Biobased Divanillin As a Precursor for Formulating Biobased Epoxy Resin

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ABSTRACT: Divanillin (DV), which can be facilely synthesized via vanillin dimerization, was employed as a building block to formulate epoxy resin. DV was synthesized through a novel approach in hot water in only 30 min with a yield of 87.5%. The process involved FeSO₄-catalyzed Na₂S₂O₈-based oxidative coupling of vanillin without any purification, followed by treatment with biobased epichlorohydin. Epoxidized-divanillin (EDV) was cured with the petroleum-based, commercially available hardener isophorone diamine (IPDA) and a biobased-diamine (GX-3090). Complete curing of the mixture was confirmed by Fourier transform infrared (FTIR) spectroscopy and statistical heat resistant-indices (Tₛ), which indicated the formation of cross-linked networks with a thermostability similar to materials prepared with diglycidyl ether bisphenol A (DGEBA, the commercial BPA-based resin). The epoxy resin developed with this new formulation had comparable storage moduli (1.7−2.3 GPa) and similar glass transition temperatures as commercial resins. The epoxy networks exhibited good solvent resistance, while the presence of aldehyde groups in EDV yielded in more readily cleavable ester and amide bonds during the cross-linking process, yielding a resin with improved degradation under acidic conditions. Almost 40% of the segments in networks cured with EDV/IPDA were solubilized in acetone after treatment with 1 M HCl at room temperature in 24 h.

KEYWORDS: Divanillin, Lignin, Bisphenol A, Biobased epoxy, Degradable thermoset

INTRODUCTION

Bisphenol A (BPA), a petroleum-based aromatic epoxy precursor, has been a commercially used building block in epoxy resins for decades. Recently, however, BPA was shown to be an endocrine disruptor, and numerous studies have demonstrated that BPA can leach from water bottles and other packaging products, potentially limiting the use of BPA-based epoxy resins in food storage applications.

Lignin is the most abundant aromatic biopolymer on earth and has been extensively investigated as a versatile renewable feedstock for both biobased fuels and chemicals. Importantly, lignin contains a number of hydroxyl groups that can be cross-linked with epichlorohydrin during the synthesis of epoxies. Unfortunately, the high polydispersity index (PDI) and complicated functionalities of lignin result in epoxies with nonuniform networks and unpredictable properties. Smaller and more homogeneous aromatic fragments obtained from lignin depolymerization, however, including vanillic acid, eugenol, C2-acetals, and vanillin, have been used to produce epoxy thermosets. Usually the monomeric products streams vary dramatically with the lignin source, the isolation process, and the method of lignin depolymerization, and it is therefore difficult to draw general conclusions about the quality of the lignin-based epoxy polymers made from these monomers. Thus, developing a generalizable approach to preparing epoxy resins using lignin-based aromatics would minimize the variables and the potential uncertainties.

Although a variety of aromatic monomers can be generated via lignin depolymerization, only vanillin is currently produced on an industrial scale, making it an especially attractive building block for epoxy resin formulations. In prior applications, vanillin is typically functionalized, often by the addition of a second alcohol required to form epoxy-based aromatics. Alternatively, divanillin (DV) can be synthesized and employed as a precursor for polymers such as polyvanillin, lignin hexamers and octamers, and Schiff base polymers including epoxies. Vanillin is directly coupled through the 5 and 5’ positions, and the absence of any spacers in DV and the shorter segments minimize the rotational motion of the backbone, thereby improving the dynamic performance of the...
networks that are formed. In contrast to the toxic bisphenol A (BPA), DV, a nonhazardous and nontoxic compound, has been approved for food use in the US as a taste enhancer and flavoring.

Currently, DV is synthesized via the oxidative-coupling of vanillin using either iron(III) chloride, laccase, persulfate salts, or electrochemistry. Ideal strategies for improving the economic and sustainable synthesis of DV include: (a) minimizing the number of synthetic steps, (b) using inexpensive catalysts, (c) identifying facile purification processes, and (d) employing water as a green solvent. Sodium persulfate (Na2S2O8), one of the most common water-soluble and inexpensive persulfate salts, is often used in industry for oxidation and polymerization reactions. Therefore, we employed Na2S2O8 in the synthesis of DV to reduce synthesis costs and reaction times, to avoid the use of organic solvents and to minimize the generation of organic wastes.

The degradation of highly cross-linked epoxy resins is usually challenging. It is both economically and environmentally problematic to dispose the thermosets via typical landfills or incineration. It is therefore advantageous to design polymers that are stable and have desirable thermodynamic performance during their service lifetime but are also readily degradable to nontoxic products in a relatively short time frame. Recently, covalent adaptable networks (CANS) have attracted extensive attention by introducing labile bonds, including esters, disulfide bonds, and imines during the cross-linking process. CANS containing these labile bonds can be rearranged by exchange reactions and degraded via acid hydrolysis. Imine bonds, which can be easily obtained from reactions between various amines and aldehydes, have been recognized as a unique dynamic covalent bond in CANS, as it can undergo a reversible degradation process through imine hydrolysis. Moreover, the presence of aldehydes in epoxidized divanillin (EDV) can lead to several other reactions during the curing process. In this report, DV was synthesized via a facile method in hot water and utilized without any purification. The DV was subsequently treated with biobased epichlorohydrin, and the EDV was then cured by a biobased hardener (Cardolite GX-3090) and a common petroleum-based hardener isophorone diamine (IPDA).

Thermal and mechanical performances, solvent resistance, and the degradability of the biobased epoxy networks formed from this process were investigated and compared to corresponding DGEBA-based references.

**EXPERIMENTAL SECTION**

**Materials.** The following materials were purchased and used without further modification: vanillin (99%; Alfa Aesar); ethyl acetate (Fisher Scientific, ACS grade); tetraethylammonium bromide (TBAB, 98%, TCI America); perchloric acid, glacial acetic acid, and NaOH (Fisher Chemical); biobased epichlorohydryd (Advanced Biochemical, Thailand Co.); Na2S2O8 (>98%) and isophorone diamine (>99%); Acros Organic; GX-3090 (Cardolite); DGEBA (EPON 828; E. V. Roberts); and FeSO4·7H2O (>99%), 1,1,2,2-tetrachloroethane, CDCl3, and DMSO-d6 (Sigma-Aldrich).

**Synthesis of Divanillin (DV).** A mixture of 6 g of vanillin (39.5 mmol), 0.2 g of FeSO4·7H2O (0.72 mmol), and 5 g of Na2S2O8 (21.0 mmol, 0.53 equiv) in 400 mL of water was stirred at 80 °C for 30 min. The precipitates were filtered and washed with hot water (80 °C) three times and lyophilized to yield 5.22 g of a gray solid (87.5%).

1H NMR (500 MHz, DMSO-d6): 9.81 (s, 2H), 7.42–7.43 (m, 4H), 3.93 (s, 6H); 13C NMR (126 MHz, DMSO-d6): 191.7, 150.8, 148.5, 128.6, 128.1, 125.0, 109.5, 56.4.

**Synthesis of Epoxidized Divanillin (EDV).** A mixture of 4 g of divanillin (13.2 mmol), 24.5 g of epichlorohydryd (0.265 mol), and 0.4 g of TBAB (1.2 mmol) was stirred at 80 °C for 2 h. NaOH (5 M, 10.6 mL) and 0.4 g of TBAB (1.2 mmol) were then added at room temperature, and the mixture was stirred for an additional 1 h. The liquid was removed by lyophilization, and the resulting residue was washed with DI water and dried in a freeze dryer overnight to yield 4.2 g of a white solid (77%).

1H NMR (500 MHz, DMSO-d6): 9.80 (d, J = 2.2 Hz, 2H), 7.41 (t, J = 2.1 Hz, 2H), 7.35 (d, J = 2.2 Hz, 2H), 4.13 (td, J = 9.5, 4.2, 2.2 Hz, 2H, 2H), 3.87 (d, J = 2.2 Hz, 6H), 2.95 (ddt, J = 13.5, 6.8, 2.1 Hz, 4H), 2.55 (tt, J = 4.6, 3.8 Hz, 2H), 2.32 (dd, J = 4.7, Hz, 4H), 2.3 Hz, 1H); 13C NMR (125 MHz, CDCl3): 191.0, 152.9, 150.9, 148.5, 131.1, 131.6, 127.4, 110.3, 74.1, 56.0, 50.2, 44.1.

**EEW Identification and AHEW Calculation.** The epoxy content of EDV was measured by two different methods. (1) The 1H autotitration method utilized was a modified version of ASTM D1652-11. Briefly, 0.2–0.3 g of EDV was dissolved in 30 mL of dichloromethane and 15 mL of a TBAB solution (100 g of tetraethylammonium bromide in 400 mL of glacial acetic acid). The resulting solution was stirred for 5 min until the EDV was completely dissolved. An autotitrator (Metrohm, 916 Titouch Swiss Mode) was used to titrate the solution with 0.1 M perchloric acid until the endpoint of titration was reached. (2) In the 1H NMR method, a mixture of 50 mg of EDV and 20 mg of internal standards (1,2,2,1,1-trichloroethane) was added to 700 mL of DMSO-d6. NMR analyses were performed using an Agilent DDR2 500 MHz NMR spectrometer (64 scans; 10 s relaxation delay) equipped with a 700A0A autosampler and running Vnmrj 3.2A.

**Preparation of Cured Epoxy Networks.** Both epoxides and DGEBA were cured with IPDA and GX-3090 based on the monomer’s EEW values. First, the mixtures were hand-stirred at room temperature for 1 min, then cured at 120 °C for 2 h and postcured at 150 °C for 1 h.

**Characterizations of Cured Epoxy Networks.** The materials were characterized by Fourier-transform infrared spectroscopy (FTIR) before and after curing to ascertain the chemical structural changes that occurred. Thermal and dynamic performance of the epoxy networks of EDV and DGEBA cured by GX-3090 and IPDA were investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA). Solvent resistance and HCl treatment of these thermostoxes were conducted to study their degradation behavior.

Cured EDV-based and DGEBA-based samples were analyzed with a Spectrum II PerkinElmer Fourier transform infrared spectroscopy (FTIR) before and after curing to ascertain the chemical structural changes that occurred. Thermal and dynamic performance of the epoxy networks of EDV and DGEBA cured by GX-3090 and IPDA were investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA). Solvent resistance and HCl treatment of these thermostoxes were conducted to study their degradation behavior.

**Dynamic mechanical analyses (DMA)** were conducted on a TA Q800 instrument with single cantilever mode under air flow and heating rate of 3.0 °C/min from room temperature to 200 °C at a constant deformation frequency of 1 Hz. The peak temperatures of the tan δ curves were recorded as the glass transition temperature (Tg). Samples were cured at 120 °C for 2 h and postcured at 150 °C for 1 h in Teflon molds with the dimensions 35 mm (l) × 25 mm (w) × 12 mm (h) with 4 cm2 resolutions and 32 scans. Dynamic scanning calorimetry (DSC, TA Analysis, Q100) was used to study the curing rate of EDV and DGEBA. Approximately 5–10 mg of each sample (mixture of resin and curing agent) was placed on an aluminum pan. A ramp test at a heating rate of 10 °C/min under a nitrogen flow of 70 mL/min was performed over 179 temperature range of 25–250 °C.

Thermogravimetric analysis (TGA, TA Analysis, Q50) was used to compare the thermal stability of cured EDV-based and DGEBA-based materials. About 5–10 mg of each sample was placed on a platinum pan and heated from 30 to 700 °C, with a heating rate of 20 °C/min under an air flow of 25 mL/min for the sample and 10 mL/min for balance.

Dynamic mechanical analyses (DMA) were conducted on a TA Q800 instrument with single cantilever mode under air flow and heating rate of 3.0 °C/min from room temperature to 200 °C at a constant deformation frequency of 1 Hz. The peak temperatures of the tan δ curves were recorded as the glass transition temperature (Tg). Samples were cured at 120 °C for 2 h and postcured at 150 °C for 1 h in Teflon molds with the dimensions 35 mm (l) × 12 mm (w) × 5 mm (t). The samples were then cut and polished to the desired rectangular dimensions (length × width × thickness = 30 mm × 12 mm × 1.2 mm) before testing.
Scheme 1. Synthesis of DV and EDV from Vanillin

**RESULTS AND DISCUSSION**

Employment of divanillin (DV) as a building block in formulating epoxy thermosets has been previously reported by Savonnets et al., in which the synthesis of DV was performed in the presence of laccase (in an acetone/buffer solution for 24 h). Additionally, the aldehyde groups in DV were reduced to hydroxyl groups to create more reactive sites for reaction with epichlorohydrin. Inspired by prior work, in the present study DV was synthesized in hot water within 30 min in which the prepared DV, in contrast with previously published data, still contained two aldehyde groups on its aromatic structures (Scheme 1). The presence of aldehyde groups in an unmodified DV provided an additional benefit of creating an epoxy network that can be degraded by mild acid hydrolysis after its service life, resulting in a cured epoxy network that is inherently different from earlier work, especially in the use of biobased epichlorohydrin and curing agents in the formulation of cured epoxy systems.

**Synthesis of Divanillin-Based Epoxy Precursors (DV and EDV).** Synthesis of DV was accomplished via oxidative coupling of vanillin in aqueous solution at 80 °C using Na₂S₂O₈ and FeSO₄ as a catalyst (Scheme 1), a procedure modified from previously published reports. Maintaining an elevated temperature (80–100 °C) was critical to complete the coupling reaction in only 30 min, as the previous method required 5 days at 50 °C. Significantly, as opposed to further modifying the DV, we then used the DV directly without any purification to synthesize EDV, following the method described by Fache et al. Although, there is still concern around the toxicity of biobased epichlorohydrin (ECH), it is widely used in industry and there are well-established methods for removing residual epichlorohydrin by quenching with NaOH and washing the product with excess water. The NMR spectra of epoxidized divanillin (EDV) confirmed the complete removal of epichlorohydrin (Figure S3–S4).

**EEW Identification and AHEW Calculation.** The epoxy contents (EC%) of EDV were measured to be 19.1% (titration method) and 19.02% (¹H NMR method), respectively, and the average (19.0%) was used to calculate the ratio of epoxy resin to various curing agents. The epoxy equivalent weights (EEW) of DGEBA and EDV were calculated to be approximately 185 and 225 g/eq., respectively, by the following equation (eq 1):

\[
\text{EEW} = \frac{4300}{\text{EC%}}
\]

Each amine hydrogen that reacts with one epoxy group corresponds to an active hydrogen equivalent weight (AHEW), and the stoichiometric ratios between the curing agents and epoxy resins can be calculated as AHEW/EEW (see Table 1).

**Table 1. Formulation of Different Epoxy Samples**

<table>
<thead>
<tr>
<th>curing agents</th>
<th>AHEW</th>
<th>DGEBA/amines</th>
<th>EDV/amines</th>
</tr>
</thead>
<tbody>
<tr>
<td>GX-3090</td>
<td>69</td>
<td>1/0.37</td>
<td>1/0.31</td>
</tr>
<tr>
<td>IPDA</td>
<td>42</td>
<td>1/0.23</td>
<td>1/0.19</td>
</tr>
</tbody>
</table>

**Curing Reactions of Epoxy Networks.** The diamines GX-3090 and IPDA were used to cure the synthesized EDV (Scheme 1). Notably, multiple reactions likely occur during the curing process due to the presence of different functional groups (aldehyde and epoxide) in EDV. Imine bonds can be introduced through the reaction of aldehyde group in EDV with the diamine (see Scheme 2, pathway 1). Moreover, in addition to the production of imine bonds, other dissociable bonds can also be formed. Amide bonds can be generated by the oxidation of methylene group or the newly formed OH group in air under elevated temperatures during the hardening process (Scheme 2, pathway 2). In addition, after the oxirane ring opens, the newly formed alkoxides can presumably behave as nucleophiles and further react with the aldehyde groups during the hardening process to form semi acetals, eventually leading to ester bonds (Scheme 2, pathway 3). Importantly, amide, imine, and ester bonds are all easily dissociable under appropriate acidic conditions, and these reactions will therefore yield a highly degradable epoxy network regardless of the specific reaction pathways.
FTIR Analysis. The curing degree of epoxy networks of DGEBA and EDV cured by GX-3090 and IPDA were characterized by FTIR. The disappearance of peaks at 913 cm\(^{-1}\) corresponding to the oxirane rings\(^49\) (Figure 1a,b) and the peaks at 1690 cm\(^{-1}\) corresponding to C=O from benzaldehydes\(^42\) (Figure 1b), in conjunction with the appearance of bands associated with the amino groups (N-H)\(^33\) at 1603 cm\(^{-1}\) suggested the complete curing of BPA and EDV by GX-3090 and IPDA (Figure 1). Notably, no significant peak associated C=N (~1635 cm\(^{-1}\))\(^33\) were observed. Instead, the new bands at 1665 cm\(^{-1}\) (Figure 1b, red trace) are likely attributed to the C=O of amides\(^47,50\) and the bands at 1720 (Figure 1b, black trace) and 1742 cm\(^{-1}\) (Figure 1b, red trace) were assigned to the C=O bands in the newly formed esters.\(^28,51,52\)

Curing Performance (DSC Analysis). The curing behavior of EDV-based and DGEBA-based epoxies was investigated by DSC (Figure 2). Values for the onset curing temperature \(T_{\text{onset}}\), the peak curing temperature \(T_p\) and the reaction enthalpy \(\Delta H\) are summarized in Table 2. EDV-based materials displayed slightly lower onset temperatures than DGEBA-based samples, suggesting that EDV is slightly more reactive, presumably due to the presence of aldehyde groups. Both EDV-based mixtures tended to cure at relatively higher temperatures, with exotherms ranging from 120 to 144 °C, compared to that of DGEBA-based mixtures (exotherms ranging from 110 to 130 °C). EDV-based mixtures exhibited lower reaction enthalpies comparing to DGEBA-based materials (374–405 J/g). Homogenous mixtures were difficult to generate due to the high viscosity of crude EDV and curing reactions might have started when the EDV was prewarmed in order to reduce the viscosity during mixing with the diamines.
Competing reactions of aldehydes and epoxies with amines may have also contributed to the lower reaction enthalpies. Shoulders were generally observed before the exothermal peak in the curing profiles of the EDV-based samples, most likely due to the different reactivities of the aldehyde and the epoxy groups toward the diamines.42

Thermomechanical Performance (DMA Analysis).

Thermomechanical performances of DGEBA-based and EDV-based epoxy thermosets were investigated by DMA using a single cantilever mode. The storage modulus, tan δ, and the loss modulus are shown in Figure 3 as a function of temperature and are summarized in Table 3. The storage modulus (E') represents the elastic response of a material and the loss modulus (E'') is its viscous response. tan δ is the ratio of the loss modulus and the storage modulus, and the peak temperature of tan δ or the loss modulus is usually recorded as the glass transition temperature (Tg), indicating the network transits from a glassy status to a rubbery stage.

The storage moduli (E') of all cured materials ranged between 1.6 to 2.5 GPa and dropped to around 0 MPa between 106 to 140 °C. Though the storage modulus of networks cured by EDV/IPDA (Figure 3a, solid red) is lower than that of DGEBA/IPDA (Figure 3a, dash red), EDV cured with the biobased diamine GX-3090 (Figure 3a, solid green) exhibited a significantly higher storage modulus than did DGEBA/GX-3090 (Figure 3a, dash green). Moreover, the storage modulus of samples cured from the EDV/IPDA system is comparable to that of samples cured from DGEBA/IPDA across the temperature range until 100 °C (Figure 3a, solid and dash red).

It was anticipated that the large chain of GX-3090 with two unsaturated bonds, in contrast to the small structure of cyclic aliphatic IPDA (Scheme S1), would result in epoxy resins with lower storage modulus (higher elasticity at room temperature). This explains the higher storage modulus of DGEBA/IPDA (2.5 GPa) compared to DGEBA/GX-3090 (1.6 GPa).

Surprisingly, however, the storage modulus of epoxidized divanillin with GX-3090 (EDV/GX-3090, 2.3 GPa) was significantly higher than EDV/IPDA. We suspect the aldehyde groups in EDV may react with the phenolic group of GX-3090, resulting in a more rigid structure with enhanced mechanical properties for EDV/GX-3090 (Scheme S2).

The tan δ peak provides important information about the cured epoxy networks. Typically, a higher tan δ peak represents improved fracture toughness.23,53 Clearly, EDV/IPDA networks exhibited a notably higher peak (Figure 3b, solid red) than did other three networks. The width of tan δ reflects the sample homogeneity; the sharper and narrower the peak, the more homogeneous the sample.23 DGEBA/IPDA displayed a significantly broader tan δ profile than the others, indicating that it is less homogeneous. When the biobased amine GX-3090 was used as the hardener; however, the EDV network displayed tan δ peaks as sharp as the DGEBA network, indicating higher homogeneity of these samples (Figure 3b, solid and dash green).

Table 2. Curing Behaviors of Different Epoxy Systems

<table>
<thead>
<tr>
<th>epoxy systems</th>
<th>T_onset (°C)</th>
<th>T_peak (°C)</th>
<th>ΔH (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDV/GX-3090</td>
<td>72</td>
<td>123</td>
<td>221</td>
</tr>
<tr>
<td>EDV/IPDA</td>
<td>59</td>
<td>89</td>
<td>24</td>
</tr>
<tr>
<td>DGEBA/GX-3090</td>
<td>128</td>
<td>144</td>
<td>405</td>
</tr>
<tr>
<td>DGEBA/IPDA</td>
<td>68</td>
<td>109</td>
<td>374</td>
</tr>
</tbody>
</table>

Table 3. DMA Performance of DGEBA and EDV Cured by 3090 and IPDA

<table>
<thead>
<tr>
<th>cure system</th>
<th>E' (GPa)a</th>
<th>Tg (°C)b</th>
<th>Tg (°C)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDV/GX-3090</td>
<td>2.3</td>
<td>103</td>
<td>91</td>
</tr>
<tr>
<td>EDV/IPDA</td>
<td>1.7</td>
<td>123</td>
<td>112</td>
</tr>
<tr>
<td>DGEBA/GX-3090</td>
<td>1.6</td>
<td>106</td>
<td>97</td>
</tr>
<tr>
<td>DGEBA/IPDA</td>
<td>2.5</td>
<td>140</td>
<td>116</td>
</tr>
</tbody>
</table>

aStorage modulus at room temperature measured by DMA.
bGlass transition temperature recorded as the peak of the loss modulus.
cGlass transition temperature recorded as the peak of tan δ.
The tan δ profile of the EDV/IPDA network was broader than usual, and although the $T_g$ was recorded at 123 °C, a significant shoulder at 140 °C was observed (Figure 3b, solid red). Residue reaction sites that react at different temperatures as well as the multiple functionalities in the network could both be responsible for the broadened tan δ profiles. In addition, the observed shoulder at 140 °C indicates a two-stage transition and agrees with the fact that when IPDA was employed as the hardener, the $T_g$ (recorded from the loss modulus profiles) of both EDV-based and DGEBA-based networks (Figure 3c, red and dash red) appeared to be very close (112 and 116 °C, respectively). The loss modulus ($E''$) measures the energy dissipated as heat (viscous response of a material), so in this respect, EDV-based and DGEBA-based networks exhibited similar abilities to dissipate deformation energy. Significantly, when the biobased amine GX-3090 was used to cure EDV, the $T_g$ from both the peak of tan δ and the loss modulus appeared to be very similar to the DGEBA references, indicating similar performance properties.

**Thermal Stability Analysis (TGA Analysis).** Thermal stabilities of cured epoxy-based and DGEBA-based epoxy networks were investigated with TGA (Figure 4). Statistical heat resistant-indices ($T_r$) were calculated from temperatures corresponding to 5% ($T_{5\%}$) and 30% ($T_{30\%}$) weight loss in eq 2 and summarized in Table 4. The maximum weight loss ($T_{\text{max}}$) values are reported in Table 4 as well.

$$T_r = 0.49(T_{5\%} + 0.6(T_{30\%} - T_{5\%})) \quad (2)$$

Two-step degradation profiles were observed for all thermosets produced under air, including a fast weight loss stage from approximately 230 to 480 °C, and another 30–40% weight loss stage above 500 °C. The first stage is primarily associated with the breaking of aliphatic chains and the loss of small molecules such as CO, CO$_2$, and water. Weight loss above 500 °C is most likely due to oxidation (combustion) of the C–C linkages and other functional groups (i.e., carbonyl and phenol) and/or the degradation of aromatic rings.

Although EDV-based thermosets started to degrade at lower temperatures (270–310 °C) than DGEBA-based materials (350–370 °C), they appeared to be more stable at higher temperatures than did DGEBA-based materials. As shown in Table 4, the $T_{\text{max}}$ of EDV-based thermosets are approximately 10–30 °C higher. Moreover, the degradation temperatures of both EDV-based thermosets are significantly higher than their $T_g$ (see Table 3), which should not affect the use of these resins in low temperature applications. All DGEBA networks showed maximum weight loss ($T_{\text{max}}$) at around 385 °C, while $T_{\text{max}}$ was approximately 50 °C higher (i.e., 435 °C) for networks cured by EDV/GX-3090. The statistical heat resistant-indices ($T_r$) of cured samples from crude EDV (175–176 °C) appears only slightly lower (7–10 °C) than those of the commercial samples (182–186 °C), indicating their similar heat tolerance. It is interesting that there is still residue remaining at 700 °C from the EDV/GX-3090 sample (Figure 4a, solid green). We surmise that the incomplete combustion may be due to carbonization of EDV/GX-3090 at higher temperatures.

**Solvent Resistance.** Solvent resistance tests of these EDV-based networks were performed following a procedure modified from a previously published method. Briefly, the thermosets cured by EDV/GX-3090 and EDV/IPDA were immersed in 6 solvents (water, DMF, acetone, THF, EtOH, and ethyl acetate) at room temperature for 4 days. Figure 5 displays how the samples appeared after 4 days in the various solvents. Importantly, both biobased epoxy resin formulated with EDV had excellent solvent resistance even after 4 days of immersion in water, acetone, tetrahydrofuran (THF), ethanol (EtOH), and ethyl acetate, and it exhibited only a slight weight loss (~4%) in DMF after 4 days.

**Degradation Analysis.** After their service life, current commercial epoxy networks are usually disposed in a landfill or incinerated. The high cost and greenhouse gases released from these disposal methods presents both economic and environmental challenges. Rapid chemical degradation of networks...
back to their initial building block constituents or to other useful, nontoxic products is an obvious promising alternative path.\textsuperscript{35} Notably, the dissociable amide and ester bonds in the backbone of these biobased epoxy thermosets described here can theoretically be cleaved under mild acidic conditions.\textsuperscript{33,42}

Degradation tests of epoxy networks cured by EDV/IPDA and DGEBA/IPDA were therefore conducted with 1 M HCl at room temperature for 24 h (Figure 6 and Table 5).

\begin{table}[h]
\centering
\caption{Weight Loss of Networks of DGEBA and EDV Cured by IPDA after Treatment with 1 M HCl for 24 h in Different Solvents at Room Temperature}
\begin{tabular}{|c|c|c|c|c|}
\hline
resin & H\textsubscript{2}O & DMF & EtOH & acetone \\
\hline
EDV & 15.5 & 30.3 & 29.5 & 37.4 \\
DGEBA & 4.0 & 2.5 & 7.0 & 3.5 \\
\hline
\end{tabular}
\end{table}

While the ether bonds in polymers composed of DGEBA/IPDA were only slightly cleaved, leading to a marginal weight loss of 3–7% following treatment with HCl (Figure 6b), significant cleavage of the network cured by EDV/IPDA was observed with far fewer solids remaining (62%–84%). The cleavage of the network cured by EDV/IPDA was especially pronounced when acetone was used, with almost 40% of the segments being solubilized (Figure 6a). The disappearance of the bands at 1720 cm\textsuperscript{-1} associated with the carbonyl in ester bonds, the appearance of the peaks at 1743 cm\textsuperscript{-1} corresponding to C=O in acids, and the appearance of the broad peak at 2500–2800 cm\textsuperscript{-1} all indicated full hydrolysis of esters to acids (Figure 7). We tested the degradation of EDV/GX-3090 as well, but unfortunately, significant portions of this sample were not solubilized in acid. We suspect this is due to the additional reactions between the aldehydes in EDV and the phenol in GX-3090, which presumably led to a more rigid skeleton. Additional work is needed to optimize the formulation to improve its degradability.

\section{CONCLUSIONS}

Utilization of renewable biomass as building blocks to replace toxic bisphenol A (BPA) in epoxy resin formulations was the major motivation of this study. Oxidative coupling of vanillin was shown to be an effective method to produce divanillin in water at elevated temperatures (80 °C) in only 30 min. The epoxy resins formulated via the reaction of divanillin with biobased epichlorohydrin and cured with a biobased hardener (GX-3090) exhibited excellent thermal stability, mechanical properties, and solvent resistance when compared with commercial bisphenol A epoxy resin. The presence of aldehyde and epoxy groups in the biobased epoxy (EDV) created an opportunity to employ mild acid to degrade the resin after its service life. Moreover, the C–C aromatic bonds in divanillin...

Figure 5. Immersion of epoxy networks cured by EDV/GX-3090 (a) and EDV/IPDA (b) in different solvents at room temperature for 4 days.

Figure 6. Treatment with 1 M HCl in acetone of networks cured by (a) EDV/IPDA and (b) DGEBA/IPDA.

Figure 7. FTIR spectrum of a network cured by EDV/IPDA before and after HCl (1M) treatment in acetone for 24 h.

GX-3090 as well, but unfortunately, significant portions of this sample were not solubilized in acid. We suspect this is due to...
(DV) are analogous to the 5–5 linkage in lignin that is usually challenging to cleave. Thus, the application of DV in epoxy resins can provide insight into future lignin valorization strategies.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c02351.

1H and 13C spectra of divanillin (DV) and epoxidized divanillin (EDV) (Figures S1–S4); proposed cross-linking reactions of DGEBA/IPDA and EDV/IPDA (Scheme S1); proposed additional reaction of EDV/GX-3090 (Scheme S2) (PDF)

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