Original article

Jaka Gašper Pečnik*, Andreja Kutnar, Holger Militz, Matthew Schwarzkopf and Hannes Schwager

Fatigue behavior of beech and pine wood modified with low molecular weight phenol-formaldehyde resin

https://doi.org/10.1515/hf-2020-0015
Received January 15, 2020; accepted April 14, 2020

Abstract: Modification of wood improves certain properties of natural wood and presents competitive alternatives to synthetic materials that may have larger environmental impacts. One aspect of modified wood that is currently not fully understood is the dynamic performance and how it is affected by the modification process. In this study, low-molecular weight phenol formaldehyde (PF) resin was applied to Scots pine (*Pinus sylvestris* L.) and European beech (*Fagus sylvatica* L.) wood. The effect of this modification was evaluated using a three-point bending test undergoing cyclic loading. Compared to reference samples, modified wood showed higher static performance but revealed a reduction in cyclic fatigue strength (9% for pine and 14% for beech). Cyclic fatigue strength of unmodified wood was found to be 67% of the static modulus of rupture for both species. With PF resin modification, the fatigue strength dropped to 58% for pine and 53% for beech. While fatigue strength decreased, there was no reduction in cyclic modulus or change in the creep rate within the stationary creep phase. It is important to consider the reduction in fatigue strength when using PF modified wood for any construction purposes with expected cyclic loading conditions.

Keywords: beech; creep rate; fatigue strength; phenol formaldehyde; pine; stress level; wood modification.

***Corresponding author: Jaka Gašper Pečnik**, Innorenew CoE, Izola, Slovenia, Livade 6, Izola, 6310, Slovenia; and Andrej Marušič Institute, University of Primorska, Koper, Slovenia,
E-mail: jaka.pecnik@innorenew.eu
Andreja Kutnar and Matthew Schwarzkopf: Innorenew CoE, Izola, Slovenia, Livade 6, Izola, 6310, Slovenia; Andrej Marušič Institute, University of Primorska, Koper, Slovenia
Holger Militz and Hannes Schwager: Wood Biology and Wood Products, University of Göttingen, Goettingen, Germany

1 Introduction

Energy and resource efficiency have become two major topics for future development of engineering products. This has led to an enormous interest in lightweight design with advanced materials, such as high-performance alloys or fiber-reinforced composites, that might enhance mechanical performance during service life (Klein 2009). Recently, focus has returned to wood as a construction material. Wood is appealing not only for its low ecological impact but also for its beneficial physical properties in relation to its low density. Being a renewable resource, wood provides inherent advantages such as climate neutrality and environmental sustainability. It is also a domestically produced material with short transport links to processing facilities and provides good machinability (Ramage et al. 2017).

From an engineering point of view, wood exhibits specific mechanical properties comparable to most metals and many fiber composites (Ashby 2010). But technical use requires taking wood's particular characteristics, originating from its former function as a living organism, into account. One major restriction for technical application of wood arises from its moisture behavior. The capillary porous structure and strong hygroscopicity of wood cell walls, which results from their chemical composition, lead to fast water uptake that affects several other physical and biological properties such as dimensional stability, mechanical properties or durability. Modification of wood species by thermal, chemical, or mechanical treatment can improve service life, dimensional stability and, in many cases, mechanical properties (Hill 2006; Sandberg et al. 2013). A well-established wood modification process is chemical modification with thermosetting resins by impregnating wood with monomers and oligomers of low molecular weight. While curing, a cross-linked polymer matrix is formed from these monomers within the wood cell walls, which helps to prevent water penetration at a later time. One such resin is phenol formaldehyde (PF). PF has a long service record

(>50 years) in the wood industry as an adhesive used for manufacturing engineered wood products such as plywood or glue laminated timber. More recently, studies have focused on the use of PF to enhance wood and wood-composite properties related to dimensional stability, color stability, exterior exposure, acoustics and resistance against fungi, termites, and other pests (Ahmed and Adamopoulos 2018; Franke et al. 2017; Gabrielli and Kamke 2010; Gascon et al. 2015; Kielmann et al. 2018; Klüppel, 2017; Klüppel et al. 2015; Stamm et al. 1947; Xie et al. 2013). PF resin has also been used to improve mechanical properties of wood. Deka and Saikia (2000) reported increases in modulus of elasticity (MOE) by 12% and modulus of rupture (MOR) by 21% for wood impregnated with PF resin. Huang et al. (2013) treated Chinese fir (*Cunninghamia lanceolate*) with a low molecular weight PF resin and reported a 31% increase in MOE. Wan and Kim (2006) found slight improvements in MOE values for strand board treated with low molecular weight PF resin. Previous studies explained that cell wall bulking caused by thermosetting resins like PF reduced the flexibility of cell wall compounds (Hosseinpourpia et al. 2016). In addition, alkaline components in phenolic resins might also cause changes in cell wall components, which can lead to decreased elastic properties (Furuno et al. 2004). The brittle behavior of wood treated with PF resin can be attributed to PF molecules occupying the cell wall and cell lumina as well as by catalysts of acidic polymers establishing new cross-linking of the cell wall network, leading to a rigid, non-pliable cell wall (Mai and Elder 2016). Dynamical mechanical behavior of modified wood with thermosetting resins is greatly affected by this increased rigidity. Kielmann et al. (2013) modified ash (*Fraxinus excelsior* L.), beech (*Fagus sylvatica* L.), and maple (*Acer platanoides* L.) wood with methylated N-methylol melamine (NMM) and reported decreased impact bending strength (IBS) for treated samples against controls, with decreased IBS between 35 and 48% for ash and beech and an even higher decrease between 55 and 67% for maple. One large study on modifying wood's mechanical and physical properties with different chemicals was carried out by Epmeier et al. (2004). IBS of pine wood (*Pinus sylvestris* L.) treated with methylated melamine formaldehyde (MMF) was found to be reduced by more than 50%. Bicke et al. (2012) modified beech (*F. sylvatica* L.) veneers with PF resins for plywood and reported 34% lower IBS values in a parallel orientated direction. One method used to assess and characterize dynamic properties of a material is fatigue testing. There is currently a lack of knowledge concerning the cyclic fatigue life of modified wood due to demanding testing, high natural variability and anisotropy. Fatigue performance in wood is driven by many parameters. One of the most important is the stress level under which a specimen is tested. The ratio of maximum and minimum stress applied to the test specimen (R ratio) must be considered. For example, R ratio with −1 would mean fully reverse loading. In other words, this would mean that the specimen is under constant load where maximum and minimum positions are extremes of the amplitude. In bending, this would mean that the specimen bends down and upwards. When R is 0, (unidirectional) specimen is loaded and unloaded between maximum positive load and initial unloaded starting position. Tsai and Ansell (1990) tested fatigue life in flexure and reported increasing damage with decreasing R values from 0.5 to −1. The waveform under which the specimen is tested also plays an important role in fatigue life. It has been reported that a square wave loading form, compared to sinusoidal or triangular, causes the most damage for solid wood and some other wood composite materials (Gong and Smith 2003; Sasaki et al. 2014; Sugimoto and Sasaki 2007; Sugimoto et al. 2006). Another important parameter is loading frequency. A shorter number of cycles is given by lower loading frequencies (Gong and Smith 2003; Sugimoto et al. 2007). Regarding modified wood, there are even fewer studies that have investigated fatigue performance. Ratnasingam and Mutthiah (2017) investigated fatigue strength of oil palm (*Elaeis guineensis*) wood from different positions in the stem. As density increased, improved fatigue life was observed in the middle and center parts of the tree treated with PF. Sharapov et al. (2016) investigated how cyclic bending influenced residual strength in thermally modified wood and effects of different moisture content levels for pine (*P. sylvestris* L.), reporting that initial moisture content before the fatigue test and highest thermal treatment play the most important roles in residual strength.

To better understand behavior of modified wood under cyclic loading, it is important to know if modification has a positive or negative effect on wood properties. Based on progress from initial studies on modified wood, there is now a need to assess the dynamic performance of other wood species that are commonly used in structural applications. Scots pine (*P. sylvestris* L.) and European beech (*F. sylvatica* L.) represent economically important softwood and hardwood species, respectively, as both are widely used in the European wood industry. Most structural timber and wood-based composites used in buildings are softwood species; however, more and more hardwood species are gaining attention for use in building applications. The objective of this study has been, to investigate static and dynamic mechanical properties such as impact bending, cyclic fatigue behavior and cyclic creep of PF modified pine and beech wood.

2 Materials and methods

2.1 Specimen preparation: modification procedure

Specimens of Scots pine sapwood (*P. sylvestris* L.) and heartwood-free European beech (*F. sylvatica* L.), with length of 180 mm in longitudinal, height of 10 mm in tangential and width of 10 mm in radial wood direction, were prepared. Before further processing, specimens from each species were distributed into two samples of 150 specimens, described in Table 1. One sample was modified (Mod) with phenol formaldehyde (PF) resin, while the other served as a reference (Ref).

Initially, all specimens were conditioned in a controlled environment at a temperature of 20 °C and relative humidity (RH) of 65% for two weeks. Following this initial step, the specimens designated for modification were stacked in containers and submerged in aqueous PF solution with 30% PF mass content and an average PF molecule weight of 440 g/mol. In order to ensure a maximum solution uptake, specimens were degassed in a vacuum chamber at a low pressure of 100 mbar for 30 min and subsequently infiltrated with PF resin by reverting to atmospheric pressure. Afterwards, specimens were desiccated in a slow drying regime. First, specimens were air dried overnight and then put into the oven to 60 °C. After 24 h, temperature was increased to 103 °C for another 24 h. This drying regime ensured smooth water removal from the specimens and prevented the formation of drying cracks. Final curing phase took place at 140 °C for 2 h. Before further investigation steps, specimens were conditioned again at 20 °C and 65% RH.

2.2 Evaluation of modification

Dimensions of all specimens along the three anatomical wood directions, longitudinal length (l_{long}), tangential height (h_{tang}), and radial width (w_{rad}), were measured with a sliding caliper after initial conditioning before infiltration and after finial conditioning after curing. Specimen mass (m) was measured by two decimal number precision balance. With these values, bulk density (ρ) of the specimens was calculated.

Permanent relative change in dimension, the so-called bulking of wood, in all three anatomical stem directions (Bul_{dir}) after modification referred to the unmodified state is given by Eq. (1):

$$Bul_{dir} = \frac{(x_{dir,1} - x_{dir,0})}{x_{dir,0}} \times 100\,[\%] \tag{1}$$

where x_{dir} represents the dimensional values for longitudinal length l_{long}, tangential height h_{tang} or radial width w_{rad} and the index t where numbers are designating the modification state after initial conditioning (0) and after modification (1).

Weight percentage gain (WPG) after modification referred to the unmodified state was calculated according to Eq. (2):

$$WPG = \frac{(m1 - m0)}{m0} \times 100\,[\%] \tag{2}$$

with initial (m_O) and final (m_I) mass of the specimens.

Moisture content (MC) of a specimen was calculated from absolute dry state mass after exposure to 103 °C for 48 h in a ventilated oven and mass after reconditioning at 20 °C and 65% RH for three weeks.

2.3 Microscopic analyses

For both reference and modified samples, images of cross-sections were made with a scanning electron microscope (SEM), Supra-35 (Carl Zeiss AG, Germany), to demonstrate the distribution of PF molecules in the material. Specimens were dried overnight in a ventilated oven at 103 °C. A clear, smooth cut was created with a microtome, and specimens were coated by carbon sputtering. Analyses were conducted at 5 kV.

2.4 Mechanical test program

The mechanical test program used in this study combined static and dynamic tests with a three-point flexural test set-up and a central force application in tangential wood direction. All specimens were tested in static bending tests, following the recommendations of DIN 52186 (1978), to determine the modulus of elasticity (MOE). From each sample, selected specimens were tested until failure to determine the modulus of rupture (MOR). Charpy impact bending tests referred to DIN 52189 (1981) to determine the effect of modification on impact bending strength (IBS). Cyclic fatigue strength (CFS) was determined in a Wöhler test series under three-point bending test regime.

2.4.1 Static bending tests: Static bending tests were performed on a universal testing machine (Zwick/Roell Z010, supported by TestXpert software) with a span (l_S) between the support rollers of 150 mm. During the test, applied force (F) and corresponding deflection (d) were recorded. Test speed was set to 5 mm/min to ensure a test duration of 90 ± 30 s until failure in tests for determining MOR (DIN 52186 1978). MOE was calculated by using linear regression in the range of 50–200 N. Limit of proportionality (LOP) equals the stress level where the stress-strain curve deviates from the calculated regression line; ergo, the material behavior changes from strictly linear-elastic to plastic was as well. Determined total strain ($\mathcal{E}_{max}$) at maximum force (F_{max}) is given by Eq. (3):

$$\varepsilon_{max} = \frac{6 \times d_{max} \times h_{tang}}{l_S^2}\,[-] \tag{3}$$

from which elastic ($\mathcal{E}_{el}$) is calculated as follows in Eq. (4):

Table 1: Description of samples and number of specimens designated for testing: modulus of elasticity, (MOE), modulus of rupture (MOR), impact bending strength (IBS), cyclic fatigue strength (CFS) and moisture content (MC).

Treatment type	Label	Resin average molecular weight	Total no. of specimens	Distribution no. of specimens included in the test program				
				MOE	MOR	IBS	CFS	MC
Reference	Ref	–	150	150	30	50	50	10
PF modifiaction	Mod	~440 g/mol	150	150	30	50	50	10

$$\varepsilon_{el} = \frac{MOR}{MOE}\,[-] \tag{4}$$

and plastic ($\mathcal{E}_{pl}$) results from the difference between $\mathcal{E}_{max}$ and $\mathcal{E}_{el}$ as shown in Eq. (5):

$$\varepsilon_{pl} = \varepsilon_{max} - \varepsilon_{el}\,[-] \tag{5}$$

Ratio of plastic to total deformation might be regarded as a measure for brittleness of the material.

2.4.2 Impact bending test: An impact pendulum machine (CEAST Resil Impactor) was equipped with an instrumented 25 J hammer. The span between the support rollers was set to 115 mm, according to standard DIN 52189-1 (1981). IBS is given by the absorbed energy during fracture referred to the cross-sectional area of the specimen.

2.4.3 Cyclic bending tests: Cyclic bending tests were performed in a Wöhler-test series on fatigue testing machine DHM-Prüfsysteme (Clausthal–Zellerfeld, Germany, supported by SysCon easyTest software). In addition to the driving force generated with a pneumatic cylinder instead of a servomotor, the bending test set-up resembled those used for static testing: two lateral support rollers with a span of 150 mm and a central force application.

Tests were performed with pulsating loads until specimen failure, whereby the upper and lower stress limit were calculated according to Eq. (8) and the corresponding maximum and minimum strain values according to Eq. (7).

Upper stress limit (σ_{up}) was given by the intended load level and lower stress limit (σ_{low}) was set to a value close to zero. A sinusoidal waveform with a constant mean stress (σ_{mean}) was calculated by Eq. (6):

$$\sigma_{mean} = \frac{(\sigma_{up} + \sigma_{low})}{2} = const. \tag{6}$$

and constant stress amplitude (σ_{ampl}) in Eq. (7):

$$\sigma_{ampl} = \sigma_{\max} - \sigma_{mean} = \sigma_{mean} - \sigma_{mim} = const. \tag{7}$$

was chosen to avoid high dynamic damaging effects caused by abrupt load reversion like in triangular or square waveforms (Gong and Smith 2003; Smith et al. 2003). The test frequency of 10 Hz was a trade-off between an opportune test duration and prevention of thermal degradation by rapid internal friction. Specimens designated for one Wöhler-test series were distributed into sub-samples of five specimens. The stress level (*SL*) of one single test is given by σ_{up} and individual strength of the tested specimen ($MOR_{spec.}$) as inEq. (8):

$$SL = \frac{\sigma max}{MORspec.}. \tag{8}$$

During one Wöhler series, the *SL* per sub-sample was decreased stepwise, beginning at ~95%, to a stress level where the specimens (theoretically) would never fail.

In the present study, the $MOR_{spec.}$ of each specimen was estimated from its individual $MOE_{spec.}$ and correlation between the average $MOR_{mat.}$ and average $MOE_{mat.}$ of the examined material that had been determined in the preceding static three-point bending tests, used under static bending test, as in Verkasalo and Leban (2002) and Baar et al. (2015), shown in Eq. (9):

$$MORspec. = \frac{MOEspec \times MORmat.}{MOEmat.}. \tag{9}$$

The number of cycles to failure (N_f) was recorded for each specimen. A threshold of one million cycles without any visible crack was regarded as fatigue limit. The belonging load level gives cyclic fatigue strength (CFS) of the wood in its modification state.

A more detailed view into the fatigue behavior of a single specimen is gained by contemplating weakening of the material during the fatigue test and creep behavior within the phase of stationary (secondary) creep. Figure 1 represents increasing minimum and maximum strain throughout the testing phase. The initial phase (I – phase of primary creep) is characterized by a low amount of creep and decreasing creep rate (see also Figure 2), followed by the quasi-linear secondary stage (II – phase of secondary, stationary creep) where we observed slow proportional linear increase as a result of time-dependent constant loading. The final stage (III – phase of tertiary creep) resulted in accelerated and sudden increase in strain and fatigue failure. The blue line represents cyclic creep and the red line represents maximum deflection.

Figure 1 aims to show behavior of increasing travel of a specimen and, on the other hand, its reduction in modulus. These indicat our measure of fatigue.

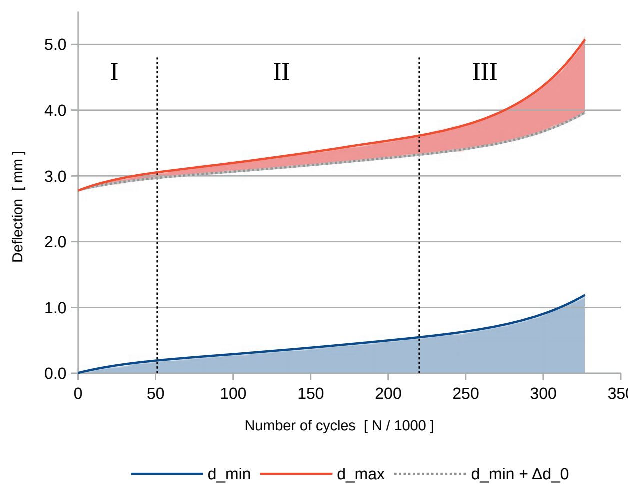

Figure 1: *d_min* and *d_max* represent increasing minimum and maximum strain. Lines present a measure of fatigue upper (red) and lower (blue) minimum strain through number of cycles and typical creep behavior.

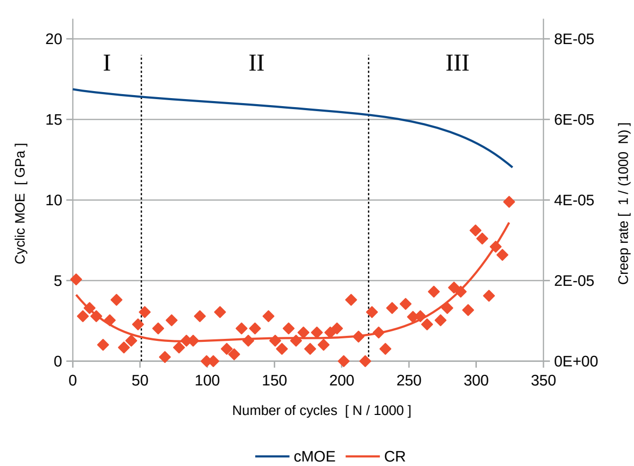

Figure 2: (I) Primary phase with decreasing CR and decelerated reduction of cMOE; (II) stationary creep with low CR and linear decrease of cMOE; (III) accelerated creep with increasing CR and rapidly decreasing cMOE.

Figure 2 presents decreasing cyclic modulus of elasticity in the upper blue line (cMOE) throughout the three phases as caused by weakening of the material. The lower red line indicates creep rate (CR). Initial high CR is a result of specimen positioning, followed by the linear secondary stage. After a certain number of cycles, fatigue effect was observed in a sudden CR increase that ended with failure of the specimen and, thus, end of the test.

Specimen weakening due to cyclic fatigue manifests in a decreasing cyclic modulus of elasticity (cMOE) throughout the fatigue test. The cMOE of a designated load cycle (N) is calculated according to Eq. (10):

$$cMOE_N = \frac{\Delta\sigma_N}{\Delta\varepsilon_N} = \frac{\sigma_{up,N} - \sigma_{low,N}}{\varepsilon_{max,N} - \varepsilon_{min,N}} \quad (10)$$

with stress values ($\sigma_{up,N}$ and $\sigma_{low,N}$) and corresponding strain values ($\mathcal{E}_{max,N}$ and $\mathcal{E}_{min,N}$) at the load reversion points of the contemplated load cycle. Cyclic creep caused by so-called mean stress (σ_{mean}) effect (constant σ_{mean} throughout testing time) manifests in a progression of minimum strain ($\mathcal{E}_{min,N}$) throughout the fatigue test. Within the phase of stationary creep, cyclic creep rate (CR) per load cycle might be determined by linear regression between minimum strain values and number of load cycles as in Eq. (11):

$$CR = \frac{\Delta\varepsilon_{min,N}}{\Delta N} \quad (11)$$

with $\Delta\mathcal{E}/\Delta N$ representing slope of the regression line.

3 Results

3.1 Results of the modification: WPG bulking and density

Results for WPG, bulking, density after modification and moisture content of modified and reference pine and beech wood specimens are shown in Table 2. WPG for pine and beech was found to be 31.7 and 24.2%, respectively. As expected, bulking in tangential direction was larger than in radial direction for both wood species. Bulking in longitudinal was found to be very low, with almost no increase. Increase in the density from initial state was found to be 20% for pine and 25% for beech. It must be pointed out that calculations were performed within the same sample and cannot be comparable with values from the reference sample. Determined WPG for pine and beech was similar to values obtained by other studies. Franke et al. (2017) impregnated beech wood with different PF molecular sizes and different concentrations and obtained 25% WPG by using 20% PF concentration and 450 Mn molecular weight. Xie at el. (2016) modified Scots pine with different PF concentrations and molecular weight around 400 Mn and obtained various WPG, some with an increase similar to 35%. Increase in density and bulking can be one of the first indicators of successful impregnation. In this study, higher WPG was found for pine, which is related to wood density, and a solid content of PF resin. WPG can be calculated to any desired increase for every wood species as a ratio between cell wall density and wood density. Penetration of low molecular weight PF resin into the cell wall was already provided in a study done by Furuno at al. (2004). Incorporating the polymer into the wood structure causes a so-called bulking effect that results in the increase in volume of a specimen towards its original volume (Hill 2006). Wood species with higher density reach higher volumetric swelling (Kollman and Côté 1968). Kollman and Côté, in their book, explained how helical arrangement of fibrils affect radial and tangential shrinking for softwoods. A few other theories regarding swelling and shrinking were described by Skaar (1988), i. e., how arrangement of various tissues and cell types, fibril alignment, cell-wall layering and difference in early – and latewood can differentiate in shrinking and swelling. Any of these reasons can contribute to the differences observed in our case as penetration of molecules can affect the same spots.

Moisture content (MC) after three weeks of conditioning was equilibrated on average 10.2% for reference specimens and 4.5% for modified specimens. Furthermore, it is necessary to mention that lower MC for modified wood due to the effects of impregnation was expected. It has to be taken into account that modification slows down the effect of water vapor sorption. This means that MC of 4.5% might not be the equilibrium moisture content at standard climate conditions. Hosseinpourpia (2016) confirmed lower MC and different behavior for PF impregnated wood species. PF-occupied molecules in the wood structure

Table 2: Calculated average properties of pine and beech samples after treatment with standard error in parentheses, bulking in radial (Bul_{rad}), tangential (Bul_{tan}), and longitudinal (Bul_{lan}) direction and an average MC at 65% relative humidity.

Sample	TT	WPG (%)	Bul_{rad} (%)	Bul_{tan} (%)	Bul_{lon} (%)	ρ_1 (kg/m³)	MC (%)
Pine	Ref	–	–	–	–	535 (3.8)	10.1
	Mod	31.7 (0.36)	1.65 (0.03)	3.44 (0.03)	0.06 (0.00)	682 (2.2)	4.5
Beech	Ref	–	–	–	–	654 (2.1)	10.2
	Mod	24.2 (0.27)	2.77 (0.06)	8.17 (0.13)	0.06 (0.01)	803 (1.8)	4.5

prevent water vapor from penetration into the wood as well as closing gaps and diffusion paths.

One of the main contributions of resin mono/oligomers is, subsequently, polymerization within the cell, creating a matrix formation between PF molecules and wood. In addition to reduction in MC of wood, polymerization causes side effects such as cross-linking molecules forming a rigid matrix and poor pliability of the cell wall (Mai 2016). In Figure 3, SEM images of the Ref (a) and Mod (b) cross-sections for pine are presented. Pine structure consists of tracheids building early – and latewood and creating different cell wall and lumen sizes. Two observations can be indicated from Figure 3. One is the shape of cell walls and deposition of material in the free voids. In the case of modification (Figure 3b), more rounded cell lumina indicate buckling of the cell wall. In addition, thicker cell walls are observed. There is clear differentiation between early – and latewood for Ref; in the case of modified wood, this is less evident.

Figure 4 shows SEM images from cross-section for reference (a) and modified (b) beech. The main difference between pine and beech is in the wood anatomical structure. Diffuse porous beech consists of fibers and vessels. The penetration of PF resin into the fibers, resulting in bulking, indicates the difference between reference (a) and modified (b) samples. Another observation was found inside the lumina where, in the case of modification, resin covered some of the visible pits (not shown). Overall, both wood species have presence of bulking effect and surface roughness after cutting the specimen.

3.2 Mechanical test: static test

Summary of the static test is provided in Table 3. Modification with PF resin influenced both the MOE and MOR for pine and beech specimens. Mean MOE of modified specimens was 21.4% higher than values for unmodified pine and 29.0% higher than values for unmodified beech. MOR of modified wood also increased, counting 17.8% higher MOR for pine and 18.0% higher MOR for beech.

Rowell (1998) attributed strength properties of lignocellulose materials as very dependent on MC of the cell wall, i.e., fiber stress at proportional limit and maximum

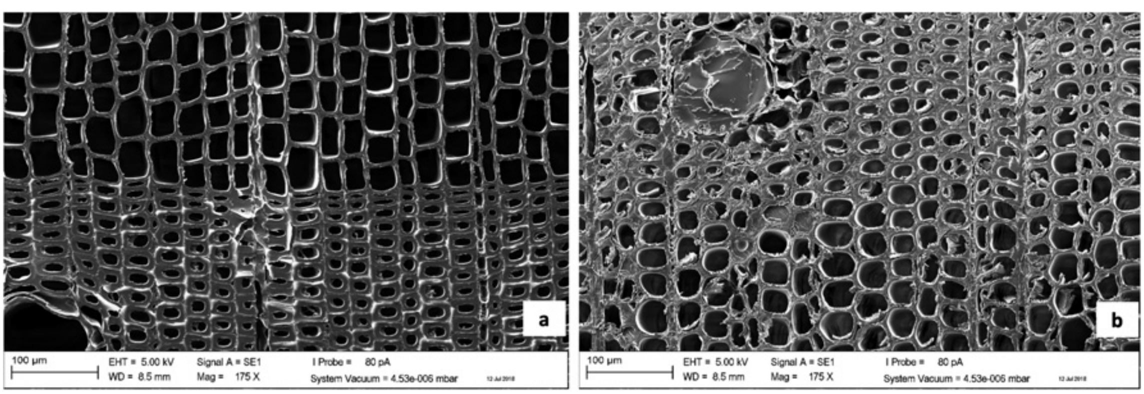

Figure 3: SEM cross-section image of pine Ref (a) and Mod (b).

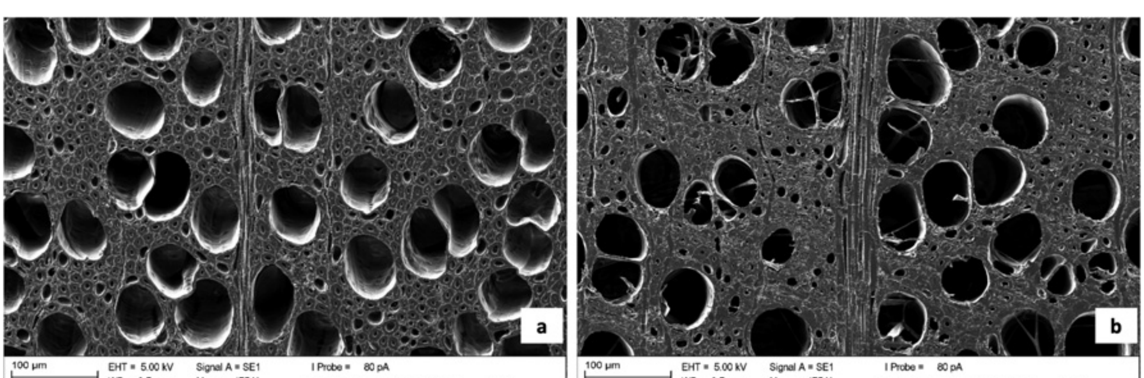

Figure 4: SEM cross-section image of beech Ref (a) and Mod (b).

Table 3: Calculated average values for MOE, MOR, total strain ($\mathcal{E}_m$), plastic strain ($\mathcal{E}_{pl}$), ratio between plastic deformation and total strain and LOP, with the standard error values in parenthesis.

	TT	MOE (GPa)	MOR (MPa)	$\mathcal{E}m$ (-)	$\mathcal{E}pl$ (-)	$\mathcal{E}pl/\mathcal{E}m$ (%)	LOP (MPa)
Pine	Ref	11.9 (0.1)	102 (1.3)	0.013 (0.03)	0.009 (0.01)	66.7	63.3 (1.3)
	Mod	14.5 (0.7)	120 (2.5)	0.008 (0.01)	0.000 (0.00)	~0	112.7 (3.5)
Beech	Ref	11.8 (0.7)	125 (1.6)	0.017 (0.04)	0.006 (0.04)	36.4	70.6 (1.4)
	Mod	15.2 (0.9)	148 (2.5)	0.010 (0.01)	0.000 (0.01)	~0	126.0 (4.7)

strength. In this study, MC was highly affected by modification resulting in 55% lower MC compared to reference samples. A study from Deka and Saikia (2000) showed improved mechanical properties of PF modified hardwood *Anthocephalus cadamba*. Huang et al. (2013) also obtained improved MOE and MOR properties by modifying Chinese fir (*C. lanceolate*) with low molecular weight PF resin. However, Xie et al. (2013), in their review of the effect of chemical modification on mechanical properties of wood, pointed out that this is not always the case. Another example from a recent study, Wang et al. (2019), investigated properties of elastic modulus, hardness and storage modulus under quasi-static and dynamic mechanical testing by using nanoindentation technique on PF-impregnated Masson pine (*Pinus massoniana* Lamb.) using different resin concentrations. Results revealed that properties only improved with lower concentrations up to 20%. Properties above this level of concentration were found to remain the same or even start to decrease as an effect of increased bulking.

One major drawback was contributed to change in original elasto-plastic behavior. Elastic and plastic deformation were determined on measured specimens from the stress strain diagrams. A high $\mathcal{E}_p$ deformation at break was visible for reference samples at 36.4 and 66.7% for pine and beech, respectively. Generally, ~0% plastic deformation was observed for Mod samples in both wood species. LOP for modified specimens was found to be only 7.3% lower than average MOR for pine and 14.7% lower than average MOR for beech. While in the case of unmodified wood, pine and beech met 38.0 and 43.6% lower LOP, respectively.

The unexpected low mechanical performance of modified beech wood could be attributed to insufficiencies of the modification process. Deka et al. (2002) demonstrated that resin treatment with PF increases MOE and MOR with no remarkable effect on the specific gravity. Furthermore, it was shown that by increasing WPG using PF, the mechanical performance improves. This might help to understand the better performance of pine reported in the present study as the density of reference beech was only around 120 kg/m³ higher than the one of pine. Total bulking was also greater in the case of beech, which in turn, leads to lower strength because the breaking force is referred to a larger cross section area.

3.3 Dynamic test: impact bending strength (IBS) and cyclic fatigue test

Results from impact bending strength (IBS) are represented by peak energy in Table 4. The modification was found to have greater effect on pine. Decrease in IBS for modified pine compared to reference was 59.8% while for beech it was 35.9%. This can be attribute this to higher WPG, which resulted in rigid matrix creation between the wood and adhesive. According to Kollman and Cote (1968), differences between pine and beech could originate from the initial properties of the material. Beech and pine both gain on the impact work with increasing density. Coniferous wide annual rings are related to low toughness, due to broad rings resulting in lower density of wood. Diffuse-porous beech was found to have greater toughness. High energy absorbance can be explained by energy transmission through long splits and coarse splinters. Type of rupture in modified wood was significantly different from the reference, showing shorter splits than those found in reference wood.

The effect of modification with PF resin expresses an important reduction in dynamic impact bending strength (Mai 2016). According to Xie et al. (2007), this phenomenon is typical when it comes to chemical modification with curing resins for the cell wall as deposits cause reduction of movement in polysaccharides and cell wall matrix. For

Table 4: Impact bending strength with peak energy (w_{peak}), standard error (StErr), and number (*N*) of evaluated specimens.

TT	Pine			Beech		
	W_{peak}	StErr	*N*	W_{peak}	StErr	*N*
Ref	16.26	0.53	49	18.59	0.54	50
Mod	6.54	0.22	47	11.91	0.47	47

modified samples, high reduction was recorded in fragile brittle breaking of wood, showing no ability to absorb energy while in contact. This type of behavior was expected due to high increased brittleness of the material.

3.3.1 Cyclic fatigue strength

Cyclic fatigue strength decreased with increasing *SL* for all the samples as presented in Figure 5. Fatigue limit for reaching 10^6 loading cycles for reference pine and beech was 67%. For modified samples, 58 and 53% fatigue strength were found for pine and beech, respectively.

In this case, reaching 10^6 cycles was a measure of fatigue life. However, not all of the values undergo 10^6 repetitions as not all of the designated specimens in a particular *SL* were able to fulfill the desired number of cyclic repetitions.

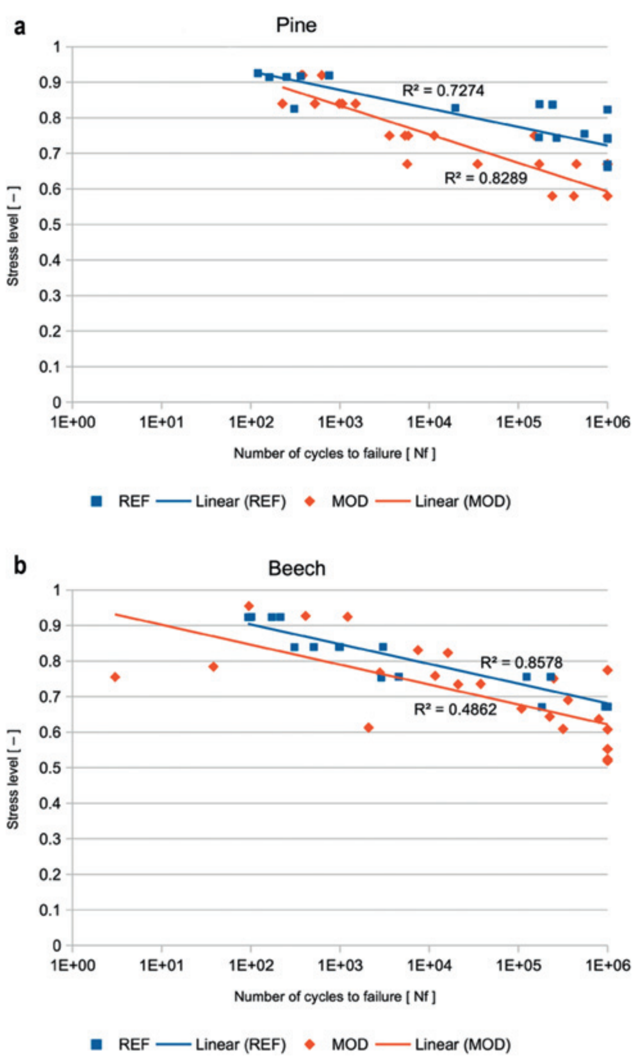

Figure 5: Cyclic SN fatigue diagram for pine (a) and beech (b).

The relationship between SL_{real} and number of cycles to failure (*Nf*) for pine and beech are presented in Figure 5. Measure of fatigue strength is the number of cycles for each individual specimen at a certain stress level, which is plotted with colored points. Color is typical for treatment type: blue indicates reference specimens and red indicates modified specimens. The linear regression line represents a trend in behavior of tested specimens under a different *SL*. It can be seen that shortened *Nf* is given by treated samples, meaning higher stress level resulted in lower number of cycles.

In both modified wood cases, additional *SL* lower than 60% has been introduced to gradually reach desired number of cyclic repetitions. All results for lowest *SL* in Mod are plotted within one single point, as all of the specimens reached the final number of cycles. It was observed that, on average, pine Ref specimens survived the highest number of loading cycles overall (4.71×10^5), followed by Mod beech (3.39×10^5), Mod pine (3.21×10^5), and Ref beech (2.81×10^5). In total, 32 and 17% decrease in average number of cycles was found between Ref and Mod for pine and beech, respectively. For pine specimens, high variability in the *SL* was observed. The slope in Figure 5 is a linear regression line, showing intensity of reduction in CFS. One can see that more intense reduction was observed in the number of cycles for modified wood. This evidence was more typical for pine, meaning that high *SL* had greater effect on modified pine. For beech, a lower regression line was found, showing similar behavior to Ref. In the case of beech, higher number of cycles was recorded throughout the test for modified wood compared to pine. Due to low number of evaluated specimens and high variability in wood, it is difficult to say which modification was more affected by the treatment. By linear regression line, one can observe that pine experienced higher reduction; however, low R^2 is not a strong indicator. Finally, this kind of observation was already supported with IBS tests.

3.3.2 Creep rate for identifying the range of stationary (secondary) creep

Results for pine and beech creep rate are summarized in Figure 6. Specimens loaded under higher *SL* experienced higher creep rate.

This correlates with the completely different material behavior. Modified samples showed linear elastic behavior up to the MOR, while reference material switched from elastic to plastic far below the MOR. The LOP of pine referred to MOR is 62% in case of beech this ratio is 57%. Even though the drop of the CR occurs at a SL of around

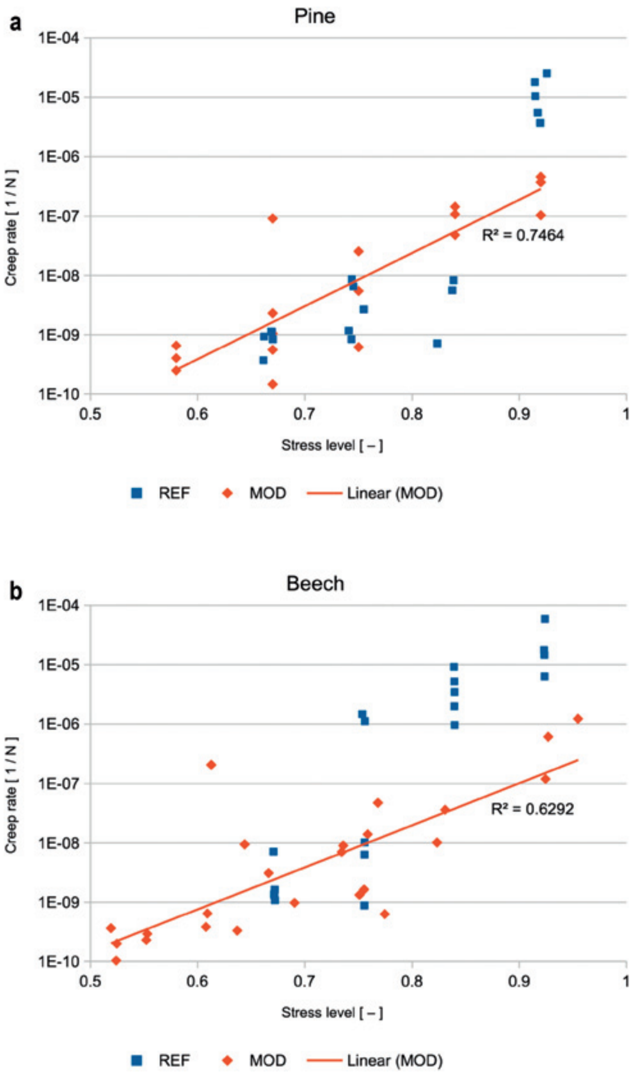

Figure 6: Creep rate (CR) for pine (a) and beech (b). A linear regression line was better fitting for CR in modified samples. Reference samples had higher CR at high *SL* until a sudden sharp drop occurred, usually bellow 75% *SL*.

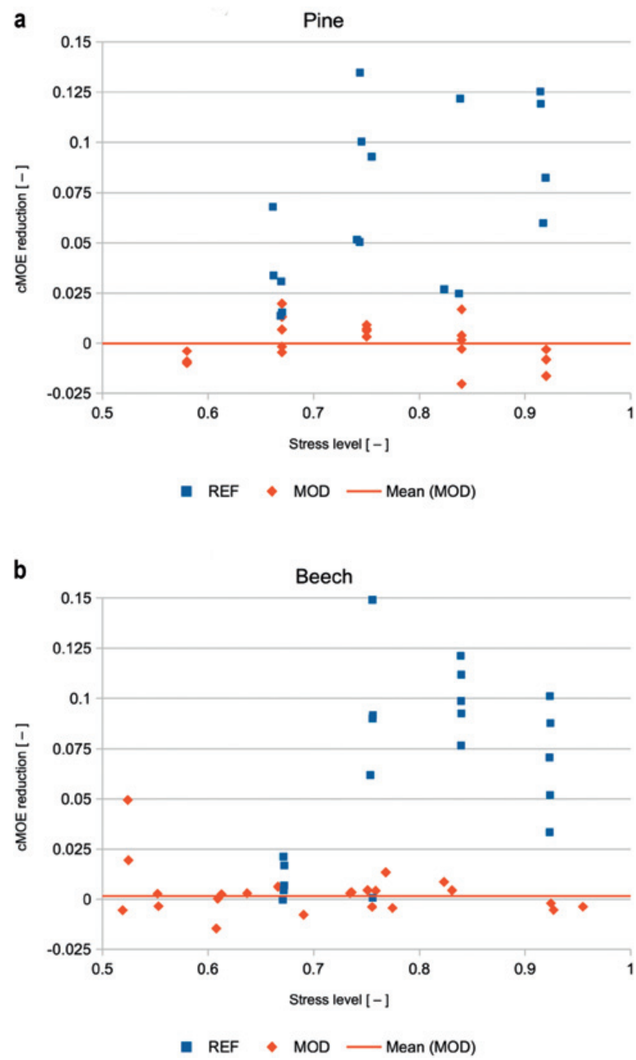

Figure 7: Reduction in cMOE as a function of stress level for pine (a) and beech (b).

75%, a change of the material behavior from elastic to plastic as a reason for this finding appears to be plausible.

3.3.3 Cyclic modulus of elasticity

Plotted samples in Figure 7, are showing average values of cMOE for pine and beech. Based on previous results, it was expected that increasing accumulative travel of a specimen, as the effect of cyclic creep, would result in reduction of elasticity as fatigue under constant force loading causes weakening of the material. The main variable here is changing $dl_{\_max}$ (Figure 1) as load is constant. It was observed that, in the case of modified specimens, $dL_{\_max}$ remains unchanged, resulting in constant linear cMOE. This is indicated by the red linear line in Figure 7. This can be related to high LOP for modified samples calculated under the static tests. It has been described before, that modified wood has limited ability for absorbing plastic deformation, which was accumulating in the reference samples.

Results obtained in the state of stationary creep level show that modulus of elasticity was decreasing for reference samples. Constant modulus was observed for Mod samples with more stable behavior. This may be explained as follows: in the case of modified wood, one can see no reduction in cMOE, showing no fatigue failure leading to unpredictable failure of specimen. The cMOE for Mod was constant throughout all *SL*. On the other hand, specimens from the Ref sample show weakening in the material while tests were causing softening, resulting in decreasing cMOE. Therefore, it could be concluded that cMOE can be used as an indicator of fatigue in material, which can ultimately lead into failure. Modulus remained constant when approaching CFS. Good correlation between CR and *SL* was found, but no relation between cMOE and *SL*. For the Ref sample, when reduction in cMOE is present one can be able to predict failure of the specimens.

4 Conclusions

Cell wall modification with low molecular weight phenol formaldehyde (PF) resin impregnation successfully contributed to improved performance of three-point bending in MOE with 21.4% increase for pine and 29.0% increase for beech. MOR improved close to 18% for both wood species. High limit of proportionality for modified wood species, describes the brittle material behavior that was identified as a main drawback for dynamic test in impact bending strength (IBS) and cyclic fatigue strength (CFS). CFS experienced negative effect of modification. Fatigue limit for reaching 10^6 loading cycles was 67% for reference sample, 58% for modified pine and 53% for modified beech from overall average static strength. Cyclic loading repetitions were found to cause decrease in cyclic creep with decreasing stress. The cyclic modulus of elasticity did not change in the case of modification at any stress level and remained constant. It can be concluded that pine and beech wood, impregnated with low molecular weight PF resin, perform much differently from unmodified wood. Therefore, it is important to take into account that dynamic mechanical properties, no matter the improved static performance, suffer greater reduction in IBS and CFS and show different creep rate level. High rigidity of modified material resulting in reduced ability for plastic deformation, prevents prediction when material starts to fatigue. More research is needed to get clearer results with greater variety of specimens.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The authors gratefully acknowledge the European Commission for funding the InnoRenew project (grant agreement #739574) under the Horizon2020 Widespread-Teaming program and the Republic of Slovenia (investment funding from the Republic of Slovenia and the European Union's European Regional Development Fund) as well as the Slovenian Research Agency (ARRS) for funding infrastructural program IO-0035 and bilateral project BI-DE/17-19-15.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

Ahmed, S.A., and Adamopoulos, S. (2018). Acoustic properties of modified wood under different humid conditions and their relevance for musical instruments. Appl. Acoust. 140: 92–99.

Ashby, M.F. (2010). *Materials selection in mechanical design*, 4th. ed. Butterworth-Heinemann, Oxford. p. 640.

Baar, J., Tippner, J., and Rademacher, P. (2015). Prediction of mechanical properties - modulus of rupture and modulus of elasticity - of five tropical species by nondestructive methods. Maderas. Cienc. Tecnol. 17: 2.

Bicke, S., Mai C., and Militz H. (2012). Modification of beech veneers with low molecular weight phenol formaldehyde for the production of plywood: durability and mechanical properties. In: *Conference: ECWM6 - The Sixth European Conference on Wood Modification*. Ljubljana, Slovenia.

Deka, M., and Saikia, C.N. (2000). Chemical modification of wood with thermosetting resin: effect on dimensional stability and strength property. Bioresour. Technol. 73: 179–181.

Deka, M., Saikia, C.N., and Baruah, K.K. (2002). Studies on thermal degradation and termite resistant properties of chemically modified wood. Bioresour. Technol. 84: 151–157.

DIN 52186. (1978). *Testing of wood; bending test*. DIN German Institute for Standardization, Berlin, German.

DIN 52189-1. (1981). *Testing of wood; determination of impact bending strength*. German Institute for Standardisation, Berlin, German.

Epmeier, H., Westin, M., and Rapp, A. (2004). Differently modified wood: comparison of some selected properties. Scand. J. Forest. Res. 19: 31–37.

Franke, T., Axel, M., Lenz, C., Nadine, H., and Pfriem, A. (2017). Microscopic and macroscopic swelling and dimensional stability of beech wood impregnated with phenol-formaldehyde. PRO LIGNO 13: 373–378.

Furuno, T., Imamura, Y., and Kajita, H. (2004). The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: a properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls. Wood Sci. Technol. 37: 349–361.

Gabrielli, C.P., and Kamke, F.A. (2010). Phenol-formaldehyde impregnation of densified wood for improved dimensional stability. Wood Sci. Technol. 44: 95–104.

Gascon, G.P., Militz, H., Mai, C., and Thévenon, M.F. (2015). Enhanced termite resistance of scots pine (*Pinus sylyvestris* L.) solid wood by phenol - formaldehyde treatment. Wood Res. 60: 873–880.

Gong, M., and Smith, I. (2003). Effect of waveform and loading sequence on low-cycle compressive fatigue life of spruce. J. Mater. Civ. Eng. 15: 93–99.

Hill, C. (2006) *Wood modification*. Wiley, Chichester. p. 239.

Hosseinpourpia, R., Adamopoulos, S., and Mai, C. (2016). Dynamic vapour sorption of wood and holocellulose modified with thermosetting resins. Wood Sci. Technol. 50: 165–178.

Huang, Y., Fei, B., Yu, Y., and Zhao, R. (2013). Effect of modification with phenol formaldehyde resin on the mechanical properties of wood from Chinese fir. Bio Resour. 8: 272–282.

Kielmann, B.C., Butter, K., and Mai, C. (2018). Modification of wood with formulations of phenolic resin and iron-tannin-complexes to improve material properties and expand colour variety. Eur. J. Wood Wood Prod. 76: 259–267.

Kielmann, B.C., Militz, H., Mai, C., and Adamopoulos, S. (2013). Strength changes in ash, beech and maple wood modified with a N-methylol melamine compound and a metal-complex dye. Wood Res. 58: 343–350.

Klein, B. (2009). *Leichtbau-Konstruktion – Berechnungsgrundlagen und Gestaltung*, 6th ed. Vieweg, Wiesbaden. p. 493.

Klüppel, A. (2017). Hardness and indentation modulus of resin-treated wood. Int. Wood Prod. J. 8: 41–44.

Klüppel, A., Cragg, S.M., Militz, H., and Mai, C. (2015). Resistance of modified wood to marine borers. Int. Biodeterior. Biodegrad. 104: 8–14.

Kollmann, F.F.P., Côté, W.A.J. (1968). *Principles of wood science and technology - solid wood*, Vol. 1. Springer, Mu¨ nchen.

Mai, C., Elder, T. (2016). Wood: chemically modified. In: *Reference module in materials science and materials Engineering*. Encyclopedia of Materials: Science and Technology, 2001: pp. 9603–9606.

Ramage, M.H., Burridge, H., Busse Wicher, M., Fereday, G., Reynolds, T., Shah, D. U., Wu, G., Yu, L., Fleming, P., Densley-Tingley, D., et al. (2017). The wood from the trees: The use of timber in construction. Renew. Sustain. Energy Rev. 68: 333–359.

Ratnasingam, J., and Mutthiah, N. (2017). Fatigue life of oil palm wood (OPW) for furniture applications. Eur. J. Wood Wood Prod. 75: 473–476.

Rowell, R. M. (1998). Property enhanced natural fibre composite materials based on chemical modification. In: *Science and technology of polymers and advanced materials*. Pra- sad, P. N., Mark, J. E., Kandil, S. H., and Kafafi, Z. H. (Ed.) Plenum, New York, NY. pp. 717–732.

Sandberg, D., Haller, P., and Navi, P. (2013). Thermo-hydro and thermo-hydro-mechanical wood processing: an opportunity for future environmentally friendly wood products. Wood Mater. Sci. Eng. 8: 64–88.

Sasaki, Y., Oya, A., and Yamasaki, M. (2014). Energetic investigation of the fatigue of wood. Holzforschung 68: 843–848.

Sharapov, E., Mahnert, K.C., and Militz, H. (2016). Residual strength of thermally modified *Scots pine* after fatigue testing in flexure. Eur. J. Wood Wood Prod. 74: 875–884.

Skaar, C. (1988). *Wood–water relations*. Springer, Berlin. p. 283.

Smith, I., Landis, E., and Gong, M. (2003). *Fracture and fatigue in wood*. Wiley, Chichester. p. 242.

Stamm, A. J., and Tarkow H. (1947). Dimensional stabilization of wood. J. Phys. Chem. 51: 493–505.

Sugimoto, T., and Sasaki, Y. (2007). Fatigue life of structural plywood under two-stage panel shear load: a new cumulative fatigue damage theory. J. Wood Sci. 53: 211–217.

Sugimoto, T., Sasaki, Y., and Yamasaki, M. (2007). Fatigue of structural plywood under cyclic shear through thickness I: fatigue process and failure criterion based on strain energy. J. Wood Sci. 53: 296–302.

Sugimoto, T., and Sasaki, Y. (2006). Effect of loading waveform on the fatigue of structural plywood in shear through thickness. In: *Proceedings of 9th World Conference on Timber Engineering (WCTE 2006)*. Portland, Oregon, pp 1818–1825.

Tsai, K.T., Ansell, M.P. (1990). The fatigue properties of wood in flexure. J. Mater. Sci. 25: 865–878.

Verkasalo, E., and Leban, J.M. (2002). MOE and MOR in static bending of small clear specimens of Scots pine, Norway spruce and European fir from Finland and France and their prediction for the comparison of wood quality. Pap Puu Pap Tim. 84: 332–340.

Wan, H., and Kim, M.G. (2006). Impregnation of southern pine wood and strands with low molecular weight phenol-formaldehyde resins for stabilization of oriented strandboard. Wood Fiber Sci. 38: 314–324.

Wang, X., Chen, X., Xie, X., Yuan, Z., Cai, S., Li, Y. (2019). Effect of phenol formaldehyde resin penetration on the quasi-static and dynamic mechanics of wood cell walls using nanoindentation. Nanomaterials 9(10): 1409.

Xie, Y., Krause, A., Militz, H., Turkulin, H., Richter, K., and Mai, C. (2007). Effect of treatments with 1,3-dimethylol-4,5-dihydroxy-ethyleneurea (DMDHEU) on the tensile properties of wood. Holzforschung 61: 43–50.

Xie, Y., Fu, Q., Wang, Q., Xiao, Z., and Militz, H. (2013). Effects of chemical modification on the mechanical properties of wood. Eur. J. Wood Wood Prod. 71: 401–416.

Xie, Y., Xu, J., Militz, H., Wang, F., Wang, Q., Mai C., and Xiao Z. (2016). Thermo-oxidative decomposition and combustion behavior of Scots pine (*Pinus sylvestri*s L.) sapwood modified with phenol- and melamine-formaldehyde resins. Wood Sci. Technol. 50: 1125–1143.