Choosing the Right Lignin to Fully Replace Bisphenol A in Epoxy Resin Formulation

Saeid Nikafshar,[a] Jiarun Wang,[b] Kevin Dunne,[c] Prakrit Sangthonganotai,[d] and Mojgan Nejad*[a,c]

Thirteen unmodified lignin samples from different biomass sources and isolation processes were characterized and used to entirely replace bisphenol A (BPA) in the formulation of solubilized epoxy resins using a developed novel method. The objective was to measure the reactivity of different lignins toward bio-based epichlorohydrin (ECH). The epoxy contents of various bio-based epoxidized lignins were measured by titration and 1H NMR spectroscopy methods. A partial least square regression (PLS-R) model with 92% fitting accuracy and 90% prediction ability was developed to find correlations between lignin properties and their epoxy contents. The results showed that lignins with higher phenolic hydroxy content and lower molecular weights were more suitable for replacing 100% of toxic BPA in the formulation of epoxy resins. Additionally, two epoxidized lignin samples (highest epoxy contents) cured by using a bio-based hardener (Cardolite GX-3090) were found to show comparable thermomechanical performances and thermal stabilities to a petroleum-based (DGEBA) epoxy system.

Introduction

Epoxy resins, mainly produced from petroleum-derived chemicals, are used for adhesive, coating, and composite applications due to their versatile properties.[1,2] One of the most common types of epoxy resin is diglycidyl ether bisphenol A (DGEBA), which has excellent chemical and mechanical properties.[1] This resin forms a crosslinked network by adding different hardeners, like polyamines, polyamides, anhydrides, and mercaptans, to cure epoxy resin at different temperatures.[3] In recent years, due to fluctuations in the price of oil, increased greenhouse gas emissions, and health and environmental issues, there have been serious efforts in replacing fossil-fuel based chemicals with bio-based materials.[4–6] Bisphenol A (BPA), which is used as the main raw material in the production of DGEBA epoxy resin, comprises more than 67% of the molar mass of DGEBA.[7] It has detrimental effects on human health and the environment, and has been shown to act as an endocrine disruptor that is highly toxic for living organisms.[5] BPA has been banned for use in food packaging, food-related materials, and baby bottles.[8–10] Therefore, it is of great interest to identify alternative, renewable, and sustainable raw materials that can substitute BPA in the epoxy resin formulation.

Several bio-based aromatic compounds have been used to synthesize epoxy resin, including itaconic acid,[5] eugenol,[11] rosins,[12] gallic acid,[13] vanillic,[14] vanillic acid,[15] as well as lignin.[15–17] Renewable compounds like lignin, which are widely available, sustainable, and inedible, are more desirable, because they do not compete with food resources like other renewable materials like vegetable oils. Lignin is the most abundant aromatic natural polymer, isolated from biomass as a byproduct of the pulp and bioethanol processes.[18,19] Lignin has different hydroxy groups, including aliphatic, phenolic, and carboxylic acid groups. Phenolic OH groups are categorized into three moieties: syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H). Hardwood lignin is composed of G and S units with low H units, while softwood lignin mostly consists of G units with traces of H units.[16] In contrast, lignin from herbaceous plants includes both G and S units and a high amount of H units.[20] Owing to the presence of phenolic hydroxy groups in lignin’s structure, lignin is widely recognized as an alternative raw material to substitute BPA in epoxy resin formulation.[21]

Epoxy resin is conventionally prepared by reacting epichlorohydrin (ECH) with the hydroxy groups of BPA under alkaline conditions and using sodium hydroxide as a catalyst.[3] There are some challenges in using lignin to replace BPA, such as high polydispersity index and molecular weight, different types of hydroxy groups, and low solubility in organic solvents and water.[22] These attributes cause lignin to have lower reactivity toward ECH than BPA and possibly result in resin with lower homogeneity. Lignin can be incorporated into epoxy resin via three different methods: 1) blending with petroleum-based epoxy resin,[23] 2) modification of lignin followed by epoxidation,[24,25] and 3) epoxidation of unmodified lignin.[26–30] Although many studies have focused on utilizing lignin in epoxy resin,[26,27,31,32] they mostly used modified lignin

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[a] S. Nikafshar, Dr. M. Nejad
Department of Forestry
Michigan State University, East Lansing, MI 48824 (USA)
E-mail: nejad@msu.edu
[b] J. Wang
Department of Chemistry
Michigan State University, East Lansing, MI 48824 (USA)
[c] K. Dunne, Dr. M. Nejad
Department of Chemical Engineering and Materials Science
Michigan State University, East Lansing, MI 48824 (USA)
[d] P. Sangthonganotai
Advanced Biochemical (Thailand) Co., Ltd
No. 944 Mittrtown Office Tower, 14th Floor, Rama 4 Road
Wongmai Sub-District, Pathumwan District, Bangkok 10330 (Thailand)
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Lignin characterization

Lignin source and isolation method are the two main factors that affect the composition of lignins and their structures. Table 1 shows the measured physicochemical properties of different lignin samples. In the kraft process, sodium sulfite (Na2S) is used during the pulping process, while soda and organosolv processes use aqueous alkali solution (sulfur-free) and organic solvents, respectively. Overall kraft and soda lignins had higher ash content than organosolv lignins. This is due to residual sodium hydroxide and sodium sulfate that were used during pulping processes and the isolation of lignin from black liquor by using sulfuric acid, as in LignoBoost or Lignoforce methods. Moreover, the use of sodium sulfite in the kraft pulping process contributes to higher sulfur contents compared to soda and organosolv lignin samples.14

On average, softwood lignins had higher molecular weights (average \( M_w = 8300 \) Da) than hardwood lignin (average \( M_w = 6800 \) Da), as expected (Table 1). In softwood, 90% of lignin is composed of coniferyl alcohols, while in hardwoods, the amount of coniferyl alcohol is roughly equal to the amount of sinapyl alcohol. The presence of two methoxy groups on the sinapyl alcohol in hardwood lignin versus one methoxy group in coniferyl alcohol would limit the formation of 5–5 and dibenzodioxins linkages in the hardwood lignin. Therefore, hardwood lignins have a more linear structure and lower molecular weight compared to softwood lignin. Moreover, during the pulping process, some intermolecular linkages (like \( \beta-O-4 \)) in lignin are broken, affecting lignin properties. For example, on average, kraft lignins had lower molecular weights (\( M_w = 7100 \) Da) than organosolv lignins (\( M_w = 10000 \) Da). This could be related to the harsh conditions of the kraft process (high temperature, high pH, and longer time), which might have caused the repolymerization of lignin.42–44

Both the lignin source and extraction method affect the \( T_g \) of lignin (Table 1). \( T_g \) of lignin is increased by decreasing methoxy content. On average, herbaceous lignins (130°C)

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### Table 1. Measured lignin properties.

| Sample ID | Ash content [%] | C [%] | H [%] | N [%] | S [%] | \( M_w \) [Da] | \( M_n \) [Da] | PDI | \( T_g \) [°C] |
|-----------|----------------|-------|-------|-------|-------|----------------|----------------|-----|-------------|
| 1-K-SW    | 0.52 (0.10)    | 62.9  | 5.9   | 0.1   | 1.7   | 1800           | 7000           | 3.9 | 144         |
| 2-K-HW    | 1.39 (0.14)    | 60.5  | 5.8   | 0.2   | 0.3   | 2700           | 12400          | 4.6 | 164         |
| 3-S-HW    | 4.84 (0.11)    | 58.5  | 5.8   | 0.8   | 1.9   | 1900           | 6400           | 3.4 | 158         |
| 4-O-CS    | 0.50 (0.20)    | 63.7  | 5.7   | 0.5   | 0.1   | 1900           | 5380           | 2.8 | 174         |
| 5-O-Ba    | 3.37 (0.04)    | 61.1  | 5.5   | 0.7   | 0.1   | 2300           | 11500          | 5.0 | 130         |
| 6-O-Ps    | 0.88 (0.02)    | 63.9  | 6.6   | 1.8   | 1.1   | 1750           | 9300           | 5.3 | 83          |
| 7-O-HW    | 0.47 (0.02)    | 62.9  | 6.0   | 0.2   | 0.2   | 1800           | 8200           | 4.6 | 79          |
| 8-K-SW    | 0.54 (0.02)    | 62.7  | 6.0   | 0.1   | 1.4   | 2000           | 8700           | 4.4 | 159         |
| 9-K-SW    | 0.65 (0.01)    | 62.9  | 6.0   | 0.1   | 1.3   | 1900           | 7200           | 3.8 | 150         |
| 10-K-HW   | 5.19 (0.01)    | 58.7  | 5.7   | 0.1   | 1.9   | 1600           | 4000           | 2.5 | 167         |
| 11-K-HW   | 1.62 (0.01)    | 60.9  | 5.8   | 0.2   | 0.3   | 1400           | 3200           | 2.3 | 146         |
| 12-O-WS   | 1.73 (0.06)    | 58.1  | 5.8   | 2.1   | 0.2   | 3100           | 15300          | 4.9 | 123         |
| 13-K-SW   | 0.75 (0.02)    | 63.7  | 6.0   | 0.1   | 1.8   | 2000           | 9300           | 4.7 | 143         |

[a] K: kraft, S: soda, O: organosolv, SW: softwood, HW: hardwood, CS: corn stover, Ba: bagasse, PS: peanut shell, and WS: wheat straw. [b] PDI = polydispersity index.
and lignins isolated through organosolv processes (118 °C) had lower $T_g$ than kraft hardwood (143 °C) and softwood (149 °C) lignins.

Figure 1 illustrates the $^{31}$P NMR spectrum of 1-K-SW, which was used to measure different types of hydroxy groups. As suggested by recent studies, for softwoods, the signal integrations of syringyl-OH and condensed 5-substituted phenolic-OH were combined since there is no syringyl in softwood.

Figure 2 shows the hydroxy contents of various lignin samples based on different substitutes. Kraft lignin samples, on average, had higher aliphatic OH (2.14 mmol/g), phenolic OH (3.13 mmol/g), and total OH (5.68 mmol/g) contents compared to the other lignin samples isolated through soda and organosolv processes. The higher aliphatic and phenolic OH contents of kraft lignins are results of the cleavage of phenolic ether linkages ($\beta$-O-4, $\alpha$-O-4, and 4-O-5), then subsequent potential recondensation of non-classical linkages, occur as a result of the severity of the cooking process. In addition, a high amount of 5-substituted OH (condensed phenolic) groups in kraft lignin are further evidence that confirms recondensation of new ether bonds and C–C coupled units. Carboxylic acid content was also higher in most isolated kraft lignins, which could be related to the overlapping of aldehyde groups in the lignin structure, which causes overestimation of carboxylic acid content. The presence of thiol groups in alkaline lignins can also cause a reaction with phospholane reagent that forms thiol-phospholane compounds, leading to the overestimation of carboxylic acid content.

**Lignin epoxidation**

The epoxy contents of different epoxidized lignin were measured by titration and $^1$H NMR methods. Figure 3 shows the $^1$H NMR spectrum of epoxidized lignin (1-K-SW). The results of these tests on all lignin samples, based on epoxy content and epoxy equivalent weight (EEW), are reported in Table 2. Epoxy contents measured by titration are based on three replicates, while epoxy contents based on $^1$H NMR are based on one replicate. As shown, there were no significant differences (p-value: 0.671) between the results of the two methods, which confirms both are reliable methods for measuring the epoxy content of epoxidized lignin samples.

The yields of epoxidation based on the total hydroxy content of lignin are given in Table 2. Samples 4-O-CS and 10-K-SW had the highest yield (89.9% and 66.9%, respectively). In addition, the average numbers of epoxy groups ($n$) in each macromolecule [epoxy content (mol g$^{-1}$) × $M_n$] are given in Table 2. The reactivities of hydroxy (OH) functional groups in lignin toward ECH, in decreasing order, are phenolic-OH > carboxylic acid > aliphatic-OH. It has been reported that the phenol epoxidation mechanism has three steps. During the epoxidation reaction, a phase transfer catalyst (TBAB) transfers...
Figure 2. Hydroxy contents (mmol g⁻¹) of different lignin samples obtained by ³¹P NMR. *K: kraft, S: soda, O: organosolv, SW: softwood, HW: hardwood, CS: corn stover, Ba: bagasse, PS: peanut shell, WS: wheat straw.

Figure 3. ¹H NMR spectrum of epoxidized lignin (1-K-SW).
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Table 2. Properties of epoxidized lignins including epoxy content and the epoxy equivalent weight measured by titration and 'H NMR methods, yield (\%) based on total hydroxy content, and average number of epoxy groups in each lignin macromolecule.

| Sample ID[a] | Epoxy content by titration [\%] | EEW by titration | Epoxy content by 'H NMR [\%] | EEW by 'H NMR | Yield [%] | n |
|---------------|-------------------------------|-----------------|-------------------------------|---------------|-----------|---|
| 1-K-SW        | 9.56 ± 0.26                  | 450             | 9.72                          | 442           | 39        | 4.0 |
| 2-K-HW        | 6.79 ± 0.12                  | 633             | 7.00                          | 614           | 26        | 4.4 |
| 3-S-HW        | 8.59 ± 0.35                  | 501             | 8.21                          | 524           | 39        | 3.5 |
| 4-O-CS        | 12.40 ± 0.31                 | 347             | 12.53                         | 343           | 90        | 5.6 |
| 5-O-Ba        | 5.93 ± 0.13                  | 725             | 5.87                          | 732           | 25        | 3.1 |
| 6-O-PS        | 5.18 ± 0.12                  | 830             | 4.93                          | 872           | 35        | 2.0 |
| 7-O-HW        | 8.75 ± 0.19                  | 491             | 8.93                          | 481           | 42        | 3.7 |
| 8-K-SW        | 7.97 ± 0.15                  | 539             | 7.88                          | 546           | 31        | 3.8 |
| 9-K-SW        | 10.01 ± 0.24                 | 430             | 9.81                          | 438           | 44        | 4.2 |
| 10-K-HW       | 11.27 ± 0.28                 | 381             | 11.50                         | 374           | 67        | 4.1 |
| 11-K-HW       | 12.14 ± 0.15                 | 354             | 11.98                         | 359           | 46        | 3.7 |
| 12-O-WS       | 4.35 ± 0.08                  | 988             | 3.81                          | 1129          | 19        | 2.5 |
| 13-K-SW       | 8.63 ± 0.18                  | 498             | 8.98                          | 479           | 32        | 4.1 |

[a] K: kraft, S: soda, O: organosolv, SW: softwood, HW: hardwood, CS: corn stover, Ba: bagasse, PS: peanut shell, WS: wheat straw.

the phenolate ion into the organic solution. In the second step, deprotonated lignin (phenolate ion) reacts with ECH via two mechanisms: 1) SN2, and 2) ring-opening reactions. In the third step, the chlorinated intermediate is closed in the presence of NaOH to form the epoxy ring. It was found that the hydroxy groups of lignin could only partially react with ECH. The reaction was also incompletely quenched due to side reactions between lignin’s OH groups, ECH, and epoxidized lignin.\(^{[51]}\) This may lead to the formation of ether bonds between epoxidized lignin functional groups and ECH. In addition, unreacted hydroxy groups could potentially react with epoxy groups and form crosslinked products.\(^{[52]}\) The formation of crosslinked epoxidized lignin reduces its solubility in organic solvents, negatively affecting the curing reaction of epoxidized lignin with a hardener.

Samples 2-K-HW, 4-O-CS, 9-K-SW, 10-K-HW, and 13-K-SW had higher \(n\) values than the other lignin samples. The higher \(n\) indicates that the crosslinking density of the cured sample is higher.

The weight of epoxidized lignin after the reaction was precisely measured for 11-K-HW to be 4.8 g. Although lignins 4-O-CS, 10-K-HW, and 11-K-HW all have high epoxy contents, based on the overall data, the organosolv corn stover lignin (4-O-CS) seems to be a better lignin for epoxy resin applications due to its low ash content, low molecular weight, and low polydispersity index. In addition, this lignin has low carboxylic acid content, which will reduce potential hydrolysis and increase the service life of epoxy systems after crosslinking with a hardener.\(^{[53]}\)

Modeling

Partial least-square regression modeling was used to find correlations between different lignin properties and their epoxy contents after epoxidation (reaction with ECH). The PLS model was developed with two PLS components, which had 92% fitting accuracy (\(R^2_Y = \) the explained variation) and 90% prediction ability (\(Q^2_Y = \) the predicted variation) based on a cross-validation method. Two PLS components were shown to be optimal for the model. Figure 4 plots the components’ contributions, showing R2 as an indicator of how well the model fits the measured data for each performance criterion (light blue bars) and \(Q^2\) as an indicator of how well the model can predict the epoxy content of a new lignin sample based on its measured properties (dark blue bars).

According to the loading plot (Figure 5), \(M_n\), \(M_w\), PDI, and nitrogen content have strong negative (opposite side) correlations with epoxy content. In contrast, phenolic hydroxyl content has strong positive correlation (same side) with the epoxy content of lignin. In other words, lignins with lower molecular weights, molecular numbers, PDI, nitrogen, and higher phenolic hydroxy contents are more suitable for replacing BPA in epoxy resin formulation. We believe the reason that higher nitrogen content seems to have a very high negative effect on epoxy content is because there is a strong negative correlation (\(r = −73\%\)) between the nitrogen content of the lignin samples used in this study with their total phenolic hydroxy groups. Rather than higher nitrogen content being a fact that contribute to the reaction of lignin and ECH. It simply indicates that among the lignins used in this study, most of them that had nitrogen content (mainly from annual crops) had relatively lower phenolic hydroxy content, which resulted in lower epoxy content.

DMA analysis of cured samples (Thermodynamic performance)

Thermodynamic performances of lignin-based epoxy and DGEBA-based thermosets cured by GX-3090 (bio-based hardener) were studied by DMA using a single cantilever mode. Figure 6 shows storage modulus, tan \(\delta\), and loss modulus as a function of temperature; these parameters are summarized in Table 3. The storage modulus (\(E'\)) and loss modulus (\(E''\)) represent the elastic and viscoelastic response of a material, respectively. The ratio of loss modulus to storage modulus is tan \(\delta\). The peak temperatures of tan \(\delta\) and loss modulus are usually reported as glass transition temperature, where a network transits from a glassy state to a rubbery state.
The storage moduli \((E')\) of all cured samples ranged between 1.3 to 1.6 GPa at 25°C (Table 3). The storage moduli of lignin-based epoxy networks (1.3–1.4 GPa) were lower than the DGEBA system (1.6 GPa), which could be related to the lower epoxy content of the epoxidized lignins compared to DGEBA resin. This shows that the lignin-based epoxy system had a lower crosslinking density than the petroleum-based epoxy system (DGEBA) prepared using bisphenol A. The organosolv corn stover lignin (4-O-CS) had a much higher storage modulus

![Figure 4. Component contribution plot for the response variable (epoxy content) measured both by titration and \(^1\)H NMR methods.](image)

![Figure 5. Loadings plot of PLS–R modeling of epoxy content based on lignin properties.](image)

| Sample ID         | \(E'\) [GPa, 25°C] | \(E'\) [GPa, 100°C] | \(\tan \delta\) |
|-------------------|--------------------|--------------------|-----------------|
| 4-O-CS/GX-3090    | 1396               | 701                | 181             |
| 11-K-HW/GX-3090   | 1275               | 613                | 173             |
| DGEBA/GX-3090     | 1557               | 331                | 106             |

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than kraft hardwood (11-K-HW). This could be due to the higher average number of epoxy groups ($\bar{n}$) and lower molecular weight of 4-O-CS compared to 11-K-HW. At the higher temperature ($100^\circ C$), the storage moduli of 4-O-CS and 11-K-HW samples were higher than that of DGEBA, possibly due to the higher glass transition temperature of cured lignin-based epoxy systems. The loss moduli ($\mathcal{E}''$) of 4-O-CS and 11-K-HW thermosts were also higher than that of the DGEBA sample at higher temperatures ($120–200^\circ C$), which shows they can better dissipate deformation energy at higher temperatures.[54]

The tan $\delta$ peak gives valuable information regarding cured epoxy networks; generally, higher tan $\delta$ peaks correspond to better fracture toughness and higher $T_g$. The width of tan $\delta$ represents sample homogeneity, with broader peaks indicating less homogeneous samples.[43] Both lignin-based epoxy thermosts showed significantly broader tan $\delta$ peaks, meaning that they are less homogeneous than the DGEBA system, as expected due to the high polydispersity index of lignin compared to BPA. Side reactions at different temperatures[56] as well as multiple functionalities[43] in the system could also result in observing broader tan $\delta$ peaks. Moreover, the glass transition temperatures ($T_g$, recorded from tan $\delta$ profile) of epoxidized lignin samples ($181^\circ C$ and $173^\circ C$) were significantly higher than the $T_g$ of the DGEBA system ($106^\circ C$), which indicates that lignin-based epoxy systems have higher toughness.

**TGA analysis of cured samples (thermal stability)**

Thermal stabilities of cured lignin-based and DGEBA thermosts were evaluated by using thermal gravimetric analysis (TGA; Figure 7).

The temperatures at 5% ($T_{d5\%}$), 30% ($T_{d30\%}$), and maximum weight loss ($T_{\text{max}}$), as well as the statistic heat-resistance index temperature ($T_s$) for different samples are summarized in Table 4. $T_s$ was calculated from $T_{d5\%}$ and $T_{d30\%}$ according to Equation (1), which represents the thermal stability of the crosslinked polymers.[29,55]

![Figure 6. Storage modulus (a), loss modulus (b), and tan $\delta$ (c) of cured epoxidized lignin samples (4-O-CS and 11-K-HW) and DGEBA with GX-3090.](image)

![Table 4. Thermal stability of cured epoxidized lignin and DGEBA networks.](table)
All epoxy thermosets showed two-step degradation profiles, including a considerable weight-loss stage around 400°C and another weight-loss stage at above 500°C. The first stage of degradation is primarily due to the breaking of aliphatic chains and releasing small molecules like CO, CO₂, and water.[54] The second stage of degradation is most likely associated with the degradation of aromatic rings and oxidation of C–C linkages and different functional groups such as methoxy, phenol, and carbonyl.[55] Although the degradation of lignin-based thermosets was started at lower temperatures (241–245°C) compared to the DGEBA thermoset (350°C), the difference was smaller at higher temperatures. According to TGA analysis results (Table 4), T₅₀% values for the lignin-based thermosets were 40–50°C lower than that for the DGEBA thermoset. Moreover, the degradation temperatures of both lignin-based thermosets are remarkably higher than their T₅₀ values (Table 1), indicating that they can be used for applications that do not require high-temperature stability.[56] The statistical heat resistant-indices (Tₛ) of cured lignin-based samples were about 33–36°C lower than Tₛ of cured DGEBA, showing their lower heat tolerance.[57] The epoxy system made with organosolv lignin (4-O-CS) had higher thermal stability than the epoxy made with Kraft hardwood (11-K-HW). This can be explained by higher n of 4-O-CS thermoset, which resulted in an epoxy system with higher crosslinking density. The lower thermal stability of lignin-based thermosets is probably due to the lower crosslinking density of epoxidized lignin and lignin’s lower thermal stability.[58]

Conclusions

This study was focused on evaluating the suitability of different lignins as replacements for bisphenol A (BPA) in epoxy resin formulations. Following previously reported procedures resulted in epoxidized lignins that were insoluble in all tested solvents (such as acetone, dichloromethane, acetonitrile, and dimethyl sulfoxide); therefore, a new method was developed for lignin epoxidation to ensure that epoxidized lignins were soluble in most organic solvents. This enabled us to accurately measure and compare the epoxy content of different lignin samples while also providing a benchmark to formulate fully bio-based epoxy resins. The goal was to evaluate the efficacy of a wide range of commercially available unmodified lignins in replacing 100% of bisphenol A in the reaction with bio-based epichlorohydrin (ECH). Lignins with lower molecular weights (Mₕ) and higher phenolic hydroxy contents had higher reactivities towards ECH. Among tested lignins, an organosolv corn stover lignin (4-O-CS) and two Kraft hardwood lignins (10-K-HW and 11-K-HW) had the highest epoxy contents. Our preliminary data indicated that among tested lignin samples, the organosolv corn stover lignin (4-O-CS) was a better candidate for epoxy resin formulations, owing to its low ash content, low molecular weight, low polydispersity, and high epoxy content. Dynamic mechanical analysis (DMA) showed that the fully bio-based cured systems containing epoxidized lignin and bio-based diamine as a hardener had comparable thermomechanical properties to the petroleum-based epoxy system (diglycidyl ether bisphenol A) but had lower thermal stability based on TGA results. This is an important step forward in establishing the possibility of formulating a fully bio-based epoxy resin using unmodified lignin, bio-based ECH, and bio-based hardener with comparable performance to petroleum-based resins.

Experimental Section

Materials

Thirteen commercially available lignin samples from different plant sources and isolation processes (Table 1) were provided by Advanced Biochemical (Thailand) Co., Ltd. Other chemicals used in this study were: N, N Dimethylformamide (DMF; 99.8%); extra dried, Acros, Acros Organics; tetrabutylammonium bromide (TBAB; Tokyo Chemical Industry Co., LTD, Purity > 98%); bio-based ECH (Advanced Biochemical Thailand Co., Ltd, 99.9%); GX-3090 and DGEBA (EPON 828) were obtained from Cardolite and E. V. Roberts, respectively. Additional reagents were purchased from Fisher Scientific, Alfa Aesar, Sigma-Aldrich, and Acros Organics and were used as received.

Synthesis of epoxidized lignin

First, each lignin sample (4 g) was dissolved in N,N-dimethylformamide (DMF; 20 g) and stirred for 10 min at room temperature (DMF was used as co-solvent since all lignin samples were completely soluble in DMF). Then tetrabutylammonium bromide (TBAB; 0.4 g) and bio-based ECH (40 g) were added to the lignin/DMF solution and stirred for 3 h at 60°C under reflux conditions (Scheme 1). The mixture was then cooled down to room temperature, and 2 wt% NaOH solution (50 mL) containing 1.2 wt% TBAB was gradually added to the mixture dropwise (one drop every 5 s). The reaction then continued at room temperature for 8 h while stirring at 500 rpm. After that, deionized (DI) water (1000 mL) was added to the solution to precipitate epoxidized lignin. The epoxidized lignin was collected by vacuum filtration and washed
several times with DI water to remove formed salt and unreacted ECH. Finally, a vacuum oven was used to dry the epoxidized lignin samples at 40 °C and 76 kPa for 48 h.\textsuperscript{[60]}

Characterization of lignin samples

The ash contents of all lignin samples were measured according to TAPPI T 212 om-93 standard method. Briefly, each oven-dry lignin sample (1–2 g) was added to a pre-weighed crucible and heated in a muffle furnace. The temperature was gradually increased from room temperature to 525 °C at a ramp rate of 5 °C min\textsuperscript{-1} and then kept at 525 °C for 4 h. The molecular weight of lignin samples was measured using gel permeation chromatography (GPC). Since unmodified lignin has very poor solubility in tetrahydrofuran (THF), the mobile phase used in the GPC column, lignin samples were first acetylated to improve their solubility in THF.\textsuperscript{[61]} One gram of each lignin sample was mixed with 40 mL pyridine-acetic anhydride solution (50–50% v/v) and stirred for 24 h at room temperature and 500 rpm. Then acetylated lignin was precipitated with 150 mL hydrochloric acid solution (pH = 1), and the precipitate particles were vacuum filtered (Whatman filter paper grade 1). Next, the residual solids were washed with HCl (1 M) solution three times, followed by DI water several times. Finally, the acetylated lignin samples were left to dry overnight in a vacuum oven at 40 °C. The acetylated lignin samples were dissolved in THF (HPLC grade; 5 mg mL\textsuperscript{-1}), and filtered using a syringe filter (PTFE, 0.45 μm). The filtrate was injected into the GPC system (Waters, Milford, MA, USA), including a separations module (Waters e2695). The mobile phase was THF (HPLC grade), with a 1 mL min\textsuperscript{-1} flow rate. Three 300 mm × 7.8 mm Ultrastyragel columns from Waters (100–10 K, 500–30 K, and 5 K–600 K Å) with THF as the mobile phase were used. Polystyrene standards with molecular weights of 162, 370, 580, 945, 1440, 1920, 3090, 4730, 6320, 9520, 16700, and 42400 Da were used for calibration. The molecular weights of samples were calculated using Empower GPC Software.

The carbon, hydrogen, and nitrogen contents of lignin samples were measured using a PerkinElmer 2400 Series II CHN elemental analyzer (with helium as carrier gas). After calibration of the instrument with K-factors, each sample (2–3 mg) was inserted into the machine with a minimum of four replicates. The sulfur contents of all lignin samples were measured using Inductively coupled plasma optical emission spectroscopy (ICP-OES), iCAP Duo 6000 series, Thermo Fisher, according to the Association of Official Agricultural Chemists (AOAC) official methods of analysis (922.02 and 980.03).\textsuperscript{[62]}

The glass transition temperatures ($T_g$) of the lignin samples were measured using a differential scanning calorimeter (DSC–Q100). Oven-dried lignin (ca. 5–10 mg) was placed on an aluminum pan with a heating rate of 20 °C min\textsuperscript{-1} under a nitrogen flow of 70 mL min\textsuperscript{-1} in a heat/cool/heat cycle from 30 to 200 °C for lignin samples. The second cycle was used to calculate $T_g$.

The hydroxy contents of lignins were measured using $^{31}$P NMR according to a slightly modified reported method by Asgari and Argyropoulos.\textsuperscript{[63]} Dry lignin (ca. 40 mg) was dissolved in an anhydrous pyridine/deuterated chloroform mixture (1.6:1 v/v; 325 μL) and anhydrous DMF (300 μL). Since not all lignins were 100% soluble in the pyridine/chloroform mixture, DMF was added,
which resulted in all lignin samples becoming 100% soluble in \(^{31}\)P NMR solvents. After that, cyclohexanol (100 \(\mu L\), 22 mg mL\(^{-1}\)) in anhydrous pyridine/deuterated chloroform (1:6.1, v/v) was added as an internal standard, and chromium(III) acetylacetone solution (50 \(\mu L\), 5.6 mg mL\(^{-1}\)) in 1.6:1 v/v anhydrous pyridine/deuterated chloroform was added as a relaxation reagent. Finally, phosphorylating reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphosphepin (TMDDP; 100 \(\mu L\)) was added to the mixture. Then, the mixture (600 \(\mu L\)) was transferred to a 5 mm NMR tube, and NMR analyses were performed using an Agilent DDR2 500 MHz NMR spectrometer equipped with 7600AS, running VnmrJ 3.2 A, with a relaxation delay of 5 \(s\), and 128 scans. The hydroxy content of each lignin sample was calculated based on the ratio of the internal standard peak area (cyclohexanol) to integrated areas over the following spectral regions: aliphatic hydroxy groups (149.1–145.4 ppm), cyclohexanol (145.3–144.9 ppm), condensed phenolic units (144.6–143.3; and 142.0–141.2 ppm), syringyl phenolic units (143.3–142.0 ppm), guaiacyl phenolic units (140.5–138.6 ppm), \(p\)-hydroxyphenyl phenolic units (138.5–137.3 ppm), and carboxylic acids (135.9–134.0 ppm).

**Characterization of epoxidized lignins**

**Epoxy content measurement (auto-titration)**

The epoxy content of epoxidized lignin was measured according to a modified version of ASTM D1652-11 using an auto-titrator (Metrohm, 916 Ti-touch Swiss Mode). Owing to the dark color of lignin, it was impossible to use a color-changing indicator; instead, the electric potential was measured to determine the endpoint of the titration. Briefly, 0.2–0.3 g epoxidized lignin was dissolved in 400 mL of glacial acetic acid. The resulting solution was stirred for 5 min to ensure the epoxidized lignin was entirely dissolved in the solution. The titration is based on the in-situ formation of hydrobromic acid by the reaction of perchloric acid with excess tetraethylammonium bromide. Initially, the produced hydrobromic acid (HBr) immediately reacts with epoxy rings; thus, there is no change in potential. After all epoxy rings are consumed, the formed HBr drops the pH and increases the potential of the solution, which is used as the endpoint. The auto-titrator was used to titrate the solution with 0.1 N perchloric acid reagent until the endpoint is used as the endpoint. The auto-titrator was used to titrate the titration. Briefly, 0.2–0.3 g epoxidized lignin was dissolved in 400 mL of glacial acetic acid. The resulting solution was stirred for 5 min to ensure the epoxidized lignin was entirely dissolved in the solution. The titration is based on the in-situ formation of hydrobromic acid by the reaction of perchloric acid with excess tetraethylammonium bromide. Initially, the produced hydrobromic acid (HBr) immediately reacts with epoxy rings; thus, there is no change in potential. After all epoxy rings are consumed, the formed HBr drops the pH and increases the potential of the solution, which is used as the endpoint. The auto-titrator was used to titrate the solution with 0.1 N perchloric acid reagent until the endpoint (Figure 8).

![Figure 8. Auto-titrator used to measure epoxy content of epoxidized lignin.](image)

**Epoxy content measurements (\(^{1}H\) NMR)**

Epoxy contents of epoxidized lignin samples were measured by \(^{1}H\) NMR according to a previously reported method. Each epoxidized lignin sample (ca. 50 mg) was dissolved in 700 \(\mu L\) of deuterated dimethyl sulfoxide (DMSO). As an internal standard, 1,1,2,2-tetrachloroethane (20 mg) was added. NMR analysis was performed using an Agilent DDR2 500 MHz NMR spectrometer equipped with 7600AS, running VnmrJ 3.2 A, with a 10 s relaxation delay, and 64 scans. The epoxy content of each epoxidized lignin was calculated based on the ratio of the following peaks \(\delta\) (ppm, [D] DMSO): 2.77 (m, 1H); 2.92 (m, 2H); 3.41 (m, 1H); 4.32 (dd, 1H), and 4.64 (m, 1H); these peaks are assigned to the epoxy ring chemical shifts and peaks of internal standard (6.89 ppm, 5, 1H). In addition, the average number of epoxy groups in each macromolecule was calculated according to the following Equation (2):

\[
\text{\% epoxy content} = \frac{4300}{\text{Epoxide content (mol g}^{-1}\text{)} \times M_n}
\]

**Curing epoxy resins**

The two epoxidized lignin samples (4-O-CS and 11-K-HW) with the highest epoxy contents and a commercial DGEBA epoxy resin were cured with a bio-based diamine (GX-3090; Scheme 1). The epoxy equivalent weight (EEW) of epoxidized lignin was calculated by using Equation (3):

\[
\text{EEW} = \frac{4300}{\% \text{ epoxy content}}
\]

Each hydrogen of the amine group could react with one epoxy group based on active hydrogen equivalent weight (AHEW), then the stoichiometric ratio between the hardener epoxy resins can be calculated as AHEW/EEW (Table 5). First, epoxidized lignin samples were dissolved in acetonitrile, then a specific amount of GX-3090 was added and mixed according to Table 5. To evaporate the solvent, epoxidized lignin systems were heated at 50°C for 1 h. All samples were cured at 130°C for 2 h and post-cured at 150°C for 1 h (as recommended by the supplier of hardener).

**Chemometric modeling**

UMetric Simca 16.0.2 software was used to model the correlation between lignin properties and their reactivity toward ECH. The partial least square regression (PLS–R) modeling method was used, as it can tolerate highly correlated variables (lignin properties). To build the model, the properties of lignin such as ash content, elemental analysis, hydroxy content, and molecular weight of lignin samples were considered as inputs (X-variables). The epoxy content (measured reactivity of lignins with ECH, using both titration and \(^{1}H\) NMR techniques) were considered as responses or Y-variables.

| Sample ID       | EEW | Mass ratio (epoxy resin/hardener) |
|-----------------|-----|----------------------------------|
| 4-O-CS/GX-3090  | 346.8 | 1:0.21                          |
| 11-K-HW/GX-3090 | 354.2 | 1:0.20                          |
| DGEBA/GX-3090   | 185  | 1:0.37                           |
Thermomechanical properties of cured epoxy systems

The thermomechanical properties of two cured epoxidized lignin samples and a cured DGEBA-based sample were analyzed using a dynamic mechanical analyzer (DMA), a TA Instrument Q800 with a single cantilever under airflow, and a heating rate of 3.0 °C min⁻¹ from room temperature to 250 °C, with a constant deformation frequency of 1 Hz was used to analyze properties of cured epoxy systems. All samples were cured at 130 °C for 2 h and post-cured at 150 °C for 1 h in Teflon molds measuring 35 mm (length) by 12 mm (width) by 3 mm (depth). Samples were polished (by different sandpaper grits 1500, 2000, 2500, 3000, 5000, and 7000) to have smooth surfaces before analysis.

Thermal stability of cured epoxy systems

Thermogravimetric analysis (TGA, TA Analysis, Q100) was carried out to compare the thermal stability of cured lignin-based epoxy samples with a DGEBA-based sample as a reference. Briefly, each sample (5–10 mg) was placed on a platinum pan and heated from 30 to 700 °C, with a constant heating rate of 20 °C, under an airflow of 25 mL min⁻¹ for the sample, and 10 mL min⁻¹ for balance.

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Conflict of Interest

The authors declare the following competition financial interest (s): M. Nejad, and S. Nikafshar are listed as inventors on a related patent (“U.S. Provisional Patent Application No. 63/129,433 (filed December 22, 2020”). As a holder of this patent, we may financially benefit from technology discussed in this paper.

Keywords: bisphenol A • biomass • epoxidation • lignin • polymers

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