Structural and other properties of modified wood

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ABSTRACT

Wood is not under all circumstances an appropriate building material. Beside others, structural properties and biological durability determine the limits for the use of wood. Until recently, the only industrial applied method to improve the durability of wood was impregnating with toxic wood preservatives. Although much progress has been made in improving the fixation of preservatives (i.e. emissions during use are very low), the general public regards them as environmentally unfriendly.

Modification of wood aims at improving the durability in an environment friendly way, not by toxifying but by altering the substrate. Apart from durability, properties like dimensional stability, hardness, UV-resistance and adsorption behaviour are improved by modification. These improvements make wood an appropriate material in much more applications than untreated wood.

In this paper two modification methods are discussed:

- Acetylation of wood, a chemical modification process, which recently resulted in the completion of a seem-industrial pilot plant.
- The development of timber modified with the so-called Plato process, a hydro-thermal method, which recently resulted in the construction of a commercial plant.

Besides the increase of durability, the reduced shrinkage and swelling and the increase of UV-resistance, the mechanical properties are also affected by modification treatments. This is also discussed in this paper.

THE PRINCIPLE OF WOOD MODIFICATION

The polymeric structure of a wooden cell wall mainly consists of cellulose, hemicellulose and lignin. All of these components contain hydroxyl groups. These hydroxyl groups play a key role in the interaction between water and wood. At the same time these groups are the most reactive sites. If wood takes up water (in moist conditions) water molecules are settling between the wood polymers forming hydrogen bonds between the hydroxyl groups and individual water molecules. This water needs space between the cell wall components, which results in swelling of the wood.

All possible types of wood treatments affect the above-described mechanisms in one way or another. For instance, filling lumina, which a substance, without altering the cell walls. Or, bulking the cell wall, where the cavities in the cell wall are filled and thereby the pathways for water are blocked. An example of bulking is a treatment with resins that do hardly react with the wood. Since hardly any molecular alteration of the wood is achieved, bulking is not regarded as being wood modification.

Modification of wood is a wood treatment, where the cell wall polymers of the molecular structure of the cell wall polymers (cellulose, hemicellulose and lignin) are altered.

In thermal wood modification (parts of) the cell wall polymers are altered. This may lead to cross-linking, reduction of OH-groups and/or (undesired) cleavage of the chains. The reduction of accessible OH-groups leads to a limited interaction with water compared to untreated wood. Examples of thermal treatments are the Perdure process, the Stellac process and the Plato process.

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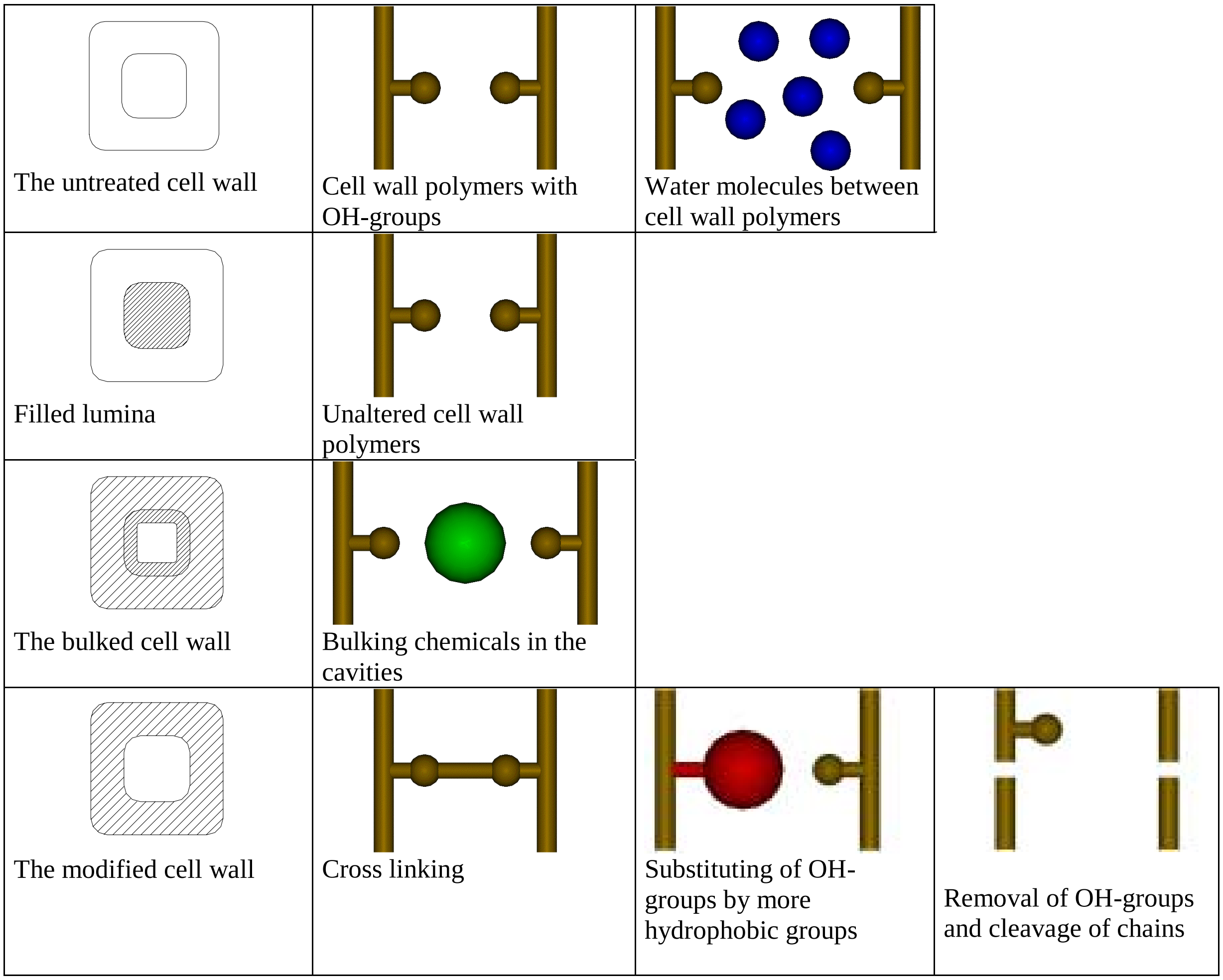
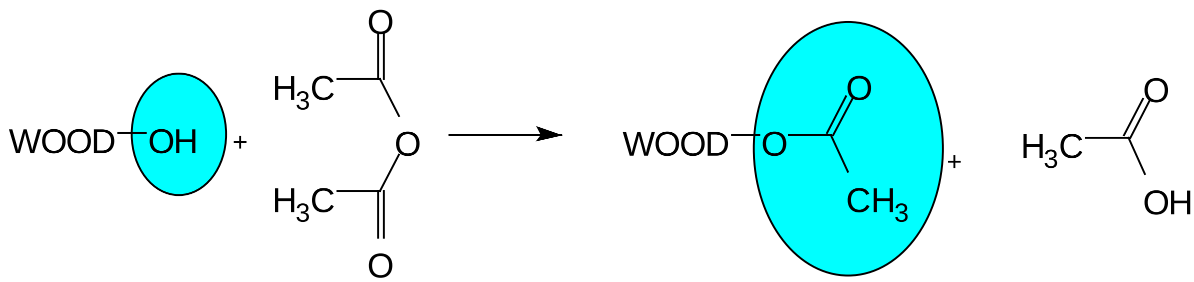


Figure 1: Different wood treatments.

In chemical modification, more hydrophobic chemical groups replace the OH-groups. This can be done by: etherification, esterification, urethanes, oxidation, silylation and many more chemical reactions. An overview of possibilities is given by Militz, Beckers and Homan (1997). An example of these types of treatments is the acetylation of wood.

ACETYLATION

Wood itself by nature already contains some minor amounts of acetyl groups, which is increased by acetylation. Off all chemical treatments, acetylation with uncatalysed acetic anhydride has been studied most and shown to be one of the most promising methods. Acetylation is a well-known technique in many industrial and scientific areas. It is widely used in textile fabrication and filters of cigarettes are made of acetylated cellulose. During the reaction of wood with acetic anhydride hydroxyl groups of the cell wall polymers are converted into acetyl groups (see figure 2) which are hydrophobic. Thus the molecules of wood are altered. During acetylation acetic acid is formed as a by-product which can be converted into acetic anhydride and be used again. Because small hydroxyl groups are substituted with larger acetyl groups, the wood will remain in a permanently swollen state and become heavier. The effect of the treatment can therefore be expressed as a weight percent gain (WPG). A higher WPG represents a higher degree of acetylation. Like untreated timber, acetylated wood only consists of carbon, hydrogen and oxygen and, consequently, disposal of acetylated waste wood can be handled as untreated wood.



Wood + acetic anhydride → acetylated wood + acetic acid

Figure 2: Acetylation: replacing OH-groups by larger and heavier CH_3-groups

<u>Material properties of acetylated wood</u>

Research has shown that acetylation of wood can considerably improve certain properties of this material.

- If wood is acetylated well enough it will have a durability comparable to durability class 1: it does not rot at all in ground contact for more than 25 years (comparable to teak or even better). A WPG of 15% is sufficient to prevent degradation of wood by white rot and brown rot fungi such as the dry rot fungus and the cellar fungus. Acetylated wood with a WPG of 10% is fully protected against soft rot degradation, which plays an important role for wood in ground contact.
- Due to acetylation the equilibrium moisture content of wood becomes very low. And the wood will stay very dry. If acetylated up to 20% WPG the wood moisture content will never exceed 10%. Furthermore it takes the acetylated wood a considerable longer time to reach this equilibrium compared to the untreated wood.
- After acetylation swelling and shrinkage of wood can be reduced by up to 80%. The swelling and shrinking of wood is directly related to the moisture content of the cell wall. Pine sapwood with a 20% degree of acetylation will swell less than 3% tangential from oven dry to fibre saturation point.

  Figure 3 shows the hygroscopicity, which is strongly correlated to the shrinkage and swelling, of acetylated wood (and thermally treated wood) compared to untreated wood.

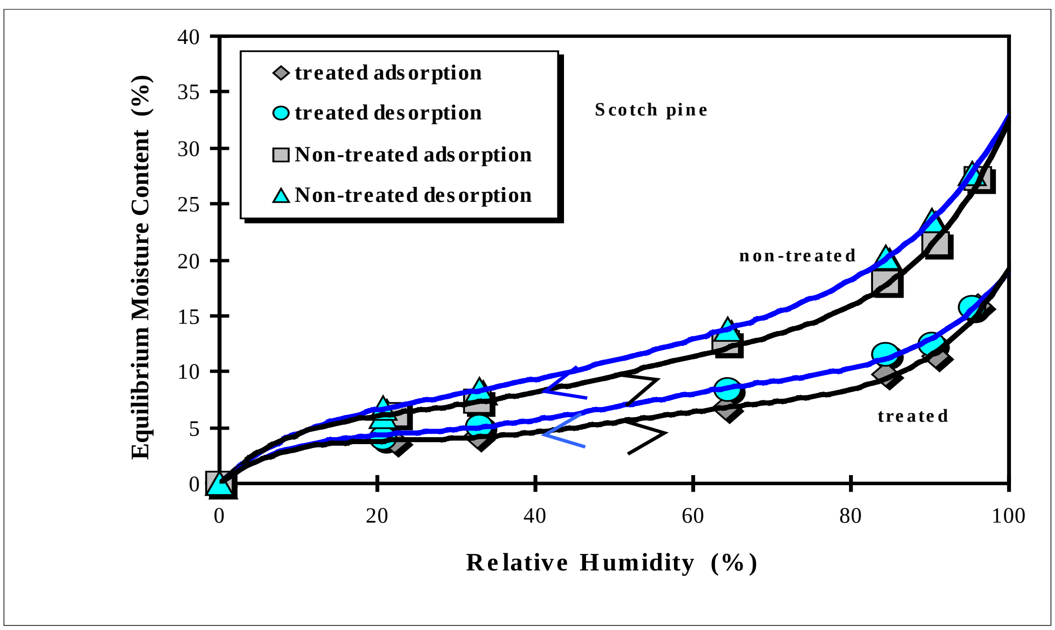


Figure 3: Hygroscopicity of treated (chemically or thermally) and untreated Scotch pine.

The hygroscopicity can be reduced to less than 50% of the untreated wood.

- Since the shrinkage and swelling is small, paint on acetylated wood will stay good for a very long time and not require extensive maintenance. The acetylation has made the wood dimensionally stable and as a result, stresses are low on the paint film, which, consequently, will stay longer intact. This has been shown both in accelerated and outdoor weathering tests.
- Acetylation of wood cell wall polymers protects them against UV-degradation. UV radiation causes darkening of untreated wood. Acetylated wood retains its original colour, which, in combining with the dimensional stability of acetylated wood, gives good opportunities for transparent paints, such as varnishes and stains. Accelerated and outdoor weathering tests pointed out these possibilities.
- Acetylation improves acoustical and di-electric properties of wood as shown by the production of two violins, a piano board and a xylophone.
- Dried wood is technically not necessary for chemical modification according to the acetylation process. However, the more water in the wood, the more acetic anhydride is needed to bond the water and to form hydrophobic groups, which replace the water bonded OH-groups. Consequently, the acetylation process is more expensive for wet (green) than for dry wood.

<u>Mechanical properties of acetylated wood</u>
Mechanical properties of wood are influenced in various ways by acetylation. Research by Dreher (1964) showed that the compressing strength increased by 6-36% and hardness increased by 22-31%. Bending strength and E-modulus in bending were not influenced while shear strength was slightly reduced (Akitsu et al., 1993; Goldstein et al., 1961; Dreher et al., 1964; Larsson and Tillman, 1989; Militz, 1991; Rowell, 1991). Hillis (1984) found that bending strength and hardness of Scots pine increased by 15-20%, which still was the case after a long term exposure to high relative humidity. This in contrast to untreated pine of which the mechanical properties decrease when exposed to high relative humidity.

Changes in mechanical properties due to acetylation can have various causes. The moisture content of the wood influences mechanical properties. At the same relative air humidity, acetylation results in a lower wood moisture content compared to untreated wood. Furthermore, the wood density influences the mechanical properties. Due to acetylation wood swells because of added acetyl groups, while weight is increased to a higher percentage and, consequently, the density increases.

Swelling also results in lesser lignocellulosic fibres per cross section, which has a negative effect on mechanical properties, mainly on the shear strength. For E-modulus the positive and negative effects seem to keep each other in balance (lower moisture content and higher density (+), lesser fibres per volume (-)). For compression strength and hardness the positive effects overrule the negative ones and they are slightly improved. More research is carried out at the SHR Timber Research Laboratory to determine effects of acetylation on mechanical properties of wood.

<u>State of the art of chemical modified wood</u>
Many laboratories around the world have performed research into acetylation of wood and other lignocellulosic materials. Earliest reports date back to 1936. The research on wood modification has intensified in the last 10-15 years due to a change in views towards the use of tropical hardwood and timber treated with toxic preservatives. In the Netherlands a pilot plant for acetylation of solid wood has been constructed and is operational since 1999. Preparations for industrial production of acetylated wood are made and the first industrial plant is expected to run at the end of 2001.

THERMALLY TREATED WOOD

Ever since the early part of this century numerous thermal treatment processes of wood have been investigated and developed. Heat-treatment of wood has been known for long as an effective method to modify the properties of wood (Runkel and Witt, 1953; Seborg et. al., 1953; Stamm, 1956; Kollmann and Schneider, 1963; Kollmann and Fengel, 1965; Hillis, 1984). The main effect obtained by a heat-treatment of wood is a reduced wood hygroscopicity. Foremost advantages of wood treated in this manner are its increased resistance to different types of biodegradation and its improved dimensional stability. Many methods of thermal modification of wood have been reported in the literature (Seborg et. al., 1953; Burmester, 1973, 1975; Burmester and Wille, 1976; Giebeler, 1983). Yet undesired side effects, in particular loss of strength and increased brittleness of the treated wood, have prevented a commercial utilisation of thermal modification so far (Runkel and Witt 1953. Davids and Thompson (1964) have reported a reduction in toughness after different heat-treatments. Giebeler (1983) found a reduction of the modulus of rupture of wood of 20 % to 50 % after thermal treatment at 180 °C to 200 °C.

Recent efforts on thermal treatment of wood have lead to the development of Thermowood (Stellac) in Finland (Viitaniemi *et al.* 1994), Torrefaction (Perdure) in France (Weiland and Guyonnet 1997) and Plato wood in the Netherlands. The process for Plato wood is different from the other processes. Three steps can be defined for the process to obtain Plato wood, which is different from the other thermal treatments where usually one treatment step under relatively dry conditions is used. In the proces for Platowood a hydrothermolysis (heating of the wood under wet conditions) is combined with a dry curing step (heating of the altered wood). The typical difference of the Plato-process to known thermal treatment processes is the appearance of the hydrothermolysis. The impact of the thermolysis in the Plato treatment results in the occurrence of many other chemical transformations. The presence of abundant water in the thermolysis results in increased reactivity of the wood components under low temperature. In order to reach a specific degree of depolymerisation of the lignin and the hemicellulolose, relative mild conditions can be applied and the unwanted side reactions, which influence the mechanical properties of wood negatively, can be minimised.

<u>An example of thermally treated wood: the Plato process</u>

The Plato process principally consists of three steps:

1. Hydro thermal treatment (hydro thermolysis)
2. Drying
3. Curing (heating of the altered wood)

In the first step of the process, green or air dried wood is hydro thermally treated at a temperature between 160 °C - 190 °C under increased pressure (6-8 bar). The second step is a conventional wood drying process, in which the treated wood is dried to a low moisture content (ca. 10%). The third step is the curing step, in which the dry intermediate product is heated again to temperatures typically between 170 °C - 190 °C.

<u>Modification principle of Plato process</u>

The Plato process consists of three succeeding steps in which the cell wall material is modified. Step one is a hydrothermal phase, which is characterised by a partial depolymerisation of the cell wall components. In principle, transformations of the chemical wood structure are caused by autocatalytic reactions of the cell wall constituents. The wood cell wall primarily is composed by the three polymeric components cellulose, hemicellulose and lignin. It is known that during a thermal treatment of wood, carbonic acids, mainly acetic acid, will be formed as a result of cleavage of the acetyl groups of particular hemicelluloses (Kollmann and Fengel 1965; Dietrich et al. 1978; Bourgois and Guyonnet 1988). Depending on acid concentration and applied temperature, hemicellulose, as the most reactive wood component, will be hydrolysed into oligomeric and monomeric structures. The monomeric sugar units, subsequently will be dehydrated to aldehydes, of which furfural is being formed out of pentoses and hydroxymethylfurfural out of dehydration of hexose sugar units. Lignin is the least reactive wood component, but at high temperatures, bonds within the lignin complex will be cleaved resulting in a higher concentration of phenolic groups. Since in this first step the wood is heated under wet conditions, it is not necessary to start with dried wood.

The second step is a conventional wood drying process, in which most of the water will be removed in order to facilitate the reactions during the third step. The third step is dominated by curing reactions where reaction products are (re)condensed into a modified polymeric complex.

<u>Material properties of thermally treated wood</u>

It is known that thermal treatment of wood improves several important properties of wood (Tjeerdsma et al. 1998, Boonstra et al. 1998 etc.). Although the classification “thermal treatment” suggests one general type of treatment, miscellaneous thermal treatments result in various different chemical transformations. The investigated properties of thermal treated wood have been found stongly dependant on the applied process and process conditions. However, regardless of the applied process, hygroscopicity, dimensional stability and durability will be improved substantially.

A thermal treatment always results in darkening of the wood. Plato treated wood has a light brown colour, but still retains the appearance of natural wood. Tjeerdsma published about research carried out on Plato wood (Tjeerdsm*a et al*. 1998) and found that the hygroscopicity of the wood decreases and the durability increases substantially after treatment. An average improvement in hygroscopicty of 40% has been found. The dimensional stability showed a strong correlation with the hygroscopicity resulting in a Anti Shrinking Efficiency (ASE) average of 40 %. The resistance against brownrot fungi was improved, but also a considerable improvement of the resistance against white and softrot was found.

Mechanical properties of thermally treated wood

Thermally treated wood shows a decrease in mechanical properties. Thermally treated wood according to the Plato process showed an average loss in bending strength varying from 5% to 18% depending on the applied process conditions, which is considerably better than the strength reductions due to other thermal treatments.

Davids and Thompson (1964) have reported a reduction in toughness after different heat-treatments. Giebeler (1983) found a reduction in bending strength of 20 % to 50 % after thermal treatment at 180 °C to 200 °C. The much smaller reduction found in tests on Plato wood is believed to be caused by the relative mild conditions (time - temperature) applied in the Plato process compared to other thermal treatment methods.

Another typical result of thermal treatment of wood is the increase of the modulus of elasticity. For thermally treated wood the brittleness is much higher than for untreated wood or acetylated wood.

State of the art of thermal`ly treated wood

In the Netherlands a production plant, which will start up in 2000, is presently under construction, arranged to treat initial 50.000 m^3 according to the Plato process. The initial aim for applications will be on claddings, garden fences and furniture, poles and sheds, but also in canal linings, jetties etc.

SUMMARY AND CONCLUSIONS

In this paper the development of modified wood according to chemical- and thermal processes were introduced. Both processes are rather old and were already discussed in the nineteen thirties. However, since modified wood was not commercially available it was never regarded as an engineering material. This might change, because several processes were commercialised (Thermowood, Stellac, in Finland and Torrefaction, Perdure, in France, being thermal treatments) or are about to be commercialised (Plato, which is a thermal treatment and Acytelated wood, being a chemical treatment, both in the Netherlands).

Wood mainly consists out of cellulose, hemicellulose and lignin. Both thermal and chemical modification treatments result in a hydrophobic hemicellulose and lignin, which protect the cellulose. During thermal modification treatments wood is cleaved into components, which are chemically glued together in a polymeric structure. During chemical modification treatments hydroxyl groups are replaced by hydrophobic groups.

Properties of softwood, e.g. spruce and pine, like durability (resistance agaunst fungi), hygroscopicity and, consequently, the dimension stability, and UV-resistance improve considerably by modification. Therefore, modified wood can be applied in hazardous conditions where untreated wood rots.

The mechanical properties also change. Compared to untreated wood, thermally modified wood shows on average lower strength values, while the failure mode for tension and bending is very brittle. The strength seems to be higher for thermally modified wood according to the Plato process than for wood treated according to other thermal processes. The failure modes of acetylated wood are comparable to the failure modes of untreated wood.

Further research is presently carried out in orther to provide values for mechanical properties on a characteristic level.

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