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Formaldehyde-Free Method for Incorporating Lignin into Epoxy Thermosets

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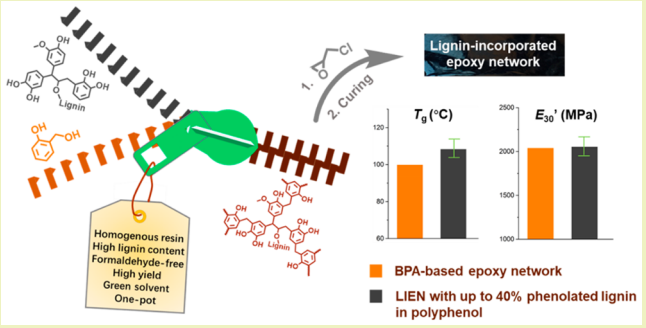
Supporting Information

ABSTRACT: A series of liquid and curable lignin-containing epoxy prepolymers were prepared for making renewable epoxy thermosets. First, lignin was modified to phenolated lignin (PL) in a solvent-free reaction. PL was subsequently co-oligomerized with salicyl alcohol (SA) in water without the use of formaldehyde to obtain fully bio-based polyphenols (PL-SA). Glycidylation of lignin-based polyphenols yielded exclusively liquid epoxy prepolymers without production of solid co-products. The liquid epoxy prepolymers (with lignin content up to 21 wt %) were curable with amine hardener (diethylenetriamine) to generate homogeneous thermosets, which required no epoxy co-prepolymer. The structural evolution from starting monomers to epoxy thermosets was followed by nuclear magnetic resonance and Fourier transform infrared spectroscopy. Compared to common syntheses in which lignin is glycidylated prior to being blended with epoxy co-prepolymers, the herein reported methodology conferred networks with increased α-relaxation temperature (106−114 vs 96 °C), storage modulus (1843−2151 vs 1828 MPa), cross-link density (8.2−16.0 vs 5.4 mmol/cm^3) and tensile properties (stress of 66.9−68.1 vs 28.7 MPa, and strain of 3.3−3.7 vs 1.4%). Moreover, bio-based thermosets exhibited comparable or superior thermomechanical properties to conventional bisphenol A (BPA)-based counterpart. By producing liquid-phase lignin-containing epoxy prepolymers, this study provides a formaldehyde-free method for incorporating lignin into epoxy thermosets without the need for additional co-prepolymers.



KEYWORDS: *Lignin, Thermoset, Liquid epoxy prepolymer, Homogenous, Phenolation, Formaldehyde-free*

INTRODUCTION

Recent years have witnessed rapid development of materials made from renewable sources.[1−5] Lignin has been widely viewed as a promising renewable starting material because it is abundant, low-cost and the sole large-volume aromatic feedstock.[6] It is especially reasonable to use lignin-derived chemicals to synthesize thermosetting materials, as the aromatic structure provides good thermal and mechanical performance.[7,8] Because of the relatively straightforward structure, lignin-derived phenol monomer (LDPM) and partially depolymerized lignin (PDL) are often utilized to make thermosets like epoxy.[8−23] However, LDPM and PDL need to be depolymerized from lignin through chemical transformations including oxidation, catalytic reduction and cracking processes etc., which are associated with intensive energy consumption as well as several separation and purification steps.[24] By comparison, bulk lignin is abundant and cheap. It is reported that the total availability of technical grade lignin in the biosphere exceeds 300 billion tons,[25] while its price is 10 times cheaper than phenol.[26] Thus, it would be advantageous to replace petroleum-based phenolics (e.g., BPA) with lignin as prepolymers for thermosets. However, only 2% of lignin is being used for value-added products,[27] which is limited by its low reactivity and incompatibility with polymeric compounds.

Epoxy thermoset is one of the most versatile thermosetting materials that has been utilized in coatings, composites, adhesives and electrical/electronic laminates, etc. By far, methods of incorporating bulk lignin into epoxy thermosets can be summarized into three categories:[28] (1) using lignin derivatives as fillers to directly blend into general epoxy thermosets; (2) modifying lignin by direct epoxidation; and

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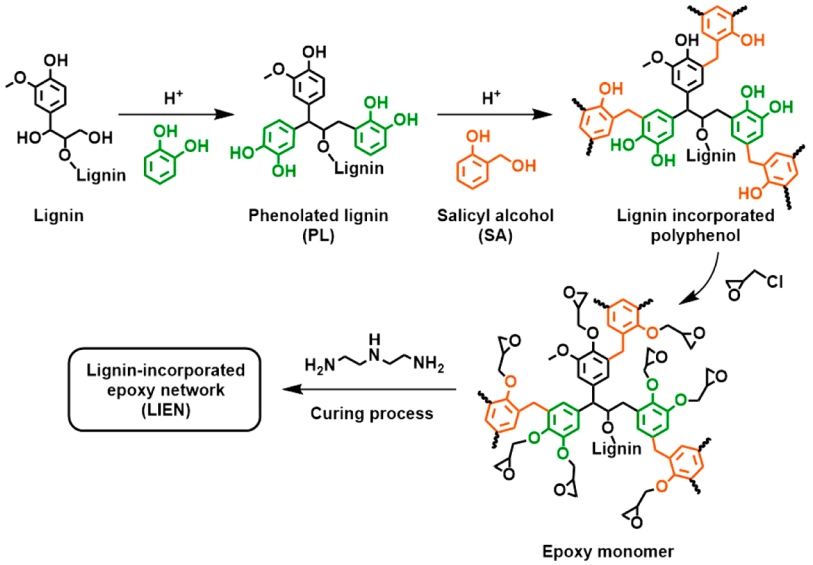

Figure 1. Synthesis route of lignin-incorporated epoxy network (LIEN). Lignin is modified through phenolation and formaldehyde-free oligomerization to yield lignin-incorporated polyphenol. Benzodioxane derivatives produced by glycidylation of catechols are not shown for clarity.

(3) modifying lignin derivatives to improve its reactivity, followed by epoxidation. It is noteworthy that epoxy prepolymers (or glycidyl ethers) should be liquid at ambient or elevated temperature for sufficient contacting and reacting with curing agents to form a homogeneous cross-linked network. For example, epoxy resins used for encapsulation and potting must melt and flow rather freely to ensure complete filling of the voids prior to cross-linking. Solvents are not preferably used in most instances due to the difficulty of solvent removal before curing.[29] However, most of reported epoxidized lignin are infusible solids, which cannot be directly cured by hardeners, and at least one epoxy co-prepolymer needs to be introduced.[30−34] Glycidylation of pre-modified lignin could produce simultaneously solid and liquid phase epoxy prepolymers.[35] However, the liquid phase is often in a small portion and needs to be separated from the mixture sophistically. For example, Hofmann et al. prepared epoxy prepolymers using hydroxyalkyl lignin derivatives.[36] Hydroxyalkylation of lignin was conducted by reacting lignin with propylene oxide to improve the solubility and then with ethylene oxide to transform secondary hydroxyls into primary hydroxyls. Glycidylation of hydroxyalkylated lignin with epichlorohydrin yielded an epoxy prepolymer mixture, while the curable liquid prepolymer had to be collected after several sophisticated solvent fractionation treatments. By reacting methylolated lignin with epichlorohydrin, Mansouri et al. synthesized solid and liquid phase of epoxidized lignin simultaneously.[37] Even though the liquid phase could be separated by filtration, its epoxy content only accounted for <20% in the mixture. Huo et al. modified lignin with cardanol-based oligomer and then glycidylated with epichlorohydrin to obtain a viscous liquid.[38] However, only curing kinetics of epoxy−anhydride reactions were reported, while neither the structure of epoxy prepolymer nor the property of obtained thermosets was characterized. By successive demethylation, phenolation, phenol−formaldehyde reaction and glycidylation of organosolv lignin, we reported the synthesis of a liquid lignin-containing epoxy prepolymer.[39] However, lignin content in starting polyphenol could not exceed 12 wt % due to compatibility issue, while the synthesis process involved unfavorable reagents including hydrobromic acid and formaldehyde.

Phenolation has been reported as an effective lignin modification method.[34,40−42] Acid-catalyzed incorporation of the ortho or para−phenyl substituent to the α-hydroxyl of lignin increased the reactive phenolic hydroxyl at ortho/para sites, while the molecular weight of lignin was simultaneously decreased by acid-catalyzed cleavage of the lignin backbone.[40] Direct glycidylation of phenolated lignin (PL) barely produces liquid epoxy prepolymer with decent yield;[43] however, the increased content of phenolic ortho/para sites in PL enhances its reactivity for phenol−formaldehyde condensation to produce a novolac oligomer, which is a common precursor for liquid epoxy prepolymers.[29] As inspired by these phenomena, we reported herein a route to synthesize liquid lignin-containing epoxy prepolymers (Figure 1). First, lignin was phenolated by catechol, a renewable building block that is available from lignin through demethylation of lignin-derived guaiacol or by lignin pyrolysis.[44−47] Compared to phenol, catechol is more reactive for phenolation and has increased number of hydroxyl group and phenolic para/ortho site for condensation.[14] Second, phenolated lignin was condensed with salicyl alcohol (SA, a renewable compound that can be derived from willow bark)[48] to yield lignin-incorporated novolac oligomers (PL-SA), with PL content could reach up to 40 wt %. As SA bears both hydroxymethyl group and reactive phenolic para/ortho sites, it could simultaneously react with the para/ortho sites of phenolics in PL and undergo self-condensation without the need for coupling agents like formaldehyde. Although willow bark-derived SA is more expensive than phenol and formaldehyde, the use of SA is more attractive in terms of environmental safety and sustainability when effective and economic SA extraction and separation methods are available. PL-SA was then glycidylated with epichlorohydrin to generate exclusively liquid epoxy prepolymers with no solid prepolymer obtained. These epoxy prepolymers were curable by diethylenetriamine (DETA) to yield homogeneous lignin-incorporated epoxy networks (LIEN). In their liquid phase, lignin-containing epoxy

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prepolymers would find much wider applications compared to their solid phase counterparts.

EXPERIMENTAL SECTION

General. Organosolv lignin was provided by Archer Daniels Midland Co. Lignin was used after washing five times with 2 M HCl solution to remove water-soluble impurities and ash. The resulting solid was washed with water and dried under vacuum overnight. The hydroxyl content of the lignin was measured to be 4.32 mmol/g as previously reported.[39] In brief, acetylation was performed by dissolving 200 mg of lignin in 4 mL of pyridine to form a homogeneous solution. 4 mL of acetic anhydride was added, and the solution was stirred at room temperature for 48 h. The resulting mixture was added dropwise to cold water, followed by centrifuging at 10,000 rpm for 15 min to isolate acetylated lignin. The isolated solid was washed with water and dried overnight under vacuum. ^{1}H NMR spectra of lignin samples (25 mg) were recorded in 0.7 mL of DMSO-d_6 containing 10 μL of pentafluorobenzaldehyde as an internal standard.

Catechol, salicyl alcohol (2-hydroxybenzyl alcohol), epichlorohydrin, tetrabutylammonium bromide, diethylenetriamine (DETA), diglycidyl ether of bisphenol A (DGEBA) and pentafluorobenzaldehyde were purchased from Aldrich Chemical Co. Sulfuric acid (98%) was obtained from Fisher Scientific. All chemicals were used as received without further purification. Glycidyl ethers of lignin (GEL) was prepared according to a previous method.[39]

Preparation of Phenolated Lignin. Catechol (7.0 g) was heated at 115 °C in a 100 mL round-bottomed flask until melting. Then, 3.50 g of organosolv lignin and 0.70 g of sulfuric acid were subsequently added and a homogeneous mixture was obtained. Weight ratio of reagents (catechol/lignin = 2, with 6.7 wt % of catalyst) was consistent with previous study, which could produce phenolated lignin with optimal degree of phenolation.[40] The mixture was stirred at 110 °C for 2 h, cooled to room temperature, and 100 mL H_2O was added. Phenolated lignin precipitated immediately. The precipitate was collected via filtration and washed with H_2O several times with the help of sonication until no catechol residue was detected as indicated by high-performance liquid chromatography (HPLC). The unreacted catechol can be recycled and reused by facile solvent extraction and drying process. Drying the solid under vacuum afforded PL as a black powder (4.28 g, 83% yield based on a lignin in which hydroxyl groups were completely substituted by catechol). Yield of PL was in accordance with a previous study.[40] Lignin content in PL was calculated based on lignin's hydroxyl content (4.32 mmol/g, sum of aliphatic and aromatic hydroxyls). Assuming all hydroxyl groups were substituted by catechol, lignin content in PL was ca. 68 wt %. However, considering the aromatic hydroxyls are not reactive with catechol and the aliphatic hydroxyls may not be completely substituted, lignin content in PL should be higher than 68 wt %.

One-Pot Preparation of Glycidyl Ethers. *Preparation of Oligomers from PL and Salicyl Alcohol.* Oligomers with various PL weight ratios (10, 20, 30 and 40 wt %) were synthesized using a formaldehyde-free method, and water was employed as solvent. $PL_{10}SA_{90}$, a phenolic oligomer containing 10 wt % of PL and 90 wt % of salicyl alcohol, was prepared as follows: salicyl alcohol (2.0 g, 16.1 mmol) was dissolved in 20 mL of H_2O at 100 °C in a 100 mL round-bottomed flask. To this mixture was added 0.22 g of phenolated lignin, and the powder was dispersed through stirring using a magnetic stirring bar. A mixture of sulfuric acid (1.6 mL) and H_2O (10 mL) was dropwise added to the flask. The mixture was stirred at 110 °C for 30 min. During the period, it was observed that dark viscous oil was gradually formed and accumulated on the magnetic bar. When the reaction was complete, the mixture was cooled to room temperature and the dark oil became solid. The acidic solution was discarded, and the afforded solid was washed with H_2O several times to remove H_2SO_4 residue.

Preparation of Glycidyl Ethers. In the same flask, 30 g of epichlorohydrin was introduced to react with $PL_{10}SA_{90}$ to make the glycidyl ether ($GE\text{-}PL_{10}SA_{90}$). Excess epichlorohydrin was used as solvent to reduce the viscosity and hydrolyzable chlorine content in epoxy prepolymers.[49] A small amount of leftover water in the flask did not influence the glycidylation reaction. 0.21 g of tetrabutylammonium bromide was used as a phase transfer catalyst. The mixture was heated at 85 °C for 3 h, and cooled to room temperature prior to the dropwise addition of 5 g of 20% w/w KOH solution. The reaction was then heated to 85 °C and kept for 2 h. When the reaction was complete, the mixture was introduced with 30 mL of acetone to precipitate the formed KCl, filtered to remove KCl, washed with water, dried with Na_2SO_4 and concentrated with a rotary evaporator to yield $GE\text{-}PL_{10}SA_{90}$ as a dark oil (3.06 g, Figure S1).

To measure the yield of polyphenol, in a separate reaction, the oligomer product $PL_{10}SA_{90}$ was scratched from the stirring bar and dried overnight in an oven at 60 °C to give the polyphenol product of 2.11 g, 95% yield based on mass. Other oligomers with various PL contents (0, 20, 30 and 40 wt %) and their glycidyl ethers (denoted as $GE\text{-}PL_0SA_{100}$, $GE\text{-}PL_{20}SA_{80}$, $GE\text{-}PL_{30}SA_{70}$ and $GE\text{-}PL_{40}SA_{60}$, respectively) were synthesized using the same method as for $GE\text{-}PL_{10}SA_{90}$, with comparable yields. Epoxy equivalent weight (EEW) was determined to be 178−207 g/equiv , using the HCl/acetone titration method.[50]

Formation of Epoxy Networks. Glycidyl ethers with different weight ratios of PL ($GE\text{-}PL_0SA_{100}$ to $GE\text{-}PL_{40}SA_{60}$) were respectively mixed with diethylenetriamine with 1:1 molar ratio of epoxy vs −NH for curing. The mixtures were stirred for 10 min, degassed under vacuum to remove entrapped air and poured into silicone molds for curing with the profile: 65 °C for 12 h, 90 °C for 2 h and 120 °C for 2 h. Cured lignin-incorporated epoxy networks were expressed as $EN\text{-}PL_0SA_{100}$, $EN\text{-}PL_{10}SA_{90}$, $EN\text{-}PL_{20}SA_{80}$, $EN\text{-}PL_{30}SA_{70}$ and $EN\text{-}PL_{40}SA_{60}$, respectively. Meanwhile, by blending GEL into $GE\text{-}PL_0SA_{100}$ co-prepolymer to form 20 wt % GEL in the mixture (LBEN approach, Figure 2), an epoxy network $EN\text{-}BL\text{-}GEL_{20}SA_{80}$ was also prepared according to the above curing profile and used for comparison.

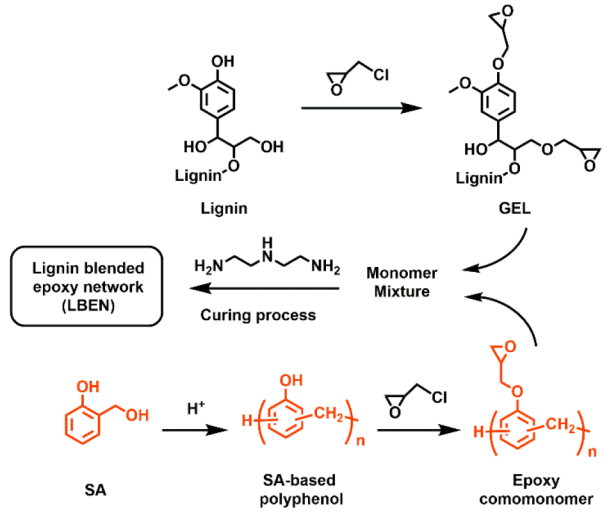

Figure 2. Synthesis route of lignin-blended epoxy network (LBEN), which is used to compare with the proposed LIEN route in Figure 1. Lignin is glycidylated prior to being blended with glycidyl ether of SA self-condensed oligomer for curing.

Analysis Methods. Chemical structure of new compounds was followed using nuclear magnetic resonance (NMR) spectroscopy. NMR spectra were collected on a Varian Unity Inova 600 MHz spectrometer. Deuterated acetone, chloroform or DMSO were used as solvent. To obtain the NMR spectra of lignin-based polyphenols, 0.5 g samples were dissolved in 0.7 mL of acetone-d_6 solvent (DMSO-d_6 for lignin) and 10 μL of pentafluorobenzaldehyde was employed as an internal standard. Fourier transform infrared (FTIR) analyses were conducted using a Thermo-Nicolet Nexus 470 FTIR Spectrometer

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equipped with an ultra-high-performance, versatile Attenuated Total Reflectance (ATR) sampling accessory. The spectra were scanned over a wavenumber range of 400−4000 cm^{-1} with a resolution of 4 cm^{-1}. High-performance liquid chromatography (HPLC) was performed on an Agilent 1260 Infinity Quaternary, with a Zorbax Eclipse XDB-C_{18} Column (250 × 74.6 mm).

Differential scanning calorimetry (DSC Q2000, TA Instruments) was conducted under dry nitrogen atmosphere to monitor exothermic peak temperature and enthalpy of curing reaction. Samples of 5−10 mg were placed in sealed aluminum pans for all DSC runs. Peak temperature and enthalpy were obtained through heating the samples from 10 to 180 °C at a rate of 10 °C/min.

Dynamic mechanical properties were characterized using a DMA 2980 (TA Instruments). Rectangular specimens with dimensions of 30 mm length, 10 mm width and 2.5 mm thickness were measured in a single-cantilever mode. The measurements were conducted from 25 to 180 °C at a heating rate of 3 °C/min and a frequency of 1 Hz. The temperature at the maximum in the tan δ curve was taken as α-relaxation temperature (T_α, related to glass transition). Cross-link density (ν) of thermoset was calculated from the equilibrium storage modulus in the rubber region over T_α according to the rubber elasticity theory using eq 1.[51−53]

$$\nu = E'/(\Phi RT) \quad (1)$$

where E' is the storage modulus at T_α + 30 °C. ϕ is the front factor (approximated to 1 in the Flory theory[52,54]), while R and T are the gas constant and absolute temperature at T_α + 30 °C, respectively.

Tensile testing was performed on dog-bone shaped specimens according to the ASTM D638 standard, on a custom-built setup on a vertical TwinRail positioning table (Lintech, CA) with a 100 N load cell. Crosshead speed was set to 0.5 mm/min.

Thermal stability studies were carried out on a Discovery Thermo-Gravimetric Analyzer (TGA, TA Instruments) under a nitrogen flow of 40 mL/min. Samples (5−10 mg) were placed in a platinum pan and scanned from 40 to 600 °C at a ramp rate of 20 °C/min.

RESULTS AND DISCUSSION

Structure of Lignin-Incorporated Polyphenols and Their Glycidyl Ethers. Figure 3 shows the ^{1}H NMR spectra of lignin, phenolated lignin, PL_0SA_{100} and PL-incorporated oligomers ($PL_{10}SA_{90}$, $PL_{20}SA_{80}$, $PL_{30}SA_{70}$ and $PL_{40}SA_{60}$). Figure 3a exhibits integral ratio of aromatic (6.0−7.3 ppm) vs aliphatic (3.5−4.1 ppm) protons of lignin is 0.34. When lignin is modified with catechol to make PL, this ratio increases to 1.43 (Figure 3b). As there is no catechol residue detected in PL, the enhanced aromatic content indicates the substitution of lignin aliphatic hydroxyls by catechols. Figure 3c exhibits the spectrum of PL_0SA_{100} (oligomer from self-condensation of salicyl alcohol). The peak at 3.8 ppm corresponds to the methylene bridge between repeating phenolic units. Integral ratio of aromatic vs aliphatic protons of PL_0SA_{100} is 1.7, which is lower than the corresponding ratio of 2 for salicyl alcohol monomer. This indicates the formation of oligomers connected by methylene linkages at the phenolic para/ortho site. For PL-incorporated polyphenols, the aromatic and aliphatic integrals decrease with increasing percentages of PL from $PL_{10}SA_{90}$ to $PL_{40}SA_{60}$ (Figure 3d−g). This is attributed to the lower integrals of PL in aromatic (3.24) and aliphatic (2.26) compared to those of PL_0SA_{100} (8.58 and 5.02, respectively). Moreover, Figure 4 reveals the integrals of aromatic and aliphatic regions decrease linearly with PL percentage. This relationship confirms the integration of PL with SA-based oligomers. Glycidyl ethers of PL_0SA_{100} and PL-incorporated polyphenols are shown in Figure S2. Compared to polyphenols, glycidyl ethers exhibit new epoxy peaks at 2.67

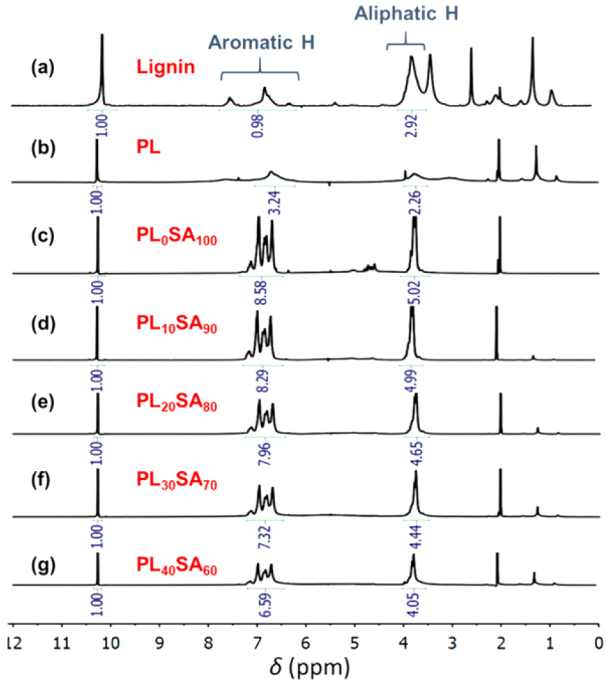

Figure 3. ^{1}H NMR spectrum of (a) lignin, (b) phenolated lignin, (c) PL_0SA_{100} (oligomer from self-condensation of SA) and PL-incorporated polyphenols: (d) $PL_{10}SA_{90}$, (e) $PL_{20}SA_{80}$, (f) $PL_{30}SA_{70}$ and (g) $PL_{40}SA_{60}$. Solvent: DMSO-d_6 for lignin and acetone-d_6 for other polyphenols.

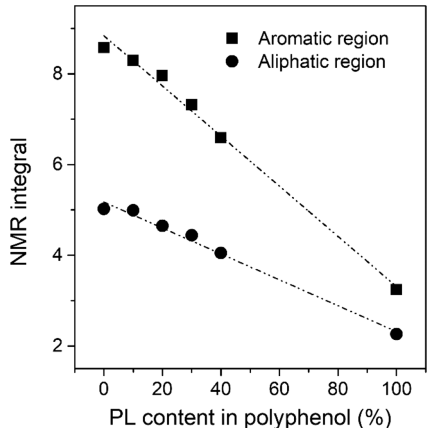

Figure 4. Correlations between PL contents and NMR integrals of aromatic and aliphatic regions of different polyphenols. Integrals of aromatic and aliphatic regions were obtained from the ^{1}H NMR spectra in Figure 3, in which integrals of internal standard (pentafluorobenzaldehyde) were set as 1.

and 2.88 ppm (−CH_2− in oxirane), 3.22 ppm (−CH− in oxirane) and 3.54 and 3.64 ppm (−O−CH_2−).

IR analyses were also conducted to confirm the structure. Figure 5a,d illustrates the characteristic absorption bands of PL_0SA_{100} and $PL_{40}SA_{60}$ appear at around 3318 cm^{-1} (O−H stretching), 2857−3005 cm^{-1} (alkyl C−H stretch) and 1602, 1504 and 1457 cm^{-1} (aromatic C−C bond). After polyphenols were reacted with epichlorohydrin, the afforded glycidyl ethers exhibit significantly decreased hydroxyl band and newly formed C−O−C ether band at 1028 cm^{-1} and epoxy band at 912 cm^{-1}, which confirms the formation of epoxy groups (Figure 5b,e). When these glycidyl ethers were cured with

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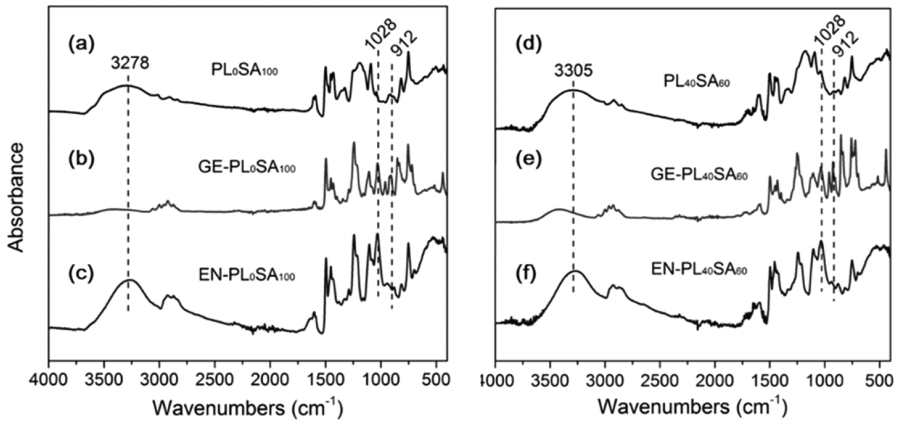

Figure 5. FTIR spectra of PL_0SA_{100} (a) and $PL_{40}SA_{60}$ (d), their glycidyl ethers (b and e) and cured epoxy networks (c and f).

diethylenetriamine, the active amine protons opened epoxies while hydroxyls were created at the same time. As shown in Figure 5c,f, cured samples exhibit no epoxy band at 912 cm^{-1}, while the broad hydroxyl band increases, which indicates significant conversion of the epoxy group. Other lignin-incorporated polyphenols, their glycidyl ethers and cured networks are shown in Figures S3–S5, which exhibit similar patterns to Figure 5.

Effect of Lignin on Curing Behavior. The effect of lignin on curing behavior was studied via DSC analysis. Table 1 exhibits enthalpy (ΔH) values gradually decreased as lignin content increased. This trend was expected because PL-incorporated polyphenols have relatively more complicated structure, lower reactivity and possibly yield non-curable benzodioxane byproduct caused by the catechol moiety.[12,39] Thus, PL-incorporated epoxy prepolymers could have less epoxy content and release lower heat compared to neat sample ($GE\text{-}PL_0SA_{100}$). Table 1 demonstrates peak curing temperatures of lignin-incorporated samples ($GE\text{-}PL_{10}SA_{90}$ to $GE\text{-}PL_{40}SA_{60}$) exhibit no obvious change compared to $GE\text{-}PL_0SA_{100}$ (72.7–74.9 °C versus 75.6 °C). Meanwhile, epoxy prepolymer prepared from the LBEN route ($GE\text{-}BL\text{-}GEL_{20}SA_{80}$) exhibits similar peak temperature of 73.4 °C. These observations indicate lignin does not have an impact on the curing process, which is consistent with previous studies.[39] Extent of curing was determined using two cycles of heating/cooling. As shown in Figures S6–S11, all epoxy prepolymers were most cured as reflected by the lack of exotherm on the second heating.

Table 1. DSC Curing Data for Epoxy/Amine Systems Exhibiting Onset Curing Temperature (T_i), Peak Curing Temperature (T_p) and Enthalpy of Reaction (ΔH)

entry	epoxy prepolymer	T_i (°C)	T_p (°C)	ΔH (J/g)
1	$GE\text{-}PL_0SA_{100}$	42.7	75.6	449
2	$GE\text{-}PL_{10}SA_{90}$	39.4	74.9	464
3	$GE\text{-}PL_{20}SA_{80}$	34.9	72.7	445
4	$GE\text{-}PL_{30}SA_{70}$	36.1	73.9	432
5	$GE\text{-}PL_{40}SA_{60}$	36.0	74.1	420
6	$GE\text{-}BL\text{-}GEL_{20}SA_{80}$	39.2	73.4	431

Effect of Lignin on Thermomechanical Properties. Table 2 and Figure 6 illustrate α-relaxation temperature (T_α,

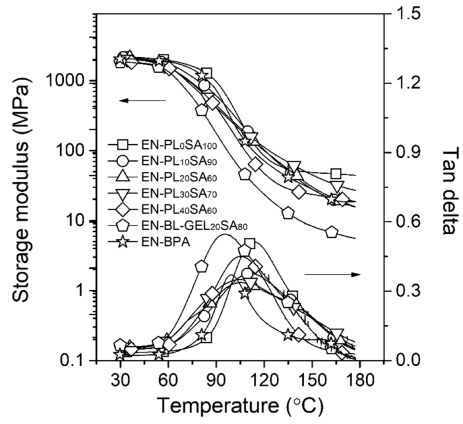

Figure 6. Storage modulus and tan δ curves of epoxy networks as a function of temperature.

Table 2. α-Relaxation Temperature (T_α), Glassy Storage Modulus at 30 °C (E_{30}') and Cross-Link Density (ν) of Epoxy Networks Prepared from LIEN and LBEN Approaches[a]

entry	epoxy networks	T_α (°C)	E_{30}' (MPa)	E' at T_α + 30 °C (MPa)	ν (10^{-3} mol/cm^3)
1	$EN\text{-}PL_0SA_{100}$	114	2151	50	16.0
2	$EN\text{-}PL_{10}SA_{90}$	112	2146	38	11.1
3	$EN\text{-}PL_{20}SA_{80}$	106	2118	52	15.4
4	$EN\text{-}PL_{30}SA_{70}$	106	2024	68	19.9
5	$EN\text{-}PL_{40}SA_{60}$	106	1843	28	8.2
6	$EN\text{-}BL\text{-}GEL_{20}SA_{80}$	96	1828	18	5.4
7	EN-BPA	100	2042	48	14.4

[a]BPA-based epoxy network (EN-BPA) was also prepared using the same curing profile as other networks for comparison.

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ACS Sustainable Chem. Eng. 2018, 6, 10628–10636

related to glass transition temperature) and storage modulus of biobased epoxy networks. Lignin loading is found to affect the mechanical performance. Compared to the neat network (EN-PL_0SA_{100}, exclusively prepared from GE-PL_0SA_{100} and DETA, T_α = 114 °C), lignin incorporation diminished the T_α of all networks (96.0−112 °C). This could be related to the relatively lower reactivity and incompatibility of lignin. Meanwhile, steric hindrance of lignin limits the development of polymer networks. Impacts of lignin are especially evident when higher contents of PL are incorporated, as T_α decreases gradually from EN-PL_0SA_{100} to EN-$PL_{40}SA_{60}$ (entries 1−5).

The synthesis route also impacts thermoset properties. As shown in Table 2 and Figure 6, T_α and E_{30}' of EN-BL-$GEL_{20}SA_{80}$ (LBEN route) are 96.0 °C and 1828 MPa respectively, which are lower than the values of LIEN-derived networks. As illustrated in Figure 2, linkages between GEL and GE-PL_0SA_{100} in LBEN are mainly realized via connecting with the amine hardener. However, these linkages are often compromised by the poor reactivity of lignin. Besides, compatibility between GEL (in solid state) and GE-PL_0SA_{100} (in oily state) is low and the mixture was heterogeneous after blending. The poor compatibility causes insoluble defects within the network, which result in decrease in cross-link. As shown in Table 2, cross-link density (ν) of the LIEN samples is in the range of 8.2−19.9 × 10^{-3} mol/cm^3, which is much higher than for the EN-BL-$GEL_{20}SA_{80}$ (5.4 × 10^{-3} mol/cm^3). This phenomenon highlights the merits of the LIEN approach: (1) as sulfuric acid was used in the phenolation and condensation process, the backbone of lignin was cleaved and the compatibility of lignin with polymeric compounds improved. Meanwhile, intermolecular hydrogen bonds, van der Waals interactions between polymer chains, and $\pi-\pi$ stacking of aromatic groups of lignin were reduced during the modifications, which prevented lignin from aggregating.[55] (2) covalent cross-links between lignin and SA-based oligomers have been established through condensation before curing, (3) improved solubility of lignin-incorporated polyphenols, which leads to improved degree of glycidylation than direct epoxidation of lignin, and (4) the afforded epoxy prepolymers are homogeneous liquid, which shows improved compatibility with amine hardener. The enhanced uniformity of LIEN is depicted pictorially in Figure 7, pictures of EN-BL-GEL_5SA_{95}, EN-PL_5SA_{95} and EN-PL_0SA_{100} (neat sample with no lignin addition). Reduced amount of lignin (5 wt %) is employed to illustrate clearly the interactions of lignin with the polymer network. Compared to the homogeneous texture of EN-PL_5SA_{95} and EN-PL_0SA_{100}, it is easy to see lignin particles unevenly dispersed in EN-BL-GEL_5SA_{95}. This inhomogeneity causes flaws within the network and significantly decreases the tensile properties of LBEN sample. As shown in Figure 8, the max stress and strain of EN-BL-$GEL_{20}SA_{80}$ are 28.7 MPa and 1.4%. By comparison, EN-$PL_{20}SA_{80}$ and EN-PL_0SA_{100} are tougher with stress of 66.9 and 68.1 MPa, and strain of 3.3 and 3.7%, respectively.

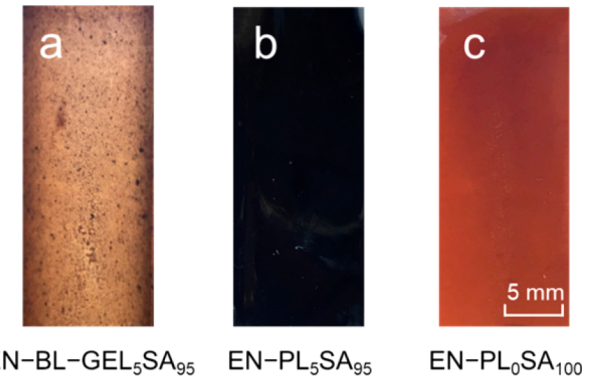

Figure 7. Image of epoxy networks (a) EN-BL-GEL_5SA_{95} (LBEN approach) and (b) EN-PL_5SA_{95} (LIEN approach, 5 wt % of GEL or PL in epoxy prepolymers were employed for clear illustration of panels a and b). (c) EN-PL_0SA_{100}, neat network with no addition of organosolv lignin.

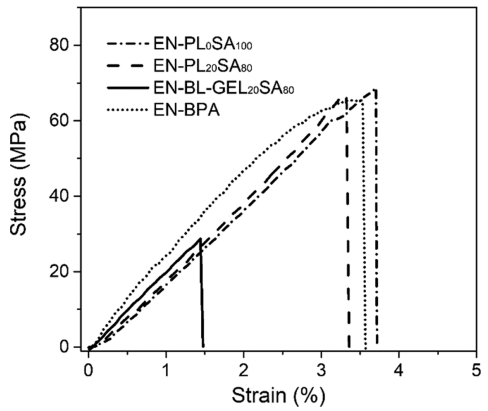

Figure 8. Tensile tests of EN-PL_0SA_{100}, EN-$PL_{20}SA_{80}$, EN-BL-$GEL_{20}SA_{80}$ and EN-BPA.

Traditional DGEBA/DETA epoxy network (EN-BPA) was also prepared using the same curing profile. Table 2 compares T_α, E_{30}' and ν of biobased epoxy networks with the BPA-based counterpart. It is found that LIEN-derived polymers have T_α, modulus and cross-link density that are comparable or superior to the BPA-based materials (T_α of 100 °C, E_{30}' of 2042 MPa and ν of 14.4 × 10^{-3} mol/cm^3). Meanwhile, Figure 8 demonstrates EN-$PL_{20}SA_{80}$ has comparable tensile properties to EN-BPA. These results highlight the potential of replacing or supplementing petroleum-based thermosets with lignin-containing materials.

Effect of Lignin on Thermal Stability. Figure 9 demonstrates thermal degradation of neat and lignin-loaded thermosets in the range of 40 to 600 °C. It is observed from Figure 9 and Table S1 that thermal stability of lignin-loaded

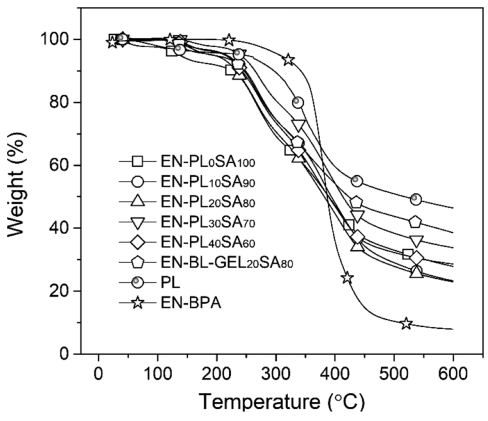

Figure 9. Thermogravimetric analysis thermograms of epoxy networks as a function of temperature.

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ACS Sustainable Chem. Eng. 2018, 6, 10628−10636

Table 3. Weight Percentage of Bulk Lignin, PL and Biomass in Polyphenols, Epoxy Prepolymers and Thermosets

	polyphenol			epoxy prepolymer			thermoset		
samples	lignin[a] (wt %)	PL (wt %)	biomass[b] (wt %)	lignin (wt %)	PL (wt %)	biomass[c] (wt %)	Lignin (wt %)	PL (wt %)	biomass[d] (wt %)
EN-PL_0SA_{100}	0	0	100	0	0	71	0	0	65
EN-$PL_{10}SA_{90}$	7	10	100	5	7	72	4	6	66
EN-$PL_{20}SA_{80}$	14	20	100	10	15	73	9	14	66
EN-$PL_{30}SA_{70}$	20	30	100	16	23	75	14	21	67
EN-$PL_{40}SA_{60}$	27	40	100	21	31	77	19	28	69

[a]content of lignin in PL was calculated to be ca. 68 wt % as demonstrated in the Experimental Section. [b]Considering lignin, catechol and salicyl alcohol are all available from bio-based sources, biomass contents in polyphenol for all samples are 100 wt %. [c]Weight ratio of biomass in epoxy prepolymer (B/EP) is in the range of 71−77 wt %. This ratio is calculated by experiments, for example, 1 g of polyphenol ($PL_{40}SA_{60}$) reacts with epichlorohydrin to yield 1.3 g of GE-$PL_{40}SA_{60}$. Thus, weight ratio of $PL_{40}SA_{60}$ in epoxy prepolymer GE-$PL_{40}SA_{60}$ is calculated to be 1/1.3 = 0.77. Contents of lignin and PL in epoxy prepolymer are calculated by multiplying their contents in polyphenol with corresponding B/EP ratios. [d]Weight ratio of biomass in thermoset (B/T) is in the range of 65−69 wt %. This ratio is calculated by, for example, 1 g of epoxy prepolymer (GE-$PL_{40}SA_{60}$, EEW = 178 g/equiv) is cured with 0.12 g of DETA (1:1 ratio of epoxy/−NH) to yield 1.12 g of thermoset. Thus, weight ratio of $PL_{40}SA_{60}$ in thermoset EN-$PL_{40}SA_{60}$ is calculated to be 0.77*1/1.12 = 0.69. Contents of lignin and PL in thermoset are calculated by multiplying their contents in polyphenol with corresponding B/T ratios.

samples is clearly higher than the neat networks, which is suggested by the onset degradation temperature (expressed as T_{d5}, temperature at 5% weight loss) of lignin-loaded ones (191−239 °C) and neat sample (136 °C). Meanwhile, T_{d30} (temperature at 30% weight loss) exhibits the same trend with T_{d5}. The improved thermal properties of lignin-loaded thermosets are consistent with previous studies,[56] which is explained by the lignin matrix that acts as a thermal barrier hindering mass exchange. To highlight the barrier role of phenolated lignin, thermal analysis of PL was also conducted, and it revealed high stability as indicated by T_{d5} (245 °C), T_{d30} (363 °C) and $Char_{600}$ (46%). The way lignin incorporates into network does not have impact on thermal performance, as EN-BL-$GEL_{20}SA_{80}$ has comparable thermal parameters with thermosets prepared from LIEN. As for the BPA-based network, it exhibits the highest thermal stability when temperature is relatively low, as reflected by T_{d5} (305 °C) and T_{d30} (371 °C). However, when temperature reaches 330 °C, EN-BPA exhibits a fast degradation behavior and only 8 wt % char was left when the temperature reaches 600 °C. As for the lignin-loaded samples, they start to exhibit higher stability over EN-BPA above 374 °C, with 23−39 wt % char formed at 600 °C.

Content of Lignin and Biomass in Thermosets. Table 3 lists the weight percentages of lignin, PL and biomass in polyphenols, epoxy prepolymers and thermosets. Although there are discrepancies between real and model feed experiments, this calculation could provide a straightforward idea of the compositions of these thermosets. Considering lignin, catechol and salicyl alcohol are all available from renewable sources as stated above, the starting polyphenol precursors are fully bio-based. As calculated above, lignin content in PL was ca. 68 wt %. Thus, lignin content in polyphenol could be up to 27 wt %. When polyphenols are glycidylated to epoxy prepolymers, the biomass content is reduced to the range of 71−77 wt %, while the rest is occupied by the glycidyl ether groups. These values are consistent with the weight ratio (75 wt %) of 2-methoxy-4-propylphenol (a typical lignin building block) in its glycidylated form. Because reacting with epichlorohydrin is the most commonly method to convert phenol into its glycidyl ether, it is inevitable to dilute the biomass content in the epoxy prepolymers. It is noteworthy that lignin content could reach up to 21 wt % in the homogeneous liquid epoxy prepolymer, with no solid phase formed. To our knowledge, this is the highest value and most efficient approach that has ever been reported for a liquid lignin-containing epoxy prepolymer. For the cured epoxy thermosets, the content of biomass decreases slightly to 65−69 wt %, while lignin content is up to 19 wt %. This decrease in biomass content depends on the properties of hardeners and is inevitable unless renewable hardeners like succinic anhydride are employed.

CONCLUSIONS

A series of liquid and curable lignin-containing epoxy prepolymers were prepared. Compared to previous lignin-containing prepolymers that are mainly infusible solids, the prepared liquid epoxy prepolymer can yield homogeneous thermoset without the need for additional epoxy co-prepolymer. The prepared thermosets have high content of biomass (up to 69 wt %), and they exhibit mechanical properties that are comparable or superior to conventional BPA-based counterpart. Meanwhile, these networks are prepared using several green approaches: formaldehyde-free preparation of oligomers using water as solvent; solvent-free synthesis of PL; one-pot synthesis of epoxy prepolymers; and use of high boiling point sulfuric acid as catalyst. Without lignin formed as the low-reactivity solid phase epoxy prepolymer, the described method represents a promising route for making lignin-containing thermosets with multiple purposes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b01962.

FTIR spectra of new compounds and DSC scans of epoxy/amine reaction (PDF)

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Notes

The authors declare no competing financial interest.

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