

Lignin Phenol Formaldehyde Resoles: The Impact of Lignin Type on Adhesive Properties

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Lignin-phenol-formaldehyde (LPF) resoles were prepared using different types of lignin at various levels of phenol replacement by lignin (0 to 40 wt.%). Adhesive properties including thermal behavior as determined by differential scanning calorimetry (DSC), time-dependent development of bond strength during hot pressing as determined by automated bonding evaluation system (ABES), tensile shear strength of solid beech wood lap-joints, and free formaldehyde content of the adhesives were investigated. Preparation of phenol-formaldehyde (PF) resole was accomplished using molar ratios of formaldehyde/phenol and NaOH/phenol of 2.5 and 0.3, respectively. Four different types of technical lignins were studied: Sarkanda grass soda lignin, wheat straw soda lignin, pine kraft lignin, and beech organosolv lignin. The synthesis of the resoles was optimized for 20 and 40 wt.% phenol replacement by lignin. Increasing substitution of phenol resulted in faster gain of LPF viscosity for all studied lignins. The best curing performances of the LPF resoles were observed for pine kraft lignin at both 20 and 40% phenol replacement. The amount of formaldehyde not consumed during cooking increased with increasing level of phenol replacement. However, no differences in free formaldehyde content were observed between the different lignin samples at comparable levels of phenol replacement.

Keywords: Phenol-formaldehyde adhesive; Lignin-phenol-formaldehyde adhesive; Lignin; ABES; DSC

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INTRODUCTION

Phenol-formaldehyde (PF) adhesives are frequently used for the production of particular wood-based composites, such as plywood, laminated veneer lumber, glue laminated timber, fiberboard, and particleboard (Malutan *et al.* 2008a; Bertaud *et al.* 2012). Furthermore, they are frequently used as binders for the production of mineral fiber-based insulation materials and impregnated paper. PF resins were the first full-synthetic polymers produced on an industrial scale in 1909 (Campo 2007), and they are synthesized by classical “Baekeland chemistry”. The reaction of phenol with formaldehyde can be conducted under either alkaline conditions, which affords self-hardening resoles that set at higher temperatures, or acidic conditions, which affords non-reactive novolacs that are typically cross-linked in a second step using formaldehyde releasers (*e.g.*, hexamethylenetetramine). Physical and chemical properties of both resoles and novolacs can be largely controlled by varying the phenol/formaldehyde ratio, pH, time, and temperature of both the cooking and curing steps, in addition to the optional use of divalent

cations, such as Ca^{2+} , that govern the position of methylation of phenolic moieties. This includes molecular weight characteristics, degree of cross-linking, viscosity, curing performance, and mechanical properties of the final glued product (Xu *et al.* 2012). In the plywood industry, resole pre-condensates of lower molecular weight are synthesized in the temperature range of 80 to 100 °C (Malutan *et al.* 2008a) to achieve a target viscosity that allows for reasonable processing; the adhesive is finally subjected to thermal curing at elevated temperature. Typical hot pressing temperatures of 120 to 165 °C are reported for plywood production (Dunky and Niemz 2002; Sedliacik 2010), which results in adhesive temperatures at the bond line that range from 60 to 120 °C (Sellers 1985).

Replacement of synthetic phenol with lignin—an irregular biopolymer composed of different phenolic and etherified phenolic units—is one of the hot topics in PF resin research (Pilato 2010). Besides the fact that lignin is an abundant renewable resource comprising 15 to 40% of woody biomass, its considerably lower price is another driving force for this vivid field of research. The actual price of technical lignins isolated from various pulping processes is estimated to be 600 to 800 € per ton on a dry basis, while the price of phenol was 1350-1550 € per metric ton in 2014 according to ICIS pricing (ICIS). The year 2015 was a weak phenol trading year, as supply outstripped demand. Currently, the phenol price climbs slowly again and amounts to about 1070 € per metric ton on the European market (S&P Global Platts 2016).

Plywood production using lignin-based phenolic resins is an area of highly focused research (Zhang *et al.* 2013; Yang *et al.* 2015). However, the lower reactivity of lignins towards formaldehyde, which is due to “dilution” of their phenolic core moieties by aliphatic side chains, less available and partly less reactive activated aromatic sites available for methylation reactions, and the required higher curing temperatures, are key disadvantages that prevented lignin-phenol-formaldehyde (LPF) resins and adhesives hitherto from large-scale production (Siddiqui 2013). In phenol, electrophilic aromatic substitution can take place at the *para* and the two *ortho* positions, while in lignin fewer reactive sites are available at the aromatic nuclei, supposedly reducing the number of cross-links in the non-linear step-growth polymerization. This is due to the different phenolic moieties present in lignin (hydroxyphenyl, H; guaiacyl, G; syringyl, S) which contain substituents in *para*-position (relative to hydroxyl group) and in one or both *ortho* positions excluding H units. Additionally, not all phenolic units present in lignin carry free phenolic hydroxyl groups. Some of them are involved in ether linkages connecting other parts of the lignin macromolecule and are thus unavailable to form phenolate ions, which are strongly electron donors and highly susceptible to electrophilic aromatic substitution (Olivares *et al.* 1995; Ek *et al.* 2009; Akhtar *et al.* 2011). To overcome the problem of lower lignin reactivity, many researchers have attempted to modify lignin reactivity (Laurichesse and Averous 2014). Xu *et al.* (2012) identified two main strategies of lignin modification for its use in adhesives. The first strategy increases the accessibility of lignin reactive sites by reducing the steric hindrances by hydrolytic or oxidative depolymerisation. The second strategy involves introduction of reactive sites by lignin phenolation, demethylation, and methylation. However, only the latter approach has been implemented on the industrial scale for plywood production within the last twenty years (Pizzi 2013). The demethylation process (Mankar *et al.* 2012) has not yet been used in industry.

This study investigated the impact of partial phenol replacement by lignin in LPF resoles on the kinetics of viscosity gain (target viscosity 1000 mPa·s) during resin cooking, on its curing characteristics (onset, peak temperature), residual free formaldehyde content,

and mechanical bonding properties (bonding strength in different conditions, tensile shear strength of solid wood joints). Including the physical properties of LPF adhesive bonds as a function of curing time (bond strength development), the most relevant technological factors for adhesives and the generated bonds are covered. Different from other studies, the present work includes a set of lignins available on large scale, representing four main lignocellulosic resources, *i.e.* grass, straw, softwood, and hardwood, as well as the major pulping technologies (soda, kraft, and organosolv pulping). Beyond the above described goals, the conducted work provides an important set of reference data for our ongoing work on the synthesis of novel resole resins from nitrogen-modified lignins.

EXPERIMENTAL

Materials

Sarkanda grass soda lignin (SGS-L) and wheat straw soda lignin (WSS-L) were purchased from Granit Technologies SA (Orbe, Switzerland); pine kraft lignin (PK-L), Indulin AT™, was purchased from MeadWestvaco Corp. (Richmond, VA, USA). Beech organosolv lignin (BO-L) was a donation from the Fraunhofer Center for Chemical-Biotechnological Processes CBP (Leuna, Germany). All lignins were received as dry powders and used without further purification. Phenol ($\geq 99.5\%$) and formaldehyde (Formalin; 37% aqueous solution) were purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). Sodium hydroxide (NaOH; 97%) was obtained from Sigma-Aldrich Co. LCC (Steinheim, Germany).

Chemicals required for the determination of free formaldehyde content, *i.e.* isopropanol, distilled water, hydroxylamine hydrochloride, sodium hydroxide solution (1 mol/l) and hydrochloric acid (1 mol/l), were purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany).

Preparation of Phenol-Formaldehyde (PF) Adhesives

The synthesis of the PF adhesives was performed as described (Herwijnen and Prock 2009) with slight modifications. Briefly, 58.42 g of phenol (0.62 mol) was placed in a 500-mL three-neck round-bottom flask equipped with a condenser, electronic temperature controller, and magnetic stirring bar. The flask was heated to 45 °C to melt the phenol; 15.07 g of a 50 wt.% aqueous sodium hydroxide (NaOH) solution (0.19 mol), which corresponded to a molar NaOH-to-phenol ratio of 0.3, was added with stirring. The addition of NaOH increased the temperature of the mixture (up to 90 °C) due to the exothermic acid-base reaction with phenol.

The alkaline mixture (pH 12 to 12.5 at 25 °C) was cooled to 65 °C, and 115 mL of an aqueous 37 wt.% formaldehyde (HCHO) solution (1.54 mol) corresponding to a HCHO-to-phenol ratio of 2.5 was added at a flow rate of 8.43 mL·min⁻¹ using an automatic burette (TitroLine® 6000/7000). After all formaldehyde was added, the mixture was heated to the final cooking temperature of 80 °C. When the resin viscosity approached 600 mPa·s, the temperature was reduced to 70 °C to better control the resin viscosity to the target of approximately 1000 mPa·s. The pre-condensate (adhesive) was cooled in an ice bath to slow down the polymerization reaction.

Preparation of Lignin-Phenol-Formaldehyde (LPF) Adhesives

Following the above procedure, phenol was replaced by different quantities of lignin up to a maximum of 40 wt.%. For phenol substitution up to 20 wt.%, the entire amount of lignin was added to the hot (65 °C) concentrated aqueous solution of sodium phenolate. At the 40% replacement level, lignin was added step-wise.

The 20 wt.% replacement of phenol by pine kraft lignin was performed as follows. Phenol (46.74 g; 0.5 mol) was melted at 45 °C, and 15.07 g of a 50 wt.% aqueous NaOH (0.19 mol), which corresponded to a molar NaOH-to-phenol ratio of 0.38, was added. The alkaline mixture was cooled to 65 °C, and 11.68 g (0.06 mol C₉ units) of lignin was added and dissolved while stirring.

The 40 wt.% replacement of phenol by pine kraft lignin followed the same procedure with the following modifications: phenol, 35.05 g (0.37 mol); NaOH, 15.07 g of a 50 wt.% aqueous solution (0.19 mol), corresponding to a molar NaOH-to-phenol ratio of 0.51; and lignin, 23.37 g (0.13 mol C₉ units). The lignin was added step-wise over 15 min and dissolved while stirring.

Viscosity Measurements

The polymerization progress was monitored by measuring the viscosity of the reaction mixture according to the German DIN 16916-2 standard (DIN 16916-2 1987) using cooled (20 °C) aliquots (1.1 mL) of the respective LPF pre-condensates. A cone-plate rheometer (Bohlin CVO; Malvern Instruments Limited, Malvern, UK) equipped with a temperature control unit was used.

Free Formaldehyde Content

The free formaldehyde content of all adhesives was determined by sodium hydroxide back-titration according to the ISO 11402 standard (2004).

Solid Content

The solids content of the adhesives was determined according to ISO 3251 standard (ISO 3251 2008). Prior analyses of all samples were cured and equilibrated in a ventilated oven at 135 °C for 24 h as recommended for liquid phenolic resins.

Automated Bonding Evaluation System (ABES)

The adhesive bonding strength of each batch (8 replicates) was determined by use of a self-constructed ABES device, which evaluates the development of bonding strength during hot pressing of the adhesives joints. This ABES device was mounted on a Zwick/Roell Z100 universal testing machine (Zwick GmbH & Co. KG, Ulm, Germany) using a controlled hot press temperature of 120 °C (Sedliacik 2010; Ferra *et al.* 2011). For this test, two beech veneer strips (0.58 mm thickness, 20 mm width, and 147 mm length) stored at 20 °C and 65% relative humidity were glued together with an overlap length of 4 mm using a spread rate of 200 g·m⁻² and a relative pressure of 1.36 N·mm⁻² (Eder 2014). Tensile shear strength was measured in hot state immediately after the pressing time had elapsed and then after 30, 60, 90, 120, 240, 360, 420, 480, and 720 s.

Tensile Shear Strength of Solid Wood Joints

PF adhesives typically reach their ultimate tensile shear performance after an additional post curing. This phenomenon is characterized by the European test standard EN

302-1 (EN 302-1 2013), which assesses the suitability of an adhesive for its use in load bearing timber constructions. In brief, two beech wood lamellas (5 mm thick) were glued together by applying the adhesive at a spread rate of $200 \text{ g}\cdot\text{m}^{-2}$ (based on the liquid phase) and hot pressing ($120 \text{ }^\circ\text{C}$ at $0.8 \text{ N}\cdot\text{mm}^{-2}$). Pressing time was derived from the curing time as determined in the ABES test and was 20 ± 2 min for all adhesives. Prior to ultimate tensile shear testing, the respective samples were subjected to two different treatments (A1 and A2) according to the EN 302-1 standard. For treatment A1, the samples were conditioned at $20 \text{ }^\circ\text{C}$ and 65% RH for 7 days. For treatment A2, the samples were additionally stored in water at $20 \text{ }^\circ\text{C}$ for 4 days and tested in the wet state. Tensile shear strength of the overlapping area of the lap-joints was determined using a Zwick/Roell Z020 universal testing machine (Zwick GmbH & Co. KG, Ulm, Germany).

Dynamic Differential Scanning Calorimetry (DSC)

A precise amount of the adhesive, between 15 and 20 mg, was weighed into a high-pressure gold-plated steel crucible equipped with gold sealing. After tightening the lid, the crucible was transferred to a DSC 200 F3 Maia[®] differential scanning calorimeter (Erich Netzsch GmbH & Co. Holding KG, Selb, Germany). Thermal analysis was conducted in the temperature range of 20 to $250 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Thermograms were recorded using the Netzsch Proteus[®] 4.8.2 software package (Selb, Germany).

Table 1. Sample Codes and Key Characteristics of the Studied Lignins

Sample Code	Lignin (L) Type	Lignin Characteristics			
		Ash [%]	Lignin [%]	Total OH [mmol g^{-1}]	Phenolic OH [mmol g^{-1}]
PK-LF	pine kraft				
SGS-L _x PF	Sarkanda grass soda	4.1 ^a	89 ^a	5.84 ^a	1.8-1.9 ^a
WSS-L _x PF	wheat straw soda	2.5 ^a	91 ^a	6.13 ^a	1.7-1.8 ^a
PK-L _x PF	pine kraft	3.0 ^b	91.7 ^b	7.53 ^b	3.71 ^b
BO-L _x PF	beech organosolv	0.22 ^c	94 ^c	1.27 ^c	0.77 ^c

NaOH, sodium hydroxide; x, wt.% phenol substitution

^a Malutan *et al.* 2008a; Tyhoda 2008;

^b Aldeus *et al.* 2011

^c Hansen *et al.* 2016

RESULTS AND DISCUSSION

Samples were prepared as shown in Table 1. Initial experiments examined the impact of cooking time on the viscosity of the resins. The experiments revealed that pre-condensate formation at $90 \text{ }^\circ\text{C}$ was so fast that it was virtually impossible to achieve the target end viscosity of $1000 \text{ mPa}\cdot\text{s}$ (Fig. 1A). Pre-condensate formation at $65 \text{ }^\circ\text{C}$, however, resulted in excessively long cooking; thus, $80 \text{ }^\circ\text{C}$ was chosen as the cooking temperature for all subsequent adhesive batches. To better control the desired end viscosity of $1000 \text{ mPa}\cdot\text{s}$, the cooking temperature was reduced to $70 \text{ }^\circ\text{C}$ when the resole reached $600 \text{ mPa}\cdot\text{s}$.

Replacement of phenol by pine kraft lignin dramatically decreased the cooking time required to reach a 1000 mPa·s viscosity for PK-LPF resins with different levels of phenol substitution (0 to 40 wt.%; Fig. 1B), which was in accordance with Wang *et al.* (2009) and Siddiqui (2013). This effect is attributed to the considerable PF network extension caused by technical lignins. Thus, the lignins contained sufficient amounts of available and accessible reactive sites for electrophilic aromatic addition of formaldehyde and/or condensation with methylolated phenol or low-molecular weight PF resoles (Wang *et al.* 2009; Siddiqui 2013).

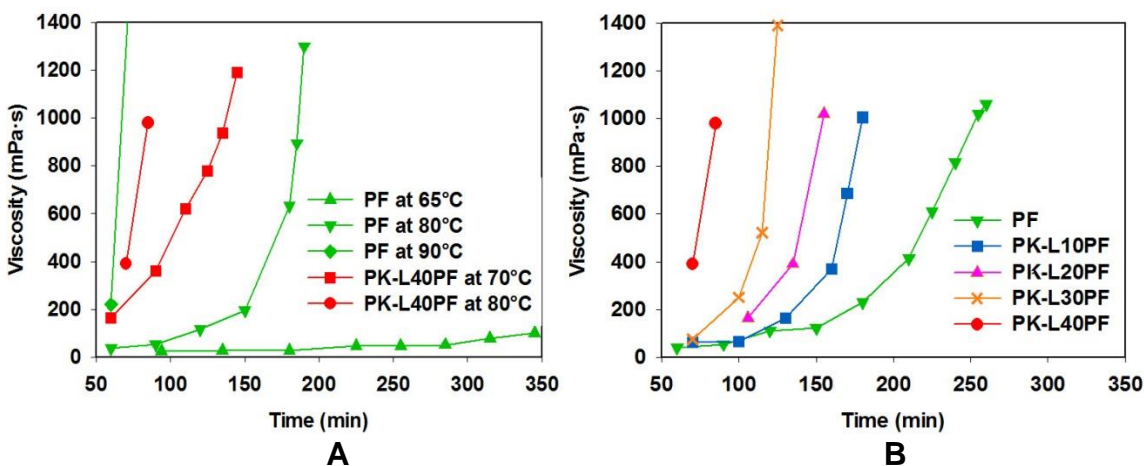


Fig. 1. Impact of cooking temperature (65 to 90 °C) and time (A) and level of phenol substitution (0 to 40 wt.%) by pine kraft lignin (PK-L; cooking temperature 80°C) on the viscosity gain of respective PF and PK-LPF resins (B).

After comparing different types of lignin obtained from grass, softwood, and hardwood *via* alkaline and organosolv pulping, it was observed that pine kraft lignin had the largest impact on viscosity. Figure 2 compares these lignins at 20 and 40 wt.% phenol replacement. This observation is mainly attributed to differences in lignin molecular weights, branching, and available reactive sites.

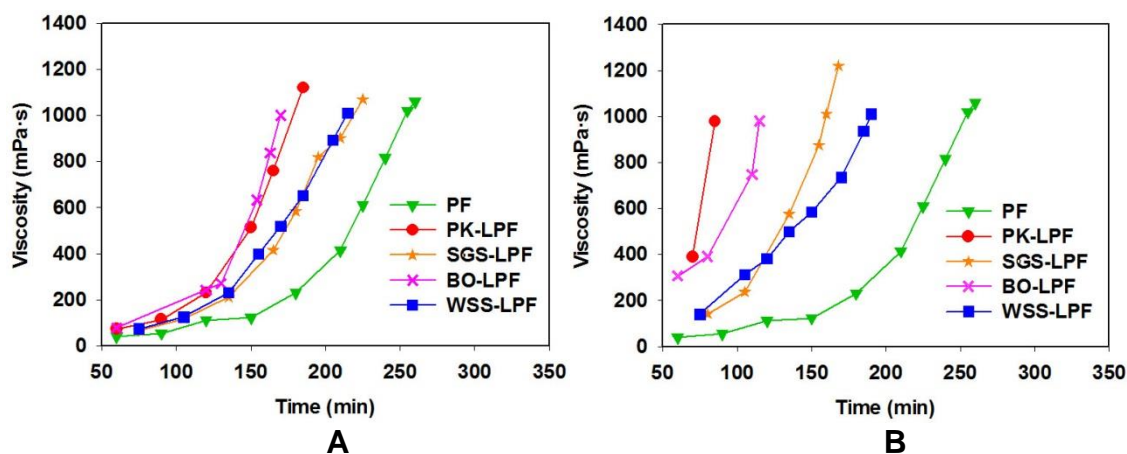


Fig. 2. Impact of the type of technical lignin on the viscosity using 20 wt.% (A) and 40 wt.% (B) phenol substitution

Grass lignins from soda pulping, such as those of sarkanda grass (*Saccharum bengalense*) (M_w of 4310 $\text{g}\cdot\text{mol}^{-1}$) and wheat straw (M_w 3510 of $\text{g}\cdot\text{mol}^{-1}$) (Malutan *et al.* 2008b), as well as hardwood lignin from organosolv pulping have lower molecular weights compared with softwood kraft lignin (M_w of 6500 to 8000 $\text{g}\cdot\text{mol}^{-1}$) (Doherty *et al.* 2011; Asikkala *et al.* 2012)). Therefore, it can be assumed that the former lignins would have a less pronounced PF network extension effect than softwood kraft lignin. Furthermore, SGS, WSS, and BO lignins are less branched than PK lignin due to several factors. One factor is the comparatively high content (30%) of hydroxyphenyl units (H units) contained in grass lignins that imparts larger sections of this type of lignin characteristics of a linear polymer (Rio *et al.* 2012). Another factor is the pronounced cleavage of β -O-4 bonds in hardwood organosolv lignin, as evident from measured lower T_g values (Baumberger *et al.* 2002; Doherty *et al.* 2011). Both softwood and hardwood lignin have higher molecular weights and are more branched compared to grass lignins, which supposedly boost PF network expansion and favors chain entanglement. Therefore, a faster viscosity gain is observed when these lignins are incorporated into the macromolecular structure during PF resole condensation than in the case of using grass lignin (Fengel and Wegner 1984). Besides mass fraction, molecular weight characteristics and steric demand of the respective lignins, which decide about the extent of PF network extension, their proportions of H, G, and S moieties, should govern the extent and kinetics of the methylation reaction as well which should have therefore an important impact on the viscosity gain during resole cooking. Grass lignin consists of approximately equal proportions of H, G, and S moieties, softwood lignin is strongly dominated by G units (95% G and 5% S), while hardwood can contain up to 50% of S building blocks and is largely free of H units like softwood (Fengel and Wegner 1984).

The impact of the different H, G, and S ratios in technical lignins on the reactivity of the latter towards methylation and hence the rate of viscosity gain is due to differences with regard to activation of the remaining free positions of the aromatic ring systems. Both phenolate ions and methoxyl groups are strong electron donators that activate the aromatic ring towards electrophilic substitution and that direct substitutions at free *ortho* and/or *para* positions. This effect is amplified by a weaker but still activating effect of alkyl substituents, which are predominantly located in *para* position relative to the phenolic groups of the respective H, G and S units. G-type lignins offer a combination of both strongly activating phenolic hydroxyls and methoxyl groups, and they are assumed to be less sterically hindered with regard to electrophilic aromatic substitution compared with S-type lignins. Hence, G units are supposedly more reactive towards formaldehyde.

The observed differences in time-dependent increases in viscosity are also related to the content of free phenolic groups. These groups form active phenolate ions at least for H and G-type lignins, which either have two (for H units) or one (for G units) non-substituted *ortho*-position relative to the phenolic group. As the studied softwood kraft lignin Indulin ATTM has nearly twice the amount of free phenolic groups (3.7 $\text{mmol}\cdot\text{g}^{-1}$) (Tyhoda 2008; Passauer *et al.* 2011)) compared to the two commercial soda lignins (sarkanda grass: 1.8 to 1.9 $\text{mmol}\cdot\text{g}^{-1}$; wheat straw: 1.7 to 1.8 $\text{mmol}\cdot\text{g}^{-1}$; (Malutan *et al.* 2008b; *cf.* Table 1)) it was hypothesized that among the set of studied lignins softwood kraft lignin would feature the highest reactivity in methylation and subsequent condensation.

This has been confirmed by experimental data which demonstrate that pine kraft lignin has superior reactivity because of its pronounced network expanding effect (highest

molecular weight), highest content of activated aromatic moieties for electrophilic aromatic substitution at moderate sterical hindrance, and highest content of free phenolic hydroxyl groups. This result was in good agreement with Tejado *et al.* (2007), who showed that among soda-anthraquinone flax lignin (grass lignin), pine kraft lignin (softwood lignin), and organosolv tamarind lignin (hardwood lignin), the G-type pine kraft lignin is superior with regard to phenol replacement in PF due to both its higher amount of activated free ring positions and its comparatively high molecular weight.

Key factors controlling both curing speed and physical bond properties of LPF resole adhesives in wood composite bonding include viscosity, final pH, solid content, and free formaldehyde content of the pre-condensates. The cooking procedures chosen for this study afforded adhesives, whose solid contents were between 41.7 to 46.5%, and pH values ranged from 10.3 to 10.9 (Table 2). However, for the target viscosity of approximately 1000 mPa·s, there were considerable differences between PF and LPF pre-condensates with regard to free formaldehyde content, which increased nearly linearly within the studied range. The PF resin had a free formaldehyde content of 2.2 wt.%, whereas for the four LPF resins, it averaged 5.9% (Δ 3.7% units) for 20% phenol substitution and 9.2% (Δ 3.3% units) for 40% phenol substitution (Table 2). This observation was indicative of a relatively high amount of formaldehyde that had not reacted with the lignin. Although the free formaldehyde content of the LPF adhesives is clearly too high to fulfil standard requirements, it does indicate that formaldehyde consumption is lower when lignin is used as substitute for phenol in corresponding adhesives. Thus, the molar ratio of formaldehyde to phenol and lignin needs to be optimized.

As stated above, the substitution of phenol with lignin accelerated changes in viscosity due to its considerable contribution to both PF network expansion and branching. As a result, the target adhesive viscosity of 1000 mPa·s was reached for the LPF resins with lower formaldehyde consumption *versus* the reference PF resin, as determined by the free formaldehyde content of the samples.

Table 2. Selected Properties of Prepared Adhesives

Resin Type	Viscosity (mPa·s)	Final pH	Solid Content (wt.%)	Free HCHO (wt.%)
PK-LF	-	-	-	14.2
PF	1000	10.9	46.5	2.2
PK-L20PF	1120	10.5	43.7	5.5
PK-L40PF	1190	10.4	42.0	9.1
SGS-L20PF	1050	10.6	45.3	5.6
SGS-L40PF	1210	10.3	42.9	9.2
WSS-L20PF	1010	10.4	42.9	6.1
WSS-L40PF	1010	10.4	41.7	9.3
BO-L20PF	1000	10.6	44.9	6.3
BO-L40PF	907	10.8	43.2	9.2

The residual free formaldehyde levels in the lignin-free PF and phenol-free (PK-LF) reference samples reflect the semi-empirical C₉ formula of the studied softwood kraft lignin (Passauer *et al.* 2011). The value of 182.9 Da used for lignin originates from the same batch as used by Passauer *et al.* (2011), while 0.74 molecules formaldehyde react with the G-type C₉ unit of the studied pine kraft lignin only (PK-L100PF). These numbers are very well reflected in the PK-L20PF and PK-L40PF variants. The theoretical and actual

amounts of consumed formaldehyde were very close to one another for PK-L20PF (1.16 vs. 1.18 mol, respectively) and PK-L40PF (0.92 vs. 0.95 mol, respectively).

The mechanical bond properties of the LPF adhesives were investigated after a final curing step in order to determine their potential applications. Tensile shear strength was assessed by the ABES technique. This method evaluates how fast the bond strength develops under a wide range of precisely controlled hot pressing conditions. The tests revealed that the bonding strength of the adhesives increased appreciably as pressing time increased (Fig. 3). However, the developed bonding strength of each of the adhesives varied considerably depending on the type of lignin used to replace phenol.

Figure 3 illustrates that none of the prepared LPF adhesives reached the ultimate strength of the PF adhesive after a pressing time of 760 s at 120 °C and 1.36 MPa. After an initial stage of rapid increase ($t \leq 240$ s), the tensile shear strength of all LPF bonds developed rather slowly, except for the adhesives prepared using pine kraft lignin (Fig. 3D). In this particular case, the ultimate strength of PF adhesive ($7.7 \text{ N}\cdot\text{mm}^{-2}$) was matched with the PK-L₂₀PF adhesive with a phenol replacement level of 20 wt.%; doubling the lignin content of PK-L₂₀PF adhesive reduced the tensile shear strength (Fig. 3D).

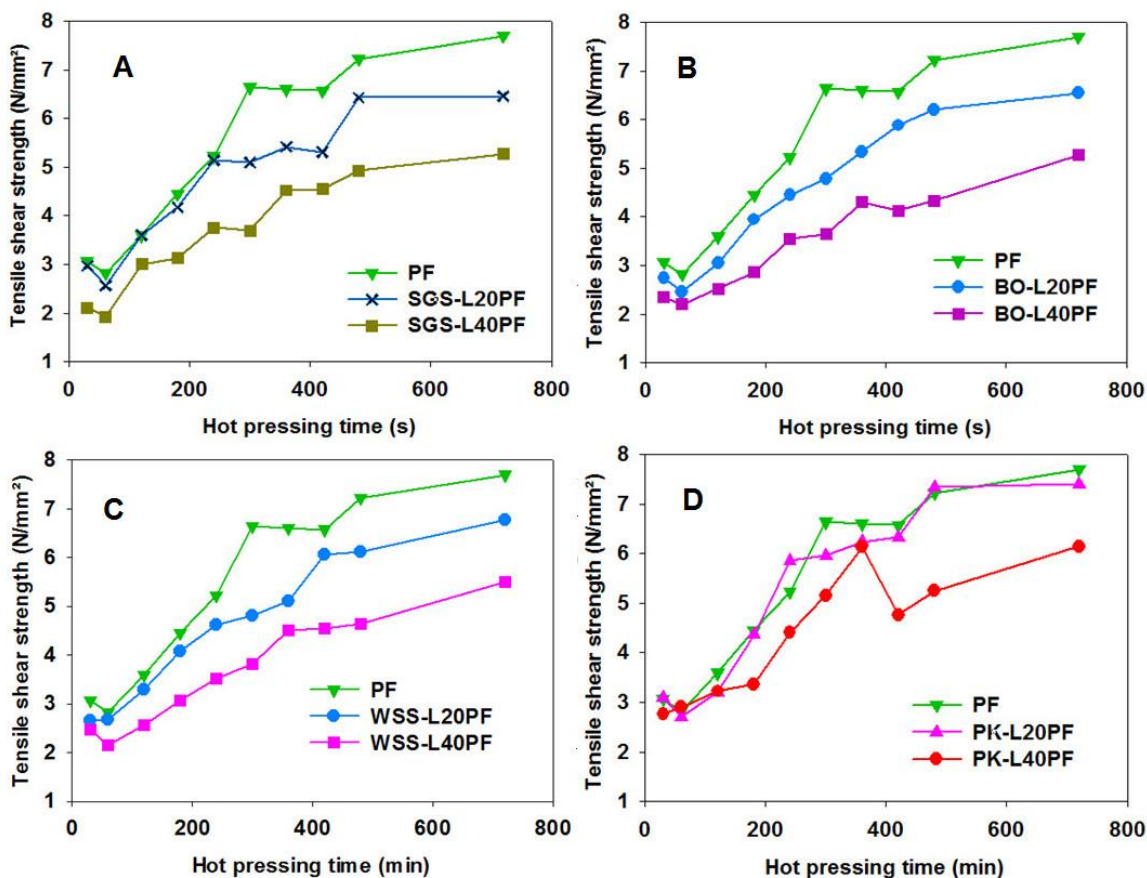


Fig. 3. Development of tensile shear strength as a function of hot pressing time of PF and LPF adhesives bonds as measured by ABES for sarkanda grass soda lignin (A), beech organosolv lignin (B), wheat straw soda lignin (C), and pine kraft lignin (D)

Selected adhesives were prepared from pine kraft lignin and sarkanda grass soda lignin, which were the most promising substitutes for phenol. These selected adhesives were used to bond wood samples, and the samples were subjected to tensile shear strength

testing in accordance with European standard EN 302-1 (2013). After equilibration at 20 °C and 65% relative humidity for 7 days (A1 treatment), the specimens bonded with lignin-free PF resin (22 tested specimens) and the two LPF resins prepared with pine kraft lignin (20 and 40 wt.% phenol replacement, 12 specimens each) surpassed the level indicated in the standard (Fig. 4), whereas the specimens bonded with sarkanda grass soda LPF failed in both dry and wet states. Interestingly, PK-L₂₀PF and PK-L₄₀PF adhesives surpassed the EN 302-1 standard of tensile shear strength in the A2 treatment conditions (storage in water for 4 days), whereas the lignin-free PF adhesive did not. It should be noted that commercial PF adhesives typically perform well in both dry and wet conditions. In this study, solid wood bonding was conducted with an extremely low adhesive spread of 200g·m⁻² (based on wet adhesive), which resulted in approximately 85 to 95 g·m⁻² solid adhesive at the bond line. Assuming more or less proper adhesive performance, the dominating failure mode of this standard test set up is wood failure, which requires a certain minimum strength in the adhesives used. Consequently, the values typically indicate the strength of wood and do not allow differentiation between the adhesives (Konnerth *et al.* 2006). In this investigation, a low adhesive spread rate was used to shift the weak link of the bond towards the bond line, which distinguished the bonding strength of the various adhesives. The results presented here suggested that the pine kraft lignin adhesives had the highest tensile shear strength of all the adhesives examined. One possible reason, which has not been further validated in the present study, could be the penetration of adhesive into the wood substrate (Kamke and Lee 2007) due to differences in molecular size distribution. However, using spread rates typically recommended for poly-condensate adhesives in load-bearing timber structures (250 to 400 g·m⁻², solid content of 60 to 67%), it is expected that specimens bonded with the PF adhesive would surpass the standard requirements.

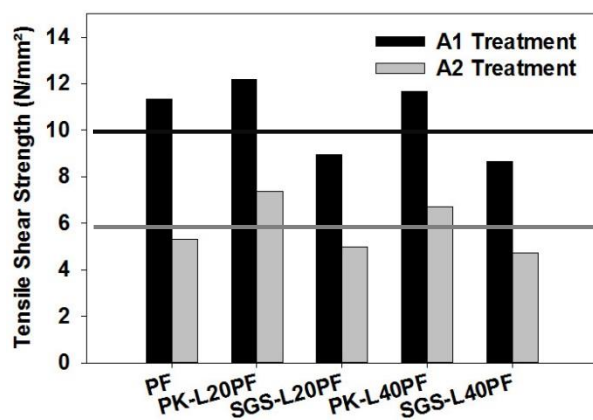


Fig. 4. Tensile shear strength of PF and LPF adhesives prepared with pine kraft lignin (PK-L) and sarkanda grass soda lignin (SGS-L). The black and grey horizontal lines present the EN 302-1 standard requirements of the A1 and A2 treatments, respectively, for adhesives used in load-bearing timber structures. The number of specimens tested for the PF and LPF adhesives is 22 and 12, respectively.

In summary, the ABES and EN 302-1 tests indicated that that pine kraft lignin is a promising candidate for replacing phenol in PF adhesives. Adhesives made with 20% pine kraft lignin have similar ultimate strength development with hot pressing time as lignin-free PF adhesive; additionally, the incorporation of pine kraft lignin (up to 40 wt.% phenol substitution) did not have any negative effects in the tensile shear strength under wet

conditions. These observations contradict the conclusions of Siddiqui (2013), who indicated that the adhesive strength of PF adhesives were higher than LPF resins using unmodified lignin, which required longer pressing times and higher hot press temperatures.

The thermal behaviors of all prepared adhesives were studied by differential scanning calorimetry (DSC); representative DSC curves for pine kraft lignin (PK-LPF) and phenol (PF) adhesives are shown in Fig. 5. The exothermic events observed during heating from 128.3 to 201.4 °C (Table 3) provided evidence that curing of the lignin-free PF adhesive started at 128.3 °C, whereas a higher temperature was required if phenol was partly substituted by lignin. This observation is in good agreement with Siddiqui (2013) and is assumed to be associated with the higher sterical demands of the lignin blocks incorporated, which require a certain degree of longer-range segmental motion and conformational freedom for setting compared to lignin-free resoles and with different reactions taking place when lignin is involved in PF curing. The relative shift of the DSC peak towards higher temperature was an unambiguous function of the amount of lignin added. The onset temperature was about 143 °C for 20% replacement of phenol (peak temperature 156.6 °C), whereas it was 177 °C (peak temperature 188.2) for 40% replacement. Deconvolution of the DSC curves provided some evidence for the occurrence of two independent setting mechanisms. Exothermic events centered at approximately 143 °C for both PF and PK-LPF adhesives, which indicated a common curing mechanism, such as phenol ether (<150 °C) and methylene linkage (>150 °C) formation. The peaks at 157 °C and 188 °C were most likely caused by other reaction mechanisms or sterical reasons. Mahendran *et al.* reported similar findings for lignin-based phenol formaldehyde adhesive prepared with lignosulfonates (2013).

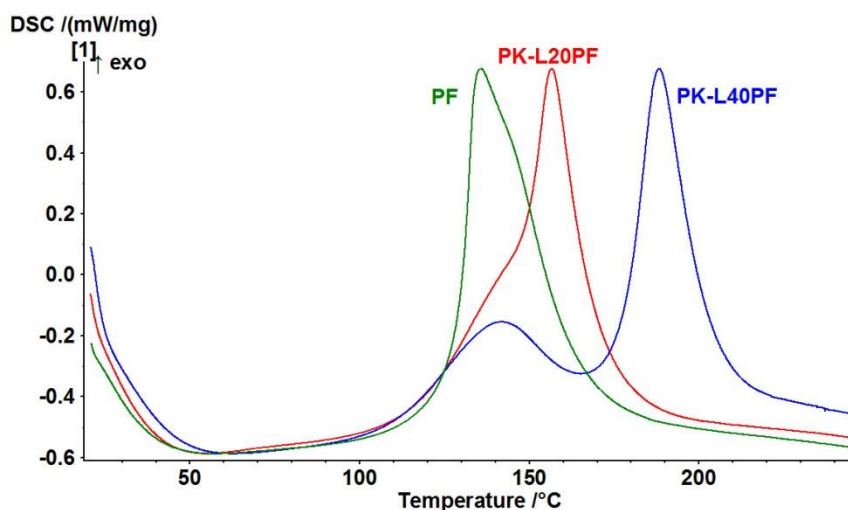


Fig. 5. DSC curves of the synthesized PF and PK-LPF adhesives

Table 3. Main Peak Temperature of Selected PF and PK-LPF Adhesives

Adhesive	Onset Temperature (°C)	Peak Temperature (°C)	Endset Temperature (°C)
PF	128.3	135.6	165.2
PK-L20PF	143.3	156.6	171.3
PK-L40PF	177.2	188.2	201.4

The same trend was observed for the other lignins used, whereas the individual lignins with single degrees had no considerable difference at their crosslinking peak temperature. Previous studies (Alonso *et al.* 2004; Wang *et al.* 2009; Mahendran *et al.* 2013) have shown similar trends for crosslinking peak temperature shift for PF versus LPF adhesives, which suggests that partial phenol replacement by lignin defers the adhesive curing process.

CONCLUSIONS

1. Four lignins were utilized to synthesize lignin-based phenolic resole adhesives. All resole adhesives showed a significant acceleration in polymerization rate during adhesive synthesis.
2. Preceding a lignin substitution degree of up to 40% the adhesive bonding performance was completely preserved, even in wet conditions, when substituting up to 40% of the phenol with pine kraft lignin.
3. The curing characteristics assessed by the ABES method showed a general decline as degree of phenol substitution increased.
4. The best results were obtained for pine kraft lignin with a phenol substitute degree of 20%, which performed almost identical to the reference PF.

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