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Preparation of carboxylated lignin-based epoxy resin with excellent mechanical properties

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ABSTRACT

Lignin, a renewable biopolymer recovered from the chemical processing of woody biomass, has potential to enhance the mechanical properties of epoxy resins with the added benefit of reduced contents of non-renewable petroleum-based polymers. Lignin-based epoxy resins were prepared by employing a carboxylated lignin as a co-hardener using a "one-pot" method. The effect of lignin content and preparation method on mechanical properties, apparent morphology, and thermodynamic properties of the resulting epoxy resins were then studied. The results showed that elongation at break increased from 2.2 to 5.7%, and flexural strength increased from 23.3 to 101 MPa, with the addition of lignin up to 20 wt%. The highest increase in tensile strength was obtained for the lignin-based resin having a lignin content of 10 wt%. The incorporation of carboxylated lignin at an appropriate amount demonstrated simultaneous reinforcing and toughening effects on the epoxy resin, which can be attributed to the rigid and highly-branched structure of lignin.

1. Introduction

Biobased polymers are under development as substitutes for petroleum-based polymers because they are renewable and usually have lower environmental impacts for production and/or use [1,2]. Greater heat resistance, higher mechanical strength properties, and preferred electrical performance properties in biobased epoxy resins containing lignin are attributed to the lignin aromatic ring structure [3]. Briefly, lignin is the renewable aromatic polymer found in land plants, comprising up to 15–35 wt% of woody biomass [4]. It is generally viewed as a three-dimensional and highly-branched polymer of monomeric phenylpropanoid units mainly linked by ether bonds [5,6]. Although lignin is the most abundant phenolic substance found in nature, only a small amount of lignin extracted by industrial processing is converted into products such as dispersants and fillers [7]. The bulk of the lignin recovered by the pulp and paper industry is burned as fuel to recover its energy value. This is due to its complex and variable structure, high polydispersity, and immiscibility with many polymer matrices [8–10].

Currently, epoxy resins represent a major class of thermosetting resins widely used in coatings and adhesives industries, with global production estimated to be 2 million tons in 2010 [11]. The development of partial or fully biobased epoxy resins has been studied, with lignin receiving attention as a component [11–13]. Lignin can be used in epoxy resins as so-called lignin-based epoxy monomers [11], with the reactive phenolic and aliphatic hydroxyl groups in lignin being chemically modified. Epoxy monomers from lignin have been obtained through the epoxidation reaction of the lignin hydroxyl groups with either epichlorohydrin or diglycidyl ether. Organosolv lignins and partially depolymerized industrial lignins are the preferred feedstocks because of their solubility in organic solvents and higher hydroxyl contents [14]. Alternatively, lignin can be used in epoxy resins as a hardener. Although lignin phenolic groups can react with epoxy monomers, the introduction of carboxylic acid or amino groups can enhance the miscibility of lignin with the epoxy monomers. For example, carboxylic acid functionalized lignin can be synthesized by ozonating lignin aromatic rings in the presence of NaOH, or esterifing lignin hydroxyl groups with an anhydride [15].

The use of lignin-based epoxy monomers or hardeners often results in unsatisfactory mechanical properties for the resulting epoxy composites,

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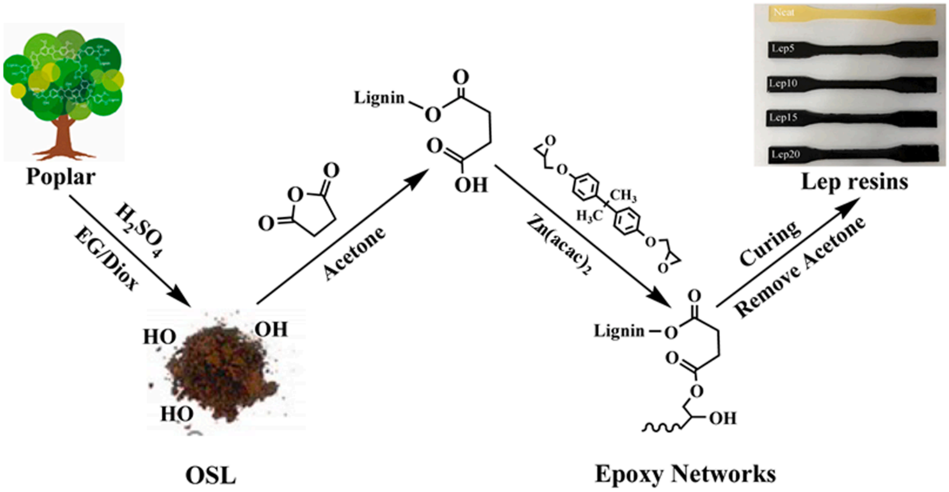

Fig. 1. Synthesis route for the lignin-based epoxy resin.

especially with high lignin contents [16]; however, with only limited additions of lignin (usually less than 10 wt%), the mechanical properties of epoxy resins can be enhanced [17,18]. It is still a challenge to prepare lignin-containing epoxy resins with improved mechanical properties by using lignin-based hardeners at high lignin contents. In some cases, epoxy resins have been prepared with lignin as a co-curing agent (i.e. co-hardener) along with an amine curing agent [19,20]. The development of biobased curing agents is also a research need for renewable epoxy materials; thus far, biobased anhydride hardeners (e.g. succinic anhydride) need higher hardening temperatures and the resulting epoxy resins often have poor mechanical properties.

In this study, lignin-based epoxy resins with high lignin contents were prepared by employing a carboxylated lignin as a co-hardener with succinic anhydride, and not an amine, as the curing agent. The lignin was extracted from poplar wood by the organosolv process to achieve a lower molecular weight and better solubility in organic solvents compared to alkali lignins [21]. The organosolv lignin was carboxylated by reacting with an excess of succinic anhydride. Remaining succinic anhydride was then available to cure the epoxy resin. A small amount of 1-methylimidazole (1-MI) was added to the mixture at the beginning of the reaction to catalyze the esterification reaction between succinic anhydride and lignin hydroxyl groups; this reagent also functioned as initiator in the subsequent curing process [22]. The mechanical properties of neat epoxy resin (no lignin) and lignin-based epoxy resins with two preparation processes were compared. Lignin functional groups changes were investigated by ^{1}H NMR and FT-IR analysis. Differences in mechanical properties, apparent morphology, and thermodynamic properties between the lignin-based epoxy resins and the neat epoxy resin (control) were explored by mechanical testing, FT-IR spectroscopy, scanning electron microscopy (SEM), and thermal analyses (TGA, DMA).

2. Materials & methods

2.1. Materials

Poplar wood chips were obtained from a wood processing facility near Nanjing, China. All chemicals used in this study, including sulfuric acid, methanol, ethylene glycol, dioxane, acetone, and succinic anhydride were of analytical grade, commercially available, and ready for use. 1-Methylimidazole (1-MI) and zinc acetylacetonate ($Zn(acac)_2$) were purchased from TCI Chemicals Co. Ltd. (Shanghai, China). The epoxy resin (DER 332) was purchased from the Dow Chemical Company (Midland, Michigan, USA) and had an epoxy equivalent weight of 171–175 g/eq.

2.2. Isolation of organosolve lignin

An organosolv lignin (OSL) isolated from poplar wood was used for the current study since it would have improved solubility over commercial lignin products (e.g. kraft lignin). The ethylene glycol/dioxane binary solvent system used to prepare the OSL was based on our previous study in which the OSL had desired properties of low molecular weight and high solubility [21]. In brief, poplar wood chips were ground in a Wiley mill to obtain particles that passed through an 80-mesh sieve. The wood particles were then dried in an oven at 105 °C for 24 h before use. For the extraction of the lignin, the wood particles (6 g) were added to ethylene glycol/dioxane mixture (2/1, w/w, 59.4 g) in a 350 ml pressure tube with a magnetic stir bar. A small amount (0.981 g) of concentrated sulfuric acid (98%) was then added as a catalyst. After heating at 140 °C for 40 min, with continuous stirring (500 r/min), the reaction mixture was filtered and the residue rinsed with 20 ml dioxane, followed by 50 ml methanol. The dioxane and methanol in the filtrate were removed using a rotary evaporator. The concentrated viscous liquid was added dropwise to an excess of deionized water (500 ml) to precipitate the lignin, which was vacuum filtered in a sand core funnel and washed repeatedly until the filtrate pH was neutral. The lignin was then collected and freeze-dried. The resultant lignin powder was stored in a tightly sealed container until needed. The procedure was repeated to obtain enough material to prepare a modified lignin and the lignin-based epoxy resins. The yield of the lignin powder (OSL) was 65 wt% based on the mass percentage of lignin in the poplar wood. The number-average (Mn) and weight-average (Mw) molecular weights of the OSL powder were 701 and 1135 g/mol, respectively, based on an analysis method provided in literature [23].

2.3. Preparation of carboxylated lignin

The carboxylation of OSL was performed following a modified method in literature [24]. Briefly, 415 mg OSL and 2.6 g succinic anhydride were dissolved with 100 ml acetone in a pressure tube, with 0.05 g 1-MI then added as catalyst. The mixture was heated at 60 °C for 6 h, and then cooled to room temperature before being added drop wise to an excess of deionized water (250 ml). The precipitate was vacuum filtered in a sand core funnel, collected, and freeze dried to obtain the carboxylated OSL (labeled as L-COOH) as a powder.

2.4. Preparation of lignin-based epoxy resin

The “one-pot/one-step” method to prepare lignin-based epoxy resin is schematically displayed in Fig. 1. Upon the end of carboxylation of

Table 1
Formulation and labeling of lignin-based epoxy resins.

Resin sample	DER 332 (g)	Lignin[a] (g)	Succinic anhydride (g)	1-MI (g)	$Zn(acac)_2$[b] (g)
Neat epoxy	53	–	26	0.5	0.80
Lep5	53	4.15	26	0.5	0.84
Lep10	53	8.78	26	0.5	0.88
Lep15	53	13.94	26	0.5	0.93
Lep20	53	19.75	26	0.5	0.99
Lep10-control[c]	53	8.78	26	0.5	0.88

[a] The mass of L-COOH accounts for 0, 5, 10, 15, and 20 wt% of total reaction system.
[b] The mass of $Zn(acac)_2$ accounts for 1 wt% of the total reaction system.
[c] Prepared by "one-pot/two-step" method.

OSL described above, the reaction system was cooled to room temperature before directly adding the desired amounts of epoxy resin (i.e. DER 332) and $Zn(acac)_2$, the latter used as a catalyst for both curing and dynamic transesterification [25]. The resultant mixture was placed in oil bath heating at 80 °C for 30 min with continuous magnetic stirring (500 r/min). After cooling to room temperature, the acetone in the mixture was removed using a rotary evaporator. The viscous lignin-based epoxy resin was poured into steel molds and kept under vacuum until bubbling ceased. All poured epoxy resin samples were cured in an oven using the following temperature profile: 120 °C for 1 h, 160 °C for 3 h, and 180 °C for 30 min. The final stoichiometric ratio of epoxy groups to anhydride groups was 100:85. Three replicates of testing samples were prepared from a same batch for each epoxy resin formulation; the detailed shapes and sizes of the testing samples are shown in Fig. S1.

To compare the influence of L-COOH content on the properties of resulting lignin-based epoxy resins, 4 lignin contents were selected to prepare lignin-based epoxy resins, those being 5, 20, 15, and 20 wt% based on the weight of the epoxy resin, and designated as Lep5, Lep10, Lep15, and Lep20, respectively. In addition, the effect of the preparation method on the properties of the epoxy resin was also studied by comparing the Lep10 resin with the Lep10-control resin. The latter was prepared by a "one-pot/two-step" method. Briefly, the carboxylated lignin was first separated from the carboxylation step and dried as L-COOH powder. Then, the pre-obtained L-COOH powder was mixed directly with the DER 332, acetone and $Zn(acac)_2$ into a pressure tube and reacted under the same conditions as Lep10. The curing process of Lep10-control is also the same as Lep10. The gel contents (by Soxhlet extraction) showed that the Lep10 and Lep10-control resins were completely cured, evidenced by values of 98.72 and 97.94 wt%, respectively. The formulations and designations for all prepared epoxy resins are summarized in Table 1.

2.5. *Characterization of lignin and epoxy resins*

The hydroxyl content of the OSL sample and the carboxyl content of L-COOH sample were determined by ^{1}H NMR according to a method in literature [17]. Firstly, the hydroxyl groups of OSL sample was acetylated and converted to acetoxy groups with acetic anhydride and pyridine. Briefly, a 200 mg of OSL sample was dissolved in 8 ml of acetic anhydride/pyridine mixture (1/1, v/v) and stirred for 48 h at room temperature. The reaction solution was added dropwise to cold water and the resultant precipitate then vacuum filtered in a sand core funnel. After complete removal of acetic acid by repeatedly washing with water, the acetylated sample was vacuum dried at 40 °C and stored in a desiccator. Acetylated OSL and L-COOH (20 mg each) were prepared for ^{1}H NMR analysis by dissolving in DMSO-d_6 (0.6 ml) with 10 mg of *p*-nitrobenzaldehyde added as an internal standard. The original OSL sample was also subjected to ^{1}H NMR analysis. All ^{1}H NMR spectra were collected on an AVANCE III HD 600 MHz spectrometer (Bruker Biospin, Switzerland).

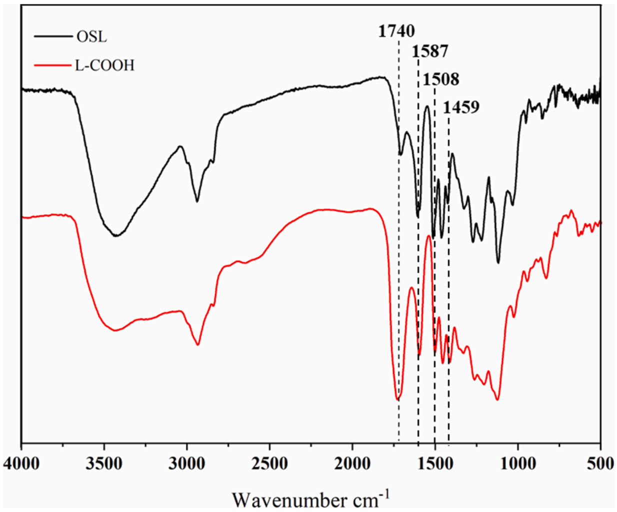

Fig. 2. FT-IR spectra of OSL and carboxylated OSL (L-COOH).

All resin and lignin samples (OSL and L-COOH) were each mixed with KBr powder and pressed into pellets for FT-IR analysis using a Nicolet 380 spectrometer (Thermo Fisher Scientific, USA). At least 32 scans were taken with a resolution of 2 cm^{-1} between the regions of 400 and 4000 cm^{-1}.

Thermal gravimetric analyses (TGA) of lignin and resin samples were performed using a TA-60H thermogravimetric analyzer (Shimadzu Corporation, Japan) under air atmosphere. The analysis was carried over a temperature range of 30–800 °C at 5 °C/min heating rates.

Tensile and flexural tests were performed using a SANS CMT4000 Series universal testing machine (MTS Systems, China) with a 5 kN load cell at a crosshead speed of 2 mm min^{-1}. Dog-bone-shaped tensile test samples (Fig. S1a) and cuboid-shaped flexural test samples (Fig. S1b) were prepared according to Chinese National Standard GB/T 2567-2008. For each test, at least 3 samples were prepared for testing and the average value was taken as the report value.

Morphological features of the fracture surfaces from tensile tests were characterized using a field-emission scanning electron microscope (SEM), model JSM-7600F (JEOL, Japan). Dynamic mechanical analyses (DMA) were performed using a Q800 dynamic mechanical analyzer (TA Instruments, USA). The test conditions used as follow: heating rate, 3 °C min^{-1}; frequency, 1 Hz; air atmosphere. The shape of test samples was cuboid with dimensions of 65 × 10 × 3.5 mm^3.

3. Results & discussion

3.1. *FT-IR spectroscopy of lignins*

To provide a qualitative assessment of OSL carboxylation with succinic anhydride, FT-IR spectra of OSL and L-COOH samples were collected (Fig. 2). The characteristic peaks of lignin, such as 1587, 1508, and 1459 cm^{-1}, assigned to aromatic skeletal vibrations, and 1028 cm^{-1}, corresponding to aromatic in plane C—H deformations, were observed in the spectrum of the OSL [26]. Evidence of esterification appears in the spectrum of the L-COOH sample with a strong signal at 1740 cm^{-1} assigned to C═O stretch (aromatic and aliphatic) in ester groups. The increase in peak intensity at 1740 cm^{-1} coincided with decreasing absorption intensities of the peaks between 3000 and 3650 cm^{-1}, together being indicative of the esterification of hydroxyl groups [26]. Elemental analysis results provided in Table S2 were similar to those reported by Li et al. [27] for an organosolv lignin and its carboxymethylated derivative. Altogether, the data demonstrated the esterification reaction between the lignin hydroxyls and succinic anhydride proceeded under the reaction conditions used.

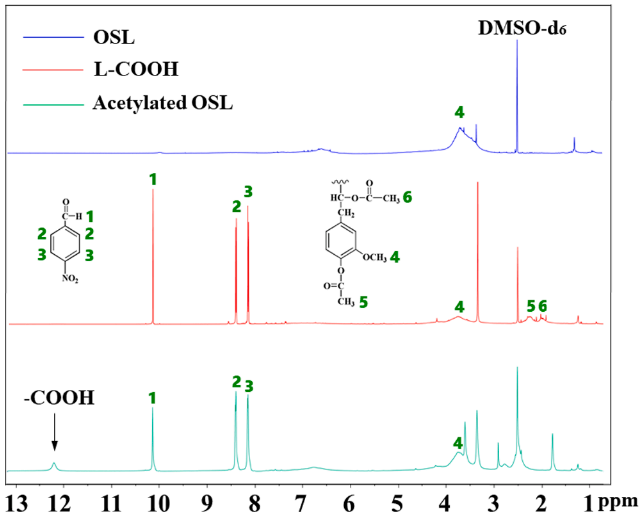

Fig. 3. ^{1}H NMR spectra of OSL, acetylated and carboxylated OSL (L-COOH).

Table 2

Mechanical properties of neat epoxy and lignin-based epoxy resins.

Resin sample	Lignin content (%)	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)
Neat epoxy	0	45.42 ± 2.33	2.1 ± 0.20	23.30 ± 3.2
Lep5	5	65.27 ± 1.45	4.4 ± 0.42	47.42 ± 4.7
Lep10	10	68.62 ± 2.67	4.6 ± 0.33	64.53 ± 6.2
Lep15	15	63.78 ± 2.29	5.1 ± 0.54	93.23 ± 3.4
Lep20	20	60.63 ± 3.02	5.7 ± 0.42	101.47 ± 4.5
Lep10-control	10	36.39 ± 4.10	1.5 ± 0.58	31.22 ± 5.2

3.2. ^{1}H NMR spectroscopy of lignins

The key reactive sites of lignin functionalization are the phenolic and aliphatic hydroxyl groups [28]. The total hydroxyl concentration in the OSL was determined by ^{1}H NMR analysis, using the proton resonance integrals of acetoxy groups (1.5–2.4 ppm) and *p*-nitrobenzaldehyde (8.10, 8.38 ppm) as the internal standard [29]. The ^{1}H NMR spectra of acetylated OSL is shown in Fig. 3; the calculation results are provided in Table S1. The total hydroxyl group content of the OSL was 4.65 mmol/g. A broad proton resonance at 12.2 ppm in the ^{1}H NMR spectrum for the L-COOH gave a calculated carboxylic acid group content of 2.28 mmol/g. This result also confirms that the OSL had been successfully carboxylated under the reaction conditions used. Similar results were obtained by Scarica et al. [24] when modifying a commercial lignin (Indulin AT) with succinic anhydride.

3.3. FT-IR spectroscopy of epoxy resins

Fig. S2 shows the FT-IR spectra of neat epoxy and lignin-based epoxy resins. Bands in common with the lignin samples can be observed at 3000–3650 cm^{-1} (O—H stretch), 2800–2900 cm^{-1} (C—H stretch), and 1514 cm^{-1} (aromatic skeletal vibrations). No epoxy group peak at 910 cm^{-1} was found, indicating the complete conversion of epoxy groups during curing [19,30,31]. The strong absorption band at 1745 cm^{-1} in the lignin-based epoxy resins is assigned to the carbonyl stretch of ester groups formed by the reaction between the succinate carboxylic acid moiety of the L-COOH and resin epoxy groups. Slightly greater peak intensities of hydroxyl groups at 3400 cm^{-1} and the carbonyl stretch at 1745 cm^{-1} may be attributed to these functionalities that are inherent to the OSL.

3.4. Mechanical properties of epoxy resins

The lignin-based and neat epoxy resins were subjected to tensile and flexural testing according to Chinese National Standard GB/T 2567–2008. The results are summarized in Table 2. Representative stress/strain curves are shown in Fig. S3 (mechanical property results are compared to literature values in Table S3). It can be seen that all lignin-based epoxy resins exhibited improved mechanical properties over the neat epoxy resin prepared using the same method. The highest tensile strength was obtained with the Lep10 resin, which was 51% greater than that for the neat epoxy resin. The tensile strengths of the Lep resins were slightly lower at lignin contents of 15% and 20%. Unlike the tensile strength, the flexural strength and elongation at break of the Lep resins both continued to increase with higher additions of lignin, up to a lignin content of 20%. It is also worth noting that lignin-based epoxy resin produced in the current study, with lignin contents up to 20%, exhibited comparable tensile strengths to similarly-prepared lignin-based epoxy resins reported in literature [18]; however, the lignin contents they use were much lower. Altogether, we found that the incorporation of carboxylated lignin can simultaneously impart reinforcing and toughening effects on the epoxy resin.

Since lignin has a rigid and highly-branched structure, it would be expected that the incorporation of lignin in an epoxy resin would affect mechanical performance [17]. The improvement in the tensile strength of the Lep resins at lower lignin contents can be attributed to the incorporation of rigid lignin segments into the epoxy network [32]. However, as a natural polymer, variability in lignin molecular structures could be rationalized to impart lower tensile strengths to lignin-based epoxy resins, especially at higher lignin contents. In a study on hyperbranched epoxy resins as a toughening agent, the hyperbranched topological structure could have causes intramolecular defects in the epoxy resin, resulting in improved toughness of the resultant epoxy resin due to the free volume fraction effect [33]; however, such intramolecular defects would have a negative effect on the tensile strength when they are present in large amounts [34].

The preparation method showed significant effect on the mechanical properties of the Lep resins listed in Table 1. The Lep10-control sample prepared with “one-pot/two-step” method exhibited markedly lower mechanical properties than its counterpart, Lep10, prepared with the one-step method. The inhomogeneous mixing of pre-obtained L-COOH sample to a viscous epoxy resin could cause microphase separation in the cured epoxy resin, causing the deterioration in mechanical performance. The SEM image of Lep10-control (Fig. 4f) confirms the inhomogeneous mixing of the “one-pot/two-step” method, where the aggregations of lignin could be clearly observed.

3.5. Morphology of resin fracture surfaces

The fracture surfaces of the neat epoxy, Lep10, and Lep10-control resins after tensile testing were observed by SEM and representative images are shown in Fig. 4. The neat epoxy resin shows relatively smooth fracture surface except for some sweeping lines (Fig. 4a and b), which is typical for brittle material without any ductility [18]. On the other hand, the fracture surface of the Lep10 resin is rougher and shows relatively bigger polymeric pullout than the neat epoxy, indicating a larger plastic deformation during fracture [18] (Fig. 4c and d). The plastic deformation means significant energy absorption during rupture and therefore indicates that the incorporation of lignin makes the epoxy resins more ductile. The neat resin (Fig. 4g and h) and Lep10 resin exhibit a relatively smooth surface (Fig. 4e) while the Lep10-control resin shows a rough surface with unevenly scattered particles (Fig. 4f). The SEM results of the Lep resins are consistent with those from mechanical analysis. In other words, the incorporation of carboxylated lignin improved the flexibility of the resultant epoxy resin. The “one-pot/two-step” method is not only less cost-effective, but could also lead to inhomogeneous distribution of lignin in epoxy matrix and resulted in

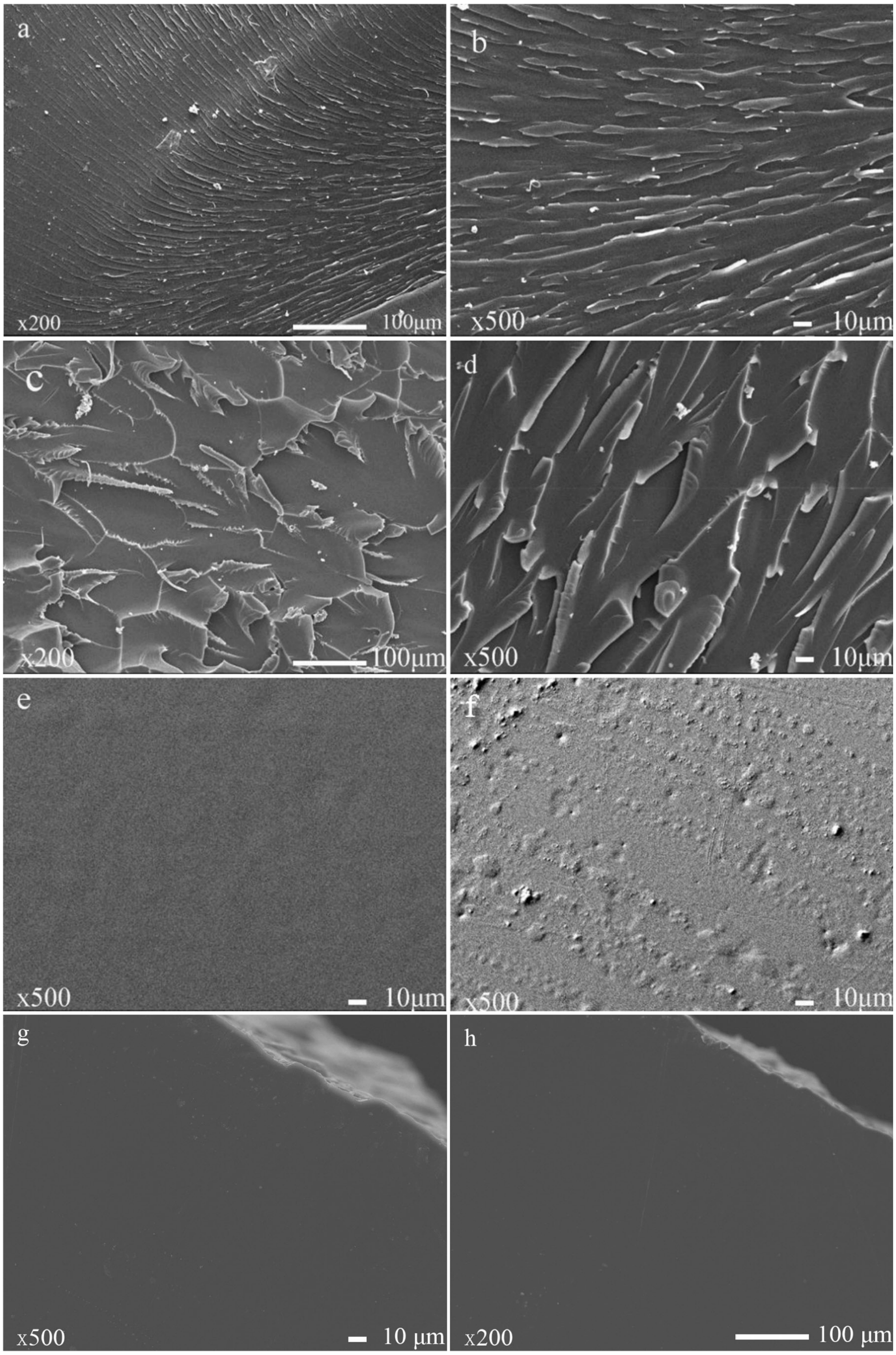

Fig. 4. Fractured surface images of neat epoxy resin (a) ×200, (b) ×500 and Lep10 resin (c) ×200, (d) ×500; surface smoothness at ×500 magnification for (e) Lep10 and (f) Lep10-control resins.

the deterioration of the mechanical properties.

3.6. Dynamic mechanical analysis of epoxy resins

Dynamic mechanical analysis (DMA) was applied to investigate the thermal dynamic properties of the neat epoxy and Lep resins. The curves of the storage modulus (E'), loss modulus (E''), and tan δ versus temperature are given in Fig. 5, and the corresponding data are summarized in Table 3. Compared with neat epoxy resin, lignin-based epoxy resins show continuous improvement in storage modulus in the glassy region (40 °C) coinciding with the increase in lignin content; the the opposite trend was observed in the rubbery region ($T_g + 30$ °C). The increased storage modulus in the glassy region may owe to the segmental motion restriction imposed by the uniform dispersion of the rigid carboxylated lignin in the epoxy matrix [30]. Similar results were reported by other researchers [18]. The cross-linking density (ρ) of a cured epoxy network is directly proportional to its storage modulus in the rubbery region according to the theory of rubber elasticity, which can be calculated by Eq. (1) [30,35]:

$$\rho = E'/3RT \tag{1}$$

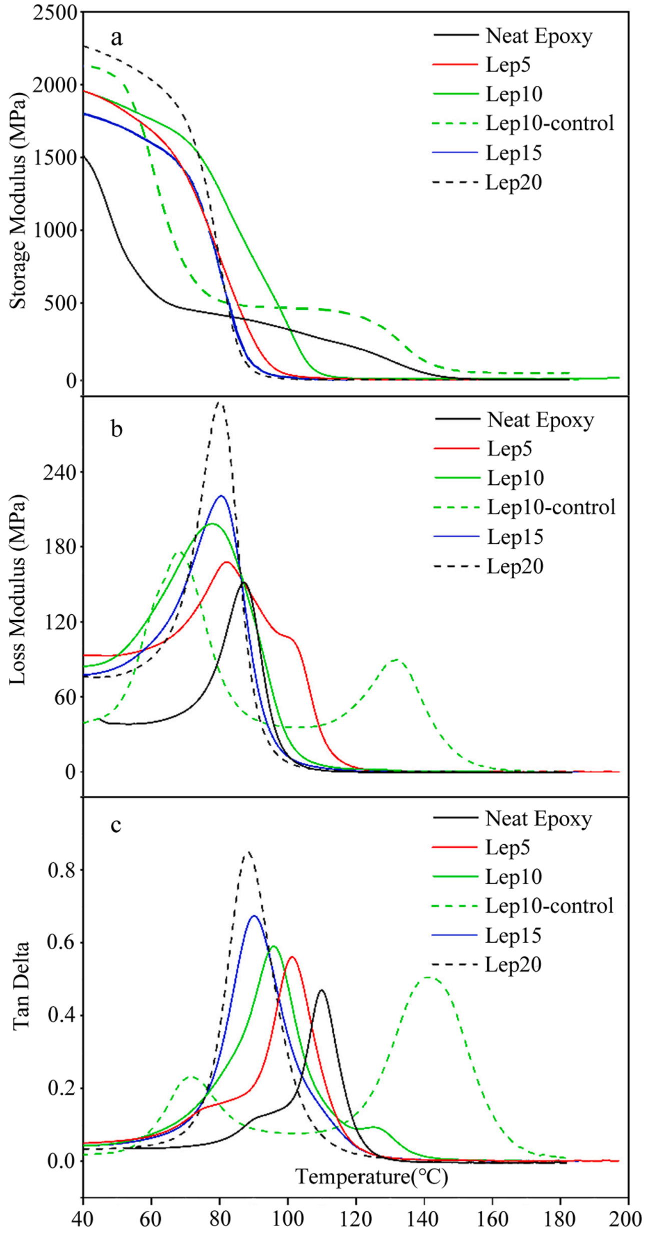

Fig. 5. DMA plots for (a) storage modulus, (b) loss modulus, (c) tan δ for the neat epoxy resin and lignin-based epoxy (Lep5 thru Lep20) resins by the one-pot method; control epoxy resin (Lep10-control) prepared by direct addition of carboxylated lignin (L-COOH).

where R is the gas constant, E' and T is the storage modulus and absolute temperature at $T_g + 30$ °C, respectively. The calculated results of the cross-linking density (ρ) shows, comparing to the neat epoxy resin, that the cross-linking densities of the Lep resins steadily decrease with the increase in lignin content (Table 3). It is expected that natural lignin, even that which is modified, is less reactive than commercial epoxy resin during the curing process. This would result in less complete cross-linking, and therefore, lower the cross-linking density. In addition, the curing reaction of bulk lignin can also be restricted by steric hindrance [17]. The decreasing storage modulus in the rubbery plateau with increasing lignin content can also be attributed to decreasing cross-linking densities in the cured Lep resins [36]. A significantly lower cross-linking density for the Lep10-control substantiates its inferior mechanical properties compared to its counterpart, Lep10, and is attributed to the unevenly dispersed lignin significantly hindering the cross-linking reaction.

The loss modulus (E'') represents the energy dissipation caused by the internal friction associated with the motion of polymer chains. As shown in Table 3, the maximum loss modulus increases continuously from 141 to 295 MPa as the lignin content increased from 0 to 20 wt%, indicating that the introducing of lignin into the epoxy resin increases the mobility of its polymer chains during the glass transition process. This result can also be explained by the decreased cross-linking densities with increased lignin contents in Lep resins [37]. The glass-transition temperature (T_g) is defined as the peak of the tan δ versus temperature curve, where Tan δ is the ratio of the loss modulus to the storage modulus [15,38]. As shown in Fig. 5c, all of the epoxy resin samples except the Lep10-control have a smooth α-relaxation peak corresponding to the glass transition [39,40]. In the tan δ diagram of the Lep10-control resin, two peaks were observed, indicating the phase-separated nature of the Lep10-control sample. It is believed that two constituent domains in T_g demonstrate a common phenomenon in the immiscible polymer blend systems [40]. As suggested by the SEM analysis, aggregated L-COOH particles were embedded and scattered in the epoxy matrix (Fig. 4f). Therefore, the first T_g at 71.04 °C should be assigned to the less cross-linked epoxy matrix while the second T_g around 140 °C is likely attributed to the lignin moiety, which has a glass-transition temperature ranging from 130 °C to 190 °C depending on its origin or separation methods [41]. The T_g values of lignin-based epoxy resins were all lower than that of neat epoxy resin (111 °C) and gradually decreased as the lignin content increased in the Lep resins. This result is believed to correlate to the low cross-linking densities of lignin-based epoxy resins [17]. It is also noted that broad shoulders appeared on the tan δ peaks of most Lep samples. This phenomenon indicates heterogeneous and broadly-distributed cross-linked structures, namely, different cross-linking densities in the cured matrix [13]. Based on the above results, it could be inferred that the carboxylated lignin was covalently incorporated in the epoxy matrix and introduced heterogeneity to the homogenous matrix at the same time. Nevertheless, the combination of the rigid structure and the lower cross-linking density induced from the heterogeneous structure of lignin somehow exhibited a simultaneous reinforcing and toughening effect on the resultant epoxy resins [34].

Table 3
DMA results for neat epoxy resin and lignin-based epoxy (Lep5 thru Lep20) resins having 5, 10, 15, and 20 wt% lignin contents.

Resin sample	Storage modulus (MPa)		Maximum loss modulus (MPa)	ρ[a] (mmol/cm^3)	T_g (°C)
	Glassy region a (at 40 °C)	Rubbery region b (at T_g + 30 °C)			
Neat resin	1500	60.0	141	6.26	111.20
Lep5	1949	28.0	176	2.95	107.46
Lep10	1952	24.6	198	2.67	95.91
Lep15	2125	19.9	219	2.20	90.11
Lep20	2275	18.0	295	2.00	88.36
Lep10-control	1760	10.2	179	1.09	71.04

[a] $\rho = E'/3RT$, $R = 8.314$.

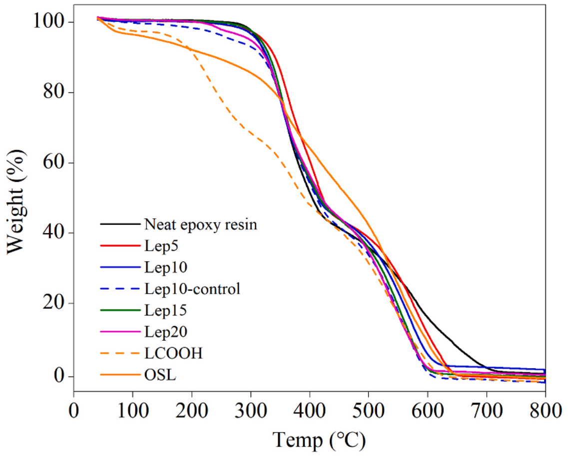

Fig. 6. TGA curves of OSL, L-COOH, neat epoxy resin, lignin-based epoxy (Lep5 thru Lep20) resins by the one-pot method, and control epoxy resin (Lep10-control) prepared by direct addition of carboxylated lignin (L-COOH).

Table 4
TGA results for OSL, L-COOH, neat epoxy resin, lignin-based epoxy (Lep5 thru Lep20) resins by the one-pot method; control epoxy resin (Lep10-control) prepared by direct addition of carboxylated lignin (L-COOH).

Lignin and resin samples	T_d5% (°C)
OSL	145
L-COOH	177
Neat epoxy	312
Lep5	320
Lep10	310
Lep15	316
Lep20	298
Lep10-control	270

3.7. TGA analysis of epoxy resins

The thermal stabilities of the lignin and lignin-based epoxy resins were measured under air atmosphere (Fig. 6). Only the two lignin samples (OSL and L-COOH) exhibited a significant weight loss below 120 °C, which can be attributed to water volatilization and thereby confirming their highly hydrophilic character [26]. The TGA traces of the neat epoxy and lignin-based epoxy resins show two degradation stages around 350 °C and 550 °C (Fig. 6), which represented the degradation of aliphatic and aromatic components in epoxy matrices, respectively [42]. The 5% decomposition temperatures (T_d5%) of the lignin and lignin-based epoxy resins are shown in Table 4. It can be seen that the T_d5% of neat epoxy and Lep resins (except for Lep10-control) with lignin contents less than 20% are close, ranging from 310 to 320 °C, and indicating that in general terms, our incorporation of carboxylated lignin had no significant effect on the thermal stability of the epoxy resin. When the lignin content reaches 20%, the T_d5% of lignin-based epoxy resin decreased to 298 °C. Also, the Lep10-control resin showed significantly lower thermal stability than the other Lep resins. Altoghether, the low thermal stabilities of the Lep20 and Lep10-control resins can be attributed to their low degree of crosslinking density, especially for the Lep10-control sample.

4. Conclusions

In this study, an organosolv lignin from poplar wood was modified with succinic anhydride in a one-pot method to prepare lignin-based epoxy (Lep) resin with lignin contents up to 20%. Tensile strength, elongation at break and flexural strength properties of the Lep resins were all improved over that for the neat epoxy resin. The highest increase in tensile strength (51%) was obtained for the Lep10 resin, with 10 wt% lignin content. Elongation at break increased from 2.2 to 5.7%, and flexural strength increased from 23.3 MPa to 101 MPa, with the increase of lignin content from 0 to 20 wt%. Microscopic observations of the fracture surfaces further confirm the toughening effect of the functionalized lignin. Combining the results of FT-IR, SEM, DMA, and TGA it appears that a carboxylated lignin can be covalently incorporated in an epoxy resin. The rigid and highly-branched structure of lignin imparted both reinforcing and toughening effects on the resultant lignin-based epoxy resins.

CRediT authorship contribution statement

Yongjian Zhang: Conceptualization, Methodology, Writing - original draft. **Hao Wang:** Methodology, Writing - original draft, Investigation, Data curation. **Thomas L. Eberhardt:** Supervision, Validation, Writing - review & editing. **Qiang Gu:** Visualization. **Hui Pan:** Project administration, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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References

[1] P. Figueiredo, K. Lintinen, J.T. Hirvonen, M.A. Kostiainen, H.A. Santos, Properties and chemical modifications of lignin: Towards lignin-based nanomaterials for biomedical applications, Prog. Mater. Sci. 93 (2018) 233–269, https://doi.org/10.1016/j.pmatsci.2017.12.001.

[2] S. Laurichesse, L. Avérous, Chemical modification of lignins: Towards biobased polymers, Prog. Polym. Sci. 39 (7) (2014) 1266–1290, https://doi.org/10.1016/j.progpolymsci.2013.11.004.

[3] T. Koike, Progress in development of epoxy resin systems based on wood biomass in Japan, Polym. Eng. Sci. 52 (2012) 701–717, https://doi.org/10.1002/pen.

[4] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B. H. Davison, R.A. Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T. J. Tschaplinski, G.A. Tuskan, C.E. Wyman, Lignin valorization: Improving lignin processing in the biorefinery, Science 344 (6185) (2014) 1246843, https://doi.org/10.1126/science:1246843.

[5] R. Rinaldi, R. Jastrzebski, M.T. Clough, J. Ralph, M. Kennema, P.C.A. Bruijnincx, B. M. Weckhuysen, Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis, Angew. Chemie Int. Ed. 55 (29) (2016) 8164–8215, https://doi.org/10.1002/anie.201510351.

[6] C. Sasaki, M. Wanaka, H. Takagi, S. Tamura, C. Asada, Y. Nakamura, Evaluation of epoxy resins synthesized from steam-exploded bamboo lignin, Ind. Crop. Prod. 43 (2013) 757–761, https://doi.org/10.1016/j.indcrop.2012.08.018.

[7] W. Zhao, B. Simmons, S. Singh, A. Ragauskas, G. Cheng, From lignin association to nano-/micro-particle preparation: Extracting higher value of lignin, Green Chem. 18 (21) (2016) 5693–5700, https://doi.org/10.1039/C6GC01813K.

[8] W.O.S. Doherty, P. Mousavioun, C.M. Fellows, Value-adding to cellulosic ethanol: Lignin polymers, Ind. Crop. Prod. 33 (2) (2011) 259–276, https://doi.org/10.1016/j.indcrop.2010.10.022.

[9] A. Duval, M. Lawoko, A review on lignin-based polymeric, micro- and nano-structured materials, React. Funct. Polym. 85 (2014) 78–96, https://doi.org/10.1016/j.reactfunctpolym.2014.09.017.

[10] Z. Ma, J. Wang, H. Zhou, Y. Zhang, Y. Yang, X. Liu, J. Ye, D. Chen, S. Wang, Relationship of thermal degradation behavior and chemical structure of lignin isolated from palm kernel shell under different process severities, Fuel Process. Technol. 181 (2018) 142–156, https://doi.org/10.1016/j.fuproc.2018.09.020.

[11] R. Auvergne, S. Caillol, G. David, B. Boutevin, J.-P. Pascault, Biobased thermosetting epoxy: Present and future, Chem. Rev. 114 (2) (2014) 1082–1115, https://doi.org/10.1021/cr3001274.

[12] M. Cui, N.A. Nguyen, P.V. Bonnesen, D. Uhrig, J.K. Keum, A.K. Naskar, Rigid oligomer from lignin in designing of tough, self-healing elastomers, ACS Macro Lett. 7 (11) (2018) 1328–1332, https://doi.org/10.1021/acsmacrolett.8b00600.

[13] J. Sun, H. Li, C. Wang, D.u. Yuan, L.P. Stubbs, C. He, The effect of residual solvent N,N′-dimethylformamide on the curing reaction and mechanical properties of epoxy and lignin epoxy composites, Macromol. Chem. Phys. 217 (9) (2016) 1065–1073, https://doi.org/10.1002/macp.v217.910.1002/macp.201500453.

[14] L.C. Over, E. Grau, S. Grelier, M.A.R. Meier, H. Cramail, Synthesis and characterization of epoxy thermosetting polymers from glycidylated organosolv lignin and bisphenol A, Macromol. Chem. Phys. 218 (2017) 1–11, https://doi.org/10.1002/macp.201600411.

[15] J. Qin, M. Woloctt, J. Zhang, Use of polycarboxylic acid derived from partially depolymerized lignin as a curing agent for epoxy application, ACS Sustain. Chem. Eng. 2 (2) (2014) 188–193, https://doi.org/10.1021/sc400227v.

[16] J.R. Gouveia, G.E.S. Garcia, L.D. Antonino, L.B. Tavares, D.J. Dos Santos, Epoxidation of kraft lignin as a tool for improving the mechanical properties of epoxy adhesive, Molecules 25 (2020) 1–18, https://doi.org/10.3390/molecules25112513.

[17] W. Liu, R. Zhou, H.L.S. Goh, S. Huang, X. Lu, From waste to functional additive: Toughening epoxy resin with lignin, ACS Appl. Mater. Interfaces. 6 (8) (2014) 5810–5817, https://doi.org/10.1021/am500642n.

[18] J. Sun, C. Wang, L.P. Stubbs, C. He, Carboxylated lignin as an effective cohardener for enhancing strength and toughness of epoxy, Macromol. Mater. Eng. 302 (12) (2017) 1700341, https://doi.org/10.1002/mame.v302.1210.1002/mame.201700341.

[19] S. Zhao, M.M. Abu-Omar, Biobased epoxy nanocomposites derived from lignin-based monomers, Biomacromolecules 16 (7) (2015) 2025–2031, https://doi.org/10.1021/acs.biomac.5b00670.

[20] C. Ding, A.S. Matharu, Recent developments on biobased curing agents: A review of their preparation and use, ACS Sustain. Chem. Eng. 2 (10) (2014) 2217–2236, https://doi.org/10.1021/sc500478f.

[21] Y. Zhang, J. Feng, Z. Xiao, Y. Liu, H. Ma, Z. Wang, H. Pan, Highly efficient and selective fractionation strategy for lignocellulosic biomass with recyclable dioxane/ethylene glycol binary solvent, Ind. Crop. Prod. 144 (2020) 112038, https://doi.org/10.1016/j.indcrop.2019.112038.

[22] J.-M. Pin, N. Sbirrazzuoli, A. Mija, From epoxidized linseed oil to bioresin: An overall approach of epoxy/anhydride cross-linking, ChemSusChem 8 (7) (2015) 1232–1243, https://doi.org/10.1002/cssc.v8.710.1002/cssc.201403262.

[23] Y. Zhang, Z. Wang, J. Feng, H. Pan, Maximizing utilization of poplar wood by microwave-assisted pretreatment with methanol/dioxane binary solvent, Bioresour. Technol. 300 (2020) 122657, https://doi.org/10.1016/j.biortech.2019.122657.

[24] C. Scarica, R. Suriano, M. Levi, S. Turri, G. Griffini, Lignin functionalized with succinic anhydride as building block for biobased thermosetting polyester coatings, ACS Sustain. Chem. Eng. 6 (3) (2018) 3392–3401, https://doi.org/10.1021/acssuschemeng.7b03583.

[25] T. Liu, C. Hao, S. Zhang, X. Yang, L. Wang, J. Han, Y. Li, J. Xin, J. Zhang, A self-healable high glass transition temperature bioepoxy material based on vitrimer chemistry, Macromolecules 51 (15) (2018) 5577–5585, https://doi.org/10.1021/acs.macromol.8b01010.

[26] F. Monteil-Rivera, L. Paquet, Solvent-free catalyst-free microwave-assisted acylation of lignin, Ind. Crop. Prod. 65 (2015) 446–453, https://doi.org/10.1016/j.indcrop.2014.10.060.

[27] S. Li, D. Ogunkoya, T. Fang, J. Willoughby, O.J. Rojas, Carboxymethylated lignins with low surface tension toward low viscosity and highly stable emulsions of crude bitumen and refined oils, J. Colloid Interface Sci. 482 (2016) 27–38, https://doi.org/10.1016/j.jcis.2016.07.063.

[28] S. Sen, H. Sadeghifar, D.S. Argyropoulos, Kraft lignin chain extension chemistry via propargylation, oxidative coupling, and claisen rearrangement, Biomacromolecules 14 (10) (2013) 3399–3408, https://doi.org/10.1021/bm4010172.

[29] J. Li, J. Zhang, S. Zhang, Q. Gao, J. Li, W. Zhang, Fast curing bio-based phenolic resins via lignin demethylated under mild reaction condition, Polymers (Basel) 9 (12) (2017) 428, https://doi.org/10.3390/polym9090428.

[30] C. Hao, T. Liu, S. Zhang, L. Brown, R. Li, J. Xin, T. Zhong, L. Jiang, J. Zhang, A high-lignin-content removable, and glycol-assisted repairable coating based on dynamic covalent bonds, ChemSusChem 12 (2019) 1049–1058, https://doi.org/10.1002/cssc.201802615.

[31] J. Xin, M. Li, R. Li, M.P. Wolcott, J. Zhang, Green epoxy resin system based on lignin and Tung oil and its application in epoxy asphalt, ACS Sustain. Chem. Eng. 4 (5) (2016) 2754–2761, https://doi.org/10.1021/acssuschemeng.6b00256.

[32] J. Sun, C. Wang, J.C.C. Yeo, D.u. Yuan, H. Li, L.P. Stubbs, C. He, Lignin epoxy composites: preparation, morphology, and mechanical properties, Macromol. Mater. Eng. 301 (3) (2016) 328–336, https://doi.org/10.1002/mame.201500310.

[33] X. Ma, Y. Liang, Z. Xu, S. Chen, J. Cheng, M. Miao, D. Zhang, The versatility of hyperbranched epoxy resins containing hexahydro-s-triazine on diglycidyl ether of bisphenol-A composites, Compos. Part B Eng. 196 (2020) 1–9, https://doi.org/10.1016/j.compositesb.2020.108109.

[34] X. Chen, S. Chen, Z. Xu, J. Zhang, M. Miao, D. Zhang, Degradable and recyclable bio-based thermoset epoxy resins, Green Chem. 22 (13) (2020) 4187–4198, https://doi.org/10.1039/D0GC01250E.

[35] M. Kaji, K. Nakahara, T. Endo, Synthesis of a bifunctional epoxy monomer containing biphenyl moiety and properties of its cured polymer with phenol novolac, J. Appl. Polym. Sci. 74 (1999) 690–698, https://doi.org/10.1002/(SICI)1097-4628(20000124)75:4<528::AID-APP8>3.0.CO;2-A.

[36] E. Feghali, D.J. van de Pas, K.M. Torr, Toward bio-based epoxy thermoset polymers from depolymerized native lignins produced at the pilot scale, Biomacromolecules 21 (4) (2020) 1548–1559, https://doi.org/10.1021/acs.biomac.0c00108.

[37] S. Zhao, X. Huang, A.J. Whelton, M.M. Abu-Omar, Renewable epoxy thermosets from fully lignin-derived triphenols, ACS Sustain. Chem. Eng. 6 (6) (2018) 7600–7608, https://doi.org/10.1021/acssuschemeng.8b00443.

[38] H. Jiang, L. Sun, Y. Zhang, Q. Liu, C. Ru, W. Zhang, C. Zhao, Novel biobased epoxy resin thermosets derived from eugenol and vanillin, Polym. Degrad. Stab. 160 (2019) 45–52, https://doi.org/10.1016/j.polymdegradstab.2018.12.007.

[39] Y. Jiang, D. Ding, S. Zhao, H. Zhu, H.I. Kenttämaa, M.M. Abu-Omar, Renewable thermoset polymers based on lignin and carbohydrate derived monomers, Green Chem. 20 (5) (2018) 1131–1138, https://doi.org/10.1039/C7GC03552G.

[40] X. Guo, J. Xin, J. Huang, M.P. Wolcott, J. Zhang, Preparation and toughening of mechanochemically modified lignin-based epoxy, Polymer (Guildf) 183 (2019) 121859, https://doi.org/10.1016/j.polymer.2019.121859.

[41] R.J. Sammons, N. Labbe, D.P. Harper, T. Elder, T.G. Rials, Characterization of lignins using thermal and FT-IR spectroscopic analysis, Bioresources 238 (2013) 2752–2767.

[42] D.H. Wang, S. Sihn, A.K. Roy, J.-B. Baek, L.-S. Tan, Nanocomposites based on vapor-grown carbon nanofibers and an epoxy: Functionalization, preparation and characterization, Eur. Polym. J. 46 (7) (2010) 1404–1416, https://doi.org/10.1016/j.eurpolymj.2010.04.025.