

## Properties of thermally modified wood

All the properties described are based on the results of a range of tests, conducted over a period of several years by VTT, the Helsinki University of Technology and the University of Helsinki. Several scientific papers have been published about chemical changes in heat-treated wood as part of their joint project entitled 'Reaction Mechanisms of Modified Wood' during 1998–2001. In addition, Risto Kotilainen from the University of Jyväskylä has written a dissertation called 'Chemical Changes in Wood during Heating at 150–260 °C'. The properties described should be used as a guide only and are subject to variation due to the natural differences between timber pieces.

Understanding the numerous changes that take place in the physical and chemical structure of wood during the heating process requires a good basic knowledge of its chemical composition, structure, and physical properties.

The main components of wood (cellulose, hemicelluloses, and lignin) degrade in different ways under heat. Cellulose and lignin degrade more slowly and at higher temperatures than the hemicelluloses. The extractives in the wood degrade more easily, and these compounds evaporate from the wood during the heat treatment.

### Carbohydrates

Cellulose and hemicelluloses are carbohydrates that are structural components in wood. Cellulose constitutes 40–50% and hemicelluloses 25–35% of wood. Cellulose is a long chain (DP 5000–10000) made up of units of glucose, while hemicelluloses are shorter chains (DP 150–200) made up of various mono-saccharides. The composition and contents of hemicelluloses vary from one wood species to another. During the heat treatment, both groups undergo changes, but the majority of the changes occur in hemicelluloses with high oxygen content.

Cellulose components,  $\beta$ -D-glycopyranoses, are joined by (1 $\rightarrow$ 4)-glycoside bonds. Cellulose chains are joined by bonds between hydroxyl groups. At temperatures under 300°C, the degree of polymerization in cellulose decomposition decreases; water is eliminated; and free radicals, carbonyl, carboxyl, and hydro-peroxide groups, as well as carbon monoxide, carbon dioxide, and reactive wood charcoal, are generated. The components of the hemicelluloses include D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, and small amounts of L-rhamnose, 4-O-methyl-D-glucuronic acid, and D-galacturonic acid. They are joined by (1 $\rightarrow$ 4) - or (1 $\rightarrow$ 6)-bonds. As wood is heated, acetic acid is formed from acetylated hemicelluloses by hydrolysis. The released acid serves as a catalyst in the hydrolysis of hemicelluloses to soluble sugars. In addition, the acetic acid that has formed depolymerises the cellulose microfibrils in the amorphous area. The acid hydrolyses the bonds joining the units of glucose, breaking cellulose into shorter chains.

After the heat treatment, the wood contains a substantially lower amount of hemicelluloses. As a result of this, the amount of fungi susceptible material is significantly lower, providing one reason for heat-treated woods improved resistance to fungal decay compared with normal kiln dried wood. With the degrading of the hemicelluloses, the

concentration of water-absorbing hydroxyl groups decreases and the dimensional stability of treated wood is also improved compared to normal kiln dried wood. The decomposition temperature of the hemicelluloses is about 200–260 °C, and the corresponding temperature for cellulose is about 240–350 °C. Since the amount of hemicelluloses in hardwood species is higher than in softwood species, degrading is also easier in hardwoods than softwoods. However, the breaking of a hemicellulose chain does not reduce as much the strength of the wood as breaking of cellulose chains would do. Instead, breaking of a hemicellulose chain improves the pressability of wood and reduces the generation of stresses and resilience of wood.

### **Lignin**

Lignin holds the wood cells together. The dark matter of wood cells' middle lamellae is mainly lignin. It is also found at the primary and secondary cell walls. Lignin constitutes 25–30% and 20–25% of softwoods and hardwoods, respectively. The precise chemical structure of lignin has not yet been determined, but its precursors - i.e., components - have been known for decades. Lignin is primarily composed of these phenylpropane units, which are typically joined by ether- and carbon-carbon bonds (DP 10–50). Softwoods contain mainly guaiacyl units of phenylpropane, and hardwoods contain almost equal amount of guaiacyl and syringyl units of phenylpropane. Both contain minor amounts of p-hydroxyl phenylpropane. During the heat treatment, bonds between phenylpropane units are partly broken. Aryl ether bonds between syringyl units break more easily than bonds between guaiacyl units. Thermochemical reactions are more common for allylic side chains than aryl-alkyl ether bonds. The longer the autohydrolysis time is, the more condensation reactions occur. Products of condensation reaction include  $\beta$ -ketone groups and conjugated carboxylic acid groups.

Of all wood's constituents, lignin has the best ability to withstand heat. Lignin's mass starts to decrease only when the temperature exceeds 200 °C; when the  $\beta$ -aryl ether bonds start to break. At high temperatures, lignin's methoxy content decreases and some of lignin's non-condensed units are transformed into diphenylmethane-type units. Accordingly, diphenylmethane-type condensation is the most typical reaction at the 120–220 °C temperature range. This reaction has a significant effect on lignin's properties in heat treatment, such as its color, reactivity, and dissolution.

### **Extractives**

Wood contains minor amounts of small-molecule constituents. Extractives constitute less than 5% of wood. This group includes, for example, terpenes, fats, waxes, and phenoles. Extractives are of heterogenic nature in various wood species, and the number of compounds is very high. Extractives are not structural components in wood, and most of the compounds evaporate easily during the heat treatment.

### **Toxicity**

The ecotoxicity of the leachates of heat-treated spruce has been tested at CTBA (an EU project - Upgrading of non-durable wood species by appropriate pyrolysis thermal treatment, 1998). The tests were carried out on leachates obtained after an EN 84 test. This test is applied to evaluate the fixation of the biocides in wood cells. Small specimens were

leached with water, and the water was tested according to NF-EN ISO 506341 against *Daphnia magna* (small freshwater shellfish) and micro toxicity tests on marine luminescent bacteria. The test results showed that leachates do not contain toxic substances for *Daphnia magna* and are harmless to bacteria.

## **Physical changes**

### **Density**

Density is determined by measuring the weight and the dimensions of the sample. Thermally modified wood has a lower density than untreated wood. This is mainly due to the changes of the sample mass during the treatment when wood loses its weight. Density decreases as higher treatment temperatures are used. However, deviation is high and the coefficient of determination is low, due to natural variation in wood density.

### **Strength**

The strength of wood has a strong correlation with density. Thermally modified wood has slightly lower density after the treatment. However, the weight-to-strength ratio can remain practically unchanged. The strength of wood is also highly dependent on the moisture content and its relative level below the grain saturation point. Thermally modified wood can benefit due to its lower equilibrium moisture content. Substantial strength is lost at temperatures over 220 °C.

### **Equilibrium moisture content**

Heat treatment of wood reduces the equilibrium moisture content. Comparisons have been made of heat-treated wood with normal untreated wood at various levels of relative humidity. Heat treatment clearly reduces the equilibrium moisture content of wood, and at high temperatures (220 °C) the equilibrium moisture content is about half that of untreated wood. The difference in wood moisture values is higher when the relative humidity is higher.

### **Swelling and shrinkage due to moisture**

Heat treatment significantly reduces the tangential and radial swelling. The effect of heat treatment in terms of reduced swelling and shrinkage of wood was clearly shown in relation to cupping of the final product. According to VTT tests, heat-treated wood both with and without a coating maintained its form but CCA-treated and untreated wood were affected by cupping. Unlike timber in general, heat-treated wood does not feature drying stress. This is a clear advantage, seen when, for example, splitting the material and manufacturing carpentry products. In addition, the wood's swelling and shrinkage is very low.

### **Permeability**

The water permeability of heat-treated wood has been tested by CTBA, examining end grain penetration. Samples were dipped in demineralised water and then kept in a room with a relative humidity of 65% and a temperature of 20 °C. The samples were periodically weighed over a period of 9 days. The conclusion was that during a short period

the water permeability of heat-treated spruce was 20–30 per cent lower than that of normal kiln dried spruce.

### **Biological durability**

VTT carried out three tests to determine the biological durability of heat-treated timber. The test fungi were *Coniophora puteana* and *Poria placentia* regarded as the most common and problematic fungi. The results revealed a remarkable ability of the heat-treated wood to resist decay by brown rot. Against the two fungi, the heat-treated wood showed varying results. The heat-treated wood required a higher treatment temperature in order to gain maximum resistance against *Poria placentia* compared to resistance against *Coniophora puteana*). The biological resistance test in accordance with EN 113 revealed very good durability depending on the treatment temperature and time. In order to treat the wood to meet the class 1 (very durable) requirements, temperatures of over 220 °C for 3 hours are required, and to gain class 2 (durable) status, the desired result is achieved at about 210 °C. Based on the results, it is **recommended that thermally modified wood not be used in deep ground applications where structural performance is required**. It is assumed that the indicated loss of strength is due to moisture and not caused by any micro-organism.

### **Resistance to insects**

Tests were carried out by the CTBA in France. Longhorn beetles are found in sapwood of softwoods. The common furniture beetle (*Anobium punctatum*) attacks hardwoods in particular. *Lyctus Bruneus* is found in some hardwood species. The tests showed that thermally modified wood was resistant to all three of the above insects. Tests made at the University of Kuopio also prove that thermally modified wood has good resistance against longhorn beetles. The test report concludes that beetles recognize pine from its terpene emissions to be a suitable place for egg laying. Because terpene emissions from thermally modified wood are drastically reduced in comparison to normal wood, it is expected that beetles will choose normal wood over thermally modified wood, whenever possible. According to the report, the same phenomena can apply also to termites. However, more testing is needed in this area.

Concerning termites, the problem is currently more apparent in Southern hemisphere locations, but termites have already spread through France and cases have also been reported in countries further north in Europe. Termites attack buildings from the earth below, avoiding direct sunlight whenever possible. Termites will attack both wood and concrete-based materials in their quest for nutrition. Various measures have been developed to control the problem; these include polythene membranes being installed in the foundations of the building. Also, various bituminous paint products are available to seal possible routes up the building. So far, the test results indicate that thermally modified wood is not resistant to termites. However, local tests are recommended since termite types vary from one region to another. In addition, more research into termite attack is needed.

## **Weather resistance**

### **Weather resistance without surface treatment**

#### **Rain**

Various field tests have been carried out to study the performance of thermally modified wood against natural weathering. Material that had been treated at 225 °C for 6 hours had about half the moisture content of untreated wood; this difference remained after five years' exposure. Surface mould growth can appear on due to bacteria in the air or dirt carried in the rain. As with all materials exposed to the natural environment, Fungi can grow on the untreated surface. However, this is on the surface only and can be removed by wiping or scraping.

#### **Sun**

Field tests have been conducted to measure thermally modified wood's resistance to the effect of sunlight (ultraviolet radiation). As with most natural materials, thermally modified wood is unable to resist UV radiation. As a result, the color changes over a period of time from the original brown appearance to a grey weathered color when exposed to direct sunlight. The original color can be preserved with pigmented or UV-protective preservatives. Although moisture content and swelling and shrinkage due to moisture are greatly reduced, the ultraviolet radiation causes small surface shakes to occur on uncoated panels when exposed. It can be easily concluded from the effects of sunlight (ultraviolet radiation) that, with the application of surface treatments containing pigment thermally modified wood performs to a good level with respect to surface shakes. Surface treatment is therefore highly recommended.

### **Weather resistance of surface-treated thermally modified wood**

Field testing with five years' outdoor exposure was carried out by VTT to study the performance of coatings on the surface of thermally modified wood and to compare it with untreated wood. It was found that the moisture content of thermally modified wood was about half that of untreated wood. The unpigmented or low-build stains and oils protected neither thermally modified wood nor untreated wood. These coatings wore away and annual rings started to loosen just as in the panels without coating. The panels coated with low-build stains showed a strong tendency to crack.

The effect of the thermally modified wood substrate on the joinery paint performance was observed after five years of exposure. The acid-curable and water-borne acrylic paint had better performance on the heat-treated panels than on the untreated panels. The panels coated with these paints showed no flaking on the thermally modified wood substrate.

The exterior wall paints performed well on both thermally modified wood and an untreated substrate, and no significant effects could be found. The results indicated that the best coating systems for thermally modified wood consisted of the priming oil and solvent-based alkyd or water-based acrylic topcoat.