Depolymerization of renewable resources—lignin by sodium hydroxide as a catalyst and its applications to epoxy resin

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ABSTRACT: Alkali lignin was successfully depolymerized into polyols with high hydroxyl number via direct hydrolysis using sodium hydroxide (NaOH) as a catalyst, without any organic solvent agent. Hydrolysis of lignin can produce a multitude of high-value products via alkali-catalyzed cleavage. This process usually gives good results with respect to the yield of phenols. Through this method, the numbers of the hydroxymethyl and phenolic hydroxyl groups of lignin had been dramatically increased, reaching 2.11%, nearly four times higher than that in the original one. Meanwhile, we added the same amounts (20 wt %) of different depolymerization of lignin (DL) into epoxy resin (EP), and the results showed that DL could not only increase the decomposition temperature of EP, but also remarkably improve its mechanical properties. The optimum reaction time was 1.5 h, the reaction temperature was 250°C, and the optimum sodium hydroxide concentration was 15 wt % for depolymerizing lignin. The mechanical and thermal properties of cured lignin-based epoxy resin (LEP) were compared with cured neat EP. The cured DL-based epoxy resin (DLEP) showed the highest adhesive shear strength up to 2.66 MPa, which displayed 122% of the adhesive shear strength of EP. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42176.

INTRODUCTION

Increasing worldwide energy consumption and limited petroleum resources combined with economic, environmental, and societal concerns have boosted research on the development of new processes for the production of renewable fuels and chemicals.[1–5] Lignin has received great attention as a sustainable precursor for basic aromatic building blocks, such as phenols, which are currently obtained by synthetic chemistry from fossil-based feedstocks.[6–9] Lignin—a natural phenolic macromolecule present in vegetal cell walls comprising three kinds of phenylpropane units (as shown in Figure 1), namely guaiacyl alcohol (G), syringyl alcohol (S), and *p*-coumaryl alcohol (H)[10–13]—accounts for 20–30 wt % of lignocellulosic biomass,[14,15] and it is a highly complex three-dimensional structured macromolecule in which large number of aromatic rings link together through C—O—C[16–19] and C—C bonds,[16,20] and major linkages include β-O-4, 5-5-, α-O-4, β-5, β-β, 4-O-5, and β-1 as shown in Figure 2.[16–20] Aryl ether linkages can be more easily cleaved than the C—C linkages since the latter is stable and resistant to chemical depolymerization.[21] Lignin contains various functional groups,[22] but it could hardly participate in the process of making polymer materials with the lower reactivity. Therefore, DL through chemical method, which can not only increase the molecular activity of lignin but also reduce the molecular weight of lignin, is beneficial to the preparation of lignin-based polymer materials.[23]

Various methods for the production of phenols from lignin have been investigated, such as hydrolysis,[24,25] pyrolysis,[26] alkaline oxidation,[27–29] and hydrocracking.[30–34] Among these methods, hydrolysis process usually gives good results with respect to the yield of phenols.[35–37] Hydrolysis of lignin can produce a lot of high-value products via acid- and alkali-catalyzed cleavage of ether bonds.[38] Alkaline catalysis or organic solvents are preferable in this regard. However, organic solvents have the disadvantage of increased costs and process complexity arising from the requirement to recover spent solvent.[22] DL by NaOH also occurs through the rupture of ether bonds[39] and the alkaline catalyst at the same time hinders coke/char formation and decreases the molecular weight of depolymerization products.[40]

Up to now, using DL to synthesize in situ EP has not been reported without any organic solvent/capping agent yet. DL extracted from hydrolysis by NaOH as a catalyst is rich in phenolic hydroxyl groups due to cleavage of the ether bonds in the lignin. This produces increased reactivity with the epoxidation reagent epichlorohydrin. So we used NaOH as a catalyst for DL.
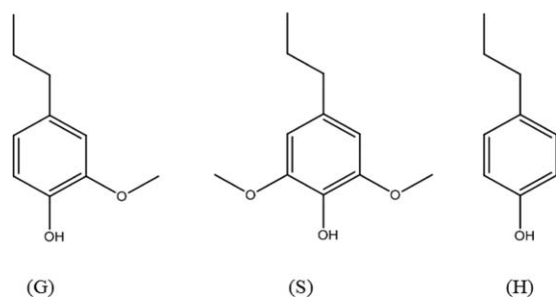
Figure 1. Three kinds phenylpropane units of lignin.

The presence of phenolic hydroxyls in the lignin macromolecule catalyzes its valuable realizations as a substitute of bisphenol A in the process of EP synthesis. Epoxidization is an interesting way to develop a new application of lignin, which therefore improves its utilization potential.[41] This process not only greatly reduced the environmental pollution caused by lignin, but also decreased the production cost of EP. The mechanical and thermal properties of LEP were compared with the neat EP. The aromatic structure of lignin enhanced the rigidity and improved the thermal stability of obtained EP. In this study, the influences of lignin with various reaction time, reaction temperatures, and sodium hydroxide concentrations were also investigated in the preparation of EP by NaOH as a catalyst.

EXPERIMENTAL

Materials
Alkali lignin was obtained from Liuan city, Anhui province.[42] Epichlorohydrin was purchased from the BASF Co. Ltd. Bisphenol A and ethylenediamine (EDA) were purchased from SINO-PHARM. Other basic reagents such as acetone, anhydrous ethanol, formaldehyde, sulfuric acid, and NaOH used in the synthetic process were purchased from the Beijing Chemicals Co. Ltd. These reagents are all of analytical grade and distilled water was applied for all synthesis and treatment processes.
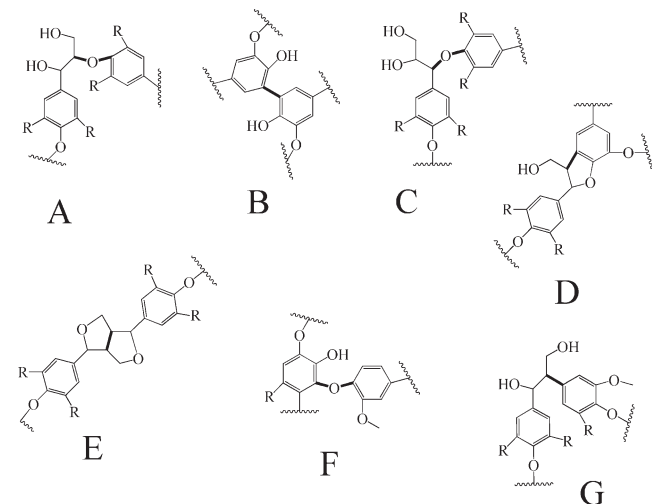
Depolymerization of Original Lignin
The hydrolysis experiments were carried out in a 250 mL reactor equipped with a pressure gauge. 60 g of original lignin (OL, that is, alkali lignin), 75 g of distilled water, and 150 mL of NaOH (15 wt %) were loaded into the reactor. During the reaction, the pressure of the reaction system will increase depending on the temperature which is mainly due to the water vapor pressure (e.g., 5 MPa at 250°C, 8 MPa at 300°C, up to 16 MPa at 350°C).[22] The reaction mixture could be directly used in the preparation of EP by NaOH as a catalyst. Part of the reaction mixture was adjusted to pH = 2.0 with sulfuric acid (2 mol/L) and filtered out the extracted mixture. The residues were washed with distilled water until pH = 7.0 and dried in the oven at 80°C for subsequent use.

Preparation of LEP
In the experiment of preparing neat EP, bisphenol A was mixed with epoxy chloropropane in a 250 mL three-neck round-bottom flask equipped with a thermometer and mechanical stirrer, and the mixture was heated until bisphenol A dissolved completely into solution at 50°C. Then 1 mL of NaOH (30 wt %) solution was dropwise added as a catalyst into the mixture to keep reaction for 30 min. The water bath was set to the specified temperature with 90°C. After 1 h, we would obtain neat EP.[23,42]

For synthesis of LEP, we took the same method as that of neat EP. There was only a small difference in a typical procedure of preparing the LEP, that was, 1 mL OL or DL solution instead of 1 mL 30% NaOH solution dropwise added into the three-neck round-bottom flask and keep reaction for 30 min. Then the water bath pot was set to the specified temperature with 90°C and the residual lignin was dripped into the reaction system. We would obtain OL-based EP (OLEP) and DLEP after 1 h when the dropping process was accomplished. All data were the mean value of these independent experiments which were performed in triplicates.
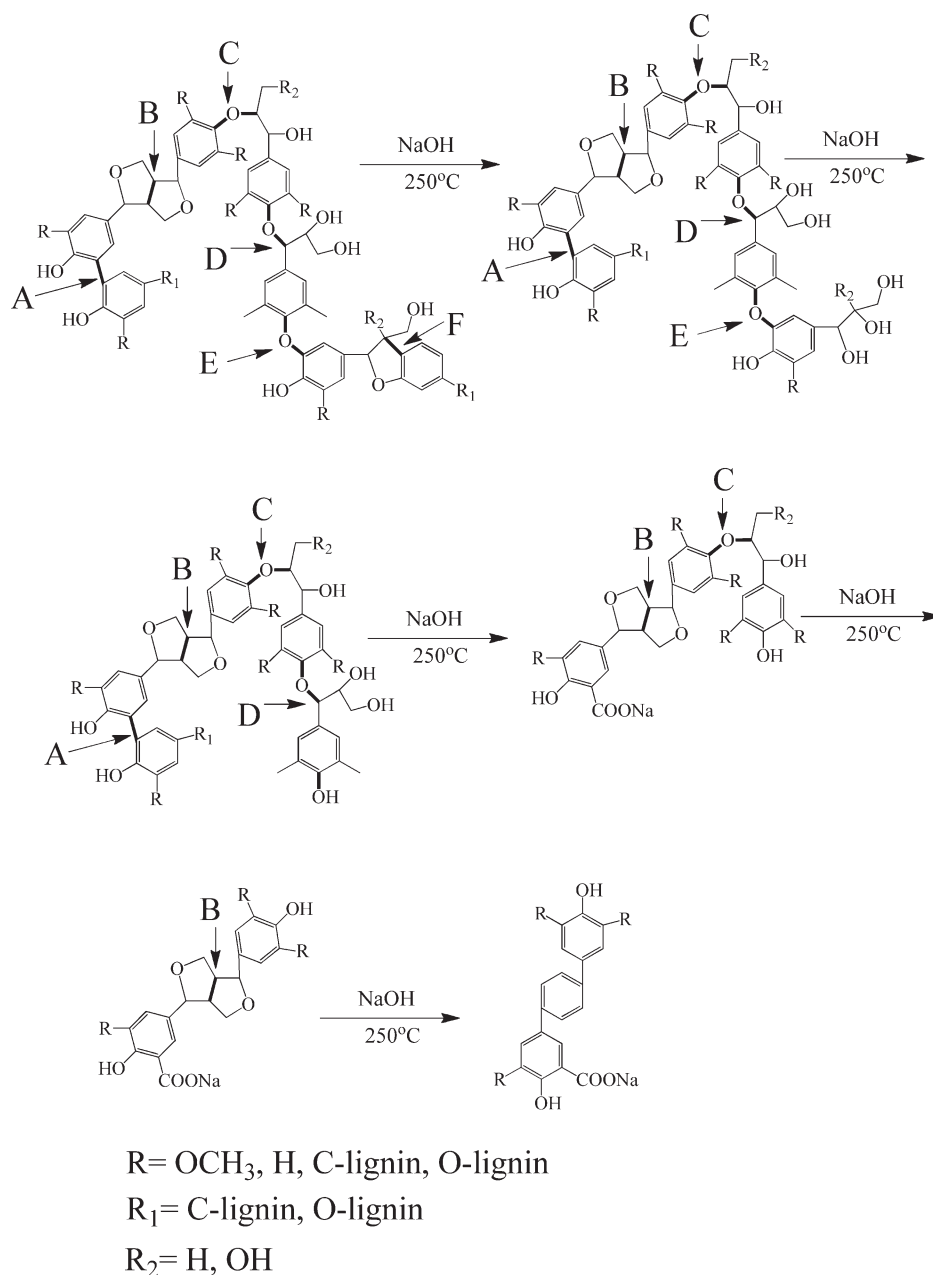
Characterizations
The microstructure of neat EP and LEP was characterized by using JEOL JSM-6700F scanning electron microscopy (SEM) to examine at 5.0 kV. The neat EP and LEP were dispersed completely into ethanol before SEM characterization, then dropped to copper grid with carbon film attachment and dried for using.

The content of phenolic hydroxyl was examined by using the SHIMADZU UV-2450 ultraviolet spectra (UV) in the range of 200–800 nm. We put samples into acid (pH = 6) and alkali (pH = 12) solution, respectively, and made them all dissolve in the case of ultrasonic.

And other functional groups were examined by the SHIMADZU FTIR-8400S. Fourier transform infrared (FT-IR) spectra were obtained by using the KBr method with the spectral range of 400–4000 cm^{-1}.

Thermal gravimetric analysis (TGA), a valuable technique for studying the thermal properties of various compounds, was carried out by means of a DTG-60H analyzer (SHIMADZU). The measurements were performed with about 5 mg of samples at

Figure 2. The major linkages include β-O-4, 5-5, α-O-4, β-5, β-β, 4-O-5, and β-1.

R= OCH$_3$, H, C-lignin, O-lignin
R$_1$= C-lignin, O-lignin
R$_2$= H, OH

Figure 3. Linkage A is the 5–5 bond, linkage B is the β–β bond, linkage C is the β-O-4 bond, linkage D is the α-O-4 bond, linkage E is the 4-O-5 bond, and linkage F is the β-1 bond in the aromatic ring.

the heating rate of 20°C/min^{-1} in air atmosphere, and weight losses were calculated from the TGA using tabular α-Al$_2$O$_3$ as reference.

The hydroxymethyl content of lignin and the epoxide value (EV) of LEP were measured by ASTM D 1763-00 (2005) and ASTM D 1652-11 (2004).

The mechanical property of EP was estimated in accordance with universal materials tester which could evaluate the compression stress and compression strength. We chose EDA as the curing agent in this experiment. First of all, LEP and EDA were mixed uniformly, coating on an aluminum plate with a range of effective area, curing for 4 h at 100°C in the drum wind drying

oven. We measured the tensile properties of the cured EP through the use of the universal materials tester (CRS-UTM50CS) under 20 kN.[42]

RESULTS AND DISCUSSION

Lignin is generally believed to be a random C$_3$ aryl polymer. The cleavage of the β-O-4 ether bond takes place in the sodium cation and the hydroxide ion participates (Figure 3). The sodium cations catalyze the reaction by forming cation adducts with lignin and thus polarizing the ether bond which leads to increase of negative partial charge on the oxygen atom and reducing of the energy required for bond cleavage. Linkage A is

Table I. Phenolic Hydroxyl and Hydroxymethyl Contents at Various Sodium Hydroxide Concentrations (wt %) (Reaction Temperature: 250°C; Reaction Time: 1.5 h)

Sodium hydroxide concentration (wt %)	Phenolic hydroxyl group (%)	Hydroxymethyl group (%)
0	0.50	13.39
5	0.50	14.73
10	0.79	16.38
15	2.11	19.24
20	0.91	21.97

Table II. Phenolic Hydroxyl and Hydroxymethyl Contents at Various Reaction Temperatures (15 wt % Sodium Hydroxide Concentration and Reaction Time: 1.5 h)

Reaction temperature (°C)	Phenolic hydroxyl group (%)	Hydroxymethyl group (%)
200	0.50	18.07
250	2.11	19.24
300	0.75	21.19
350	2.49	23.40

the bond 5-carbon to 5-carbon in the aromatic ring (5–5 bond). Linkage B is the bond cross-linking hydroxylated alkyl chains through C—C bonds at the β-position (β—β bond). Linkage C is the bond between oxygen and the side-chain β-carbon (β-O-4 bond). Linkage D is the bond between oxygen and the side-chain α-carbon (α-O-4 bond). Linkage E is the bond between oxygen and the 5-carbon in the aromatic ring (4-O-5 bond) and linkage F is the bond between the side-chain β-carbon and 1-carbon in the aromatic ring (β-1 bond).[43,44]

Influence Factors of DL
Many factors, such as the sodium hydroxide concentration, the reaction temperature, and the reaction time can influence the performance of DL. Therefore, those factors were investigated, respectively.

UV-spectroscopic methods are based on the wavelength shift between ionized and protonated phenolic hydroxyl groups. The intensities of the absorbances in the ionization difference spectra are proportional to the content of phenolic hydroxyl groups.[45] The method chosen for this work is based on the intensities of the maxima (Δa_{max}), which was the absorbance peak of above acidic (pH = 6) and alkaline (pH = 12) solution with the detection wavelength at 279 nm.[23,42]

The phenolic hydroxyl group content of lignin samples was calculated using the Δa_{max} as follows.

$$\text{Phenolic hydroxyl} = \Delta a_{max} \times 0.41078 \times 100\% \qquad (1)$$

Hydroxymethyl content was examined according to the ASTM D 1763-00 (2005) for different DL with the same reaction temperature (90°C), reaction time (1 h), and amounts of lignin added (20 wt %), which are shown in Tables I—III.

The Change of Phenolic Hydroxyl and Hydroxymethyl Contents. *Effects of sodium hydroxide concentration.* The effect of sodium hydroxide in the hydrolysis of lignin was determined by varying sodium hydroxide concentration from 10 to 20 wt %, while keeping all other variables or process parameters constant. The changes of phenolic hydroxyl contents and hydroxymethyl contents are shown in Table I.

Table I displays the phenolic hydroxyl and hydroxymethyl contents at 250°C for 1.5 h with various sodium hydroxide concentrations. From Table I, we could see that the contents of phenolic hydroxyl in lignin increased after decreased first which increased faster than the increasing of sodium hydroxide con-

centration and the contents of hydroxymethyl in lignin were increased continuously. Phenolic hydroxyl and hydroxymethyl contents were higher than that of OL, which displayed that DL by NaOH as a catalyst could increase the activity of functional groups. We also found that using lignin instead of bisphenol A for synthesis of LEP was due to the contents of phenolic hydroxyl. So we choose the optimum conditions: the sodium hydroxide concentration was 15 wt %. At this time, the contents of phenolic hydroxyl and hydroxymethyl in lignin reached the degree of 2.11 and 19.24%, respectively.

Effects of reaction temperature. Temperature is the critical parameter for lignin hydrolysis in water by NaOH as a catalyst. Table II shows the effects of reaction temperature on the phenolic hydroxyl and hydroxymethyl contents of DL from the tests carried out at a temperature ranging from 200 to 350°C for 1.5 h. From Table II, we could see that the contents of phenolic hydroxyl were curved with an upward trend until the temperature reaching 250°C, then it exhibited a downward trend. When the temperature reaches 350°C, the contents of phenolic hydroxyl got a maximum. In this process, the hydroxymethyl contents were increased from 200 to 350°C. The reason could be attributed to lignin carbonization. That is to say, we found obvious solid residue from the process of depolymerized lignin when the temperature arrived at 350°C. On the other hand, the high temperature needed more energy to meet the experimental conditions. So we got the optimum conditions that the contents of phenolic hydroxyl in lignin got 2.11% in this process and the contents of hydroxymethyl could get up to 19.24% at the same temperature.

Effects of reaction time. Table III shows that reaction time (from 1 to 3 h) affected the contents of phenolic hydroxyl and

Table III. Phenolic Hydroxyl and Hydroxymethyl Contents at Various Reaction Time (h) (15 wt % Sodium Hydroxide Concentration and Reaction Temperature: 250°C)

Reaction time (h)	Phenolic hydroxyl group (%)	Hydroxymethyl group (%)
1.0	0.50	15.60
1.5	2.11	19.24
2.0	1.08	18.59
2.5	1.89	16.78
3.0	3.02	20.28
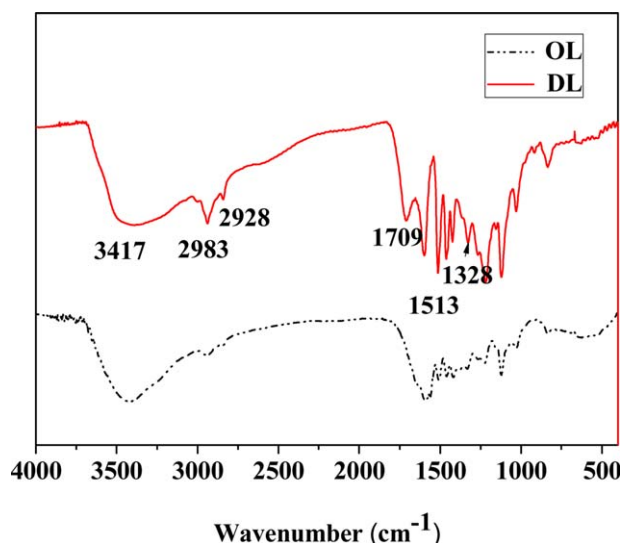
Figure 4. FT-IR spectra of original lignin (OL) and depolymerization of lignin (DL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydroxymethyl in lignin during the depolymerization process when the temperature was 250°C with 15 wt % sodium hydroxide concentration. As shown in Table III, when the reaction time reached 3 h, lignin carbonization, obvious solid residue formation from depolymerized lignin, would happen and it was bad for the synthesis of LEP shown in Figures 11(a) and 12(c). We selected the optimum conditions for the reaction time as 1.5 h. The contents of phenolic hydroxyl in lignin got a degree of 2.11% in this process and the contents of hydroxymethyl could get up to 19.24% at the same condition.

FT-IR Spectra of DL. The FT-IR spectra recorded between 4000 and 400 cm^{-1} were used to determine which functional groups would be present in the samples. The FT-IR spectroscopy data indicated that DL (shown in Figure 4 DL) had different frameworks comparing with OL (Figure 4 OL). From Figure 4, we found that the peak of 3417 cm^{-1} showed the existence of hydroxyl vibrating; the characteristic peak of 2983 and 2928 cm^{-1} was C—H deformations in methyl molecule; 1328 cm^{-1} showed the aliphatic in —CH stretch in —CH$_3$ and —OH phenol; 1513 cm^{-1} indicated the existence of vibration in the aromatic rings skeleton.

Comparing the two sets of FT-IR spectroscopy data, we could find that there were some other different peaks. In the FT-IR spectra of DL, 1709 cm^{-1} was the characteristic peak of C=O vibration in aromatic rings, which could not be found in the original one (shown in Figure 4 OL). This illustrates that C=O was added to DL molecules. These results demonstrated that hydrolysis by NaOH as a catalyst could not only increase the molecular activity of lignin but also reduce the molecular weight of lignin.

Change of the Lignin Morphology. The microstructure of DL was characterized by using SEM. Figure 5 shows the effect of hydrolysis on the morphology of lignin. Figure 5(a) represents

OL, and Figure 5(b) shows DL which was hydrolysis by NaOH as a catalyst.

From Figure 5(a), we could see that the morphology of OL was irregular, heterogeneous, cross-linked, nonuniform cluster, and particle size of about 1–3 μm. Meanwhile DL in Figure 5(b) was spherical, homogeneous, and small particle size under 0.2 μm. So we could realize that hydrolysis by NaOH as a catalyst could make the macromolecule lignin more dispersed than the OL and reduce the molecular weight of lignin. Depolymerization reaction via NaOH as a catalyst in lignin increased the numbers of lignin active groups exposing to the external, which would improve the chemical reactivity of lignin.

Thermal Analysis of OL and DL. OL and DL at various sodium hydroxide concentrations were further analyzed by TGA and DTA to confirm the initial decomposition temperature and the content of ash with different morphologies, as shown in Figure 6. Figure 6(a) shows the TGA results of OL and DL at various sodium hydroxide concentrations. The thermal stability and the decomposition temperature of DL at various sodium hydroxide concentrations were clearly improved. The initial weight loss for all the samples occurred at the range from 100 to 200°C due to the water loss. The second part of the weight
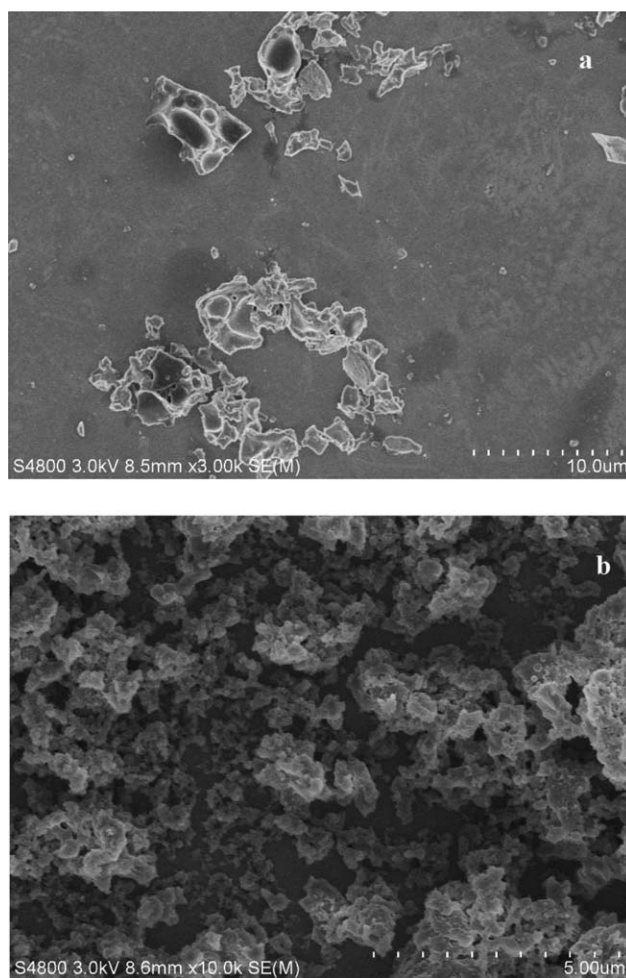
Figure 5. SEM image of samples: (a) original lignin (OL) and (b) depolymerization of lignin (DL).
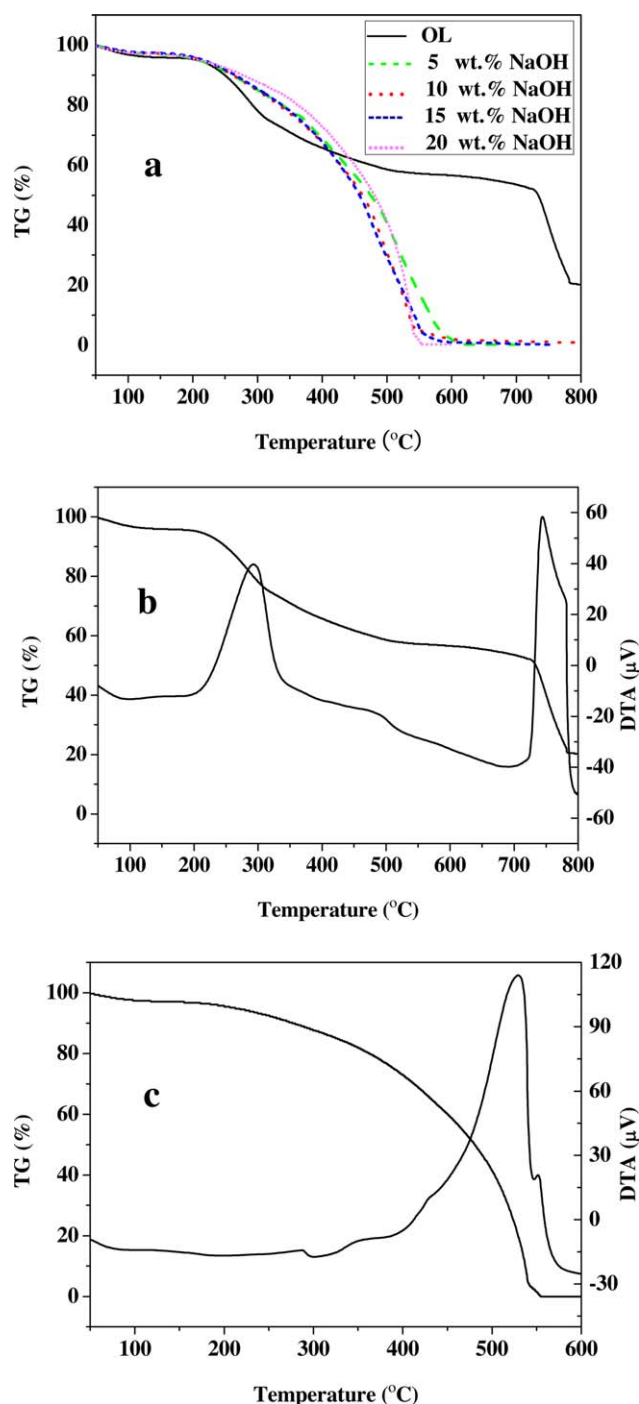
Figure 6. (a) TG of original lignin (OL) and depolymerization of lignin (DL) at various substrate concentrations (original lignin with 5 wt % NaOH, 10 wt % NaOH, 15 wt % NaOH, and 20 wt % NaOH); TG and DTA of (b) OL and (c) DL with 20 wt % NaOH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

loss for OL and DL was from 200 to 650°C because of their decomposition of low-molecular-weight lignin which could be shown in Figure 6(b,c), respectively. Meanwhile, there was an obvious peak from 700°C to 750°C [shown in Figure 6(b)] which was not found in Figure 6(c). Figure 6(c) shows that DL could be resolved completely at 650°C, while OL was still unde-

composed partly at 800°C [shown in Figure 6(b)]. The OL obtained from the factory directly without any purification included about 20 wt % of impurity. The depolymerization of alkali lignin can eliminate the redundant impurities from the process of dissolving extraction, which was beneficial to the subsequent application of lignin.

### Structural and Morphological Characteristics of LEP

The sodium hydroxide concentration, the reaction temperature and the reaction time can influence the performance of DL. Also, the factors can influence the performance of LEP. The DL with the same amount (20 wt %) of lignin added, reaction temperature and reaction time was investigated for the preparation of LEP.

FT-IR Spectra of LEP. From the FT-IR spectra of neat EP and LEP, we could also see some characteristic peaks of functional groups as shown in Figure 7. The peak near 3354 cm^{-1} was hydroxyl vibration. The peaks of 2969 cm^{-1} and 2866 cm^{-1} showed C—H stretching vibration in —CH$_3$ and —CH$_2$. Peak at the 1609 cm^{-1} indicated the existence of the vibration in the aromatic rings skeleton. Peak at 1510 cm^{-1} was the existence of asymmetric deformation of epoxy groups. Peak at 1246 cm^{-1} indicated the C—O and C=O asymmetric stretching vibration. Peak at 830 cm^{-1} was the vibration peak of substituent groups on the benzene ring. We could see from the FT-IR spectra that LEP and neat EP had the same structure. Therefore, we could draw the conclusion that DL by hydrolysis had higher reactivity than the original one and they both could replace bisphenol A to synthesize EP.

SEM of LEP. We used the SEM micrograph to observe the morphology of LEP. Figure 8(a) showed neat EP, and Figure 8(b,c) showed OLEP and DLEP, respectively. The quantity of added lignin in all kinds of LEP was 20 wt %. From Figure 8(b,c), we could see that LEP existed obvious particles, which might be the macromolecules of LEP. Because the molecular weight of
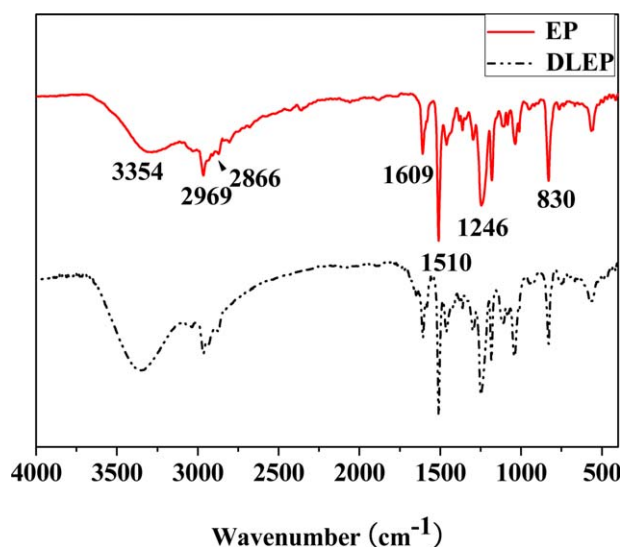
Figure 7. FT-IR spectra of the neat epoxy resin (EP) and DL-based epoxy resin (DLEP). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
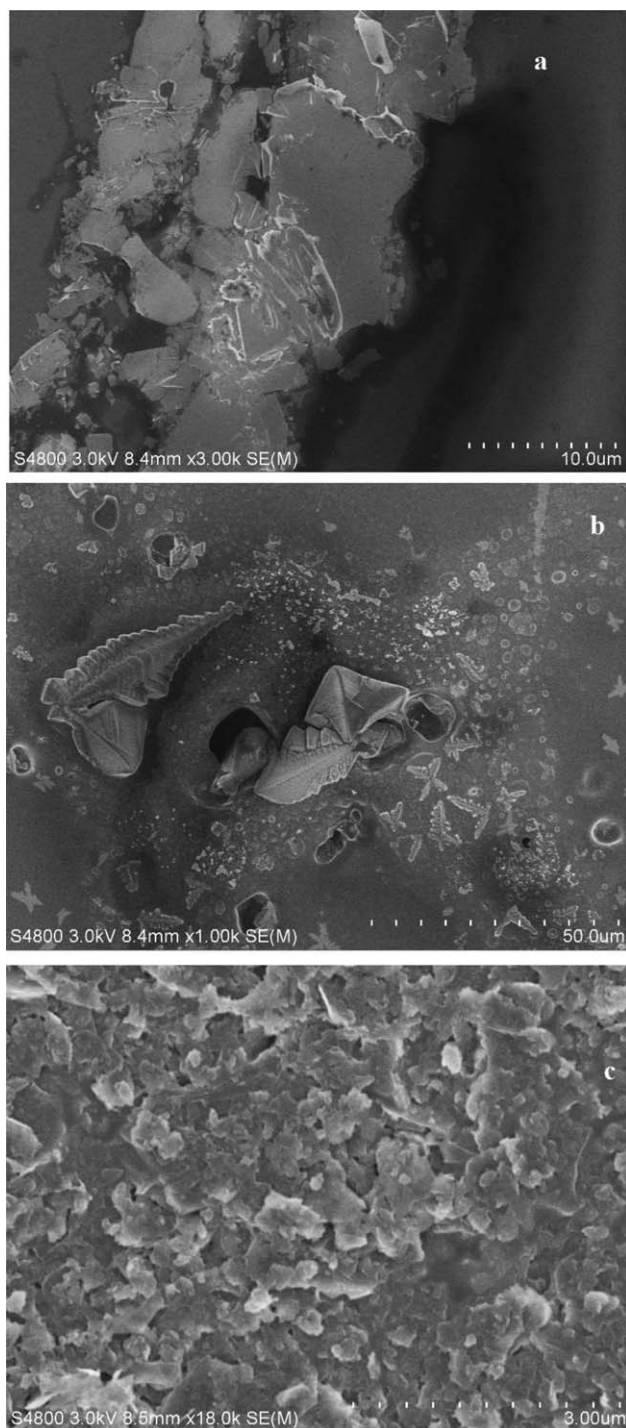
Figure 8. SEM image of samples: (a) neat epoxy resin (EP), (b) original lignin-based epoxy resin (OLEP), and (c) depolymerized lignin-based epoxy resin (DLEP).

lignin is much bigger than that of bisphenol A, the molecular weight of LEP is bigger than that of neat EP, when we used the same synthesis method. And the particles of LEP were more branched than those of neat EP. From Figure 8(b), we could find clear particles which were exposed at the surface of EP, which displayed lignin was not fully involved in the synthesis of EP. The reason was attributed to the fact that OL has low activ-

ity. From Figure 8(c), we could find that DLEP was spherical, homogeneous with small particle size distribution, which displayed that DL could increase the reactivity of functional groups.

TGA and DTA of LEP. The thermal decomposition of polymers was investigated by TGA and DTA. This parameter could be used to give a better understanding of the thermal stability of LEP.

The thermal stability and the decomposition temperature of DLEP were obviously improved [shown in Figure 9(a,b)]. In EP, the decomposition starts at 240°C with a slight that could be assigned to the relatively weak bonds break. The maximum degradation rate takes place at 312°C during EP decomposition from Figure 9(b). From TGA curves, we also can see that the decomposition temperature of LEP was divided into two stages. The first stage of decomposition temperature is from 153 to
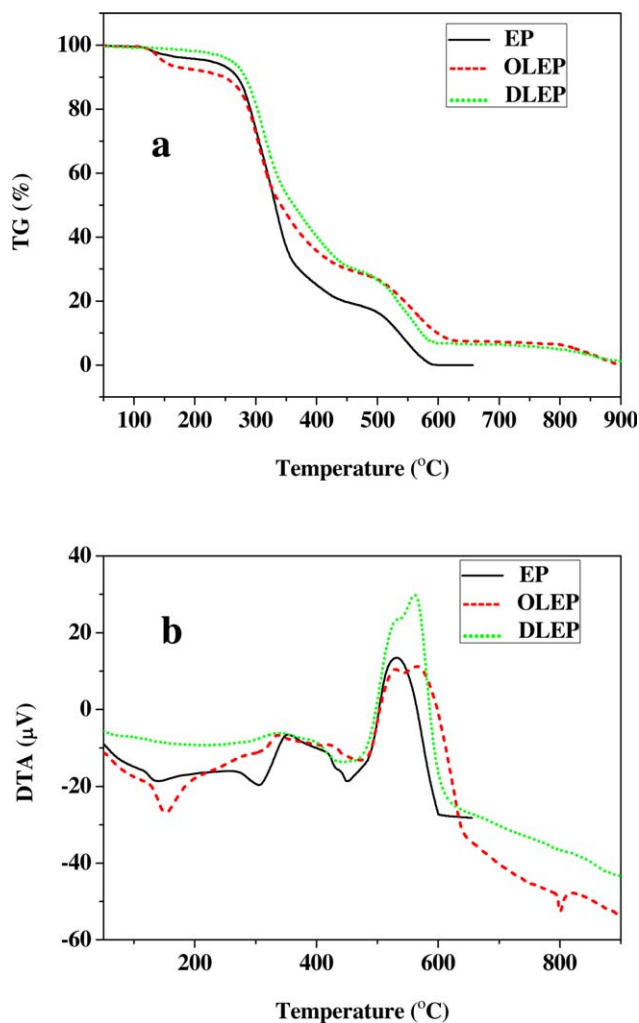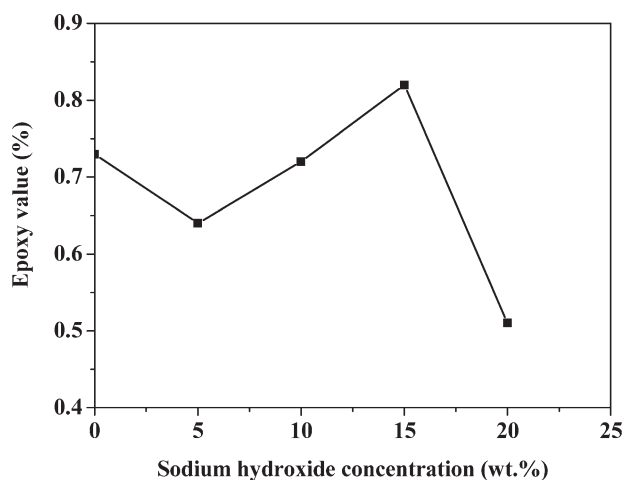

Figure 9. (a) TG results of neat epoxy resin (EP), original lignin-based epoxy resin (OLEP) and depolymerized lignin-based epoxy resin (DLEP) (The amount of added lignin was 20 wt %, reaction temperature: 90°C, reaction time: 1.5 h). (b) DTA results of EP, OLEP and DLEP from 50 to 650°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Epoxy Value of Epoxy Resin for Depolymerization of Lignin with Various Sodium Hydroxide Concentrations

| Sodium hydroxide concentration (wt %)	Epoxy value of epoxy resin (%)
0	0.73
5	0.64
10	0.72
15	0.82
20	0.51

400°C and the second stage is from 400 to 650°C. Before 400°C, the decomposition temperature of OLEP was 244°C and DLEP was 258°C. We can clearly draw a conclusion that the decomposition temperature of DLEP was increased by 18°C and OLEP was increased by 4°C compared to neat EP [shown in Figure 9(a)]. In the second stage, the decomposition temperatures of OLEP and DLEP were increased from 448 to 480°C and 470°C after 400°C which can attributed to the cleavage of stronger bonds (such as C—C and O—CH$_2$ bonds) in the aromatic rings of the cross-linked resin network.[46] The major exothermic peak of EP, OLEP, and DLEP was observed at 532, 552, and 565°C from Figure 9(b), respectively. Pyrolysis and carbonization of EP could be explained by these results. We could draw a conclusion that lignin obviously improved the thermal resistance of EP. The mechanism was that the macromolecular structure of lignin that has more active groups to synthesize of EP increased the decomposition temperature of neat EP.[42] From Figure 6(a), we found neat EP almost has no residue at 600°C, while both OLEP and DLEP could be exhausted completely without any residue at 900°C. From Figures 6 and 9(a), we could draw a conclusion that the decomposition of OLEP and DLEP from 600 to 900°C was ascribed to the decomposition of lignin. Therefore, only a small part of lignin (OLEP was 9.24% and DLEP was 6.47%) failed to participate in the reaction for the synthesis of EP completely.

Epoxy Value (EV) of LEP. We examined EV according to the ASTM D 1652-11 (2004) for different DL with the same reaction temperature (90°C), reaction time (1 h), and amounts of lignin added (20 wt %), which are shown in Table IV and Figure 10. EV was expressed to the mass fraction (wt %).

From Table IV and Figure 10, we could see that EV of LEP tended to increase after decrease first while the additive content of OL was stayed the same. EV would reach the maximum of 0.82 when the sodium hydroxide concentration was 15 wt % and only EV of EP with 15 wt % sodium hydroxide concentration of lignin was above to one of OLEP, so we set the sodium hydroxide concentration with 15 wt % of NaOH in the later experiments.

From Tables II and III and Figure 11, the proportion of phenol hydroxyl could affect EV of EP. When the reaction temperature reached 350°C and reaction time is 3 h, EV of EP was obviously increased. The reason could be attributed to the lignin carbonization. From Figures 10 and 11, we also set the optimum conditions with DL, that is, substrate concentration was 15 wt % of NaOH, reaction temperature was 250°C and reaction time was 1.5 h.

Figure 10. Epoxy value of epoxy resin (depolymerization of lignin with various sodium hydroxide concentrations).
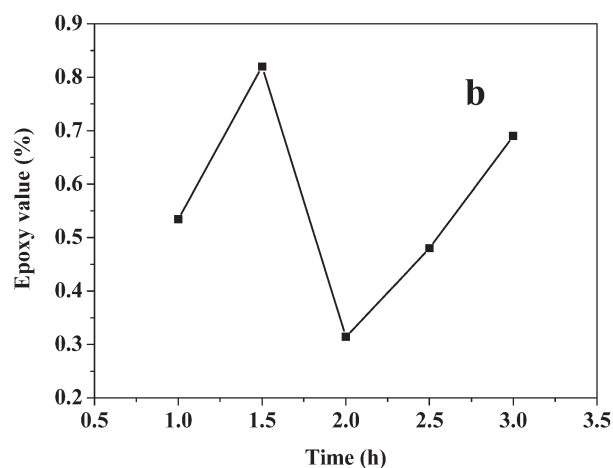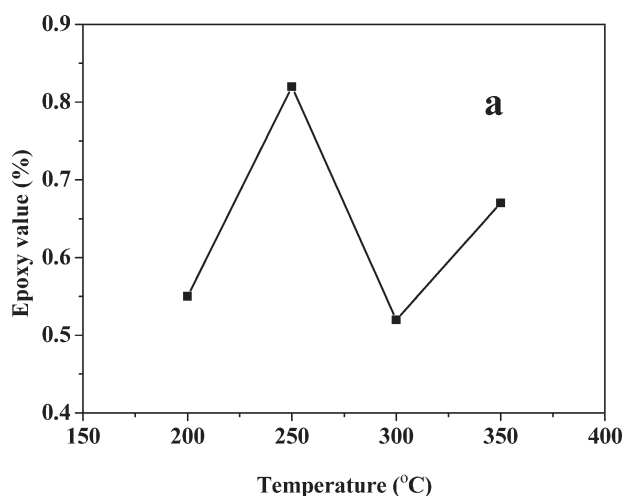
Figure 11. EV of DLEP for depolymerization of lignin: (a) with different reaction temperatures and (b) with different reaction time.
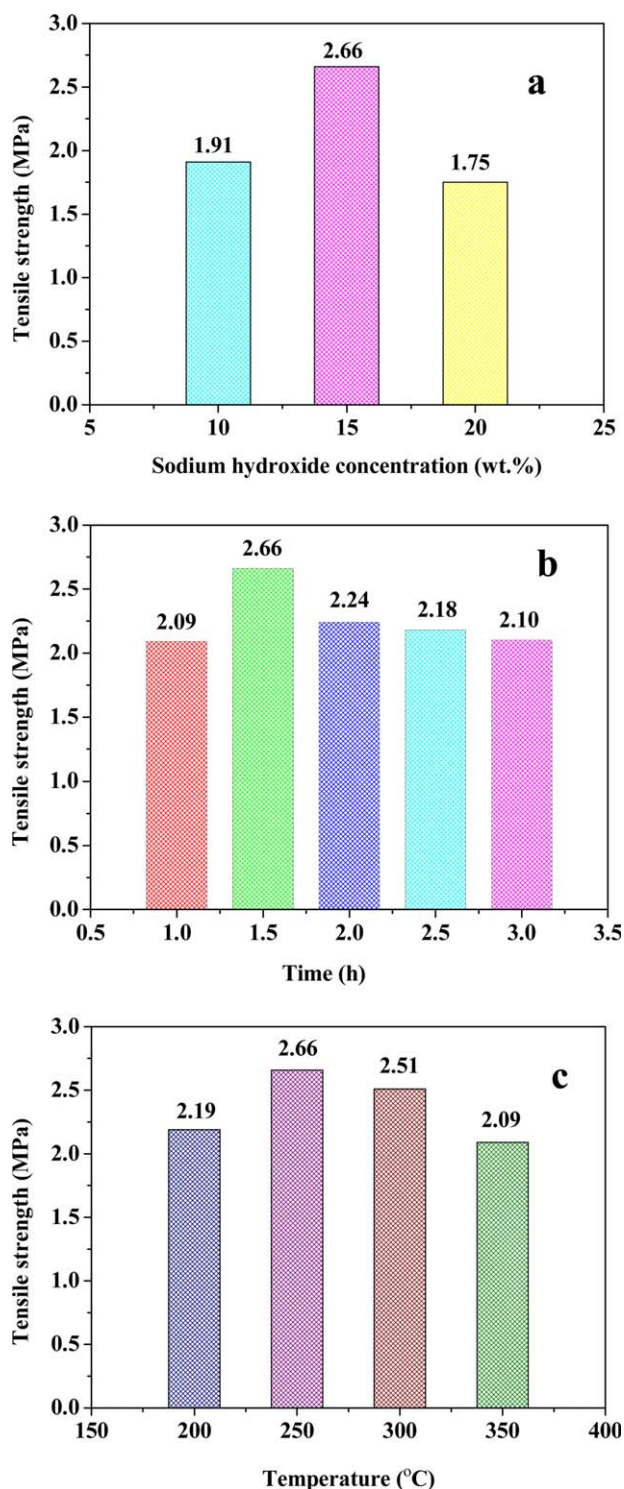
Figure 12. Tensile strength of lignin-based epoxy resin added the same amounts (20 wt %) of different depolymerized lignin: (a) with various sodium hydroxide concentrations, (b) with different reaction time and (c) with various reaction temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Tensile Property Analysis of DLEP. *The effect of DL with various sodium hydroxide concentrations on the tensile property of EP and LEP.* The tensile strength of the neat EP was 2.18 MPa. The tensile strength of OLEP was 1.16 MPa. The tendency of other DLEP was shown in Figure 12(a). We could find that the tensile strengths of all DLEPs were greater than that of OLEP, but only the tensile strength of DLEP with DL of 15 wt % sodium hydroxide concentration was greater than that of EP.

The effect of DL with different reaction time on the tensile property of EP and LEP. As shown in Figure 12(b), the reaction temperature of DL is a critical factor for preparation of EP. When the reaction temperature was 250°C, the tensile strength achieved the maximum with 2.66 MPa. All DLEPs were greater than that of OLEP, but only the tensile strength of DLEP with DL at the reaction temperature (350°C) was lower than that of EP. The reason could be explained that high temperature lead lignin to carbonization, which resulted in the decrease of the reactivity of lignin.

The effect of DL with different reaction temperatures on the tensile property of EP and LEP. From Figure 12(c), we could also find that the tensile strengths of all DLEP were greater than that of OLEP, which displayed a rule that the reactivity of DL was increased than that of OL. When the reaction time was 1.5 h, the tensile strength of DLEP reached the maximum. While the reaction time was 3 h, the tensile strength of DLEP was declined because lignin was carbonized at the long reaction time. DL by NaOH could increase the amounts of functional groups (—OH). Using lignin instead of bisphenol A for synthesis of EP not only greatly reduced the environmental pollution caused by lignin, but also reduced the cost of production of EP.

CONCLUSION

We took the way of DL by NaOH as a catalyst with different sodium hydroxide concentrations, reaction temperatures, and reaction time, which effectively improve the chemical reactivity of the lignin. The EV reached a maximum of 0.82 when the additive amount of DL was 20 wt % at 250°C with 15 wt % of NaOH concentration for 1.5 h. Moreover, phenolic hydroxyl groups of lignin by NaOH as a catalyst was the highest, reaching 2.11%, nearly four times higher than that in the original one. The decomposition temperature of DLEP was 18°C higher than that of neat EP. These results suggested that the thermal stability of EP was improved by the addition of DL, that is, LEP will be used in many fields. The cured DLEP showed the highest adhesive shear strength up to 2.66 MPa, which displayed 122% of the adhesive shear strength of the EP. By adding DL to EP, it can not only increase the decomposition temperature of EP, but also remarkably improve its mechanical properties.

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