Wood Science and Technology (2022) 56:1527–1549
https://doi.org/10.1007/s00226-022-01408-8

ORIGINAL

Synthesis of phenolic resins by substituting phenol with modified spruce kraft lignin

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Received: 14 August 2021 / Accepted: 16 August 2022 / Published online: 2 September 2022

Abstract

In this study, a commercial kraft lignin (KL) was used as the raw material to prepare phenolic resin (PF) based on a detailed analysis of its molecular structure. To further increase the viscosity of the phenolic resins and improve their environmental performance, demethylated and hydroxymethylated KL (DKL and HKL) were also prepared and used to produce DKLPF and HKLPF. Compared with the methoxy content of KL, that of DKL was lower by 39.34%, and the alcoholic hydroxyl contents of HKL were higher by 59.39%. Therefore, the increased active sites on the benzene ring of DKL promote the hydroxymethylation reaction, and HKL adds more methylol groups, which is more conducive to the condensation reaction to produce PF. The synthesis process and properties of the lignin-based PF with high phenol substitution rates were investigated. The results showed that the maximum substitution rates of KL, DKL, and HKL to replace phenol to prepare phenolic resin were 70%, 50%, and 30% (w/w). The viscosity, free formaldehyde content, and other important indices of LPF meet the requirements of the GB/T14732-2017 standard. Besides, as the substitution rate of phenol by lignin increases, the viscosity of DKLPF and HKLPF performance is higher. When the 30% (w/w) phenol was replaced by lignin, the adhesive strengths of KLPF, DKLPF, and HKLPF all reached the maximum, and the trend of adhesive strengths was KLPF < DKLPF < HKLPF.

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Introduction

Owing to their high heat resistance and adhesive strength, phenolic resins are widely used in various applications in the transportation, construction, and defense industries. Given the recent developments in the economy and advancements in science and technology, the demand for phenolic resins suitable for use in various new materials is increasing. In 2017, the domestic consumption of phenolic resins in China was 601,000 tons, their annual production was approximately 1.08 million tons, and their import and export volume was approximately 100,000 tons. However, the market price of phenol, a synthetic raw material for phenolic resins, was relatively high at approximately 9500 yuan/ton, resulting in a high price for phenolic resins at approximately 14,600 yuan/ton (Xu et al. 2019). Because phenol is a nonrenewable oil-based resource in the short term, many researchers have begun to explore the suitability of the natural and renewable alternative lignin for preparing phenolic resins. Lignin is an aromatic compound that can help reduce the production cost of phenolic resins and realize the high value of plant resources, resulting in significant economic and social benefits.

Although there are many reports on the preparation of phenolic resins by replacing phenol with lignin, the substitution rate in the reported literature is not high, and the substitution rate of most lignin is in the range of 20–50% (Gravitis et al. 2010; Zhang et al. 2013a). Moreover, the structure of the lignin-based raw materials used to synthesize phenolic resins remains unclear. Therefore, the preparation of phenolic resins from lignin instead of phenol is not being performed on an industrial scale in China.

In addition to the alkaline lignin obtained from pulping black liquor, lignin produced by other methods has been used to prepare phenolic resins. Stücker et al. (2016) used two different methods, namely enzymatic hydrolysis and alkali extraction, to obtain lignin. The free formaldehyde content of the lignin-based phenolic resin (LPF) was 0.12% at a substitution rate of 20%. Qiao et al. (2015) prepared phenolic resins by enzymatic hydrolysis of lignin, with 30% substitution rate. Moreover, the adhesive strength (0.76 MPa) of the prepared phenolic resins met the national standard (0.7 MPa). However, their free formaldehyde content was 0.35% and did not meet the requirements of the GB/T 14,732–2010 standard ($\leq$0.3%) (Qiao et al. 2015). Zhang et al. (2013a) prepared phenolic resin adhesives using butanol lignin. When the phenolic ratio was 3:1 and catalyst mass fraction was 20%, the optimal replacement amount of lignin was 50% of the mass fraction of phenol. Gravitis et al. (2010) used lignin obtained by enzymatic hydrolysis to prepare a phenolic resin with a replacement rate of 20%; however, in this case too, the content of free formaldehyde was high. Thus, when different types of separated lignin were used to replace phenol in the preparation of phenolic resins, the resulting resins exhibited low substitution rates and adhesive strengths.

To solve these problems, it is necessary to obtain homogeneous lignin with a stable structure and properties and to modify its molecular structure for improving its reactivity and increase the number of beneficial functional groups present.

This can be achieved by introducing hydroxymethyl and phenolic hydroxyl groups in the lignin molecules (Fleckenstein et al. 2018). In the phenylpropane unit of lignin, the ortho-position of the phenolic hydroxyl group is naturally replaced by one or two methoxy groups ($-OCH_3$), and hence, the reactivity of the free phenolic hydroxyl groups is being hindered. If these methoxy groups can be removed, the amount of reactive-free phenolic hydroxyl groups will increase, thereby enhancing the reactivity of lignin (Okamoto et al. 1996). To increase the reactivity of lignin to cross-linking agents such as formaldehyde, a chemical modification technique called hydroxymethylation or methylation is usually applied (Zhao et al. 1994; Malutan et al. 2008). Methylolation improves the reactivity of lignin by introducing active functional groups into the ortho-position of the phenolic hydroxyl group of the lignin molecule and the side chain of the benzene ring.

Gilca et al. (2014) modified lignin by hydroxymethylation and used it to prepare a lignin-based phenolic resin. When the phenol substitution rate of the hydroxymethylated lignin was 50%, it acted as an adhesive, resulting in good bond strength and low free formaldehyde and phenol contents. Khan and Ashraf (2005) modified a lignin phenol–formaldehyde resin by first subjecting lignin from bagasse to hydroxymethylation and then using it to replace some of the phenol. The results showed that when the maximum phenol substitution rate of the hydroxymethylated lignin was 50%, the adhesive strength remained high, and so did the curing rate of the resin. Wu and Zhan (2001) used alkaline lignin from wheat straw as the raw material, subjected it to demethylation, and used the demethylated lignin to replace phenol at a rate of up to 60%. The adhesive strength of the plywood prepared in this manner reached the requirements for national class I boards. Chai et al. (2016) subjected lignin to phenolic modification and used it to replace 70% of the phenol to prepare a lignin-based phenolic resin, which was then used as an adhesive. The adhesive strength of the resin (1.65 MPa) still met the national standard. However, its free formaldehyde content (0.89%) exceeded the standard limit. Moreover, the environmental performance of the resin was poor. In summary, using lignin obtained from different sources by various separation methods and subjected to different chemical modification treatments can improve its phenol substitution rate during the preparation of phenolic resins. However, these processes have not been scaled industrially, and industrially produced alkaline lignin continues to be used in large amounts.

The synthesis of lignin-based PF (LPF) resins occurs through the electrophilic substitution of formaldehyde at the ortho-position of the phenolic hydroxyl group of lignin (Vishtal and Kraslawski 2011). In the S-type unit, both C_3 and C_5 positions are occupied by methoxy groups and thus have the lowest reactivity compared to the G-type and H-type units (Mohamad et al. 2007). Therefore, lignin G and H-type units have reactive sites for formaldehyde, which makes softwood lignin more desirable for the synthesis of LPF resins. Therefore, we chose the kraft lignin (KL) of softwood as the raw material. The macromolecular structure of lignin polyphenols has fewer ortho- and para-reactive sites and more steric hindrance, which is the main reason for the low reactivity of lignin (Alonso et al. 2004; Effendi et al. 2008). For these reasons, proper modification is required to enhance the reactivity of lignin before it can be used as a feedstock for various other valuable applications.

In this study, demethylated and hydroxymethylated lignin (DKL and HKL) was prepared from KL through demethylation and hydroxymethylation reactions. KL, DKL, and HKL substitute some phenol to produce phenolic resins, and then, the properties and bond strength of phenolic resins were analyzed.

Materials and methods

Experimental raw materials and reagents

UPM BioPiva™ spruce commercial kraft lignin (KL) was purchased from UPM with a purity of 90%. The lignin structure and functional group content were determined by the laboratory team (Zhang et al. 2021), and the data are summarized in Table 1.

Sodium hydroxide, hydrochloric acid, and phenol were purchased from Nanjing Chemical Reagent Co., Ltd; hydroxylamine hydrochloride, potassium bromide, and p-nitrobenzaldehyde were purchased from Sinopharm Chemical Reagent Co., Ltd; formaldehyde, acetic anhydride, and pyridine were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd; tetrahydrofuran and deuterium chloroform were purchased from Sigma-Aldrich Co. Ltd.

Lignin modification

Demethylation modification of KL

Kraft lignin (60 g), sodium sulfite (9 g) and sodium hydroxide (6 g) were added to a three-pot flask for mixing. The pH of the solution was adjusted to 12 ± 0.1, and the reaction was done for 2 h in a water bath of 80 °C. The pH of the solution was adjusted to about 3 to produce a precipitate. After centrifugation, the supernatant was removed to collect the precipitate. The solid precipitate was washed with distilled water to neutral. After freeze-drying, the solid precipitate was fully dried in a vacuum dryer at 40 °C to obtain demethylated lignin (DKL).

Table 1 Structural analysis of UPM BioPiva™ lignin (KLignin)

Structural characterization	UPM BioPiva™ lignin (KL)
Alcohol hydroxyl content	2.93 mmol/g
Phenolic hydroxyl content	4.55 mmol/g
Mw	6348 g/mol
Mn	1631 g/mol
Mw/Mn	3.86

Hydroxymethylation modification of KL

Lignin (45 g) and formaldehyde (15 g) were added into a three-pot flask with the ratio of m(alkali lignin)/m(formaldehyde) = 3:1. Then, 30 mL of 5% NaOH was added, the pH was adjusted to 12 ± 0.1 with water, and the reaction time was set at 80 °C for 3 h. The pH of the solution was adjusted to about 3 ± 0.1 to produce a precipitate. After centrifugation, the supernatant was removed to collect the precipitate. The solid precipitate was washed with distilled water to neutral. After freeze-drying, the solid precipitate was fully dried in a vacuum dryer at 40 °C to get hydroxymethylated lignin (HKL).

Lignin acetylation

The lignin was acetylated according to a reported procedure (Li et al. 2018). About 100 mg of lignin sample (KL or DKL or HKL) was placed into a 5 mL vial, 1 mL pyridine was added and evenly mixed with a vibromixer. After the solution is fully dissolved, 1 mL acetic anhydride solution was added, mixed well, and kept away from light for 48 h. Then, a 50 mL conical flask was prepared, and an appropriate amount of distilled water was added. Then, a rotor was put in the conical flask and stirred under the ice water bath. After 48 h of reaction in the capped bottle, the mixed solution was dropwise dropped into the conical flask. After dropping, by centrifuge, the precipitate in the mixture was obtained. After drying, acetylated alkali lignin (AcKL), acetylated demethylated modified lignin (AcDKL), and acetylated hydroxymethylated modified lignin (AcHKL) were obtained.

Characterization and comparison of basic structural properties of KL, DKL, and HKL

FTIR analysis

The Fourier transform infrared spectrum of lignin (KL, DKL, and HKL) was determined by Bruker vertex 80 V spectrometer. Using potassium bromide as the background, the tablet was scanned 32 times in transmission mode, and the test range was 4000–400 cm^{-1}. 3 mg of sample was weighed, ground with 300 mg of potassium bromide, and the tablet was pressed and put on the stage for testing.

Characterization of methoxy contents of KL, DKL, and HKL by ^{1}H NMR

Acetylated lignin (AcKL, AcDKL, and AcHKL) samples and *p*-nitrobenzaldehyde internal standard were dissolved in a mixture of deuterated pyridine and deuterated chloroform. Regarding the specific sample preparation and ^{1}H NMR specific test method reference is made to a reported procedure (Zhang et al. 2021) and samples detected by Bruker AVANCE III 600 nuclear magnetic resonance instrument.

Characterization of hydroxyl group and carboxyl group contents of KL, DKL, and HKL by ^{31}P NMR

Lignin (KL, DKL, and HKL) samples were dissolved in pyridine-d_5/$CDCl_3$ followed by the addition of N-hydroxy-5-norbene-2,3-diimide and chromium(III) acetylacetonate solution. After thorough mixing, the resulting mixture was reacted with a phosphitylating agent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, TMDP) for approximately 10 min and then transferred into a 5 mm NMR tube for subsequent NMR detection using a Bruker AVANCE III 600 MHz nuclear magnetic resonance instrument. The specific sample preparation and NMR test methods have been reported in the literature (Li et al. 2017). Chemical shifts were calibrated relative to N-hydroxy-5-norbene-2,3-diimide as the internal standard ($\delta = 152$ ppm). The hydrogen and carboxyl contents were calculated according to reference (Argyropoulos et al. 1994; Zhang et al. 2021).

GPC to determine the molecular weight of lignin and its modified products

The lignin was acetylated according to a reported procedure before GPC analysis was conducted (Li et al. 2018). KL, AcDKL, and AcHKL samples were dissolved in tetrahydrofuran solution and filtered through an organic syringe filter with a pore size of 0.22 µm. The molecular weight of lignin was determined by a Shimadzu high-performance gel permeation chromatographer (Shimadzu, Kyoto, Japan) equipped with a SPD-20A detector and LC20AB pump. Chromatography analysis was performed with Asahipak Shodex KF-804L (Showa Denko, Tokyo, Japan) polymer-based columns (300 mm, 8 mm ID). The injection volume was 25 µL, the flow rate was 1 mL/min, and the column temperature was 40 °C. The weight average molecular weight (Mw), number average molecular weight (Mn), and polydispersity (Mw/Mn) were calibrated using standard polystyrene with molecular weights of 46,300, 30,000, 20,000, 10,000, 4050, 2400, 1000, and 500.

Synthesis process and basic property characterization of lignin phenolic resin (KLPF, DKLPF, and HKLPF)

Synthesis process of lignin phenolic resin

The molar ratio of formaldehyde and phenol is 1:2, and NaOH (30 wt%) is 15% of the phenol content. They are all added to a four-neck round-bottom flask and the mixture was reacted at 90 °C for 90 min. After cooling to below 40 °C, phenolic resin (PF) was obtained.

According to the synthesis method, phenol resin was prepared by partially replacing phenol with KL, and the replacement mass of phenol accounted for 10%(w/w), 20%(w/w), 30%(w/w), 40%(w/w), 50%(w/w), 60%(w/w), 70%(w/w), 75%(w/w) of the total weight of phenol. The prepared lignin phenolic resins were expressed as 10%KLPF, 20%KLPF, 30%KLPF, 40%KLPF, 50%KLPF, 60%KLPF, 70%KLPF, 75%KLPF, respectively. Phenol was partially replaced by DKL, and the replacement quality of phenol accounted for 10, 20, 30, 40, 50, 60, 70% of the total weight of phenol. The denaturated lignin-based phenolic resin prepared was expressed as 10%DKLPF, 20%DLPF, 30%DKLPF, 40%DKLPF, 50%DKLPF, 60%DKLPF, 70%DKLPF, respectively. The replacement of phenol by HKL was 10, 20, 30, and 10% of the total weight of phenol. The lignin phenolic resin was expressed by 10%HKLPF, 20%HKLPF, and 30%HKLPF, respectively.

Characterization of the properties of lignin phenolic resin

The solid content, pH, viscosity, free formaldehyde content, and gelation time of phenolic resin were tested according to the national standard of the People's Republic of China (GB/T 14,074–2017).

Solid content

The thermostat was adjusted to 120 °C. The container used in the experiment was put into a thermostat for 30 min. 4 g of the phenolic resin sample was weighed and placed in a container. The samples were placed on a thermostat and dried at 120 ± 1 °C for 120 min. Samples were weighed after 15 min in a desiccator.

The resin solid content is calculated by Eq. 1:

$$C = \frac{m_3 - m_1}{m_2 - m_1} \times 100\% \tag{1}$$

C_1—Resin solid content, %, m_1—Weight of the container, g, m_2—Weight of container with resin before drying, g, m_3—Weight of container and resin after drying, g

pH test

The sample, 2 g, was accurately weighed in a beaker and dissolved in 100 mL distilled water. The pH value was adjusted to 3.5 ± 0.1 with the hydrochloric acid solution of 0.1 M, and the volume of the standard hydrochloric acid solution consumed was recorded.

The sodium hydroxide content is calculated by Eq. 2:

$$S = \frac{c \times V \times 0.04}{m} \times 100\% \tag{2}$$

S—Sodium hydroxide content, %, c—Concentration of a standard solution of hydrochloric acid, M, V—Volume of the hydrochloric acid standard solution consumed for titrating the sample, mL. 0.040 mL of c(HCl) = 1 mol/L of the standard solution of hydrochloric acid is equivalent to the molar mass of sodium hydroxide, g/mmol. m—Weight of the sample, g

Viscosity

The viscosity of the phenolic resin was measured using an NDJ-1 rotational viscometer. An appropriate rotor and speed were selected to stir the adhesive evenly, and it was ensured that the reading range is between 20 and 80%. Then, three samples were placed in a container, and the container was placed in a constant temperature water bath to keep the sample temperature uniform so that the sample temperature was in balance with the test temperature. The rotor of the viscometer was dipped into the center of the container vertically so that the liquid surface of the sample reached the rotor line. The viscometer was opened and the reading on the disk was recorded after the viscometer pointer had stopped rotating. Each sample was measured three times.

Free formaldehyde content

2.0 g of the sample was weighed and placed in a 0.25 L beaker. 0.1 L methanol was added and stirred until the resin dissolves. The pH meter electrode was inserted into the solution, the pH value was adjusted to 3.5 with 0.1 M hydrochloric acid solution, 20 mL of 10% hydroxylamine hydrochloride solution was added, stirred well, and the measured solution was titrated to 3.5 ± 0.1 with 0.1 M sodium hydroxide solution.

Blank test: same determination with the same procedure and the same reagent (without sample).

The free formaldehyde content is calculated by Eq. 3:

$$w = \frac{3c(V_1 - V_0)}{m} \times 100\% \tag{3}$$

w—Free formaldehyde content, %; c—Concentration of NaOH, M; V_0—Volume of NaOH solution used in blank test, L; V_1—Volume of NaOH solution, L; m—Weight of the sample, g.

Gelation time

5.0 g of the liquid adhesive was weighed and transferred to the test tube (16 × 160 mm). The test tube was transferred to an oil bath at 130 °C and moved up and down with a metal rod with a diameter of 3 mm. The time required for the adhesive to reach the wire-drawing state on the metal rod is the gel time.

Adhesive strength of phenolic resins

Three-ply laboratory plywood panels of dimensions 400 × 400 × 4.5 mm were prepared from 1.5 mm thick poplar veneers of 10% moisture content at a glue mix spread of 250–280 g/m^2 single glue line. Lignin-PF resin was assembled and hot pressed under 8 bar at 20 ± 2 °C for 6 min. Then, a hot press under 12 bar at 130 ± 2 °C for 15 min was used to assure full reaction.

The adhesive strength of plywood was tested according to the national standard GB/T17657-2013. Poplar plywood was stored at 20 ± 5 °C for 24 h before testing the dry adhesive strength, then soaked in water at 25 ± 5 °C for 24 h before testing the wet adhesive lightness, and soaked in hot water at 63 ± 2 °C for 3 h before testing the hot water adhesive strength. The universal electronic adhesive testing machine (CMT6140) stretched the plywood sample along the grain direction of the wood at a speed of 5 mm/min until it broke; the tensile strength of the two pieces poplar veneer failure was recorded, and the actual glue at the failure point was measured. The adhesive strength test results are the average of 36 specimens.

The adhesive strength is calculated by Eq. 4:

$$\sigma = P/(A \times B) \tag{4}$$

σ—Adhesive strength (MPa); P—Maximum tensile strength when the specimen fails (N); A—Length of the glued surface of the specimen (mm); B—Width of the glued surface of the test piece (mm).

Results and discussion

Analyses of basic structures of lignin and its modified products

FTIR analyses of KL, DKL, and HKL

The infrared spectra of KL, DKL, and HKL are shown in Fig. 1. In the case of DKL, the peak related to the stretching vibrations of the hydroxyl group at 3433 cm^{-1} increased in intensity and moved to lower wave number (3414 cm^{-1}), and the peak related to the presence of C-O stretching vibration of phenolic OH group at 1218 cm^{-1} also increased in intensity (Tejado et al. 2007). This indicated that the hydrogen bond interactions in the DKL were enhanced, and the content of phenolic hydroxyl groups was increased (Li et al. 2016). The decrease in the amplitudes of the peak related to the benzene cyclic C-O vibrations at 1270 cm^{-1} and the peak related to the guaiac-based unit and stretching vibrations of the C-O (methoxy group) at 1145 cm^{-1} indicated that some of the methoxy groups in KL were decomposed, resulting in the formation of phenolic hydroxyl groups and degradation of the lignin macromolecules.

The intensity of the peak related to the stretching vibrations at 3433 cm^{-1} was higher in the case of HKL, and the peak was shifted to a lower wave number (3420 cm^{-1}). This indicated that the content of hydroxyl groups in the DKL was increased. In addition, the amplitude of the peak at 2935 cm^{-1} increased in intensity, which was related to the stretching vibrations of the methylene C-H bond being higher, primarily due to the hydroxymethylation reaction that increases the hydroxymethyl (-CH_2OH) groups of the lignin phenol hydroxyl group in the ortho-para position (Aini et al. 2019), and so did the peak related to

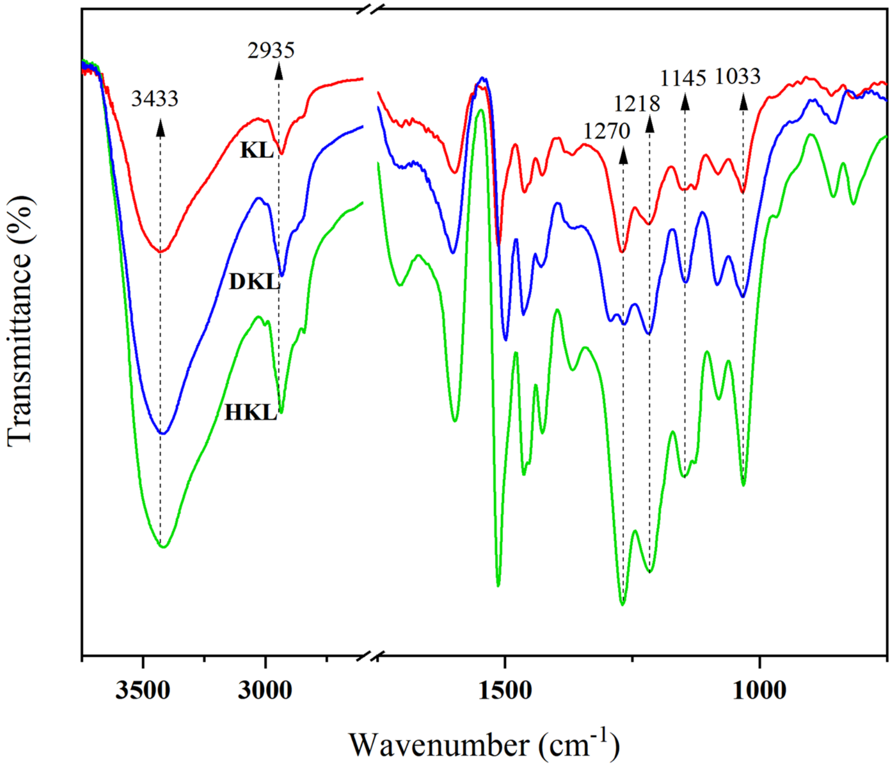

Fig. 1 FTIR spectra of KL, DKL, and HKL

the C-O vibrations of the aliphatic OH at 1033 cm^{-1} (Tejado et al. 2007). These results confirmed that the hydroxymethyl group was successfully introduced into KL after the hydroxymethylation reaction.

^{1}H NMR spectroscopy analyses of KL, DKL, and HKL

The ^{1}H NMR spectra of acetylated KL, DKL, and HKL are shown in Fig. 2. The protons in the–CHO of p-nitrobenzaldehyde can be observed at 10.15 ppm and the aromatic protons in p-nitrobenzaldehyde were present at 8.36 and 8.06 ppm, and the integral of proton signals between 6.0 and 8.0 ppm can be attributed to the aromatic protons in G units. The methoxyl protons give an intense proton signal at around 3.82 ppm (Alvaro et al. 2007). The aromatic and aliphatic acetyl groups were shifted slightly (2.3 and 2.08 ppm, respectively), giving rise to separate peaks.

In the spectrum of DKL, the proton peak at 3.82 ppm is weakened, indicating that some of the methoxy groups of KL had been removed by the catalytic action of sodium sulfite. Compared to KL, the methoxy content of DKL decreased

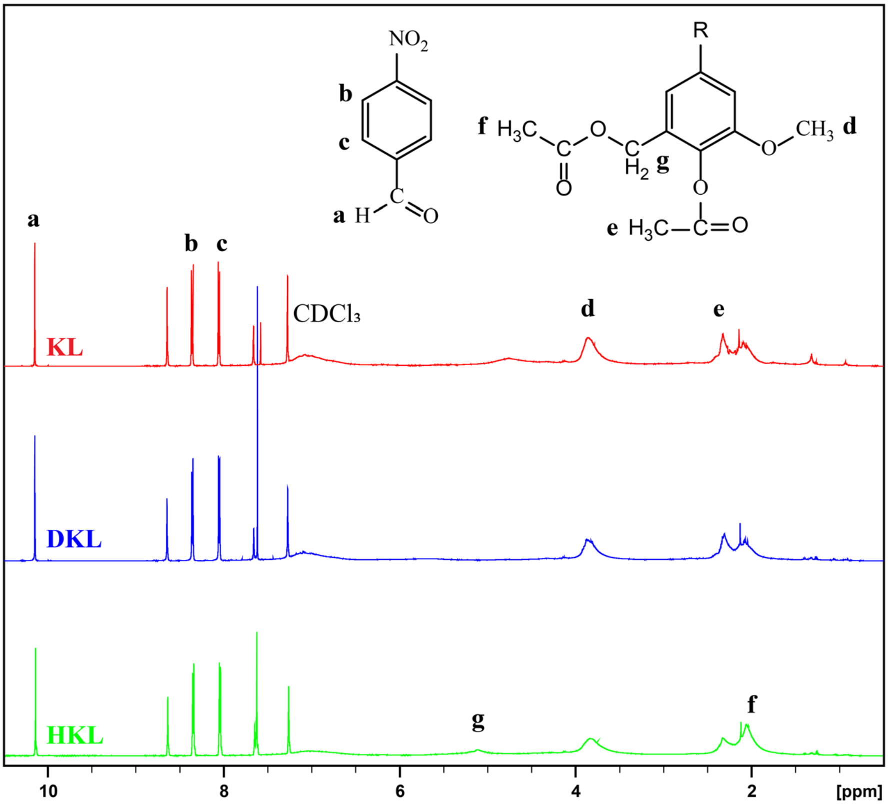

Fig. 2 ^{1}H NMR spectra of KL, DKL, and HKL

by 39.34%, higher than that reported in previous studies (Hussin et al. 2013). In addition, compared with KL, the intensities of the proton peaks at 2.27 and 2.03 ppm in the case of DKL were higher, indicating that the contents of the aromatic and aliphatic acetyl groups in DKL had increased. This may be owing to the nucleophilic substitution reaction of the methoxy group under the attack of sodium sulfite, which is a nucleophile; the attack transformed the methoxy group into the phenolic hydroxyl group. In addition, the depolymerization of lignin during the reaction also leads to an increase in the hydroxyl content.

In addition, after the modification of KL by hydroxymethylation, a peak was observed at 5.1 ppm. This was related to the hydrogen proton of the methylene unit connected to the benzene ring after hydroxymethylation, thereby indicating that the lignin and formaldehyde had undergone a hydroxymethylation reaction (Xia et al. 2016). In addition, the area of the peak at 6.4–7.1 ppm, which was related to the hydrogen of the aromatic nucleus, was significantly reduced. This indicated that the lignin and formaldehyde had undergone a nucleophilic reaction; this also indirectly confirmed that the lignin had undergone a hydroxymethylation reaction. Finally, the hydrogen proton peaks of the phenolic hydroxyl acetyl and

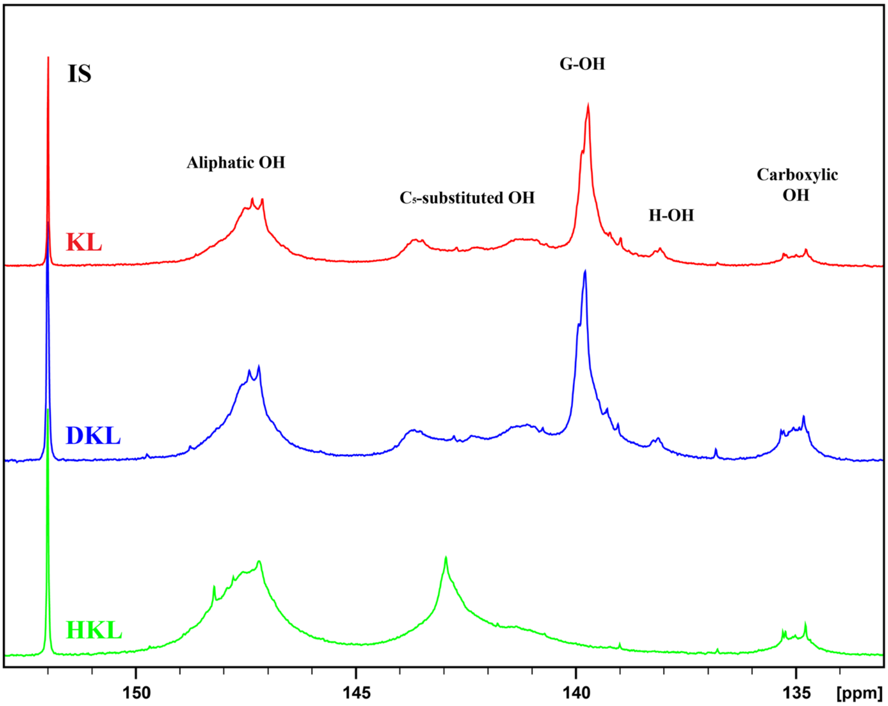

Fig. 3 Quantitative ^{31}P NMR spectra of KL, DKL, and HKL

Table 2 Quantitative analysis of KL, DKL, and HKL based on ^{31}P NMR

Hydroxyl type	Hydroxyl content (mmol/g)		
	KL	DKL	HKL
Aliphatic OH	2.93	3.46	4.67
Condensed phenolic OH	1.39	2.46	3.87
Guaiacyl OH	2.85	3.13	0.63
p-Hydroxyphenyl OH	0.31	0.31	0.09
Total aromatic OH	4.55	5.7	4.59
Carboxylic OH	0.38	0.52	0.42

alcohol hydroxyl acetyl groups were observed at. 2.27 and 2.02 ppm, respectively. In the spectrum of HKL, the peak at 2.02 ppm is stronger than that at 2.27 ppm, indicating that the content of the alcohol hydroxyl groups increased after hydroxymethylation and that the hydroxyl group was mainly the alcohol hydroxyl group (Zhang et al. 2013b).

Hydroxyl and carboxyl group contents of KL, DKL, and HKL as determined by ^{31}P NMR spectroscopy

To further understand the changes in the hydroxyl content of KL after modification, ^{31}P-NMR spectroscopy was used to quantitatively analyze the hydroxyl contents of the various lignin samples (Springer et al. 2016). The integral phosphorus spectra of KL, DKL, and HKL are shown in Fig. 3, while the contents of the various functional groups are listed in Table 2.

The peak at 145.2–149.5 ppm is the characteristic peak of the aliphatic OH group (Ahvazi et al. 2016). The intensity of this peak in the case of DKL was higher than that for KL. Moreover, the content of the aliphatic OH groups increased from 2.93 mmol/g for KL to 3.46 mmol/g for DKL (Table 2). This can be attributed to the breakage of the alkyl aryl and/or alkyl ether bonds (Hu et al. 2014). The peaks at 144.5–144.9 and 140.4–138.4 ppm represent the characteristic peaks of the condensed phenolic OH group and guaiacyl OH group (G), respectively (Xie et al. 2017). The intensities of these peaks were also significantly higher in the case of DKL. This may be owing to the breakage of the other ether bonds in lignin because of the demethylation reaction and the formation of phenolic OH groups (Wang et al. 2019). Table 2 also shows that the contents of the condensed and guaiacyl OH groups (G) increased from 1.39 mmol/g for KL to 2.46 mmol/g for DKL and from 2.85 mmol/g for KL to 3.13 mmol/g for DKL, respectively. This led to an increase in the total phenolic OH groups from 4.55 mmol/g for KL to 5.7 mmol/g for DKL. This was consistent with the reduction in the amplitude of the peak related to the stretching vibrations of the phenyl cyclic ether bonds (methoxy group) at 1145 cm^{-1} in the FTIR spectrum. This indicates that the methoxy group in the lignin breaks down to form a phenolic OH group, leading to the degradation of the lignin molecule. Furthermore, the intensities of the proton peaks at 2.27 and 2.03 ppm in the ^{1}H NMR spectrum were higher.

The aliphatic OH group (peak at 145.2–149.5 ppm) was dominant in lignin, with the strength of this peak in the case of HKL being higher than that for KL owing to the hydroxymethylation reaction (Fig. 3). Furthermore, while the content of the aliphatic OH group increased from 2.93 mmol/g for KL to 4.67 mmol/g for HKL, that of the phenolic OH group remained unchanged (Table 2). This is consistent with the introduction of hydroxymethyl groups, as discussed in Sect. ^{1}H NMR spectroscopy analyses of KL, DKL, and HKL. Thus, hydroxymethylation primarily results in an increase in the content of the aliphatic OH group (Chen et al. 2020). In addition, after KL was modified by hydroxymethylation, the content of the guaiacyl OH group decreased from 2.85 mmol/g to 0.63 mmol/g. Repolymerization and cross-linking of lignin polymers were accomplished through the formation of methylene (CH_2) bridges and new, strong C–C bonds after the condensation reaction (Teodor et al. 2007); this

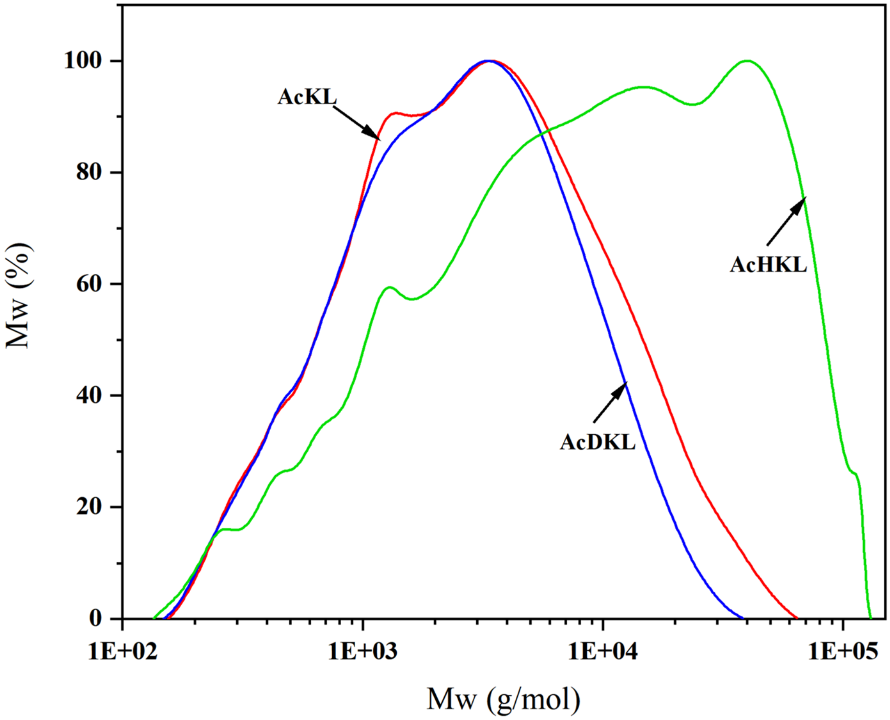

Fig. 4 Molecular weight distribution of AcKL, AcDKL, and AcHKL

Table 3 Mn, Mw, and PDI of AcKL, AcDKL, and AcHKL

Sample	Mw (g/mol)	Mn (g/mol)	Mw/Mn
AcKL	6348	1631	3.86
AcDKL	4468	1468	3.04
AcHKL	27,332	3266	8.36

would be consistent with the increase in the content of the condensed phenolic OH group.

Comparison of molecular weights and polydispersities of KL, DKL, and HKL

Before determining the molecular weights of the various lignin samples (KL, DKL, and HKL), to increase their solubilities in tetrahydrofuran, they were acetylated to obtain acetylated KL (ACKL), acetylated DKL (ACDKL), and acetylated HKL (ACHKL), respectively. Their molecular weight distributions results are shown in Fig. 4 and Table 3.

Weight average molecular weight (Mw), number average molecular weight (Mn), and polydispersity index (PDI) of KL decreased after the demethylation reaction

Table 4 Influence of lignin substitution rate on properties of lignin-based phenolic resin

KL substitution rate	pH	Alkalinity %	Free formaldehyde content %	Solid content %	Gel time (s)	Viscosity (mPa·S)
0	11.31	4.20	0.036	62.86	450	182
10% KLPF	10.69	3.65	0.058	56.72	360	300
20% KLPF	10.66	3.61	0.087	55.97	385	275
30% KLPF	10.63	2.65	0.115	52.83	390	250
40% KLPF	10.52	2.23	0.174	43.77	398	215
50% KLPF	10.42	1.59	0.211	42.20	463	175
60% KLPF	10.17	1.31	0.233	42.06	492	168
70% KLPF	9.91	1.07	0.284	41.62	527	142
75% KLPF	9.69	1.07	0.311	40.71	564	87
GB/T14732-2017	≥ 7.00		≤ 0.30	≥ 35.00		≥ 70

(Table 3). This was because the methoxy functional group broke during the demethylation process. The molecular weight and PDI of HKL were greatly increased by hydroxymethylation modification. Because during the hydroxymethylation reaction, the ortho-positioned or side-chain C_α and C_β carbons of the phenolic hydroxyl group of lignin reacted with formaldehyde to introduce a hydroxymethyl group, and further formation of prepolymers (Zhang et al. 2013b), resulting in an increase in the relative molecular weight and dispersion coefficient of HKL (Fig. 4). These results confirmed that both demethylation and hydroxymethylation have an effect on the molecular size of lignin.

Analysis of basic properties of lignin-based phenolic resins (KLPF, DKLPF, and HKLPF)

Phenolic resins basic properties (viscosity, pH, alkalinity, free formaldehyde content, solid content) and the phenol replacement rates of the various resin samples were analyzed as per the method described in section characterization of basic properties of lignin phenolic resin.

Basic performance analysis of KLPF

As shown in Table 4, when the replacement rate of phenol by KL was 70%, the properties of the resulting resin met the requirements of the national standard GB/T14732-2017, which is significantly higher than those reported in most similar studies. Of course, KL's high substitution rate for phenol inevitably reduces the viscosity performance of phenolic resin. When the replacement rate of KL was less than 50%, the viscosity of KLPF was greater than that of PF (182 mPa·S). This is due to the KL molecular weight being greater than that of phenol, so the viscosity of KLPF was greater than that of pure PF (Li et al. 2016). As the replacement rate of KL increased, the number of active sites available for the reaction with formaldehyde decreased, resulting in a decrease in the viscosity. When the phenol replacement rate of KL was 75%, the viscosity of KLPF decreased to 87 mPa·S, and the free formaldehyde content of the resulting resin was slightly higher than the requirements of the national standard.

When the phenol substitution rate of KL was increased, the pH of the resulting phenolic resin gradually decreased. In the presence of a certain amount of NaOH, with an increase in the phenol substitution rate of lignin, the amount of alkali consumed by KL increased. In other words, the amount of free NaOH in the solution decreased. Therefore, the solution alkalinity decreased with an increase in the lignin substitution rate (Li et al. 2019).

In addition, the free formaldehyde content increased and solid content of KLPF decreased with an increased replacement rate of KL. Although KL has a polyphenol structure similar to phenol, KL's large molecular weight, low activity, and large steric hindrance hinder the progress of the polycondensation reaction to a certain extent. This can be attributed to the fact that the ortho-para position of the phenolic hydroxyl group of lignin may be occupied, so the number of active sites in the benzene ring structure of lignin per unit mass was lower than that in the case of phenol (Ma et al. 2011). Therefore, as the rate of KL substitution for phenol increases, the consumption of formaldehyde in the reaction process is reduced, and the yield of KLPF is reduced.

Basic performance analysis of DKLPF

Based on a complete understanding of the structure of DKL, the effect of the phenol substitution rate of DKL on the performance of DKLPF was explored. Table 5 lists the pH, basicity, free formaldehyde content, solid content, gel time, and viscosity of DKLPF at different substitution rates.

For the same phenol replacement rate, the free formaldehyde content of DKLPF was lower than that of KLPF, and its viscosity was higher. This is because after the demethylation of KL, the content of the methoxy group decreased and that of

Table 5 Effect of substitution rate of DKL on properties of phenolic resin based on DKLPF

DKL substitution rate	pH	Alkalinity %	Free formaldehyde content %	Solid content %	Gel time (s)	Viscosity (mPa·S)
0	11.31	4.20	0.036	62.86	450	182
10% DKLPF	11.16	3.92	0.041	52.11	311	550
20% DKLPF	10.94	3.48	0.056	50.94	286	1650
30% DKLPF	10.92	2.71	0.089	47.46	267	1925
40% DKLPF	10.87	2.11	0.156	39.95	333	22,250
50% DKLPF	10.55	2.07	0.187	37.92	352	23,000
60% DKLPF	10.30	1.34	0.211	36.13	381	> 100,000
70% DKLPF	9.98	1.07	0.272	34.87	425	> 100,000
GB/T14732-2017	≥ 7.00		≤ 0.30	≥ 35.00		≥ 70

the hydroxyl group increased. Although DKL modified by demethylation has higher molecular activity than KL, the structure of lignin limits the number of active sites on the benzene ring that can be substituted less than phenol. Therefore, the free formaldehyde content in DKLPF is higher than that in pure PF and it is lower than KLPF at the same phenol replacement rate.

The viscosity of DKLPF was greater than that of pure PF because the molecular weight of DKL is much higher than that of phenol. Besides, under the same phenol replacement rate, the viscosity of DKLPF is better than KLPF, and as the substitution rate increases, the viscosity performance is better. This may be because DKL has better reactivity than KL after demethylation, and more DKL participates in the hydroxymethylation and polycondensation reactions. Compared with KL, the number of DKL active sites increases leading to an increase in the reactivity of lignin and an increase in the degree of cross-linking between lignin and formaldehyde, so the obtained DKLPF has a better viscosity. It can be seen that, when the phenol replacement rate of DKL was 60% and 70%, the viscosity of DKLPF was too high, which may be detrimental to the practical application of the gluing process.

Generally speaking, longer gel time is more dominant in actual production. When the DKL substitution rate exceeded 50%, the viscosity of the adhesive increased, and its gel time also increased. This may be owing to the fact that when the amount of DKL substituted was too large, its reactivity was lower than that of phenol, and it acted as a filler in the reaction system (Khan and Ashraf 2005). Accordingly, the degree of condensation with formaldehyde did not increase significantly, thus resulting in an increase in the gel time. To sum up, when DKL replaces 50% of phenol, the applicability of the prepared phenolic resin is relatively better.

Basic performance analysis of HKLPF

HKL was used to prepare a phenolic resin (HKLPF), according to the analysis of its structure, and the effect of the phenol substitution rate of HKL on the basic properties of HKLPF was analyzed. Table 6 lists the pH, alkalinity, free formaldehyde content, solid content, gel time, and viscosity of HKLPF at different substitution rates.

Under the laboratory conditions, the maximum replacement rate of HKL used in this study was kept at 30% and met the requirements of GB/T14732-2017. When

Table 6 Effect of substitution rate of HKL on properties of phenolic resin based on HKLPF

HKL substitution rate	pH	Alkalinity %	Free formaldehyde content %	Solid content %	Gel time (s)	Viscosity (mPa·S)
0	11.31	4.20	0.036	62.86	450	182
10% HKLPF	11.23	3.69	0.173	57.40	256	3200
20% HKLPF	11.37	3.47	0.175	56.19	240	17,000
30% HKLPF	11.27	2.60	0.186	53.89	240	20,000
GB/T14732-2017	≥ 7.00		≤ 0.30	≥ 35.00		≥ 70

the phenol replacement rate of HKL exceeded 30%, this resulted in a solid-state gel without fluidity. Because of the large molecular weight of HKL, the reaction rate was low, and the viscosity of the reaction system was high.

As the phenol replacement rate of HKL increased, the viscosity of HKLPF also increased significantly (Table 6). Because an active functional group is introduced after the modification of lignin by hydroxymethylation, the degree of condensation with phenol increases with the increase in the hydroxyl content of HKL. Consequently, the viscosity of HKLPF increased with increase in the phenol substitution rate of HKL.

In addition, at the same lignin replacement rate, the viscosity of HKLPF was higher than those of KLPF and DKLPF (Tables 4, 5). This may be due to the change in the molecular weight of the reactants. Compared with phenol, the molecular weight of HKL ($M_w > 20{,}000$) is larger than that of phenol, KL, and DKL, which leads to a further increase in the molecular weight of the synthesized HKLPF, resulting in increased intermolecular friction (Chen et al. 2019), the viscosity of HKLPF was much higher than those of PF, KLPF, and DKLPF.

As stated previously, the replacement of phenol with HKL increased the free formaldehyde content of the HKLPF. As the replacement rate of HKL increases, the viscosity during the formation reaction of HKLPF was higher because the mass transfer resistance during the reaction was increased, thereby reducing the chance of HKL reacting with formaldehyde. This led to a high free formaldehyde content of HKLPF (Lin et al. 2010).

In general, the larger the molecular weight of an adhesive, the shorter its gelation time will be (Khan and Ashraf 2005). Therefore, when the HKLPF substitution rate was 30%, the shortest gelation time was 240 s. The high viscosity and reduced gel time of lignin-based phenolic resins are beneficial to improve the thermal curing efficiency of plywood, but may affect the expiration date of the resin glue and the gluing process.

Table 7 Influence of lignin substitution rate on dry tensile strength (σ_{dry}) of three lignin-based phenolic resins

Lignin substitution rate	KLPF (MPa)	DKLPF (MPa)	HKLPF (MPa)
0%	1.43	1.43	1.43
10%	2.18	2.33	2.25
30%	2.28	2.43	2.55
50%	1.99	2.18	NA
70%	1.28	1.34	NA
GB9846.2	≥ 0.70	≥ 0.70	≥ 0.70

Adhesive strength of lignin-based phenolic resins (KLPF, DKLPF, and HKLPF)

Dry adhesive strength of three lignin-based phenolic resins

To characterize the effect of KL, DKL, HKL substituted phenol on the dry adhesive strength properties of phenolic resin, KLPF, DKLPF and HKLPF with 0%, 10%, 30%, 50% and 70% substitution rates were selected to prepare three-ply poplar plywood. All plywoods were stored at 20 ± 5 °C for 24 h before testing the dry adhesive strength, and the results are shown in Table 7. With the increase in the substitution rate of phenol, the adhesive strength of the three lignin-based phenolic resins showed a trend of increasing first and then decreasing. When the maximum substitution rate of phenol in KLPF, DKLPF, and HKLPF is 70, 70, and 30%, respectively, their wet adhesive strength meets the national standard requirements. When the 30% phenol was replaced, the adhesive strengths of KLPF, DKLPF, and HKLPF all reached the maximum, which were 2.28, 2.43, and 2.55 MPa, respectively. Compared with PF without lignin replacement, their adhesive strengths increased by 59.09, 70.60, and 79.02%. When the substitution rate of phenol is less than or equal to 30%, the adhesive strength increases with the increase in substitution rate; this is mainly because lignin is a phenolic polymer, and the addition of some lignin increases the toughness of the adhesive, so the glue strength increases with the increase in lignin content. Since the activity of lignin at the same mass is lower than that of phenol, when the content of lignin in the system increases and the content of phenol decreases, the active sites for the reaction of lignin, phenol, and formaldehyde per unit mass decrease, resulting in a decrease in the condensation strength during thermal curing. The bond strength decreases gradually. Under the same lignin replacement rate, DKLPF has higher adhesive strength than KLPF, which may be because the molecular weight of KL decreases after demethylation and the hydroxyl content in lignin increases at the same time, so the condensation of lignin and formaldehyde degree increases, increasing the bond strength of DKLPF. When the lignin replacement rate is 70%, the adhesive strength of DKLPF and KLPF is lower than that of PF, which may be due to the decrease in the condensation degree of lignin with formaldehyde and phenol with increasing lignin content, which is only equivalent to the effect of fillers. As a result, the viscosity of the adhesive increases, but the

Table 8 Influence of lignin substitution rate on wet tensile strength (σ_{wst}) of three lignin-based phenolic resins

Lignin substitution rate	KLPF (MPa)	DKLPF (MPa)	HKLPF (MPa)
0%	0.84	0.84	0.84
10%	0.97	1.14	1.77
30%	1.04	1.16	1.99
50%	0.72	1.04	NA
70%	0.62	0.68	NA
GB9846.2	≥ 0.70	≥ 0.70	≥ 0.70

condensation reaction during thermal curing decreases, which in turn leads to a decrease in adhesive strength.

Under the condition of the same lignin substitution rate, HKLPF has higher adhesive strength than KLPF and DKLPF, which may be due to the increased hydroxyl content of HKL, so after lignin is modified by methylol, the functional groups of lignin formaldehyde increase. The increased molecular weight of HKLPF results in the highest viscosity and highest bond strength.

Wet adhesive strength of three lignin-based phenolic resins

To characterize the effect of KL, DKL, and HKL substituted phenols on the wet adhesive strength properties of phenolic resins, KLPF, DKLPF, and HKLPF with 0, 10, 30, 50, and 70% substitution rates were selected to prepare three-ply poplar plywood. All plywoods were treated by soaking in water at 25 ± 5 °C for 24 h before testing the wet adhesive strength, and the results are shown in Table 8. The wet adhesive strengths of KLPF, DKLPF, and HKLPF reached the composite strengths required by national standards when the maximum substitution rates of phenol were 50%, 50%, and 30%, respectively. Among them, the wet adhesive strength of KLPF, DKLPF, and HKLPF reached the maximum values of 1.04, 1.16, and 1.99 MPa, respectively, when the phenol substitution rate was 30%, which increased by 23.10, 37.91, and 135.31%, respectively, compared with PF without lignin substitution. It was also found that the water resistance of DKLPF and HKLPF was slightly increased compared to KLPF, which was attributed to the KL modification increasing the degree of cross-linking of lignin with formaldehyde and increasing the viscosity of the lignin-based phenolic resin, which in turn led to an increase in the wet glue strength of DKLPF and HKLPF.

Hot water adhesive strength of three lignin-based PF resins

To characterize the effect of KL, DKL, and HKL substituted phenols on the hot water adhesive strength properties of phenolic resins, KLPF, DKLPF, and HKLPF with 0, 10, 30, 50, and 70% substitution rates, respectively, were selected to prepare three-ply poplar plywood. All plywoods were treated by soaking in hot water at

Table 9 Influence of lignin substitution rate on hot-water tensile strength (σ_{hwt}) of three lignin-based phenolic resins

Lignin substitution rate	KLPF (MPa)	DKLPF (MPa)	HKLPF (MPa)
0%	0.78	0.78	0.78
10%	0.77	1.21	1.23
30%	0.89	1.09	1.02
50%	0.64	0.79	NA
70%	0.62	0.64	NA
GB9846.2	≥ 0.70	≥ 0.70	≥ 0.70

63 ± 2 °C for 3 h before testing the hot water adhesive strength, and the results are shown in Table 9.When the maximum substitution rate of phenol in KLPF, DKLPF, and HKLPF is 30, 50, and 30%, their hot water adhesive strength meets the national standard requirements. When the substitution rate of phenol was 30%, the hot water-resistant adhesive strength of KLPF, DKLPF, and HKLPF reached the maximum value, which was 0.89, 1.09, and 1.02 MPa, respectively. Compared with the PF without lignin replacement, they increased by 13.66, 39.39, and 30.81%. When the substitution rate of phenol is 30%, the adhesive strength of the three lignin-based phenolic resin plywood can reach the national standard in dry, wet, and hot water environments.

Conclusion

In this study, based on the structural and chemical characteristics of a commercially available kraft lignin (KL), the properties of its demethylated lignin (DKL) and hydroxymethylated lignin (HKL) products were analyzed in detail. In addition, the feasibility of preparing phenolic resins from the three types of lignin (KL, DKL, and HKL) at high phenol replacement rates was studied. The results showed that the maximum substitution rates of KL, DKL, and HKL to replace phenol to prepare phenolic resin were 70, 50, and 30% (w/w), respectively. The results showed that the maximum replacement rate of phenol by KL can be as high as 70% (w/w), which is higher than the rates reported previously. The viscosity, free formaldehyde content, and other important indices of LPF meet the requirements of the GB/T14732-2017 standard. Besides, as the substitution rate of phenol by lignin increases, the viscosity of DKLPF and HKLPF performance is higher.

After the moderate demethylation of KL, its methoxy group content was reduced by 39.34% while its hydroxyl group content increased by 25.27%. After KL was modified by hydroxymethylation, its alcoholic hydroxyl group content increased by 59.39%, and its Mw increased to more than 27,000 g/mol. Besides, as the substitution rate of phenol by lignin increases, the viscosity of DKLPF and HKLPF is higher. Under the same phenol replacement rate, the HKLPF exhibited high viscosity and the shortest gel time. This is beneficial to improve the thermal curing efficiency of plywood, but may affect the pot life of the resin glue and the glue application process. When the 30% (w/w) phenol was replaced by lignin, the dry, wet, and hot water adhesive strengths of KLPF, DKLPF, and HKLPF all reached the maximum, and the trend of adhesive strengths was KLPF < DKLPF < HKLPF.

In summary, UPM BioPiva™ can be used to replace phenol at a high substitution rate to produce phenolic resins. Based on a detailed analysis of its molecular structure, it can be modified by appropriate reaction (demethylation and hydroxymethylation). Moreover, the characteristics of the thus-produced phenolic resins can be tailored to meet the market demand. Hence, UPM BioPiva™ has the potential to replace phenol in the industrial production of phenolic resins in the future as well as meet the increasingly stringent environmental protection requirements.

Acknowledgements The project was supported by the foundation (No. KF 201803) of state key laboratory of biobased material and green papermaking, Qilu University of Technology, Shandong Academy of Sciences. The authors are also grateful for the support of the National Key Basic Research Program of China (No. 202010298105Y). The work was also supported by the Nanjing Forestry University Outstanding Youth Fund (No. NLJQ 2015-5). The research did not receive any specific Grant from funding agencies in the public, commercial, or not-for profit sectors.

Declarations

Conflict of interest The authors declare that there is no conflict of interest related to this article.

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