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Wood modification developments

Waldemar J. Homan[1] and André J.M. Jorissen[2]

[1] SHR Timber Research, Wageningen, The Netherlands

[2]: Eindhoven University of Technology, Eindhoven, The Netherlands

The last decades developments in the arena of wood modification have accelerated considerably. This acceleration is due to a number of circumstances of which the environmental awareness, the increasing demand for high and constant quality and the increasing prices and availability of tropical hardwood species. This has led to the up-scaling and the market introduction of a number of wood modification techniques. Modification can be done without added chemicals by heat treatment only, or with the aid of added chemicals. Examples of both principles are given. Several products of thermally modified wood are already available on the market. More recently the first chemical modification processes have reached (or are about to reach) market introduction. Chemical modification makes wood with superior qualities of tailor-made products possible. The variability in degree of modification within wood is discussed with acetylated wood as an example. Different treatabilities in different wood species also reflect in acetic anhydride impregnation. However, in contrast to waterborne systems this does not result in sharp fronts but in more gradual profiles. The gas diffusion of the chemical into the wood plays an important role in this phenomenon. In the further process developments these effects need to be taken into account.

keywords: wood, modification

1 Introduction

This article gives an extended introduction on the state of the art of wood modification world-wide and then zooms in on the variability in degree of modification within pieces of wood. Timber is available in many diverse species that vary in density, colour, strength and durability. As main renewable resource wood is part of cyclic ecosystem transformations. Biodegradation is a significant factor in this process. Wood as a natural composite is also very sensitive for moisture. Instability under changing moisture regimes is considered next to biodegradability as a second major disadvantage of wood compared to other materials.

Most fast grown wood species tend to deteriorate rapidly under biological and physical influences. In particular the sapwood of most species has a low durability. The most important biological decay is caused by fungi. Many wood species from temperate and boreal forests have insufficient durability for the intended applications. At this moment this problem is solved partly by using biocides (containing for example: creosote, arsenic, zinc, copper, chromium, etc.) and partly by using tropical hardwoods. Since both the traditional wood preservation and the use of tropical species are under political and consumer pressure, the timber industries are seeking alternatives. The use of home grown species with enhanced qualities would be the ultimate solution to this problem.

Wood modification aims at altering the molecular structure of the cell wall components. Wood properties can be improved considerably by converting hydrophilic OH-groups into larger more hydrophobic groups. Dimensionally stable material is created because the cell wall itself will be in a permanently swollen state that will attract no or very little water. Often the treated wood is no longer recognised as a nutrient medium by the very specific enzyme systems of degrading fungi or the lowered equilibrium moisture content no longer promotes decay.

One of the bonuses of modified wood is that it brings new applications of wood within reach. Therefore it should not be considered merely either a replacement for preservative treated wood or tropical hardwood.

The different technologies of wood modification have been known for a long time, but in the past there was no economic or environmental urgency to develop these technologies. More recently there has been growing environmental and legislative pressure on the use of biocides and traditional biocide based wood preservatives, that has created new opportunities for wood modification. At present several processes for modifying wood have been demonstrated on laboratory and semi-industrial scales and continued advances in process development will see these materials becoming more commonplace in the near future.

Wood modification can change important properties of the wood including biological durability, dimensional stability, hardness and UV-stability. Controlling the moisture content of the wood is a very effective way to protect timber. In many wood applications improving the dimensional stability also helps by reducing the formation of cracks and thus keeping water out of the construction. A secondary effect of dimensional stability is the improved performance of paint coating systems. Improving the dimensional stability can also function as a first objective, especially in applications at lower moisture risk but with high requirements for exact and constant dimensions.

In summary the broad range of possible wood modification treatments can be divided into three categories related to the mode of action of the chemicals:

1. Lumen filling with a substance, usually a resin can be an option. These treatments might increase strength properties and slow down the process of water (vapor) uptake, but they do not change the sorption behavior of the wood over a longer period of time.

2. Bulking to fill the cavities in the cell wall as well as the cell lumen is a more general approach. Bulking treatments tend to reduce the swelling and shrinkage of the wood. They might even have a beneficial effect on the long-term sorption behavior.
3. Modifying treatments are usually the most effective. The chemical structures of cell wall components (lignin, cellulose and hemi-cellulose) are altered and covalent bonds are formed. Modification in this stricter sense can be divided into heat treatments, chemical modification and enzymatic treatments. Many properties can be improved permanently, in particular durability, dimensional stability and reduced equilibrium moisture content.

Strength and stiffness properties are, however, mostly reduced due to the modification treatment. For heat treatments this is generally shown in figure 1. Strength and stiffness values used in practice are valid for temperatures below 60 °C. Since the temperature within the wood raises, depending on the type of modification, up to sometimes over 200 °C these values cannot be used. Even the relations between these properties change and consequently the strength and stiffness values must be determined for each wood species and for each treatment. Since this activity is not carried out yet, modified wood cannot be used structurally.

2 Overview of scaling up

2.1 Introduction

Many definitions of wood modification are given in old and recent literature. Some of them include the demand of a change in chemical structure of the cell wall components. Recent insights have shown that in many cases it might be very hard to proof whether this demand is met or not (Hill *et al* 2004). Besides that, chemicals that merely bulk the cell wall would not fall under this definition. A wider definition of wood modification involves a treatment of wood to enhance its properties, but that does not involve the production of a product that contains toxic residues. This last premise excludes the use of biocidal treatments and thus separates wood preservation from wood modification.

In 2003 the first European Conference on Wood Modification was held in Gent, Belgium. The meeting was the final result of a EU supported thematic network entitled: "Wood modification, the novel base, providing materials with superior qualities without toxic residue" (co-ordinator: SHR Timber Research) (Van Acker and Hill 2003). In the final conference it became clear that wood modification is no longer an academic topic. Thermal treatments have already been penetrating the market for a number of years and several chemical modification processes are just emerging. The industrial input was noteworthy. In fact the success of the conference, and the network, was such that the organizing committee decided to have a new conference in 2005.

A distinction can be made between three main "wood modification" processes: thermal treatments, chemical modification and hydrophobation. Additionally enzymatic modifications can be identified especially in relation to wood fibres.

2.2 Thermal treatments

Burmester (1973) published the basic principles of the so-called FWD-process ("Feuchte, Wärme und Druck"). Thermal treatments are controlled pyrolysis of wood being heated (> 180 °C) in absence of oxygen (O_2) inducing as such chemical changes. Several different technologies are introduced using different media including nitrogen gas, steam and hot oil.

In Finland, France, Germany and the Netherlands laboratories have been experimenting with modification of wood by heat treatments. By applying heat some of the wood polymers are broken down, influencing negatively the strength properties, and new water insoluble polymers are formed. Most of these processes are performed under low oxygen atmosphere since the presence of oxygen can result in severe degradation of the cellulose thus reducing the strength of the timber even more. As for all modification treatments the chemical structures of cell wall components (lignin, cellulose and hemi-cellulose) are altered. The function of these components can be explained generally by making a comparison with concrete:

Wood	**Concrete**	**Function**
Lignin	sand, small stones	compression forces
Cellulose	reinforcement	tension forces
Hemi-cellulose	cement	bonding

Consequently, the strength properties are changed by altering the chemical structure of these components.

Keeping the strength reduction and the increasing of the brittleness under control are two of the biggest challenges of thermal treatments. Some processes are out of the scaling-up phase and entered the stage of commercial production for non structural use. Additional research is needed before structural use is possible.

In 2001 in a special seminar of COST Action E22 heat treatments of wood were reviewed (Rapp 2001) and later also summarized by Militz (2002). At present there are four groups of treatments, all of which are on the market: the Finnish Thermowood, the Dutch Plato Wood, the French Retification and the Oil Heat Treatment (Chanrion and Schreiber 2002).

2.2.1 Thermowood

In 2000 eight heat treatment plants were operating in Finland (in 2004 twelve) with a capacity a little under 50000 m^3 / year. Big international timber companies like Finnforest and Stora Enso are producing under the Thermowood patents. In the Thermowood process the wood is heated in the presence of steam. Water steam is used to replace air by water vapor. Air contents are typically under 3.5% (Syrjanen 2001). Low oxygen contents prevent the wood from burning at high temperature. Temperatures for the actual heat treatment period range from 150 °C to 240 °C, the time of the period is 0.5 to 4 h. Starting with non durable (class 5) softwood species, durability class 1-3 can be obtained depending on the process. In general the bending strength is reduced up to 30% with higher temperatures. A reduction in shrinking and swelling up to 50-90% is reported. Because of limited resistance against decaying soil organisms, use in ground contact is not recommended (Jamsa and Viitaniemi 2001).

2.2.2 Plato

The Plato process was invented in the 80's by Shell (Ruyter 1989) and is now executed by the Plato Company in the Netherlands. It consists of three steps. The first step is a hydrothermolysis. The wood is heated under wet conditions (under steam pressure, thus under low oxygen atmosphere). In this step it is believed that aldehydes and phenols are released from the hemi-cellulose and the lignin. The second step is a drying process, which is needed because in the third step the curing is executed under dry conditions. The aldehydes and phenols react with each other during the curing and form new polymers around the existing structures in the cell wall. In the first step temperatures typically are between 160 °C and 190 °C. In the curing step the temperatures are between 170 °C and 190 °C. The duration of the process steps is as follows 4-5 hours for the thermolysis, 3-5 days drying, 14-16 hours curing and finally 2-3 days conditioning (Boonstra *et al* 1998, Militz and Tjeerdsma 2001). The durability depends on the exact process conditions but typically is between class 1 and 3 (Tjeerdsma *et al* 2000). Reduction in bending strength varies from 5% to 18%. Reduction in tangential swelling and shrinking (ASE) vary between 15% and 40%. Similar work (Jones *et al* 1999) has also shown that fibreboards may be produced from fibres treated by a “hygrothermal” process.

2.2.3 Retification and Perdure

In France at the Ecole des Mines de Saint-Etienne, the process called retification (retified wood) has been developed. The Company New Option Wood now operates under the license. The process consists of slow heating up pre-dried wood of around 12% MC up to 210 °C to 240 °C, in a nitrogen atmosphere with less than 2% oxygen content (Vernois 2001). In 2001 three plants were operating. A second French process is named Perdure. This process starts with fresh wood. The first step is artificial drying in the oven. Then the wood is heated up to 230 °C under steam atmosphere (low O_2). The steam is generated from the water of the fresh timber.

With both processes the maximum temperature influences durability and mechanical properties. The higher the temperature the more durable the wood becomes, however this also induces more strength loss. Bending strength losses up to 40% are reported. Both processes are very sensible to slight temperature changes. This needs to be controlled precisely. The paint adhesion of this wood is drastically reduced. This is believed to arise from exudation of the resin from resinous species. Durability is very dependent on species, process temperature, process time, and accuracy of the process. Swelling and shrinkage are reduced with a factor 2. Equilibrium moisture content typically is 4-5% instead of 10-12% for untreated wood.

2.2.4 Oil heat treatment

Most heat treatments are carried out at temperatures between 180 °C and 260 °C under low oxygen conditions. This has lead to the idea of heating up the wood in hot oils. The Company Menz Holz in Germany started with a hot oil treatment. (Vernois 2004) It proved to be necessary to maintain the desired temperature (e.g. 220 °C) in the wood's core for 2-4 h (Rapp and Sailer 2001). The oil medium can be rape seed oil, linseed oil or sunflower oil. The oil provides in good heat transfer and separates the oxygen from the wood. The obtained durability is very depending on wood species and temperature. For spruce temperatures up to 220 °C are needed to reach durability class II for pine 200 °C is sufficient. With the Menz process no reduction in stiffness was observed. However the strength was reduced by 30% when heated at 220 °C. Paintability with acrylic waterborne systems was reported to be good and even better than with gas-heat-treated material. Typical improvement in dimensional stability is 40%.

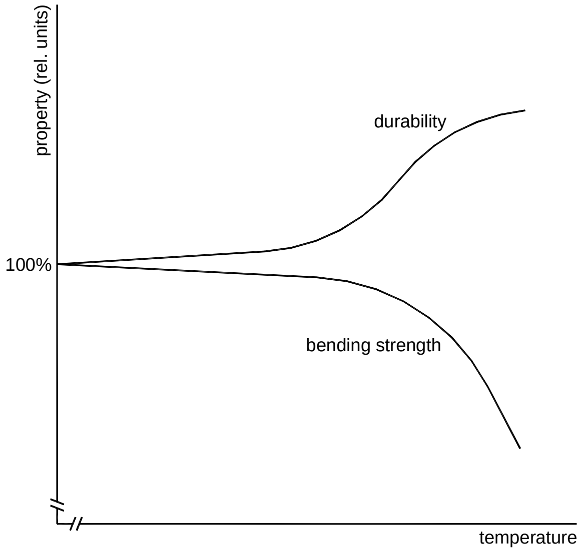

Figure 1. Interdependency of durability and bending strength with thermal treatments.

2.3 Chemical modification process

2.3.1 Background

In many papers the possible methods in chemical modification are described. A good overview is given in papers by Militz *et al* (1997) for solid wood and by Jones (1999) related to fibres.

The main chemical modification systems are esterifications. Esters are formed by reaction of wood with carboxylic acids or acid anhydrides. Ester bonds can be liable to acid or base attack, which leads to hydrolysis. During the esterification of wood with anhydrides the acid within the anhydride is produced as the by-product if an alkylic anhydride is used. A new hydroxyl group is formed when esterification is performed with the use of a cyclic anhydride. This new hydroxyl group can cross link with another hydroxyl group of cell wall polymers in a possible acetalation reaction. An advantage of many acylations with anhydrides is that for most of them no catalyst is required. Several anhydrides have been examined such as propionic and butyric anhydride (Goldstein *et al.* 1961), phthalic anhydride (Popper and Bariska 1975) and maleic anhydride (Matsuda, 1993).

Like many other anhydrides, esterification with acetic anhydride proceeds well even in the absence of catalysts (Rowell *et al.* 1986). Other reagents may in theory produce favourable products, but have difficult processing requirements. The majority of work in this area of esterification deals with acetic anhydride treatments (i.e. acetylation). Acetylation was recognised as a potential method for commercialisation both for solid wood and fibre treatments (Sheen 1992, Beckers et al 1994, Larsson-Brelid *et al* 2000).

There has also been work using other straight chain anhydrides (Hill and Jones 1996, Li *et al* 2000). It has been suggested that the effects of modification are solely a bulking effect (Hill and Jones 1999). Further investigations (Hill *et al* 1998) have indicated that the reaction kinetics obey a diffusion type model, whilst studies on the individual components suggest several concurrent pathways (Ramsden and Blake 1997). Activation energies for the reactions approximate to those of hydrogen bonding, suggesting that the rate-determining step is the breaking of these bonds. Work has not been restricted to wood, as seen by the successful production of acetylated bamboo particleboards (Rowell and Norimoto 1988). The use of cyclic anhydrides avoids the release of by-products, with the formation of a carboxy ester. More recent studies (Hill and Mallon 1998) have shown the reaction of Scots pine (*Pinus sylvestris*) with succinic anhydride and octenyl succinic anhydride.

Most laboratory-based experiments have involved the use of solvents (which is not really suitable for commercial processes), especially those containing heteroatoms, since they offer the benefits of both swelling the substrate, and catalysing the reactions. One way of avoiding the use of solvents is where the reagent acts also as a solvent. The use of acetic anhydride under these conditions has been documented (Rowell *et al* 1986, Rowell *et al* 1991). Other anhydrides studied by this method were maleic anhydride and succinic anhydride (Rowell and Clemons 1992).

Whilst esterification represents the most common form of chemical modification of lignocellulosics, other reactions are also possible. Among the reagents used are isocyanates (Rowell and Ellis 1979, Quinney *et al* 1995) and thio-isocyanates (Kalnins 1982) to form urethanes. In the reaction of wood hydroxyl groups with isocyanate a urethane bond (nitrogen-containing ester) is formed. Unlike mono-isocyanates, a reaction of wood with di- and poly-isocyanates can result in polymerization or self polymerization / bulking. A frequently used isocyanate in fibre technology is 4,4'-diphenylmethane diisocyanate (MDI). Isocyanates swell wood and react with it at 100 to 120 °C without a catalyst or with a mild alkaline catalyst such as triethylamine (TEA). The resulting urethane bond is very stable to acid and base hydrolysis. There are no by-products generated from the chemical reaction of isocyanate with dry wood. Another chemical modification is the formation of ether bonds. During etherification the hydrogen within the hydroxyl group of a cell wall polymer is substituted by an alkyl group. The formation of an ether bond can be the result of an alkylation or epoxidation of the wood. The reaction of wood with epoxides is an example of a polymerizing addition. The chemical used reacts initially with a wood cell wall hydroxyl group and subsequently polymerizes by addition to the new formed hydroxyl group which arises from the epoxide. Several epoxides have been used the past decades for wood modification purposes. They include ethylene oxide (EO), propylene oxide (PO) and butyleneoxide (BO) (Norimoto et al., 1992). Epoxidation takes place at elevated temperature and pressure. Usually the reaction is catalysed under mild basic conditions. In most experiments triethylamine (TEA) is used as a catalyst. N-methylolacrylamide (NMA) has also been mentioned as a special case of ether formation (Goethals & Stevens, 1994).

By addition of an alcohol (hydroxyl group of the wood cell wall polymers) to a carbonyl group of a modifying agent (aldehyde or keton) a half acetal is formed. This half acetal can further react with a second hydroxyl group of the cell wall polymers (cross linking) and an acetal bond is formed. One of the aldehydes used and most frequently reported in literature is formaldehyde (Stevens *et al* 1979). Akitsu *et al.* (1993) used sulfurdioxide as catalyst. Yano and Minato (1993) and Yasuda and Minato (1994) treated wood samples using formaldehyde and SO_2 at 120 °C for 24 hours. Besides formaldehyde other crosslinking chemicals have been used too. They include glyoxal, glutaraldehyde and dimethylol dihydroxyethylene urea (DMDHEU). Besides other catalysts which have been used with DMDHEU are aluminium chloride, citric acid and tartaric acid. Treatments were carried out with aqueous solutions of 10 - 95% at temperatures of 80-175 °C (Militz, 1993).

In general in laboratories world-wide many chemical possibilities have been investigated, however most of them were never brought in the up scaling process. Some of them however (like acetylation and furfurylation) are becoming commercially available now.

As for all modification processes the chemical structure of the lignin, cellulose and hemi-cellulose is altered and consequently, the strength properties are changed. Therefore, the chemical modified wood, which becomes commercially available now, may not be used structurally without further research.

2.3.2 Acetylation

In many chemical modification reactions the hydroxyl groups play the leading role. Esters are formed by the reaction of wood with carboxylic acids or anhydrides. Most studied and reported by dozens of authors is the acetylation of solid wood, wood fibres, chips, veneers etc. with acetic anhydride. In Europe, at Chalmers University (Sweden) efforts are focussing on the use microwave technology for fast heating during the treatment (Larsson and Simonson 1994), while SHR Timber Research (the Netherlands) has developed a method to overcome the problem of the residual by-product acetic acid, a process now coming in the full scaling-up phase (Bongers and Beckers 2003).

From a chemical reaction point of view, acetylation of wood with uncatalysed acetic anhydride is relatively simple. Acetylation processes of wood have been described already in the beginning of the 20th century. Research efforts since the late 80's and in the 90's have led to the scaling up of the acetylation process. The process basically consists of an impregnation step followed by heating up to start the exothermic reaction (at approximately 70 °C). After the reaction the mixture of acetic acid and acetic anhydride is removed from the wood. A post treatment process removes the residual acetic acid (Bongers and Beckers 2003, Homan and Bongers 2004).

Acetylation with uncatalysed acetic anhydride has been studied extensively and has shown to be one of the most promising methods for improvement of technical properties of wood products. During the reaction of the wood with acetic anhydride, hydroxyl groups of the cell wall polymers are converted into acetyl groups. The principle was proven initially at laboratory scale. After some years of work, a pilot plant (2500 litres with 0.6 m^3 wood capacity per batch) was built by Acetyleer Kennis BV (AKBV) in 1999 in the Netherlands. Since the establishment of the pilot plant, SHR Timber Research has conducted several experiments and results indicate good potential for the commercial acetylation of wood.

The construction of a 20000 m^3 full-scale production plant has started. The company that will bring acetylated wood to the market is called Titan Wood. Their aim is to provide an economic acetylation system and a range of products that exceeds the wood industry's expectations in terms of quality and performance. The biological durability class is always in class I at WPG levels of over 20 %, dimensional stabilisation is 75% or more, strength properties are not influenced by the treatment (except a slight increase in hardness), the material is UV-stable and paint tests have shown remarkably good results. Termites do not prefer the material (choice test) but can eat it although not digest it.

2.3.3 Furfurylation

Furfurylation of wood (modification of wood with furfuryl alcohol resin) is known to be an extremely efficient method to obtain wood products with high dimensional stability, high durability and resistance towards alkalis and acids. Furfuryl alcohol is a renewable chemical derived from furfural, produced from hydrolysed biomass waste (e.g. molasses). The acid catalyst reaction chemistry of furfuryl alcohol in wood is very complex. The result is a highly branched and cross-linked furan polymer grafted to wood cell wall polymers.

Furfurylation of wood was no longer commercial since the early 1970s in USA. The Norwegian company Wood Polymer Technologies AS (WPT) developed new processes which have recently become commercial.

Westin *et al* (2003) explained the many ways of polymerisation of this molecule. Important is that the molecule in theory also forms covalent bonds with the lignin.

Wood Polymer Technology (WPT) has made the process industrial. In Lithuania and in Norway the first plants have been built. Further expanding is foreseen by licensing the process. The wood is first impregnated with the treating solution by a full cell process. Then an intermediate drying step is needed and after that the reaction curing-step is carried out. During the curing step the wood is brought to temperatures of 80-140 °C by injection of steam. The curing period is 6-8 h. Finally the wood is dried in a kiln to minimize emissions and to ship dry timber.

The impact strength of the treated wood is strongly reduced, ranging from -25% at 15% WPG (weight percent gain) to -65% at 125% WPG. The stiffness however always increases from 30 to 80%. ASE figures range from 30% to 80% (ASE = Anti Swelling / Shrinkage Efficiency: a measure for the dimensional stabilization of the treated wood). Durability against fungi can be very good (class 1) at high weight gains. High weight gains also lead to insect resistance even for the aggressive Formosan termites. Influence of the treatment on paintability has not been reported.

2.3.4 N-methylol (DMDHEU)

Dimethylol dihydroxyl ethylene urea, better known as DMDHEU is used world wide in textile industry as an anti-wrinkling agent. It can react with hydroxyl groups of lignin and of hemi-cellulose, but it can also form complex polymers with itself (cross linking agent). Krause *et al* (2003) gave an overview of DMDHEU and derivatives and their ability to modify wood. Typical ASE's are in the range of 30 to 40% at 40% WPG. Strength properties are not or hardly influenced by DMDHEU treatments. The attainable durability class was not reported. Although adaptations to conventional wood preservative plants to make them suitable for DMDHEU treatments are relatively easy and cheap, to date no companies are known to prepare commercial introduction of this type of modification.

A problem for the application of DMDHEU in the textile industry is the emission of formaldehyde. The same problem for the use of DMDHEU with wood could be expected. The textile industry therefore developed novel chemicals based on DMDHEU, which release a lower amount of formaldehyde, or are completely formaldehyde free. These chemicals are modified DMDHEU (mDMDHEU) or dihydroxydimethylimidazolidinone (DHDMI). These novel chemicals are now under test to enhance the dimensional stability and reduce the emission of formaldehyde.

2.3.5 Reactive oil treatments

At SHR Timber Research, modification systems have been developed using modified linseed oil as part of EU funded projects (Nurmi 1998, Van Acker 2001). This linseed oil has been altered by an ene-reaction followed by a Diels-Alder-reaction to provide the molecule with a maleic anhydride group. The use of this chemical for wood modification has been patented by DSM Resins (Dekker 2001). The combination of this reactive oil with heat treatments is new. It has lead to high durability, high ASE and no losses in strength in laboratory conditions. At present, the scaling up is being done and the timber treater Foreco in Dalfsen (NL) is the main industrial partner in that project. If the scaling up is successful, the time to market will be relatively short. Any timber treater with a heated autoclave (old creosote equipment) can by means of only slight modifications treat with reactive oils. Consequently, reactive oil treatments have great commercial potential.

2.4 Hydrophobation

Changing the nature of the cell wall from hydrophilic to hydrophobic has been a topic to improve wood quality using several types of natural oils (e.g. tall oils and linseed oil) and synthetic resins (e.g. melamine resins). The last 5 years hydrophobation of wood has gained more interest. It is believed, that hydrophobation helps to reduce the average time that timber is wet under use class 3 exposure conditions.

2.4.1 Organic silicon compounds

The most interesting group of chemicals used for hydrophobation are the organic silicon compounds (silanes, siloxanes, silicons, etc) (Mai *et al* 2003, Ritschkoff *et al* 2003). The potential of silicon-based hydrophobation agents for improvement of wood properties is at the moment evaluated and demonstrated within the new European project “Hydrophob” (full name "Improvement of wood product properties by increased hydrophobicity obtained by the use of silicon compounds"). Some commercial products are tested at present on one of the wooden gantries over Motorway A9 in the Netherlands.

2.4.2 Resin and oil treatments

Recent work performed on the treatment with resins and oils was organised in a European project called “Natural resins as a potential wood protecting agent” (Nurmi 1998). The project studied the whole range of natural based resins and their usability as wood protecting agents. With respect to oil treatments focus was on linseed and hemp oil as water repellent agents. The BFH (Bundesforschungsanstalt für Forst- und Holzwirtschaft) at Hamburg (Sailer *et al* 2000) compared those methods with e.g. melamine resin treatments, described hereafter. Focus on field testing revealed that moisture control can be of major benefit in retarding the onset of decay. It was interesting to notice that the *laboratory assessment* of the anti-swell-efficiency (ASE) revealed low dimensional stability of wood treated with oils, whereas *in the field* oil treated lap-joints (ENV 12037) changed their dimension only to a very small extent and few cracks were detected.

The natural resin project widely covered the evaluation of tall oil resins (TOR) as wood protecting agents. From a huge number of potential candidates a few were chosen to determine the properties of treated wood. Mainly TOR resin and non-volatile solvent ester mixtures were selected. This enabled application methods known as “hot oil” treatments or “Boultonising” techniques. Most resin systems decrease liquid water uptake. However, the ultimate equilibrium moisture content in constant climate room did hardly differ from untreated wood samples.

2.4.3 Melamine treatments

Melamine resins are forming a stiff solid network with themselves. There are many formulations of melamine. The amount of research on modification with melamine is quite high (Lukowsky 1999, Gsöls *et al* 2003, Rosca *et al* 2003, Hansmann *et al* 2003). In general it is reported that in use class 3 conditions (according to European standard EN 335, e.g. exterior joinery) the behavior of melamine treated wood is good. Micro-checks are prevented under normal exposure conditions. The top surface of the wood is much more stable. Durability tests also show good results, mainly depending on the amount of resin used. ASE values up to 40% are reported. There is a distinct industrial interest to start with melamine treatments of wood on a commercial scale.

2.4.4 Hot oil treatment

The treatments described here are not to be compared to creosote treatments.

In France a hot oil treatment of green chestnut has been developed. The process uses relative low temperature (120 °C – 140 °C) and is not regarded as heat treatment in the narrow sense, but merely an improved oil treatment system.

Another oil heat treatment process, developed at CIRAD (Grenier *et al* 2003), can be divided into two phases. The first phase consists of submerging the wood into an oil bath at 160 °C – 200 °C. In the presence of strong heat flows, the material warms up to over 100 °C. The water, which is contained in the cells, evaporates creating an overpressure inside the wood. This vaporization moves from the surface to the centre. There is steam repulsion outside the wood, mostly in the fiber direction. In the second phase, the wood piece is soaked into an oil bath at a temperature lower than the boiling temperature of water, at the pressure in the cold bath. The wood then cools down leading to water condensation. The created low pressure causes oil penetration. The work was performed using groundnut oil for the hot bath as it is resistant to high temperatures and raw linseed raw oil (cold squeezed) for the cold bath.

2.4.5 Royal process

Recently much research effort has gone in the improvement of the Royal treatment (Treu *et al* 2003). In this treatment the curing of wood preservatives is done by hot oil treatments. Since biocides are used in this case it does not come under the given definition of wood modification. Oil and water repellents are well known in different applications. As wood treatments they are beginning to attract more interest for practical applications especially in combination with known wood preservatives. Because of their water repellent effect they can improve the hydrophobicity of surfaces of wood. Therefore they also have a positive effect against leaching of preservative compounds.

Several authors report results from durability tests against micro-organisms on wood samples treated with different natural oils only. Their findings indicate that an oil treatment alone (even at higher retention) does not increase the resistance of non durable wood species like pine and spruce sufficiently for most outside applications, especially related to long term stability.

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

2.5 Conclusions

In the last 5 years the commercialization of thermal wood modification has become a fact. In the Netherlands there are at present some 10 different brands of thermally modified wood available on the market. The present production of thermally modified wood worldwide is estimated to be about 50 000 m^3 per annum and is still growing almost completely used for non-structural hazard class 3 conditions. The conclusion, that thermally modified wood has got a foot on the ground, is therefore justified.

More recently the first chemical modification processes have reached the market or are in the process of coming to the market. In general the diversity of properties that may be reached by chemical modification is much bigger compared to other modification processes. In the laboratory it has been proven that almost any desired property can be improved with chemical modification. This may lead to either wood with superior qualities or to tailor-made products, which potentially lead to the use of wood in areas where it has never been used before. It is expected that the market for chemically modified wood will increase dramatically in the coming 5 years.

Specific wood modification processes designed for the wood based panel sector and probably also for the production of wood plastic composites, will be developed based on the principles of timber modification. Inevitably new options will become commercial in future dealing with properties of the wood component in the composites, but also with improved interaction e.g. by means of grafting processes.

The fact that modified wood now has established its name and is becoming a commercial success is very promising. Firstly because it will enable environmental responsible use of wood, secondly because it helps to preserve our natural resources and thirdly because it promotes the use of one of the most important renewable resources.

3 Variability in degree of modification within wood

3.1. Introduction

In all treatments of wood the variability in the material plays a key role. This variability exists between species, between growing areas, between individual trees but even in wood of the same tree and furthermore on an anatomical and ultrastructural level. In this chapter the treatability of beech and spruce with respect to acetylation are given as an example of this phenomenon.

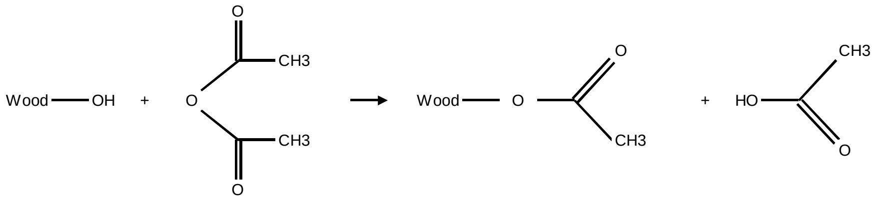

Figure 2. The reaction of wood with acetic anhydride

In order to be acetylated (see reaction equation figure 2), the cell wall material needs to be in intimate contact with the acetylation agent (acetic anhydride). The crucial part of the acetylation process therefore is the impregnation step before actual chemical acetylation process (part of the box "acetylation" in figure 3). The penetration of liquid into the wood is a process that needs to be described at three different levels. At the first level (anatomical level) it is important to get the liquid from the wood surface deeper into the wood. At this level the cell lumina are filled. Also at this level, the treatability of wood comes to expression. In species that close their cell structure, like spruce, liquid penetration is difficult. The second level is the penetration of the liquid from the cell lumina into the cell wall (ultra structural level). Even within the same genus the width of cell wall cavities may differ. This influences the maximum molecule size that can enter the cell wall. At the third level the penetration of the molecules between the cell wall polymers takes place (chemical level). The size and nature of the molecules are a key factor at this level.

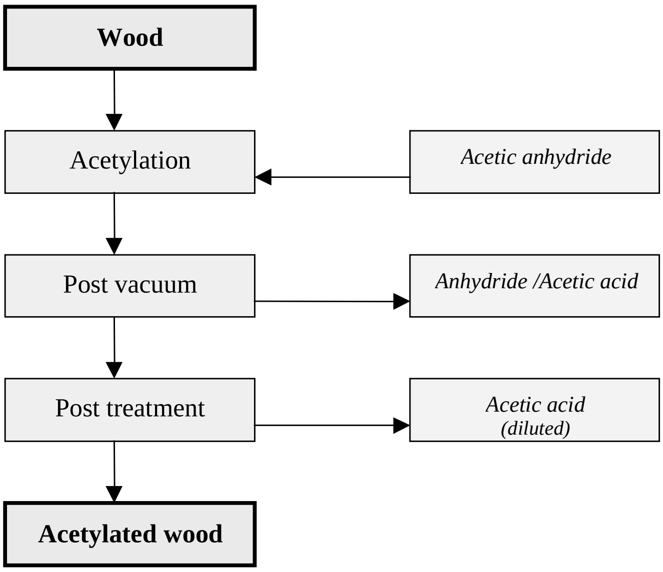

Figure 3. Major steps in the acetylation process

At laboratory scale impregnation with acetic anhydride is a well-known and relatively easy process. Complete impregnation can easily be reached in small samples. In up-scaling, the process, the dimension of the wood and the wood species play an important role. Sharp gradients in acetyl contents in the wood can be the result of poor penetration. Acetylation is swelling the wood, which, if inhomogeneous, results in internal tension and cracking. Treatability of a wood species, as well as the acetylation process are critical. Refractory (difficult to impregnate) wood species, like spruce and Douglas fir, are therefore in general not suited for acetylation if large dimensions are considered. Methods to improve the impregnability of a wood species, such as fungal pre-treatment, oscillating pressure methods and incising (Messner et al., 2003), could be a solution to upgrade the treatability of refractory wood species and allow them to be treated by acetylation. Treatment with gas instead of liquid can be an other, since the diffusion of gases through cell wall material is an order of magnitude faster than that of most liquids. The treatability classification of wood species, as given in the EN 350-2, is mainly based on impregnation of waterborne systems or on creosote oils. In the case of acetylation, acetic anhydride is used, which behaves differently compared to water. But even so, there is a clear need to improve the penetration of the liquid in refractory species.

As part of a research program on how to improve the treatability of wood with respect to acetic anhydride, it was necessary to gain a good impression on the normal permeability of beech and Norway spruce for liquid anhydride. Therefore boards of various thicknesses and lengths of Norway spruce and beech were treated in a number of not optimised acetylation processes.

3.2. Materials and Methods

Boards of Norway spruce (*Picea abies* (L.) Karst) and beech (*Fagus sylvatica* L.) of different sizes (length and thickness) were acetylated in a pilot plant. In order to get good comparison data the impregnation process for this research was kept constant. It consisted of a period of 30 minutes vacuum and a period of 15 minutes at 1,0 MPa pressure. This is, on purpose, not an optimised system. An optimised system relates the impregnation process to the timber species and dimensions. In the first batch samples with various thicknesses have been acetylated (see table 1), and in the second batch the length as well as the thickness of the samples was varied.

Table 1. Batch 1 - Norway spruce and beech (width 120 mm, length 1.2 m) of various thicknesses.

Wood species	**Thickness (mm)**											
	3	**5**	**7**	**9**	**11**	**13**	**15**	**20**	**25**	**30**	**40**	**50**
Norway spruce	x	x	x	x	x	x	x		x[1]			
Beech	x	x	x	x	x	x	x	x	x	x	x	x

[1] the 25-mm board of Norway spruce had the radial face on the largest side, the other samples had the tangential face on the largest side.

Table 2. Batch 2 – Norway spruce and beech of various lengths and thicknesses.

Wood species	**Thickness (mm)**	**Length (mm)**
Norway spruce	27	500, 1500
	40	500, 1500
Beech	27	500, 1500
	60	500, 1500

After the treatment, consisting of impregnation, acetylation reaction, post-vacuum and post-treatment (see figure 2), samples were taken of the boards. The samples have been obtained by using a top router. The shavings were collected in plastic sample bags and then further processed for the analyses. At least two boards per category were sampled in this way and analysed. The analysis method consists of a saponification step followed by High Performance Liquid Chromatography (HPLC) conform SHR Internal Standard Operation Procedure WVS_SHR_056-EN. The method has been published (Beckers et al., 2003). The samples of batch 1 have been taken at various depths in the middle of the board's length. The samples of batch 2 (length experiment) have been analysed over a length gradient by analysing the core of the sample. In this way the gradient in acetyl content was determined both in the direction of the height of the board and in the length of the board.
From the acetyl contents and the depths of the samples gradients have been calculated. The acetyl content as a function of depth is presented in figures 4 – 7, the gradient (i.e. the difference in acetyl content per unit of length) as a function of depth is presented in a graph (fig. 8).

3.3. Results

The acetyl content in the middle of the sample's length at various depths is graphical expressed in figures 4 and 5 for respectively beech and Norway spruce acetylated in batch 1. The values represent the average acetyl content (i.e. relative mass of acetyl groups compared to the total mass of the treated wood) of two boards per category. In figures 6 and 7 the results of batch 2 are plotted. The length of the board is set along the X-axis. A clear effect of the longitudinal penetration can been seen for spruce, and especially in the 40 mm thick samples (figure 7).

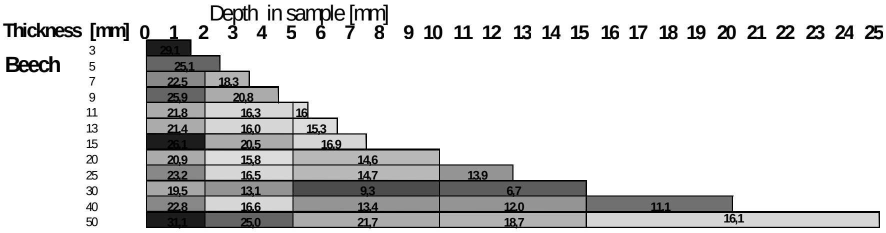

Figure 4. The achieved acetylation content in depth for various wood dimensions of beech acetylated within one batch.

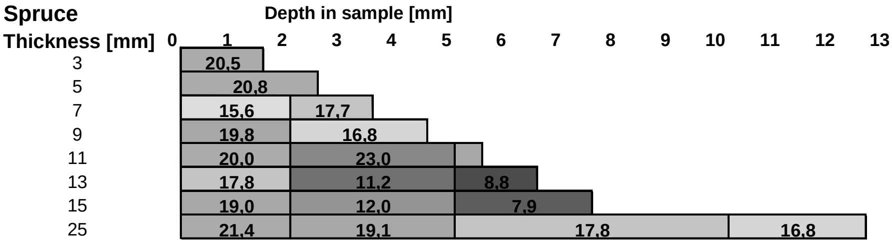

Figure 5. The achieved acetylation content in depth for various wood dimensions (up to 25 mm) of Norway spruce acetylated within one batch.

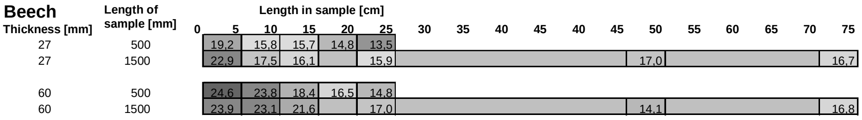

Figure 6. The achieved acetylation content in length for 27 and 60-mm thick and 500 and 1500 mm long beech acetylated within one batch.

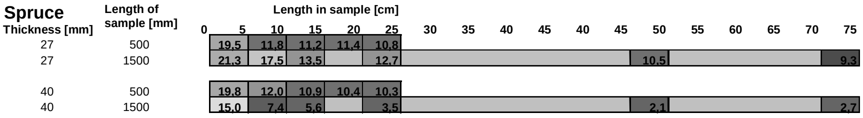

Figure 7. The achieved acetylation content in length for 27 and 40-mm thick and 500 and 1500 mm long Norway spruce acetylated within one batch.

The penetration in depth of acetic anhydride in Norway spruce during the first batch is lower than that in beech. Under the used process conditions, a steep gradient in acetyl content (in depth) is observed for Norway spruce dimensions of 13 mm and up, while sharper gradients in depth are starting at 30 mm for beech.

In the graph (figure 8) the gradient, that is the decline in acetyl content per distance into the wood (in -% / mm), is plotted against the depth of the board.

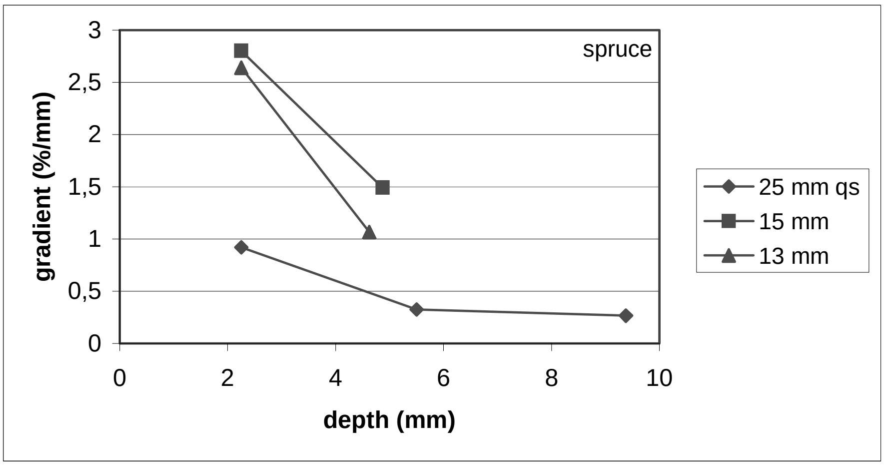

Figure 8. Acetyl gradient as a function of depth in spruce. Remark: The 25 mm sample is quarter sawn (indicated as qs).

In figures 5 and 8 the effect of sawing patron is visible in the 25 mm board of Norway spruce, which was quarter sawn while the other samples are plain sawn.

3.4. Discussion

Known differences in treatability of wood species, related to liquids, also reflect in liquid acetic anhydride impregnation. According to EN 350-2 the treatability of Norway spruce is classified as 3-4 (sapwood 3 variable, 3-4 heartwood), while beech heart- and sapwood are classified as 1 (4 if red-heart is present). Treatability class 1 gives good penetration of the anhydride, treatability class 4 poor. Liquid acetic anhydride seems to penetrate deeper into wood than water. Here even in the core (i.e. heartwood) increased acetyl contents are found, whereas waterborne systems in spruce usually result in an envelope pattern, i.e. only a few mm are penetrated.

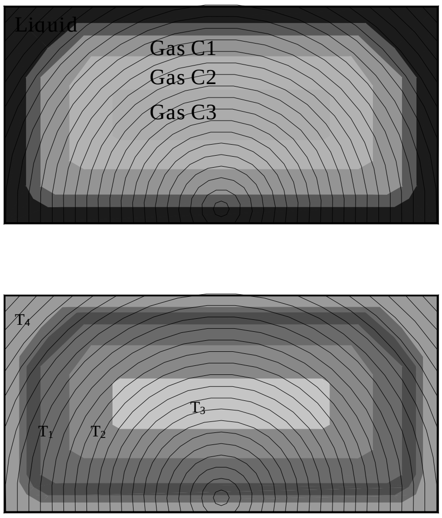

Figure 9. Liquid and gas penetration (upper drawing) and thermal profile (lower drawing) during reaction phase (C1 > C2 > C3 and $T_1 > T_2 > T_3 > T_4$*)*

The main difference with water borne systems is that, probably during the reaction step, acetic anhydride penetrates the cell walls as gas and migrates deeper into the wood structure than the liquid. Even at temperatures below the boiling point of acetic anhydride this occurs. Locally in the wood, because of the exothermic reaction of the hydroxyl groups with the anhydride and the reaction of water with anhydride (also exothermic), the temperature is likely to be well above the boiling point of acetic anhydride (t > 139 °C). This means that locally the pressure of the anhydride gasses, combined with that of the acetic acid that is formed, can be raised and that the anhydride can penetrate the cell walls and adjacent cells as a consequence. There it will react easily with the available hydroxyl groups in the wood, thus, because of the exothermic reaction, even increasing the temperature. Because of the difficult transport of heat through wood this may lead to internal burning if not well controlled. At those places where liquid is present in the wood the heat can be lead away relatively easily. However in the core of the wood where the liquid has not penetrated these burning effects can be seen, if the process is not well adapted to control this phenomenon.

A typical liquid front situation, as known in envelope treatments where only the outer surface is treated, does not appear in acetylated wood. Even in a refractory species like Norway spruce the acetyl content and gradient is not very steep, albeit that in the outer mm’s the gradient is the highest. In a more open species like beech the highest concentrations are still to be found in the outer layers, but even so, the gradient is rather smooth. Consequently, it is very unlikely that tension stresses in the wood, caused by the differences in swelling, will be raised to such an extent, that cracks or distortions will occur. This partly explains the fact that there are only small differences in mechanical properties between treated and untreated wood.

However, the acetyl content in the deeper layers of the spruce is still not at a desirable level. This means that the chosen process conditions are not ideal. Experience with long processes learns that even in spruce of bigger dimensions the wanted acetyl content can be obtained. In order to limit the process times and thus making the processes more economical, acceleration of these processes is wanted. Further optimisation of the acetyl processes is still going on. The focus is on gas diffusion with controlled temperature and on methods to improve the accessibility. Another easily way to overcome treatability problems is to treat wood of small dimensions only and use all sorts of wood engineering techniques to obtain the desired products. For instance, to date it is already very easy and economically viable to make real exterior plywood. In that case the veneer sheets need to be treated before gluing them together. The strongly reduced swelling and shrinkage behaviour of such a product allows leaving away dilations. With a board like that, using a transparent coating, the attractiveness of wood really comes to expression.

3.5. Conclusion

The results show that process conditions and the wood species have a clear influence on the acetyl content gradients to be expected in the wood. The treatability classification of wood species as given in EN 350-2 does not apply when systems other than strictly liquid penetrations are considered. Even the liquid front, with acetylation processes, penetrates deeper than the waterfront with waterborne systems such as many contemporary biocide systems. In spruce the effects of the crosscut sides is limited to the outer 10 cm. In general it is very complicated to separate the crosscut side effect and the lateral effect. Especially with the more open wood species this is a research methodology challenge. With acetylation there is evidence that at least part of the penetration takes place in the gas phase.

When scaling up processes in wood modification, it is important to be able to control the process conditions in such a way that gradients are limited. This is valid for both the impregnation and reaction conditions. Though very different in treatability, both a refractory species like spruce and a very open species like beech, require well-defined and controlled processes. The steering of the process conditions in order to control and limit the temperature in the wood, is the most important challenge here.

References

Akitsu, H., Norimoto, M., Morooka, T. and Rowell, R.M. (1993) Effect of humidity on vibrational properties of chemically modified wood. *Wood and Fiber Science*, **25**(3), 250-260.

Beckers, E.P.J., Militz, H. and Stevens, M. (1994) Resistance of acetylated wood to basidiomycetes, soft rot and blue stain. *International Research Group on Wood Preservation.* Document no. IRG / WP 94-40021.

Bongers, H.P.M. and Beckers, E.P.J. (2003) Mechanical properties of acetylated solid wood treated on pilot plant scale. *Proceedings of the first European Conference on Wood Modification*, Ghent, Belgium, 341-350.

Boonstra, M, Tjeerdsma, B.F. and Groeneveld, H.A.C. (1998) Thermal Modification of Non-Durable Wood Species. 1. The PLATO Technology: Thermal Modification of Wood. *International Research Group on Wood Preservation.* Document no. IRG / WP / 998-40123.

Burmester, A. (1973) Einfluss einer Warme-Druck-Behandlung halbtrockenen Holzes auf seine Formbeständigkeit. *Holz als Roh- und Werkstoff*, **31**, 237-243.

Chanrion, P. and Schreiber, J. (2002) Bois traité par haute température. *Éditions CTBA*. ISBN 2-85684-053-1, 115 pages.

Chen, G. and Rowell, R. (1989) Fungal and termite resistance of wood reacted with periodic acid or sodium periodate. *Wood and Fiber Science,* **21**(2), 163-168.

Dekker, G.H. (2001) European Patent appl. EP 1 174231 A1.

Felby, C., Pedersen, L.S. and Nielsen, B.R. (1997) Enhanced Auto Adhesion of Wood Fibers Using Phenol Oxidases. *Holzforschung,* **51**, 281-286.

Grenier, D., Baillères, H., Méot, J-M., Langbour, P. and Lanvin, J-D. (2003) A study of water loss and oil absorption during oleothermic treatment of wood. *Proceedings of the first European Conference on Wood Modification,* Ghent, Belgium, 23-32.

Goethals, P.; Stevens, M. (1994) Dimensional stability and decay resistance of wood upon modification with some new type chemical reactants. *International Research Group on Wood Preservation*. Document No. IRG / WP / 94-40028.

Goldstein, I.S., Jeroski, E.B., Lund, A.E., Nielson, J.F. and Weaver, J.W. (1961) Acetylation of wood in lumber thickness. *Forest Products Journal,* **11**(8), 363-370.

Gsöls, I., Rätzsch, M. and Ladner, C. (2003) Interactions between wood and melamine resins - effect on dimensional stability properties and fungal attack. *Proceedings of the first European Conference on Wood Modification*, Ghent, Belgium, 221-225.

Hansmann, C., Gindl, W., Zargar-Yaghubi, F. and Wimmer, R. (2003) Melamine modification of acetylated spruce wood. *Proceedings of the first European Conference on Wood Modification,* Ghent, Belgium, 365-369.

Hill, C.A.S., Hale, M. and Forster, S.C. (2004) Investigations of the role of cell wall moisture content and micropore blocking in the decay protection mechanism of anhydride modified wood. Presentation given at the *Final Conference of COST Action E22*, Estoril, Portugal.

Hill, C.A.S. and Jones, D. (1996) The Dimensional stabilisation of Corsican pine sapwood by reaction with carboxylic acid anhydrides. *Holzforschung,* **50**(5), 457-462.

Hill, C.A.S and Jones, D. (1999) Dimensional changes in Corsican pine sapwood due to chemical modification with linear chain anhydrides. *Holzforschung*, **53**(3), 267-271.

Hill, C.A.S., Jones, D., Strickland, G. and Cetin, N.S. (1998) Kinetic and Mechanistic Aspects of the Acetylation of Wood. *Holzforschung,* **52**(6), 623-629.

Hill, C.A.S. and Mallon, S. (1998) The Chemical Modification of Scots Pine with Succinic Anhydride or Octenyl Succinic Anhydride. I. Dimensional Stabilisation. *Holzforschung,* **52**, 427-433.

Homan, W.J. and Bongers, H.P.M. (2004) Influence of up-scaling processes on degree and gradient of acetylation in spruce and beech. Presentation given at the *Final Conference of COST Action E22*, Estoril, Portugal.

Jamsa, S. and Viitaniemi, P. (2001). Heat treatment of wood - Better durability without chemicals. Review on heat treatments of wood, *Proceedings of the special seminar of COST Action E22,* Antibes, France.

Jones, D. (1999). Recent Advances in Treatments of Wood and Plant Fibres: Chemical, Pressurised Thermal and Steam Treatments. Technical University of Denmark*, Publication I-23, ISBN 87-7740-258-8*, pp41

Jones, D. (2001) The potential for modified materials in the panel products industry – a thematic network approach. *Proceedings of the fifth panel products symposium*, Llandudno, Wales, U.K., 184-197.

Jones, D., Stromdahl, K., Hoffmeyer, P., Folting, P., Fischer, G. and Bjerring Olesen, A. (1999) The Hygrothermal Treatment of Natural Fibres: Part 1-Spruce. *Proc. Eur. Panel Prod. Symp. 3*, 54-65.

Kalnins, M.A. (1982). Chemical modification of wood for improved decay resistance. *Wood Science*, **15**(2), 81-89.

Krause, A., Jones, D., van der Zee, M. and Militz, H. (2003) Interlace treatment – wood modification with n-methylol compounds. *Proceedings of the first European Conference on Wood Modification*, Ghent, Belgium, 317-327.

Larsson, P. and Simonson, R. (1994) A study of strength, hardness and deformation of acetylated Scandinavian softwood. *Holz als Roh- und Werkstoff*, **52**, 83-86.

Larsson-Brelid, P., Simonson, R., Bergman, O. and Nilsson, T. (2000) Resistance of acetylated wood to biological degradation. *Holz als Roh- und Werkstoff*, **58**, 331-337.

Li, J.-Z., Furuno, T., Katoh, S. and Uehara, T. (2000). Chemical Modification of Wood by Anhydrides without Solvents or Catalysts. *J. Wood Science*, **46**, 215-221.

Lukowsky, D. (1999) Holzschutz mit Melaminharzen, Dissertation. University of Hamburg.

Mai, C., Donath, S. and Militz, H. (2003) Modification of wood with silicon compounds. *Proceedings of the first European Conference on Wood Modification*, Ghent, Belgium, 239-251.

Matsuda, H. (1993) Preparation and properties of oligoesterified wood blocks based on anhydride and epoxide. *Wood Science and Technology*, **27**, 23-34.

Militz, H. (1993) Treatment of timber with water soluble dimethylol resins to improve their dimensional stability and durability. *Wood Science and Technology,* **27**, 347-355.

Militz, H. (2002) Heat treatment technologies in Europe: scientific background and technological state-of-art. *International Research Group on Wood Preservation*. Document No. IRG / WP 02-40241.

Militz, H., Beckers, E.P.J. and Homan, W.J. (1997) Modification of solid wood: research and practical potential. *International Research Group on Wood Preservation*, Document No. IRG / WP 97-40098.

Militz, H. and Tjeerdsma, B. (2001) Heat treatment of wood by the PLATO-process. Review on heat treatments of wood, *Proceedings of the special seminar of COST Action E22*, Antibes, France.

Norimoto, M., Gril, J. and Rowell, R.M. (1992) Rheological properties of chemically modified wood: relationship between dimensional and creep stability. *Wood and Fiber Science,* **24**(1), 25-35.

Nurmi, A. (1998) EU research project FAIR CT95-0089: Natural Resins as a Potential Wood Protecting Agent. 1995- 1998.

Popper, R. and Bariska, M. (1975) Die Azylierung des Holzes - Dritte Mitteilung: Quellungs- und Schwindungseigenschaften. *Holz als Roh- und Werkstoff,* **33**, 415-419.

Quinney, R.F., Banks, W.B. and Lawther, J.M. (1995) The activation of wood fiber for thermoplastic coupling, the reaction of wood with a potential coupling agent. *J. Wood Chem. Technol*, **15**(4), 529-544.

Ramsden, M.J. and Blake, F.S.R. (1997) A Kinetic Study of the Acetylation of Cellulose, Hemicellulose and Lignin Components of Wood. *Wood Science and Technology*, **3**(1), 45-50.

Rapp, A.O. (2001) Review on heat treatments of wood, *Proceedings of the special seminar of COST Action E22,* Antibes, France.

Rapp, A. (2001) Review on heat treatments of wood. *Proceedings of Special Seminar*, Antibes, France, COST Action E22 ‘Environmental optimization of wood protection’, 65 pages.

Rapp, A. O. and Sailer, M. (2001) Oil heat treatment of wood in Germany - State of the art. In: Review on heat treatments of wood, *Proceedings of the special seminar of COST Action E22*, Antibes, France.

Ritschkoff, A.-C., Mahlberg, R., Suomi-Lindberg, L., Viikari, L. and Nurmi, A. (2003) Properties of Wood Treated with Hydrophobisation Agents. Poster presentation. *Proceedings of the first European Conference on Wood Modification*, Ghent, Belgium, 267-271.

Rosca, I., Gsöls, I., Rätzsch, M. and Schmidt, H. (2003) Short duration impregnation of wood with melamine resins. Poster presentation. *Proceedings of the first European Conference on Wood Modification*, Ghent, Belgium, 273-277.

Rowell, R.M. and Ellis, W.D. (1979) Chemical Modification of Wood: Reaction of Methyl isocyanate with Southern Pine. *Wood Science*, **12**(1), 52-58.

Rowell, R.M. and Norimoto, M. (1988) Dimensional Stability of Bamboo Particleboards made from Acetylated Particles. *Mokuzai Gakkaishi*, **34**(7), 627-629.

Rowell, R.M., Simonson, R. and Tillman, A.M. (1991) A Process for Improving Dimensional Stability and Biological Resistance of Lignocellulosic Materials. Eur. Patent EN 021352 B1.

Rowell, R.M., Tillman, A.M. and Simonson, R. (1986) Vapor phase acetylation of southern pine, douglas-fir and aspen wood flakes. *J. Wood Chem. Technol*, **6**(3), 427-448.

Ruyter, H.P. (1989) European patent Appl. No. 89-203170.9.

Sailer, M., Rapp, A.O., Leithoff, H. and Peek, R.-D. (2000) Vergütung von Holz durch Anwerdung einer Öl-Hitzebehandlung (Upgrading of Wood by Application of an Oil-Heat Treatment). *Holz als Roh-und Werkstoff*, **58**(1), 15-22.

Sheen, A.D. (1992) The preparation of acetylated wood fibre on a commercial scale. *FRI Bulletin* **176**, 1-8.

Stevens, M. (1985) Restrictions on the use of chlorosilanes as wood preservatives. *International Research group on Wood Preservation*. Document No. IRG / WP / 3345.

Stevens, M., Schalk, J. and Van Raemdonck, J. (1979) Chemical modification of wood by vapour-phase treatment with formaldehyde and sulphur dioxide. *Int J. Wood Preservation*, **1**(2), 57-68.

Syrjanen, T. (2001) Production and classification of heat treated wood in Finland. In: Review on heat treatments of wood, *Proceedings of the special seminar of COST Action E22*, Antibes, France.

Tjeerdsma, B.F., Stevens, M. and Militz, H. (2000) Durability aspects of (hydro)thermal treated wood. *International Research Group on Wood Preservation*, Doc. No. IRG / WP 00-40160.

Treu, A., Habicht, J., Klaucke, R. and Militz, H. (2003) Improvement of wood properties by combined impregnation process - the Royal Process. *Proceedings of the first European Conference on Wood Modification*, Ghent, Belgium, 3-13.

Van Acker, J. (2001) EU research project FAIR CT97-3187: Process Development and Technological Evaluation of Final Products Based on New Methods for Chemical Modification of Solid Wood. 1997-2001.

Van Acker, J. (2002) The way forward: testing and specifying wood protective systems. Presentation given at the Workshop of COST Action E22, Reinbek, Germany.

Van Acker, J. (2003) Assessing performance potential of modified wood focusing on dimensional stability and biological durability In: *Proceedings of the first European Conference on Wood Modification*, Ghent, Belgium, 2003

Van Acker, J. and Hill, C.A.S. (2003) *Proceedings of the first European Conference on Wood Modification*, Ghent, Belgium, EUR 20639, ISBN 9080656526. 414 p.

Van Acker, J., Nurmi, A., Tomkinson, J., Van der Werf, B., Van der Zee, M. and Westin, M. (2003) Scaling up some new chemical modification systems. *Proceedings of the first European Conference on Wood Modification*, Ghent, Belgium. 329-340.

Vernois, M. (2001) Heat treatment of wood in France - State of the art. In: Review on heat treatments of wood, *Proceedings of the special seminar of COST Action E22*, Antibes, France.

Vernois, M. (2004) Menz Holz: une première unité industrielle de traitement oléothermique. *CTBA Info,* **104**, 25-27.

Westin, M., Lande, S. and Schneider, M. (2003) Furfurylation of wood -Process, properties and commercial production. *Proceedings of the first European Conference on Wood Modification,* Ghent, Belgium, 289-306.

Yano, H., Minato, K. (1993) Controlling the timbre of wooden musical instruments by chemical modification. *Wood Science and Technology,* **27**, 287- 293.

Yasuda, R., Minato, K. (1994) Chemical modification of wood by nonformaldehyde cross-linking reagents - Part 1. Improvement of dimensional stability and acoustic properties. *Wood Science and technology,* **28**, 101-110.

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