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Phenol-formaldehyde resins with suitable bonding strength synthesized from “less-reactive” hardwood lignin fractions

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Abstract: The substitution of phenol by lignin in phenol-formaldehyde (PF) resins is one of the most promising end uses of lignin valorization. Lignin from grasses and softwood has been the focus of the studies in this field as they present a higher number of theoretical reactive sites for resin synthesis. Herein we examined the composition and chemical reactivity of “less-reactive” hardwood lignin fractions and their performance in PF resins, synthesized by substituting 50 wt% of the phenol with lignin. Before resin synthesis, the samples were hydroxymethylated and the maximum formaldehyde consumption was recorded. By doing so, we observed that hardwood fractions consumed formaldehyde close to the theoretical calculation, whereas the reference softwood lignin consumed only about ¼ of the theoretical value. In the resin synthesis, we added formaldehyde to the formulation according to the measured maximum formaldehyde consumption. Thus, low values of free formaldehyde in lignin-PF (LPF)

resins were achieved (<0.23%). Moreover, the resin bonding strength displayed similar performance irrespective of whether the LPF resins were made with softwood or hardwood lignin (range of 3.4–4.8 N mm⁻² at 150°C and 45–480 s of press time). Furthermore, we concluded that hardwood kraft lignins present no disadvantage compared to softwood lignins in PF resin applications, which have significant practical implications.

Keywords: formaldehyde consumption, kraft, phenolic resins, reactive sites, technical lignin

Introduction

Phenol-formaldehyde (PF) resins are thermosetting polymers resulting from the condensation of petroleum-based phenol with formaldehyde. These phenolic resins have been used in many industrial applications such as automotive, computing, aerospace and buildings (Gardziella et al. 2000), and are widely used in the manufacture of engineered wood products such as plywood, particleboard, laminated veneer lumber and oriented strand board (Stark et al. 2010; Hong et al. 2018). The cost and availability of phenol depend heavily on petroleum prices, and this becomes one of the biggest disadvantages of PF adhesives. Furthermore, growing socio-environmental-economic concerns about the scarcity of fossil feedstock have been encouraging the search for petroleum replacements. In this timely topic, some research has been focused on the production of phenolic resins using a natural aromatic material, lignin, to replace phenol (El Mansouri and Salvadó 2006; Kalami et al. 2017; Lorente et al. 2017). Lignin is the most abundant source of aromatic compounds in nature and can be recovered in large quantities as a byproduct during pulp and paper production. The kraft process is the main method used for pulping and, according to ICIS Chemical Business (2017), the production of this technical lignin is estimated to reach 1.7 million tons by 2025. Kraft lignin has been considered to be a realistic proposition as a precursor to produce high value-added bio-based

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products (Schorr et al. 2014), highlighted by the fact that it forms a large proportion of non-food biomass (Doherty et al. 2011).

The replacement of a fossil resource by a natural polymer should in itself be enough to justify significant efforts in this area. Additionally, however, recent statistics show that the estimated average price for technical lignins ranges from 600 to 800 € per ton, whilst the average price for phenol is 1350–1550 € per ton (ICIS Chemical Business 2017), making the lower price another driving force in this scenario. Nevertheless, despite clear evidence of the benefits and the research conducted in the area, there are currently still challenges to be addressed in order to make it to the market.

Phenolic hydroxyl groups with unsubstituted C3 and/or C5 positions in addition to relatively low and narrow apparent molar mass have been cited as desirable properties of lignins for the efficient synthesis of lignin-PF (LPF) resin (El Mansouri and Salvadó 2006; Yang et al. 2015). These characteristics depend on the tree species used to isolate the lignin. Softwood (e.g. pines) and hardwood (e.g. eucalypts) are the main raw materials used in the kraft process, whereas grasses are used in soda and organosolv processes. Each starting material provides lignin with specific properties. For instance, softwood lignin is composed exclusively of guaiacyl (G) units and traces of *p*-hydroxyphenyl (H), whereas hardwood lignin is usually composed of syringyl (S) units, lower amounts of G and traces or none of H type. Lignins from grasses present the HGS lignin type, with similar levels of S and G and higher amounts of H (Lin and Dence 1992). The majority of studies have focused on the use of softwood (El Mansouri and Salvadó 2006; Ghorbani et al. 2016) or grasses (Khan et al. 2004; Kalami et al. 2017; Pang et al. 2017) for LPF resins, as their lignins are richer in G and H units. These specific units (G and H) exhibit free C3 and/or C5 positions and, theoretically, are fully able to react with formaldehyde during resin synthesis. However, the calculated theoretical number of lignin reactive sites (Yang et al. 2015) cannot be considered to be the only factor affecting the performance of lignin in LPF resins. As hypothesized recently by Balakshin and Capanema (2016), hardwood lignins consisting of a “lower amount of reactive sites” could still be targeted as a phenol substitute in PF resins, as factors such as molecular branching and conformity, steric availability, molar mass, and its distribution could also play important roles in the resin synthesis and subsequent performance, and should be taken into account. It is worth noting at this point that Brazil, for instance, produces an enormous amount of kraft lignin that is generated as a byproduct of the eucalypt-based pulp and

paper industry (IBÁ 2016). Finding a use for this byproduct in LPF resin could provide enormous opportunities for addressing current challenges faced by the industry in identifying high value-added applications for this economically important technical lignin.

Herein, we investigated the chemical composition and structure of the hardwood lignin fractions, obtained by the previously described sequential acidification process (Lourençon et al. 2015), and analyzed the correlations between the number of reactive sites and the performance of the lignins in LPF resins.

Materials and methods

Procurement and characterization of the lignin fractions: The lignin used in this study refers to fractions precipitated from eucalypt kraft black liquor provided by the Suzano Pulp and Paper industry (Limeira, Brazil). The fractionation method was described in a previous work (Lourençon et al. 2015). Briefly, diluted hydrochloric acid was slowly added to the black liquor to reach pH 9, and then it was centrifuged resulting in a supernatant and a precipitate. The supernatant was subsequently acidified to reach pH 7 and centrifuged again to obtain the next supernatant and precipitate. This procedure was repeated to obtain further samples at pH 5 and 3. The precipitated material at each pH step (i.e. pH 9, 7, 5 and 3) was filtered off, washed with acidified water (ca. pH 2), oven-dried (50°C) and milled in a mortar. The yield (%) recovered in each fraction was 50 ± 0.1 (fraction, pH 9), 38 ± 2.3 (fraction, pH 7), 7.5 ± 2.6 (fraction, pH 5) and 5.1 ± 0.9 (fraction, pH 3). Industrial softwood kraft lignin was used for comparison (chemical composition detailed in Table 1). It was an industrial lignin precipitated using carbon dioxide from the black liquor of a pulp mill that produces paper-grade kraft pulp and was kindly gifted by Metsä Fibre (Äänekoski, Finland).

Physicochemical characterization of lignin fractions

Overall chemical composition

To determine the carbohydrate and lignin composition, the samples were hydrolyzed with sulfuric acid and the resulting monosaccharides were determined by high-performance anion-exchange chromatography (HPAEC) with pulse amperometric detection (Dionex ICS 3000A equipped with a CarboPac PA1 column) (NREL standard 2008). The polysaccharide content in the samples was calculated from the corresponding monosaccharides using an anhydro correction of 0.88 for pentoses and 0.9 for hexoses. Klason lignin content i.e. the insoluble residue from the hydrolysis was determined gravimetrically. Acid-soluble lignin in the hydrolysate was quantified by ultraviolet spectroscopy at 215 and 280 nm, as described by Goldschmid (1971).

Elemental analysis (C, H, N, S and O) was determined from 20 to 30 mg of dried fractions (105°C overnight) using a FLASH 2000 series elemental analyzer (Thermo Scientific, Bremen, Germany). The molar mass measurements of the lignin fractions are described in the section “Measurement of the molar mass with size exclusion chromatography (SEC)”.

Table 1: Overall chemical composition of the hardwood kraft lignin fractions and softwood kraft lignin, and their functional groups obtained by ^{31}P NMR (all units are mmol g^{-1} without correction for lignin impurities).

Lignin samples		9	7	5	3	Softwood ^a
Klason lignin	(%)	70.4 ± 0.4	73.0 ± 0.9	83.5 ± 0.8	78.3 ± 0.2	92.3
Soluble lignin		9.7 ± 0.1	9.2 ± 0.3	10.6 ± 0.5	16.6 ± 0.7	2.5
Polysaccharides		1.9 ± 0.0	2.0 ± 0.03	2.1 ± 0.02	2.5 ± 0.01	1.1
C		50.8	51.2	57.6	57.9	65
H		4.5	4.6	5.1	5.1	5.7
N		0.03	0.05	0.06	0.12	0.12
S		2.3	2.5	2.8	3.3	1.62
O		28.6	27.3	27.5	27.6	–
Total aliphatic OH	mmol g^{-1}	0.99	0.98	0.92	0.83	1.88
Total phenolic OH		2.94	3.19	3.79	3.83	4.15
S + G _{cond}		2.20	2.39	2.87	2.86	1.83
G		0.65	0.71	0.82	0.83	2.05
H		0.09	0.10	0.12	0.14	0.26
COOH		0.63	0.59	0.58	0.89	0.50
Total OH		4.56	4.76	5.30	5.54	6.53

S + G_{cond}, 5-substituted phenolic hydroxyls (S-units and 5-condensed G units); G, free phenols in guaiacylic structures; H, free phenols in *para*-hydroxyphenyl structures and COOH = carboxylic acids.

^aChemical composition previously reported in Jäskeläinen et al. (2017).

Quantitative determination of functional groups in the lignin fractions

The number of hydroxyl groups was determined indirectly using ^{31}P nuclear magnetic resonance (NMR) spectroscopy by using a modified procedure proposed by Granata and Argyropoulos (1995), and using a Bruker 500 MHz (Bruker, Billerica, MA, USA) spectrometer. The hydroxyl groups in the lignin samples were derivatized with an excess of a phosphorus-containing reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane). After the total dissolution of lignin in *N,N*-dimethylformamide and pyridine, an internal standard solution (*endo*-N-hydroxy-5-norbornene-2,3-dicarboximide in pyridine/ CDCl_3) and $\text{Cr}(\text{acac})_3$ (in pyridine/ CDCl_3) were added. Then the phosphitylation reagent followed by chloroform-*d* (CDCl_3) were added. A total of 1024 scans with a pulse delay of 5 s, 90° pulse, line broadening of 2 and default baseline correction were used in the spectral collection. The quantification limits applied were 150–146 ppm for aliphatic OH groups, 144.2–140.3 ppm for 3- and 5-substituted OH groups, 140.3–138.5 ppm for guaiacylic OH groups, 138.5–137 ppm for *p*-hydroxyphenyl groups and 135.7–134 ppm for carboxylic acid groups (Balakshin and Capanema 2015).

Hydroxymethylation and resin synthesis: Before resin synthesis, a pre-polymerization (hydroxymethylation) experiment was carried out in order to understand the lignin reactivity and the maximum consumption of formaldehyde. Lignin was mixed with NaOH using 0.65 mol equivalent based on total acidic functionalities (phenolic OH + COOH) and formaldehyde (37% aqueous solution) in double dosage relative to the theoretical reactive sites, calculated based on ^{31}P NMR. Water was added to achieve 10% of dry matter content. The samples were heated for 4–6 h at 60°C, under stirring. The content of residual formaldehyde was measured by gas chromatography-mass spectroscopy (GC-MS; see section “Formaldehyde and phenol by GC-MS”). Then, based on the known amount of formaldehyde added, the maximum formaldehyde consumption (mmol g^{-1}) was calculated for each lignin.

After this step, the LPF resins were prepared using lignin to replace 50 wt% of the phenol. Lignin, NaOH (0.65 mol equivalent based on total acidic functionalities) and water were mixed at 60°C overnight, to ensure total dissolution. Formaldehyde (37% aqueous solution) was added according to maximum consumption – measured by the hydroxymethylation experiment as described earlier – and mixed at 60°C for 90 min to make sure that the lignin reacted with the formaldehyde. Then, phenol, NaOH (0.65 mol equivalent to phenol) and formaldehyde (37% aqueous solution; 0.67 mol equivalent to formaldehyde reactive sites in phenol) were added. Under mechanical stirring, the mixture was maintained at 60°C for 30 min to ensure hydroxymethylation. The temperature was increased to 73°C (measured directly from the reaction mixture). The viscosity was monitored by a viscometer, with the target viscosity being in the range of 3.5–4.5 poise (P). When ca. 4P was achieved, the reaction was stopped, and the resin was immediately cooled in an ice bath. A reference sample without a lignin increment – PF resin – was made following the same procedure as noted earlier. The resins were synthesized in two-neck sealed flasks to avoid formaldehyde losses.

Evaluation of LPF resins

Physical properties of the resins

The pH values of the LPF resins were measured at 25°C using a digital pH meter. Gel times were measured after preparation of the resins. Starting at room temperature, about 0.5 g of each resin was placed in a glass test tube and immersed in an oil bath at 100 ± 2°C. The resin was stirred continually with a glass rod until the gel point was reached, when no further stirring was possible. Gel time was measured by using a stop-watch.

Measurement of the molar mass with size exclusion chromatography (SEC)

The molar mass measurements of the lignin fractions and resins were performed by SEC using an alkaline eluent (0.1 M NaOH). For the

molar mass measurements, the samples were diluted with 0.1 M NaOH for the measurement concentration. In all cases, the samples were filtered (0.45 μm) before the measurement. The SEC measurements were performed in 0.1 M NaOH eluent (pH 13, 0.5 ml min⁻¹, T = 25°C) using PSS MCX 1000 and 100000 Å columns with a pre-column. The elution curves were detected using a Waters 2998 Photodiode Array detector at 280 nm. The molar mass distributions (MMDs) were calculated against polystyrene sulfonate (8 $\times$ PSS, 3420–148500 g mol⁻¹) standards, using the Waters Empower 3 software.

Formaldehyde and phenol by GC-MS

Free formaldehyde was analyzed as oxime by using the Agilent 7697A Headspace Sampler coupled with Agilent 7890B gas chromatography, and the compounds were detected using a micro-electron capture detector (HS-GC-ECD). For calibration, a stock solution containing formaldehyde in water was prepared at a concentration of 1000 ppb. The calibration range was 5–40 ppb and calibration solution dilutions were done in water. An aqueous solution of the derivatization agent O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA) (Sigma-Aldrich) was prepared at a concentration of 6 g l⁻¹. One hundred microliters of PFBOA solution (6 g l⁻¹) and 10 ml of diluted sample were placed in a 20-ml glass vial and sealed with a crimp cap (Agilent), and run using HS-GC-ECD. For hydroxymethylated lignin and resin samples, the free formaldehyde measurements were performed by HS-GC-ECD using a HP-5 capillary column, 50 m $\times$ 0.32 mm $\times$ 1.05 μm (J&W Scientific, Folsom, CA, USA). Helium was the carrier gas at a flow rate of 1.0 ml min⁻¹. For ECD, nitrogen make-up gas was applied at a flow rate of 30 ml min⁻¹.

Phenol was analyzed from 10-mg samples of the resins. The samples were directly trimethylsilylated in pyridine (0.2 ml) with a 0.4-ml mixture (3:1) of *N,O*-bis(trimethylsilyl)trifluoroacetamide and trimethylchlorosilane, after addition of 3-methoxyphenol as the internal standard. The trimethylsilylated samples were then analyzed by GC-MS, using an Agilent 6890 series GC system, equipped with an Agilent 5973 mass selective detector and a DB-5 MS capillary column (30 m $\times$ 0.25 mm, film thickness 0.25 μm). The temperature program applied was 1 min at 70°C, 10°C min⁻¹ to 300°C, and 9 min at 300°C. A split ratio of 50:1 was used in the injection. The phenol concentrations were calculated from the peak areas, with the help of a calibration curve (for phenol concentrations from 20 to 60 g l⁻¹). The analyses were performed in triplicates.

Automated bonding evaluation system (ABES)

The bonding strengths of five replicates of each LPF resin (50 wt% replacement) were tested using the ABES (Adhesive Evaluation Systems, Inc., Corvallis, OR, USA) equipment. Matched, conditioned silver birch (*Betula pendula* Roth) rotary cut veneer plies (20 $\times$ 150 $\times$ 0.8 mm) were used. Using a micropipette (HandyStep electronic, BRAND GMBH + CO KG, Wertheim, Germany), each resin was applied to an area of 4 $\times$ 20 mm² at one end of the veneer plies to give a resin spread rate of ca. 237 g $\cdot$ m⁻². The shear strength was measured at three different pressing temperatures with a fixed press time of 90 s, based on which 150°C was chosen to be analyzed at various pressing times (45, 90, 180, 300 and 480 s). The press pressure was 2.0 MPa. All resins were tested the day following their preparation.

Thermal behavior evaluation of the resins

Thermal properties of the resins were studied by thermogravimetric analysis (TGA). TGA was carried out in a Netzsch STA 449F1 under a nitrogen atmosphere at 20 ml min⁻¹. The weight loss (TG) and the

mass loss rate (DrTG) were determined. About 5 mg of the sample was heated from 35°C up to 800°C at 10°C min⁻¹.

Two-dimensional heteronuclear single quantum coherence NMR spectrum (2D HSQC NMR)

In order to investigate the reactions of lignin during the synthesis of LPF resin, the relative amounts of different structural units were characterized by volume integration of the signals representative to those structures observed in a 2D HSQC NMR spectrum. 2D HSQC NMR spectra were recorded using a Bruker AVANCE III 600 NMR spectrometer with a magnetic flux density of 14.1 T, and equipped with a cryogenically cooled 5-mm TCI probe head with inverse geometry (i.e. optimized for proton signal detection). A sensitivity-enhanced pulse program (hsqcetgpsisp2.2) that utilizes adiabatic pulses on carbon channel was used in acquisition. All samples were first freeze-dried, after which they were dissolved in D₂O (Sigma Aldrich, 99.96% deuterated), with a concentration of 80 mg in the 600- μl sample volume. Recorded spectral widths were 14 ppm (180 ppm) for proton (carbon), spanning a range from -2 to 12 ppm (0–180 ppm for carbon). The average value for one-bond J-coupling between protons and carbons was set as 145 Hz. The number of scans was 128 for each 256 increments in the indirect detected dimension, delay between successive scans was 1 s and acquisition time was 120 ms. Prior to Fourier transformation, the data in the directly detected dimension were zero-filled to 2048 real data points; for ¹³C dimension, the data were zero-filled to 1024 points. Gaussian window functions were used for both dimensions. All data were processed using Bruker BioSpin's TopSpin 3.5 software. The integrals were normalized to the integral of methoxyl signal, as the methoxyl group has been considered to be the most stable structure in the present reaction conditions (Yelle and Ralph 2016). The units in PF resin correspond to ratios between CH₂OH and methylene bridges (ratios are per 100 methoxyls). The integration precision was estimated by repeating the integration process (*n* = 10) with varied integration areas. The relative error for integral values was found to be 3%. Note that comparison between raw material types (hardwood, softwood and phenol) is not relevant due to their different degrees of methoxylation.

Results and discussion

Physicochemical characterization of lignin fractions and evaluation of their hydroxymethylated forms

Hardwood kraft lignin fractions obtained from a simple acid fractionation process exhibited different compositions (Table 1). The carbohydrate amounts were very low and similar among the fractions (see also Supplementary material). Regarding the total lignin content, fractions obtained at pH 5 and 3 exhibited a higher purity of 94.1 and 94.9%, respectively. These variances among the fractions make them very attractive to be evaluated in PF resins, as they come from the same source but present specific characteristics.

The number of hydroxyl groups in aliphatic, phenolic and carboxylic acid moieties (Table 1) were determined from the ^{31}P NMR spectra after derivatizing the hydroxyl groups in the lignin samples with phosphorus-containing reagents (Balakshin and Capanema 2015). As a consequence of the stepwise fractionation process used, all types of phenolic units (S, G and H) increased gradually in the fractions obtained at lower pH (5 and 3). Furthermore, with the increasing G and H content at fractions 5 and 3, the number of theoretical reactive sites increased as a consequence. Similar numbers of reactive sites have been estimated for lignins isolated from a number of different lignocellulosic sources and reported in the literature, such as corncob (1.72 mmol g^{-1}) (Yang et al. 2015), poplar wood ($0.91\text{--}1.39 \text{ mmol g}^{-1}$) (Yang et al. 2014), distinct hardwood lignins ($0.65\text{--}1.37 \text{ mmol g}^{-1}$) and softwood kraft lignin (2.36 mmol g^{-1}) (Balakshin and Capanema 2016).

The number of theoretical reactive sites was first calculated based on ^{31}P NMR. Then, the maximum formaldehyde consumption was determined by the hydroxymethylation reaction in the presence of excess formaldehyde. At this point, methyl guaiacol was used as a model compound. As can be observed in Figure 1, methyl guaiacol consumed 96% of the theoretical number of reactive sites. This confirms that formaldehyde is not consumed to a significant extent in competing reactions, e.g. via the Cannizzaro mechanism, and the formaldehyde consumption can be used as a means to evaluate its reactivity with lignin. The formaldehyde consumptions determined for all the lignins were in the same range; such an observation could also be tracked by 2D NMR of hydroxymethylated (no phenol addition) samples (see Supplementary material).

Figure 1: Monitoring formaldehyde consumption by hardwood lignin fractions, softwood lignin and methyl guaiacol model compound.

The empty bar represents the theoretical number of reactive sites (measured by ^{31}P NMR) and the solid bar represents the actual formaldehyde consumption (as described in the section “Hydroxymethylation and resin synthesis”).

Furthermore, for hardwood fractions, the theoretical reactive sites were very close to the actual formaldehyde consumption, while for softwood the actual consumption was only one quarter of the theoretical calculation.

Despite the fact that softwood lignin exhibits a higher number of theoretically reactive sites with formaldehyde, they do not seem to be fully available. This steric barrier may be due to the significantly higher molar mass of softwood lignin (Table 2). Thus, even if hardwood lignin only has a few reactive sites, they mostly react with the added formaldehyde. Balakshin and Capanema (2016) observed recently that the amount of reactive sites is not the only important factor in LPF blends, suggesting that other characteristics such as steric factors and the flexibility of lignin macromolecules could play a more important role.

Evaluation of the synthesized LPF resins

The LPF resins were prepared by substituting 50 wt% of the phenol with lignin. The viscosity of the resins was a stipulated parameter to stop the resin synthesis when it reached about 4P. The pH and gel time measured for LPF resins were very similar to those of PF resin. The pH values were all about 11–12 and the gel times were 31–43 min (see Supplementary material). The content of free-formaldehyde was very low for PF resin ($<0.05\%$) and all synthesized LPF resins ($\leq 0.23\%$). This is an encouraging result for such LPF resins as other studies have reported high residual formaldehyde when phenol was substituted by lignin (Lee et al. 2011; Ghorbani et al. 2016; Kalami et al. 2017). The analyses indicated that free-phenol concentrations in the resins were in the range of $0.5\text{--}1.5 \text{ g l}^{-1}$. Such results could also be considered satisfactory, mainly if it is compared to other studies using lignin to substitute phenol (Zhang et al. 2013; Pang et al. 2017).

Table 2: Weight average (Mw) and number average (Mn) molar mass and PDIs of starting lignins and PF/LPF resins.

	Lignins			Resin (50 wt% replacement)		
	Mw	Mn	PDI	Mw	Mn	PDI
9	1870	970	1.9	2370	992	2.4
7	1840	960	1.9	2250	953	2.4
5	1850	980	1.9	2290	982	2.3
3	1730	960	1.8	2100	960	2.2
Softwood	4100	2100	2.0	5180	970	5.3
PF resin				4780	1300	3.7

LPF, Lignin phenol-formaldehyde; PDI, polydispersity; PF, phenol-formaldehyde.

The calculated average molar mass values of the resins as well as starting lignins were obtained by SEC and are given in Table 2. Among the starting lignins, fraction 3 shows a slightly lower weight-average molar mass (M_w), and softwood lignin presents much higher M_w compared to hardwood fractions. Despite these differences, the increase in the M_w of all resins (ca. 21–27%) was in the same range. This shows a similar degree of polymerization during LPF resin synthesis irrespective of the molar mass or wood origin.

Clear differences among resins were better observed in the MMDs of LPF and PF resins. Figure 2 shows rather similar distributions for LPF resins from hardwood lignin fractions. On the other hand, these fractions showed pronounced differences, when compared to softwood LPF resin and PF resin. The hardwood lignin resins show clearly narrower MMDs compared to softwood lignin, which yielded a resin with a significant fraction of high molar mass.

There are some controversies in the literature about the effect of molar mass on resin synthesis. On the one hand, it is believed that due to the larger number of phenylpropane units per molecule in higher molar mass lignin, the chances of contributing to polymerization are higher, compared to monomeric and dimeric fractions (Tejado et al. 2007). On the other hand, low molar mass molecules, characterized by cleaved main internal linkages, would be more suitable to condense with formaldehyde as the cleavage introduces more active sites (Pang et al. 2017).

These molar mass differences as such cannot be used as a predictor of the performance of LPF resins. From the ABES results, all LPF resins at distinct temperatures and press times (Figure 3a and b, respectively) in general showed a comparable bonding strength.

The increment of 50 wt% of lignin in the phenolic resins led to a reduced bonding performance in the LPF resins when compared to PF (without lignin) in all cases, which was expectable. A similar pattern with increasing

Figure 2: Molar mass distribution of LPF resins and PF resin.

Figure 3: Bonding strength of resins at three different temperatures and a fixed press time at 90 s (a) and bonding strength of resins at five different press times and a fixed temperature at 150°C (b).

bonding strength as the temperature was increased can also be noticed (Figure 3a). Besides, for most of the resins, the bonding strength increased with press time at 150°C (Figure 3b) and this corroborates with the literature (Balakshin and Capanema 2016; Ghorbani et al. 2016). Among the hardwood resins, differences in composition (high purity of fractions 5 and 3) and the small M_w of fraction 3 were not enough to highlight a better performance of a specific fraction when incorporated into PF resin. Such observations corroborate with earlier studies in which different lignins (with distinct structures, purities and molar masses) were tested and the bonding strengths were found to be similar (Yang et al. 2015; Balakshin and Capanema 2016; Pang et al. 2017). This indicates that the correlation of an isolated feature of lignin with its performance in LPF is not straightforward.

The thermal behavior of PF and LPF resins was evaluated by TG and their DrTG (Figure 4a and b, respectively). Post-curing, thermal reforming and ring stripping are the three major thermal events reported for PF resins (Zhang et al. 2013; Chaouch et al. 2014). From the thermogram profiles, it is possible to observe that LPF resins degraded in a broad temperature range.

The initial weight loss in the temperature range of 90–300°C for all resins included water, phenol and

Figure 4: (a) Thermograms (TG) and (b) derivative thermograms (DrTG) of PF and LPF resins.

formaldehyde evaporation triggered by the reaction of hydroxymethyl groups with each other (Khan et al. 2004). In this initial stage, LPF resins showed a higher thermal stability than PF resins.

The mass loss observed in the second event, at 390°C for PF resin, might be due to the loss of water as a consequence of the breakdown between phenolic-OH and methylene linkages (Khan et al. 2004; Zhang et al. 2013), as well as between two hydroxyl functional groups (Lee et al. 2011). This peak was shifted to a lower temperature in the presence of lignin (350°C). At this point, the higher molar mass softwood lignin (Table 2) showed higher thermal stability among the LPF resins. The lower chemical activity of lignin compared to phenol and the relatively high substitution level of phenol by lignin, may lead to weak cross-linked networks, which may affect the thermal stability of the LPF resins (Chaouch et al. 2014). Besides, from ca. 300°C, aliphatic side chains of lignin start to break down, up to cleavage of more stable carbon-carbon bonds, which arises at 370–400°C (Nassar and MacKay 1984). The third thermal event at 500°C for PF resin was the most drastic thermo-degradation. This peak was also shifted to a lower temperature when phenol was substituted by 50 wt%

lignin. This last event is associated with released methane and carbon monoxide formed by the reaction of eliminated hydrogen and water with methylene, respectively (Lee et al. 2011). From 600°C, the lower, but continuous, rate of weight loss is caused by the dehydrogenation of aromatic structures in the LPF resins (Khan et al. 2004).

Among all resins, including PF without lignin, the LPF resin from fraction 3 showed the highest thermal stability in the initial stage. On the other hand, this fraction showed a wider and faster decomposition pattern from 250°C and lower char content at 800°C. Such thermal behavior can be associated with its lower molar mass (Table 2) (Lee et al. 2011). From about 250°C, PF resin had better thermal resistance than all the LPF resins. The higher hydroxymethyl groups and methyl bridges (Figure 5) confirmed from 2D NMR might be associated with such an observation.

As can be seen in Figure 5, the frequency of methylol (CH_2OH) substitution is slightly higher in the pH 7 and 9 samples compared to pH 3 and 5. The same order of reactivity is also detected for the formation of ortho-para and para-para methylene bridges ($\text{CH}_2\text{-op}$ and $\text{CH}_2\text{-pp}$). In the case of softwood lignin, only traces of methylene bridges were detected in comparison to the frequency of methylol substitution (see also Supplementary material). Such observation could be related to steric hindrance, high molar mass, the rigid polymer and intermolecular associations. PF resin had the highest substitution, as expected, due to its higher reactivity. The easier formation of methylene bridges in hardwood resins may thus compensate for the lower degree of hydroxymethylation (lower frequency of CH_2OH groups) in addition to the narrow MMD (when compared to softwood) and this could explain their good performance as adhesives, observed in bonding strength tests (Figure 3).

Conclusions

In this study, hardwood lignin fractions were tested as a 50 wt% substitute for phenol in PF resins. Softwood lignin was also tested in LPF resins and compared with the hardwood lignin samples. The hardwood fractions consumed formaldehyde close to the theoretical calculation (^{31}P NMR), whereas softwood lignin consumed only about 1/4 of the theoretical value. Low values of free formaldehyde in LPF resins were achieved by applying in the formulation the determined maximum amount of consumed formaldehyde, instead of the theoretically calculated amount. When the bonding strength of resins was evaluated by ABES, hardwood LPF resins performed in a

Figure 5: LPF resins evaluated by 2D HSQC NMR.

The frequency of CH₂OH groups indicates the maximum amount of methylol substitution in the first stage of resin reaction due to the addition of formaldehyde. The presence of methylene bridges [CH₂-op (ortho-para) and CH₂-pp (para-para)] indicates a second stage of resin polymerization. The units are relative to the methoxyl signal integral of each resin. Comparison between different lignin types is not relevant due to their different degrees of methoxylation. The units in PF resin correspond to ratios between CH₂OH and methylene bridges.

similar way to that of softwood LPF resin. Furthermore, up to 200°C, LPF resins showed higher thermal stability than PF resin. Despite the fact that softwood lignin exhibits a higher number of reactive sites, they do not seem to be fully available. The higher molar mass of softwood lignin and steric effects might decrease its polymerization, confirmed by the lower level of methylene bridge formation observed by 2D HSQC NMR. Thus, even if hardwood lignin has only a few theoretically reactive sites, they are mainly reactive with formaldehyde and also polymerize easily. It may be also favored by its lower molar mass.

Furthermore, a practical outcome can be derived from our results: hardwood kraft lignins present no disadvantage over the softwood counterpart for LPF application. This creates opportunities for the industry's efforts toward value-added applications for such economically important technical lignin. Nonetheless, additional comprehensive studies on the fundamental structure-performance correlations are still required to fully understand the lignin behavior when applied to LPF resins.

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