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# Lignocellulosic ethanol residue-based lignin–phenol–formaldehyde resin adhesive

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ABSTRACT

Phenol–formaldehyde (PF) adhesive is usually used to bond exterior grade plywood for high bonding strength and water resistance. However, all components are based on petrochemicals, nonrenewable materials from fossil fuel. Lignocellulosic ethanol residue (ER), as the by-product of lignocellulosic ethanol production, is rich in activated lignin and usually treated as waste. In this work, the ER was used as a renewable and valuable resource to partially replace phenol in the range of 10–70% to prepare lignin–phenol–formaldehyde (LPF) adhesive. The composition, functional groups and molecular weight of the ER were characterized. The result revealed that ER, with rich hydroxyl group and less methoxyl group as well as lower molecular weight, was suitable for the synthesis of LPF adhesive. The synthesis process parameters of ER-modified PF (ERPF) adhesives were optimized. It was found that the phenol could be replaced by ER for 50% at most, without much free formaldehyde and free phenol in the ERPF adhesives and the performance of plywood bonded by ERPF adhesives met the requirement of exterior grade according to the Chinese National Standard (GB/T 9846.3-2004). FT-IR, solid state $^{13}$C-NMR and TGA were used to characterize the PF and ERPF adhesives. FT-IR and solid state $^{13}$C-NMR spectra of the adhesives showed structural similarity between them. With the increase of substitution rate, the content of aliphatic OH group in the ERPF adhesive increased. Thermal stability of ERPF adhesives was better than that of PF adhesive in the initial thermal degradation. After scale up production, the industrial feasibility of preparing ERPF adhesives had been confirmed.

## 1. Introduction

The most common adhesives used in plywood industry are phenol–formaldehyde (PF), urea–formaldehyde (UF) and melamine–urea–formaldehyde (MUF) adhesives [1,2]. Particularly, PF adhesive is more widely used due to its high weather-resistance and water-resistance, which makes it suitable for exterior applications [1–4]. But the rapidly rising oil price has increased the cost of petro-chemicals. As a result, the high price of phenol has been the main reason for the restriction of PF adhesive for broad applications. On the other hand, the use of renewable nature resources has been afforded a lot of attention, as they can potentially replace petro-chemicals.

Several attempts have been made to replace phenol by lignin [4–6] or tannin [7] based on the structural similarity. Lignin is an amorphous, polyphenolic material derived from three phenylpropanoid monomers: coniferyl, sinapyl and p-coumaryl alcohols. These structures are linked by a multitude of interunit bonds that include several types of ether (β-O-4, α-O-4, 4-O-5) and carbon–carbon linkages. Lignin is a highly branched, three-dimensional polymer with a wide variety of functional groups providing active centers for chemical and biological modification [8]. The conventional technical lignin (kraft lignin, soda lignin, lignosulfonate etc.) is the by-product of pulping industry. During the pulping process, most hydroxyl groups are oxidated due to high temperature and high alkaline condition, resulting in low substitution rate and poor performance of lignin–phenol–formaldehyde (LPF) adhesive. Their free formaldehyde and phenol contents are much higher than PF adhesive [4] and wet bonding strength is difficult to meet the requirement for exterior plywood [9]. Therefore, conventional technical lignin has to be purified or modified before incorporating into LPF adhesive. This adds up to the cost of LPF adhesive production. It is desirable to find a biomass resource with high activity and low cost to develop a new wood adhesive for exterior plywood.

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In the last few years, the production of bioethanol as a transportation fuel has increased significantly. At present, bioethanol is mainly produced from food sources, particularly corn and sugarcane [10]. However, these resources compete for arable land with crops intended for human and animal consumption [11]. Meanwhile, lignocellulosic feedstocks are the largest sources of hexose ($C_6$) and pentose ($C_5$) sugars with the potential for production of bioethanol [12]. In the whole world, lignocellulosic materials could produce up to 442 billion liters per year of bioethanol [13]. The lignocellulosic ethanol is produced from non-food raw materials, such as energy crops, straw, wood and various agricultural and wood processing waste products [14].

As literature reported [15], the basic process steps in producing bioethanol from lignocellulosic materials are pretreatment (steam explosion, acid or alkali treatment), enzymatic hydrolysis, fermentation and distillation. The lignocellulosic ethanol residue (ER), as the by-product of enzymatic hydrolysis, is rich in highly activated lignin. It can condense with phenol and formaldehyde under alkaline condition to synthesize the ethanol residue-modified phenol–formaldehyde (ERPF) adhesive used for exterior plywood. The lignin and phenol can undergo hydroxymethylation by reacting with excess formaldehyde in the presence of NaOH as catalyst, and the hydroxymethyl lignin and the PF prepolymer can then copolymerize to produce a lignin–phenol–formaldehyde (LPF) copolymer to combine phenolic and lignin parts [16,17].

Apart from optimizing the process parameters, full utilization of the ER is a desirable method to reduce the overall cost of bioethanol production [18]. The lignin in lignocellulosic bioethanol residue has higher activity than conventional technical lignin, because the condition of enzymatic hydrolysis process is more smooth and moderate to retain a large number of active groups. However, most residues have been used as fuel for power generation to drive the fermentation and distillation [19]. It makes a great waste of high value bioresource. The viability of lignocellulosic bioethanol production would be greatly enhanced by the development of lignin-derived products.

It is inferred from early work [18] on LPF adhesive based on ER that the lignin must be purified ahead of the preparation of LPF adhesive. Because the synthesis method and process were not optimized, the substitution rate was low, and the free phenol content was high. We recently studied the use of different biorefinery residues for the preparation of LPF resins [20]. The main objective of this study was to examine the potential for full utilization of ER in the ERPF adhesive and to investigate the optimized process for preparation of ERPF adhesives for bonding exterior plywood.

## 2. Experimental

### 2.1. Materials

The lignocellulosic ethanol residue (ER), was purchased from Tianguan group company in Henan province of China. Phenol, formaldehyde solution (37–40%) and sodium hydroxide were AR grade reagents purchased from commercial resources.

### 2.2. Preparation of PF adhesive

The PF adhesive was synthesized by batch polymerization according to the phenol and formaldehyde in the molar ratio of 1:2.0. In the first step, phenol with one third of the formaldehyde and NaOH were mixed in a flask. The mixture was heated for 1 h at 80 °C. In the second step, another one third of the formaldehyde and NaOH were added in the flask for 1 h at 80 °C. In the third step, the rest of the formaldehyde and NaOH were added in the flask for 1 h at 80 °C. When the viscosity is 100–150 mPa s, it should be rapidly cooled to 40 °C to yield PF adhesive.

### 2.3. Preparation of ERPF adhesives

The ERPF adhesives were prepared by batch polymerization according to the ER substitution rate which was in the range of 10–70%. In the first step, phenol, ER, one third of the formaldehyde and NaOH were mixed in a flask. The mixture was heated for 1 h at 80 °C. The rest of the synthesis processes were the same as those for phenol–formaldehyde resin. When the viscosity is 150–300 mPa s, it should be rapidly cooled to 40 °C to yield ERPF adhesive.

### 2.4. Preparation of plywood

The three-layer plywood (400 mm × 400 mm × 6 mm) was prepared with a single poplar veneer in the middle and two eucalyptus veneers on the top and bottom simulating actual industrial parameters. The poplar veneer was coated with 250–300 g/m$^2$ adhesive on both sides. The plywood was cold-pressed under 0.8 MPa for 0.5 h, and then hot-pressed at 135 °C under 1.2 MPa for 7 min.

### 2.5. Characterization of the lignocellulosic ethanol residue

The moisture content of ER was determined by drying samples at 105 °C to constant weight with corresponding JIS Standard P8002-1996. The ash content of ER was obtained after it was placed in muffle furnace for 4 h at 575 °C with corresponding TAPPI Standard T211om-1993. The acid-insoluble lignin content was determined by fraction left insoluble after two-step acid hydrolysis with corresponding TAPPI Standard T222om-02. The acid-soluble lignin content was determined by applying the spectrophotometric method with corresponding TAPPI Standard T250. The content of holocellulose in ER was measured by the acidic chlorite method [21]. The polysaccharide content was obtained through the determination of furfural content generated by polysaccharide with 12% hydrochloric acid with corresponding TAPPI Standard T223cm-01. Total hydroxyl content was determined by acetylation with acetic anhydride catalyzed by pyridine at 50 °C for 2 h. After acetylation, titration was carried out with NaOH [22]. Phenolic hydroxyl groups were determined using UV-spectroscopy method ($\Delta 3$ method). The content of various phenolic units in the lignin samples was determined using a method based on the difference in absorption at 300 and 360 nm between phenolic units in neutral and alkaline solutions [23]. The content of ionizing phenol hydroxyl groups was quantitatively evaluated by comparing the $\Delta 3$ values of substances studied at certain wavelengths to the $\Delta 3$ values of the respective model compounds (types I, II, III, IV). The methoxyl group content in acid-insoluble lignin was determined according to the Viebock–Schwappach method [23]. Carbon, hydrogen, sulfur and nitrogen contents of acid-insoluble lignin were determined using a Perkin Elmer Series, 2400 Analyzer. The percentage of oxygen was calculated by subtracting the C, H, S and N contents from 100% [17,24]. The $C_9$ formula was calculated according to former research [25]. The percentage of protein content was calculated as N (%) × 6.25 [17,24] and the double bonds equivalent (DBE) were calculated from the elemental analysis result [17]. The metal elements content analysis of the ash was determined using a Thermo Fisher ARL-9800+ X-ray fluorescence spectrometer.

### 2.6. Characterization of the PF and ERPF adhesives

The non-volatile (solid) contents of the resol resins were determined in accordance with ASTM standard D4426-01. Free formaldehyde was determined by the hydroxylamine hydrochloride method in accordance with DIN EN ISO 9397-1997. Free phenol content was determined in accordance with ASTM D 1312-93. The viscosity of resin was measured in a viscosimeter at 25 °C according to the standard of ASTM 1084-08.

### 2.7. Characterization of the plywood

The shear strength was measured as per ASTM D906-98. Formaldehyde emissions were measured with the acetylactone method [26]. For this testing, 10 specimens with the dimension of 15 cm × 5 cm were put into a desiccator that had the capability of 10 L and contained 300 mL of distilled water at the bottom. After 24 h at 20 °C, the concentration of formaldehyde absorbed in the distilled water was determined by the acetylactone method with the ultraviolet spectroscope (UV) with the wavelength of 412 nm.

### 2.8. GPC analysis of lignocellulosic ethanol residue

The ER was subjected to acetylation in order to enhance their solubility in organic solvents for GPC technique. This reaction implies the substitution of all the hydroxyl functions by new acetyl groups [27]. With that purpose, acetylation was performed using the method of Vázquez et al. [28]. Briefly, 30 mL of a 1:1 ($v/v$) mixture of pyridine and acetic anhydride was added to 2 g of lignin in a 100 mL conical flask, and, after stirring for 48 h at room temperature the mixture was treated with 10 volumes of 1% HCl at 0 °C. The resulting precipitate was filtered, washed with distilled water to neutral pH, and dried at room temperature.

The molecular weight distribution of ER and acetylated ER was determined by gel permeation chromatography (GPC). Tetrahydrofuran (HPLC grade) was used as the mobile phase with a flow rate of 1.0 mL/min using Water 1515 Isocratic HPLC Pump. Two Water Stryragel® columns of HR 1 THF and HR 2 THF as well as a Water 2414 Refractive Index detector were used. The columns were calibrated using narrow molecular weight monodisperse polystyrene standard ranging from 580 to 19,600 g/mol in the eluent. The molecular weight and molecular number must be considered relative because they were compared with polystyrene standard.

### 2.9. FT-IR analysis of PF and ERPF adhesives

The resins were placed in 1.0 MPa vacuum at 60 °C for 4 h to dry to non-volatility. FT-IR spectra of vacuum-dried PF and ERPF adhesives were performed in a Nicolet(USA)IS10 instrument. Each spectrum was recorded in a frequency range of 600–4000 $cm^{-1}$ using attenuated total reflection method using diamond as crystal.

### 2.10. Solid state $^{13}$C-NMR analysis of PF and ERPF adhesives

The solid state CP MAS (Cross-Polarization Magic-Angle-Spinning) *$^{13}$CNMR* spectra of vacuum-dried PF and ERPF adhesives were acquired at ambient temperature by using a Bruker-avance 400 MHz spectrometer at a frequency 100 MHz and at a contact time of 3 ms. Chemical shifts were determined relative to tetramethyl silane (TMS) used as control. Aquisition time was 0.01 s with the number of transients being about 6000. All the spectra were run with a relaxation delay of 1.0 s and spectral width of 100,000 Hz.

### 2.11. TG analysis of cured PF and ERPF adhesives

Thermogravimetric Analysis (TGA) of vacuum-dried cured PF and ERPF adhesives was performed with Netzsch STA 409 in a nitrogen atmosphere and at a temperature range from room temperature to 900 °C, with a heating rate of 20 °C/min.

## 3. Results and discussion

### 3.1. Analysis for raw material

The composition and functional groups content of ER and the element analysis of acid-insoluble lignin in ER were characterized to determine the industry feasibility of ER incorporated into ERPF adhesives. Meanwhile, the elements of the ash were detected to generally analyze the pre-treatment method in the preparation of lignocellulosic ethanol.

#### 3.1.1. Composition content

Table 1 shows the fractions of moisture, ash, acid-insoluble lignin, acid-soluble lignin, holocellulose and polysaccharide in ER. The data of kraft lignin [24] from pulping industry was also given for comparison. The moisture of ER accounted for 11.3%, much higher than that of the kraft lignin that was usually dried. Ash content of ER accounted for 22.7%, less than that of kraft lignin (27.1%). In the case of ER, the high ash content was due to raw material (e.g., corn and wheat straw) of lignocellulosic ethanol that was rich in ash. The higher ash content of kraft lignin was attributed to the addition of a lot of alkali in the pulping process. The content of total lignin (acid-insoluble lignin and acid-soluble lignin) in kraft lignin was higher than that in ER. Holocellulose, including cellulose and hemicellulose, should have hydrolyzed into monosaccharides in the enzymatic hydrolysis process. But this process could not be completed, because of the cellulose

**Table 1**
The composition, functional group content and element analysis of ER.

| Properties | ER | Kraft lignin[a] |
|---|---|---|
| Moisture (%) | 11.3 | 3.9 |
| Ash (%) | 22.7 | 27.1 |
| Element analysis of the ash (%) | | |
| Si | 21.8 | NA |
| Ca | 9.0 | NA |
| K | 9.0 | NA |
| Fe | 5.8 | NA |
| S | 1.5 | NA |
| Na | 0.9 | NA |
| Acid-soluble lignin (%) | 3.7 | 4.9 |
| Acid-insoluble lignin (%) | 38.8 | 61.2 |
| Element analysis of the acid-insoluble lignin (%) | | |
| Carbon | 50.6 | 65.0 |
| Hydrogen | 4.3 | 5.4 |
| Oxygen | 42.2 | 28.2 |
| Nitrogen | 2.0 | 0.1 |
| Sulfur | 0.9 | 1.3 |
| Methoxyl group of the acid-insoluble lignin (%) | 10.1 | 10.5 |
| $C_9$ formula of the acid-insoluble lignin | $C_9H_{7.61}O_{5.35}N_{0.33}(OCH_3)_{0.75}$ | $C_9H_{7.76}O_{2.45}N_{0.01}S_{0.07}(OCH_3)_{0.60}$ |
| $M_w$ of $C_9$ formula (g/mol) | 229 | 176 |
| DBE | 6.1 | 5.5 |
| Protein (%) | 12.5 | 0.3 |
| Holocellulose (%) | 25.2 | NA |
| Polysaccharide (%) | 1.1 | 3.3 |
| Total hydroxyl (%) | 23.2 | 14.2 |
| Phenolic hydroxyl (%) | 1.6 | 4.1 |
| Phenolic hydroxyl I (%) | 0.3 | NA |
| Phenolic hydroxyl II (%) | 0.1 | NA |
| Phenolic hydroxyl III (%) | 1.1 | NA |
| Phenolic hydroxyl IV (%) | 0.1 | NA |
| Aliphatic hydroxyl (%) | 21.6 | 10.1 |

NA: not analyzed.

[a] Data of kraft lignin are from El Mansouri et al. [24].

crystalline structure and low activity of biological enzymes. The polysaccharide content in ER was lower, only 1.1%. The presence of polysaccharide lowered the reactivity of lignin and, therefore, affected the strength and water resistance of the resins [29].

### 3.1.2. Functional groups content

Table 1 shows the results of total hydroxyl, phenolic hydroxyl, aliphatic hydroxyl and methoxyl groups content obtained for ER, compared with that of the kraft lignin [24]. Four types of phenolic structures were determined by UV-spectroscopy. The results showed that ER had lower proportion of phenolic group due to the lower lignin content found in composition analysis. Among the four types, phenolic structure had the highest activity attributed to the empty ortho positions of phenolic hydroxyl and carbonyl groups of $\alpha$ position on side chains. Both can undergo addition reactions with formaldehyde. Table 1 shows that the total hydroxyl groups of ER were much more than that of the kraft lignin. More hydroxyl groups per phenylpropane unit are more suitable for preparation of PF adhesive [5]. The methoxyl group content of acid-insoluble lignin was lower than that of kraft lignin. The lower methoxyl contents indicated that the residues had more activated positions of their phenyl rings unblocked by methoxyl groups and were therefore suitable for producing LPF adhesive [24].

The data of functional groups content of ER suggested that the ER had a greater potential to replace the phenol to synthesize PF adhesive, compared to conventional technical lignin.

### 3.1.3. Element analysis

Table 1 also reveals the C, H, O, N and S element contents of the acid-insoluble lignin in ER and compares them with those in kraft lignin [24] from pulping industry. The approximate $C_9$ formula of lignin structure was derived from element analysis and the methoxyl content. The double bond equivalent (DBE) and protein content were given as well as the molecular weight corresponding to the $C_9$ formula. Element analysis showed that acid-insoluble lignin in ER had lower carbon content and higher oxygen content than kraft lignin because of the moderate condition of enzymatic hydrolysis process and the dehydration of lignin was low to prevent hydroxyl group cracking. It was consistent with the result of hydroxyl group content. The sulfur content in kraft lignin may be derived from sulfide added during the pulping process. The $C_9$ formula was a relative value to describe the elemental ratios in lignin structure. Table 1 shows that the $C_9$ formula of acid-insoluble lignin in ER was similar to that of kraft lignin. Corresponding to the $C_9$ formula, the molecular weight of lignin in ER was higher than in kraft lignin due to a higher degree of polymerization. DBE of acid-insoluble lignin implied the degree of lignin condensation and the presence of aromatic ring structure [17,24]. The DBE of acid-insoluble lignin in ER was higher than that in kraft lignin. It was in agreement with the molecular weight of $C_9$ formula. The protein content was calculated by the nitrogen element content. The protein residue attached to acid-insoluble lignin suggested a strong chemical bond between lignin and protein [17]. The content of protein in acid-insoluble lignin of ER was higher than that of conventional technical lignin due to the enzymatic hydrolysis process.

**Table 2**
Results of weight-average ($M_w$) and number-average ($M_n$) molecular weights and polydispersity of lignocellulosic ethanol residue before and after the acetylation.

| Sample | Molecular weight | | |
|---|---|---|---|
| | $M_n$ (g/mol) | $M_w$ (g/mol) | Polydispersity ($M_w/M_n$) |
| ER | 450 | 760 | 1.7 |
| Acetylated ER | 480 | 1280 | 2.6 |
| Kraft lignin[a] | 950 | 1370 | 1.5 |
| Acetylated Kraft lignin[a] | 1100 | 1800 | 1.6 |

[a] Data of kraft lignin and acetylated Kraft lignin are from Ibrahim et al. [17].

### 3.1.4. GPC analysis

$M_n$, $M_w$ and the polydispersity ($M_w/M_n$) of the ER were given in Table 2. Both $M_w$ and $M_n$ of ER were lower than that of the conventional technical lignin. This result suggested that ER was more suitable for the condensation with phenol and formaldehyde because the smaller molecular structure has less steric hindrance. Similar to kraft lignin, it was observed that both $M_n$ and $M_w$ of ER before acetylation were lower than those after acetylation. The polydispersity of ER was also increased after acetylation. It was indicated that the solubility of lignin in tetrahydrofuran was enhanced after acetylation.

### 3.2. Optimization of process parameters for the preparation of ERPF adhesives

The synthesis processes of ERPF adhesives were optimized by controlling ER to phenol weight ratio, formaldehyde to phenol molar ratio and catalyst concentration. The influence of these parameters on the performances of adhesives and plywood were investigated.

### 3.2.1. ER to phenol weight ratio

Table 3 shows the viscosity, solid content, free formaldehyde and free phenol content of PF and ERPF adhesives. The bonding strength and formaldehyde emission of plywood samples were

**Table 3**
Adhesives with different substitution ratios of ER and their performance.

| Adhesive | Resin performances | | | | Plywood performance | |
|---|---|---|---|---|---|---|
| | Viscosity (mPa s) | Solid content (%) | Free formaldehyde (%) | Free phenol (%) | Bonding strength (MPa) | Formaldehyde emission (mg/L) |
| PF | 100 | 48.9 | 0.10 | 0.65 | 1.65 | 0.13 |
| 10% ERPF[a] | 127 | 45.0 | 0.10 | 0.31 | 1.40 | 0.24 |
| 30% ERPF | 175 | 47.3 | 0.23 | 0.15 | 1.06 | 0.11 |
| 30% ERPF[c] | 100 | 48.7 | 0.31 | 0.13 | 1.32 | 0.10 |
| 50% ERPF | 235 | 50.0 | 0.32 | 0.24 | 0.98 | 0.23 |
| 50% ERPF[c] | 160 | 49.5 | 0.47 | 0.26 | 1.31 | 0.11 |
| 70% ERPF | 260 | 46.3 | 0.12 | 0.33 | 0.65 | 0.21 |
| EHL-PF[b] | 1880 | 71.1 | 0.49 | 5.40 | 1.80 | NA |
| GB/T14732 | $\geq 60$ | $\geq 35$ | $\leq 0.3$ | $\leq 6$ | $\geq 0.7$ | $\leq 0.5$ |

[a] 10% ERPF means the adhesive with ER substituted phenol by 10%.

[b] EHL-PF is the adhesive of enzymatic hydrolysis lignin 20% substituted phenol. The data is from Jin et al. [18].

[c] Adhesives were produced in adhesive factory and used in plywood industry actually.

also detected. The data of EHL-PF [18] were shown in the Table for comparison.

With the increase of the substitution rate from 10% to 70%, the solid content was almost the same, but the viscosity increased from 127 mPa s to 260 mPa s for incorporation of lignin macromolecule. The free formaldehyde content was higher with the substitution rate increased, because lignin was generally less reactive than phenol. The free phenol content of ERPF adhesives was much lower than PF resin. Especially, the free phenol content of 30%ERPF adhesive was only 0.2%, because the amount of phenol in the synthesis process was reduced when the residue substitution rate increased. As a result, the phenol can be fully hydroxymethylated in our synthesis process.

The bonding strength was characterized after 4 h boiling. The results showed that with increase of the replacement rate of ER to phenol, the bonding strength of plywood decreased from 1.7 MPa to 0.7 MPa. The water resistance of ERPF adhesives was weaker than that of PF adhesive because the reactivity of lignin was lower than that of phenol and there were sugar and ash in ER. The formaldehyde emissions of plywood samples bonded by ERPF adhesives were all below 0.5 mg/L, meeting $E_0$ grade.

It was found that the substitution rate can reach 50% at most, without influencing the properties of adhesives. Compared with EHL-PF, the synthesis process of adhesives was much different. As reported, EHL-PF adhesive was synthesized by the one-pot method. In our process, the ERPF adhesives were synthesized by batch polymerization. The hydroxymethylation reaction of phenol and lignin was accelerated and the activity of ERPF adhesives was higher, too. As a result, both the free formaldehyde and free phenol contents of ERPF were lower than those of the EHL-PF. Although the bonding strength of EHL-PF adhesive was higher, actually, its hot-pressed pressure (6.5 MPa) was too high to apply in industry. Meanwhile, there was difficulty in coating the EHL-PF adhesive on the wood, owing to its higher viscosity.

### 3.2.2. *Formaldehyde to phenol molar ratio*

Fig. 1 shows the effect of formaldehyde to phenol (*F*/*P*) molar ratio at 50% ER substituted on physico-mechanical properties. All adhesives were prepared with catalyst concentration (weight ratio of NaOH to phenol and ER together) at 20%. It was observed that with the increase of *F*/*P* molar ratio, free formaldehyde content became higher and the free phenol content decreased. When the molar ratio was 3.0, both were optimized to satisfactory values. Gel time is defined as the conversion time of the prepolymer transforming into 3-dimensional macromolecular structure under certain conditions, which can be used to evaluate the molecular activity [30]. *F*/*P* molar ratio was increased by adding formaldehyde, which improved the hydroxymethylation degree of resin and molecular activity, resulting in shorter gel time. Fig. 1 shows that the gel time was gradually shortened with the increase of *F*/*P* molar ratio and therefore the molecular activity gradually increased to form more crosslinks between the hydroxymethyl phenol and lignin. Values of bonding strength further supported this result. With the increase of *F*/*P* molar ratio, the bonding strength was higher due to the shorter gel time and the more complete curing.

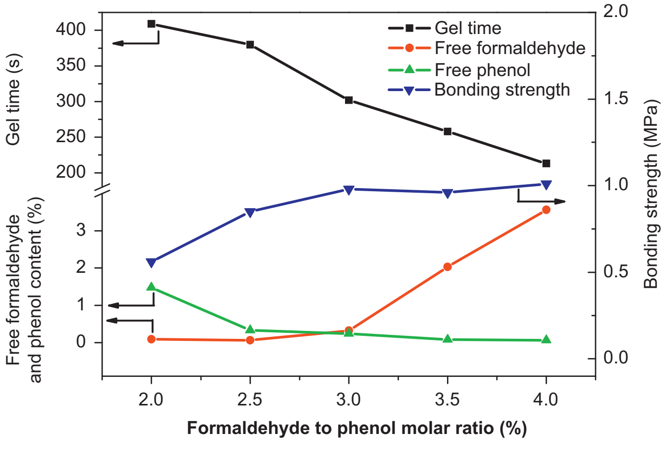

**Fig. 1.** Effect of formaldehyde to phenol molar ratio on physico-mechanical properties of 50% residue substituted ERPF adhesive.

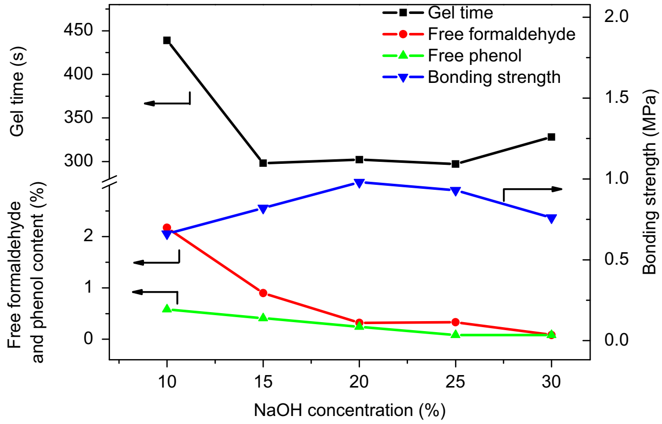

**Fig. 2.** Effect of catalyst (NaOH) concentration on physico-mechanical properties of 50% residue substituted ERPF adhesive.

From these observations it was concluded that formaldehyde to phenol molar ratio of 3.0 was optimal for the preparation of ERPF adhesives to get the best properties.

### 3.2.3. *Catalyst concentration*

Effects of catalyst concentration on the above properties are given in Fig. 2. Five different concentrations of NaOH were used for the preparation of ERPF adhesive at 50% ER substituted while keeping the *F*/*P* molar ratio at 3.0. It was observed that with the catalyst increase, the free phenol and formaldehyde content decreased and the gel time was shorter because the degree of hydroxylmethlation was enhanced. When the catalyst concentration was above 25%, the gel time became longer. This could be explained by the Cannizzaro reaction [31]. The formaldehyde could undergo self-condensation at high alkali concentration [32]. The bonding strength confirmed this explanation. With an increase of catalyst concentration, the bonding strength became lower, because the gel time was longer and the curing process could not be completed under the same hot-pressed condition.

From these observations it could be concluded that the optimized process for preparation of ERPF adhesives was substitution rate at 50%, formaldehyde to phenol molar ratio of 3.0 and catalyst concentration at 20%. These conditions resulted in the free formaldehyde content at 0.3%, free phenol content at 0.2% and bonding strength at 1.0 MPa. All properties satisfied the requirements of exterior grade plywood according to the Chinese National Standard (GB/T 9846.3-2004).

## 3.3. *Chemical structure of PF and ERPF adhesives*

### 3.3.1. *FT-IR spectroscopy*

To investigate the structural changes that took place in ERPF adhesives with the increase of substitution rate, FT-IR spectra (Fig. 3) of samples obtained after vacuum-drying were characterized.

There were no significant differences between the spectra of PF and ERPF adhesives which indicated structural similarity

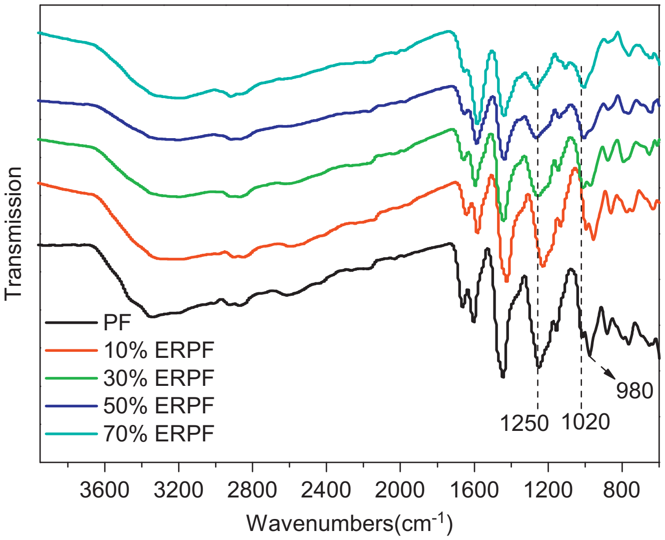

**Fig. 3.** FT-IR spectra of PF resin and ERPF adhesives.

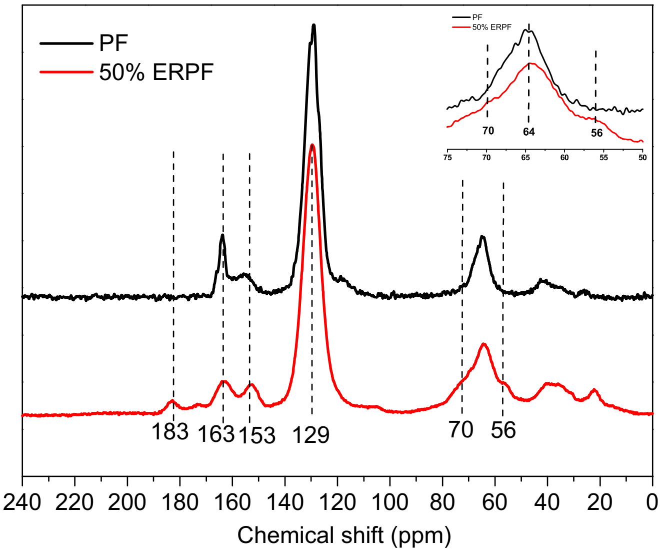

**Fig. 4.** Solid state CP-MAS $^{13}$C-NMR spectra of PF and 50% ERPF adhesives.

**Table 4**
Thermal properties of cured PF and RRPF adhesives (The temperature is in celsius).

| Resin | First thermal event $T_{max}$ (°C) | Second thermal event $T_{max}$ (°C) | Third thermal event $T_{max}$ (°C) | Weight residue (%) |
|---|---|---|---|---|
| PF | 191 | 395 | 534 | 65.0 |
| 10% ERPF | 195 | 394 | 517 | 65.6 |
| 30% ERPF | 214 | 428 | 494 | 59.4 |
| 50% ERPF | 191 | 405 | 479 | 54.9 |
| 70% ERPF | 194 | 307 | 388 | 48.4 |

between them. Bands at 1250 cm$^{-1}$ can be ascribed to the presence of C–O stretching vibration of phenolic C–OH, and phenolic C–O(Ar), meanwhile bands at 1020 cm$^{-1}$ can be attributed to the presence of C–O stretching vibration of aliphatic C–OH, aliphatic C–O(Ar), and methylol C–OH [33–35]. Peaks at 980 cm$^{-1}$ were assigned to C–H stretching vibration of vinyl on the PF [36].

With increase of substitution rate, the peak at 980 cm$^{-1}$ became weaker until it disappeared. The peaks at 1020 cm$^{-1}$ of ERPF became wider, because there were not only methylol OH but also aliphatic OH groups in the ER. The bond at 1250 cm$^{-1}$ of PF adhesive was sharper than that of ERPF adhesives, which means that there was more phenolic OH in PF resin. That was because in ERPF adhesives the phenol was substituted by ER which had both phenolic and non-phenolic units in their structures. And with the increase of substitution rate, the content of phenolic OH in ERPF adhesives decreased.

From FT-IR analysis, it could be concluded that with the increase of substitution rate, the content of aliphatic OH group increased as well as phenolic OH group decreased in the ERPF adhesives.

### 3.3.2. *Solid state $^{13}$C-NMR*

The solid state CP-MAS $^{13}$C-NMR spectra of vacuum-dried PF and 50% ERPF adhesives are shown in Fig. 4. The dominant peaks at 129 ppm were assigned to the ortho and para carbon sites on aromatic ring which have been substituted [37,38]. The peaks at 64 ppm were assigned to the methylol OH on the para position of phenolic OH of phenol or lignin [37,38].

Some differences between PF and 50% ERPF adhesives could be observed in Fig. 4. The peak at 183 ppm in 50% ERPF was related to carbon of $\gamma$-position carbonyl on the lignin side chain which was involved by ER [39]. The signals at 152–155 ppm and 163–164 ppm were assigned to carbon on benzene ring to which phenolic hydroxyl [37,38] and methylene ether groups [36,37] were connected. Increase of the signal at 163 ppm was accompanied by decrease at 153 ppm. It meant the condensation of phenolic OH group occurred with methylol OH to generate methylene ether bonds in the copolymerization. It is well known that the higher the degree of condensation, the better the bonding strength and water resistance of adhesive. It could explain why the bonding strength of ERPF adhesives decreased with the increase of substitution rate. Comparing with the PF, signals at 70 ppm and 56 ppm, found in the 50% ERPF adhesive, were attributed to the carbon of $\beta$-position in $\alpha$-O-$\beta$ unit and the carbon of methoxyl group of lignin structure [40], respectively. It could be recognized as the evidences of copolymerization of lignin with phenol and formaldehyde in ERPF adhesive preparation.

### 3.4. *Thermal behavior of cured PF and ERPF adhesives*

In order to avoid the evaporation of water, PF and ERPF adhesives cured under 120 °C for 2 h were used for TGA analysis [26,32,41].

To characterize the thermal stability of PF and ERPF adhesives, TGA analysis was carried out. Temperatures (celsius) at which maximum degradation took place ($T_{max}$) in different thermal events of cured PF and ERPF adhesives are shown in Table 4.

It was known that phenolic resin degraded in three steps: postcuring, thermal reforming and ring stripping [42]. In the initial stage, the mass loss was due to the evaporation of water which was formed by condensation reaction of methylol groups [26]. The mass loss in the second event was due to the loss of water formed by condensation reaction of methylene and phenolic OH as well as between two hydroxyl functional groups [26]. In the third event, the mass loss was due to the loss of carbon monoxide and methane formed by degradation of methylene bridge [26]. Fig. 5 shows TG-DTG curves of cured PF and ERPF adhesives, and the data of their thermal degradation was given in Table 4. It was observed that compared to PF adhesive, ERPF adhesives show higher thermal stability in the initial stage. That was due to the fact that methylol OH content in PF resin was more than that of the ERPF resin which can be found in $^{13}$C-NMR spectra at 64 ppm. With the increase of substitution rate, the $T_{max}$

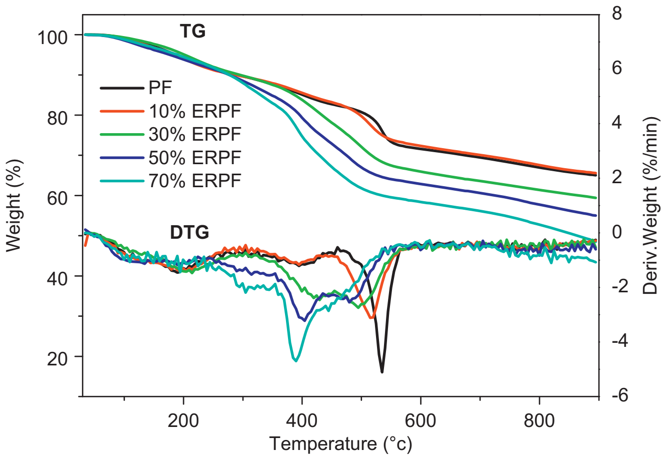

**Fig. 5.** TG-DTG curves of the cured PF and RPF adhesives.

of ERPF adhesives in the first thermal event increased in the beginning and then decreased when substitution rate was higher. It announced that ER incorporated into the ERPF adhesives will make better thermal stability for ERPF adhesives in the initial stage, but the substitution rate should not be too high. The performances of thermal degradation of ERPF in the second thermal event were similar to those in the former stage. In the third thermal event, PF had better heat resistance than ERPF adhesives because $T_{\max}$ and weight residue at 900 °C of PF in the third thermal event were higher than those of ERPF. With the increase of substitution rate, the $T_{\max}$ of ERPF adhesives in the third thermal event decreased obviously. At 900 °C the weight residue decreased, that was because the total lignin in ER was only 42.5% as shown in composition analysis, and compositions like polysaccharide would be decomposed soon before 900 °C.

### 3.5. Scale up production

The PF adhesive modified by lignin used for bonding plywood has been investigated for a long time. A number of technologies for their formulation and application have been proposed. However, they are still far from industry production [43].

Because the activity of the conventional technical lignin was low, the purification [18] and modification [3–5] treatments for the lignin were needed that would increase the cost and difficulty in application. In most of the reports, LPF had too high viscosity [44] that was not suitable to coat the wood and the hot-pressed process needed higher temperature and longer time [1].

The LPF adhesives suitable for industry application primarily depend on the following three factors: (1) the overall cost is low; (2) the technology is simple and feasible; (3) the adhesive is suitable to coat the wood and the wet bonding strength is high enough.

As shown in Table 1, the 30% ERPF and 50% ERPF adhesives have been scaled up in 100 L reactor. They were then used to produce exterior grade plywood in a plywood mill. The activity of ER was higher than that of the conventional technical lignin, as shown by the above discussion. The performance of ERPF adhesives was very similar to that of PF adhesive. The scale up production was adopted by the same parameters as the factory conventional method. The bonding strength of seven-layer plywood met the standard for exterior grade panels.

## 4. Conclusions

As the by-product of lignocellulosic ethanol process, ER was characterized to evaluate the suitability for incorporation into phenolic resins. The results demonstrated that the ER had lower content of polysaccharide, higher content of hydroxyl group, and lower molecular weight than conventional technical lignin. Meanwhile the acid-insoluble lignin in ER had lower methoxyl group, leading to higher activity and greater potential to substitute phenol in the production of PF adhesive.

The optimized conditions for preparation of ERPF adhesive were substitution rate at 50%, *F*/*P* molar ratio at 3.0 and catalyst concentration at 20%. A replacement of 30% or 50% of phenol by ER appeared more feasible with this process. Higher levels of substitutions with ER were limited by the decrease of the bonding strength.

With the increase of substitution rate, the content of aliphatic OH group increased as well as phenolic OH group decreased in the ERPF adhesives. ER incorporated into the ERPF adhesives will make better thermal stability for ERPF adhesives in the initial stage, but the substitution rate should not be too high.

The preparation of ERPF adhesives was scaled up to explore the possibility for industry production and use in making exterior grade plywood. The industrial feasibility was confirmed.

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