Pyrolysis oil substituted epoxy resin: Improved ratio optimization and crosslinking efficiency

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ABSTRACT: The objective of this study was to determine the compatibility of whole pyrolysis oil (PO) of pine as a substitute for the phenolic component of epoxy resins (ER). Pyrolysis oil-based epoxy resin (POBER) was synthesized by modification of EPON828 ER with PO at various mixing ratios (1 : 3–1 : 8, PO:EPON828, w/w). Acetone extraction determined that a ratio of 1 : 7–1 : 8 resulted in a fully reacted thermoset, leaving neither PO nor EPON828 in a significantly unreacted state. Dynamic mechanical analysis (DMA) revealed that a ratio of 1 : 8 produced the highest storage modulus (E'); in addition, it was determined that this ratio provided a superior glass transition temperature (Tg) of 120°C and crosslinking density of 1891 mol/m^3. FTIR spectra concluded that the reaction between the EPON828 and PO was complete at the 1 : 8 ratio, citing the removal of hydroxyl and epoxide peaks within the cured product. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42239.

KEYWORDS: bio-oil; biopolymers and renewable polymers; properties and characterization; thermosets
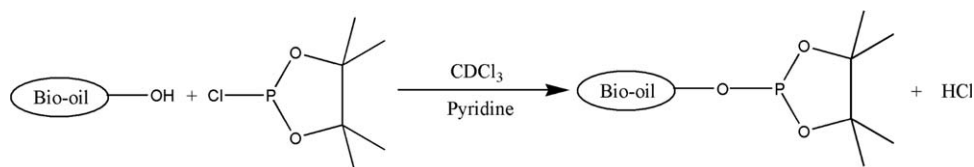
INTRODUCTION

Epoxy resins are an important class of thermosets which are widely used in the field of automotive, aerospace, insulation, and electronics due to their superior properties such as low density, high toughness, excellent thermal and mechanical properties, and flame and chemical resistance.[1–4] ERs owe their excellent properties to epoxide functionality and aromatic/phenolic backbone. When ER is cured, epoxide groups provide a highly crosslinked matrix which enhances thermal and mechanical properties. The phenolic backbone, on the other hand, provides flame resistance and stiffness.[2,5] The global epoxy production is predicted to be 3 million tons by 2017[6] with a market size of US$21.5 billion.[6] Today epoxy and other plastic production processes rely on petroleum resources to assist in the reaction. Current petroleum use is large and creates significant problems such as air pollution, promotion of the greenhouse effect, and depletion of petroleum reserves.[7] Therefore, environmental concerns, as well as instability in the petrochemical market, have recently increased in using more sustainable and renewable chemical resources.

Lignocellulosic biomass is considered the most abundant natural resource with an annual production of 1.3 billion dry tons in the USA.[8] The U.S. Department of Energy (DOE) and the U.S. Department of Agriculture (USDA) have prioritized the development of bioenergy and bioproducts, and they have a goal to produce 18% of the current U.S. chemical commodities from biomass by 2020, and 25% by 2030.[8] Increased research on the utilization of lignocellulosic biomass to produce bio-based ER has also occurred recently. Valuable reviews on bio-based epoxy systems to date can be found in the literature.[6,9–12] Among lignocellulosic biomass, bark[13], woody biomass[14], bamboo,[15] and switchgrass[16] have been previously studied in the bio-based epoxy systems. These studies mainly focused on the production of bifunctional or polyfunctional alcohol (polyol) from biomass as a substitution of bisphenol A (BPA) for epoxy synthesis. Researchers reported promising results, for instance, a high degree of substitution (up to 50%)[16] and a low curing activation energy[13]; however, thermal and mechanical properties still needed to be improved. Most recently, Tiimob *et al.*[17] has reinforced a bio-based ER with sustainable β-CaSiO₃ nanoparticles prepared from egg shell to improve resin properties. During the past decade, lignin has also attracted interests in the bio-based epoxy systems as hardeners[18,19] and polyols[20,21] because of its natural aromatic structure. However, a complex and variable chemical structure and high polydispersity index[22] of lignin restrain its feasibility.

Figure 1. Phosphitylation of free OH group with TMDP in the solvent system of CDCl₃/Pyridine.

PO is a product of the controlled heating of lignocellulosic biomass within a controlled atmosphere in which a rapid quenching of the vapors and aerosols result in PO. In the pyrolysis process, biomass is converted to vapors, aerosols, and chars in the absence of oxygen at elevated temperatures (400–600°C). Vapors and aerosols are then rapidly condensed, and bio-oil is produced. Bio-oil yield is around 60–75% depending on process parameters (temperature, residence time, etc.).[23] The rapid cooling of these vapors produces a highly reactive, two-phase chemical, comprised of an aqueous, hydrophilic phase and a tarry, hydrophobic phase. This hydrophobic phase is rich in pyrolytic lignin, which has been demonstrated as a viable partial replacement (up to 50%) for phenol during the production of phenol formaldehyde (PF) resin.[24] Therefore, PO of lignocellulosic biomass could be considered as a promising natural phenolic resource.[25–28]

ER can utilize PO as a phenolic source due to the high concentration of phenolic hydroxyl groups found within the PO.[26] ER have been used sparingly in the wood products industry, primarily due to the increased cost associated with these types of adhesive systems.[29] However, with the increase in the production of PO, the cost of this product is expected to be less than the traditional petroleum-based phenol used in epoxy-phenolic production.[29] In addition, these adhesives are formulated without the use of formaldehyde, circumventing the current problems associated with off-gassing. After adjustment for inflation, it is anticipated that the significantly cheaper cost of bio-oil ($0.20–0.35/lb) than epoxy ($1.50/lb) will result in an opportunity to make epoxies that are more cost effective and competitive to other adhesive systems.[24,30,31]

PO as substitutes for phenolics into epoxies is lacking and the OH distribution within PO is currently unknown but is important during crosslinking. Therefore, the objective of this study is to determine the compatibility of whole PO as a substitute for the phenolic component of ER. Whole PO utilizes both the hydrophobic and hydrophilic phase, increasing the potential yield and industry profits. There may be additional challenges associated with using the resource in this form. Therefore, this research has the potential to provide interesting results and introduce new possibilities in the field of bio-based industrial adhesives. To explore this question, the stoichiometric ratio for proper PO was determined finding out the optimum mixing ratio of PO and ER, and the chemistry behind PO and ER was investigated using both chemical and physical analysis.

EXPERIMENTAL

Materials

Loblolly pine wood chips, *Pinus spp*, (20 mesh), obtained from a local chipping plant in Opelika, AL. All chemicals were purchased from VWR; except phosphorylating agent, 2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP), which was purchased from Sigma Aldrich. All chemicals were reagent grade and used as received.

Preparation of Pyrolysis Oil (PO)

The PO was a combination of four batches produced using an auger style reactor at temperatures ranging from 425–500°C for approximately 10 s according to the method reported by Thangalazhy-Gopakumar *et al.*[32] The whole PO was methylated using methanol at a rate of 50% (v/v). The resulting homogenized PO product was vacuum filtered 5 times using #1 Whatman paper in order to make sure that all the ash and char components were removed. Excess methanol was removed by rotary evaporation for 45 min. at 60°C under 27" Hg vacuum.

³¹P NMR Analysis of Pyrolysis Oil

³¹P-NMR provides great deal of information to determine the content of OH groups present in the PO. In this technique, OH groups belonging to aliphatic, phenolic, carboxylic units are phosphitylated by TMDP followed by quantitative ³¹P-NMR. In the phosphitylation reaction (Figure 1), TMDP reacts with the free OH groups in the PO, and yields to derivatized compound and hydrochloric acid (HCl). Since HCl may cause to decomposition of derivatized compound, pyridine is used in the solvent system as the based to capture HCl. The reasons of using deuterated chloroform (CDCl₃) in the solvent system are (1) to dissolve derivatized sample, (2) to inhibit precipitation of pyridine-HCl salt, and (3) to get a deuterium signal for NMR experiment.[33]

Phosphitylation of PO was performed as follows: Stock solution was prepared by dissolving 40 mg N-Hydroxy-5-norbornene-2,3-dicarboximide (NHND) as the internal standard, and 40 mg chromium (III) acetylacetonate as the relaxation reagent in a solvent system of pyridine and chloroform (1.6/1, v/v). Approximately 20 ± 2.5 mg of bio-oil was completely dissolved in 500 μL of stock solution at room temperature, and then 150 μL TMDP (derivatization agent) was added to sample vials and vortexed for 2 min. After phosphitylation, the mixture was transferred to an NMR tube for analysis. Peaks were integrated relative to the NHND peak in order to quantitatively calculate the OHN. ³¹P NMR spectra were acquired with a Bruker Avance II 250 MHz spectrometer using inverse gated decoupling pulse sequence, 90° pulse angle, 25 s pulse delay and 128 scans as per the methods of Ben and Ragauskas.[34]

Preparation of Pyrolysis Oil-based Epoxy Resin (POBER)

EPON828 (average molecular weight of ~377g/mole, epoxide equivalent of 185–192 g/eq) was used as the ER in this study. PO was mixed with ER until homogenized at ratios of 1 : 3 to 1 : 8 (PO:ER, w/w) at one part increments. Triphenylphosphine

(TPP), 0.5% TPP based on EPON828 weight, was added to the mixture to catalyze the reaction. To aid in the homogenization of the components during mixing, tetrahydrofuran (THF) was used as the solvent. After blending PO and ER, the mixture was poured into an aluminum weighing dish (10 cm), and then cured using a temperature ramp of 1h at 80°C, 2 h at 150°C, 2h at 200°C and allowed to cool slowly to 25°C within the oven as suggested by Wei et al.[16]

ATR-FT-IR

Attenuated total reflection Fourier Transform Infrared (ATR-FT-IR) spectra of the PO, ER (EPON828), and the POBER resin were acquired between 4000 and 650 cm^{-1} with an ATR-FT-IR spectrometer (Model Spectrum400, Perkin Elmer Co., Waltham, MA) with 4.00 cm^{-1} resolution and 32 scans to determine the functional groups. All ATR-FT-IR spectra were collected at room temperature (22 ± 1°C).

Thermo-Mechanical Analysis of POBER Resin

Dynamic mechanical analysis (DMA) was conducted on a TA Instruments RSAIII Dynamic Mechanical Analyzer (DMA) using samples approximately 26 × 8 × 2 mm according to the method described by Auad et al.[35] A three-point bending configuration at 1% strain and an oscillating frequency of 1 Hz was utilized. Runs were conducted between 35°C and 200°C with a temperature ramp of 10°C/min. The number of active chain segments in the network per unit volume (n), which is also called crosslink density, was calculated using physical data acquired through DMA according to the following equation:

$$E' = 3nRT \quad (1)$$

where, E' is the storage modulus at rubbery region (Pa) at rubbery plateau region; n is the number of active chains (mol/m^3), which is proportional to the crosslinking density of the crosslinked network; R is the gas constant (8.31 Pa.m^3/mol.K); T is the temperature at rubbery region (K).[36]

Solubility of POBER Resin

POBER resin was grounded to 40 mesh by Wiley Mini Mill (Thomas Scientific, model no: 3383-L10, Swedesboro, NJ.) for acetone extraction. The soxhlet extractor was obtained from Ace Glass Incorporated (Vineland, NJ.). An extraction thimble filled with an appropriate amount of grounded POBER resin was placed into the soxhlet system, and then the extraction flask was filled with 150 mL acetone. The soxhlet system was heated up and allowed to reflux for 4 h. After extraction, acetone was evaporated and the solid residue was dried in an oven for 1 h at 105°C. The weight loss (%) was then calculated by deduction of weight of residue from the weight of starting grounded POBER resin.

RESULTS AND DISCUSSION

^{31}P NMR Analysis of Pyrolysis Oil

^{31}P-NMR provides a great deal of information to determine the content and origin of OH groups present in PO. In this technique, OH groups belonging to aliphatic, phenolic, and carboxylic units are phosphitylated by TMDP. Quantitative ^{31}P-NMR analysis have been extensively employed by many researchers to characterize the OH groups in lignin[33], PO[34], bio-diesel[37],

hydrothermal liquefaction oil of algae[38], and bio-oil produced by organic solvent liquefaction (hereafter referred to as liquefaction oil) of biomass.[39] However, no research works could be found in which the OH groups were partitioned into aliphatic, phenolic, and acidic categories prior to epoxy reaction. Such understanding is important if we are to overcome the variability and complexity of bio-oil, which can complicate and vary the reaction with epoxy.
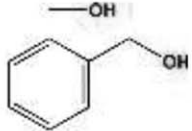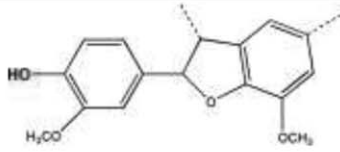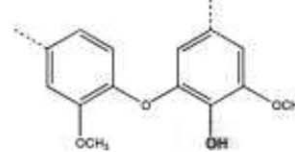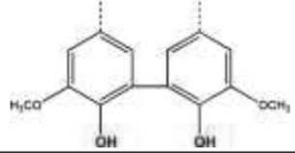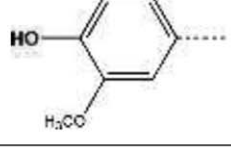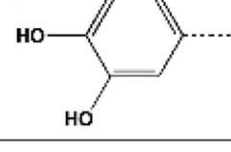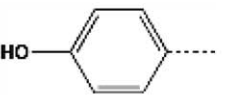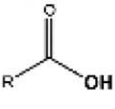
The hydroxyl number (OHN) of pure ethylene glycol (EG) was also calculated by ^{31}P-NMR in order to confirm the accuracy of the method. OHN of EG was calculated to be 31.75 mmol/g which was quite close to the theoretical OHN value of EG, 32.23 mmol/g. Table I shows the OHN of PO calculated by quantitative ^{31}P-NMR analysis, the integration region and an example of the chemical structures for each classification. Total OHN of PO was calculated to be 10.83±1.08 mmol/g. High OHN (5.35–10.70 mmol/g) is required for a bio-oil to be considered as a high quality bio-based polyol.[40] Therefore, the PO produced in this study is a good candidate to be used as a bio-based polyol. It was also found that aliphatic, phenolic, and acidic hydroxyl groups accounted for 49%, 28%, and 23% of the total OHN, respectively. Aliphatic type of OHs was most likely due to the degradation of cellulose, hemicellulose, and lignin[41] while monomeric phenols, guaiacyl, p-hydroxyphenyl, and catechol type of OH groups in PO can be attributable to the cleavage of ether bonds in lignin during pyrolysis.[42,43] Phenolic OH groups are important in the synthesis of bio-oil based polymers because aromatic groups provide strength to the resulting polymer system.[5] It was previously reported that acids and furfurals were the major component found in the PO of xylan[43]; thus, it could be conjectured that hemicellulose made more contribution to concentration of acidic OH than cellulose and lignin in the PO produced in our study.

ATR-FT-IR

The IR spectra of POBER (mixing ratio of 1 : 8), commercial unmodified ER (EPON828) and PO are shown in Figure 2, and band assignments are summarized in Table II. The peak at around 3400 cm^{-1} was due to the presence of OH groups, indicating that PO had a significant amount of OH groups, as confirmed by ^{31}P-NMR analysis. The peak at around 1750 cm^{-1} was due to the carbonyl (C=O) groups in the PO which are generated by the decomposition of cellulose and hemicellulose during pyrolysis.[44] Aromatic components in the PO, which have been previously proved by GC-MS analysis by other researchers[32,44] resulted in the peaks at 1000–1150, 1214–1233, 1600, and 1500 cm^{-1}. And finally, the peak at 910 cm^{-1} is the characteristic peak of epoxide ring.

FTIR analysis of the individual components and cured ER illustrate the completeness of the reaction. As illustrated in Figure 1, PO contains a significant number of hydroxyl groups as indicated by a peak at 3400 cm^{-1}. However, POBER resin exhibited a weak hydroxyl peak at 3400 cm^{-1}. The peak area at 3400 cm^{-1} of the PO and POBER resin was calculated to be 26.0458 and 4.5802 A cm^{-1}, respectively, which clearly indicates that OH groups in the PO was consumed during the curing. On the other hand, the epoxide groups within the EPON828

Table I. Hydroxyl Number (OHN) of the Pyrolysis Oil Determined by Quantitative ^{31}P-NMR after Derivatization with TMDP.

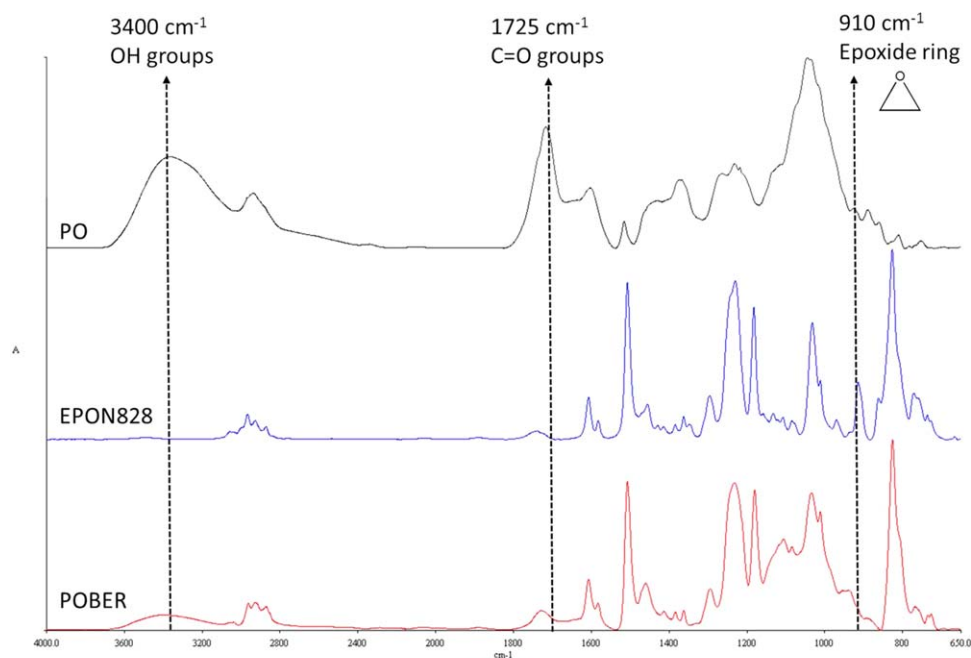| Type of OH			Example of Chemical Structure	OHN[a] (mmol/g)	Integration Region[b] (ppm)
Aliphatic OH				5.33 ± 0.28	150.0 - 145.5
Phenolic OH	C5 substituded Condensed phenolic OH	β-5		0.04 ± 0.01	144.7 - 142.8
		4-O-5		0.18 ± 0.01	142.8 - 141.7
		5-5		1.28 ± 0.14	141.7 - 140.2
	Guaiacyl phenolic OH			0.44 ± 0.12	140.2 - 139.0
	Catechol type OH			0.76 ± 0.48	139.0 - 138.2
	p -hydroxy-phenyl OH			0.33 ± 0.26	138.2 - 137.3
Acidic OH				2.48 ± 0.31	136.6 - 133.6
Total OHN (mmol/g)				10.83 ± 1.08	

[a] OHN values were calculated by integrating of peaks relative to NHND peak. Values are means of three independent replicates, and numbers after-± are the standard deviation.
[b] Integration regions were identified according to ^{31}P-NMR chemical shifts reported by Ben and Ragauskas.[34]

are indicated by the sharp peak at the 910 cm^{-1}. Following the reaction, both of these groups are nearly completely removed within the cured epoxy spectra. This analysis indicates that the

EPON828 and PO provided a complete reaction, consuming these components and thus removing their signatures within the spectra. Another change in the IR spectra was observed at

Figure 2. FT-IR spectrum of POBER (mixing ratio of 1 : 8), EPON828 (commercial unmodified epoxy resin), and PO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the carbonyl peak (1725 cm^{-1}). As the PO was consumed by EPON828, the peak at 1725 cm^{-1} was not observed in the POBER resin suggesting that carbonyl groups within the PO contributed the curing of EPON828 resin along with the hydroxyl groups.

Thermo-Mechanical Analysis of POBER Resin

The viscoelastic behavior of POBER resin at different mixing ratios was analyzed by DMA, and the E' and tan δ versus temperature is shown in Figure 3. As shown in Table III, the E' at 30°C and 160°C were found to be in the range of 1.03–2.85 GPa and 0.006–0.018 GPa, respectively, which is in agreement with Qin et al.[19] and Hu et al.[45] where ER was cured with lignin and furan based curing reagents. Tg is determined by the temperature at maximum tan δ [Figure 3(b)] which is measured as the angle between the in-phase and out-of-phase components of the cyclic motion during DMA.[36] Tg of the POBER resin was found to be in the range of 96.5–120.1°C depending on the mixing ratio (Table III) which is comparable to traditional EPON828 resin cured with different curing agents, for instance, 134°C when cured with diethylenetriamine,[45] 111°C with triethylene tetramine,[46] 93°C with aliphatic triamine.[45] This is a promising finding because PO could be utilized to improve the Tg of ER without using any petroleum-based curing agent. The Tg of the POBER resin is also found to be relatively higher as compared to other bio-oil-based epoxy studies. For example, Wei et al.[16] modified ER with a liquefaction oil of switchgrass with diethylene glycol, and the Tg was in the range of 35–65°C. In another study, ER was synthesized using commercial ER and the liquefaction oil of Japanese cedar with PEG400/glycerol solvent mixture, and the Tg of the resulting epoxy system was in the range of $-40 - 50$°C.[47] Unlike PO, there is significant amount of unreacted liquefying solvent (24–

75% of the bio-oil weight depending on the liquefaction conditions) retained in the liquefaction oil[39] which acts like a plasticizer when liquefaction oil is used to modify the ER.[16] Therefore, unreacted liquefying solvent left in the liquefaction oil is attributed to the low Tg in these studies cited above. PO, on the other hand, is a solvent free product of pyrolysis process of biomass; thus, a higher Tg can be achieved with PO in ER systems.

The Tg of the POBER resin synthesized in this study is higher than the lignin-based epoxy systems which could be defined as the epoxy systems that are either cured or modified with lignin. Lignin has received increased attention for epoxy systems because of its natural aromatic structure and phenolic hydroxyls. Qin et al.[19] studied the curing behavior of ER with partially depolymerized lignin, and they reported Tg to be 62.3–78.5°C. In another study, alkaline solution of industrial kraft lignin was utilized to cure two commercial ER, polyethylene glycol diglycidyl ether (PEGDE) and diglycidyl ether of bisphenol A (DGEBA), and the Tg of the resulting ER were 30–110°C depending on the resin type used.[48] Delmas et al.[49] blended PEGDGE ER with wheat straw Biolignin^{TM} at different ratios, and found the Tg to be 70°C. Most recently, Mannich-functionalized lignin was incorporated into DGEBA resin to create epoxy composite where authors reported that Mannich-functionalized lignin acted as a plasticizer and decreased the Tg of the ER.[50] Another reason for low Tg of lignin-based epoxy systems might be the unreacted lignin components which cause less oriented crosslinked structures.[11] One of the main differences between solid lignin powder and PO is the difference in concentration of OH groups which is an important parameter for the curing of epoxies. It is conjectured OH groups in the PO react with the betaine which is the product of ring opening
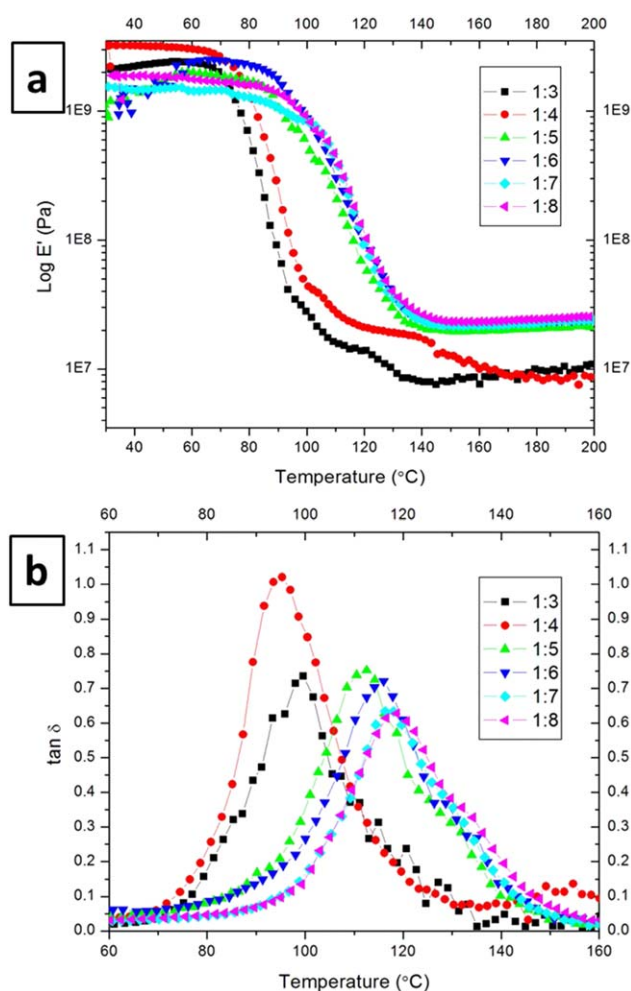
Table II. Characteristic FT-IR Band Assignment of POBER (Mixing Ratio of 1 : 8), ER (Commercial Unmodified Epoxy Resin, EPON828), and PO (Pyrolysis Oil)

Wavenumber (cm^{-1})	Band Assignment	Sample
3400	O—H stretching vibration	PO
3000–3040	Aromatic ring C—H stretching	PO + ER
1725	C=O stretch in unconjugated ketones, carbonyl, and ester groups	PO
1600, 1500	C—C stretch (in-ring)	PO + ER + POBER
1214–1233	C—C, C—O and C=O stretching	PO + ER + POBER
1000–1150	Deformation vibration of C—H bonds in benzene rings	PO + POBER
1050	=C—H bend	ER
910	Epoxide ring	ER

reaction of epoxide in the presence of TPP by nucleophilic attack[51] [Figure 4(a)], and then three dimensional crosslinked epoxy matrix is created[51] [Figure 4(b)]. It should be taken into account that carbonyl groups in the PO contributed to the

Figure 3. (a) Storage modulus and (b) tan δ versus temperature for the PO:ER resin at different mixing ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

curing of EPON828 as discussed in the FTIR analysis. In the Figure 3, however, the curing mechanism between epoxy and hydroxyl groups was illustrated in order to simplify the reaction. PO of previous lignin based feedstock has higher OH numbers than lignin itself because of the cleavage of ether and ester bonds during the pyrolysis process.[34,42] Therefore, there are more likely less unreacted components in the PO than lignin indicating that more components were incorporated into the epoxy matrix during crosslinking. Thus, the higher Tg in this study, as compared to lignin-based ER, could be attributable to the higher OH number of PO.
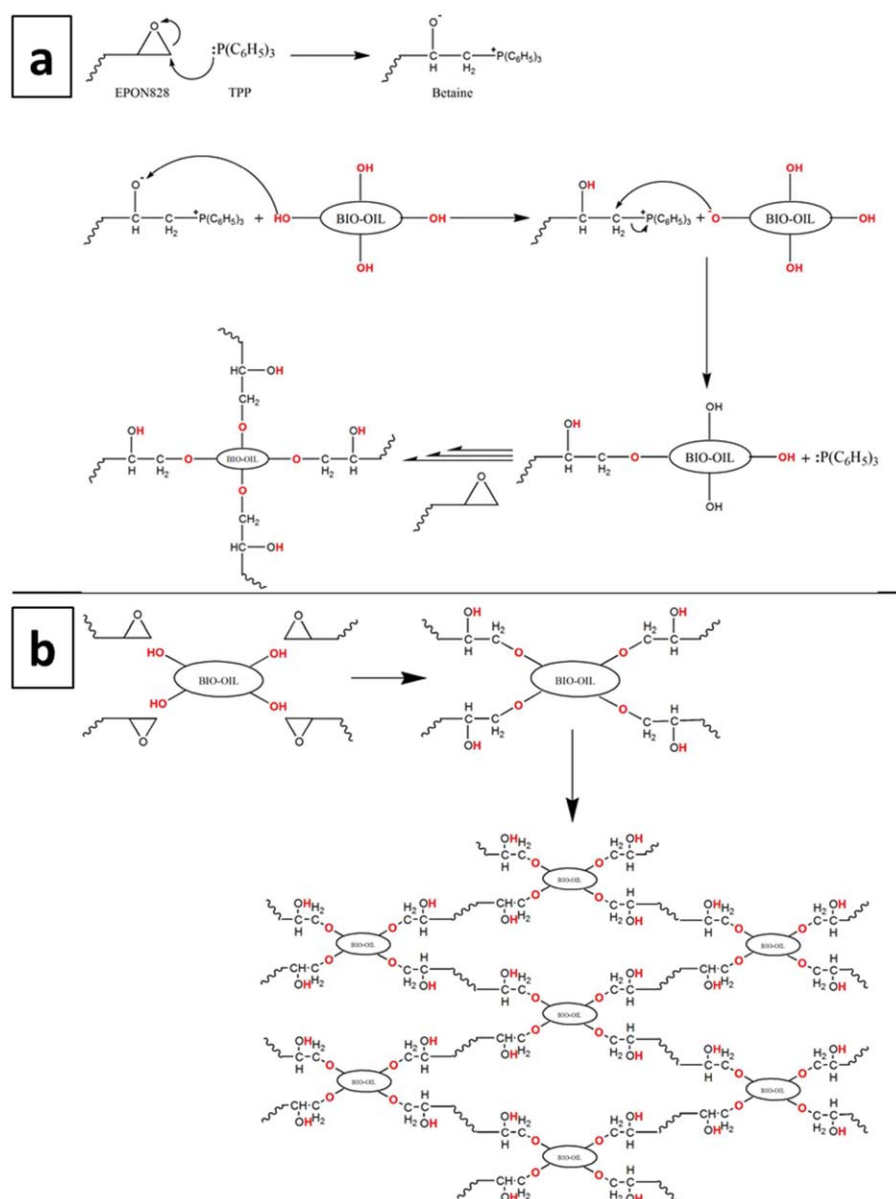
Table III shows how the Tg and crosslinking density increases as the amount of EPON828 resin is increased. The crosslinking density is defined as the number of active segments per unit volume.[36] As the crosslinking density increased, the chain mobility was restrained; therefore, an increase in the Tg and the E' at the rubbery plateau were observed as the crosslinking density increased. The crosslink density was found to fall in the range of 583–1891 mol/m^3 depending on the mixing ratio of PO to EPON828. It was found that the crosslinking density increased in a linear fashion ($R^2 = 0.88$) as the amount of EPON828 was increased. A similar trend was also observed by Wu and Lee[52] where the cure temperature of the ER increased as more liquefaction oil of Japanese cedar was introduced into system. Hirose et al.[53] witnessed an increase in Tg with increased lignin concentration, contributing this to a disruption in the in the polymer network, thereby stiffening the matrix. The authors reacted alcoholysis lignin with EG and further reacted the components with dimethylbenzylamine, a crosslinking agent, to form ester ER. Additionally, one underlying assumption in this study was that PO probably resulted in low molecular weight polymers which can probably help to explain the high reactivity of the ER to such low levels of bio-oil (1 : 8). This theory agrees with El Mansouri et al.[54] who found a decreased molecular weight opens up more hydroxyl groups available for consumption during the cure of bio-based ER. In order to evaluate the reaction within this system, experiments were conducted using EPON828 and TPP without the addition of PO and a reaction was not achieved, indicating that PO acts as a cross-linking agent within the system.
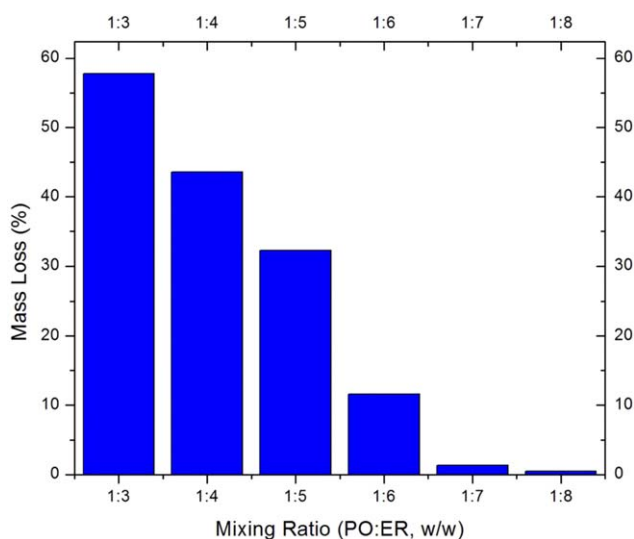
Table III. Glass Transition Temperature (Tg), Crosslinking Density (*n*), and Storage Modulus (E') at 30°C and 160°C

Sample composition (PO:ER)	Tg (°C)	n (mol/m^3)	E' (GPa) at 30°C	E' (GPa) at 160°C
1 : 3	96.5 ± 4.4	583 ± 171	2.34 ± 0.46	0.006 ± 0.002
1 : 4	97.2 ± 2.6	992 ± 90	2.85 ± 0.51	0.011 ± 0.001
1 : 5	109.2 ± 2.7	1127 ± 110	1.07 ± 0.07	0.015 ± 0.005
1 : 6	114.7 ± 4.0	1436 ± 135	1.03 ± 0.06	0.015 ± 0.006
1 : 7	113.6 ± 2.9	1651 ± 46	1.24 ± 0.43	0.016 ± 0.007
1 : 8	120.1 ± 2.0	1891 ± 125	2.55 ± 0.12	0.018 ± 0.006

[a] Values are mean of repeated analysis and numbers after ± are standard deviation.

Figure 4. Proposed reaction mechanism between OH groups of pyrolysis oil and epoxide groups of EPON828 in the presence of TPP (**a**), and the generation of 3-D crosslinked structure (**b**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. Mass loss (wt %) of POBER resin synthesized at different mixing ratios extracted under acetone for 4 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Solvent Resistance of POBER Resin

Figure 5 illustrates the mass loss of POBER resin synthesized at different PO:ER ratios. To determine the solubility of the POBER resin and determine the minimum epoxide content for stability of the final product, an acetone extraction was conducted. Acetone is an effective solvent for PO and therefore removes unreacted PO from the polymer matrix.[23] A decrease in mass loss from 57.74% to 0.49% was observed as the content of EPON828 was increased which indicates that the polymer became more completely reacted, resulting in a less soluble product. Nonaka et al.[48] supported this observation, where lignin was reacted with epoxide to form a three-dimensional cross-linked network, and a decrease in mass loss was reported as more lignin was incorporated to the ER. Auad et al.[2] reacted EPON826 with synthetic phenol at near-stoichiometric ratio, and they observed that no mass loss under acetone extraction occurred at complete crosslinking. In our study, the progressive increase in insolubility, as well as the crosslinking density (Table III), indicates that the stoichiometric ratio was approaching equilibrium and was met at approximately 1 : 7 to 1 : 8 PO:ER ratio. At this point, a three-dimensional network (highly cross-linked network) dominated the composite's structure.

CONCLUSION

POBER was synthesized by mixing PO with commercial ER (EPON828) at different mixing ratios of 1 : 3–1 : 8 (PO:ER, w/w) to investigate the compatibility of PO of loblolly pine as a substitute for phenolic component of ER. Total OHN of PO was calculated to be 10.83 mmol/g by 31P-NMR analysis. It was also calculated that PO has enough number of aliphatic and phenolic OH numbers 5.33 and 2.87 mmol/g, respectively, which makes it a suitable alternative phenol resource to petroleum-based phenols. FT-IR analysis of PO, EPON828 resin, and POBER resin supported that hydroxyl and carbonyl groups in the PO opened up the epoxide rings of EPON828 during curing. DMA of POBER resin suggested that resins synthesized

at 1 : 7 and 1 : 8 mixing ratios had the highest Tg and cross-linking densities, 113–120°C and 1651–1891 mol/m^3, respectively. Moreover, acetone extraction supported the superior crosslinked structure at 1 : 7 and 1 : 8 mixing ratios since around 0.5% mass loss was observed at those mixing ratios. Overall, the system developed herein has the potential to utilize a naturally derived cross-linking agent.

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