Impact of Molecular Weight of Kraft Lignin on Adhesive Performance of Lignin-Based Phenol-Formaldehyde Resins*

Pia Solt Anna-Stiina Jääskeläinen Peter Lingenfelter
Johannes Konnerth Hendrikus W. G. van Herwijnen

Abstract

This study describes the influence of improved lignin homogeneity on the adhesive properties of lignin-based phenolic resins. Softwood kraft lignin was separated by applying an ethanol-based solvent fractionation to obtain three lignin fractions with a narrow molar mass distribution (smallest [M_w 1,590 g/mol] to largest [9,570 g/mol]). Lignin-phenol-formaldehyde (LPF) adhesives were prepared by 50 percent (by weight) substitution of phenol with an adjusted formaldehyde-to-phenol molar ratio. For investigating the storage stability of the resin, viscosity was monitored, curing behavior was determined by differential scanning calorimetry (DSC), and development of the bonding strength was analyzed via tensile shear strength as a function of press time. An acceleration of the condensation process for LPFs with higher molecular mass was observed. DSC signal indicated that LPFs need a slightly higher temperature for a complete curing than the phenol-formaldehyde reference resin. Furthermore, it was found that the tensile shear strength decreases with the use of fractionated kraft lignin in phenolic adhesives. No significant difference in reactivity was found for the resins making up the different lignin fractions.

Phenol-formaldehyde (PF) resins belong to a major class of adhesives and are widely used as binders in the wood panel industry for the production of plywood, oriented strand board, hardboard, or glulam. PF resins have excellent properties, such as high bonding strength and good resistance against moisture and temperature. Resoles are generally synthesized in multilevel processes using fossil components, such as phenol and formaldehyde (Knop and Pilato 1985, Pilato 2010). An increasing ecological awareness is a major driving force to search for alternative resources to replace such fossil components (Effendi et al. 2008).

Lignin is the second most abundant polymer from biomass following cellulose and is the main one based on aromatic units (Ragauskas et al. 2014). It is considered the most promising renewable feedstock to replace petrochemical-based aromatics. Large quantities of lignin (60×10^6 tons/acre worldwide; Feldman 2002) are isolated from wood in various pulping processes, and more than 95 percent of isolated lignin is used as an energy source.

Not only is lignin abundant, but the chemical resemblance of lignin precursors to phenol makes the development of lignin-based phenolic resins (lignin-phenol-formaldehyde

The authors are, respectively, Research Associate, Wood K plus, Competence Center of Wood Composites and Wood Chemistry, Linz, Austria, and Inst. of Wood Technol. and Renewable Materials, Dept. of Material Sci. and Process Engineering, BOKU-Univ. of Natural Resources and Life Sci., Tulln, Austria (p.solt@wood-kplus.at [corresponding author]); Principal Scientist, VTT Technical Research Center of Finland Ltd., Espoo, Finland (Anna-Stiina.Jaaskelainen@vtt.fi); Technology Manager of Construction, Prefere Resins Oy, Hamina, Finland (peter.lingenfelter@prefere.com); Associate Professor, Inst. of Wood Technol. and Renewable Materials, Dept. of Material Sci. and Process Engineering, BOKU-Univ. of Natural Resources and Life Sci., Tulln, Austria (Johannes.konnerth@boku.ac.at); and Deputy Area Manager, Wood K plus, Competence Center of Wood Composites and Wood Chemistry, Linz, Austria (e.herwijnen@wood-kplus.at). This paper was received for publication in November 2017. Article no. 17-00079.

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[LPF]) attractive for research. However, at the moment, lignin finds its utilization in PF resins mostly as a filler to increase the cold tack, thus reducing resin costs (Pilato 2010).

Dunky (2002) outlined the low reactivity of lignin with formaldehyde as an obstacle for a widespread commercialization. Nevertheless, some commercialization could be realized. For a period of time in the past, particleboard and fiberboard had been produced on an industrial scale using phenolic resin wherein 25 percent of phenol was replaced by kraft lignin (Fliedner et al. 2010). Prefere Resins (Hamina, Finland) announced on its home page to be the first company to produce a binder for panel application materials in which 50 percent of the phenol has been substituted by lignin (Prefere Resins 2017). Otherwise, higher substitution volumes with high lignin proportion (up to 80% substitution of petro-based phenol) could be achieved only under pilot plant conditions (UPM Bio Chemicals; Valkonen and Hübsch 2017). However, the limited usage of lignin is attributed to a nonuniform structure, complicating market penetration. This is due to the fact that the quality of the collected lignin is determined mainly by the quality of the feedstock as well as the pulping conditions. Unlike phenol, lignin is already a cross-linked polymer in which most of the reactive sites of the aromatic ring are methoxylated or occupied by other groups; further cross-linking reactions with formaldehyde are prevented (Hu et al. 2011). To overcome the challenge of reactivity, different lignin modification strategies have been proposed, such as methylolation (Zhao et al. 1994, Wang et al. 2009, Ghorbani et al. 2017), phenolation (Effendi et al. 2008, Ma et al. 2011), or demethoxylation (Olivares et al. 1988, Campion and Suckling 1998).

Another challenge is the heterogeneous nature in both composition and structure and an irregularity that defies exact description (Ralph et al. 2004). Moreover, native lignin is changed on isolation. There is a significant variety in molar mass and functional groups of different lignin isolation techniques that will impair its applicability in high-value lignin applications (Zinovyev et al. 2017, Domínguez-Robles et al. 2018). Regarding the synthesis of LPF resins, two possible theories on the effect of molar mass of lignin are known from the literature. On the one hand, the smaller lignin fractions are expected to be more reactive owing to an increase in the content of phenolic units from the depolymerization of kraft lignin (Mahmood et al. 2013, Siddiqui 2013). On the other hand, Tejado et al. (2007) assumed that large fragments have a better chance to contribute to polymerization because of the presence of a larger number of phenylpropane units.

The improvement of lignin homogeneity could be achieved by solvent fractionation to gain fractions with narrower molecular weight distributions (Ropponen et al. 2011, Duval et al. 2016, Jääskeläinen et al. 2017a, Domínguez-Robles et al. 2018). A fractional precipitation procedure that has been published recently by Jääskeläinen et al. (2017a) provides an easily controllable process to manipulate the yield and structural composition of the produced lignin fractions without the use of harmful or hazardous solvents or expensive instrumentation. It is assumed that separated lignin molecules with well-defined properties, such as the amount of free phenolic hydroxyl groups, carboxylic acid moieties, or low polydispersity, will have the highest potential in different product applications (Jääskeläinen et al. 2017b).

The aim of this article is to describe the influence of improved softwood kraft lignin homogeneity by ethanol-based solvent fractionation on the resin properties of lignin-based phenolic resins, such as storage stability and curing behavior, as determined by differential scanning calorimetry (DSC) and tensile shear strength development.

Materials and Methods

Materials

Precipitated pine kraft lignin from industrial softwood black liquor was provided as dry powder by Metsä Fibre Oy (Espoo, Finland).

Chemicals for the adhesive preparation (i.e., formaldehyde [formalin; 37% aqueous solution] and phenol [$\geq$99.5%]) were purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). Sodium hydroxide (NaOH; 97%) was obtained from Sigma Aldrich Co. LCCC (Steinheim, Germany).

Chemicals used for the determination of free formaldehyde content are isopropanol, distilled water, hydroxylamine hydrochloride, sodium hydroxide solution (1 mol/liter), and hydrochloric acid (0.1 mol/liter) and were purchased from Carl Roth GmbH.

For mechanical testing, beech veneer strips with a thickness of 0.58 mm were acquired at J. u. A. Frischeis Gesellschaft m.b.H (Stockerau, Austria). The veneer was selected by focusing on homogeneous and straight fiber alignment.

Solvent fractionation of kraft lignin

Technical softwood kraft lignin was fractionated in the pilot facilities of VTT (Espoo, Finland) and using the same principle as described by Jääskeläinen et al. (2017a). In this process (Fig. 1), the unfractionated lignin (UNF) was added to aqueous ethanol (80% by volume) solution and mixed at room temperature. The insoluble lignin fraction (INS) was recovered by filtration and dried under vacuum at 40°C. The lignin-containing filtrate was replaced in a reactor followed by water addition under constant mixing to reach a solvent concentration of 50 vol%. The precipitated lignin (PREC) was recovered and dried as the second fraction. The most soluble lignin fraction (SOL) was recovered from the second filtrate by evaporating the solvent under vacuum at 40°C. The chemical characterization of the unfractionated and fractionated lignin samples was performed as has been described elsewhere (Jääskeläinen et al. 2017a).

Resin preparation

For the PF-prepolymer, formaldehyde, and phenol, NaOH and water were mixed in a 500-mL three-necked flask equipped with an electronic temperature controller, according to a recipe by Prefere Resin Oy (Hamina, Finland) originally developed for plywood production. The synthesis was performed on a magnetic/hot plate stirrer (IKAWorks, Inc., Wilmington, NC, USA) at 80°C. The cooking procedure was stopped when the resin reached a target viscosity of 500 $\pm$ 50 mPa·s.

For the LPF resin manufacturing, each lignin fraction (UNF, SOL, PREC, and INS) was dispersed in 50 percent

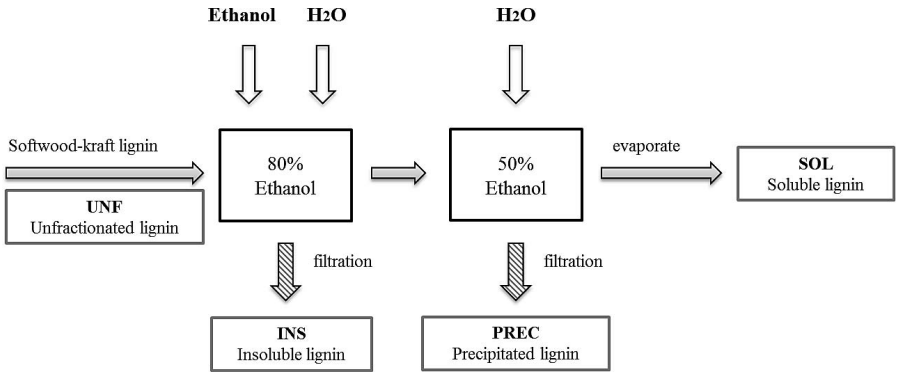

Figure 1.—Schematic description of the aqueous ethanol solvent fractionation of softwood kraft lignin.

NaOH solution and mixed until a homogeneous slurry was achieved. Following the principle recipe of PF, for the case of LPF resins, 50 wt% of phenol was substituted by the corresponding kraft lignin fraction. Including the caustic used to disperse the lignin fraction, all the LPF resins contained the same amount of NaOH, which was generally more than the reference PF resin. Moreover, the amount of formaldehyde was adjusted to obtain resins containing similar free monomers as the reference PF resin at the final viscosity of 500 ± 50 mPa·s. The target values were free phenol ≤0.1 percent and free formaldehyde ≤0.5 percent. This adaptation resulted in less formaldehyde used for the LPF resins than for the PF resin and also in a lower ratio of formaldehyde to (phenol plus lignin building stone) compared with the ratio of formaldehyde to phenol of the reference resin. Thus, lignin replaced not only a part of the phenol but also, to a lesser extent, a part of the formaldehyde. Yet the formaldehyde amount was identical for all LPF resins independent of the lignin fraction used.

Physiochemical resin characterization

Solid content of the resoles were measured according to ISO-3251 (International Organization for Standardization [ISO] 2008). Therefore, 2 ± 0.2 g of each resin sample was cured in an aluminum cup and equilibrated in a ventilated oven at a temperature of 135°C for 24 hours.

Viscosity of the adhesives was determined in accordance with the DIN-16916-2 (German Institute for Standardization 1987) standard at 20°C. Therefore, 1.2 mL of the sample was measured with a temperature-controlled cone plate rheometer (Bohlin CVO; Malvern Institute Limited, Malvern, UK). The average value of three samples was used.

The pH value of the phenol resins and the lignin slurries was measured in a aqueous medium (ratio 1:1 weight) with a glass electrode according to DIN-16916-2 (German Institute for Standardization 1987).

Free formaldehyde content was evaluated based on ISO-11402 (ISO 2004). Therefore, a well-defined amount (9.0 ± 0.2 g) of adhesive was dissolved in an isopropanol–water mixture (3:1). With 0.1 M hydrochloric acid, the pH was then adjusted to 3.5 using automatic titration equipment (TitroLine 6000/7000; SI Analytics, Mainz, Germany). Twenty-five milliliters of hydroxylamine hydrochloride solution (10 wt%) was added under continuous stirring. After a reaction of 10 minutes, the solution was back-titrated to pH 3.5 using 1 M aqueous sodium hydroxide. The calculated free formaldehyde content had to be below a target value of 0.5 ± 0.1 percent.

Free phenol in the phenolic adhesives was determined by Prefere Resins Austria (Krems, Austria) on an ICS 5000 HPLC system (Thermo Scientific, Waltham, MA, USA) equipped with a UV detector (271 nm) and Chromolith RP-18e 100 by 4.6-mm column using phenol as an external standard. The measured value had to be below the limit of 0.1 ± 0.03 wt%.

Thermal analysis (DSC)

The DSC of PF and LPF resins was performed on a DSC 200 F3 Maia instrument (Erich Netzsch GmbH & Co. Holding KG, Selb, Germany). For the dynamic DSC experiment, a precise amount of each resin sample (10 to 12 mg) was weighed in a high-pressure, gold-coated stainless steel crucible (30 µL). The crucible lid was tightened and transferred to the instrument. The analysis was conducted in a range of 10°C to 250°C at a heating rate of 5°C/min under nitrogen atmosphere. The heat flow was recorded and analyzed using the Netzsch Proteus 4.8.2 software package.

Development of bonding strength

To evaluate the development of the bonding strength during hot pressing, a self-constructed hot press was mounted in a Zwick/Roell Z100 universal testing machine (Zwick GmbH & Co. KG, Ulm, Germany). The setup was selected in order to allow testing according to ASTM-D7998-15 (ASTM International 2015) as originally proposed by Humphrey (1990). This instrument allows adhesive curing between two overlapping veneer strips during hot pressing, with a subsequent testing of the tensile shear strength.

For this measurement, 0.58-mm-thick beech veneer strips with dimensions of 20 by 150 mm were stored at standardized atmosphere (20°C, 65% relative humidity) for 2 weeks prior to testing. One veneer was coated with 180 g/m^2 of resin and glued together with an overlapping area of 20 by 5 mm. The samples were hot pressed at 120°C at a relative pressure of 1.5 N/mm^2. Immediately after expiration of the press time (0.5, 1, 2, 5, 10, and 20 min), the tensile shear strength of the sample was tested with a testing speed of 60 mm/min. During testing, the bond line had a residual temperature of 70°C to 80°C.

Results and Discussion

Chemical resin characterization

Kraft lignin was fractionated into three fractions using an aqueous ethanol fractionation process with two steps. In this process, each fraction consisted of approximately one-third of the original lignin. The purpose of the fractionation was to produce lignin feedstock with constant quality by separating lignin into fractions based on their solubility in selected solvents. In general, the solubility of lignin moiety is defined by the chemical structure, namely, molar mass, number of functional groups, and content of impurities (e.g., carbohydrates) (Brodin et al. 2009). In aqueous solvent fractionation, the chemical structures of lignin fractions follow a distinct pattern: the insoluble fractions possess typically high molar mass and wide molar mass distribution with a low number of phenolic or carboxylic acid moieties, while the most soluble fractions have the opposite characteristics (Jääskeläinen et al. 2017a, Domínguez-Robles et al. 2018). For this specific fractionation, the chemical characterization data of the lignin and the supernatants are collected in Table 1.

The molar mass distribution of the unfractionated and fractionated lignin samples showed significant differences between the fractions (Fig. 2). The INS fraction possessed the highest weight-average molar mass (M_w) compared with other fractions or with the unfractionated lignin and furthermore the highest polydispersity index (PDI) of 3.2. However, even this fraction possessed a small proportion of low-molar-mass lignin, indicating the presence of lignin moieties with low solubility but still low molar mass. SOL had the narrowest molar mass distribution (PDI of 1.5) with M_w of ~1,500 g/mol, which corresponds to lignin polymer of ~8 monomeric units (Jääskeläinen et al. 2017a).

The chemical analysis of the lignin fractions showed that INS had the highest amount of aliphatic hydroxyl groups, followed by the SOL and PREC fractions. These structures originate mostly from residual carbohydrates attached to lignin moieties, and it has been reported that they accumulate in both the INS and the SOL fractions (Domínguez-Robles et al. 2018). The number of phenolic hydroxyl groups decreased with the molecular weight of the lignin fraction. A low M_w results in a high amount of phenolic hydroxyl groups due to depolymerization of the lignin because the cleavage of β-O-4 structures result in the lowering of molar mass and the formation of a free phenolic hydroxyl group (Mahmood et al. 2013). Furthermore, it is also expected that because of the better solubility of fragments bearing more phenolic hydroxyl groups, this characteristic plays a role in the fragmentation. To facilitate creating a resin with homogeneous properties, lignin slurries were prepared in advance. As expected, the viscosity showed a significant coherence to M_w of the lignins, where smaller lignin moieties give rise to a lower viscosity in the slurry. INS slurry achieved a viscosity >5,000 mPa·s and was not measurable with the rheometer. The pH was similar for all prepared slurries.

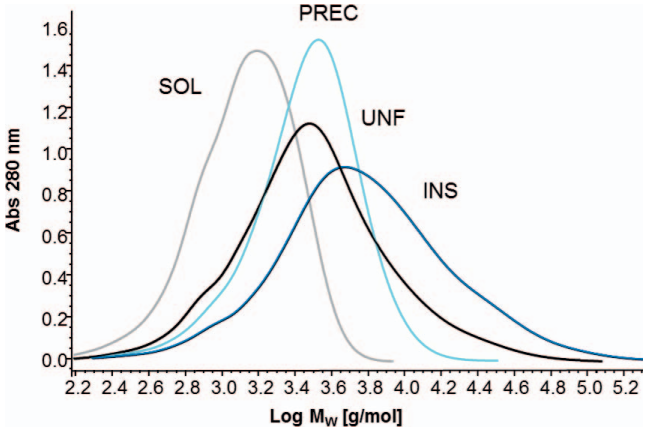

Figure 2.—Molar mass distribution of precipitated lignin fractions (PREC) and unfractionated lignin (UNF). SOL = soluble lignin fraction; INS = insoluble lignin fraction. (Color version is available online.)

The properties of the final resin, such as free formaldehyde and free phenol or viscosity, are important parameters for the usability of an adhesive. Furthermore, reactivity is an important factor of the adhesive production capacity. The properties of the LPF and the PF reference resins are compiled in Table 2.

The duration of condensation demonstrates that the resin preparation is strongly affected by the different lignin fractions. Higher molar mass of the fractionated lignin accelerates the increase of viscosity during cooking and results in shorter condensation process time during synthesis. At 5.2 hours, LPF-INS required the shortest condensation time, whereas the condensation time needed to include LPF-SOL (8 h) was longest. Similar observations have already been reported (Van der Klashorst 1989, Tejado et al. 2007) and are attributed to the larger number of phenylpropane units, which accelerates expansion of the LPF network, compared with smaller molar mass fraction.

Table 1.—Lignin raw material and lignin slurry characteristics.[a]

	Lignin					Slurry
Sample/ fraction	M_w (g/mol)	Polydispersity index	Aliphatic OH (mmol/g)	Phenolic OH (mmol/g)	pH	Viscosity (mPa·s)
UNF	5,014	2.2	1.86	4.30	12.4	4,300
INS	9,571	3.2	2.00	3.86	12.5	>5,000
PREC	3,386	1.7	1.37	4.35	12.5	780
SOL	1,590	1.5	1.61	5.56	12.4	90

[a] M_w = weight-average molar mass; UNF = unfractionated lignin; INS = insoluble lignin fraction; PREC = precipitated lignin; SOL = soluble lignin fraction.

Table 2.—Characteristics of phenol-formaldehyde (PF) and lignin-phenol-formaldehyde (LPF) resins (data are the average of at least two cooks).[a]

	Condensation time (h)	Viscosity (mPa·s)	Solid content (%)	Final pH	Free HCHO (wt%)	Free phenol (wt%)
PF	5.5	580	43.6	12.1	0.22	<0.01
LPF-UNF	7	520	46.7	13.2	0.37	0.13
LPF-INS	5.2	570	46.2	12.7	0.39	0.10
LPF-PREC	5.5	480	46.7	12.8	0.67	<0.01
LPF-SOL	8	450	46.3	13.1	0.37	0.07

[a] UNF = unfractionated lignin; INS = insoluble lignin fraction; PREC = precipitated lignin; SOL = soluble lignin fraction.

Other resin properties did not vary significantly between the LPF resins, such as final pH (12.7 to 13.2) or solid content (46.3% to 46.7%). Only standard PF showed lower values for both pH and solid content.

Free formaldehyde content of all LPF resins as well as of the reference resin was in the range of 0.22 to 0.67 wt% and thus was close to the selected target value of $\leq$0.5 wt%. Only LPF-PREC showed a slightly higher free formaldehyde content of 0.67 wt%, which was rated as acceptable for the type of laboratory production applied. Compared with the standard PF resole, the lignin-based adhesives showed similar higher values.

Free phenol contents showed that all samples reached the selected target values below 0.1 wt%. The highest value was obtained for LPF-UNF and the lowest for LPF-PREC and the reference resin.

Storage stability

Storage stability, or shelf life, is an important process parameter from an industrial point of view and is typically investigated by monitoring the viscosity behavior over time. The storage stability of commercial PF resoles is specified by the adhesive manufacturer and ranges in general from 2 to 4 weeks for standard PF-based plywood adhesives.

In the case of the produced resins, a significant difference between the set of LPF and the PF reference resin can be seen starting from day 23, visible at a disproportionately high increase in viscosity for the case of PF resin, as illustrated in Figure 3. Until day 23, only marginal viscosity changes were observed, followed by a fast increase until a leveling off was detected after 30 days. Compared with PF resin, all lignin-containing resoles were found to have a slower increase in viscosity. This may be owing to a higher reactivity of the phenolic resin or to physical gelation of the network. The different lignin fractions did not show an influence on the storage stability of the synthesized LPF prepolymers. Phase separation was not observed for any resin at any time during the monitoring of the storage stability.

Thermal analysis (DSC)

DSC was used to measure the temperature-dependent heat flow occurring during polymerization reaction of the adhesives. Typical curves of all resins are illustrated in Figure 4. In addition, corresponding onset temperature, peak temperature, and offset temperature of the main peak are given in Table 3.

Christiansen and Gollob (1985) found two exothermic peaks for phenolic resins and assigned the lower peak maximum in range of 98°C to 129°C to methylolation reactions and the higher peak maximum in the range of 139°C to 151°C to condensation reactions. Figure 4 shows only one broad exothermic peak for the PF resin with a maximum at 145.7°C, wherein the condensation polymerization signal overlaps the methylolation reaction. Because of the low free formaldehyde content (0.22%) of the resin, the contribution of methylolation reaction is expected to be low.

The LPF resins also show this broad peak but with a maximum at a 5°C higher temperature, indicating a lower reactivity of these resins. Siddiqui (2013) observed an additional clear signal at higher temperatures for lignin-modified phenolic resins. In this work, the LPF resins show an additional signal only as a weak shoulder. The higher the molecular weight of the lignin fraction, the higher the temperature of this shoulder signal, whereby the shoulder signal of the LPF making up the INS fraction could not be unequivocally determined. The signal of the LPF made with unfractionated lignin is approximately an average value of the other LPF shoulder signals.

Development of bonding strength

The development of the bonding strength was determined by testing the tensile shear strength of two glued veneer strips immediately after hot pressing. This method evaluates the bonding strength development as a function of pressing temperature and time. By using thin veneer strips as adherends, target temperature within the bond line is

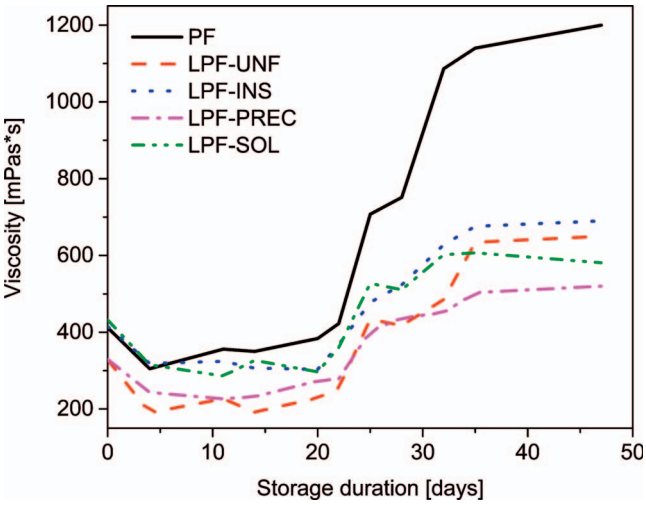

Figure 3.—Storage stability of lignin-phenol-formaldehyde (LPF) and phenol-formaldehyde (PF) samples at 20°C, illustrated by viscosity increase as a function of time. Lignin fractions: UNF = unfractionated; INS = insoluble; PREC = precipitated; SOL = soluble. (Color version is available online.)

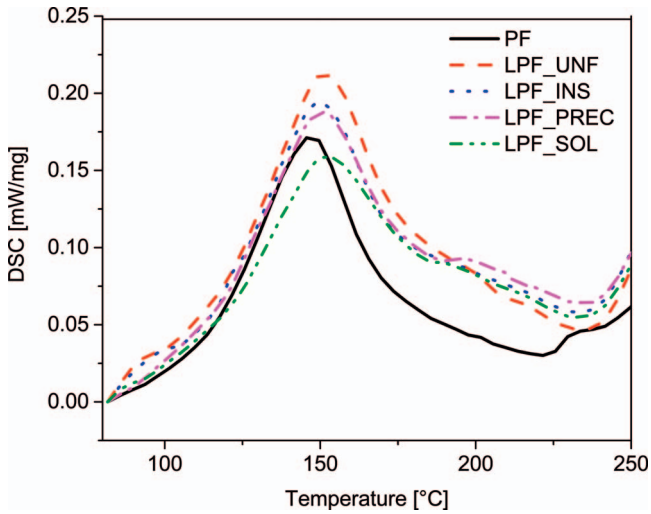

Figure 4.—Differential scanning calorimetry (DSC) curves of lignin-phenol-formaldehyde (LPF) and phenol-formaldehyde (PF) resins at a heating rate 5°C/min. Lignin fractions: UNF = unfractionated; INS = insoluble; PREC = precipitated; SOL = soluble. (Color version is available online.)

Table 3.—Reaction temperature of phenol-formaldehyde (PF) and lignin-phenol-formaldehyde (LPF) resins, measured with differential scanning calorimetry (DSC).[a]

	Temperature (°C)			Shoulder signal (°C)[b]
	Onset	Peak	Offset	
PF	115.1	145.7	170.5	
LPF-UNF	116.8	150.9	171.1	203.7
LPF-INS	115.7	150.1	174.6	—
LPF-PREC	118.6	150.3	174.9	204.9
LPF-SOL	119.7	150.9	177.4	199.7

[a] UNF = unfractionated lignin; INS = insoluble lignin fraction; PREC = precipitated lignin; SOL = soluble lignin fraction.
[b] Defined as the local minimum of the first derivative of the DSC signal.

achieved very quickly, and a near-isothermal bond formation can be evaluated (Humphrey 2005). Heinemann (2004) and Ferra et al. (2011) explained that, due to polymerization, the tensile shear strength of the adhesive bond increases until the curve levels off to reach a plateau at the maximum value. Figure 5 shows the time-dependent development of the shear strength for all tested resins at a pressing temperature of 120°C. PF showed faster bond strength development than LPF. PF reached the cohesive wood failure after a pressing time of 10 minutes, whereas the lignin-containing adhesives were not able to achieve significant wood failure up to the investigated 20 minutes of hot-pressing time. Within the hot-pressing time monitored, no LPF achieved the ultimate strength of the reference resin. Furthermore, the LPF resins did not reach a plateau. In this particular case, all the solvent-fractionated lignin types performed similarly, and no improvement in reactivity was found.

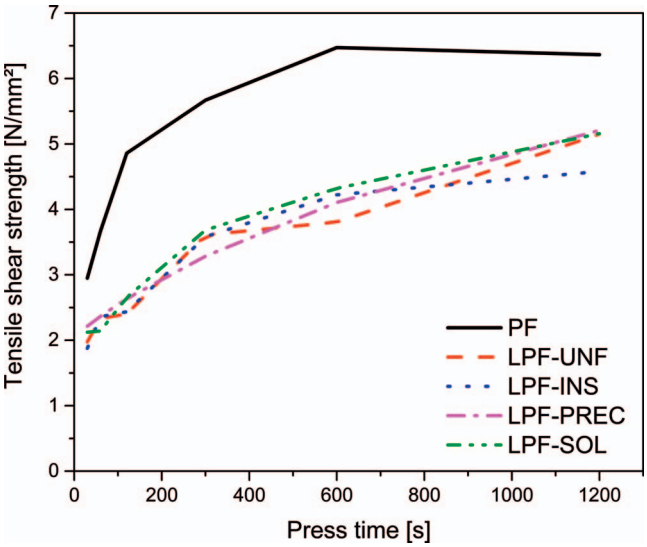

Figure 5.—Development of tensile shear strength at 120°C hot-pressing temperature as a function of hot-pressing time of phenol-formaldehyde (PF) and lignin-phenol-formaldehyde (LPF) resins. Lignin fractions: UNF = unfractionated; INS = insoluble; PREC = precipitated; SOL = soluble. (Color version is available online.)

Conclusions

1. Lignin was fractionated using ethanol into three homogeneous fractions with different molecular weight distributions. These lignins were then used to produce lignin-based phenolic resins with 50 wt% substitution of phenol.
2. It was found that condensation time decreases with an increasing molecular weight of the fractionated kraft lignin.
3. The lignin-containing resins showed a longer storage stability compared with the PF reference resin.
4. DSC analysis suggests that the LPF resins need higher temperatures to fully cure compared with PF adhesive. Also, the development of bonding strength is slower when lignin is used in the adhesive system and does not reach the final strength of the reference phenolic resin.
5. No significant influence of ethanol fractionation on the performance of LPF adhesives could be ascertained.

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