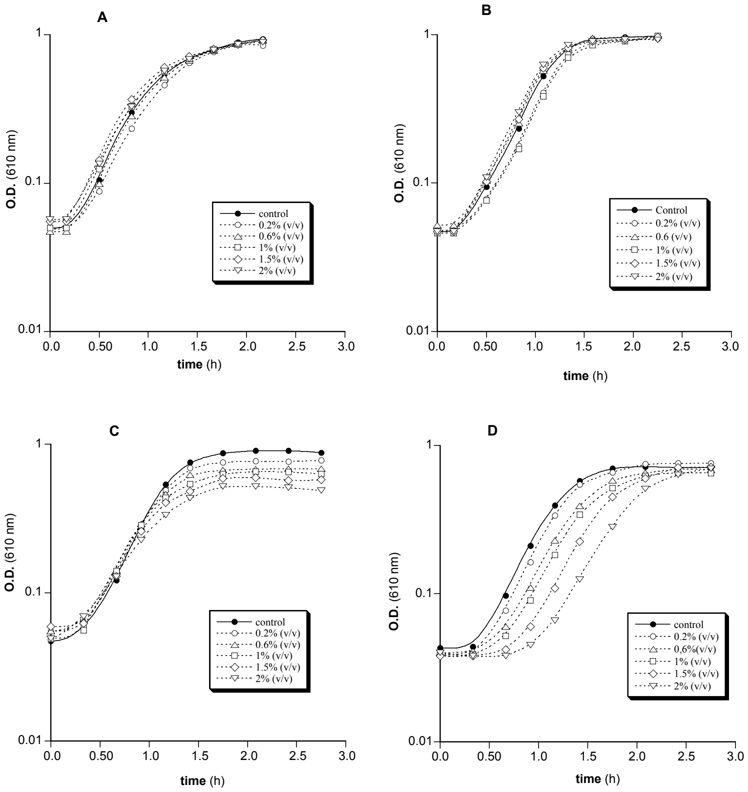

Figure 2: Effects of the water extractives of untreated (A) and heat treated (B) pine wood on the growth of cultures of Bacillus stearothermophilus. C and D show, respectively the effects of the ethanol extractives of untreated and heat treated pine wood on bacterial growth.

Data of Figure 2 show that increasing concentrations of water extracts of untreated (A) and heat treated pine wood (B) have no significant effects on the bacterial growth. In fact, the water extractives are mainly sugars (Esteves 2006), which are not toxic to bacteria. On the other hand, growth in media with increasing concentrations of ethanol extracts is differently affected by the ethanol extractives obtained with untreated and heat treated pine wood (C, D), reflecting the differences in extracts composition (Table 1). The increasing concentration of ethanol extract of untreated pine wood induces a progressively decrease of the specific growth rate and of the final cell density. However, the ethanol extract of heat treated pine wood promotes a progressively increase of the length of the lag phase and a decrease of specific growth rate. For example, the addition of 2% (v/v) of ethanol extracts of untreated pine wood to the basal medium promoted a decrease of the specific growth rate to 76.2 % and a decrease of the optical density in a stationary phase. In comparison, the same concentration of the ethanol extracts of heat treated pine wood duplicated the length of the lag period and decreased the specific growth rate to 81.3 % without any effects on the final cell density (Table 2).

Table 2: Specific growth rate

Extract concentration % (v/v)	**Specific growth rate (% of control)**			
	Untreated pine wood	**Heat treated pine wood**	**Untreated pine wood**	**Heat treated pine wood**
0.0	100.0	100.0	100.0	100.0
0.2	93.9	95.7	98.4	102.4
0.6	100.4	96.9	92.3	93.4
1.0	100.8	96.1	96.1	89.0
1.5	99.2	101.1	88.4	83.3
2.0	95.1	101.9	76.2	81.3

CONCLUSIONS

Wood chemical composition changed with the heat treatment by the degradation of both structural and extractable compounds. Hemicelluloses were the first to degrade, mainly in relation to arabinose and galactose moieties followed by xylose and mannose, leading to degradation products such as anhydrosugars like galactosan, two C_5 anhydrosugars, possibly 1-5-anhydroarabinofuranose and 1-5-anhydro-β-D-xylofuranose and mannosan. At the same time fats and fatty acids were removed from the wood followed by resin acids. Cellulose was only degraded for mass losses higher than 3.5% with the formation of levoglucosan. Lignin started to degrade already for small mass losses (0.4%) but at a slower rate than the sugars leading to the formation of soluble phenolic compounds. The overall toxicological results obtained with water and ethanol extracts indicate that heat treatment of the pine wood do not induces additional toxicity to bacteria.

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Session 7: Thermal Modification.

Near Infrared Spectroscopy Assay for Thermal Treatment of Wood

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Keywords: Acetylation, hydroxyl group, Near infrared spectroscopy, thermal treatment

ABSTRACT

This paper deals the evaluation of thermally treated wood by near infrared (NIR) spectroscopy. In the NIR second derivative spectrum, the peak at 6913 cm^{-1}, which has not been reported, appeared with the procession of heat treatment. It was assumed that it should be assigned to phenolic hydroxyl group originated from lignin because the acetylated wood did not have any peak at 6913 cm^{-1} in the second derivative spectrum. Moreover, the NIR spectra in the region of hydroxyl groups (7200 – 6100 cm^{-1}) was separated by Gauss – Newton method, and the changes in the ratio of peak area after thermal treatment to that before treatment was discussed. As a result, it was assumed that the hydroxyl groups in cellulose degraded those in amorphous, in semi-crystalline, and in crystalline region, in that order.

INTRODUCTION

The thermal modification of wood has been studied for a long time. Although there is a disadvantage that the thermal treatment of causes the decrement of strength (Stamm 1956, Millett and Gerhards 1972, Mitchell 1988, Bekhta and Niemz 2003), there are some advantages such as the increment of dimensional stabilization of wood (Stamm *et al*. 1946, Burmester 1975, Inoue *et al.* 1993, Bekhta and Niemz 2003) and colouration without the emission of harmful volatile organic compounds (Morita and Yamazumi 1987, Tolvaj *et al*. 2000, Mitsui *et al*. 2001, 2004). The dimensional stabilization is caused by the decrement of hydroxyl group of cellulose and hemicellulose, and Fengel and Wegener (1989) have shown the probable thermal degradation pathway for cellulose and hemicelluloses.

Near Infrared (NIR) spectroscopy is one of the useful methods for non-destructive measurement. Recently there have been various reports on NIR spectroscopy assay for wood (Tsuchikawa *et al*. 2003, 2004, Tsuchikawa and Siesler 2003a, b, Yonenobu and Tsuchikawa 2003, Hinterstoisser *et al*. 2003, Mitsui and Tsuchikawa 2003, Kelley *et al*. 2004, Schimleck and Evans 2004, Schimleck *et al*. 2004, Schwanninger *et al*. 2004, Fackler *et al*. 2005). In comparison with infrared (IR) spectroscopy, it is difficult to assign functional groups because of obscureness or overlapping of peaks in NIR spectrum; however, in the region of hydroxyl groups clear spectrum is obtained.

On the experiment of wood, Tsuchikawa and Siesler (2003a) reported that amorphous, semi-crystalline, and crystalline regions were discriminated.

However, there are no reports on detail discussion on hydroxyl groups of thermally treated wood using NIR measurement. In this study, the behaviour of hydroxyl groups in wood by thermal treatment was monitored using NIR spectroscopy. In addition, acetylated wood which is typical chemically modified wood for hydrophobicity was also discussed.

EXPERIMENTAL

Materials

The species used in this study was Sitka spruce (*Picea sitchensis*) having 50 × 10 × 1 mm in the longitudinal, tangential, and radial directions, respectively.

Thermal treatment

The unacetylated specimens were treated by steaming at 140 °C for 5, 10, 20, 50, and 100 hours.

Acetylation

The oven-dried specimens were treated with acetic anhydride in the liquid phase without catalyst for 6 hours at 120 °C. At the end of the reaction, the specimens were fully washed with water and dried P_2O_5, at room temperature. The weight percent gain was 20.8 ± 0.9 %.

NIR spectroscopic measurement

Before NIR measurement, the specimens were dried under reduced pressure at 60 °C. NIR spectra were measured with FT-NIR spectrophotometer (F-MATRIX, Bruker Optics Inc., Ettlingen, Germany). The wavelength of incident light varied from 10000 to 4000 cm^{-1} with a step size of 8 cm^{-1}.

RESULTS AND DISCUSSION

Changes in weight of wood by thermal treatment

Figure 1 shows the changes in weight of spruce wood by thermal treatment. The residual weight decreased with treatment time. This result concurred with previous reports (Stamm 1956, Rusche 1973, Fung *et al*. 1974).

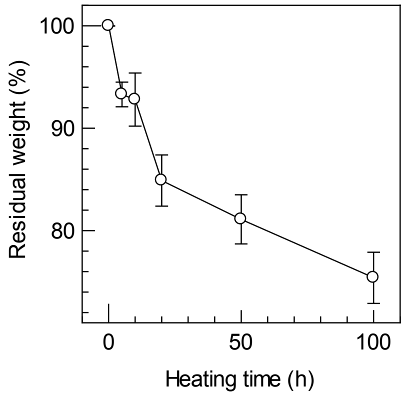

Figure 1: Changes in weight of spruce wood by thermal treatment

Changes in NIR spectra by thermal treatment

Figure 2 and Table 1 show the NIR spectra of untreated, thermally-treated for 100 hours, and acetylated wood, and the assignment of absorption bands, respectively. The absorbance from 10000 cm^{-1} to 7200 cm^{-1} in the spectrum of control sample was higher than that of acetylated or thermally treated one. It was caused by the remarkable darkening of wood by thermal treatment. In the case of acetylated wood, the absorbance at wavenumbers (7003, 6722, 6460, and 6281 cm^{-1}) assigned to hydroxyl groups in cellulose was lower, and that at 5981 and 5800 cm^{-1} assigned to CH stretching first overtone of aromatic skeletal due to lignin and CH stretching first overtone of furanose or pyranose due to hemicellulose, respectively, was higher than control one. These results indicate that acetyl groups reacted to cellulose, hemicellulose, and lignin. It was guessed that the hydroxyl group at 4808 cm^{-1} was assigned to that of cellulose or hemicellulose because it decreased by thermal treatment or acetylation. Moreover, the peak at 4281 cm^{-1} assigned to CH is due to hemicellulose, and it was guessed the increment of the absorbance by acetylation was originated from acetyl group reacted to hemicellulose and the decrement by thermal treatment was due to degradation of hemicellulose.

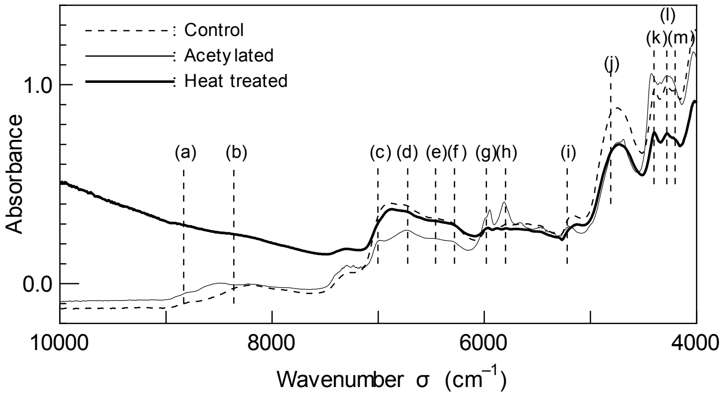

Figure 2: NIR spectra of untreated, thermally-treated, and acetylated spruce wood

Table 1: Assignment of absorption bands of NIR spectrum

	Wavelength [cm^{-1}]	**Assignment**
a	8834	CH str. second overtone, aromatic skeletal due to lignin (*1, *2)
b	8361	CH str. second overtone, CH_3 (*1, *2)
c	7003	OH str. first overtone, amorphous regions (*3)
d	6722	OH str. first overtone, semi-crystalline regions (*3)
e	6460	OH str. first overtone, crystalline regions in cellulose (*3)
f	6281	OH str. first overtone, crystalline regions in cellulose (*3)
g	5981	CH str. first overtone, aromatic skeletal due to lignin (*1, *2)
h	5800	CH str. first overtone, furanose or pyranose due to hemicellulose (*4)
i	5219	OH str. + OH def., H_2O (*1, *2)
j	4808	OH str. + OH def., OH (*1, *2)
k	4401	CH str. + CH def., CH_3 (*1, *2)
l	4281	CH str. + CH def., due to hemicellulose (*4)
m	4202	OH def. second overtone, OH (*1, *2)

**1: Osborne and Fearn 1988, *2: Siesler et al. 2002, *3: Tsuchikawa and Siesler 2003a, *4: Williams and Norris 1990.*

Figure 3 shows the expanded second derivative spectra of spruce wood. The peak at 6913 cm^{-1} which has not been reported on wood, was observed after thermal treatment. It is clear that the peak overlapped to that of amorphous region in cellulose was separated by thermal treatment, by comparison with the spectrum of control specimen. Furthermore, it is guessed that the peak at 6913 cm^{-1} is assigned to the stable substances against thermal treatment because second derivative values ($d^2A/d\sigma^2$) around 6913 cm^{-1} before and after treatment have almost same. On the other hand, there was no peak around 6910 cm^{-1} in the spectrum of acetylated wood. That is, it is guessed that the peak is assigned to the function groups which have high reactivity to acetylation. Therefore, this peak (6913 cm^{-1}) should be assigned to phenolic hydroxyl groups originated from lignin.

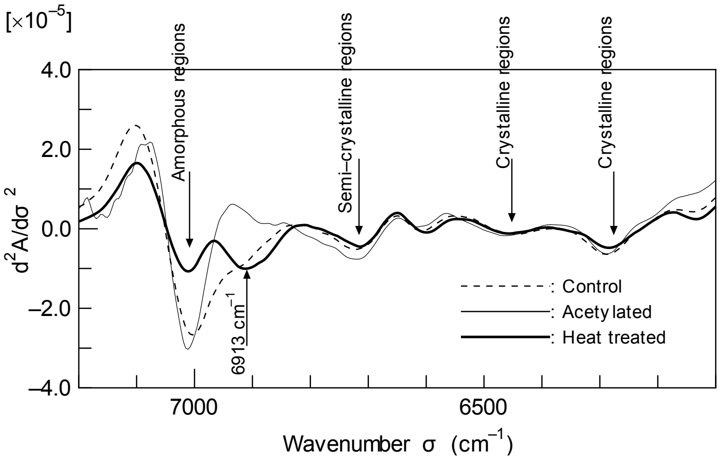

Figure 3: Expanded second derivative spectra of spruce wood

Next, the spectra was separated by Gauss – Newton method after baseline correction between 7200 cm^{-1} and 6100 cm^{-1} as shown in Figure 4 to discuss the thermal degradation of hydroxyl groups. Figure 5 shows the changes in ratio of peak area after thermal treatment to that before treatment. The ratio of peak area of all the hydroxyl groups decreased with thermal treatment time. The order of degree of decrement was that of amorphous region > semi- crystalline region > crystalline region (6460 cm^{-1}) =

crystalline region (6285 cm^{-1}) in cellulose > phenolic hydroxyl group. That is, hydroxyl group in cellulose starts from amorphous region, and the degradation follows to semi-amorphous and crystalline regions.

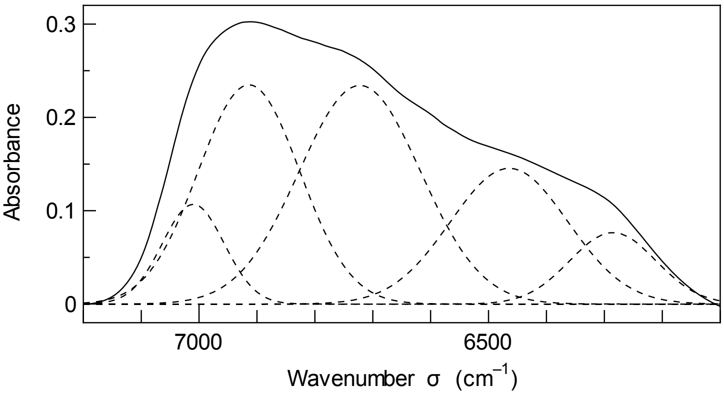

Figure 4: Spectral separation based on Gauss-Newton method

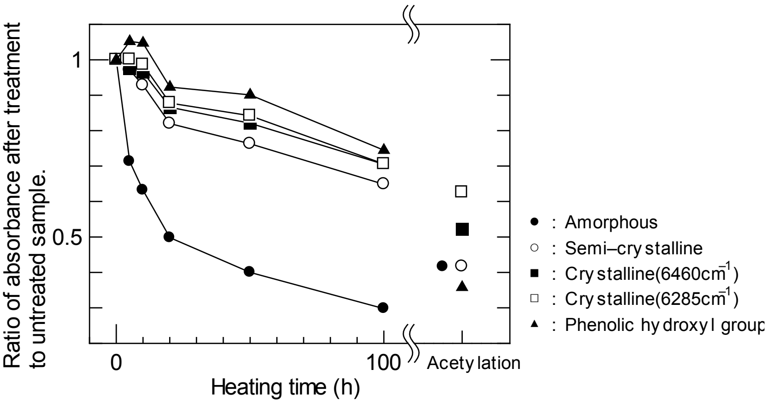

Figure 5: Changes in ratio of peak area after thermal treatment to that before treatment

The discussion on hydroxyl groups in hemicellulose has not been carried out yet. In a future study, we will discuss the assignment of hydroxyl groups in hemicellulose.

CONCLUSIONS

We discussed the evaluation of thermally treated wood using NIR spectroscopy. We concluded that the peak at 6913 cm^{-1} was assigned to the phenolic hydroxyl groups originated from lignin in comparison with the spectrum of acetylated spruce. Furthermore, it was guessed that the hydroxyl groups in cellulose degraded those in amorphous, in semi-crystalline, and in crystalline region, in that order.

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Anatomical and Molecular Reasons for Property Changes of Wood after Full-scale Industrial Heat Treatment

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Keywords: Thermal wood modification, dimensional stability, strength, durability

ABSTRACT

Thermal modification or heat treatment is an effective method to improve the dimensional stability and biological durability of wood. An undesired side effect is the reduction of mechanical properties of wood, mainly due to the high temperatures involved (150-280 °C). In this study the effects of heat treatment on wood properties have been discussed in relation to anatomical and molecular changes found in wood after heat treatment. The results are based on investigations of a full-scale industrial heat treatment method under relative mild conditions (< 200 °C) including a moist and dry treatment stage. Several changes and or modifications of the main components of wood (cellulose, hemicelluloses and lignin) appear to be involved in the effects of heat treatment on important wood properties like dimensional stability, strength/stiffness and biological durability. Although the effect of heat treatment on the anatomical structure of wood is limited, changes have been found affecting the properties of wood. This paper provides a better understanding of thermal modification which probably contributes to a more controlled use of heat treated wood in service conditions.

INTRODUCTION

All over the world there is an increasing demand for sustainable building materials in order to reduce the CO_2 emission and energy consumption. Wood is a ubiquitous and dependable material for construction works and used in a very broad range of applications like furniture, building, road works, water works etc. The huge diversity in timber species guarantees that there is always a species with the required properties for a specific purpose. The economic impact of timber products is therefore considerable. However, the growth of the human population is causing an increasing pressure on forests with high quality timber for construction and other purposes. Furthermore, deforestation which results in the green house effect, erosion of fertile soil, and a reduction of the bio diversity. There is clearly a declining production of high quality or more specifically of durable timber from the current forests available. In future as a consequence of increased introduction of governmental restrictive regulations protecting the environment the availability of this material will be even more reduced. A solution to this could be the increased use of the adequate reserve of less durable timber species. To that end, technologies for improving timber dimensional stability and/or durability are indispensable.

Thermal modification or heat treatment is such a technology enabling the upgrading of lower durability softwood and hardwood species like Scots pine, Norway spruce, birch, and poplar into wood products of constant quality. These can be used for a broad range of applications such as garden fences and channel linings or even cladding, decking and exterior joinery. The main effect gained by a heat treatment of wood is reduced wood hygroscopicity. Foremost advantages of wood treated in this manner are increased resistance to different types of biodegradation and improved dimensional stability. However, originally some undesired side effects, in particular loss of strength and increased brittleness of the treated wood were the main objections for overall commercial utilisation of heated timber. Development of suitable thermal modification techniques are in essence optimisation of the process for a maximum increase of the dimensional stability and durability, while minimising the decrease of the strength. The Plato process embodies an effective two-step process under relatively mild conditions (<200 °C) minimising these disadvantages and hence yielding more noticeable and consistent improvements. This effective two-step heat treatment is based on five distinct process stages:

1. Pre-drying stage in a conventional industrial wood kiln to a moisture content of 14-18%;
2. Hydro-thermolysis stage, the timber is heated to 150 °C-180 °C in an aqueous environment at superatmospheric pressure;
3. Drying stage in a conventional industrial wood kiln using common procedures to a moisture content of 8-9%;
4. Curing stage, the timber is heated once again to 150 °C-190 °C, but now under dry and atmospheric conditions;
5. Conditioning stage, the moisture content of the timber is elevated to a level which is necessary for manufacturing. Conditioning is done in the same conventional industrial wood kiln as the drying stage.

Experimental work revealed the hydro-thermolysis stage to be the most critical process stage in the two-step heat treatment method, affecting both wood quality and wood properties (Tjeerdsma *et al*. 1998b and 2002, Tjeerdsma and Militz 2005, Boonstra and Tjeerdsma 2006, Boonstra *et al*. 2006a and 2006b). Variations of the process conditions (e.g. temperature, effective process time) during the hydro-thermolysis stage showed a larger impact on the quality and properties of treated wood than variations during the curing stage. For this reason much attention has been focussed on the development of the first treatment stage and its effect on the anatomical structure and wood properties.

In order to optimise the process it is of considerable importance to understand which modifications and reactions occur in wood resulting in environmental and performance advantages. In this paper the effects of the two-step heat treatment on physical and strength properties of wood are discussed in relation to the chemical and physical changes of wood after heat treatment. This provides a better understanding of thermal modification which probably contributes to a more controlled use of heat treated wood in service conditions.

CHEMICAL, MICROSTRUCTURAL AND PHYSICAL ASPECTS OF HEAT TREATMENT

Chemical changes of wood after heat treatment

In the moist treatment stage, the hydro-thermolysis, hemicelluloses are depolymerised by hydrolysis reactions to oligomers and monomers (Tjeerdsma *et al.* 1998a, Boonstra and Tjeerdsma 2006). This involves cleavage of the side chain constituents (arabinose and galactose), followed by degradation of the main chain constituents (mannose, glucose and xylose). The corresponding pentoses and hexoses are dehydrated to respectively furfural and hydroxymethylfurfural (Bobleter and Binder 1980, Abatzoglou *et al.* 1990). Other aldehydes such as formaldehyde have also been found due to cleavage of the carbohydrates C6 as well as from the Cγ of lignin (Fengel and Wegener 1989, Tjeerdsma *et al.* 1998a). Furthermore, cleavage of acetic acid from acetyl side chains of hemicelluloses occurs and reduces the acetyl content of wood (Tjeerdsma *et al.* 1998a, Tjeerdsma and Militz 2005, Boonstra and Tjeerdsma 2006). Hydronium ions generated by water autoionization are thought to act as catalists in the initial reaction stages. In further reaction stages, the hydronium ions generated from acetic acid autoionization (and possibly some other acids such as levulinic and formic acid) also acts as catalists and their contribution become more important than that of water autoionization (Garrotte *et al.* 1999). The degradation of the hemicelluloses and the release of acids depend on the process conditions applied, such as process temperature, treatment time and pressure (Belkacemi *et al.* 1991). However, it appears that it is the process temperature and possibly the corresponding pressure which play an important role in the degradation of hemicelluloses during the hydro-thermolysis stage (Tjeerdsma and Militz 2005, Boonstra and Tjeerdsma 2006). The presence of water is of eminent importance since no reactivity of wood components and especially the hemicelluloses are observed at a treatment temperature below 180 °C under dry and atmospheric conditions (Weiland and Guyonnet 1997). Indeed, during the second heat treatment stage (curing) performed under dry and atmospheric conditions at a very low oxygen level, no further degradation of the remaining hemicelluloses were observed (Boonstra and Tjeerdsma 2006).

Degradation of cellulose is limited since the temperatures used during this heat treatment process are too low (165-185 °C). According to Torres *et al.* (1986) very little cellulose passes into solution at temperatures below 200 °C, whereas the solubilization of cellulose becomes important beyond 220 °C. Cellulose has a highly ordered crystalline structure which provides a high stability to the cellulose chains and protects them against acid attack during hydrolysis (Fengel and Wegener 1989). Although no cellulose degradation occurs during the hydro-thermolysis of wood (Boonstra and Tjeerdsma 2006) heat treatment under moist conditions, such as the hydro-thermolysis stage, appears to have a stimulating effect on the crystallization of amorphous cellulose (Bhuiyan and Hirai 2000). During curing some (amorphous) cellulose degradation is observed, probably due to the different process conditions applied (dry atmospheric heat treatment) and/or due to a longer effective treatment time (4-6 hours at 180 °C instead of 30 minutes at 165 °C). Thus, an increase of the relative amount of crystalline cellulose is observed, but it can be questioned whether this is due to the degradation or to the crystallization of amorphous cellulose (or both).

During heat treatment lignin can be subject to degradation, but also to condensation or repolymerization reactions (Burmester 1975, Bobleter and Binder 1980, Tjeerdsma *et al.* 1998a, Sivonen *et al.* 2002, Hakkou *et al.* 2005). The covalent bonds between lignin and hemicelluloses will be broken and low molecular weight lignin fragments with high reactivity are produced. Demethylation or more likely demethoxylation of the methoxy groups at the C3 position of the aromatic nuclei of lignin has been observed during the hydro-thermolysis treatment stage (Tjeerdsma *et al.* 1998a). This results in a higher number of aromatic lignin sites available for reactions and an increased reactivity of the aromatic nuclei of lignin. An increase in the proportion of methylene bridges connecting two phenolic nuclei has been noticed. Formaldehyde and furfuraldehyde which are produced during the hydro-thermolysis stage are the likely contributors to the formation of these methylene bridges. Lignin cleavage at the O4 and at the Cα of some lignin units appears to occur followed by autocondensation of the reactive -CH2 group formed with a free reactive site on the phenolic nuclei of another lignin unit. Stable free radical centres have been found after a dry heat treatment and they are most likely involved in the condensation reactions of lignin (Sivonen *et al.* 2002). A decrease of the C=O absorption band at 1650 cm-1 and 1740 cm-1 has been observed in the FTIR spectra of wood after the hydro-thermolysis stage (Tjeerdsma and Militz, 2005). This is an indication of degradation of conjugated *p*-substituted aryl ketones (1640 cm^{-1}) and of unconjugated ketone, carbonyl and ester groups (1740 cm^{-1}). It is expected that the functional groups of lignin are mainly involved since these absorption bands are characteristic for lignin and to a much lesser extend hemicelluloses (Baeza and Freer 2001). After the curing stage a noticeable increase of the C=O absorption band at 1650 cm^{-1} and 1740 cm^{-1} was observed. According to Tjeerdsma and Militz (2005) this is due to esterification reactions and the newly formed carbonyl groups were mainly linked to the lignin complex. However, an increase of these absorption bands after the curing stage might be related to the formation of esters, but also to the formation of ketons and carbonyl groups. In ^{13}C NMR spectra of treated wood a decrease of the C=O peak at 175 ppm (esters and/or organic acids) is observed after the hydro-thermolysis stage whereas this peak increased after the curing stage (Tjeerdsma *et al.* 1998a). Since the aldehyde and ketone peaks at respectively 190 and 200 ppm are unchanged this favours the formation of esters and/or organic acids during the curing stage (or both). The organic acids can be situated free in the woody structure or they are bounded to the remaining and/or modified wood components (Gerardin *et al.* 2007). Interesting are the UV absorption spectra of the secondary cell wall and middle lamella, before and after heat treatment (Boonstra and Tjeerdsma 2006). The UV spectrum of the secondary cell wall shows a clear increase of the maximum absorption at 280 nm, much higher than that of the middle lamella. This can be caused by condensation reactions in which the lignin complex is involved and/or to the formation of other aromatic structures during heat treatment, such as furfural and hydroxymethylfurfural. The secondary cell wall contains more hemicelluloses than the middle lamella (Fengel and Wegener 1989) and thermal depolymerisation results in a higher production of furfural from them.

An important reason to perform the second heat treatment stage (curing) is that condensation reactions are relatively slow. This enables further autocondensation reactions (repolymerisation) resulting in new lignin based polymers (Garrotte *et al.* 1999) and/or in an increased cross-linking of the existing lignin network. The formation of a lignin-cellulose complex due to condensation reactions has also been suggested (Košíková *et al.* 1999).

Microstructural and physical changes of wood after heat treatment

The wood colour after the first treatment stage (hydro-thermolysis) varies from was light to dark brown, caused by the formation of quinones (Tjeerdsma *et al*. 1998a) or the caramellization of holocellulose components (Boonstra and Tjeerdsma 2006). An increase of the treatment temperature changed the colour into a darker tinge. Most of the colour changes occur during the hydro-thermolysis, whereas treatment of wood specimens without the first treatment stage (only the curing) resulted in a light brown colour, much lighter than after the hydro-thermolysis. The colour change also depends on the timber species used and is correlated to the density of the wood since the colour is becoming darker with an increasing density. A microscopic analysis revealed that the colour of the cell wall changes from white to brown. This colour change involves both the compound middle lamella and the secondary cell wall. This is believed to be due to the formation of reaction products in the cell wall or to the diffusion of such reaction products within the cell wall.

The effects of heat treatment on the anatomical structure of wood is rather limited, although this depends on the wood species considered and on the process method and conditions used (Boonstra *et al*. 2006a and 2006b). Softwood species with narrow annual rings and/or an abrupt transition from earlywood into latewood are sensitive to tangential cracks in the latewood section. Radial cracks occur mainly in impermeable wood species such as Norway spruce, caused by large stresses in the wood structure during treatment. Sapwood of treated pine species reveal some damage to parenchyma cells in the rays and epithelial cells around resin canals, whereas this phenomenon has not been noticed in the heartwood section. Treated radiata pine results in a very open and permeable wood structure limiting the applications of this species.

Hardwood species such as beech and poplar, are predominantly sensitive to collapse of the vessels and some deformation of the libriform fibres directly near the vessels. In treated beech and birch radial cracks are observed near the rays. Optimisation of the process conditions including the application of a steam hydro-thermolysis stage reduced such damages to a minimum.

Broken cell walls perpendicular to the fibre direction resulting in transverse ruptures have been noticed in treated softwood and hardwood species. This contributes to abrupt fractures of treated wood as observed in bending tests which can lead to considerably different failure behavior after impact or mechanical stress. In some treated softwood and hardwood species maceration (small cracks between tracheids) was noticed after heat treatment. Heat treatment does not cause damage to the ray parenchyma pit membranes, bordered pits and large window pit membranes; the margo fibrils appear without damage.

PHYSICAL PROPERTIES

One of the most striking effects of heat treatment is a reduction of the hygroscopicity while the typical sigmoid curve of the hysteresis is maintained (Tjeerdsma *et al.* 1998b). A positive effect of the hysteresis is that small changes in relative humidity do not immediately result in a change of the moisture content of the treated wood. This contributes to the dimensional stability of the treated wood, because swelling and shrinkage is due to the water absorption and desorption of wood. Moreover, a reduction in water absorption reduces the overall swelling and shrinkage of wood, hence improving its dimensional stability (Seborg 1953, Kollmann and Schneider 1963, Hillis 1964, Stamm 1964, Burmester 1973 and 1975, Giebeler 1983, Bourgois and Guyonnet 1988, Boonstra *et al.* 1998, Tjeerdsma *et al.* 1998b).

It has been found that wood hygroscopicity is influenced by the process conditions (temperature, time, pressure) and the process temperature appears to be the most influential parameter (Tjeerdsma *et al.* 1998b, Tjeerdsma *et al.* 2002, Tjeerdsma and Militz 2005). The availability and/or accessibility of the free hydroxyl groups of the wood carbohydrates play an important role in the process of water adsorption and desorption (Boonstra and Tjeerdsma 2006). Heat treatment results in a reduction of free hydroxyl groups which might hinder the accessibility to water (Pizzi *et al.* 1994). Several causes have been reported, *e.g* depolymerisation of the carbohydrates and especially hemicelluloses causing a reduction of the total amount of hydroxyl groups, including the free hydroxyl groups (Burmester 1975, Kollmann and Schneider 1963); an increase of the relative proportion of the crystalline cellulose, in which the hydroxyl groups are not easily accessible to water molecules (Pott 2004, Tjeerdsma *et al.* 1998a); and cross-linking of the lignin network which decreases the accessibility of the free hydroxyl groups (Bobleter and Binder 1980, Burmester 1975, Pizzi *et al.* 1994, Tjeerdsma *et al.* 1998a).

A material property which is clearly altered during heat treatment is the density of wood. The main reasons for the decrease of the density of wood after heat treatment are: the degradation of wood components (mainly hemicelluloses) into volatile products which evaporate during treatment; the evaporation of extractives; and a lower equilibrium moisture content since heat treated wood is less hygroscopic.

MECHANICAL PROPERTIES

It is well known that heat treatment causes a reduction of mechanical properties of wood, due to the relative severe process conditions used, especially at high temperatures between 150-280 °C (Seborg *et al.* 1953, Stamm 1964, Davis and Thompson 1964, Rusche 1973, Giebeler 1983, Tjeerdsma *et al.* 1998b, Kubojima *et al.* 2000, Bekhta and Niemz 2003, Boonstra *et al.* 2007a). The industrial two-step heat treatment method also revealed a clear effect on the mechanical properties of wood (Boonstra *et al.* 2007a and 2007b). The tensile strength parallel to the grain shows a large decrease and it is expected that also the shear strength reduces after heat treatment. On the other hand, the compressive strength parallel to the fibre and hardness increases after heat treatment. The bending strength which is a combination of the three primary stresses (tensile, compressive and shear stress), is lower after heat treatment. However, this decrease is not as high as the decrease of only the tensile strength. An increase of the modulus of elasticity (MOE) during the bending test has been noticed, whereas the impact strength shows a rather large decrease after heat treatment.

The mechanical properties of wood are closely related to the moisture content of the timber. Increased amounts of bound water interferes with and reduce hydrogen bonding between the main polymeric components of the cell wall and thereby decreases the strength properties of wood since strength is related to covalent but also to hydrogen intrapolymer bonds (Fengel and Wegener 1989, Winandy and Rowell

1984). Therefore, heat treatment shows a positive contribution to the strength properties since heat treated wood is less hygroscopic and the (maximum) amount of bound water is reduced (Boonstra *et al*. 2007a).

According to a hypothetical model by Winandy and Rowell (1984) the main components of the cell wall (cellulose, hemicelluloses, lignin) contribute in different degrees to the strength of wood. A chemical or thermal modification method that affects the individual wood components and their interaction must therefore affect the mechanical properties of wood (Rowell 1996). Cellulose is thought to be primarily responsible for strength in the wood fibre because of its high degree of polymerisation (DP 5000-10000 units) and linear (crystalline) orientation (Stamm 1964, Pettersen 1984, Fengel and Wegener 1989). Heat treatment results in a small but noticeable degradation of amorphous cellulose causing some disturbance and/or depolymerisation of the cellulose polymer (Boonstra and Tjeerdsma 2006). This could be an important reason for the observed decrease of the tensile strength. However, according to Stamm (1964) internal stresses are distributed among several cellulose microfibrils/fibrils. Furthermore, the effect of the cellulose polymer length on the strength is limited since the tensile strength is not changing at DP's over 300. Whether or not the crystallization of amorphous cellulose is involved in the decrease of the tensile strength is not clear.

Since crystalline cellulose shows significant anisotropy, its stiff and rigid structure might contribute to the increase of the compressive strength in longitudinal direction. Due to this anisotropic character the compressive strength is limited in the radial and tangential direction. The decrease of the radial compressive strength after heat treatment might be caused by small radial fissures which were noticed in Scots pine after heat treatment (Boonstra *et al*. 2006a). Another reason might be the damage of parenchyma cells in the rays and epithelial cells around resin canals during heat treatment (Boonstra *et al*. 2006a). Rays contributes to the compressive strength in radial direction (Kennedy 1968, Ellis and Steiner 2002) and damages of the rays might decrease the compressive strength.

It has been suggested that degradation and/or modification of the hemicelluloses are primarily responsible for the initial loss of bending strength, since no depolymerisation nor degradation of cellulose and lignin were observed after heat treatment (Sweet and Winandy 1999, Winandy and Lebow 2001). Raising the effective treatment temperature and/or increasing the treatment time during the hydro-thermolysis stage resulted in a further decrease of the bending strength (Boonstra *et al*. 2007a). Hemicelluloses are the most thermal-chemically sensitive component of wood and it has been found that more severe process conditions during this hydro-thermolysis stage resulted in a further degradation of the hemicelluloses confirming a possible relationship (Boonstra and Tjeerdsma 2006). LeVan (1990) proposed that cleavage of the sidechains of hemicelluloses within the lignin-hemicelluloses matrix caused disruption of load-sharing capacity and therefore might be responsible for the observed strength losses. Another explanation which is given for the observed initial strength loss was a reduction of the DP of hemicelluloses, which means a degradation of the hemicelluloses backbone.

The small but noticable increase of the MOE is probably due to the increase of the relative amount of crystalline cellulose after heat treatment, although degradation and/or modification of the hemicelluloses, disrupting the load-sharing capacity of the lignin-hemicelluloses matrix, might also have an effect on the MOE. Furthermore, heat treated wood is less hygroscopic than untreated wood (it contains less bound water in the cell wall), which affects the MOE making wood less elastic.

Whether or not lignin is directly involved in the effect of heat treatment on the mechanical properties is not clear. Lignin acts as a stiffener of the cellulose microfibrils/fibrils (Sweet and Winandy 1999) and an increased cross linking of this polymer appears to prevent or limit movement perpendicular to the grain. Furthermore, lignin is the main component of the middle lamella (Fengel and Wegener 1989) and an increased cross linking of the lignin polymer network improves the strength of the middle lamella which subsequently affects the strength properties of the cell wall. This can be an indication that the lignin polymer network contributes directly to the strength of wood. Findings of Banoub and Delmas (2003) indicating a regular structure within the lignin polymer network support this statement, since regular structures are expected to add a constructive contribution to the strength of wood.

In most studies defect free specimens are used to determine the effect of heat treatment. Defect free specimens can be used to compare the effects of different treatment processes and/or different treatment conditions but not for the calculation of constructive elements, at least not without the use of several safety factors (Brown *et al.* 1952, Kollmann 1968, McKenzie 2000, Natterer *et al.* 2004). Large scale experiments of full construction Norway spruce timber revealed a decrease of the bending strength after heat treatment, much higher than the decrease of defect free specimens (Boonstra *et al.* 2007a and 2007b). The effect of natural defects, such as knots, resin pockets, deviating slope of grain and reaction wood, on the strength properties of timber appeared to be affected by heat treatment. At failure heat treated timber reveals a rather large and abrupt fracture, whereas untreated timber shows a more gradual decrease of the stress. The external forces heat treated wood can bear after initial failure are much lower than for untreated wood. Broken cell walls perpendicular to the grain appears to be the cause for this phenomenon (Boonstra *et al.* 2006a and 2006b), although changes of the main wood components might also be involved, especially degradation of the carbohydrates and/or crystallization of amorphous cellulose (making wood more brittle). The displacement until failure is much lower for heat treated timber confirming a rather stiff and brittle character. Contrary to the bending strength the modulus of elasticity of full construction timber is still increased after heat treatment. Since MOE is often the most critical parameter for a construction, higher stiffness results in lower deflection for a given load, heat treatment appears not to lower the potential for constructive applications. The effect of a three year period of outdoor exposure on the strength properties of heat Norway spruce timber was limited (Boonstra *et al.* 2007b). Especially for the 5%-value low strength range where wood defects strongly determines the mechanical properties of timber, a three years outdoor exposure did not change the bending strength and modulus of elasticity of heat treated timber. Thus heat treated timber shows potential for use in constructions. However, it is important to carefully consider the stresses that occur in a construction and some practical consequences when heat treated timber is used since the impact of heat treatment on different strength properties is not proportional. Heat treated timber might therefore respond different to stresses applied on the construction, limiting or favouring this material for constructions.

DURABILITY AGAINST FUNGAL ATTACK

Many organisms can deteriorate wood and fungal decay is the prominent kind of microbiological deterioration since it can cause (a rapid) structural failure. Fungal decay is a very complex process and depends on the fungi (brown rot, white rot and/or soft rot) and wood species involved, wood structures, (micro)environments, as well as interactive competition. During decay the main wood components (cellulose, hemicellulose and lignin) are depolymerised and/or modified in order to provide energy and metabolites for fungal growth. Other important requirements for fungal growth are the occurrence of free water and oxygen, a favourable pH and temperature, the occurrence of chemical growth factors, and the absence of toxic extractives (Highley *et al.* 1992, Zabel and Morell 1992). Since heat treatment improves the resistance against biodegrading organisms it must affect one or more requirements necessary for fungal growth.

Although heat treatment reduces the water absorption of wood (Tjeerdsma *et al.* 1998b), it does not prevent the occurrence of free water on the surfaces of cell lumina (the moisture content can increase much higher than the fibre saturation point). Free water can therefore still serve as reactant in chemical decay processes (e.g. hydrolysis), as a diffusion medium for enzymes and solubilized substrate molecules, and as a solvent or medium for life systems within the fungal hyphea. However, heat treatment causes a significant reduction of the fibre saturation point of the cell wall: 16-18% whereas 28-30% is commonly found for untreated wood (Tjeerdsma *et al.* 1998b). This reduces the swelling of the cell wall preventing or limiting the penetration of (non-)enzymatic systems necessary for fungal decay. Furthermore less water is available in the cell wall to allow diffusion of degradation products of carbohydrates to the fungal hyphae in the cell lumina. The obligate aerobic fungi require free oxygen for several metabolic reactions (e.g. energy release, synthesis) and it is expected that heat treatment does not affect the occurrence of free oxygen in wood (in cell lumina and cell wall).

Heat treatment reduces the pH of wood to 3.5-4.0 due to the production of acetic acid and formic acid, whereas a pH of 5.0-5.5 is commonly found for untreated wood (Boonstra *et al.* 2007c). The significant higher hydrogen concentration probably affects decay processes, e.g. it inhibits minor metal solubilities affecting exocellular decay processes in wood and/or it destabilises exoenzymes. Changes of the pH during the service life of heat treated wood products, resulting in a higher pH, might alter the sensitivity of heat treated wood to wood-decaying fungi. Most wood-decaying fungi grow best within a 15 to 40°C temperature range (Zabel and Morrel 1992), but it is not expected that heat treatment does have an effect on the temperature requirement of fungi.

Heat treatment could affect chemical growth factors (nitrogen, vitamins, minor metals and mineral elements) which are necessary for fungal growth. For example, heat treatment results in the degradation of thiamine and the absence of growth factors like thiamine could contribute to decay resistance (Baechler 1959). However, it is expected that wood destroying fungi can still get access to such components since such growth factors are still available from sources outside the wood in the form of surface molds, air-borne spores, organic dust, washings from overhanging trees, and others.

During heat treatment several phenolic compounds, polynuclear hydrocarbon derivates of phenantrene and acenaphtylene and other classes of polyaromatic compounds are produced (Kamden *et al.* 2000, Boonstra *et al.* 2007c). Such compounds can be toxic to wood degrading fungi and prevent or slow down fungal growth. However, no effect on fungal decay after removal of such compounds by extraction was reported and the contribution of toxic compounds to decay resistance seems therefore limited (Kamden *et al.* 2002).

As described above, heat treatment causes a modification of the main components of wood and changes the composition of these components. This plays an important role in the resistance of heat treated wood against fungal attack. Changes of the main wood components which are necessary to provide energy and metabolites for fungal growth, might affect the enzymatic and non-enzymatic mechanism of wood decay. In wood decay hemicelluloses are often the first cell-wall components degraded, probably owing to their shorter chain lengths, solubility, and exposed locations around the cellulose microfibrils (Zabel and Morell 1992). Heat treated wood contains a significant lower hemicelluloses content and most of the remaining hemicelluloses are modified (e.g. cleavage of acetyl side chains). As a result less hemicelluloses are available to provide energy and metabolites for fungal growth, especially in the initial stage of decay. It appears that hemicelluloses and perhaps lignin are critical to the mechanism involved in degradation of cellulose (Lyr 1960, Highley 1977, Enoki *et al.* 1988) and less or modified hemicelluloses might therefore affect cellulose degradation. On the other hand, the access to cellulose might be easier since less hemicelluloses surround the cellulose microfibrils.

Oxidation and hydrolysis appears to be the mechanism involved in cellulose degradation and this mechanism is rather similar for brown-rot and white-rot fungi (Cowling and Brown 1969, Koenigs 1974, Zabel and Morell 1992). Although the changes of cellulose are limited after heat treatment there might be a direct or indirect effect on the decay processes during fungal exposure. The increase in the crystalline cellulose proportion might limit or slow down the initial attack of non-enzymatic oxidizing agents and/or prevent diffusion of soluble oligosaccharides or monosaccharides to the wood cell lumen.

Although brown rot fungi do not produce ligninolytic enzymes, they do have a non-enzymatic mechanism that results in oxidative demethylation and oxidation of the propyl side chains of lignin. According to Goodell (2003) both the level and the type of lignin have very little effect on the decay of brown rot fungi. This indicates that lignin changes which occur during heat treatment should have no direct effect on the decay resistance against brown rot fungi. White rot fungi are capable to degrade lignin due to a non-enzymtic and enzymatic (ligninolytic) mechanism. Heat treated birch showed a clear improvement of the resistance against white rot attack, *Coriolus versicolor* and especially *Stereum hirsutum* (Boonstra 2007c). These fungi are capable to degrade both the carbohydrates and lignin and there is probably more than one reason for this heat treatment effect, *e.g.*

- changes of the external conditions affecting the microenvironment (extracellular slime layer) needed for lignin degradation. Exoenzymes can be destabilized which then prevent production of non-enzymatic oxidizing agents and/or prevent degradation reactions by ligninolytic enzymes. However, exoenzymes were found to be quite stable (Micales *et al.* 1987, Highley and Micales 1990), so this effect might be limited;

- blocking the (radical) reactions of non-enzymatic oxidizing agents in initial stages of decay. Phenolic compounds, formic acid (or formate) and acetic acid (or acetate) present in heat treated wood can act as scavengers of the hydroxyl radical affecting Fenton reactions; and
- changes (modification) of the substrate, especially hemicelluloses and lignin. Non enzymatic oxidizing agents can still be active, but the enzymatic mechanism in the outer decay zone can be affected since enzymes are highly specific to the substrate.

A solid state CP MAS ^{13}C NMR study of heat treated Norway spruce revealed similarities but also clear differences after exposure to brown-rot and white-rot fungi when compared to untreated Scots pine sapwood (Boonstra *et al.* 2006c). Brown rot fungi appears to have a preference to attack the carbohydrates at C4 and especially C1 cleaving the skeleton of cellulose and glucomannans. In untreated Scots pine sapwood this attack mainly occured at C4, the non-reducing end of the glucose unit. Attack on the out-of-the-ring alcoholic group CH_2OH of the carbohydrates of heat treated Norway spruce is observed but less obvious than in untreated Scots pine. The fungus possibly tried to cleave the out-of-the-ring CH_2OH group on the main H-bond fixing sites of the crystalline structure in order to open the cellulose crystalline structure to an amorphous structure to decrease its water repellency and facilitate enzymatic cellulose degradation. Remarkable is the attack on the C3/C5 of the carbohydrates, indicating ring opening of the glucose units, which was not observed in untreated Scots pine sapwood. Lignin degradation is limited to demethoxylation and low or no aromatic ring opening is observed, even after exposure to the white-rot fungus *C. versicolor*. Fungal exposure in ground contact revealed an attack of the carbohydrates of heat treated wood at C1 and possibly at C4 in order to cleave and eventually depolymerise cellulose and hemicelluloses (Boonstra *et al.* 2006d). An attack on the out of the ring alcoholic group, -CH_2OH, of the carbohydrates was also observed. The opening of the glucose pyranose ring in heat treated tropical wood species Simaruba after ground contact exposure, not observed in untreated wood, was remarkable. Demethoxylation and some ring opening of the aromatic structure of lignin has been observed, for treated and untreated wood species.

Fungal attack of heat treated wood can be affected by the treatment conditions used, e.g. process time and especially temperature (Boonstra *et al.* 2007c). An increase of the temperature and process time during the hydro-thermolysis stage causes a further degradation and/or modification of the hemicelluloses in the cell wall (Boonstra and Tjeerdsma, 2006). Since there are more reactive intermediates (*e.g.* furfural) available more cross linking reactions (e.g. polycondensation) occur increasing the lignin polymer network. More severe process conditions probably also increases the relative proportion of the crystalline cellulose. The decay of heat treated wood during exposure to the brown rot fungus *Coniophora puteana* decreased after increasing the temperature and/or process time during the hydro-thermolysis treatment. The increased changes of the wood components during these severe heat treatment conditions might have contributed to this improved resistance against *C. puteana* decay. The minimal effect of more severe treatment conditions on the attack of the brown-rot fungus *Poria placenta*, is remarkable. It is known that hemicelluloses are necessary for the degradation of cellulose by *P. placenta* (Lyr 1960, Highley 1977, Enoki *et al*. 1988). An increased degradation and/or modification of the hemicelluloses did not affect the *P. placenta* decay of heat treated wood. It is possible that the amount of hemicelluloses still available is high enough to initiate *P. placenta* decay and/or that the role of hemicelluloses in the mechanism of decay is of less importance than previously assumed. Similar results were obtained when heat treated wood was exposed to the white rot fungus *C. versicolor*. More severe process conditions during the hydro-thermolysis stage revealed no or low effect on the decay of heat treated wood after exposure to *C. versicolor*. This is in agreement with results of an initial study in which was found that variations of the process conditions during the second process stage (curing) affected the resistance against *C. versicolor* attack more than process variations of the hydro-thermolysis stage (Tjeerdsma *et al*. 2002). Degradation and modification of the hemicelluloses which occur mainly during the hydro-thermolysis stage (Tjeerdsma *et al*. 1998a, b, Boonstra and Tjeerdsma 2006) appeared to have no or low effect on the resistance against *C. versicolor* attack. Degradation of amorphous cellulose which occurs mainly during the second process stage and/or modification of the lignin network (cross linking reactions) are therefore believed to affect *C. versicolor* attack.

Heat treatment did not affect the growth of non-decaying wood fungi on the surface of wet wood (Boonstra *et al*. 2007c). Molds and sap stain fungi use wood extractives (e.g. proteins) for their metabolism (Fengel and Wegener 1989, Zabel and Morrell 1992). Substrate changes of the main components of wood appeared not to affect the growth of such fungi. Degradation products of the hemicelluloses (e.g. sugars) might even accelerate the growth of moulds, as found on heat treated radiata pine.

Whether heat treated wood is suitable for a certain application depends on the wood species involved and on the typical (biological) hazards of such an application. For instance, heat treated radiata pine appeared to be resistant against *C. puteana* attack, but its resistance against *P. placenta* was limited (Boonstra *et al* 2007c). Therefore, the application of heat treated radiata pine should be restricted to applications in which no or low fungal decay of *P. placenta* is expected. Heat treated Norway spruce revealed a higher resistance against *P. placenta* which might enable the application of heat treated Norway spruce poles since *P. placenta* occurs frequently in poles. However, other possible biological hazards of a certain application should also be taken into account, such as soft rot fungi, bacteria, maritime organisms, insects and termites. Furthermore, (semi-) practice or service commodity tests at different locations are inevitable to predict the suitability of heat treated wood for a certain application.

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Modelling of Wood Thermotransformation Process

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Keywords: Wood heat treatment furnace, heat transfer, high temperature heat treatment of wood, mass transfer, mathematical modelling

ABSTRACT

A three-dimensional, unsteady-state mathematical model of a wood heat-treatment furnace has been developed using the CFX commercial code. In this model, the simultaneous heat and mass transfer taking place both in wood and gas as well as the interactions between them are taken into account. The model uses the diffusion model to represent the mass transfer in wood. The wood thermophysical properties are expressed as a function of temperature and moisture content except for the thermal conductivity. This property is taken as a function of spatial direction as well as temperature and moisture content. The results of the model predictions are compared with the industrial data, and a good agreement is found.

INTRODUCTION

Mathematical modelling is a highly useful tool in industrial processes. A validated mathematical model can be used in designing new furnaces as well as in improving the existing ones. In addition, it can also be used for training the personnel who will have to control the process and have to make critical decisions at certain stages of the operation. During thermotransformation, the wood is heated to temperatures higher (up to 230 °C) than those used in conventional drying (80-100 °C). The final product has a dark color. In addition, the heat-treated wood is dimensionally more stable and biologically more resistant compared to the untreated wood. The thermotransformation of wood is a complex process during which simultaneous heat and mass transfer take place. As it is well known, wood is non-isotropic, and its properties are different in radial, tangential, and axial directions. Therefore, modelling only the thermotransformation of wood without considering the furnace environment is already rather complex. Also, the modelling of the wood thermotranformation at high temperatures is quite recent. The Research Group on the Thermotransformation of Wood (GRTB – Groupe de recherché sur la thermotransformation du bois) at the University of Quebec at Chicoutimi in Canada has a unique research infrastructure (a laboratory furnace, a prototype furnace, and an industrial furnace). The group has developed various furnace models as well as different fundamental models for the wood thermotransformation using different approaches. The Luikov approach (Younsi *et al*. 2006a, Kocaefe *et al*. 2006), the diffusion model (Younsi *et al*. 2006b Kocaefe *et al*. 2006), and the multiphase model (Younsi *et al*. 2006c, Kocaefe *et al*. 2006) were used in the fundamental model development. The predictions of these models were compared (Kocaefe *et al*. 2007). Although the multiphase model was found to represent the above phenomena most accurately, the predictions of the diffusion model were reasonably similar to those of the multiphase model, but it required the least number of constants and the shortest computation time among the models studied. A furnace model has to represent not only the heat and mass transfer taking place in the wood but also in the gas. It also has to take into account the interactions between wood and gas and represent the furnace geometry realistically. A furnace model was previously developed using Luikov's approach for the wood side (Osma et al., 2007). In the current study, a 3D unsteady state wood heat-treatment model was developed, and the diffusion model was used to represent the phenomena taking place in wood. The model predictions were compared with the industrial data.

MATHEMATICAL MODEL

The furnace model solves the heat and mass transfer equations both in gas and in wood. The gas and the wood sides are interrelated through the boundary conditions and the sink and source terms of the corresponding equations. The equations describing both gas and wood sides and the interface between them are explained in more detail in the following sections.

Gas Side

The continuity equation and the momentum conservation equations in three spatial directions are given as:

$$\frac{\partial \rho_g}{\partial t} + div\,(v.\rho_g) = 0 \tag{1}$$

$$\frac{\partial \rho_g v}{\partial t} + div\,(\rho_g v \otimes v) - div\,(\mu_{eff}\ gradv) = B - divP + div(\mu_{eff}\, divv) \tag{2}$$

The turbulence is represented by the k-ε model. The physical properties used for the gas and water are taken from the material properties database of the software used. No slip condition at the wall and known inlet velocities at the gas inlet are used as the boundary conditions of the momentum equations in three directions. All the velocity components are taken as zero for the initial conditions. The heat transfer equation giving the temperature profile in gas is:

$$\rho_g c_q \frac{\partial T_g}{\partial t} = -div\,(v\,\rho\, c_p T_g) + div(k_g \nabla T_g) + S_q \tag{3}$$

The mass transfer equation solving for the humidity distribution in gas is:

$$\rho_g \frac{\partial M_g}{\partial t} = -div(\rho_g v M_g) + \rho_g div\left(D_g \nabla M_g\right) + S_m \tag{4}$$

The initial temperature and the initial humidity of the gas are taken as those of the entering gas. The inlet temperature and the humidity of the gas at any given time are the boundary condition of the above equations.

Wood Side

To represent the heat and mass transfer in wood, the heat and mass transfer equations are solved simultaneously. It was assumed that the diffusion is the only mass transfer mechanism in wood (Baronas *et al.* 1999, Raisul *et al.* 2003). The heat transfer in wood and the boundary conditions are given by Equations (5) and (6), respectively. The initial wood temperature was taken equal to that of the initial gas temperature.

$$\rho_{mix}\frac{\partial h_{mix}}{\partial t}=\vec{\nabla}\bullet\left[k_w\vec{\nabla}T_w\right] \tag{5}$$

$$k_w\frac{\partial T_w}{\partial j}=\alpha_q(T_w-T_g)+\alpha_q\lambda(M_w-M_g) \tag{6}$$

The mass transfer in the wood and its boundary conditions are represented by the Equations (7) and (8), respectively. The initial moisture content of the wood is used as the initial condition in the mass transfer equation.

$$\frac{\partial M_w}{\partial t}=\vec{\nabla}\bullet\left[D_w\vec{\nabla}M_w\right] \tag{7}$$

$$-D_w\frac{\partial M_w}{\partial j}=\alpha_m(M_w-M_g) \tag{8}$$

Both the inter gas diffusion (diffusion of water vapor in lumen cells) and the bound water diffusion (diffusion of water through the cell wall) are taken into account (Siau, 1984). Below the fiber saturation point, the diffusivity coefficient is expressed as a function of local moisture content and temperature. Above this point, it is expressed as a function of wood moisture content at the fiber saturation point and temperature (Baronas *et al.* 1999). The thermopysical properties of wood are expressed as a function of temperature, moisture content and the spatial direction depending on the property. These are given elsewhere (Younsi *et al.* 2006, Kocaefe *et al.* 2007).

Wood/Gas Interface

The temperature and the humidity of gas calculated in the cells around the wood layers are taken as the boundary conditions of the heat and mass transfer equations for the wood side. The heat transferred from gas to wood is represented as a heat sink for the gas side heat transfer equation whereas the moisture transferred from wood to gas is taken into account as the source term in gas mass transfer equation (Equations 3 and 4). The equations are solved using the CFX commercial code and the finite volume approach. Due to the geometry of the furnace, one symmetrical section of the furnace is represented in the model using 204000 cells for the gas side and 12000 cells for the wood side. The computation time for a typical run was 8 hours.

RESULTS AND DISCUSSION

Comparison of Model Predictions with the Plant Data

Figure 1 compares the measured and predicted temperatures of the wood layers at the bottom, middle, and top of the wood block. Both the plant data and the model results showed that the temperature of the top layer was the highest and that of the bottom layer is the lowest. The model predicts the plant results very well. The slight differences in the temperature values is most probably due to the lack of detailed thermophysical wood properties which is the greatest obstacle in furnace modelling. Also, the model assumes that the properties of all wood layers are uniform, which, most probably, is not the case, especially for the wood humidity. This might also contribute to the differences observed.

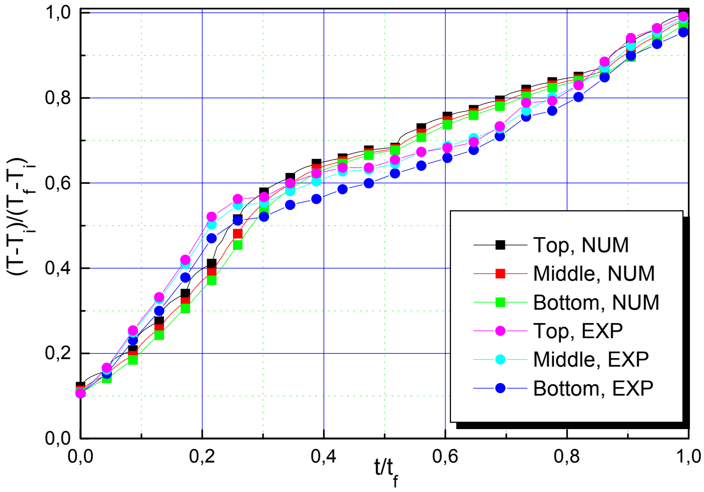

Figure 1: Comparison of Predicted Normalized Temperatures with the Plant Data at the Bottom, Middle, and Top Wood Layers During Heat Treatment ($T_{g,final}$=220°C, M_0=13%)

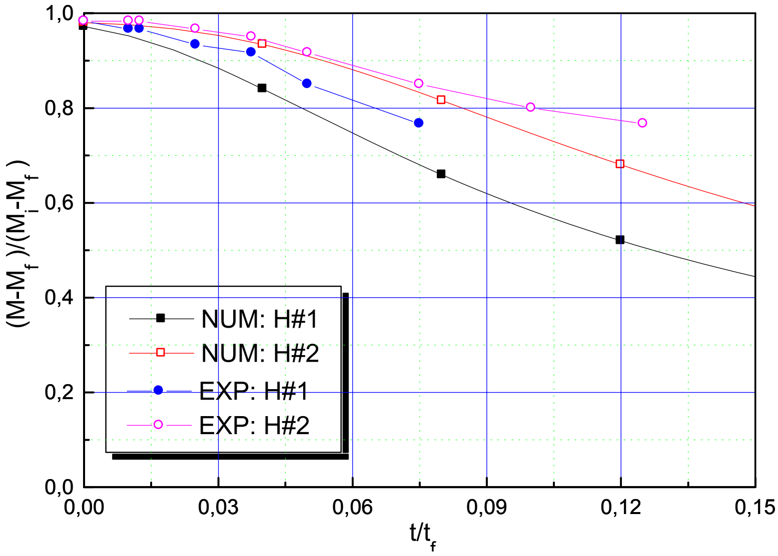

Figure 2: Comparison of Predicted Normalized Surface and Center Moisture Contents with Experimental Results During Heat Treatment (Jack Pine, Tg_{final}=180°C, M_0=6%; H1-H2: Hygrometers at the surface and center, respectively)

Figure 2 illustrates the predicted and the measured normalized moisture contents as a function of time at the centre and on the surface of the sample. During heating, the moisture content decreases with time almost linearly. The heat coming from the gas is used to vaporize the moisture at the surface. The comparison shows that, in general, the model predictions are in good agreement with the experimental data.

Moisture Content and Temperature Profiles within the Sample

Figures 3 (a) and (b) present the predicted temperature and moisture content profiles along the thickness for the midsection of central plane at different times. The wood temperature increases and the moisture content decreases with time as expected. The temperature is highly uniform showing a slight decrease towards the center due to the small thickness of the layer. Initially, the moisture content profile is very flat in the middle with a sharp gradient at the surfaces. As time passes, a gradient develops within the wood; and finally when it reaches its final value, it becomes uniform.

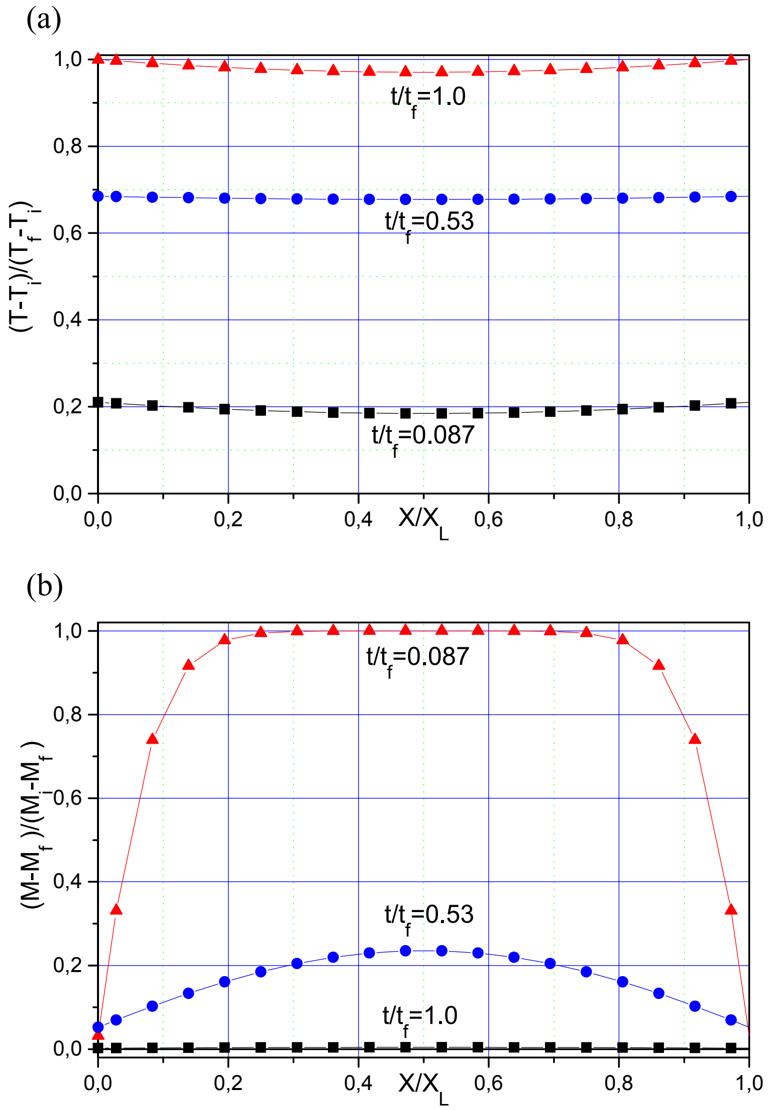

Figure 3: Spatial Profiles of: (a) Normalized Temperature and (b) Normalized Moisture Content During Heat Treatment ($T_{g,final}$=220°C, M_0=13%)

Parametric Study

A parametric study was carried out to investigate the effects of the convective heat and mass transfer coefficients on the average moisture content and the temperature distribution.

The effect of the convective heat transfer coefficient is presented in Figures 4(a) and 4(b). As this coefficient decreases, the temperature decreases, and the wood moisture content increases.

Figures 5(a) and 5(b) show the effect of the convective mass transfer coefficient on the heat and mass transfer. It seems that the change in this coefficient doesn't affect the wood temperature. This might be attributed to the initial low moisture content of wood. However, it affects the moisture content significantly. The lower the mass transfer coefficient is, the higher the moisture content of the wood is.

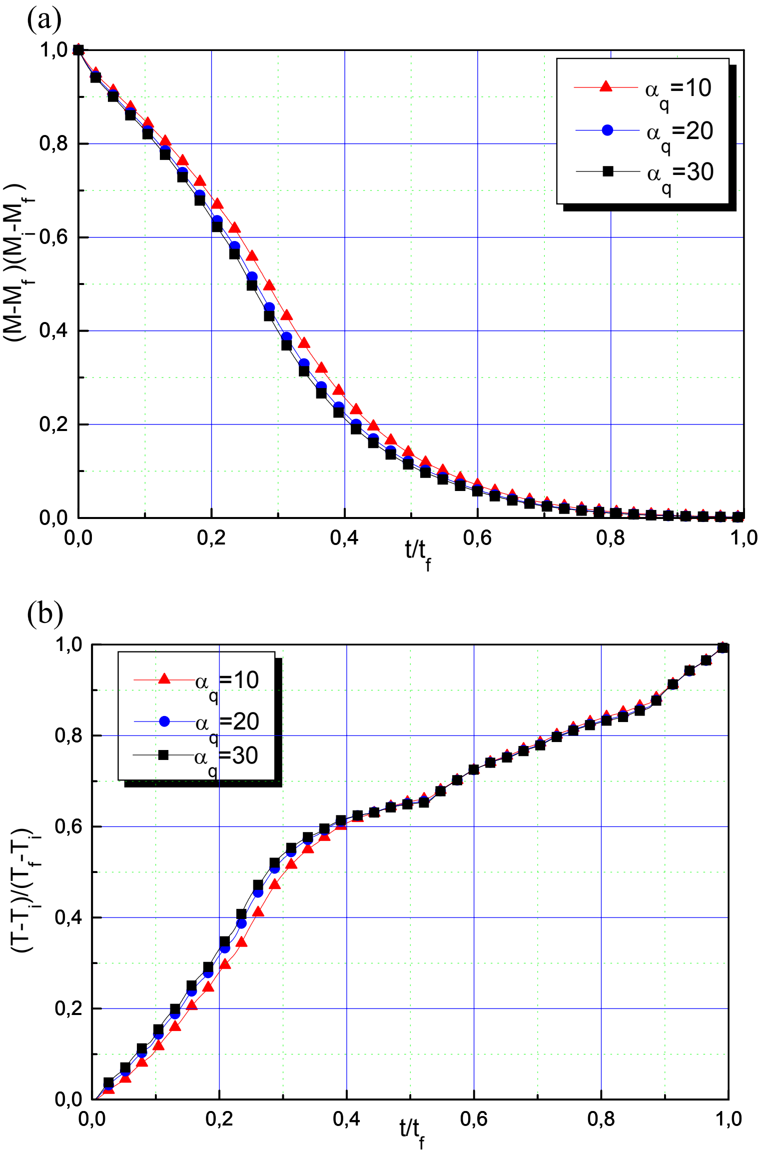

Figure 4: Effect of Convective Heat Transfer Coefficients; Predicted: (a) Normalized Center Temperature Evolution, (b) Normalized Average Moisture Content Evolution During Heat Treatment ($T_{g,final}$=220°C, M_0=13%)

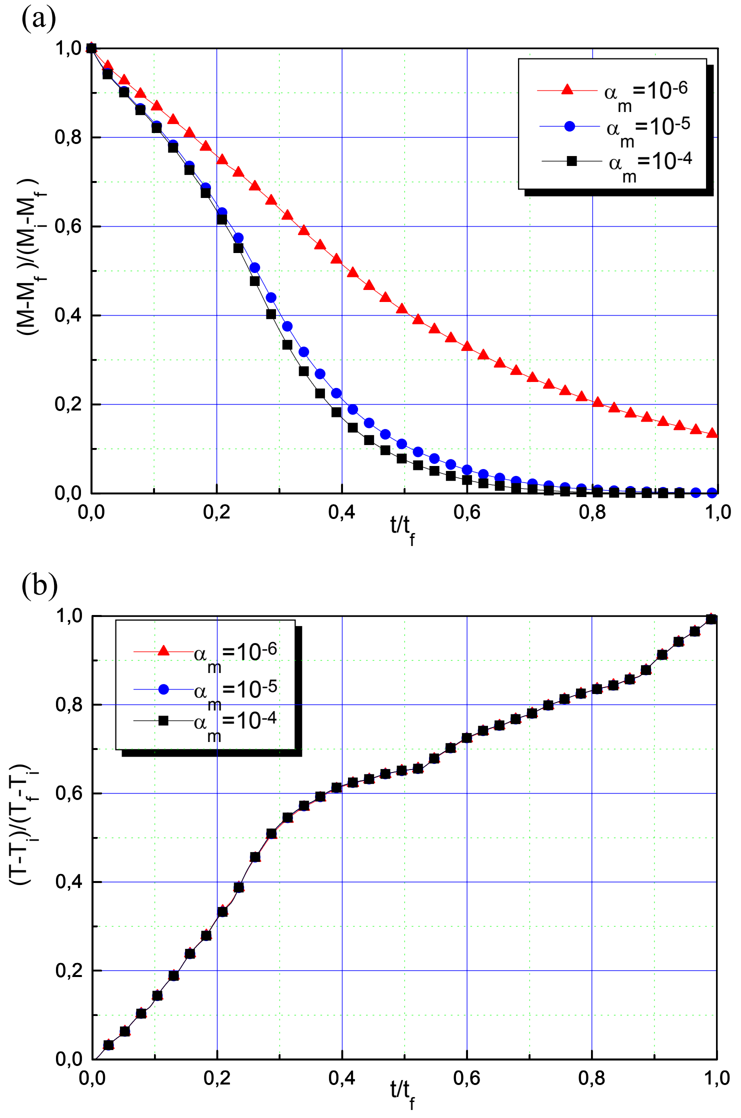

Figure 5: Effect of Convective Mass Transfer Coefficients; Predicted: (a) Normalized Center Temperature Evolution, (b) Normalized Average Moisture Content Evolution During Heat Treatment ($T_{g,final}$=220°C, M_0=13%)

CONCLUSIONS

The model seems to predict all the trends observed in the plant. It is a highly useful tool for optimizing the process and the design of the furnace. It has been used successfully by the industry for various applications. The model predictions can be further improved by incorporating better wood properties into the model.

ACKNOWLEDGEMENT

Authors would like to thank the University of Quebec at Chicoutimi (UQAC), especially Mr. Sylvain Tremblay, the Foundation of the University (FUQAC), our industrial partner PCI Industries, especially, M. Denis Lapointe, our technicians, Mr. Jacques Allaire and Mr. Pascal Vandal for their support and contributions.

NOMENCLATURE

B	= Body force, N m^{-3}	Greek letters	
c_p	= heat capacity, $Jkg^{-1}K^{-1}$	α_q	= convective heat transfer coefficient, $Wm^{-2}K^{-1}$
D	= diffusion coefficient, m^2s^{-1}	α_m	= convective mass transfer coefficient, m^2s^{-1}
h	= enthalpy, Jkg^{-1}	ρ	=dry wood density, kg/m^3
j	= spatial directions x, y, z	μ	= viscosity, $kgm^{-1}s^{-1}$
k	= thermal conductivity, $Wm^{-1}K^{-1}$	λ	= latent heat, J kg^{-1}
M	= moisture content, $kg_{(moisture)}kg^{-1}{}_{(dry\ material)}$	Subscripts	
P	= Pressure, Pa	eff	= effective
S_m	=Source or sink in mass transfer equation kg $m^{-3}s^{-1}$	g	=gas
S_q	= Source or sink in heat transfer equation $Jm^{-3}s^{-1}$	w	=wood
t	= time, s	mix	= mixture of wood and its moisture
T	= temperature, K	m	= mass
v	= Velocity vector	q	=heat
		final	=final

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Influence of a Thermally Modification of Spruce to Unsteady-state Sorption Processes and Wood Moisture-dependent Elasticity

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Keywords: Elasticity, thermal modification, sorption process, unsteady state sorption

ABSTRACT

The aim of the investigations was to evaluate the influence of a thermal modification on the kinetics of the water vapour sorption of spruce (*Picea abies* (L.) Karst.). In addition the unsteady-state sorption process between two equilibria of humidity was modelled as a diffusion process. After recording the rate of sorption of wood samples by the gravimetric method a water vapour diffusion coefficient of the material could be determined through inverse parameter identification. Further the trend of the decrease of the modulus of elasticity with increasing moisture content of wood is well-known from earlier investigations. In a second step this behaviour was analysed with thermally modified and unmodified samples in the 3-point bending test with seven different stages of air humidity.

INTRODUCTION

The ability of a material to transport dampness is of vital importance for the time interval, in which its moisture content adapts to a change of the air humidity. Investigations to the changed kinetics of the water vapour sorption as a result of a thermal modification were so far not the subject of purposeful scientific investigations. By the simultaneous examination of modified and unmodified twin samples of spruce (*Picea abies* (L.) Karst.) the influence of the thermal modification to the unsteady water absorption could be determined. For the investigations of unsteady water absorption an experimental rig according to Wadsö (1992) and Viiri and Tyrväinen (1999) was prepared, which permitted the simultaneous gravimetric analysis of the sorption behaviour of the modified and unmodified wood twin samples with identical test conditions.

The trend of the decrease of the modulus of elasticity with increasing moisture content of wood is well-known from earlier investigations (Kollmann and Krech 1960). In earlier investigations of the authors an increase of the modulus of elasticity as a result of a thermal modification under identical site conditions could be proven (Wagenführ *et al.* 2006). Investigations to the dependence of the modulus of elasticity of thermally modified woods to the relative humidity and/or the wood moisture content were so far not the subject of purposeful investigations. This behaviour was analysed with thermally modified and unmodified spruce samples in the 3-point bending test with seven different stages of air humidity.

EXPERIMENTAL

The investigations were carried out on unmodified and thermally modified wood twin samples of spruce (*Picea abies* (L.) Karst.) supplied by Thermoholz Austria GmbH. A weak modification level (180 °C) was used.

Unsteady-state sorption processes

During a sudden change of humidity water vapour is taken up to the wood and into the pore system by diffusion procedures (Figure 1).

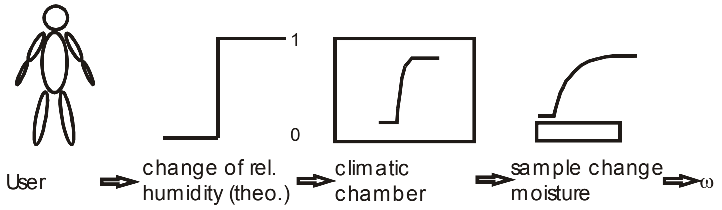

Figure 1: Process chain to the analysis of unsteady state sorption behaviour (Pfriem 2006)

For the examination of unsteady state sorption behaviour of thermally modified and unmodified spruce samples an experimental rig (Figure 2) as well as a computing routine for the evaluation of the tests were developed. Because the sorption curves show Fickian behaviour the sorption process was modelled by Ficks second law (Equation 1).

$$\frac{\partial c}{\partial t} = \left(D(c) \cdot \frac{\partial c}{\partial x} \right) \cdot \frac{1}{\partial x} \qquad (1)$$

The experimental rig (Figure 2) for continuous plot of unsteady water absorption permits a simultaneous examination of 36 wood samples with identical test conditions.

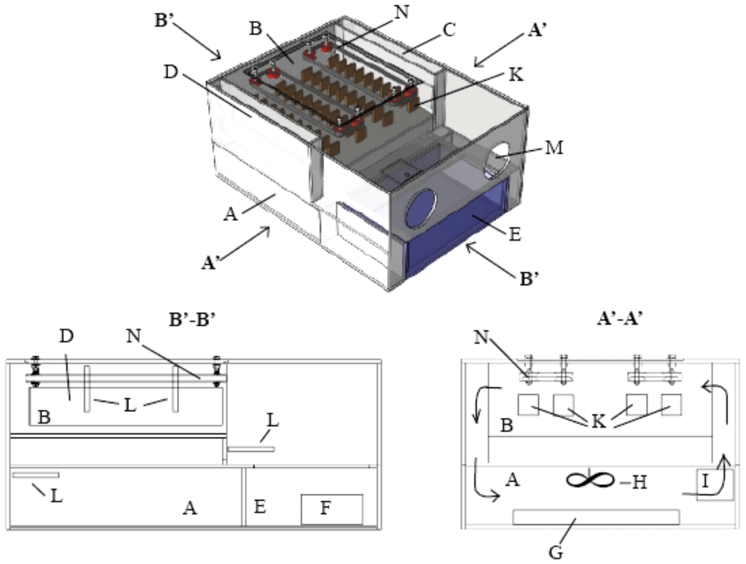

Figure 2: Experimental rig for continuous plot of unsteady water absorption (Sproßmann 2007)

The notation in Figure 2:
A lower air-conditioned compartment; **B** upper air-conditioned compartment; **C** flow channel; **D** Sealing flap; **E** Drawer; **F** a pair of scales; **G** saturated salt solution; **H** vertical fan; **I** tangential fan; **K** wood samples; **L** coupled temperature and moisture meter; **M** aperture for glove; **N** mobile toothed belt from which the specimen is suspended.

In the lower air-conditioned compartment (A) air flows over the saturated salt solution (G) away and adapts thereby its relative humidity of the salt solution accordingly. Subsequently, it is carried over tangential fan (I) by a flow channel (C) into the upper compartment (B). There the wood samples (K) are attached at a mobile toothed belt (N). By streaming around the wood samples the air delivers a part of their dampness to the samples. Afterwards air arrives over a further flow channel (C) again into the lower air-conditioned compartment, in order to adjust their relative humidity. The closed cycle lets to keep constant the climate in the compartment and to realize continuous flow conditions at all wood sample surfaces. The climatic data is taken up in four places with climatic sensors. The change of mass of the samples is realized with a pair of precision scales (F) in the drawer (E).

The sorption measurements are made by registering the weight of the specimens after a sudden step in relative humidity in the apparatus. The following test steps have been performed: 32 to 41 % RH, 41 to 53% RH, and 56 to 73% RH. The investigations were accomplished under isotherms conditions (22 °C).

Wood moisture-dependent elasticity

For 16 weakly thermally modified spruce samples and the unmodified twin samples, the moduli of elasticity were determined at different air humidity levels (0%, 25%, 35%, 65%, 75%, 85% and 93% relative humidity).

For evaluation for each wood twin samples with each humidity level the measured modulus of elasticity was referred to the modulus of elasticity of the unmodified sample under dry condition. This results in each case a modulus of elasticity normalized on 0% relative humidity.

The mean values and the standard deviations of this normalized modulus of elasticity were determined for each humidity level. They were calculated as a function of the relative humidity. Furthermore the normalized modulus of elasticity and their standard deviations were calculated as a function of the parallel measured wood moistures.

RESULTS AND DISCUSSION

Unsteady-state sorption processes

The sorption behaviour of wood is affected clearly by thermal modification processes. Depending upon modification temperature and duration the equilibrium moisture content (EMC) is reduced up to 50%. The influence of a thermal modification on the kinetics of the water vapour sorption of spruce is shown in Figure 3. The unsteady-state sorption process between two equilibria of humidity (in this case: a change in humidity of 56 to 73%) was modeled as a diffusion process. It is plotted in Figure 4 (Grothe 2006, Pfriem *et al.* 2007). It shows the place and time-dependent adjustment of the moisture content in unmodified and thermally modified spruce samples with the change of relative humidity calculated by Ficks second law.

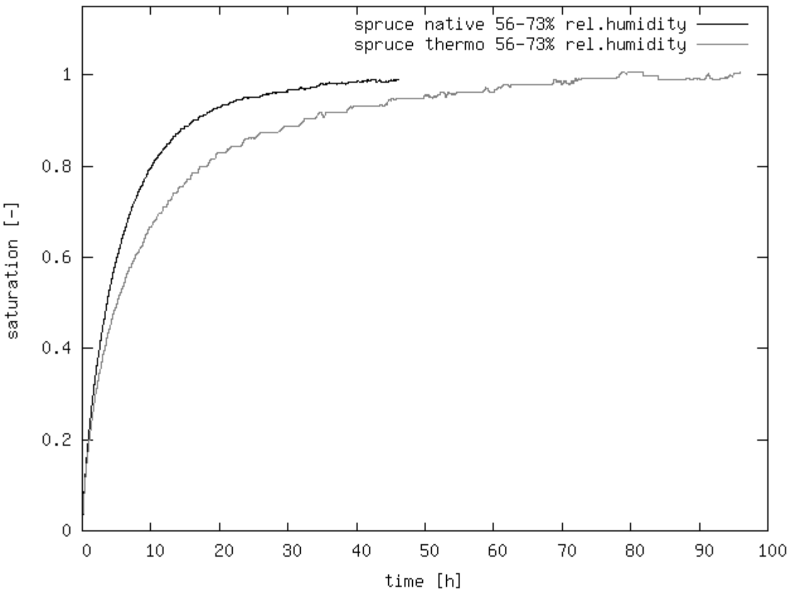

Figure 3: Measured data of rate of sorption of modified and unmodified spruce twin samples by change of 56 to 73% relative humidity

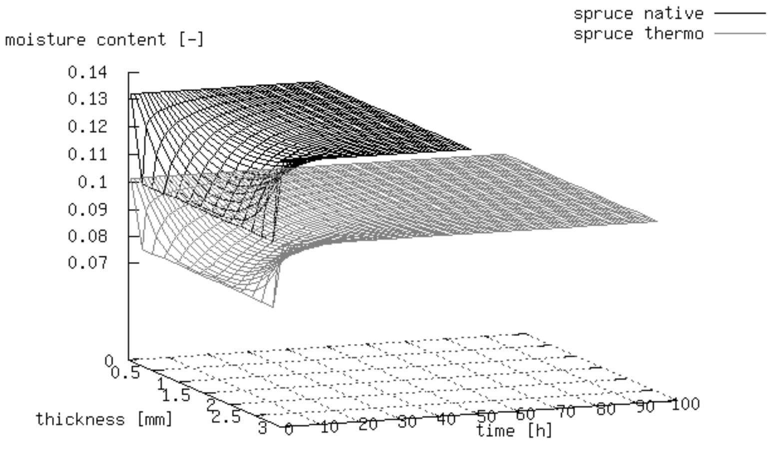

Figure 4: Place and time-dependent adjustment of the moisture content in natural and thermally modified spruce wood samples with the change from 56 to 73% of relative humidity

The determined diffusion coefficients of unmodified and modified spruce are shown in Figure 5. The Interrelation of the diffusion coefficient on the wood moisture content is evident. Furthermore thermally modified spruce show a clearly reduced diffusion coefficent than unmodified samples under the same conditions. For this the reduced moisture content of the thermally modified woods could be responsible.

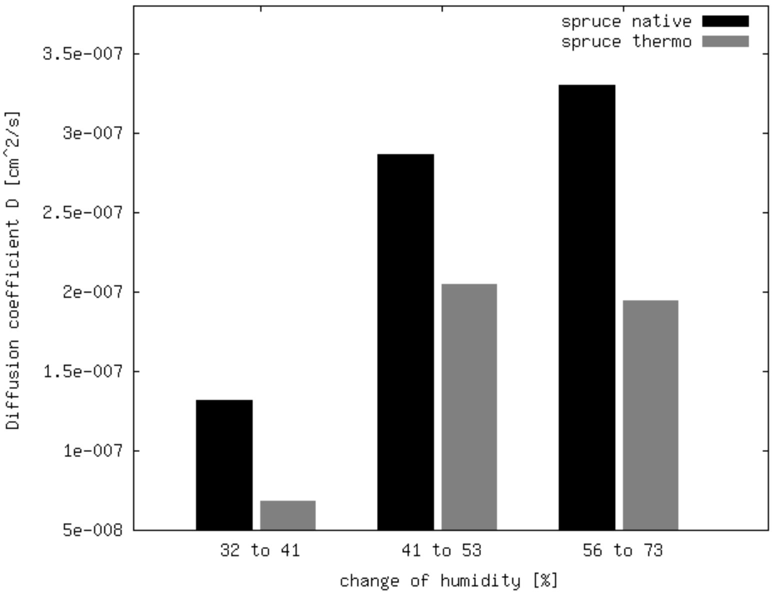

Figure 5: Determined diffusion coefficients for thermally modified and unmodified spruce

In summary it can be held that thermally modified spruce compared to unmodified spruce shows a clearly reduced water vapour sorption, but beyond that also a clearly reduced reaction to climatic variability. By comparing of same site conditions reduced diffusion coefficients for thermally modified samples could be proven, as for unmodified samples.

Wood moisture-dependent elasticity

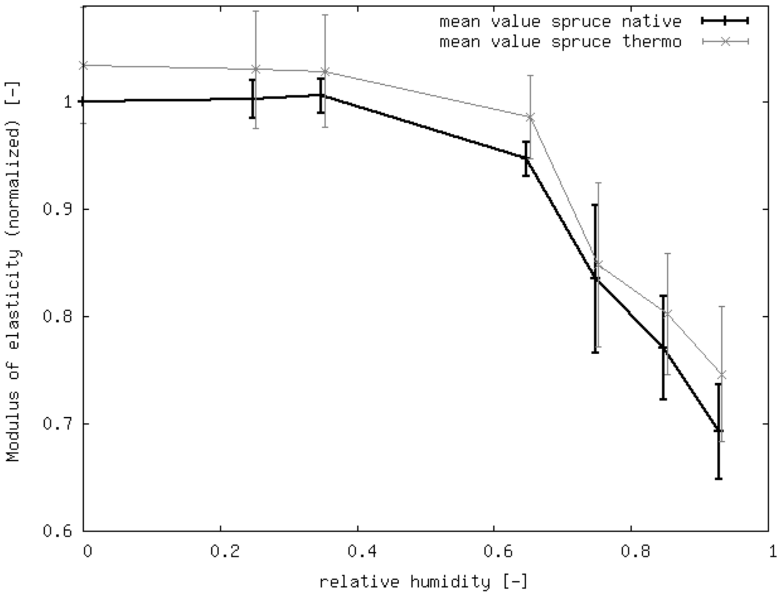

Figure 6: Averaged normalized bending modules of elasticity of modified and unmodified spruce twin samples as a function of the relative humidity

Within the range between 0 and 93% of relative humidity a higher modulus of elasticity could be proven for thermally modified samples, than for unmodified comparison samples (Figure 6).

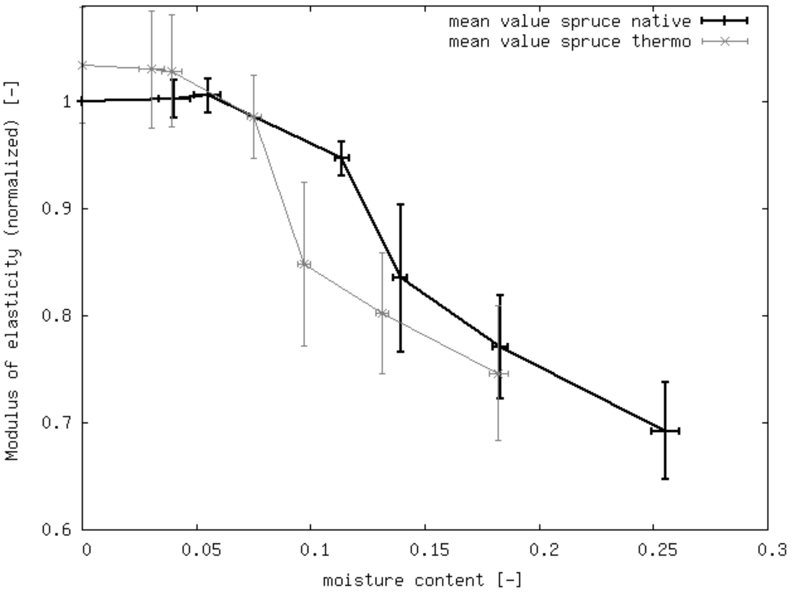

Figure 7: Averaged normalized bending modules of elasticity of modified and unmodified spruce twin samples as a function of the wood moisture

The unmodified wood samples showed that functional interrelation between the modulus of elasticity and the wood moisture could be confirmed for modified twin samples (Figure 7). Within the range to approximately 7% wood moisture weakly thermally modified samples exhibit higher elasticity modules than the unmodified paired samples with the same wood moisture. Starting from this wood moisture value thermally modified samples show a clear reduction of the modulus of elasticity. With unmodified samples this reduction arises with higher wood moisture values around approximately 12% wood moisture. Starting from this wood moisture value the elasticity modules approach.

The statement of Junghans and Niemz (2006) can be thus not completely confirmed, according to which alone the reduction of the wood moisture as a result of a thermal modification is responsible for the increase of the modulus of elasticity. Rather additionally the changes of the cellulose and the hemicelluloses in the course of the modification must be considered which lead to an embrittlement of the material.

CONCLUSIONS

For thermally modified and unmodified spruce twin samples the functional interrelation of the increase of the diffusion coefficient with increasing wood moisture could be determined on the basis of unsteady state sorption experiments and comparatively by stationary diffusion experiments. Both by stationary and by unsteady-state diffusion experiments in tangential diffusion direction the measured values for thermally modified as well as the unmodified twin samples can be arranged in the same functional curves. Because of the smaller equilibrium moisture content thermally modified spruce responded therefore under same site conditions (relative air humidity) more slowly to humidity swaying than unmodified spruce. The thermal modification leads thus also to an improved dimensional stability by temporary and short changes of air humidity. Thermally modified wood is thus interesting for applications, with which matched parts from wood are manufactured or wooden construction units in the manufacturing or transportation process brief, extreme changes of air humidity are expected.

ACKNOWLEDGEMENTS

Parts of the results this publication based on have been financially supported by the German Research Foundation (WA 1540/7-1). Special thanks to Timo Grothe and Robert Sproßmann for their work in this project.

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Nail-Holding Capability and Surface Hardness of a Thermally Modified Oriented Strandboard (OSB)

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Keywords: Oriented strandboard, surface properties, thermal treatment.

ABSTRACT

A very promising method of improving the dimensional stability of oriented strandboard (OSB) has been studied in Brazil since 2001. According to this method, the OSB is thermally treated in mild conditions using a hot-press, but without a high level of compression stress. The properties of treated OSB panels are different and enhanced from untreated OSB. This means that treated OSB can be used in more severe end-uses, like concrete formwork. This paper aims at evaluating the effect of the proposed thermal treatment on the nail-holding capability and on the surface hardness of OSB. Samples from 42 commercial OSB were thermal treated at two levels of temperature (190 ºC and 220 ºC) and three heating times (12, 16 and 20 min) using a single opening hot-press. For comparison, control panels were kept untreated. Eighty-four samples were cut from treated and untreated material to evaluate the nail-holding capability in a normal plane to the face (F⊥), in the edge of the panel (E//) and Janka hardness (JH) according to the ASTM D1037-99 standard. According to the Dunnett test significant differences between treated and untreated panels for F⊥ and E// for the material treated at 220 ºC were identified. The JH values of the untreated material were slightly higher than those of the treated one, but no significant difference was identified. The factorial ANOVA showed that temperature is the factor governing the improvement of the nail-holding capability while the duration of the treatment did not have any effect. It was concluded that the proposed thermal treatment did not affect adversely the nail-holding capability and the surface hardness of the treated OSB, may even improve the former. These conclusions confirm the results obtained for other mechanical properties that have been examined.

INTRODUCTION

Oriented strandboard (OSB) is a based panel used mainly for structural purposes. It has very good mechanical, physical and technological properties when compared with other composite panels made from wood particles. In comparison with plywood, OSB has lower mechanical properties, but in spite of this it has been replacing plywood mainly because of the possibility to use low quality species and logs and the low availability of veneer logs.

The dimensional stability of the OSB is worse than that of plywood: its thickness swelling is sometimes 7 to 10 times higher than that observed in plywood. That is why it is necessary to improve the dimensional stability of OSB to expand its market.

Many researches on treatments for the improvement of dimensional stability have been carried out and these can be divided into three types according to the stage to which they are applied: before panel consolidation (furnish pre-treatment); in the course of hot-pressing (steam injection press, not exactly a treatment); or after pressing (panel post-treatment).

Pre-treatments were evaluated by Paul *et al*. (2006), Goroyias and Hale (2002), and very good results were obtained, but some adverse effects are common such as decreasing of the wood bonding and flexural properties. Pétrissans *et al*. (2003) identified also that wood wettability is decreased on thermally treated wood. On the other hand, it is possible to use a post-treatment as done by Suchsland and Xu (1991) in which the board is treated after its consolidation.

A very promising post-treatment of improving the dimensional stability of oriented strandboard (OSB) has been studied in Brazil since 2001. According to this method, OSB is thermally treated in mild conditions using a hot-press, and the pressure is applied just to provide the contact between the press plates and surfaces of the board. The main differences from other well known thermal processes are the use of lower temperature, but fast heating by conduction, and a shorter time. Thus, the results obtained until this moment show an improvement of dimensional stability by reducing thickness swelling, equilibrium moisture content and permanent thickness swelling, as observed by Del Menezzi and Tomaselli (2006).

It has been observed that treated OSB has longer service life than untreated one because it has both higher resistance against fungi and better weathering behaviour as reported by Del Menezzi (2006). These improvements could be obtained without any severe effect on mechanical properties, which always happens when wood and wood products are thermally treated for a longer time. Although the post-treatment is recommended for boards produced with thermal-resistant resins, recently Okino *et al*. (2007) thermally treated urea-formaldehyde-bonded OSB and stimulating results have been reached.

Thus, the properties of treated boards are different and enhanced from those untreated ones. It means that treated OSB can be used in more severe end-uses, *e.g.* concrete formwork. In this end-use two properties play an important role: nail-holding capability and surface hardness. These properties are not usually determined for wood based panels, but some studies about them have been done (Falk *et al*. 2001, Viswanathan and Gothandapani 1999).

The lack of this kind of data especially for heat-treated wood and wood products is evident. However, some works have related that thermal treatments can increase the corrosion of fasteners (Jermer and Anderson 2005) and decrease the surface hardness of wood (Brischke *et al*. 2005) or even improve it, depending on how intensive the applied treatment was, as argued by Syrjänen and Kangas (2000).

In this context, the present work aims at gathering the technological data on this kind of treated material by evaluating the effect of the proposed thermal treatment on the nail-holding capability and on the surface hardness, which are important properties mainly when OSB is used in more severe end-uses.

EXPERIMENTAL

Wood Material

The samples (50 x 50 x 1.25 cm) cut from 42 commercial OSB panels had the following characteristics: made from *Pinus* sp, nominal density 640 kg/m^3, three layers, 40% di-isocyanate resin on the core layer and 60% on the surface layer. The samples (boards), were kept in a conditioning room (65%; 20 ºC) until to reach constant mass. From each board a 5 x 5 x 1.25 cm piece was cut to determine the moisture content.

Thermal Treatment

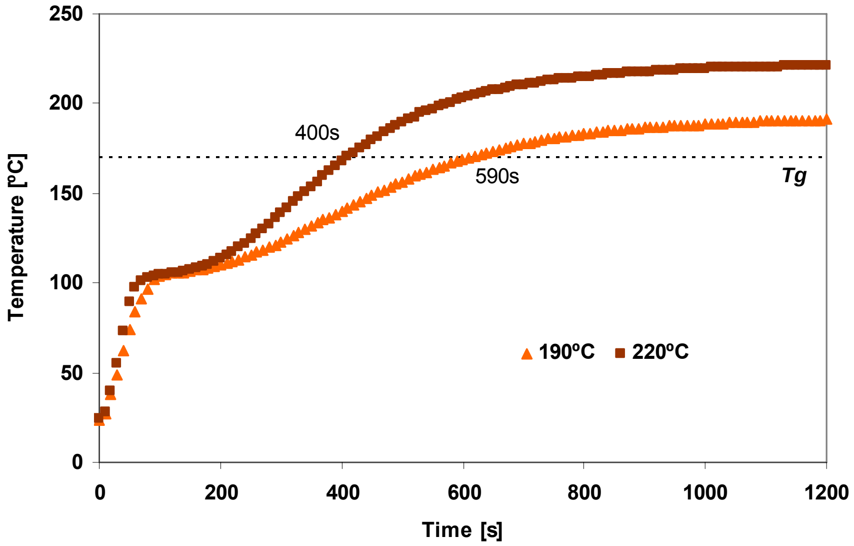

Figure 1: Temperature increasing into the board when is treated at 190 ºC and 220 ºC.

The thermal treatment was applied using a laboratory single-opening press. The boards were put into the press and were repressed and re-heated, but without a high level of compression stress. The pressure was only sufficient to provide the contact between the press plates and both surfaces of the boards.A preliminary study was done to evaluate the time needed to heat the boards above 170 ºC, which had been admitted to be the minimum temperature at which the compression stresses could be released. This is known as glass transition temperature (T_g) and the wood matrix above this temperature loses its stiffness. It could be expected that also more severe chemical degradation can occur. At an OSB industrial plant the pressing temperature varies from 190 ºC to 210 ºC, which is the range needed to promote the resin polymerization. Thus, two temperature levels were chosen: 190 ºC, industrially minimum; and 220 ºC, slightly above the maximum. The results indicated that at least 590 s were necessary for the boards reach the admitted T_g at 190 ºC and at least 400 s at 220 ºC (Figure 1). This meant the minimum treatment should be 8 minutes, but it was necessary that board temperatures were kept for a certain time to release the compression stresses. Thus, at least 4 minutes were chosen and added to the minimum required.

The boards were treated according to the following schedule: two temperature levels, 190 ºC and 220 ºC, during 12, 16 and 20 minutes. For each temperature-time combinations six boards were thermally treated and additional six boards were kept untreated (control samples), totalizing 42 boards (Table 1). After the thermal treatment the boards were returned to the conditioning room to cool down and reach constant mass.

Table 1: Experimental design employed.

Treatment	Temperature [ºC]	Time [min.]	Boards [n.]
Control	-	-	6
T1	190	12	6
T2	190	16	6
T3	190	20	6
T4	220	12	6
T5	220	16	6
T6	220	20	6

Mechanical Testing

The following mechanical properties were evaluated according to the ASTM D1037 (1999): nail-holding capability in a normal plane to the face (F⊥) and in the edge of the panel (E//), and Janka hardness (JH). Both nail-holding tests were done on the same sample. To achieve the minimum thickness for the JH test two pieces needed to be glued to obtain one sample. For each mechanical property two samples from each board were tested, totalling 84 samples.

Statistical Analysis

Initially the comparison between the treated and control boards for each mechanical property was evaluated by a running Dunnett test at 5% level of probability. This test compares control and treated board means, pair to pair, instead of comparing whole treatment. To evaluate the effect of temperature (Tp), time (Tm) and its interaction (Tp x Tm) a factorial (3 x 2 levels) analysis of variance (ANOVA) without control values was run.

RESULTS AND DISCUSSION

Comparison between Control and Heat Treated Boards

Figure 2 presents the results of the properties for both control and treated boards. As can be seen in this figure, the JH of the treated boards presented values slightly lower then those observed in control. However, the Dunnett test did not identify these differences were statistically significant. The moisture content of the board was about 9.2%.

It is well known that thermal treatment makes wood more brittle and degrades the wood polymers of the cellular wall causing mass loss. The higher and the longer the treatment was, the more intense these effects became. According to Militz (2002) the absence of oxygen plays also an important role on these effects. Brischke *et al*. (2005) observed the decrease of the Brinell hardness of thermally treated wood from silver fir and beech. The higher the mass loss, the lower the Brinell hardness.

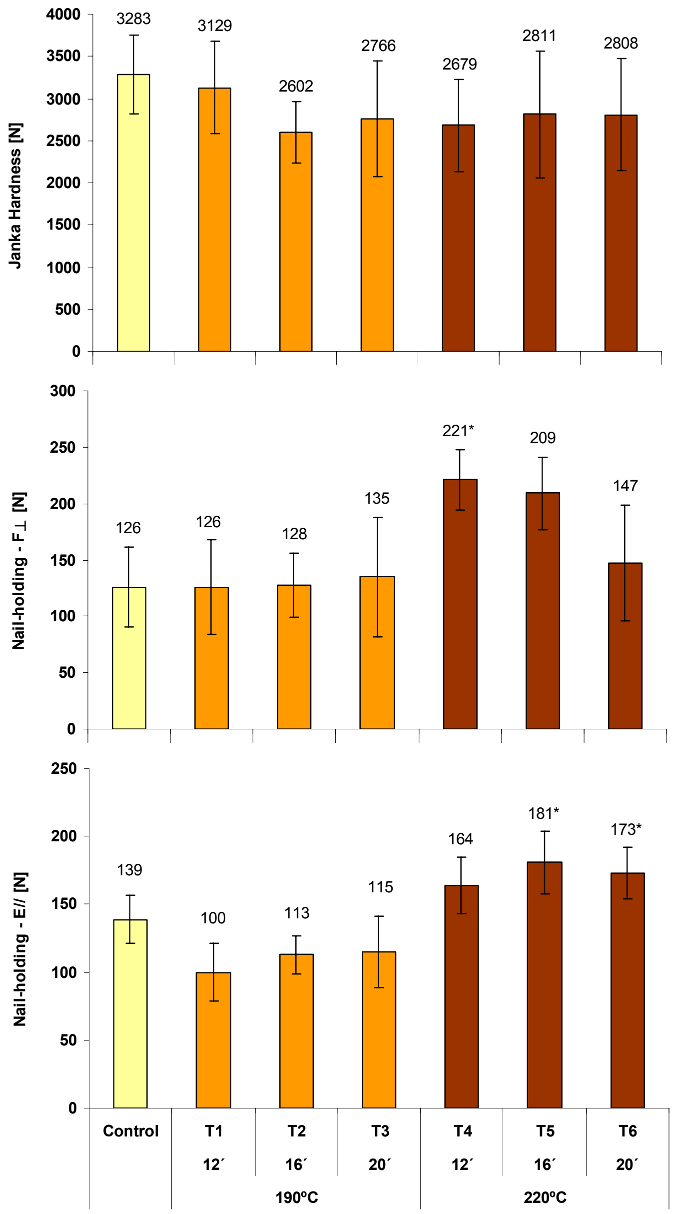

Figure 2: Janka hardness and nail-holding capability of control and thermally treated OSB (* statistically significant according to the Dunnett at 5% of probability).

The thermal treatment was applied in relatively mild conditions compared to the well known thermal wood processes, such as: atmosphere pressure, low moisture content and fast heating. Okino *et al*. (2007) have recently applied the same thermal treatment on UF-bonded OSB and JH the values were also slightly decreased, but not statistically. According to Del Menezzi (2004) the permanent mass loss for this process is less than 5%, and it is much lower than those observed in other processes, which can explain the results observed here.

On the other hand, according to Figure 1 the treatment seems to be suitable for OSB because of the improvement for both F⊥ and E//. However, these improvements were statistically significant only for boards treated at 220 ºC, while at 190 ºC the values observed were similar to those from control boards. Any explanation of these results is presented above.

It has been extensively reported that wood based particle/fibre products such as OSB, PB and MDF have an unequal distribution of density through the thickness: the density is higher on the surface, and lower in on the core. This characteristic is called vertical density profile (VDP) and is originated during the hot-pressing. As the surface layers are hotter than the core layer during the early stages of hot-pressing, it is compressed more intensively because of the loss of stiffness of the wood matrix, while the core it remains stiffer.

It can be argued that the thermal treatment used here acted as a re-pressing stage and it also succeeded in improving the density of the surface layers. The F⊥ test was done on the nail driven through the sample from surface to surface, and the regions of higher density regions probably helped to retain the nail, improving the observed values. It can be assumed that some core densification also took place because of the improvement of the E// values. Nevertheless, these assumptions cannot be used to explain the observed JH values.

Effect of Temperature and Time

The results of factorial ANOVA are presented on Table 2. As expected, the JH was not affected by the treatment while both F⊥ and E// were affected. Nevertheless, it can be observed that only temperature had effect on these results and the higher it was, the higher both nail-holding capacities were (Figure 3).

Table 2: Summary of the factorial analysis of variance.

	Temperature [Tp]		Time [Tm]		Tp x Tm	
Property	**F**	**Significant**	**F**	**Significant**	**F**	**Significant**
Janka hardness	0.054	0.817	0.742	0.480	2.169	0.123
Nail-holding - Face ⊥	5.091	0.028*	0.525	0.594	0.865	0.426
Nail-holding - Edge //	16.604	0.000**	0.353	0.704	0.042	0.959

***, * significant at the level α=0.01 and α=0.05.*

As for thermal treatments, the temperature has been identified as a very important factor affecting the extent of the changes in thermally treated wood (Del Menezzi 2004, Militz 2002, Syrjänen and Kangas 2000). None of the evaluated properties were affected by time and which confirms the previous study done by Del Menezzi (2004) which evaluated several mechanical properties of thermally treated OSB. This means that even if a shorter treatment were applied (12 min.) it would be already possible to improve those properties.

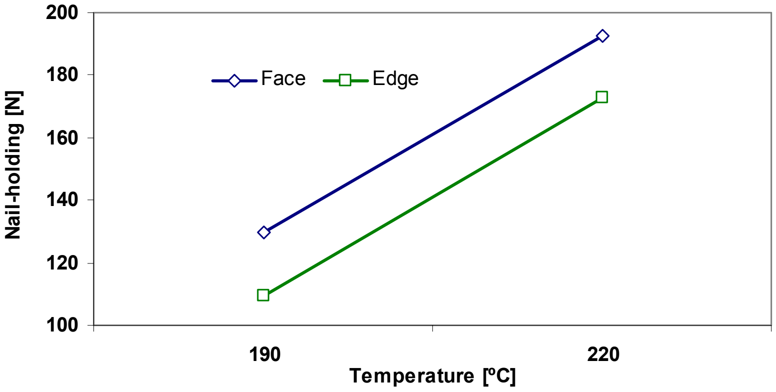

Figure 3: The effect of the treatment temperature on the OSB nail-holding capability.

CONCLUSIONS

It can be concluded that the proposed thermal treatment did not affect adversely the nail-holding capability and the surface hardness of the treated OSB, may even improve the former. The temperature of the treatment was the factor affecting the changes observed, while time did not have any effect. These conclusions confirm the results obtained for other mechanical properties that were examined. Additional tests will be done to evaluate the effect of this thermal treatment on joints made with others fastenings.

ACKNOWLEDGEMENTS

The team is very grateful to the IBAMA/Forest Products Laboratory (Brasília, Brazil) and the UFPR/Forest and Wood Science Centre (Curitiba, Brazil), where part of this work were done and to the UnB/Department of Forest Engineering (Brasília, Brazil) for the complementary financial support which made it possible for me to attend this conference.

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Susceptibility of Thermo-hydro-mechanically (THM) Densified Wood to Colonization and Degradation by Soft Rot Fungi

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Keywords: Beech, Norway spruce, soft-rot fungi, thermally treated wood, thermo-hygro-mechanically (THM) treated wood, wood densification.

ABSTRACT

Recent studies showed that in comparison to untreated wood thermo-hygro-mechanical (THM) densified wood is more resistant to colonisation and degradation by brown-rot fungi. Since one potential field of THM-treated wood is utility class four, colonisation and degradation by soft-rot fungi was investigated in Norway spruce (*Picea abies*) and beech (*Fagus sylvatica*). Wood specimens were subjected to three different treatments: thermal-hygro (TH), mechanical densification and THM-treatment including densification and post treatment under saturated steam conditions at different temperatures. For comparison additional wood specimens were treated with two concentrations of a chromium-copper (CC) wood preservative. After 32 weeks incubation, weight losses induced by soft-rot fungi were lowest in wood treated with CC. Highest weight losses were recorded from TH-treated wood in which soft rot type 2 attack was exclusively observed in spruce. In comparison to controls, significantly lower weight losses by soft-rot fungi were recorded in THM-treated spruce wood, but no such differences were found in beech wood. Microscopical examination showed that in THM-treated wood of spruce, soft rot type 1 commenced from the outer wood surfaces and cavity formation was not found in deeper regions of the wood samples. THM-treated beech wood was more susceptible to degradation than that of spruce which can be partly explained by the higher syringyl lignin content in beech wood, which promotes degradation by soft-rot fungi. In addition hyphal colonisation and soft rot within deeper regions of beech wood was facilitated by the non-occluded lumina of parenchyma cells in multiseriate xylem rays. On the basis of these results it must be concluded that TH-treated spruce wood and THM-treated beech wood is susceptible to soft rot and therefore inappropriate for use in utility class 4.

INTRODUCTION

Wood is a natural material appreciated for its appearance, high strength to low density ratio and suitability as a construction material. In addition, wood is sustainable, non-toxic, recyclable and biodegradable. The latter fact is however also one important drawback for extensive use of wood. The other significant disadvantage of wood is its low dimensional stability. Wood adsorbs and desorbs water under different moisture conditions resulting to swelling and shrinking. The natural resistance of most European wood species restricts its use without chemical preservation in outdoor applications. As an alternative to chemical preservation, a range of non-biocidal wood modification processes have been developed in recent years (Mai *et al.* 2004; Hill 2006; Rowell 2006).

THM-densified wood is a unique material in a field of engineered wood products. High temperature, moisture and compression are used to manufacture a wood product with higher strength properties than natural wood. Navi *et al.* (2000) found that wood compressed using a THM process showed decreased shape recovery, increased shear and strength parallel to the grain as well as increased surface hardness.

Recent investigations show that in comparison to untreated wood, THM-densified wood is more resistant to colonisation and degradation by brown-rot fungi (Schwarze and Spycher 2005; Welzbacher and Rapp 2005). Microscopical examination of colonised THM-densified wood 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 (Schwarze and Spycher 2005). 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 (Schwarze and Spycher 2005). However, if a high proportion of lumina are completely occluded, this will clearly restrict fungal ingress overall, sufficiently to explain why the wood is more durable.

One potential field of application for THM-densified wood is utility class four (wood exposed to the soil), its resistance to soft-rot fungi, however, has not been investigated to date. In contrast to brown rot fungi, soft-rot fungi are known to degrade wood in terrestrial as well as aquatic environments (Eriksson *et al.* 1990). They play a significant role in wood decay in utility class 4 (CEN 1996), particularly under conditions such as high moisture content and preservative loading of wood, which inhibits colonisation and attack by the more aggressive basidiomycetes. The characteristic feature of soft rot is its pattern of development, which involves T-branching or L-bending and hyphal tunnelling inside lignified cell walls (Hale and Eaton 1985a, b). In addition to cavities formed by hyphae growing within the cell wall discrete notches of cell wall erosion by hyphae growing within the cell lumina are also frequently found in wood degraded by soft-rot fungi. These erosion troughs, which are indistinguishable from those of white rot fungi, have been attributed to a soft rot known as “type 2”, whereas internal cavity formation is typical for “type 1” attack (Hale and Eaton 1985a,b).The objective of the present study was to test the soft 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. For comparison a chromium/copper salt solution (CC) was used as a reference preservative. Wood specimens of Norway spruce (*Picea abies*) and beech (*Fagus sylvatica*) were used for this purpose and exposed to soft-rot fungi according to EN 807 (CEN 2001).

EXPERIMENTAL

Thermo-hygro-mechanical densification

A total of 80 wood specimens of Norway spruce (*Picea abies* Karst), and beech (*Fagus sylvatica* L.), dimensions 50 x 150 x 50 mm (L x R x T) were subjected to the two-stage THM procedure of Navi and Giradet (2000), involving densification and post-treatment in saturated steam at 140 °C, 160 °C and 180 °C and at 80% relative humidity (RH) and 180 °C. From each wood specimen six sub-samples with the dimensions 30 x 10 x 5mm (L x R x T) were cut. A total of 480 sub-samples were used for the soft rot test described below.

Inoculation of wood specimens

A slightly modified soil bed test according to ENV 807 (CEN 2001) was carried out in order to determine the resistance of THM-densification against soft-rot fungi and other soil-inhabiting micro-organisms. Six wood specimens for each treatment method were placed in a soil substrate. Soil substrate used in the study was a natural top soil from a test field in Thurgau, Switzerland. A chromium/copper salt solution (CC) was used as a reference preservative ($CuSO_4$. $5H_2O$ – 50%, $K_2Cr_2O_7$ – 48%, CrO_3 – 2%). Concentrations of CC solution 0.4% and 1.6% were selected for beech wood specimens, 0.16% and 0.4% for spruce wood specimens respectively.

All test, reference and virulence control wood specimens were incubated for 8, 16, 24 and 32 weeks in a conditioning room at 28±1 °C and 95-100% RH. After incubation the specimens were removed from the soil substrate, cleaned of adhering soil particles and weighed. Determination of the initial dry mass and the final dry mass after soil exposure was carried out by oven drying the wood specimens at 103°C and weighing to the nearest 0.001g. The mass loss of each specimen was calculated as a percentage of the initial dry mass.

One-way analysis of variance (ANOVA) of the recorded dry weight losses was performed for all wood samples in Excel with the significance level set at $P<0.01$. A Tukey HSD *post hoc* test was performed in SPSS to demonstrate differences in mean values.

Light microscopy

The incubated wood specimens were cut into sub-samples of approximately 20 mm x 5 mm x 5 mm, with transverse, radial and tangential surfaces exposed to examination. These were fixed in a 2% glutaraldehyde buffered at pH 7.2 -7.4, dehydrated with acetone and embedded in a methacrylate medium. They were then sectioned at approximately 2 and 4 µm using a rotary microtome (Leica® 2040 Supercut) fitted with a diamond knife. In order to compare the rate of wood colonisation and degradation by decay fungi, transversal longitudinal sections (TLS) were cut at the surface and in depth of 10 mm of the sub-samples. For general observations of cell wall degradation and hyphal growth, sections were stained for 12 h in safranine and then counter-stained for 3 min in methylene blue and in 30 min in auramin. Micrographs were taken with a microscope fitted with camera system (Leica® DC 50, TWAIN).

RESULTS AND DISCUSSION

Densification resulting from wood treatment

THM-treatments resulted in increases of densities ranging from four-fold for Norway spruce and two-fold for beech wood (Table 1). THM wood post-treated at 140 °C compressed the vessels of beech wood to a radial width from 20-24 µm to 2 - 7 µm in the late- and to 5 - 10 µm in the early wood. After post treatment at 180°C the corresponding values were 0.5 - 5 µm in the latewood and 4 - 8 µm in the early wood. Occlusion of the cell lumina of tracheids in spruce wood was within the range previously described by (Schwarze and Spycher 2005).

Table 1: Condition and mean density of beech and Norway spruce wood samples before incubation

Treatment		**Density [kg/m^3]**	
		Norway spruce	**Beech**
Control	Untreated	352	651
TH 160 °C	Heat treatment at 160°C under SSC	373	648
TH 180 °C	Heat treatment at 180°C under SSC	365	648
Densified	Mechanical densification under SSC without post-treatment	1297	1140
THM 140 °C	Densification and post-treatment at 140°C under SSC	1334	1213
THM 160 °C	Densification and post-treatment at 160°C under SSC	1296	1229
THM 180 °C/ 80%RH	Densification under SSC and post-treatment at 180°C under 80% RH	1254	1167
THM 180 °C	Densification and post-treatment at 180°C under SSC	1279	1196

After 32 weeks the lowest dry weight losses were recorded in wood treated with CC (Figure 1). All specimens modified by THM-treatment showed an inverse relationship between susceptibility to fungal degradation and increase in density (Figure 1). In beech wood most THM-treatments resulted in a significant reduction in weight losses ($P<0.01$) by soft rot during initial stages of soil exposure but after 32 weeks failed to inhibit degradation (Figures 1). In spruce wood all THM treatments resulted in a significant reduction ($P<0.01$) in weight losses regardless of the incubation period.

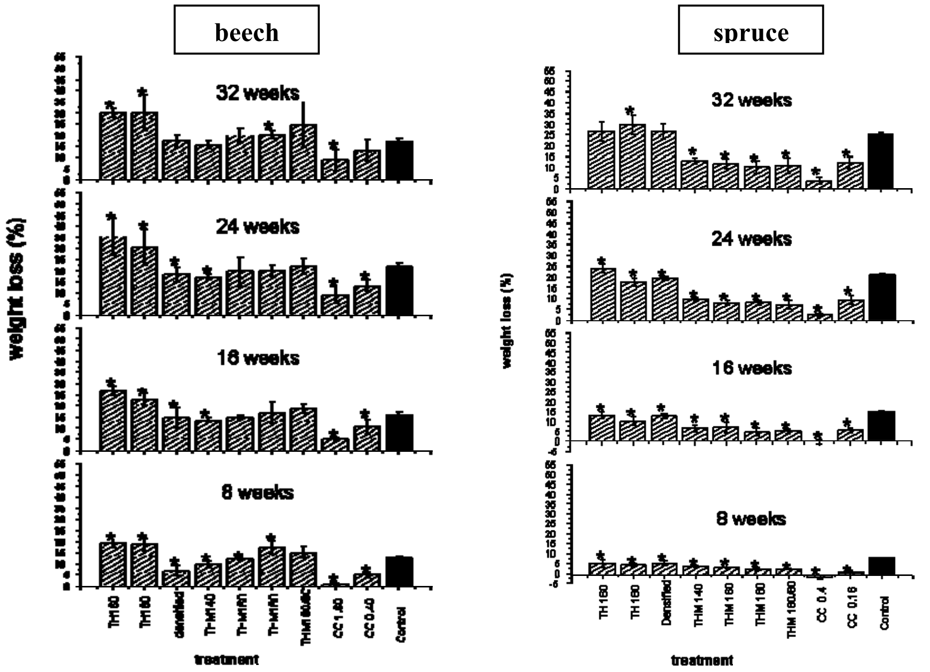

Figure 1: Dry weight losses of Norway spruce and beech wood specimens in untreated controls, TH-treated wood (160 and 180 °C), densified wood without thermal treatment, THM-densified wood (140, 160, 180 °C and 180 °C/80%RH) and CC (1.6 and 0.4 %) impregnated wood incubated for 6, 12, 18 and 32 weeks. (n=6) Bars show standard deviation. Columns marked with asterisk show significant difference in comparison to untreated control (P< 0.01)

The density of wood specimens exposed to TH-treatment was slightly reduced in comparison to untreated controls (Table 1) and resulted in higher weight losses by soft-rot fungi than in the untreated controls in both beech and spruce wood specimens after 32 weeks incubation. The adverse affect of TH-treatment on wood resistance was previously also recorded for brown rot fungi (Schwarze and Spycher 2005). It is well established that thermal treatment decreases the amount of accessible hydroxyl groups and results in a reduction in the hygroscopicity of treated wood (Tjeerdsma *et al.* 2000). TH treatment contributes to depolymerisation of polysaccharides and shifts the T_g of lignin. However, in the present study, the moisture content of incubated TH-treated wood specimens was found to be well above the fibre saturation point. During incubation a higher moisture content developed in spruce than in beech wood specimens. After eight weeks, the moisture content of the modified wood specimens was in the range of 130 ± 10% for TH-treated and 48 ± 10% for THM-treated beech specimens, whereas TH- and THM-treated spruce wood specimens had a moisture content of 225 ± 40% and 51 ± 15% respectively.

Fungal colonisation and degradation

In THM and TH-treated wood of spruce and beech the impact of thermal treatment resulted in distinct alterations in the micro-morphology of cell walls in close proximity to the specimen surface. The combustion of cellulose and hemicelluloses resulted in a conspicuous reddish appearance of the outer cell rows due to staining of lignin with safranine (Figure 2a).

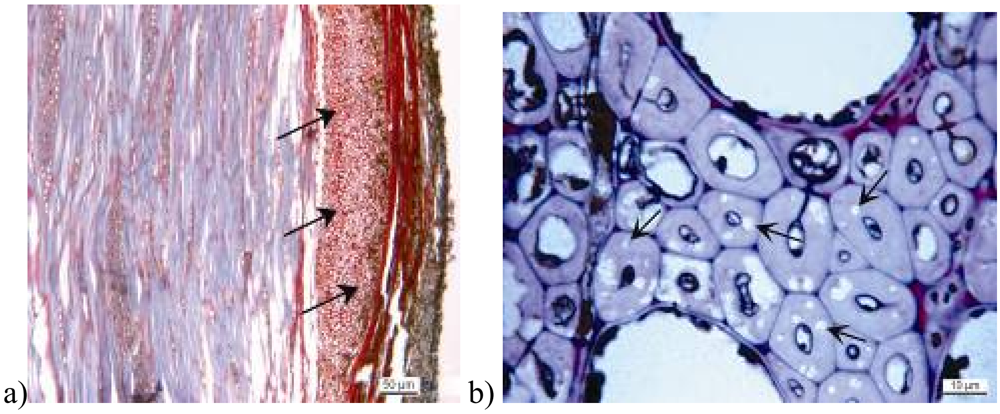

Figure 2: a) Tangential longitudinal section (T.L.S.) of TH-treated beech wood at 160 °C. Note reddish staining of fibre-tracheids and multiseriate xylem ray parenchyma (arrows) with safranine due to combustion of polysaccharides; b) Transverse section (T.S.) of TH-treated beech wood showing cavities (arrows) within secondary walls of fibre-tracheids

Moreover, loss of birefringence was apparent from the cell walls in this region which appeared dark when viewed between crossed Nicol prisms. In THM-treated wood of spruce modified regions were superficial and were merely recorded in a depth of 40 - 45 µm, whereas in beech modifications by thermal treatment were more extensive and apparent in a depth of 170 - 220 µm (Figure 2a). Even in cell regions close to the surface, parenchyma cells of multiseriate xylem rays in beech wood did not appear to be affected by heat treatment and cellulose maintained a distinct birefringence.

In control specimens of beech and spruce wood, hyphae had completely colonised the wood specimens. Cell wall degradation by soft-rot fungi was induced either by formation of cavities by hyphae in the S_2 layer (type 1) or erosion troughs (type 2). Soft rot type 1 was characterized as a series of successive cavities with conical pointed ends which followed the direction of microfibrils within S_2 layer (Figures 2b, 3a). Soft rot type 1 was most prevalent in control and treated wood specimens of spruce. The latter observation is in good agreement with former studies showing that soft rot type 1 occurs in secondary walls with high concentration of guaiacyl, whereas soft rot type 2 is often associated with syringyl rich cell walls (Anagnost 1989; Schwarze *et al.* 2004). Norway spruce wood has a high concentration of guaiacyl, and thus is moderately resistant to soft-rot fungi, whereas wood of beech that consists predominantly of syringyl-rich fibre tracheids is which is more susceptible to soft-rot fungi (Schwarze *et al.* 2004). The latter differentces in the lignin composition partly explains the higher weight losses recorded by soft-rot fungi in beech wood.

Interestingly, soft rot type 2 was exclusively observed in TH-treated wood of spruce. Former studies show that many species that only cause soft rot type 2 in hardwoods, failed to exhibit any decay features or weight losses in softwoods (Anagnost 1998). One reason for this selection process appears be related to the extremely resilient S_3 layer of tracheids that hampers degradation by hyphae from within the cell lumen outwards (Schwarze *et al.* 2004). This does not deter brown rot fungi, which are able to degrade the cell wall by means of diffusible secretions from hyphae within the tracheid lumen, but a resistant S_3 layer is a considerable barrier to fungi that cause soft rot type 2 or a simultaneous rot (Schwarze *et al.* 2004). In TH-treated wood it seems that thermal treatment induces chemical alterations in the S_3 layer which strongly reduces its resistance to soft-rot type 2 attack *i.e.* formation of erosion troughs by hyphae growing within the lumen.

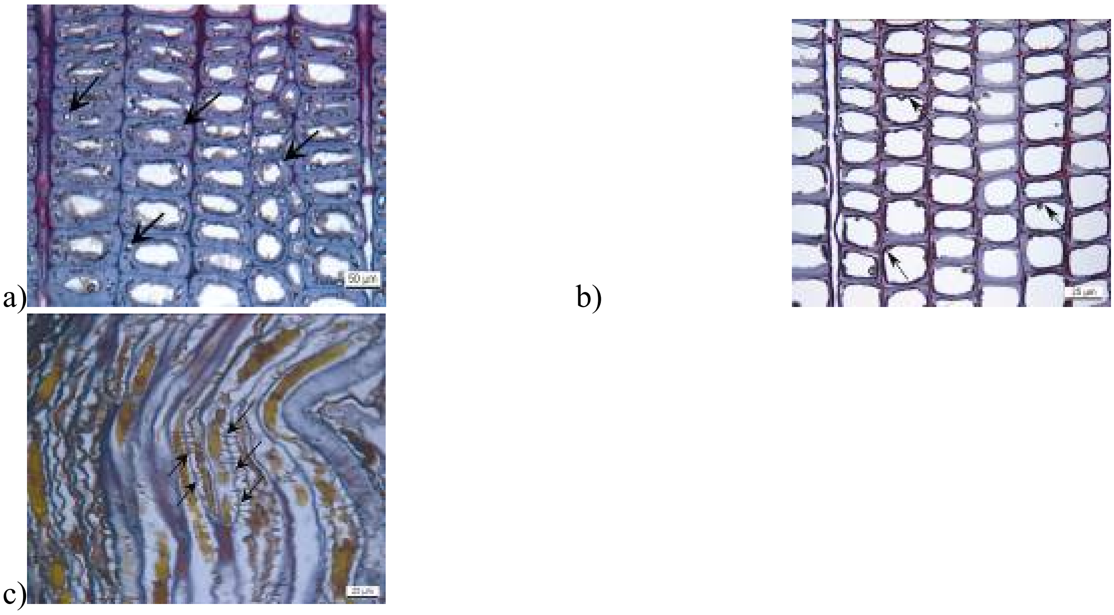

Figure 3: a) T.S. of untreated Norway spruce wood showing cavities (arrows) within the secondary walls of tracheids; b) T.S. of TH-treated Norway spruce wood showing soft rot type 2 attack in secondary walls of tracheids. Note formation of hyphal sheaths and cell wall erosion troughs (arrows); c) T.S. of THM-treated beech wood post-treated at 160 °C showing soft rot attack within a multiseriate xylem ray. Note complete degradation of the secondary walls (arrows) in xylem ray parenchyma

In THM-treated spruce wood colonisation of tracheids by soft-rot fungi was evidently hampered by densification. Hyphae were not detected in deeper parts of the wood specimens and cell wall degradation was restricted to the outer surface of the wood specimens (Figure 3b). Interestingly, THM–treated beech wood post treated at 180 °C showed similar weight losses as controls. Thus, even a complete occlusion of cell lumina could not inhibit decay by soft-rot fungi as the occlusion was simply counteracted by directional growth within the cell wall (Figures 3b).

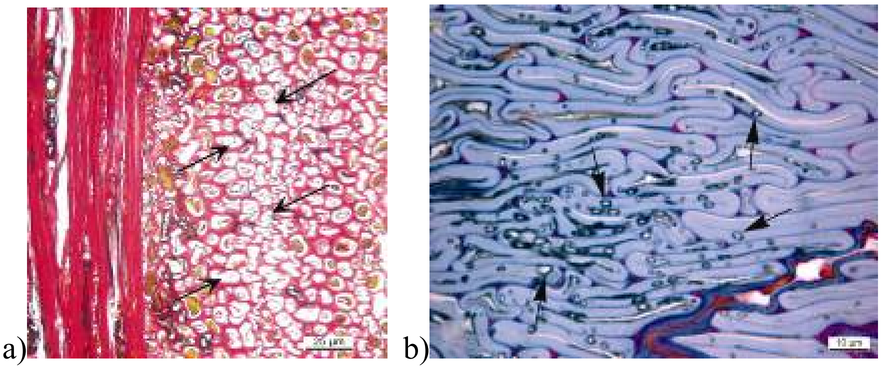

Figure 4: a) T.L.S. showing THM-treated beech wood post-treated at 180 °C showing non-occluded xylem ray parenchyma cells. Note: complete degradation of the S2-layer (arrows) in secondary walls of xylem ray parenchyma. b) T.S. of THM-treated spruce wood post treated at 180 °C showing cavities (arrows) within the secondary walls of tracheids

Another important factor affecting resistance of THM-treated wood is the impact of the wood structure on compression and vice versa on hyphal colonisation and degradation. Norway spruce wood has a very homogenous structure and consists predominantly of axially aligned tracheids (90 – 95 %) and a low proportion of radially aligned uniseriate xylem rays. Thus, in THM-treated wood of spruce, post treated at 180 °C most cells were almost completely occluded, regardless whether wood specimens were compressed in the radial or tangential direction. In contrast the structure of beech wood is more heterogeneous as it consists of vessels, fibre-tracheids, axial parenchyma and prominent multiseriate xylem rays. In THM-treated wood of beech, post treated at 180 °C the multiseriate xylem rays counteracted compression in the radial direction and cell lumina of xylem ray parenchyma were only slightly occluded, facilitating hyphal colonisation and access from the surface of the deeper wood regions. Thus, the strongest soft rot attack in beech was observed in the secondary walls of xylem ray parenchyma and in fibre tracheids in close proximity to multiseriate xylem rays (Figures 3c, 4a).

The results show that before selecting potential wood species for THM-treatment for Utility Class 4 it is essential to consider whether the lignin composition and anatomical features such as multiseriate xylem rays may promote wood colonisation and degradation by soft-rot fungi despite thermal treatment and/or considerable increases in density.

CONCLUSIONS

The process of THM-treatment increased the resistance of spruce but not of beech wood to degradation by soft-rot fungi. Microscopical examination showed that in THM-treated wood of Norway spruce soft rot commenced from the outer wood surfaces and cavity formation was not found in deeper regions of the wood specimens. In beech wood hyphal colonisation and degradation was facilitated by the non-occluded lumina of parenchyma cells in multiseriate xylem rays. Moreover, due to the higher syringyl lignin content of beech wood renders it more susceptible to decay by soft-rot fungi than spruce wood. TH-treated wood of beech and spruce was highly susceptible to soft-rot fungi and cell wall modification due to thermal treatment induced soft rot type 2 attack in latter host. On the basis of the results obtained it must be concluded that TH-treated Norway spruce wood and THM-treated beech wood are highly susceptible to soft-rot attack and therefore inappropriate for application in utility class 4.

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Changes in the Wood Cell Wall Microstructure as a Result of Modification Processes

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Keywords: Wood modification, sorption, hygroscopicity, durability.

ABSTRACT

The structure and hydrophobic properties of the wood cell wall, as well as durability changes as a result of different modification treatments were assessed. The studies were carried out with the wood of most typical European coniferous tree species, modified using a variety of technologies (Plato, Lignius, NOW processes, acetylation, furfurylation, treatment with UZA hot oil). The evaluation of the effect of the hydrophobisation and the structural changes of wood at different types of thermal and chemical modification was carried out on the basis of the measurement and analysis of the isotherms of sorption-desorption with water vapours in two sorption cycles. The characteristics of the microstructure were determined and the hygroscopic properties of wood were characterised. The method makes it possible to compare the hydrophobisation effect obtained by different modification processes and its stability. To evaluate durability in connection with the water sorption changes as a result of modification, tests applying modified standard EN 113 method were performed. An essential hydrophobisation effect of all modification treatments has been established. As a rule, the thermal treatment results in obtaining of a non-equilibrium structure of wood, which then is relaxed in the water vapours atmosphere and is accompanied by the some decrease in the hydrophobisation effect. Among the presented methods for modification of wood, the most efficient one is acetylation – the “water surface” decreases almost twice. In this case, the hydrophobisation effect after saturating with water vapours is retained and even increases in some cases. The treatment of wood with furfuryl alcohol and hot oil is less efficient, but is stable in water vapours. Based on the analysis of the obtained results, we conclude that the main reason for hydrophobisation upon thermal modification is the decrease of the “water surface” owing to the formation of strong contacts between the structural elements at high temperature. In chemical modification, the decrease or blocking of hydrophilic centres plays a major part.

INTRODUCTION

In the last 10-20 years, industry and the leading wood research centres have looked for methods for ensuring non-biocide safety of wood, changing material properties by physical or chemical way. In this case, studies are under way in parallel with applying patents and implementation of modification methods on an industrial scale. At the same time, the mechanisms of the improvement of wood durability by different modification methods are not yet known unambiguously, and the information on forecasting the modified wood's living cycle in different application conditions is not sufficient. The aim of the study was, applying sorption study methods, to gain information on the changes of the structure and hydrophobic properties of wood in different modification processes, to assess the treatment efficiency's stability and to try to understand the reasons for the biological durability of modified wood.

Sorption methods were used for assessing the changed structure and hygroscopic properties of modified wood. Wood, similarly to other plant materials, is characterised by an enhanced hygroscopicity. The reason is the chemical structure of all wood components, containing alcohol hydroxyl groups (hemicelluloses > cellulose > lignin), forming strong hydrogen bonds, whose energy in force is between chemical and dispersion forces. Therefore, wood belongs to non-rigid or swelling sorbents, because, in the atmosphere of active vapours (namely, those that are also capable of forming hydrogen bonds – water, alcohols, amines, *etc.*), there is a competition between the interstructural bonds and the outer agent. In this case, the inner bonds are deformed up to pseudo-cleavage. Since there is a hierarchy of structures, obviously, the bonds between the large structures are the first to cleave. As a result, microvoids or micropores arise, and a new surface appears (Chirkova *et al.* 2004). This process is indicated as "swelling". Thus, inert sorbates (for example, nitrogen) enable the study of the intact structure of wood, while active sorbates (water, alcohols) make it possible to investigate the structure of the wood cell wall in the sorbate vapours atmosphere. Besides, the study of water vapours enables a quantity characterisation of the concentration of hydrophilic centres in the sample under study.

EXPERIMENTAL

All the samples investigated (see Table 1) are treated under standard treatment conditions. Whilst some of the processes are commercialised the regimes used to modify these specimens were not optimised for each timber species.

Experimental methods

The change in the hygroscopic properties of wood of different species in the process of thermal and chemical modification was investigated by the method of cyclic sorption-desorption of water vapours. The two-cycle sorption of water vapours was measured on a vacuum balance with quartz spirals as the sensible 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. The following characteristics of the samples' microstructure were determined: accessible specific surface A, m^2/g ("water surface"), mass concentration of hydrophilic centres H, mMol/g (the monolayer capacity according to BET equation (Gregg and Sing 1982)) and surface concentration of hydrophilic centres α, groups/nm^2, and $\alpha = H/A$. From the desorption branches of isotherms, curves of the distribution of pore volumes by pore sizes were calculated by the BJH method (Barrett *et al.* 1951).

Nitrogen sorption isotherms were measured on an automatic sorptometer Kelvin 1042, degassing temperature 40 °C. using helium as carrier gas. The specific surface of the samples in terms of nitrogen ("nitrogen surface") was determined by the BET-method, the distribution of pore volume by pore sizes – by the BJH-method. Chemically modified and untreated wood samples were subjected to the effect of brown rot fungi *Coniophora puteana* in compliance with the modified procedure of the EN 113 standard. The test duration was 6 weeks. The samples were dried before and after fungi tests at (103±2 °C). Microscopic studies were carried out using an electron microscope Tescan Vega TS 5136MM.

Table 1: Wood samples investigated

Wood species, suppliers	**Thermal treatment, estimated temperature [°C]**	**Chemical modification estimated temperature [°C]**
Sitka spruce (Scotland)	NOW (180, N_2)	Furfuryl alcohol (80-140) Acetylation (max 140) UZA hot oil (180-200)
Sitka spruce (Novar estate, Scotland)	PLATO (160-200) NPC (200-220)	-
Douglas Fir (UK)	NOW (180, N_2)	Furfuryl alcohol (80-140) Acetylation (max 140)
Douglas Fir (Novar estate, Scotland)	PLATO (160-200) NPC (200-220)	-
Western hemlock (Novar estate, Scotland)	PLATO (160-200) NPC (200-220)	-
Larch (UK)	NOW (180, N_2)	Furfuryl alcohol (80-140) Acetylation (max 140)
Scots pine (UK)	NOW (180, N_2)	Furfuryl alcohol (80-140) Acetylation (max 140)
Corsican pine (UK)	NOW (180, N_2)	Furfuryl alcohol (80-140) Acetylation (max 140) UZA hot oil (180-200)

Process designations: PLATO (the Netherlands); UZA modified linseed oil (the Netherlands); NOW (New Option Wood, France); NPC (Lignius, the Netherlands, there are no data on treatment).

RESULTS AND DISCUSSION

Two sorption-desorption cycles were carried out for untreated and modified wood to assess the stability of hygroscopic properties in water vapours. Table 2 summarises hygroscopicity characterising values for untreated wood of different species.

Table 2: Hygroscopic properties of untreated wood

Wood species	**I cycle**			**II cycle**		
	A[a] $[m^2/g]$	H[b] [mMol/g]	α[c] $[groups/nm^2]$	A[a] $[m^2/g]$	H[b] [mMol/g]	α[c] $[groups/nm^2]$
Sitka spruce (Scotland)	309	2.64	5.14	327	2.73	5.04
Sitka spruce (Novar)	344	2.96	5.86	347	2.80	5.84
Scots pine (UK)	320	3.01	5.82	321	3.10	5.03
Scots pine (Latvia)	336	2.81	5.04	-	-	-
Douglas fir (UK)	247	2.13	5.20	307	2.57	5.04
Douglas fir (Novar)	302	2.62	5.22	304	2.67	5.29
Western hemlock (Novar)	289	2.77	6.44	325	3.11	5.76
Corsican pine (UK)	256	1.72	4.04	328	2.70	4.95
Larch (UK)	310	2.86	5.55	326	2.74	5.06
On the average	317	2.81	5.58	323	2.80	5.25

[a] *Accessible specific surface area,* [b] *mass hydrophility,* [c] *surface concentration of hydrophilic centres.*

The “water surface” area (A) for all the species is close to 315 m^2/g. In the second cycle, when the inner tension disappears, it is about 325 m^2/g everywhere. However, for some samples, A in the first cycle is considerably lower (Douglas fir (UK), Corsican pine (UK)). We propose that, before the treatment, these samples had been subjected to drying, inclusing water. Under the action of water vapours, the system opens up, therefore, in the second cycle, A values grow and become similar to those of the wood of other species. The microstructure and hydrophilic properties of untreated wood of all the species under study are stable, and their characteristics, obtained in two sorption cycles, are practically equal.

Table 3 shows the effect of wood hydrophobisation under different conditions of thermal modification.

Table 3: Hygroscopicity changes for wood of different species as a result of thermal modification

Wood species	**$A/A_{untreat.}$ in I cycle [%]**	**$A/A_{untreat..}$ in II cycle [%]**	**Change of $A/A_{untreat.}$ in II cycle [%]**	**$a_m/ a_{m\ untreat.}$ in II cycle [%]**
Treatment: NOW (180 °C, N_2)				
Sitka spruce (Scotland)	72.2	85.5	11.3	76.9
Scots pine (UK)	65.9	77.0	11.1	66.5
Corsican pine (UK)	62.9	75.9	10.0	87.0
Larch (UK)	55.2	66.8	11.6	68.6
Douglas fir (UK)	67.6	81.8	14.2	85.2
Treatment: PLATO (160-200 °C)				
Sitka spruce (Novar)	56.4	62.5	6.1	72.9
Western hemlock (Novar)	55.4	79.7	24.3	89.1
Douglas fir (Novar)	65.6	75.3	9.7	76.8
Treatment: NPC (200-220 °C)				
Sitka spruce (Novar)	49.4	57.9	3.2	57.1
Western hemlock (Novar)	58.8	65.9	7.1	58.2
Douglas fir (Novar)	48.0	65.8	17.8	64.8

As a result of the thermal treatment in the temperature range 160-220 °C, mass hydrophobisation of wood due to the lessening of the surface accessible for water occurs. The “water surface” decreases due to the closing up of the structural elements of wood upon heating, with the formation of closed pores. In saturated water vapours, the structure is partially relaxed, and the hydrophobisation effect tends to decrease. The “water surface” in the second sorption-desorption cycle increases in a wide range from 6 to 24% and is not unequivocally connected with a definite treatment method. The results show a partial reversibility of the hygroscopic properties of thermally modified wood, which, as is indicated by the coincidence of the desorption curves of cycles I and II, is caused by the water encapsulated in the cell wall.

Similarly, it has been shown (Obataya and Tomita 2002) that thermal treatment has a reversible and irreversible effect on the wood hygroscopicity. In their opinion, the reversible effect is based on the cell wall matrix softening and relaxation at high temperatures, which causes the matrix structure to fold when cooling. As a result, the polymer chains’ mobility decreases. At a low relative moisture, the folded structure hampers the water adsorption, while, at a high relative moisture, the material gets moistened, the polymer chains recover mobility, and water adsorption proceeds again.

Irreversible effects are caused by the material's chemical modification. Our results do not contradict Obataya's conclusions. The changes of the accessible specific surface by chemical modification of wood are summarised in Table 4.

Table 4: Hygroscopicity changes in wood of different species as a result of chemical modification

Wood species	**$A/A_{untreat.}$ in I cycle [%]**	**$A/A_{untreat.}$ in II cycle [%]**	**Change of $A/A_{untreat.}$ in II cycle [%]**	**$a_m/a_{m\ untreat.}$, in II cycle [%]**
Treatment: Acetylation				
Sitka spruce (Scotland)	45.0	46.2	1.2	49.5
Scots pine (UK)	54.1	54.5	0.4	44.8
Corsican pine (UK)	48.8	35.1	-13.7	37.4
Larch (UK)	56.8	54.3	-2.5	54.8
Douglas fir (UK)	112.6	96.1	-16.5	82.9
Treatment: Furfurylation				
Sitka spruce (Scotland)	79.6	80.4	0.8	62.8
Scots pine (UK)	74.7	73.8	-0.9	66.1
Corsican pine (UK)	91.4	74.7	-16.7	81.9
Larch (UK)	70.3	68.7	-1.6	74.5
Douglas fir (UK)	76.1	75.9	-0.2	75.9
Treatment: UZA hot oil				
Sitka spruce (Scotland)	69.3	77.7	8.4	93.8
Corsican pine (UK)	44.1	49.4	5.3	49.6

From the treatments studied, acetylation is most efficient from the viewpoint of hydrophobisation. Only in one case (for Douglas fir), some mass loss in the water vapour atmosphere was observed. The effect of closed pores, observed in the case of thermal treatment, is absent: the microstructure of the modified samples is stable, the sorption cycles are repeatable. Modification with furfuryl alcohol also gives a similar hydrophobisation effect, where there is medium stability to water vapour; the hydrophobisation effect is lower than in the case of acetylation. In all samples considered during this study, mass losses were observed (although minor ones) in moist medium.

For the samples modified with modified linseed oil (UZA), the results are too different for Sitka spruce and also for Corsican pine to judge the treatments hydrophobising efficiency. The surface of the obtained samples is very heterogeneous, which is testified by the poor obedience to sorption equations.

The best results are shown by Corsican pine treated by acetylation and UZA hot oil, although, similarly, as has been shown also by Jones and Howard (2004), Sitka spruce reaches essential improvement in the case of acetylation (envelope effect), while the effect in the case of UZA oil is limited.

Structural features of modified wood

As has been shown earlier, when investigating wood, each sorbate creates its structure depending on the energy of its interaction with wood. The characteristics of the microstructure of Sitka spruce wood, based on the isotherms of nitrogen and water vapours sorption show, that the "nitrogen surface" and pore volume of both untreated and modified wood are hundreds times less than the corresponding characteristics in terms of water. For instance, the “nitrogen surface” of Sitka spruce is about 1 m^2/g and the “water surface” is more than 300 m^2/g, the full pore volume is 0.002 cm^3/g and 0.2 cm^3/g for nitrogen and water vapours, respectively. Inert nitrogen is adsorbed on the surface of cell walls, not penetrating their structure. The curves of pore volumes distribution in size, calculated from the desorption branches of isotherms in the size region 2.6-30.0 nm, indicate the presence of several narrow maxima in the initial wood in the region 4-18 nm. In the case of thermal modification (both NPC and PLATO), the number of maxima decreases from 5 to 3, while, in the case of hydrothermal modification, the pore volumes in the region 4 nm and 7 nm exceed almost twice the corresponding volumes in the initial and NPC-modified wood.

The curves of pore size distribution in size, obtained from the desorption branches of water vapours sorption isotherms in the pore volume (1-11 nm) and characterising directly the cell wall structure in moist medium, show that the prevailing pore volume in the initial wood (including also for other species, in particular, Scots pine) falls within the region of sizes 1 nm and less, and there is also a small maximum close to 3 nm. After thermal modification, the pattern of distribution is not changed qualitatively, although the volume of all pores decreases, especially after modification in an inert medium. Considerable changes in the pore structure occur as a result of acetylation, namely, the volume of pores 1 nm in diameter decreases from 0.115 cm^3/g to 0.045 cm^3/g, while a small maximum appears close to the pore sizes 2 nm; in this case, the pore volume of all sizes decreases.

Results of fungi test

Biological tests were carried out with brown rot fungi *Coniophora puteana* for untreated and chemically modified wood alone. Scots pine *(Pinus sylvestris)* was used as the control.

Mass losses were 34% on average for unmodified softwood of different species, and 43% for control wood. Samples’ moisture after fungi for unmodified wood and the control was 34% and 56%, respectively. Mass losses for virulence samples were 32.8%.
The results of the brown rot test for acetylated, furfurylated and UZA hot oil modified wood are summarised in Table 5.

Only in some cases, minor mass losses were observed for acetylated wood. The losses of control samples show the normal development of fungi. The moisture of the modified wood after the fungi is lower than for the control samples, which can influence the wood degradation rate. SEM pictures show that the fungus penetrates the surface of the acetylated wood’s lumens and surface cracks.

Table 5: Minimum and maximum values of mass losses and wood moisture after the fungi test with Coniophora puteana for chemically modified wood

Treatment	Mass losses, %		Moisture after fungi, %	
	Modified wood	Control	Modified wood	Control
Acetylation	0-5.6	38.0-53.0	11.0-33.3	46.4-68.7
Furfurylation	0	12.5-14.4	57.7-82.3	58.0-69.6
UZA hot oil	2.2-16.9	46.1-48.3	12.9-13.7	50.5-51.7

For wood modified with furfuryl alcohol, mass losses were observed in no cases, although the control samples' losses were also comparatively low, which could testify the release of the substances from the modified material, hampering the fungi growth. The high moisture content in modified wood after fungi is also large, in comparison with the moisture of the adjacent control sample, which could testify an increased binding of the moisture of modified wood, but, at the same time, could not hamper the fungi development.

The biological durability of the UZA oil-modified wood against *C. puteana* is ambiguous. The better stability of Corsican pine (max. mass loss 3.6%) can be explained by the hydrophobising effect (see Table 4) in comparison with the case of Sitka spruce (average mass loss 16.9). Undoubtedly, oils decrease the moisture absorption during the fungi test (moisture after the fungi test - 13.3% on average), although do not prevent their degradation.

The durability against microorganisms is one of the improvements, which is reached by modification methods. The reasons and mechanisms of the durability of modified wood are not known precisely, although they are connected with changes in the wood structure. Several possible reasons for the improvement of the durability of thermally modified wood are mentioned in the literature, namely, low moisture of wood, which is not sufficient for fungi growth, formation of toxic compounds in the modification process; modification of the wood components' complex, which is not recognised by the fungi and is not degraded by them; degradation of hemicelluloses - an important source for fungi nutrition. The results of different experiments testify that none of these factors alone ensures the durability of wood against fungi (Weiland and Guyonnet 2003; Kamdem *et al.* 2002 *etc.*). Andersson *et al.* (2005), carrying out X-ray scattering studies of thermally modified wood, have found that, up to 200°C, the wood structure does not change essentially. They have concluded that the reason for the properties' changes is the change in the chemical composition and not the structural change. Obataya and Tomita (2002) also believe that the modification of the lignin and lignocellulose complex during thermal treatment is mainly responsible for the irreversible decrease in the wood hygroscopicity.

Hill *et al.* (2005) indicate three possible mechanisms of stability against fungi for wood, chemically modified with anhydrides, namely, chemical substitution of hydroxyl groups, reduced cell wall moisture, and blocking of the enzymes' access to the cell wall. Modification diminishes the water amount in the cell wall necessary for diffusion. The authors conclude that acetylation influences the rate of degradation with fungi, either decreasing the cell wall moisture or blocking the micropores, or as a result of the combination of these two effects. The substitution of hydroxyl groups is an important protection factor, which is still to be investigated.

In their turn, Mohebby *et al.* (2002), referring to Rowell (1989), indicate that hydroxyl groups are not only water adsorption sites, but also biological enzymes' reaction sites. The substitution of these groups with less reactive ones can possibly improve the properties and bio-stability of wood

In our opinion, obviously, the decrease in the affinity of the cell wall relative to water vapours and, respectively, the decrease of its ability to swell complicates the processes of the diffusion of active agents.

CONCLUSIONS

Samples of different coniferous wood species, subjected to thermal modification at the temperatures 160-220 ^{o}C in the inert gas or water vapours medium and chemical modification (treatment with acetic anhydride, furfural alcohols, UZA hot oil), were investigated. The decrease in the “water surface” at thermal modification (by 20-40%) is the main reason for hydrophobisation. In parallel, changes in the surface concentration of hydrophilic centres occur, although the effect of this factor is not unambiguous. The efficiency of thermal treatment after enduring the wood samples in saturated water vapours is retained, although tends to decrease. The best results are obtained in the NPC process, probably owing to the higher treatment temperature.

Chemical modification, especially acetylation, ensures an essential hydrophobisation of wood. In this case, the obtained effect is stable and is retained also in the moist medium. In the case of furfurylation, the obtained results are worse, although, as in the case of acetylation, the wood’s durability against rot fungi improves dramatically. Further studies of the properties of oil-modified wood are necessary.

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Session 8: The Future.

Acetylated wood in exterior and heavy load-bearing constructions: building of two timber traffic bridges of acetylated Radiata pine

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Keywords: Accoya, acetylated, load-bearing construction, radiata pine, traffic bridges

INTRODUCTION

Modification of wood opens a whole new and broad range of innovative or renewed applications for timber. Applications of which until now architects and designers only considered using steel, synthetic materials or concrete are now coming accessible. The initiative and implementation of the province of Fryslân in the Netherlands to build two heavy load-bearing traffic bridges of timber offers a unique chance for modified timber to demonstrate what will be possible using this innovative material. From an early stage it was clear that this specific design of the traffic bridges, chosen by the local inhabitants in a contest, could not be built using the known natural wood species.

The design consists of structural parts of three dimensional double bended glue-laminated beams, with exceptional dimensions of 140 by 108 cm in cross-section and specific wood-wood-connections to join these elements in the construction (Figure 1). The minimal required life-expectancy of these bridges is 80 year, with minimal maintenance efforts and a high safety level. For this purpose, durability, dimensional stability, mechanical strength, bending- and glue-ability, should be combined within one single timber species.

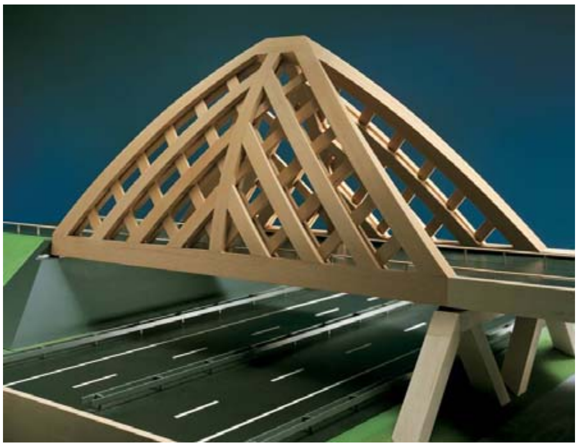

Figure 1: Model of the traffic bridges

In the same period the world's first industrial scale production plant of acetylated wood was launched by Titan Wood B.V., starting production in the beginning of 2007, marketed under the trademark Accoya^{TM}. This enabled the constructors and designers to explore the possibilities of using this novel material for the bridges and to proceed with their challenging plans. The initial design of the bridges by the architects was further developed into the technical design by the constructor with support of a specific composed "technical team timber bridges".

Numerous studies (Hill, 2006) over the past decades had already shown that acetylated wood meets the highest standards concerning biological durability and dimensional stability. For this exclusive application also additional proof was required for acetylated wood on: mechanical properties of structural timber sizes, compatibility with metal fasteners and specific wood joints and the suitability for industrial lamination for exterior and load-bearing application. This paper gives merely an overview of part of the specific research and general results performed within the framework of the development of the timber traffic bridges. Results of the specific parts of these studies will be published in more detail elsewhere.

EXPERIMENTAL

Study of the results of the extensively performed studies and tests worldwide on acetylated wood were used as the bases for further development. The high durability (class 1) and dimensional stability (improvement of 80% compared to the untreated wood), together with the reduced water adsorption (80% reduction) and the increased UV-stability known for acetylated wood did not need any additional support. The additional studies performed within the framework of the timber traffic bridges are divided in four major aspects:

- mechanical properties on structural timber sizes and strength grading,
- compatibility with metal fasteners
- gluability and (industrial) lamination
- strength properties and assembling of specific wood joints

Mechanical properties

Based on calculations of the constructive design and the dimensions of the elements, the required specifications regarding the mechanical properties of the timber to be used were defined. The required specifications are:

- average bending stiffness (MOE) $\geq$ 11.065 N/mm^2
- minimum (individual) MOE of 8.000 N/mm^2
- characteristic bending strength (MOR), within class C30, MOR $\geq$ 30 N/mm^2
- density (volumetric weight) of the wood, $\rho_{rep} \geq 380$ kg/m^3

The *primary research* questions regarding mechanical properties were:

1. can the intrinsic strength properties of the wood species radiata pine, or a sorted selection, meet the required specification?
2. can Accoya^{TM} (acetylated radiata pine) meet the required specification?

Secondary to this were:

3. what is the impact of the treatment on the strength properties and its distribution?
4. what is the influence of moisture content of acetylated wood on the strength properties?

Strength grading of Accoya^{TM} and radiata pine

The individual lamellas are machine stress graded according to EN 408. Boards of radiata Pine and acetylated radiata Pine were tested. Characteristic strength and stiffness properties of both boards and glulam are derived according to the European Standards EN 338, EN 384, EN 408 and EN 1194. In order to assess the complete strength characteristics, measurements were done during the whole production line, from the tree until after the acetylation treatment. In New Zealand 120 stems of radiata pine trees, origination from three different growth areas were measured non-destructively using acoustic velocity and density. After cutting and drying 90 boards (4000 x 205 x 25 mm) were selected and machine strength graded. From the 90 boards 360 pared samples (2000 x 100 x 25 mm) were cut. 50 boards of untreated radiata pine were tested on a bending machine and MOE and MOR were determined. The corresponding 50 matched-samples were pre-bent on a bending machine (to 40% of max. load) in order to determine the MOE before treatment of each individual sample. After acetylation the MOE and MOR of all boards were determined. Parallel to all strength measurements non-destructive measurements using speed of vibrations in wood were performed in order to determine the correlation between destructive and non-destructive strength measurements.

Influence of moisture content on strength properties of Accoya^{TM}

Since strength grading is performed on conditioned wood (20 °C, 65% RH) and the traffic bridges will be exposed to a wet outdoor climate, it is important to study the impact of higher moisture load on the strength properties. For this purpose the MOE and MOR at three moisture conditionings of structural size boards (200 x 100 x 22 mm) were performed. Boards were conditioned at 65% RH, 90 % RH and water soaked.

Compatibility with metal fasteners

From previous studies on acetylated wood it is known that due to the residual (low) concentration of acetic acid in the wood after acetylation, a higher risk on increased speed and intensity of corrosion of metal components in acetylated wood can be expected. The study was divided in two phases:

1. Search for a suitable corrosion protection system
2. Testing the, for the traffic bridges typical, steel fasteners on acetylated wood

For both studies, 1 and 2, tests samples of radiata pine and acetylated radiata pine with several types of fasteners and several types of corrosion protecting systems were prepared. In study 1, different types of metal protection systems (zinc, aluminium, etc) were tested. In study 2, duplex coated (epoxy layer with polyester top coating) were used. Also samples with glued-in rods were prepared for the corrosion tests. The samples were exposed for minimal 6 months in an accelerated weathering test and in an outdoor field test.

Glue-ability and (industrial) lamination

The study consisted of two parts:

1. influence of process parameters on the glue-ability of acetylated radiata pine
2. delamination testing

The suitability of different structural adhesives for the production of glulam from acetylated boards of radiata pine was studied and the parameters influencing the shear strength of the bond line were varied. The variation of parameters is shown in table 1. Both phenol resorcinol (PRF) and polyurethane (PU) adhesives were tested. The tests are performed according to EN 301 and EN302.

Table 1: Overview variables of the gluability testing

Parameter	**PRF resin**			**PU-resin**		
	Min	**Max**	**Standard**	**Min**	**Max**	**Standard**
Pre-conditioning RH [%]*	50	95	65	50	95	65
Residual acid concentration [%][a]	0	1	0,5	0	1	0,5
Resin yield [g/m^2]	300	500	400	150	300	210
Harder [% m/m]	15	35	25	-	-	-
Open-closed-time [min]	30	90	60	30	150	60
Pressure [N/mm^2]	0.6	1.4	1.0	0.6	1.2	0.8
Pressing time [hours]	16	48	24	3	16	6

[a] *moisture content acetylated wood between 3% (50% RH) and 9% (95% RH)*

The delamination tests are performed according to EN 391 and EN386. Three different types of adhesives (two types PRF, one PU) were used to produce sections of glued laminated timber of both untreated and acetylated radiata pine, using different quantities of adhesive per area, open times, and pressure times. The sections were 500 mm long, 100 mm wide and consisted of 4 laminations of each 30 mm thickness.

Strength properties and assembling of specific wood joints

The most important wood-wood-connections in the bridges will be constructed using glued-in rods. Usually glued-in rods are not recommended in an outdoor climate where changing moisture conditions lead to high tension laterally to the grain of the wood. However in the case of acetylated wood, the low moisture uptake and high dimensional stability the use of these connections in outdoor climate conditions. Due to the exceptional size of the foreseen glued-in rods, the load-carrying capacity of the glued-in rods when axially and laterally loaded needed to be determined experimentally. For each test 5 glulam blocks of radiata pine blocks with glued-in rods were prepared. Dimensions and test set-up can be seen in Figure 2. A selected epoxy resin (Wevo Specialharz) was used for the gluing. Besides the strength test also

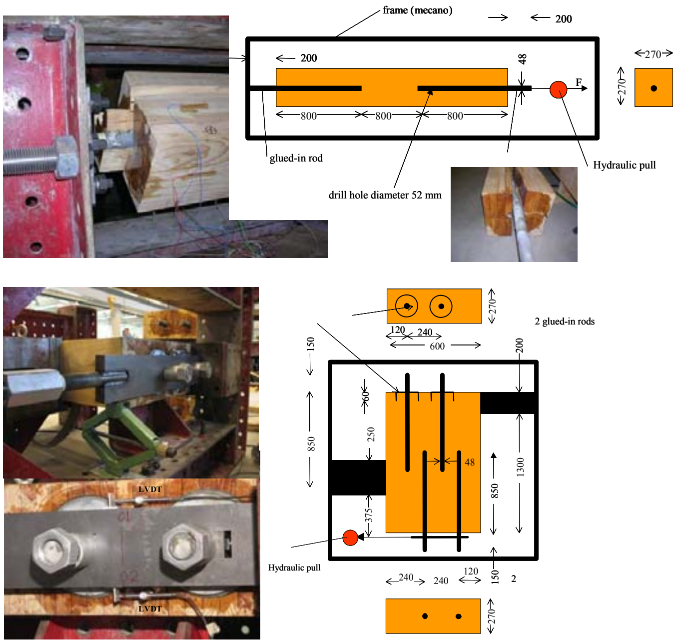

Figure 2: Experimental set-up of mechanical testing glued in rods. Above: axially loaded. Under: laterally loaded

a study was done in order to find the best method for injection of the joints with epoxy resin in order to gain a complete filling of the cavities around the rods.

RESULTS AND DISCUSSION

Mechanical properties

In Table 2 the mean and characteristic values of MOE and MOR of radiata pine before and after acetylation are shown.

Table 2:Strength properties of selected group of radiata pine boards before and after acetylation

		Before acetylation		**After acetylation**	
		MOE $[\mathrm{N/mm^2}]$	MOR $[\mathrm{N/mm^2}]$	MOE $[\mathrm{N/mm^2}]$	MOR $[\mathrm{N/mm^2}]$
Mean value	X_m	10540	63,6	10602	64,4
Standard deviation	S	2150	9,5	2430	12,1
Characteristic value	$X_{char} = X_m - (k_f \cdot s)$[a]	-	47,4	-	43,7
	X_{med}[b]	10570	-	10963	-

[a] *k_f =fractile factor = 1,7;* [b] *median value*

Influence of the acetylation on (structural) strength properties

The results (Table 1) of the strength grading show some influence of the acetylation on the strength properties of radiata pine. The mean values of both MOE and MOR increased slightly after the acetylation treatment. However the deviation in strength properties of the acetylated wood was also slightly higher compared to the untreated radiata pine. The higher deviation results in a reduction of the characteristic MOR of approximately 7%. The distribution of MOR in different strength fractions is shown in figure 3. On the basis of the results it can be calculated that 84 % of the tested acetylated radiata pine meets the required strength specifications for the timber bridges.

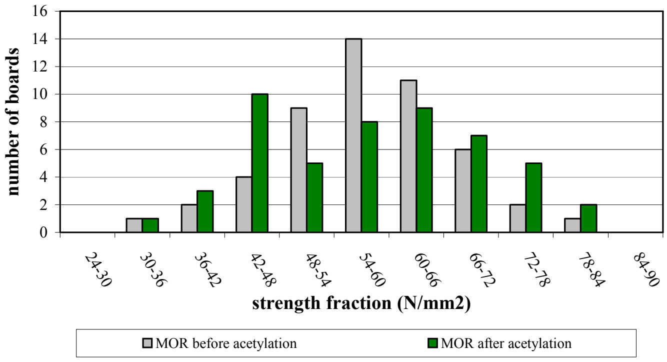

Figure 3: Distribution of the bending strength

Influence of moisture content on strength properties of Accoya^{TM}

The results of the influence of moisture content and stiffness are shown in Table 3. The tests are according to EN 408 performed in climate class I. For exterior use, as in the case of bridges, the construction will be exposed in climate class III. Both 90 % RH and water soaked conditions belong to climate class III, although water saturated wood in most instances is not acceptable for wooden constructions. According to Eurocode 5 a reduction of 20% of the MOE is used. This value corresponds with the value found (Table 3) for untreated radiata pine, going from conditioned in 65% RH to 90% RH. Acetylated radiata pine shows only half of this stiffness reduction. Even more remarkably is the different behaviour under the water soaked condition. The acetylated wood shows no further reduction of the stiffness, where the stiffness of untreated wood decreases with app. 36% compared to climate class I. For the MOR a similar effect has been found.

Table 3: Decrease of bending stiffness(MOE) with increasing moisture content (reference 65% RH)

	Condition		
	65% RH	**90% RH**	**Water soaked**
		[%]	[%]
Radiata pine	-[a]	-20,0[b]	-35,9[c]
Acetylated radiata pine	-[d]	- 9,6[e]	- 8,6[f]

Moisture content: [a] 3,7%; [b] 6%, [c] 36%, [d] 12%, [e] 17%, [f] 52%

Compatibility with metal connection materials

The results of the corrosion test in general are:

- Corrosion on acetylated wood occurs faster and stronger compared to the untreated wood.
- All metallurgic systems (zinc, aluminium, *etc.*) do not offer a long-lasting protection
- Only stainless steel shows no corrosion
- Duplex coated metal shows good protection; risk on damaging the coating during assembly needs to be avoided.
- Glued-in rods are enduring protected by the epoxy covering.

Figure 4: Samples acetylated Radiata Pine from the corrosion test: left different types of corrosion protection systems; right types of fastener to be used in the bridges, incl. glued-in rods

Based on the results of the corrosion tests for the timber bridges, the non-replaceable connection materials will be embedded in the epoxy covering. Replaceable fasteners will be duplex coated and in some cases stainless steel will be used.

Gluability and (industrial) lamination

The results of the influence of process parameters on the gluability of acetylated radiata pine with the PU-resin is shown in figure 5. From the 7 studied parameters and the 343 possible combinations 19 per resin were selected by the used a statistical model. As can be seen from Figure 5, for the PU-resin, all but one combination met the requirement of a minimal shear strength of 6 N/mm^2. For the PRF-resin comparable results were found. Of all parameters studied only the moisture content had a critical impact on the results. Although the moisture content of the acetylated wood (9% mc at 95% RH) was still considerably lower than the untreated at standard conditioning (12% mc at 65% RH), the higher moisture content of the acetylated wood had a negative influence on the glue-ability. This rejects the hypothesis that pre-moistening the acetylated wood might improve the gluability. The results of the delamination tests are shown in Table 4 and Figure 6. As can be seen in Table 4 one of the examined phenol resorcinol resin as well as the polyurethane resin fulfil the requirements for gluability of laminated beams for load-bearing constructions in exterior use (climate class III) and are therefore suitable for the production of the glulam members for the two timber bridges. The results confirm the positive results of the shear tests mentioned above. According to EN 386 a maximum of 5% open glue-line is acceptable. Also the high percentage of wood failure after opening the test blocks (Figure 6) confirm the suitability of acetylated radiata pine for the examined resin types. Hence both adhesives may be used for the bridges it is recommended to use a PRF resin type for the lamination of the glulam beams with large dimensions, since PRF resin tolerates thicker glue-lines, where the PU resin is more critical on this point.

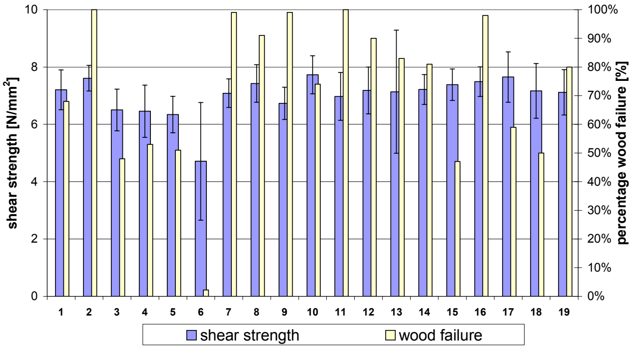

Figure 5: Influence of process parameters on the gluability of acetylated radiata pine with the PU-resin

Table 4: Delamination test of gluaminated acetylated radiata pine(EN 386, EN391)

Resin type	Code	Open glue-line [mm]	Wood failure [%]
PRF[a]	A1[a]	0	87
	A2[a]	2	75
	A3[a]	0	92
	E1[b]	29	13
PU	P1[c]	1	89
	P2[c]	0	93

[a] *Dynea, Aerodux 185,* [b]*Enocol RL490*
[c] *Purbond, HB181*

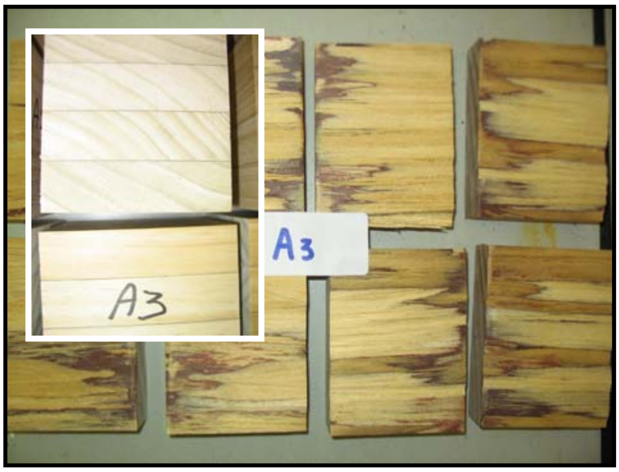

Figure 6: Test sample delamination test acetylated radiata pine, after cyclic test, left: glue-line cross section, right after opening test samples

Strength properties and assembling of specific wood joints

The determined load-carrying capacity of the axially loaded glued-in rods is shown in Table 5. The glued-in rods appeared to be very strong. However one of the most important conclusions was that the strength was very dependant on the angle between glued-in rod and the load direction. A relative small angle already can lead to a substantial decrease of the strength of the connection, as can be seen by the results of test 5 (Table 5), were an angle of approx. 3° was measured. This will mainly be caused by crooked drilling of the hole for the rod. Based on results of this study an angle of maximum ±0.5° can be tolerated for the bridge construction. The characteristic strength of axially loaded glued-in rods as a function of the bond length are shown in Table 6. The laterally load-carrying capacity of the glued-in rods appeared to be high. However the tests also confirmed the ductile behaviour of this type of connections. In order to avoid preliminary brittle tensile failure perpendicular to the grain, it is recommended to reinforce the timber perpendular to the grain.

Table 5:measured load-carrying capacity of axially loaded glued-in rods (Ø 48mm; bond length 800mm)

test	**Max load [kN]**
1	612
2	577
3	788
4	713
5	379[a]

[a] *low value due to crooked drill; oblique angle with axial load direction*

Table 6: Suggested characteristic load For axially loaded glued-in rod Ø 48 mm

bond length glued-in rod [mm]	**Characteristic load [kN]**
800	445
1000	470
1200	490
1400	505

CONCLUSIONS

Based on the results of the research performed within the framework of the timber bridges it can be concluded that:

- The intrinsic strength properties of the wood species radiata pine are sufficient to provide a representative fraction that can meet the required strength specifications, whereas preceding strength grading will be required.
- The mechanical properties of the acetylated radiata pine meet the required specification for the timber bridges.
- Only a minor impact of the acetylation treatment on the structural strength properties of radiata pine has been found: a slight increase of the mean values for MOE and MOR are diminished by a small increase of the deviation.
- The known reduction of strength properties of wood with increasing moisture content was found to be substantial lower for acetylated radiata pine.
- Corrosion on acetylated wood occurs faster and stronger compared to the untreated wood. Provided that the recommended procedures are engaged, the risk of critical corrosion of metal fasteners can be minimised.
- Both a phenol resorcinol adhesive as well as the tested polyurethane adhesive fulfilled the requirements of EN 386 and are therefore suitable for the production of the Glulam members for the timber bridges.

- The load-carrying-capacity of the glued-in rods connection meets the strength properties needed for the timber bridges. However the angle between glued-in rod and the load direction is critical and only a very small angle can be tolerated. In order to avoid preliminary brittle tensile failure perpendicular to the grain, it is recommended to reinforce the timber perpendular to the grain.

ACKNOWLEDGEMENTS

The authors would like to thank the following organisations and persons for their indispensable contribution; the province of Fryslân for the initiative and providing the means to perform the research, the other members of the technical team “timber bridges Sneek” for the complete development of the technical design of the timber bridges and establishing all the necessary research presented in this paper: Niek Kaptijn, Jan Bos, Emiel Lüning, Hans van der Grinten and Jaap Stro.

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Thermally Modified Timber (TMT) Facing European Standards

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Keywords: Thermally modified timber, standards, quality securing

ABSTRACT

Thermally modified timber (TMT) is defined as a material, whose properties are permanently changed by thermal treatment at temperatures above 160 °C in conjunction with reduced oxygen availability. The individual TMT assortments are defined by wood species, process and treatment level, and should be regarded like individual wood species.

Previously, TMT has not been considered within standards. Deviations from currently valid characteristic values, *i.e.* from untreated wood, particularly consist in equilibrium moisture content and strength properties.

The European Technical Specification for TMT, elaborated by CEN/TC 175, is the first available standardisation document (publication due mid-2007). The CEN/TS gives basic definitions, addresses important properties and the way how they are to be determined.

Despite this, different systems for quality assurance of TMT have been developed in Finland, the Netherlands and Germany. These systems, as well as the CEN/TS, commit the manufacturers of TMT to providing their customers with information and data concerning specifics and with deviations from standards. Further requirements will arise in the future from CE-marking.

INTRODUCTION

Thermally modified timber (TMT) was introduced into the European market 10 years ago and has been available ever since. However, the world of standardisation is just beginning to take note of it. An important first step to accept TMT – or wood modification in general – as a material capable of being standardised is the CEN/TS for TMT which was undertaken by CEN TC175/WG3/TG6 and which is just about to be published. Moreover, wood modification is not considered in current standards. The German Institute for Standardisation (DIN e.V.) initiated a project in 2006 to investigate how TMT fits, or does not fit, both testing and product wood standards.

EXPERIMENTAL

Terminology

Standardisation has just started to clearly regulate the terminology. There are some insufficiently defined terms, like "Thermoholz", as well as brands. For being technically correct, the term “modified wood” should be used. In analogy to OSB or MDF, the abbreviation TMT for thermally modified timber has been accepted by the above mentioned CEN/TG 6. In contrast to this, "ThermoWood" is the brand for processes and products of the Finnish Thermowood Association and its members.

The definition of TMT, according to CEN/TS, is given below. It was created to be open to the four relevant industrial types used today. These differ in the way the oxygen content is reduced during the process: atmosphere from wood gases and steam ("Finnish" process), thermohydrolysis and heat curing (the Plato process), oil bath (OHT process), and nitrogen atmosphere (rétification).

Single TMT assortments differ not only in the wood species, but also in both the manufacturer/process and the treatment level, and are therefore defined by a specific property profile. Thus, TMT should be considered as an own group of wood species, and single TMT assortments as single (artificial) "wood species". TMT mostly appears as a semi-finished product, such as boards, beams and poles. Additionally, it should be mentioned that chemical wood modification is currently starting to be introduced into the market. Here, acetylated wood (Accoya), furfurylated wood (Kebony/Visorwood) and resin-cross-linked wood (Belmadur) is to be mentioned.

As a logical consequence and in analogy to TMT, for chemically modified timber, the abbreviation CMT is proposed to the 3rd ECWM conference 2007.

The German project "Standardisation of thermally modified timber"

This project was processed in 2006 by IHD on order of the German Institute for Standardisation (DIN e.V.), in cooperation with the Federal Research Centre for Forestry and Forest Products Hamburg (BFH), the Institute for Wood Biology and Wood Technology Göttingen and the German Association of Wood Traders (GD Holz e.V.).

The objective of the project was to support the introduction of TMT into the market, regarding its conformity with relevant standards, in order to reduce uncertainties and limitations when TMT is used within standardised applications, and to avoid problems resulting from standard requirements on the one hand and specialties of TMT on the other. Furthermore, testing standards and methods were to be compiled and developed, which are suitable to determine and to describe the properties of TMT.

Within this project, 134 product and application standards as well as 120 testing standards have been checked, with regard to their relevance to TMT and to critical aspects and deficits, respectively. Furthermore, specific test methods for TMT have been compiled and proposed.

Product standards

As a result, some advice has been produced to be used by the standardisation groups for the preparation and revision of standards as well as by the users of standards, *e.g.* for planning, preparation of achievement lists or for contracts. This advice helps to improve communication between the market and contract partners and to reduce problems and disputes. An extract of the product standard overview is given in Table 1.

It was shown that wood modification has so far not been respected within standards. There is need for clarification and adaptation, with particular view of the moisture content (MC), sizes at specific MC and strength properties. Therefore it is necessary and recommended to determine specific equilibrium moisture content (EMC) for each TMT assortment. Furthermore, it is not possible to obtain strength values for TMT by density, as it is usual in some standards; this means, minimum strength for TMT cannot be deduced from minimum density. Some standards for floorings offer the opportunity to declare TMT as a free class. Until now, it has frequently been asked if TMT is applicable to load bearing components. Here it has to be stated that TMT is not a regulated construction product. Its use in load bearing applications is only legal if applicability has been proved. Currently, no sufficient data for TMT assortments are available for determining characteristic strength values.

Table 1: Extract of comments for products standards

Standard	Title	Part	Specific relevance to TMT	Measure, e.g. at revision
EN 844-12:2001-03	Round and sawn timber – terminology	part 12: additional terms and general index	no	possibly notes from 844-10 into this part (additional terms); take up into general index: fr: modification thermique du bois en: thermal wood modification de: thermische Holzmodifizierung
EN 1001-1:2005-10	Durability of wood and wood products – terminology	part 1: List of equivalent terms	yes	add: thermal wood modification modification thermique du bois thermische Holzmodifizierung
EN 1001-2:2005-10	Durability of wood and wood products – terminology	part 2: vocabulary	yes	add (analogous to EN 844-10): fr: modification thermique du bois Traitement par températures hautes > 160 °C, consistant à augmenter la résistance du bois aux altérations biologiques et la stabilité de la dimension en: thermal wood modification treatment at temperatures > 160 °C to improve the resistance of timber against biodeterioration and dimensional stability de: thermische Holzmodifizierung Behandlung des Holzes mit Temperaturen > 160 °C, um die Widerstandsfähigkeit gegen biologischen Abbau zu Verbessern und die Dimensionsstabilität zu erhöhen

Recommendations for durability test methods and standards

In principle, realistic test methods to determine the durability of wood (ISO 15686-2, 2001) are to be preferred. This means that field test methods (long-term exposure) should be preferred in contrast to laboratory tests (short-term exposure). According to the use classes of EN 335-1 (2006), various field methods are needed to fit the different conditions in practice. For determining durability in ground contact (use class 4), the field test according to EN 252 (1989) has proved valuable. Existing durability test methods for the durability out of ground contact (e.g. CEN/TS 12037, 2003) are time-consuming and have been designed for preservative testing so that testing naturally durable timber and modified wood is difficult. The double layer test method (Rapp and Augusta, 2004), already introduced as a standard proposal, seems to be a reasonable alternative.

The applicability of both the EN 252 and the double layer test to thermally modified wood has yet to be validated. Since both tests are based on a so-called "picking test" to quantify fungal attack, the reduced strength properties of TMT are to be taken into consideration.

For supplying the market with new materials as soon as possible, short-term laboratory tests, apart from field tests, are of interest, too. EN 113 (1996) has been established in order to determine the effectiveness of preservatives. prCEN/TS 15083-1 is foreseen for the purpose of determining in the laboratory the natural durability against wood destroying basidiomycetes. Both methods are carried out with selected basidiomycetes in pure-culture and under aggravated artificial testing conditions. To create a testing situation suitable for TMT, an adaptation of lab tests is necessary, *e.g.* regarding the selected test fungi (in field tests, TMT showed a weakness against white rot which could not be realised in the laboratory), and regarding the reduced equilibrium moisture content of TMT. Due to the fact that the durability of TMT particularly depends on treatment intensity, fast test methods for its control (and possibly for durability prediction) immediately after the process are of interest. For this purpose, the High Energy Multiple Impact Test (Brischke *et al.* 2006; Rapp *et al.* 2006) and the colour measurement acc. to CIE L*a*b* system (Brischke *et al.* 2007) are proposed as suitable methods.

Recommendations for future standardisation work

For future standardisation work concerning durability and life cycle prediction, the main conclusions made by BFH are as follows:

- There is no field test to determine the resistance of solid wood against wood-destroying insects as a reference, but for termites. Results of existing laboratory methods (*e.g.* EN 20-1, EN 20-2, EN 46, EN 47, EN 22) for the determination of resistance of wood against wood-destroying insects are not to be transferred to field conditions or conditions of use, respectively.
- The common use classes from EN 335 are to be revised, in particular regarding use class 3, which requires further specification in order to better and more realistically take the use conditions into consideration.
- Existing laboratory tests (*e.g.* EN 113, EN 807, prCEN/TS 15083) should be revised and adapted, in particular regarding the changed properties of TMT (reduced EMC, chemical composition, hydrophobicity and unsuitable criteria of exclusion (e.g. minimum MC after testing).

Possibly, laboratory tests acc. to the systematic method provided for by ISO 15686 should be adapted. For this purpose it is particularly necessary to adapt the corresponding short-term laboratory tests to the field tests, considering comparable deterioration patterns.

Recommendations for standards concerning moisture content and swelling

The thermal modification process changes the hygroscopic properties of wood. TMT has a reduced equilibrium moisture content (EMC) compared to untreated wood

(Militz 2002; Militz 2005). This reduction depends on the treatment process, wood species and climatic conditions. After thermal treatment for increased durability, the EMC is approximately 50 % of the EMC of untreated wood. The moisture content of TMT can be measured by gravimetric methods (*e.g.* according EN 13183-1). The measurement of EMC by the use of electrical resistance results in a higher moisture content than the TMT really has, during the treatment process the ion concentration within the wood is being changed. The electrical resistance method has to be adopted by any combination of treatment process and wood species.
Many standards for wood and wood products require a certain EMC of wood. Often this moisture content is derived from special climatic conditions for this test or product. In these cases the users of TMT have to consider that TMT requires another EMC, which can be calculated from isotherms. The producer of TMT should provide the customers with such isotherms for their TMT to make sure that the wood is used in the accurate EMC.

Swelling and shrinking of wood is often specified in relation to the change of the moisture content (differential swelling) or relative humidity (swelling coefficient). In the practical application these values are used for calculations where changed EMC should be considered. In these calculations the changed EMC must be considered. The increased hydrophobicity of TMT can be shown by reduced capillary water uptake. The standard (EN ISO 15148) provides a simple and accurate method to evaluate the capillary water uptake of TMT.

Recommendations for standards concerning mechanical properties

During the thermal modification process many mechanical properties (mp) of wood are changed. Therefore, the mp differs between untreated wood and TMT (Militz 2005). For the measurement of certain mp such as bending strength, tension strength, hardness and especially impact bending strength, the common standards for untreated wood can be used under consideration of the changed EMC. Because of the high decrease in impact bending strength (DIN 52189-1), this property should be considered in a product standard for TMT as required data for product description.

Recommendations for standards concerning surface properties (glueability and coatability)

The chemical changes during the thermal treatment process influences the surface properties of TMT (Hietala *et al.* 2002; Sivonen *et al.* 2002). As all the conventional coating and gluing systems cannot be used with TMT in the same way, it is necessary to evaluate the compatibility between TMT and gluing or coating. In Germany as well as in Europe, there are no established standards to evaluate wood concerning gluability or coatability. However, standards for the evaluation of glues and coatings exist for different applications. These standards use untreated European beech (*Fagus sylvatica*) or spruce (*Picea abies*) as a substrate. Some of these standards are suitable for an evaluation of glue/TMT or coating/TMT systems. Certain strength values required to accomplish a valid test could not be obtained by TMT due to its reduced mechanical properties resulting from the treatment process. A recommendation for a validation criterion for glue/TMT or coating/TMT systems is that the test is failed or passed by TMT.

An overview of standards for the evaluation of glueability and coatability is given in Table 2:

Table 2: Comments on standards concerning surface properties

Standard	Title	Comment
EN 301	Adhesives, phenolic and aminoplastic, for load-bearing timber structures: classification and performance requirements	Developed for assessment of gluing
EN 302-1 to EN 302-4	Adhesives for load-bearing timber structures - Test methods -	Developed for assessment of gluing
EN 204	Classification of Thermoplastic Wood Adhesives for Non-Structural Applications	Developed for assessment of gluing
EN 205	Adhesives - Wood adhesives for non-structural applications - Determination of tensile shear strength of lap joints	Developed for assessment of gluing
EN 927-3	Paints and varnishes - Coating materials and coating systems for exterior wood - Part 3: Natural weathering test; Amendment AC	Developed for assessment of coating
EM927-6	Paints and varnishes - Coating materials and coating systems for exterior wood - Part 6 : exposure of wood coatings to artificial weathering using fluorescent UV lamps and water	Developed for assessment of coating
EN 927-8	Paints and varnishes - Coating materials and coating systems for exterior wood - Part 8 : Assessment of adhesion	Developed for assessment of coating

European Technical Specification (CEN/TS) for TMT

The CEN/TS for thermally modified timber was compiled by CEN/TC175/WG 3/TG 6 under WI 00175118. Its title is "Thermally Modified Timber – definitions and Characteristics". The document has been prepared by the Technical Committee CEN/TC 175 “Round and sawn timber”, the secretariat of which is held by AFNOR.

The introduction describes improved dimensional stability (by a reduced equilibrium moisture content), increased durability against wood destroying fungi and – in some cases – changed colours as desired effects of the thermal treatment. The alteration of strength properties as a negative secondary effect is considered with the note that, if TMT shall be used in load bearing applications, the relevant requirements of European and national standards are to be taken into consideration.

An important principle is that TMT which the CEN/TS refers to usually is a semi-finished product. Therefore, the user has to take into consideration specific product standards (depending on the application) beyond the CEN/TS. Within the scope of the CEN/TS, service conditions are defined as interior (dry, humid) and exterior conditions, referring to service classes according to EN-1995-1 and to Use Classes according to EN 335.

TMT is defined as wood in which the composition of the cell wall material and its physical properties are modified by the exposure to temperature higher than 160 ºC and to conditions of reduced oxygen availability. The wood is altered in such a way that at least some of the wood properties are affected permanently and throughout. Meanwhile it is known that TMT shows lower moisture contents than untreated wood. Thus, if standards, respectively data, refer to MC values for untreated wood in specific climates (*e.g.* 12 % in climate 20 °C and 65 % rH), the EMC value in the concerning climate shall be used for TMT. As a suitable parameter to describe the treatment effect, the anti swelling/shrinkage efficiency (ASE) is mentioned. The requested data shall be calculated according to EN 1910.

In order to determine the biological durability towards fungi, the test method and rating have to be determined based on the end use class – Lap Joint test or double layer test combined with laboratory tests according EN 113 or ENV 839. The necessary tests depend on the application case (Table 3). Both laboratory and field tests are possible to determine durability, but field tests are to be preferred. Durability is not compulsory to be declared for products which are used only in service class 1 and Use Class 1 conditions, except if required by national regulation.

Table 3: Biological durability tests towards fungi

Use class according to EN 335	Laboratory test	Field test
3 (wood exposed to weathering, above ground	EN 113	Lap-Joint CEN/TS 12037 Double layer test (IRG/WP 04-2029).
4 (wood in contact with ground or fresh water, frequently exposed to moisture)	ENV 807	EN 252
5 (wood in contact with sea water)		EN 275

The TMT producer who is referring to the CEN/TS has to declare the following characteristics at least:

- Equilibrium moisture content
- Dimensional stability
- Biological durability towards fungi

Other characteristics shall be determined if they are relevant to the end application or region. Compliance of TMT with the requirements of the CEN/TS and with the values and classes of the characteristics declared by the manufacturer shall be demonstrated by type testing by the manufacturer or assessment and factory production control. Testing or assessment of TMT shall be performed to demonstrate conformity with the declared values or classes of the characteristics. Compliance criteria for a characteristic is its declared value.

Additionally to the product-related requirements of the CEN/TS, the producer of TMT shall establish, document and maintain a factory production control system to ensure that products placed on the market conform with the declared values or classes of the characteristics. In factory production control, the following characteristics shall be controlled by direct testing:

- Modification temperature,
- Moisture content,
- Colour,
- Surface shakes, internal shakes,
- Knot holes,
- Form defects.

The product marking for TMT according to the CEN/TS shall include at least:

- Name of producer,
- Traceability of production unit and production control,
- Manufacturer's product grade or identification code,
- Reference to this CEN/TS,
- Name of wood species,
- Product service class or use class for conditions

Quality assurance

Specific systems for quality assurance of TMT production and TMT products, respectively, have been established in Finland, in the Netherlands and in Germany. Despite this, the TMT manufacturers, e.g. in Austria, France and Switzerland, have established their own variants of quality assurance and factory production control.

Together with an independent national certification organisation, the members of the Finnish Thermowood Association have established the "ThermoWood® Production and Product Quality Control System". It focuses on raw material grading and process control.

In the Netherlands, construction products may be certified with a KOMO®-Certificate. For modified timber, a "National assessment directive for the KOMO® product certificate Timber modification" is available. It was introduced by Homan and Tjeerdsma 2005 at 2nd ECWM. The Dutch certificate particularly focuses on reproducibility of properties and traceability of products, as it is requested in the scope of CE marking, too.

In Germany, the quality label "Gütezeichen TMT" has been developed. It is awarded by the Entwicklungs- und Prüflabor Holztechnologie GmbH (EPH), Dresden. The label is registered as a common European label. A first certification procedure is currently running.

CONCLUSIONS

Unfortunately, the CEN/TS does not meet the expectation to classify TMT. Due to the multitude of TMT assortments and products, of the small market volume and of the insufficient data, it is currently impossible to define characteristic values for TMT and to match them with classes. By the time this will become possible, the relevant testing and product standards are to be considered in every application case, *e.g.* requirements of Brinell hardness for floorings or of durability for exterior uses. Further requirements are expected within the scope of CE marking, *e.g.* for windows and floorings.

ACKNOWLEDGEMENTS

We thank the German Federal Ministry of Economic Affairs and Labour for funding the project within the Federal Programme "Innovation with regulations and standards" (INS).

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Quality Control of Furfurylated Scots pine by TGA

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Keywords: Furfurylation, quality control, Thermogravimetric analysis (TGA), weight percent gain (WPG), wood modification.

ABSTRACT

Furfurylated wood is an environmentally friendly, chemically treated, wood product with improved characteristics. Quality control of furfurylated wood is still performed manually by subtracting the initial weight of a treated sample from its final weight, then dividing the result by the initial weight. Expressed as a percentage, this results in a value that represents the weight percent gain (WPG) of the treated sample and thus the degree of modification. The major disadvantage of this quality control method is that the production parameters are needed to determine WPG, since the initial weight cannot be deduced from a treated wood sample. In this paper the use of ThermoGravimetric Analysis (TGA) is presented as a potential quality control method for furfurylated Scots pine (Pinus *sylvestris L.*). The technique is independent of production parameters and, therefore, enables third parties to determine the WPG of any furfurylated wood product. Three validation trials have been performed with the same validation samples, but varying TGA settings and with different Partial Least Square regression models (PLS-models). Although the method needs further improvement, it has shown good accuracy and precision. Therefore, it is concluded that the proposed quality control methods using TGA can be used to estimate the treatment level of furfurylated pine sapwood.

INTRODUCTION

The use of furfuryl alcohol (FA) as a wood modification agent has been known for some decades. In the 1990s, new catalytic systems for the furfurylation of wood were developed that resulted in relatively cheap modification process. Furfurylated wood has good properties with respect to mechanical strength, dimensional stability and resistance to biological deterioration (Lande *et al.* 2004a,b).

Since Kebony ASA (formerly Wood Polymer Technologies ASA) started with the production of furfurylated wood, the quality control has been dependent on the production parameters and internal control of the specific batch produced. It is a disadvantage to not have a quality control system independent of the process. A crucial aspect in the quality control is the assessment of the degree of modification, which is expressed as weight percent gain (WPG) of the treated wood in comparison to the untreated reference. The weight increase, which is caused by the polymerization of furfuryl alcohol (FA) in the wood, is measured manually. Therefore, a method is needed that is partly independent of process parameters so that third parties can undertake quality control checks and also to enable subsequent quality control by Kebony ASA.

In this paper a method will be presented that fulfils all criteria mentioned and that has possibilities to be implemented by Kebony ASA. The method is based on the use of ThermoGravimetric Analysis (TGA), which makes it possible to quantify the amount of polymerized furfuryl alcohol, furan polymer (FP) in pine sapwood (*Pinus sylvestris L.*). Earlier, an attempt was made to quantify FP with the use of FT-NIR (Eikenes *et al.* 2004).

Thermogravimetry is a branch of thermal analysis that examines the mass change of a sample as function of temperature and time as it is subjected to a controlled temperature programme in a controlled atmosphere. Not all thermal events cause a change in the sample mass (*e.g.*, melting, crystallization or glass transition), but there are some important exceptions; such as desorption, absorption, oxidation and, in particular, decomposition (PerkinElmer 2004).

The decomposition of wood is characterized by differences in thermostability of the three major wood constituents; hemicellulose, cellulose and lignin (Beall and Eickner 1970). This difference in thermostability makes wood a suitable material for thermal analysis. When wood is analysed thermogravimetrically the result will be a thermogram with weight loss relative to temperature and time.

EXPERIMENTAL

Wood samples

Sound sapwood samples of Scots pine (*Pinus sylvestris L.*), originating from three different sources, were treated with different FA solutions to obtain various WPG. The first group of samples (A001 to A140; 140 samples), measuring 20_r x 20_t x 50_l mm^3 was made in the laboratory of the Norwegian Forest and Landscape institute. The second group (A201 to A262; 38 samples) was selected from a pool of EN-113 samples, which were treated in the laboratory of Wood Polymer Technologies under supervision of an engineer from the Norwegian Forest and Landscape institute. The third group of samples (144 to 206; 37 samples) originated from Kebony Products DA, where quality control sticks (20_r x 50_t x 300_l mm^3) are used in the industrial furfurylation process.

Sample preparation

Firstly, all wood samples were chopped into smaller pieces with a knife and hammer to make grinding into powder easier. Samples from groups 1 and 2 were chopped into pieces completely; from samples of group 3, only a representative part was used to obtain powder. The small pieces of wood were then processed in an IKA® MF 10 Basic grinding mill, with cutting-grinding head and 0.5 millimetre mesh. The wood powder was collected in a transparent plastic container of 100 ml. After every sample the equipment was cleaned in order to prevent cross contamination. When preparing the samples it is important to work carefully: contamination is a significant threat for the purity of the samples and separation may lead to loss of homogeneity resulting in test samples that are not representative. The friction caused during chopping and grinding should be kept to a minimum, in order to avoid loss of material by evaporation of Volatile Organic Compounds (VOC), such as fatty acids, resins and residues of furfuryl alcohol.

Thermogravimetric Analysis

The analysis was performed on a Pyris 1 TGA, produced by PerkinElmer Inc, at the Norwegian Forest and Landscape institute. The TGA is equipped with an auto sampler, which makes it possible to test 20 specimens in a row without human interference.

Different temperature programmes have been developed in order to improve the separation of wood components combined with a short process time. The settings for the three most recently developed temperature programmes, compared in this paper, can be observed in Table 1.

Table 1: The three temperature programmes, between brackets is the temperature increase per minute

	Temperature Programme 11		**Temperature Programme 12**		**Temperature Programme 13**	
Step	Action	Time [mins]	Action	Time [mins]	Action	Time [mins]
1	Hold at 35 °C	1:00	Hold at 35 °C	1:00	Hold at 40 °C	1:00
2	Heat to 160 °C (20)	6:15	Heat to 230 °C (30)	6:30	Heat to 600 °C (20)	28:00
3	Hold at 160 °C	45:00	Hold at 230 °C	45:00		
4	Heat to 230 °C (30)	2:20	Heat to 300 °C (20)	3:30		
5	Hold at 230 °C	40:00	Hold at 300 °C	50:00		
6	Heat to 300 °C (20)	3:30	Heat to 600 °C (40)	7:30		
7	Hold at 300 °C	45:00	Hold at 600 °C	6:00		
8	Heat to 310 °C (5)	2:00				
9	Hold at 310 °C	40:00				
10	Heat to 600 °C (40)	7:15				
11	Hold at 600 °C	10:00				
Total		3:22:20		1:59:30		29:00

The tests carried out with temperature programmes 11 and 12 used air as a sheath purge gas with a flow rate of 45 ml/minute until the moment that 300 °C was exceeded. Then the sheath gas switched to oxygen at a similar flow rate. The change to oxygen is absent in temperature programme 13 and air flows at 40 ml/minute. In all situations the balance purge gas was nitrogen at a flow rate of 45 ml/minute. For every analysis six milligrams (+/- 10%) of ground wood powder was used.

Data handling and statistics

In the chemical modification of wood, the level of treatment is expressed as WPG. In analytical chemistry substances are commonly expressed by their concentrations. The relation between those two expressions is not linear and needs to be converted by means of Equation 1.

$$FP\ (\%) = 100 * WPG / [100 + WPG] \qquad (1)$$

The response from the TGA was transferred to Excel data files. Although the data recorded from each sample consists of thousands of measurement points, not all data points were used in the statistical calculations. For temperature programmes 11 and 12, 5 and 4 points respectively were chosen, based on prior internal research regarding the thermal stability of cellulose, lignin and FP.

This data handling method was changed when temperature programme 13 was implemented. From the data collected during the sample analysis, all data points between 70 °C and 600 °C were transferred to an Excel database. For statistical analysis, the software programme Unscrambler 9.2 developed by CAMO Inc., was used. Partial Least Square Regression models (PLS-models) were build based on the response from sample groups 1 and 2 (calibration samples). The validation of the PLS-model was performed with the response from sample group 3 (validation samples).

RESULTS AND DISCUSSION

Thermal Analysis

When a sample has been analyzed by the TGA, the response is expressed in a thermogram. Figures 1, 2 and 3 are examples of how the response is presented. Each figure has a thick black line for the weight loss and a thin dotted line that shows the temperature applied to the sample. The scale of the weight loss in percentage is shown on the left axis, the temperature on the right axis, and the time on the x-axis (bottom).

In this project, the TGA only registered weight loss relative to time and temperature. Based on these outcomes it is not possible to identify the concentration of FP, because of the overlap in the combustion of the major wood constituents. Therefore, a PLS-model was created in order to predict the concentration of FP based on the data collected in the thermograms.

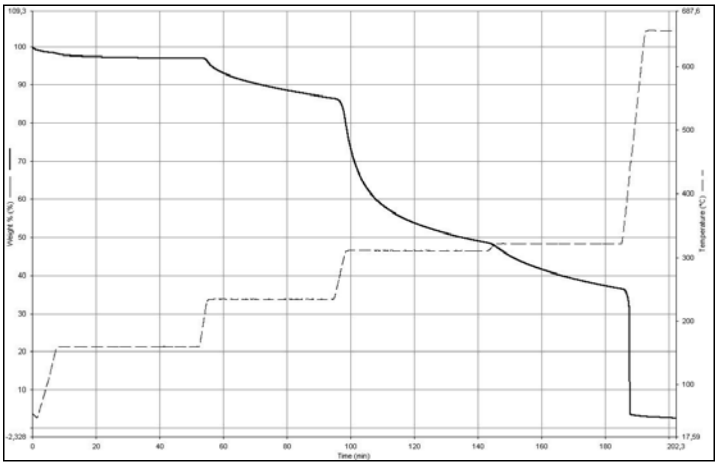


Figure 1: Sample 145 analyzed with temperature programme 11

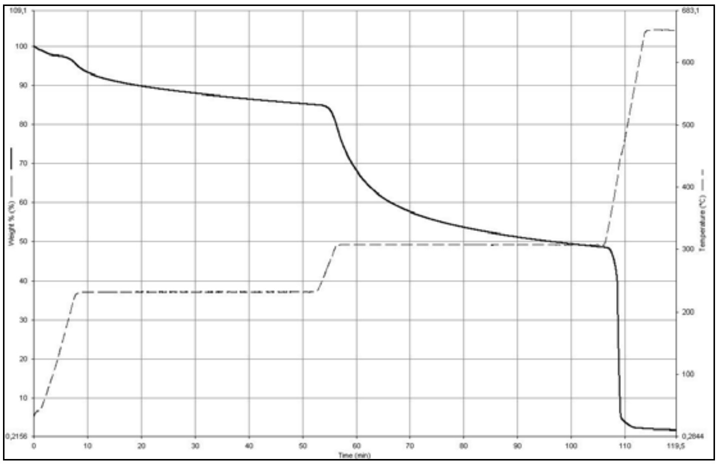


Figure 2: Sample 145 analyzed with temperature programme 12

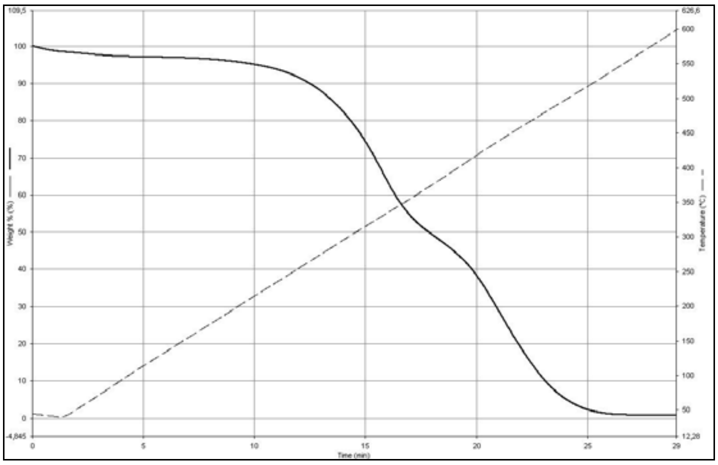


Figure 3: Sample 145 analyzed with temperature programme 13

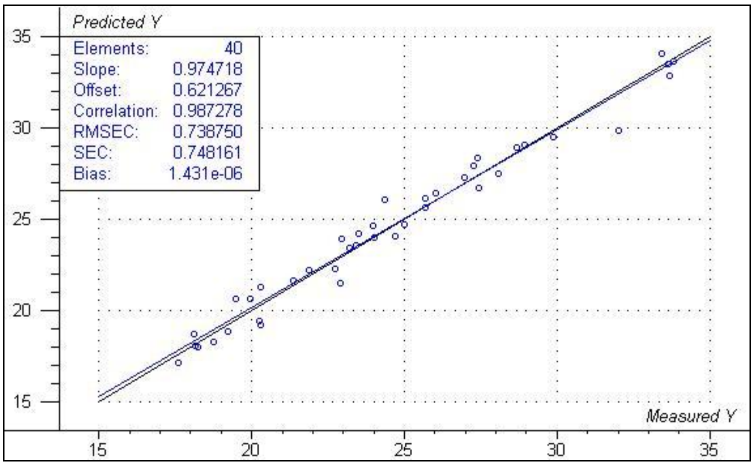
PLS Regression

Partial Least Square Regression is used to predict dependent variables from independent variables. In this study PLS regression was used to predict the amount of FP based on the measurements undertaken by TGA.

The bases of the PLS-models are known values of the samples; in this case the amount of FP. Therefore, all test samples were analysed using the manual method. The outcome of this manual method was the WPG of each sample, which then needed to be converted into FP by means of Equation 1.

The PLS regression models were based on a limited number of samples from groups 1 and 2. Model number 1 was the first result that provided an accurate prediction for the FP. It was based on the samples analyzed with temperature programme 11, of which only 5 measurement points were used. The PLS regression model used 1 principal component (PC).

The second model was based on samples analyzed with temperature programme 12 and also used 1 PC. The third model, made with temperature model 3, used 3 PC. All three PLS regression models are shown in Figures 4, 5 and 6.



. Figure 4: PLS-model 1, based on samples from temperature programme 11

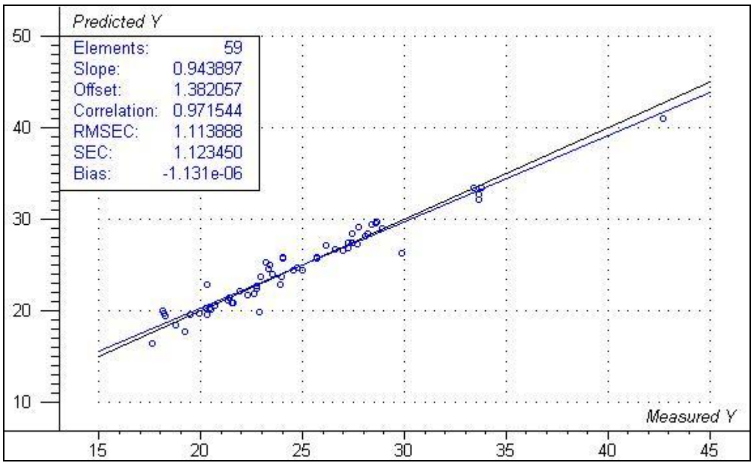


Figure 5: PLS-model 2, based on samples from temperature programme 12

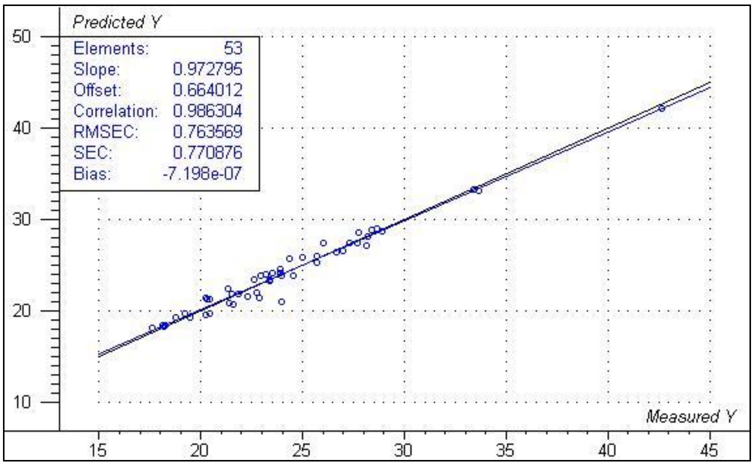


Figure 6: PLS-model 3, based on samples from temperature programme 13

Notice the different scaling in Figures 5 and 6 compared to Figure 4. The first PLS-model used fewer test samples (elements) and excluded in this way a sample with a high FP concentration.

Root Mean Square Error of Calibration (RMSEC) is, together with the slope, the most important figure to pay attention to in the above figures from the PLS-models. RMSEC is a measurement of the average difference between predicted and measured response values, at calibration stage. A lower RMSEC means a higher accuracy of the PLS-model.

Validation of PLS-models

The accuracy and precision of the developed PLS-models were tested through external validation. This was accomplished by analyzing six replicates of three different samples with different levels of treatment. These three samples were taken from group 3, the industrially produced samples, while the PLS-models were calibrated with samples from group 1 and 2. The results of the validation are shown in Tables 2, 3 and 4.

Table 2: Eikenes, Temperature Programme 11, PLS-model 1

Sample	Reference	AVG	STDEV	Rel STDEV	Rel.dev. FP
Val 145	30.0	32.4	0.36	1.11 %	8.0 %
Val 176	21.4	22.0	0.32	1.47 %	2.9 %
Val 198	15.7	15.8	0.57	3.63 %	0.4 %

Table 3: Fongen, Temperature Programme 12, PLS-model 2

Sample	Reference	AVG	STDEV	Rel STDEV	Rel.dev. FP
Val 145	30.0	31.1	0.25	0.81 %	3.6 %
Val 176	21.4	23.1	0.24	1.03 %	7.8 %
Val 198	15.7	16.6	0.16	0.95 %	5.2 %

Table 4: Van Riel, Temperature Programme 13, PLS Model 3

Sample	Reference	AVG	STDEV	Rel STDEV	Rel.dev. FP
Val 145	30.0	28.4	0.64	2.27 %	-5.4 %
Val 176	21.4	22.4	0.36	1.63 %	4.5 %
Val 198	15.7	16.9	0.58	3.45 %	7.5 %

Note: the validation of temperature programme 13 and PLS-model 3 used four replicates of sample Val 145 and five replicates of sample Val 198.

The tables present the sample numbers followed by the true FP value, which was measured manually. The third column shows the average of the six predicted values, followed by the standard deviation of those predicted values. Finally the deviation of the predicted outcomes is given in percentages (Rel STDEV), and also the deviation of the prediction from the reference is given in percentages (Rel.dev.FP). This last figure reveals which method can determine a particular FP concentration most accurate.

Despite the differences in the working methods, it can be stated that the relative deviation from the reference value is relatively small. Whether the test samples are analyzed for more than 3 hours (temperature programme 11) or within 30 minutes (temperature programme 13), the accuracy and precision remain comparable. The basic assumption is that the prediction with a PLS-model should not divert more than

10% from the true value of FP. This objective is realised with all three PLS-models and temperature programmes.

Wood samples

It should be taken into account that the three groups of samples were produced at three different locations under different circumstances. Ideally all samples would come from one source only, with preference for the industrial process. Likely, this would result in an even more accurate and precise PLS-model.

Thermogravimetric Analysis

Temperature programme 13 lacks a step that takes the moisture content into account. The other two temperature programmes do have such a step. It is necessary to include such a step in order to have a robust PLS-model the whole year round.

CONCLUSIONS

After having made three PLS-models based on three different TGA temperature programmes, it can be stated that this approach for predicting the amount of FP in furfurylated wood is accurate and precise. Furthermore, it is practical, affordable, reliable and independent of the production parameters.

Further improvements need to be made when one PLS-model is desired that can predict the WPG of any commercially furfurylated wood product. The test samples need to be selected more carefully, the number of samples needs to be increased in order to obtain a more robust PLS-model and the range of treatment level needs to be considered.

ACKNOWLEDGEMENTS

The authors would like to thank Monica Fongen and Eva Grodås for their laboratory work and Professor Mark Hughes for his editorial contribution. Kebony ASA is thanked for the supply of test materials and the funding. Furthermore, the Research Council of Norway is thanked for their financial support

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Accoya™

An Opportunity for Improving Perceptions of Timber Joinery

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Keywords: Acetylated wood, Accoya™, joinery, windows, markets.

ABSTRACT

This paper offers a short overview of the UK window sector and an opportunity for introduction of a high performance modified wood product to the market. The domestic window market is dominated by non-wood materials for reasons of cost, performance, perception, and effective marketing of competitor materials. The decline of timber in window market share, resulting in today's minority position, is beginning to show signs of arrest and slow reverse. BSW Timber's objective in the UK market development of Accoya™ is to offer the wide audience of professionals participating in the window supply chain a dramatically improved alternative to non-wood products. Success depends on the alternative offering strong advantages and no characteristic disadvantages compared to traditional timber and non-timber products. The opportunity exists to increase the share of timber in the UK window market at a faster rate, to a higher level and for a sustained period.

INTRODUCTION

While acetylated wood has been previously unheard of in the UK wood industry it has had a long history of development at universities and institutes around the world since the 1920's. The incentive for this continued development, requiring substantial funding and professional commitment, is largely due to the opportunity presented by the product. Quality acetylation of sustainably grown, short rotation timber species produces a modified product with wide ranging improvements over the best tropical timbers. This is not limited to solely environmental considerations, but also includes key material properties such and durability, stability, coating life and ease of processing.

Unfortunately, this quality academic work and equally intense proprietary work by companies around the world has not had the success in developing methods for cost effective production of acetylated wood. Titan Wood's work since 2003 (Kattenbroek, 2007) has been successful in achieving this critical cost effective production requirement. Acetylated timber has been in production and sold in commercial volumes, for the first time, from mid 2007, under the Accoya™ brand. BSW Timber, the largest sawmilling company in the UK, have been working with Titan Wood since mid-2003 under an exclusivity agreement in the UK and Ireland.

Accoya's performance property improvements (Hill 2006), and important absence of any property deterioration such as strength (Jorissen 2005), coating compatibility (Sikkens and Teknos) or impact strength (Tjeerdsma 2006) make it an ideal material for a wide variety of applications. Commercial projects are on-going in applications ranging from boat building, canal lining, highway bridge construction through to bee hive manufacture. This review focuses on windows. However, similar general assumptions may be made for doors and cladding (siding).

EXPERIMENTAL

Commercial production of Accoya™ from a foundation of comprehensive academic, largely laboratory based, research on acetylated wood required an intense product development period. It is interesting to consider examples from other industry sectors when seeking to assess what makes notable product development.

A strong product development case from the consumer sector has been the evolution of music players in the past ten years. The switch from record players to CD's and now I-pods has been dramatic. Gulfs in respective product capabilities have been large, clear and sufficiently relevant to cause the market to switch.

A view of the UK window sector in the same period by many important professionals in the construction sector will not feel anywhere near the same level of improvements have occurred in the timber window sector. This is not to say there's been an absence of any change or improvement. Changes have taken place but could be viewed as incremental and frequently only evident to manufacturing companies or specialist in the field.

Poor performing timber products from fencing through to joinery are regrettably familiar in the UK and many other countries. In this environment, a likely effect of change being somewhat incremental in the joinery sector has been the declining share of timber in the UK window market (Figure 1). A ten year period has seen timber go from mainstream to minority in short time. The impact on the joinery manufacturing sector and their suppliers of raw materials has been dramatic. The volume use of less sustainable materials has been equally pronounced and is widely anticipated to have strong consequences for the future (Thompson, 2005).

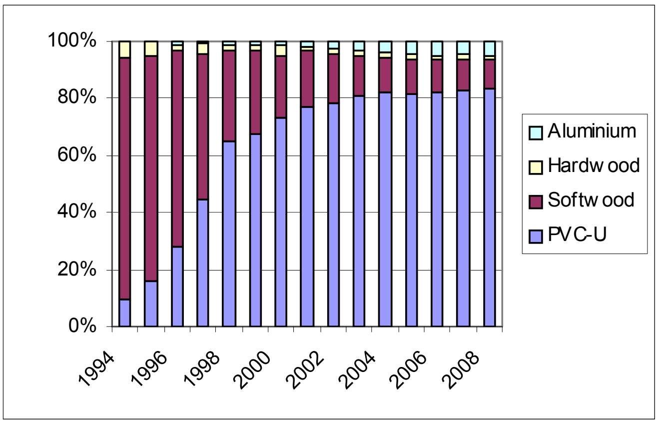

Figure 1: UK Window Market. New Build Residential

Timber's loss of market share does create an opportunity for a wood product which offers dramatically improved performance. Critically, this improved performance must be sufficiently robust to allow simple explanation to the construction and client sector with a minimum degree of technical clauses. The properties achieved by Accoya™ through the Acetylation modification may offer this required dramatic, robust level of performance.

RESULTS AND DISCUSSION

This section focuses on the relevant performance areas where dramatic, robust improvements are required to enable change in the perception of timber for windows in the construction sector.

Durability

Durability has many meanings to non wood scientists. The emphasis here is decay resistance and resultant life expectancy in the target hazard class 3 application. This type of acetylated wood durability testing has been well researched through laboratory exposures and field trials for decades. It is possible to achieve the highest level of durability – Class 1 – with the acetylation reaction. The acetylation reaction process has been extensively developed and scaled to a commercial point where all Accoya™ is guaranteed to achieve Durability Class 1 completely through the cross section of the timber. This absence of non durable zones of timber is quite different to traditional envelope impregnations of preservatives or modifying polymers. Envelope treated wood is highly susceptible to decay if the protective envelope is compromised by nails, drill holes, abrasion, impact damage, cracks or profiling to highlight a few common circumstances.

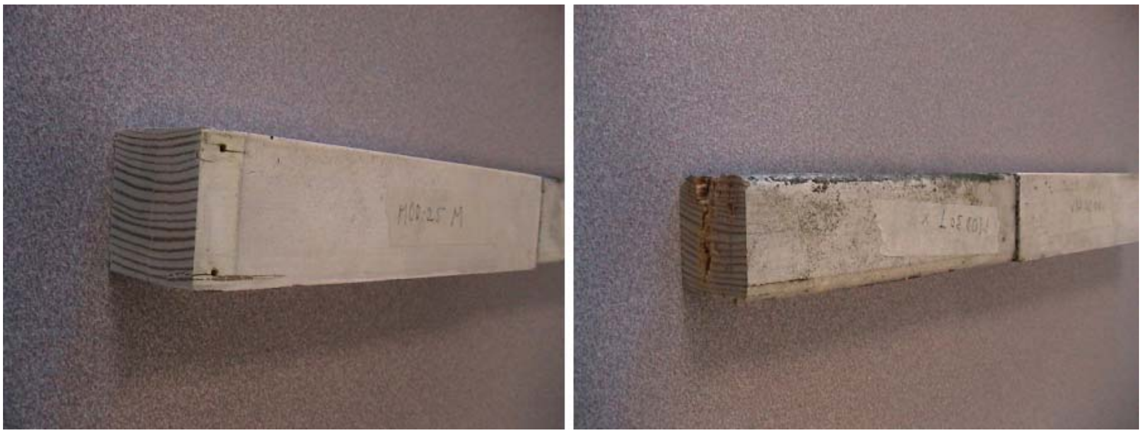

Figure 2: L-Joint samples after 9 year exposure. Acetylated left. Standard Joinery redwood right

Durability in real life is best evaluated by lengthy field trials where the product is placed in situations far worse than their design is intended to encounter in an ideal world. The L-Joint assessment represents this type of evaluation and Figure 2 illustrates the results for acetylated timber alongside standard timber after a 9 year L-Joint field exposure. The L-Joint test requires a mortice and tennon corner joint are machined and coated. The coating film is then broken around the joint and the assembly positioned at a negative incline towards the joint on an outdoor exposure rack. The timber joint has a severe exposure to decay mechanisms in this situation. No decay was encountered with the acetylated wood sample over the 9 year period.

The market is familiar with rot in timber windows, particularly if the coating fails or the window is damaged. This level of Accoya™ durability prevents rot in the most adverse use situations. The improvement cannot be considered incremental and the opportunity exists to make this durability benefit clear to the market.

Stability

Stability improvements resulting from cell wall moisture exclusion in acetylated wood (Hill, 2006) are significant when comparing Accoya™ to traditional timber species. Stability has a particular benefit on ease of use for timber as a raw material and for finished timber products. A simple method of comparing stability amongst timber species is though exposure of samples to conditions of varying humidity for prolonged periods of time. Figure 3 illustrates reductions in equilibrium moisture content in varying conditions of humidity for Accoya™ as compared to the unmodified pine control.

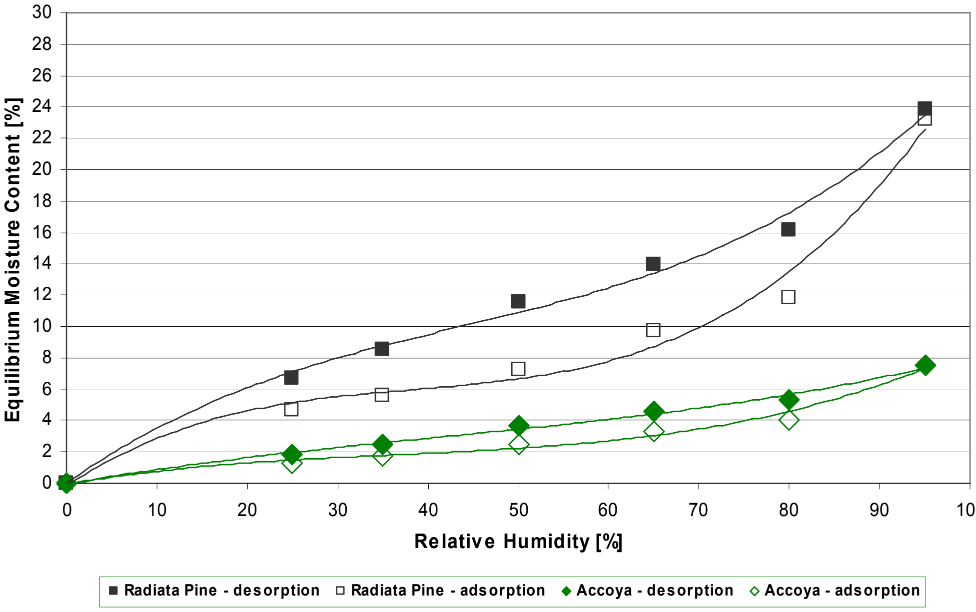

Figure 3: Comparison of hysteresis curves for Accoya™ and pine control

Similar information for other species can be drawn upon to compare Accoya™ stability to other species commonly used in hazard class 3 applications such as windows. Figure 4 illustrates the new level of stability for a timber product that's achieved by Accoya™. Again, the improvement cannot be considered incremental and the opportunity exists to make this stability benefit clear to the market.

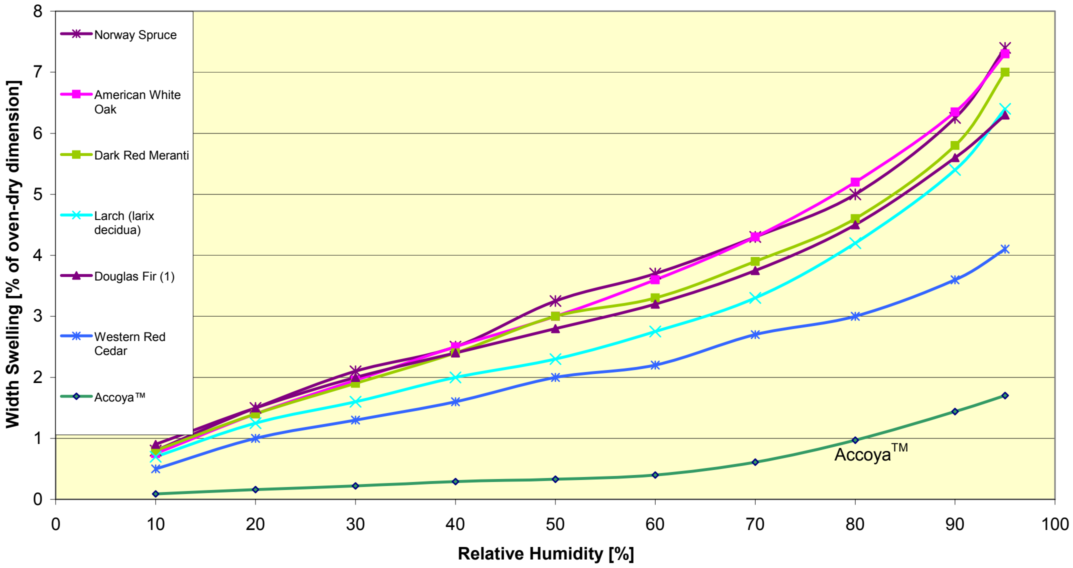

Figure 4: Comparison of stability for Accoya™ and commonly used joinery timbers

Extended Coatings Life

Coatings form an important element of a window system. Frequent coating maintenance of windows and the associated costs are a significant factor in consideration window options by specifiers and clients. Coating compatibility with acetylated wood has been extensively researched in lab evaluations and field trials at institutes and R&D departments around the world. Intuitively the improvements in stability and increased UV stability should extend coating life on an acetylated substrate. This has been repeatedly proven in rigorous assessments. Figure 5 shows at coating exposure rack at SHR in the Netherlands where a wide range of timber substrates and coatings were exposed at 45° elevation to a south facing situation.

Performance of coatings on acetylated wood demonstrated new levels of coating integrity on wood substrates over such an extended period. Studies such as these, in parallel with significant evaluation at coatings companies, has resulted in extended warranties for coatings on windows produced from Accoya™. Painted Accoya windows can be situated on an exposed elevation of a building and not require brush applied maintenance for 12 years. Stained finishes for the same situation have a 10 year interval. This compares to 3 to 6 years and 2 to 4 years for paints and stains on traditional timber windows respectively. The improvement cannot be considered incremental and the opportunity exists to make this maintenance benefit clear to the market.

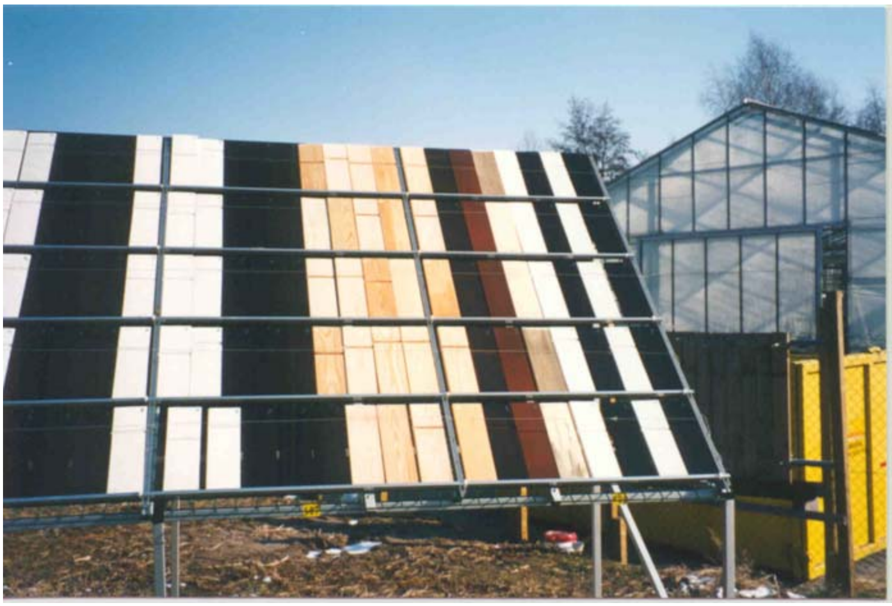

Figure 5: SHR 10 year coating exposure field trial

Processing

Figure 6: Profiled Accoya™ window sections

The benefits section concludes on an area which has until now been impossible to report on; experience of processing the material in large scale timber joinery factories with particular emphasis on profiling and coating.

Profiling and coating characteristics are less visible to the construction sector compared to durability, stability and extended coating maintenance. However, they are very important to the joinery manufacture and improvements serve as an added incentive to work with and promote the product. Poor definition of profiled sections, tear out, increased brittleness or raised grain create quite the opposite response.

Experience of machining Accoya™ for production of windows across the UK has been positive. The response is improved compared to common joinery soft woods and hardwoods. The clean finish is best appreciated by touch. A representation is shown in Figure 6.

A second window manufacturing process, heavily influenced by the wood substrate, is factory coating after assembly. Widely used water-based coatings are absorbed by surface wood fibres causing them to swell and create a 'raised grain' situation. Raised grain requires manual surface preparation (de-nibbing) before application of the subsequent coat in order to achieve a suitable quality finish. Grain raising is minimal with Accoya™ and de-nibbing requirements are dramatically reduced.

Figure 7: Factory coating Accoya™ windows

CONCLUSIONS

Experience in the introduction of acetylated wood under the Accoya™ brand has demonstrated an opportunity in the UK for a wood substrate offering dramatic improvements. The challenge is translating this through sound commercial practice into an increased share for timber in the window and other markets. Indications suggest that similar opportunities exist for development of other domestic markets by a number of companies around the world.

This will be relevant to:

- Sustainable forest owners
- The sawmilling industry
- Timber processing companies

- Timber window manufacturers
- System partners (coatings, adhesives etc.)
- Specification groups requiring high performance sustainable products
- Clients requiring long life, low maintenance and cost effective solutions
- Local authorities requiring materials which can be easily recycled or re-used at end of life.

ACKNOWLEDGEMENTS

A large number of companies and stakeholders have played active parts in the period of market development and commercial launch of Accoya™ in the UK. In this technical arena it’s important to make reference to those who have committed significant R&D resource to ensuring excellent proof of synergy between Accoya™ and related system products such as coatings and adhesives. Sikkens – Akzo Nobel, Teknos Coatings UK and Collano Purbond have all been valuable partners in this field.

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The Commercialisation of Wood Modification – Past, Present and Future

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Keywords: Wood modification, commercialisation, market opportunities, standardization.

ABSTRACT

The modification of wood has progressed considerably over the past decade, progressing from laboratory-based experiments to commercial ventures in some cases. Whilst the concept of wood modification is well established, commercial production still represents an emerging technology for enhancing the properties of European timber species, though there are now several commercialised processes. Among the selling points for these commercial ventures are that selected properties (such as dimensional stability and durability) may be increased. This has led to several claims of timber behaving in similar fashion to tropical hardwood species, and given the sustainable source of many European species, the environmental marketing angle has also been a key area of focus. Recent commercialisation has been due to a variety of reasons for the successful implementation of these processes, including advances in process technology, increased demand for high performance material, as well as environmental drivers. However there is a fine balance between a product with excellent properties and one that can viably compete in today's aggressive market. This paper will look at a variety of factors as to why these technological advances have taken several decades to come to fruition, as well as considering how timber processing needs to continue to evolve. Having a good product is not enough to ensure long term prosperity, due to aggressive marketing from other sectors. The potential of legislative changes will be explored, along with perceived views of treatment costs. This will help define medium to long term strategies for the continued success of commercialised wood modification processes.

INTRODUCTION

The commercialisation of wood modification processes has become a reality in the past 5 years for a variety of reasons. The main driver behind this has been the desire of end-users to use what is perceived a more environmentally friendly product than currently available. These developments have been borne out by legislative changes within the conventional wood protection industry, specifically within the Biocidal Products Directive (BPD 1998). The core objective of the BPD was to abolish trade barriers through the harmonisation of additives based on their efficacy. This led to the development of a pan-EU registration scheme, resulting in a standardised approval system. This increased registration led to a reduction in available active components, as companies did not wish to invest in compounds where there may be a limited production lifetime. This has been exemplified by arsenic and chromium. These changes occurred at a time when there were also increased public environmental awareness in both the components used in treating wood and in how to ultimately dispose of the treated wood. The marketing strategies of wood modification processes have taken advantage of such increased awareness, resulting in a 'green' image for the technology, which has partly been questioned during this conference (Saunders 2007). However, this has mainly led to a competition between modified wood and preservative treated wood, so limiting the potential of wood within the construction and related industries. It is the recovery of markets previously lost to other materials, such as PVC-u and aluminium, that must be viewed as major priorities, and one where the wood industries would benefit form working together.

Whilst this paper refers to wood modification in the past, it is not the aim of the author to review this subject, as this has been comprehensively covered (Rowell 1983, Jones 1999, Rapp 2001, Hill 2006). The important factor with all previous developments has been the inability to convert promising results into a commercially viable business venture. To date, the most long standing attempt to commercialise acetylation has been in Japan by the Daiken company, in the production of acetylated flooring, marketed as alpha-wood. This venture, started in the 1980's, has been reported as continuing to this day (Rowell 2006), though only to a limited national market. The inability to realise sound commercial activity within wood modification in general has been due to a variety of factors, including:

- Too high a market entry price
- Incomplete market survey
- Technologies insufficiently advanced
- Lack of supporting codes and standards.

This paper attempts to address these issues, observing where changes in technology and market perception has led to changes to previous commercialisation attempts, such that market entry points are now being established.

CURRENT AND FUTURE TRENDS IN WOOD MODIFICATION

As reported in reference texts (*e.g.* Hill 2006), there are a range of wood modification methods available: chemical, thermal, impregnation/polymerisation and enzymatic treatments. Many of the processes reaching commercialisation have been based on 'traditional' wood modification methodologies, based on the findings of pioneering wood scientists over the past several decades. The reason for the uptake of these technologies at this time can be attributed to advances in processing technologies as well as acceptance of the market to the products. However, several groups have been applying technologies from non-wood systems. An example of such technology transfer in recent years has been the development of wood treatments based on 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), whose use is commonplace within the fabric and textile industries in the production of wrinkle-free fabrics. From some of the earliest examples of the use of DMDHEU in wood treatment (Militz 1993), the process has undergone considerable evaluations (for example Krause *et al.* 2003, Xie *et al.* 2005), from which commercial application has been achieved with the launch of Belmadur®. Other recommended methods for the processing of fabrics are also beginning to feature more prominently in wood technology, namely the processing with citric acid (Katovic *et al.* 2005) and polycarboxylic acids. Future developments from the textile industry may see implementation of combination treatments, such as those of citric acid polymaleates (Yang *et al.* 1998). Indeed it is only the limitation and/or imagination of wood scientists that may prevent the implementation of concepts already in use within several product ranges, including agrochemical, food and sugar, coating, paper and resin industries respectively, as well as from other industrial sectors.

Similar trends have also been noted in the application of silicon-based treatments. Traditionally, silicon treatments have been used as a means of establishing a water barrier, particularly for surface treating brickwork. Over the past 15 years there have been considerable advances in applying this technology to wood (Mai *et al.* 2003), with possibilities existing in the use of:

- Fluorine containing compounds
- Inorganic silicates (“water glass”) and silicic acid condensates
- Wood-inorganic composites by sol-gel process
- Organo-functional silanes (sol-gel process)
- Micro-emulsion technology
- Chlorosilanes and trimethylsilyl derivatives
- Surface modification and hexamethyldisiloxane-plasma coating

It is impossible for the author to try and identify all possible aspects of process development, though it is certain that further advances in wood modification (including surface treatments) will occur. This is necessary to maintain market positions against other technologies. Wood modification has gained a place in today’s market through the application of technology, to stand still and bask in current successes would be unwise, as this may allow the competition to overtake you in the market place. Given the recent history of wood treatment development, such advances can be expected to take between 10-15 years to reach commercial possibility, which is a similar time delay as in other industries.

MEETING END-USER REQUIREMENTS

Much has been said of the benefits gained from wood modification processes, and it is not the intention to restate these in this paper. Whilst it is possible to provide vast amounts of technical data relating to treatments of single batches, it is the continued demonstration of quality control between batches that must be achieved. In order to better assess the requirements, it is necessary to look at the KOMO-system developed in The Netherlands (Homan and Tjeerdsma 2005).

Any company wishing to apply for the so-called KOMO®-certificate would need to comply with Assessment Directive (BRL) BRL0605 (“National assessment directive for the KOMO® product certificate timber modification”). A BRL will be compiled when sufficient demand for a certified product has been identified, with the evaluating committee comprising experts in the fields of study involved in the process under evaluation. The BRL, upon completion, will then undergo technical appraisal by a registered company, and if found acceptable be presented to and accepted by the Building Harmonisation Committee of the Building Quality Foundation.

The BRL is made up of several topics, each requiring a product to conform to strict guidelines. The topics include:

1. Process requirements – covering equipment, raw materials, process conditions and reproducibility
2. Product requirements – covering aspects such as durability, EMC / water absorption, dimensional stability, glueability, suitability for finishing systems, colour, mechanical properties, processing properties, fire behaviour, emission of harmful material
3. Quality system – both internal and external quality control systems
4. Control by the certification body – including regular inspections
5. Requirements regarding the marking, identification and trace ability

Provided a product meets with all these factors, it will be deemed suitable to carry:

- the KOMO®-logo
- the certificate number and/or the name of the certificate holder
- a unique production/run number-the field of application of the treated timber by means of a colour or letter coding
- the original timber species.

The colour and lettering will define the particular use of the modified timber, and is shown in Table 1.

Table 1: Colours and coding used in KOMO® scheme

Hazard Class	Description	Colour	Letter Code
1	Above ground, covered (dry)	Black	L
2	Above ground, covered (risk of wetting)	Orange	L
3	Above ground, not covered	Blue	L
4	In permanent contact with ground or groundwater	White	G
	In permanent contact with fresh water	Green	W
5	In permanent contact with salt or brackish water	Red	Z

Having a product with enhanced properties is one thing, successfully marketing it is another. In order to achieve this, it is necessary to engage with architects and specifiers – i.e. those who will recommend the use of the material. To gain acceptance, it is necessary to provide a considerable amount of information in the form of accredited results and certification, demonstrating a product conforms with current national and international codes and standards. Aspects for marketing will be covered later in this paper.

CO-OPERATION BETWEEN COMPANIES

In today's marketplace, technological and marketing aspects are recognised as providing advantages over competitors. Whilst this is also true in wood modification, there is a perceivable business benefit to be gained from working with other companies in the wood modification sector. This idealistic viewpoint has been shown to be possible through the creation of the ThermoWood network in Finland, where the best interests of product development have been placed ahead of individual company domination. Whilst it is true that some of the companies within the ThermoWood association operate at significantly larger scale than others, the benefits gained from a collective operation have been clearly demonstrated.

The need for a collective approach in marketing and development has been considered by the Task Group dedicated to thermal modification processes (CEN TC175/WG3/TG6). Part of the remit of this group has been to identify what are the current requirements for product conformation according to European standards, along with the aim of increasing the marketability of thermally modified wood. This group is expected to deliver its recommendations by late-2007, and these recommendations may play a significant role in the marketability of all forms of modified wood. The actions of this group have been reported previously (Scheiding *et al.* 2005), with an update to be presented at this conference (Scheiding *et al.* 2007).

The recent change of name by IRG (from the International Research Group for Wood Preservation to International Research Group for Wood Protection) demonstrates the increasing awareness of many companies of the increasing importance of non-traditional methods of increasing the durability of timber species. The degree of co-operation typified by the traditional wood preservation industry to encompass wood modification needs to be repaid by the creation of new markets for modified wood, not through the capturing of markets currently held by preserved wood. It will be through the interaction of companies in several sectors (including wood modification, wood preservation, coatings technologies, product manufacturers and architects / specifiers) that will provide some of the emerging technologies with entry points into today's markets. Attempting to develop the complete chain from wood treatment to final product for each process would appear a financially unsound option, it is better to use the expertise in each sector to your personal benefit.

MARKETING ASPECTS

It is only through a well planned and orchestrated marketing policy that a product can hope to succeed in today's aggressive market place. The main aims can be summarised as (1) identify the market area; (2) who are the main competitors; (3) understand the product; (4) perfect the sales pitch; and (5) make a profit. An obstacle of wood modification several years ago was the impression that the product was the replacement for all treatments and alternative materials. This has been re-evaluated to the point that selected wood modification techniques are aimed towards specific markets. Table 2 (Westin 2001) shows the perceived areas where selected wood modification techniques could be successfully applied.

Table 2: Overview of perceived market opportunities for modified wood (Westin 2001)

Type of product range	**Most belief in**
Garden wood (furniture)	Thermally modified wood
Window frames	Acetylated wood
Exterior doors and frames	Acetylated wood and MDF
Flooring	Several types of modified wood / fibres
Wet room & façade panels	Acetylated fibres
Building products etc.	Acetylated / Heat modified wood
Automotive / nautical applications	Furfurylated wood
Use by architects /government organizations	Acetylated /Heat modified wood

Whilst the information in Table 2 represents an interesting insight into the thoughts of companies several years ago, it is important to realise that the listed modification methods are not the only options. Table 2 has been used by several groups to provide an insight into which market should be targeted. Once the product range has been identified, it is necessary to undertake a SWOT (Strengths, Weaknesses, Opportunities and Threats) analysis. The aim of this is to rationally evaluate the potential of a product / method within the selected market. Table 3 shows a SWOT analysis for acetylated timber, though the findings may also be applied to many other wood modification methods.

Table 3: SWOT analysis for acetylated timber

Strengths	**Weaknesses**
▪ Stability of product ▪ Enhanced durability ▪ Potentially improved environmental profile ▪ Use of (European) softwoods ▪ The aesthetics of wood ▪ Extended maintenance intervals for coatings	▪ Dependency on timber supplies (e.g. radiata pine) ▪ Treatments adversely affect some properties ▪ Limited or no long-term performance data ▪ Lack of dedicated standards ▪ Limited public perception ▪ Lack of knowledge in market ▪ High investment costs in equipment ▪ High cost of modified wood
Opportunities	**Threats**
▪ Recovery of markets lost to wood ▪ Establishment of new markets for wood ▪ Greater use of FSC timber (or equivalent) ▪ Increased liaison with affiliated industries	▪ Supply of timber of adequate quality ▪ Supply and cost of chemicals / energy ▪ Aggressive marketing of competing materials ▪ Customers not willing to change ▪ New cheaper products entering the market

A major breakthrough in recent years has been the marketing of modified wood through a new brand name. Some examples of these are shown in Figure 1. The use of a brand name instead of ‘modified wood’ represents a major step forward, providing a more recognisable product. In addition, it provides the perception of a new timber species, which has been recognised as a marketing advantage. The use of a brand name may be further enhanced with strong environmental credentials. The author wishes to stress that previous claims of wood modification having environmental benefits over conventional preservative treated wood could be regarded as misguided, as many forms of modified wood are often not capable of achieving similar service lives to those of wood that has undergone conventional treatment. The aim of modified wood should be to re-establish markets lost to non-wood materials. However the environmental benefits should, wherever possible be promoted, through the use of life cycle analyses (LCA) and whole life costings (WLC). Furfurylation was the first wood modification system to be recognised as exempt from the Biocidal Products Directory (BPD), given the absence of active compounds in the processing. The process also gained further recognition through its award of the ‘Nordic Swan’ ecolabel. Other modification companies are developing similar environmental profiles.

Figure 1: Some examples of branded modified wood

THE FUTURE

Predicting the future is fraught with danger, especially when concerning emerging technologies. What is certain is that wood modification is here to stay. It has taken several decades to achieve this, though serious commercial development has only been established in the last 10-15 years. It is likely that several new methods will emerge over the next 10-15 years, possibly as a result of technology transfer from other non-wood industries. It is also likely that as production and availability of modified material increases, some of the elevated costs will reduce. However these prices will not drop to those currently achieved by preservative treated wood, but expectations are for prices to match those of imported tropical hardwoods. It is for this reason that there should be a recognition for a market for both preservative treated and modified wood. Modified wood should compete with alternative non-wood materials, and companies need to address markets currently held by non-wood materials to assess market potential.

CONCLUSIONS

At the time of the First European Conference on Wood Modification, the number of companies producing modified wood was fairly limited, though commercial involvement has increased since that time. At the time of the Third European Conference on Wood Modification, new production plants have come on line. Wood modification has become an established method for treating wood within Europe, backed up by considerable quantities of scientific and environmental data. The development of new treatments will continue, providing a greater choice for architects in near future of products with superior profiles to many of today’s favoured materials, at affordable prices for high end-value products.

ACKNOWLEDGEMENTS

The author would like to thank persons within the wood modification industry who have provided information prior to and during the compilation of this paper, as well as the many persons form the Thematic Network for Wood Modification, who helped define many of the changes now being applied within the wood modification industry.

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