

1 Biobased Divanillin As a Precursor for Formulating Biobased Epoxy Resin

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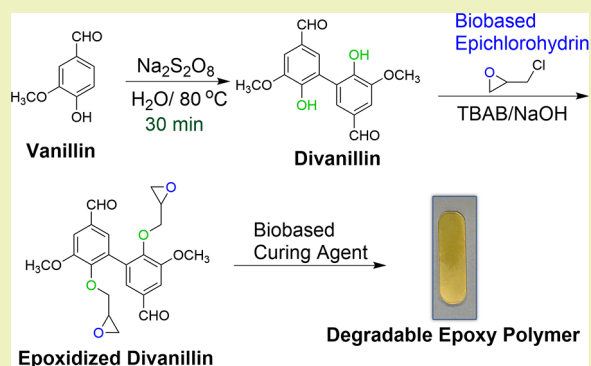
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4 **ABSTRACT:** Divanillin (DV), which can be facilely synthesized via
5 vanillin dimerization, was employed as a building block to formulate
6 epoxy resin. DV was synthesized through a novel approach in hot water
7 in only 30 min with a yield of 87.5%.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

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



23 ■ INTRODUCTION

24 Bisphenol A (BPA), a petroleum-based aromatic epoxy
25 precursor, has been a commonly used building block in
26 epoxy resins for decades.¹ Recently, however, BPA was shown
27 to be an endocrine disruptor,² and numerous studies have
28 demonstrated that BPA can leach from water bottles and other
29 packaging products,³ potentially limiting the use of BPA-based
30 epoxy resins in food storage applications.

31 Lignin is the most abundant aromatic biopolymer on earth
32 and has been extensively investigated as a versatile renewable
33 feedstock for both biobased fuels and chemicals.^{4–8}
34 Importantly, lignin contains a number of hydroxyl groups
35 that can be cross-linked with epichlorohydrin during the
36 synthesis of epoxies. Unfortunately, the high polydispersity
37 index (PDI) and complicated functionalities of lignin result in
38 epoxies with nonuniform networks and unpredictable proper-
39 ties. Smaller and more homogeneous aromatic fragments
40 obtained from lignin depolymerization, however, including
41 vanillic acid,⁹ eugenol,¹⁰ C2-acetals,¹¹ and vanillin,^{6,12–15} have
42 been used to produce epoxy thermosets. Usually the
43 monomeric products streams vary dramatically with the lignin
44 source, the isolation process, and the method of lignin
45 depolymerization, and it is therefore difficult to draw general
46 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,⁷ only vanillin is currently
produced on an industrial scale, making it an especially
attractive building block for epoxy resin formulations.⁶ In prior
applications, vanillin is typically functionalized,^{13,16,17} often by
the addition of a second alcohol required to form epoxy
resins.¹⁸ Alternatively, divanillin (DV) can be synthesized and
employed as a precursor for polymers such as polyvanillin,¹⁹
lignin hexamers and octamers,²⁰ and Schiff base polymers,²¹
including epoxies.²² Vanillin is directly coupled through the 5
and 5' positions, and the absence of any spacers in DV²² and
the shorter segments minimize the rotational motion of the
backbone, thereby improving the dynamic performance of the

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64 networks that are formed.²³ In contrast to the toxic bisphenol
65 A (BPA), DV, a nonhazardous and nontoxic compound,²⁴ has
66 been approved for food use in the US as a taste enhancer²⁵ and
67 flavoring.²⁶

68 Currently, DV is synthesized via the oxidative-coupling of
69 vanillin using either iron(III) chloride,²⁷ laccase,^{22,24,28}
70 persulfate salts,^{29–31} or electrochemistry.¹⁹ Ideal strategies for
71 improving the economic and sustainable synthesis of DV
72 include: (a) minimizing the number of synthetic steps, (b)
73 using inexpensive catalysts, (c) identifying facile purification
74 processes, and (d) employing water as a green solvent. Sodium
75 persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), one of the most common water-soluble
76 and inexpensive persulfate salts, is often used in industry for
77 oxidation and polymerization reactions.³² We therefore
78 employed $\text{Na}_2\text{S}_2\text{O}_8$ in the synthesis of DV to reduce synthesis
79 costs and reaction times, to avoid the use of organic solvents
80 and to minimize the generation of organic wastes.

81 The degradation of highly cross-linked epoxy resins is
82 usually challenging. It is both economically and environ-
83 mentally problematic to dispose the thermosets via typical
84 landfills or incineration.^{33,34} It is therefore advantageous to
85 design polymers that are stable and have desirable thermody-
86 namic performance during their service lifetime but are also
87 readily degradable to nontoxic products in a relatively short
88 time frame.³⁵ Recently, covalent adaptable networks (CANs)
89 have attracted extensive attention by introducing labile bonds,
90 including esters,^{34,36–38} disulfide bonds,^{39–41} and imines^{14,33,42}
91 during the cross-linking process. CANs containing these labile
92 bonds can be rearranged by exchange reactions and degraded
93 via acid hydrolysis.^{42,43} Imine bonds, which can be easily
94 obtained from reactions between various amines and
95 aldehydes, have been recognized as a unique dynamic covalent
96 bond in CANs, as it can undergo a reversible degradation
97 process through imine hydrolysis.^{14,33} Moreover, the presence
98 of aldehydes in epoxidized divanillin (EDV) can lead to several
99 other reactions during the curing process.⁴² In this report, DV
100 was synthesized via a facile method in hot water and utilized
101 without any purification. The DV was subsequently treated
102 with biobased epichlorohydrin, and the EDV was then cured
103 by a biobased hardener (Cardolite GX-3090) and a common
104 petroleum-based hardener isophorone diamine (IPDA).
105 Thermal and mechanical performances, solvent resistance,
106 and the degradability of the biobased epoxy networks formed
107 from this process were investigated and compared to
108 corresponding DGEBA-based references.

109 ■ EXPERIMENTAL SECTION

110 **Materials.** The following materials were purchased and used
111 without further modification: vanillin (99%, Alfa Aesar); ethyl acetate
112 (Fisher Scientific, ACS grade); tetraethylammonium bromide (TBAB,
113 98%, TCI America); perchloric acid, glacial acetic acid, and NaOH
114 (Fisher Chemical); biobased epichlorohydrin (Advanced Biochemical
115 Thailand Co.); $\text{Na}_2\text{S}_2\text{O}_8$ (+98%) and isophorone diamine (+99%;
116 Acros Organic); GX-3090 (Cardolite); DGEBA (EPON 828; E. V.
117 Roberts); and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (+99%), 1,1,2,2-tetrachloroethane,
118 CDCl_3 , and $\text{DMSO}-d_6$ (Sigma-Aldrich).

119 **Synthesis of Divanillin (DV).** A mixture of 6 g of vanillin (39.5
120 mmol), 0.2 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.72 mmol), and 5 g of $\text{Na}_2\text{S}_2\text{O}_8$ (21.0
121 mmol, 0.53 equiv) in 400 mL of water was stirred at 80 °C for 30 min.
122 The precipitates were filtered and washed with hot water (80 °C)
123 three times and lyophilized to yield 5.22 g of a gray solid (87.5%).

124 ¹H NMR (500 MHz, $\text{DMSO}-d_6$): 9.81 (s, 2H), 7.42–7.43 (m,
125 4H), 3.93 (s, 6H); ¹³C NMR (126 MHz, $\text{DMSO}-d_6$): 191.7, 150.8,
126 148.5, 128.6, 128.1, 125.0, 109.5, 56.4.

Synthesis of Epoxidized Divanillin (EDV). A mixture of 4 g of
127 divanillin (13.2 mmol), 24.5 g of epichlorohydrin (0.265 mol), and
128 0.4 g of TBAB (1.2 mmol) was stirred at 80 °C for 2 h. NaOH (5 M,
129 10.6 mL) and 0.4 g of TBAB (1.2 mmol) were then added at room
130 temperature, and the mixture was stirred for an additional 1 h. The
131 liquid was removed by lyophilization, and the resulting residue was
132 washed with DI water and dried in a freeze drier overnight to yield 4.2
133 g of a white solid (77%).

134 ¹H NMR (500 MHz, $\text{DMSO}-d_6$): 9.80 (d, $J = 2.2$ Hz, 2H), 7.41 (t,
135 $J = 2.1$ Hz, 2H), 7.35 (d, $J = 2.2$ Hz, 2H), 4.13 (tdd, $J = 9.5, 4.2, 2.2$
136 Hz, 2H), 3.92–3.88 (m, 2H), 3.87 (d, $J = 2.2$ Hz, 6H), 2.95 (ddt, $J =$
137 4.8, 3.3, 1.8 Hz, 2H), 2.55 (td, $J = 4.6, 2.0$ Hz, 2H), 2.32 (dt, $J = 4.7,$
138 2.3 Hz, 2H); ¹³C NMR (126 MHz, CDCl_3): 191.0, 152.9, 150.9,
139 132.1, 131.6, 127.4, 110.3, 74.1, 56.0, 50.2, 44.1.

EEW Identification and AHEW Calculation. The epoxy content
141 of EDV was measured by two different methods. (1) The
142 autotitration method utilized was a modified version of ASTM
143 D1652-11. Briefly, 0.2–0.3 g of EDV was dissolved in 30 mL of
144 dichloromethane and 15 mL of a TBAB solution (100 g of
145 tetraethylammonium bromide in 400 mL of glacial acetic acid). The
146 resulting solution was stirred for 5 min until the EDV was completely
147 dissolved. An autotitrator (Metrohm, 916 Ti-touch Swiss Mode) was
148 used to titrate the solution with 0.1 M perchloric acid until the end
149 point of titration was reached. (2) In the ¹H NMR method, a mixture
150 of 50 mg of EDV and 20 mg of internal standard (1,1,2,2-
151 tetrachloroethane) was added to 700 μL of $\text{DMSO}-d_6$. NMR analyses
152 were performed using an Agilent DDR2 500 MHz NMR spectrometer
153 (64 scans; 10 s relaxation delay) equipped with a 7600AS autosampler
154 and running VnmrJ 3.2A.

Preparation of Cured Epoxy Networks. Both epoxides (EDV
156 and DGEBA) were cured with IPDA and GX-3090 based on the
157 monomer's EEW values. First, the mixtures were hand-stirred at room
158 temperature for 1 min, then cured at 120 °C for 2 h and postcured at
159 150 °C for 1 h.

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

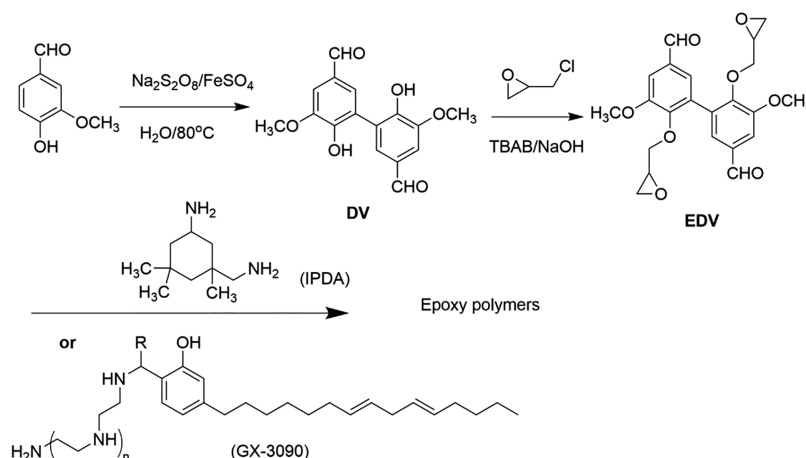
169 Cured EDV-based and DGEBA-based samples were analyzed with
170 a Spectrum II PerkinElmer Fourier transform infrared spectropho-
171 tometer in attenuated total reflectance mode (ATR-FTIR). The
172 transmittance mode was used with wavenumbers ranging from 400–
173 4000 with 4 cm^{-1} resolutions and 32 scans.

174 Differential scanning calorimetry (DSC, TA Analysis, Q100) was
175 used to study the curing rate of EDV and DGEBA. Approximately 5–
176 10 mg of each sample (mixture of resin and curing agent) was placed
177 on an aluminum pan. A ramp test at a heating rate of 10 °C/min
178 under a nitrogen flow of 70 mL/min was performed over a
179 temperature range of 25–250 °C.

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

186 Dynamic mechanical analyses (DMA) were conducted on a TA
187 Q800 instrument with single cantilever mode under air flow and
188 heating rate of 3.0 °C/min from room temperature to 200 °C at a
189 constant deformation frequency of 1 Hz. The peak temperatures of
190 the $\tan \delta$ curves were recorded as the glass transition temperature
191 (T_g). Samples were cured at 120 °C for 2 h and postcured at 150 °C
192 for 1 h in Teflon molds with the dimensions 35 mm (l) \times 12 mm (w)
193 \times 5 mm (t). The samples were then cut and polished to the desired
194 rectangle dimensions (length \times width \times thickness = 30 mm \times 12 mm
195 \times 1.2 mm) before testing.

Scheme 1. Synthesis of DV and EDV from Vanillin



197 Solvent resistance tests were conducted by immersing cured epoxy
198 networks in 6 different solvents (water, DMF, acetone, THF, EtOH
199 and ethyl acetate) for 4 days at room temperature using a modified
200 version of a previously reported procedure.^{33,43}

201 Degradation tests were conducted by adding a stir bar and 50–150
202 mg of cured samples to a mixture of 1 mL HCl (1 M) and 1 mL of
203 either DI water or organic solvent (DMF, EtOH, and acetone). After
204 stirring at room temperature for 24 h, the residual solid was
205 lyophilized and weighed, and the solid remaining was calculated based
206 on the initial mass of the samples.

207 ■ RESULTS AND DISCUSSION

208 Employment of divanillin (DV) as a building block in
209 formulating epoxy thermosets has been previously reported
210 by Savonnet et al.,²² in which the synthesis of DV was
211 performed in the presence of laccase (in an acetone/buffer
212 solution for 24 h). Additionally, the aldehyde groups in DV
213 was reduced to hydroxyl groups to create more reactive sites
214 for reaction with epichlorohydrin. Inspired by prior above
215 work, in the present study DV was synthesized in hot water
216 within 30 min in which the prepared DV, in contrast with
217 previously published data, still contained two aldehyde groups
218 on its aromatic structures (Scheme 1). The presence of
219 aldehyde groups in an unmodified DV provided an additional
220 benefit of creating an epoxy network that can be degraded by
221 mild acid hydrolysis after its service life, resulting in a cured
222 epoxy networks that is inherently different from earlier work,
223 especially in the use of biobased epichlorohydrin and curing
224 agents in the formulation of cured epoxy systems.

225 **Synthesis of Divanillin-Based Epoxy Precursors (DV
226 and EDV).** Synthesis of DV was accomplished via oxidative
227 coupling of vanillin in aqueous solution at 80°C using
228 $\text{Na}_2\text{S}_2\text{O}_8$ and FeSO_4 as a catalyst (Scheme 1), a procedure
229 modified from previously published reports.^{30,31} Maintaining
230 an elevated temperature ($80\text{--}100^\circ\text{C}$) was critical to complete
231 the coupling reaction in only 30 min, as the previous method³⁰
232 required 5 days at 50°C . Significantly, as opposed to further
233 modifying the DV,²² we then used the DV directly without any
234 purification to synthesize EDV, following the method
235 described by Fache et al.¹³ Although, there is still concern
236 around the toxicity of biobased epichlorohydrin (ECH), it is
237 widely used in industry and there are well-established methods
238 for removing residual epichlorohydrin by quenching with
239 NaOH and washing the product with excess water.^{14,22,44} The

NMR spectra of epoxidized divanillin (EDV) confirmed the 240
complete removal of epichlorohydrin (Figure S3–S4). 241

EEW Identification and AHEW Calculation. The epoxy 242
contents (EC%) of EDV were measured to be 19.1% (titration 243
method) and 19.02% (^1H NMR method), respectively, and the 244
average (19.0%) was used to calculate the ratio of epoxy resin 245
to various curing agents. The epoxy equivalent weights (EEW) 246
of DGEBA and EDV were calculated to be approximately 185 247
and 225 g/eq., respectively, by the following equation⁴⁵ (eq 1): 248

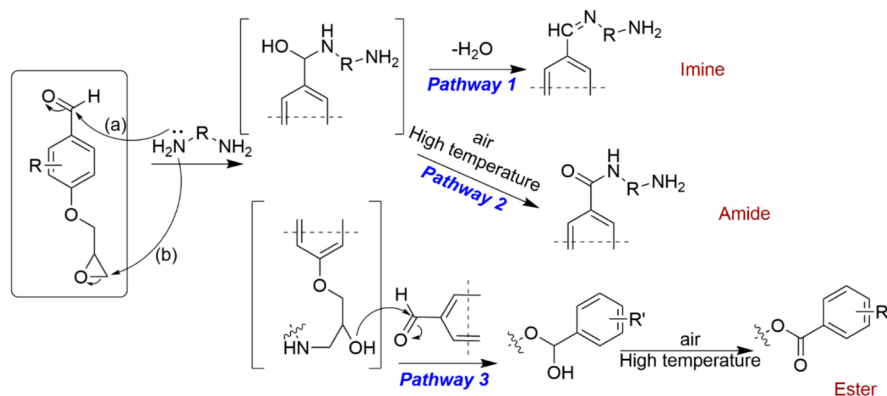
$$\text{EEW} = \frac{4300}{\text{EC}\%} \quad (1) \quad 249$$

Each amine hydrogen that reacts with one epoxy group 250
corresponds to an active hydrogen equivalent weight (AHEW), 251
and the stoichiometric ratios between the curing agents and 252
epoxy resins can be calculated as AHEW/EEW (see Table 1). 253

Table 1. Formulation of Different Epoxy Samples

curing agents	AHEW	mass ratio(g/g)	
		DGEBA/amines	EDV/amines
GX-3090	69	1/0.37	1/0.31
IPDA	42	1/0.23	1/0.19

Curing Reactions of Epoxy Networks. The diamines 254
GX-3090 and IPDA were used to cure the synthesized EDV 255
(Scheme 1). Notably, multiple reactions likely occur during the 256
curing process due to the presence of different functional 257
groups (aldehyde and epoxide) in EDV. Imine bonds can be 258
introduced through the reaction of aldehyde group in EDV 259
with the diamine (see Scheme 2, pathway 1).^{14,22,33,42} 260
Moreover, in addition to the production of imine bonds, 261
other dissociable bonds can also be formed. Amide bonds can 262
be generated by the oxidation of methylene group^{46,47} or the 263
newly formed OH group in air under elevated temperatures 264
during the hardening process (Scheme 2, pathway 2). In 265
addition, after the oxirane ring opens, the newly formed 266
alkoxides can presumably behave as nucleophiles and further 267
react with the aldehyde groups during the hardening process to 268
form semi acetals, eventually leading to ester bonds⁴⁸ (Scheme 269
2, pathway 3). Importantly, amide, imine, and ester bonds are 270
all easily dissociable under appropriate acidic conditions, and 271
these reactions will therefore yield a highly degradable epoxy 272
network regardless of the specific reaction pathways. 273

Scheme 2. Formation of Dissociable Bonds when EDV Was Cured with Diamines^a

^aThe diamine can react with both the aldehyde (a) and the epoxy (b) moiety.

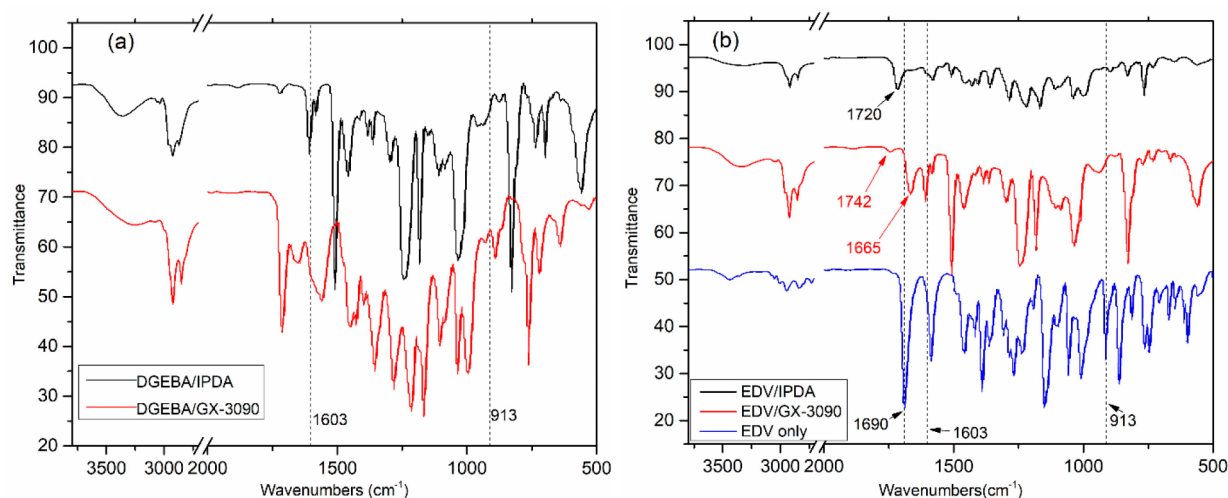


Figure 1. FTIR spectra of networks composed of DGEBA (a) and EDV (b) cured with IPDA and GX-3090.

274 **FTIR Analysis.** The curing degree of epoxy networks of
 275 DGEBA and EDV cured by GX-3090 and IPDA were
 276 characterized by FTIR. The disappearance of peaks at 913
 277 cm^{-1} corresponding to the oxirane rings⁴⁹ (Figure 1a,b) and
 278 the peaks at 1690 cm^{-1} corresponding to C=O from
 279 benzaldehydes⁴² (Figure 1b), in conjunction with the
 280 appearance of bands associated with the amino groups (N–
 281 H)³³ at 1603 cm^{-1} suggested the complete curing of BPA and
 282 EDV by GX-3090 and IPDA (Figure 1). Notably, no
 283 significant peak associated C=N ($\sim 1635 \text{ cm}^{-1}$)³³ were
 284 observed. Instead, the new bands at 1665 cm^{-1} (Figure 1b,
 285 red trace) are likely attributed to the C=O of amides^{47,50} and
 286 the bands at 1720 (Figure 1b, black trace) and 1742 cm^{-1}
 287 (Figure 1b, red trace) were assigned to the C=O bands in the
 288 newly formed esters.^{28,51,52}

289 **Curing Performance (DSC Analysis).** The curing
 290 behavior of EDV-based and DGEBA-based epoxies was
 291 investigated by DSC (Figure 2). Values for the onset curing
 292 temperature (T_{onset}), the peak curing temperature (T_p) and the
 293 reaction enthalpy (ΔH) are summarized in Table 2. EDV-
 294 based materials displayed slightly lower onset temperatures
 295 than DGEBA-based samples, suggesting that EDV is slightly
 296 more reactive, presumably due to the presence of aldehyde
 297 groups. Both EDV-based mixtures tended to cure at relatively
 298 higher temperatures, with exotherms ranging from 120 to 144

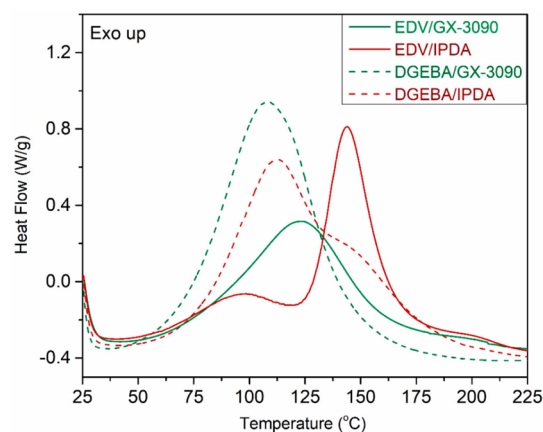


Figure 2. DSC profiles of different cured samples from EDV and DGEBA.

°C, compared to that of DGEBA-based mixtures (exotherms 299
 ranging from 110 to 130 °C). EDV-based mixtures exhibited 300
 lower reaction enthalpies comparing to DGEBA-based 301
 materials (374–405 J/g). Homogenous mixtures were difficult 302
 to generate due to the high viscosity of crude EDV and curing 303
 reactions might have started when the EDV was prewarmed in 304
 order to reduce the viscosity during mixing with the diamines. 305

Table 2. Curing Behaviors of Different Epoxy Systems

epoxy systems	T_{onset} (°C)	T_p (°C)	ΔH (J/g)
EDV/GX-3090	72	123	221
EDV/IPDA	59	89	24
DGEBA/GX-3090	128	144	148
DGEBA/IPDA	68	109	405
DGEBA/IPDA	75	113	374

306 Competing reactions of aldehydes and epoxies with amines
 307 may have also contributed to the lower reaction enthalpies.
 308 Shoulders were generally observed before the exothermal peak
 309 in the curing profiles of the EDV-based samples, most likely
 310 due to the different reactivities of the aldehyde and the epoxy
 311 groups toward the diamines.⁴²

312 Thermomechanical Performance (DMA Analysis).

313 Thermomechanical performances of DGEBA-based and
 314 EDV-based epoxy thermosets were investigated by DMA
 315 using a single cantilever mode. The storage modulus, $\tan \delta$, and
 316 the loss modulus are shown in Figure 3 as a function of
 317 temperature and are summarized in Table 3. The storage
 318 modulus (E') represents the elastic response of a material and
 319 the loss modulus (E'') is its viscous response. $\tan \delta$ is the ratio
 320 of the loss modulus and the storage modulus, and the peak
 321 temperature of $\tan \delta$ or the loss modulus is usually recorded as
 322 the glass transition temperature (T_g), indicating the network
 323 transits from a glassy status to a rubbery stage.

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

336 It was anticipated that the large chain of GX-3090 with two
 337 unsaturated bonds, in contrast to the small structure of cyclic
 338 aliphatic IPDA (Scheme S1), would result in epoxy resins with
 339 lower storage modulus (higher elasticity at room temperature).
 340 This explains the higher storage modulus of DGEBA/IPDA
 341 (2.5 GPa) compared to DGEBA/GX-3090 (1.6 GPa).
 342 Surprisingly, however, the storage modulus of epoxidized
 343 divanillin with GX-3090 (EDV/GX-3090, 2.3 GPa) was
 344 significantly higher than EDV/IPDA. We suspect the aldehyde
 345 groups in EDV may react with the phenolic group of GX-3090,
 346 resulting in a more rigid structure with enhanced mechanical
 347 properties for EDV/GX-3090 (Scheme S2).

348 The $\tan \delta$ peak provides important information about the
 349 cured epoxy networks. Typically, a higher $\tan \delta$ peak represents
 350 improved fracture toughness.^{23,53} Clearly, EDV/IPDA net-
 351 works exhibited a notably higher peak (Figure 3b, solid red)
 352 than did other three networks. The width of $\tan \delta$ reflects the
 353 sample homogeneity; the sharper and narrower the peak, the
 354 more homogeneous the sample.¹² DGEBA/IPDA displayed a
 355 significantly broader $\tan \delta$ profile than the others, indicating
 356 that it is less homogeneous. When the biobased amine GX-
 357 3090 was used as the hardener; however, the EDV network
 358 displayed $\tan \delta$ peaks as sharp as the DGEBA network,

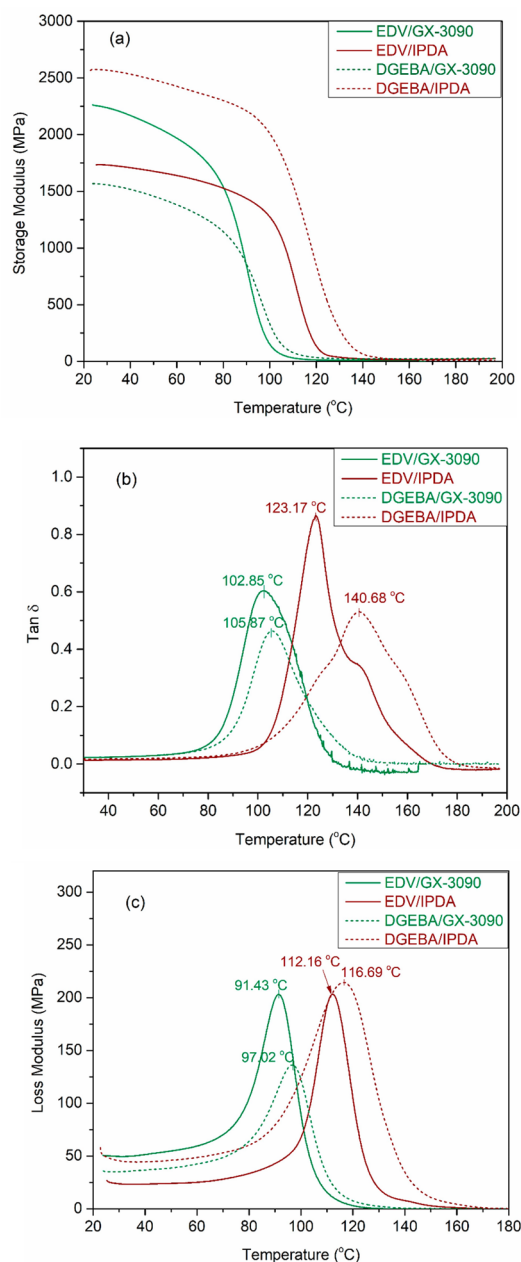


Figure 3. Storage modulus (a), $\tan \delta$ (b), and loss modulus (c) of networks containing EDV and DGEBA cured by GX-3090 and IPDA.

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

cure system	E' (GPa) ^a	T_g (°C)	
		from $\tan \delta$ ^b	from loss modulus ^c
EDV/GX-3090	2.3	103	91
EDV/IPDA	1.7	123	112
DGEBA/GX-3090	1.6	106	97
DGEBA/IPDA	2.5	140	116

^aStorage modulus at room temperature measured by DMA. ^bGlass transition temperature recorded as the peak of $\tan \delta$. ^cGlass transition temperature recorded as the peak of the loss modulus.

indicating higher homogeneity of these samples (Figure 3b, 359 solid and dash green). 360

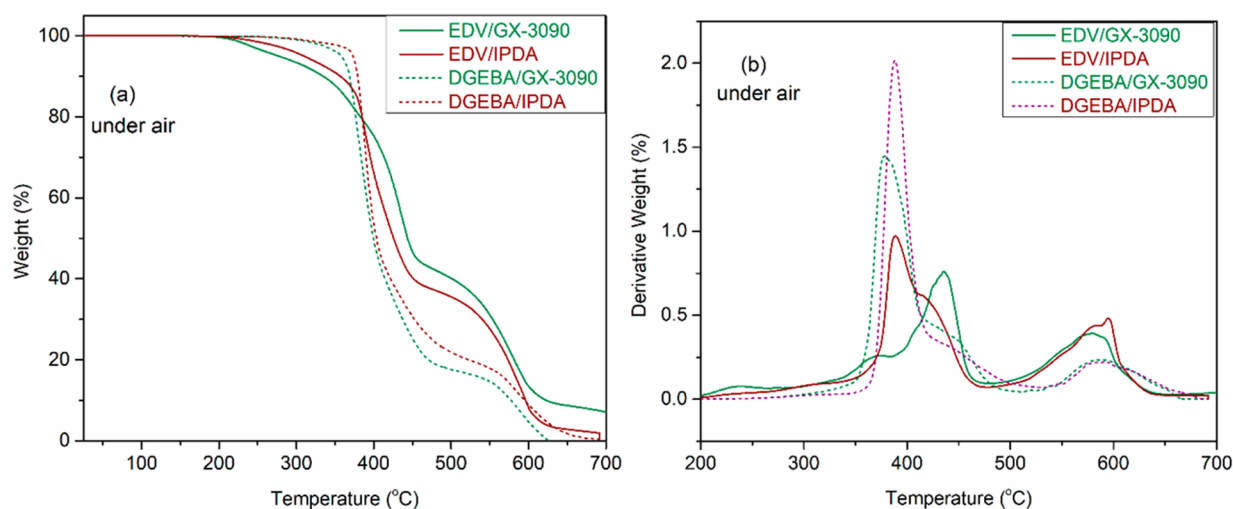


Figure 4. Thermal degradation of polymers cured from EDV and DGEBA with either GX-3090 or IPDA; weight loss (a) and derivatized weight loss (b) as a function of temperature.

361 The $\tan \delta$ profile of the EDV/IPDA network was broader
 362 than usual, and although the T_g was recorded at 123 °C, a
 363 significant shoulder at 140 °C was observed (Figure 3b, solid
 364 red). Residue reaction sites that react at different temper-
 365 atures²² as well as the multiple functionalities in the network¹²
 366 could both be responsible for the broadened $\tan \delta$ profiles. In
 367 addition, the observed shoulder at 140 °C indicates a two-stage
 368 transition and agrees with the fact that when IPDA was
 369 employed as the hardener, the T_g (recorded from the loss
 370 modulus profiles) of both EDV-based and DGEBA-based
 371 networks (Figure 3c, red and dash red) appeared to be very
 372 close (112 and 116 °C, respectively). The loss modulus (E'')
 373 measures the energy dissipated as heat (viscous response of a
 374 material), so in this respect, EDV-based and DGEBA-based
 375 networks exhibited similar abilities to dissipate deformation
 376 energy.²² Significantly, when the biobased amine GX-3090 was
 377 used to cure EDV, the T_g from both the peak of $\tan \delta$ and the
 378 loss modulus appeared to be very similar to the DGEBA
 379 references, indicating similar performance properties.

380 **Thermal Stability Analysis (TGA Analysis).** Thermal
 381 stabilities of cured EDV-based and DGEBA-based epoxies
 382 were investigated with TGA (Figure 4). Statistical heat
 383 resistant-indices (T_s) were calculated from temperatures
 384 corresponding to 5% ($T_{5\%}$) and 30% ($T_{30\%}$) weight loss^{54,55}
 385 in eq 2 and summarized in Table 4. The maximum weight loss
 386 (T_{max}) values are reported in Table 4 as well.

$$387 \quad T_s = 0.49(T_{d5\%} + 0.6(T_{d30\%} - T_{d5\%})) \quad (2)$$

388 Two-step degradation profiles were observed for all
 389 thermosets produced under air, including a fast weight loss
 390 stage from approximately 230 to 480 °C, and another 30–40%
 391 weight loss stage above 500 °C. The first stage is primarily

Table 4. Thermal Degradation of Networks Cured by DGEBA and EDV with Either GX-3090 or IPDA

epoxy polymers	$T_{d5\%}$ (°C)	$T_{d30\%}$ (°C)	T_{max}	T_s (°C)
EDV/GX-3090	276	412	435	175
EDV/IPDA	309	394	388	176
DGEBA/GX-3090	350	385	379	182
DGEBA/IPDA	366	388	385	186

associated with the breaking of aliphatic chains and the loss of
 small molecules such as CO, CO₂, and water.⁵⁶ 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 phenols) and/or the degradation of aromatic rings.⁵⁷
 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
 temperature than did DGEBA-based materials. As shown in
 Table 4, the $T_{d30\%}$ 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.¹⁸ All DGEBA networks
 showed maximum weight loss (T_{max}) at around 385 °C, while
 T_{max} was approximately 50 °C higher (i.e., 435 °C) for
 networks cured by EDV/GX-3090. The statistical heat
 resistant-indices (T_s) 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.⁵⁸ 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.^{33,43} 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 environ-
 mental challenges. Rapid chemical degradation of networks

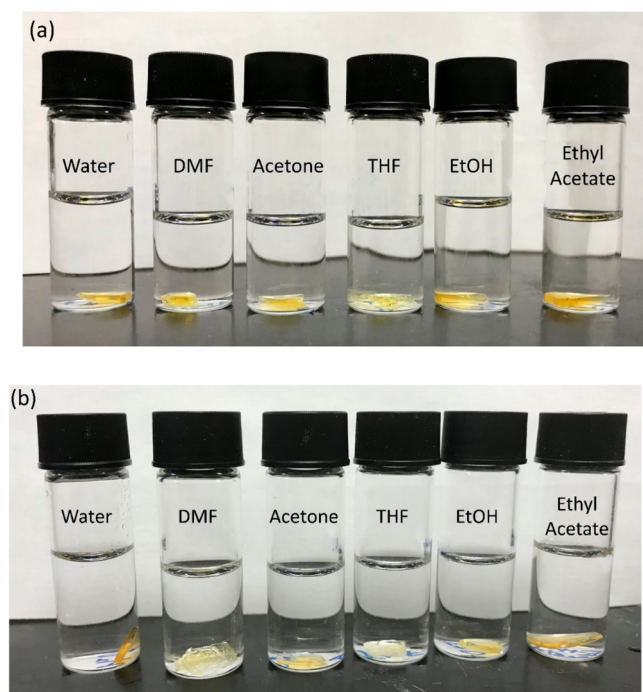


Figure 5. Immersion of epoxy networks cured by EDV/GX-3090 (a) and EDV/IPDA (b) in different solvents at room temperature for 4 days.

Table 5. 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

resin	% weight loss in different solvents			
	H ₂ O	DMF	EtOH	acetone
EDV	15.5	30.3	29.5	37.4
DGEBA	4.0	2.5	7.0	3.5

While the ether bonds in polymers composed of DGEBA/ 442 IPDA were only slightly cleaved, leading to a marginal weight 443 loss of 3–7% following treatment with HCl (Figure 6b), 444 significant cleavage of the network cured by EDV/IPDA was 445 observed with far fewer solids remaining (62%–84%). The 446 cleavage of the network cured by EDV/IPDA was especially 447 pronounced when acetone was used, with almost 40% of the 448 segments being solubilized (Figure 6a). The disappearance of 449 the bands at 1720 cm^{-1} associated with the carbonyl in ester 450 bonds, the appearance of the peaks at 1743 cm^{-1} 451 corresponding to C=O in acids, and the appearance of the 452 broad peak at $2500\text{--}2800\text{ cm}^{-1}$ all indicated full hydrolysis of 453 esters to acids (Figure 7). We tested the degradation of EDV/ 454 17

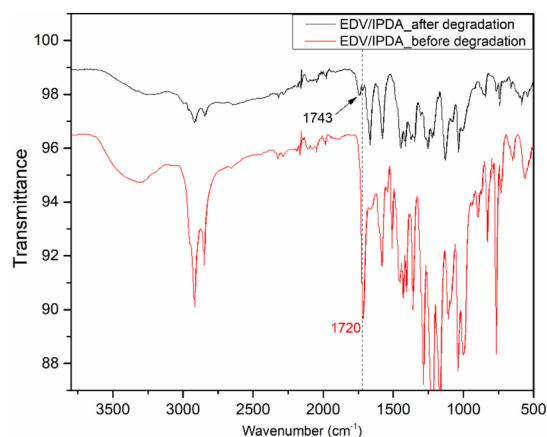


Figure 7. FTIR spectrum of a network cured by EDV/IPDA before and after HCl (1M) treatment in acetone for 24 h.

434 back to their initial building block constituents or to other 435 useful, nontoxic products is an obvious promising alternative 436 path.³⁵ Notably, the dissociable amide and ester bonds in the 437 backbone of these bio-based epoxy thermosets described here 438 can theoretically be cleaved under mild acidic conditions.^{33,42} 439 Degradation tests of epoxy networks cured by EDV/IPDA and 440 DGEBA/IPDA were therefore conducted with 1 M HCl at 441 room temperature for 24 h (Figure 6 and Table 5).

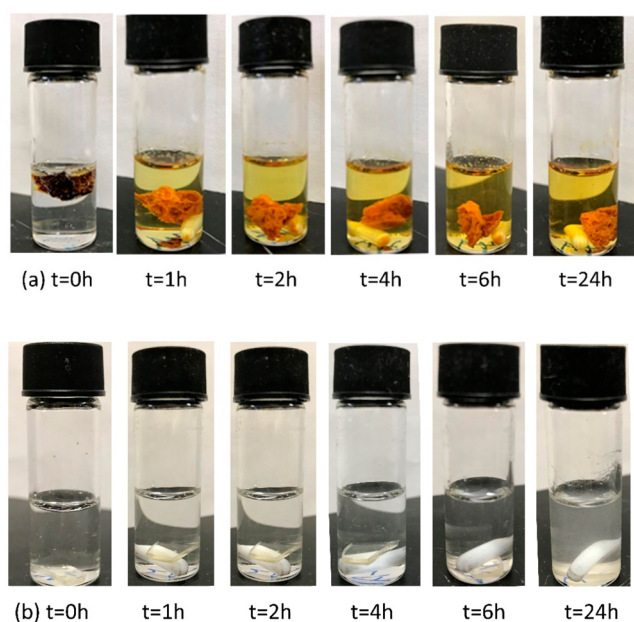


Figure 6. Treatment with 1 M HCl in acetone of networks cured by (a) EDV/IPDA and (b) DGEBA/IPDA.

GX-3090 as well, but unfortunately, significant portions of this 455 sample were not solubilized in acid. We suspect this is due to 456 the additional reactions between the aldehydes in EDV and the 457 phenol in GX-3090, which presumably led to a more rigid 458 skeleton. Additional work is needed to optimize the 459 formulation to improve its degradability. 460

CONCLUSIONS

461 Utilization of renewable biomass as building blocks to replace 462 toxic bisphenol A (BPA) in epoxy resin formulations was the 463 major motivation of this study. Oxidative coupling of vanillin 464 was shown to be an effective method to produce divanillin in 465 water at elevated temperatures ($80\text{ }^{\circ}\text{C}$) in only 30 min. The 466 epoxy resins formulated via the reaction of divanillin with 467 bio-based epichlorohydrin and cured with a bio-based hardener 468 (GX-3090) exhibited excellent thermal stability, mechanical 469 properties, and solvent resistance when compared with 470 commercial bisphenol A epoxy resin. The presence of aldehyde 471 and epoxy groups in the bio-based epoxy (EDV) created an 472 opportunity to employ mild acid to degrade the resin after its 473 service life. Moreover, the C–C aromatic bonds in divanillin 474

475 (DV) are analogous to the 5–5 linkage in lignin⁸ that is usually
476 challenging to cleave. Thus, the application of DV in epoxy
477 resins can provide insight into future lignin valorization
478 strategies.

479 ■ ASSOCIATED CONTENT

480 ■ Supporting Information

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

483 ¹H and ¹³C spectra of divanillin (DV) and epoxidized
484 divanillin (EDV) (Figures S1–S4); proposed cross-
485 linking reactions of DGEBA/IPDA and EDV/IPDA
486 (Scheme S1); proposed additional reaction of EDV/GX-
487 3090 (Scheme S2) (PDF)

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