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IMPROVING THE PROPERTIES OF SOLID SCOTS PINE (PINUS SYLVESTRIS) WOOD BY USING MODIFICATION TECHNOLOGY AND AGENTS

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Suvorov auditorium of Technopolis, Lappeenranta, Finland on the 14th of October, 2016, at noon.

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Abstract

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The main aim of the study is to improve or upgrade the material properties of solid wood with substances and methods that do not cause undue strain on the environment. Traditionally, the qualities of wood have been enhanced with various preservatives, but wood preservation has undergone great changes worldwide due to environmental concerns and governmental regulations. This has increased the demand for the development of wood properties in other ways, for example by using modification technology and agents which will increase the usability of wood in current and future applications. The modification methods used in this study are impregnation and heat treatment. The impacts of modifications on the functional properties of solid wood are studied and the factors affecting the treatment are discussed. The study shows that wood impregnation is a challenge at some instances, but successful impregnation contributes to various wood properties. Heat treatment, as a post-treatment for impregnated wood, increases the beneficial properties of wood. Especially, the properties of moisture and discoloration resistance are improved significantly after the combination treatment of melamine and heat. Additionally, beneficial alterations are observed in strength and fire performance. The achieved results are mostly comparable with the modified wood products that are currently on the market. According to the findings, thermal modification with moderate temperature to melamine-impregnated wood appears to be advantageous, depending on the parameters used.

Keywords: wood, Scots pine, modification, impregnation, thermal modification, properties

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Ville Lahtela
September 2016
Lappeenranta, Finland

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List of publications

This thesis is based on the following papers, which are referred to in the text by their Roman numbers. The rights to include the papers in the thesis have been granted by the publishers.

- I. Lahtela, V., Hämäläinen, K., and Kärki, T. (2014). The effects of preservatives on the properties of wood after modification (Review paper). *Baltic Forestry*, 20(1), pp. 189-203.
- II. Lahtela, V., and Kärki, T. (2014). Improving the UV and water-resistance properties of Scots pine (*Pinus sylvestris*) with impregnation modifiers. *European Journal of Wood and Wood Products*, 72(4), pp. 445-452.
- III. Lahtela, V., and Kärki, T. (n.d.). Improving the mechanical properties of Scots pine (*Pinus sylvestris*) with impregnation modifiers. To be submitted for *Drvna Industrija* journal publication 2016, in review.
- IV. Lahtela, V., and Kärki, T. (2016). Effects of impregnation and heat treatment on the physical and mechanical properties of Scots pine (*Pinus sylvestris*) wood. *Wood Material Science & Engineering*, 11(4), pp. 217-227.
- V. Lahtela, V., and Kärki, T. (2016). The influence of melamine impregnation and heat treatment on the fire performance of Scots pine (*Pinus sylvestris*) wood. *Fire and Materials*, 40(5), pp. 731-737.
- VI. Lahtela, V., and Kärki, T. (2015). Determination and comparison of some selected properties of modified wood. *Wood Research*, 60(5), pp. 763-772.

Author's contribution

In Paper I, the author had the responsibility of collecting the data and writing the text.

In Papers II-VI, the author had the responsibility of sampling, measuring, and analysing the research material, as well as writing the text.

Abbreviations

ΔE^*	Colour difference
a^*	Colour space coordinate (from red to green)
b^*	Colour space coordinate (from yellow to blue)
BC	Bulking coefficient
BDP	Biocidal Product Directive
°C	Celsius
CCA	Chromated copper arsenate
CO ₂	Carbon dioxide
CTO	Crude tall oil
DMDHEU	Dimethyloldihydroxy-ethyleneurea
DP	Degree of polymerization
EMC	Equilibrium moisture content
EPA	Environmental Protection Agency
ECWM	European Conference on Wood Modification
FAO	Food and Agriculture Organization of the United Nations
FSP	Fibre saturation point
g/cm ³	Gram per cubic centimetre
GDP	Gross domestic product
Ha	Hectare
HRR	Heat release rate
HT	Heat treated
kg/m ³	Kilogram per cubic meter
kW/m ²	Kilowatt per square meter
L	Litre
L^*	Colour space coordinate (lightness, from white to black)
LCA	Life cycle assessment
ML	Mass loss

MLR	Mass loss rate
μm	Micrometre
m^3	Cubic meter
ml	Middle lamella
mm	Millimetre
mm/a	Millimetre per year
MPa	Megapascal
mPas	Millipascal-second
M_m	Oven-dry mass of the modified wood
M_u	Oven-dry mass of the unmodified wood
m_1	Mass before heat treatment
m_2	Mass after heat treatment
N/A	Not available
nm	Nano meter
%	Percent
p	Primary wall
pH	Acidity of an aqueous solution
OH	Hydroxyl group
PDMS	Polydimethylsiloxane
R	Radial
RSU	Relative solution uptake
s_1, s_2, s_3	Secondary cell wall layers
SCE	Specular component excluded
SEM	Scanning electron microscopy
SD	Standard deviation
T	Tangential
TH	Thermo-hydro treatment
THM	Thermo-hydro-mechanical treatment
THR	Total heat release rate
TSP	Total smoke production

UV	Ultra violet
VC	Volume change
WCWM	World Conference on Wood Modification
WPC	Wood polymer composite
WPG	Weight percent gain
W_1	Oven-dry mass before impregnation
W_2	Mass of the conditioned sample before impregnation
W_3	Mass of the sample after impregnation

1 Introduction

Solid materials are classified into a few main groups, such as, metals, ceramics, polymers, and composites. Naturally-occurring wood is classified into the composite group, and it is one of the oldest materials utilized by human beings. Today, several different materials are available to meet the needs of the modern society, and selecting the right material may be a problem in many places. However, the economic point of view can be the deciding factor in the material selection. A material may contain an ideal set of properties but be prohibitively expensive (Callister 2007).

Globally, forests and wood have a significant influence on and contribution to the humankind and economy. The demand for wood is about three billion cubic meters per year and 30.6 percent of the global land area is covered by forests, whereof about 30 percent is designated as production forest, according to the assessment of the Food and Agriculture Organization of the United Nations (FAO 2015a). The forest area in Europe is 33 percent of the total land area (FAO 2015b), and correspondingly in Finland, 86 percent of the land area is forestry land (Metsäntutkimuslaitos 2014). In 2011, the forest sector employed about 13.2 million people across the world, and in addition, about 41 million were employed indirectly. The total employment means about 1.7 percent of the global workforce. Forests have even greater significance in Europe, and especially in Finland. The contribution of the forest sector to the gross domestic product (GDP) is 0.9 percent globally, and in Europe as well. In Finland, the corresponding figure is 4.3 percent (FAO 2014). The importance of wood and its applications has been grown with the increasing population and economics, and for example, over half of the wood consumed in the world is used for fuel. Additionally, some characteristics of wood, such as renewability, biodegradability and carbon sequestration are generally accepted as good for the environment (Risbrudt 2013).

In addition to the positive environmental impact, wood has a large number of favourable properties which contribute to its use in many applications. Favourable properties are, inter alia, easy workability, good insulation, and high strength compared to weight. However, some of the inherent properties of wood impair its competitiveness, such as vulnerability to moisture, biological organisms, and weathering. Due to its hygroscopic nature, several physical properties of wood become undesired with the moisture change. Wood starts to shrink when moisture is removed below the fibre saturation point (FSP), and contrarily, dry wood starts to swell with water contact. The shrinkage and swelling of wood varies between the growing directions due to its anisotropic nature (Rowell 2013a). Depending on the temperature and moisture conditions, biological organisms may attack wood and degrade its quality (Ibach 2013). Environmental factors, such as solar radiation, can destroy the texture of the wood surface, which is reflected as a grey, cracked, or rough surface (Evans 2013). These susceptibilities have led to the development of wood protection to enhance the qualities of wood. Several countries have made significant investments in the research of wood preservation (Preston and Jin 2008).

The modern wood preservation industry started in the 1830s, when the most common wood preservatives, such as creosote and chromated copper arsenate (CCA) were introduced. Until the 21st century, CCA was the major preservative around the world, due to its low cost and efficiency (Freeman et al. 2003; Barnes 2008; Preston and Jin 2008). Also boron-containing wood preservatives are often used due to, inter alia, their property of decay resistance, but their weakness is susceptibility to leaching (Manning 2008). Wood preservatives are generally classified into two categories; oil-borne and water-borne preservatives, and pressure and optionally also a vacuum can be utilized in the treating process, leading to controlled results (Nicholas 2001; Archer and Lebow 2006). Even though the pressure-treating processes have remained almost constant for the last century, the industry of wood preservatives has experienced changes worldwide due to environmental concerns. For example, the use of CCA is limited in most European countries, and Japan has prohibited the utilization of arsenic and chromium in preservatives (Barnes 2008). The use of preservatives is authorized and controlled by different enactments, such as the Environmental Protection Agency (EPA) in the United States, or the Biocidal Product Directive (BDP) in Europe (Barnes 2007). The aim of the enactments is to provide safe products and production, without a negative impact on human health and the environment. This will help to develop wood preservatives in a direction which will further reinforce the image of wood as a natural, valuable, high-tech, and sustainable resource (Leithoff et al. 2008).

In addition to the tightened enactments on wood preservatives, environmental awareness is one of the key drivers for the increased demand of research and development for improving wood properties. Finding alternatives to tropical hardwood and energy-consuming material processes are essential, and this will increase the need for new wood modification technologies (Navi and Sandberg 2012). Especially, finding alternatives to tropical wood is relevant because the forest area decreased by 129 million ha between the years 1990 and 2015, and the forest area decline is greatest in the tropics, due to population growth and the conversion of forest land to other purposes. While the forest areas have diminished in the southern hemisphere, they have increased in the northern hemisphere (FAO 2015a). Additionally, the demand of sawn tropical hardwood decreased by fifteen percent in the European Union during the years 2005-2010 (Jones 2012). The properties of solid wood can be developed by wood modification technologies to bring in products for various applications such as decking, cladding, and environmental constructions, for example. In addition to solid wood, the modification technology can be also exploitable in other processed wood products, such as plywood, particleboard, or wood polymer composites (WPC).

The development towards urbanization and demographic evolution will affect the requirements of building products (Mayes 2015). The competing products can reduce the use of wood. For example, plastic lumber is the major competitor of solid wood in the American decking market. People consider plastic lumber as a modern high-performance material, while wood is a cheap product with inferior properties (Schultz et al. 2007). The construction industry is a big user of wood products, and wood-frame buildings have

become common in several European countries. The share of wood-frame residential buildings of all kinds is high in the Nordic countries, New Zealand, and North America, but for example in Western and Eastern Europe, the corresponding shares are low (Eriksson et al. 2012, Mahapatra et al. 2012). Hence, the demand of wood products would seem to have potential for growth in Western and Eastern Europe. Wood is a safe material under high stress conditions, but the challenge for wider utilization is national fire regulations, which restrict the use of wood in many countries. However, it should be remembered that a layer of char is created when wood burns, and this char layer ensures the structural integrity of wood, reducing the risk of collapsing concurrently (European Economic and Social Committee 2015). The opportunities relating to the use of wood in construction are not fully exploited. At the moment a positive building policy toward wooden multi-storey construction can lead to a larger use of wood (Tykkä et al. 2010, Mahapatra et al. 2012, Anon 2016), and using more wood in construction could save global carbon dioxide (CO₂) emissions and fossil fuel consumption substantially (Oliver et al. 2014).

1.1 Structure of wood material

Wood is a renewable natural material with a large number of applications. To understand wood and its behaviour for the purpose of wood modification, fundamental knowledge of its structure is needed. Traditionally, wood is classified into two categories – softwood and hardwood, which have a different cellular structure from the microscopic point of view. Softwoods consist mainly of axially-elongated, long, and pointed cells called tracheids. Radially-elongated cells are known as rays. The flow in softwood occurs via tracheids and from cell to cell through bordered pits. Hardwoods do not have as simple and regular structure as softwoods. The water conducting cells of hardwood, called vessels, stand out from the transverse section of the wood microstructure (Figure 1). The diameter of a tree is increased by dividing cells near the outside of the stem just beneath the bark, known as the vascular cambium. The cyclic production of new wood cells leave a pattern that is known as annual growth ring. In softwoods, growing season tracheids with larger lumens and thin walls are termed earlywood, and the tracheids with smaller lumens and thicker walls at the end of the growing season are termed latewood. The core of a tree is often harder and darker, and it is known as heartwood, which is difficult to penetrate. The outside of the stem is usually paler, and it is called sapwood, which is active in water transport and other physiological activities. (Butterfield 2006)

Wood can be observed from three main perspectives, which are the transverse plane (the cross section), the radial plane, and the tangential plane. These planes are detectable in Figure 1a (Wiedenhoef 2013).

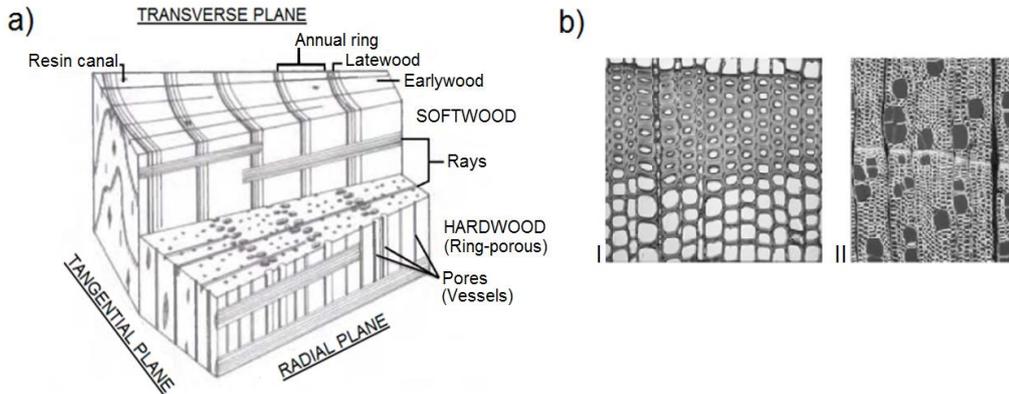


Figure 1. Models of softwood and hardwood structures with cutting planes (a), and their microstructural transverse sections [pine (I) and birch (II)] (b). Adapted from Fengel and Wegener (1989) and Daniel (2009).

The main structural components of wood are cellulose, hemicellulose, and lignin. In addition, there are extraneous chemicals known collectively as extractives, as well as small amounts of inorganic elements. Cellulose and hemicellulose are polysaccharides, and their combined content is about 70 % of the dry weight of wood. Lignin consists of phenylpropane units, and its content varies from about 25 % to 30 % (Walker 2006a). The role of lignin is to act as an adhesive in wood, holding the cellulose fibres together (Rowell 1984). Wood contains also a few percents of extractives which provide natural durability to wood (Walker 2006a).

Cellulose is the ruling organic chemical, consisting of linear chains of glucose units. Native wood cellulose has the degree of polymerization (DP) of approximately 10 000 and the linear chain length is approximately 5 micrometre (μm). However, the DP varies in different parts of wood. Linear cellulose molecules have a tendency to form bonds with each other, in which case microfibrils have been formed. Cellulose microfibrils are partially organized (crystalline), and partially not (amorphous), which has an effect on the sorption of water molecules, for instance. Cellulose is water-insoluble. Hemicelluloses are located in the cell wall between the cellulose microfibrils. In general, the hemicellulose consists of branched polysaccharides, but hardwood and softwood have different hemicellulose compositions and contents. The hemicelluloses of hardwood is mainly xylan, while in softwood the hemicellulose is mostly glucomannan. Hemicellulose has an average DP of 100-200. The nature of hemicellulose is hydrophilic, it is partially soluble in water. Lignin is a branched and reticulated polymer, which has hydrophobic nature. In softwood, lignin is called guaiacyl lignin, while in hardwood it is called syringyl-guaiacyl lignin. The extractives consist of a wide group of compounds. In general, softwoods have a higher extractives content than hardwoods, and most of the extractives are located in the heartwood (Jääskeläinen and Sundqvist 2007; Rowell et al. 2013).

All wood species have a regular cell wall structure, consisting of three main regions: the middle lamella, the primary wall, and the secondary wall, as depicted in Figure 2. The outermost layer between the cells is the middle lamella, followed by a thin primary wall, both of which are mainly composed of lignin. The layer interior to the middle lamella and the primary wall is the secondary wall which is composed of three layers, distinguished on the basis of the different angle than the helically oriented microfibrils with the long axis of the cell. The first-formed secondary cell wall layer is s_1 , which is thin and characterized by a large microfibril angle ($50-70^\circ$). The next layer s_2 is the thickest secondary cell wall layer, and for this reason it is probably the most important cell wall layer in determining the properties of the cell. The s_2 layer is cellulose-rich and has a low microfibril angle ($5-30^\circ$). The innermost layer of the cell is the relatively thin s_3 layer, which has a high microfibril angle ($>70^\circ$) and a high percentage of hemicelluloses (Rowell et al. 2013; Wiedenhoef 2013).

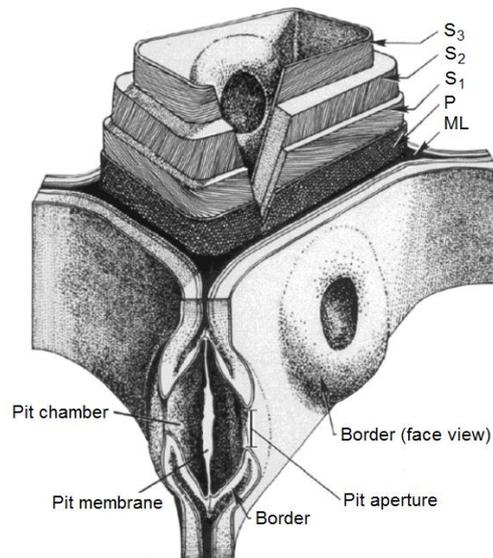


Figure 2. Schematic of the ultrastructure of the wood cell wall, including the relative thickness of the layers, the illustration of microfibril angles, and the structural details of a bordered pit. The layers of the cell wall are detailed at the top of the drawing; the middle lamella (ml), the primary wall (p), and the secondary wall in its three layers (s_1 , s_2 , s_3). (Wiedenhoef 2013, p. 18)

Intercellular communication and transport between the cells occur via pit-pairs, called also pits, which have three sections: pit membrane, pit aperture, and pit chamber, which are noticeable in Figure 2. The pits have overarching walls and they are named bordered pits (Wiedenhoef 2013).

1.2 Properties of wood material

Wood is a widely used material in many applications due to, inter alia, its good strength properties compared to its weight. The natural growth characteristics of wood affect the mechanical properties, which are also known as strength properties. For example, specific gravity correlates positively with wood strength, while the moisture content correlates negatively with strength (Kretschmann 2010). The structural components of wood have individual mechanical properties, which vary with respect to three mutually perpendicular axes. Cellulose is the strongest component in wood and is thus highly responsible for the strength of wood because of its high degree of polymerization and linear orientation. Hemicelluloses act as a link between cellulose and lignin which holds the fibres together, and they also act as a stiffening agent for cellulose within the cell wall. Environmental agents and some treatment compounds can alter the mechanical properties of wood (Winandy and Rowell 2013). The most commonly studied mechanical property of wood is the bending strength, because it reflects the strength that is needed in many structural applications (Kärkkäinen 2003). Stiffness, which describes the momentary maximum force (Kretschmann 2010), is often measured at the same time and the same way as bending strength. The measurement of wood hardness is also quite common due to the ease of measurement, and because it does not break the material (Kärkkäinen 2003).

Unprotected wood is susceptible to weathering, which means the outdoor and above ground degradation of materials. Weathering depends on many environmental factors, such as solar radiation, moisture, temperature, oxygen, and air pollutants. However, it is generally accepted that UV light is responsible for the primary photochemical process in weathering (Hon 2001). A typical feature for weathered wood is grey colour, and the surface is often cracked and rough (Evans 2013). Weathering influences the wood components individually. For example, celluloses and hemicelluloses are quite resistant to UV degradation, but they are more sensitive to moisture. Lignin is sensitive to UV radiation, and also the extractives change colour in UV radiation (Williams 2010). In addition to UV light, acid rain may have significant influence in the deterioration of wood surface quality (Hon 2001).

Wood has a tendency to reach equilibrium moisture content (EMC) with the surrounding relative humidity and as noted above, wood shrinks when the moisture is below the fibre saturation point (FSP), and dry wood swells with water contact. These moisture relationships have important influence on the properties and performance of wood, because several properties of wood depend upon the moisture content. The completely saturated wood cell walls without water in the cell lumina is called the fibre saturation point, above which the properties of wood do not change as a function of moisture content. For example, wood is dimensionally stable when its moisture content is greater than the FSP. Usually, the FSP of wood means an approximately 30 % moisture content, but it can vary depending on the species and pieces of wood. Below the FSP, the dimensions of wood change, which can appear as shrinking or swelling, and because wood is an anisotropic material, the dimensional change varies according to the growing direction (Glass and Zelinka 2010). The wood cell wall can adsorb or desorb moisture

from the surrounding air, due to the presence of accessible hydroxyl groups throughout its structure. When the wood cell wall adsorbs water, the water forms hydrogen bonds with accessible hydroxyl groups in amorphous regions (Walker 2006b). The sorption of water in wood at a defined temperature is referred to as a sorption isotherm, which is described in Figure 3. The differences in moisture content from wet to dry and dry to wet are known as hysteresis (Rowel 2013a).

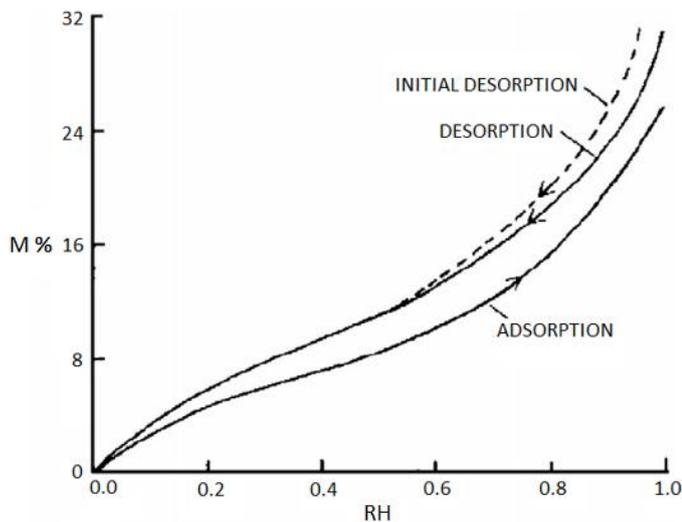


Figure 3. Sorption isotherm for wood, including moisture lost from green wood (initial desorption), following different curves of rewetting (adsorption) and redrying (desorption). The adsorption curve is always lower than the desorption curve. (M % = moisture content, RH = relative humidity) Adapted from Rowell (2013a)

Wood material is sensitive to fire, which restricts its utilization in many places. Wood does not burn directly, but combustion takes place as a reaction between oxygen and the gases released from the material (Rowell and Dietenberger 2013). The combustion and ignition of wood materials is based on the thermal decomposition of cellulose and the reactions of thermal decomposition products with each other and the surrounding gases (Hakkarainen et al. 2005). The chemical components of wood begin to decompose at different temperatures. Hemicelluloses, lignin, and celluloses components are thermally decomposed in the range of 200 to 300 °C, 225 to 450 °C, and 300 to 350 °C, respectively (White and Dietenberger 2010). Even though the fire performance of wood material is unfavourable, it must be remembered that after ignition, the surface of wood begins to char at a rate of approximately 0.8 mm/min. The charring rate will decrease slightly when the combustion progresses, and it is dependent on several factors, such as the moisture content and the anatomical features of the wood (White and Dietenberger 2010). The charring of wood retards the progress of fire, which can be taken into account in the designing of the structure.

1.3 Wood modification

As stated above, wood has a great number of favourable properties, but also a few disadvantages which restrict its end uses. These inherent properties can be altered by modification, to bring about an improvement in one or more of its disadvantages. The improvements must be carried out so that during the lifetime of a product no loss of the enhanced performance of the wood should occur. In addition, modified wood is prepared in such a way that it does not contain hazardous residues once the modification process is complete (Hill 2006). According to Militz and Lande (2009), the treatment of wood with hazardous methods is also presented as wood modification, and consequently non-toxicity should be seen as an important recommendation, not as a prerequisite. However, the growing environmental awareness increases the demand of harmless materials. The sustainable use of resources has dominated in public discussion during the last decades, and its importance will only increase in the future (Hill 2011a). The term “environmentally friendly” is often used incorrectly because it is impossible to describe. The method which exhibits the greatest relative environmental, social, and economic benefit should be selected (Hill 2006).

The modification of wood material has been exploited already ages ago. For example, the Vikings burned the outsides of their ships to make them water and flame resistant (Rowell 2006). Today, international wood modification work is mainly centred in Europe, where the European Conference on Wood Modification (ECWM) has been organized since 2003 (Barnes 2008). Participation in ECWM from outside Europe has been growing recently, and therefore a new name for the conference has been suggested: World Conference on Wood Modification (WCWM) (Militz 2015a).

Wood modification can be active or passive. Active modification alters the chemical nature of the material, and passive modification alters the properties without an alteration in the chemistry of the material (Hill 2006). There are several ways and methods to classify the modification of wood. The ruling classification of wood modification is divided to four categories according to Hill (2006): chemical, thermal, surface, and impregnation modification. Navi and Sandberg (2012) divide wood modification to two main categories, chemical modification and thermo-hydro-mechanical processing, followed by several sub-categories, for example thermo-hydro treatments (TH) and thermo-hydro-mechanical (THM) treatments.

The surface modification of wood can involve chemical, biological, or physical modification with an agent to wood surface. For example, UV stability improvement is a commonly used surface modification of wood. Most of the chemical modification methods contain a chemical reaction of a reagent with the cell wall polymeric hydroxyl groups. The modification of wood with acetic anhydride, also known as acetylation, is a noted chemical modification method. There are a lot of surveys on the chemical modification of wood, but commercialization has been limited due to the price of the reagent and the handling of large amounts (Hill 2006). Generalizing, true chemical modification must be separated from the modifications which change the wood properties

only by filling cell lumens (Militz and Lande 2009). Thermo-hydro-mechanical processing methods are combined use of temperature and moisture (TH), and additional mechanical action (THM). With the TH and THM treatments, several properties of wood are improved which can increase the use of local wood material instead of imported rare hardwoods (Navi and Sandberg 2012).

The result of modification must be proved. Weight percent gain (WPG) is a common method in measuring, and it is calculated as follows:

$$WPG(\%) = \left[\frac{M_m - M_u}{M_u} \right] \times 100 \quad (1.1)$$

where M_m is the oven-dry mass of modified wood and M_u is the oven-dry mass of unmodified wood.

Similar indicators to WPG are volume change (VC) and the bulking coefficient (BC), where the masses are replaced by volumes (Hill 2006). Moreover, same type of modification figures have been used by Sint et al. (2013) and Tondi et al. (2013), for example. In these figures, the solution uptake or the ratio between wet and dry weights have been determined.

A small percentage of modified wood has been commercialized. The commercialization of wood modification is divided into four levels. The first level includes small-scale laboratory experiments, where treatments are identified. On the second level, the laboratory treatments take place on a larger scale, including also field tests and product evaluation, such as gluing and painting. The third level of development examines technological and economic feasibility, and it also includes a pilot plant and industrial implementation. On the last level, modified wood is produced industrially. A significant limitation of commercialization is the high cost of the production method (Suttie and Thompson 2001).

Wood modification technology is still quite a new industry sector. Chemical, thermal and impregnation modification methods have been exploited commercially in the 2010s (Hill 2011b). Dunningham and Sargent (2015) have estimated that the total production volume of modified wood was over 190 000 m³ in 2015, but in the estimation of Militz (2015b), the production volume in Europe is believed to be far higher. The production volume of the most successful thermal modification of wood was nearly 150 000 m³ in 2014 (ThermoWood 2015). Although there is disagreement in the estimation of the total production volume, it is undeniable that the known modification methods have been growing rapidly in the last years (Dunningham and Sargent 2015; ThermoWood 2015).

Some of advantages and disadvantages of wood modification are presented in Table 1. A clear advantage for modified wood is the environmental benefits that are detectable by the reduced toxicity and reduced carbon footprint, inter alia. Life cycle assessment (LCA)

is one tool which can be used to evaluate the total environmental impact of a modified wood product. The generally lower maintenance, for example prolonged time for re-painting, and thereby increased life span of the modified wood, will reduce costs and have also a positive environmental impact. Hill and Norton (2014) estimated that the life extension of two modified wood products increased 2.5 times, approximately. Due to the novelty of modified wood, there is a lack of data of for example long-time performance in exterior applications, which may raise questions relating to the usability of modified wood. Different countries and regions have different demands and resources, such as dependency on timber suppliers, which can be a barrier for modified wood (Dunningham and Sargent 2015). Although the high cost of modified wood has been mentioned as a disadvantage, it should be remembered that an increasing number of people are willing to pay a premium for wanted features (Schultz et al. 2007).

Table 1. Some advantages and disadvantages of wood modification and modified wood. (Jones 2007, Dunningham and Sargent 2015)

Advantages	Disadvantages
<ul style="list-style-type: none"> - a “green” image - environmental benefits - remained native wood aesthetics - increased product life - increased stability - lower maintenance - local production with local species - co-operation - new markets for wood 	<ul style="list-style-type: none"> - lack of data - limited long-term performance - fire performance - differences between regions - high investment cost - cost of production (i.e. energy) - high cost of modified wood - cheaper alternative products

1.3.1 Impregnation modification

The impregnation modification of wood results in filling of the wood substance with an inert material, providing a desired performance change. The presence of material in the wood cell wall can affect several properties of wood. The fixation of the impregnator within the cell wall of wood can take place by two main mechanisms: by monomer impregnation or by diffusion. Generally, a monomer (or oligomer) solution penetrates into the cell wall, followed by subsequent polymerization. In the other fixation mechanism, a soluble material is diffused into the cell wall so as to render the material insoluble afterward (Hill 2006).

The best known impregnation methods are full cell treatment Bethell and empty cell treatments Lowry and Rueping (Rüping). The initial vacuum in the full cell treatment method, which evacuates air from the wood, is the most noticeable difference to the empty cell methods. Full cell treatment is generally used for water-borne solutions, where maximum solution retention is desired. The empty cell treatment is often used with oil-borne solutions, whose requirement for net solution retention is much lower (Nicholas 2001; Archer and Lebow 2006).

The chemical structure of wood components has an influence on wood penetration and reactivity. The hydroxyl group is the main chemical group in wood cell wall biopolymers, and it is mostly responsible for the chemical reactivity of wood (Gérardin 2015). It should be mentioned in this context that the water content of wood is critical because the hydroxyl in water is more reactive than the hydroxyl groups available in wood components. The cell wall must be in a swollen state during the impregnation phase to ensure the accessibility of the impregnator. A catalyst or a workable cosolvent may be added to cause the wood to swell, and almost all chemical reactions require a catalyst. However, it would be desirable to avoid multicomponent systems in the treatment as they require complex separation procedures at a later stage. An increase in temperature may improve the penetration, but the temperature of about 120 °C is the safe upper limit in the reaction. Generally, the reaction conditions must be mild enough in order to avoid undesirable properties of wood. Of the structural components of wood, lignin is more sensitive to substitution than the carbohydrate components (Rowell 1984).

The properties of the impregnation solution have an effect on the impregnation result. It is a foregone conclusion that the molecular components of the impregnator should be small, so that it can gain access to the cell wall interior. Some studies have shown that a molecular diameter of approximately 0.68 nm is the limit for the penetrating liquid, but its hydrogen-bonding ability has also a significant effect. Molecules with a greater tendency to form or break hydrogen bonds show greater penetrating ability. A chemical bond between the impregnator and cell wall may occur, but it is not a requirement for impregnation. However, the impregnator must be nonleachable in service conditions (Hill 2006).

The status of the bordered pits has a great effect on the treatment of wood. The pit membrane is composed of a network of microfibrils, called the margo, with a central thickened area, called the torus. When wood dries, the pit membranes move toward the pit apertures, isolating the conducting pits. This process is known as aspiration, and is illustrated in Figure 4. Microscope pictures of unaspirated and aspirated bordered pits are presented in Figure 5.

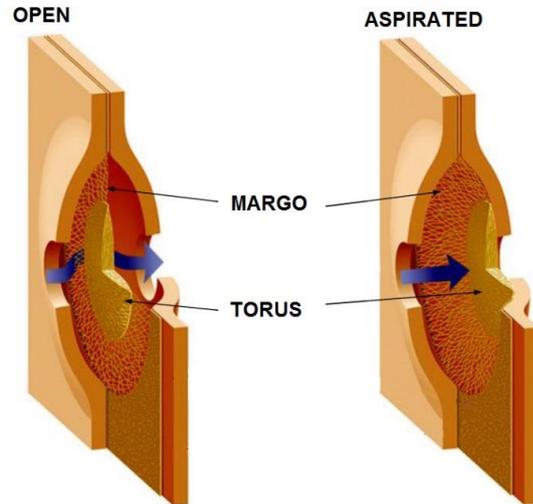


Figure 4. Simple illustration of pit aspiration. In the open system, conduction via the pit (*the blue arrow*) occurs through the margo, while in the aspirated system, the torus has moved and conduction is inhibited. Adapted from Lehringer (2011).

The once aspirated pits remain at the aspirated status. A majority of the pits are unaspirated in green sapwood, while after drying, a majority of the earlywood pits and about half of the latewood pits are aspirated. The weaker aspiration of latewood is due to a thicker margo and the different shape of the pit, and therefore the pits of latewood do not close as easily as those of earlywood (Langrish and Walker 2006). Also, the thicker S_2 layer in the cell wall of latewood results in less pit aspiration. The penetration of liquids into latewood takes place partly by capillary action in the small lumens and passage through unaspirated pits (Rowell 1984). In addition to aspiration, the more suitable treatability of pine sapwood compared to other softwoods is explained by the opportunity of collapse of the thin-walled cells on drying (Langrish and Walker 2006). The most sensitive part of wood is from one to three growth rings -wide transition zone, which is less permeable than sapwood and less durable than heartwood (Wang and DeGroot 1996).

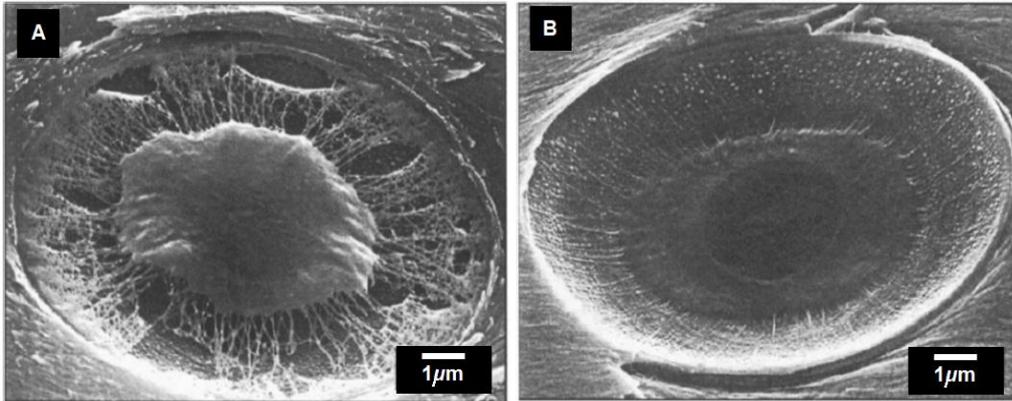


Figure 5. Microscope picture of unspirated (A) and aspirated (B) states of bordered pits of pine (*Pinus sylvestris*) sapwood. Adapted from Olsson et al. (2001).

Generally, a high density of wood makes penetration more difficult (Ajdinaj et al. 2013), but penetrability varies also between wood species. In softwood, longitudinal permeability is dominant compared to transverse permeabilities which are approximately 10^4 times less in number. The permeability of hardwood is limited due to the pits between contiguous vessels. In addition, the vessels are not very long (Langrish and Walker 2006). Earlywood has thinner cell walls which contributes to and accelerates the penetration of earlywood compared the latewood. In addition, a raised temperature and pressure increase the penetration due to softening of the pit structure and displacement of the pit membrane (Rowell 1984). In the study of Larnøy et al. (2005) it is proven that the uptake of pine is double in the radial and tangential directions, compared to the corresponding uptake of beech, birch, and spruce. Pine has good penetrability in the radial direction, where the liquid can pass through the radially orientated large size ray tracheids of the average diameter of 15-35 μm (ibid.).

In the case of adhesive penetration, two levels of penetration are discussed: micrometre level (gross penetration) and nanometre level (cell wall penetration). In gross penetration, a liquid agent with low viscosity flows into the porous structure of wood, filling the microscopic cell cavities. In cell wall penetration, the agent is diffused into the cell wall or micro fissures if the agent is composed of small-molecular weight components (Kamke and Lee 2007, Qin et al. 2016).

The substance uptake and penetration can be enhanced by a selective degradation of bordered pits (bioincising), but it has also been shown to have some negative effects (Lehringer et al. 2009). Also, the treatment method can minimize the effect of pit aspiration on the permeability. For example in the oscillating pressure method, the repeated pressure variation from vacuum to high pressure forces the agent into green sapwood, and thus aspiration does not occur prior to treatment (Archer and Lebow 2006).

In addition to the properties of the impregnator, also the size of the sample and the treatment variables have an effect on the penetration. For example, a sufficient time will ensure that the impregnator molecules diffuse into the intracellular spaces. This may take several days for large wood samples (Hill 2006).

1.3.2 Thermal modification

The thermal modification of wood is the most advanced wood modification method commercially. It causes a desired improvement in the wood material by heat. Thermal modification is usually performed between the temperatures of 180 °C and 260 °C (Hill 2006). At these temperatures, wood undergoes important chemical transformations. At lower temperatures, between 20-150 °C, the wood dries with loss of free and bound water. The substrate of wood degrades undesirably, starting a carbonization process with the formation of CO₂ and other pyrolysis products (Esteves and Pereira 2009). Several variables have an effect on the treatment and the properties, such as the wood species, the sample dimensions, the treatment time and temperature, together with the treatment atmosphere and systems (Hill 2006).

Thermal modification modifies the structure of wood cell wall polymers, creating new properties to the material (Hill 2006). The general changes of wood components are depicted in Figure 6. Microscopic examination has demonstrated that the cell walls were decomposed to lamella and the walls were broken to sharp-edged chips (Viitaniemi and Jämsä 1996). In thermally modified wood, the percentage of carbon increases, and the amount of oxygen and hydrogen decreases (Esteves and Pereira 2009). The main volatile compounds are water, formic acid and acetic acid furfural (Gérardin 2015). The thermal stability of polymers differs according to their chemical structure, and the presence of oxygen during treatment has a significant effect on the degradation of wood. It is generally recognized that hardwoods are more susceptible to thermal degradation than softwoods. Due to the amorphous structure of hemicelluloses, thermal treatment degrades most of the structural components of wood, which further increases the amount of crystallinity and re-organize the amorphous region of cellulose. Cellulose demands a higher temperature for changes, but lignin is the most thermally stable component (Hill 2006, Gérardin 2015). The stability of cellulose is probably due to its crystalline nature. Most extractives disappear or degrade during thermal modification (Esteves and Pereira 2009), but the extractives can also move to the surface of the sapwood due to moderate thermal modification (Nuopponen et al. 2003).

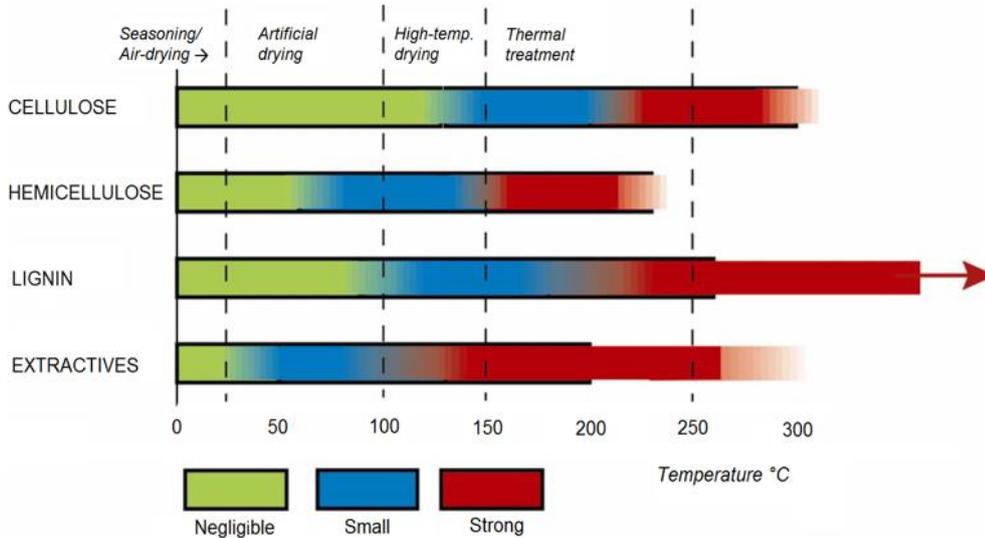


Figure 6. General changes of wood components due to thermal modification. Adapted from Sundqvist (2004).

The thermal modification of wood causes changes in the wood properties, for instance the colour darkens and density decreases. The darkened colours of various thermally modified woods are presented in Figure 7. Improved dimensional stability and decay resistance, together with reduced strength properties, are the characteristic alterations in thermally modified wood. The modulus of elasticity may increase slightly with the lightweight process parameters, but it too will decrease with the increased mass loss. A sufficient treatment time can increase the decay resistance of thermally modified wood to the same level with CCA-treated wood, which has 1 % retention (Hill 2006). The permeability of wood is increased after thermal modification (Viitaniemi and Jämsä 1996).

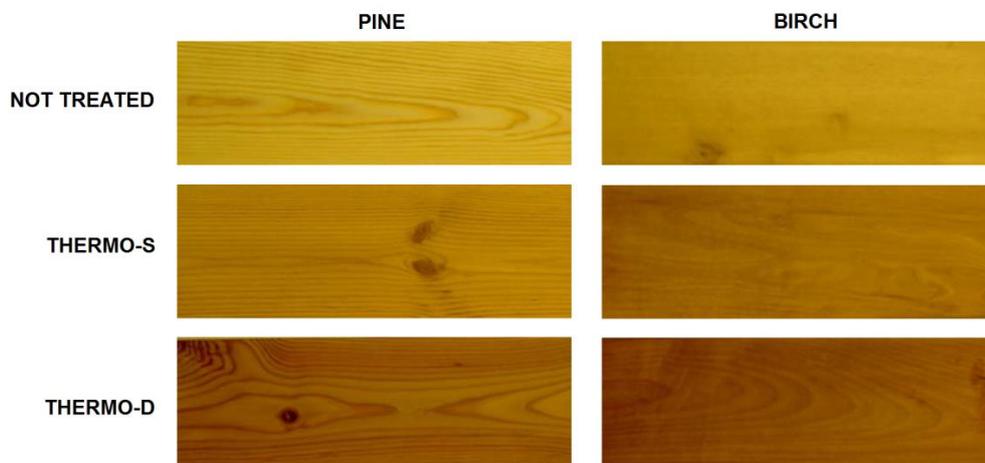


Figure 7. The effect of Thermo-wood- treatment on the colour of softwood and hardwood. The treatment temperatures for Thermo-S wood were 190 °C (softwood) and 185 °C (hardwood), and for Thermo-D wood the temperatures were 212 °C (softwood) and 200 °C (hardwood). Adapted from Puuinfo (2010).

1.3.3 Trial agents for solid wood modification

There are several possible agents for wood modification which have nontoxicity nature from the environmental perspective. In recent years, tests with some of these agents have been performed with varying success, for example resins, oils, silicon compounds, and biopolymers, just to name a few.

Various resin formulations have been studied, such as phenol formaldehyde, and urea- and melamine-based resins (Hill 2006). Melamine is used in widely applications, such as adhesives, laminates and coatings, but it is difficult to characterize by chemical methods (Crews et al. 2012). The influence of melamine formaldehyde resin on the wood has been studied. It has been detected that the lowest and the highest formaldehyde content, together with high contents of cell wall moisture and water in the resin, are favourable factors for melamine uptake (Lukowsky 2002, Gindl et al. 2003).

Oil can be used in wood modification, and also as a part of thermal treatments, which result in improved properties with increasing treatment temperature (Wang and Cooper 2005). However, the increased heating may result in slight decrease in WPG, due to the increased viscosity (Dubey et al. 2011). Tall oil may act as a protection agent for wood (Koski 2008). Crude tall oil (CTO) is composed of a mixture of fatty acids, rosin acids, and unsaponifiable matter. Total sapwood penetration needs a high amount of oil, and it tends to be exuded out from the wood (Hyvönen et al. 2006).

The term silicone means a polymeric material based on a silicon-oxygen backbone with hydrocarbon radicals combined directly with silicon. The dominant product in the silicone

market is polydimethylsiloxane (PDMS) (Owen 2007). The particle size of silicone affects its penetration into the cell wall (Mai et al. 2007). Potassium or sodium silicates or solutions thereof are known as water glass, which is produced by melting quartz sand together with sodium or potassium carbonate at temperatures of 1400-1500 °C, whereupon carbon dioxide is released. The alkaline nature of water glass may destroy the polymeric structure of wood, due to hydrolysis (Mai and Militz 2004). In addition, water glass may be polymerized from the wood acidity, and thus it is unable to penetrate into the cell wall and remains on the surface layers (Chen 2009).

Waxes are often complex mixtures, which can be classified according to various criteria. For example, the classification can be a division into two groups, natural and synthetic waxes. Natural waxes are formed by biochemical processes, whereas synthetic waxes have been modified with a chemical reaction (Wolfmeier et al. 2000). The dry content and viscosity of wax emulsions have an influence on their uptake into wood (Lesar and Humar 2011). A complete filling of wood with waxes is challenging due to the shrinkage of wax after congealing and the non-penetrability nature of the parenchyma tissue (Scholz et al. 2010a).

Citric acid is produced by fermentation of glucose- and sucrose-containing materials. It reacts with wood cellulose but not lignin, providing good adhesiveness and physical properties (Miklečić and Jirouš-Rajković 2011, Umemura and Kawai 2015). Chitosan is partially deacetylated chitin from crustacean shells, which are a by-product of the seafood refining industry. The penetration of chitosan into wood correlates with the molecular weight and concentration (Larnøy et al. 2005, Eikenes et al. 2005)

Other preliminary research with different agents has been performed, such as paraffin, extracts, or various biopolymers (Esteves et al. 2012, Tondi et al. 2013, Noël et al. 2015)

The chemical composition of the impregnator has an effect on the wood properties. For example, Ozdemir et al. (2015) noted that waterborne agents generally increased the surface roughness of wood while organic-based agents decreased it. The adhesion was also decreased with the organic-based agents but the gloss value was increased. Waterborne treatment reduces the mechanical properties of wood due to the reaction with the wood cell wall material. Some waterborne agents contain metallic oxides, which react with the cell wall components by undergoing hydrolytic reduction with wood sugar (Simsek et al. 2010).

1.4 Modified wood products

The commercial activity of the wood modification sector has taken significant steps mainly in Europe in the past decade. A few of the methods have been introduced into the market, such as acetylation, heat treatments, and furfurylation. Some modified wood products are presented in Figure 8.

Thermal modification is the most advanced wood modification method, and several processes have been commercialized in the past decades, such as Thermowood, Plato, and Retification, as noted processes. Thermowood consists of three process steps; drying, heat treatment, and cooling. It has been developed in Finland and its trade name is licensed to members of the Finnish ThermoWood Association. The Plato process is operated in the Netherlands and it involves four process stages; hydrothermolysis, drying, curing, and conditioning. The Retification process, also known as Retitech, has been introduced in France, and it is a one-step process for relatively dry wood in a nitrogen atmosphere (Hill 2006, Militz 2008). Other less known commercialized thermal modification processes are, inter alia, Perdure, Stellac, and FirmoLin (Hill 2006, Lallukka 2007, Segerholm et al. 2015). Additionally, there are a few oil heat treatment processes, such as Menz Holz, Royal, and Ecotan (Hill 2006).

Acetylated wood is available under the names of Accoya and Tricoya, whose commercial production were started in 2007 and in 2011, respectively. Accoya means the treatment of solid wood, and Tricoya is a treatment for wood-based panels (Lankveld et al. 2015). A full scale acetylation mill is located in the Netherlands, and it is able to produce 35 000 m³ of acetylated solid wood per year (Dunningham and Sargent 2015).

Commercial production based on the furfurylation process, where wood is impregnated with mixes of furfuryl alcohol, was started in Norway in 2004, titled as Kebony and VisorWood. Their annual output capacity is 20 000 m³, and cladding and decking products cover the bulk of production (Brynildsen and Bendiktsen 2009). DMDHEU (dimethyloldihydroxy-ethyleneurea) is an agent used in the textile industry, and it can increase the dimensional stability of wood and wood-based composites (Krause et al. 2008). Its commercialization was meant to be done under the name Belmadur (Jones 2007), but a full-scale production plant was never built. New commercial development with DMDHEU-modified wood is planned in New Zealand and Australia, named as HartHolz (Dunningham and Sargent 2015).

There are also some other wood modification operators globally. Sodium silicate -treated wood has been presented on the markets, called TimberSil, S-treat, and Q-treat (Flynn 2006, Pynnönen et al. 2014). The impregnation of wood with a water-soluble polysaccharide solution is known as the Indurite process. Its main target is the improvement of the wood hardness and it has been created to meet the expectations of furniture manufacturers (Hill 2006, Franich 2007). Also, a technology named Lignia has been started for furniture applications (Dunningham and Sargent 2015). Today, the trademarks of Lignia and LigniaXD are registered by Fibre7, which produces and markets resin-modified wood (Anon 2013). The exact production information of the above-mentioned operations are not readily available.



Figure 8. Modified wood products for e.g. decking. From left to right: ThermoWood, Accoya, Kebony, and Q-Treat.

2 Aims of the study

The objective of this study is to investigate the impacts of selected modification substances and methods that improve or upgrade the material properties of solid wood. The study focuses on modification substances that do not cause undue strain on the environment. Also, the overall usability of such materials is discussed, as well as the effects of treatment parameters. The best substances and methods are studied in depth. In order to understand the different effects of modification on the various properties, the work is divided into sub-categories as follows:

- 1) Study of diverse modification substances and their effects on several properties of wood (Paper I)
- 2) The impact of modification on the UV and moisture resistance behaviour of wood (Paper II)
- 3) The impact of modification on the mechanical properties of wood (Paper III)
- 4) Mechanical properties of thermally modified wood (Paper IV)
- 5) Fire performance of modified wood (Paper V)
- 6) Properties of selected modified wood products (Paper VI)

The synthesis presented here is based on the papers. The main idea of the synthesis is to describe how the potential modification substances, methods and combinations thereof, affect the functional properties of solid wood. A flowchart of the structure of the thesis is presented in Figure 9.

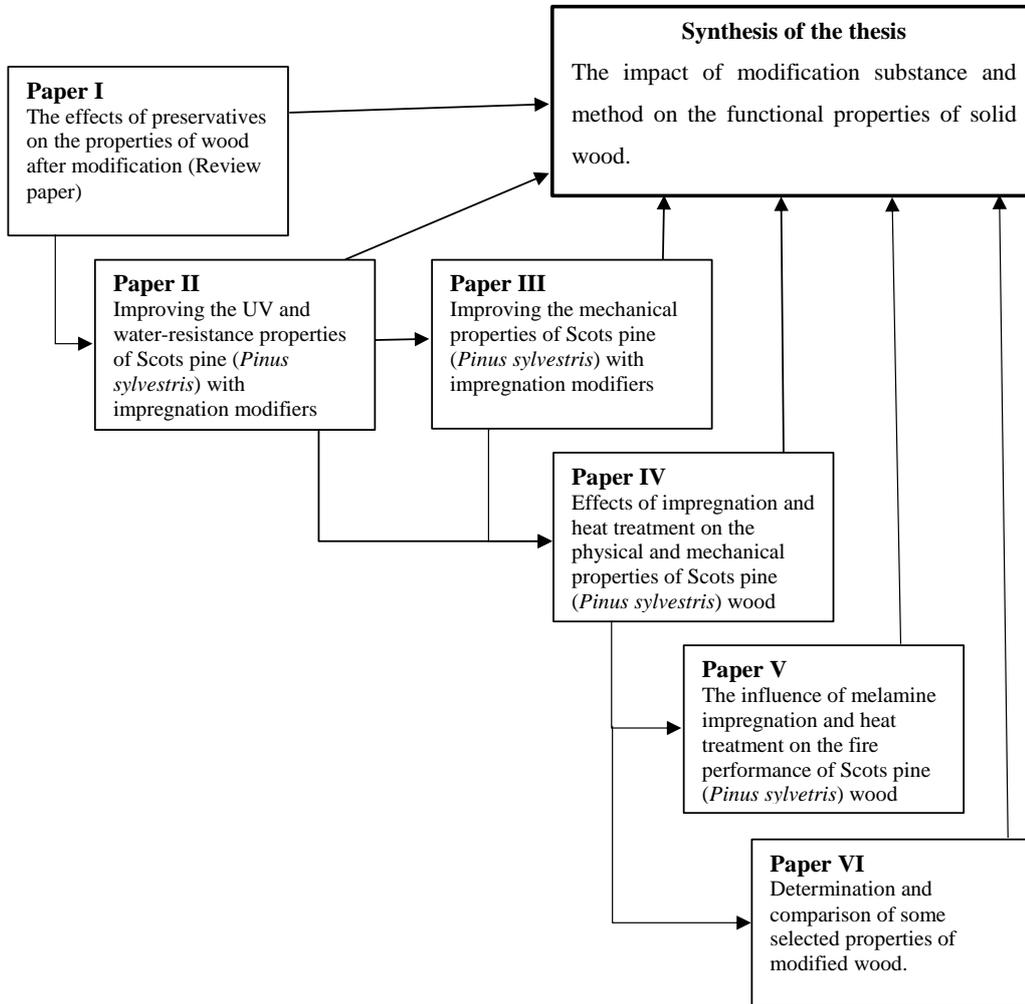


Figure 9. Structure of the thesis.

3 Materials and methods

The materials and methods of the studies included in this thesis (Papers I-VI) are presented in closer detail in each article. This chapter presents outlines of the materials and methods generally. An overview of different substances is presented first (Paper I). In the experimental part, wood samples were impregnated with the selected modifiers first, and some physical and mechanical properties were determined (Paper II, Paper III). After that, the wood samples were additionally treated with heat, and analysed by physical and mechanical tests (Paper IV). The investigation continued with the most promising results, and the fire performance was tested (Paper V), and compared with modified wood products available on the market currently (Paper VI). A General description of each article is presented in Table 2.

Table 2. Outlines of the materials and methods.

Paper	Materials	Methods
I	A review on the impact of modification substances on wood properties	Literature review
II	Scots pine, impregnation, water glass, silicone, melamine, tall oil	Determination of physical properties; WPG, SEM images, thickness swelling, water absorption, colour change
III	Scots pine, impregnation, water glass, silicone, melamine, tall oil	Determination of mechanical properties; WPG, (+SU, RSU, I.R.), bending, hardness, impact strength
IV	Scots pine, impregnation, heat treatment, water glass, silicone, melamine, tall oil	Determination of physical and mechanical properties; WPG, mass loss, swelling, water absorption, bending, impact strength
V	Scots pine, impregnation, heat treatment, melamine	Determination of fire performance properties; WPG, mass loss, heat release rate, total heat release, total smoke production, mass loss rate, residual mass
VI	Melamine (impregnated & heat-treated), acetylation, furfurylation, sodium silicate	Determination and comparison of physical and mechanical properties; colour change, swelling, water absorption, bending

Planed Scots pine (*Pinus sylvestris*) was used as research material in this study, and its features were measured before the first treatment. The density, moisture content and rate

of growth were 447.6 (kg/m³), 11.7 (%), and 2.7 (mm/a), respectively. Exceptionally, the corresponding values of Scots pine were 477.5 (kg/m³), 13.4 (%), and 3.4 (mm/a) in the fire performance study (paper V), where the research material was different. Before impregnation, the size of the sample was 20 × 95 × 1000 mm, with the exception of the fire performance test, where samples with the dimensions of 20 × 100 × 160 mm were impregnated. The research material was manufactured by impregnation with various solutions, the properties of which are presented in Table 3. As with the wood material, also the impregnation solution (melamine) was slightly different in the fire performance study, and according to the manufacturer its properties were the following: viscosity 85–100 mPas (20 °C) and pH 9.4–9.8. The commercial modified wood products were purchased from an importer and a retailer.

Table 3. Properties of the used modifiers.

	Water glass	Silicone	Melamine	Tall oil
Density (g/cm ³)	1.38*	1.00**	1.19*	0.86**
Solid content (%)	37.0	–	46.2 – 48.2	–
pH	11.2	c. 7	9.7 – 10.0	
Viscosity (mPas)	250	–	8 – 14	4 000

*at 20 °C

**relative density

The impregnation was executed without added heat, by using a registered pressure apparatus consisting of a 600 L tank with an individual treatment bin, where the treated samples were set and filled with the impregnation solution. After that, the hatch was closed and treatment was performed. Reduction of pressure and removal of unabsorbed solution were the last steps in the impregnation stage. After impregnation, the samples were dried in an oven. Part of research material was heat-treated in a heating oven without an added catalyst, at selected temperatures and times. The results of impregnation were measured by WPG and the influences of the heat treatment were determined by mass losses. The mass loss (ML) was determined according to the following equation:

$$ML(\%) = \frac{m_1 - m_2}{m_1} \times 100 \quad (3.1)$$

where m_1 is the mass before heat treatment, and m_2 is the mass after heat treatment.

WPG is a commonly reported value related to wood modification (Hill 2006), but the results can be reported also in other ways, such as relative solution uptake (RSU), which is determined as follows:

$$RSU(\%) = \frac{W_3 - W_2}{W_1} \times 100 \quad (3.2)$$

where W_1 is the oven-dry mass of the sample before impregnation, W_2 is the mass of the conditioned sample before impregnation, and W_3 is the mass of the sample after impregnation Sint et al. (2013). The equation of WPG (1.1) was presented in chapter 1.2 above.

In addition, some specimens were examined with a scanning electron microscope (SEM), Jeol JSM-5800 LV. The different processing times of the research materials and their parameters are presented in Table 4.

Table 4. Compositions of the research materials.

No.	Presented in paper	Wood	Substances	Treatment	Pressure (MPa) / [Time (min)]	Temperature (°C) / [Time (min)]
1	II, III	<i>Pinus sylvestris</i>	Water glass	Impregnation	1 / [120]	
2	II, III	<i>Pinus sylvestris</i>	Silicone	Impregnation	1 / [120]	
3	II, III, VI	<i>Pinus sylvestris</i>	Melamine	Impregnation	1 / [120]	
4	II, III	<i>Pinus sylvestris</i>	Tall oil	Impregnation	1 / [120]	
5	IV	<i>Pinus sylvestris</i>	Water glass	Impregnation Heat treatment	1 / [120]	180 & 212 °C / [180]
6	IV	<i>Pinus sylvestris</i>	Silicone	Impregnation Heat treatment	1 / [120]	180 & 212 °C / [180]
7	IV	<i>Pinus sylvestris</i>	Melamine	Impregnation Heat treatment	1 / [120]	180 & 212 °C / [180]
8	IV	<i>Pinus sylvestris</i>	Tall oil	Impregnation Heat treatment	1 / [120]	180 & 212 °C / [180]
9	V	<i>Pinus sylvestris</i>	Melamine	Impregnation Heat treatment	1 / [120 & 240]	180 & 212 °C / [180]

The moisture properties were determined by swelling and water absorption tests. The sizes of the test pieces were 20 × 50 × 50 mm (Paper II) and 20 × 20 × 30 mm (Paper IV and Paper VI). The pieces were conditioned at 20 °C and 65 % relative humidity before testing. The weights and dimensions of the pieces were measured before immersion into water for a duration of 14 (Paper II) and 28 days (Paper IV), and also during water immersion, by comparing measurement results to the initial measurements.

Discoloration was determined (Paper II and Paper VI) by measuring the surface colour with a spectrophotometer (Minolta CM-2500d, Konica Minolta Sensing Inc. Japan) during an accelerated weathering test in a test chamber (Q-Sun Xe-3 Xenon Test Chamber). The settings of the spectrophotometer were the following; reflectance SCE, illumination D65, observer 2°, and illumination area 8 mm. The accelerated weathering test was based on intervals of UV-light and water spray, according to standard SFS-EN ISO 4892-2 (2006). The colour change was measured according to the CIELAB system, which is a three-dimensional colour space with L^* , a^* , and b^* coordinates. L^* represents the lightness from white ($L^* = 100$) to black ($L^* = 0$), a^* represents red ($+a^*$) to green (-

a^*), and b^* represents yellow ($+b^*$) to blue ($-b^*$). On the basis of the $L^*a^*b^*$ -coordinates, the colour difference (ΔE^*) is defined by the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (3.1)$$

where: ΔL^* , Δa^* , and Δb^* illustrate the differences between the initial and measured values of L^* , a^* , and b^* , individually.

The mechanical properties were determined by bending (Paper III, Paper IV, and Paper VI), hardness (Paper III), and impact strength (Paper III and Paper IV) tests. The three-point bending and hardness tests were performed with a testing machine (Zwick Roell Z020) according to standards ISO 3133 and SFS-EN 1534, respectively. The size of the specimens for the bending test was $20 \times 20 \times 380$ mm and for the hardness test $20 \times 50 \times 100$ mm. The impact strength was determined with an impact tester (Zwick 5102) in accordance with EN ISO 179. The size of the impact strength test specimens was $4 \times 10 \times 80$ mm.

Fire performance (Paper V) was tested according to standard ISO 5660-1 with a cone calorimeter device (Fire Testing Technology). The size of the test pieces was $20 \times 100 \times 100$ mm and the directions of annual rings were vertically close to 90 degrees. The test pieces were wrapped in aluminium foil covering the sides and the bottom. The specimens were exposed in the horizontal orientation to an external heat flux of 50 kW/m^2 with a cone heater located 25 mm above the specimen. Prior testing, the pieces were conditioned at $23 \text{ }^\circ\text{C}$ and 50 % relative humidity. The cone data presented here are the averages of three replicated experiments. During the test, the heat release rate (HRR), total heat release rate (THR), total smoke production (TSP), average specific mass loss rate (MLR), and residual mass were obtained. The cone calorimeter includes also a simulation software, which can predict the fire performance class.

4 Review on the results and discussion

A brief description of the work and the findings of the individual articles are presented in the following. The sections are named according to the sense and purpose the articles are referred to in this work. More detailed information is presented in each article.

4.1 Properties of the modification substance

Paper I presents the effects and features of the modification agent on the various properties of wood material, as a literature review with no practical experiments included. The effects of the agents are classified into different categories.

Mechanical properties are one of the properties studied in wood material. The mechanical properties can change significantly as a result of treatment, as for example hardness, but on the other hand, the change may be a quite neutral, such as the bending strength (Esteves et al. 2011). The critical factors of the modification agent related to wood strength are, inter alia, aqueous, metallic oxides, and pH. An aqueous solution increases the rate of hydrolysis in the wood, causing a loss of strength. In addition, the metallic oxides used in the aqueous solution react with the wood cell wall components by undergoing reduction in contact with wood sugars. This is also known as fixation that reduces wood strength (Simsek et al. 2010). Fire-retardant treatment has been shown to reduce the strength of wood by 10-20 percent. Especially, elevated temperatures and a low pH of the agent contribute to a decrease of strength (Nurmi et al. 2010).

An effective modification method for wood is chemical modification, which improves weathering and moisture resistance. For example, chemical modification restricts lignin degradation to some extent (Pandey et al. 2010) and blocks the hydroxyl (OH) groups in wood (Hill 2006). The wood components are cross-linked with a double bond with the modification solution after chemical modification, which decreases the water absorption of wood (Devi and Maji 2012). The particle size of the emulsion has significance in wood impregnation because small particles cover only the inner surface of tracheids, which does not give the best possible protection (Ghosh et al. 2009).

A lower moisture content also contributes to the biological resistance of wood, which is the traditional studied property. Resins with low molecular weights have been shown to penetrate into the cell walls, contributing to the enhancement of decay resistance (Furuno et al. 2004). Many agents need a combination with another compound to give effective resistance against decay. Unexpectedly, the fire resistance of wood has received minor attention in the wood modification field.

4.2 The effect of treatment on wood

In **Paper II** and **III**, the wood samples were impregnated, and the result of the modification was studied by WPG, which is a commonly reported value related to wood

modification (Hill 2006). In addition to WPG, the modification figures can be reported in other ways, for example by RSU. In **Paper IV**, heat treatment at two temperatures was added as a part of the study. The effect of heat treatment was determined by mass loss measurements.

The impregnation results are presented in Table 5. The WPG results show that the melamine samples have impregnated best. The uptake results, like RSU, show that the high water content of the impregnation solution may result in a weak WPG. For example, silicone- and melamine-impregnated wood have nearly the same values in the RSU results, but in the WPG, the results are different. The melamine- and tall oil –impregnated samples have minor relative evaporation in the RSU and the WPG compared to the results of the water glass- and silicone-impregnated wood. Due to the heterogeneous nature of the wood material, the standard deviations of the results are remarkably high. The results of the analysis show that an uptake test is needed to give more information in addition to WPG.

Table 5. Average WPG and RSU, together with standard deviations (SD).

	Water glass	Silicone	Melamine	Tall oil
WPG	2.76 (6.24)	6.85 (8.72)	38.71 (24.68)	7.28 (5.29)
RSU	20.01 (13.21)	67.69 (36.40)	76.57 (47.55)	11.42 (6.03)

(Values in parentheses indicate SDs)

The results show that parts of the wood were penetrated differently, for example, the impregnation solution penetrated better into sapwood compared to heartwood. The impregnation of heartwood is challenging due to pit aspiration and a high content of extractives (Kärkkäinen 2007; Olsson et al. 2001). Generally, the uptake of the impregnation solution is better in the longitudinal direction than in the transverse directions due to the longitudinal positions of transport cells (Larnøy et al. 2005). The comparison of transverse directions shows deeper penetration in the radial direction than in the tangential direction due to, inter alia, the ray tracheids of pine (Scholz et al. 2010b). Penetration depends also on the wood parts. For example, the permeability of late wood is higher than that of early wood, due to the rigid and thicker margo of late wood pits, which do not close in the natural drying of wood (Kärkkäinen 2007).

In addition to wood properties, the features of the treatment solution and the parameters have an effect on the results. The uptake of the impregnation solution increases with increasing pressure and time (Larnøy et al. 2005). However, the treatment solution may be strongly alkaline at elevated temperatures and pressures, and it can polymerize from wood acidity and be unable to penetrate into the cell wall layers. This phenomenon has been perceived in treatment of wood with water glass (Mai and Miltz 2004, Chen 2009). It has been noted previously that a sufficiently small molecular size of the solution is needed to allow penetration of the cell wall. In addition, the molecules should be soluble in polar solvents, and exhibit sufficient polarity (Hill 2006). Studies have shown that the

viscosity of the impregnation solution affects the uptake of a solution in pine wood (Tondi et al. 2013). Higher viscosity results in a weaker uptake (Larnøy et al. 2005).

The effects of heat treatment are presented in Table 6 by mass loss. The mass loss results show that the higher temperature causes greater mass loss, which is in agreement with previous studies (Welzbacher et al. 2007; Metsä-Kortelainen and Viitanen 2010).

Table 6. Average mass loss and standard deviations (SD).

	Reference	Water glass	Silicone	Melamine	Tall oil
180 °C	7.49 (0.78)	8.20 (0.93)	7.21 (0.48)	8.14 (0.54)	7.33 (0.53)
212 °C	10.24 (1.00)	13.00 (1.63)	10.44 (0.78)	11.00 (0.80)	11.01 (1.67)

(Values in parentheses indicate SDs)

In Papers II and IV, modified sapwood specimens were examined with a scanning electron microscope (SEM), Jeol JSM-5800 LV. The effects of heat treatment were detectable in SEM micrographs (Paper IV). For example, water glass-impregnated samples which were heat-treated at higher temperatures had visible cracks. Other findings from the SEM graphs were the melting of melamine into the wood and the boiling of tall oil after heat treatment at higher temperatures.

4.3 The effect of impregnation on the functional properties of solid wood

In Papers II and III, the effects of impregnation on the functional properties of solid wood were examined by performing water absorption, weathering, and some mechanical property tests. The effect of impregnation on the fire performance of wood is presented in Paper V.

4.3.1 Moisture resistance properties

The water absorption of the melamine-impregnated wood decreased clearly compared to the control wood, and that curve which describes its absorption is the lowest the all. Also, the silicone-impregnated wood absorbed less water than the control wood throughout the test, and especially in a short period. Tall oil and water glass impregnation had a negative effect on the moisture compared to the control. Figure 10 shows the water absorption of the impregnated wood as a point chart, in which a trend line has been added between the points by using a two-period moving average.

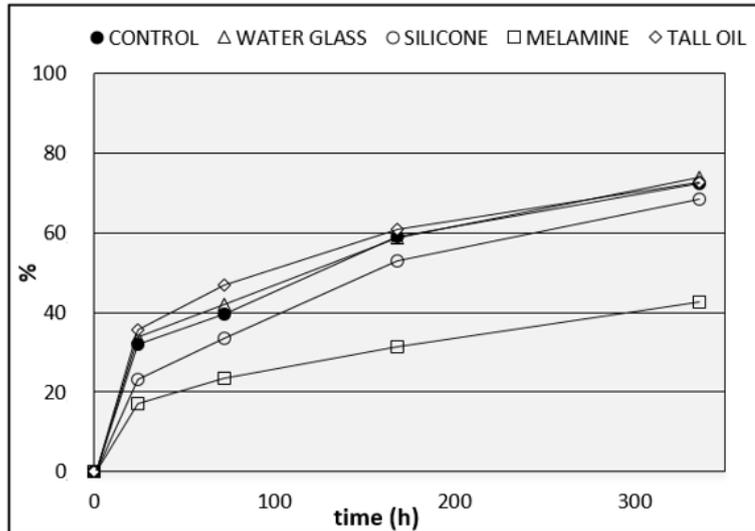


Figure 10. Water absorption as a function of immersion time of impregnated materials.

This study demonstrated that the melamine-impregnated wood had stable and smooth faces after water immersion. Similar results relating to the moisture behaviour of melamine have been achieved previously with wood and a wood-plastic composite (Shukla and Kamdem 2010, Butylina et al. 2011). Although the tall oil -impregnated wood does not have favourable properties with moisture, a previous study has shown that it can restrain the penetration of water into wood (Koski 2008). The moisture behaviour of water glass -impregnated wood will require more study because it is a water-soluble solution that leaches away during water immersion.

4.3.2 Weathering properties

Table 7 presents the weathering performance of impregnated wood after artificial weathering. The colour change of the silicone-impregnated wood is linear with time, which is different compared to the other wood samples within the test period. After the exposure of 200 h, the colour change values are similar, with the exception of the water glass -impregnated wood, the colour change of which differs clearly from the other wood samples.

Table 7. Total colour change (ΔE) of impregnated materials in artificial weathering for 100, 200, and 300 hours.

Sample	100 h	200 h	300 h
Control	9.47 (2.48)	11.14 (1.84)	10.95 (3.54)
Water glass	19.54 (4.83)	25.15 (4.38)	26.14 (6.32)
Silicone	6.53 (1.63)	11.02 (1.27)	14.59 (1.68)
Melamine	9.73 (3.08)	8.99 (1.99)	8.23 (1.38)
Tall oil	12.14 (7.76)	10.08 (4.21)	10.72 (4.53)

(Values in parentheses indicate SDs)

Different parts of wood behave differently in weathering exposure. Kataoka et al. (2005) have found that the photodegradation of wood depends on wood density and consequently, for example earlywood erodes more rapidly than the denser latewood. In addition to higher density, latewood is more resistant to UV radiation due to its lower lignin content (Turkulin and Sell 2002). The general change of wood colour is the change towards grey (Kärkkäinen 2007). A study of Müller and Steiner (2010) indicates that melamine impregnation reduces lignin degradation and the greying of wood.

4.3.3 Mechanical properties

In Paper III, the mechanical properties of impregnated wood were presented. The investigated mechanical properties included Brinell hardness, bending strength, and impact strength. The strength properties of wood are unique.

Hardness properties

Due to the soft nature of wood material, determining the hardness may require changes in the measurements (Esteves et al. 2014), but Brinell hardness is a reliable and widely used method in Europe to measure the hardness of wood (Heräjärvi 2004). The hardness of the impregnated wood specimen is shown in Figure 11. The melamine-impregnated wood has the highest hardness and its sapwood hardness is higher than the hardness of heartwood, which is an inverse phenomenon compared to the control wood, for example. Water glass and tall oil -impregnation have stabilized the hardness of wood the between sapwood and heartwood. The standard deviations of the hardness results are quite high.

The properties of native wood affect the hardness of the wood. For example, hardness is greater in the tangential direction versus the radial direction, as well as hardwood versus softwood, and latewood versus earlywood (Kurt and Özçifçi 2009, Grekin and Verkasalo 2013). Studies have indicated that the hardness of wood is increased by impregnation. The increase of hardness is proportional to the weight gain (Esteves et al. 2014), and it

may be caused by increased density (Atar et al. 2011). Gindl et al. (2004) have noted that melamine can alter the hardness of softwood to same level with the hardness of hardwood, but 2 mm is a minimum penetration depth to achieve an increase in hardness.

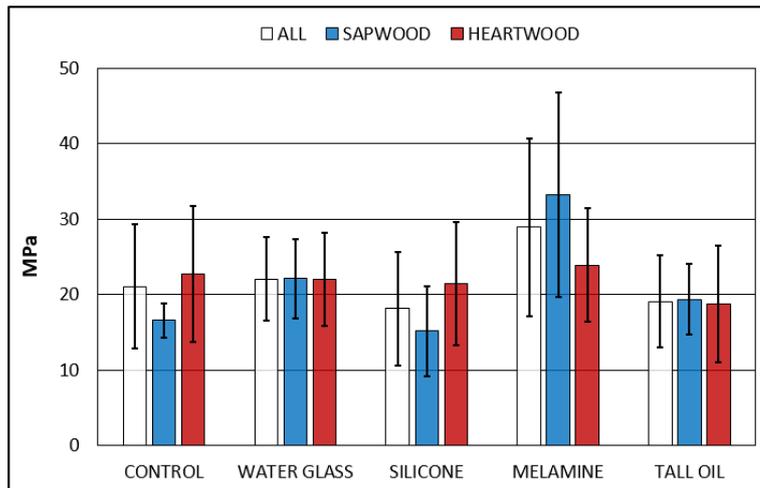


Figure 11. Hardness of impregnated materials, presented separately for all, sapwood and heartwood samples. The error bars indicate SDs.

Bending strength

Bending strength is the most commonly used property because it corresponds to the strength that is required in many practical applications. Hardness is a property that measures the penetration force of a solid piece into wood. Impact strength measures the effect of a short-term load (Kärkkäinen 2007). The bending strength of wood decreased when impregnation was added as a part of treatment (Figure 12). At worst, the bending strength decreased by over 20 % compared to the unimpregnated control wood. The differences were rather insignificant between the sapwood and heartwood samples.

Previous studies have reported that impregnation can be able to increase the bending strength of wood (Esteves et al. 2011, Esteves et al. 2014). According to Kielmann et al. (2013), the WPG plays in a minor role in bending strength. However, the features of wood, like density and species influence the bending strength (Shi et al. 2007, Kielmann et al. 2013).

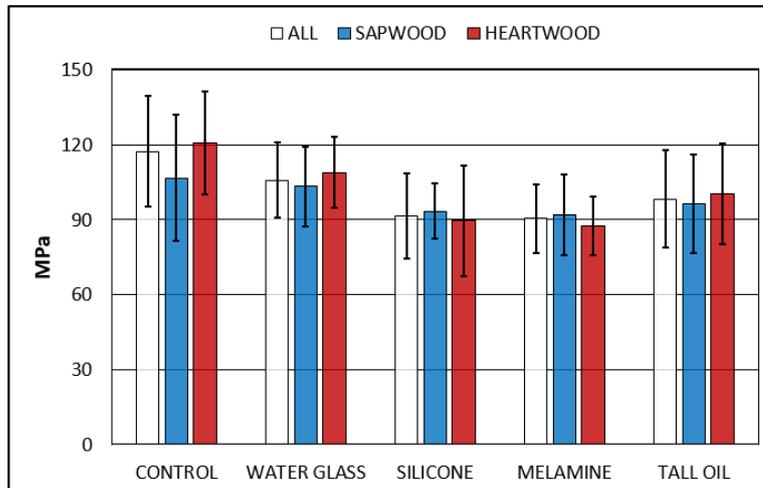


Figure 12. Bending strength of impregnated materials, presented separately for all, sapwood and heartwood samples. The error bars indicate SDs.

Impact strength

The impact strength, which had a shorter loading time than in the other mechanical tests, was decreased significantly when the impregnation was successful. For example, the impregnation of wood with melamine decreased the impact strength by almost 50 % compared to the control wood. The standard deviations of the impact strength were quite high. The impact strengths of the impregnated wood are shown in Figure 13.

Kärkkäinen (2003) has stated that impact bending strength is sensitive for changes of wood. Modified wood is fragile because the mobility of the cell wall components is decreased (Dieste et al. 2008). Epmeier et al. (2004) found that the impact strength of modified wood correlated negatively with dimensional stability. The treatment of wood with melamine decreased the impact strength because cured resin is rigid and brittle in the wood structure (Kielmann et al. 2013).

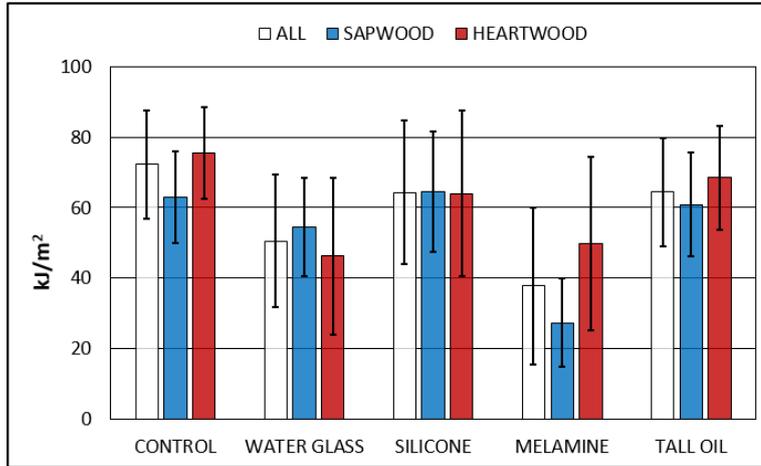


Figure 13. Impact strength of impregnated materials, presented separately for all, sapwood and heartwood samples. The error bars indicate SDs.

4.3.4 Fire performance

Some traditional fire-retardant chemicals contain elements which may produce unwanted secondary side effects on the wood, for example the degradation of wood strength (LeVan and Winandy 1990). It has not been found that melamine would have a similar negative impact on wood. Melamine has been used as a flame-retardant additive in other applications, but the fire performance of melamine-treated solid wood has not been studied thoroughly, and therefore it was studied here.

In the evaluation of fire performance, the heat release rates and mass loss rates of the impregnated wood were studied. The heat release rates of the wood are presented in Figure 14. Due to the high standard deviations of the different time periods of impregnation, the samples have been classified two groups, 10 and 20 WPGs, according to the target WPGs. The curve of heat release rate usually consists of two peaks (Schartel and Hull 2007). The first peak describes the commencement of combustion when oxygen and volatile gases are formed under the influence of heating. After the first peak, an insulating char layer is formed and heat transfer becomes more difficult. The second peak at the end is caused by decomposition of the char layer, and volatile gases escape through small cracks (Marney et al. 2008).

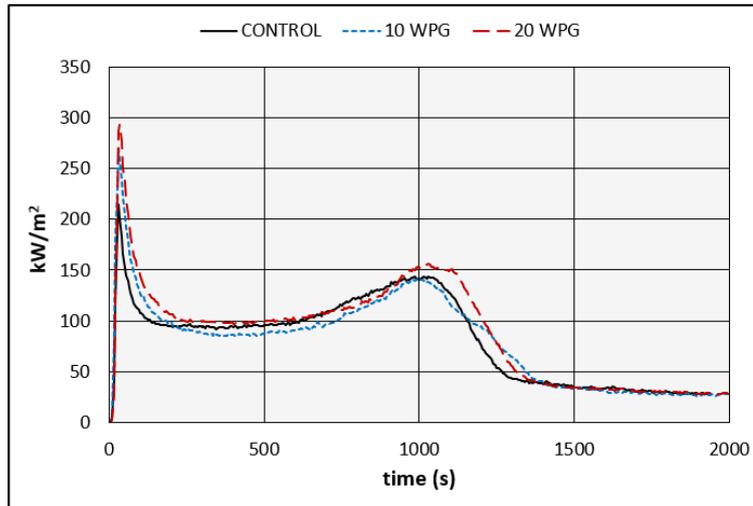


Figure 14. Heat release rate curves of the control and different impregnation levels versus time.

Melamine impregnation did not cause a significant difference in the HRR curve compared to the control wood, with the exception of the first peak. The first peak in the HRR was higher for the melamine-impregnated wood but the second peak was equal to the control wood. The analyses indicated that the mean HRR values of the control and melamine-impregnated wood correlated positively with mass. The residual masses of wood after the fire performance test are presented in Table 8. Melamine impregnation did not change the residual mass percentages significantly compared to the control wood.

Table 8. Residual masses and mass loss percentages of the tested materials.

Target / Real WPG	Original mass (g)	Residual mass (g)	Percentage of original mass (%)
0	103.90 (8.58)	11.75 (0.53)	11.38 (1.26)
10 / 11.93	114.32 (10.26)	14.74 (3.32)	13.14 (4.12)
20 / 20.49	114.69 (7.62)	13.05 (0.25)	11.40 (0.69)

(Values in parentheses indicate SDs)

4.4 The effect of impregnation and heat treatment on the functional properties of solid wood

In **Paper IV**, the effects of heat treatment after impregnation on the properties of solid wood are reported after performing swelling, water absorption, and mechanical properties tests. Weathering tests of selected impregnated and heat-treated wood were performed in the studies presented in **Papers II** and **VI**. The effect of impregnation and heat treatment on the fire performance of wood was presented in **Paper V**. The heat treatment was performed at the temperatures of 180 °C and 212 °C for three hours.

4.4.1 Moisture resistance properties

The water absorption of impregnated and heat-treated wood are presented in Figure 15 as a point chart, in which a trend line has been added between the points. The results are presented separately at different temperatures, and untreated wood as a control result has been added into both results. It was found that a higher heat-treatment temperature reduced water absorption, especially at the beginning of the test. The water glass-impregnated and heat-treated wood absorbed more water than the control wood at the beginning of the test, and more than merely heat-treated wood (reference) throughout the test. At lower heat treatment temperatures, the tall oil-impregnated wood absorbed water similarly with merely heat-treated wood, but at higher temperatures it had less absorption. Melamine impregnation and heat treatment affected the water absorption of the wood notably. At both treatment temperatures, the melamine-impregnated and heat-treated wood absorbed less water than any other tested wood material. Silicone treatment restrained water absorption, particularly at the beginning of the test.

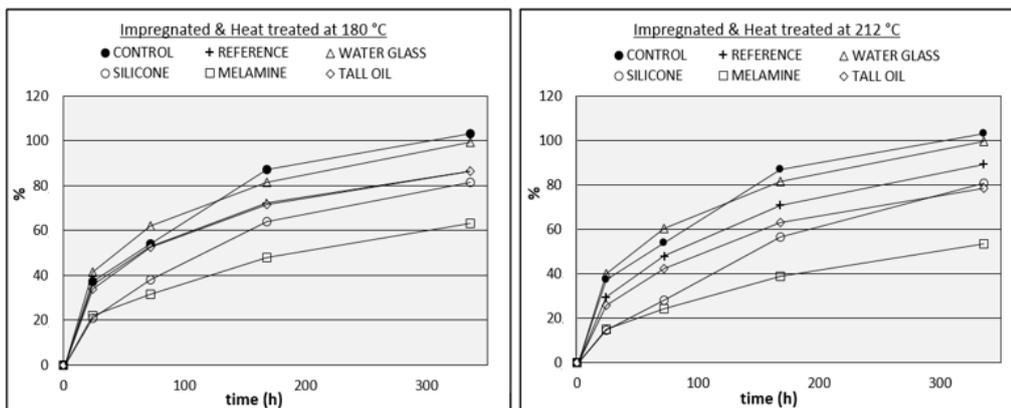


Figure 15. Water absorption as a function of immersion time of impregnated and heat-treated materials.

The swelling of the impregnated and heat-treated wood is presented in Figure 16 as a bar chart for the tangential and radial directions. It can be seen that the higher heat treatment temperature has decreased the swelling. All impregnated and heat-treated wood have swelled less than the untreated control wood, and also less than merely heat-treated wood at the lower temperatures. The results indicate that mass loss is related to the moisture properties. The results of swelling showed somewhat surprisingly, that the melamine-treated wood swelled the most in the radial direction. Tangential swelling is usually twice that of radial swelling in untreated and heat-treated wood (Rowell 2013a, Korkut and Bektaş 2008). The melamine-impregnated and heat-treated wood has a minor swelling ratio between the tangential and radial directions.

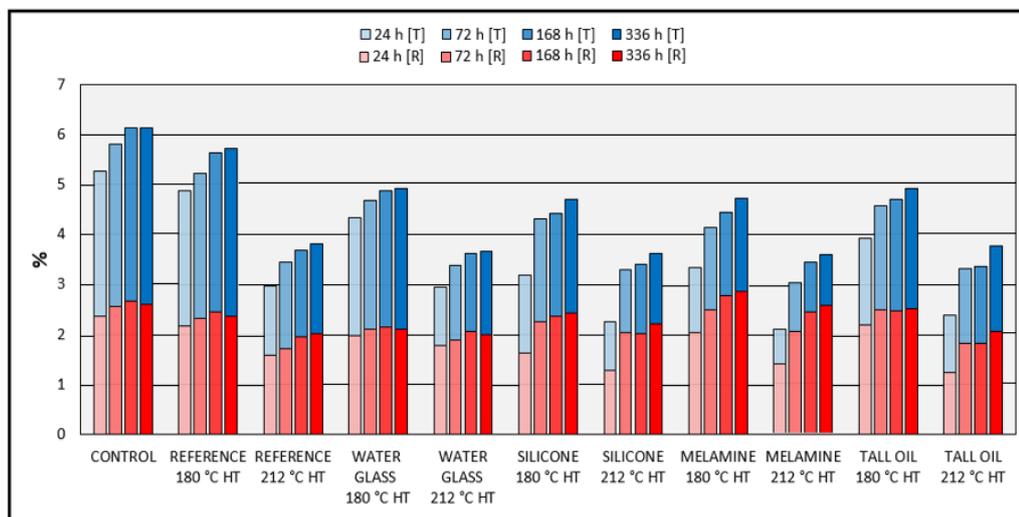


Figure 16. Tangential and radial swelling of impregnated and heat-treated materials with time (HT=heat treated, T=tangential, R=radial)

The impact of heat treatment temperature was as expected because thermal modification of wood is known to reduce hygroscopicity (Hill et al. 2012) and thus improve dimensional stability (Korkut and Bektaş 2008). The decreased hygroscopicity of heat-treated wood is due to the reduced amount of hydroxyl groups and the degraded hemicellulose, which is the hydrophilic component in the wood cell wall (Gündüz et al. 2008, Walker 2006a). Also, the relative proportion of crystalline cellulose and the new linkages of lignin may restrain the accessibility of water and hydroxyl groups (Boonstra et al. 2007). The heat treatment temperatures have an effect on the moisture properties of softwood (Metsä-Kortelainen et al. 2006). It has been found that at a low heat-treatment temperatures, the extractives move onto the edges of pine sapwood, which is not detected at higher temperatures (Nuopponen et al. 2003). The migration of extractives mentioned above may have an effect on the wettability of Scots pine wood (Metsä-Kortelainen and Viitanen 2012).

4.4.2 Weathering properties

In Paper II, the effects of artificial weathering on the properties of impregnated wood were explored. A similar study for impregnated and heat-treated wood was done in Paper VI. The weathering performance results have been collected to Table 9. The exposure in artificial weathering for 300 hours resulted in similar colour change with the melamine-impregnated wood and the untreated control wood. However, the heat treatment of the melamine-impregnated wood influenced the colour change significantly, especially the treatment temperature. The wood treated at the lower treatment temperature had the lowest changes of colour and restrained standard deviations, while at the higher temperature, the colour was changed more intensively.

Table 9. The effect of heat treatment on the total colour change (ΔE) of the treated materials in artificial weathering for the 100, 200, and 300 hours.

Sample	100 h	200 h	300 h
Control	9.47 (2.48)	11.14 (1.84)	10.95 (3.54)
Melamine	9.73 (3.08)	8.99 (1.99)	8.23 (1.38)
Melamine 180 °C HT	2.39 (0.89)	3.58 (2.16)	6.29 (3.35)
Melamine 212 °C HT	13.79 (7.29)	19.96 (9.92)	23.76 (9.59)

(Values in parentheses indicate SDs)

The leaching of lignin and extractives cause greying of wood (Evans 2013), which is a typical phenomenon for wood in weather exposure, but treatment with melamine can reduce discoloration and retain the natural appearance of wood (Hansmann et al. 2006). The colour differences in the heat-treated wood are congruent with previous knowledge, as it has been stated that the darkness of thermally modified wood increases with the increasing temperature (Thermowood 2003). However, the colour of thermally modified wood turns grey relatively quickly at weather exposure (Jämsä et al. 2000). Tangential colour change is more powerful than radial (Huang et al. 2012), which is in agreement with the colour change of melamine-impregnated and heat-treated wood.

4.4.3 Mechanical properties

In Paper IV, the mechanical properties of impregnated and heat-treated wood were examined. The investigated mechanical properties included bending strength and impact strength tests, which are presented in Figures 17 and 18 as bar charts with standard deviations added as error bars. In addition, polynomial trend lines have been added to the figure.

Bending strength

The bending strength of the wood decreased after all treatments (Figure 17), and the increased treatment temperature usually decreases the strength more intensively. However, improved bending strength of impregnated wood was observed after heat treatment. The melamine-impregnated and at 180 °C heat-treated wood had 10 % better bending strength compared to the merely heat-treated wood at the same temperature. Additionally, the bending strength of melamine-impregnated wood increased even more compared to the corresponding wood which was not impregnated but heat-treated at the same higher temperature (212 °C). Also, silicone and tall oil -impregnated wood had almost 10 % better bending strength than the merely heat-treated wood after heat treatment at 212 °C.

The treatment conditions have an influence on the bending strength of heat-treated wood, for example the species, treatment time, and temperature (Shi et al. 2007, Rowell et al. 2009, Kocaefe et al. 2010). A slight increase in the bending strength was noticed after low treatment temperatures, which may have been due to the reduced moisture content (Zhang et al. 2013). The favourable effect of melamine and heat treatment on the bending strength of wood was observed also in the study of Sun et al. (2013). In the study of Deka and Saikia (2000) it is indicated that thermosetting resins increase the bending strength by 12-20 % when the WPG is over thirty.

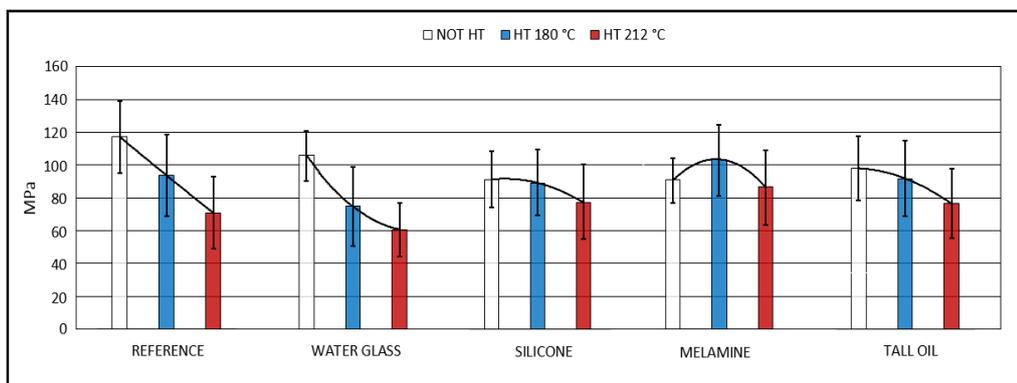


Figure 17. Bending strength of impregnated and heat-treated materials. The error bars indicate SDs.

Impact strength

As stated above (in 4.3.3 Mechanical properties), the impact strength of wood was decreased by successful impregnation, and heat treatment had a parallel effect. The impact strength was impaired with the increasing treatment temperature, as can be seen in Figure 18. In a previous study (Boonstra et al. 2007), congruent results were observed in impact strength with the values presented in Figure 18 after heat treatment. The lower heat treatment temperature for the melamine-impregnated wood can be able to maintain the same level of impact strength as the merely melamine-impregnated wood. A conspicuous fact in the results is the remarkably high standard deviation.

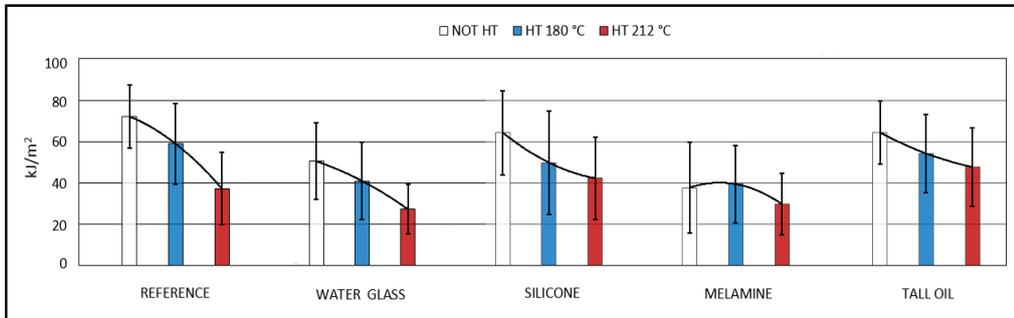


Figure 18. Impact strength of impregnated and heat-treated materials. The error bars indicate SDs.

The degradation of hemicellulose causes strength loss in wood (Sweet and Winandy 1999) and in heat-treated wood (Rowell et al. 2009). It has been found that hemicellulose degradation is responsible for the decrease of impact and bending strength (Boonstra et al. 2007, Weigl et al. 2012). The loss of hemicelluloses increases the crystalline part in the wood material and replaces the flexible hemicellulose-cellulose-hemicellulose bond with a more rigid cellulose-cellulose bond. These alterations have an effect on the changed mechanical properties (Boonstra et al. 2007, Kocaefe et al. 2008).

4.4.4 Fire performance

The fire performance of heat-treated wood has been reported to be equal with that of untreated wood (ThermoWood 2003), but differences between wood species have been noticed (Müllerová 2013). The heat release rates and mass loss rates were studied to evaluate the fire performance of impregnated and heat-treated wood. The HRR results are presented as a scatter chart with lines in Figure 19. Even though the mere melamine impregnation did not cause significant changes in the HRR (see 4.3.4 Fire performance), the impact of heat treatment can be seen in the results. The HRR values of the mere heat treated wood decreased, but melamine impregnation before the heat treatment was able to raise the HRR values to a higher level, especially in the case of higher heat treatment temperatures. A second peak value of HRR was brought forward as a result of the treatments.

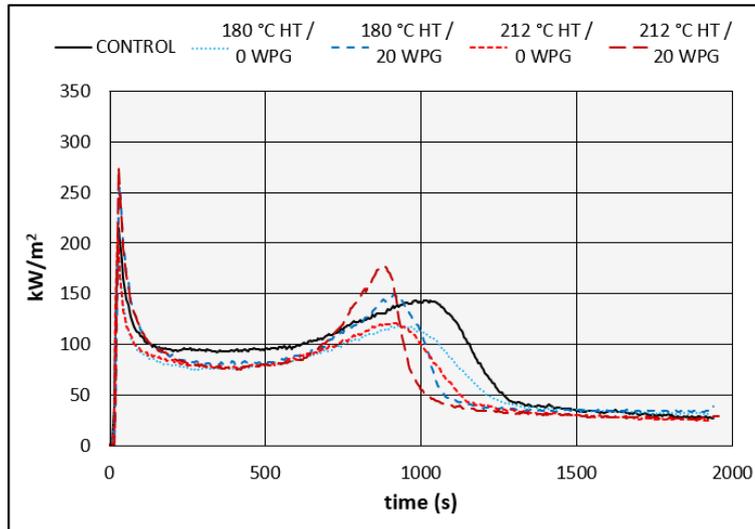


Figure 19. Heat release rate curves of control and different treatment levels versus time.

The residual masses of impregnated and heat-treated wood after the fire test are presented in Table 10. The combination of melamine impregnation and heat treatment caused bigger residual mass percentages compared to the untreated and merely heat-treated wood. In addition to the results presented in Figure 19 and Table 10, it must be mentioned that there was reduced smoke production in the heat-treated wood during the fire test. The total smoke production (TSP) of the heat-treated wood was decreased, by at least over 60 per cent. The melamine-impregnated and heat-treated wood had even higher TSP reduction after heat treatment. Smoke production is an important factor for evaluating a fire hazard (Lee et al. 2011), and it may be a critical problem with a fire retardant (Rowell and Dietenberger 2013). Therefore, the reduced smoke production of the heat-treated wood can be considered an improved feature.

Table 10. Residual masses and mass loss percentages of the tested materials

Heat treatment (°C) / Target WPG	Original mass (g)	Residual mass (g)	Percentage of original mass (%)
- / 0	103.90 (8.58)	11.75 (0.53)	11.38 (1.26)
180 / 0	84.56 (2.03)	8.72 (1.97)	10.28 (2.08)
180 / 20	103.03 (1.65)	16.61 (1.71)	16.10 (1.41)
212 / 0	79.84 (2.66)	7.52 (1.16)	9.40 (1.23)
212 / 20	100.93 (0.63)	18.40 (1.35)	18.23 (1.22)

(Values in parentheses indicate SDs)

4.5 Properties of treated wood compared with commercial modified wood products

The main aim in **Paper VI** was to compare the properties of modified wood products. Three commercial modified wood products from different manufacturers were chosen, and their water absorption, swelling, colour change, and bending strength were analysed. In addition to the commercial products, in-house manufactured modified wood products were used as contenders. The commercial modified wood products were selected on the basis of treatment with a modifier agent, and on the utilization of thermal modification. In the test circumstances, the treatment of the commercial products corresponded to the treatment of the contenders. The commercial modified wood products were acetylated, furfurylated, and sodium silicate -impregnated wood. The contender specimens were impregnated with melamine and heat-treated at the temperatures of 180 °C and 212 °C.

4.5.1 Moisture properties

As Thygesen and Elder (2008) have stated, moisture has an influence on many properties of wood, like the dimensions and mechanical and biological properties. Due to this, moisture is an important property and it needs to be investigated. The water absorption of the modified woods is presented in Figure 20 as a point chart with trend lines. It can be seen that the sodium silicate -impregnated wood absorbed the most water during the test period. At the beginning of the test, the amount of water absorption varied between the different modified woods, but after the immersion time of a few hundred seconds, the water absorption was quite similar for most of the samples, except for sodium silicate wood. The melamine-impregnated wood, which was heat-treated at the higher temperature, absorbed the least water.

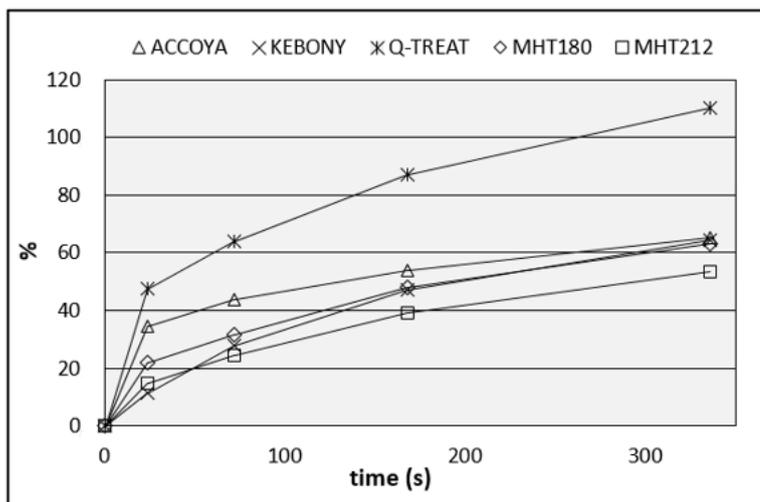


Figure 20. Water absorption as a function of immersion time.

The swelling of the modified wood is presented as a bar chart in Figure 21, for tangential and radial directions. The swelling increased with the progressing immersion time, but already successfully modified wood products, for example acetylated and furfurylated wood, had very restrained swelling immediately in the beginning of the test.

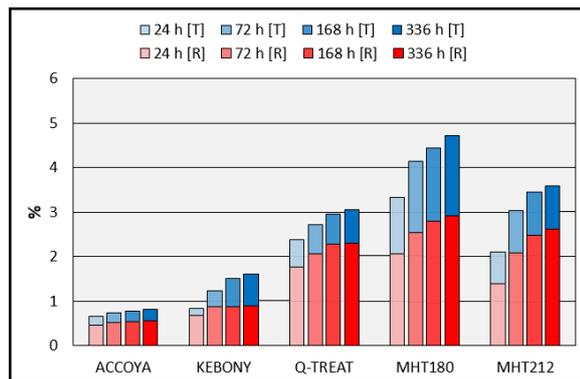


Figure 21. Tangential and radial swelling with time (T=tangential, R=radial).

The results presented in Figures 20 and 21 show that the method of wood modification has an effect on the moisture properties of wood. It has been reported that the successful methods, acetylation and furfurylation, make the cell walls of wood more hydrophobic, and thus water in the lumens becomes freer (Thygesen and Elder 2008). Ageing increases the hydrophobicity for unmodified wood, due to the migration of extractives and reorientation of functional groups, which may be possible for heat-treated and furfurylated wood, according to Bryne (2008). The unfavourable moisture properties of water glass -treated wood indicate in turn that the hygroscopic solution has not reacted with the wood material (Pfeffer et al. 2011). Generally, the tangential swelling of wood is twice compared to swelling in the radial direction (Rowell 2013a), but in modified wood this phenomenon is almost reverse.

4.5.2 Weathering

The weathering properties of the modified wood products are presented in Table 11. The properties were measured after 24 and 48 hours, and after that every hundred hours. The results are presented in Table 11 spaced from 200 hours forward. The weathering property varied depending on the product and review timing. Low heat-treated melamine-impregnated wood and sodium silicate-impregnated wood had the most restrained colour change at the beginning of the test. The colour change of the low heat-treated melamine wood was almost stable until about halfway of the test period. The colour change of acetylated wood was the greatest at the start but its colour altered the least from 24 hours to 1000 hours. The colour of furfurylated and high heat-treated melamine wood altered the most in the end of the test. The analysis of colour space indicated that in every type of modified wood, colour had a tendency to become lighter, bluer, and greener when the exposure proceeded.

Table 11. Total colour change (ΔE) in artificial exposure for 1000 hours.

Sample	24 h	48 h	100 h	200 h	400 h	600 h	800 h	1000 h
Melamine 180 °C HT	2.89 (1.05)	2.90 (0.93)	2.39 (0.89)	3.58 (2.16)	8.82 (3.86)	15.66 (3.67)	19.52 (2.52)	22.47 (2.39)
Melamine 212 °C HT	7.13 (4.43)	9.63 (5.11)	13.79 (7.29)	19.96 (9.92)	26.62 (8.32)	32.11 (6.63)	35.81 (5.07)	37.99 (4.69)
Q-Treat	2.15 (1.23)	3.51 (1.61)	5.23 (1.49)	8.48 (2.22)	12.45 (1.76)	16.22 (2.65)	18.60 (3.54)	20.38 (1.81)
Accoya	15.29 (1.44)	17.50 (1.72)	19.90 (1.75)	21.57 (1.88)	24.40 (2.02)	26.39 (1.98)	27.30 (2.02)	27.99 (2.14)
Kebony	7.75 (0.80)	9.59 (2.00)	14.61 (2.98)	22.80 (4.24)	31.86 (4.01)	38.54 (4.17)	41.27 (4.32)	44.45 (4.06)

(Values in parentheses indicate SDs)

Changes in the colour of modified wood products are detectable after artificial exposure. As mentioned above, greying is a common change of colour for wood (Kärkkäinen 2007, Evans 2013). Rowell (2013b) has noted that acetylation changes dark wood to lighter and light wood to darker. According to Oltean et al. (2008), the colour of softwood was altered rapidly in the first 24 hours, and therefore the restrained colour change of the low heat-treated melamine wood and sodium silicate wood is a notable improvement, because Scots pine was the species for both products. The colour change of sodium silicate-impregnated wood was quite linear, but according to Pfeffer et al. (2012) it cannot prevent discoloration during outside weathering.

4.5.3 Mechanical properties

The investigated mechanical property of modified wood was bending strength. The results are presented in Figure 22 as bar charts with standard deviations added as error bars. Acetylated wood and a low heat-treated melamine-impregnated wood received an over 100 MPa average in the bending strength, and furfurylated wood reached almost the same threshold value. However, the standard deviations of melamine-impregnated wood were the highest. The average bending strength of sodium silicate-impregnated wood was significantly lower compared to the three other modified wood samples, but it had the lowest standard deviation.

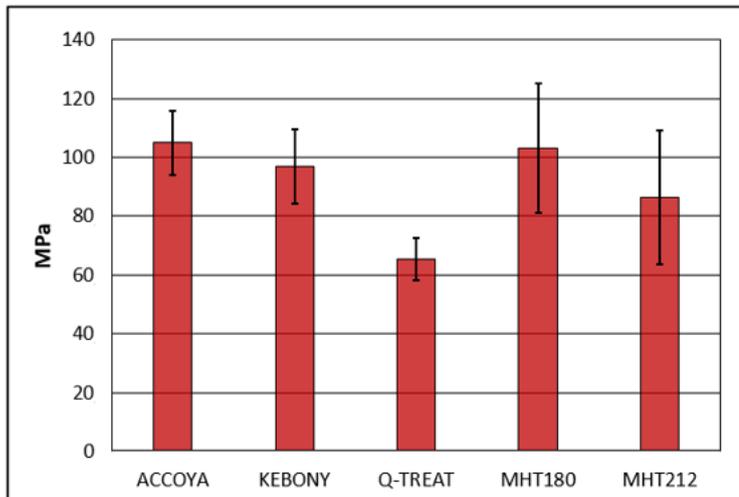


Figure 22. Bending strength of the tested materials. The error bars indicate SDs.

As can be seen in Figure 22, a separate modification method affects the bending strength individually. For example, it has been observed that the effects of acetylation on the strength is negligible (Papadopoulos and Tountziarakis 2011) or slightly improving (Epmeier et al. 2004). The strength of acetylated wood depends e.g. on the wood species (Bongers and Beckers 2003). The effect of heat treatment temperature on the bending strength of the melamine-impregnated wood converges with a previous study (Sun et al. 2013), where it was observed that the bending strength decreased with increasing temperatures and times. A sodium silicate solution has been found to reduce the bending strength due to hydrolysis of the cell wall polysaccharides, which is caused by a high pH of the wood (Mai and Militz 2004).

4.6 Synthesis of the study

As a summary, the effects of the studied treatments on the functional properties of solid softwood are shown in Table 12. Five main parameters – penetration ability, moisture resistance, weathering resistance, mechanical properties, and fire resistance, were chosen for comparative analysis based on individual estimation without a numerical scale. Functional improvement in a property is marked with the “+” sign while decline in a property is marked with the “-” sign. The number of signs describes the magnitude of the impact, the higher number, the bigger impact.

Table 12. Impact of modification on the properties of Scots pine (*Pinus sylvestris*) wood. (N/A = not available. *a* = 180 °C. *b* = 212 °C.)

Treatment	Penetration ability	Moisture resistance	Weathering resistance	Mechanical properties	Fire resistance
Water glass impregnation	-	-	--	-	N/A
Silicone impregnation	+	++	+	-	N/A
Melamine impregnation	+++	+++	++	-	+/-
Tall oil impregnation	+	+	+	-	N/A
Water glass impregnation & heat treatment	N/A	-	N/A	-	N/A
Silicone impregnation & heat treatment	N/A	++	N/A	-	N/A
Melamine impregnation & heat treatment	N/A	++	a: +++ b: --	+	+
Tall oil impregnation & heat treatment	N/A	+	N/A	-	N/A

The properties of the modifier solution had an effect on the penetration. The lower viscosity of the solution raised the amount of WPG while a higher water content of the solution affected the WPG results negatively due to the drying of wood. Therefore, a solution uptake parameter is necessary in addition to WPG. It was assumed that the uptake of the impregnation solution was generally better in the longitudinal direction, and drying would reduce the penetration ability. However, it was observed that the ability of the impregnation solution to penetrate into the wood in the transverse direction was due to, inter alia, the different properties of the wood parts. Some parts of wood remained difficult to impregnate and treat, for example heartwood and the transition zone. The high standard deviation of the results did not verify the image of being watertight. Impregnation as pre-treatment for heat-treated wood did not alter the properties of wood aberrantly, but different effects were detectable between the modifier solutions in micrographs.

The effect of impregnation on the wood properties were occasional. The moisture resistance properties were significantly improved with melamine impregnation but on the

other hand, some modifiers had an unfavourable effect compared to the unimpregnated reference wood. Greying is a general to wood, which was the case with the impregnated wood. Some impregnated wood samples reached a significant colour change rapidly, while the colour of some impregnated wood samples was not stabilized within the used weathering test run. The weight gain of impregnated wood influenced the mechanical properties individually. Hardness and impact strength were affected by the changed WPG substantially, while in bending strength it was found to be in a minor role. The fire performance of the treated wood stayed almost the same as with the reference wood in spite of the impregnation.

A significant improvement of properties was observed when the wood was treated twice, by impregnation and by heat treatment. The moisture properties of impregnated wood were further improved by the addition of heat treatment and increasing treatment temperature, due to the reorganization of wood components in the cell wall. In addition, heat treatment showed clear differences in the moisture tests compared to the merely impregnated wood. Swelling testing according to the direction of wood growth was a successful measurement, as it revealed pronounced swelling of melamine wood in the radial direction. Rather unexpectedly, a weak result in water absorption did not appear in the swelling test. A negative effect was noticed in the absorption test with the treatment combination of water glass and heat but generally, the combination treatment improved the moisture resistance properties of the treated wood. The mechanical properties of wood were expectedly decreased with increasing heat. However, a moderate temperature in the treatment had the ability to increase or maintain the strength properties. The temperature of heat treatment had also a clear effect on the colour change of wood. It has been reported that the colour of thermal modified wood changes relatively quickly (Jämsä et al. 2000). The correct modifier and temperature can be able to reduce the rapid colour change of thermally modified wood. According to the literature, thermally modified wood has equal fire performance with untreated wood (ThermoWood 2003), but the combination treatment alters also the fire properties of wood.

Table 13 shows the classification of commercial modified wood compared with possible contenders according to their functional properties. The possible contenders were modified wood which had the best results in the tests described above. The moisture resistance, mechanical properties, and start and final weathering resistance were evaluated at a three-level scale. The number of the “+” signs shows the state of quality of the property.

Table 13. Scoring of modified wood products evaluated by a three-phase system, +- markers one (worst), two, or three (best) times.

Treatment	Swelling	Water absorption	Weathering (100 h)	Weathering (1000 h)	Strength
Accoya	+++	++	+	++	+++
Kebony	+++	++	+	+	++
Q-Treat	++	+	++	++	+
MHT180	++	++	+++	++	+++
MHT212	++	++	+	+	++

The results of moisture resistance tests are quite congruent with our test (Paper IV), because sodium silicate wood absorbed clearly most water. The successful commercial modified wood had hydrophobic cell walls, and therefore swelling was restrained effectively. The traditional swelling coefficients into different directions seems to have changed in modified wood compared to untreated wood. A weak result in the moisture test does not correlate with the weathering test, where the wood species may have significance. The dense and long-term measurements in the weathering tests were informative, as for example acetylated wood had the biggest alteration at the beginning but after that the alteration was the least of all. There were differences in the bending strength of modified wood, but most of the modifications had an insignificant effect on bending, albeit the deviations were high. Only sodium silicate wood had reduced strength, due to hydrolysis of the cell walls.

It is obvious that the low cost of the modifier solution may be a major factor for choosing it. A rough comparison of the estimated average costs of modifiers is presented in Table 14, which is based on indicators from manufactures and markets. However, several manufactures emphasize that the price depends considerably on the use volume and costs of raw materials, and of course, the prices are negotiable. The comparison was not made by using actual prices, but by using ratios, by giving number 1 to the most economical solution. The estimated costs were based on the solution package used in this study, and market prices in the spring 2016, in Finland. The cost estimations include only the starting price for impregnation, and for example, the consumption of the modifiers or evaporation in the drying phase were not taken into account.

Table 14. Comparison of the estimated average costs of the modifiers.

Solution	Price
Water glass	1
Melamine	12
Tall oil	17
Silicone	30

Even though water glass -treated wood did not reach excellent material properties, its price is well competitive compared to the other modifier solutions. Melamine is an interesting solution for wood modification because it does not have the highest cost, but it had quite excellent properties in several tests. The used silicone solution is an expensive modifier solution but its costs could have been significantly lower if it had been acquired from an importer, for example. However, an expensive modifier solution is not necessarily an obstacle in wood modification. For example, in the commercialized Kebony wood furfuryl alcohol is used, the price of which has been stated to be high (Boren 2010).

It is obvious that modified wood has a higher price compared to untreated wood, and this will limit its use if consumers are not sure of its properties. Therefore, the consumer should consider the total benefit during the entire life cycle of the product. In addition to the original cost, costs related to its use should be taken into account, like lifetime and maintenance costs. Also, the disposal of the product may cause costs after the use.

5 Conclusions

The aim of this study was to investigate the impacts of selected modification substances and methods that improve or upgrade the material properties of solid wood without undue strain on the environment. The studied properties were weathering, moisture and mechanical properties, and fire performance. Also the effects of the modifier and the treatment parameters were assessed. The study revealed that wood modification can succeed and improve the properties of solid wood with certain parameters.

Based on the findings, it can be ensured that the properties of the modification substance, the wood material, as well as the treatment parameters have an effect on the modification and the properties. It is known that the properties of the solution, such as particle size, pH, and metallic oxides, will affect the final features. Due to the anatomy of wood, the uptake of the solution works differently depending on the direction. Additionally, pre-treatment, e.g. drying, impair the penetration of a substance into wood. The difference between the uptake and the remaining part of solution may be conspicuous. Therefore, the modification result should be checked by several tests, such as weight gain and solution uptake. One major property of the modification substance is viscosity, which, when low, has been found to have advantageous influence on the modification. As known, thermal modification causes chemical changes in the wood material, but impregnation did not seem to have a divergent effect because the traditional indicator of heat treatment, mass loss, was altered similarly in spite of impregnation with any of tested substances.

It was found in the study that impregnation with melamine worked best. The successful impregnation contributed to the other properties of wood, like moisture resistance and reduced discoloration. Moreover, heat treatment improved the properties even more, depending on the treatment temperature.

The moisture behaviour of wood is an important property because good moisture resistance can advance the other properties. The impregnation of wood did not automatically improve the moisture resistance properties, as some modification substances had a negative effect on the moisture behaviour, which was verified also with the commercial wood products. However, the heat treatment had a positive influence on the moisture resistance of wood, which was further improved with the increasing treatment temperature. In addition, heat treatment clarified the differences between the modifier substances, especially with a short treatment period. The differences became steady in the moisture tests in the long term. The well penetrated wood had different moisture anisotropy compared to the general swelling ratio of wood. Generally, the commercial wood products had good moisture resistance which appeared as a restrained swelling.

The discoloration of wood depends on the parts and properties of wood, but melamine treatment can help to retain the natural appearance of wood. Heat treatment had an influence on the weathering properties of melamine-impregnated wood, and the treatment

temperature had a remarkable effect on the discoloration. At first, it seemed that the discoloration were moderated after a few hundred exposure hours, but color changes occurred also after hundreds of hours. Hence, long-term weathering tests are necessary. The greying of wood may not be preventable, but a specific modification can restrain it. Additionally, modified wood may be an excellent base for surface finishing, which would restrain greying even more.

Strength is one of the most important properties of wood, and it altered individually according to the processing, and depending on the treatment and the examined property. Generally, wood modification did not cause remarkable alterations in the mechanical properties. However, the somewhat wide standard deviation in the strength results can impair the credence of the implications, but the commercial modified wood products had restrained standard deviation in the strength test. Successful impregnation increased the hardness with weight gain, but the bending strength and impact strength were impaired. The impact strength is very sensitive to any changes, due to alterations in wood material that were noted also after heat treatment. Even though the bending strength was decreased after impregnation, a certain combination treatment of impregnation and heat was able to increase it, compared to merely heat-treated wood. This happened when solid wood was impregnated with melamine and heat-treated at a low temperature after that. Strength has been a weakness for thermally modified wood, but in the light of the results described above, this problem will not necessarily play a significant role in the future.

In this work, the influence of impregnation on the fire performance of wood was found to be marginal, but heat treatment as a post-treatment for impregnated wood had an effect on the results such as decreased smoke production and altered values and time in heat releases. The combination treatment of impregnation and heat often has a reverse effect on the fire performance in comparison with the effect of mere heat treatment. The combination treatment increased the amount of residual mass after combustion, and therefore it should be intriguing to know the alterations of mechanical properties in a fire situation. However, the completed treatments did not seem to have any negative effect.

The melamine solution exhibited good penetration into the wood structure. In more detailed studies related to the structure of wood cell wall it could be found out whether melamine can improve the most critical parts in the wood structure, such as the transition zone. Thus, it would prevent potential decomposition and cracking that would occur afterwards. The melamine-treated wood achieved outstanding results in the moisture resistance tests, which were done quite laboriously. Accordingly, melamine-treated wood could be applied in marine use, for example wharf applications. In addition, the hardness of melamine-treated wood is high, so it can be utilized in applications where a harder surface is required. The melamine-impregnated and heat-treated wood had the most advanced properties in a number of the tests, and it was a promising way to contribute to the utilization of wood in the future. The commercial modified wood products that are currently on the market have at least one excellent property. The melamine-impregnated and at low temperatures heat-treated wood has features which may challenge the current

commercial modified wood products if production is done cost-effectively. Suitable uses for melamine-heat-treated wood may be outdoors, for example in gardens. However, further studies of the treated wood are still needed treated wood to ensure reliability and market acceptability, for example studies relating to environmental performance. Treated wood may have favourable properties which did not come out in this work. Some outdoor testing could be useful, for example, studying real photo degradation and bio deterioration. These effects are difficult to simulate in laboratory conditions a short period. In order to achieve the best possible properties for treated wood, various temperatures in heat treatment should be tested in further studies.

In conclusion, the functional properties of solid wood can be improved by a combination modification of impregnation and heat treatment. The effect of modification depends on the type of substance and the parameters used in the treatment phases.

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Publication I

Lahtela, V., Hämäläinen, K., and Kärki, T.

The effects of preservatives on the properties of wood after modification (Review paper)

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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 hygroscopic 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 Shirai-shi 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 treat-

ment 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 sylvestris 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 furfurylation (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 furfurylation 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 sylvestris* 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 pre-cured 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 ac-

ording 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), phenylisothio-

cyanate (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)

Samples	Immersion time (h)								
	24	48	72	96	168	192	240	264	336
Control	62.20 (5.96)	63.84 (5.76)	64.54 (5.91)	67.99 (6.25)	80.01 (7.66)	83.02 (7.55)	85.84 (7.07)	87.00 (7.11)	90.55 (7.16)
Silicon 15	61.37 (4.34)	64.21 (4.19)	67.00 (4.57)	72.55 (4.90)	75.61 (4.77)	76.16 (4.91)	77.64 (4.99)	78.32 (5.05)	80.17 (5.17)
Silicon 30	46.08 (2.58)	48.06 (1.78)	49.36 (1.92)	53.89 (2.37)	57.52 (1.94)	58.00 (2.04)	58.87 (2.00)	59.36 (2.09)	60.43 (2.12)
Acetylated	47.56 (3.26)	51.27 (3.49)	55.81 (4.04)	66.61 (5.51)	74.57 (4.61)	75.88 (4.83)	78.84 (5.00)	79.77 (5.02)	83.74 (5.12)
Heat treated	24.70 (1.78)	32.66 (2.05)	38.67 (1.95)	40.10 (1.94)	56.00 (1.77)	60.38 (1.78)	67.56 (1.78)	68.19 (1.83)	79.39 (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 (Umamura 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 (%)
<i>Betula sp.</i>	0.8 M	33.48	7.48
	1.3 M	43.49	18.76
	2.3 M	50.10	35.32
<i>F. sylvatica</i>	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 unrepresentative 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 (Seegerholm et al. 2012). For example, acetylated 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 sylvestris* 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 (Hos-

seini 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 exam-

ple, 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

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

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

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).

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

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 Giudice 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 extrac-

tives 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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Publication III

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Improving the mechanical properties of Scots pine (*Pinus sylvestris*) with impregnation modifiers

in review

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1 **Improving the mechanical properties of Scots pine (*Pinus sylvestris*) with impregnation**
2 **modifiers**

3

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5

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7

8 **Abstract**

9

10 Wood modification is a promising alternative to improving the performance of wood without
11 harmful side effects. This study investigates impregnation modification and its effects on the
12 mechanical properties of solid wood, which has been paid limited attention to previously. Scots
13 pine (*Pinus sylvestris*) wood was impregnated with four modifiers with a pressure device. The
14 mechanical properties of the modified samples were determined with bending strength,
15 hardness, and impact strength tests. The modifiers penetrated into the wood differently,
16 depending on the quality of the modifier. The melamine-impregnated samples attained the best
17 impregnation, which had an influence on the mechanical properties, but the orientation of the
18 effect varied. It is concluded that the significance of each mechanical property in the modified
19 wood product must be evaluated case by case.

20

21 **Keywords**

22

23 Impregnation, Scots pine, mechanical properties, bending, hardness, impact strength

24

25 **1 Introduction**

26 It is well known that wood is a natural structural material with a great number of applications.
27 Although wood has many excellent material properties, such as good isolation and high
28 strength in relation to weight, some of its inherent properties restrain its comprehensive
29 utilization. These properties can be improved by modification, which means improvement of
30 one or more of the disadvantages of wood (Hill 2006).

31 One of the methods of wood modification is impregnation, where the desired performance
32 changes are achieved by filling the wood substance with an inert material. The fixation of the
33 impregnator within the cell wall can occur either by monomer impregnation or by diffusion. In
34 monomer impregnation, impregnate polymerization within the cell wall occurs afterwards,
35 while in diffusion, a soluble material is diffused into the cell wall, making it insoluble (Hill
36 2006).

37 Impregnation depends on several variables, such as the material and process properties. The
38 longitudinal position of transport cells contributes to better penetration of the impregnator in
39 the longitudinal direction compared to radial or tangential directions. In radial directions, the
40 penetration passes through parenchyma rays (Larnøy et al. 2005; Tondi et al. 2013). The
41 properties of the impregnate liquid, for example the maximum molecular diameter or
42 hydrogen-bonding ability, also affect the penetration (Hill 2006). Additionally, the impregnator
43 may polymerize due to the acidity of wood, making it unable to penetrate into the cell wall
44 layers (Chen 2009).

45 The moisture properties and weathering performance of the selected modifiers have been
46 presented previously in the study of Lahtela and Kärki (2014). In addition, some studies have
47 reported the effects of each modifier. It has been found that melamine treatment can protect
48 solid wood against weathering and reduce the water absorption (Hansmann et al. 2006; Lahtela
49 and Kärki 2014). Some studies have shown that potassium or sodium silicate, commonly
50 known as water glass, treatment enhances the durability of wood and decreases fungal growth
51 (Mai and Militz 2004; Pfeffer et al. 2011). Hydrophobicity and resistance against decay and
52 mould have been found to improve after tall oil derivate and silicone emulsion treatment
53 (Temiz et al. 2008; Ghosh et al. 2009). In spite of several studies with selected modifiers,
54 investigations into their mechanical properties are limited. Generally, strength losses have been
55 found after waterborne-preservative treatment (Winandy and Rowell 2013) due to waterborne
56 preservative chemicals reacting with the wood cell wall components (Simsek et al. 2010).

57 In this study, solid wood was treated with environmentally nontoxic modifiers, and the
58 mechanical properties were investigated. Advanced modified wood products have been found
59 to have improved moisture features, but significant improvements in wood strength have not
60 been recorded. Improved strength properties could allow the utilization of wood in more
61 demanding applications. Therefore, the aim of this paper is to find out the influence of
62 modifiers on the mechanical properties of wood. Impregnation modification is also a relatively
63 unexplored method (Hill 2006), which also creates challenges for its research.

64

65

66 **2 Materials and methods**

67 Scots pine (*Pinus sylvestris*) wood samples were impregnated with four modifiers, melamine,
68 water glass, silicone, and tall oil. Before the impregnation, the samples were cut and planed
69 into the size 20 × 95 × 1000 mm. The features of the wood material were measured before
70 treatment, and the values are given in Table 1.

71

72 Table 1 Average properties before treatment

Feature	Value
Density (kg/m^3)	447.6
Moisture content (%)	11.7
Rate of growth (mm/a)	2.7
Heartwood ratio (%)	45.7

73

74 The impregnation was carried out by using a registered pressure apparatus, at a pressure of 10
75 bars for 120 min, without added heat. After impregnation, the samples were dried in an oven
76 at 103 °C for 24 h. Due to the more responsive qualities of the modifier, the melamine- and tall
77 oil -impregnated samples required slightly different treatment. The tall oil -impregnated
78 samples were allowed to stabilize for a day before drying and the melamine-impregnated
79 samples were dried at a lower (90 °C) temperature.

80 Impregnation was performed individually by each of the four modifier sets, consisting of 15,
81 both sapwood and heartwood, samples. The modifiers were melamine, water glass, silicone,
82 and tall oil. The melamine solution (Preferre 70 0592 L) was supplied by Dynea Chemicals Oy
83 (Hamina, Finland). The water glass solution, specifically sodium silicate (Zeopol 33), was
84 acquired from J.M. Huber Finland Oyj (Hamina, Finland) and diluted 1:1 with water. The
85 silicone solution was made of a silicone product (001 7100) from Tikkurila Oy (Vantaa,
86 Finland), mixed with water at the ratio 1:9. The tall oil (EP608) was obtained from Ekopine
87 Oy (Oulu, Finland) and diluted 1:1 with wood turpentine (T2501) from Kiilto Oy (Lempäälä,
88 Finland). The properties of the modifiers are presented in Table 2.

89

90 Table 2 Properties of used modifiers

	Melamine	Water glass	Silicone	Tall oil
Density (g/cm^3)	1.19 *	1.38 *	1.00**	0.86**
Solid content (%)	46.2 – 48.2	37.0	–	–
pH	9.7 – 10.0	11.2	c. 7	
Viscosity ($mPas$)	8 – 14	250	–	4 000

91 *at 20 °C **Relative density

92

93 The results of the modification were measured by weight percent gain (WPG) according to the
94 following equation:

$$WPG(\%) = \frac{Mm - Mu}{Mu} \times 100 \quad (1)$$

where Mm is the mass after modification, and Mu is the mass before modification.

Weight gain is a commonly reported value related to wood modification (Hill 2006). In addition to WPG, similar modification figures have been reported in other ways. For example, Sint et al. (2013) and Tondi et al. (2013) have determined other values for treated samples. These values, solution uptake (SU (kg/m^3)), relative solution uptake (RSU), and impregnation rate (I.R.), have been determined as follows:

$$SU(kg/m^3) = \frac{W_3 - W_2}{V_{AD}} \quad (2)$$

$$RSU(\%) = \frac{W_3 - W_2}{W_1} \times 100 \quad (3)$$

$$I.R.(%) = \frac{W_w - D_w}{D_w} \times 100 \quad (4)$$

where W_3 is the mass of the sample after impregnation (kg), W_2 is the mass of the conditioned sample before impregnation (kg), W_1 is the oven-dry mass of the sample before impregnation (kg), V_{AD} is the volume of the conditioned sample before impregnation (m^3), W_w is the wet weight, and D_w is the dry weight (Sint et al. 2013; Tondi et al. 2013).

The mechanical properties of the modified wood were determined by bending, hardness, and impact strength tests. The tests were carried out with 15 samples of each category, without visible cracks and knots. The set of samples consisted of 7 heartwood and 8 sapwood samples. The three-point bending and hardness (Brinell) tests were performed with a Zwick Roell Z020 testing machine in accordance with ISO 3133 and SFS-EN 1534, respectively. The specimens for the bending test were $20 \times 20 \times 380$ mm in size, and for the hardness test they were $20 \times 50 \times 100$ mm in size. The bending strength specimens were set on the testing machine in the longitudinal direction, and the penetrated surfaces of the specimens were located horizontally. This setting ensured that the effects of the modifiers were congruent in every specimen, regardless the magnitude of penetration, and the grain direction was not changed. The impact strength was determined with a Zwick 5102 Model impact tester according to EN ISO 179. The size of the impact test specimens was $4 \times 10 \times 80$ mm.

121

122 3 Results and discussion

123 3.1 Treatment

124 The impregnation results are listed in Table 3 by different parameters. The results show that
 125 the properties of the treatment solution have an effect on the penetration into wood. The WPGs
 126 of the treated wood are rather small, expect for the melamine-treated wood, whose favourable
 127 result may be caused by lower viscosity (Tondi et al. 2013). It has been assumed previously
 128 that the high water content of the impregnation solution may result in a weak WPG (Lahtela
 129 and Kärki 2014), which can be confirmed by the analysis of the uptake results (SU, RSU, I.R.).

130 For example, the silicone-treated wood has nearly the same average values as the melamine-
 131 treated wood in the uptake results, but not in the WPG. The results of the WPG show great
 132 evaporation for the water glass- and silicone-treated samples compared to the uptake results,
 133 whereas the melamine- and tall oil -treated samples have minor relative evaporation from the
 134 uptake results to the final results (WPG).

135

136 Table 3 Average treatment results and standard deviations

	Melamine	Water glass	Silicone	Tall oil
WPG	38.7 (24.7)	2.8 (6.2)	6.9 (8.7)	7.3 (5.3)
SU	352.6 (202.5)	93.6 (64.3)	315.8 (153.4)	52.7 (26.7)
RSU	76.6 (47.5)	20.0 (13.2)	67.7 (36.4)	11.4 (6.0)
I.R.	69.6 (42.9)	18.5 (12.2)	60.9 (31.2)	10.5 (5.8)

137 *Values in parentheses indicate standard deviations*

138

139 The impregnation is also dependent on the wood material properties, like aspiration,
 140 penetration direction, and the ratio of wood parts. Drying aspirates to the wood pits, which
 141 reduces the wood permeability (Langrish and Walker 2006). The penetration of the solution
 142 across the grain is more limited compared to the movement along the grain (Archer and Lebow
 143 2006). Permeability varies between wood parts, for example heartwood is impermeable due to,
 144 inter alia, aspiration and extractives (Langrish and Walker 2006). The results of the analysis
 145 show that in addition to WPG, an uptake test is needed to confirm the results.

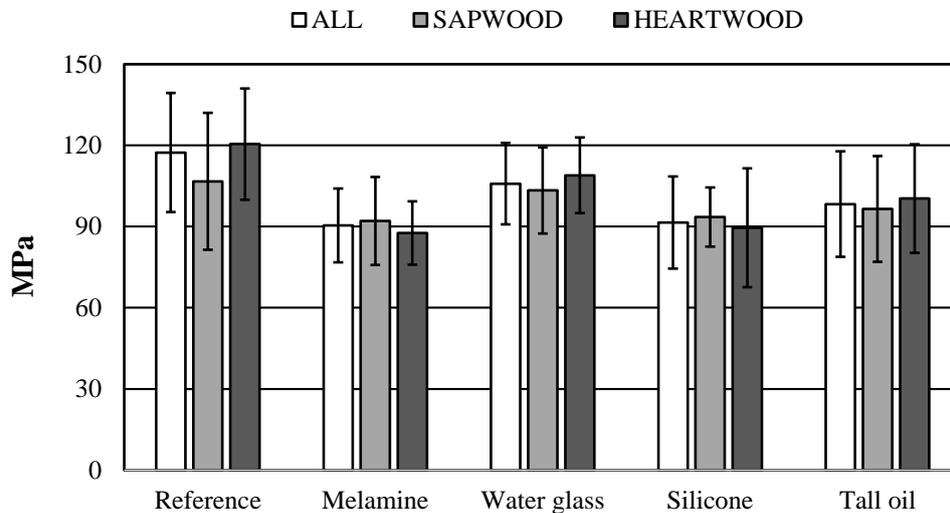
146 **3.2 Mechanical properties**

147 The mechanical properties are presented in Figures 1-3. The average results are presented as
 148 bar charts with error bars, which reflects the standard deviations.

149 **3.2.1 Bending**

150 The effect of impregnation on the bending strength is presented in Figure 1. The results show
 151 that the bending strength is decreased for the all impregnated samples, with a decline of 22.9
 152 % at worst. The differences between the sapwood and heartwood samples in bending are close
 153 to insignificant. The standard deviations of the bending results are slightly controlled after the
 154 impregnation.

155



156
 157 Figure 1. Bending strength of impregnated wood: *white bars* correspond to all specimens, *light*
 158 *grey bars* correspond to the sapwood specimens, and *dark grey bars* correspond to the
 159 heartwood specimens.

160

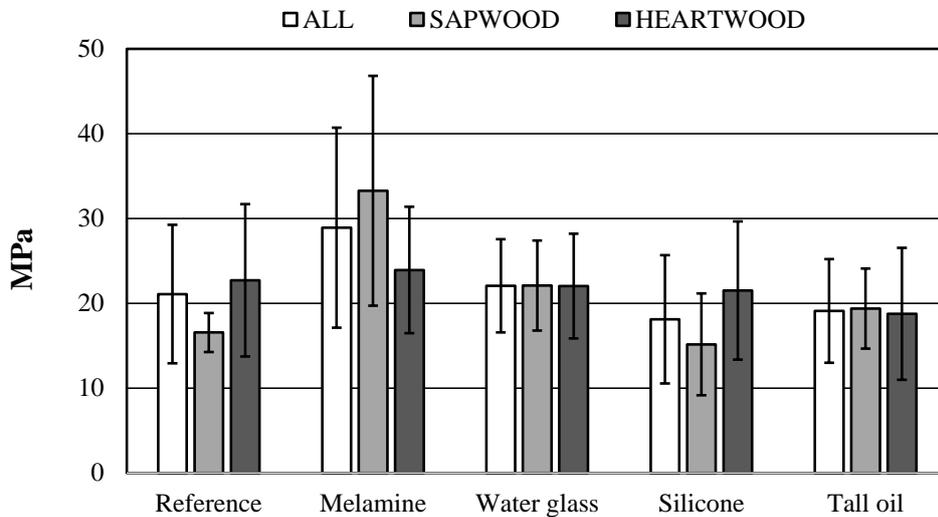
161 Previous studies have noted that impregnation with various modifiers may improve the bending
 162 strength of wood (Esteves et al. 2011, Esteves et al. 2014). The bending strength depends on
 163 the treatment parameters. For example, the bending strength is decreased with increasing
 164 treatment temperature (Poncsak et al. 2006), but a moderate treatment temperature may
 165 improve it (Rautkari et al. 2014). Also specific gravity, the total processing time, initial
 166 moisture content, and wood species influence the bending strength (Wang and Wang 1999; Shi
 167 et al. 2007; Kielmann et al. 2013). Kielmann et al. (2013) state that WPG has no major effect
 168 on the bending properties. An analysis of measurements revealed that the bending result
 169 decreased with increasing specimen dimensions (Scholotzhauer et al. 2015).

170 3.2.2 Hardness

171 Hardness was measured by Brinell hardness, and the results are given in Figure 2. The Brinell
 172 hardness is a reliable and widely used method in Europe for determining the hardness of wood
 173 (Heräjärvi 2004). Other test methods may require changes in the measurements due to the soft
 174 nature of wood material (Esteves et al. 2014).

175 As can be seen in Figure 2, the melamine treatment has produced the highest increment on
 176 hardness. Gindl et al. (2004) have previously stated that melamine can alter the hardness of
 177 softwood to correspond the hardness of hardwood. Water glass and tall oil treatment have
 178 stabilized the hardness of the wood between sapwood and heartwood. The hardness of the
 179 silicone-treated samples is similar to the hardness of the untreated wood. The standard
 180 deviations of the hardness results are remarkably high after impregnation modification, which
 181 may be due to the heterogeneous nature of wood.

182



183
 184 Figure 2. Hardness of impregnated wood: *white bars* correspond to all specimens, *light grey*
 185 *bars* correspond to the sapwood specimens, and *dark grey bars* correspond to the heartwood
 186 specimens.

187

188 The hardness of wood is dependent on the properties of native wood, for example grain
 189 direction and density (Holmberg 2000; Heräjärvi 2004). In addition, the viewing direction has
 190 an influence on the magnitude of hardness. For example, hardness is a greater in the tangential
 191 direction than in the radial direction (Kurt and Özçifçi 2009) and latewood is harder than
 192 earlywood (Rautkari et al. 2009; Grekin and Verkasalo 2013).

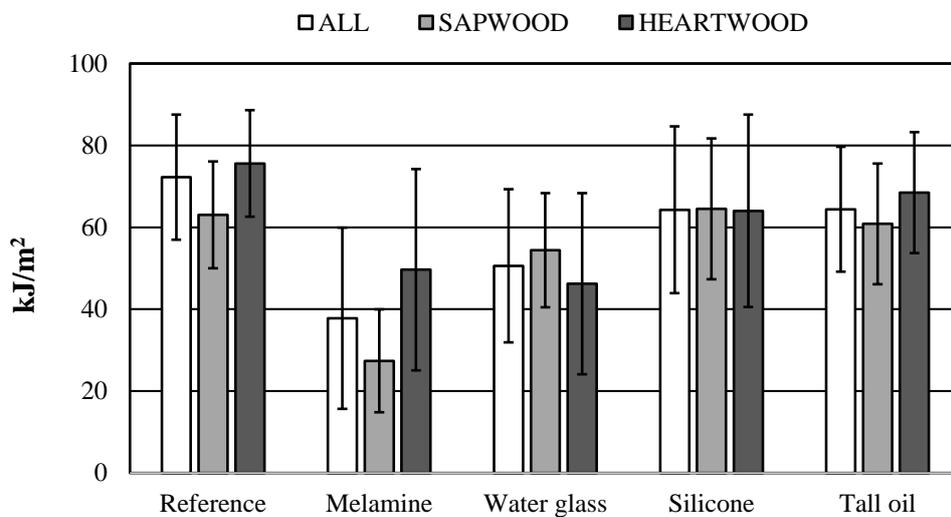
193 Treatment also influences on the hardness of wood, depending on the parameters. The hardness
 194 of densified wood has been found to increase (Rautkari et al. 2009; Candan et al. 2013), but for
 195 example, the effects of heat treatment on the hardness appear to be slightly ambiguous (Kocaefe
 196 et al. 2010; Priadi and Hiziroglu 2013). However, it has been observed that the treatment
 197 parameters have a significant effect on the hardness (Shi et al. 2007; Laine et al. 2013). The
 198 impact of the variables mentioned above can be minimized by using the same species and
 199 treatment conditions in all tests, and then the different parts of the wood cannot cause a
 200 significant deviation on the results. The impregnation solution was a singular variable in this
 201 study.

202 Several studies have indicated that the impregnation of wood can increase the hardness
 203 (Hansmann et al. 2006; Esteves et al. 2011, Atar et al. 2011). Esteves et al. (2014) have noted
 204 that the increase of hardness is proportional to the weight gain. The increased hardness of
 205 impregnated wood may be caused by increased density (Atar et al. 2011), but according to
 206 Epmeier et al. (2004), the denser wood does not automatically cause an increase in hardness.
 207 Gindl et al. (2004) have found that 2 mm is a minimum penetration depth to achieve increase
 208 in hardness.

209 3.2.3 Impact strength

210 Impact strength represents a distinct mechanical property which is affected by the dynamic
 211 load. Also the shorter loading time separates it from the other mechanical tests. The impact
 212 strength properties are presented in Figure 3. Significant deteriorations were observed in the
 213 impact strength when the impregnation was successful, for example in the melamine-treated
 214 samples, of which the average value was 52.3 % from the corresponding result of the reference
 215 samples. According to Kielmann et al. (2013), the impact strength of melamine-treated wood
 216 is reduced because the cured resin is rigid and brittle in the wood structure. The standard
 217 deviations of the impact strengths are relatively high.

218



219 Figure 3. Impact strength of impregnated wood: *white bars* correspond to all specimens, *light*
 220 *grey bars* correspond to the sapwood specimens, and *dark grey bars* correspond to the
 221 heartwood specimens.
 222

223

224 Modified wood is fragile due to the decreased mobility of the cell wall components (Dieste et
 225 al. 2008). The impact bending strength is sensitive for changes of wood (Kärkkäinen 2003),
 226 and the increased WPG value and heat treatment parameters reduce the impact strength (Lande
 227 et al 2004, Korkut et al. 2008, Rautkari et al. 2014). Epmeier et al. (2004) indicate that several
 228 modification methods reduce the impact strength of wood, correlating negatively with
 229 dimensional stability. Therefore, attention has to be paid to the crucial requirements of
 230 modified wood material, for example the strength and moisture properties.

231 The limited number of studies and a wide variation in the reference values suggest that further
 232 studies of the impact strength are needed to get more knowledge. Kärkkäinen (2003) has stated
 233 that the impact bending strength of wood must be considered as valid only within the standard
 234 used.

235

236 **4 Conclusions**

237 The effect of impregnation on the mechanical properties of wood was investigated in this study.
 238 The penetration of the impregnation solution into the wood was also assessed. Awareness of
 239 the features of modified wood may allow the utilization of wood in wider applications where
 240 for example a harder surface is required.

241 It was found that, in addition to material properties, the qualities of the impregnation solution
 242 affected the results. The changes to the mechanical properties of the impregnated wood were
 243 different. The bending strength stayed close to stable, but the hardness and impact strength
 244 were sensitive to the modification, and the WPG played a significant role. The typical
 245 heterogeneous nature of wood material led to wide deviations in the results, which may have
 246 confused the analysis.

247 In the light of the results, the mechanical properties altered after impregnation depending on
 248 the impregnation solution. Some post-treatment, e.g. thermal modification, could have a more
 249 favourable effect on the wood qualities, which should be investigated in further research.

250

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Publication IV

Lahtela, V., and Kärki, T.

**Effects of impregnation and heat treatment on the physical and mechanical properties
of Scots pine (*Pinus sylvestris*) wood**

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ORIGINAL ARTICLE

Effects of impregnation and heat treatment on the physical and mechanical properties of Scots pine (*Pinus sylvestris*) wood

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Abstract

Wood modification, of which thermal modification is one of the best-known methods, offers possible improvement in wood properties without imposing undue strain on the environment. This study investigates improvement of the properties of heat-treated solid wood. Scots pine (*Pinus sylvestris*) was modified in two stages: impregnation with modifiers followed by heat treatment at different temperatures. The impregnation was done with water glass, melamine, silicone, and tall oil. The heat treatment was performed at the temperatures of 180°C and 212°C for three hours. The modified samples were analyzed using performance indicators and scanning electron microscope micrographs. The mechanical and physical properties were determined with water absorption, swelling, bending strength, and impact strength tests. All the modifiers penetrated better into sapwood than hardwood; however, there were significant differences in the impregnation behavior of the modifiers. As regards the effect of heat treatment, generally the moisture properties were improved and mechanical strengths impaired with increasing treatment temperature. In contrast to previous studies, the bending strength increased after melamine impregnation and mild heat treatment. It is concluded that the properties of impregnated wood can be enhanced by moderate heat treatment.

Keywords: *Impregnation, mechanical properties, physical properties, Scots pine, thermal modification*

Introduction

Wood is a widely used natural structural material in many applications. The modification of wood, for example, by impregnation or thermal treatment, is a possible option for improving the performance of wood material, thus permitting its utilization in a wider variety of applications. Impregnation modifies wood properties by filling the wood substance with an inert material. Thermal modification causes chemical changes in the wood material by heat (Hill 2006).

The exposure of wood to a controlled elevated temperature has been known to modify its properties since the mid-twentieth century (Stamm *et al.* 1946). The thermal modification of wood reduces its hygroscopicity (Borrega and Kärenlampi 2010, Hill *et al.* 2012), thus improving its dimensional stability (Korkut and Bektas 2008, Kocaefe *et al.* 2008a). The color of thermally modified wood is darker (Esteves *et al.* 2011, Poncsak *et al.* 2011, Akgül and Korkut

2012) and the strength properties are reduced (Kocaefe *et al.* 2010, Pfriend *et al.* 2010, Rowell *et al.* 2013). The treatment of wood at elevated temperatures causes mass loss because wood cell wall polymers degrade thermally. Mass loss is an important variable in the heat treatment of wood (Esteves and Pereira 2008). Hemicelluloses degrade earlier than other wood cell wall compounds with increasing temperature (Esteves *et al.* 2011), and hence hemicellulose degradation has a significant impact on the strength and dimensional stability properties of heat-treated wood (Müller *et al.* 2003, Weiland and Guyonnet 2003, Kocaefe *et al.* 2008b, Rowell *et al.* 2009, Weigl *et al.* 2012).

Thermal modification is the most advanced wood modification process commercially (Hill 2006) and various thermal modification processes have become widespread over the past decade, for example, the ThermoWood (Finland), Plato (Netherlands), Reticification (France), and Oil Heat Treatment (OHT) (Germany) processes. A common factor in these

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processes is thermal treatment at elevated temperatures with low oxygen content. The oxygen content is minimized in a variety of ways, for example, by nitrogen in the Retification process or by oil in the OHT process (Rapp 2001, Militz 2008). The ThermoWood (2003) process operates with the presence of water vapor, which also protects the wood. The thermal modification of wood has been studied with various wood species; pine wood is a commonly used material in such research.

To meet social demands, the wood products industry needs new innovative products that are based on environmentally nontoxic agents and methods. Research into novel wood modification approaches contributes to the removal of barriers to new applications for solid wood products. The effects of thermal modification on the properties of pine are well known, but combining such modification with another treatment has not been widely researched. However, some treatment combinations have recently been tested, for example, heat treatment and borate impregnation (Awoyemi and Westermarck 2005) and preboiling (Awoyemi *et al.* 2009) as a pretreatment. Sun *et al.* (2013) have studied the combination of melamine-urea-impregnation and heat treatment.

The aim of this study is to investigate the influence of impregnation on subsequently heat-treated pine wood. The impregnation pretreatment was performed with four different solutions (water glass, melamine, silicone, and tall oil) and the heat treatment was performed at two temperatures. The impregnation solutions were selected focusing on environmentally nontoxic agents with different compositions. The selected solutions have previously been found to give improved wood properties (Hansmann *et al.* 2006, Temiz *et al.* 2008, Ghosh *et al.* 2009, Pfeffer *et al.* 2010). The major motivation for this study was enhancement of the mechanical properties of heat-treated wood.

Material and methods

Scots pine (*Pinus sylvestris* L.) wood samples were first impregnated with the solutions studied, followed by treatment of the impregnated samples. Heat treatment was carried out at two different temperatures: 180°C and 212°C. Density, moisture content, heartwood ratio, and the rate of growth were measured before the treatment. The values are presented in Table I.

The samples were cut and planed into the size 20 × 95 × 1000 mm, and impregnated with four different modifiers. The impregnation was carried out using registered pressure apparatus, at a pressure of 10 bars for 120 min. The capacity of the pressure

Table I. Average properties of samples (62 pieces) before treatment.

Density (kg/m ³)	447.6 (46.9)
Moisture content (%)	11.7 (2.5)
Rate of growth (mm/a)	2.7 (1.5)
Heartwood ratio (%)	45.7 (43.3)

Value in parentheses indicate standard deviation.

apparatus is 600 l, and it contains an individual bin into which the test samples are placed with the impregnation solution.

After impregnation, the samples were dried in an oven at 103°C for 24 h, with the exception of the melamine- and tall oil-treated samples which have a more responsive flash point and thus required slightly different treatment. The melamine-treated samples were dried at 90°C for 24 h, and the tall oil-treated samples were allowed to stabilize for a day before drying, ensuring that the responsive agent had evaporated. The result of the impregnation was measured by weight percent gain (WPG).

Impregnation was performed with different modifiers, and each treatment had 15 samples, consisting of both sapwood and heartwood. The modifiers used were water glass, melamine, silicone, and tall oil. Water glass, specifically sodium silicate (ZEOPOL 33), was obtained from J.M. Huber Finland Oy (Hamina, Finland) and diluted 1:1 with water. Melamine (Preferre 70 0592 L) was supplied by Dynea Chemicals Oy (Hamina, Finland). The silicone emulsion was made of silicone (001 7100) from Tikkurila Oy (Vantaa, Finland) and water, mixed at the ratio 1:9. Tall oil (EP608) was acquired from Ekopine Oy (Oulu, Finland) and diluted 1:1 with wood turpentine (T2501) from Kiilto Oy (Lempäälä, Finland). The properties of the impregnation solutions are presented in Table II.

The heat treatment was performed based on the ThermoWood process, but without water vapor in the process. The samples were treated in a heating oven, at temperatures of 180°C and 212°C for 180 min.

Table II. Properties of impregnation solutions.

	Water glass	Melamine	Silicone	Tall oil
Density (g/cm ³)	1.38 ± 0.015 (20°C)	1.19 (20°C)	1.00 ^a	0.86 ^a
Solid content (%)	37.0	46.2–48.2	–	–
pH	11.2	9.4–10.0	c. 7	
Viscosity (mPas)	250	8–14	–	4000

^aRelative density.

After the heat treatment, the mass loss was determined.

The impregnated heat-treated specimens were examined with a scanning electron microscope (SEM), Jeol JSM-5800 LV. Prior to the analysis, the surfaces of the samples were covered with a layer of gold using a sputter coater. In view of the poor impregnation of the heartwood, only the treated sapwood specimens were analyzed by SEM microscopy.

The moisture properties were determined with thickness swelling and water absorption tests. The size of the test pieces was $20 \times 20 \times 30$ mm. The test pieces were conditioned at 20°C and 65% relative humidity before testing. The weights and dimensions of the pieces were measured before immersion into water for a duration of 28 days. The pieces were periodically taken out of the water, surface-dried with absorbent paper, re-measured, and returned to the water immediately.

Swellings were determined in the radial and tangential directions. Swelling in the axial direction has been noted to be insignificant (Poncsak *et al.* 2011). Swelling (S) was calculated according to the following formula:

$$S = \frac{T_1 - T_2}{T_2} \times 100 \quad (1)$$

where T_1 is the thickness of the specimen after immersion, and T_2 is the thickness of the specimen before immersion.

The water absorption values (WA) were calculated as follows:

$$WA = \frac{W_1 - W_2}{W_2} \times 100 \quad (2)$$

where W_1 is the mass of the specimen after immersion, and W_2 is the mass of the specimen before immersion.

The mechanical strengths of the heat-treated wood were determined by three-point bending and impact strength tests. The bending strength was determined with a Zwick Roell Z020 testing machine in accordance with ISO 3133. Fifteen test samples of each category, with dimensions $20 \times 20 \times 380$ mm, were tested. Before the test, the specimens

were conditioned at 20°C and 65% relative humidity for over 24 h. The impact strength was determined with a Zwick 5102 Model impact tester in accordance with EN ISO 179. The impact strength testing was carried out with 15 samples with the dimensions $4 \times 10 \times 80$ mm. The test pieces were conditioned at 23°C and 50% relative humidity for over 24 h before the impact test was performed.

Results and discussion

Results for the control and reference samples are presented below. The control sample was not subjected to elevated temperature heat treatment, only kiln-dried at the temperature of 103°C for 24 h. The reference samples were heat-treated, but not impregnated. The mechanical properties data contain also the results of impregnated samples that were not heat-treated but only kiln-dried as described above.

Treatment

The impregnation results are presented in Table III by WPG. Results for the sapwood specimens are presented separately as they clearly differ. Some samples exhibited no impregnation, which, after drying, gives negative results for WPG in a few categories. The results show that the melamine samples were impregnated best, especially in sapwood. The effects of heat treatment are presented in Table IV by mass loss. It can be seen that the higher temperature causes greater mass loss.

The effects of the heat treatment are also presented in Figures 1–5, which show SEM micrographs of the surface of the samples. Cracks can be seen in the samples after heat treatment, especially in the water glass-impregnated sample treated at the higher temperature (Figure 2). Based on Figure 3, melamine seems to have melted into the wood during the heat treatment. The tall oil seems to have boiled during heat treatment at the temperature of 212°C (Figure 5).

It can be seen in Table III that the sapwood specimens have been well impregnated. The solutions penetrate into sapwood better due to a lower proportion of extractives, and because the pit

Table III. Average WPG and standard deviations.

	Water glass	Melamine	Silicone	Tall oil
Average (%)	2.76 (6.24)	38.71 (24.68)	6.85 (8.72)	7.28 (5.29)
Sapwood average (%)	3.48 (4.75)	57.04 (15.60)	12.09 (6.70)	7.73 (3.26)

Values in parentheses indicate standard deviations.

Table IV. Average mass loss and standard deviations.

	Reference	Water glass	Melamine	Silicone	Tall oil
180°C	7.49 (0.78)	8.20 (0.93)	8.14 (0.54)	7.21 (0.48)	7.33 (0.53)
212°C	10.24 (1.00)	13.00 (1.63)	11.00 (0.80)	10.44 (0.78)	11.01 (1.67)

Values in parentheses indicate standard deviations.

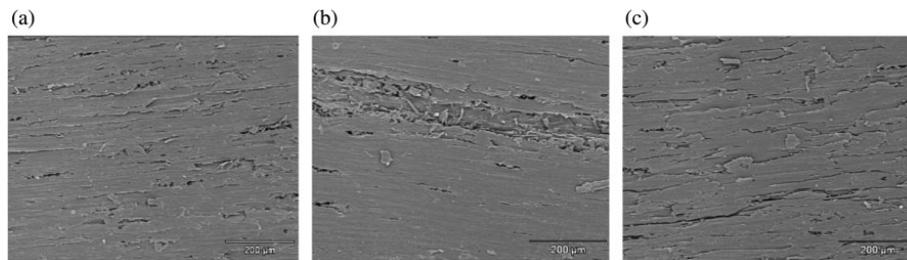


Figure 1. SEM micrographs of untreated control (a), heat-treated at 180°C (b), and at 212°C (c) reference samples.

membranes are not aspirated in sapwood (Archer and Lebow 2006). The excellent impregnation of the melamine samples may be due to the lower viscosity of the modifier. Viscosity has been found to affect the uptake of a solution (Larnøy *et al.* 2005, Dubey *et al.* 2011), especially in pine wood (Tondi *et al.* 2013).

The results show that increased treatment temperature enhances mass loss, as presented in previous studies (Welzbacher *et al.* 2007, Metsä-Kortelainen and Viitanen 2010). In addition to the temperature, longer treatment time has also been found to increase mass loss (Alén *et al.* 2002, Esteves *et al.* 2007). Density, which has been found to correlate with mechanical properties (Mahnert and Militz 2012), is also reduced by heat treatment (Boonstra *et al.* 2007a, Metsä-Kortelainen and Viitanen 2010). The mass loss in heat treatment is caused by degradation of the hemicelluloses (Esteves and Pereira 2008, Esteves *et al.* 2011).

The temperature of the heat treatment plays significant role; for instance, the tall oil-impregnated heat-treated samples seem to undergo a boiling effect at the temperature of 212°C (Figure 5c) but not at 180°C (Figure 5b). The melamine samples that were treated at the temperature of 212°C have unusual patterns on the surface of the samples (Figure 6a, 6b) and there are areas with no patterns (Figure 6c). The patterns appear to occur randomly on the surface (Figure 6a, 6b) and resemble condensation on the surface of the wood.

Moisture properties

Data on the moisture properties are presented in Figures 7–10. The water absorption properties are presented as a point chart in Figures 7 and 8, to which a trend line has been added between the points using a two-period moving average. The results for water absorption are presented separately

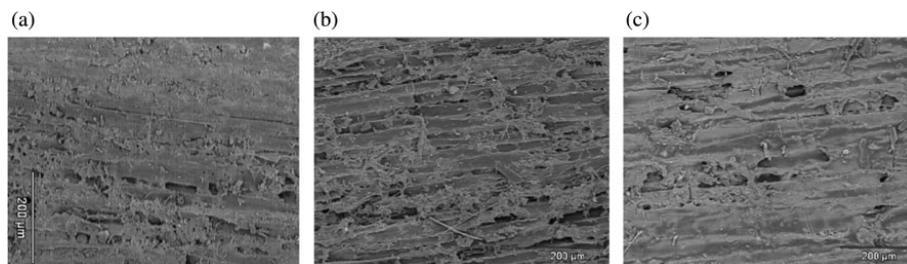


Figure 2. SEM micrographs of water glass-impregnated (a), water glass-impregnated and heat-treated at 180°C (b), and water glass-impregnated and heat-treated at 212°C (c) samples.

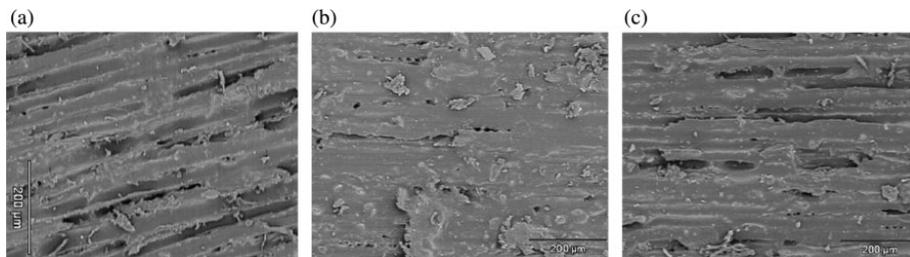


Figure 3. SEM micrographs of melamine-impregnated (a), melamine-impregnated and heat-treated at 180°C (b), and melamine-impregnated and heat-treated at 212°C (c) samples.

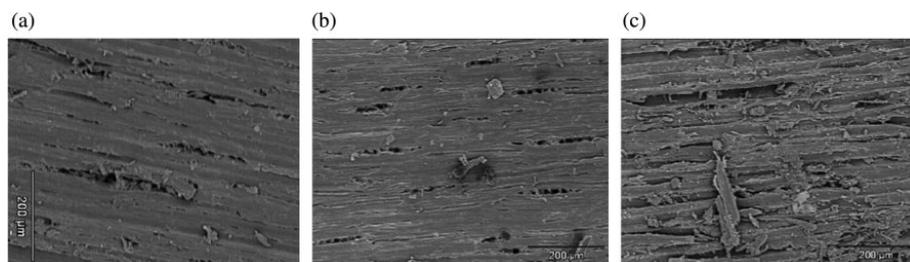


Figure 4. SEM micrographs of silicone-impregnated (a), silicone-impregnated and heat-treated at 180°C (b), and silicone-impregnated and heat-treated at 212°C (c) samples.

at the different temperatures. The samples treated at the higher temperature absorbed less water during the first 7 days of the water absorption test than the samples treated at the lower temperature. Some samples absorbed the same amount or more water than the reference samples regardless of the treatment temperature. The melamine-impregnated heat-treated samples absorbed least water throughout the test at both temperatures. The silicone-impregnated heat-treated samples absorbed water with restraint at the beginning of the test. Water glass impregnation followed by heat treatment had a negative effect on water absorption, i.e. more water was absorbed than the untreated reference sample.

The swelling properties are presented as bar charts in Figures 9 and 10. The swelling is presented separately for the tangential and radial directions. The higher treatment temperature restrains swelling in the tangential and radial directions. The benefit of impregnation can be seen at the lower temperature in the tangential directions, where all impregnated heat-treated samples have swelled less than the reference samples. The samples heat-treated at 212°C swelled similarly despite the impregnation. The melamine samples swelled most in the radial direction. By comparison with the data in Table IV, it can be seen in Figures 7–10 that mass loss is related to the moisture properties of the wood.

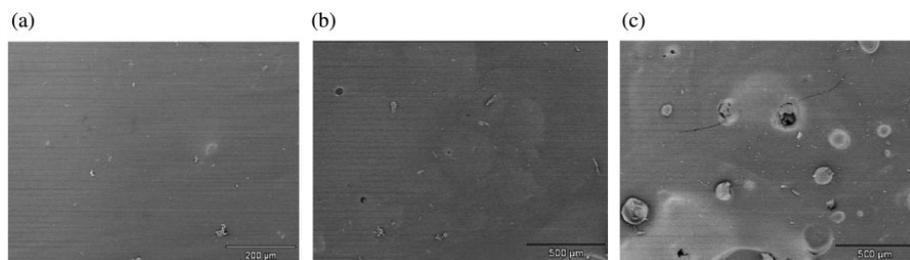


Figure 5. SEM micrographs of tall oil-impregnated (a), tall oil-impregnated and heat-treated at 180°C (b), and tall oil-impregnated and heat-treated at 212°C (c) samples.

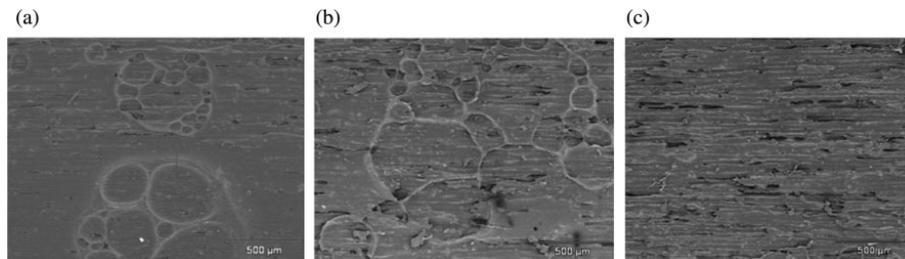


Figure 6. SEM micrographs of melamine-impregnated samples heat-treated at 212°C.

The higher treatment temperature stabilized the moisture properties of the samples, which is in agreement with earlier studies (Welzbacher *et al.* 2007, Gündüz *et al.* 2008, Korkut and Bektas 2008, Jalaludin *et al.* 2010, Cao *et al.* 2012, Priadi and Hiziroglu 2013). Longer treatment time could restrain moisture absorption, but not as efficiently as increased temperature (Cao *et al.* 2012, Priadi and Hiziroglu 2013).

Improvement in the moisture-resistance properties with increasing temperature and time is not always unambiguous. Metsä-Kortelainen *et al.* (2006) noted that the water absorption of pine sapwood increased after heat treatment at the temperatures of 170°C, 190°C, and 210°C compared to normally kiln-dried reference samples when the specimens were floated for 146 hours. Only heat treatment at the temperature of 230°C reduced the water absorption of pine sapwood. In addition, the differences in water absorption between pine sapwood and heartwood were significant in this study,

which could be explained by the migration of extractives onto the wood surface (Metsä-Kortelainen and Viitanen 2012). Nuopponen *et al.* (2003) found that during heat treatment at a low temperature the extractives moved onto the edges of pine sapwood. Extractives were not detected in the sapwood edges after the heat treatment at a higher temperature in this study, which could be due to degradation and evaporation of the extractives. Another option could be softening of the lignin that enables the diffusion of the extractives deeper into the battens (Nuopponen *et al.* 2003).

In untreated wood, tangential swelling is usually twice that of radial swelling (Rowell 2013), which appears to be valid also in heat-treated Scots pine (Korkut and Bektas 2008). However, the dissimilar anisotropy of different wood species together with the different treatment temperatures and times affects the swelling ratio (Welzbacher *et al.* 2007, Priadi and Hiziroglu 2013). The melamine-impregnated heat-treated samples swelled about one and a half times in

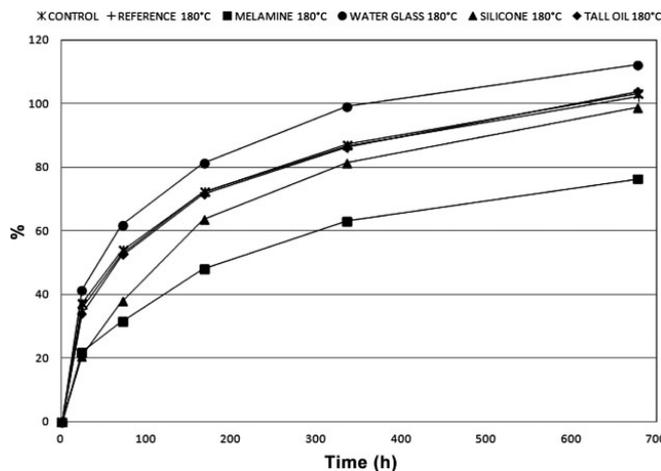


Figure 7. Water absorption at 180°C with time.

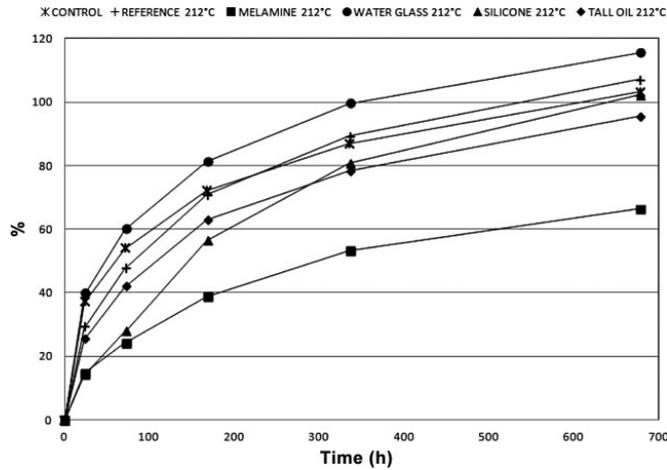


Figure 8. Water absorption at 212°C with time.

the tangential direction compared to the radial direction. The swelling and absorption are lower after heat treatment because the amount of wood hydroxyl groups are reduced (Gündüz *et al.* 2008) due to the formation of an ether linkage by the splitting of two adjacent hydroxyl groups (Kamdem *et al.* 2002). Furthermore, hemicellulose degradation in heat-treated wood reduces the hygroscopicity of the wood, because hemicellulose is the hydrophilic component in the wood cell wall (Walker 2006). In addition, depolymerization of hemicelluloses increases the relative proportion of crystalline cellulose and cross-linking of the lignin network, which inhibits the encounter of water and hydroxyl groups (Boonstra *et al.* 2007b).

Mechanical properties

The mechanical properties are presented in Figures 11 and 12. The average results are presented as bar

charts with standard deviations added as error bars. In addition, polynomial trend lines have been added to the figures.

The higher temperature usually decreases the bending strength. None of the treated samples achieved the same or better bending strength than the normal kiln-dried sample. Melamine improved the bending strength after heat treatment. Melamine-impregnated samples heat-treated at 180°C had 10.0% better bending strength compared to the reference samples treated at the same temperature. The melamine-impregnated samples heat-treated at 212°C had 21.7% better bending strength compared to the reference sample heat-treated at the same temperature. The bending strengths of the samples impregnated with silicone and tall oil and heat-treated at 212°C were 9.2% and 8.2% better than that of the reference sample after heat treatment at the same temperature. The bending strengths of the water glass-impregnated heat-treated samples were

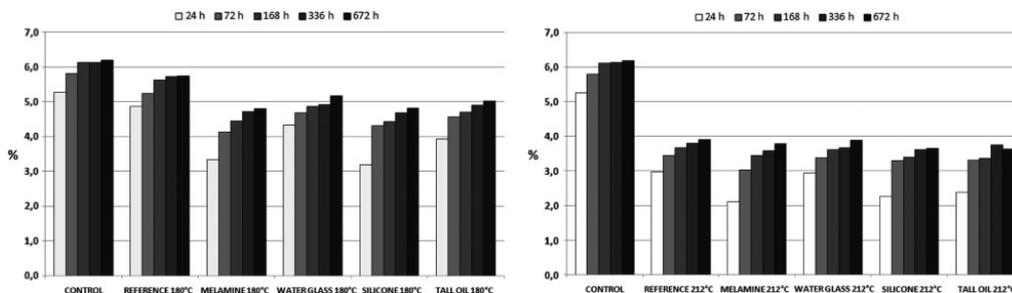


Figure 9. Tangential swelling at 180°C (left) and 212°C (right) with time.

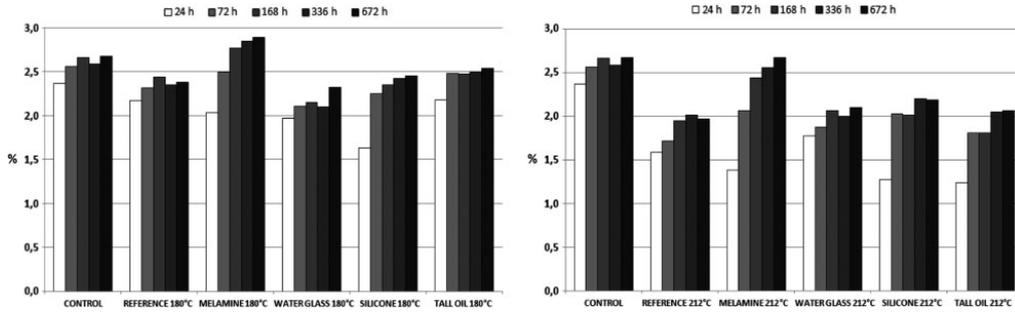


Figure 10. Radial swelling at 180°C (left) and 212°C (right) with time.

reduced close to half after heat treatment at the higher temperature. The water glass-impregnated samples achieved 51.7% of the bending strength of the control sample after 212°C heat treatment. The bending strengths of silicone- and tall oil-impregnated heat-treated samples were not increased, but the reduction appeared to be smaller than that of the reference samples.

The heat treatment impaired the impact strength of the wood. The melamine-impregnated and lower temperature heat-treated samples were able to maintain the same level of impact strength as the melamine-impregnated sample without heat treatment, but it was weaker by a half compared to the control

sample. On the basis of Figure 12, it can be concluded that the impact strength of wood is impaired with increasing heat treatment temperature.

Impregnation makes the wood more fragile because the mobility of the cell wall components is reduced by the impregnation solution (Dieste *et al.* 2008). The bending strength of the melamine-impregnated samples was improved after heat treatment at 180°C. The study of Deka and Saikia (2000) indicated that the bending strength increases by 12–20% due to the thermosetting resin. The study of Boonstra *et al.* (2007b) gives impact strength results similar to the result for the untreated control samples in this study.

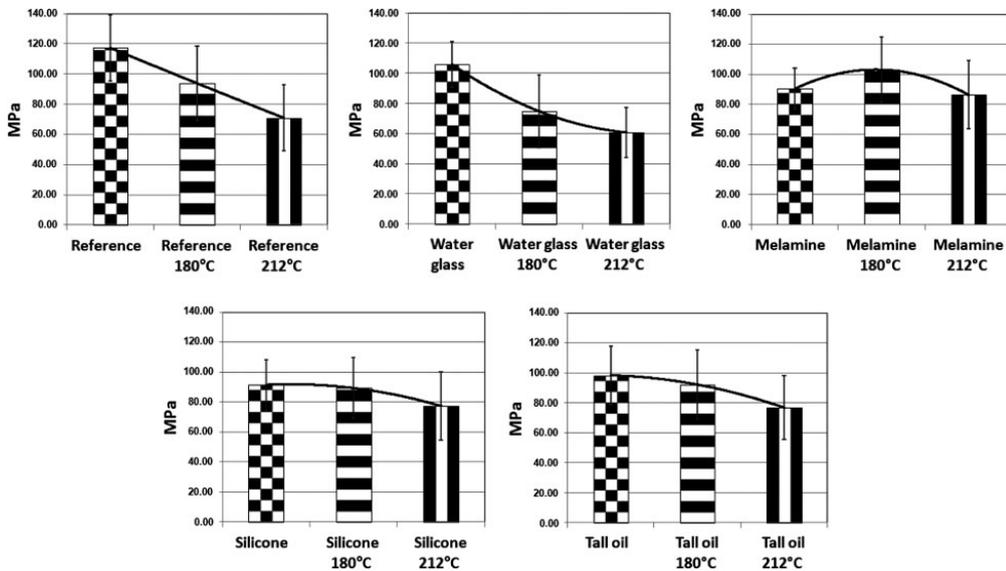


Figure 11. Effect of impregnation and heat treatment on bending strength.

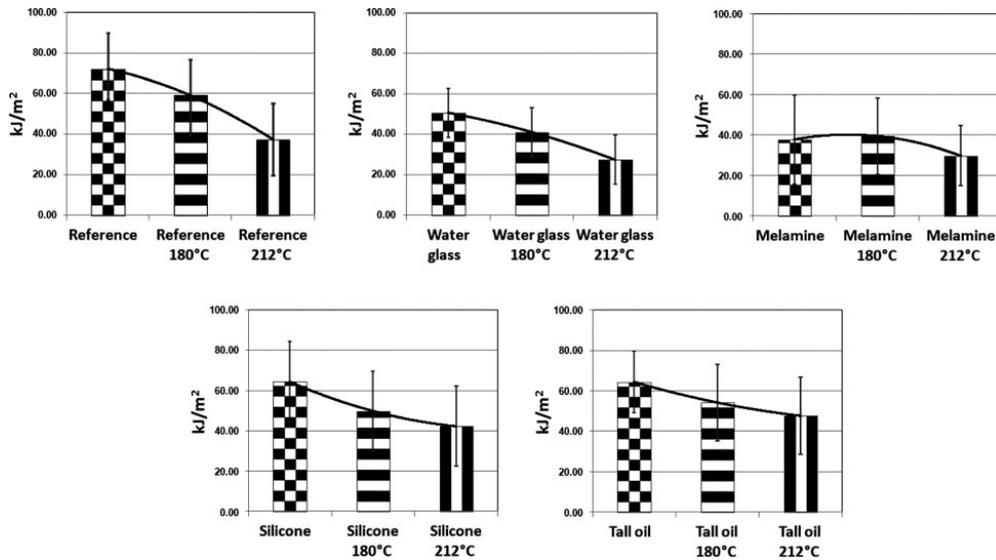


Figure 12. Effect of impregnation and heat treatment on impact strength.

The higher treatment temperature reduced the bending strength, in agreement with previous studies (Kocaefe *et al.* 2010, Poncsak *et al.* 2011, Welzbacher *et al.* 2011, Surini *et al.* 2012). In addition to temperature, the treatment time and atmosphere affect the bending strength (Rowell *et al.* 2009), as does the wood species (Shi *et al.* 2007). For example, hardwood is more sensitive to mechanical changes than softwood (Kamdern *et al.* 2002), which is thought to be due to lignin condensation (Wikberg and Maunu 2004). A slight increase in the bending strength after mild heat treatment may be due to the decreasing moisture content (Zhang *et al.* 2013). Kocaefe *et al.* (2010) have found that heat treatment up to 160°C temperature improves bending strength. Sun *et al.* (2013) impregnated *Eucalyptus pellita* wood with melamine-urea-formaldehyde resin and then heat-treated it at different temperatures. They noted that the changes in the mechanical properties were minimal below 200°C, which is in agreement with the present study. The impact strength is strongly dependent on the treatment method. Heat treatment in an air atmosphere decreases the impact strength more than to oil heat treatment or heat treatment in nitrogen air (Kubo-jima *et al.* 2000, Rapp 2001). Winandy *et al.* (1983) state that higher retention of an impregnation solution decreases toughness, which is congruent with our results. Well-penetrated melamine impaired the impact strength of the wood.

Degradation of hemicellulose between microfibrils is the main mechanism of strength loss in wood (Sweet and Winandy 1999), and the reduced strength properties of heat-treated wood are attributed to the loss of hemicelluloses (Rowell *et al.* 2009). When flexibility decreases, the hemicellulose-cellulose-hemicellulose bond is replaced with a more rigid cellulose-cellulose bond (Boonstra *et al.* 2007b, Kocaefe *et al.* 2008b). The reduction in bending strength is correlated with the degradation of hemicelluloses (Weigl *et al.* 2012). Boonstra *et al.* (2007b) have characterized that the impact strength is determined by secondary bonds between cellulose and hemicelluloses, therefore degradation of hemicelluloses is also responsible for the decrease in impact strength. The mass losses were similar in every sample at the same temperature, so it can be assumed that the degradation of hemicelluloses is similar after impregnation. The better bending strength of the melamine-impregnated heat-treated samples thus is unlikely to be due to the minor degradation of hemicellulose. In addition to the degradation of hemicellulose, previous studies have assumed that the changed mechanical properties may be explained by the increasing crystalline cellulose content (Boonstra *et al.* 2007b, Kocaefe *et al.* 2008b). Furthermore, heat-treated wood has lower plastic ductility, which makes crack initiation easier (Majano-Majano *et al.* 2012).

Conclusions

The effect on pine wood of impregnation with different modifiers together with heat treatments was investigated in this work. The combination of two treatment methods can improve some properties of wood, but the type of modifier and the treatment conditions affect the results.

On the basis of the tests, the moisture properties of wood were improved by the heat treatment, with greater improvement found at higher treatment temperature. It was found that the mechanical properties decreased after impregnation compared to untreated wood but the impregnation solutions had a favorable effect on the mechanical properties after heat treatment at a low temperature. The most significant property change was the bending strength of melamine-impregnated wood improved with the mild heat treatment temperature.

This study shows that moderate heat treatment of impregnated solid wood can improve, or at least will not reduce, the mechanical properties of Scots pine wood. Solid wood treated in this way may be suitable for various uses, for example, in outdoor use and furniture. The promising results for melamine-impregnated wood suggest that future research should focus on more detailed study of its properties and suitability for various applications.

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Publication V

Lahtela, V., and Kärki, T.

The influence of melamine impregnation and heat treatment on the fire performance of Scots pine (*Pinus sylvestris*) wood

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The influence of melamine impregnation and heat treatment on the fire performance of Scots pine (*Pinus sylvestris*) wood

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SUMMARY

Wood, as a natural and renewable resource, is a popular material for construction, but its fire performance restricts its utilization. In addition, for example, the mechanical properties of wood have up till now been impaired by the most common fire retardants, and therefore, the investigation of wood modification with not-weakening flame retardants is essential. This study investigates the effects of melamine impregnation and heat treatment on the fire performance of Scots pine (*Pinus sylvestris* L.). The treated samples were tested with a cone calorimeter, and the following features were studied: time to ignition, heat release, smoke production, and mass loss. The heat-treated samples became more homogenous as regards the results of fire performance. Some of the examined fire behavior values decreased because of heat treatment, while the same values increased after the combination of melamine impregnation and heat treatment. The smoke production was reduced the most for the samples that were both impregnated and heat treated. Although the influence of treatment on the fire behavior properties of solid wood was relatively marginal, it was assumed that these treatments will not have a negative impact on the fire-resistance properties of pine wood. Copyright © 2015 John Wiley & Sons, Ltd.

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KEY WORDS: wood; modification; melamine; impregnation; heat treatment; cone calorimeter

1. INTRODUCTION

Wood is a renewable resource with a large number of applications as a structural material as it is easy to work with, has good isolation properties, and high strength compared with weight. However, wood has some weaknesses, such as vulnerability to moisture and further to decay. These inherent properties can be developed by wood modification, which is an option for improving the quality of wood during its lifetime [1]. Wood modification methods are, inter alia, impregnation and thermal treatment. The impregnation modification of wood creates the desired changes by filling the substrate of wood with an inert material, utilizing, for example, vacuum and pressure processes [1, 2]. In thermal modification, the chemical structure of wood is changed by high processing temperatures [3].

The most restrictive property for the use of wood is its sensitivity to fire, which requires investments in fire safety. However, it must be remembered that after ignition, the surface of wood begins to char at a rate of 0.8–0.9 mm/min [4], retarding the progress of fire, which may be taken into account in the designing of the structure. To meet the fire safety codes, the treated wood must be tested and classified, for example, according to the Euroclass system. This is a widespread system for the fire performance of construction products, which relieves the barriers of wood applications. In the Euroclass system, construction products can be classified to seven categories, in the order of merit:

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A1, A2, B, C, D, E, and F. The basic class for untreated wood-based products is D, if the density is at least about 400 kg/m³, and fire-retarded wood products can achieve B class at best [5].

A number of theories of the mechanism of fire retardants have been presented quite a long time ago [6], and the traditional fire retardants for wood are based on phosphorus, nitrogen, and boron [7]. Some fire-retardant chemicals contain elements that have a negative impact on the wood, such as vulnerability to leaching and corrosion, and dimensional instability properties [8, 9]. Furthermore, some fire retardants can degrade the strength properties of wood in synergy with high temperature and high acid concentration environments [10].

The purpose of this study was to investigate the fire-resistance properties of melamine-treated and thermally modified solid wood. Also, the effect of treatment parameters on the results is discussed. The melamine treatment of wood has a positive influence on some properties, such as protection against weathering, decay, and moisture [11–13]. It has not been found that melamine would cause similar problems like the aforementioned traditional fire retardants. The thermal modification of wood improves its dimensional stability and decay resistance, but some strength properties are decreased [1,3]. Several thermal modification processes have been commercialized, for example, ThermoWood, which exploits a steam and a temperature of at least 180 °C [14]. From the fire safety point of view, thermally modified wood is equal to untreated wood [14], but there are differences between wood species [15]. It has also been noted that the treatment of wood at elevated temperatures, 180 and 212 °C, influences some properties of melamine-impregnated wood favorably [16]. Melamine has been used as a flame-retardant additive in other applications, such as plastics [17]. Nonetheless, the fire-resistance properties of melamine-treated solid wood have not been studied thoroughly, and therefore, this study is necessary. In addition, the fire behavior of thermally modified wood has not been examined thoroughly, even though it is the most advanced wood modification process commercially [1].

2. EXPERIMENTAL

2.1. Materials

Scots pine wood (*Pinus sylvestris* L.) was used in the investigation. Wood material properties, density, moisture content, and the rate of growth, were measured before the treatment. The values are given in Table I. Based on the rate of growth and density, the untreated wood material corresponded to normal values [18, 19].

The samples (20 × 100 × 160 mm) were treated by impregnation with melamine in a registered pressure apparatus, at a pressure of 10 bar for 120 and 240 min. Melamine (EXPH 522) was obtained from Dynea Chemicals Oy (Hamina, Finland). According to the manufacturer, the viscosity of melamine was 85–100 mPa · s (20 °C), and the pH value of 9.4–9.8.

After impregnation, the samples were dried in an oven at 95 °C for 24 h. The result of the impregnation was measured by weight percent gain (WPG) (Eqn 1).

$$WPG (\%) = \frac{Mm - Mu}{Mu} \times 100 \quad (1)$$

where *Mm* is the oven-dry mass of the modified wood and *Mu* is the oven-dry mass of the unmodified wood.

Table I. Average properties before treatment.

Property	Value
Density (kg/m ³)	477.46 (38.09)
Moisture content (%)	13.39 (1.17)
Rate of growth (mm/a)	3.40 (1.16)

Values in parentheses indicate standard deviations.

A portion of the samples impregnated for 120 min were heat treated at two different temperatures according to the ThermoWood process [14], without water vapor in the process. Because of the minor effect of impregnation time, the heat treatment was performed only for the 120-min-impregnated samples. The samples were treated in a heating oven, at temperatures of 180 and 212 °C for 180 min. The effect of heat treatment was measured by mass loss (ML) (%) (Eqn 2).

$$ML(\%) = \frac{m_1 - m_2}{m_1} \times 100 \quad (2)$$

where m_1 is the mass before heat treatment and m_2 is the mass after heat treatment.

2.2. Fire testing

The fire testing was conducted according to standard ISO 5660–1 with a Fire Testing Technology cone calorimeter whose function is based on the amount of oxygen required for combustion. The samples for the tests were 20×100×100 mm in size. The grain orientation of all samples was by radial section when the directions of annual rings were vertically close to 90°. All the samples were wrapped in aluminum foil covering the sides and the bottom. The samples were exposed in the horizontal orientation to an external heat flux of 50 kW/m² with the cone heater located 25 mm above the sample. The samples were conditioned at 23 °C and 50% relative humidity before testing. The cone data presented in this paper are the averages of three replicated experiments. During the test, heat release rate (HRR), total heat release (THR) rate, total smoke production (TSP), and average specific mass loss rate (MLR) were calculated according to standard ISO 5660–1. The cone calorimeter includes a simulation software, which can predict the fire performance class, based on fire growth rate values, W/s, which is defined as the rate of heat release divided by time [5].

2.3. Statistical analyses

The results of the fire-resistance tests were analyzed statistically by the Pearson product moment correlation coefficient, which reflects the extent of a linear relationship between two data sets, giving a value between –1 and +1. The sign (–/+) indicates the direction of the relationship, and the magnitude of the values demonstrates the strength of the relationship. The significance of correlation coefficient requires that variables based on same standard [20, 21].

3. RESULTS AND DISCUSSION

There were no significant differences between 120 and 240 min of impregnation, 16.76 and 19.06 WPG, respectively, but the standard deviations were remarkably high, 10.77 and 7.12, respectively, because of the heterogeneous nature of wood. Therefore, we classified the impregnated samples according to two target WPGs, 10 and 20, in order to detect differences. Every reclassified group consisted of three samples in fire testing. The values after reclassification are presented in Table II.

Table II. Average properties of WPG, mass loss, initial mass, and time to ignition.

HT (°C)	Aim WPG	Real WPG ± SD	HT mass loss ± SD	Initial mass [g] ± SD	Time to ignition [s] ± SD
*	0	—	—	103.90 ± 8.57	12.33 ± 2.89
*	10	11.93 ± 4.84	—	114.32 ± 10.26	12.33 ± 5.86
*	20	20.49 ± 0.70	—	114.69 ± 7.63	15.00 ± 6.56
180	0	—	10.76 ± 0.05	84.56 ± 2.03	11.33 ± 0.58
180	20	17.89 ± 0.35	8.44 ± 0.08	103.03 ± 1.65	16.00 ± 1.00
212	0	—	13.59 ± 0.15	79.84 ± 2.66	12.33 ± 0.58
212	20	17.89 ± 0.35	10.66 ± 0.24	100.93 ± 0.63	15.67 ± 0.58

*No heat treatment.

WPG, weight percent gain; HT, heat treatment; SD, standard deviation.

The penetration of the solution depends on various factors of wood, for example, on porosity and growth increment [22, 23]. In a previous study, better melamine penetration was achieved [13], which may have been due to the different viscosity of the solution. The viscosity of the solution has been found to affect the penetration in Scots pine [24, 25]. The low average WPG value is not likely to be a problem in this study, as Ma *et al.* [26] have found that a too high melamine content could decrease the fire-retardant property. Looking at the initial mass in Table II; we can see that the rates of standard deviations are minor for the heat-treated samples. The initial mass of the samples ranged from 76.77 to 123.60 g, and it is generally approximately 80 g in the cone calorimeter apparatus [27]. The MLRs decreased after the melamine treatment compared with the purely heat-treated samples at the same temperature. The ML was increased because of higher treatment temperature, which is in agreement with previous studies [28, 29].

The fire behavior of the melamine-impregnated and heat-treated wood is presented in Figure 1 and Tables II–IV. Table II shows the ignition time of the samples. The heat treatment decreased the ignition time [14]. It has been stated that wood density correlates with ignition time [30, 31], which is in agreement with this study, as the ignition of untreated wood correlated with density negatively, at the value of -0.97 . The impregnation increased the density, and correspondingly, the heat treatment decreased the density.

The HRR and specific MLR curves versus time of different treatment levels are shown in Figure 1. The HRR curves are presented as a scatter chart with lines, and the specific MLR curves are presented as a scatter chart, to which trend lines have been added using a 10-period moving average. The HRR curve of wood burning usually consists of two peaks [32]. The first peak is the commencement of combustion, which is compounded by the reaction between oxygen and volatile gases under the influence of heating. After that, heat transfer becomes difficult because an insulating char layer has been formed. The second peak is a consequence of decomposition of the char layer, which produces small cracks, and these cracks allow volatiles to escape [33]. Even though the previously presented ignition times did not change significantly, differences can be seen in the HRR curves. The melamine-treated samples had quite similar values in the HRR curves compared with the curve of untreated wood, but the values of mere heat treatment had decreased. The combination of melamine impregnation and heat treatment increased and brought forward HRR in the case of the second peak.

Figure 1 shows also the specific MLR curves versus time of different treatment levels. It can be seen that the melamine impregnation causes greater MLR, which sustained longer compared with untreated samples (0 WPG). The means of the HRR peak values are presented in Table III, together with time and standard deviations. The initial peaks were higher than the second peaks, and they appeared within 35 s. The second peaks appeared in a wider area, between 805 and 1080 s. For the non-impregnated and heat-treated samples, there was a decrease in the HRR peaks.

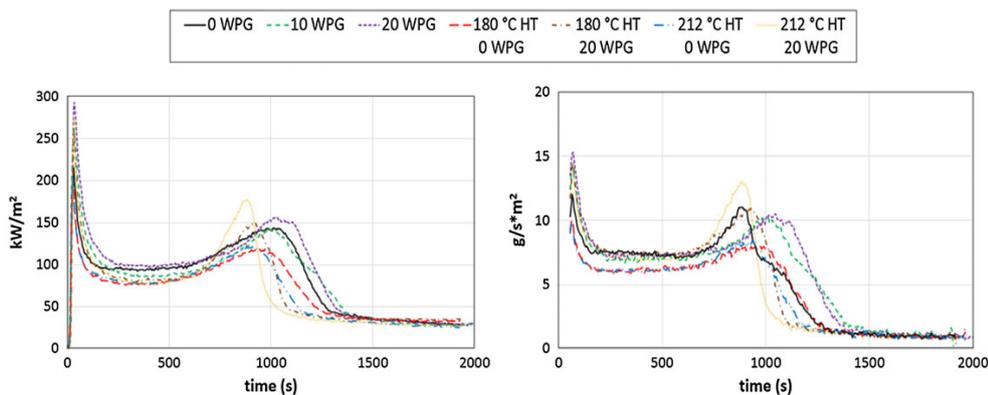


Figure 1. Heat release rate (left) and specific mass loss rate (right) curves of different treatment levels versus time.

Table III. Average peak values of the HRR and the time of peaks, together with SDs.

Heat treatment (°C)	Aim WPG	HRR (first peak, 0–300 s) kW/m ² ± SD Time ± SD	HRR (second peak, 500–1500 s) kW/m ² ± SD Time ± SD
*	0	214.95 ± 27.00 30 ± 0	152.87 ± 28.39 985 ± 66
*	10	305.69 ± 104.46 28 ± 8	150.17 ± 7.51 1027 ± 50
*	20	324.56 ± 44.34 30 ± 5	157.92 ± 7.99 1042 ± 16
180	0	198.85 ± 10.16 28 ± 3	118.99 ± 4.81 932 ± 19
180	20	258.42 ± 41.53 32 ± 3	153.28 ± 19.48 893 ± 27
212	0	209.92 ± 6.05 27 ± 3	123.34 ± 10.96 893 ± 37
212	20	275.06 ± 6.63 30 ± 0	203.96 ± 34.18 865 ± 54

*No heat treatment.

HRR, heat release rate; WPG, weight percent gain; SD, standard deviation.

Table IV. Sample averages of cone calorimeter data with regard to THR, TSP, and MLR.

Heat treatment (°C)	Target WPG	THR (MJ/m ²) ± SD	TSP (m ³) ± SD	Average specific MLR (g/s*m ²) ± SD
*	0	156.47 ± 28.24	11.80 ± 10.30	8.01 ± 0.57
*	10	156.47 ± 31.36	12.17 ± 14.68	7.88 ± 0.25
*	20	171.07 ± 11.87	13.63 ± 8.39	8.10 ± 0.26
180	0	131.80 ± 5.06	4.47 ± 0.59	6.49 ± 0.08
180	20	136.73 ± 9.19	2.30 ± 0.40	8.08 ± 0.06
212	0	125.60 ± 5.30	4.27 ± 1.21	6.41 ± 0.20
212	20	130.43 ± 4.40	2.84 ± 0.32	7.81 ± 0.08

*No heat treatment.

THR, total heat release; TSP, total smoke production; MLR, mass loss rate; WPG, weight percent gain; SD, standard deviation.

Considering the HRR results in Figure 1 and Table III, it can be seen that the melamine treatment caused an increase especially in the first HRR peak. For example, the biggest result is seen with the high melamine impregnation (20 WPG), the first HRR peak increased by 51%. The heat treatment reduced the HRR values, but melamine impregnation before the heat treatment was able to raise it to a higher level. It can be inferred from the results that the decomposition of wood takes place more strenuously, due to melamine treatment. According to the statistical analyses, the mean HRR values correlated positively with mass, especially for untreated and melamine-impregnated wood, which correlation coefficients were 0.98 and 0.94, respectively.

The average and standard deviations of the results of THR, TSP, and MLR are given in Table IV. The melamine treatment does not appear to affect to the values of THR significantly, but heat treatment has a lowering effect thereto. According to Scharrel and Hull [32], THR is connected with HRR in a cone calorimeter test, which is agreement with this study. The results show that the growth of THR values are refracted approximately at same time with the second peak values of HRR.

Table V. Data of residual mass with SD.

Heat treatment (°C)	Target WPG	Original mass [g] ± SD	Residual mass [g] ± SD	Percent of original mass ± SD
*	0	103.90 ± 8.58	11.75 ± 0.53	11.38 ± 1.26
*	10	114.32 ± 10.26	14.74 ± 3.32	13.14 ± 4.12
*	20	114.69 ± 7.62	13.05 ± 0.25	11.40 ± 0.69
180	0	84.56 ± 2.03	8.72 ± 1.97	10.28 ± 2.08
180	20	103.03 ± 1.65	16.61 ± 1.71	16.10 ± 1.41
212	0	79.84 ± 2.66	7.52 ± 1.16	9.40 ± 1.23
212	20	100.93 ± 0.63	18.40 ± 1.35	18.23 ± 1.22

*No heat treatment.

WPG, weight percent gain; SD, standard deviation.

The pure melamine treatment did not result in significant changes in the TSP, contrary to the heat treatment, when compared with untreated wood. Looking at the TSP results in Table IV, a high decrease of the TSP can be seen in the heat-treated samples, at least over 60%. The melamine-impregnated and heat-treated samples have even higher TSP reduction than previously, 81% and 76% after heat treatment at 180 and 212 °C, respectively. The lignin content increases, the hemicelluloses degrade, and most of the extractives evaporate during the heat treatment [34]. These chemical changes of wood may be the cause of the different TSPs.

Smoke production is an important factor for evaluating a fire hazard [35]. According to the tests, it can be concluded that melamine treatment did not seem to increase smoke production significantly compared with untreated wood. Depending on the nature of the smoke, the decreased smoke production of heat-treated samples can be classified as an improved property, because smoke is a critical problem with some fire retardants [8]. The smoke production must be studied more exactly, because there have been irregular measurements in smoke production after heat treatment of wood [14, 15, 36].

It can be seen in Tables II and IV that the results of MLR are comparable with the initial mass. The relationship between ML and initial mass is provable by the correlation coefficient, which is on average 0.91 in all samples. When reviewing the residual mass in Table V, it can be concluded that the melamine-treated and heat-treated samples have bigger residual mass percentage than the merely heat-treated samples.

Unambiguous differences in the HRRs could be achieved with changing of the heat flux density, which has a significant influence on the combustion, according to Martinka *et al.* [37]. On the basis of fire growth rate values, the classification of fire performance did not advance significantly.

4. CONCLUSIONS

In this work, the fire-resistance properties of melamine-impregnated and thermally treated solid wood were studied. Because of the standard deviation of the results, it can be stated that the fire behavior of wood is strongly dependent on the properties of an individual sample, but heat treatment makes wood more homogenous. Melamine impregnation increased the fire behavior rates, like ignition time and heat release, while heat treatment decreased them. The combination of impregnation and thermal modification of wood increased and brought forward HRR in the case of the second peak. Moreover, reduction of TSP was caused by combination treatment, and especially by heat treatment. The combination treatment also increased the amount of residual mass after combustion. It is concluded that melamine impregnation and heat treatment do not appear to have a negative impact on the fire-resistance properties of solid wood.

The decreased amount of smoke could contribute to survival in conflagration, depending on the toxicity of the smoke. Therefore, the nature of smoke is a feasible topic for further study of the melamine-impregnated heat-treated wood. In addition, the information of the changes of charring rates and mechanical strengths in fire situations can contribute to the utilization of wood in the future.

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Publication VI

Lahtela, V., and Kärki, T.

Determination and comparison of some selected properties of modified wood

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DETERMINATION AND COMPARISON OF SOME SELECTED PROPERTIES OF MODIFIED WOOD

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ABSTRACT

Modification of wood has become increasingly significant in recent decades due to e.g. growing environmental awareness, and a number of modified wood products are available. Some inherent qualities of wood may, however, raise questions about the durability of modified wood. This study investigates the properties of modified wood products. Three commercial modified wood products and two possible future contenders of our own production are studied and their resistance to artificial weathering, water absorption, swelling, and bending strength are analyzed. The results show that weathering caused notable and interesting differences among the tested materials. The moisture properties of the commercially available modified wood products remained on a restrained level compared to the contenders, but in the bending strength, the contender achieved equal values with the commercial products. It is concluded that each of the modified wood products had some outstanding properties.

KEYWORDS: Wood, modification, acetylation, furfurylation, sodium silicate, melamine, properties.

INTRODUCTION

Wood is a natural material which has been used in many applications for centuries. However, some of its weak inherent features, for example water susceptibility and biodegradability, reduce its quality. Wood modification is a way to advance these features to increase the usability of wood products.

Modification of wood alters its properties in such a way that during the lifetime of a product, loss of the enhanced performance of the wood should not occur. In addition, it is desirable that the modification of wood would be carried out with no release of toxic substances (Hill 2006). Although, the demand for non-toxicity has been abandoned slightly (Militz and Lande 2009), the growing environmental awareness has turned the focus on non-hazardous chemicals and processes and also natural materials (Németh et al. 2015). The first studies relating to wood

modification were done in the 1930s, but the wood modification technology is still relatively new. Some methods have been introduced in the European market, such as acetylation, heat treatments, furfurylation, and use of DMDHEU (dimethyloldihydroxyethylurea) (Militz and Lande 2009). In addition, wood plastic composite (WPC) products are also an alternative to modified wood in some outdoor applications (McGraw and Smith 2007; Stark and Matuana 2007; Clemons et al. 2013).

The properties of the studied materials have been investigated quite widely. Research of acetylated wood has been done since 1928. Today, the most common acetylation reaction is performed by acetic anhydride without a catalyst as a liquid phase. The reaction of acetic anhydride with wood forms acetic acid as a by-product, which must be removed from the final product. The acetylation treatment process of solid wood consist of a vacuum and a drying step before and after the anhydride processing, respectively (Rowell 2006; Rowell et al. 2009; Rowell 2013). The acetylation of wood reduces the number of hydroxyl groups, which results in a reduction of the equilibrium moisture content. Hence, dimensional stabilization increases and fungal attack decreases. The strength properties are retained almost unchanged after acetylation. (Rowell et al. 2009). The trade name Accoya is a known acetylated wood product.

Investigations of wood modification with furfuryl alcohol were started in the 1930s and 1940s, and the method is known as furfurylation (Lande et al. 2004); Kebony is the known trade name for furfurylated wood. Furfurylation is usually defined as impregnation modification (Esteves et al. 2011), the process of which is based on the full cell method with water-borne solution of furfuryl alcohol and its additives. An intermediate vacuum drying step before steam curing and drying is also possible, for example within the Kebony process (Pilgård et al. 2010). Furfurylated wood has good dimensional stability and resistance to decay and insect attack (Lande et al. 2004). The changes of the mechanical properties depend on measurable features. Some properties show insignificant change, but hardness can increase about 50 %, for instance (Esteves et al. 2011).

Water glass means potassium or sodium silicates, or solutions thereof, and it is utilized in many applications. Its beneficial properties are non-toxicity, low price and availability, inter alia (Mai and Militz 2004; Chen 2009). Water glass is soluble in water and forms an alkaline solution at elevated temperatures and pressures (Mai and Militz 2004). The strongly alkaline solution can polymerize from wood acidity when it is unable to penetrate into the cell wall layers (Chen 2009). The treatment of wood with water glass can reduce fungal growth and change of color, and in addition, it can increase the fire resistance (Mai and Militz 2004; Pfeffer et al. 2012). The number of commercially available silicate-based wood preservatives is difficult to determine (Mai and Militz 2004), but examples of commercialized wood products based on sodium silicate can be found. Such examples are the trade names TimberSil (Flynn 2006), S-Treat, and Q-Treat, of which the latter includes also thermal modification (Pynnönen et al. 2014).

From the commercial point of view, wood treatment with melamine does not have a significant role yet. However, its penetration into wood has been studied for years (Lukowsky 2002; Gindl et al. 2003). Melamine can protect wood against weathering, it reduces water uptake, and improves the strength and decay-resistance of wood on its own (Deka et al. 2002, Hansmann et al. 2006; Lahtela and Kärki 2014a) and in synergy with moderate heat treatment (Lahtela and Kärki 2014b).

The aim of this study is to compare the properties of commercial, and potential future modified wood products. There are several modified wood methods and products, but the selected products are based on treatment with a modifier agent, and possibly by the utilization of thermal modification. The comparisons of the products are done by measuring the weathering, moisture, and mechanical properties of the wood.

MATERIAL AND METHODS

The commercial modified wood products were purchased from an importer (Accoya and Kebony) and a retailer (Q-Treat). In addition to the commercial modified wood products, Scots pine (*Pinus sylvestris*) samples (20 x 95 x 1000 mm) were impregnated with melamine (Prefere 70 0592 L), at a pressure of 10 bars for 120 min. After that, the samples were dried at 90°C for 24 h, and the measured weight percent gain (WPG) that was 38.7 %. Finally, the samples were heat treated, at temperatures of 180°C (MHT180) and 212°C (MHT212) for 180 min. The densities of the tested materials are presented in Tab. 1.

Tab. 1: Average densities and standard deviations.

	MHT180	MHT212	Q-Treat	Accoya	Kebony
Density (kg.m ⁻³)	599.61 (76.32)	569.45 (93.94)	420.81 (18.54)	619.26 (26.21)	626.72 (17.92)

Values in parentheses indicate standard deviations.

The weathering performance of the tested materials was evaluated by an accelerated weathering test in a test chamber (Q-Sun Xe-3 Xenon Test Chamber) with intervals of UV-light and water spray based on the standard of SFS-EN ISO 4892-2 (2006). The effect of the weathering test was analyzed through measurement of the surface color with a Minolta CM-2500d spectrophotometer (Konica Minolta Sensing Inc., Japan) with the following settings: Reflectance SCE, illumination D65, observer 2°, and illumination area 8 mm. The surface color was calculated before the test and after every 100 h up to the end of the test, 1000 h. In addition, the surface color was calculated in the beginning of the test, 24 and 48 h after test start. In the spectrophotometer measurement, the CIELAB color space was measured in L*, a*, and b* coordinates. The value of L* indicates the lightness coordinate and varies from 100 (white) to 0 (black), a* indicates the red (+a*) to green (-a*) coordinate, and b* indicates the yellow (+b*) to blue (-b*) coordinate. The color difference (ΔE^*) is defined by the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where: ΔL^* , Δa^* , and Δb^* illustrates the differences between the initial and measured values of L*, a*, and b*, individually. The surface color for each product was measured from six specimens, by 18 measurements in total.

The moisture properties were determined with swelling and water absorption tests for pieces with the size 20 × 20 × 30 mm (RxTxL). The test pieces were conditioned at 20°C and 65 % relative humidity for over 24 h before the test. The specimens were then weighed and the dimensions were measured before immersion into water for the duration of 28 days. The specimens were periodically taken out of the water, surface-dried with absorbent paper, re-measured, and returned to the water immediately.

Swelling (S) was determined in radial and tangential directions according to the following equation:

$$S = \frac{T_1 - T_2}{T_2} \times 100 \quad (2)$$

where: T_1 - the thickness of the piece after immersion,
 T_2 - the thickness of the piece before immersion.

The water absorption values (WA) were calculated as follows:

$$WA = \frac{W_1 - W_2}{W_2} \times 100 \tag{3}$$

where: W_1 - the mass of the specimen after immersion,
 W_2 - the mass of the specimen before immersion.

Mechanical strength was determined by three-point bending strength tests with a Zwick Roell Z020 testing machine in accordance with ISO 3133 (2008). Fifteen test samples of each product, with dimensions 20 × 20 × 380 mm, were tested. The test samples were conditioned at 20°C and 65 % relative humidity for over 24 h prior to testing. The moisture and mechanical properties were determined of 15 specimens per product.

RESULTS AND DISCUSSION

Weathering

The weathering performance of the tested specimens is presented as point charts in Figs. 1-2, with an added trend line between the points. Fig. 1 shows weathering behavior based on the first three measurements, and the weathering performance of the whole test period is presented in Fig. 2.

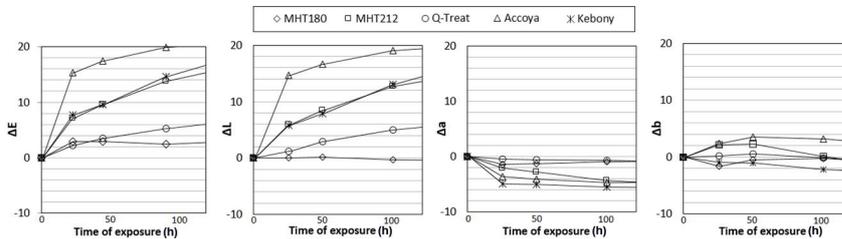
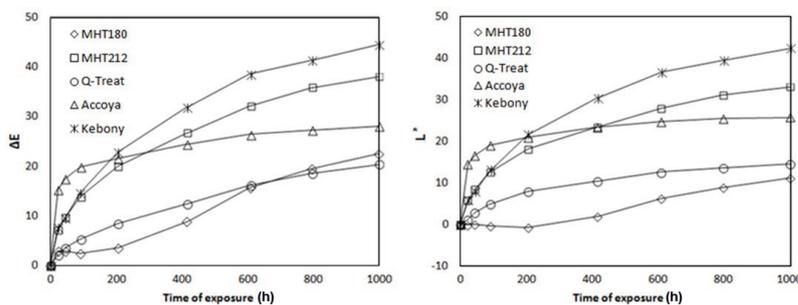


Fig.1: Total color change (ΔE) and changes of three color parameters (L^* , a^* , b^*) of tested specimens in artificial weathering for the first 100 hours.



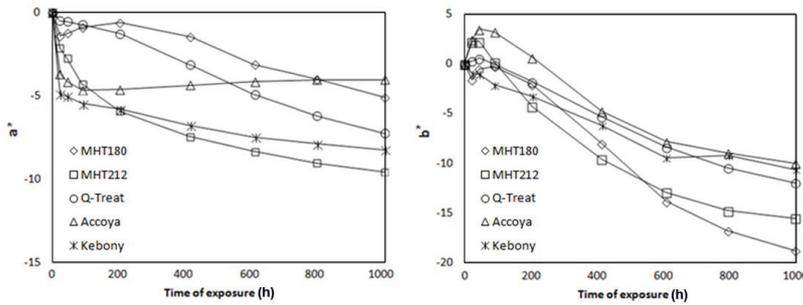


Fig. 2: Total color change (ΔE), and changes of lightness (L^*), and the red/green (a^*) component and yellow/blue (b^*) component as a function of artificial exposure of the tested materials for 1000 hours. The results are presented as spaced from 200 h forward.

The graying of wood is the most obvious feature of weathered wood, which is due to leaching of extractives and lignin, resulting in cellulose-rich surface layers (Evans 2013). One ΔE is the smallest change in color which the human eye can detect (Sachs 2001-2003), and we could detect the color change already in the first measurement. All specimens showed a tendency to become lighter, bluer, and greener when the weathering test proceeded. The melamine-impregnated and heat-treated (MHT180) samples together with the Q-Treat samples had the lowest changes of color in the beginning of the weathering test. The MHT180 samples had the lowest color change until about halfway of the test period, after which the color change increased slightly. It has been found in previous studies that melamine treatment can reduce wood discoloration and retain its natural appearance (Hansmann et al. 2006). The weathering performance of the Q-Treat specimens was nearly linear for the whole test period. Water glass treatment can curb the decrease of lightness particularly in the case of Scots pine, but it cannot prevent discoloration during long-term weathering (Pfeffer et al. 2012). This kind of function is possible with the Q-Treat specimens. The total color change was greatest with the Kebony specimens, the lightness of which increased most, which is in agreement with a previous study (Temiz et al. 2007). Furfuryl alcohol is a colorless liquid which forms a hydrophobic dark brown polymeric gel in the presence of heat and an acidic catalyst (Thygesen et al. 2010). The color change of the melamine-impregnated specimens heat treated at 212°C (MHT212) were congruent with the Kebony specimens, only the b^* color value was reversed compared to the color parameters in the beginning of test. The change of lightness was higher with the MHT212 specimens compared to the MHT180 specimens, which may be due to the color function of thermally modified wood. Generally, the darkness of thermally modified wood increases with the increasing temperature (Thermowood 2003) but fades relatively quickly at weather exposure (Jämsä et al. 2000, Bak et al. 2012). The color change of the Accoya specimens was significant in the beginning, after which it became stable. According to Rowell (2013), acetylation changes dark woods to lighter and light woods to darker. Weathering changed the color of the Accoya samples rapidly, after which the surfaces remained stable, as well as lighter and cleaner by visual review.

It has been found that the surface color alters more tangentially than radially (Huang et al. 2012). In this study, the surfaces of the Accoya and Kebony specimens were tangential, those of the Q-Treat mainly radial, and the MHT samples (MHT180 and MHT212) consisted of both kinds of surfaces. Analysis of the tangential and radial surfaces of the MHT samples showed that the tangential surfaces altered more, and the effect was highlighted in the MHT212 samples.

Moisture properties

Data on the moisture properties are presented in Figs. 3-4. The water absorption (WA) properties are presented as a point chart in Fig. 3, to which a trend line has been added. The Q-Treat specimens absorbed the most water during the test while the other specimens absorbed considerably less water, and the MHT212 absorbed the least. The Accoya specimens absorbed water slightly more in the beginning of the test but it leveled off when the test proceeded.

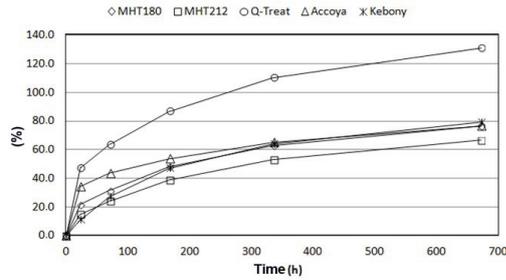


Fig. 3: Water absorption as a function of immersion time of the tested materials.

The swelling properties are presented as a bar chart in Fig. 4 for the tangential and radial directions. The swelling increased with the progressing immersion time, but part of the specimens reached quickly a status where no more swelling occurred. For example, the swelling of the Accoya specimens was diminished significantly in both directions, starting from the first measurements. Generally, the swelling of the commercial wood products was almost stabilized after a week of water immersion at the latest.

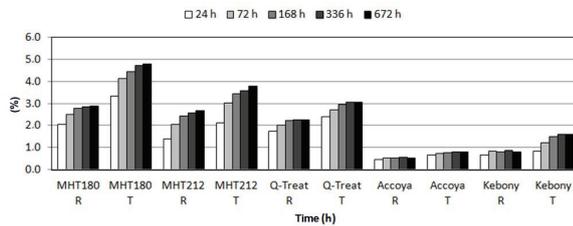


Fig. 4: Radial (R) and tangential (T) swelling with time.

The significance of moisture must not be underestimated, as it affects many properties of wood. Generally, tangential swelling is twice compared to radial swelling (Rowell 2013) but in modified wood this difference did not seem to be so notable. Further study showed that although the swelling anisotropy decreases as a result of heat treatment, it will not disappear (Bak and Németh 2012). It has been reported that the cell walls of Accoya and Kebony specimens are more hydrophobic owing to treatments, in which case swelling does not have a normal influence (Thygesen and Elder 2008). The water absorption function of the Q-Treat specimens was similar to a previous study where heat treatment had a negative effect on the water absorption of water glass-treated wood (Lahtela and Kärki 2014b). It has been stated that the high moisture content of water glass-treated specimens proceeds from hygroscopicity of unreacted solution in the lumen of the cell and on the specimen surface (Mai and Militz 2004; Pfeffer et al. 2011). It can be seen on the basis of the study that the method of wood modification has an effect on the moisture properties of wood.

Mechanical properties

The averages of bending strengths are presented in Fig. 5, as bar charts with standard deviations added as error bars. Accoya and MHT180 have the best values, 104.92 and 103.15 MPa, respectively while the bending strength of Q-Treat reached 62.5 % of the best strength.

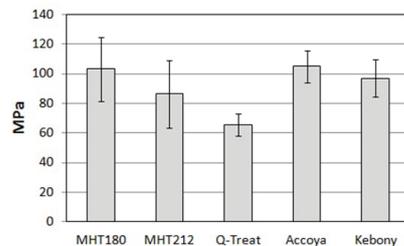


Fig. 5: Bending strength of the tested materials.

The modification affects the bending strength individually. For example, furfurylation increases to strength (Esteves et al. 2011) but the effects of acetylation is insignificant (Papadopoulos and Tountziarakis 2011; Rowell et al. 2009) or at most slightly increased (Epmeier et al. 2004). The strength property of acetylated material depends on the species and treatment processes (Bongers and Beckers 2003). It has been found that melamine can increase the strength of wood on its own (Deka and Saikia 2000) and in combination with moderate heat treatment (Lahtela and Kärki 2014b), but immoderate treatment temperature and time reduce the strength (Sun et al. 2013). Water glass treatment with elevated temperatures decreases the bending strength because a high pH produces hydrolysis of the cell wall polysaccharides (Mai and Militz 2004). Although Q-Treat achieved the weakest bending strength, its lowest standard deviation must be noted, which expresses controlled manufacture and product. It can be noted on the basis of the study that bending strength depends on the way of modification.

A high treatment temperature causes strength loss in wood (Thermowood 2003; Lekounougou and Kocaefe 2014). Therefore, the process values must be selected carefully when exploiting heat in wood modification. The bending strength depends on many properties, like specific gravity (Winandy and Rowell 2013) and it has been found that the bending strength reduction is aligned with hemicelluloses degradation (Weigl et al. 2012). For modified wood, the bending strength increases with increasing weight gain (Minato et al. 2003), but it is not always automatic (Epmeier et al. 2004).

CONCLUSIONS

In this work the effect of weathering, moisture, and mechanical properties of modified wood products were investigated. The tested products had different properties and there was variation in the results, showing that there was a need for this study. Superiority ranking between the investigated samples is challenging, but each type of modified wood has at least one excellent material property.

On the basis of the promising results of the weathering test, the color change of modified wood can be minimal or stable, especially in the beginning of weathering. The most significant changes in moisture took place quickly and the commercial modified wood products had controlled swelling. The mechanical properties were quite identical in the MHT180, Accoya, and Kebony samples.

This study has demonstrated that modified wood products have improved properties. However, none of the modified products had superior features in every test, and consequently wood modification is still a subject for further development. Modified wood products may have some other excellent properties which did not come out in this study. The choice of the modified wood product must be done according to intended use.

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