

# Use of Polycarboxylic Acid Derived from Partially Depolymerized Lignin As a Curing Agent for Epoxy Application

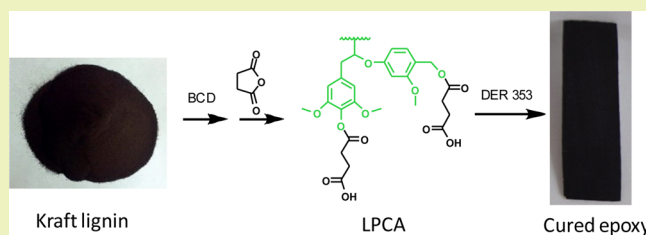
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## Supporting Information

**ABSTRACT:** In this study, Kraft lignin was partially depolymerized through base catalyzed depolymerization (BCD) in supercritical methanol to increase its solubility in organic solvents. The resulting partially depolymerized lignin (PDL) was then converted to lignin-based polycarboxylic acid (LPCA) by reacting with succinic anhydride. The hydroxyl value of PDL and acid value of LPCA were determined using  $^{31}\text{P}$  NMR. LPCA was used as a curing agent to cure a commercial epoxy (DER353). Because LPCA was a soft solid, glycerol tris(succinate monoester) (GTA) which was liquid at room temperature was also synthesized and used as cocuring agent and a diluent for LPCA. Dynamic mechanical properties and thermal stability of the cured epoxy resins were examined using dynamic mechanical analysis and thermogravimetric analysis, respectively. Results showed that curing of DER353 with the LPCA resulted in an epoxy resin with a moderate glass transition temperature ( $T_g$ ) and a storage modulus comparable to the resin cured with the commercial hexahydrophthalic anhydride (HHPA). However, thermal and thermal mechanical properties of the cured resins could be greatly regulated by using GTA or HHPA as a cocuring agent.

**KEYWORDS:** Lignin, Biobased material, Polycarboxylic acid, Curing agent



## INTRODUCTION

With growing concerns over sustainable development and environment impact of petrochemical polymer products, researchers are paying more attention to biobased and eco-friendly materials. Lignin exists in many different biomasses and can constitute up to 25–35 wt % of woody biomass. However, only a small portion of lignin resulted from the pulping process is extracted and converted to other commercial products, and the rest is burned as fuel to recover heat and energy. Because of its complicated branched/cross-linked structure, lignin is insoluble in most organic solvents and incompatible with many other materials. Lignin is biologically synthesized from three precursor monomers which all contain the basic phenylpropane units, so it is considered an important alternative resource for aromatic chemicals, and various lignin liquefactions have been attempted to prepare aromatic compounds and fuel additives.<sup>1–9</sup> However, it is very difficult to cleave the linkages in lignin effectively,<sup>10,11</sup> and the liquefied products are very complicated mixtures.<sup>2,4,12–16</sup> Researchers also make effort to modify lignin via various chemical methods to improve its solubility in reaction media. Lignin contains a certain amount of hydroxyls which can be functionalized by various reactions. Direct methylation and acylation make the lignin more soluble in organic solvents and/or compatible with other materials,<sup>17,18</sup> and partially hydrothermal depolymerization such as phenolation can decrease the molecular weight and then improve its solubility and miscibility.<sup>17–22</sup>

Compared to depolymerizing lignin to monomeric molecules, partial depolymerization and using the modified lignin as

a feedstock for polymer application is a more practical approach in terms of economics and energy efficiency. To date, uses of lignin for phenolics,<sup>1</sup> epoxies,<sup>17,19,23</sup> and polyurethanes<sup>6,20,24,25</sup> have been attempted by many researchers, but the properties of resulting materials are usually not satisfactory when lignin content is high. Hirose et al. prepared a lignin-based polycarboxylic acid by reacting alcoholysis lignin with succinic anhydride. Because ethylene glycol or glycerol was used as the solvent for the alcoholysis lignin, the resulting product was actually a mixture of lignin-derived polyacid and ethylene glycol bis(succinate monoester) or glycerol tris(succinate monoester). That mixture polyacid was used to cure glycerol diglycidyl ether or ethylene glycol diglycidyl ether. Because a flexible epoxy was used and a large amount of flexible cocuring agents was present in the system, the  $T_g$ s of the cured resins were very low (0–20 °C).<sup>26–28</sup> Furthermore, the lignin content was less than 10% in the cured resins.

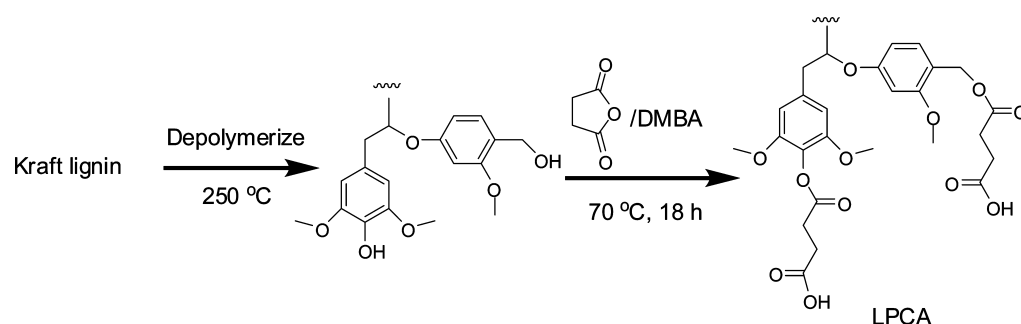
Since most lignins are not soluble in organic solvents like organosolv lignin and most modifications require organic solvents as reaction media, partial depolymerization can significantly modify the solubility of lignin for further applications. Base-catalyzed depolymerization (BCD) is frequently used to liquefy lignin under harsh reaction conditions in the literature, and the resulting products are mainly mixtures of monomeric compounds.<sup>3</sup> In contrast, the

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Scheme 1. Schematic Preparations of Partially Depolymerized Lignin (PDL) and Lignin Polycarboxylic Acid (LPCA) from Kraft Lignin



BCD reaction under mild conditions can also depolymerize lignin with relatively high yield.<sup>29</sup> The product obtained at mild BCD reaction conditions is expected to be a mixture of low molecular weight fragments of lignin. Compared to the phenol used in phenolation liquefaction of lignin which is also to fragment lignin, the solvents used in the BCD process, such as methanol and ethanol, are of low boiling points and can be easily removed.

In this study, KL was partially depolymerized under base catalysis in supercritical methanol, and then, the resulting PDL was converted to lignin-derived polycarboxylic acid (LPCA) by reacting with succinic anhydride (Scheme 1). Application of LPCA as a curing agent for a commercial epoxy was subsequently studied. Since succinic acid can also be obtained from renewable feedstock through fermentation technology,<sup>30</sup> it is reasonable to regard the LPCA as a fully biobased curing agent. Since LPCA was a soft solid at room temperature, glycerol tris(succinate monoester) (GTA) which was liquid at room temperature was also synthesized and used as cocuring agent and a diluent for LPCA. In addition, a commercial liquid curing agent (HHPA) as a reference was also used to cure the same epoxy. Curing kinetics and mechanical properties of the cured epoxy resins were studied using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermogravimetry analysis (TGA). The major objective of this study is to explore the use of PDL for the preparation of curing agents and study the properties of the epoxy resins cured using LPCA.

## MATERIALS AND METHODS

**Materials.** Kraft lignin (KL) Indulin AT (NJ 23) was obtained from Westvaco Co. Ltd., Virginia, USA. Glycerol (>99%), succinic anhydride (SA, >98%), and hexahydrophthalic anhydride (HHPA) were obtained from Sigma-Aldrich, St. Louis, USA. Commercial epoxy DER353 (epoxy equivalent weight: 190–200 g/mol) was provided by Dow Chemicals. 2-Ethyl-4-methyl-imidazole (EMID), dimethylbenzylamine (DMBA; >98%), sodium hydroxide, methanol, acetone, and other solvents were chemical reagents and used as received.

**Partial Depolymerization of Kraft Lignin in Supercritical Methanol.** Partial depolymerization of KL was performed following the base catalyzed depolymerization (BCD) method according to the literature with slight modification.<sup>12,21</sup> A typical example of this process is given as follows. A 4 g portion of KL, 2 g of NaOH, and 50 mL methanol were added to a 100-mL pressure reactor (Parr Inst. Co. Ltd.). The reaction was performed at 250 °C for 90 min under stirring, and the pressure was about 1400 psi. After

cooling to room temperature, the reaction solution was adjusted to be neutral and then filtrated. Subsequently, methanol was evaporated and the residue was dissolved in acetone and filtrated again to further remove the salt. The acetone was evaporated, and the product was dried in vacuum oven overnight to obtain 2.8 g solid PDL (yield 70%). The PDL product was a solid but could be dissolved in some organic solvents like THF, acetone, and methanol.

**Lignin-Derived Polycarboxylic Acids (LPCAs) and Glycerol-Derived Triacid (GTA).** A 10 g portion of PDL (71.5 mmol hydroxyl groups), 7 g succinic anhydride (SA, 70 mmol), and 0.10 g DMBA were dissolved in 50 mL acetone, and the solution was refluxed at 70 °C for 18 h. After acetone was removed under vacuum, a black solid named LPCA was obtained. The acid value of the resulting LPCA was 229 g mol<sup>-1</sup> as determined by <sup>31</sup>P NMR. Similarly, 6.2 g glycerol (0.1 mol), 20 g (0.2 mol) of SA, and 0.27 g DMBA were reacted in a 100-mL flask at 80 °C for 6 h with stirring to obtain glycerol-derived triacid (GTA) with acid value of 133 g/mol.

**Sample Preparation and Characterization.** DER 353, curing, and/or cocuring agents in a predetermined equivalent ratio were heated to 70 °C in an oven and ground to a homogeneous mixture, then 1 wt % EMID as a catalyst was added and mixed again. Curing kinetics was studied using DSC, and the temperature was scanned from room temperature to 250 °C with a heating rate of 10 °C/min. For TGA and DMA characterizations, the samples were cured at 150 °C for 2 h and then at 200 °C for 4 h. Thermogravimetric analysis (TGA) was performed on a TA Q600 instrument by scanning the cured resins from 30 to 600 °C at a heating rate of 10 °C/min in the air atmosphere. Dynamic mechanical analysis (DMA) was carried out on a TA Q800 analyzer under the single cantilever mode and a frequency of 1 Hz at a heating rate of 3 °C/min. The glass transition temperature ( $T_g$ ) was determined from the peak temperature of the damping ( $\tan \delta$ ) curve. Fourier transform infrared (FTIR) spectra were recorded on a NEXUS 670 FTIR spectrometer. The hydroxyl value of PDL and acid value of LPCA was determined using <sup>31</sup>P NMR. The <sup>31</sup>P NMR spectra were obtained on Bruker 300 NMR following a method in the literature.<sup>31,32</sup> Approximately 25.0 mg of lignin derivative with excess 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) were dissolved in a mixed solvent of pyridine/CDCl<sub>3</sub> (1.6:1 v/v). Chromium acetylacetonate was used as relaxation agent and cyclohexanol as internal standard. The <sup>31</sup>P NMR spectra were acquired using an inverse gated decoupling pulse sequence, 90° pulse angle, and 25 s pulse delay.

## RESULT AND DISCUSSION

**Synthesis and Characterization of LPCA.** After partial depolymerization in supercritical methanol, the resulting PDL had a hydroxyl value of 7.15 mmol/g. Moreover, the DPL was soluble in a variety of solvents, which would make functionalization reactions more effectively in solution reactions. Figure 1 shows the  $^{31}\text{P}$  NMR of PDL. It was noted

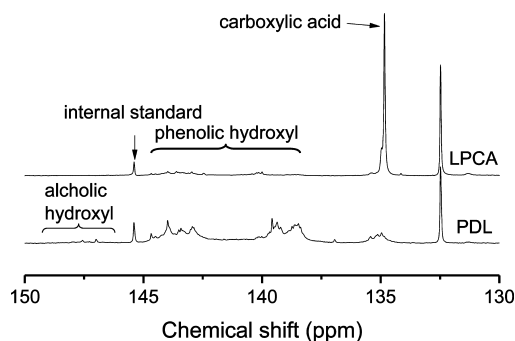


Figure 1.  $^{31}\text{P}$  NMR of PDL and LPCA.

that most of the hydroxyl groups of DPL had reacted with succinic anhydride to form succinate monoesters, meaning that free carboxylic acid groups were introduced to DPL. The acid value of LPCA was found to be 229 g/mol by comparing the peak areas of the acid and internal standard. There was a small amount of unreacted hydroxyl groups in the product because the hydroxyl groups were in slight excess during the reaction. Figure 2 shows the FT-IR spectra of KL, PDL, LPCA, and the

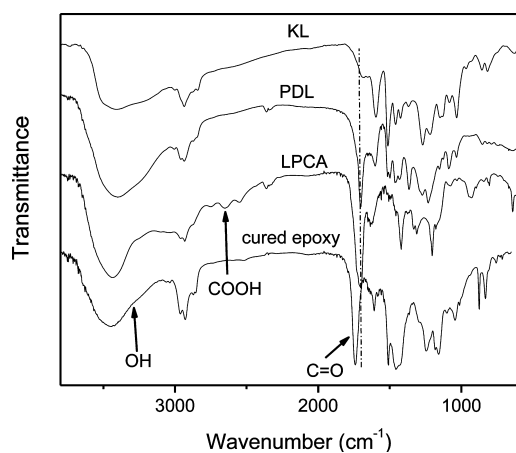


Figure 2. FT-IR spectra of lignin and derivatives.

LPCA cured DER353. Compared to the spectrum of KL, the absorption of the carbonyl groups in PDL at  $1700\text{ cm}^{-1}$  increased, indicating some carbonyl groups were formed during the BCD process. After DPL was reacted with succinic anhydride, the resulting LPCA exhibited another great increase in the absorbance at  $1700\text{ cm}^{-1}$ . At the same time, a new peak appeared at  $2700\text{ cm}^{-1}$ , suggesting that the product contained a lot of carboxylic acid groups.

To confirm that succinic anhydride was reacted completely with the hydroxyls of PDL, phenol as a model compound was reacted with an equal equivalent of succinic anhydride under the same condition and the resulting product was analyzed by DSC. There was neither a peak around the melting point of phenol ( $41\text{ }^\circ\text{C}$ ) nor a peak around that of SA in the DSC

thermogram. Instead, a new melting peak appeared at  $88.4\text{ }^\circ\text{C}$ , which was attributed to the melting of phenol succinate (Supporting Information Figure S1). This result suggested that succinic anhydride could effectively react with phenolic hydroxyl groups.

**Curing using LPCA and Dynamic Mechanical Properties of the Cured Resins.** Curing of DER 353 and LPCA in different equivalent ratios with 1 wt % EMID on the basis of total weight of resin was studied using DSC. Figure 3 shows

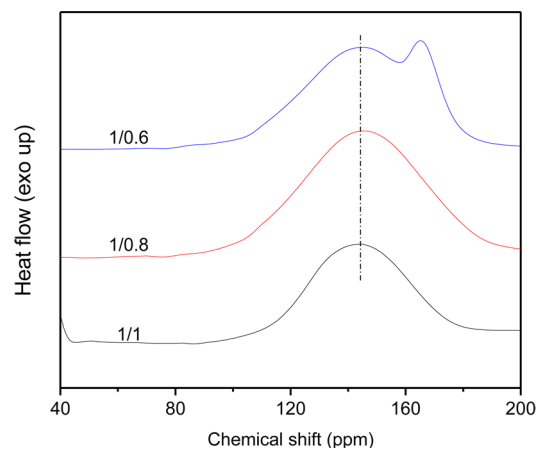
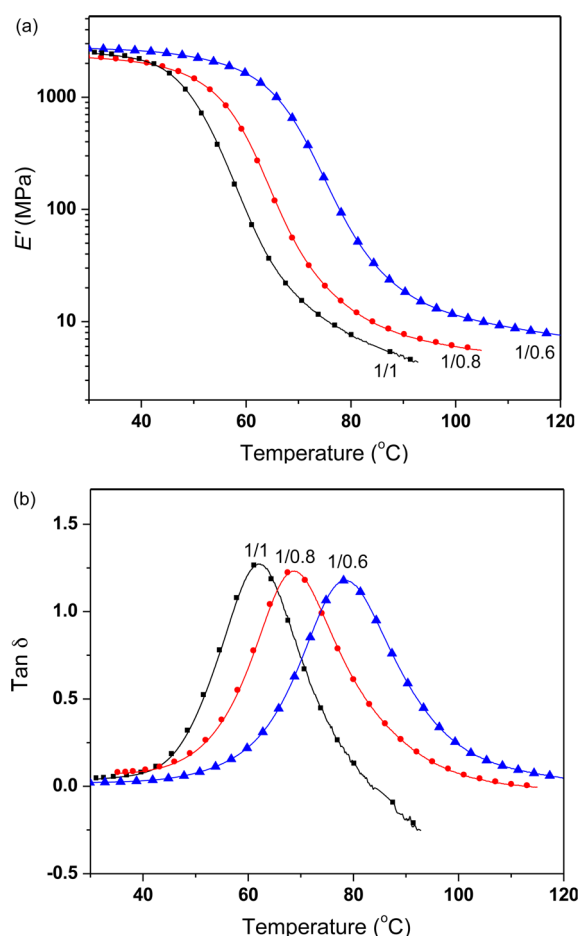


Figure 3. DSC thermograms of curing of DER 353/LPCA with different equivalent ratios.

that the curing for all formulations started and peaked at similar temperatures ( $\sim 145\text{ }^\circ\text{C}$ ). However, when the DER353/LPCA ratio was 1/0.6, another peak appeared at a higher temperature ( $\sim 165\text{ }^\circ\text{C}$ ). This result indicated there probably were two types of reactions involved because of the shortage of carboxylic acid groups (Supporting Information Scheme S1). When the DER353/LPCA ratio was 1/0.8, a broad exothermic peak was noted in the DSC thermograms. As the equivalent of LPCA increased further in the formulation, i.e., at the DER353/LPCA ratio of 1/1, the exothermic peak of curing narrowed slightly. This result might suggest that in the latter two cases the curing involved only one major reaction, i.e., the reaction of the carboxylic acid group and epoxide. In Figure 1, the absorption of carbonyl groups of the unreacted LPCA at  $1700\text{ cm}^{-1}$  shifted to  $1740\text{ cm}^{-1}$  in the cured DER353/LPCA (1/1), while the peak of carboxylic acid groups at  $\sim 2700\text{ cm}^{-1}$  disappeared, indicating that the carboxylic acid group had reacted with the epoxy groups to form ester bonds.

Figure 4 shows the dynamic mechanical properties of the LPCA cured DER353. As the DER353/LPCA equivalent ratio varied from 1/0.6, 1/0.8, to 1/1, the  $T_g$  of the cured resins decreased from  $78.5$ ,  $69.4$ , to  $62.3\text{ }^\circ\text{C}$ , while the storage moduli ( $E'$ s) at room temperature were comparable ( $2.4\text{--}2.7\text{ GPa}$ ). The introduction of the linear succinate monoester enhanced the flexibility of the lignin molecules. Therefore, increasing the content of curing agent (LPCA) in the formulation tended to reduce the  $T_g$  of cured resins. On the other hand, lignin contents in these three samples were 24.8, 29, and 32.3%, respectively.

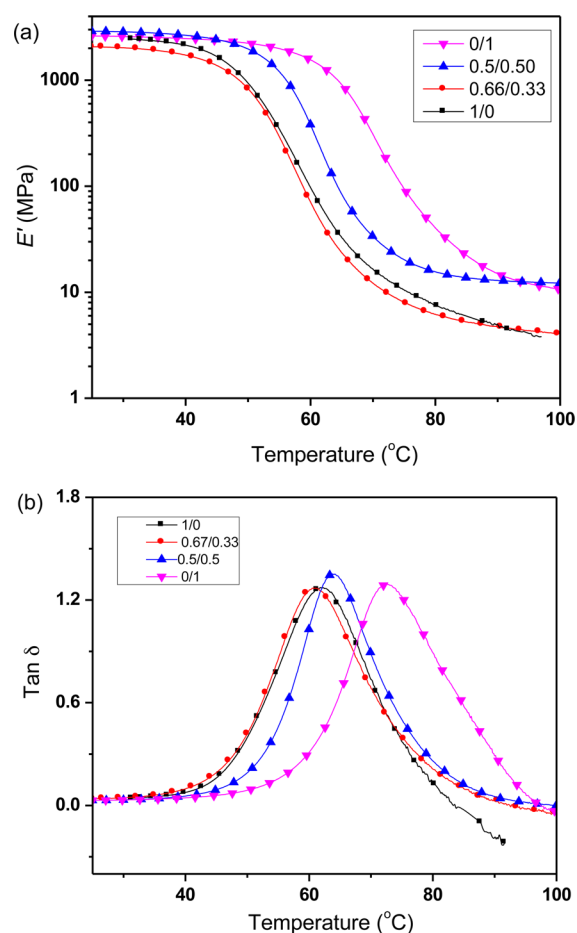
**Effects of Cocuring Agent on Dynamic Mechanical Properties.** Because LPCA was solid, liquid cocuring agents were selected to reduce the viscosity of the resin system. Because LPCA cured epoxies only exhibited some moderate  $T_g$ s, the selected cocuring agent was also intended to increase



**Figure 4.** Storage modulus (a) and  $\tan \delta$  (b) versus temperature for the cured DER 353/LPCA with different equivalent ratios.

the  $T_g$  and stiffen the cured resins. In this study, GTA or HHPA was used as cocuring agent with LPCA to cure DER353. In all formulations, the epoxy and the total curing agent were in equal equivalents. With a 0.5 equiv of cocuring agent, all samples exhibited similar curing temperature ranges with negligible differences in peak curing temperatures (Supporting Information Figure S2). At other LPCA/cocuring agent ratios, the curing thermograms also behaved similarly (data not shown). This result means that addition of cocuring agents did not affect the curing temperature of the epoxy resins, which was most likely due to similar reactions involved during the curing.

Figure 5 shows the dynamic mechanical properties of the DER 353 cured with LPCA/GTA. It was noted that at different LPCA/GTA ratios the storage moduli ( $E'$ s) of cured epoxy resins were comparable. Meanwhile, the  $T_g$ s of the epoxies cured by LPCA/GTA also showed little differences since the DER 353 cured by 1 equiv GTA was just 10 °C higher than that cured by 1 equiv LPCA. At different curing agent ratios, the  $T_g$ s of the cured epoxies are listed in Table 1. GTA seemed to render the cured epoxy a higher cross-link density than LPCA, as evidenced by the higher  $E'$  in the rubbery state. In contrast, use of HHPA as a cocuring agent increased the  $T_g$  of the cured resins gradually (Figure 6) because of the rigid molecular structure and low molecular weight of HHPA. The HHPA cured epoxy exhibited a  $T_g$  of  $\sim 110$  °C, being the highest among all cured epoxies. Figure 6 also shows that the  $E'$  of LPCA cured DER 353 was very similar to that of the pure HHPA cured one. The  $E'$  for the epoxy cured with 1 equiv



**Figure 5.** Storage modulus (a) and  $\tan \delta$  (b) versus temperature of the DER 353 resins cured with LPCA/GTA.

LPCA was 2.44 GPa at 30 °C and was comparable to that of the HHPA cured DER 332 and some other bio-based epoxies reported in our previous study.<sup>33,34</sup>

**Thermal Stability of Cured Resins.** When LPCA was used as the sole curing agent at different stoichiometric ratios, the TGA curves of the cured epoxy resins exhibited similar thermal stability (Supporting Information Figure S3). Figure 7 shows the effects of cocuring agents on the thermal stability of the cured epoxy resins. Compared to the thermograph of the LPCA cured epoxy, replacing half of the LPCA by the cocuring agent had little influence on the degradation temperatures. The reason for this phenomenon is that most of the cross-links in the cured resin are ester bonds that have very similar bond strengths. All samples were decomposed with a negligible amount of residue when the samples were heated to 600 °C. The temperatures at which 5% weight loss was incurred,  $T_{d5}$ , are also listed in Table 1. It is noted that  $T_{d5}$  of the LPCA cured epoxy was 269.3 °C. With GTA as a cocuring agent, the  $T_{d5}$  was increased to  $\sim 300$  °C. This increase in thermal stability was possibly due to the increased cross-linking density caused by the higher functionality of GTA. When HHPA was used as a cocuring agent, the thermal stability increased gradually with HHPA content.

## CONCLUSIONS

Base-catalyzed depolymerization at mild conditions could partially depolymerize lignin which had improved solubility in organic solvent. Compared to the starting lignin, the received



Table 1. Effect of Cocuring Agents on  $T_g$  and Thermal Stability of the Cured Epoxy Resins

cocuring agent and equivalent	LPCA		LPCA/GTA		LPCA/HHPA		
	1	0.67/0.33	0.5/0.5	0/1.0	0.67/0.33	0.5/0.5	0/1
$T_g$ ( $^{\circ}\text{C}$ )	62.3	60.5	63.8	72.3	76.4	85.3	109.9
$T_{ds}$ ( $^{\circ}\text{C}$ )	269.3	302.8	302.3	301.4	282.0	297.2	339.0

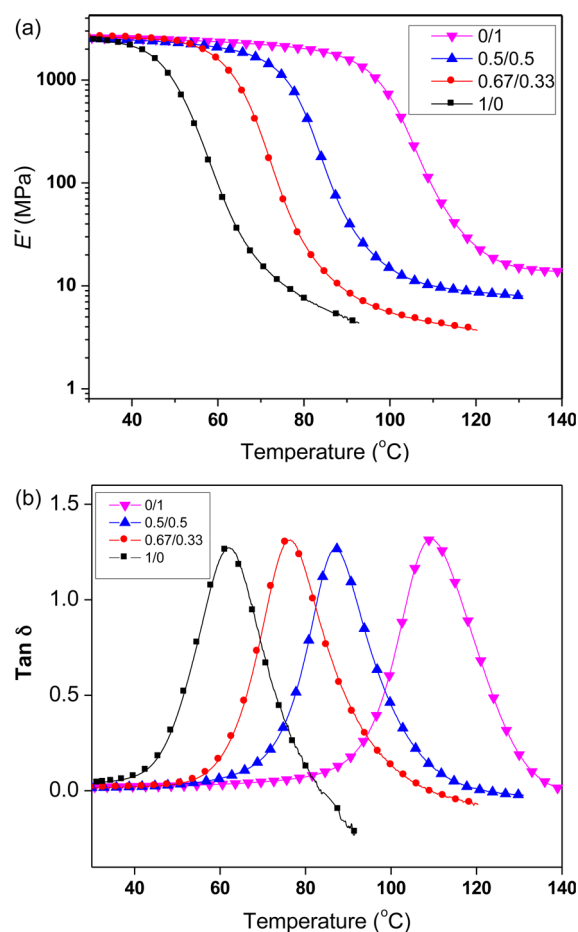
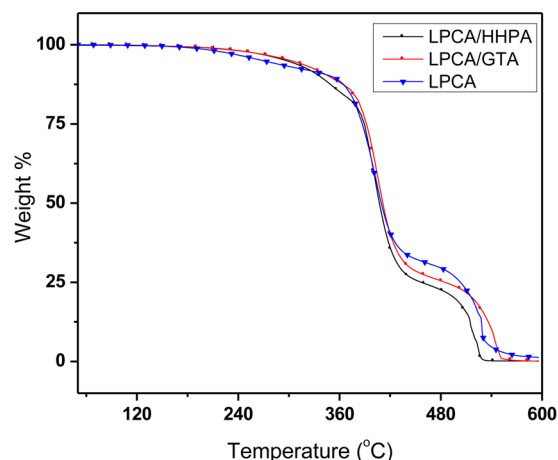
Figure 6. Storage modulus (a) and  $\tan \delta$  (b) versus temperature of the DER 353 resins cured with LPCA/HHPA.

Figure 7. TGA curves of epoxies cured with LPCA (1 equiv) and LPCA/cocuring agent (0.5/0.5 equiv/equiv).

PDL exhibited increased hydroxyl value and reduced molecular weight. The PDL was successfully converted to lignin-based

polycarboxylic acid (LPCA) by reacting with succinic anhydride. LPCA could act as a curing or cocuring agent in the preparation of epoxy resins. It was noted that LPCA could act as a curing agent to cure a commercial epoxy (DER 353) in a similar temperature range as the commercial anhydride type curing agents. The LPCA cured DER 353 resin exhibited a moderate  $T_g$  and comparable storage modulus to that cured with a commercial anhydride curing agent. The solid LPCA could be used together with other liquid curing agents such as glycerol tris(succinate monoester) (GTA) and commercial hexahydrophthalic anhydride (HHPA) to cure epoxies. The result indicated that using mixture of LPCA and a liquid curing agent not only adjusted the viscosity of the resin system but also greatly regulated the dynamic mechanical properties and thermal stability of the cured resins. This study demonstrates that partially depolymerized lignin can serve as a feedstock in the preparation of curing agent and be used for epoxy applications.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The reaction mechanism of glycerol with succinic anhydride, the mechanism of  $^{31}\text{P}$  NMR characterization, curing of epoxy with carboxylic acid, and some DSC and TG curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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