



Substituting phenol in phenol–formaldehyde resins for wood modification by phenolic cleavage products from vacuum low-temperature microwave-assisted pyrolysis of softwood kraft lignin

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Abstract Wood modification by impregnation and curing inside of the cell wall using phenol–formaldehyde resins (PF resins) is a well-known and commercialized method to improve, amongst others, the dimensional stability and the durability of wood. However, phenol is mainly obtained from non-renewable resources, and the substitution of phenol by renewable resources has been a topic of research interest for years. Due to the high availability of technical lignins, lignin-derived cleavage products are promising candidates. In this study, organic cleavage products obtained from vacuum low-temperature microwave-assisted pyrolysis of softwood kraft lignin were used to substitute up to 45% of phenol in PF

resins. The curing behavior and the free formaldehyde content of the resins was studied. Pine sapwood was treated with these resins by a vacuum pressure treatment, and the weight percent gain, leaching, and dimensional stability of the species were examined. Selected samples were analyzed with bright-field microscopy. The results indicate that up to 30% substitution of phenol by lignin-based organic products does not lead to significantly inferior quality of wood modification. Additionally, the amount of formaldehyde added to the resin can be reduced. The method described in this study could be a way to improve the environmental footprint of wood modification by PF resins.

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Introduction

The demand for timber as a renewable material has increased and is expected to increase further. Reason for this are not only the good properties, such as a good strength to weight ratio, and the pleasant appearance, but also that it can substitute non-renewable materials, and in addition function as a carbon repository. However, being a biological material, wood has the disadvantage that it can be affected by a number of biotic and abiotic factors, including

degradation by fungi or insects. Hence, wood often is protected by biocidal wood preservatives, especially for applications in the outdoor sector (Hill 2006). Being by definition harmful to organisms, these preservatives have been topic of a number of governmental regulations, such as the regulation (EC) No 1907/2006 (REACH) or the Biocidal Products Regulation (EU) No 528/2012 (Council of the European Union 2006, 2012). Therefore, the market for non-biocidal wood protection, often referred to as wood modification, has significantly increased in recent years, and is expected to increase further (Jones and Sandberg 2020).

Currently, the commercially most applied wood modification methods are acetylation, furfurylation, and thermal modification. During acetylation, the hydroxyl groups of wood are replaced with acetyl groups, reducing the water uptake of the wood samples. Furfurylation is the impregnation of furfuryl alcohol followed by curing inside of the wood material, increasing amongst other properties the dimensional stability and resistance against fungal decay. During thermal modification, the wood is degraded by heat, leading to complex changes in the chemical structure. Other methods, which are commercialized on a smaller scale are impregnation of wood with thermosetting resins and charring of wood. (Zelinka et al. 2022).

During wood impregnation with thermosetting resins, monomers of a resin are brought into the cell walls of the wood in swollen state, and cured therein (Hill 2006; Jones and Sandberg 2020). This increases not only the dimensional stability, but also the resistance against biological and physical decay (Stamm and Baechler 1960). There are different commercial resins used for wood impregnation, for example phenol-, urea-, or melamine-based resins. Wood treated with PF-resin is sold for example under the trademark Compreg™, however, this product is not produced with wood impregnation alone; compressive forces are applied during the curing of the impregnated resin. (Jones and Sandberg 2020).

A disadvantage of PF resins is that phenol is obtained mainly from non-renewable petroleum-based chemicals, and that monomeric phenol is highly toxic to humans, even at low quantities (Klašnja and Kopitović 1992; Sarika et al. 2020). Searching for alternatives, many researchers have shifted their attention to biomass as alternative source for organic

chemicals as a substitute for phenol, with a promising candidate being lignin (Sarika et al. 2020).

Lignin is the most abundant aromatic polymer in nature and one of the main components of wood (Qu et al. 2015; Wang et al. 2020). In paper production, it is cleaved from the wood during the pulping process. As such, more than 50 million tons of lignin are generated each year as a byproduct of the pulping industry; this amount is expected to increase further (Luo and Abu-Omar 2017). The process used during pulp production in most cases is the so-called kraft process. During the kraft process, the lignocellulosic material is treated with high temperature and pressure under basic conditions. The lignin is dissolved in the pulping liquor. Due to the harsh conditions, the lignin is chemically changed during the pulping process. Easily cleavable ether bonds are cleaved, while new bonds emerge through recondensation (Rinaldi et al. 2016; Crestini et al. 2017). Hence, the structure of the treated lignin, the so-called technical lignin, is vastly different than that of natural lignin. It is unreactive, heterogeneous and complex. Due to this, technical lignins are usually not converted into higher-value chemicals, but instead burned to regain energy and inorganic pulping chemicals (De Wild et al. 2014; Rinaldi et al. 2016).

Due to its high availability and aromatic structure, attempts to find other uses for lignin have been a topic of interest in research. A well-described potential application of lignin is to substitute phenol in PF resin used as an adhesive for wood, for example in wood-containing boards (Sarika et al. 2020; Huang et al. 2022). While the extensive research underlines the potential of lignin as phenol-substituent in PF-resins used as adhesives, the substitution cannot be identically applied for impregnation modification of wood. For effective wood modification, the resin has to be located inside of the cell wall. To access the cell wall, the resin has to pass micropores, which in swollen state have a maximum diameter of 2–4 nm, allowing only molecules with low molecular weight to enter (Furuno et al. 2004; Hill 2006; Biziks et al. 2019). Lignin, being a polymer, has large molecules, which makes it unsuitable for these methods. To overcome this problem, lignin can be cleaved, by which also the reactivity of the components can be improved, and the steric hinderance decreased (Hu et al. 2011). A promising method for the cleavage of lignin is pyrolysis, which is thermal treatment

under oxygen-free atmosphere (De Wild et al. 2014). Pyrolysis methods are divided into two categories, first conventional heating pyrolysis and second microwave-assisted pyrolysis, during which the heat is generated by microwave radiation. The latter brings several advantages, such as a better energy efficiency, a more homogeneous heating in the inner and outer material layers, and higher yields of short-chained organic cleavage products (Farang et al. 2016).

In literature, several publications describe the cleavage of lignin by microwave-assisted pyrolysis at temperatures of 500 °C or higher (Farang et al. 2014, 2016; Morgan et al. 2018; Yerrayya et al. 2018; Fan et al. 2019; Bu et al. 2019; Arapova et al. 2020). However, cleavage at lower temperatures has also been discussed (Bu et al. 2014; Morgan et al. 2018; Bartoli et al. 2020; Nde et al. 2021; Karthäuser et al. 2022).

The resulting organic cleavage fraction often primarily contains guaiacolic or phenolic compounds (Bu et al. 2014, 2019; Farang et al. 2016; Nde et al. 2021; Karthäuser et al. 2022). Due to the similar structures of the lignin cleavage products and phenol, a research goal is to substitute phenol with it. The partial or even complete substitution of phenol in PF resin by different lignin cleavage products has been described before. However, in literature these resins are mainly applied for adhesive purposes, and not for wood modification. Experiments on wood modifications with partial or complete substitution of the phenol were described by Fleckenstein et al. (Fleckenstein 2018; Fleckenstein et al. 2018). Herein, 40% and 100% of the phenol was substituted by base-catalyst, pyrolytic, and microwave cleaved lignin, additionally pretreated in different ways. The resins were diluted to a solid content of 25%, and pine sapwood was impregnated using a vacuum-pressure-process. Afterwards, the resin was cured at 140 °C. The results indicate that 40% substitution of phenol by base-catalyzed and pyrolytic lignin cleavage products do not significantly influence the ASE of the wood samples compared to pure phenol formaldehyde resin (PF resin). The microwave cleaved lignin performed worse, compared to the other substituents. 100% substitution lead to less quality of the wood modification. While this research lays a foundation for wood modification with lignin cleavage products as substituent of phenol in PF resins, there are several open questions remaining. In the publication, the lignin cleavage products were

commercially bought and not further specified, leaving unclear their production process, chemical nature, and properties. In addition, only 40% or complete substitution were tested (Fleckenstein 2018; Fleckenstein et al. 2018).

In this publication, 15%, 30%, and 45% of phenol in a PF resin for wood modification by impregnation were substituted by softwood kraft lignin (SKL) cleavage products. The SKL was cleaved using vacuum low-temperature microwave-assisted pyrolysis. The known pyrolysis procedure and chemical components of the cleavage products can help evaluating lignin cleavage methods and products for phenol substitution in future research or applications. The properties of the resins, such as free formaldehyde content, curing behavior, and solid content, were compared. Pine sapwood was modified with the obtained resins, and the weight percent gain (WPG), the leaching of the cured resin, and the anti-swelling efficiency (ASE) were determined.

Experimental section

Bio-oil production and characterization

Herein, bio-oil refers to the organic pyrolysis cleavage products, which are obtained and separated from the aqueous products as described below. The setup for the vacuum low-temperature microwave-assisted pyrolysis of lignin, as well as the work-up and characterization methods for the bio-oil are described in detail elsewhere (Karthäuser et al. 2022), with the differences that the final temperature of the pyrolysis was selected as 200 °C, and the weigh-in mass of lignin as 200–300 g. The pyrolysis of lignin was performed in a “Milestone flexiWAVE” reactor (MWS Mikrowellensysteme Vertriebs GmbH, Leutkirch, Germany). An amount of 200–300 g of commercial SKL with the trademark Lineo™ (Stora Enso Oyj, Helsinki, Finland) were filled into a quartz glass reactor. Vacuum was applied and the lignin was heated from 30 to 200 °C under slow rotation. The heating rate was set to 3.5 K/min from 30 to 110 °C, and 5 K/min from 110 to 200 °C. The condensate was collected and separated into two phases by liquid/liquid extraction with trichloromethane (TCM; ≥ 99,9%, Th. Geyer GmbH & Co. KG, Renningen, Germany). The

bio-oil was obtained from the TCM-soluble phase by evaporating the TCM.

To determine the qualitative composition of the bio-oil, gas chromatography – mass spectrometry (GC–MS) was applied. A DSQ mass spectrometer with a Trace GC gas chromatograph provided by Thermo Electron Corporation (Waltham, Massachusetts, USA) and a VF-5 ms capillary gas chromatography column (Agilent J&W, length 30 m, ID 0.25 mm, d_f 0.25 μm) was used. A solvent solution was prepared by adding 20 mg of the internal standard iodobenzene (>98%, Acros Organics Bvba, Geel, Belgium) to 20 ml of acetone (\geq 99.8%, Merck KGaA, Darmstadt, Germany), and 10 μl of bio-oil were diluted in 990 μl of this solution. After introducing 0.5 μl of the sample with a split/splitless injector at a temperature of 250 °C with a split ratio of 1:10, the temperature in the GC column was increased from 50 to 250 °C with a heating rate of 15 °C/min. Structural identifications are supported by NIST and Wiley mass spectra databases.

The quantitative analysis of the components of the bio-oil was done via GC – flame ionization detector (FID), using a 7890A GC System with a 7683B Series Injector (both Agilent Technologies, Santa Clara, California, USA). The gas was chromatographically separated in a DB-5MS GC column (Agilent, 30 m \times 0.25 mm, d_f 0.25 μm). The samples were prepared similarly as for the GC–MS measurements. 1 μl of the samples was injected in a split/splitless injector at 250 °C with a split ratio of 1:20. The GC column was heated from 50 to 250 °C with a heating rate of 15 °C/min. The peak area of the substances was determined automatically in tangent skim mode. Standard solutions containing the five main constituents of the bio-oil were prepared. Concentrations of 0.5 mg/ml, 0.25 mg/ml and 0.1 mg/ml of guaiacol (98%, Carl Roth GmbH + Co. KG, Karlsruhe, Germany), 4-methyl guaiacol (99%, J&K Scientific Ltd., Beijing, China), 4-ethyl guaiacol (98.1%, HPC Standards GmbH, Cunnorsdorf, Germany), 4-propyl guaiacol (99%, Sigma-Aldrich, Co., St. Louis, Missouri, USA), and 4-(1-propenyl) guaiacol (95%, Fluorochem Ltd., Hadfield, UK) diluted in acetone were prepared. A quantity of 1 mg/ml of iodobenzene was added to each of the standard solutions, and the ratio between the peak area of the bio-oil compounds compared to iodobenzene was determined. The quantity of the

compounds in the samples was calculated with help of a calibration line.

Resin synthesis

The resins synthesized were a PF resin as reference, as well as PF resins in which 15, 30, and 45 weight% of the phenol was replaced by bio-oil obtained from SKL. For the synthesis of the pure PF resin, a molar ratio of 1:1.5:0.1 of phenol:formaldehyde:NaOH was applied. Two batches of samples containing bio-oil were produced. In the first batch, the molar ratio of 1:1.5:0.1 was continuously used, with the only difference being that the molar ratio of phenol was exchanged with the molar ratio of phenol and bio-oil. For the bio-oil, a molar weight of $M=266.3$ g/mol was assumed, as indicated by earlier gel permeation chromatography measurements. While this value is most likely not the precise average molar weight of the bio-oil because of the precision of the method, it is a good benchmark for the calculation of the weigh-ins. The phenol (99.5%, Th. Geyer GmbH & Co. KG, Renningen, Germany) and depending on the sample bio-oil were weighted into a flask and melted at about 55 °C. Afterwards, the NaOH (50% solution, AppliChem GmbH, Darmstadt, Germany) was added and nitrogen atmosphere was applied. Carefully pouring the formaldehyde (37% solution, Th. Geyer GmbH & Co. KG, Renningen, Germany) into the flask, the temperature was increased to 65 °C. This temperature was kept for 4 h before the final resin was obtained. For additional insights, resin samples were collected after 1 h, 2 h, and 3 h.

In a second batch, samples with reduced formaldehyde were produced. The resins were synthesized in a way that the higher the bio-oil content, the less formaldehyde was added, to account for the lower reactivity of biooil compared to pure phenol.

The samples with a phenol (and biooil) to formaldehyde content of 1:1.5 are referred to as hF (high formaldehyde), while those with reduced formaldehyde content are referred to as lF (low formaldehyde). All of the resins were synthesized and characterized at least two times, the molar ratios for the different syntheses are listed in Table 1.

Table 1 Molar ratios of the educts in the different resins

Resin	Mass ratio Phenol:Biooil / %	Molar ratio P + BO:F:NaOH	Repetition 1	Repetition 2
100 PF	1	1:1.50:0.10	1:1.50:0.10	1:1.50:0.10
85/15 hF	0.85	1:1.51:0.10	1:1.50:0.10	
70/30 hF	0.7	1:1.51:0.10	1:1.50:0.10	
55/45 hF	0.55	1:1.49:0.10	1:1.50:0.10	1:1.50:0.10
85/15 IF	0.85	1:1.44:0.10	1:1.44:0.10	
70/30 IF	0.7	1:1.38:0.10	1:1.38:0.10	1:1.38:0.11
55/45 IF	0.55	1:1.33:0.11	1:1.32:0.10	

Resin characterization

The free formaldehyde content of the resins was determined according to ISO 9397:1997. For this, about 3 g of the resin were weighed in and mixed with methanol. While stirring the solution, the pH-value was adjusted to 3.5 using hydrochloric acid. 25 ml of 10% hydroxylamine hydrochloride solution were added, and the solution was stirred for 10 min. Due to reactions between formaldehyde and the hydroxylamine hydrochloride (see Fig. 1), hydrochloric acid is set free and the pH-value decreases. Sodium hydroxide was added until the pH was 3.5 again. The amount of NaOH added to the solution was determined and used to determine the quantity of free formaldehyde in the solution.

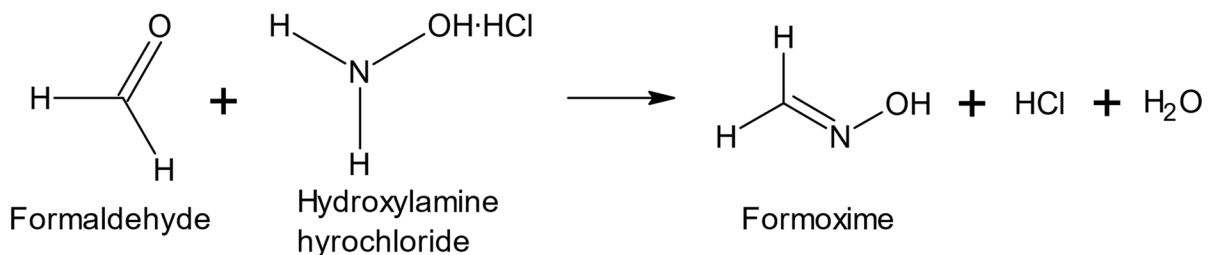
The pH-values of the resins were obtained with a pH-meter (EC-30 pH, Phoenix Instrument GmbH, Garbsen, Germany).

The solid contents of the resins were determined by weighing 2 g of the resin into an aluminum pan. Butanol was added to obtain a flat, thin surface. The resin was heated to 135 °C for two hours. Afterwards, the remaining weight was determined, and the solid content was calculated.

Differential scanning calorimetry (DSC) measurements were performed to determine the curing temperature and the enthalpy of the curing process using a DSC 200 F3 by Netzsch (NETZSCH-Gerätebau GmbH, Selb, Germany). For this, about 20 µg of the resin was weighed into a 200 µg gold-plated high-pressure crucible. The sample was heated to 250 °C with a heating rate of 10 °C/min. After cooling the sample, it was heated with the same heating program once more as a background correction. Measurements were repeated thrice per resin for one resin of each composition. The energy input curve of the first heating process, during which the resin is cured, is subtracted by the energy input curve of the second heating process. The signal onset-, maximum-, and end-temperature as well as the signal area, which is the reaction enthalpy, were determined using the Netzsch analysis tool.

Sample preparation for leaching and anti-swelling efficiency tests

The pine (*Pinus sylvestris*, Bavaria, Germany) sapwood samples were treated with resin with molar ratios described in Table 1, column “Molar ratio P + B:F:N”. Considering the solid content, the resins

**Fig. 1** Chemical equation of the reaction taking place during the free formaldehyde content analysis

were mixed with water so that a final solid content of 12.5% was achieved. For each resin and curing temperature set, ten $25 \times 25 \times 10 \text{ mm}^3$ scots pine sapwood samples were dried at $103 \text{ }^\circ\text{C}$ for three days. Their weight and dimensions were measured, and their average density was calculated. The samples were submerged in the resin/water solution, and treatment with 1 h of reduced pressure (80–100 mbar), followed by 2 h of high pressure (11 bar) was applied. The weight and dimensions of the wet samples were determined directly after the treatment. The samples were carefully dried first at room temperature, then by gradually increasing the temperature inside a furnace over several days. Finally, the resin was cured at $120 \text{ }^\circ\text{C}$ or $140 \text{ }^\circ\text{C}$ for two days in a furnace. Again, weight and dimensions of the samples were measured. The solution uptake (SU) of the liquid resin was calculated (Kupfernagel et al. 2022) and the WPG, and bulking of the wood samples were determined (Emmerich and Militz 2020).

Leaching of resin

The leaching of resin after curing was determined according to EN-84, with the difference that the samples were dried in a furnace before weighing. The samples were impregnated with demineralized water under vacuum. Then, the water was exchanged ten times in the following 14 days. The weight of the dry wood samples was determined before and after the tests. The mass loss as a function of the weight of the wood samples ML_{Wood} by leaching was calculated. Additionally, to better understand the influence of the resin on the leaching, the mass loss per resin mass in the sample ML_{Resin} was calculated.

Anti-swelling efficiency tests

Ten unmodified wood samples were used as reference material for the ASE tests. Dimension and weight of the dry samples were determined. The samples were impregnated with water under reduced pressure (80–100 mbar, 30 min). The samples were submerged under water for 24 h. Afterwards, the wet weight and dimensions were determined and the samples were dried for the next cycle. The procedure was repeated five times, after which a constant ASE was reached. The ASE was calculated according to the following Eq. (1) using the swell rate of untreated reference

wood samples SW_{ref} and the swell rate of the treated wood samples SW_{T} .

$$ASE = \frac{SW_{\text{ref}} - SW_{\text{T}}}{SW_{\text{ref}}} \cdot 100\% \quad (1)$$

The swell rate of the wood samples was calculated as follows (2) with the area of the wet sample A_{W} and the area of the dry sample A_{D} .

$$SW = \frac{A_{\text{W}} - A_{\text{D}}}{A_{\text{D}}} \cdot 100\% \quad (2)$$

Microscopy

For microscopy, samples treated with 100 PF, 70/30 IF, and 55/45 hF were selected. Additionally, untreated reference samples were prepared. Small blocks with dimensions of about $5 \times 5 \times 10 \text{ mm}^3$ were cut from the samples. The more brittle samples treated with resins were submerged in $60 \text{ }^\circ\text{C}$ warm water over night, while the less brittle reference samples were only wetted with water before cutting. The samples were cut with a microtome (HistoCore Autocut, Leica Biosystems, Wetzlar, Germany) to a thickness of $25 \text{ }\mu\text{m}$. For each sample half of the slices were stained with Safranin (Euromex PB.5295, Euromex Microscopen B.V., Arnhem, Netherlands). The coloration with safranin was performed to inspect the location of the resin in the cell wall, as described in literature (Biziks et al. 2019). The assumption hereby is that safranin cannot enter cell walls that are already filled with cured resin, and thus coloration is not possible, leading to an optical representation of resin load of cell walls. The samples with and without safranin treatment were dewatered with a six-step alcohol dewatering procedure, and afterwards fixated to a microscope slide with Euparal (Plano GmbH, Wetzlar, Germany). The Euparal was cured for 24 h at $55 \text{ }^\circ\text{C}$. The measurements were performed on an All-in-One fluorescence microscope BZ-X810 (Keyence Corporation, Osaka, Japan). Pictures were obtained with bright-field microscopy using the same exposure for each measurement.

Results and Discussion

Chemical composition of the bio-oil

A dark-brown bio-oil with a strong odor was obtained with a yield of $11.7 \pm 1.7\%$. The GC-FID chromatogram obtained for the bio-oil is depicted in Fig. 2. Proposed assignments for the signals were done with GC-MS and are listed in Table 2. While there are some small signals, the chromatogram indicates that several clear main products are present in the bio-oil.

The proposed main products marked in Fig. 2 with the numbers 2 – 6 are guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol, and 4-prop-1-enylguaiacol. The highest yield was detected for 4-methylguaiacol with $13.8 \pm 0.8\%$ (weight percent of the bio-oil), followed by guaiacol with $8.1 \pm 0.9\%$ and 4-ethylguaiacol with $6.8 \pm 0.5\%$. Both the 4-propylguaiacol and the 4-prop-1-enylguaiacol have yields below 5% (Table 2).

During the synthesis of PF resins, the formaldehyde reacts with the phenol on its ortho- and para-positions (Frihart 2012). Considering that the main products of the microwave-assisted pyrolysis are ortho- and para-substituted phenolic compounds, the reactivity of them with formaldehyde is expected to be lower than that of pure phenol. Hence, the resulting polymers after condensation will be less large and a smaller macromolecule will be created. Thus, it is expected that the performance of the resin for wood modification decreases with increasing substitution of phenol – a 100% replacement is most probably not suitable. At the same time, the amount of formaldehyde added to the mixture can be decreased, as less reactive positions remain.

The few signals in the chromatograms combined with the measured bio-oil composition indicate that there are additional molecules in the bio-oil, which have a higher boiling-point and thus cannot be detected with the given measurement parameters.

Fig. 2 Signal intensity as a function of time of the GC-FID measurement of the bio-oil. The numbers refer to the proposed assignment in Table 2

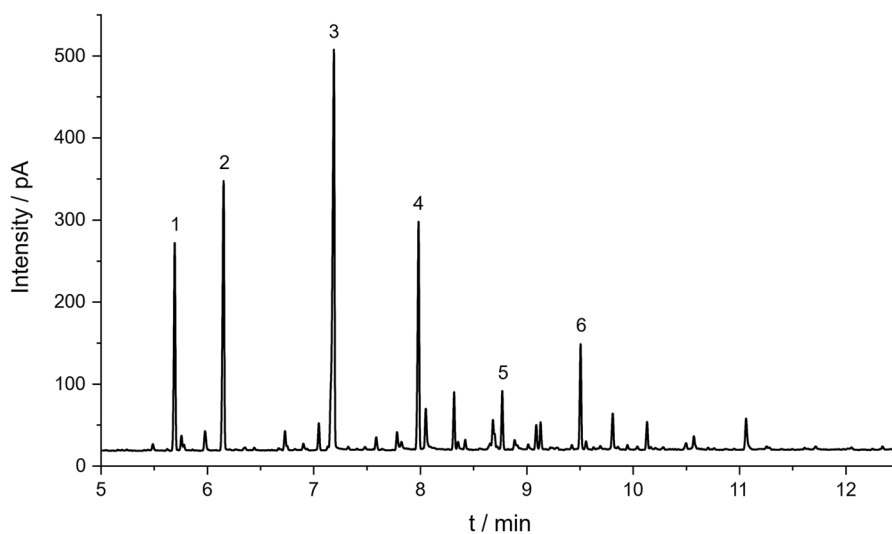


Table 2 Propose assignment, retention time, and yield of the main components of the bio-oil

Proposed Assignment	Number in Fig. 2	Retention time / min	Molar Mass / g/ mol	Yield / %
Iodobenzene (IS)	1	5.7	204	
Guaiacol	2	6.2	124	8.1 ± 0.9
4-Methylguaiacol	3	7.2	138	13.8 ± 0.8
4-Ethylguaiacol	4	8.0	152	6.8 ± 0.5
4-Propylguaiacol	5	8.8	166	1.4 ± 0.0
4-Prop-1-enylguaiacol	6	9.5	164	3.2 ± 0.0

These larger molecules probably also have an influence on the properties of the resin, as they are less likely to enter the cell wall and may consume different amounts of formaldehyde compared to the detected components.

Microwave pyrolysis was chosen as a method to produce the bio-oil, because it has several advantages over conventional pyrolysis (Farag et al. 2016). However, the upscaling of microwave pyrolysis apparatuses is connected to electrical and chemical engineering challenges (Suresh et al. 2021). Because of this, it is important to mention that the method described herein may, due to similarities in the organic cleavage products mentioned above, also be applied with lignin cleavage products obtained from conventional lignin pyrolysis.

Free formaldehyde content of resins

The free formaldehyde content of the resins is depicted in Fig. 3 and listed in the supplementary information (Table S1). For all resins, the free formaldehyde content decreases with longer reaction time. At low reaction times, the deviation of the free formaldehyde content between individual samples of the same resin is much higher than at later stages. The free formaldehyde content increases with increasing bio-oil content of the resin, however, up to 30% substitution the differences are still modest, with significant increase at 45% substitution. As expected, the samples synthesized with higher formaldehyde

amounts also have a higher free formaldehyde content compared to those with lower formaldehyde amounts.

The high standard deviation at early synthesis times is likely due to slight differences between the synthesis processes. Due to the exothermic nature of the reaction between formaldehyde and phenol (or other phenolics), the temperature is not always accurately set during the first hour. However, after four hours the deviation has decreased in all samples. The increasing free formaldehyde content with increasing substitution of bio-oil was expected due to the lower amount of free ortho- and para-positions of the main bio-oil components, which are usually occupied by formaldehyde in PF resins.

The increase in free formaldehyde content of the resin can be a challenge for applications of the resins with substituted phenol. Reason for this are the high toxicity of formaldehyde and strict regulations on formaldehyde emission or content of products worldwide (Salthammer et al. 2010). Hence, additives for reduction of free formaldehyde content, for example amines, may be required (Chaussoy et al. 2022). Predicting the formaldehyde release of the final product is complicated, as it can depend on monomer content in the resin, changes in the cured resins chemical structure (due to formaldehyde release by hydrolysis), or remaining lignin-type structures from bio-oil in the resin (lignin in wood is known to release more formaldehyde than hemicelluloses or cellulose) (Schäfer and Roffael 2000; Carvalho et al. 2012). Hence, additional studies are required to make sure that the

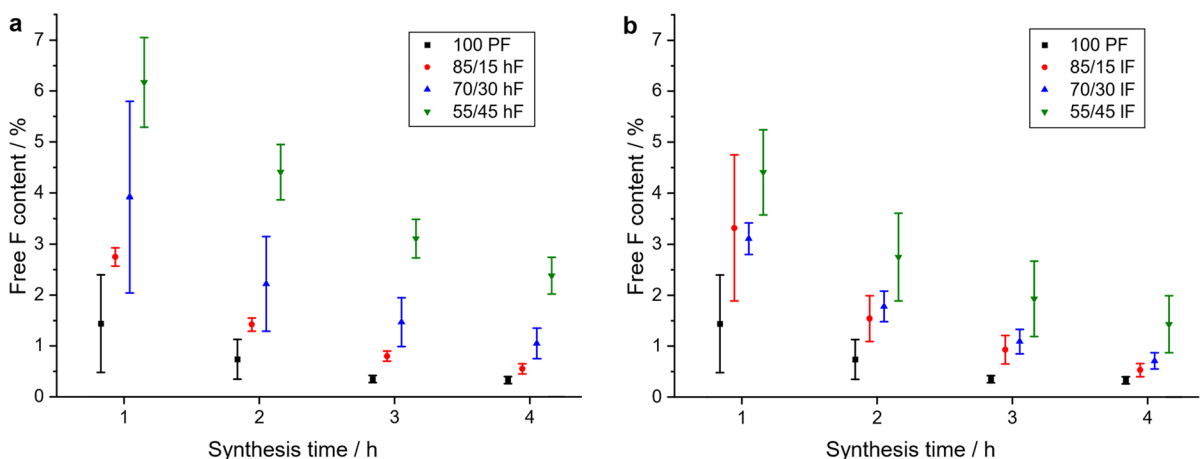


Fig. 3 Free formaldehyde content of the resins synthesized with high formaldehyde content (a), as well as reduced formaldehyde content (b) at different times of synthesis

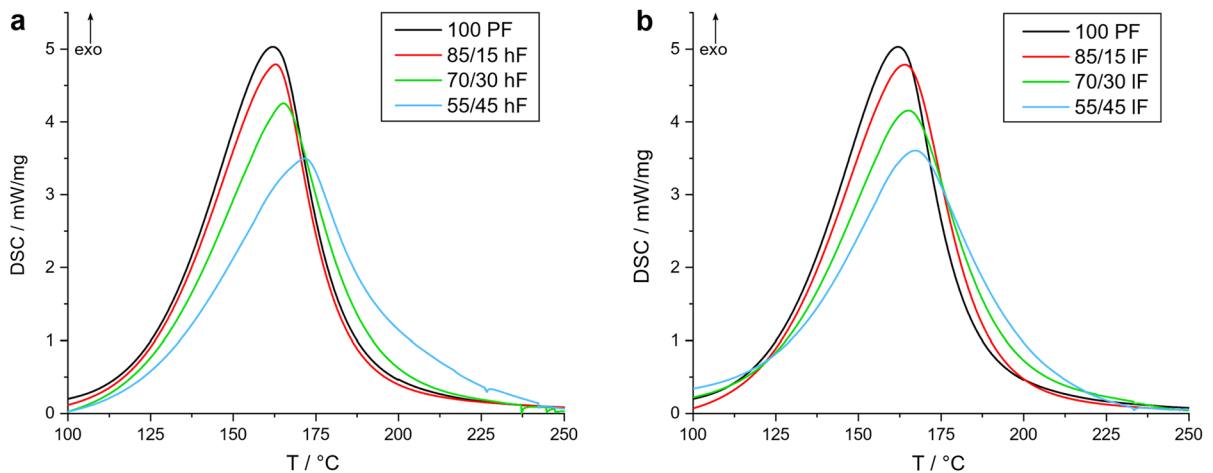


Fig. 4 DSC curves of the resins with high formaldehyde content (**a**) and low formaldehyde content (**b**)

Table 3 Onset, maximum, and endpoint temperature, as well as enthalpy of the different resins measured by DSC

Resin	Onset T / °C	Maximum T / °C	Endpoint T / °C	ΔH / J/g
100 PF	127.2 ± 0.2	162.0 ± 0.1	182.8 ± 1.2	1074.7 ± 45.0
85/15 hF	125.1 ± 0.4	162.9 ± 0.0	182.4 ± 0.5	1087.0 ± 11.6
70/30 hF	123.9 ± 2.2	165.2 ± 0.1	190.5 ± 0.3	1141.7 ± 29.0
55/45 hF	132.5 ± 0.6	171.6 ± 0.2	191.6 ± 0.8	908.6 ± 60.7
85/15 IF	123.9 ± 0.7	164.0 ± 0.1	189.0 ± 0.2	1269.7 ± 9.4
70/30 IF	122.5 ± 0.6	165.1 ± 0.1	206.5 ± 18.9	1124.0 ± 22.0
55/45 IF	127.6 ± 0.5	167.3 ± 0.1	200.2 ± 0.6	1042.3 ± 25.4

substitution of phenol does not affect the formaldehyde emission of the cured wood samples.

DSC of resins

The curing behavior of the resins was analyzed by DSC. The results indicate that higher substitution levels lead to an increase in the temperature, at which the maximum of the curing can be observed, while at the same time the maximum energy release is reduced (Fig. 4; Table 3). An effect on the overall energy consumption of the curing could not be observed.

The changed curing behaviors of the samples with phenol substitution indicate that a higher temperature is needed for curing. This could be relevant for industrial processes, where a slightly increased curing temperature or small differences in required energy could have a significant financial influence.

Table 4 pH-value and solid content of the different resins

Resin	pH value	SC / %
100 PF	9.6 ± 0.1	54.3 ± 1.4
85/15 hF	9.8 ± 0.2	55.5 ± 1.5
70/30 hF	9.0 ± 0.3	54.7 ± 2.7
55/45 hF	8.8 ± 0.4	54.6 ± 2.3
85/15 IF	9.5 ± 0.0	56.8 ± 1.8
70/30 IF	9.4 ± 0.1	55.7 ± 2.3
55/45 IF	9.4 ± 0.2	57.3 ± 1.1

Other resin characteristics

In addition to the measurements above, the pH-value and the SC of the resins were determined. The pH-value is similar for most resins, with the exception of the 70/30 hF and the 55/45 hF samples. The solid content is slightly higher for the samples with low

formaldehyde content, due to reduced water addition from formaldehyde solution (Table 4).

The obtained bio-oil had a dark color and a strong odor. This was reflected in the appearance of the resin: resin containing bio-oil was much darker than resin without bio-oil. With 45% substitution, the resin was not homogeneous anymore: a darker layer formed at the bottom of the flask. After curing, the samples of the wood had a darker color with increasing bio-oil content. The strong odor of the bio-oil disappeared when the sample was cured.

Wood treatment

Experiments on the suitability of the resins for wood treatment were carried out on pine sapwood samples. The solution uptake of the wood samples with the different resins is depicted in Fig. 5. The solution uptake varies between 138 to 195%. Higher solution uptakes were achieved with 100 PF, 70/30 hF, and 55/45 hF, while lower solution uptakes were observed for 85/15 hF, and 85/15 IF. For the other resins, namely 70/30 IF and 55/45 IF, the uptake varied.

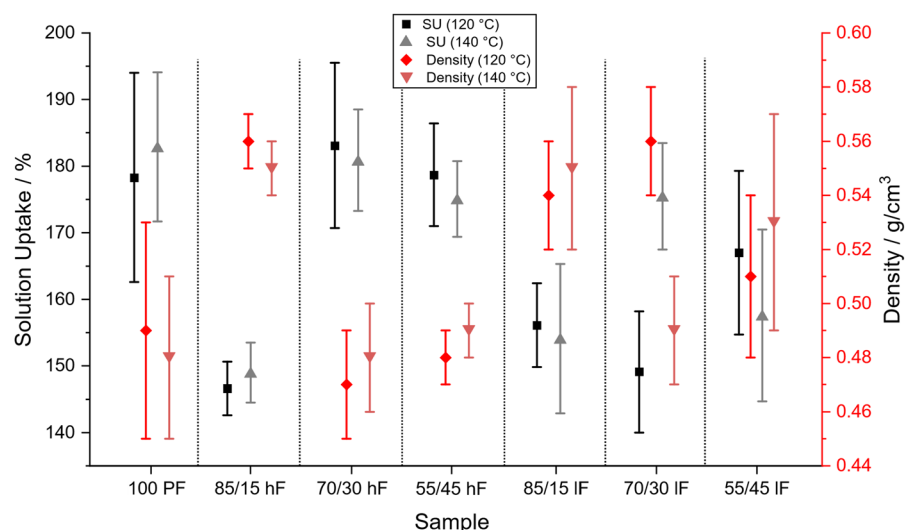
The density of the untreated wood samples ρ_{w_0} , solution uptake, WPG, and Bulking of the pine samples treated with different resins are listed in the supplementary information (Table S2) and are presented and discussed below.

While there are differences in the solution uptake of the different samples, even the lower solution uptakes measured are adequate values for a good

modification. The high range of solution uptake values does not correlate with the type of resin, as indicated by the seemingly random distribution of high and low solution uptakes. Hence, the reason for the variation are most likely differences in the properties of the wood samples. The density of the untreated wood samples was calculated and is depicted in Fig. 5. The results indicate, that there is a high correlation between the density and the solution uptake; lower density favors higher solution uptakes and vice versa. These observations are in line with results described elsewhere (Kupfernagel et al. 2022). To confirm the influence of the density on the solution uptake, the density was depicted as a function of the solution uptake (Fig. 6a). For this, each single measured wood sample, independent of the curing temperature, was depicted. A linear fit was applied, and a R^2 -factor of 0.975 was determined.

The R^2 -factor of 0.975 indicates that the solution uptake is highly dependent on the density. As an additional confirmation, the residuals (the difference between expected and experimental value) to the linear fit are depicted in Fig. 6b. The residuals are not high, and they are distributed statistically. Small exceptions to this are, that some slight trends can be observed for example for the 85/15 hF resin, which only has negative residuals. The indication of this is, that the resin did have a slight influence on the solution uptake. However, compared to the influence of the density on the solution uptake, the influence of the resin type seems insignificant. Thus, concerning

Fig. 5 Solution uptake of the pine samples cured at 120 °C (black; square), and 140 °C (grey, triangle), as well as density of the pine samples before curing at 140 °C (red, rotated square) and 140 °C (light red, triangle)



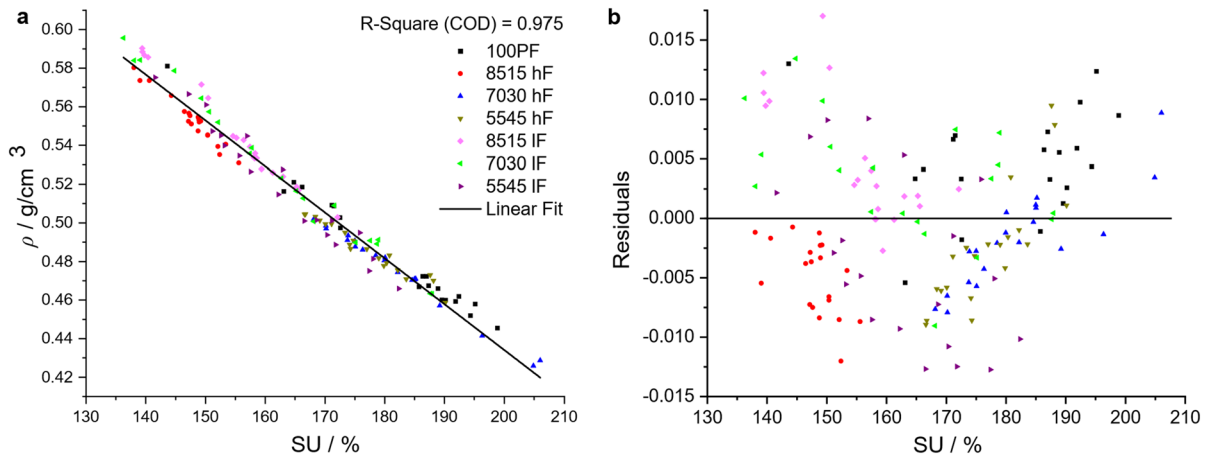


Fig. 6 Linear fit of the density as a function of the SU (a) and residuals to the linear fit (b)

the solution uptake, substitution of phenol by bio-oil in PF-resins has no significant negative effects.

While the solution uptake is a good indicator for a thorough impregnation, other factors such as the WPG and the bulking have to be considered as well. Both values help to observe the uptake of resin into the wood samples. While the WPG outlines the overall uptake of resin, the bulking shows the permanent swelling of the wood in dry state, and can be seen as an indicator for the uptake of resin into the cell wall. The WPG for the pine samples are depicted in Fig. 7a. In general, the WPG for PF 100 was higher than for the resins containing bio-oil. Between the

samples with different amounts of substitution or different amount of added formaldehyde, there were no clear trends. However, with higher bio-oil content the standard deviation of the WPG often increased, especially in case of the 55/45 IF samples.

Similar to the WPG, the bulking of the pine samples indicated that most resin uptake into the cell wall took place with 100 PF samples, and that the amount of substituted phenol was not relevant for the uptake of resins into the cell wall (Fig. 7b). The high variation of the WPG for the 55/45 IF sample was less pronounced for the bulking.

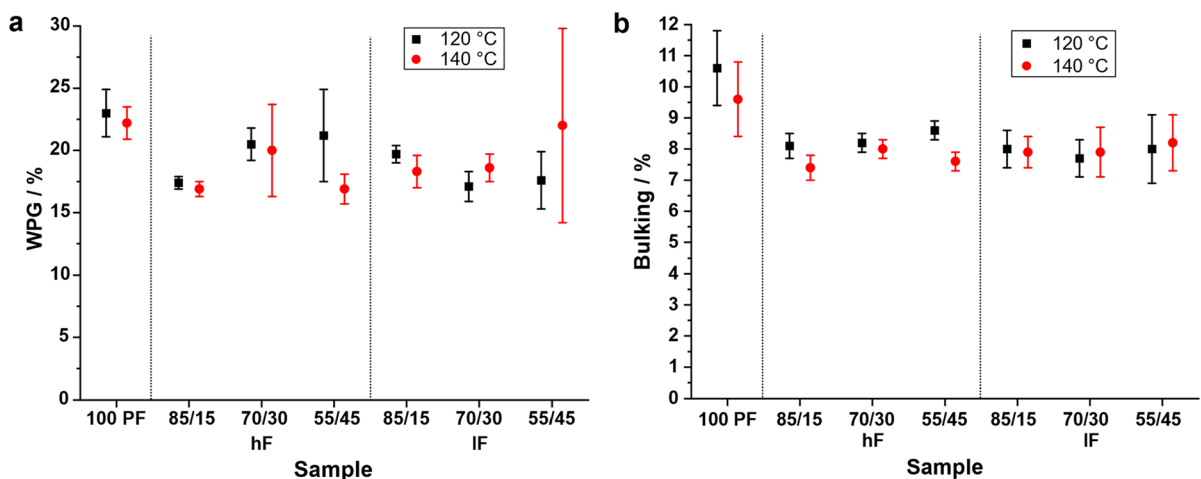


Fig. 7 WPG (a) and bulking (b) of the pine samples cured at 120 °C (black; square), and 140 °C (red; circle) treated with different resins

Because of the larger molecular size of the bio-oil components compared to pure phenol, the uptake in the cell wall is hindered. Thus, the higher WPG for 100 PF resin was expected, under the premise that few resin hardens in the lumen. Reason for the high variation in the WPG of the samples containing a lot of bio-oil was most probably the low solubility of bio-oil in water. Upon addition of little amounts of bio-oil, the prepolymers could still be dissolved, and a uniform resin was obtained. Upon addition of more bio-oil, however, the limit of solubility was reached, and a phase separation took place. This effect was strongest for the 55/45 IF solution. It has to be mentioned that a similar high divergence between the WPG of the samples treated at 120 °C and at 140 °C was observed, which is not depicted in Fig. 7a. Reason for this is that only the samples used for ASE tests were considered in the figure. However, additional samples were produced for other tests not described herein, which had a similarly high standard deviation. The effect, which led to a high variation in the WPG, could prove to be a challenge for industrial application of the method, because the heterogeneity of the resin can also lead to heterogeneous wood properties after treatment.

The lower standard deviation of the bulking compared to the WPG of the 55/45 IF indicates that the deviation did not originate from the uptake of resin into the cell walls, but into the lumen. The large bio-oil particles have a higher viscosity than the PF-resin. Due to this high viscosity and high molecular size, the phase of the inhomogeneous resin containing more of the large bio-oil components could not enter the cell walls, but was stuck inside the lumen, which led to a high WPG, but not a higher bulking.

Leaching of resin

The mass loss ML_{Wood} by leaching was determined according to EN-84, and the mass loss in relation to resin mass ML_{Resin} was calculated (supplementary information, Table S3). The ML_{Resin} of the different pine sapwood samples is depicted in Fig. 8. Both mass losses were higher for samples cured at 120 °C than for samples cured at 140 °C. Additionally, higher substitution of phenol led to increased mass loss. As for the WPG, a high standard deviation was measured for the 55/45 IF samples.

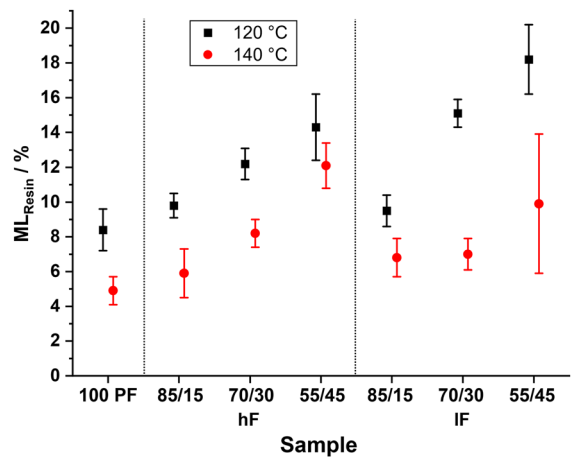


Fig. 8 Mass loss in relation to resin mass of the pine samples cured at 120 °C (black; square), and 140 °C (red; circle) treated with different resins

The main reason for the increasing mass loss with higher substitution of phenol is most likely a reduced fixation of the resin in the wood cell wall. The lower reactivity of the phenol substitutes led to less intermolecular bonds, and thus smaller molecules, which could be leached from the cell wall more easily. Similarly, the higher mass loss for samples cured with 120 °C was due to less thorough curing. The final molecule sizes are probably on average smaller than for the samples cured at 140 °C. The high deviation for the samples with high phenol substitution are in line with results reported above. As mentioned before, the high span of WPGs can be explained by a high viscosity phase due to low solubility of bio-oil in water, which remains in the lumen after impregnation. Chemicals in the lumen can be leached more easily than those in the cell wall, leading to a higher mass loss. Thus, since the resin was heterogeneous, some of the samples with 55/45 substitution had an increased mass loss. Another factor, which could have influenced the mass loss could be molecules in the bio-oil, which cannot be included into the polymeric network, however, for the main products this is not expected.

Anti-swelling efficiency tests

To verify the quality of the modification, the ASE was determined as a representative for the dimensional stability. The ASE of the pine samples treated

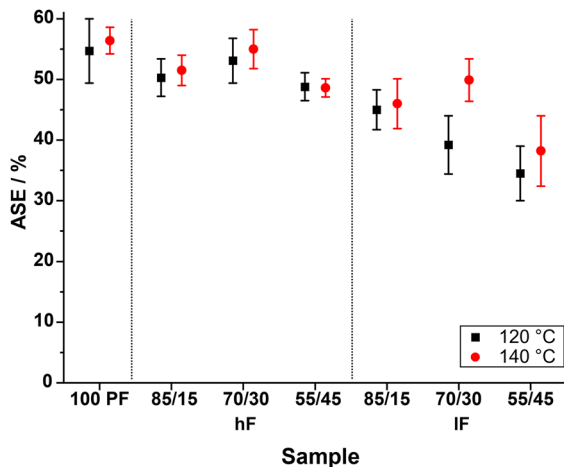


Fig. 9 ASE of the pine samples cured at 120 °C (black; square), and 140 °C (red; circle) treated with different resins

with different resins are depicted in Fig. 9 and listed in the supplementary information (Table S4). A trend for higher ASE values with increased curing temperatures can be observed for almost all sample sets. The highest ASE was measured for the samples with 100 PF resin. Higher bio-oil contents led to lower ASE, and a lower formaldehyde content had a negative effect on the ASE.

The decreased ASE of the resins with higher bio-oil content, especially the samples 55/45 IF, are

in line with earlier results. In general, samples with high formaldehyde content had similar performance compared to 100 PF resin. The samples with lower formaldehyde content performed less, however, the 85/15 IF and the 70/30 IF cured at 140 °C had high ASE values. The decreased ASE of the other resins indicated that the additional formaldehyde solution acted as a solvent and had a positive effect on the resin properties. Overall, up to 30% substitution of phenol at 140 °C curing temperature was possible without significantly decreasing the ASE. The ASE achieved with the given resin load are in range with results described in literature (Furuno et al. 2004; Fleckenstein 2018).

The repeated treatment of the samples during the ASE tests give insight into the long-term stability of the polymers inside the cell wall. Thus, the ML_{Resin} after ASE tests was calculated, and compared to the ML_{Resin} of the samples after the EN-84 leaching procedure. The mass loss of all samples increases after ASE, however, the amount of increase differs from sample to sample. The samples synthesized with bio-oil and a high formaldehyde amount have significantly increased mass losses compared to the 100 PF resin regardless of curing temperature (Fig. 10a, supplementary information Table S5 and Fig. 10b, supplementary information Table S5). The samples synthesized with low amounts of formaldehyde seem to be more stable over longer periods of time. All of

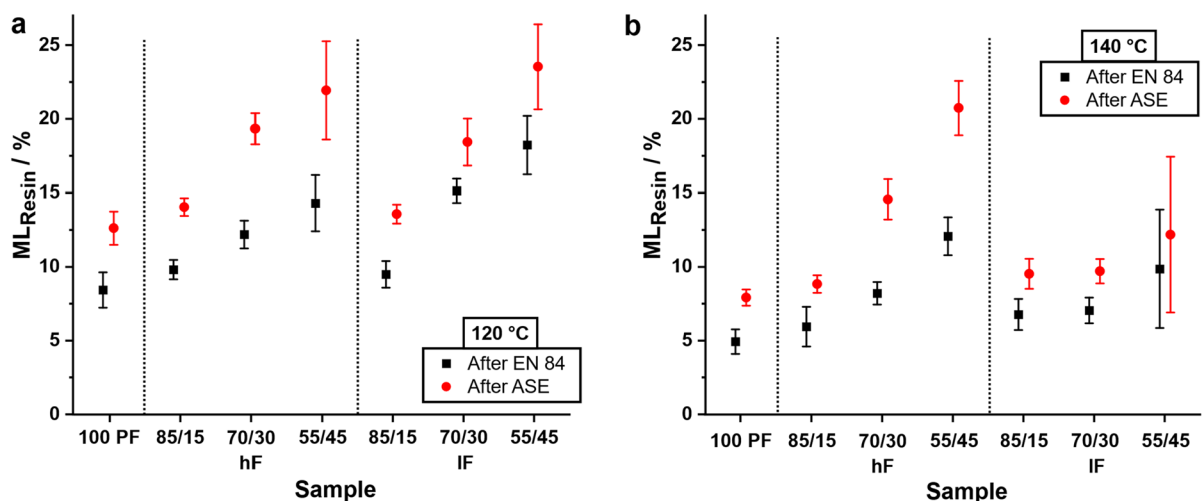


Fig. 10 ML_{Resin} after EN-84 (black; square), and ASE-tests (red; circle) of pine sapwood samples treated with different resins and cured at 120 °C (a), and 140 °C (b)

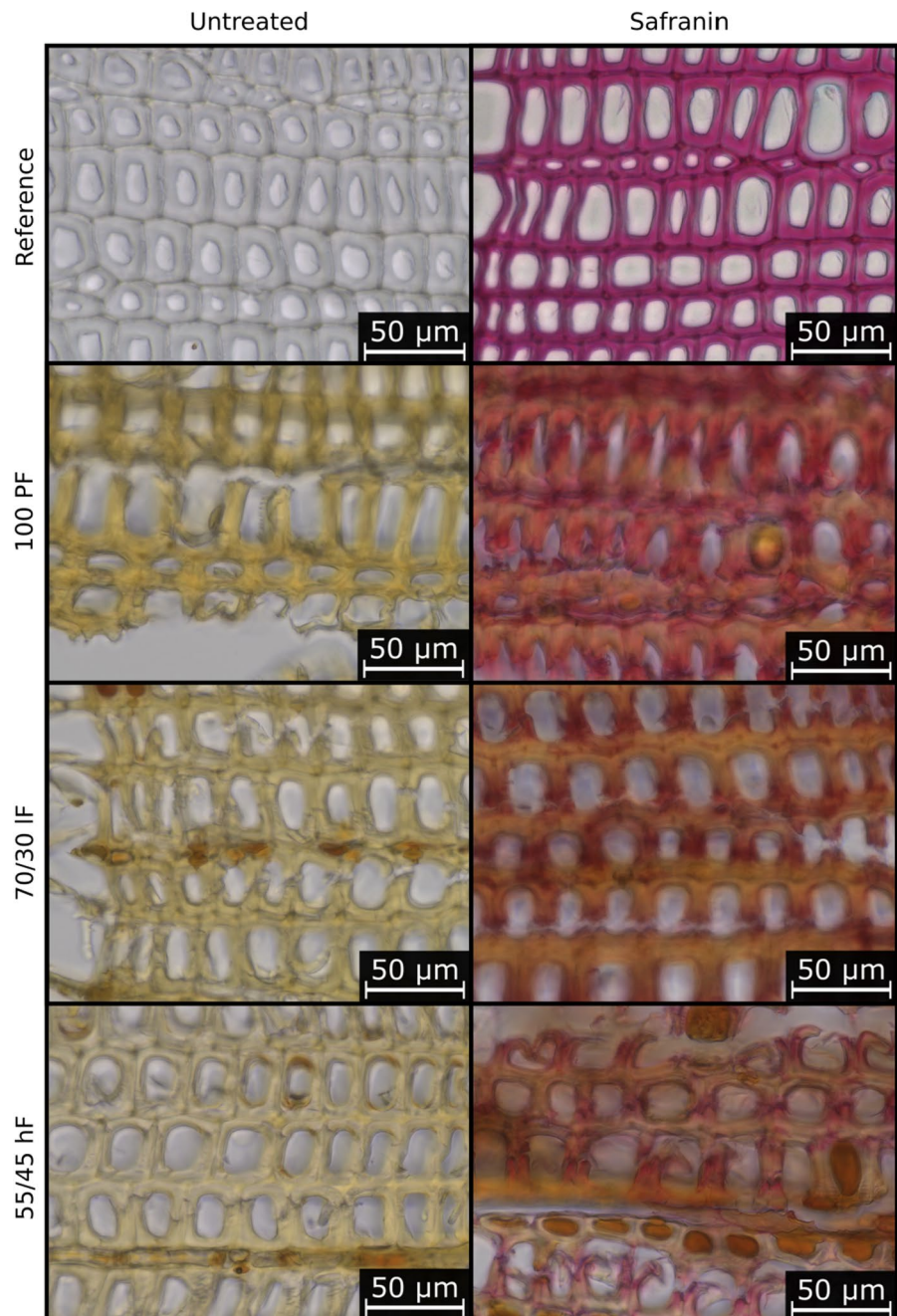
the samples cured at 120 °C had higher leaching than those at 140 °C.

The results agree with earlier results, indicating a better stability of the 100 PF samples, as well as those cured at higher temperatures.

Microscopy

To obtain additional information on the location of the resin in the wood, three selected pine samples, namely those treated with 100 PF, 70/30 IF and 55/45 hF, were observed with a microscope with and without safranin staining treatment (Fig. 11). For this, thin

Fig. 11 Microscopy with 40× magnification of pine sapwood samples treated with different resins, with and without safranin staining



slices of the samples were prepared. However, the vacuum pressure process and the curing at elevated temperature already destroy part of the wood structure. In addition, wood treated with PF-resins is significantly more brittle than untreated wood, complicating the sample preparation. Because of this, only samples with small size and from latewood of the modified wood were obtained.

Nevertheless, the pictures obtained are useful to investigate the wood treatment. As visible in the samples without staining, the cell walls containing cured resin could be differentiated from the unmodified ones by color, as the modified cells are brown. Similarly, the modified and unmodified wood could be differentiated via the safranin staining method, because the violet safranin stains untreated wood stronger than treated wood (Biziks et al. 2019). The pictures indicate that part of the resin was indeed cured in the lumen and not in the cell walls. The differences between the samples treated with bio-oil containing resins and those treated with pure PF-resin were only marginal.

The results indicate that microscopy is a suitable method to observe where the resin is cured, however, differences between the resins with or without bio-oil were not visible. The resin is mainly deposited inside of the cell-walls, with some exceptions of resins cured in the lumen.

Conclusions

The purpose of this study was to develop a PF resin for wood modification where phenol is partly replaced by the phenolic fraction from lignin pyrolysis bio-oil. Up to 45% of phenol has been substituted with the phenolic fraction obtained from vacuum low-temperature microwave-assisted pyrolysis of softwood kraft lignin. The substitution of up to 30% of the phenol had no large influence on the performance of the modification; at higher substitution levels the performance is decreased slightly. The method additionally enables the reduction of formaldehyde in the resin mixture, due to lower formaldehyde consumption of the substituent. Application of the described method could improve the environmental impact of modified wood products, while at the same time providing a higher value use for the pulping byproduct kraft lignin. Further steps will be to assess the suitability

of the method for treatment of different wood species, and upscaling of the method for modified plywood production.

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Declarations

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

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