REVIEW

The Effects of Preservatives on the Properties of Wood after Modification (*Review paper*)

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Abstract

Wood is a material that is widely used in many applications but it has some weak properties which can be modified with various solutions. The aim of this study is to examine how preservatives affect wood properties. The effects of preservatives are classified into five categories: mechanical properties, weathering, moisture resistance, biological durability and fire resistance. The different properties have been studied at varying intensity in wood science: for example, moisture resistance and biological durability have been studied quite a lot, while weathering is a rather new issue. Preservatives have a minor effect on wood, depending on the solution, treatment, and wood species. However, generally preservatives cannot cause dramatic changes to the properties of wood, whereas the moisture content has a great effect on the characteristic of wood. In addition to the properties of wood and the weight percentage gained after modification, the crucial properties of modifiers are for example the pH value and the comparison between water- and oil-based solutions.

Key words: wood, modification, property, preservative

Introduction

Wood is porous and hydroscopic material with some weaknesses, such as decay resistance, and swelling by water. The weaknesses can be reduced by modifying the properties of wood by utilizing some substances or methods. The structure of all kinds of wood is made up mainly of cellulose, hemicelluloses, lignin and extraneous chemicals, which are collectively known as extractives (Walker 2006). Wood modification refers to method of improvement of one or more of the disadvantages of wood, which can be performed for example chemically, by heat-treatment, or by impregnation. Hill (2006, p. 20) defines the aim of wood modification as follows *"applies to the application of a process that alters the properties of the material such that during the lifetime of a product no loss of the enhanced performance of the wood should occur"*. The modification of wood is not a totally new invention, as references indicating an interest in wood modification can be found far back in history. Early references to wood modification are when Noah built an ark or when the Vikings burned their ships. Noah used the wood which he knew to be resistant to decay while the Vikings burnt the outsides of their ships to make them water and flame resistant (Rowell 2006). It must also be possible to use wood in technical wood products after modification, such as particle board, plywood, or wood-plastic composites (WPC).

Chemical modification refers to treatment where a reagent reacts on within the wood cell wall component. The reactions may also be formed by filling the cell lumens with resins or chemicals (Hon and Shiraishi 2001). Most of examinations of chemical wood modification concentrate on substitutive reactions with hydroxyl (OH) groups (Rowell 2005). The chemical reaction may form a single chemical bond with a singular OH group or a cross-link between multiple OH groups changing the chemical character of the cell wall polymers (Hill 2006). Rowell (2005) states, that the most desirable reaction is the reaction between a single reagent molecule and a single hydroxyl group. Cross-linking, where more than one reactive groups of the reagent react with a hydroxyl group, may cause brittleness in the wood (Rowell 2005).

Impregnation refers to methods where the wood substance is filled with an inert material, in other words, with material or solution incapable of making chemical bonds with other materials. Also the optimal solution should have to be non-leaching after the treatment and in service conditions. For the outcome to be most successful, the molecular size of the solution should be small enough to enter the wood cell wall interior. In addition, the cell walls must be in a swollen condition to ensure the access of the solution. The method can be executed by impregnating the wood with monomers or oligomers, following polymerization within the cell wall. It is also possible to impregnate wood with a diffusion of a soluble material and use subsequent treatment to immobilize the solution (Hill 2006). Increased pressure and sufficient treatment time are commonly utilized in wood impregnation, to achieve better uptake and a more even result. The best known impregnation methods are those of Bethell, Lowry and Rueping (*Rüping*), among others. The Bethell method is also known as full cell treatment, in which an initial vacuum is the first step in the process. The vacuum is maintained for at least fifteen minutes, after which the solution is absorbed into the wood by using pressure. The Bethell method ends in a final vacuum which lasts a few minutes. The Lowry method is known as the empty cell treatment, where the aim is to achieve maximum penetration simultaneously with a low net retention of the solution. The Lowry method does not have an initial vacuum, but otherwise it is similar to the Bethell method. The Rueping method is also an empty cell treatment like the Lowry method, but it has a lower initial pressure. The oscillating pressure method exploits repeated applications of high pressure and vacuum to force the preservative into green wood. Green wood can also be impregnated by utilizing the Boulton method where wood is treated with an oil preservative under vacuum. The Boulton method is a suitable alternative for wood species that are especially susceptible to collapsing at high temperatures (Archer and Lebow 2006). Wood impregnation has been done by various techniques on a small scale, in addition to the above-mentioned methods (Freeman et al. 2003). Larnoy et al. (2005) state that the uptake of the preservative after impregnation depends on the pressure, time, preservative, and wood species. The uptake of the preservative is better in the longitudinal direction than in the radial or tangential directions, due to the longitudinal positions of the wood cells. The penetration during impregnation increases with increasing pressure and time. Low viscosity of the preservative will increase the penetration into wood. According to Hill (2006), the molecular diameter of the solution should be less than 0.68 nanometers (nm) to ensure full access into the cell walls. At the same time, the solution should have good ability to form hydrogen bonds. It is possible to use carrier liquids which will swell the wood cells to a greater extent than the solution would do solely. This provides a path of better access for the solution because at the same time with the cell itself the swelling applies to the micropores of the cell wall. It is also important to reserve enough time for the solution molecules to diffuse into the spaces between the cell walls. It often takes days, even weeks to reach sufficient results. Pressure treatment will improve the penetration into cells but will not help the cell wall penetration because it is purely a diffusion-type process.

In this article, the properties of wood modification are examined, especially those properties which have been in view in recent years. It is examined what a modifier can make to wood and how it can influence the wood properties. The wood properties are discussed in the following sections:

- effects on mechanical properties are presented in the first section;
- weathering and especially color changes are presented in the second section;
- the third section concerns the effects of treated wood after water immersion, and it concentrates on thickness swelling, water absorption, and dimensional stability;
- the fourth section discusses the effects of decay; and
- the fifth section presents the fire resistance properties of wood.

The conclusions of the study are presented in the last section. The aim of the study is to find out which properties need more attention and more research.

Mechanical properties

Various mechanical properties can be examined simultaneously. The most commonly studied mechanical property of wood is the modulus of rupture (MOR). The modulus of elasticity (MOE) has been studied almost as often as the MOR, because the MOE can be often performed simultaneously with the MOR. Other mechanical properties which have been examined often are the hardness, tensile strength, impact strength, and compression strength. Epmeier and Kliger (2005) have also studied creeping and some researchers have studied the internal bonds of wood panels like Papadopoulos and Traboulay (2000), Wan and Kim (2007), and Pedieu et al. (2012). In addition to these, there are some relatively new mechanical test methods like the one by Avramidis et al. (2011), who performed a peel-test after plasma treatment. Tondi et al. (2012) point out that attention should be paid to the bonding potential of treated wood. There are many standards which are suitable for the measurement of mechanical properties. This study is not focused on the standards of comparison.

The modulus of rupture, in other words, bending strength is usually tested with a three-point or a four-point flexural test. The test is usually performed by applying a load to the center of a specimen supported at two points. The modulus of rupture reflects the maximum load carrying capacity in bending (Kretschmann 2010). It is very common that the bending strength does not change significantly after the treatment of wood. The change in the bending strength may be neutral after treatment as Dieste et al. (2008) have noted. They impregnated veneers with a solution of dimethylol dihydroxy ethylene urea (DMDHEU) and did not observe significant reduction in the bending strength. Also Rowell et al. (2008) and Esteves et al. (2011) have observed an almost neutral effect on the bending strength after treatments. Rowell et al. (2008) modified wood by acetylation, and Esteves et al. (2011) by furfurylation. However, some treatments may improve bending strength. For example, Deka and Saikia (2000) tested the strength property of softwood with thermosetting resins and found that the bending strength was increased with the increasing chemical content. Devi et al. (2003) have also observed that the moduli of rupture values were increased by treatment with styrene and in the combination of styrene with a cross-linked glycidyl methacrylate. Impregnation with urea-formaldehyde prepolymer by a pulse-dipping machine increased the bending strength significantly (Wu et al. 2010), as did impregnation with synthesis of methylourea performed by the same method (Wu et al. 2012). Some treatments decrease the bending strength. Impregnation of beech (*Fagus orientalis L.*) and pine (*Pinus sylvetris L.*) with aqueous solutions of borates decreases the MOR value according to Simsek et al. (2010). Wood particle impregnation with the mimosa bark extracts also decreases the MOR value (Nemli et al. 2004), and the MOR value of pine wood and strands impregnated by butanetetracarboxylic acid decreases (Wan and Kim 2007). The treatment of WPC raw material has not been found to improve its bending strength, but a decreasing effect has been noted. This kind of decreasing effect has been found in acetylated (Ibach et al. 2007, Segerholm et al. 2012) and chemically modified WPC raw material with benzene diazonium salt and alkylene epoxides (Pandey et al. 2010, Islam et al. 2012).

The modulus of elasticity (MOE) or Young's modulus refers to bending stiffness. The MOE value is usually determined with at the same time and the same way as the MOR value. The MOE implies the momentary maximum force whereof deformations will return after the load is removed (Kretschmann 2010). The treatment of wood with tannin resin can increase its elasticity due to effective penetration, according to Tondi et al. (2012). The treatment of wood should be done with restraint, taking the solution into account. Too heavy treatment decreases elasticity, as shown in the research of Umemura et al. (2012), where wood was impregnated with citric acid. In general, the treatment of wood does not cause significant changes to elasticity according to the literature reviewed for this study. For example, the elasticity of acetylation (Rowell et al. 2008), impregnation of DMDHEU (Dieste et al. 2008), and furfyrylation (Esteves et al. 2011) have stayed unaffected after treatment. The treatment of WPC raw material causes slight changes to elasticity (Farsi 2010, Segerholm et al. 2012).

There are a few methods to perform measurements of hardness, for example, Brinell, Janka, and Shore-D. Nowadays the Brinell hardness method is widely used to measure hardness (Rautkari 2012). In general, hardness has increased regardless of which treatment has been used. In a study of Papadopoulos and Tountziarakis (2011), hardness increased slightly after acetylation, but it may have been due to lower moisture content rather than the effect of acetylation. According to Esteves et al. (2011), furfurylation increases hardness very significantly, as can be seen in Table 1. Epmeier et al. (2004) report even more significant results, where the hardness of furfurylated wood increased by 100%. The hardness of furfyrylation depends on the weight percentage gain (WPG). Esteves et al. (2011) have impregnated wood with 38% WPG, while the better results of Epmeier et al. (2004) were produced by 92% WPG. According to Hansmann et al. (2006), melamine treatment increased hardness significantly, and a different type of resin and different method could improve hardness as well. There were minor differences between the radial and tangential surface, but not substantial.

Compressive strength and tensile strength can be measured parallel to the wood grain or perpendicular to the wood grain. Parallel to the wood grain is the most frequently used method. The results of compression resistance depend on the preservative, treatment, and wood species. Aqueous solutions decrease compressive strength with increasing concentration, according to Simsek et al. (2010). The treatment of fir

Table 1. Hardness of untreated and furfurylated sapwood according to ISO 3350 standard. (Esteves et al. 2011)

Sample		Hardness (N)	
		Radial	*Tangential*
Untreated	*Average*	4505	4363
	Std. Dev.	322	668
Treated	*Average*	7013	6534
	Std. Dev.	416	454

(*Abies alba* Mill) with citric acid improved compression strength after curing, but compression strength stayed unchanged after microwave treatment, according to a study of Sefc et al. (2012). Tondi et al. (2012) have impregnated pine (*Pinus sylvetris* L.) and beech (*Fagus sylvatica* L.) wood with a tannin-boron solution. They noted that the compression resistance of pine increased by 30% due to impregnation with a 10% tannin solution and the compression resistance of beech also increased by 15% with a 20% tannin solution. The tensile strength is a frequently measured property of WPC. The treatment of wood fiber or wood flour with chemicals increases tensile strength in WPC products (Farsi 2010, Gwon et al. 2010). The increased tensile strength may be attributed to the chain structure that has developed a double bond in the structure of the WPC (Gwon et al. 2010). The better tensile strength of WPC may also be attributed to the improvement of the bonding strength between the wood flour and the plastic matrix (Farsi 2010).

Some properties have received a little attention, e.g. the internal bond, which is an important property of treated strand boards, like particle boards and oriented strand boards (OSB). The behavior of the internal bond is not congruent in every treatment. Hence, there are results where the internal bond decreases (Papadopoulos and Traboulay 2000, Wan and Kim 2007) and results where the internal bond increases with increasing solution (Pedieu et al. 2012). Impact strength and bending creep are also relatively rarely studied properties. Epmeier and Kliger (2005) have determined the creep deformation and relative creep with various methods after acetylation, melamine treatment, and heat treatment. They noticed that all modifications reduced the relative creep. The impact strength has decreased with a number of wood treatment methods (Ibach 2010). The study of Nurmi et al. (2010) reveals that fire-retardant treatment decreases the strength of wood. Nurmi et al. have investigated fire retardant -treated timber, on the basis of information from their own investigations and studies of the USDA Forest Service in the last decades (LeVan and Collet 1989, LeVan et al. 1990, Winandy et al. 1991, Wang et al. 2005, Laufenberg et al. 2006). The fire retardants have been said to reduce the strength of wood between 10 to 20% immediately after treatment. The problem has been assessed to be due to the fact that elevated temperatures activate the fire retardants prematurely. The power of the reaction to fire depends on the pH value of the preservative and the temperature of the environment, especially a low pH value of the used chemicals will cause a decrease of strength. Nurmi et al. (ibid.) state that the critical pH value of wood is 4.2 after impregnation, and if the pH of impregnated wood is over 4.2, there is no reason to suspect loss of strength in the practical structure.

Improved mechanical properties may be due to increased density (Wu et al. 2010), but the bulked volumes of treated specimens have also remained the same after curing (Deka and Saikia 2000). Rautkari (2012) states that the hardness of wood depends on the density and the thickness relation between the surface and the core. Devi et al. (2003) note that increased mechanical properties may be attributed to cross-linking a solution with wood. The cross-linking of a solution with wood has provided better interaction between the preservative and the wood. Treatment with waterborne solutions has reduced the mechanical properties compared to treatment by an oil-type solution, because treatment by aqueous solutions increases the rate of hydrolysis in the wood, thereby causing a loss of strength. Also metallic oxides will react with the cell wall components by undergoing hydrolytic reduction upon contact with wood sugars, which oxidizes the wood cell wall components and may reduce the strength of wood. This method is also known as fixation (Simsek et al. 2010). According to Nemli et al. (2004), the curing rate of formaldehyde-based resins influences the mechanical properties in further processing in for example particle board production. If the curing rate is low, pre-curing takes place, and in particle board production the precured resin bonds break-down when the pressing device closes. The curing rate depends on the pH of the environment in which the curing takes place (Nemli et al. 2004). Further processing can also influence the mechanical properties after treatment, like Wan and Kim (2007) indicate in their study. The mechanical properties also depend on the wood properties (Islam et al. 2012). Reduced impact strength indicates that the modified wood is more fragile. This might be due to cross-linking between the cell wall and the chemical, which has decreased the mobility between the cell wall components (Dieste et al. 2008).

Weathering

The term weathering describes the outdoor degradation of materials. The degradation of wood depends on moisture, temperature change, freeze-thaw cycles, abrasion by windblown particles, growth of micro-organisms, and especially ultraviolet radiation from sunlight. Weathering will impact the wood components in a different way. Carbohydrates (cellulose and hemicelluloses) are resistant to ultraviolet degradation, but they absorb and desorb moisture, which causes dimensional changes. Lignin is very sensitive to ultraviolet radiation and it begins to degrade within a few hours. Extractives change color in ultraviolet radiation. (Williams 2010)

Parts of a weathering test are among others discoloration, fungal staining, cracking, and deformation. Dimensional stability can be a part of weathering, but it is presented in the next section. One of the most typical weathering tests is color measurement with a spectrophotometer. Color measurement is performed before and after the test which calculates color differences. On the basis of the results of color differences it is possible to make conclusions of how efficiently wood can be protected against weathering. The CIE-L*a*b* is a general color measurement method where the three values (L, a, and b) describe coloration in the color space. The properties of untreated wood will affect the color change, for example high extractive contents and high density may appear as lower discoloration (Oltean et al. 2008). Lignin absorbs more light, resulting in more degradation than other wood polymers (Hon and Shiraishi 2001). This shows that lignin and ultraviolet radiation have a big role in weathering properties.

The weathering properties can be tested with a natural or artificial weathering test. It is not unusual that both tests are done in the same study, as in the study of Donath et al. (2007). A number of studies have been done to test the weathering of more than one treatment, and reliable and comparable results have been obtained this way. A weathering test takes a long time compared to measuring the other properties, and especially a natural weathering test will take time. For instance, Adamopoulos et al. (2011) have tested DMDHEU-treated wood outdoors for over six years. However, a lot has not been published about weathering tests, and the available articles are quite recent. This shows that the interest in weathering features has increased recently. Additionally, the commercially successful treatment methods exhibit good color permanence. This can be observed in the study of Temiz et al. (2006), where acetylated and heat-treated wood had a clearly lower color change value than that of silicon-treated wood. Acetylation and heat treatment have been successfully commercialized, in contrast to silicon.

Xiao et al. (2012) treated chemically pine sapwood with glutaraldehyde. They found fewer cracks on the surface of chemically modified boards, due to lower moisture content. Pandey et al. (2010) investigated also chemical modification of wood with epoxides and noted that a chemical can inhibit lignin degradation to some extent. Also Chang and Chang (2006), together with Prakash and Mahadevan (2008) noted that esterification improved the photostability of wood. Respectively, silicone cannot protect lignin from degradation, although silicone compounds did not leach during a weathering test (Ghosh et al. 2009). Siloxane-treated pine sapwood resembles untreated pine sapwood according to a study of Pfeffer et al. (2012), where DMDHEU and water glass -treated pine could reduce the change of color slightly. On the basis of the study of Pfeffer et al. (ibid), it can be concluded that the predominant change in color occurs in the beginning of the test. Wax and melamine have also used to protect wood against weathering. Lesar et al. (2011) have studied wax treatment of wood by three different waxes. Waxes can protect wood from photodegradation to a certain extent, and therefore Lesar et al. recommend improving performance for example by heating wax-treated wood above the melting point of wax. Hansmann et al. (2006) have examined melamine-treated solid wood with an artificial weathering test. They observed that melamine may protect solid wood against weathering, and its natural appearance did not change. Melamine protects lignin and it also retards the leaching of degradation products.

Wood panels are also interesting products for weathering tests. The edges of panels are vulnerable to absorption of water (Williams 2010). Trinh et al. (2012) have investigated plywood and De Vetter et al. (2011) have investigated OSB, medium density fibreboard (MDF) and plywood together with solid wood. Treatment with organosilicons caused negative results in the study of De Vetter et al. (ibid.) because OSB and MDF increased the moisture uptake of the edges. Trinh et al. (2012) treated veneers by two formulations based on N-methylol-melamine. They got better properties by treatment compared to the control veneers. The modification of veneers is necessary because plywood is vulnerable to moisture changes due to the adhesive bonding between the veneer layers. Although N-methylol-melamine has improved the properties of veneer, it may cause problems during drying and curing, resulting in homogenous distribution of resin, which might cause additional stress leading to crack formation (Trinh et al. 2012). The changes in the structure of wood after modification and weathering can be analyzed microscopically, for example, with FTIR-spectroscopy. The chemical modification of wood reduces photodegradation best. The chemical modification of wood inhibits lignin degradation to some extent (Pandey et al. 2010). For example, as a result of esterification, more stable groups in the structure of wood are formed (Prakash and Mahadevan 2008).

Moisture resistance

Wood has a tendency to reach equilibrium in moisture content with the relative humidity of the surrounding air. Controlled moisture content will reduce the dimensional changes of wood, swelling or shrinkage (Bergman 2010). Wood shrinks or swells tangentially about half as much as radially, and longitudinally the changes of dimensions are slight (Glass and Zelinka 2010). Water resistance properties can be measured by values like anti-swelling efficiency or anti-shrink efficiency (ASE), thickness swelling (TS), linear expansion (LE), weight gain (WG), resistance of water absorption (RWA), and water-repellent effectiveness (WRE). The most common indicator of moisture properties are TS and ASE. Thickness swelling means the relative growth of piece dimensions before and after testing. Thickness swelling is usually determined by immersing the test pieces in water. Anti-swelling efficiency is the opposite of thickness swelling, and it means the ability of a piece to resist swelling, where a higher ASE value means better dimensional stability. This part of the article focuses on the water resistance of wood, including among other things dimensional stability, thickness swelling and water absorption.

The best known modification methods have a good ability to resist moisture. Acetylation reduces the hygroscopicity of the wood material. The dimensional stability of acetylated wood depends on the weight gain percentage, where a higher level of acetylation decreases the saturation point of wood fiber (Rowell et al. 2008). Acetylation blocks the OH groups in wood, which causes better dimension stability. A similar conclusion can be reached also with wood modified with anhydride reagents (Hill 2006). Buchelt et al. (2012) note that the dimensional stability of furfurylated wood depends on the concentration of furfuryl alcohol. Also the weight gain percentage influences the dimensional stability. The anti-swelling efficiency of furfurylated wood increased with the increasing WPG (Lande et al. 2004). Esteves et al. (2011) have measured anti-swelling efficiency within various relative humidities. Anti-swelling efficiency was higher in the tangential direction than in the radial direction, due to wood anisotropy. Unlike in former studies, WPG had no importance in the study of Esteves et al. (ibid).

Chemical modification of wood is an efficient way to improve dimensional stability. This has been concluded in various studies with several chemicals, for instance various anhydrides (Li et al. 2000), styrene and its combination with glycidyl methacrylate (Devi et al. 2003), butyric anhydride (Chang and Chang 2003), propionic anhydride (Papadopoulos 2006), butanetetracarboxylic acid (Wan and Kim 2007), palmitoyl chloride (Praskash and Mahadevan 2008), phenylisothiocyanate (Pandey et al. 2009), and alkylene epoxides (Pandey et al. 2010). Due to the chemical modification, wood components and solutions become cross-linked with a double bond, which improves the water resistance properties (Devi and Maji 2012). Chemical modification also blocks the hydroxyl groups in wood and improves water resistance (Islam et al. 2012). Chemical modification needs often a solvent with the solution. Li et al. (2010) have treated wood with maleic anhydride dissolved with acetone. Wood treatment with this solution can reach about 30% resistance to water absorption, which means that the solution has entered into the wood matrix and has reacted chemically with the hydroxyl groups on wood cell walls.

Modifications cannot totally prevent the water uptake, but they may curb the water uptake significantly for a longer period of time. For example, in a study of Wu et al. (2010), chemically modified and untreated poplar wood absorbed water quickly within 24 hours and the absorption continued even after this, but the water uptake of the treated wood was nearly stable after 24 hours. Similar behavior has been observed in other treatments as well, like by organosilicon-treated pine wood in a study of De Vetter et al. (2011). Shukla and Kamdem (2010) studied pine swelling with polyvinyl alcohol (PVA), melamine, and urethane. All three chemicals improved the tested properties, but PVA and melamine were the most efficient chemicals. PVA and melamine are classified as water repellents, because they do not swell more than 1.0%. These results are presented in Table 2 below (Shukla and Kamdem 2010).

Ghosh et al. (2009) studied wood treatment with three silicones, one micro-emulsion with particles below 40 nm in size, and two macro-emulsions with particles of 110 nm and 740 nm. They noted that the macro-emulsions reduced the water uptake more than the micro-emulsion. The silicone of the macro-emulsions filled the tracheid lumens partly, while the silicone of the micro-emulsion covered only the inner lumen surface of tracheids. Similar results were obtained also by Temiz et al. (2006) in a water immersion test which lasted 14 days. They treated samples with two dispersions of silica with different particle sizes. The silicon with 15 nm particle size absorbed water like the untreated control sample at the early stage of the test. The silicon of 30 nm particle size gave better

Table 2. Properties of PVA, urethane, and melamine -treated samples. (Shukla and Kamdem 2010)

Chemicals	Density (g/cm^3)	Total weight gain (%)	Water uptake (%)	Total tangential swelling (%)	Water-repellency efficiency (%)
PVA	0.49 ± 0.05	150.0 ± 22.2	37.4 ± 4.5	1.0 ± 0.3	82.1 ± 5.8
Urethane	0.46 ± 0.05	166.9 ± 25.9	61.5 ± 7.1	2.3 ± 0.2	58.9 ± 4.4
Melamine	0.45 ± 0.01	186.8 ± 3.2	49.9 ± 1.7	0.8 ± 0.2	85.6 ± 3.2
Untreated	0.42 ± 0.01	-	96.5 ± 1.7	6.0 ± 0.5	-

results at the same period and resembled acetylated wood. The wood treated with the silicon of 30 nm particle size absorbed the least water in the end of the test compared to acetylated and heat-treated wood, as can be seen in Table 3 (Temiz et al. 2006).

to have poor dimensional stability, while chitosan has been used to improve the water resistance of paper products. Chitosan improves the dimensional stability of particle board significantly, especially in a short time. The better dimensional stability may be attribut-

Table 3. Water absorption of treated and untreated wood expressed as a percentage of absolute dry weight of the sample. (Temiz et al. 2006)

	Immersion time (h)								
Samples	24	48	72	96	168	192	240	264	336
Control	62.20	63.84	64.54	67.99	80.01	83.02	85.84	87.00	90.55
	(5.96)	(5.76)	(5.91)	(6.25)	(7.66)	(7.55)	(7.07)	(7.11)	(7.16)
Silicon 15	61.37	64.21	67.00	72.55	75.61	76.16	77.64	78.32	80.17
	(4.34)	(4.19)	(4.57)	(4.90)	(4.77)	(4.91)	(4.99)	(5.05)	(5.17)
Silicon 30	46.08	48.06	49.36	53.89	57.52	58.00	58.87	59.36	60.43
	(2.58)	(1.78)	(1.92)	(2.37)	(1.94)	(2.04)	(2.00)	(2.09)	(2.12)
Acetylated	47.56	51.27	55.81	66.61	74.57	75.88	78.84	79.77	83.74
	(3.26)	(3.49)	(4.04)	(5.51)	(4.61)	(4.83)	(5.00)	(5.02)	(5.12)
Heat treated	24.70	32.66	38.67	40.10	56.00	60.38	67.56	68.19	79.39
	(1.78)	(2.05)	(1.95)	(1.94)	(1.77)	(1.78)	(1.78)	(1.83)	(1.87)

Values below in parentheses indicate standard deviations

Waxes have been used for wood panel production, where they have been shown to reduce the water uptake and improve the dimensional stability (Lesar and Humar 2011). It has also been reported that wax treatment can reduce the capillary uptake of water in solid wood (Scholz et al. 2009). Wang and Cooper (2005) noted that slack wax reduced water absorption more than palm oil or soy oil. Lesar and Humar (2011) treated spruce wood by montan wax and state that montan wax can reduce the water uptake. Waxing can make the surface of the wood more hydrophobic, and montan wax can form a film on wood which can slow down the movement of water. The cell lumens were also partly filled with wax, which prevents moisturizing physically. Wax emulsions can also be combined with traditional preservatives to improve the water repellency (Evans et al. 2009). High levels of wax cannot be used because it weakens the adhesion of binders (Wan and Kim 2007).

According to Furuno et al. (2004), the low molecular weight resin penetrated easily into cell walls and reduced swelling most effectively. Gabrielli and Kamke (2008) treated hybrid poplar with three different chemicals, phenol-formaldehyde resin, tung oil, and acetylation with acetic anhydride. After the chemical modification, they treated the wood with viscoelastic thermal compression. Only tung oil weakened the dimensional stability. In contrast to tung oil, tall oil treatments can reduce the water uptake of wood according to Hyvönen et al. (2006).

Like noted above, wood panels like particle board, plywood, OSB, and MDF are very sensitive to moisture at the edges. For example De Vetter et al. (2011) have noticed that wood-based materials increase the moisture uptake at the edges, and consequently the swelling increases. Basturk (2012) has examined chitosan in particle board. Particle board is considered

ed to a chitin film encapsulating the wood particles and blocking some of hydrophilic hydroxyl groups. Additionally, chitosan is insoluble in water, which may explain the good dimensional stability. Boric acid may impair the thickness swelling of particle boards (Pedieu et al. 2012), which it is not a surprise because wood treatment with boron compounds will make the wood more hygroscopic than untreated wood (Lesar et al. 2010). Mantanis and Papadopoulos (2010) have treated particle board, OSB, and MDF with a new nanotechnology compound and tested the thickness swelling. The results with the MDF panel improved more than with OSB or particle board, which was attributed to the more homogenous structure, making it possible for the small size nanoparticles to penetrate into the wood more easily and thus protect the wood against moisture. Hundhausen et al. (2009) investigated the modification of particle board chips by alkyl ketene dimer (AKD), which is a widely used paper sizing agent. The AKD improved the water resistance if the chips were previously impregnated and cured. Nemli et al. (2004) have treated particle board with a mimosa bark extract, which improved the thickness swelling. Papadopoulos and Traboulay (2000) investigated dimensional stability of acetylated OSB. They noted that acetylated OSB absorbed less water and the swelling was lower than with the control samples. Acetylation makes the wood less hygroscopic and improves the dimensional stability, but the method is expensive for OSB (Wan and Kim 2007). MDF board has been treated with maleated polypropylene wax and has been found to absorb less water (Garcia et al. 2006).

The water resistance of most solutions increases with the increasing solution content. For example the ASE of DMDHEU treated plywood has a positive effect on the DMDHEU concentration; the higher concentration implies higher dimensional stability, as can be seen in Table 4 (Dieste et al. 2008). Also resin and citric acid have the same effect. The water uptake decreases with increasing resin levels (Zhang et al. 2007) and citric acid content (Umemura et al. 2012). The dimensional stability and water absorption improve with increasing the impregnation time, which is attributed to the increasing of the amount of solution penetrating through the wood (Fadl and Basta 2005). Sahin (2008) has observed that in addition to density, the structure of the wood also has an effect on swelling and water absorption; cellulose is more hydrophilic than lignin. Especially hemicelluloses are the most hygroscopic polymers in the wood cell wall (Temiz et al. 2006).

Table 4. Correlation between anti-swelling efficiency (ASE) thickness and weight gain percentage (WPG) for DMDHEU-modified plywood. (Dieste et al. 2008)

Species	DMDHEU concentration	ASE thickness (%)	WPG (%)
Betula sp.	0.8 M	33.48	7.48
	1.3 M	43.49	18.76
	2.3 M	50.10	35.32
F. sylvatica	0.8 M	36.92	5.97
	1.3 M	40.81	15.18
	2.3 M	47.95	28.64

Most of the treated samples absorbed water rapidly at the early stage of the tests of the water resistance of wood, but later the results were more restrained. Hill (2006) has proposed that the results of the first cycle should be ignored because they are generally unpresentative due to the presence of non-bonded chemicals which are not leached, but are used as bulking. Unger et al. (2013) present in their study two possibilities of improving the dimensional stability of wood. The first possibility is artificial swelling where a solid substance is pressed into the cell walls in such a quantity that there is no space for water. Another possibility is chemical reaction where the OH groups of cellulose react with the OH groups of the solution. As a result, the OH groups of the wood are blocked by the solution when water cannot attack the OH groups of wood.

Biological durability

Biological degradation may be due to various causes like bacteria, mold and stain, decay fungi, insects, and marine borers. Bacteria can slowly degrade wood when it is saturated with water over a long period of time. Bacteria do not have a huge effect on the properties of wood, but they can make it more absorptive, which again can make it more susceptible to decay. Mold and stain cause damage to the surface of wood, especially on sapwood. Mold and stain fungus make the material more absorptive, which makes the wood more susceptible to moisture and decay fungi. Toughness and shock resistance are altered by molds and stains, but the main strength properties stay almost unchanged. Decay fungi and insect are more advanced organisms than bacteria or mold and stain. Decay fungi (brown-, white- and soft rot fungi) and insects (termites, carpenter ants, carpenter bees, and beetles) use wood as nutrition, causing serious problems to quality. Marine borers (shipworms, pholads, and crustaceans) can cause extensive damage to wood especially in warm water temperatures. (Ibach 2013)

Biological resistance is the most commonly studied property of wood, especially for treated wood. Ibach (2013) states, that some beetles can become active and cause damage when the moisture content of wood is between 10 and 20%. In addition to moisture, wood species and part of wood are resistant to decay; for example, heartwood has natural biological resistance. Traditionally, wood has been protected with pressure treatment using the copper chrome arsenic (CCA) preservative. It is known nowadays that CCA-treated wood poses risks to the public and hence alternative preservatives have replaced CCA. The degree of the protection of wood treatment depends on four basic requirements: toxicity, permanence, retention, and depth of penetration into wood (Ibach 2013). Biological resistance can be tested either in laboratory or field tests or both, when the reliable results can support each other. Biological resistance is usually measured by the percentage of weight loss. Biological resistance has been examined in several studies for both hardwood and softwood. That is advisable, because as it is generally known, the structure of wood is different between hardwood and softwood.

Chemical modification has a positive effect also on decay resistance. For example, anhydride modification can resist microbial attack (Abdul Khalil et al. 2010) and glutaraldehyde treatment restricts the penetration of blue stain fungi into deeper layers of wood (Xiao et al. 2012). Chang and Chang (2006) have noted that etherified wood is very resistant to fungus. Islam et al. (2012) modified tropical woods by various chemicals that inhibited mycelia spread. Williams and Hale (2003) modified wood chemically with isocyanates. The best known chemical modification method, acetylation, increases decay resistance with increasing WPG (Rowell et al. 2008). Hill (2002) states that acetylation requires WPG levels of circa 20% for full protection, depending on the species of wood and fungi. Acetylated wood flour and fiber can also import decay resistance (Segerholm et al. 2012). For example, acetylating wood components in wood plastic composites are highly decay-resistant (Westin et al. 2008). An acetylated wood component in wood plastic composites, however, cannot inhibit the formation of mold on the surface of a wood-plastic composite (Ibach et al. 2007). Acetylation is not the only method whose decay resistance increases with increasing WPG. Papadopoulus (2006) has made the same observation with the propionic anhydride, which required a WPG of approximately 17% to ensure protection. Jayashree et al. (2011) found that acid chloride-modified wood exhibited good resistance to fungus, but according to Habu et al. (2006), acid anhydride-modified wood has better durability than acid chloride-modified wood. According to Hill et al. (2005), anhydride-modified wood improved decay resistance through a reduction in cell wall moisture content or by the blocking of cell wall micropores, or through a combination of the two effects. The decay resistance of chemically modified wood increases due to increased hydrophobicity induced by the replacement of accessible hydroxyl groups in wood polymers (Pandey et al. 2009). Furfurylation has good resistance against degradation. For example, Esteves et al. (2011) tested the durability of furfurylated pine by wet rot and brown rot, and the mass loss decreased significantly due to furfurylation. Hadi et al. (2005) have examined the resistance to termite attack. They noted that furfurylated wood appeared to be immune to termites, provided that there was an adequate level of furfurylation. Low-furfurylated wood could not protect wood from a termite attack. According to a marine field test by Lande et al. (2004), furfurylated wood can challenge even CCA-treated wood.

Biological resistance with wood extractives has been topical in recent years. Especially new and promising researchers have studied wood treatment with extractives. Tascioglu et al. (2012) have treated pine (*Pinus sylvetris* L.), beech (*Fagus orientalis* L.) and poplar (*Populus tremula* L.) with wood and bark extracts. They have got the excellent results by mimosa (*Acacia mollissima*) and quebracho (*Shinopsis lorentzii*) extractives, especially at the higher concentration level, whereas the treatment of wood with a half lower concentration of extractives did not show significant improvements. Pine (*Pinus brutia*) bark extract treated wood gave unsuccessful results regardless of the concentration of extract. Feraydoni and Hosseinihashemi (2012) treated beech with walnut heartwood extractives, acid copper chromate and boric acid, and investigated decay resistance. None of the extractives were able to protect wood from decay by themselves, but the combination of the extractives with boric acid and acid copper chromate protected the wood from decay. The same kind of the result was reached in a previous study where walnut extractive increased protection against decay but could not prevent it (Hosseini Hashemi and Jahan Latibari 2011). The tannin extract by itself also showed poor inhibitory effect against fungus, but the combination with $CuCl_2$ solutions showed a better effect (Lomeli-Ramirez et al. 2012), and adding preservative salts to extracts decreased fungal penetration in wood (Sen et al. 2009). Bernardis and Popoff (2009) have also tested wood treatment with extracts and CCA, which increased the resistance to fungal degradation. The combination solutions are effective protection against decay. In addition to extracts, oil-based emulsions can also protect wood from degradation. Kaps et al. (2012) have developed an effective emulsion against fungal decay. Their emulsion is based on rapeseed oil in water emulsion, and it includes also boron compounds and acid oil. Tall oil alone cannot protect wood from decay, but tall oil combined with boron compounds is effective (Temiz et al. 2008). Boron has been found to be an effective agent against decay resistance also in other studies. Simsek et al. (2010) note that even with low loading levels of borate-treated wood can be protected wood degradation.

Wood can be treated with a variety of waxes. Wax treatment can reduce biological degradation, but it cannot prevent it (Scholz et al. 2010). Lesar and Humar (2011) have studied wax emulsions for wood preservation. The biological resistance of wood after wax treatment depends on the waxes and the fungus. The concentration of some waxes also influences the protection of wood from decay fungi. Higher concentrations protect better than lower concentrations. According to Lesar and Humar (2011), the most important reason for improved performance against wood decay fungi is the lower moisture content of wax-treated wood. Biological durability of wood has been tested also with resin, silicone, DMDHEU, citric acid, and water glass. According to Furuno et al. (2004), treatment of wood with phenol-formaldehyde resin prevents biodeterioration. The most important properties of wood protection by resin are the load level and molecular weight. The best protection is achieved by low molecular weight resin when the resin penetrates easily into the cell walls (Furuno et al. 2004). All silicone emulsions can inhibit fungal growth, but especially amino-silicones are active (Ghosh et al. 2009). This is explained by the antifungal effects of the amino-functional group or by changes in the surface properties of treated wood (ibid.). Pfeffer et al. (2011) have investigated the resistance of DMDHEU and water glass -treated wood against blue stain fungus. Both treatments inhibited but did not prevent fungal penetration into the wood. Especially water glass -treated wood showed promising results (ibid.), but a sufficiently high level of solution is needed (Chen 2009). The type of wood also affects the efficiency; for example, DMDHEU-treated pine is more effective against termites than DMDHEU-treated beech (Militz et al. 2011). Citric acid is a promising alternative for increasing biological durability (Despot et al. 2008) as is sol-gel treatment (Palanti et al. 2011). Non-treated wood has a more porous surface compared to sol-gel treated wood, which has a hard surface (Tshabalala et al. 2009).

Usually, sapwood is easy to impregnate, and hence the effects are better in sapwood. Ulvcrona et al. (2012) present contrasting results. They impregnated different parts of pine wood with linseed oil. According to Ulvcrona et al., impregnated pine sapwood had no significant effect in preventing mass loss by brown rot fungus. The same test for heartwood showed a potentially positive effect.

Fire resistance

The fire resistance of wood has been studied long. Fire resistance played an important role a century ago when ships were made from wood. The research of fire resistance has been in a minor role in Europe in the last decades, but the standards and codes of buildings have increased interest to fire safety today. Fire retardants can be tested by several instruments, which measure among others ignition time, weight loss, and other parameters. The fire retardant treatments for wood can be classified to the several classes according to the influence of chemicals (Rowell and Dietenberger 2013). The time to ignition is one of the most important properties of flammable material, which is affected by the thickness of the tested material, and oxygen concentration influences the ignition time (Pedieu et al. 2012), as does the temperature (White and Dietenberger 2010). Like White and Dietenberger comment, a high temperature will cause thermal degradation of wood. The permanent reductions in strength can occur even at temperatures below 100 °C, if the other conditions are favorable for degradation. The chemical bonds of wood begin to break at temperatures above 100 °C. The hemicelluloses and lignin components start getting pyrolyzed at 200 and 225 °C. Cellulose begins to depolymerise at the temperature range of 300 to 350 °C. The ignition of wood starts with the mixing of volatiles and air at the right composition in the temperature range of about 400 to 500 °C (White and Dietenberger 2010).

Fire-retardant treatment generally decreases the mechanical properties of wood (White and Dietenberger 2010). Fire-retardant treatment decreases the strength of wood by about between 10 to 20%. More problems arise if treated wood is exposed to high temperatures. Fire-retardants are activated prematurely at a high temperature, which leads to thermally induced acid degradation. The temperature of environment and a low pH value affect the intensity of the reaction (Nurmi et al. 2010). In contrast, the treatment of wood with fire retardants will delay ignition, reduce the heat release rate, and slow the spread of flames. The fire protection of wood is usually done by impregnation with chemical solutions. Inorganic salts are the most often used fire retardants, especially for interior wood products. These salts include phosphates, ammonium sulfate, zinc chloride, sodium tetraborate, and boric acid. The excellent effects of salts can be seen in Table 5. Traditional fire-retardant salts are water soluble, which means that corrosion and leaching are weaknesses of fire-retardants, especially in exterior applications (White and Dietenberger 2010).

As stated above, boric acid can be successfully used as a fire-retardant agent. Pedieu et al. (2012) have investigated particle board treatment with boric acid. They treated birch strands with three percentages of boric acid. The flame spread speed and after-flame time decreased with increasing boric acid content in the particle boards. Tondi et al. (2012) treated pine and beech wood with tannin. They noticed that the fire resistant properties improved with increasing tannin concentration. Still better results of fire resistance will be achieved when boron and phosphorus are added to tannin. Boron has high performing anti-biological properties, so it has a doubly beneficial effect on wood preservatives (Tondi et al. 2012). In contrast to boron, some other fire retardant chemicals have poor resistance against biodegradation. For example, according to Terzi et al. (2011), fire-retardant chemicals showed poorer performance against termites.

Sol-gel technology is quite a novel method of developing the fire resistance properties of wood. According to Shabir Mahr et al. (2012), sol-gel derived materials make potential option for wood modification due to their less toxic impacts, cost effective processing, and easy handling. For example, water glass, are

Table 5. Short-exposure fire tests for Scots pine. (Tondi et al. 2012)

Parameters	Ignition time (s)	Flame time 2 min (s)	Flame time 3 min (s)	Ember time 2 min (min)	Ember time 3 min (min)
Untreated	12 ± 3	140 ± 30	120 ± 35	4.0 ± 1.0	3.9 ± 1.0
10 % Tannin	75 ± 15	35 ± 10	130 ± 30	2.5 ± 0.5	6.0 ± 1.5
20 % Tannin	>120	20 ± 10	80 ± 20	2.5 ± 0.5	7.0 ± 1.5
20 % Tannin + Boric Ac. 1 %	>120	25 ± 5	30 ± 5	0.8 ± 0.2	1.5 ± 0.5
20 % Tannin + Phosph. Ac. 1 %	>120	15 ± 5	27 ± 5	0.9 ± 0.2	2.5 ± 0.8

efficient fire retardants Pereyra and Giudice (2009) impregnated wood panels with alkaline silicates and found that they had high fire-retardant efficiency. Silicate treatment together with curing agents helps avoid the leaching of preservatives in contact with water (ibid.) Canosa et al. (2011) impregnated wood with nano-lithium silicates, which also improved the fire resistance properties as well as in the research of silica nanoparticles by Guidice and Pereyra (2009). Urea-formaldehyde resin together with other agents seems to have fire resistance properties. Shi et al. (2007) have treated poplar wood with a solution consisting of urea-formaldehyde and nano-silica. This solution compound enhanced the flame resistance of wood. Plotnikova et al. (2003) coated pinewood with urea-formaldehyde resin and mineral fillers. They found that the flame-retardant characteristics depended on the nature of the filler, not its percentage.

Conclusions

The treatment of wood does not cause dramatic changes to the mechanical properties of wood. The changes of mechanical properties mainly depend on the properties of the materials; for example, higher density improves the strength of wood. Hardness is the easiest property to improve. The cross-linking between the agent and wood also improves several of the strength properties of wood, excluding the impact strength. The impact strength decreases after treatment, because cross-linking between the cell wall and agent reduces the mobility of the cell wall components. Waterborne solutions seem to have a negative influence on the mechanical properties. Waterborne solutions cause loss in strength, because treatment by aqueous solutions increases the rate of hydrolysis in the wood. Metallic oxides, which are often used in waterborne solution formulations reacts with the cell wall components, thereby reducing the strength of wood. This process is also known as fixation. Each modifier has a special feature, like the curing rate of formaldehyde-based resins in the production of the particle board, and the pH value of fire retardant chemicals. If the resins have a low curing rate, pre-curing may take place. The pre-cured bond breaks down when for example the pressing device of particle board production is closed. A low pH value of chemicals will cause a decrease in strength. Creeping and relative creep are mechanical properties that should be more researched.

The articles dealing with weathering are quite recent. This indicates that the importance of the weathering property has increased recently. The problem with weathering tests is the long duration of tests lasting even years. The most successful wood modification methods, like acetylation and heat-treating, have good color stability. Wood components behave differently under stress by weathering. For instance, carbohydrates are resistant to UV-degradation and extractives cause change of color. Lignin is the most important wood component in weathering because it is very sensitive to UV-light; hence lignin modification has a significant role in weathering. Various modifiers can protect wood from weathering but chemical modification seems to be the most effective.

Moisture resistance and especially dimensional stability are traditional properties that can be measured from wood. The greatest change happens at the early stage of the test, which has to be taken into account when considering the results. Water resistance depends significantly on the WPG value. According to the reviewed articles, water resistance increases with the increasing WPG. Hardly, any modifier can prevent water uptake, but they can curb the water uptake in a long period. Usually, the water resistance has improved remarkably when the modifier has cross-linked by a double bond with wood, or when the modifier has blocked the hydroxyl groups in the wood. The dimensional stability has been improved by artificial swelling when there has not been space anymore for water in wood cells. The dimensional stability can also improve the chemical reaction between the OH groups of cellulose and the OH groups of the solution. Some modifiers are promising for improving the dimensional stability of wood, but the properties of the modifier have a huge role. For example, a silicone emulsion with too small particle size covers only the inner lumen and therefore it cannot protect wood as efficiently as a silicone emulsion of a little greater particle size. Many other examples also show promising results, but they still need more researching. Acetylated wood has been found to be effective material for wood panels, but is found expensive. Cost-effectiveness should be kept in mind when wood modification is concerned. Solutions from other disciplines can be a possibility to develop the water resistance of wood.

Biological durability is perhaps the most commonly studied property of wood. Biological degradation may have only an aesthetically effect, but wood can also be destroyed in the worst-case scenario. New applications are replacing traditional preservatives due to legislation and environmental aspects. The performance of effective modification methods has increased with in increasing WPG. Some studies have shown that about 20% WPG is enough to protect wood from decay. Furfurylation has a good resistance against degradation and it is suitable for applications where traditional preservatives have been used. Wood extractives are a new possibility to protect wood. Several studies have shown that the extractive alone cannot protect wood from biological degradation, but a combination with other agents will improve the durability. Many solutions can protect wood from degradation, but the wood species and type of decay affect the performance of protection significantly.

The research of the fire resistance of wood has a long history, but it has received minor attention in the last decades. For example, the fire resistance of wood has not been presented at all in a number of traditional wood modification publications. Fire retardants will generally decrease the mechanical properties of wood, especially high temperatures and a low pH value of the solution will cause problems. Boron is a well-known preservative for wood, and it can protect wood from biological degradation, and in addition from fire. Silicates are also promising solutions for fire resistance. Other properties have been found to improve with the increasing volume of solution, but fire resistance depends more on the nature of the preservative than the volume.

It can be concluded that lower moisture content can improve the quality of wood in many sections. Lower moisture content improves the dimensional stability of wood and resistance against fungus. The chemical modification of wood is the best way to control and stabilize the moisture content of wood. Chemical modification can change the structure of wood cells, which is the most crucial factor in curbing moisture in wood. Further research should concentrate also on more cost-effective methods, such traditional impregnation, where the solution fills up the lumen without hard adhesion. This method could improve dimensional stability without affecting the mechanical properties significantly. The best solutions might be oil-type solutions which do not contain metallic oxides and whose pH-value is quite neutral. Other important properties are particle size, adhesion with wood, and avoidance of premature curing. One of the most promising solutions is melamine, for example. Melamine treatment can improve the hardness and water repellent properties of wood. Melamine also protects solid wood against weathering, and its natural appearance does not change. Extractives also are a promising solution for protecting wood. Another further research target should be the fire retardant properties of wood.

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