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ORIGINAL ARTICLE

Modification of plywood with phenol–formaldehyde resin: substitution of phenol by pyrolysis cleavage products of softwood kraft lignin

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Abstract

The modification by impregnation of veneers for the production of plywood with phenol–formaldehyde resins is a well-known method to improve the dimensional stability and fungal resistance. Because phenol is obtained from non-renewable resources, finding substitutes has been a topic of research. Due to similarities in chemical structure and availability, lignin cleavage products present a promising alternative. In this study, microwave-assisted pyrolysis cleavage products of softwood kraft lignin have been used to substitute 30% of phenol in phenol–formaldehyde resins. Scots pine veneers were impregnated with the resin, and five-layered plywoods were produced. The influence of the substitution on the bonding quality, the dimensional stability, and the leaching of resin from the specimens were studied. Mechanical properties such as the bending strength, the modulus of elasticity, as well as the dynamic impact bending strength of the plywood were analyzed. Both treatments led to plywood with good dimensional stability, and the resin was stable against leaching. The substitution of phenol with lignin cleavage products led to slightly reduced brittleness of the specimens compared to pure phenol–formaldehyde resin. This study presents a method to reduce the use of non-renewable resources, increase the use of currently underutilized lignin sources, and produce plywood with promising properties for exterior applications.

1 Introduction

Plywood and other veneer-based products have several advantages over unprocessed timber. They allow the usage of smaller diameter logs, and defects, like knots, are bonded with an offset or (for larger defects) removed after peeling. These composites have more uniform properties, and are produced in standardized panels, facilitating both further processing and transport. The mechanical properties are improved compared to solid wood. Additionally, plywood is appealing due to its enhanced dimensional stability brought on by its cross-wise structure. A larger area may be covered by using plywood instead of solid wood with similar amount of raw material, utilizing the trees more effectively (Berglund and Rowell 2005; Baldwin 2016).

Wood in general is increasingly used for outdoor applications, and veneer-based products are commonly used for exterior applications such as cladding. However, weathering (which causes both discoloration and mechanical damage) and biological decay pose a major challenge. To protect the wood, several methods such as coating, wood preservatives or wood modification are applied (Bicke 2019; Grinins et al. 2021a).

There are many different methods for wood modification. The most important, according to amount of sold timber worldwide, is by far thermally modified wood (Jones and Sandberg 2020). During thermal modification, wood is heated to temperatures of up to 260 °C, leading to firstly the softening of the wood, which reduces the stress, and secondly the controlled degradation of wood, leading to higher dimensional stability and decay resistance (Sandberg and Kutnar 2016). Other commercially available methods for wood modification include acetylated wood (during which the hydroxyl groups in the wood are reduced by reaction with acetic acid anhydride), furfurylated wood (furfuryl alcohol is impregnated and cured inside the wood cell wall), and impregnation of wood with other thermoset resins (Jones and Sandberg 2020). All the above-mentioned

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methods may also be applied to veneer-based panels (Westin et al. 2009; Aro et al. 2014; Barnes et al. 2018; Slabohm et al. 2022). Examples for impregnation resins include phenolic resins, urea–formaldehyde resin, melamine–formaldehyde resins, 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), etc. (Emmerich et al. 2020; Altgen et al. 2020; Jones and Sandberg 2020). The resins are cured inside of the wood cell wall and improve the dimensional stability and the fungal resistance of wood (Stamm and Seborg 1936; Stamm and Baechler 1960; Biziks et al. 2020). A resin with good weathering stability (thus, suitable for exterior applications) is phenol–formaldehyde (PF) resin (Fleckenstein 2018; Grinins et al. 2021b). Impregnation with PF resins has also been applied to plywood and other veneer-based wood composites (Stamm and Seborg 1939; Bicke 2019; Grinins et al. 2021a, b). The treatment increases the dimensional stability (Stamm and Seborg 1939; Bicke and Militz 2014) and reduces moisture permeability, as well as fungal decay (Stamm and Seborg 1939; Andersons et al. 2018; Grinins et al. 2021a; Slabohm et al. 2023).

While PF resins have several advantages, including the ease of synthesis, excellent mechanical properties, and weathering resistance (Kalami et al. 2017; Fleckenstein et al. 2018), they have the major disadvantage that phenol is obtained from non-renewable sources. Because of this, the search for a renewable phenol substituent has been a topic of scientific interest (Dier et al. 2017; Sarika et al. 2020). Due to similarities in the chemical structure and a high availability at low price, lignin could be an alternative (Ghorbani et al. 2018; Sarika et al. 2020). Technical lignins are obtained as a side-product during paper production (dominantly by the kraft process) and currently mostly burned to regain energy and pulping chemicals (Kai et al. 2016; Rinaldi et al. 2016). Finding higher-value applications for the lignins has been subject of numerous studies. Up to date, however, these attempts have mostly not been commercially feasible, reason being the recalcitrant, heterogeneous and non-reactive lignin properties (Vishtal and Kraslawski 2011; De Wild et al. 2014).

Due to the diameter of the macropores of the wood cell wall (2–4 nm in swollen state), the lignin macromolecules (e.g., kraft lignin usually has molecular weights of $1.5 – 5 \times 10^3$ g/mol (Kai et al. 2016)) are too large to penetrate the cell walls, and have to be cleaved prior to impregnation (Furuno et al. 2004; Hill 2006; Biziks et al. 2019). Phenol substitution by lignin cleavage products and subsequently impregnation of solid wood specimens indicated that depending on pretreatment and lignin source, 30–45% of the phenol could be substituted, while maintaining the favorable resin properties (Fleckenstein 2018; Fleckenstein et al. 2018; Karthäuser et al. 2023a).

First results on the usage of PF resins in which part of the phenol was substituted by lignin cleavage products for laminated veneer lumber (LVL) were presented by Fleckenstein et al. (2018). Herein, 40% of the PF resin were substituted by different technical lignins or lignin cleavage products (which were added after the synthesis, thus, not reacting during the synthesis with the other resin constituents). Compared to LVL produced with pure PF resin, the substitution led to reduced weight percent gain (WPG), reduced leaching, higher water uptake, and roughly similar modulus of rupture (MOR) and modulus of elasticity (MOE). Overall, the results indicate that high-quality LVL may be produced with the modified resins (Fleckenstein et al. 2018). While the results of the study are promising, several questions remain unanswered, amongst them the chemical composition of the lignin cleavage products, the potential influence of adding the cleavage products already during the synthesis step, as well as the influence of the resin modification on plywood.

In this study, 30% of phenol in PF resin were substituted by cleavage products of softwood kraft lignin, obtained with microwave-assisted pyrolysis. Scots pine veneers (preferably sapwood) were impregnated and five-layered plywood was produced. The uptake of resin, leaching of resin after curing, and the anti-swelling efficiency (ASE) were determined. The bonding quality of the plywood was tested, and the mechanical properties were evaluated by three-point bending test, as well as dynamic impact bending test.

2 Experimental section

2.1 Lignin cleavage products and synthesis of impregnation resins

The lignin cleavage products were obtained by vacuum low-temperature microwave-assisted pyrolysis as described in Karthäuser et al. (2023a). The main constituents of the lignin cleavage products were guaiacol ($8.1 \pm 0.9\%$), 4-methylguaiacol ($13.8 \pm 0.8\%$), 4-ethylguaiacol ($6.8 \pm 0.5\%$), and 4-prop-1-enylguaiacol ($3.2 \pm 0.0\%$). The impregnation resins were prepared as described in Karthäuser et al. (2023a). In short: phenol and sodium hydroxide were added to a flask under nitrogen atmosphere and heated to about 55 °C to melt the phenol. Formaldehyde was carefully added, and the temperature was increased to 65 °C. The mixture was kept at 65 °C and stirred for four hours. The molar ratio of the pure PF resin (100 PF) was phenol: formaldehyde: NaOH = 1:1.5:0.1. In the resin containing lignin cleavage products (70/30 lF; lF stands for low formaldehyde), 30% of the phenol by mass were substituted, and the lignin cleavage products were added in the flask together with the phenol and the NaOH. The molar ratio was phenol + lignin cleavage products: formaldehyde: NaOH = 1:1.32:0.1. The solid content of the resin was determined by weighing in about 3 g of the resin, adding a small amount of butanol to obtain a flat surface, and curing at 135 °C for two hours. Before addition of the butanol and after curing, the weight of the resin was measured to determine the remaining solids after curing. The solid content of the resins was 53.7% for 100 PF and 54.3% for 70/30 lF. Before impregnation of the wood specimens, the resins were diluted with demineralized water to obtain impregnation resins with a solid content of 6.25%, 12.5%, and 18.75%. Further analysis of resins produced with the same method (such as curing behavior analysed by dynamic scanning calorimetry and free formaldehyde content at different stages of the reaction) may be found in the literature (Karthäuser et al. 2023a).

2.2 Plywood production

Scots pine (*Pinus sylvestris* from Bavaria, Germany, mainly sapwood) veneers with a thickness of about 3 mm were used to manufacture five-layered plywood. Half of the veneers were impregnated with the resin, while the other half remained as untreated references. The oven-dried (T = 103 °C, t = 24 h) veneers were submerged into the respective resin solution and subjected to a vacuum (80 – 100 mbar, 20 min), followed by a pressure (11 bar, 30 min) treatment. Before and after impregnation, the veneers were weighed and the solution uptake was calculated to confirm that the vacuum-pressure treatment led to a thorough impregnation. The specimens were carefully dried, first at room temperature, later-on in an oven. The final drying was performed at 80 °C, a temperature selected to ensure that the veneers were dry enough to avoid cracks during hot-pressing, but not so high that the curing of the impregnation resin would be complete before the hot-pressing of the plywood.

Five-layered plywood was produced using a commercial one-component phenol–formaldehyde adhesive. To determine the solid content of the adhesive, three specimens of the adhesive were weighed in and cured at 140 °C for 10 h. The dry weight after curing was determined, and the percentile of solids in the adhesive was calculated. For better workability, the adhesive was mixed with about 10% water for plywood production, and the final solid content was determined. The adhesive was manually brushed on four veneers of the five-layered plywood creating a uniform layer, leading to an adhesive consumption of 166.5 ± 33.2 g/m^2. The weight of the adhesive was measured, to make sure that a roughly similar amount of adhesive was used for the different veneers. The top layers had no lathe checks on the outside; the inner layers were alternately stacked. A LAP-40 hot-press (Gottfried Joos GmbH & Co.KG, Pfalzgrafenweiler, Germany) was used for hot-pressing the plywood. The pressure plates were heated to a temperature of 140 °C. The veneers were pressed to a thickness of 13–14 mm with a maximum force of 1.5 N/mm^2 for 15 min; the press was programmed to automatically adjust the used force until the final plywood thickness was reached. The hot plywood was cooled down under a pneumatic press with 4 bar pressure, to make sure that no deformation would take place while cooling. After cooling down, the plywood was transferred into an oven and heated up to 140 °C for 10 h, to ensure that the impregnation resin was thoroughly cured. This curing temperature was selected based on properties of solid wood impregnated with a similar resin (Karthäuser et al. 2023a, b).

The WPG of the plywood was calculated with Eq. 1 with the oven-dry mass of the treated plywood m_{plywood}, the mass of the solid content of the adhesive m_{adhesive}, and the average mass of one dry untreated veneer $m_{\text{untreated,dry}}$.

$$\mathrm{WPG}[\%] = \frac{\mathrm{m}_{\text{plywood}} - \mathrm{m}_{\text{adhesive}} - 5 \cdot \mathrm{m}_{\text{untreated,dry}}}{5 \cdot \mathrm{m}_{\text{untreated,dry}}} \tag{1}$$

2.3 Plywood analysis

2.3.1 Water-related properties

Ten 25 × 25 mm^2 specimens were cut from the plywood and their oven-dried (103 °C) dimensions and weights were determined. The leaching from the specimens was determined according to EN 84 (1997), with the difference that the dry weight was determined after oven drying at 103 °C. The specimens were submerged in demineralized water and vacuum (80–100 mbar, 30 min) was applied. The water was exchanged with fresh water after two hours. Afterwards, the water was again exchanged 9 times in the following 14 days. The dry weight of the specimens was determined, and the mass loss after leaching was calculated. After the leaching test, the dimensions of the dry specimens were measured to check if a set-recovery occurred.

The ASE is a value used to evaluate the dimensional stability of treated specimens. It was determined based on the methodology described in Hill (2006). The specimens measured during ASE tests were the same as those of the EN 84 tests before. The dry weight and dimensions were measured. The specimens were impregnated with water under vacuum (80–100 mbar, 30 min) and left underwater for 24 h. Then, the wet weight and dimensions were measured. This procedure was repeated five times. The swell rate of the specimens SW was calculated as described in Eq. (2) with the dry volume of the specimen V_d and the wet volume V_w. The ASE was calculated Eq. (3) using the swell rate of untreated reference wood specimens SW_{ref} and the swell rate of the treated wood specimens SW_T. It is important to mention that all values were calculated with the swell rate of the reference material during the first cycle. Reason for this is that during the ASE tests the dimensions of the reference material permanently changed (for example due to set-recovery), while the treated plywood remained more stable.

Thus, it was considered to be more accurate to determine the ASE in comparison to the unchanged reference.

$$\mathrm{SW}[\%] = \frac{V_\mathrm{W} - V_\mathrm{D}}{V_\mathrm{D}} \cdot 100 \quad (2)$$

$$\mathrm{ASE}[\%] = \frac{\mathrm{SW}_\mathrm{ref} - \mathrm{SW}_\mathrm{T}}{\mathrm{SW}_\mathrm{ref}} \cdot 100 \quad (3)$$

2.3.2 Bonding quality

The bonding quality was analyzed according to EN 314-1 (2004). The tests were carried out on the specimens treated with resins with a solid content of 12.5%. Due to low availability of the lignin cleavage products for the bonding quality and the mechanical properties tests, only one resin solid content, and not three as for the tests described above, was selected. In short, plywood specimens were sawn to dimensions of 150 × 25 mm^2 so that the long side of the top veneer was in longitudinal direction. The specimens were grooved to the middle veneer twice, on opposite sites, with cuts 25 ± 1 mm apart. The exact area between the grooves was determined. The specimens were submerged in boiling water for 4 h, heated to 60 °C in a furnace for 16 h, submerged in boiling water for 4 h, and finally stored in cold water for 22 h before measurement (according to the standard, two tests, one with storing in water for 24 h and one with the boiling procedure herein followed by storing in water for at least one hour should be done. Due to the long storage time in water after boiling done herein, the authors decided that the first test could be neglected, because the test described herein would subject the specimens to significantly harsher conditions and include the first test due to the long storage in water). A minimum of 11 specimens were prepared for the reference, PF 100 treated and 70/30 lF treated specimens, respectively.

The measurements were carried out on a table-top testing machine Z010 (ZwickRoell AG, Ulm, Germany). A preload of 5 N was applied. Then, the specimens were pulled apart in longitudinal direction with a speed of 5.4 mm/min. The dry specimens were scanned to obtain pictures of the cleaved area to determine the wood failure percentage (EN 314–1 2004).

2.3.3 Mechanical properties

Tests carried out to analyze the mechanical properties were a three-point bending strength test, as well as a dynamic impact bending test. The tests were carried out on the specimens treated with resins with a solid content of 12.5%. The bending strength (also referred to as MOR) and the MOE were determined with a method based on EN 310 (1993) on a table-top testing machine Z010 (ZwickRoell AG, Ulm, Germany). Ten specimens with dimensions of 310 × 50 mm^2 were cut from the plywood plates so that the long side of the top veneer was in longitudinal direction. The specimens were stored at 20 °C and 65% humidity until constant weight. The precise thickness and depth of the specimens were measured with a caliper (± 0.01 mm). The specimens were put onto two supports with a span of 280 mm and a radius of 15 mm. The pressure stamp with a radius of 15 mm was lowered with a preload of 0.1 N/mm^2. During the test, the stamp was lowered with a velocity of 11 mm/min. This velocity was determined for the reference specimens so that the specimen broke after 60 s and applied similarly for the treated specimens. For the reference and for each treatment, ten specimens were measured.

The dynamic impact bending test was carried out with a method based on EN 52189 (1981). At least 33 specimens per treatment method with dimensions of 310 × 13 mm^2 were cut from the plywood plates so that the long side of the top veneer was in longitudinal direction. The specimens were stored at 20 °C and 65% humidity until constant weight. The thickness and depth were determined with a caliper (± 0.01 mm). The measurements were carried out on a Resil Impactor Junior (Instron GmbH, Darmstadt, Germany). The supports with a diameter of 10 mm were set to a span of 135 mm (measured between them without adding the diameter). A dynamic impulse with an impact of 15 J was applied to the specimens perpendicular to the grain. The impact bending strength (IBS) was calculated as described elsewhere (Emmerich et al. 2021).

3 Results and discussion

3.1 Plywood production

3.1.1 Veneer and plywood production

The solution uptake of the veneers with the impregnation resin, the final WPG, the thickness, and the density of the plywood specimens are listed in Table 1. The solution uptake of the veneers is lower than that of pine sapwood with similar resins (in the mentioned study, the SU was 140–195%) (Karthäuser et al. 2023a). Reason for this might be a certain heartwood content in the veneers, which in case of Scots pine is difficult to determine. While a low solution uptake is causing also a low WPG, the uptake between the different resins is roughly similar at similar solid contents, indicating that the phenol substitution did not have a negative effect on the WPG, which is in accordance with published data (Karthäuser et al. 2023a). The thicknesses of the cooled plywoods are in similar ranges, indicating that the applied

Table 1 Solution uptake of the veneers, WPG of the plywood, and thickness of the plywood measured for the specimens treated with different treatment methods

Resin	Solid content / %	Veneer Solution Uptake / %	Plywood WPG / %	Thickness Plywood / mm	Density Plywood / g/cm^3
Reference	–	–	–	13.7 ± 0.2	0.64 ± 0.01
100 PF	6.25	113.0 ± 10.3	6.7 ± 2.1	14.2 ± 0.2	0.67 ± 0.03
100 PF	12.50	114.2 ± 15.8	13.2 ± 3.4	13.8 ± 0.5	0.70 ± 0.01
100 PF	18.75	115.8 ± 7.8	17.9 ± 2.7	13.6 ± 0.4	0.78 ± 0.02
70/30 lF	6.25	114.2 ± 15.7	6.1 ± 2.5	14.1 ± 0.2	0.67 ± 0.02
70/30 lF	12.50	125.8 ± 12.3	14.4 ± 1.8	13.8 ± 0.3	0.68 ± 0.02
70/30 lF	18.75	119.2 ± 13.1	18.9 ± 3.1	13.5 ± 0.0	0.73 ± 0.01

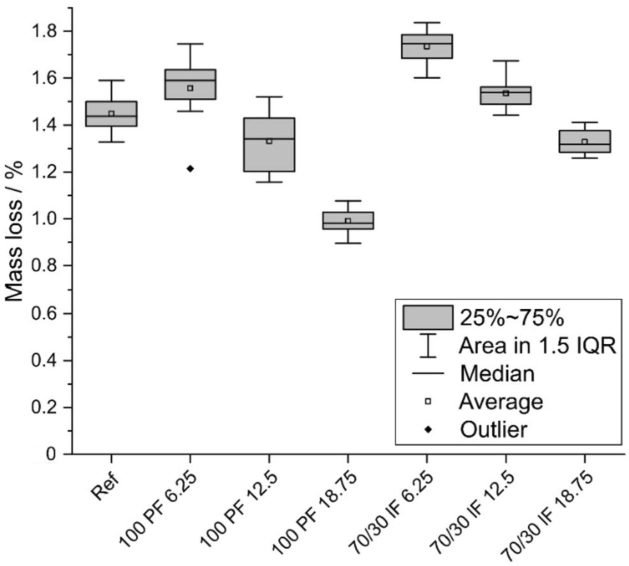


Fig. 1 Mass loss after leaching according to EN 84 of reference specimens (Ref), as well as specimens treated with 100 PF resin or 70/30 lF resin with different solid contents (6.25%, 12.50%, and 18.75%)

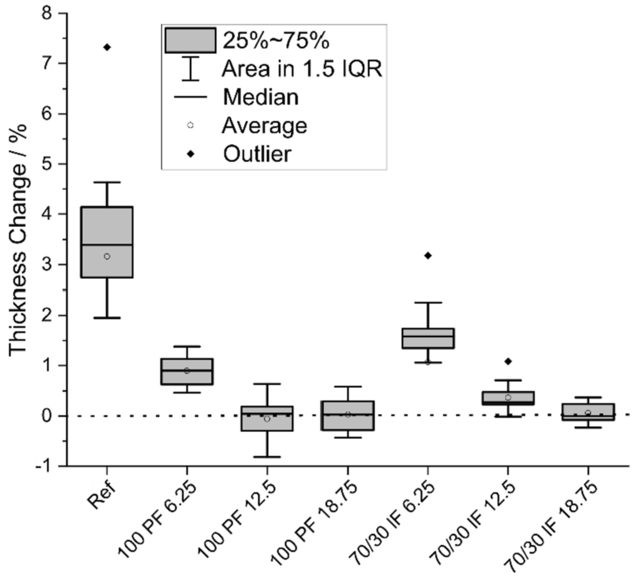


Fig. 2 Thickness change after leaching according to EN-84 of reference specimens (Ref), as well as specimens treated with 100 PF resin or 70/30 lF resin with different solid contents (6.25%, 12.50%, and 18.75%)

method was suitable, and that no direct set-recovery after hot-pressing occurred.

3.1.2 Water-related properties

The mass losses after leaching of the specimens according to EN 84 are depicted in Fig. 1. All of the treated specimens have a mass loss comparable to the reference specimens. There is a tendency for mass loss to decrease with increasing resin solid content.

The reduced leaching with increasing resin uptake indicates that the resin is well-fixated in the specimens and does not leach out to a significant degree. Reason for the decreasing (percent) mass loss might be the higher weight of the treated specimens. The leaching is lower than that of solid wood treated with the same method (Karthäuser et al. 2023a), indicating that the densification (in this study about 10%) or the different layers of the plywood lead to an improved fixation of the cured resin inside of the wood. Additionally, the reduced leaching might be due to the adhesive layer, which may create a physical barrier against leaching (Bridaux et al. 2001). While the leaching is slightly higher for the specimens treated with 70/30 lF compared to those treated with 100 PF, the low mass loss nevertheless indicates that the treatment is suitable to achieve a stable polymeric network in the wood specimens.

The percentage change in thickness in radial direction of the specimens after leaching by EN-84 is depicted in Fig. 2. The untreated reference specimens increased in thickness by roughly 3–4%. This thickness increase was lower for the treated specimens, and at a resin solid content of 12.5%, the thickness increase was close to zero for both the 100 PF and the 70/30 lF resin treated specimens. It must be mentioned that two outliers with significant decreased thickness are not presented in the graph, as they most likely originate from a measuring error. The graph with the outliers may be found in Fig. S1.

Possible densification during pressing of the plywood can be partly reversed when the specimens are swollen by water (set-recovery). The specimens treated with resins are significantly more stable. Reason for this is that the network of the resins stabilizes the specimens, hindering the thickness increase. Both the 100 PF and the 70/30 lF are suitable to stabilize the plywood when impregnated with a solid content of 12.5% or higher.

The ASE of the plywood specimens are depicted in Fig. 3a and 3b. In Fig. 3a, the ASE in each ASE cycle of the specimens treated with 100 PF are depicted; those for the 70/30 lF can be found in Fig. 3b. The untreated reference specimens significantly changed their appearance and dimensions during the ASE tests due to delamination or the formation of cracks. The treated specimens were more stable and had less deformation or damage after ASE tests. Because of this, all the ASE values were calculated with reference to the swell rate of the reference specimens during the first ASE cycle to avoid errors due to comparison to damaged specimens. The changing ASE values of the reference specimens during the ASE cycles, stemming from the permanent deformation of specimens, can be observed in Fig. 3a.

The ASE of the treated specimens does not significantly change between the first and the last cycle. The only exception is the 100 PF specimens with high resin load, where a significantly higher ASE value was detected in the first cycle. After this high value, the ASE remains constant. Reason for this could be, that during the first swelling cracks are formed, leading to a less rigid structure in the following ASE tests.

As expected, higher resin loads generally resulted in higher ASE. However, at higher resin loads, the increase of ASE is not as pronounced as for lower resin loads. Most likely the cell wall load is reaching a high level, and not much more additional resin can be added.

The ASE of the specimens treated with 100 PF are slightly higher than of those treated with 70/30 lF. The reason for this is likely that due to a larger number of reactive sites, the 100 PF forms a more interconnected molecular network, leading to less leaching and less remaining space

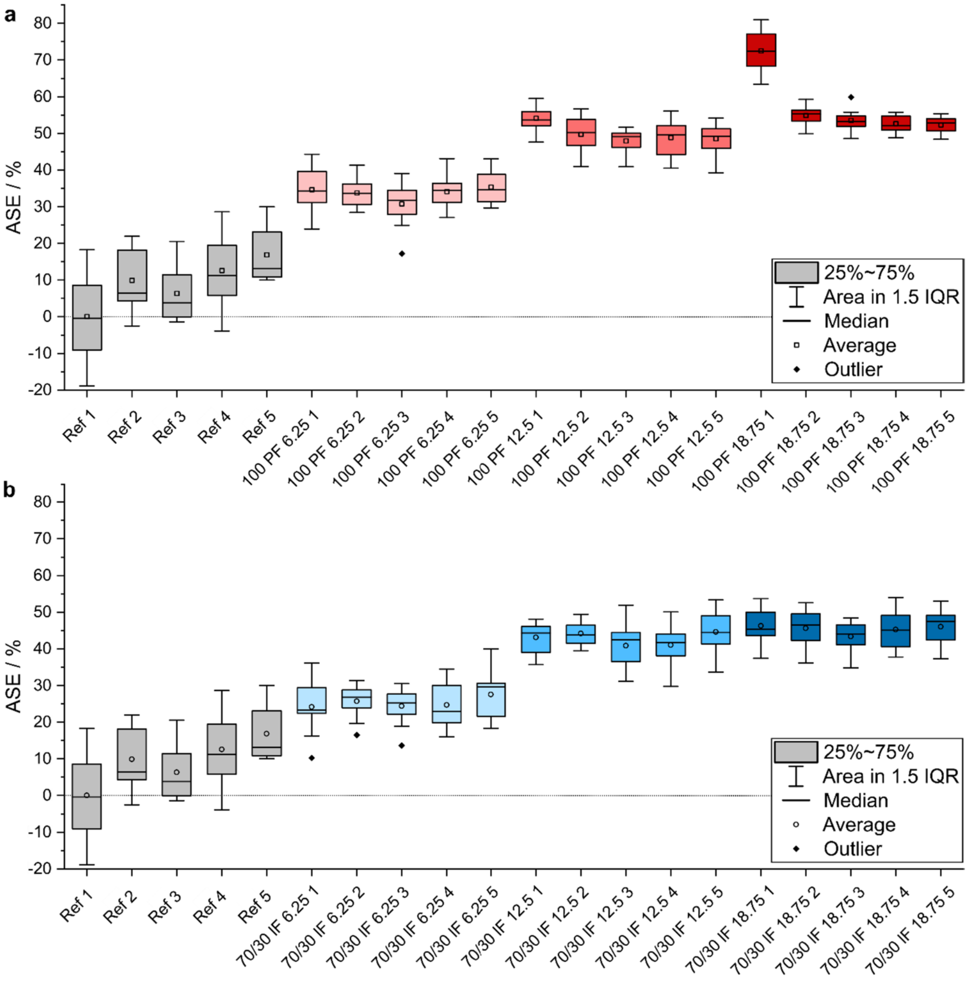


Fig. 3 ASE of reference material (Ref), as well as specimens treated with 100 PF resin (**a**) or 70/30 lF resin (**b**) with different solid contents and in different ASE cycles (1–5)

for water in the cell wall. These observations are underlined by above reported mass losses of treated specimens.

The only slightly decreased ASE of the 70/30 lF specimens, as well as the ASE values, which are in relation to the WPG and in comparison with the literature in a good range, indicate that the substitution of phenol bears composite material of high quality (in the literature source, the plywood was produced with Douglas fir veneer, which the authors consider to be comparable to the pine wood used herein) (Stamm and Seborg 1939).

3.1.3 Bonding quality

To determine if the wood modification influences the bonding interface between the plies and the adhesive, the bonding quality (shear strength and wood failure percentage) was measured. The shear force as a function of deformation in the middle layer of the plywood is depicted in Fig S2. The results indicate that the untreated reference material can be deformed about 1.9 × as much as the 100 PF samples before breaking. The 100 PF breaks at the lowest deformation, with (on average) 1.2 × higher values observed for the 70/30 lF.

This indicates that the modified plywood is more brittle than the untreated one. This effect is known from earlier work and is attributed to the rigid polymeric network of thermoset resins (Bicke 2019). The 100 PF treated wood is slightly more brittle than the 70/30 lF treated. Reason for this is the higher number of reactive sites in the 100 PF, leading to a more interconnected and stiffer polymeric network.

The shear strength measured for the specimens is depicted in Fig. 4. The stiffness does not seem to have a high impact on the shear strength. A slight decrease can be observed for the treated specimens, but the large variation between different specimens makes it impossible to make a definitive statement.

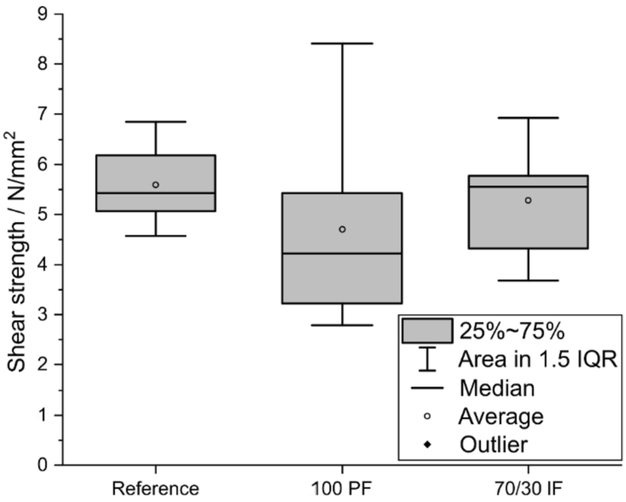


Fig. 4 Shear strength of reference plywood specimens, as well as plywood specimens treated with 100 PF or 70/30 lF resins

As an additional measure for the bonding quality, the failure of the specimens was visually inspected as described in EN 314. The resulting average wood failure is listed in Table 2; the pictures of each individual specimen and their evaluation can be found in the supplementary information (Table S1). For the reference specimens, only wood failure of 100% was observed. For the 100 PF specimens, one of the specimens had slight adhesive failure. In the 70/30 lF specimens, several cases of slight adhesive failure were observed.

All shear strengths measured are significantly higher than values found in the literature for pine plywood bound with phenol–formaldehyde adhesives (Mirski et al. 2011; Demirkir et al. 2013; Setter et al. 2021). An explanation for this could be that the adhesive performed very well, leading to almost exclusively wood failure. Additionally, the veneers used were relatively thick and a long pressing time was applied (long pressing time can increase the shear strength, according to Mirski et al. 2011). Nevertheless, considering the results obtained in the literature, the shear strength is higher than expected for plywood produced with the method described herein.

All treatments led to a good bonding quality with mainly wood failure. The treatment with 70/30 lF led to a slightly worse performance of the adhesive. Due to the complex chemical composition of the lignin cleavage products, the precise reason for this is difficult to outline, a screening with several components would have to be carried out. However, due to the good quality of the bonds, which fulfills the requirement for exterior grade applications according to EN 314, this was not further inspected.

3.2 Physical properties

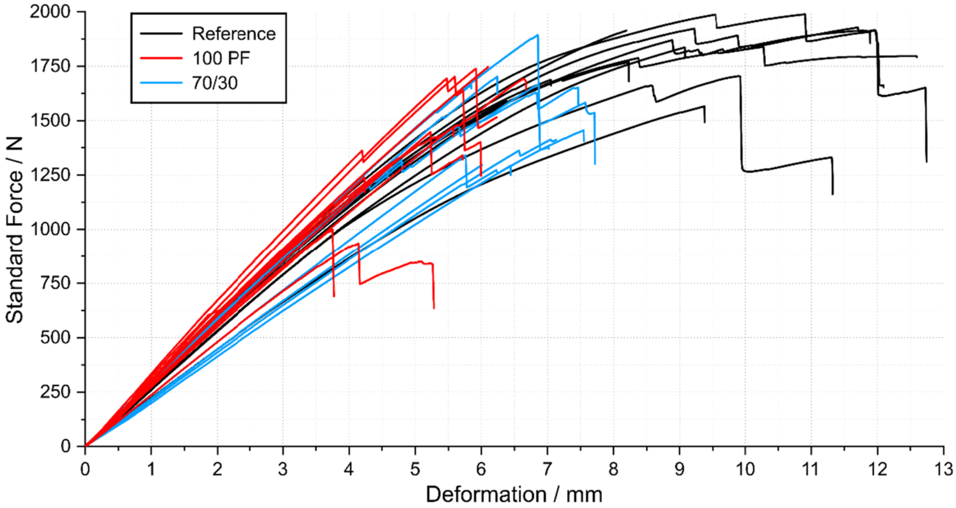
3.2.1 Three-point bending strength

Three-point bending strength tests were carried out to determine the physical properties of the untreated and treated wood specimens. The force–deformation diagram of the specimens is depicted in Fig. 5. The reference specimens can be deformed to a higher degree than the treated specimens. The deformation at which the maximum force was applied is 1.3 × higher for 70/30 lF treated samples than for 100 PF treated samples, and 1.8 × higher for untreated samples than for 100 PF treated samples. In addition, the untreated specimens take up a slightly higher force before breaking. A less pronounced difference can

Table 2 Wood failure of reference plywood, as well as plywood treated with 100 PF and 70/30 lF resin

Treatment	Reference	100 PF	70/30 lF
Wood failure / %	100	99.5	95.8

Fig. 5 Force–deformation diagram during three-point bending strength tests of the reference specimens (black), the specimens treated with 100 PF resin (red), and the specimens treated with 70/30 lF resin (blue)



be observed between the 100 PF and 70/30 lF treated specimens: the specimens with substituted phenol break at slightly higher applied force and higher deformation.

As described above, treating wood with PF resins increases the brittleness. As a result, the maximum load-bearing capacity and deformation before fracture are reduced for treated specimens. The slight difference between the 100 PF and the 70/30 lF treated specimens is most likely due to differences in the polymeric network, as mentioned above. The described increase in brittleness of the treated specimens is confirmed by the measured bending strength (Fig. 6a). In addition, the modulus of elasticity increased after treatment with the 100 PF and 70/30 resins (Fig. 6b).

For LVL with two-ply layers and low densification during pressing (in the method described herein, the densification is low as well), a slight decrease of the bending strength after treatment with PF resins was reported, which is in line with the results above (Bicke 2019). However, there are several publications reporting an increasing bending strength (Loh et al. 2010; Bicke et al. 2012; Shen et al. 2013). Reason for this may be additional factors such as the densification, which has a high impact on the bending strength (Bicke 2019). The observation that the MOE increases upon treatment with impregnation resins is confirmed in the literature (Loh et al. 2010; Bicke et al. 2012; Fleckenstein et al. 2018; Bicke 2019).

Both the bending strength and the MOE have a high deviation. Thus, trends observed for the samples should not be overinterpreted. Additional repetitions of the experiments could confirm the trends.

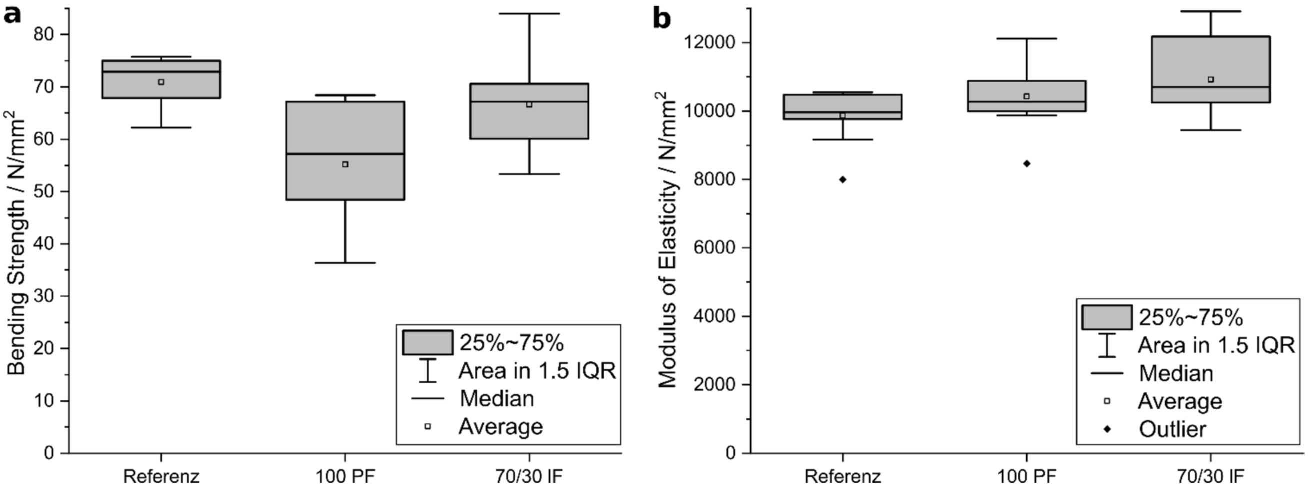


Fig. 6 Bending strength (**a**) and modulus of elasticity (**b**) of reference plywood, as well as plywood treated with 100 PF and 70/30 lF resin (color figure online)

3.2.2 Dynamic Impact Bending Strength

The IBS of the wood specimens is depicted in Fig. 7. It decreased for the treated specimens. It is slightly lower for the specimens treated with 100 PF than for those treated with 70/30 lF.

The results obtained for the IBS are in line with the results above. The treatment increases the stiffness and the brittleness, leading to a reduced IBS, which is slightly less reduced for the 70/30 treated specimens, because of the less connected polymer network.

4 Conclusion

The aim of the research was to determine if the substitution of 30% of the phenol in a PF resin used for the modification of veneers for plywood production by pyrolysis cleavage products of softwood kraft lignin is suitable to produce plywood of good quality. The results indicate that

1. The resin is bound well into the plywood, and leaching tests resulted only in minor mass losses.
2. Both pure PF resin as well as the substituted resin are suitable to improve the dimensional stability of the specimen. Both resins are resistant against leaching and reduce the thickness swelling (set-recovery) of the plywood significantly.
3. The bonding performance is only slightly influenced by the modification of the veneers, and tests of the bond quality confirm a tough bonding for all specimens, which is suitable for exterior grade applications according to EN 314.
4. As expected, the modified plywood is stiffer and more brittle than the unmodified reference. The bio-oil substitution slightly reduces the brittleness. Nevertheless, the resulting materials still have considerable bending- and dynamic impact bending strength.

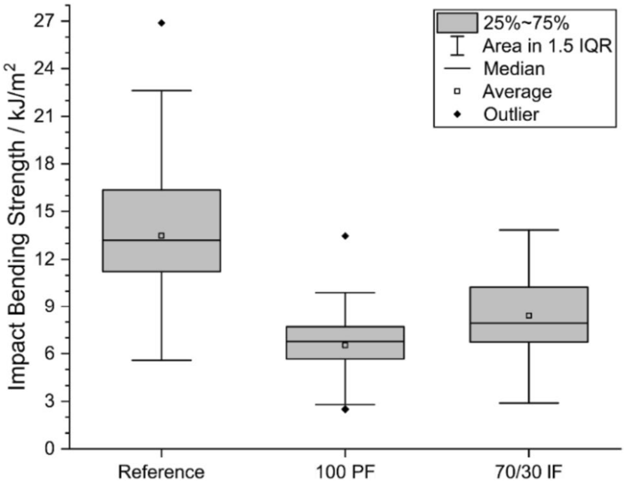


Fig. 7 Impact bending strength of the reference plywood as well as plywood modified with 100 PF and 70/30 lF resin

We conclude that the substitution of phenol with lignin cleavage products did not have a negative effect on the plywood performance compared to a treatment with pure PF resin. Thus, it is a promising method to reduce usage of non-renewable resources, and potentially improve the environmental impact of modified plywood. In future work, the fungal resistance of the modified plywood will be studied, to further evaluate the materials for potential exterior grade applications, and the formaldehyde emission of the material will be analyzed.

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

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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