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Preparing phenolic resins using pulping spent liquor

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ABSTRACT

The method of using spent liquor (SL) obtained from the chemical pretreatment stage of wheat straw semi-chemical pulping to prepare spent liquor phenolic resins (SLPR) was investigated in the present work. In this work spent liquor was modified with phenol, and then the modified spent liquor was further synthesized with phenol and formaldehyde under appropriate conditions. Experimental data shows that the substitution mass fraction of spent liquor for phenol, the mole ratios of formaldehyde and sodium hydroxide to phenol, temperature and duration time of addition and condensation reaction all show significant influence on the properties of SLPR. SLPR and pure phenolic resins (PR) exhibited almost the same macromolecular structures characterized by FT-IR, and the main properties of the SLPR such as free formaldehyde content, gel time and bonding strength demonstrated superiority to that of PR.

1. Introduction

Phenolic resins were first synthesized using phenol and formaldehyde by the German chemist Bayer in 1872, and are commonly used in various fields because of their superior bonding strength, excellent water resistance and electrical insulation and so on [1]. Aiming to reduce the cost of raw materials and improve the eco-friendliness of the products, considerable efforts have been undertaken in the past decade to replace phenol partially with biomass such as lignin and its derivatives [2–14]. Agricultural residues such as wheat straw offer a promising alternative to hardwood and softwood for papermaking in countries such as China, where forest resources are limited. In the chemical pretreatment stage of wheat straw semi-chemical pulping, a certain amount of lignin, hemi-celluloses and cellulose may undergo degradation and end up in spent liquor. The spent liquor could be used as a promising substitute for phenol in the preparation of phenolic resins, but research in this area has been limited. The aim of our research in this area has been to explore the feasibility of using pulping spent liquor as an effective substitute for phenol in the preparation of phenolic resins. In the present work, a method for preparing SLPR has been investigated and related technology parameters which affect the properties of SLPR discussed. Mechanisms responsible for the formation of the SLPR are also considered.

2. Experimental

2.1. Chemicals and materials

Phenol, sodium hydroxide, and a formaldehyde solution with an effective concentration of 37% were all analytically pure and procured from a local chemicals store. Cotton cloth with basis weight of 80 g/m^2 used to test bonding strength of adhesives was procured from a local merchandiser. Wheat straw, which was kept in storage more than 3 months, was obtained from a local paper mill having a moisture content less than 10%.

2.2. Methods

2.2.1. The preparation of spent liquor

Wheat straw was cut into pieces varying from 3.0 to 5.0 cm long and cooked with sodium hydroxide solution in a 15 L rotary electric heated digester. Prior to cooking, the raw material, sodium hydroxide of 6.0% based on oven dry straw and makeup water, was placed into the digester. The ratio of liquor (volume, mL) to wheat straw (weight, g) was 5:1. The temperature of the mixture was increased from room temperature to 110 °C over a period of 90 minutes and then maintained at this temperature for a further 60 min. Following this process, the contents of the digester were transferred into a plastic container, diluted with a certain amount of cold water and agitated vigorously for approximately 10 min to diffuse spent liquid from the straw pieces.

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The mixture was then transferred into a nylon bag of 100 mesh, and spent liquor was obtained by pressing the mixture manually. The spent liquor was then evaporated under conditions of 100 °C and atmospheric pressure to yield a higher concentration of 28.0% (solids content). Pulp obtained from the above process was then enclosed in a sealed polyethylene bag and stored for further use.

2.2.2. *Modification of spent liquor with phenol*

90.0 g of spent liquor with a solids content of 28%, 25.0 g of phenol and 4.0 g of sodium hydroxide were added into a 500 mL four-neck flask. The mixture was then heated to 45–50 °C and stirred for 20 min. The temperature was then raised to 105 °C and maintained at this temperature for 150 min. The modified product was then allowed to cool to room temperature.

2.2.3. *Synthesis of SLPR*

A predetermined amount of spent liquor modified with phenol and sodium hydroxide was added into a 500 mL four-neck flask. The reaction mixture was then stirred for 20 min at 45–50 °C, followed by the addition of an appropriate quantity of formaldehyde solution into the reaction system. The reaction system was heated to a temperature of 60–65 °C and maintained at this temperature for 1.0 h to allow completion of addition reactions. The mixture was then heated to 80 °C and maintained at this temperature for 2.0 h to allow completion of condensation reactions. Finally, the end product i.e. SLPR was cooled in a water bath to room temperature. Meanwhile, pure PR was prepared in accordance with the similar procedures to SLPR.

2.3. *Testing methods*

The solids content of the spent liquor was determined in accordance with TAPPI Standard (TAPPI T 650 OM 2005.01.01, solids content of black liquor). The lignin content of the spent liquor was determined in accordance with Chinese state Testing Standard (GB/T 2677.8-1994). The ash content of the spent liquor was determined by referring to Chinese state Testing Standard (GB/T 742–2008). Other organic components of the spent liquor can be considered as degraded carbohydrates originating from the wheat straw, and their content can be calculated by deducting lignin and ash from the solid content of the spent liquor. The pH, free formaldehyde content, gelation time and viscosity of the synthesized adhesives were all determined in accordance with Chinese state Testing Standard (GB/T 14074-2006).

The bonding strengths of the prepared adhesives were determined using a method based on Chinese State Testing Standards (GB/T 12914-2008 and GB/T 2791-1995). The testing procedure can be described as follows: Cotton cloth was cut into pieces with the size of 170 mm × 120 mm. Adhesives were coated evenly on one surface of the cloth, with coating weights (oven dry) controlled at 5.0 g/m^2. Coating area was controlled at a size of 170 mm × 80 mm by retaining a 40 mm blank space on one side of the cloth in the width direction. One piece of coated cloth and another piece of uncoated cloth were laminated together. The resulting assembly was then pressed at 0.2 MPa and room temperature for 5.0 min in a laboratory hydraulic press. The pressed assembly was then treated for 5.0 h under constant temperature and humidity conditions (23 ± 1 °C and 50 ± 2% respectively), and then cured for 30 min at 150 °C in an oven. The cured assembly was then treated for 24 h under the previously mentioned condition. Sample with dimensions of 150 mm × 100 mm was prepared by removing approximately 10 mm of material from each side of the pressed materials. The samples were then cut into ten testing specimens with dimensions of 15 mm × 100 mm. The specimens were tested by clamping two blank ends in a tensile testing machine. The remaining coating length of the specimen was controlled at 60 mm when it was stripped in testing machine, the bonding strengths was tested at room temperature, and the stripping rate was controlled at 90 ± 10 mm/min.

Table 1
Basic properties of spent liquor.

pH	Solids content (%)	Lignin content (%)	Ash content (%)	Other organics content (%)
9.9	28.0	5.91	8.57	13.52

Bond strengths were calculated using Eq. (1):

$$\delta_T = \frac{F}{B} \tag{1}$$

where δ_T is the bonding strength in kN/m. *F* is data recorded from the tensile tests, N. *B* is the width of the specimens in mm.

FT-IR spectra of spent liquor and adhesives were obtained using a Bruker VECTOR22 infrared spectrometer. The binding ability of the adhesives was tested using a Lorentzen & Wettre 062 tensile strength tester.

3. Results and discussions

3.1. *Basic properties of the spent liquor*

The basic properties of the spent liquor are presented in Table 1. The FT-IR spectrum of spent liquor is shown in Fig. 1.

As presented in Table 1, the spent liquor contains a certain amount of lignin, ash and other organics. Lignin molecular structure contains substantial benzene rings, so it can be used as a substitute for phenol in the preparation of phenolic resins [15]. Ash mainly consists of silicates which originate from the wheat straw, which can serve as a filler in phenolic resin formulations. The other organics which can include polysaccharides usually have a definite stickiness, which may improve the bonding ability of phenolic resins.

As shown in Fig. 1, the FT-IR spectrum of the spent liquor exhibits obvious molecular characteristics of lignin. Absorption peaks located at 3285 cm^{-1} and 2936 cm^{-1} can be attributed to the stretching vibration of O-H in carbonyl and -CH in methyl and methylene respectively. Absorption peaks located at 1564 cm^{-1} can be assigned to the vibration of the aromatic ring and C = O, absorption peaks located at 1404 cm^{-1} can be attributed to the plane deformation of C-H in the aromatic skeleton. The absorption peaks at 1116 cm^{-1} can be attributed to the stretching of secondary alcohols and C = O, whilst absorption peaks located at 1041 cm^{-1} may originate from the plane deformation of C-H in aryl and C-O in primary alcohol.

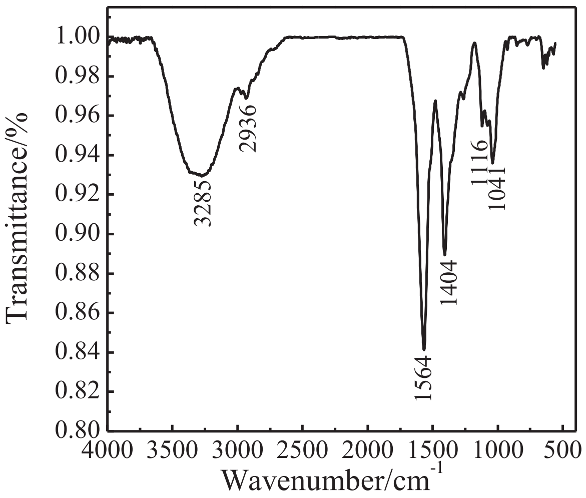

Fig. 1. FT-IR spectrum of spent liquor.

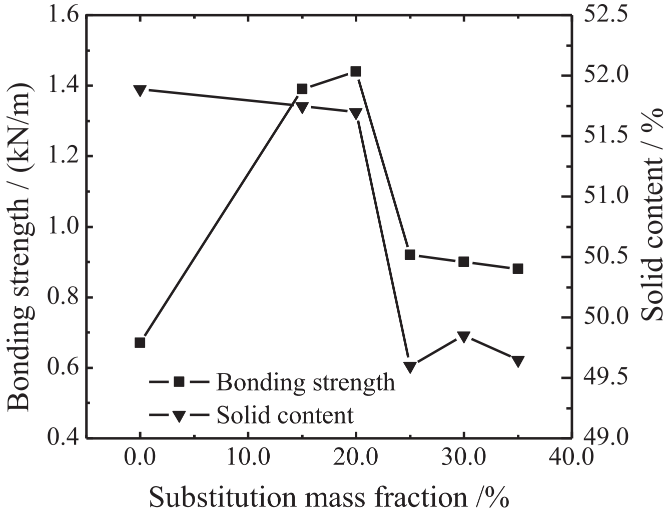

Fig. 2. Effects of substitution mass fractions on the properties of SLPR.

3.2. Analysis of the main preparation parameters of SLPR

3.2.1. Substitution mass fractions of spent liquor on phenol

As the mole ratio of formaldehyde to phenol is 2.0, the mole ratio of sodium hydroxide to phenol is 0.5, the substitution mass fractions of modified spent liquor with phenol on phenol vary from 0 to 35.0%, and the effects of substitution mass fractions on the properties of SLPR are shown in Fig. 2.

As indicated in Fig. 2, the bonding strength curve shows an increasing trend until the phenol substitution mass fraction reaches approximately 20.0% and then shows a decreasing trend. Khan et al. reported that copolymerization of lignin with phenol and formaldehyde may increase the cross link density of modified PR and thus improve its adhesive and shear strength [10]. Meanwhile, the solid content curve shows a decreasing trend as the substitution mass fraction varies from 0 to 35%, but the trend becomes precipitous after the substitution mass fraction of 20%. It can therefore be concluded that substitution mass fraction should be maintained below 20.0%.

The properties of SLPR can be associated with many factors, but the substitution mass fraction of spent liquor for phenol may be crucial. The effects of the substitution mass fraction on the properties of SLPR can be explained as follows: the reactive activity of the lignin may be lower than phenol, when the substitution mass fractions are below 20.0%, the polysaccharides in spent liquor may play a synergistic role in promoting the bonding strength of SLPR. As more spent liquor is added into the reaction system, the spent liquor may have a negative effect on the SLPR, potentially resulting in a deterioration in properties.

3.2.2. Mole ratio of formaldehyde to phenol

The effects of the mole ratio of formaldehyde to phenol (whilst maintaining preparation conditions as previously described and substitution mass fraction of modified spent liquor for phenol at 20%) on the properties of SLPR are shown in Fig. 3. As shown, the bonding strength curve reaches a maximum level at a formaldehyde-phenol mole ratio of 2.0 and then shows a decreasing trend with further increases in mole ratio. The solid content curve shows a continuing decline as the mole ratio varies from 1.4 to 2.2. However, from a bonding strength standpoint, the optimum mole ratio is clearly 2.0.

3.2.3. Mole ratio of sodium hydroxide to phenol

The effects of the mole ratio of sodium hydroxide to phenol on the properties of SLPR are shown in Fig. 4 (for systems in which preparation conditions are maintained constant and formaldehyde to phenol mole ratio set at 2.0). As shown, the solid content curve exhibits an increasing trend as the mole ratio varies from 0.25 to 0.8, and the bonding strength curve reaches a maximum at a mole ratio of 0.4. Thus it can be concluded that an appropriate mole ratio of sodium hydroxide to phenol would be 0.4.

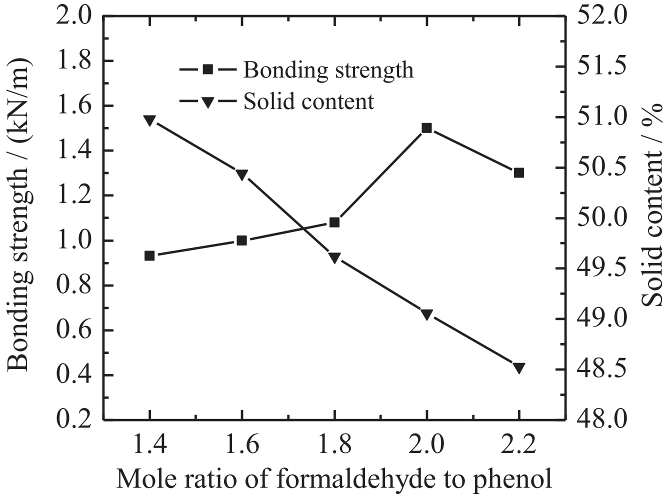

Fig. 3. Effects of mole ratio of formaldehyde to phenol on the properties of SLPR.

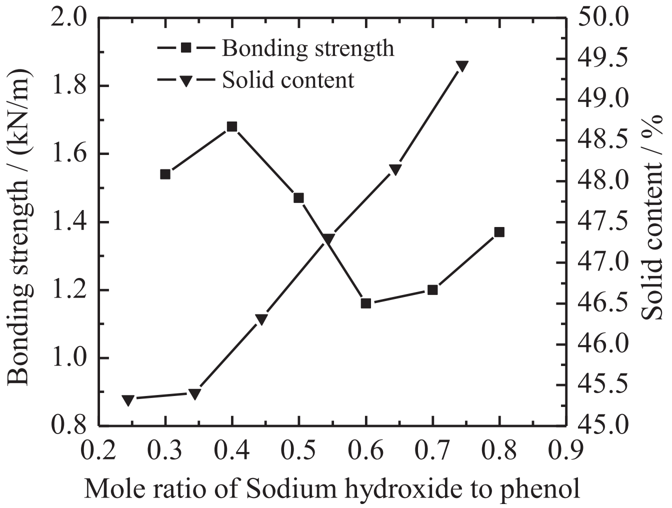

Fig. 4. Effects of mole ratio of sodium hydroxide to phenol on properties of SLPR.

3.2.4. Addition reaction temperature

With other preparation conditions being maintained constant and the mole ratio of sodium hydroxide to phenol ~~is~~ set at 0.4, the effects of addition reaction temperature on the properties of SLPR are shown in Fig. 5. As indicated, the solid content and bonding strength curves both reach a maximum level at an addition reaction temperature of 65 °C with a decreasing trend as temperature is further increased. Thus a reaction temperature of 65 °C can be considered as a reasonable condition for preparing SLPR.

3.2.5. Addition reaction time

Results showing the effects of reaction time (all other reaction conditions being maintained constant as described above) on the properties of SLPR are shown in Fig. 6. As indicated, the solid content and bonding strength curves both reach a maximum at a reaction time of 1.5 h followed by a negative trend with increasing reaction time. Thus a reaction time of 1.5 h can be considered a reasonable point for preparing SLPR.

3.2.6. Condensation reaction temperature

With the addition reaction temperature ~~is~~ set at 65 °C, and other

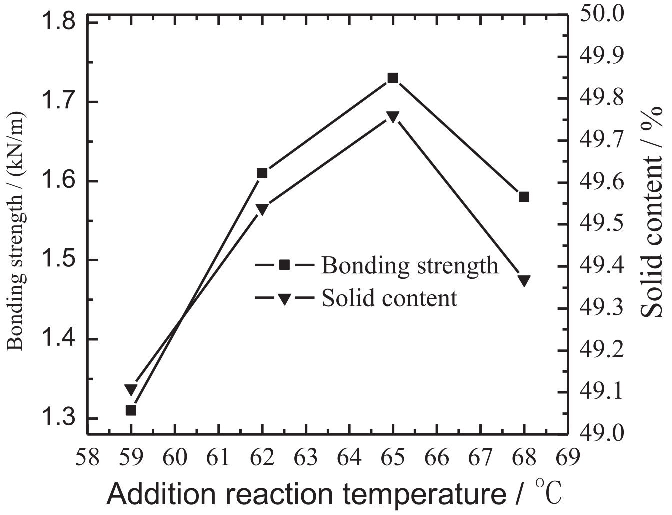

Fig. 5. Effects of addition reaction temperature on properties of SLPR.

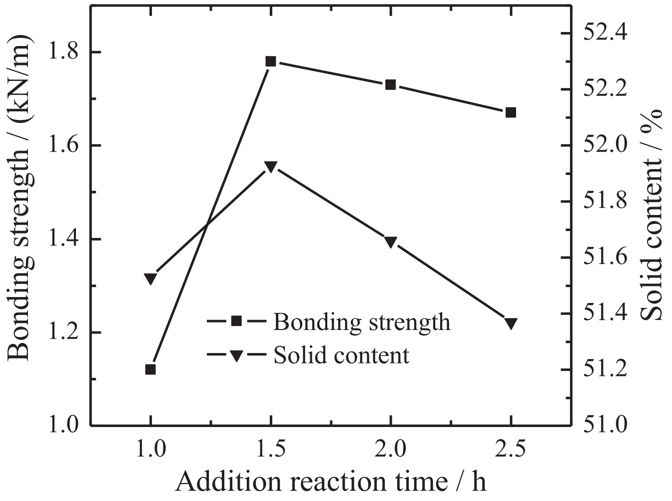

Fig. 6. Effects of addition reaction time on properties of SLPR.

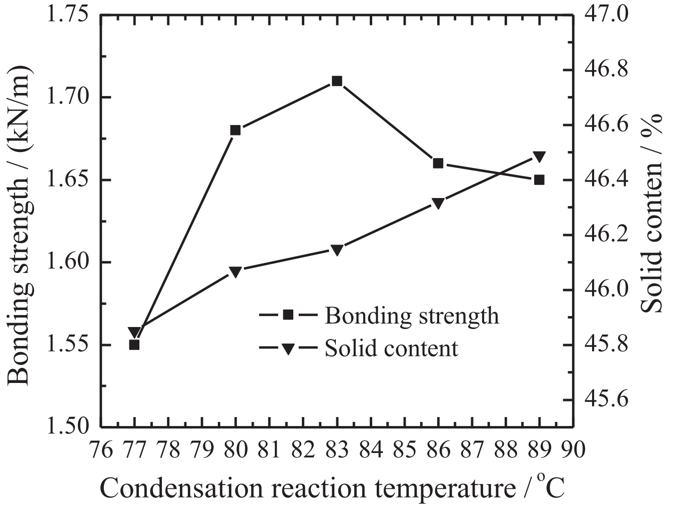

Fig. 7. Effects of condensation reaction temperature on properties of SLPR.

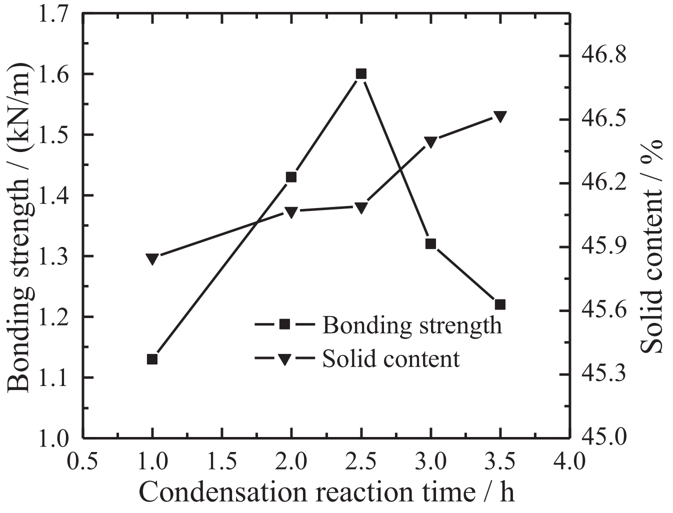

Fig. 8. Effects of condensation reaction time on properties of SLPR.

reaction conditions maintained as previously described, Fig. 7 shows the effect of condensation reaction temperature on the properties of SLPR. As indicated, the bonding strength curve exhibits a sharply increasing trend in comparison to the solid content curve as the condensation reaction temperature varies from 77 °C to 83 °C. The resin network formation rate will increase as the condensation temperature is increased, which, in all likelihood, will improve the properties of the SLPR. Thus 83 °C can be regarded as a reasonable condensation reaction temperature for the SLPR system.

3.2.7. *Condensation reaction time*

As other preparation conditions are kept the same as above and the condensation reaction temperature is set at 83 °C, the effects of the condensation reaction time on the properties of SLPR are shown in Fig. 8. As indicated, the bonding strength curve shows an increasing trend as the condensation reaction time varies from 1.0 h to 2.5 h and then shows a downward trend. The solid content curve shows an upward trend within the time range. It can be inferred that 2.5 h should be a reasonable condensation reaction time point for preparing SLPR.

3.3. *Comparison on FT-IR spectrum of SLPR and PR*

Hydroxymethylation can be considered as the main chemical reaction during the synthesis of SLPR. Some hydroxymethylation reactions may take place between some hydroxyl units such as the guaiac wood structure of lignin and formaldehyde, and other hydroxymethylation reactions may take place between formaldehyde and added phenol. The hydroxymethylation reaction of lignin is illustrated in Fig. 9.

The FT-IR spectra of SLPR and PR are shown in Fig. 10. Both SLPR and PR exhibit virtually the same characteristic absorption peaks generated by chemical functional groups of macromolecules of the two resins. Absorption peaks located at 1606 cm^{-1} can be assigned to the C=C bond stretching vibration of benzene. Absorption peaks located at 3429 cm^{-1} can be assigned to free hydroxyls (-OH) from two kinds of resins. The peak located at 2923 cm^{-1} can be assigned to methyl or methylene stretching vibrations for the two kinds of resin. The peak located at 1018 cm^{-1} can be assigned to the C-O stretching vibration of methoxy groups, whilst the absorption peak located at 1221 cm^{-1} can be assigned to the phenolic and alcoholic hydroxyl ether bond of the resins. Absorption peaks located at 1470 cm^{-1} and 1428 cm^{-1} can be assigned to the bending vibration of C-H in methoxy, and the peak of SLPR shifts to a higher wave number by about 40 units in comparison to PR. The intensities of the absorption peaks located at 3429 cm^{-1}, 2923 cm^{-1}, 1606cm^{-1} and 1221 cm^{-1} for SLPR are all attenuated compared to PR. Differences in the absorption peaks between these two resins illustrates that lignin is successfully copolymerized onto the resin molecular structures.

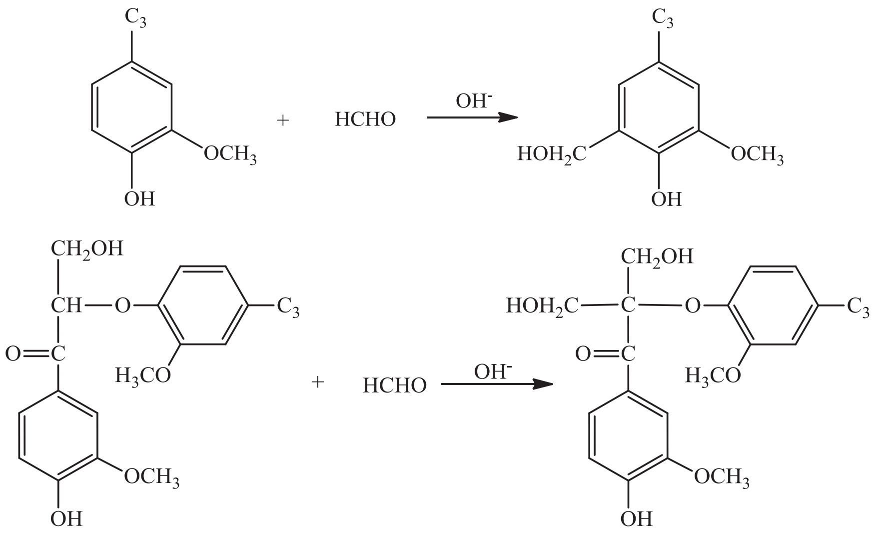

Fig. 9. Hydroxymethylation reactions of lignin with formaldehyde.

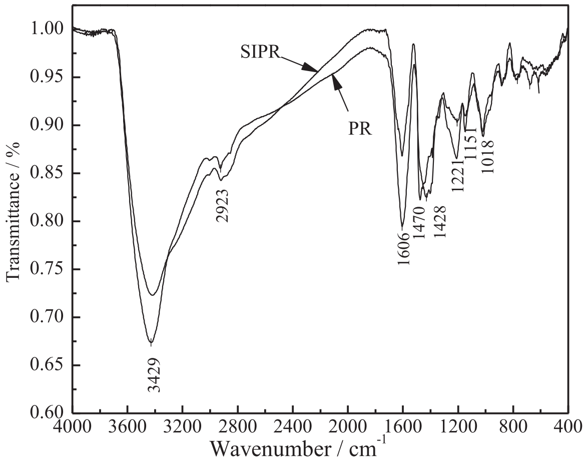

Fig. 10. FT-IR spectrums of SLPR and PR.

Table 2
Main properties of SLPR and PR.

	Resins	
	SLPR	PR
Viscosity at 20 °C (mPa s)	694.9	507.8
pH	10.8	11.5
Solid content (%)	48.36	54.76
Free formaldehyde content (%)	2.92	3.11
Gelation time (s)	412	585
Bonding strength (KN/m)	1.63	1.49

3.4. Comparison on properties of SLPR and PR

Main properties of SLPR and PR are presented in Table 2.

As shown in Table 2, the main properties of the SLPR are all similar to PR. Among them, the free formaldehyde content, gel time and bonding strength of SLPR demonstrates superiority to that of PR. The data illustrates that substitution of the mass fraction of spent liquor for phenol is feasible.

4. Conclusions

4.1 The spent liquor from the chemical pretreatment of wheat straw semi-chemical pulping can be used as a substitute of phenol to prepare phenolic resins, and the technology is useful for the comprehensive utilization of the spent liquor.

4.2 The appropriate technology conditions for preparing SLPR can be concluded as follows: the substitution mass fraction of spent liquor for phenol is 20.0%, the mole ratio of formaldehyde to phenol is 2.0, the mole ratio of sodium hydroxide to phenol is 0.4, the addition reaction temperature is 65 °C and time is 1.5 h, the condensation reaction temperature is 83 °C and time is 2.5 h.

4.3 The main properties of the SLPR such as free formaldehyde content, gelation time and bonding strength demonstrate superiority to that of PR.

Acknowledgments

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