



Utilizing pyrolysis cleavage products from softwood kraft lignin as a substitute for phenol in phenol-formaldehyde resins for modifying different wood species

Johannes Karthäuser¹ · Vladimirs Biziks² · Daniel Roggatz¹ · Holger Militz¹

Received: 15 August 2023 / Accepted: 1 February 2024 / Published online: 9 February 2024
© The Author(s) 2024

Abstract

Phenol-formaldehyde resins can be used for wood modification through an impregnation process and subsequent curing within the wood cell wall. Phenol is gained from non-renewable resources, and its substitution by renewable chemicals has been a research goal. A promising example for renewable phenol substituents are lignin-derived organic chemicals. Phenol-formaldehyde resins with such substitutions have been studied, however, knowledge of their application for wood modification is deficient. While there are attempts to modify pine and beech wood with this method, studies on other wood species are scarce. Considering the increasing use of different wood species in wood industry, determining the influence of the wood species on the modification quality is an important research goal. Therefore, in this study, vacuum-pressure impregnation of five wood species – Scots pine sapwood (*Pinus sylvestris*), Norway spruce (*Picea abies*), European beech (*Fagus sylvatica*), Silver birch (*Betula pendula*), and European aspen sapwood (*Populus tremula*) – with phenol-formaldehyde resins is described. Here, up to 45% of the phenol in the synthetic resin is substituted by vacuum low-temperature microwave-assisted pyrolysis cleavage products from commercial softwood kraft lignin. The solution uptake, weight% gain, leaching, and anti-swelling efficiency of the modified wood are analyzed and compared. The results indicate that up to 30% of the phenol can be substituted without significant decreases in the performance of the modification. The method gives comparable results for most of the wood species described herein, with exception of beech wood, for which the modification had a lower quality. The results could help to develop more environmentally friendly wood modification methods for several common European wood species.

1 Introduction

The global usage of wood as a material has significantly increased in the past years, and this trend is expected to continue in the coming decades (Sauter and Scheiding 2023). This can be explained especially by the good carbon

footprint and the renewable character of wood. Additionally, the good strength to weight ratio, the aesthetic appearance, as well as other properties make wood an excellent material for many applications (Hill 2006; Lugt and Harsta 2020). While the use of wood has environmental benefits over other materials, it also has challenges. As a biological material, wood is prone to degradation by fungi or insects, as well as weathering conditions. In addition, wood frequently interacts with water, causing it to swell and shrink, which can lead to cracks in the material and faster mechanical failure (Hill 2006; Zabel and Morrell 2020). Additionally, wood has to be grown and harvested in a responsible way, since the forests are a major source of biodiversity. Climate change poses a major threat, and increasingly extreme weather conditions already have visible effects on forests

✉ Johannes Karthäuser
jkarthaeuser@gwdg.de

¹ Department of Wood Biology and Wood Products, Georg-August University of Göttingen, Buesgenweg 4, 37077 Göttingen, Germany

² Surfactor Germany GmbH, Braunschweiger Str. 23 b, 38170 Schoeppenstedt, Germany

(Buras and Menzel 2019; Sauter and Scheiding 2023). Hence, using wood as efficiently as possible is an important task for the wood industry, amongst others because of monetary considerations. There are different strategies on how the efficiency of wood usage can be increased, two of which, wood modification to extend the lifespan of the product, and the increasing usage of a larger variety of (hardwood) species will be described in detail below.

Forestry sectors should adapt to the impact of climate change, particularly on mono-specific and even-aged forest stands. Due to this and to increase the biodiversity in forests, the European Union has implemented a strategy for European forests that promotes the planting of forests with mixed tree species (EC 2021). This will change the abundance of different wood species, and thus timber, in European forests. Currently, the most common tree species in European forests are the Scots pine (*Pinus sylvestris*), and the Norway spruce (*Picea abies*), which is in line with the most traded timber (UN and FAO 2021). However, models of the future composition of forests indicate a change in forest composition, e.g., increased occurrence of some hardwood species (Buras and Menzel 2019). Additionally, the growing demand in timber poses a challenge for wood industries and companies (Schlotzhauer et al. 2017; Stolze et al. 2022). One way to face the growing timber demand is the establishment of plantations consisting of fast-growing species, such as poplar (*Populus*) (Cheng et al. 2022; Xu et al. 2020). Changes in timber availability affect the wood industry as a whole. Currently, due to the high availability of softwood, the wood industry has much less experience on processing hardwood. Thus, new processes or methodologies have to be developed or tested for different timber feedstocks (Schlotzhauer et al. 2017; Stolze et al. 2022).

Moreover, to improve the efficiency of wood usage, the service life of wood should be increased by various treatments. To ensure a long service life of wood products, and thus make the usage of wood more effective, most wood is treated before use. This is often done by adding biocidal wood preservatives, which is consequently decreasing the wood degradation by fungi and insects (Hill 2006; Zabel and Morrell 2020). However, due to leaching in the use and waste phase, biocides can be exposed to the environment. Hence, more and more restrictions on their application are decided on by governments, for example the regulation (EC) No 1907/2006 (REACH) or the Biocidal Products Regulation (EU) No 528/2012 from the EU (Council of the EU 2006; Council of the EU 2012). Because of this, the market for non-biocidal wood modification has grown, and is expected to do so even further (Jones and Sandberg 2020).

There are various methods for non-biocidal wood modification, for example heat treatment or different chemical treatments. One way to chemically modify wood is the

impregnation with synthetic resins. During this treatment, synthetic resins are deposited inside of the cell walls and thermally cured, resulting in the permanent hardening within the wood's structure in swollen form (Hill 2006; Jones and Sandberg 2020). By this, the dimensional stability, as well as the resistance towards biological and physical decay are increased (Bicke 2019; Stamm and Baechler 1960). A well-known method is the treatment with phenol-, urea-, or melamine-based (or mixtures of those monomers) resins (Jones and Sandberg 2020).

Combining the exploitation of different timber sources and wood modification to increase the efficiency of timber usage, non-biocidal modifications on different wood species have to be evaluated.

Trials on modification of small specimens from different wood species by impregnation with phenol-urea-formaldehyde resin have been carried out, and the results indicate that one major factor, which has an influence on the impregnation, is the density of the wood. Additionally, between different wood species with similar densities, significant differences in the anti-swelling efficiency (ASE) were observed (Kupfernagel et al. 2022). It has to be considered that small specimens are easier to impregnate. For larger wood specimens, species-specific properties are expected to be a bigger factor, such as the irreversible pit closure during the drying process of spruce, which often leads to bad impregnations (Meints et al. 2018). This implies that wood products from different wood species cannot be produced with the same process parameters, but the methods have to be adjusted accordingly. With suitable methods, pine sapwood, birch, beech, and poplar may be modified by impregnation with phenol-formaldehyde (PF) resins (Bicke 2019; Wang et al. 2023; Karthäuser et al. 2023; Grinins et al. 2021).

The treatment of wood with PF resins significantly improves the above-mentioned properties of wood (Biziks et al. 2020). However, it also has several disadvantages: monomeric phenol is highly toxic to humans and is obtained from non-renewable resources. Hence, bio-based and less-poisonous substitutes have been investigated for many years (Klašnja and Kopitović 1992; Sarika et al. 2020).

Due to the high availability and the similarities in chemical structure, lignin (most prominently kraft lignin) or cleavage products of lignin are promising for the substitution of phenol. Especially in the field of adhesives, many studies on the topic have been published, indicating the high potential of the method (Sarika et al. 2020; Huang et al. 2022). During the substitution of phenol in adhesives, the lignin does not necessarily have to be cleaved, however, when it comes to modifying wood with thermosetting resins, cleavage of lignin is inevitable. The reason for this is the size of the lignin macromolecules, which are too big to access the wood cell walls via the micropores. In swollen state,

the pores have a diameter of 2–4 nm, allowing only small molecules to enter (Furuno et al. 2004; Hill 2006; Biziks et al. 2019). In attempts to valorize lignin, many methods to cleave lignin were developed. One of the most promising methods is the pyrolysis of lignin, by which often phenols or guaiacolic substances are produced (Bu et al. 2014, 2019; Farag et al. 2016; Nde et al. 2021; Karthäuser et al. 2022). The substitution of phenol in PF resins by lignin cleavage products (LCP) has been studied (Feghali et al. 2018), but trials on their application as an impregnation resin for wood are scarce (Karthäuser et al. 2021).

Wood modification with partial or complete substitution of phenol in PF resins for wood modification by LCP was first described by Fleckenstein et al. (2018). Trials with model LCP compounds indicated a high potential of resulting resins. A substitution of 40% of phenol by base-catalyst, pyrolytic or microwave cleaved lignin was performed, with base-catalyst and pyrolytic LCP not performing worse, while the microwave cleaved lignin led to slightly reduced resin uptake (Fleckenstein 2018; Fleckenstein et al. 2018). While this work indicated the potential of the method, it left questions unanswered, especially because the LCP were not chemically analyzed, and only 40 and 100% of the phenol were substituted.

In a recent study, the properties of PF resins with different substitution levels of phenol by LCP obtained by vacuum low-temperature microwave-assisted pyrolysis of softwood kraft lignin (SKL) were investigated. In addition, experiments were carried out to determine if decreasing the amount of formaldehyde used in the formulation, considering the reduced free reactive sites of the LCP compared to pure phenol, would produce good wood modification. To study the suitability of the resins for wood modification, Scots pine sapwood was treated with the different resins. The results indicated that 30% substitution of phenol by LCP only results in slightly decreased performance of the modified wood. Reduction of formaldehyde led to less uniform results particularly at higher phenol substitution levels of 45% (Karthäuser et al. 2023).

While the results described above are promising, they were carried out on easily impregnatable pine sapwood. However, the treatment of other wood species, which are going to be increasingly abundant in the future, with the

resin has not been studied, and their interaction with the resin might be different than that of pine sapwood. Hence, in this study, five common European wood species – Scots pine sapwood (*Pinus sylvestris*), Norway spruce (*Picea abies*), European beech (*Fagus sylvatica*), Silver birch (*Betula pendula*), and European aspen sapwood (*Populus tremula*) – were treated with pure PF resin, as well as PF resin, in which 30% of the phenol was substituted by vacuum low-temperature microwave-assisted pyrolysis LCP, and in which the formaldehyde content was decreased. In addition, a resin with 45% substitution of phenol by LCP, and a high formaldehyde content was selected. The resins were selected based on the results in Karthäuser et al. (2023), where easily impregnatable Scots pine sapwood (*Pinus sylvestris*) was treated with the different resins. While the resin treatment with 45% substitution gave worse results in the study mentioned above for impregnation of pine sapwood, because an as high as possible substitution of phenol is the ideal scenario, this mixture was selected. The resin uptake, weight and volume increase, leaching, as well as ASE of the modified wood specimens were studied.

2 Materials and methods

2.1 Lignin cleavage products

Commercial SKL (“Lineo™” from Stora Enso Oyj, Helsinki, Finland) obtained by kraft pulping using the LignoBoost™ process on spruce and pine wood was used to produce the LCP. SKL derived vacuum low-temperature microwave-assisted pyrolysis cleavage products were obtained as described in Karthäuser et al. (2023). The main components are 4-methylguaiacol ($13.8 \pm 0.8\%$), guaiacol ($8.1 \pm 0.9\%$), and 4-ethylguaiacol ($6.8 \pm 0.5\%$), as well as several other guaiacolic substances at lower concentrations.

2.2 Resin synthesis

Synthesized resins were a pure PF resin, in which the molar ratio between phenol and formaldehyde was 1:1.5 (100 PF), a resin in which 30% of the phenol was substituted by LCP with a molar ratio of phenol and LCP to formaldehyde of 1:1.38 (70/30 IF; IF for low formaldehyde content), as well as a resin in which 45% of the phenol was substituted by LCP with a molar ratio of phenol and LCP to formaldehyde of 1:1.5 (55/45 hF; hF for high formaldehyde content). The molar ratio of phenol (and LCP) to NaOH was 1:0.10 in all resins. The described composition and measured solid content of the resins are listed in Table 1.

The resin synthesis as well as characterization is described in Karthäuser et al. (2023). In short, the phenol

Table 1 Resin abbreviation, phenol to lignin cleavage product (LCP) mass ratio, molar ratio of the resin components, and measured solid content

Resin	Mass ratio Phenol : LCP / %	Molar ratio Phenol (+ LCP) : Formaldehyde : NaOH (± 0.01)	Solid content / %
100 PF	1	1.00 : 1.50 : 0.10	53.4
70/30 IF	0.7	1.00 : 1.38 : 0.10	54.7
55/45 hF	0.55	1.00 : 1.50 : 0.10	53.3

(99.5%, Th. Geyer GmbH & Co. KG, Renningen, Germany) and LCP were weighed into a three-neck flask and melted at about 55 °C. Nitrogen atmosphere was applied and the NaOH (50% solution, AppliChem GmbH, Darmstadt, Germany) was added. Finally, the formaldehyde (37% solution, Th. Geyer GmbH & Co. KG, Renningen, Germany) was carefully added, and the temperature was increased to 65 °C. The temperature was kept at 65 °C, and the reaction was stopped after 4 h. Considering the measured solid content, the resins were diluted to a solid content of 12.5% with demineralized water prior to impregnation.

2.3 Specimen preparation for leaching and anti-swelling efficiency tests

Ten specimens with dimensions of $25 \times 25 \times 10 \text{ mm}^3$ were cut from Scots pine sapwood (*Pinus sylvestris* from Bavaria, Germany), Norway spruce (*Picea abies* from Bavaria, Germany), European beech (*Fagus sylvatica* from Thuringia, Germany), Silver birch (*Betula pendula* from Aizkraukle Municipality, Latvia) and European aspen sapwood (*Populus tremula* from Latvia). The specimens were dried at 103 °C, and their weight and dimensions were determined. The density of the specimens was calculated. The specimens were submerged in the resins in separate containers, and treated by reduced pressure (1 h, 80–100 mbar) followed by increased pressure (2 h, 12 bar). The resin on the surface of the specimens was wiped off, and the weight and dimensions of the specimens in wet state were determined.

The solution uptake (SU) was determined using Eq. 1 with the dry mass before impregnation m_D and the wet mass after impregnation m_W .

$$SU = \frac{m_W - m_D}{m_D} \cdot 100\% \quad (1)$$

After drying with gradually increasing temperature, the specimens were cured at 140 °C for two days inside of a furnace. The dry weight and dimensions of the specimens were measured.

The weight% gain (WPG) was calculated with the dry weight before impregnation m_D and the dry weight of the treated wood specimens m_T (Eq. 2).

$$WPG = \frac{m_T - m_D}{m_D} \cdot 100\% \quad (2)$$

To obtain the bulking value of the wood specimens, the dry volume before impregnation V_D and the dry volume of the treated specimen V_T are needed (Eq. 3).

$$\text{Bulking} = \frac{V_T - V_D}{V_D} \cdot 100\% \quad (3)$$

2.4 Leaching of resin

The leaching of resin after curing was determined according to EN 84 (1997), with the difference that the drying was done at 103 °C in a furnace instead of a climate chamber. The specimens were impregnated with demineralized water under reduced pressure (30 min, 100 mbar). Two hours after impregnation, the water was exchanged for the first time. Afterwards, the water was exchanged twelve times in the following 14 days. The dry weight of the wood specimens was determined before and after the tests. The mass loss as a function of the weight of the wood specimens ML_{Wood} by leaching was calculated as described in Eq. 4, with the dry mass of the treated wood specimens m_T and the dry mass after leaching m_L .

$$ML_{\text{Wood}} = \frac{m_T - m_L}{m_T} \cdot 100\% \quad (4)$$

To better understand the influence of the resin on the leaching, the mass loss per resin mass ML_{Resin} in the specimen was calculated according to Eq. 5.

$$ML_{\text{Resin}} = \frac{m_T - m_L}{m_T - m_D} \cdot 100\% \quad (5)$$

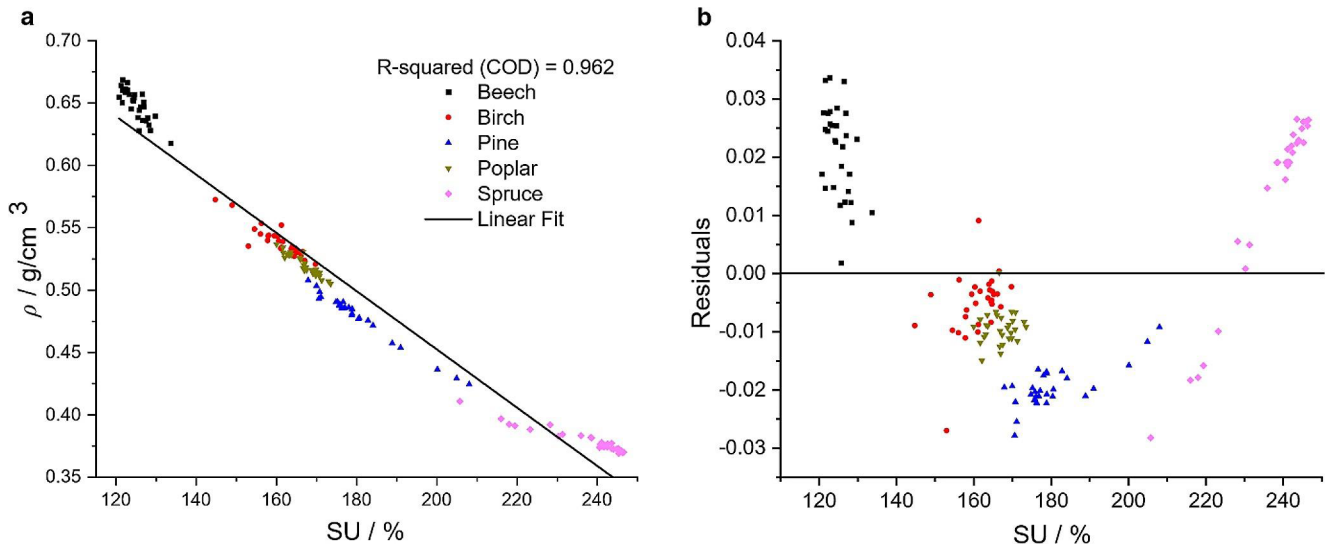
2.5 Anti-swelling efficiency tests

The ASE is a value, which represents the dimensional stability of specimens. It was determined based on the methodology described in Hill (2006). Ten untreated wood specimens were prepared as a reference material. The treated specimens after EN 84 were used. The dry specimens were measured and weighed. All specimens were submerged and impregnated in demineralized water (30 min, 100 mbar). After leaving the specimens submerged in the water for 24 h, the dimensions and weight of the wet specimens were determined. The ASE was calculated (Eq. 6) with the swell rate of untreated reference wood specimens SW_{ref} and the swell rate of the treated wood specimens SW_T . The swell rate of the wood specimens was calculated as follows (Eq. 7) with the area of the wet specimen A_W and the area of the dry specimen A_D (the area is calculated by radial width x tangential width).

$$ASE = \frac{SW_{\text{ref}} - SW_T}{SW_{\text{ref}}} \cdot 100\% \quad (6)$$

Table 2 Density (ρ_w) and solution uptake (SU) of the specimens from different wood species treated with pure PF resin (100 PF), resin with 30% substitution of phenol by lignin cleavage products (70/30 1F), and resin with 45% substitution (55/45 hF)

Wood species	100 PF		70/30 1F		55/45 hF	
	$\rho_w / \text{g/cm}^3$	SU / %	$\rho_w / \text{g/cm}^3$	SU / %	$\rho_w / \text{g/cm}^3$	SU / %
Beech	0.65 ± 0.01	125.3 ± 2.4	0.65 ± 0.02	124.8 ± 3.8	0.65 ± 0.01	124.9 ± 2.2
Birch	0.54 ± 0.01	162.3 ± 4.8	0.54 ± 0.01	160.0 ± 6.8	0.54 ± 0.01	160.5 ± 4.0
Pine	0.48 ± 0.02	178.7 ± 11.4	0.47 ± 0.02	182.4 ± 8.9	0.48 ± 0.02	179.1 ± 7.3
Poplar	0.52 ± 0.01	167.8 ± 2.7	0.52 ± 0.01	166.9 ± 3.4	0.52 ± 0.01	166.1 ± 4.2
Spruce	0.38 ± 0.01	238.4 ± 9.7	0.38 ± 0.01	231.3 ± 12.4	0.38 ± 0.01	240.8 ± 5.1

**Fig. 1** Linear fit of the density (ρ) as a function of the solution uptake (SU) (a), and the residuals to the linear fit (b) of the different wood species treated with pure PF resin (100 PF), resin with 30% substitu-

tion of phenol by lignin cleavage products (70/30 1F), and resin with 45% substitution (55/45 hF), for tested specimen dimensions

$$SW = \frac{A_W - A_D}{A_D} \cdot 100\% \quad (7)$$

This procedure was repeated five times, after which a constant ASE was reached.

3 Results and discussion

3.1 Wood treatment

As a first indicator on the quality of the impregnation, the SU should be considered (Table 2). For each individual species, the SU was independent of the resin, as indicated by similar uptakes for each resin treatment. As expected, the SU varies between the different wood species. While the birch, pine and poplar wood exhibited a roughly similar SU, it was much lower for beech wood and much higher for spruce wood. Generally, the maximum SU of lighter wood species is expected to be higher due to more pore volume. However, an important factor is the wood anatomy,

because pits, tyloses, reaction tissue etc. will strongly influence the uptake, especially in wood specimens with larger dimensions.

The results are in accordance with the literature, where the main influence on the SU of small wood specimens was attributed to the density, with additional effects for wood species (Kupfernagel et al. 2022). For the specimens measured in this work, the density also seems to be the main influence on the SU, likely due to their small size (Table 2). To confirm this, the density was depicted as a function of the SU (Fig. 1a). For this, the individual measurements, and not the average, were evaluated. The different resins were not separated herein, because the results above indicated that the resin does not have a significant influence on the SU; additional information can be found below. A linear fit was applied, and an R^2 -factor of 0.962 was determined.

The good fit and the high R^2 value confirm that the main impact on the SU is the density of the specimens. The residuals to the linear fit are depicted in Fig. 1b. The residuals are not statistically distributed; clear separations between the different wood species can be observed. This indicates that the wood species indeed had an influence, not only due

Table 3 ANOVA of the solution uptake (SU) to the factors wood species and resin

	SU ANOVA	
	f-value	p-value
Wood species	956.8	$4.3 \cdot 10^{-102}$
Resin	0.56	0.57

to the density but also due to other species specific properties, such as anatomical structure or chemical composition. However, the residuals are minor, and the main influence can be attributed to the density of the specimens.

To make sure that the resin type does not have an influence on the SU, an analysis of variance (ANOVA) was carried out (Table 3). The factors considered were the wood species (representing the density) and the resin. The significance value was set to 0.05.

The ANOVA underlines that the wood species, and thus the density, plays a significant role for the SU, while the resin only slightly influences it. Thus, the substitution of phenol by LCP did not negatively affect the SU.

In general, spruce is difficult to impregnate, due to irreversible pit closure during the drying process (Meints et al. 2018). Nevertheless, herein the SU for spruce is by far the highest. Reason for this is that the specimens are small (making thorough impregnation easier to achieve), and that the vacuum-pressure-impregnation process used herein is more harsh than necessary for such small specimens (the long exposure to resin under vacuum and pressure conditions may lead to slow diffusion over time). The process parameters were selected to ensure that a good impregnation is achieved. With larger scale specimens, however,

the known impregnation difficulties for spruce, as well as additional influences of anatomical differences between the different wood species, are expected to occur also with the resins described herein.

While the SU is a good first indicator for a successful impregnation, it does not give further insights into the location of the resin inside the specimen. Some information on this can be obtained by the WPG and the bulking. The WPG outlines the overall weight gain of the cured resin, while the bulking is attributed to resin inside of the cell wall. The WPG of the specimens is depicted in Fig. 2a and listed in Table S1 in the supplementary information. For the birch and poplar specimens, the WPG did not change a lot depending on the level of phenol substitution. For spruce, pine, and beech, the WPG decreased with substitution of phenol. This indicates that the wood species had an influence on the WPG, which is not only caused by the density of the specimens. For the birch specimens impregnated with 55/45 hF a high standard deviation was observed.

The bulking values of the specimens are depicted in Fig. 2b and listed in Table S1 in the supplementary information. Almost no decrease in bulking for the pine specimens with substitution of phenol was measured. Similarly, the bulking of the spruce and poplar specimens are relatively constant, independent of the resin used. In contrast, both the birch and the beech specimens had decreasing bulking with substitution of phenol. Even for the specimens with decreasing bulking upon phenol substitution, no significant differences between the 30% substitution and the 45% substitution were measured.

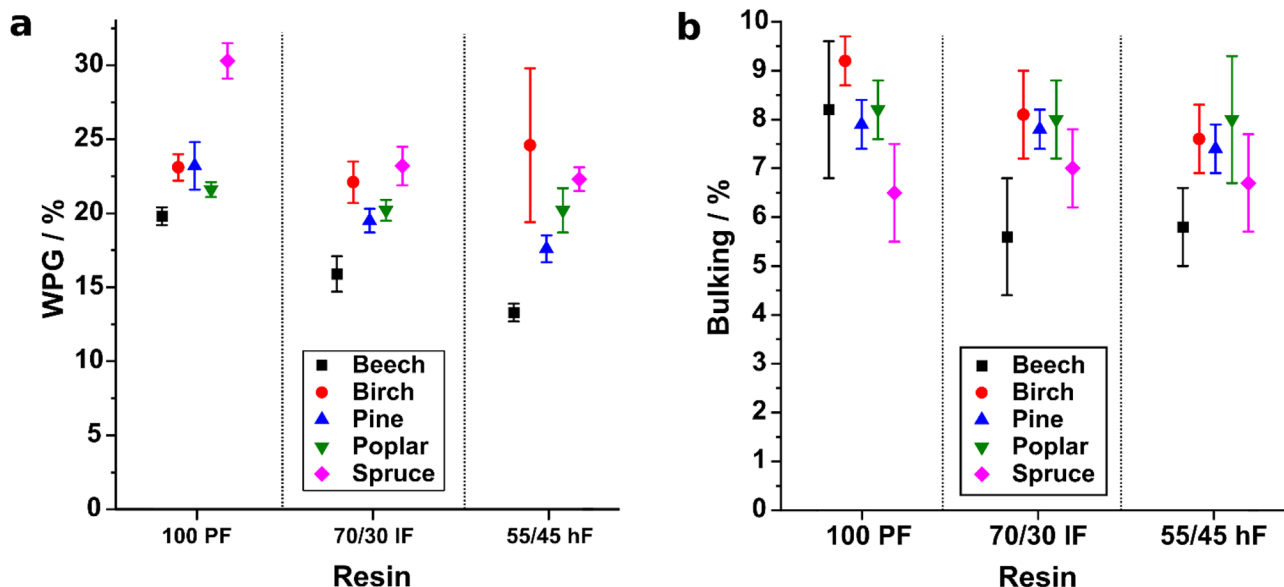


Fig. 2 Weight% gain (WPG) (a) and bulking (b) of the different wood specimens treated with pure PF resin (100 PF), resin with 30% substitution of phenol by lignin cleavage products (70/30 IF), and resin with 45% substitution (55/45 hF)

For birch no decrease in WPG because of the phenol substitution was measured, while a decrease in bulking could be observed. This indicates that while the overall uptake of resin was similar, less resin was deposited into the cell walls. The high standard deviation of the WPG of the birch specimens treated with 55/45 hF could be because of resin heterogeneity (while all the specimens were treated with the same resin, it could be that during the pouring of the resin into the impregnation containers a phase separation in the remaining resin began). This heterogeneity at high phenol substitution levels was described in recent literature (Karthäuser et al. 2023), with the reason most likely being a phase separation of the highly viscous and non-water-soluble LCP phase. This highly viscous phase could remain in the lumen, and thus contribute to the WPG while not contributing to the bulking. The resin composition and the solubility of the components in the resin could also influence the WPG, because upon taking the specimens out of the solvent, different amounts of solid content could be leached. While the WPG of the spruce and the pine specimens decreased with increasing phenol substitution, the bulking remained similar, indicating that for the PF100 specimen more resin remained in the lumen, while the resin uptake into the cell walls was similar. Both the beech and the poplar exhibit roughly similar trends for both the WPG and the bulking, indicating that most of the resin uptake is also responsible for the bulking, hence, that the resin is deposited in the cell walls. It has to be mentioned that due to the heterogeneous nature of bio-materials, a high deviation due to different specimen properties could influence the obtained results.

Comparing the results with the literature, the WPG achieved for all specimens are similar or higher to published results with PF resins with similar solid content (note that

the spruce wood in the reference is in the form of veneers, as no similar impregnation methodology to the one described herein was found for wood blocks) (Fleckenstein 2018; Yue et al. 2018; Bliem et al. 2020; Grinins et al. 2021; Altgen et al. 2023).

3.2 Leaching of resin

The results from the leaching trials according to EN 84 (1997) are depicted in Fig. 3 and listed in Table S2 in the supplementary information. For most wood species, the mass loss was higher for the specimens treated with LCP containing resins, however, between the 70/30 IF and the 55/45 hF specimen, no significant differences were observed. Exceptions are the birch specimens, where the mass loss was almost similar for all resins, and the beech specimens, for which an increasing mass loss from 30 to 45% substitution was measured. Overall, the beech specimens are the specimens with highest mass loss.

The similar results obtained for 70/30 IF and 55/45 hF with different wood species are surprising, considering that in previous measurements on pine specimens higher substitution level led to higher leaching. Despite this, problems with heterogeneous resins at 45% substitution level may occur, as described above and in Karthäuser et al. (2023). The birch specimens had no differences in ML_{Resin} for all three resins. The similar leaching implies that the resin was fixated well inside of the wood specimens, even with the treatment with phenol substitution.

In general, the increasing mass loss with substitution of phenol observed for most species was expected, due to several reasons. First, the LCP contains substances with lower number of available reactive sites than pure phenol, due to already occupied ortho- and para-positions, leading to less interconnections in the molecular network during curing, and thus smaller macromolecules. In addition, the LCP may contain chemicals that do not react with the formaldehyde at all, and can be washed out easily. Second, the average molecular size of the chemicals in the LCP is larger than phenol, making the diffusion into the cell walls more difficult. Because of this, and because of the higher viscosity, it is expected that more resin remains in the lumen, where it is more susceptible to leaching.

3.3 Anti-swelling efficiency tests

The ASE is a representative for the dimensional stability and thus an important value for the quality assessment of a wood modification. In all specimens, the substitution of phenol by LCP led to a decrease of the ASE value at 45% phenol substitution (Fig. 4; Table S3 in supplementary information; the ASE values are the average values of the

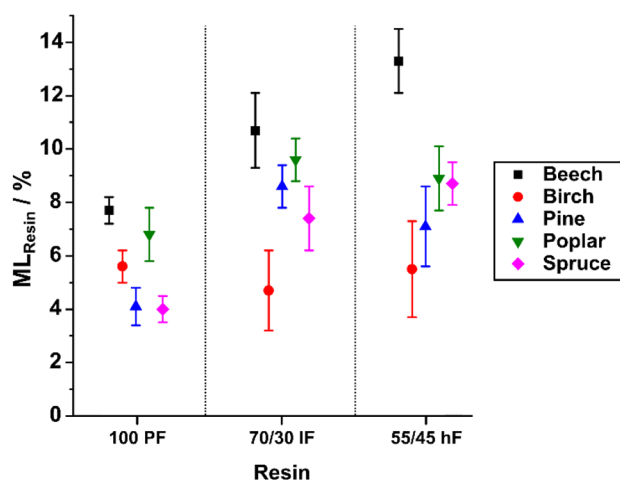


Fig. 3 Mass loss in relation to resin mass (ML_{Resin}) of the wood specimens treated with pure PF resin (100 PF), resin with 30% substitution of phenol by lignin cleavage products (70/30 IF), and resin with 45% substitution (55/45 hF)

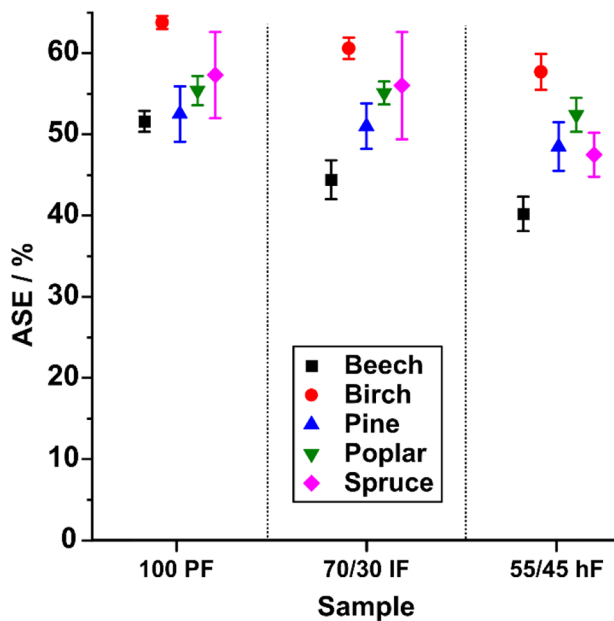


Fig. 4 Anti-swelling efficiency (ASE) of the wood specimens treated with pure PF resin (100 PF), resin with 30% substitution of phenol by lignin cleavage products (70/30 IF), and resin with 45% substitution (55/45 hF)

ASE measured in the five cycles). For the pine, poplar, and spruce specimens, the treatment with 70/30 IF led to similar ASE values, indicating similar modification qualities. Even the 55/45 hF specimens of pine and poplar were in similar ranges, while for spruce the ASE with this treatment decreased significantly. Both birch and beech had decreasing ASE values with increasing LCP content; especially for beech a drastic decrease was measured, while the decrease for the birch specimens is much less pronounced. Overall, the ASE values of the birch specimens are by far the highest – even those treated with 55/45 hF are higher than the ASE measured for the other wood species with pure PF resin. The lowest ASE values were measured for the beech specimens treated with LCP containing resins. The spruce specimens treated with 100 PF and 70/30 IF have a high standard deviation.

In most cases, the substitution of 30% of phenol by LCP leads to comparable dimensional stabilities. The exception to this is the beech wood, which had worse performance at 30% substitution. This indicates that the high density and resulting low SU of the beech wood has a negative impact on the final set resin, when phenol is substituted. The results outline that especially birch wood could be an interesting candidate for modification with bio-based resins. In addition, considering the results, even the substitution of 45% of the phenol may result in sufficiently good treatments for some wood species. The high deviation for the spruce specimens can be explained by the difficult treatability of spruce

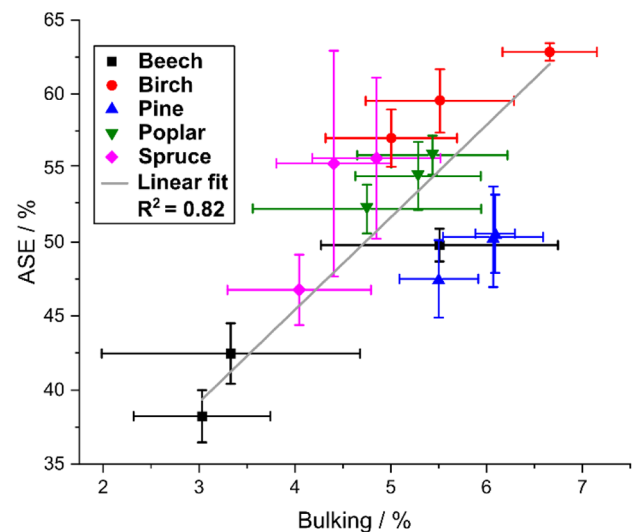


Fig. 5 Anti-swelling efficiency (ASE) as a function of bulking of the wood specimens

wood, leading to some specimens where the resin was only partially deposited in the cell walls.

The ASE is directly dependent of the bulking of the cell wall by resin. To confirm this, the ASE was depicted as a function of the bulking (both during the fifth ASE cycle), and a linear fit was applied (Fig. 5). The linear fit had a R^2 -value of 0.82, confirming the proportionality of the ASE and bulking.

Furuno et al. (2004) classified an ASE value of 60% as a high dimensional stability. Considering the low WPG, low resin SC, and the ASE values that are close to 60%, the modification herein can be considered to be effective for all resins, with slight exception to the beech specimens with phenol substitution.

The repeated leaching of the specimens during the ASE tests can be used as a first indicator of the long-term stability of the cured resin inside the wood specimens. The bulking after the ASE was calculated, and compared to the original bulking of the specimens (Fig. 6; Table S4 in supplementary information). The highest bulking losses were measured for the specimens treated with 55/45 hF for all wood species. However, the overall amount of bulking reduction and the trends differ between the wood species. As such, the modified beech and the spruce wood exhibited a significant increase in bulking loss with 30% substitution of phenol, followed by a more similar value between the 70/30 IF and the 55/45 hF treated specimens. For all other wood species, the bulking loss of the 100 PF and the 70/30 IF was similar, followed by an increase with the 55/45 hF specimens. The beech wood is the wood species with the highest bulking losses upon substitution of phenol.

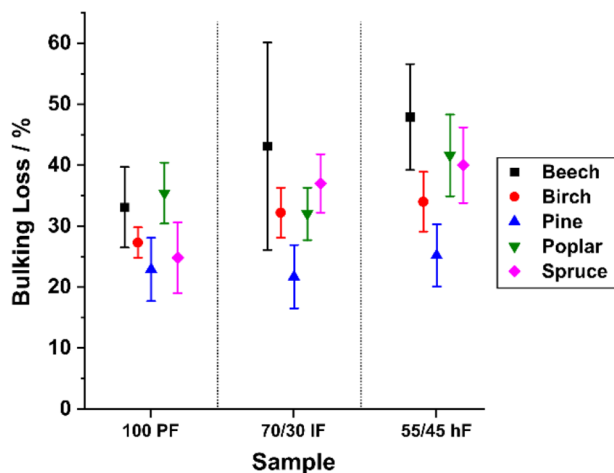


Fig. 6 Loss of bulking of the wood specimens treated with pure PF resin (100 PF), resin with 30% substitution of phenol by lignin cleavage products (70/30 IF), and resin with 45% substitution (55/45 hF)

The results confirm that the modification method described herein works least good for beech, likely due to the high density and anatomical features.

4 Conclusion

The purpose of this study was to investigate if the partial substitution of phenol by softwood kraft lignin cleavage products in PF resins used for wood modification by impregnation is suitable for different wood species. Up to 45% of phenol were substituted by LCP obtained with vacuum low-temperature microwave-assisted pyrolysis. The results indicate that PF resins with different substitution levels of non-renewable phenol by LCP are promising to be used for wood modification of different wood species. With exception of beech, the bulking of the wood after modification was in similar ranges for pure PF resin and resin with substitution of phenol by LCP. In case of beech, a significant reduction of bulking was measured with increasing LCP content. After the modification, all modified wood species had on average about 50% ASE. The level of the ASE was dependent on the resin and wood species used. In case of beech wood, the quality of the modification decreased already at 30% substitution of phenol, while in case of the other wood species tested the performance was similar. With substitution of phenol by LCP, the leaching of the resin from the modified wood increased, with exception of the modified birch. The highest leaching was observed for the beech specimens. It can be concluded that for most wood species tested herein, the substitution of 30% of the phenol, for some specimens even 45% substitution, does not have a big influence on the quality of modification (with exception of the beech wood). Thus, the method could be a good

approach to reduce the use of non-renewable resources, while at the same time providing an additional application for kraft lignin. It could be an interesting method for exterior applications where the wood is exposed to water, such as claddings. In future work, the fungal resistance of the modified wood, which is important for exterior applications, will be determined.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00107-024-02056-4>.

Author contributions Method development and conduction of experiments, V.B., J.K., and D.R.; Data curation, J.K.; Writing—original draft preparation, J.K.; Supervision, H.M.; writing—review and editing, all authors. All authors have read and agreed to the published version of the manuscript.

Funding The authors acknowledge support from the Federal Ministry of Education and Research (Germany) and its project promoter Forschungszentrum Jülich GmbH (funding number: 031B0952), as well as the Research Council of Norway (RCN Project no. 305120). The publishing of this article was supported by the Open Access Publication Funds of the Georg-August University of Göttingen. Open Access funding enabled and organized by Projekt DEAL.

Data availability The data presented in this study are available upon request from the corresponding author.

Declarations

Competing interests The authors declare no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Altgen M, Awais M, Altgen D, Klüppel A, Koch G, Mäkelä M, Olbrich A, Rautkari L (2023) Chemical imaging to reveal the resin distribution in impregnation-treated wood at different spatial scales. *Mater Des* 225:111481. <https://doi.org/10.1016/j.matdes.2022.111481>
- Bicke S (2019) Dimensionsstabile und pilzresistente Furnierwerkstoffe durch Zellwandmodifizierung mit niedermolekularem Phenol-Formaldehyd [Dimensionally stable and fungal decay resistant veneer-based materials produced by cell wall modification with low molecular sized phenol-formaldehyde]. Dissertation, Georg-August-Universität Göttingen

- Biziks V, Bicke S, Militz H (2019) Penetration depth of phenol-formaldehyde (PF) resin into beech wood studied by light microscopy. *Wood Sci Technol* 53(1):165–176. <https://doi.org/10.1007/s00226-018-1058-2>
- Biziks V, Bicke S, Koch G, Militz H (2020) Effect of phenol-formaldehyde (PF) resin oligomer size on the decay resistance of beech wood. *Holzforschung* 75(6):574–583. <https://doi.org/10.1515/hf-2020-0020>
- Bliem P, Konnerth J, Frömel-Frybort S, Gartner C, Mauritz R, Van Herwijnen HWG (2020) Influence of drying and curing parameters on phenol-formaldehyde impregnated wood veneers. *J Adhes* 96(1–4):253–271. <https://doi.org/10.1080/00218464.2019.1657015>
- Bu Q, Lei H, Wang L, Wei Y, Zhu L, Zhang X, Liu Y, Yadavalli G, Tang J (2014) Bio-based phenols and fuel production from catalytic microwave pyrolysis of lignin by activated carbons. *Bioresour Technol* 162:142–147. <https://doi.org/10.1016/j.biortech.2014.03.103>
- Bu Q, Chen K, Xie W, Liu Y, Cao M, Kong X, Chu Q, Mao H (2019) Hydrocarbon-rich bio-oil production, thermal behavior analysis and kinetic study of microwave-assisted co-pyrolysis of microwave-torrefied lignin with low density polyethylene. *Bioresour Technol* 291:121860. <https://doi.org/10.1016/j.biortech.2019.121860>
- Buras A, Menzel A (2019) Projecting tree species composition changes of European forests for 2061–2090 under RCP 4.5 and RCP 8.5 scenarios. *Front Plant Sci* 9:1986. <https://doi.org/10.3389/fpls.2018.01986>
- Cheng X, Lu D, Yue K, Lu W, Zhang Z (2022) Fire resistance improvement of fast-growing poplar wood based on combined modification using resin impregnation and compression. *Polymers* 14(17):3574. <https://doi.org/10.3390/polym14173574>
- Council of the European Union (2006) Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. *OJ* 396(49):1–849
- Council of the European Union (2012) Regulation (EU) 528/2012 of the European parliament and of the council of 22 May 2012 concerning the making available on the market and use of biocidal products. *OJ* 167:1–123
- EN 84 (1997) : Wood preservatives - Accelerated ageing of treated wood prior to biological testing - Leaching procedure (Brussels: CEN (European Committee for Standardization))
- European Commission (2021) New EU Forest Strategy for 2030. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the regions, COM(2021) 572 final. European Commission, Brussels, Belgium
- Farag S, Mudraboyina BP, Jessop PG, Chaouki J (2016) Impact of the heating mechanism on the yield and composition of bio-oil from pyrolysis of kraft lignin. *Biomass Bioenergy* 95:344–353. <https://doi.org/10.1016/j.biombioe.2016.07.005>
- Feghali E, Torr KM, van de Pas DJ et al (2018) Thermosetting polymers from Lignin model compounds and depolymerized lignins. *Top Curr Chem (Z)* 376:32. <https://doi.org/10.1007/s41061-018-0211-6>
- Fleckenstein M (2018) Technische Lignine als biobasiertes Ausgangsmaterial zur Substitution von erdölbasiertem Phenol in Phenol-Formaldehyd-Harzen [Technical lignins as a bio-based starting material for the substitution of oil-based phenol in phenol-formaldehyde resins]. Dissertation, Georg-August-Universität Göttingen
- Fleckenstein M, Biziks V, Mai C, Militz H (2018) Modification of beech veneers with lignin phenol formaldehyde resins in the production of laminated veneer lumber (LVL). *Eur J Wood Prod* 76(3):843–851. <https://doi.org/10.1007/s00107-017-1275-7>
- Furuno T, Imamura Y, 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
- Grinins J, Biziks V, Rizikovs J, Irbe I, Militz H (2021) Evaluation of water related properties of birch wood products modified with different molecular weight phenol-formaldehyde oligomers. *Holzforschung* 75(10):908–916. <https://doi.org/10.1515/hf-2020-0235>
- Hill CAS (2006) Wood modification: chemical, thermal and other processes. Wiley, Chichester, UK
- Huang C, Peng Z, Li J, Li X, Jiang X, Dong Y (2022) Unlocking the role of lignin for preparing the lignin-based wood adhesive: a review. *Ind Crops Prod* 187:115388. <https://doi.org/10.1016/j.indcrop.2022.115388>
- Jones D, Sandberg D (2020) A review of wood modification globally – updated findings from COST FP1407. *Interdiscip Perspect Built Environ* 1:1. <https://doi.org/10.37947/ipbe.2020.vol1.1>
- Karthäuser J, Biziks V, Mai C, Militz H (2021) Lignin and lignin-derived compounds for wood applications—A. *Rev Molecules* 26:2533. <https://doi.org/10.3390/molecules26092533>
- Karthäuser J, Biziks V, Frauendorf H, Mai C, Militz H (2022) Vacuum low-temperature microwave-assisted pyrolysis of technical lignins. *Polymers* 14(16):3383. <https://doi.org/10.3390/polym14163383>
- Karthäuser J, Biziks V, Frauendorf H, Hoffmann L, Raskop S, Rogatz D, Militz H (2023) Substituting phenol in phenol-formaldehyde resins for wood modification by phenolic cleavage products from vacuum low-temperature microwave-assisted pyrolysis of softwood kraft lignin. *Cellulose* 30:7277–7293. <https://doi.org/10.1007/s10570-023-05295-5>
- Klašnja B, Kopitović S (1992) Lignin-phenol-formaldehyde resins as adhesives in the production of plywood. *Holz Roh Werkst* 50(7–8):282–285. <https://doi.org/10.1007/BF02615352>
- Kupfernagel C, Spear MJ, Pitman AJ, Ormondroyd GA (2022) Wood modification with phenol urea formaldehyde (PUF) resin: the influence of wood species selection on the dimensional stability. *Eur J Wood Prod* 81:5–19. <https://doi.org/10.1007/s00107-022-01893-5>
- Meints N, Hansmann C, Müller M, Liebner F, Gindl-Altmutter W (2018) Highly effective impregnation and modification of spruce wood with epoxy-functional siloxane using supercritical carbon dioxide solvent. *Wood Sci Technol* 52(6):1607–1620. <https://doi.org/10.1007/s00226-018-1050-x>
- Nde DB, Muley PD, Sabliov CM, Nokes SE, Boldor D (2021) Microwave assisted pyrolysis of Kraft lignin in single mode high-Q resonant cavities: degradation kinetics, product chemical composition, and numerical modeling. *Energy Convers Manag* 230:113754. <https://doi.org/10.1016/j.enconman.2020.113754>
- Sarika PR, Nancarrow P, Khansaheb A, Ibrahim T (2020) Bio-based alternatives to phenol and formaldehyde for the production of resins. *Polymers* 12:2237. <https://doi.org/10.3390/polym12102237>
- Sauter UH, Scheiding W (2023) Survey on Forestry and sources of Wood. In: Niemz P, Teischinger A, Sandberg D (eds) *Springer Handbook of Wood Science and Technology*. Springer International Publishing, Cham, pp 3–24
- Schlotzhauer P, Nelis PA, Bollmus S, Gellerich A, Militz H, Seim W (2017) Effect of size and geometry on strength values and MOE of selected hardwood species. *Wood Mater Sci Eng* 12(3):149–157. <https://doi.org/10.1080/17480272.2015.1073175>

- Stamm AJ, Baechler RH (1960) Decay resistance and dimensional stability of five modified woods. *Prod J* 10(1):22–26
- Stolze H, Gurnik M, Koddenberg T, Kröger J, Köhler R, Viöl W, Militz H (2022) Non-destructive evaluation of the cutting surface of hardwood finger joints. *Sensors* 22(10):3855. <https://doi.org/10.3390/s22103855>
- United Nations and the Food and Agriculture Organization of the United Nations (2021) Forest products: annual market review 2020–2021. United Nations, Geneva
- van der Lugt P, Harsta A (2020) Tomorrow's timber: towards the next building revolution. MaterialDistrict, The Netherlands
- Wang H, Zhang Y, Li H, Hou H, Li C, Liu M (2023) Research on the impregnation process and mechanism of silica sol/phenolic resin modified poplar wood. *Forests* 14(11):2176. <https://doi.org/10.3390/f14112176>
- Xu J, Zhai Z, Yan X, Song Z, Shang S, Rao X (2020) Improvement of water resistance and mechanical properties of fast-growing poplar with bio-based isobornyl methacrylate monomer. *BioResources* 15(2):2356–2370. <https://doi.org/10.15376/biores.15.2.2356-2370>
- Yue K, Cheng X, Chen Z, Tang L, Liu W (2018) Investigation of decay resistance of alkaline copper, urea-formaldehyde, and phenol-formaldehyde resins. *WFS* 50(4):392–401. <https://doi.org/10.22382/wfs-2018-051>
- Zabel RA, Morrell JJ (2020) Wood microbiology: decay and its prevention, Second edition. Academic Press, Amsterdam, The Netherlands

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.