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Lignin-phenol-formaldehyde resin adhesives prepared with biorefinery technical lignins

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ABSTRACT: In this study, four biorefinery technical lignins were used to synthesize lignin–phenol–formaldehyde (LPF) resin adhesives with a proposed formulation that was designed based on accurate analysis of the active sites in lignin with ^{31}P nuclear magnetic resonance (NMR). The properties of the LPF resin adhesives and the plywoods prepared with them were tested. The structural features and curing behavior of the LPF resin adhesives were thoroughly investigated by solution- and solid-state ^{13}C NMR. Results indicated that the proposed formulation exhibited favorable adaptability for all four of these technical lignins for synthesis of LPF resin adhesives. High-performance plywood with low emissions of formaldehyde could be successfully prepared with the synthesized LPF resin adhesives. All the LPF resin adhesives exhibited similar structure and curing behavior with the commercial phenol–formaldehyde (CPF) resin adhesive. However, the LPF resin adhesives showed relatively higher curing temperatures as compared with the CPF resin adhesive. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42493.

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INTRODUCTION

Phenol–formaldehyde (PF) resin is classified as an exterior adhesive due to its resistance to water, weathering, and high temperatures in a cured glue line.[1] It is widely accepted that formaldehyde emissions from panels used in interior applications is a leading cause of sick building syndrome (SBS) in indoor environments.[2] However, formaldehyde emissions from PF resin-bonded wood products are very limited.[3] Thus, the PF resin adhesive is more suitable for interior applications such as decorative panels and furniture. However, PF resin adhesives have not been widely used in interior applications because of the high price of phenol, which is derived from petroleum.[4] In China, urea formaldehyde resin remains the dominant adhesive product used in indoor panels because it is cheap; however, it emits a higher level of formadehyde.[5] Another factor that has discouraged the use of PF resin adhesives is that exposure to phenol during the processes of adhesive synthesis and plywood production can be harmful to humans. Finally, the ongoing shortage of petroleum products likely will cause the price of phenol to continue to rise. All these factors restrict the sustainable development of the PF resin industry. Therefore, it is important to find a substitute for phenol that is of low cost and nontoxic.

Lignin is one of the main constituents of lignocellulosic biomass (15–30% by weight, 40% by energy), together with cellulose and hemicelluloses.[6] A large amount of technical lignins are obtained as by-products (technical lignin) in pulp and paper industry. In addition to the large quantity of industrial lignin produced annually as the waste product of the pulp and paper industry, the emerging biomass refinery industry also produces enormous amounts of technical lignin.[7] It is important to define the role that biorefinery technical lignin can play in supporting the economic health of the biorefinery industry. Most of the feedstocks for biorefinery industry are obtained from agricultural and forestry wastes.[8,9] Thus, the exploitation of biorefinery technical lignin for industrial application can indirectly promote the improvement of economic benefits of agriculture. As the most abundant renewable aromatic amorphous biopolymer in nature, lignin is expected to play an important role in the near future as a substitute for nonrenewable petrochemicals for the production of bioproduct.[10,11] The properties, such as readily available, high abundant, less toxic, and less expensive, make the technical lignin be regarded as a promising substitute for phenol in PF adhesive synthesis.[12] The process of substituting lignin for phenol may occur as follows: lignin and phenol undergo hydroxymethylation by reacting with formaldehyde in the presence of NaOH (the catalyst); then, the hydroxymethylated lignin and phenol derivatives are copolymerized to form a lignin–phenol–formaldehyde (LPF) copolymer.[13]

Numerous attempts have been made to use various lignins as substitutes for phenol in the formation of phenol–formaldehyde

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resins.[14–18] However, the complex components and low reactivity of conventional technical lignins make it difficult to use these lignins in LPF resin adhesive production.[19] A great deal of researches have been conducted to modify lignin to improve its chemical reactivity. The most commonly utilized reactivity-enhancing processes are hydroxymethylation, phenolation, and demethylation.[8,14,20,21] Phenolation treatment, in either alkaline or acid conditions, is a promising method that may enhance the reactivity of the lignin in the synthesis of LPF resin adhesive. An alkaline solution is a better reaction medium than an acid environment in terms of the subsequent synthesis of LPF resin adhesive. Phenolation adds phenol molecules into the lignin structure and could render the lignin easy to incorporate into the resin, as described in our previous work.[22] However, the common weaknesses of these LPF adhesives are high formaldehyde emissions, low bond strength when the lignin substitution rate is high, and product properties that are not consistent across different batches. It is therefore important to discover a formulation that will enhance the properties of the LPF resin adhesives, achieve high bond strength, and create plywood with low formaldehyde emissions. In terms of the chemical reaction, the active sites (mainly *ortho* position of the phenolic hydroxyl in the aromatic ring) of the technical lignin should be regarded as the basis for LPF resin adhesive formulation design.

In this study, four biorefinery technical lignins—corn cob lignin (L_1), two different kinds of poplar wood lignin (L_2 and L_3), and wheat straw lignin (L_4)—obtained from three different biorefinery mills were used to produce LPF resin adhesive as a partial substitution for phenol. The active sites and structural features of these four technical lignins were given in the previous report of this research series.[22] A special formulation was designed based on active site analysis of the technical lignins. This formulation was designed and tested to explore the feasibility of using each of these four biorefinery technical lignins as substitutes for phenol in the synthesis of high-performance LPF resin adhesives. The performance of each LPF resin adhesive created was characterized using corresponding standards. The structural properties of the LPF adhesives and their curing behaviors were characterized using the solution- and solid-state ^{13}C NMR techniques, respectively. The curing characteristic of the uncured LPF adhesives was analyzed using differential scanning calorimetry (DSC). A commercial phenol–formaldehyde (CPF) resin adhesive was used as a control sample.

MATERIALS AND METHODS

Materials

The four technical lignins used in this study are corn cob lignin (L_1), two kinds of poplar wood lignin (L_2 and L_3), and wheat straw lignin (L_4)—each was described in detail in the previous report of this research series. As reported in the previous study,[22] the active site values of L_1, L_2, L_3, and L_4 were 1.72, 0.81, 1.39, and 0.99 mmol g^{-1}, respectively. The weight-average molecular weights (M_w) of the four technical lignins were measured as 3258, 1830, 1840, and 4330 g mol^{-1} for L_1, L_2, L_3, and L_4, respectively. In addition, all the four technical lignins exhibited relatively narrow molecular weight distributions (<2.1). Because the biorefineries processed a single type of raw material and applied stable technology, the properties of biorefinery technical lignins produced were very similar among the different batches. This makes the lignins well-suited for industrial applications. The phenol, formaldehyde solution (37%), sodium hydroxide, and urea used were reagent grade and used as obtained without purification. The commercial phenol–formaldehyde (CPF) adhesive used was purchased from Beijing Taier Chemical Co., Ltd.

Preparation of LPF Resin Adhesives According to Proposed Formulation

To effectively reflect the concerned information when technical lignin was used in LPF resin adhesive synthesis, all the LPF resin adhesives were synthesized by batch copolymerization with a lignin substitution rate of 50% (in relation to the mass of phenol). The total formaldehyde consisted of two parts: one part was calculated according to the molar ratio of phenol to formaldehyde, and the other part was calculated based on the number of active sites of each technical lignin (based on accurate analysis of the active sites in lignin with ^{31}P NMR[22]). These calculations were used to discover what proportion of 1 g of technical lignin equaled the weight of pure phenol, which we consider hypothetical pure phenol. The molar ratio of this hypothetical pure phenol to formaldehyde was the same as that of pure phenol to formaldehyde. The mole ratio of the phenol to formaldehyde was set as 1 : 1.8 in this study. In the first step, phenol and technical lignin were mixed in a three-necked flask. Then, the appropriate amount of NaOH solution (30% wt) was added to adjust the pH value to 9–10. Next, the mixture was heated to 90°C and held at the temperature for 1 h. The temperature of the mixture was then dropped to 80°C, and 70% of the total formaldehyde and NaOH solution (30% wt) was added. This mixture was kept at 80°C for 1 h. The remaining 30% of the total formaldehyde and NaOH solution (30% wt) was added, and that mixture was kept at 80°C for 1 h. Finally, the temperature of the mixture was decreased to 65°C, and the solution of NaOH (30% wt) and urea (5% of the total weight of phenol and technical lignin) was added, and this mixture was held at 65°C for 30 min. When the reaction was complete, it was rapidly cooled to 40°C to yield the LPF adhesive.

Preparation and Characterization of Plywood

Three-layered poplar plywoods ($400 \times 400 \times 4.5$ mm) were prepared simulating actual industrial parameters. Wheat flour with a proportion of 10% wt to the CPF/LPF adhesives was added into the adhesive as filler. The core poplar veneer was coated with a 150 g m^{-2} adhesive on each side. The plywoods were hot-pressed at 145°C under 1.0 MPa. The hot-pressed time was 1.5 min/mm. The bonding strength and formaldehyde emissions of the plywoods were measured according to the Chinese National Standard (GB/T 17657-2013). Each of the prepared plywoods was cut into 12 specimens (25×100 mm, "A-type" specimen) for evaluating its bonding strength. The bonding strength was characterized after 4 h immersed in boiling water, dried at 60 ± 3°C for 20 h and immersed again in boiling water for 4 h. All treated specimens were chosen for testing for bonding strength by stretching loading on a WDS-50KN mechanical testing machine (CN). The treated specimens were tested in a wet state and the average bonding strength

Table I. Properties and Plywood Performances of CPF and Various LPF Resin Adhesives

	Adhesive properties					Plywood performances	
Adhesive	pH	Viscosity (mPa·s)	Solid content (%)	Free formaldehyde (%)	Free phenol (%)	Bonding strength (MPa)	Formaldehyde emission (mg L^{-1})
CPF	12.61	132.9	43.96	0.241	0.11	1.53 (0.147)[b]	0.25
L_1PF	11.86	1900.0	54.93	0.211	0.84	1.18 (0.084)	0.19
L_1PF[a]	–	445.0	45.00	–	–	1.11 (0.077)	0.27
L_2PF	11.69	459.5	55.23	0.274	0.90	1.08 (0.110)	0.22
L_3PF	11.71	889.0	54.36	0.219	0.70	1.08 (0.100)	0.37
L_4PF	11.88	1447.5	50.98	0.248	0.65	0.95 (0.172)	0.24
GB/T 14732	≥7	≥60	≥35	≤0.3	≤6	≥0.7	≤0.5

[a] This product was obtained by adjusting the solid content of L_1PF to 45%.
[b] The number in the parentheses was the standard deviation of the bonding strength of the plywood sample.

value of all the 12 specimens was recorded as the bonding strength of a plywood sample.

Characterization of CPF and LPF Adhesives

The pH, viscosity, nonvolatile content, free formaldehyde, and free phenol of the LPF adhesives were determined in accordance with the Chinese National Standard (GB/T 14704-2006). The uncured adhesives were freeze-dried before liquid-state ^{13}C-NMR and DSC analysis. For the solution-state ^{13}C-NMR analysis, the 80 mg freeze-dried uncured adhesives were dissolved in 0.5 mL of D_2O. The spectra were obtained with a Bruker AVIII 400 MHz spectrometer (GER) at 25°C. For the solid-state ^{13}C-NMR analysis, the cured adhesives were prepared by treating uncured adhesives at 120°C for 2 h in an air convection oven, as described by other published articles.[23,24] The uncured adhesives were freeze-dried before analysis. The solid-state cross-polarization/magic-angle spinning (CP/MAS) ^{13}C-NMR spectra of the uncured and cured adhesives were acquired at 100 MHz using a Bruker AV-III 400M spectrometer (GER), in accordance with techniques described in a previous article.[25] DSC analysis of the freeze-dried uncured adhesives was conducted on a Shimazu DSC-60 (JP) in a nitrogen atmosphere. Scans were run at heating rates of 5, 10, 15, and 20°C min^{-1}, respectively. The scanning temperature ranged from 40 to 200°C. The flow rate of nitrogen was 20.0 mL min^{-1}.

RESULTS AND DISSCUSSION

Performance of LPF Resin Adhesives

The prepared LPF resin adhesives using various biorefinery technical lignins were all dark-brown aqueous solutions with a water solubility that was satisfactory. Table I shows the pH, viscosity, nonvolatile contents, free formaldehyde, and free phenol contents of the LPF and CPF resin adhesives. The bonding strength and formaldehyde emissions of the plywoods were also characterized.

Although the natural polyphenol structure of lignin was similar to phenol–formaldehyde resin, the complex molecular structure and lower reactivity made the performance of the LPF resin adhesives significantly different from the CPF resin adhesive. Considerable difference in properties was also found among the various LPF resin adhesives, although the same formulation method (the same proportion of raw materials but different technical lignins) and synthesis process was applied. The viscosity of all the LPF resin adhesives was higher than that of the CPF resin adhesive—especially those of L_1 PF (1900.0 mPa s) and L_4 PF (1447.5 mPa s), which were synthesized with lignin of higher molecular weights. It is well known that such a high viscosity will obviously bring problem in the application. However, the viscosity of the synthesized LPF in this study could be adjusted to an acceptable level using water without obvious blemishing the performance of the final products as shown in Table I. The solid content of all the LPF resin adhesives was more than 50%, higher than that of the CPF resin adhesive. This was more favorable to form a continuous bond line between the two cementing limiting surfaces. The free-formaldehyde content of all the LPF resins adhesives was similar to that of the CPF resin adhesive, and less than the Chinese National Standard (GB/T 14732-2006) limitation (≤0.3%). This implied that the formaldehyde fully participated in the hydroxymethylated reaction during the synthesis process, and that only a slight amount of formaldehyde remained in the adhesive products. The content of free phenol in all the LPF resin adhesives was higher than that of the CPF resin adhesive. This may be due to that part of the formaldehyde in the formulation was consumed via Cannizzaro self-oxidation reaction occurred during the synthesizing process.[26] However, the content of free phenol in the LPF adhesives was still far below the limit requirement of the Chinese National Standard (GB/T 14732-2006), as shown in Table I. Thus, all the LPF resin adhesives could be regarded as low-toxicity adhesives. The formaldehyde emissions of the plywoods bonded by the LPF resin adhesives were higher than that of the plywood bonded by CPF resin adhesive, but they were all below 0.5 mg/L and reached the requirement of E_0 grade (≤0.5 mg L^{-1}) plywood as identified by the Chinese National Standard GB/T 9846.3–2004. The bonding strength of the plywoods bonded using LPF resin adhesives was lower, because the lignin was generally less reactive than the phenol. A lignin unit tended to average two or less positions available for polymerization, while three positions (two *ortho* and one *para*) were available in the pure phenol.[14] However, the bonding strength of the plywoods bonded using LPF resin adhesives still met the standard for exterior-grade

panels (first grade, ≥0.7 MPa). The performances of the various LPF resin adhesives were stable, which could be reflected by the relatively low standard deviation (0.077–0.172) of the bonding strength of the plywood samples. It was found that the L_1PF had the best performance among all the LPF resin adhesives, which should be due to the high active sites and the high degree of lignin purity of L_1, as shown in the previous report of this research series.[22] L_2PF and L_3PF had almost the same bond strength. Interestingly, although L_4 had more active sites than L_2, the bond strength of L_4 was the lowest among the four LPF resin adhesives. This may be attributed to the high molecular weight of L_4, which was also a considerable factor that influenced LPF resin adhesive properties. Enough active sites could ensure that the technical lignin could be embedded in an LPF resin adhesive system. However, if the molecular weight of the technical lignin rose beyond a certain limit, the cured resin structure of the LPF resin adhesive would become inhomogeneous, and the inherent drawback of the lignin macromolecular structure would become clear, especially in a condition with a high substitution rate. In addition, the high molecular weight of the lignin would also restrict the penetration of the LPF resin adhesive in the veneer and thus reduce the strength of the cured bond line of the plywood.[27] Thus, the bond strength of the LPF resin adhesive synthesized using the high-molecular-weight lignin was lower than that made from low-molecular-weight lignin. The other properties of lignin, such as the carbohydrate and ash content, may also affect the performance of the LPF resin adhesive.[12] The relevance between the properties of the LPF resin adhesives and the physicochemical properties of the technical lignins was complex, and needs to be explored further.

The actual result indicated that this formulation (designed based on accurate analysis of the active sites in lignin with ^{31}P NMR) had perfect feasibility for various technical lignins. A reasonable formulation could undoubtedly ensure that the phenol, lignin, and formaldehyde could fully react with each other in suitable proportions. The LPF resin adhesives synthesized with the different biorefinery technical lignins based on this formulation exhibit some advantages, such as satisfying performance and low formaldehyde emission, and could be used as both exterior plywood and interior E_0-grade panels. In addition, the low-cost and low-toxic features of the technical lignins would further extend the scope of the applications of the LPF resin adhesive. Although some differences in performance could be found due to the different inherent properties of the biorefinery technical lignins, all four biorefinery technical lignins obtained from different biorefinery processes could be used as substitutions for phenol at a high substitution rate in LPF resin adhesive synthesis. The overall performances of the LPF resin adhesives synthesized in this study were equal to or even better than those of the optimal LPF products with a high substitution level reported by other researchers.[28–30]

Chemical Structure of Different Adhesives

To investigate the chemical structures of the LPF resin adhesives synthesized with various biorefinery technical lignins, solution-state ^{13}C NMR spectra of the various uncured adhesives after being freeze-dried were recorded. A CPF resin adhesive was also analyzed as a comparison. Figure 1 shows the ^{13}C NMR spectra of the uncured CPF and LPF resin adhesives. The signals are assigned according to previous literatures.[3,31–33] The LPF adhesives had NMR spectra similar to those of the CPF resin adhesive, suggesting that the LPF resin adhesives exhibited similar molecular structure as compared to the CPF resin adhesive. This result was in agreement with some previous publications.[34,35] The spectra of different LPF resin adhesives were also similar with each other. However, some special signals belonging to the lignin structures were found in the spectra of the LPF resin adhesives, due to the addition of technical lignins such as the —OCH_3 at 56 ppm at the 2 and 6 positions of the lignin in S units at approximately 104 ppm.

The spectra of all the uncured adhesives showed that the intensity of the peak at 40 ppm (*para–ortho* methylene bridges between phenolic units) was higher than that of the peak at 35 ppm (*para–para* methylene bridges between phenolic units), and that the intensity of the peak at 64 ppm (methylol group on the *para* positions of phenolic —OH) was lower than that of the peak at 60 ppm (methylol group on the *ortho* positions of phenolic —OH). This could be ascribed to the higher reactivity of the aromatic hydrogen at the *para* position of the phenolic —OH than that at the *ortho* position. At the initial stage of the resin adhesive synthesis process, the hydroxymethylated reaction mainly occurred at the *para* position of the phenolic —OH in phenol. The subsequent condensation reaction would also more easily occur between the *para* methylol group and the unsubstituted *para* position of the phenolic —OH in phenol. Thus, most of the *para* positions of the phenolic —OH in phenol were consumed to form *para–para* methylene bridges.

Although the content of the *ortho* methylol groups in phenol and lignin units was greater than that of the *para* methylol groups of the phenolic —OH in phenol, reactions between these groups and the unsubstituted *ortho* positions were relatively difficult to induce. Thus, as shown in the Figure 1, the signal at 29 ppm, which was assigned to the *ortho–ortho* methylene bridge between phenolic units, was extremely weak in the spectra of the LPF resin adhesives. Only a small portion of these groups could react with the remaining unsubstituted *para* positions to form *para–ortho* methylene bridges. A brief reaction mechanism is shown in Figure 2. A group of signals around 115–118 ppm in the spectra of the LPF resin adhesives were more complex than those of the CPF resin adhesive due to the incorporation of the technical lignin. In addition to the unsubstituted *ortho* and *para* positions of the phenolic —OH in the phenol and lignin units, the C_6 positions in the G units of lignin also had a strong signal in this region.

It was known that appropriate active sites in the adhesive would promote the curing process and control formaldehyde emissions in the cured adhesive. This occurred because the low number of unsubstituted active sites in the LPF resin adhesive (i.e., relatively high methylol —OH) caused the formation of more methylene ether bonds during the curing process, and these bonds released a large amount of formaldehyde during the plywood utilization stage.

The dominant peak at around 129 ppm is assigned to the substituted *ortho* and *para* carbon sites on the aromatic ring.

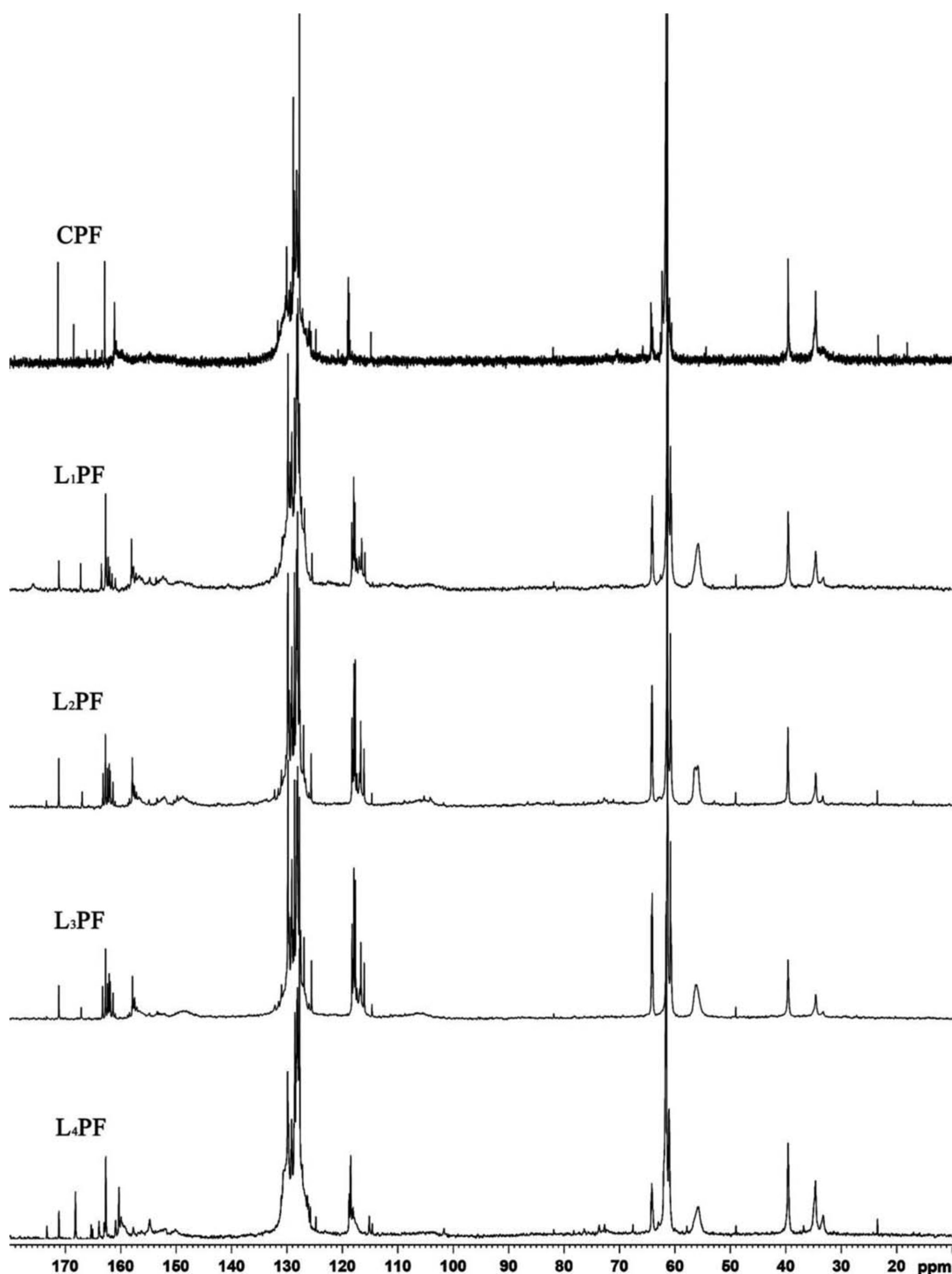

Figure 1. Liquid-state ^{13}C NMR spectra of various uncured LPF and CPF resin adhesives.

The signal at 163 ppm is assigned to the carbon on the aromatic ring to which methylene ether groups were connected. This implies that the free phenolic —OH in phenol and lignin could also be condensed with the methylol group. Thus, except for the reaction between *ortho* positions of phenolic —OH in lignin units, the reaction could also cause the lignin to become embedded in the adhesive system during the synthesizing process.

Curing Behavior of Different Adhesives

To explore the curing behavior of the various LPF resin adhesives, the uncured and cured adhesives were analyzed using solid-state CP-MAS ^{13}C NMR. The spectra are illustrated in Figure 3. Generally, the peak assignments of the ^{13}C CP-MAS NMR spectra of the PF resin are similar to those of the liquid-phase ^{13}C NMR spectra.[3]

The solid ^{13}C CP-MAS NMR spectra of the uncured adhesives were similar to that obtained by the liquid ^{13}C NMR method. However, the disadvantage of the solid-state ^{13}C NMR spectra was an overlap among different signals. The ^{13}C CP-MAS NMR spectra of different LPF resin adhesives were still very similar to each other. The signals at 56 ppm in the solid ^{13}C CP-MAS

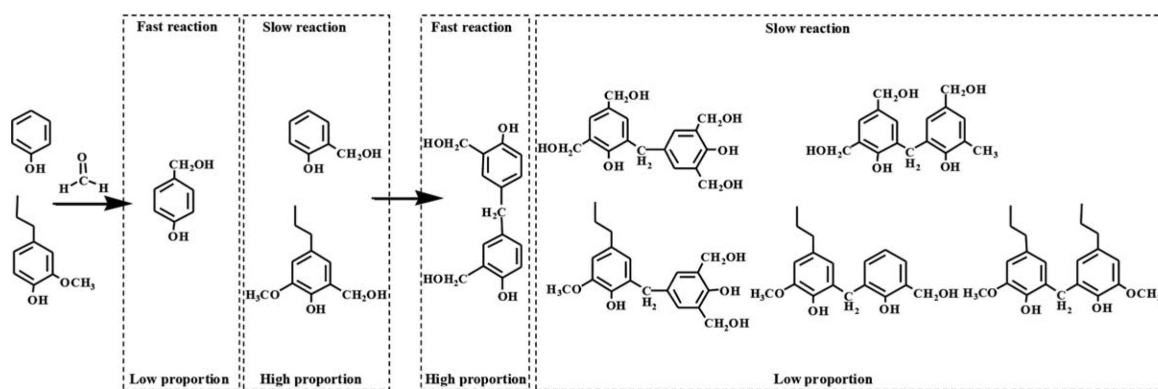

Figure 2. A brief graphical representation of synthesis mechanism of LPF resin adhesives.

NMR spectra of the uncured and cured LPF should belong to the —OCH_3 in lignin. No signals at 55 ppm could be found in the spectra of uncured and cured CPF due to the absence of lignin. The new peaks at 80 and 180 ppm in the solid-state ^{13}C NMR spectra of the uncured adhesives were considered spinning side bands.[3] An obvious peak around 150 ppm in the solid ^{13}C NMR spectra of both uncured and cured adhesives spectra is assigned to the free phenolic —OH in the aromatic ring. As compared with the spectra of all the adhesives before curing, the signals around 29–40 ppm increased obviously along with the decrease of the signals around 60–64 ppm, which were assigned, respectively, to the methylol groups and the methylene bridges between aromatic rings after the curing process. The signals around 29–35 ppm increased more obviously. The unsubstituted active sites around 115–118 ppm also decreased significantly. These results indicated that the main reaction during the curing process was the condensation reaction between *ortho* methylol groups and the remaining unsubstituted *ortho* and *para* positions. The considerable decrease of the peaks around 115–118 ppm in the spectra of the cured LPF resin adhesives indicated that all condensation reactions during the curing process were thoroughgoing and the added lignin had been embedded in the cured LPF resin adhesives. The spectra of the cured adhesives showed that the signal at 163 ppm also decreased significantly. This indicated that the methylene ether bridges were broken during the hot-pressing process. The curing behaviors of these four LPF resin adhesives were similar to each other, and no obvious differences were found as compared to the CPF resin adhesive. All these results indicated that the LPF resin adhesives produced according to the formulation (designed based on accurate analysis of the active sites in lignin with ^{31}P NMR) was reasonable. The different final performances of various LPF resin adhesives may be also caused by other factors (such as molecular weight and inherent molecular structure) of the various biorefinery technical lignins.

Adhesive Curing Kinetic Analysis

To investigate the curing kinetics of different LPF resin adhesives, DSC kinetic analysis started by obtaining kinetic parameters from the peak temperatures of DSC scans conducted at different heating rates. The curing characteristic temperatures could be determined from peak temperatures obtained from nonisothermal DSC measurements at various heating rates through linear-regression analysis. The intercept at the heating rate of 0°C min^{-1} was regarded as the characteristic curing temperature under the isothermal condition.[24,36] The activation energy could also be obtained—using both the Flynn–Wall–Ozawa and Kissinger methods—from the dependence of the peak temperature on the heating rates.[37] The peak temperatures obtained at different heating rates and their corresponding calculation results are shown in Table II. The DSC curves of the various LPF resin adhesives at the heating rate of 10°C min^{-1} are displayed in Figure 4.

As shown in Figure 4, the exothermic peaks of the all the LPF adhesives were higher than that of the CPF adhesive, indicating that the LPF adhesives underwent a reduction of its reactivity

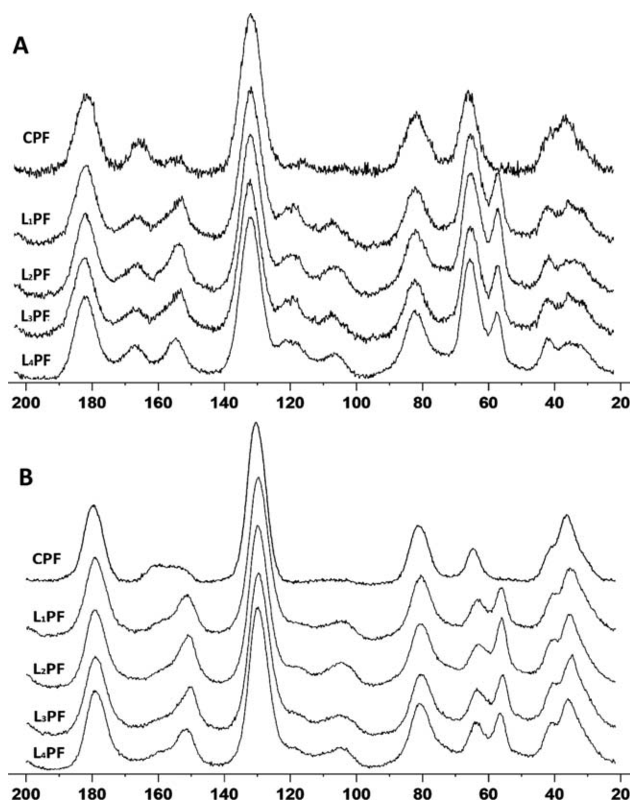

Figure 3. Solid-state CP-MAS ^{13}C NMR spectra of various (A) uncured and (B) cured LPF and CPF resin adhesives.

Table II. Thermal Cure Kinetics Parameters of CPF and Various LPF Resin Adhesives

Sample	T_p (°C)				Curing temperature (°C)[a]	E_k (kJ mol^{-1})[b]	E_o (kJ mol^{-1})[c]
	5°C min^{-1}	10°C min^{-1}	15°C min^{-1}	20°C min^{-1}			
CPF	122.8	131.1	136.5	141.3	117.7 (0.9824)	96.6 (0.9956)	103.1 (0.9970)
L_1PF	129.3	137.1	142.8	147.9	123.9 (0.9899)	98.3 (0.9903)	105.7 (0.9927)
L_2PF	129.9	137.6	143.5	148.1	124.7 (0.9870)	100.7 (0.9937)	107.6 (0.9945)
L_3PF	132.9	140.3	145.5	149.8	128.2 (0.9843)	109.8 (0.9946)	117.7 (0.9962)
L_4PF	134.2	141.8	146.9	150.4	129.9 (0.9714)	115.4 (0.9994)	122.4 (0.9994)

[a] Curing temperature was calculated based on linear regression analysis of peak temperature at various heating rates.
[b] E_k was calculated according to the Kissinger method.
[c] E_o was calculated according to the Fly-Wall-Ozawa method.
The values in parentheses are the regression coefficients.

due to the incorporation of lignin. The data in Table II also showed that the curing temperatures of the LPF resin adhesives under the isothermal condition were higher than that of the CPF resin adhesive. However, the curing temperatures of these four LPF resin adhesives were slightly diverse. As mentioned above, the differences are attributed to the different properties of the four biorefinery technical lignins.

The activation energy values produced by both the Flynn–Wall–Ozawa and Kissinger methods were similar, although the values calculated with the Kissinger method (E_k) were always slightly higher than the values calculated with the Flynn–Wall–Ozawa method (E_o) for all the adhesives. The regression coefficients were more than 0.99 for each regression analysis; that is, the curing kinetic parameters calculated by both methods were credible and consistent with each other. The data in Table II shows that the activation energy values of the four LPF resin adhesives were higher than that of the CPF resin adhesive. This likely was due to the lower chemical activity of lignin, which was caused by serious steric hindrance and the complex groups within the macromolecular structure of the lignin. In fact, this phenomenon were more obvious at relatively high substitution level.[24] Interestingly, as compared to the data in Table I, the LPF resin adhesive, possessing a lower activation energy value and curing temperature, also had high bond strength. This result indicated that, under the same curing conditions, the LPF resin adhesive with low activation energy and curing temperature would cure more completely than one having high activation energy and curing temperature; thus, the former would produce a plywood product with high bond strength. Low curing temperatures would be more favorable for the industrial application of the LPF resin adhesive.

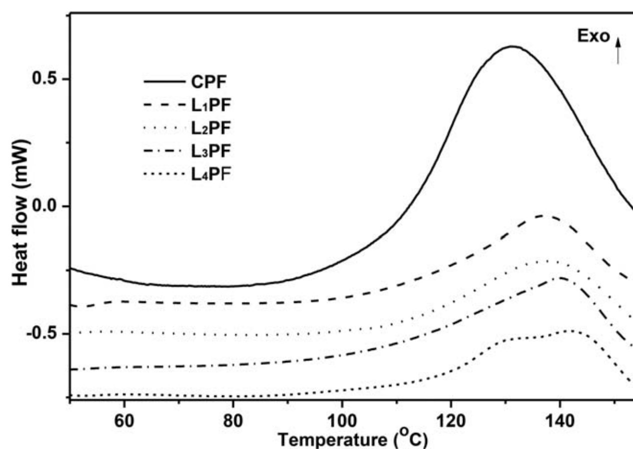

Figure 4. DSC curves of various uncured LPF and CPF resin adhesives.

CONCLUSIONS

Four technical lignins from different biorefinery processes were used to synthesize LPF resin adhesives based on a novel formulation. The results demonstrated that the formulation, which was designed based on accurate analysis of the active sites in lignin with ^{31}P NMR spectra, exhibited favorable adaptability for the four technical lignins. High-performance and low-formaldehyde-emission plywood could be successfully prepared with these LPF resin adhesives based on the proposed formulation. It could be logically deduced that this reasonable formulation may also exhibited favorable adaptability for other technical lignins. The accurate analysis of functional groups in technical lignin could undoubtedly provide a valuable reference to its modification and application.

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