

Pretreatment of Kraft Lignin by Deep Eutectic Solvent and its Utilization in Preparation of Lignin-based Phenolic Formaldehyde Adhesive

Xiteng Xian,^a Shubin Wu,^{a,*} Wenguang Wei,^b and Fengshan Zhang^b

To improve the reactive sites of kraft technical lignin, a deep eutectic solvent (DES) composed of ZnCl₂ / lactic acid was used to pretreat kraft lignin from coniferous wood. The modified and unmodified lignin were used to replace different proportions of phenol (50%, 60%, and 70%) to prepare the lignin-phenol-formaldehyde (LPF) adhesive. The phenolic hydroxyl content of DES-treated lignin increased from 3.12 wt% to 3.93 wt% and methoxy content decreased from 11.83 wt% to 6.64 wt% under optimized experimental conditions. The bond strength of LPF adhesive prepared by DES reagent activated lignin was higher than that of the control sample. When the substitution degree of modified lignin for phenol reached 70%, the bond strength of the plywood prepared by the DES-pretreated lignin was 0.79 MPa and the free formaldehyde content was 0.28%, which met the requirements of the Chinese national standard GB/T 9846 (2015). However, the viscosity was higher than the control sample, and results indicate that DES reagent modification cannot improve the viscosity of LPF resin.

Keywords: Kraft lignin; DES pretreatment; Phenolic formaldehyde resin

Contact information: a: State Key laboratory of Pulp & Paper Engineering, South China University of Technology, No. 381 Wushan Road, Guangdong Province, China; b: Shandong Huatai Paper Co., Ltd., Dongying, Shandong 257000, PR China; *Corresponding author: shubinwu@scut.edu.cn

INTRODUCTION

As the only renewable natural polymer on the earth, with guaiacol propane, *p*-syringyl propane, and *p*-hydroxyphenyl methane as its structural units, lignin has great potential. According to Liu *et al.* (2016), a large amount of lignin produced in the process of pulping and papermaking is burned or discharged as energy every year. Lignin has not been effectively utilized for high value because of its complex chemical structure and low reactivity. Scholars have conducted a lot of research on the chemical structure modification of industrial lignin and the application of modified products. Mao and Wu (2013) prepared surfactant from liquefaction products of kraft lignin and prepared a lignin-phenol nonionic surfactant, which is named ML-AL, by liquefaction modification of lignin. The results showed that the synergistic effect of the binary system of ML-AL and anionic surfactant exhibited the best performance, and the dosage ratio was about 0.4. Lignin-based phenolic resin adhesive was prepared from demethylated modification wheat straw kraft lignin (Wu and Zhan 1998, 2001) with the addition of sulfur and alkali at a temperature of 200 °C. The demethylation treatment is beneficial to the preparation of lignin phenolic resin adhesive; the methoxyl group of lignin was reduced from 10.39% to 6.09% and the content of phenolic hydroxyl group was increased from 2.98% to 5.51%. When the substitution degree of phenol is 60%, the prepared lignin-phenol-formaldehyde (LPF) adhesive is used

in plywood. At this value, the adhesive strength meets the requirements of Chinese national standard for class I outdoor plywood.

Phenolic resin is a kind of high molecular compound that is prepared by phenols and aldehydes. Since the discovery of phenolic resin by German chemists in 1872, its synthesis technology has been continuously developed. Thus far, the synthesis and commercial application of phenolic resin has been mature (Wang *et al.* 2014). However, phenolic resin also has its inherent disadvantages: its synthetic raw materials, phenol, and formaldehyde are toxic, and phenol is a non-renewable fossil raw material (Li *et al.* 2017). The lignin structural units have active phenolic hydroxyl groups; therefore, lignin has great potential in the preparation of lignin-based phenolic resin adhesive.

In order to improve the reactivity of industrial lignin and the stability of synthetic products, researchers have invented a variety of lignin modification methods in recent decades. Steam explosion was used to treat liginosulfonate, and lignin-based phenolic resin adhesive was prepared (Wang and Chen 2014). Glyoxal was used to treat lignin (Lei *et al.* 2010). Lignin was treated with sodium sulfite at low temperature and atmospheric pressure (Li *et al.* 2017), and the results showed that under the optimal conditions, the content of methoxyl lignin decreased from 1.93 mmol/g to 1.09 mmol/g, and the content of phenolic hydroxyl increased from 0.56 mmol/g to 0.82 mmol/g. Table 1 summarizes the commonly used lignin modification methods.

Table 1. Methods and Characteristics of Pretreatment of Lignin

Modification Method	Advantage	Shortcoming
Hydroxymethylation modification	The modification method is simple, and the requirement of reaction equipment is low	Formaldehyde is usually used for modification, which does not meet the requirements of green chemistry.
Hydroxyethylation modification	Avoid free formaldehyde emission	The reaction activity of modified lignin is worse than that of hydromethylation.
Demethylation modification	The reactivity of lignin was greatly improved	Most of the modification conditions are relatively harsh and the comprehensive cost is high.
Amination modification	It can be used in the production of polyurethane adhesive	Although amino groups were introduced into the lignin structure, the obtained amino groups had less active hydrogen, which affected the subsequent reaction.
Phenolic modification	The lignin reactivity and the number of active sites were increased	Phenol still needs to be used in the modification process, which does not meet the requirements of green chemistry.
Biological modification	Green environmental protection	The modification effect is not obvious.
Hydrothermal degradation	Rapid reaction, green environmental protection, good modification effect	The reaction energy consumption is high and the reaction conditions are harsh.

The emergence of ionic liquids provides a new method for lignin modification (Chew and Doshi 2011). Ionic liquid is a kind of ionic system in liquid state at room temperature, which is a type of salt material composed of organic cation and inorganic anion. Ionic liquids have been used in many chemical reactions and material separation

due to their good stability, easy reuse, pollution-free, and environmental friendliness (Fu *et al.* 2010). At present, most of the ionic liquids used to dissolve lignin are imidazolium salts and eutectic solvents. In order to recover lignin from lignocellulosic biomass, a cheap ionic liquid was used (Achinivu *et al.* 2014). [BMIM] [Ace] was used to treat eucalyptus wood powder. Under the optimal process conditions, the dissolution degree of lignin exceeded 90% (Sun *et al.* 2013). Although imidazole ionic liquids have good solubility for lignin, the synthesis process of imidazole ionic liquids is complex and the cost is high. The problem of green chemistry in the production of ionic liquids also needs to be solved. Recently, a new type of ionic liquid was synthesized for the first time, a deep eutectic solvent (DES). This was made of urea and choline chloride (Abbott *et al.* 2003, 2007). This new type of ionic liquid not only has the excellent properties of traditional ionic liquid, but it also has the advantages of low price, low toxicity, and biodegradability, so it has a great application prospect.

In recent years, DES has also been studied in the modification of lignin, showing a better application prospect. Lignin was modified with choline chloride/urea as solvent to improve its reactivity (Yang *et al.* 2017). Epoxy resin was prepared by using modified lignin (Liu *et al.* 2018), and the effects of reaction temperature, reaction time, and lignin dosage on the modification were investigated. The results showed that the content of total phenolic hydroxyl decreased, but the content of non-condensed G-type phenolic hydroxyl increased, which was beneficial to the reaction of lignin with urea, hydroxyl, and epoxy groups. Lignin-based phenolic resin adhesive was prepared by replacing phenol with modified lignin prepared by ZnCl₂/urea. The reaction activity of modified lignin was enhanced, and the curing time of the prepared lignin-based phenolic resin adhesive was significantly shortened (Lian *et al.* 2015). ZnCl₂/ChCl DES was used to modify lignin when the following conditions were met: the molar ratio of ZnCl₂:ChCl was 2:1; the reaction temperature was 80 °C; and the reaction time was 1 h. The reaction activity of modified lignin was the best, and the phenolic hydroxyl content was increased by 1.9 times. When the replacement degree of phenol by modified lignin is 40%, the bond strength of plywood can reach 1.3 MPa (Cao *et al.* 2016; Hong *et al.* 2016). Choline chloride and glycerol were used to synthesize eutectic solvent (Xie *et al.* 2016), and the experimental results showed that when the ratio of material mass is 1:2 of ChCl to glycerol is 1:2, the reaction efficiency of the system is the best, the viscosity of DES is moderate, and the system has good stability. The total phenolic hydroxyl content of lignin increased significantly after DES treatment. When phenol was replaced by 40% modified lignin, the bond strength of plywood was 0.98 MPa. Phenolic resin adhesive was prepared by treating bagasse kraft lignin with ionic liquid (Younesi-Kordkheili and Pizzi 2017). It was found that the viscosity and solid content of phenolic resin adhesive were improved by adding modified lignin. ChCl and urea were used to synthesize a deep eutectic solvent (Xu *et al.* 2015), and it was used to treat lignin. The results showed that the modified lignin had better effect when the reaction time was 2 h, the reaction temperature was 90 °C, and the amount of palladium chloride was 10% of lignin. When the replacement ratio of lignin to phenol was 40%, the bond strength can reach 1.29 MPa. A deep eutectic solvent with zinc chloride and acetamide was prepared, and experimental results showed that the lignin treated with zinc chloride / acetamide DES could effectively replace part of phenol to prepare modified lignin phenolic resin adhesive (Sun *et al.* 2016).

These studies show that pretreatment of lignin with DES reagent under certain conditions can relatively increase the phenolic hydroxyl content of lignin and have potential application in the synthesis of phenolic resin adhesive. But what is the effect of

DES on the chemical activation of kraft lignin extracted from the waste liquor of 100% softwood kraft pulping? Can DES pretreatment improve the viscosity and adhesive strength of lignin phenolic resin adhesive? This is the focus of this research work.

EXPERIMENTAL

Materials

Kraft lignin, which was extracted from 100% softwood kraft pulping waste liquor by sulfuric acid precipitation (precipitation temperature *ca.* 60 °C), filtered, washed and dried, was provided by Rizhao Huatai Paper Co., Ltd. (Rizhao, China). The ash content of the lignin was 4.95%. Poplar veneer was purchased from a local market. The chemicals, such as phenol, sodium hydroxide, ZnCl₂, lactic acid, urea, formaldehyde solution (37%), *etc.*, used in this research project were purchased from Guangzhou Qianhui Co., Ltd. (Guangzhou, China).

Methods

DES preparation

The mixture of ZnCl₂ and lactic acid solution (85 to 90%) with a molar ratio of 1:2 was heated to 80 °C in an oil bath until a uniform yellow transparent liquid was formed. After cooling, the mixture was placed in a dry environment for standby.

Pretreatment of lignin in DES reagent

A certain amount of kraft lignin and DES reagent were put into a flask, and the reaction was performed at a certain temperature, time, and mass ratio. After the reaction was completed, the whole reaction system was poured into a beaker, about twice the volume of deionized water was added, and then the reaction system was stirred for 1 h. After this time, a large number of flocculates appeared in the beaker. Contents underwent centrifugal separation. After repeated washing, the solid product was dried in an oven at 40 °C to obtain modified lignin. The unmodified lignin is expressed as L and the modified lignin is expressed as ML.

Preparation of adhesive

According to the literature (Sun *et al.* 2014), the phenolic hydroxyl content of lignin was calculated by characterization results, and the molar ratio of the phenolic hydroxyl content of lignin and phenol to formaldehyde was set as 1:9 and 1:2, respectively, so the molar mass of formaldehyde was calculated, and the mass substitution degree of lignin for phenol was approximately 50% to 70%. Lignin phenolic resin adhesive was prepared by five steps polymerization under alkaline condition. In the first step, lignin, phenol, and 1/2 formaldehyde and 1/2 NaOH solution (30 wt%) were added to a four-port flask and heated at 85 °C for 1 h; in the second step, 1/6 formaldehyde and 1/24 NaOH solution (30 wt%) were added to four port flask and kept at 85 °C for 20 min; in the third step, 1/6 formaldehyde and 1/12 NaOH solution (30 wt%) were added to four port flask and kept at 85 °C for 20 min; in the fourth step, 1/6 formaldehyde and 1/8 NaOH solution (30 wt%) were added to four port flask and kept at 85 °C for 20 min; fifth, 4.7 g formaldehyde capture agent (urea) and 1/4 NaOH solution (30 wt%) were added into the four port flask and kept at 70 to 80 °C until the proper viscosity; then, lignin-based phenolic resin adhesive was obtained by rapidly cooling to below 40 °C. The unmodified lignin phenolic resin adhesive

is abbreviated as LPF, the modified lignin phenolic resin adhesive is abbreviated as MLPF, in which MLPF-50, MLPF-60, and MLPF-70 represent the mass substitution degree of lignin for phenol, which is 50%, 60%, and 70% respectively.

The preparation method of pure phenolic resin adhesive was the same as that of lignin-based phenolic resin adhesive, except that lignin was not added. The pure phenolic resin adhesive is abbreviated as PF.

Lignin characterization

The phenolic hydroxyl content of lignin was determined by a UV spectrophotometer (UV-1990; Shimadzu Corporation, Kyoto, Japan), and the specific method followed Xie *et al.* (2016).

Headspace gas chromatography (GC-2014; Shimadzu Corporation, Kyoto, Japan) was used for the determination of methoxyl content of lignin, and the specific steps followed the method used by Li *et al.* (2012).

Fourier transform infrared (FTIR) spectroscopy analysis

Dried lignin sample was weighed (approximately 1 to 2 mg) and put into the sample tank of tablet pressing machine. KBr was added to the grinding mix, which was then pressed into a sheet. The FTIR scanning (Nicolet iS50; Thermo Fisher Scientific, Waltham, MA, USA) was conducted in the range of 4000 to 300 cm^{-1} , the resolution was 0.9 cm^{-1} , the scanning times were 32, and the ambient atmosphere is air.

Preparation of plywood

Samples of the three-layer plywood (20 cm \times 20 cm \times 2 mm) was pressed with phenolic resin adhesive. The moisture content of the poplar veneer was 12%, and all sides of the veneers were coated with approximately 175 to 200 g/m^2 adhesive. The pressing process was as follows: cold pressing at room temperature for 30 min, cold pressing pressure of 0.5 MPa; then hot pressing at 140 $^{\circ}\text{C}$, hot pressing pressure of 1.2 MPa, hot pressing time of 6 min; finally, cold pressing at room temperature, cold pressing pressure of 0.5 MPa, and cold pressing time of 6 min. The bond strength of plywood was determined according to GB/T 17657 (2013).

Determination of adhesive properties

The solid content and pH of resin were determined according to GB/T 14704 (2017). The free formaldehyde content of the adhesive was determined by headspace gas chromatography (the same instrument as above) (Li *et al.* 2013). At 25 $^{\circ}\text{C}$, the viscosity of the adhesive was measured by using Tu-4 viscosity cup meters and converted to dynamic viscosity according to the viscosity conversion table (Zhang 2004). The error range of viscosity determination was 0 to 54 $\text{mPa}\cdot\text{s}$. The resin was dried in vacuum at 60 $^{\circ}\text{C}$ and minus 0.1 MPa, and then tested by FTIR. The resolution was 0.9 cm^{-1} , the scanning times was 32, and the ambient atmosphere was air.

After curing at 120 $^{\circ}\text{C}$ for 2 h, the resin was ground into powder and determined by NETZSCH TG209F3 thermogravimetric analyzer (NETZSCH Group, Free State of Bavaria, Germany) in nitrogen atmosphere. The temperature range was 40 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$ and the heating rate was 10 $^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Properties of Lignin after Modification

Optimization of ZnCl₂ / lactic acid DES reagent treatment conditions

The effects of ZnCl₂ / lactic acid binary DES reagent on phenolic hydroxyl and methoxyl content of lignin under different treatment temperature, treatment time, and mass ratio are shown in Figs. 1, 2, and 3. The phenolic hydroxyl and methoxy content of unmodified lignin were 3.12 wt% and 11.83 wt%, respectively. Based on the initial content of the total of phenolic and methoxyl groups present in the unmodified lignin, the theoretical maximum of phenolic content was 14.95 wt%

Figure 1 shows the effect of DES reagent treatment time on phenolic hydroxyl and methoxyl content of lignin at 100 °C and mass ratio of 1:10 (lignin to DES reagent). The phenolic hydroxyl content increased from 3.93 wt% to 4.54 wt%, and the methoxyl content decreased from 10.46 wt% to 7.91wt%. Therefore, the activity of lignin increased after DES reagent treatment. However, with the extension of reaction time, the rate of reduction of methoxyl group decreased, which may be because the effect of demethoxylation reached a saturation point. However, the authors noticed that although the reaction activity of lignin was improved, with the extension of reaction time, the viscosity of the adhesive prepared by modified lignin was also increasing.

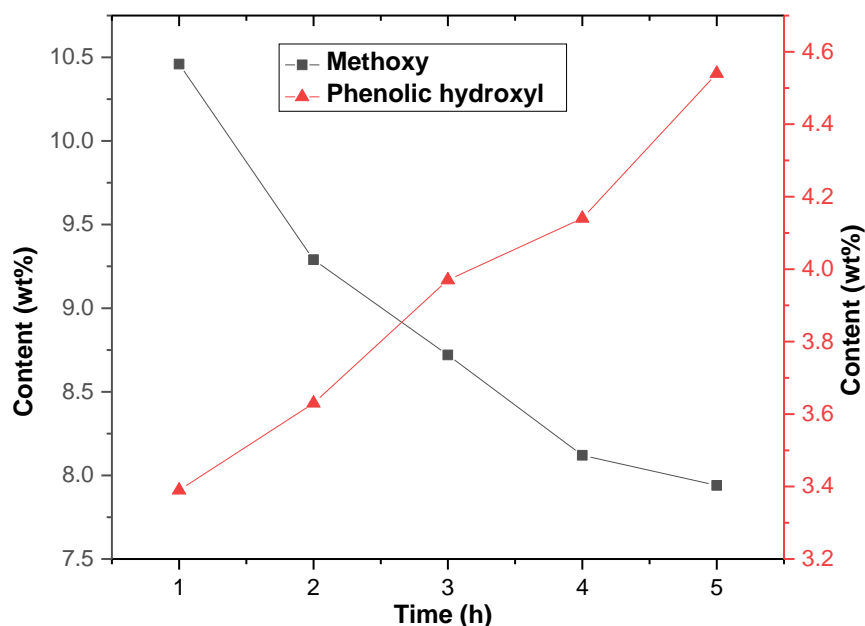


Fig. 1. The content of methoxy and phenolic hydroxyl of DES-treated lignin under different treatment time

Figure 2 shows the effect of DES reagent treatment on phenolic hydroxyl and methoxyl content of lignin at different temperatures under the conditions of reaction time of 2 h and mass ratio of 1:10 (lignin to DES reagent). With the increase of temperature, more phenolic hydroxyl groups were generated, and the content of methoxyl group decreased, which may be caused by a large number of chemical bond breaking with the increase of reaction temperature. However, there is a slight twist in the phenolic hydroxyl group of DES reagent pretreated lignin at 100 °C.

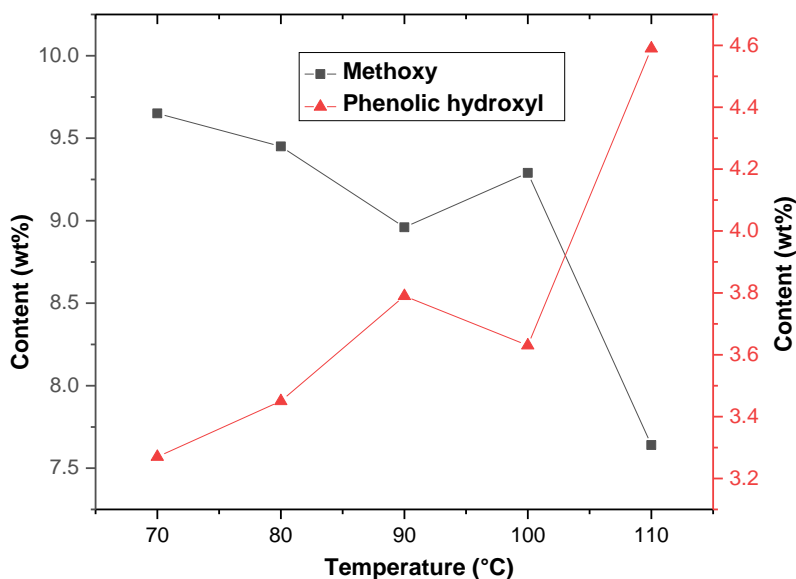


Fig. 2. Changes of the content of methoxy and phenolic hydroxyl at different DES treatment temperatures

Figure 3 shows the effect of mass ratio on phenolic hydroxyl and methoxyl content of DES-treated lignin at 80 °C for 2 h. When the mass ratio (lignin to DES reagent) ranged from 1:8 to 1:12, the content of phenolic hydroxyl group increased and the content of methoxyl group decreased. This may be because with the increase of mass ratio, DES reagent can dissolve lignin better and make lignin react better. When the mass ratio was 1:12, the phenolic hydroxyl content of the modified lignin was 3.93 wt%, and the methoxyl content was 6.46 wt%.

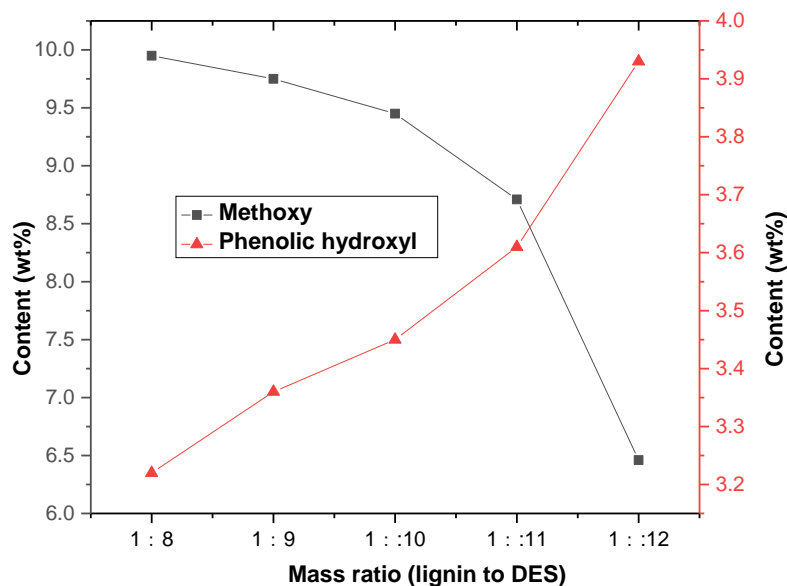


Fig. 3. Changes of the content of methoxy and phenolic hydroxyl of modified lignin (ML) of different mass ratios (lignin to DES solution, wt%/wt%)

Through the above analysis, from the point of view of obtaining lignin with high active functional groups, the optimal treatment conditions of binary DES reagent composed of ZnCl_2 / lactic acid reagent were as follows: treatment temperature $80\text{ }^\circ\text{C}$, treatment time 2 h, and mass ratio 1:12. Under the experimental conditions, phenolic hydroxyl content of modified lignin increased from 3.12 wt% to 3.93 wt% and methoxy content decreased from 11.83 wt% to 6.64 wt%.

Chemical structure characteristics of kraft lignin after DES reagent treatment

In order to further explore the structural changes of modified lignin, the lignin was analyzed by FTIR. The FTIR spectra of L and ML are shown in Fig. 4. There is a large absorption peak at 3400 cm^{-1} , which belongs to aromatic and aliphatic hydroxyl groups (Nadji *et al.* 2009). The absorption peaks at 2931 and 1459 cm^{-1} belong to the C-H vibration of methyl and methylene, and the absorption peaks at 2854 cm^{-1} is attributed with the C-H vibration of phenylpropane skeleton (Tejado *et al.* 2007). The absorption peaks at 1428 , 1513 , and 1600 cm^{-1} belong to the aromatic ring vibration in the phenylpropane skeleton of lignin. The absorption peak at 1513 cm^{-1} belongs to the coupling of aromatic ring vibration and C-H vibration; the absorption peak at 1428 cm^{-1} belongs to the coupling of aromatic ring vibration and C-H plane vibration (Ibrahim *et al.* 2011). The absorption peak of 1213 cm^{-1} is associated with the C-O of aromatic C-O (Ar) and the vibration of phenolic hydroxyl C-OH in guaiacyl-phenylpropane and syringyl-phenylpropane (Tejado *et al.* 2007). The absorption peak at 1030 cm^{-1} is associated with the C-O vibration of aliphatic C-O (Ar), alcohol hydroxyl, and hydroxymethyl C-OH in syringyl-phenylpropane. The 855 cm^{-1} absorption peak is associated with the C-H vibration of aromatic ring in guaiacyl-phenylpropane structural unit of lignin (Tejado *et al.* 2007).

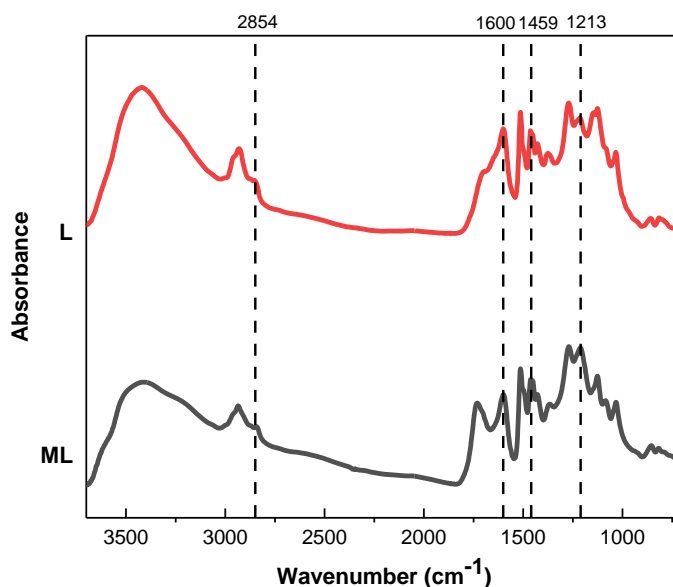


Fig. 4. FTIR spectra of L and ML (the pretreatment conditions of the ML were 2 h, $80\text{ }^\circ\text{C}$, and the mass ratio was 1:8)

According to the spectra, semi-quantitative analysis was used to verify the chemical structure change of modified lignin. The vibration of phenolic ring skeleton in lignin is approximately 1600 cm^{-1} . This absorption peak can be basically consistent in different

reaction systems and is not affected by the reaction system. Therefore, the absorption peak can be regarded as an internal standard group to calculate the relative content of other functional groups, and its relative absorbance value is set to 1.00. The relative content of other groups can be calculated by the absorbance value of the group (1600 cm^{-1}) (Li *et al.* 2016; Li *et al.* 2017).

Table 2. Relative Absorbance Values of Different Peaks in FTIR Spectra of L and ML

Wavenumber (cm^{-1})	Relative Absorbance Value		Ascription
	L	ML	
1030	0.939	0.922	N(-OH)
1213	1.031	1.520	v(-OH)
1459	1.005	1.160	δ_{am} (C-H)
1600	1.000	1.000	v(C=C)
2854	0.859	0.655	v(C-H)
2931	0.946	0.879	vip(-CH ₂ -)
3400	1.119	1.149	v(-OH)

Note: v: Stretching vibration; δ : deformation vibration; am: asymmetric vibration; ip: in-plane vibration

The relative absorbance values of different peaks in the spectra are shown in Table 2. Compared with L, ML has more phenolic hydroxyl content (1213 cm^{-1}) and less methoxyl content (2854 cm^{-1}). These data show that DES reagent treatment can effectively break the methyl aryl ether bond and increase the content of phenolic hydroxyl group. Studies have shown that the increase of phenolic hydroxyl content can improve the reaction activity of lignin with formaldehyde, so the phenolic hydroxyl content in lignin is an important factor affecting the quality of lignin phenolic resin adhesive (Doherty *et al.* 2011). Some studies have shown that a large number of phenolic hydroxyl groups in lignin can agglomerate lignin to form rigid polymer, which makes lignin show poor activity (Sarkar and Adhikari 2001). However, researchers generally believe that the higher the phenolic hydroxyl content in lignin, the higher the quality of lignin phenolic resin adhesive (Khan *et al.* 2010). In this experiment, DES reagent can increase the content of phenolic hydroxyl groups in lignin under conditions of low temperature and atmospheric pressure. Theoretically, the phenol substitution degree and bond strength of the DES reagent modified lignin adhesive can be improved.

Properties of Lignin-based Phenolic Resin Adhesive

Effects of ZnCl_2 / lactic acid DES reagent treatment conditions on the bond strength and physical properties of MLPF

Figure 5 shows that with the extension of DES reagent treatment time, the bond strength of plywood increased firstly and then decreased. This indicates that although the phenolic hydroxyl content of lignin increased after DES reagent treatment, the phenolic hydroxyl content was not the only factor affecting the bond strength of lignin-based phenolic resin plywood. The reason for this phenomenon may be that the reaction time was long. Lignin molecules agglomerate to form a rigid structure, thus reducing the reaction activity of lignin (Sarkar and Adhikari 2001; Thring *et al.* 2004). Additionally, with the extension of DES reagent treatment time, the viscosity of the adhesive increased, so the

adhesive cannot be used in actual production. Therefore, in the follow-up experiments, the pretreatment time of DES reagent was determined to be 2 h.

Figure 6 shows that the bond strength of plywood increased with the increase of the reaction temperature, and the bond strength of plywood increases from 1.32 to 1.57 MPa. The reason may be that the content of phenolic hydroxyl groups in lignin increased with the increase of the temperature of DES reagent treatment, so there were more active sites in lignin to react with formaldehyde, which made the prepared lignin-based phenolic resin adhesive have good adhesion. However, with the extension of DES reagent treatment time, the viscosity of lignin phenolic resin also increased. When the DES reagent treatment temperature was 80 °C, the viscosity and bond strength of the adhesive meet the actual production requirements.

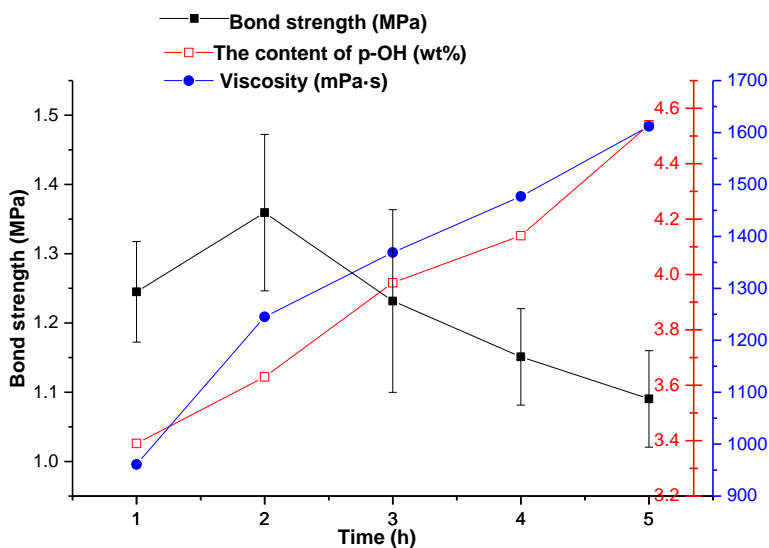


Fig. 5. The changes of phenolic hydroxyl content, MLPF viscosity, and bond strength with DES treatment time

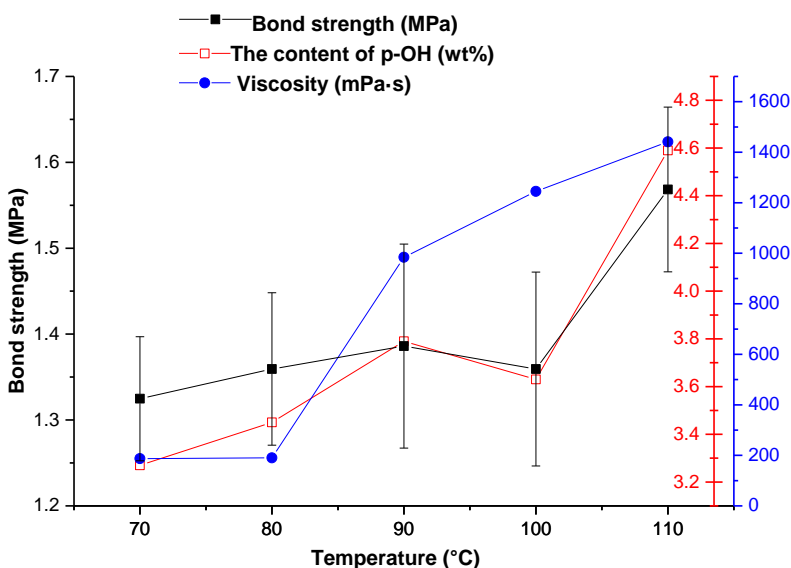


Fig. 6. The changes of phenolic hydroxyl content, MLPF viscosity, and bond strength with DES treatment temperature

It can be seen from Fig. 7 that with the increase of mass ratio, the bond strength of plywood first increased and then decreased, and its viscosity increased continuously. This may be because with the increase of mass ratio, lignin dissolves better in DES reagent. However, phenolic hydroxyl groups in lignin may agglomerate lignin into a rigid polymer structure during the reaction. The lignin showed poor properties (Sarkar and Adhikari 2001; Thring *et al.* 2004). In order to meet the viscosity of adhesive used in actual production, the mass ratio of 1:8 was selected for subsequent tests.

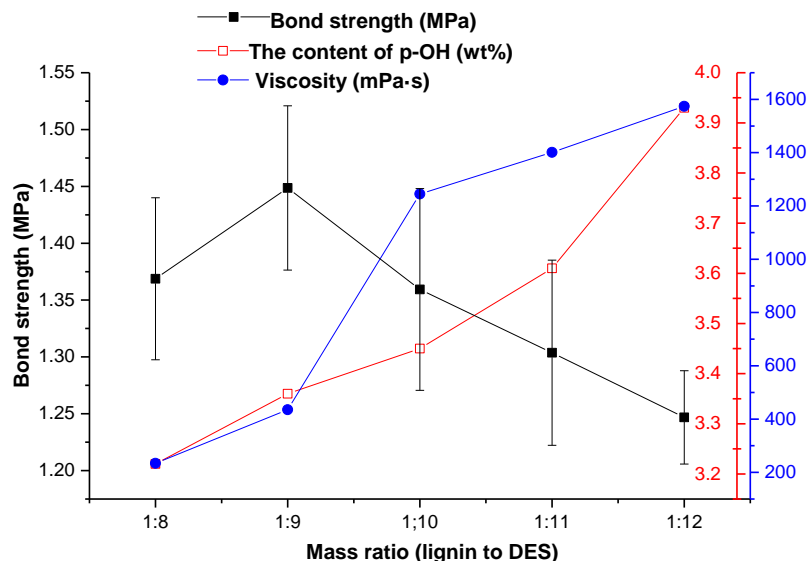


Fig. 7. The changes of phenolic hydroxyl content, MLPF viscosity, and bond strength with DES reagent treatment mass ratios

Effect of substitution degree of modified lignin for phenol on properties of lignin-based phenolic resin adhesive

The influence of different substitution degrees of lignin to phenol on phenolic resin adhesive was explored, and the experimental results are shown in Fig. 8.

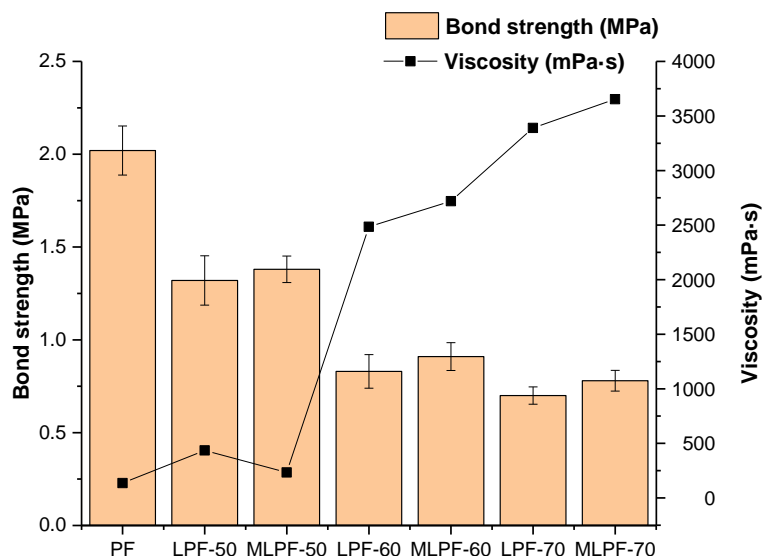


Fig. 8. Bond strength and viscosity of LPF and MLPF with different substitution degree of lignin to phenol percentage (50, 60, and 70%)

It is apparent that with the increasing of lignin substitution degree, the adhesive strength decreased and the viscosity increased. The bond strength of the MLPF were higher than that of the LPF. However, with the increase of lignin content, the viscosity of the adhesive also increased. Therefore, the relatively ideal replacement degree was 60%. Follow-up research is encouraged to look at how to reduce the viscosity of resin while improving the substitution degree of modified lignin.

Table 3 shows the physical properties of lignin-based phenolic resin adhesive. Under the same substitution degree, the free formaldehyde content of lignin-based phenolic resin adhesive prepared by ML was lower than that of L. This is because, compared with phenol, modified lignin had a larger molecule and the number of phenolic hydroxyl groups on the benzene ring was less uniform, which affects the demand for formaldehyde in the polymerization process of LPF resin.

Table 3. Physical Properties of Lignin Phenolic Resin Adhesive

Resin	Solid Content (%)	Free Formaldehyde Content (%)	Bond Strength (MPa)	pH
PF	48.30	0.16	2.00(2.15 to 1.84)	12.30
LPF-50	53.45	0.35	1.23(1.46 to 1.10)	12.51
MLPF-50	43.37	0.31	1.37(1.46 to 1.28)	12.75
LPF-60	53.88	0.36	0.83(0.97 to 0.71)	12.23
MLPF-60	45.12	0.30	0.91 (1.02 to 0.82)	12.92
LPF-70	50.33	0.29	0.7(0.78 to 0.66)	12.91
MLPF-70	47.83	0.28	0.78(0.86 to 0.68)	12.79

FTIR and thermal stability analysis of adhesives

In order to study the difference of chemical structure between different resins, the lignin-based phenolic resin adhesive was analyzed by FTIR spectra. As shown in Fig. 9, different resins had similar functional group structures, which indicates that they had similar molecular structures.

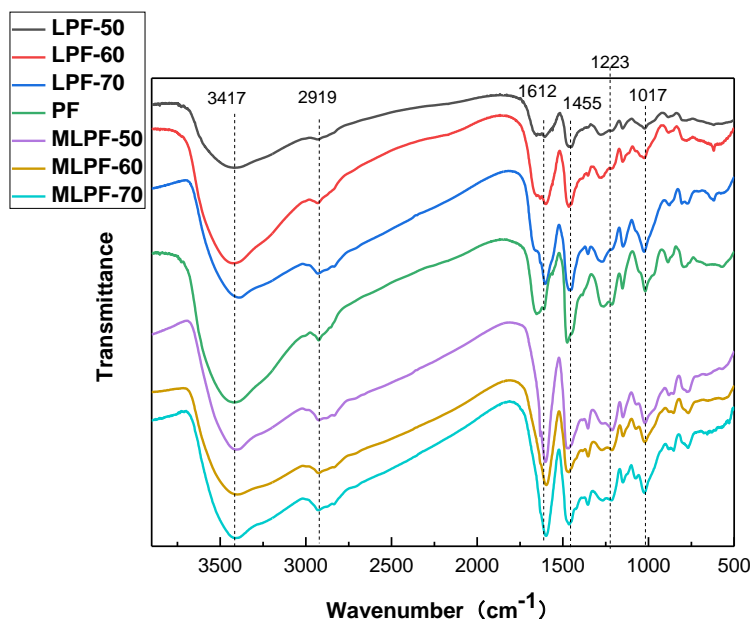


Fig. 9. FTIR spectra of PF resins, LPFs, and MLPFs

From the spectra, all adhesives exhibited an absorption peak of -OH at 3417 cm^{-1} . The absorption peak at 2919 cm^{-1} corresponds to the methylene bridge bond, and the absorption peaks at 1612 cm^{-1} and 1445 cm^{-1} belong to the vibration of aromatic ring in phenylpropane skeleton (Wang *et al.* 2009). The absorption peak at 1223 cm^{-1} is associated with the stretching vibration of C-O in phenolic hydroxyl group, and the absorption peak at 1017 cm^{-1} is associated with the stretching vibration of aliphatic C-O (Ar), C-O in aliphatic C-OH, and hydroxymethyl C-OH (Yi *et al.* 2016).

Although they have some similarities in structure, there are some differences in spectra between LPF, MLPF, and PF: the absorption band of LPF and MLPF are weaker than that of PF at 1259 cm^{-1} , which indicates that the stretching vibration of phenolic hydroxyl C-O in PF is greater than that of LPF and MLPF. Because the content of phenolic hydroxyl in LPF and MLPF is much lower than that of PF, part of phenol in LPF and MLPF is replaced by lignin, thus reducing the total content of phenolic hydroxyl in LPF and MLPF; at 1017 cm^{-1} , the absorption peak of LPF and MLPF is wider than that of PF, which is because the LPF and MLPF contain not only hydroxymethyl, but also a large number of hydroxyl alcohols due to the addition of lignin (Zhang *et al.* 2013a,b).

In order to explore the effect of lignin on the thermal stability of phenolic resin adhesive, the phenolic resin adhesive was analyzed by thermogravimetry in nitrogen atmosphere. The maximum thermal degradation temperature of different degradation stages is expressed by the peak value of DTG curve (T_{max}), which indicates the thermal stability of phenolic resin adhesive. In order to eliminate the interference of moisture and more accurately explore the thermal stability of phenolic resin adhesive at high temperature, phenolic resin was cured at $120\text{ }^{\circ}\text{C}$ for 2 h, and then ground into powder for TGA analysis (Zhang *et al.* 2013a,b). Figure 10 shows the TGA curve and DTG curve of phenolic resin adhesive. Table 3 shows the T_{max} of phenolic resin adhesive at different degradation stages and the residual mass at $600\text{ }^{\circ}\text{C}$.

The thermal degradation of phenolic resin can be divided into three stages: post curing, thermal reforming, and ring cracking (Alma and Kelley 2000). It can be seen from Fig. 10 that the range of 110 to $210\text{ }^{\circ}\text{C}$ is the first degradation stage, and the mass loss in the first stage is mainly caused by the evaporation of water produced by the condensation reaction of hydroxymethyl (Li *et al.* 2017). It can be seen that the highest degradation temperature of MLPF in this degradation stage is higher than that of PF. Therefore, the thermal stability of MLPF is better than that of PF in the first stage of thermal degradation. The second degradation stage occurs in the range of 210 to $430\text{ }^{\circ}\text{C}$. The volatilization of water generated by the condensation reaction between methylene and phenolic hydroxyl is the main reason for the mass loss in the second stage (Lee *et al.* 2012). MLPF and PF have similar thermal stability in the second thermal degradation stage. The third thermal degradation stage occurred in the range $450\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$ (Khan *et al.* 2010). The mass loss at this stage is mainly caused by the volatilization of methane and carbon monoxide produced by the fracture of methylene bridge. The T_{max} of PF at this stage is higher than that of MLPF, and at $600\text{ }^{\circ}\text{C}$, compared with MLPF, PF has higher residual mass, so in the third thermal degradation stage, the thermal stability of PF is better than that of MLPF.

According to the above analysis, the authors can draw the following conclusions: in the initial thermal degradation stage, the thermal stability of MLPF is greater than that of PF, but with the rise of thermal degradation temperature, the PF shows better thermal stability, which is consistent with the previous reports (Zhang *et al.* 2013a,b; Li *et al.* 2017).

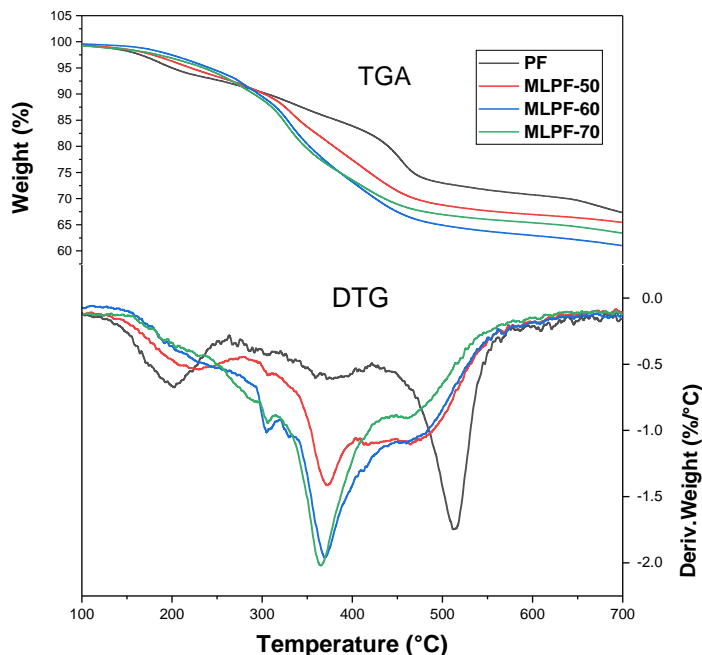


Fig. 10. TG and DTG for PF Resins and MLPFs

Table 4. Thermal Stability of Lignin Phenolic Resin

Sample	First Degradation Stage T_{max} (°C)	Second Degradation Stage T_{max} (°C)	Third Degradation Stage T_{max} (°C)	Residual Mass at 600 °C (%)
PF	200	374	510	72.2
MLPF-50	224	370	470	68.1
MLPF-60	303	369	459	64.2
MLPF-70	307	363	460	66.4

CONCLUSIONS

1. The content of phenolic hydroxyl group in lignin can be increased and the content of methoxyl group in lignin can be decreased by using a deep eutectic solvent (DES) reagent to treat lignin. This study provides a green method for the activation of kraft lignin. The results showed that the optimal treatment conditions were as follows: treatment temperature was 80 °C, treatment time was 2 h, mass ratio was 1:12. Under those conditions the phenolic hydroxyl content of lignin increased from 3.12 wt% to 3.93 wt%, while the methoxy content decreased from 11.83 wt% to 6.64 wt%.
2. The bond strength of phenolic resin adhesive prepared by DES reagent activated lignin was higher than that of control phenolic resin adhesive. When the substitution degree of modified lignin for phenol reached 70%, the bond strength of the plywood prepared by the lignin-based phenolic resin adhesive was 0.79 MPa and the free formaldehyde content was 0.28%, which meet the requirements of the Chinese national standard GB/T 9846 (2015), but the viscosity of the MLPF resin was higher than that of LPF. Therefore, the DES modification cannot improve the viscosity of

LPF resin. In the experiment, MLPF-60 showed better properties and practicality. In addition, the bond strength and free formaldehyde content are in conformity with Chinese national standard GB/T 9846 (2015).

ACKNOWLEDGMENTS

The authors thankfully acknowledge the support of Key Research and Development Program of Shandong Province (No. 2019JZZY010501); The National Natural Science Foundation of China (No. 31870558), and the Science and Technology Project of Guangzhou City (No. 202002030157).

REFERENCES CITED

- Abbott, A. P., Harris, R. C., and Ryder, K. S. (2007). "Application of hole theory to define ionic liquids by their transport properties," *Journal of Physical Chemistry B* 111(18), 4910. DOI: 10.1021/jp0671998
- Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., and Tambyrajah, V. (2003). "Novel solvent properties of choline chloride/urea mixtures," *Chemical Communications* 2003(1), 70-71. DOI: 10.1039/B210714G
- Achinivu, E. C., Howard, R. M., Li, G., Gracz, H., and Henderson, W. A. (2014). "Lignin extraction from biomass with protic ionic liquids," *Green Chemistry* 16, 1114-1119. DOI: 10.1039/C3GC42306A
- Alma, M. H., and Kelley, S. S. (2000). "Thermal stability of novolak-type thermosettings made by the condensation of bark and phenol," *Polymer Degradation and Stability* 68(3), 413-418. DOI: 10.1016/S0141-3910(00)00029-X
- Cao, X. Q., Hong, S., Ding, Q. Q., Chen, F., Q., Zhu, M. J., and Lian, H. L. (2016). "Lignin modified by DES with $\text{ChCl}/\text{ZnCl}_2$ to prepare phenol-formaldehyde resin adhesive," *China Forest Products Industry* 43(10), 25-29. DOI: 10.19531/j.issn1001-5299.2016.10.007
- Chew, J. J., and Doshi, V. (2011). "Recent advances in biomass pretreatment - Torrefaction fundamentals and technology," *Renewable & Sustainable Energy Reviews* 15(8), 4212-4222. DOI: 10.1016/j.rser.2011.09.017
- Doherty, W. O. S., Mousavioun, P., and Fellows, C. M. (2011). "Value-adding to cellulosic ethanol: Lignin polymers," *Industrial Crops and Products* 33(2), 259-276. DOI: 10.1016/j.indcrop.2010.10.022
- Fu, D., Mazza, G., and Tamaki, Y. (2010). "Lignin extraction from straw by ionic liquids and enzymatic hydrolysis of the cellulosic residues," *Journal of Agricultural & Food Chemistry* 58(5), 2915-2922. DOI: 10.1021/jf903616y
- GB/T 14074 (2017). "Testing methods for wood adhesives and their resin," Standardization Administration of China, Beijing, China.
- GB/T 9846 (2015). "Plywood for general use," Standardization Administration of China, Beijing, China.
- GB/T 17657 (2013). "Test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels," Standardization Administration of China, Beijing, China.

- Hong, S., Lian, H., Sun, X., Pan, D., Carranza, A., Pojman, J. A., and Mota-Morales, J. D. (2016). "Zinc-based deep eutectic solvent-mediated hydroxylation and demethoxylation of lignin for the production of wood adhesive," *RSC Advances* 6(92), 89599-89608. DOI: 10.1039/C6RA18290A
- Ibrahim, V., Mendoza, L., Mamo G., and Hatti-Kaul, R. (2011). "Blue laccase from *Galerina* sp.: Properties and potential for kraft lignin demethylation," *Process Biochemistry* 46(1), 379-384. DOI:10.1016/j.procbio.2010.07.013
- Khan, M. A., Ashraf, S. M., and Malhotra, V. P. (2010). "Eucalyptus bark lignin substituted phenol formaldehyde adhesives: A study on optimization of reaction parameters and characterization," *Journal of Applied Polymer Science* 92(6), 3514-3523. DOI: 10.1002/app.20374
- Lee, W. J., Chang, K. C., and Tseng, I. M. (2012). "Properties of phenol-formaldehyde resins prepared from phenol-liquefied lignin," *Journal of Applied Polymer Science* 124(6), 4782-4788. DOI: 10.1002/app.35539
- Lei, H., Pizzi, A., and Du, G. (2010). "Environmentally friendly mixed tannin/lignin wood resins," *Applied Polymer Science* 107(1), 203-209. DOI: 10.1002/app.27011
- Li, H. L., Chai, X. S., Liu, M. R., and Deng Y. H. (2012). "Novel method for the determination of the methoxyl content in lignin by headspace gas chromatography," *Journal of Agricultural and Food Chemistry* 60(21), 5307-5310. DOI: 10.1021/jf300455g
- Li, J. J., Wang, W., Zhang, S. F., Gao, Q., Zhang, W., and Li, J. Z. (2016). "Preparation and characterization of lignin demethylated at atmospheric pressure and its application in fast curing biobased phenolic resins," *RSC Advances* 6(71), 67435-67443. DOI: 10.1039/C6RA11966B
- Li, J. J., Zhang, J. Z., Zhang, S. F., Gao, Q., Li, J. Z., and Zhang, W. (2017). "Fast curing bio-based phenolic resins via lignin demethylated under mild reaction condition," *Polymers* 9(9), Article Number 428. DOI: 10.3390/polym9090428
- Li, L. V., Hui, L., Xi, H. U., Yang-Li, W., and Station, E. M. (2013). "The detection of methanal and BETX in surface water by headspace gas chromatography," *Science and Technology of West China* 12(10), 45-47. DOI: 10.3969/j. assn. 671-6396. 2013. 10. 019
- Lian, H., Hong, S., Carranza, A., Mota-Morales, J. D., and Pojman, J. A. (2015). "Processing of lignin in urea-zinc chloride deep-eutectic solvent and its use as a filler in a phenol-formaldehyde resin," *RSC Advances* 5(36), 28778-28785. DOI: 10.1039/C4RA16734A
- Liu, J., Wang, J., Fu, Y., and Chang, J. (2016). "Synthesis and characterization of phenol-furfural resins using lignin modified by a low transition temperature mixture," *RSC Advances* 6(97), 94588-94594. DOI: 10.1039/C6RA17877D
- Liu, T. Q., Lian, H. L., Hong, S., Chen, L., and Zhu, P. (2018). "Effect of modified lignin by choline chloride/urea deep-eutectic solvent on curing properties of epoxy resin," *Journal of Northeast Forestry University* 46(04), 78-82+87. DOI: 10.13759/j.cnki.dlxb.2018.04.016
- Mao, C. P., and Wu, S. B. (2013). "Synergistic effects of lignin-phenol-based nonionic surfactant with anionic surfactants in aqueous solution," *BioResources* 8(4), 5025-5035. DOI: 10.15376/biores.8.4.5025-5035
- Nadji, H., Diouf, P. N., Benaboura, A., and Stevanovic, T. (2009). "Comparative study of lignins isolated from alfa grass (*Stipa tenacissima* L.)," *Bioresource Technology* 100(14), 3585-3592. DOI: 10.1016/j.biortech.2009.01.074

- Sarkar, S., and Adhikari, B. (2001). "Jute felt composite from lignin modified phenolic resin," *Polymer Composites* 22(4), 518-527. DOI: 10.1002/pc.10556
- Sun, Y. C., Xu, J. K., Xu, F., and Sun, R. C. (2013). "Efficient separation and physico-chemical characterization of lignin from eucalyptus using ionic liquid-organic solvent and alkaline ethanol solvent," *Industrial Crops and Products* 47, 277-285. DOI: 10.1016/j.indcrop.2013.03.025
- Sun, R. C., Yuan, T. Q., Yang, S., and Wen, J. L. (2014). "Preparation method of lignin-based environment friendly phenolic resin adhesive," China Patent: CN 103804618 A.
- Sun, X., Chen, L., and Lian, H. L. (2016). "The pyrolysis and pyrolysis kinetics of phenol-formaldehyde resin modified with lignin in deep eutectic solvent," *China Forest Products Industry* 43(5), 19-24. DOI: 10.19531/j.issn1001-5299.2016.05.005
- Tejado, A., Peña, C., Labidi, J., and Mondragon, I. (2007). "Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis," *Bioresource Technology* 98(8), 1655-1663. DOI: 10.1016/j.biortech.2006.05.042
- Thring, R. W., Ni, P., and Aharoni, S. M. (2004). "Molecular weight effects of the soft segment on the ultimate properties of lignin-derived polyurethanes," *International Journal of Polymeric Materials & Polymeric Biomaterials* 53(6), 507-524. DOI: 10.1080/00914030490267627
- Wang, G., and Chen, H. (2014). "Carbohydrate elimination of alkaline-extracted lignin liquor by steam explosion and its methylation for substitution of phenolic adhesive," *Industrial Crops and Products* 53, 93-101. DOI: 10.1016/j.indcrop.2013.12.020
- Wang, T. Y., Tong, J. C., Liu, Y. L., and Cao, S. K. (2014). "New progresses on phenolic resins," *Chinese Polymer Bulletin* 12, 39-46. DOI: 10.14028/j.cnki.1003-3726.2014.12.004
- Wu, S. B., and Zhan, H. Y. (1998). "Change in physico-chemical characteristics and structures of wheat straw soda lignin after modification," *Journal of South China University of Technology (Natural Science Edition)* 11, 3-5.
- Wu, S. B., and Zhan, H. Y. (2001). "Characteristics of demethylated wheat straw soda lignin and its utilization in lignin-based phenolic formaldehyde resins," *Cellulose Chemistry and Technology* 35(3), 253-262.
- Xie, P. P., Lian, H. L., and Sun, X. (2016). "Modification of lignin-phenol-formaldehyde adhesive with ChCl/glycerol deep-eutectic solvent," *Journal of Forestry Engineering* 1(4), 107-113. DOI: 10.13360/j.issn.2096-1359.2016.04.018
- Xu, X. D., Hong, S., An, R., Huang, H. L., and Lian, H. L. (2015). "Structural features of lignin modified by palladium chloride catalyst in eutectic ionic liquids," *China Forestry Science and Technology* 29(6), 116-119. DOI: 10.13360/j.issn.1000-8101.2015.06.029
- Yi, Z., Zhang, J., Zhang, S., Gao, Q., Li, J., and Zhang, W. (2016). "Synthesis and mechanism of metal-mediated polymerization of phenolic resins," *Polymers* 8(5), Article Number 159. DOI: 10.3390/polym8050159
- Younesi-Kordkheili, H., and Pizzi, A. (2017). "Properties of plywood panels bonded with ionic liquid-modified lignin-phenol-formaldehyde resin," *The Journal of Adhesion* 94(2), 143-154. DOI: 10.1080/00218464.2016.1263945
- Zhang, X. Y. (2004). *Adhesive Analysis and Testing Technology*, Chemical Industry Press, Beijing, China.

Zhang, W., Ma, Y., Wang, C., Li, S., Zhang, M., and Chu, F. (2013a). "Preparation and properties of lignin-phenol-formaldehyde resins based on different biorefinery residues of agricultural biomass," *Industrial Crops and Products* 43, 326-333. DOI: 10.1016/j.indcrop.2012.07.037

Zhang, W., Ma, Y., Xu, Y., Wang, C., and Chu, F. (2013b). "Lignocellulosic ethanol residue-based lignin-phenol-formaldehyde resin adhesive," *International Journal of Adhesion & Adhesives* 40, 11-18. DOI: 10.1016/j.ijadhadh.2012.08.004

Article submitted: January 26, 2021; Peer review completed: February 28, 2021; Revised version received and accepted: March 7, 2021; Published: March 9, 2021.
DOI: 10.15376/biores.16.2.3103-3120