

Effects of chemical modification on the mechanical properties of wood

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Abstract Chemical modification has been recognized as an efficient strategy for dimensionally stabilizing wood and protecting it from environmental damage, such as deterioration due to weathering and fungal decay during the service period. Studies reported in the literature mainly concern the establishment of workable modification techniques, testing methodologies, and assessment of the durability of modified wood. The development of wood modification techniques has recently been reviewed; limited information is however given on the effects of chemical modification on the mechanical properties of wood that are of importance to it as an engineering material. This paper reviews the effects of wood modification, typically by heat treatments and impregnation with low molecular weight resins, reactive monomers, or hot melting paraffins on the mechanical properties of wood. The modifying variables associated with mechanical properties of wood such as wood species, treating temperature and time, catalyst, type of solvent, weight percent gain, and molecular structures of the modifying agent were analysed and the results interpreted. The reasons for changes in the mechanical properties of wood are discussed.

Einfluss chemischer Modifikation auf die mechanischen Eigenschaften von Holz

Zusammenfassung Chemische Modifikation wird als ein wirksames Verfahren zur Verbesserung der Dimensionsstabilität und zum Schutz gegen umweltbedingte Schäden wie zum Beispiel Holzzabbau aufgrund von Bewitterung oder Pilzbefall während der Gebrauchsdauer angesehen. In der Literatur vorhandene Studien befassen sich hauptsächlich mit geeigneten Behandlungsverfahren, Prüfmethoden und der Beurteilung der Dauerhaftigkeit von modifiziertem Holz. Die Entwicklung von Holzbehandlungsmethoden wurde kürzlich beschrieben, jedoch gibt es nur wenig Informationen hinsichtlich der Einflüsse einer chemischen Modifikation auf die mechanischen Eigenschaften von Holz im Hinblick auf seine Nutzung als Bau- und Werkstoff. In diesem Artikel werden die Einflüsse einer chemischen Modifikation, üblicherweise durch Hitzebehandlung oder Imprägnierung mit niedermolekularem Harz, reaktiven Monomeren oder heiß schmelzenden Paraffinen, auf die mechanischen Eigenschaften von Holz untersucht. Einflussgrößen auf die mechanischen Eigenschaften von Holz wie Holzart, Behandlungstemperatur und -dauer, Katalysator, Art des Lösungsmittels, prozentuale Gewichtszunahme und molekulare Struktur des Modifiziermittels wurden untersucht und die Ergebnisse diskutiert. Gründe für die Änderungen der mechanischen Eigenschaften wurden erörtert.

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1 Introduction

Wood is an important engineering material and commonly used in buildings and bridges (Wacker 2010); however, it is susceptible to abiotic and biotic damage during its service

period. Wood preservatives have been used for thousands of years to protect in-service wood from such damage, but the resultant environmental and health issues are of profound concern. Chemical modification can improve the properties of wood and provide a protection efficacy comparable to that given by preservatives. The chemicals used do not contain heavy metal elements and are able to react with wood cell wall polymers or condense in wood micro-structures. As a result, there is little risk of chemical leaching and therefore, protection to wood can last for a long-term service period. Consequently, chemical modification has been recognized as an important alternative to preservatives in the wood protection industry.

Wood chemical modification involves techniques where chemical and/or physical methods are applied to alter permanently the properties of wood cell walls, thereby providing a persistent protection to in-service wood (Hill 2006). Chemical modification can generally be classified as either cell wall modification, or filling of large cell cavities, or a combination of both. Cell wall modification refers to the process whereby wood cell wall constituents are altered through reacting with reactive low molecular weight monomers or oligomers, or by heating under high temperature conditions. Filling of cell cavities is the process by which chemicals are deposited in the large cell cavities such as lumens and vessels, and block the physical passages thereby reducing water/moisture access to wood cell walls. The protection mechanism of wood modification is mainly proposed to present as the bulking of cell walls, reduction of moisture content, and/or changes of molecular structure of the cell wall polymers (Hill 2006).

Laboratory studies on wood chemical modification have been carried out for several decades and many modification techniques developed have been successfully applied in industrial production in the last decade. In the current market there are almost one hundred commercial trademarks for various modified woods. Wood modification techniques normally involve the use of high temperature, catalysts, water/organic solvents, and reactive or non-reactive chemicals. Effects of chemical modification processes on the dimensional stability, moisture sorption, and durability against rot fungi and weathering have been extensively reported and reviewed (Homan and Jorissen 2004; Rowell 2005, 2006; Esteves and Pereira 2009; Hill 2011); however, to date there are few systematic reviews on the effects of chemical modification on the mechanical properties of wood that are crucial for wood used as a load bearing and non-load bearing material (Epmeier et al. 2004). Any substantial reduction in mechanical properties due to modification will greatly limit the application of modified wood as an engineering material (Kretschmann 2010).

The objective of this paper is thus to comprehensively review the literature with regard to the effects of wood

modification on the mechanical properties of wood. Typical current and potential commercial modification techniques are discussed, including heat treatment in various shield media, modification with reactive resins such as N-methylol compounds, furfurylation, grafting with vinyl monomers, acetylation, and impregnation with hot melting waxes. The effects of modifying variables such as wood species, treating temperature and period, catalyst, type of solvent, weight percent gain, and molecular structures of the modifying agent on the mechanical properties of wood are critically analysed and the results interpreted.

2 Heat treatment

Heat treatment comprises several techniques for treating wood at high temperatures (typically 150–230 °C) in a shield media such as steam, nitrogen gas, vegetable oils or under vacuum (Viitaniemi et al. 1997; Militz 2002). Heat treatments can cause a mass loss in wood, dark appearance, and create hydrophobic wood materials; dimensional stability and durability are improved (Kamdern et al. 2002; Nunes et al. 2004). Generally, wood treated at higher temperatures for longer periods exhibits a more severe loss in mass, colour, and mechanical properties, but greater improvement in dimensional stability and biological durability (Mitchell 1988).

Heat treatments lead to a reduction in most of the strength properties of wood which is dominated by the treating temperature and time (Christmas et al. 2005; Tremblay and Lihra 2005). Reduction in the modulus of elasticity (MOE) is generally less than the modulus of rupture (MOR). Both the MOR in bending and impact strength decrease by as much as 50 % (Table 1). The strength losses can even be higher as the treating temperature/time is more severe. In the load–deflection curves of the static bending test, untreated wood exhibited a plastic deformation following the initial linear elastic region of the curve (Fig. 1a); in contrast to the untreated controls, the heat-treated wood showed less deflection and a lower fracture force (Fig. 1b). These results indicate that wood appears to be more brittle after heat treatments.

A comprehensive test of 13 industrially manufactured heat-treated woods (Scots pine (*Pinus sylvestris* L.), European ash (*Fraxinus excelsior* L.), European beech (*Fagus sylvatica* L.), Norway spruce (*Picea abies* L.), and teak (*Tectona grandis* L.)) showed that wood density and several important mechanical properties were reduced following heat treatment compared to the untreated controls (Scheidig et al. 2005). Both the treated Scots pine and Norway spruce showed a decrease in density by approximately 20 % and the treated European beech by 10 %. All tested wood (hardwood and softwood) exhibited

Table 1 Effects of heat treatments on the mechanical properties of wood**Tab. 1** Einflüsse der Hitzebehandlung auf die mechanischen Eigenschaften von Holz

Wood species	Media	Temperature/duration (°C/h)	Moisture content at 20 °C, 65 % r.h. (%)		Change in mechanical properties based on untreated controls (%)			References
			Untreated	Treated	Static bending		Impact bending	
					MOE	MOR		
Pine	Steam	210/6	12.6	4.5	-40	-5	-	Esteves et al. (2007)
Eucalypt			10.5	2.8	-50	-15		
Pine	Moist/N ₂	Two stage treatment	-	-	-	-3	-	Tjeerdsma et al. (1998)
Beech						-20		
Pine	Linseed oil	220/4.5	-	-	NC	-30	-49	Rapp and Sailer (2000)
Beech	Gas exclude O ₂	220/4	11.3	4.9	11	-26	-	Arnold (2010)
Spruce			12.2	5.3	10	-19		
Softwood	-	212/-	13.5	6	-	-15	-	Mayes and Oksanen (2002)
Hardwood		200/-	10.5	6		-20		
Birch	Humid inert gas (N ₂ + CO ₂)	230/-	-	-	-7	-43	-	Poncsák et al. (2006)
Pine	Air	180/10	-	-	-32	-33	-42	Korkut et al. (2008)
Spruce	-	212/3	-	2-3	-14	-49	-	Shi et al. (2007)
Aspen		212/3			+15	-35		
Birch		200/3			+30	+6		

Positive values show an increase in percentage and negative ones for a decrease compared to the untreated wood

Only the data obtained from wood treated with the highest temperatures in each report are listed in the Table

- Unknown, NC no change

Positive Werte stehen für eine prozentuale Verbesserung und negative Werte für einen Rückgang im Vergleich zu unbehandeltem Holz

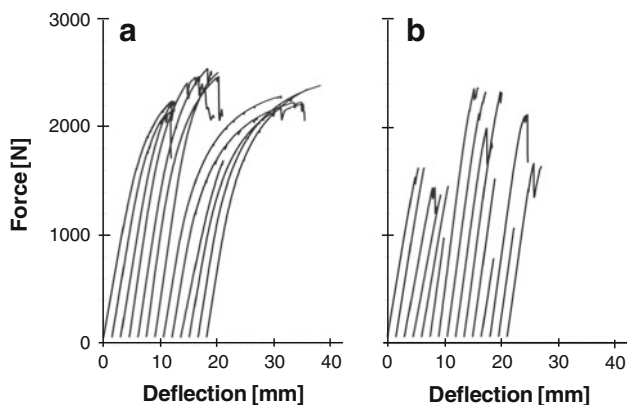


Fig. 1 Load-deflection curves for individual beech specimens (a) untreated and (b) treated at 220 °C for 4 h. Before bending test the samples were conditioned at 20 °C and 65 % r.h. Data adapted from Arnold (2010)

Abb. 1 Last-Verformungskurven einzelner Buchenprüfkörper: a unbehandelt und b bei 220 °C über 4 Stunden behandelt. Vor der Biegeprüfung wurden die Prüfkörper bei 20 °C und 65 % rel. Luftfeuchte klimatisiert. Daten von Arnold (2010)

losses in both MOE and MOR by 20–30 % and in impact strength by 30–60 %. Due to this severe decrease in mechanical properties, the use of heat-treated wood as

load-bearing structural material may be restricted (Jamsa and Viitaniemi 2001). It is normally used for non-structural elements such as furniture in the garden, kitchen, sauna, and cladding on wooden buildings (Syrjanen and Oy 2001; Militz 2002).

Shield media in treating systems have a critical effect on the mechanical properties of heat-treated wood. At the same treating temperature, wood treated in air exhibited lower impact bending strength than wood treated in plant oil (Fig. 2). A decrease in the MOE in bending was observed for woods treated in steam or under open air circumstances (Esteves et al. 2007; Korkut et al. 2008), which can be attributed to hydrolysis (steaming) or oxidation degradation (air) of cell wall polymers during treatment (Kuboijima et al. 2000). While wood treated in inert gas or vegetable oil exhibited an MOE comparable to or even higher than that of untreated controls, treated wood was less brittle than wood treated without any shield medium (Rapp and Sailer 2000; Vernois 2001). Common shield media reported are nitrogen gas, water vapour, and vegetable oils (Table 1). They perform the function of not only excluding oxygen in the treating chamber but also transferring heat to the wood interior.

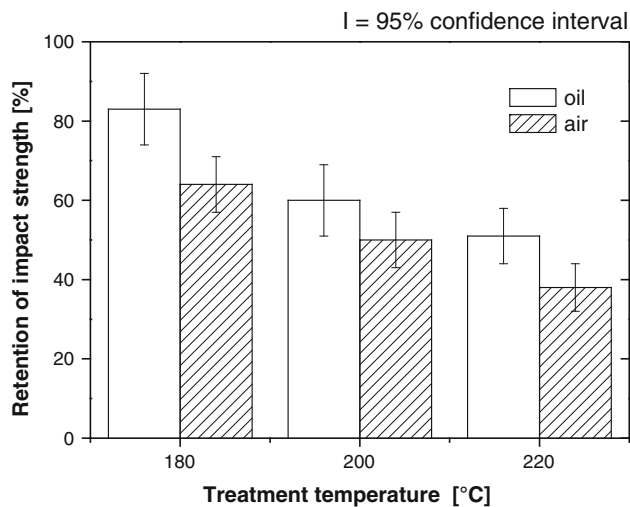


Fig. 2 Effects of temperature and shield media on the impact bending strength of wood. Data adapted from (Rapp and Sailer 2000)
Abb. 2 Einfluss der Temperatur und des Schutzmediums auf die Schlagbiegefestigkeit von Holz. Daten von Rapp and Sailer (2000)

Some studies show that heat treatments cause a greater decrease in MOR in hardwood than in softwood (Table 1). This has been explained by a higher content of hemicelluloses which are most susceptible to thermal degradation in hardwood; xylan in hardwood is more degradable by heat than is mannans in softwood (Alén et al. 1995). However, an opposite result was reported for hardwood, which is less influenced in strength than softwood during heat treatment (Shi et al. 2007).

Changes in heating rate did not substantially influence the MOE of heat-treated jack pine and birch wood; however, the treated wood exhibited greater loss in MOR at a heating rate of 10 °C than at a heating rate of 20 and 30 °C, which has been attributed to a longer time of exposure to heat (Poncsák et al. 2006; Kocaefe et al. 2010). The difference in heating rate may cause a distinct temperature and moisture content gradient between the wood exterior and interior. As a result, stresses generated in the wood can lead to its deterioration to various extents. This may explain the different results observed for the same wood species and similar treating temperatures.

Reduced moisture content is also associated with the mechanical properties of wood. Reported changes in mechanical properties are normally established by comparing the values of treated wood with those of untreated wood. Untreated and treated samples are conditioned under the same circumstances to equilibrium moisture content prior to mechanical testing. Such a comparison has an applicable but non-scientific meaning. The moisture content of heat-treated wood is considerably lower than the untreated controls and the reduction in mechanical properties of heat-treated wood is thus underestimated. This is because the mechanical strength such as bending and

tensile strength is generally reduced with increasing moisture content below fibre saturation point (Kollmann and Côté 1968; Gerhards 1982; Kretschmann 2010). For example, beech and spruce wood treated at 220 °C for 4 h in shield gas exhibited an improvement of approximately 10 % in MOE but a reduction of more than 20 % in MOR when tested after conditioning at 20 °C and 65 % r.h. (Table 1). While both the untreated and heat-treated wood were conditioned to a comparable moisture content of approximately 11 %, the MOE of treated wood did not substantially change and the MOR was reduced by up to 40 % (Arnold 2010). It has been established, below fibre saturation point, the untreated wood may exhibit decreased tensile strength but unchanged or even increased compression strength with increasing moisture content. Compared to the untreated controls, changes in the bending strength (MOR) of heat-treated wood were less sensitive to the environmental relative humidity. Therefore, by increasing the relative humidity, a reduction in MOR may be faster for the heat-treated wood than for the untreated wood (Boonstra 2008; Arnold 2010).

The decrease in mechanical strength is mainly due to thermal degradation of wood cell wall polymers, especially hemicelluloses which are susceptible to high temperature and can be chemically changed at elevated temperatures (Hillis 1984). The evidence of solid phase CP-MAS 13C-NMR spectroscopy of beech and Scots pine sapwood, heat-treated using a humid and a dry step, showed that acetic acid can be liberated from the hemicelluloses (Tjeerdsma et al. 1998). The acetic acid produced may further catalyze the depolymerization of carbohydrates and thereby eliminate parts of hygroscopic hydroxyl groups. This can explain the increased hydrophobic feature of heat-treated wood. Lignin can also be cleaved in the initial humid step and the resulting fragments auto-condense in the following dry step (at approximately 230 °C), forming methylene bridges between aromatic rings via C_{α} . Auto-condensation of lignin may lead to an increased cross-linking network, which may explain the improved dimensional stability and decreased hygroscopicity of wood (Tjeerdsma et al. 1998).

3 Modification with resins

3.1 N-methylol resin

N-methylol resins such as 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) are widely used in the textile industry as finishing agents; their use as wood modifying agents is also reported for improving the dimensional stability, durability, coating properties, and weathering resistance of wood (Militz 1993; Nurmi et al. 1999; Xie et al. 2005, 2006, 2008; Krause et al. 2008; Verma et al. 2008).

Modification processes include vacuum-pressure impregnation of wood with aqueous solutions of DMDHEU and catalysts such as magnesium chloride followed by a curing step at temperatures above 100 °C (Schaffert et al. 2005). The DMDHEU molecule has a molecular weight of 178 and its molecular size is small enough to penetrate wood cell walls. DMDHEU monomers and/oligomers can condense themselves and cross-link the cell wall polymers (Krause et al. 2003).

The modifying effects of DMDHEU on the tensile strength of wood have previously been investigated using a thin-veneer strip technique, where Scots pine sapwood was sliced into veneer strips, each measuring 100 mm × 15 mm × 100 μm (longitudinal × radial × tangential) (Xie et al. 2007). The combined treatments with DMDHEU and magnesium chloride caused a strength loss of up to 50 % in zero-span (mainly measuring the intra-fibre strength) and up to 70 % in finite-span test mode (mainly measuring the inter-fibre shear strength). Treatments with acidic magnesium chloride aqueous solution alone led to a tensile strength loss of approximately 20 % in both zero- and finite-span modes, suggesting an acid-catalyzed hydrolysis of cell wall polymers. The excess losses in tensile strength are attributed to the formation of a stiff cross-linked network in the cell walls. For commercial modified timber, the catalyst in the wood may have potential negative effects such as acid-catalyzed hydrolysis of hemicelluloses, cellulose, and ether bonds between wood and DMDHEU, thereby gradually reducing the mechanical properties of treated wood during long-term service. To date, however, there is as yet no systematic report on the long-term effect of catalysts.

An early study showed that modification of Southern pine with 10 % DMDHEU and a combined catalyst including 0.5 % AlCl₃·6H₂O and 0.5 % tartaric acid induced a reduction in MOR in bending by 37 % but did not change the MOE (Nicholas and Williams 1987). However, reliability of the results is uncertain because the number of sample replicates (two) is too few to have a statistically valid meaning. In addition, the author also observed the development of cracks in the treated samples due to uneven distribution of DMDHEU in the wood structure, which may also result in a low MOR value. Using magnesium chloride as the reaction catalyst, DMDHEU-treated beech wood exhibited a decrease in tensile strength of up to 40 % (Fig. 3a) but an increase in compression strength of up to 65 % by increasing the DMDHEU concentration (Fig. 3b). Only a slight decrease of MOR in bending was observed (Fig. 3c). This minor change in MOR can be explained by the increased compression strength on the top layer of the wood sample, which compensates the loss of tensile strength on the

bottom layer during the static bending test (Winandy and Rowell 2005).

The most adverse effect of DMDHEU treatments may be severe reduction in the dynamic mechanical properties. With increasing DMDHEU concentration, the impact strength decreased; at the highest concentration of 2.3 mol l⁻¹, the treated beech wood showed a loss in impact strength of up to 80 % (Fig. 3d). The untreated wood fractured irregularly with a jagged breakage line (Fig. 4a); however, the treated wood showed a straight breakage line almost perpendicular to the wood grain (Fig. 4b, c, d). Microscopic observation using a scanning electron microscope (SEM) revealed that some microfibril bundles were pulled out of the fractured early- and late-wood in the untreated control (Fig. 5a, b); the samples treated to 28 % weight percent gain (WPG) exhibited a regular fracture surface with some fragments (Fig. 5c, d). The results show that DMDHEU-treated wood is brittle which may limit its use as load-bearing structural elements.

3.2 Formaldehyde-based resins

Thermoset resins such as urea–formaldehyde (UF), phenol–formaldehyde (PF), and melamine–formaldehyde (MF) can be used for vacuum-pressure impregnation of wood and react in the wood structure at high temperature. Penetration of resins in the wood structures highly depends on the molecular weight of resins (Lukowsky 2002), which dominates the modification patterns (cell wall modification and/or cell lumen filling). A study has revealed that low molecular weight (290–480) PF resin can penetrate the cell walls, but those with high molecular weight (820) mostly fill the cell lumen (Furono et al. 2004). The diffusion of low molecular weight MF resins into wood cell wall layers was observed using electron loss spectroscopy (Rapp et al. 1999) and UV-microscopy (Gindl et al. 2002). Penetration of waterborne resins in wood is relatively easier if wood has a high moisture content and low extractive content, and if concentration of resins is low. Reaction of resins within the cell wall substances can dimensionally stabilize the wood, whilst filling in lumens lead to hardly any such effect on wood (Lukowsky 2002; Furono et al. 2004). Filling in lumens with resins may block the path available for moisture/water access to cell walls, thereby decelerating the moisture sorption. Therefore, it can inhibit the deformation of wood in the short term (Cai et al. 2007); physical bulking of cell walls and chemical deactivation of the hygroscopic hydroxyl groups of cell wall polymers can also facilitate improving the dimensional stability and biological durability of wood (Pittman et al. 1994; Rapp et al. 1999; Deka and Saikia 2000; Deka et al. 2002; Hansmann et al. 2006).

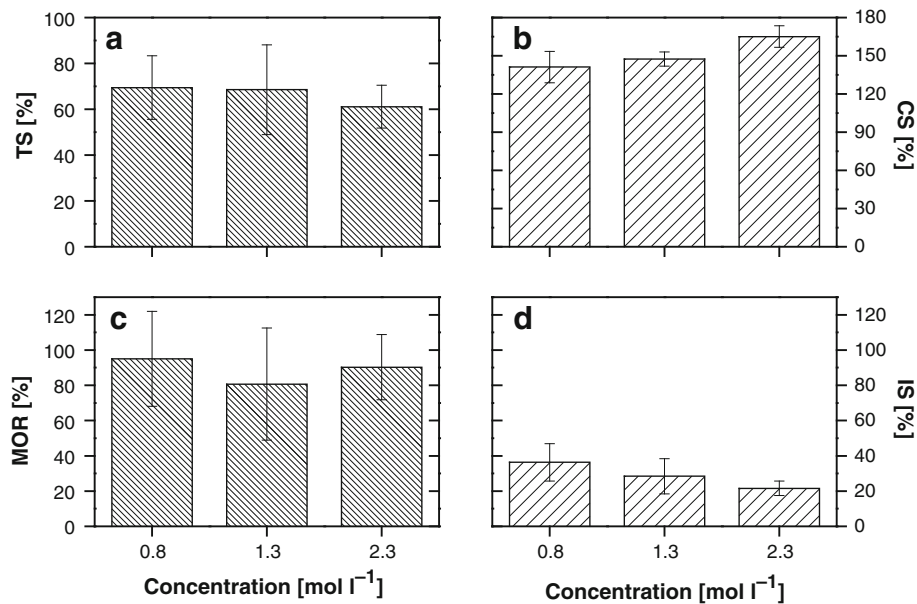


Fig. 3 Retention of tensile strength (TS) (a), increase of compression strength (CS) (b), retention of modulus of rupture in bending (MOR) (c) and impact strength (IS) (d) of wood modified with various concentrations of DMDHEU and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (5 wt % based on DMDHEU). Data adapted from Bollmus et al. (2010)

Abb. 3 Einfluss auf (a) die Zugfestigkeit (TS), (b) die Druckfestigkeit (CS), (c) die Biegefestigkeit (MOR) und (d) die Schlagfestigkeit (IS) von Holz, das mit verschiedenen Konzentrationen von DMDHEU und $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (5 Gewichts % basierend auf DMDHEU) behandelt worden war. Daten von Bollmus et al. (2010)

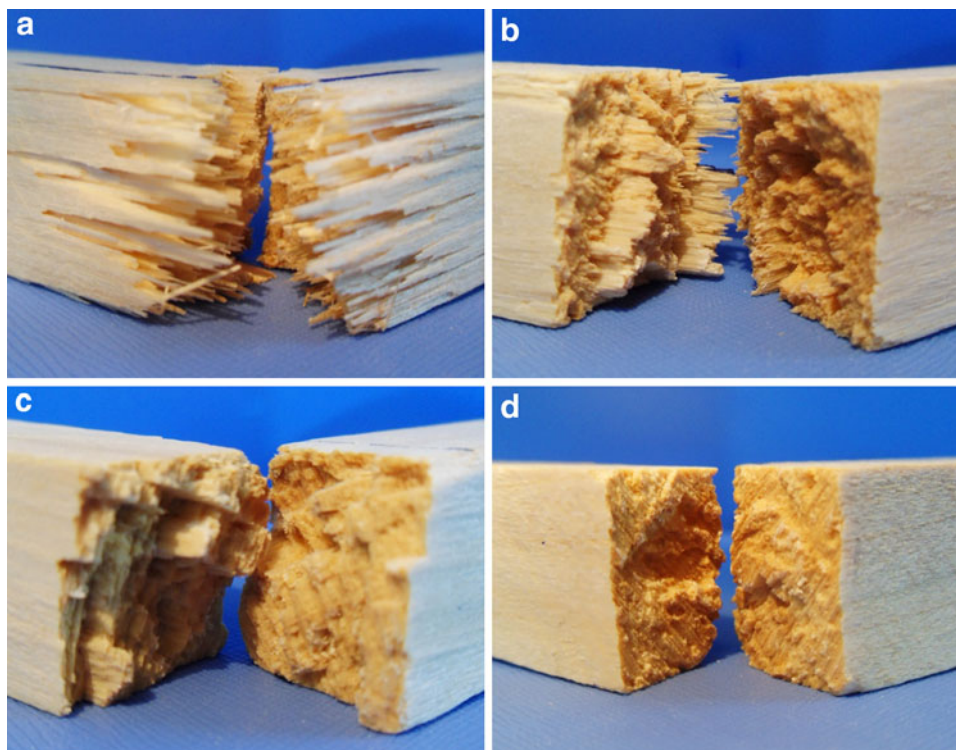


Fig. 4 Impact fractured section of wood untreated (a) and treated with 0.4 (b), 1.2 (c), and 2.0 mol l⁻¹ (d) DMDHEU, respectively. The concentration of magnesium chloride (catalyst) is 1.5 wt % for all treatments

Abb. 4 Bruchbild beim Schlagbiegeversuch von (a) unbehandeltem Holz sowie mit (b) 0,4, (c) 1,2 und (d) 2,0 mol l⁻¹ DMDHEU behandeltem Holz. Die Magnesiumchloridkonzentration (Katalysator) betrug bei allen Behandlungen 1,5 Gewichts %

Fig. 5 SEM graphs of fractured cross sections of wood untreated and treated with DMDHEU to 28 % WPG. Untreated (a) and treated (c) earlywood, and untreated (b) and treated (d) latewood

Abb. 5 REM-Aufnahmen der Bruchquerschnitte von unbehandeltem und mit DMDHEU bis 28 % Gewichtszunahme behandelten Holzprüfkörpern. a unbehandelt und c behandeltes Frühholz, b unbehandeltes und d behandeltes Spätholz

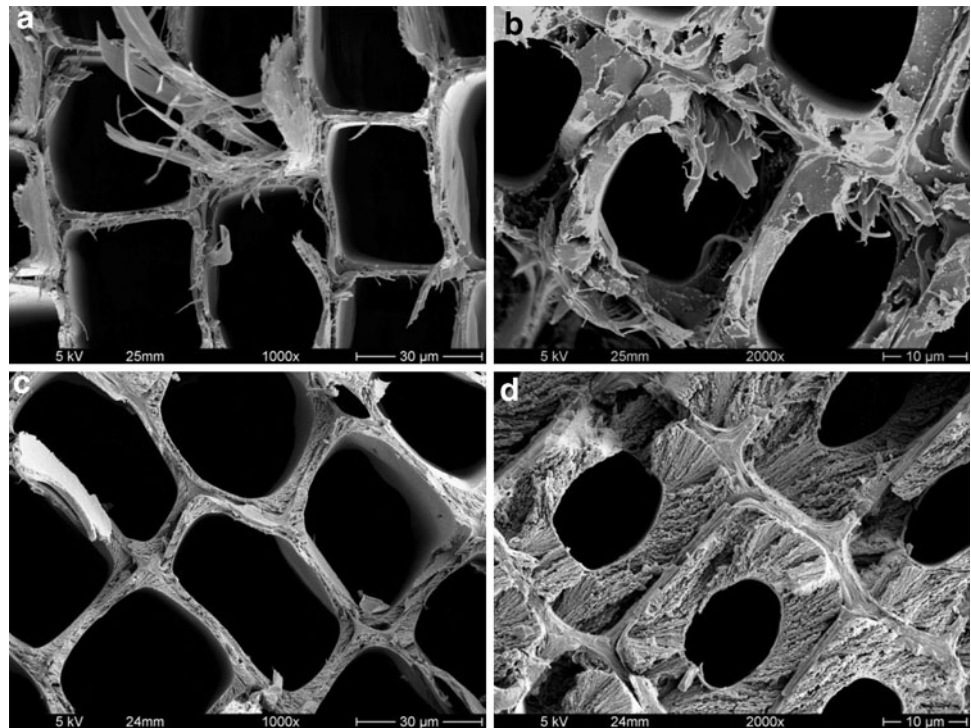
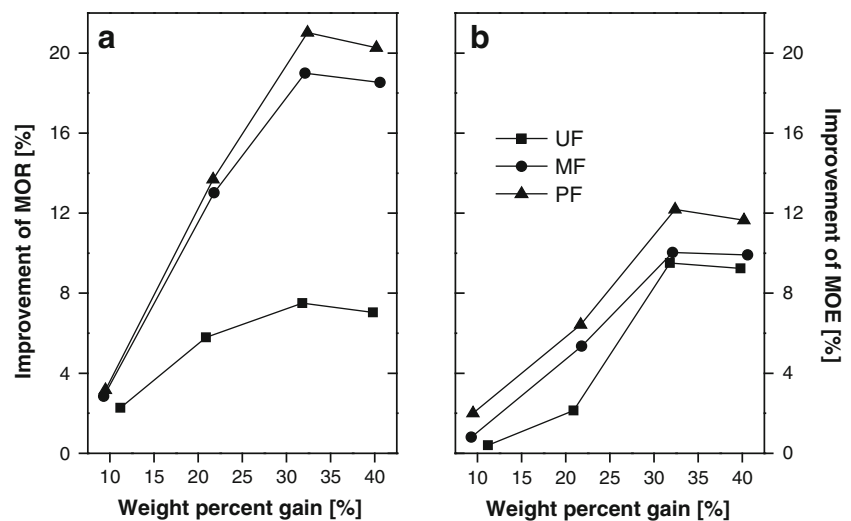


Fig. 6 Improvement of modulus of rupture (a) and modulus of elasticity (b) of *Anthocephalus cadamba* (Roxb) Miq. treated with UF, MF, and PF to different weight percent gains, respectively. Data adapted from Deka et al. (2002)

Abb. 6 Verbesserung a der Biegefestigkeit und b des Elastizitätsmoduls von *Anthocephalus cadamba* (Roxb) Miq., das mit UF, MF und PF behandelt wurde, in Abhängigkeit der prozentualen Gewichtszunahme. Daten von Deka et al. (2002)



Due to formation of a highly rigid cross-linked network of resins in/with wood, the surface hardness of modified wood was considerably enhanced (Miroy et al. 1995; Gindl et al. 2004). In the case where the secondary cell walls of spruce were treated with a low molecular weight MF to a melamine content of 24 % (v/v), the longitudinal hardness and Young's modulus of cell walls measured using a nano-indentation technique increased by 115 and 33 %, respectively (Gindl and Gupta 2002). Scots pine treated with methylated melamine formaldehyde (MMF) to low WPGs (7.5–15 %) showed an increase in MOR of 10 %, an unchanged MOE, but a decrease in impact strength of 61 %

as compared to the untreated controls (Epmeier et al. 2003; Epmeier and Kliger 2005). A comparable reduction in impact strength was also observed in the wafers of Southern yellow pine treated with MF or melamine-ammeline-formaldehyde (MAF) resins to WPGs of 60–95 % (Pittman et al. 1994). The embrittlement of wood treated with melamine resins can be attributed to the rigid structure of the cured MF resin and the cross-linking of cell wall polymers by MF resin; checking of cell walls due to stress applied by the volume contraction of the resin during thermal curing process may also cause reduced impact strength (Pittman et al. 1994; Gindl et al. 2003).

A comparative study was carried out by treating the softwood (*Anthocephalus cadamba* (Roxb) Miq) with PF, MF, and UF resins to WPGs approximately ranging from 10 to 40 %. The treated wood exhibited a bulking coefficient of 9–15 %, which shows that the resins used can penetrate the cell walls (Deka and Saikia 2000). Both MOR and MOE in bending of the treated wood increased with the WPG until 30 %, beyond which the static bending properties did not change (Fig. 6a, b). The levelling off may be explained by the cell walls having been saturated with resins at a WPG of 30 %, after which the resins mainly deposit in the lumens and influence the bending properties only slightly. The greatest improvement in MOR is 5, 17, and 21 % for UF-, MF-, and PF-treated wood, respectively (Fig. 6a). Compared to MOR, improvement in MOE was below 10 % in the WPG range obtained (Fig. 6b).

Thermoset resins are also used to fix compression (densified) wood dimensionally. They are impregnated into the wood in advance, and the impregnated wood is then transversally pressed in the thermal moulds, in which a rigid resin-cell wall network can be formed and therefore considerably inhibit the dimensional springback of compression wood. The densified poplar (*Populus sp.*) wood impregnated with a low molecule weight PF resin exhibited better dimensional stability but greater reduction in MOE than that impregnated with a high molecular weight PF resin (Gabrielli and Kamke 2010). The MOE was reduced by 37 % at a WPG of 23 % with the low molecular weight PF resin. The reduction in MOE is attributed to fracturing of the rigid network of PF resin, which was pre-cured in the press mould before applying final compression. However, Shams et al. (2004) did not find any substantial effect of impregnation with PF resin to 61 % WPG on the bending properties (Young's modulus and bending strength) of densified Japanese cedar (*Cryptomeria japonica*) wood panel.

4 Furfurylation

Furfuryl alcohol (FA) is a monomeric precursor originating from biomass feedstock (Goldstein 1955). The FA can polymerize in the presence of a catalyst at elevated temperatures through cationic condensation reactions, which finally produce a branched polymer via connection of methylene groups and/or dimethylene ether groups (González et al. 1992a, b; Barsberg and Thygesen 2009). The workable catalysts for wood treatments include zinc chloride or organic acids such as citric and maleic acids. The presence of these types of catalysts can stabilize the treating solution for a long shelf life and catalyze polymerization of FA in wood (Goldstein and Dreher 1960). In the waterborne treatment solution, the aqueous catalyst may chromatographically separate from FA. Therefore, a

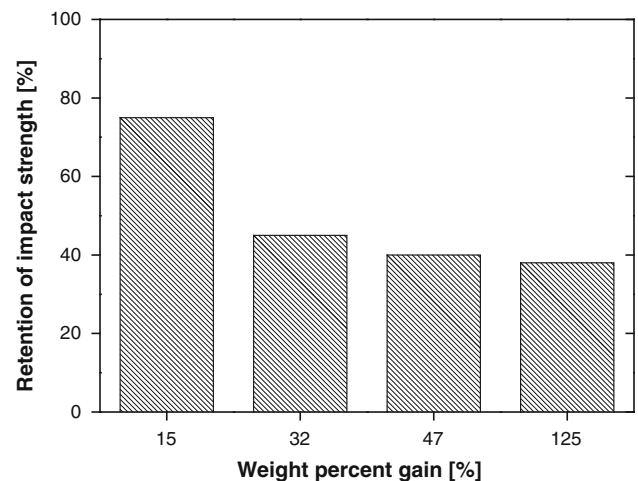


Fig. 7 Retention of impact strength of Scots pine wood treated with furfuryl alcohol to various weight percent gains. Data adapted from Westin et al. (2003)

Abb. 7 Veränderungen der Schlagbiegefestigkeit von mit Furfurylalkohol behandeltem Kiefernholz in Abhängigkeit der prozentualen Gewichtszunahme. Daten von Westin et al. (2003)

surfactant was used to prepare an even aqueous solution; the cyclic anhydrides such as maleic anhydride can be directly dissolved in FA as the reactive catalysts (Schneider 1995, 2006; Westin et al. 1998). Except for polymerization, evidence has also been found for potential grafting of FA onto cell wall polymers, especially lignin (Lande et al. 2004, 2008; Nordstierna et al. 2007; Thygesen et al. 2010). Wood modified with FA to certain WPGs showed highly improved dimensional stability, reduced water uptake, and increased resistance to biological deterioration (Ryu et al. 1992; Epmeier et al. 2004; Lande et al. 2004; Hoydonckx et al. 2007; Treu et al. 2009).

Modification with FA generally causes positive or few effects on the mechanical properties of wood, except for the impact strength. Pine (*Pinus pinaster*) sapwood treated with FA to a WPG of 38 % exhibited a MOE comparable to the untreated controls, but an increase in MOR by 6 % and in hardness by 50 %, respectively (Esteves et al. 2011). An increase of more than 30 % in MOE was observed for Scots pine sapwood treated with FA prepolymer to a WPG of approximately 35 % (Hoydonckx et al. 2007). A bending creep test for 140 days revealed that partial FA treatments of Scots pine sapwood caused a reduction in creep deflection and relative creep by 46 and 24 %, respectively. The reduction in creep deflection is mainly attributed to the reduced mechanosorptive property; the elastic part of creep deflection is influenced by FA treatments only slightly (Epmeier et al. 2007). Similar to the modification with resins described above, modification with FA resulted in severe reduction in impact strength of wood (Westin et al. 2004). Scots pine wood treated to 15 % WPG showed a 25 % loss in impact strength compared to the untreated

controls; with increasing WPG of up to 125 %, the impact strength was reduced by 65 % (Fig. 7), which demonstrates the embrittlement of wood due to FA treatments. The great decrease in impact strength has mainly been attributed to the formation of a stiff cross-linked poly(FA) network (Lande et al. 2008). In addition, the small size of the samples used for treatments may be another reason for this, because the larger samples cut from industrially treated timber only exhibited an impact strength loss of 30–40 % compared to the untreated controls (Westin et al. 2003). The lower losses in impact strength for industrially treated timber may also be due to the treatment not fully penetrating through the timber thickness.

5 Grafting with vinyl monomers

Wood products modified with thermoplastic-related vinyl monomers such as styrene (ST) and methyl methacrylate (MMA) were previously called wood polymer composites (Schneider 1994). The vinyl monomers may polymerize in the wood structure using radiation (gamma rays or X-rays) or radical initiators and heat. Several wood species (poplar, beech, alder, pine, fir, and spruce) treated with three agents (ST, MMA, and ST-MMA mixture) to a WPG of up to 64 % only exhibit minor bulking (up to 4.7 %) and anti-swelling efficient (up to 25 %), the changing extent depending on the specific wood species (Alma et al. 1996). The low bulking can be explained by the fact that the homo-polymerized monomers mainly fill in the cell lumens, as shown in Fig. 8 (Schneider 1994; Baysal et al. 2007). This is because these monomers have little swelling ability; as a result, it is difficult for them to penetrate cell walls (Siau 1969; Baysal et al. 2007). The moderate improvement in dimensional stability may be attributed to a decreased rate of moisture sorption, since the paths (cell cavities) for moisture are physically occupied by the polymerized monomers.

Treatments with vinyl monomers generally cause improvement in tensile, bending, and compression properties (Schneider and Phillips 1991; Devi et al. 2003; Yildiz et al. 2005). The treated sugar maple wood showed increases in MOE and MOR in bending by 20.0 and 28.0 %, respectively, as it was treated with a vinyl-type monomer to 51 % WPG. At higher WPG (61 %), the MOE and force to rupture in tensile strength increased by 12.9 and 21.4 % and in compression by 32.6 and 81.3 %, respectively (Fig. 9). The improved tensile strength was explained by the restricted unwinding of cell wall microfibrils by the polymerized monomers in the lumens; increased compression strength can be due to increased density of wood (Schneider et al. 1990). Both the maritime pine and poplar wood modified with ST, MMA, or ST-MMA exhibited an

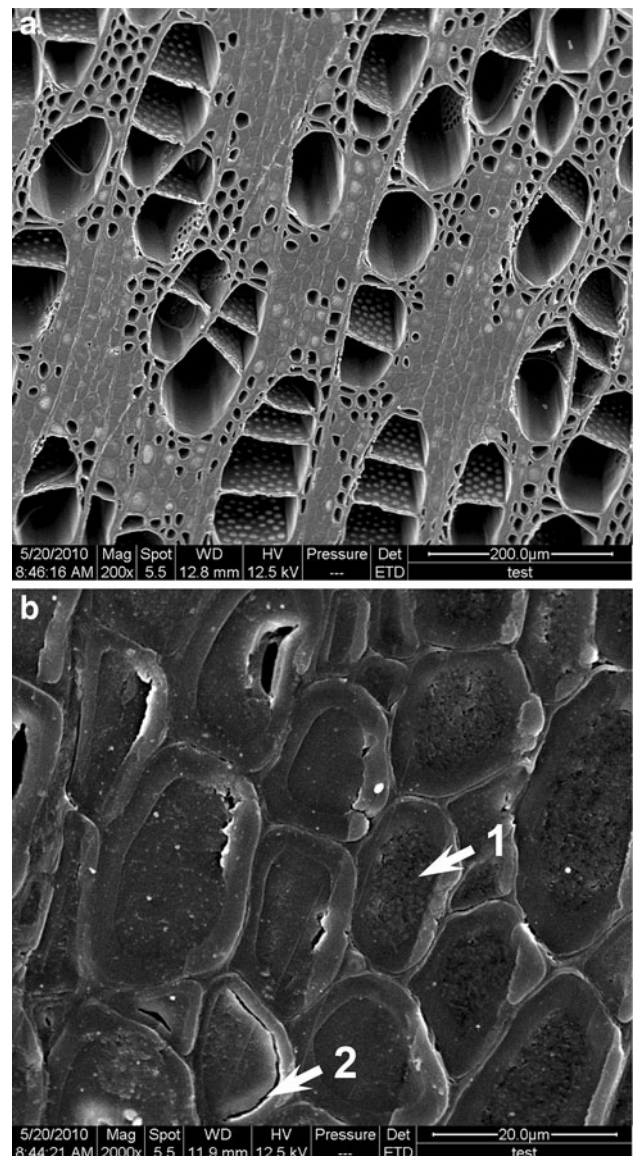


Fig. 8 Micrograph of cross-section of poplar wood treated with methylmethacrylate using AIBN as the reaction initiator. **a** $\times 200$ and **b** $\times 2000$. *Arrow 1* shows the micropores in the polymers located in the lumen and *Arrow 2* shows the separation between wood cell wall and polymer, both due to shrinkage of polymer during radial reaction
Abb. 8 Mikroskopische Aufnahme von Pappelholzquerschnitten, die mit Methylmethacrylat und AIBN als Katalysator behandelt wurden a) 200fache Vergrößerung und b) 2000fache Vergrößerung. Pfeil 1 zeigt die Mikroporen der in den Lumen befindlichen Polymere. Pfeil 2 zeigt die Trennung zwischen Holzzellwand und Polymer, beides aufgrund des Schwindens des Polymers

increase in compression from approximately 20–110 % with increasing the WPG range from 34 to 179 %; however, improvement in bending properties was generally below 30 % and little influenced by changes in WPG (Yildiz et al. 2005). A comparable result was also observed for the Southern pine that had been fully impregnated and cured with 1,6-hexanediol dimethacrylate; at a high WPG of

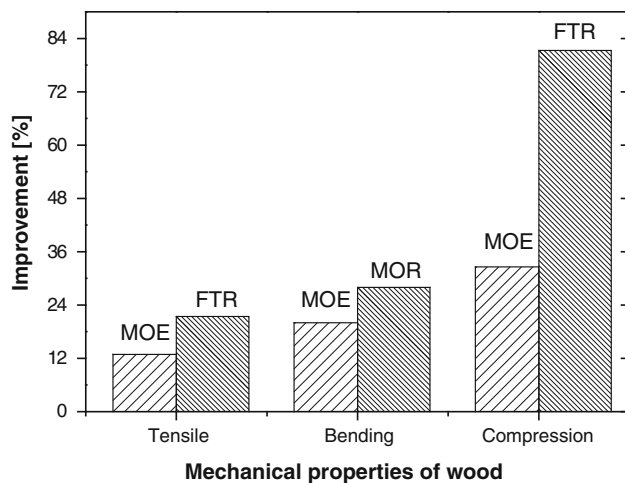


Fig. 9 Improvement in the mechanical properties of sugar maple wood treated with a vinyl-type monomer to WPGs of 51 % (for bending) and 63 % (for tensile and compression), respectively. Before measurement all samples were conditioned to a moisture content of 12 %. Legends: *MOE* modulus of elasticity, *MOR* modulus of rupture, *FTR* force to rupture. Data adapted from Schneider et al. (1990)

Abb. 9 Verbesserung der mechanischen Eigenschaften von Zuckerahornholz, das mit einem vinylartigem Monomer behandelt wurde, prozentuale Gewichtszunahme bei Biegung 51 % und bei Zug und Druck 63 %. Vor den Messungen wurden alle Prüfkörper auf einen Feuchtegehalt von 12 % klimatisiert. Daten von Schneider et al. (1990)

180 %, the MOR increased by 39 % and MOE by 27 % (Bergman et al. 2009).

In the polymerization process the formed polymer can contract in the cell lumens, which can in turn cause formation of micropores within the polymer and interfacial separation between polymers and wood cell walls (Fig. 8b). As a result, the stress may not be efficiently transferred to polymers located in the lumens as the sample is applied with load. Use of a mixture of vinyl monomers may reduce the contraction of polymers and the treated wood generally exhibits greater improvement in mechanical properties than those treated with individual monomers (Yildiz et al. 2005). A mixture of MMA, ST, and vinyl acetate (VAc) was used to treat poplar wood with 2,2'-azobisisobutyronitrile (AIBN) at an elevated temperature; the treated wood exhibited an increase in MOR and compression strength by 69 and 68 %, respectively (Li et al. 2010). Maleic anhydride (MA) was used as a coupling agent to pre-treat the wood prior to impregnation with a mixture of glycidyl methacrylate (GMA) and ST, with the aim of establishing a covalent bonding between the wood cell wall and polymerized copolymers (Li et al. 2011). The MOR in bending, compression strength, and hardness increased by 51, 131, and 153 %, respectively; however, the impact strength reduced by 34 %, which may be because of a cross-linking network formed between wood cell walls and copolymers

due to the coupling effects of MA limiting the movement of wood cells under the impact stresses applied.

6 Acetylation

In the process of acetylation various anhydrides are delivered into wood structures using vacuum-pressure and then react with wood cell wall polymers under heat conditions. The anhydrides reported in the literature include acetic, butyric, succinic, maleic, propionic, and butyric anhydride. The most commonly used is acetic anhydride, which can react with the hydroxyl groups of cell wall polymers at high temperatures in the absence or presence of a catalyst such as pyridine, forming ester bonds and simultaneously releasing acetic acid as the reaction by-product (Rowell 1982; Hon 1995; Hill et al. 1998). The reactivity of cell wall polymers with acetic anhydride proceeds in the order lignin > hemicelluloses > cellulose (Hill et al. 1988). The acetylated wood is highly dimensionally stable and can efficiently resist weathering (Plackett et al. 1992; Evans et al. 2000) and biological decay (Militz 1991).

In early studies, acetylation of wood was carried out using acidic salts or mineral acids as reactive catalysts which can cause hydrolysis of cellulose, thereby making wood brittle (Goldstein et al. 1961). Recently, a study has revealed that reactions between wood and anhydrides can also proceed at a low temperature (75 °C) in the presence of a Lewis acid such as magnesium chloride; the acetylated wood did not exhibit any changes in mechanical properties compared to the untreated controls (Li et al. 2009). Pyridine can catalyze grafting of acetic anhydride onto cell wall polymers and has little influence on the mechanical properties of wood (Goldstein et al. 1961; Minato et al. 2003); however, separation of pyridine from modified industrial timber is particularly difficult. In order to solve this problem, an uncatalyzed acetylation technique was developed where wood is impregnated with acetic anhydride alone and then cured at 120 °C (Militz 1991).

Scots pine wood treated in 50 % (v/v) acetic anhydride in xylene exhibited a tensile modulus higher than the untreated wood, but apparently lower than the wood treated with xylene alone (Ramsden et al. 1997). The shear strength parallel to the grain of wood acetylated to approximately 20 % WPG decreased by 24 %; however, the compression strength perpendicular to the grain increased by up to 39 % (Dreher et al. 1964). Improvement in compression strength is influenced by the chemical structure of anhydrides used. At a comparable WPG of approximately 15 %, the compression strength of Scots pine wood treated with acetic, propionic, butyric, valeric, and hexanoic anhydrides increased with the molecular size

Table 2 Effects of anhydride-modification on the mechanical properties of wood
Tab. 2 Einflüsse einer Anhydrid-Modifikation auf die mechanischen Eigenschaften von Holz

Treatment	Wood species	WPG (%)	Moisture content at 20 °C, 65 % rh (%)		Change in mechanical properties based on untreated controls (%)				References
			Untreated	Treated	Static bending		Impact bending	Tensile strength	
					MOE	MOR			
AA	Pine	19.1	9.8	4.1	-17.0	-5.3	-	-	Larsson and Simonson (1994)
	Spruce	23.3	12.0	2.8	+3.5	+7.4	-	-	
PA	Acacia mangium	-	-	-	+1.0	+2.1	-	+8.2	Bhat et al. (2010)
	Acacia hybrid	-	-	-	+3.6	+9.0	-	+10.0	
SA	Acacia mangium	-	-	-	+11.5	+5.5	-	+6.6	Goldstein et al. (1961)
	Acacia hybrid	-	-	-	+7.1	+2.8	-	+6.7	
AA, 125–130 °C	Southern yellow pine	18.0	-	-	-	-	-13.3	-	Dreher et al. (1964)
	Ponderosa pine	-	-	-	-	-	+15.6	-	
AA, 125–130 °C	Ponderosa pine	20.7	9.1	4.0	+2.0	+10.9	+17.5	-	Li et al. (2009)
	Red oak	21.2	8.4	4.6	-5.8	-8.3	-6.9	-	
	Sugar maple	21.4	9.2	3.4	-4.3	-8.1	-1.4	-	
AA, MgCl ₂	Sugi	25	-	-	-2 %	-1.5 %	-	-	Minato et al. (2003)
AA	Sitka spruce	Up to 30	9.5	8.5–3.0	(-20)–	(-20)–	-	-	Epmeier et al. (2003)
					(+10)	(+30)			
AA		20	-	-			+1		Jorissen et al. (2005)
AA	Radiata pine	-	13.1	5.2	-9.1	-9.3	-	-	

Positive values show an increase in percentage and negative ones for a decrease compared to the untreated wood

– Unknown, AA acetic anhydride, PA propionic anhydride, SA succinic anhydride

Positive Werte stehen für eine prozentuale Verbesserung und negative Werte für einen Rückgang im Vergleich zu unbehandeltem Holz

of the substituent groups, which shows that the improved compression strength correlates with the degree of substitution rather than with the cell wall bulking (Papadopoulos and Pougoula 2010).

The reported changes in mechanical properties of wood due to acetylation were inconsistent with one another, depending on wood species, treatment method, and WPG obtained by wood (Table 2); however, these changes, either positive or negative, were within the limits of error of measurement (Jorissen et al. 2005). Various wood species exhibited a different extent of changes in their mechanical properties after they had been acetylated (Dreher et al. 1964; Minato et al. 2003). Using the same acetylation process without catalyst on a pilot plant scale, Scots pine and poplar exhibited improvements in MOE, MOR, compression parallel to the grain, Janka hardness, and shear strength, but the MOE and MOR of radiata pine (*Pinus radiata* D. Don.) decreased. The mechanical properties of beech wood were less influenced by acetylation (Bongers and Beckers 2003). Enhancement in the mechanical properties due to acetylation may be attributed to increased density and reduced moisture content (Table 2). In addition, anhydride molecules do not

polymerize themselves or cross-link the cell wall polymers, resultantly forming a stiff network (Dreher et al. 1964; Youngquist et al. 1986; Tsoumis 1991). Therefore, the impact strength of the wood may not be substantially changed by acetylation treatments. Decrease in some mechanical properties may be explained by reduction of fibre amount per volume due to cell wall bulking (swelling), hydrolysis of lignocelluloses at high temperatures, and degradation by acetic acid (Homan and Jorissen 2004).

7 Wax treatment

Wax treatments do not strictly belong to the class of chemical modification because there is no chemical reaction throughout the treatments; however, wax treatments have a process and intention comparable to the chemical modification techniques presented above. Therefore, this technique is also included in this review. It can give insight into the effects of the physical incorporation of non-reactive macromolecules into the wood structure on the mechanical properties of wood. Several paraffin products have been used as water repellents to

reduce the moisture sorption and water uptake, and therefore improve the dimensional stability of in-service wood. The treatments are normally performed by impregnating the wood with melted waxes at elevated temperature under vacuum and pressure. Penetration depth of melted waxes in wood highly depended on their viscosity and polarity; filling of cell cavities slowed down the sorption rate of moisture/water (Scholz et al. 2010a). Beech and spruce wood fully impregnated with wax emulsions (montan wax, polyethylene, ethylene copolymer, or oxidized polyethylene) also exhibited considerable resistance against white-rot and brown-rot fungi (Lesar and Humar 2011); at high WPG the treated spruce showed improved resistance against artificial weathering (Lesar et al. 2011). However, wax treatment did not prevent wood from damage by subterranean termites *Coptotermes acinaciformis* and *Mastotermes darwiniensis* (Militz et al. 2009); the adhesion of wood was reduced when adhesives such as isocyanate copolymer, poly(vinylacetate), and phenol-resorcinol resin were tested due to the highly hydrophobic surface of the treated wood (Scholz et al. 2010c).

Different from the chemical modifications presented above, treatment of wood using waxes improved all the mechanical properties tested. The hardness of five wood species (beech, pine, birch, oak, and poplar) impregnated with a mixture of modified natural resins and waxes increased from 54 to 156 % at a WPG ranging from 20 to 73 % (Mundigler and Rettenbacher 2005). Scots pine sapwood treated with five different hot melting waxes (montan acid, amide wax, modified plant wax, Fischer-Tropsch wax, and polyethylene) showed an increase in MOR, MOE, and impact strength by 25, 11, and 31 %, respectively (Scholz et al. 2009, 2010b). Impregnation of waxes only causes physical filling in the large cell cavities such as lumens. During the treatment, wood cell wall microstructures and constituents do not change, nor do the wax molecules undergo any chemical reaction to form a stiff network. The improvements in mechanical properties can mainly be explained by the increased density and reduced moisture content (Scholz et al. 2010b); the flexible wax macromolecules may also mechanically reinforce the wood.

Combined treatments, including a preceding chemical modification (heat treatment, acetylation, DMDHEU treatment) followed by impregnation with montan wax were carried out (Scholz et al. 2012). With increasing WPG of wax, the density, hardness, compression strength, bending strength and impact strength of chemically modified wood obviously increased. The bending strength and Brinell hardness perpendicular to the grain of heat-treated wood increased by up to 45 and 420 %, respectively, following treatment with wax. The wax treated acetylated

wood showed an enhancement in compression and MOE up to 47 and 66 %, respectively, compared to the acetylated wood. The impact strength of wax-impregnated chemically modified wood increased by up to 2.5 times compared to chemically modified wood. The losses in mechanical properties due to the preceding chemical modification were compensated for by the subsequent wax treatments. Most of the mechanical properties of the chemical and wax treated wood were comparable to or even significantly greater than those of teak wood.

8 Conclusion

Wood chemical modification has been extensively recognized as an optional strategy for wood protection. However, use of high temperatures, reactive chemicals, and catalysts through the modification processes may lead to adverse effects on those wood mechanical properties which are of importance for structural materials. Based on the review of the present literature and work in the research groups, it can be summarized and concluded as follows:

- (a) Heat treatment techniques are established based on thermal reaction of wood constituents, especially hemicelluloses and lignin, to less hydrophilic structures, and on stress relaxation of the wood interior at elevated temperatures. The treated wood generally exhibits a reduction in mechanical properties such as bending, impact, and compression. Improved durability of wood due to heat treatment is normally at the expense of loss of mechanical strength. The temperature, treating period, and shield gas used dominate the degree of strength losses.
- (b) The impact bending strength of wood can be reduced in cases where a stiff network is formed due to cross-linking between chemicals and cell wall polymers and/or condensation of chemicals in the wood structures. The network can limit the movement of wood microfibrils under an applied external stress. Reduction in the impact strength is observed for almost all chemically modified wood. Hydrolysis due to the presence of acidic catalysts may also be responsible for a reduction in impact strength for some chemical modification techniques such as DMDHEU. Consequently, chemically modified wood with great loss in impact strength may have limited use for structural materials.
- (c) Incorporation of chemicals, either reactive or non-reactive, into the wood cell walls and/or lumens can always cause increased hardness and compression strength, which is mainly attributed to a resultant increase in wood density.

- (d) Wood species used can influence the extent of changes in the mechanical properties due to chemical modification since they are different in terms of permeability, moisture content, and/or varying thermal conductivity.

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