PREPARATION AND CHARACTERIZATION OF ACETIC ACID LIGNIN-BASED EPOXY BLENDS

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Lignin-based epoxy resin (LER) was prepared from phenolated lignin (PL) and epichlorohydrin (ECH) in the presence of sodium hydroxide. The eucalyptus acetic acid lignin (AAL) was first reacted with phenol in the presence of sulfuric acid to obtain PL. Then, PL was reacted with ECH in aqueous sodium hydroxide to obtain LER. LER was mixed with diglycidyl ether of bisphenol A (E-44) and then cured with triethylenetetramine (TETA). The initial thermal degradation temperature (T_d) of the cured epoxy blends decreased with the increase in LER content. The residue ratio at 500 °C of the cured epoxy blends (R_{500}), however, increased with the LER content. The maximum adhesive shear strength of the cured epoxy blends was obtained at 20 wt% of LER. The water absorption of epoxy blends increased with increasing the content of LER. SEM photos showed that increasing the content of LER increased inhomogeneity and porosity of epoxy blends.

Keywords: Lignin; Epoxy resin; Blends; Thermal stability; Adhesive shear strength

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INTRODUCTION

Second only to cellulose, lignin is the most abundant biopolymer on earth. Almost all of the lignin isolated from lignocellulosic materials in the pulp and paper industry are burnt to generate energy and to recover chemicals. Only a small portion (1% to 2%) of it is commercially used to replace a part of petrochemicals. Lignin can be used to prepare polymeric materials such as polyurethanes (Bonini *et al.* 2005; Liu *et al.* 2009), phenolic resins (Cavdar *et al.* 2008; Wang *et al.* 2009), and epoxy resins (Nieh and Glasser 1989; Zhao *et al.* 2000).

In recent decades, lignin-based epoxy resins (LER) have been prepared from lignosulfonate (Nieh and Glasser 1989; Zhao *et al.* 2000) or alkali lignin (Malutan *et al.* 2008; Mansouri *et al.* 2011) due to their potential use in adhesives or printed circuit board. Chemical modifications, *e.g.*, phenolation, hydroxymethylation, or hydroxypropylation, are sometimes needed to increase the hydroxyl content of lignin. After that, modified lignin can be reacted with ECH in the presence of sodium hydroxide. Many types of lignin-based epoxy resins are difficult to utilize due to their poor solubility in organic solvents and irreversible condensation occurring during the epoxidation reaction. The solubility of the lignin epoxides in organic solvents has been reported to be in the order shown as follows: phenolated lignin > unmodified lignin > bisguaiacylated lignin (Nieh and Glasser 1989). The results indicated that lignin should be phenolated before epoxidation to improve its solubility.

Acetic acid lignin (AAL) is isolated from acetic acid pulping. Less structural changes occurred during acetic acid pulping procedure than during Kraft pulping. Relatively low condensed structure favors the utilization of AAL because this type of lignin is relatively reactive in chemical reactions. Though the utilization of AAL in polymer material synthesis is seldom reported due to its high cost, AAL do present good performances in the preparation of polymer materials and chemicals. In this study, AAL was used to prepare LER. LER was then blended with E-44 at different ratios to investigate the possibility of replacing commercial bisphenol A epoxy resin with LER. The epoxy blends were characterized by thermogravimetric analysis (TGA), adhesive shear strength, water absorption, and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Acetic acid lignin (AAL) was obtained from the acetic acid pulping of eucalyptus chips under atmospheric pressure (Uraki *et al.* 1991). Diglycidyl ether of bisphenol A (E-44, M_w: 475, epoxy index: 4.4 kg/mol) was a commercial product of Dongfeng Chemical Co., Ltd., Guangzhou, China. Sulfuric acid, sodium hydroxide, ethyl ether, chloroform, acetic acid, acetic anhydride, pyridine, phenol, epichlorohydrin, and triethylenetetramin were of AR grade. All these reagents were used as received.

Phenolation of AAL

5.0 g of AAL, 7.5 g of phenol, and 20 mL of 2 mol/L sulfuric acid were mixed in a three-neck flask and stirred at 95 °C for 3 hours. A biphasic mixture, one brown-yellow aqueous upper phase and one black organic lower phase, was thus formed. Then the black liquid in the lower layer was isolated from the mixture, mixed with 800 mL water, and boiled for 3 hours so that the unreacted phenol and sulfuric acid could be transferred into the aqueous phase. After that, the reaction mixture was filtered. The solids were separated and washed with warm water several times (Matsushita and Yasuda 2003). Finally, the phenolated lignin (PL) was vacuum-dried at 40 °C.

Epoxidation of PL

5.0 g of PL and 15.0 g of ECH were mixed and stirred in a three-neck flask at 80 °C. Then, 20 wt% aqueous NaOH solution was added drop-wise in 30 minutes. Subsequently, the reaction was continued for a further 2.5 hours. The mixture was washed with water until the water became colorless. After that, water and excess ECH were removed by vacuum-evaporation at 90 °C with a rotary evaporator. The resulting solid was vacuum-dried at 40 °C.

Curing of Epoxy Blends

The LER and E-44 were mixed and stirred at 80 °C. The contents of LER in the mixture were varied in the range between 0 and 50%. After the mixture was cooled to room temperature, a stoichiometric amount of TETA was added and stirred. Then the mixture was cured at 100 °C for 3 hours.

Characterization of Lignin and Epoxy Resins

FT-IR spectroscopy

The Fourier transform infrared (FT-IR) spectra of AAL, PL, and LER were obtained with a NEXUS 670 FT-IR spectrometer (Nicolet Corporation, U.S.A) by the KBr-pellet method.

Phenolic hydroxyl content and epoxy index

The contents of phenolic hydroxyl in AAL and PL were determined by UV spectroscopy (Goldschmid 1954) with an S-3100 ultraviolet spectrophotometer (Scinco Corporation, South Korea). The epoxy index of LER was determined according to ISO 3001-1999.

Molecular weight and molecular weight distribution

300 mg of AAL (vacuum-dried at 40 °C for 16 hours) was dissolved in 15 mL of a 1:1 (v/v) mixture of pyridine and acetic anhydride at room temperature in a 100 mL Erlenmeyer flask. After 72 hours, the solution was diluted with diethyl ether and centrifuged several times, then vacuum dried at 40 °C. The molecular weight distributions of AAL were determined by Agilent 1100 series gel permeation chromatography (GPC) analysis system equipped with an Agilent-25 column and an R-401 differential refractometer. Tetrahydrofuran (THF) was used as the eluent. The column was calibrated by monodispersed polystyrene standards (molecular weight 1490, 3650, 10300, 25100, and 53500 g/mole, respectively). The average molecular weight and molecular weight distribution were calculated by the calibration curve and peak area integration of the chromatogram, respectively.

Thermal stability

The thermal stability of the lignin samples was determined with a Q500 thermogravimetric analyzer (TA Instruments, U.S.A.) operating from 50 ºC to 500 ºC at the heating rate 20 ºC/min with nitrogen flow rate of 40 mL/min.

Adhesive tensile shear strength

Adhesive shear strength of the epoxy blends was measured on an Instron 5565 testing machine (Instron Corporation, U.S.A.) according to ISO 4587: 2003.

Water absorption

Water absorption of the epoxy blends was performed according to ISO 62: 2008. Specimens were dried at 80 °C in a vacuum oven until constant weight was attained. Then, they were immersed in water in a thermostat water bath at 30 °C for 24 hours. After the removal of the specimens from the water bath, the specimen surface was wiped with filter paper to remove water. Then the weight gain was measured.

Scanning electron microscopy

The SEM images of the failure surface of the epoxy blends were taken with a FEI Nova Nano SEM 430 microscope with a field emission gun as the electron source. The surface was coated with gold by sputtering. The acceleration voltage was 5 kV.

RESULTS AND DISCUSSION

Synthesis of Lignin-Based Epoxy Resins

LER were prepared in reference to literature (Zhao *et al.* 2001; Malutan *et al.* 2008), as shown in Fig. 1. The synthesis comprises the phenolation of AAL and the synthesis of LER from PL. Alonso *et al.* (2005) reported that the phenolation of AAL involved the protonation of the benzyl hydroxyl group, followed by dehydration at the α-carbon, to give a carbonium ion. The phenol molecule underwent an electrophilic attack by the carbenium ion and gave a lignin-phenol condensation product. After the incorporation of the ortho- or the para-phenyl substituent to the α-hydroxyl groups on the side chains of lignin, the adduct fragmentation took place. Some side-reactions, including condensation, also occurred during the phenolation process. These reactions resulted in a decrease of molecular weight. In the epoxidization reaction, the hydroxyl groups of PL reacted with epichlorohydrin (ECH) to obtain glycidyl groups in an alkali medium. The degree of epoxidation depended on the amount of sodium hydroxide added. The amount of ECH had little impact on the epoxidation degree of PL as long as ECH was in excess. Crosslinking through polymerization was a potential problem which limits the degree of epoxidation (Nieh and Glasser 1989).

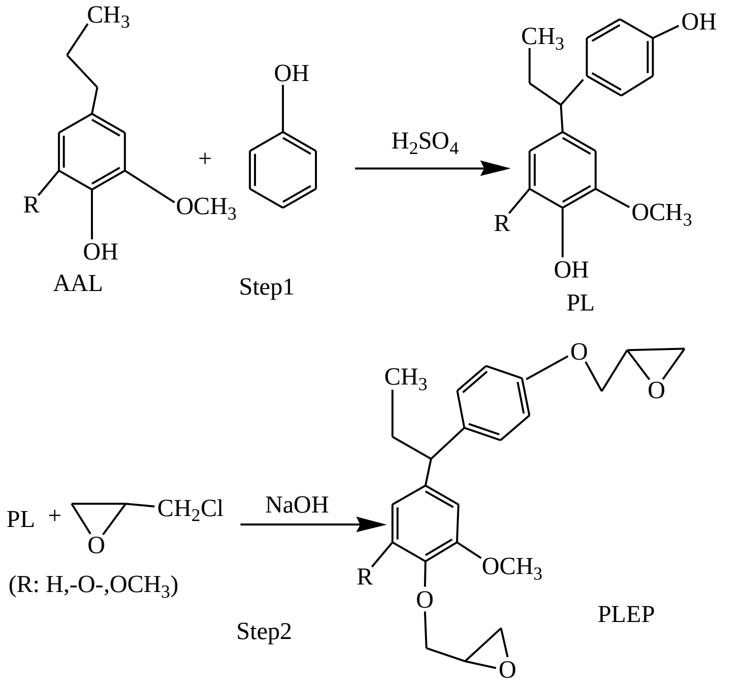

Fig. 1. Reaction scheme for the preparation of LER: phenolation of AAL (upper) and epoxidation of PL (bottom)

After the phenolation of AAL, the phenolic hydroxyl content of PL was determined to be 3.65 mol/kg, while that of AAL was 2.29 mol/kg. The results proved that the phenolic hydroxyl content of AAL was greatly increased by phenolation. During the epoxidation of PL, the weight ratio of PL to ECH was 1:2 and the reaction temperature was 80 °C, but the amount of NaOH solutions was varied. With the increase of weight ratio of sodium hydroxide to lignin, the epoxy index of LER first increased and then decreased (Table 1). The highest epoxy index of the four samples of LER was 1.25 mol/kg, which is much lower than that of E-44. This is probably due to the lower phenolic hydroxyl content of PL compared with bisphenol A (8.76 mol/kg). The crosslinking reaction between lignin units in the epoxidization reaction also leads to the reduced epoxy index of LER.

Table 1. Epoxy Indexes of Lignin-Based Epoxy Resins Prepared with Different Weight Ratio of Sodium Hydroxide to Lignin

Weight ratio of sodium hydroxide to lignin	Epoxy index(mol/kg)
0.3：1	1.09
0.5：1	1.25
0.7：1	0.96
0.9：1	0.67

FT-IR Spectroscopy of Lignin and Epoxy Resins

The FT-IR spectra of AAL, PL, and LER are shown in Fig. 2. As shown, there was a characteristic broad O–H band at 3400 cm^{-1} and an intense C–H band at 2927 cm^{-1}. The bands that appeared at 1597 cm^{-1}, 1507 cm^{-1}, and 1424 cm^{-1} in each sample could be assigned to the C=C stretching for aromatic rings. The absorption at 1734 cm^{-1} of the spectra of all the samples could be assigned to the carbonyl stretching of ester and the carboxyl groups. The change of absorption at 1734 cm^{-1} after phenolation reaction was due to the hydrolysis of acetyl group of AAL in the presence of sulfuric acid. A band was found at 755 cm^{-1} in the spectrum of PL that resulted from the reaction between phenol and α-hydroxyl groups in the side chain of lignin (Alonso *et al.* 2005). The band at 1120 cm^{-1} disappeared in the spectrum of phenolated lignin (b) demonstrating the cleavage of ether groups during phenolation reaction. The bands at 1230 to 1280 cm^{-1}, 915 cm^{-1} and 854 cm^{-1} in the spectrum of PL (c) could be assigned to the epoxy group stretching.

Molecular Weight and Distribution

The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersion coefficient (M_w/M_n) of AAL and PL are listed in Table 2. The M_n of PL was found to be higher than that of AAL, while the M_w of PL was lower than that of AAL. Correspondingly, the molecular weight distribution of PL was narrower than that of AAL. For a given polymer sample, the M_n is sensitive to low molecular weight substances, and the M_w is sensitive to high molecular weight substances. The increase in the M_n of lignin is probably due to the condensation between AAL and phenol and the removal of the low molecular weight part of phenolic compounds from the reaction mixture while removing the un-reacted phenol. The decrease in weight average molecular weight could be attributed to the fragmentation of the lignin-phenol condensation products during the phenolation reaction (Alonso *et al.* 2005). The comparison of the molecular weight of PL and LER showed that the epoxidation reaction increases the molecular weight of PL. It was due to the crosslinking reaction of PL and ECH.

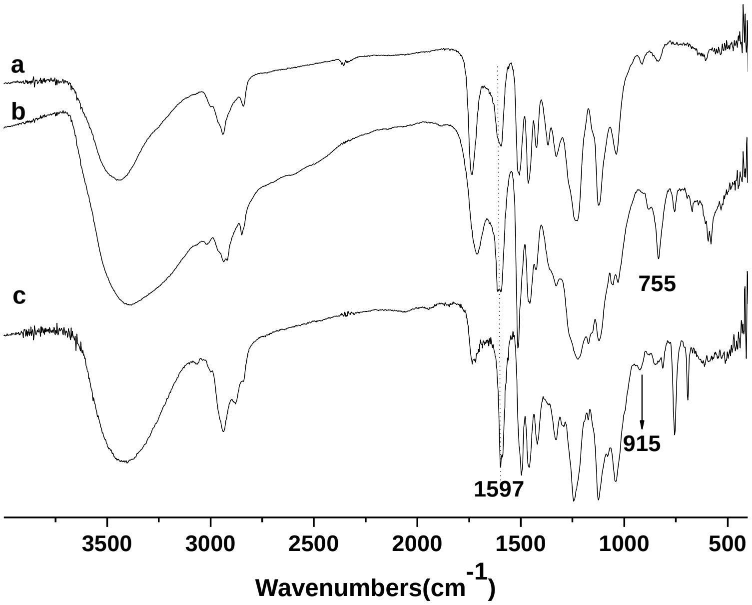

Fig. 2. FT-IR spectra of AAL (a), PL (b), and LER (c)

Thermal Stability

The initial thermal degradation temperature (T_d) and the residue yield at 500 °C (R_{500}) of AAL, PL, LER, E-44 of cured E-44 and cured epoxy blends with varied LER content are listed in Table 3. The initial thermal degradation temperature (T_d) of AAL was 244.3 °C, while the T_d of PL was 178.6 °C. The decrease in T_d was due to the formation of thermal-unstable ether linkages between AAL and phenol during phenolation reaction. The T_d of LER and that of E-44 was measured to be 242.8 °C and 269.8 °C respectively.

Table 2. Molecular Weight and Molecular Weight Distribution of AAL, PL, and LER

Sample	M_n	M_w	M_w/M_n
AAL	4539	8870	1.96
PL	4940	7830	1.59
LER	5360	9150	1.71

The residue yield at 500 °C (R_{500}) of AAL (40.6%) was lower than that of PL (48.0%) and LER (48.3%). The R_{500} of AAL, PL, and LER, however, were much higher than that of E-44 (5.7%). The increase in R_{500} could be attributed to the condensation between AAL and phenol during the phenolation and the removal of the low molecular weight

Table 3. T_d and R_{500} of the Products and Epoxy Blends

Sample	T_d (°C)	R_{500} (%)
AAL	244.3	40.6
PL	178.6	48.0
LER	242.8	48.3
E-44	269.8	5.7
Cured E-44	338.2	10.3
10% LER+90% E-44	323.0	12.0
20% LER+80% E-44	315.2	15.0
30% LER+70% E-44	296.4	18.8
40% LER+60% E-44	279.3	23.2
50% LER+50% E-44	265.1	24.3

part of phenolic compounds while removing the un-reacted phenol. The T_d of cured LER was lower than that of cured E-44, while the R_{500} of cured LER was higher than that of cured E-44. The R_{500} of the cured epoxy blends increased significantly with the increasing LER content. These results may be attributed to the poorer thermal stability of LER than that of E-44 and higher R_{500} of LER than that of E-44.

Adhesive Tensile Shear Strength

The data of adhesive shear strength of the epoxy blends are listed in Table 4. It was found that the adhesive shear strength was improved when E-44 was blended with up to 40% of LER. When the addition of LER in the epoxy blends was low, *e.g.*, 20%, the increase in the LER addition resulted in improved adhesive shear strength. The adhesive strength tended to decrease when the LER addition increased up to 50%. The maximum value appeared at a 20% of LER content, at which the adhesive shear strength of the epoxy blends was 108% higher than that of pure E-44. However, the adhesive shear strength of the epoxy blends containing 50% of LER was 24% lower than that of pure E-44. The adhesive shear strength of the epoxy resin depends on the compatibility between the major components. Both lignin and epoxy resin is polar polymers. The blends of lignin and epoxy resin presented good compatibility when the solubility parameters (δ) of the two major components were similar. The solubility parameter of E-44 epoxy resin was calculated to be approximately $20(\mathrm{J/cm^2})^{1/2}$, which was different from most kinds of lignin. For example, the solubility of Alcell lignin (an organosolv lignin) was $13.7(\mathrm{J/cm^2})^{1/2}$. It can be evaluated that the compatibility between LER and E-44 epoxy resin was low. Also, the epoxy index is an important factor that changes the adhesion behavior of the resin. As shown in Table 1, the epoxy index of LER was much lower than that of E-44. The low epoxy index of LER, which represented relatively low content of epoxy groups, resulted in a low crosslinking degree of the epoxy blends. Therefore, when the content of LER exceeded a certain value, the adhesive shear strength of the epoxy blends was decreased.

Table 4. Adhesive Shear Strength of the Epoxy Resins

LER Content (%)	E-44 Content (%)	TETA Amount (g/100g mixture)	Adhesive Shear Strength (MPa)
0	100	10.74	3.7
10	90	10.05	5.0
20	80	9.37	7.7
30	70	8.69	6.1
40	60	8.00	5.3
50	50	7.32	2.8

Water Absorption

The amount of water absorption of the epoxy blends are listed in Table 5. The water absorption of epoxy blends was found to be increased with the increase in LER content. Generally, the water sorption behavior in polymers depends on the chemical structure and the morphological structure of polymers. Increasing the amount of polar groups, *e.g.*, hydroxyls, in polymers can promote the sorption of polar penetrants (Seo *et al*. 2007). Furthermore, in the aspect of morphology, the blends became more porous when the LER content increased, and the specific surface area was thus increased, so the water adsorption increased.

Table 5. Water Absorption of the Epoxy Blends

LER Content (%)	Water Absorption (%, 24 h)
0	0.30
10	1.07
20	1.39
30	2.14
40	2.24
50	2.33

Compatibility of LER with Epoxy Resin

Figure 3 shows the scanning electron microscopy (SEM) images of the failure surfaces of the epoxy blends. As shown in Fig. 3, the cured E-44 epoxy resin is a homogeneous matrix. The epoxy blends with addition of a small amount of LER (approximately 10%) had no obvious change when compared with cured E-44 epoxy resin. Partial agglomeration of LER occurred in the epoxy blends with LER content of 30%. A lot of pores were observed in the epoxy blends with an LER content of 50%. The result may be attributed to the poor compatibility between LER and epoxy resin. The particles, which seemed not compatible with the epoxy matrix, were lignin particles. Lignin is a highly cross-linked natural polymer with a lot of polar functional groups. Due to its structural characteristics, many kinds of lignin cannot be dissolved in organic solvents completely. Neither can they be homogeneously mixed with other polymer materials. The LER epoxy blend was homogeneous when LER content was low. The compatibility became worse when the LER content increased. Obvious pores could be observed when the addition of LER was high.

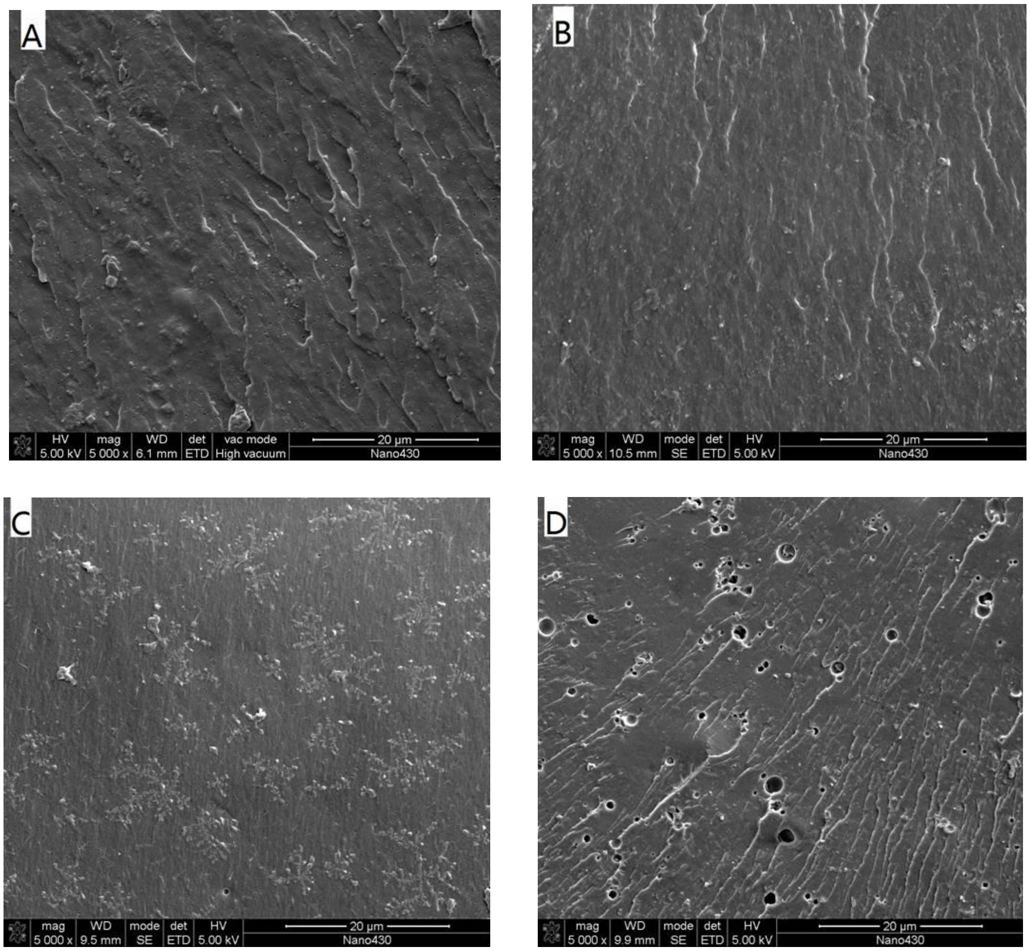

Fig. 3. SEM images of epoxy blends with 0% (A), 10% (B), 30% (C), and 50% (D) of LER content

CONCLUSIONS

Lignin-based epoxy resins were prepared from PL and ECH in the presence of sodium hydroxide. Phenolation reaction resulted in higher phenol hydroxyl content, lower molecular weight and poorer thermal stability than those of AAL. The T_d of the cured epoxy blends decreased with increasing LER content, while the R_{500} of the cured epoxy blends increased significantly with the increasing LER content. The adhesive shear strength of the epoxy blends could be improved by addition of LER. The maximum adhesive shear strength was achieved when the LER content was 20%. The water absorption of epoxy blends increased with the increasing content of LER. The SEM photos showed the increasing inhomogeneity and porosity with the increasing content of LER. Preparation of epoxy blends with LER provides a potential way of lignin utilization.

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