

# Synthesis and Characterization of a Low-Molecular-Weight Novolac Epoxy Derived from Lignin-Inspired Phenolics

Kelli M. Hambleton and Joseph F. Stanzione, III\*



Cite This: *ACS Omega* 2021, 6, 23855–23861



Read Online

ACCESS |



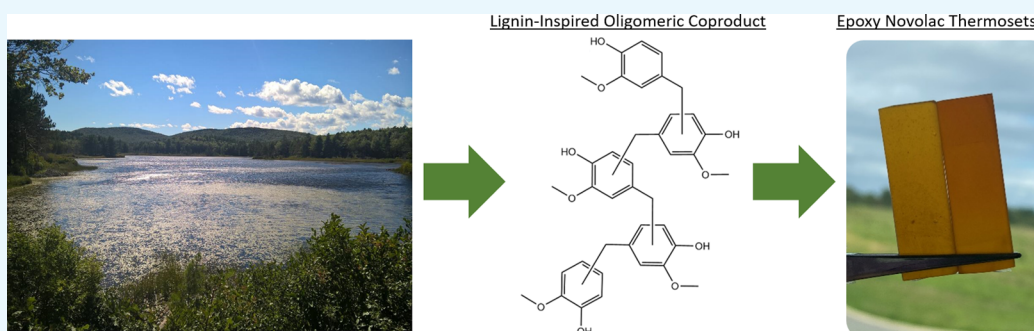
Metrics & More



Article Recommendations



Supporting Information



**ABSTRACT:** The need for renewable polymers capable of replacing their petrochemical counterparts continues to grow as sustainability concerns rise. Bisguaiacol (BG), a bioinspired alternative to bisphenol-A (BPA), has been synthesized using vanillyl alcohol and guaiacol via an electrophilic aromatic condensation. Purification provides both BG and an oligomeric coproduct with a consistent number average molecular weight and dispersity of  $\sim 650$  Da and  $\sim 1.00$ , respectively. This coproduct has been well characterized as a low-molecular-weight novolac averaging five hydroxyls per molecule and was transformed into an epoxy resin suitable for use in thermosetting resins. The bioinspired thermoset produced in this work, consisting of the epoxidized coproduct and an amine curing agent (Epikure W), exhibited a glass transition temperature over  $100$  °C and glassy storage modulus value of  $\sim 3$  GPa at  $25$  °C. When compared to a commercial cresol novolac epoxy, the cured epoxidized coproduct resin shows comparable thermal and thermomechanical properties. When compared to a commercial BPA-based resin, the cured epoxidized coproduct resin shows improved mode I fracture values of  $1.34$  J m $^{1/2}$  ( $K_{IC}$ ) and  $448.16$  J/m $^2$  ( $G_{IC}$ ). By utilizing the coproduct strategically, the overall production of BG has the potential to become more economically feasible.

## INTRODUCTION

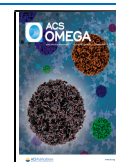
Thermosetting polymers, those which typically cannot be reshaped with the addition of heat, are favorable in many applications because of their great thermal stabilities, chemical resistances, and durable mechanical properties.<sup>1–6</sup> Epoxy resins are one of the most popular thermosetting polymers,<sup>7</sup> making up about 70% of all such polymeric systems.<sup>8</sup> Common applications of epoxy resins are coatings, adhesives, electronic materials, metal can linings, and thermosetting plastics.<sup>1–7</sup> Unfortunately, most commercial epoxy resins are derived from petrochemicals, an unsustainable feedstock. The most popular epoxy resin is diglycidyl ether of bisphenol-A (DGEBA), which is synthesized by reacting bisphenol-A (BPA) with a molar excess of epichlorohydrin under basic conditions.<sup>1,3,7</sup> Furthermore, in the past few decades, BPA has fallen under scrutiny as it is a proven endocrine disruptor and, therefore, poses a health risk to consumers.<sup>9–11</sup> It was recently reported that  $\sim 20\%$  of all BPA consumption was for the production of epoxy resins.<sup>9</sup> Despite this, BPA is still widely used in consumer products and produced at over 2 million tons per year.<sup>8</sup>

Thus, there is an immediate need for the development of sustainable thermosetting polymers that also potentially pose a lower toxicity threat to consumers and the environment. In recent years, researchers have looked to lignocellulosics as a source for chemical building blocks to create bio-based materials.<sup>8,12,13</sup> Lignocellulose is comprised of cellulose, hemicellulose, and lignin.<sup>8,14,15</sup> While cellulose and hemicellulose typically have aliphatic structures, lignin has an irregular structure of highly crosslinked phenolics.<sup>12,15–17</sup> It is estimated that lignin is naturally produced in millions of metric tons per year by the biosphere, making it one of the most abundant materials on Earth.<sup>13,15,18</sup> Despite this, lignin is mainly viewed as a waste material of the paper and pulping industry, typically being burned as fuel.<sup>13,19</sup> Less than 5% of

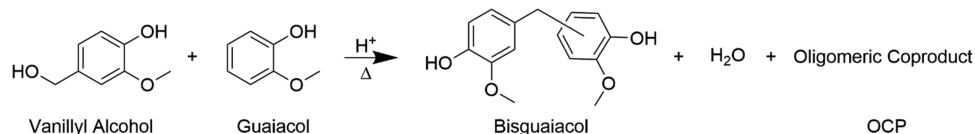
Received: May 28, 2021

Accepted: August 5, 2021

Published: September 3, 2021



## Scheme 1. General Reaction Scheme for the Synthesis of Bisguaiacol (BG) and the Oligomeric Coproduct



lignin being used is processed to become goods and products.<sup>13,19</sup> While lignin is a valuable renewable resource in itself, it can also be depolymerized to form useful phenolic building blocks, such as guaiacol, vanillin, creosol, and syringol.<sup>13</sup> These substituted phenols have been shown to be viable alternatives to petrochemical-based phenolics in the synthesis of polymers, including many thermosetting polymers.<sup>8,20–28</sup>

The synthesis of bisguaiacol (BG), a lignin-inspired bisphenol, was reported by Hernandez et al. as a greener alternative to typical bisphenol synthetic routes by condensing vanillyl alcohol with an excess of guaiacol.<sup>20</sup> This synthesis produces an isomeric mixture of BG, water, and an oligomeric coproduct (OCP), as shown in Scheme 1, with an OCP yield of about 30% on average and a BG yield of about 51% on average.<sup>20</sup> From BG, the diglycidyl ether of BG (DGEGB) was synthesized via epoxidation with epichlorohydrin and blended with a commercially available DGEBA resin.<sup>20</sup> Through thermomechanical testing, it was determined that the presence of the methoxy substituent causes a decrease in  $T_g$ , but increases the glassy storage modulus ( $E'$ ).<sup>20</sup> Furthermore, recent toxicity assessments performed by Peng et al. and Hong et al. showed that the presence of the methoxy moiety reduced the estrogenic activity of BGs compared to bisphenols, thus demonstrating BG (referred to as BGF) as a less toxic alternative to BPA or BPF.<sup>29–31</sup> Peng et al. studied six BGs with varying numbers and locations of methoxy moieties using two in vitro assays at both the whole-cell and RNA-expression levels.<sup>29,31</sup> This study concluded that BG has a significantly lower estrogenic activity than that of BPA at concentrations of  $10^{-10}$ – $10^{-7}$  M.<sup>29,31</sup>

In the work presented herein, we utilized an adapted BG synthesis technique in an effort to improve the ease of processability. The reaction mixture was separated into BG, excess guaiacol, and the OCP. The OCP, which is the main focus of the presented work, was thoroughly characterized and functionalized for use in epoxy-amine thermosetting resins. This was performed to elucidate the potential utility of the epoxidized OCP (E-OCP) in the development of useful thermosets for high-performance applications, which, in turn, could promote the overall production of BG in becoming more economically feasible.

## EXPERIMENTAL METHODS

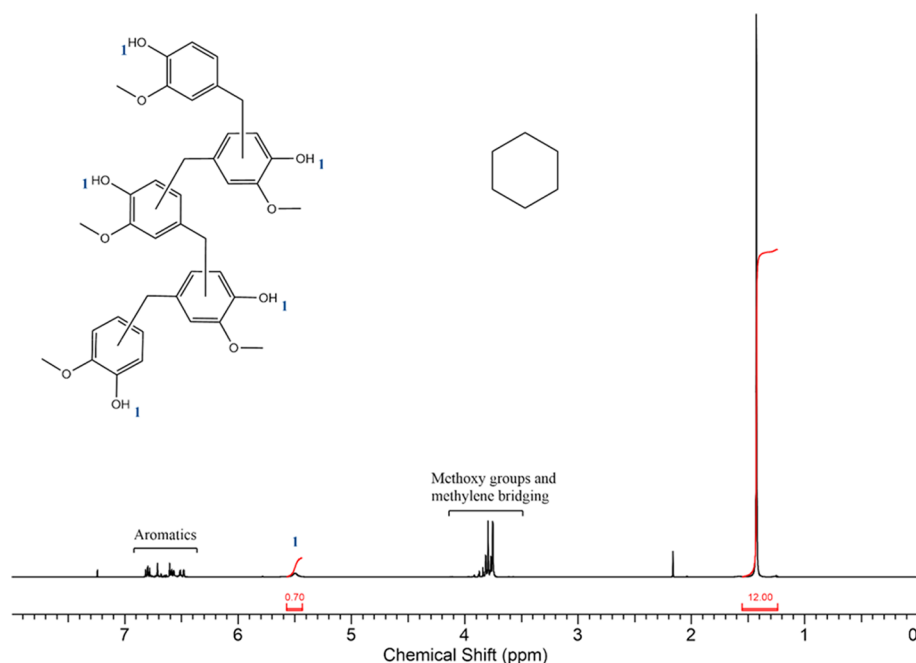
**Materials.** Vanillyl alcohol (4-hydroxy-3-methoxy benzyl alcohol, 99%), guaiacol (2-methoxyphenol,  $\geq 99\%$ ), epichlorohydrin ( $>99\%$ ), tetraethyl ammonium bromide (TEAB,  $>99\%$ ), and deuterated chloroform ( $CDCl_3$ , 99.8% d) were purchased from Acros Organics. Tetrabutylammonium bromide (TBAB,  $\geq 99\%$ ), glacial acetic acid ( $>99\%$ ), cyclohexane ( $\geq 99\%$ ), and sodium hydroxide (NaOH, 98%) were purchased from Sigma-Aldrich. Dichloromethane (DCM, 99.9%) was purchased from VWR. Tetrahydrofuran (Optima THF, 99.9%), sodium sulfate (anhydrous, granular), and perchloric acid (60%) were purchased from Fischer Scientific. Amberlyst

15 hydrogen form ion exchange resin (dry) was purchased from Alfa Aesar. Crystal violet in glacial acetic acid solution (1% w/v) was purchased from RICCA Chemical Company. Epon 164 resin (solid at 25 °C), Epon 828 resin (moderately viscous resin; 110–150 P at 25 °C), and Epikure W curing agent (low-viscosity aromatic amine-based curing agent with a sufficient pot life with epoxy resins that assists in proper mixing and resin transfer before reaction which also provides stiffness and thermal stability to cured epoxy systems; 22 P at 25 °C) were received from Hexion; see Figure S1 for chemical structure representations. Compressed nitrogen ( $N_2$ , 99.9998%) and liquid  $N_2$  were purchased from Airgas. Advanced Polymer Chromatography (APC) standards were purchased from Waters Corporation. All chemicals were used as received. Bisguaiacol (BG) was synthesized using a method adapted from Hernandez et al. with the OCP separated from BG and excess guaiacol with assistance from Cardolite Corporation (Bristol, PA).<sup>20</sup>

**Characterization of the OCP and E-OCP.** The OCP and E-OCP were characterized via  $^1H$  NMR spectroscopy using a Bruker 400 MHz NMR spectrometer. Exemplar spectra can be found in the Supporting Information (SI). The number ( $M_n$ ) and weight ( $M_w$ ) average molecular weights and dispersities ( $\mathcal{D}$ ) of the OCP and E-OCP were estimated using a Waters Acquity APC instrument with Optima THF as the solvent. Twelve polystyrene standards with  $M_n$  values ranging from 2.52 MDa ( $\mathcal{D} < 1.1$ ) to 390 Da ( $\mathcal{D} < 1.1$ ) were used as calibration references. The number of hydroxyl groups present in each mole of the OCP was determined using  $^1H$  NMR spectroscopy. Method details are provided in the SI. The epoxy equivalent weight (EEW) of the E-OCP was determined using ASTM D1652.<sup>32</sup>

**Epoxidation of OCP.** A round-bottom flask equipped with a mechanical stirrer and thermometer was charged with 1.0 equiv of OCP, 15.0 equiv. of epichlorohydrin, and 0.1 equiv of TBAB, where TBAB was utilized as the phase transfer catalyst. The reaction mixture was placed in an oil bath kept at 65 °C for 6 h with continuous stirring. Then, the flask was immediately placed in an ice bath, where 12.0 equiv of NaOH in a 33 wt % aqueous solution was added dropwise to the reaction mixture. The reaction proceeded with continuous stirring overnight at ambient conditions. The reaction mixture was dissolved in DCM and then washed twice with deionized water in a separatory funnel. The neutralized solution was then washed twice with a basic water solution. The organic layer was dried over anhydrous sodium sulfate, reduced via rotary evaporation, and dried under vacuum. This procedure was also completed using 30.0 equiv of epichlorohydrin. The comparison of the resultant epoxy resin from either equivalent of epichlorohydrin was used to help verify the extent of the epoxidation.

**Curing of E-OCP.** The synthesized epoxidized oligomeric coproduct (E-OCP) was cured with the appropriate stoichiometric quantity of Epikure W. Upon the addition of Epikure W, the resulting uncured resin was thoroughly mixed using a Thinky ARE-310 planetary centrifugal mixer for 10 min



**Figure 1.** Representative  $^1\text{H}$  NMR spectrum of the OCP spiked with  $\text{C}_6\text{H}_{12}$  (1.43 ppm) for hydroxyl content determination as well as the proposed chemical structure of OCP isomers.

at 2000 rpm and defoamed for 5 min at 2200 rpm. After mixing, the uncured resin was transferred to round aluminum pans of uniform dimensions (44 mm ID) and subsequently degassed under vacuum for 15 min. In the aluminum pans, the epoxy-amine resins were further degassed under vacuum in the oven for approximately 15 min before beginning the cure schedule. Samples were cured at  $90\text{ }^\circ\text{C}$  for 4 h and postcured at  $180\text{ }^\circ\text{C}$  for 2 h. All samples were allowed to cool to room temperature overnight.

**Curing of Epon 164 and Epon 828.** Commercial resin Epon 164, which has structural similarities to that of the E-OCP (see Figure S1 for a representative structure), was cured with the appropriate stoichiometric quantity of Epikure W. The EEW of the Epon 164 used was 213 g/equiv as per the certificate of analysis. Because Epon 164 is a solid at room temperature, the epoxy cresol novolac was heated past its melting point ( $\text{mp} = 80\text{--}85\text{ }^\circ\text{C}$ ) to aid in processability. Before mixing, the Epikure W was also heated to avoid temperature shock when combining the epoxy resin and the curing agent. Heated Epon 164 and Epikure W were poured into round aluminum pans of uniform dimension (44 mm ID) and quickly mixed before being placed in a thermal oven to cure. Samples were cured at  $90\text{ }^\circ\text{C}$  for 4 h and were postcured at  $180\text{ }^\circ\text{C}$  for 2 h. All samples were allowed to cool to room temperature overnight. A representative structure of Epon 164 can be found in the Supporting Information (see Figure S1). The EEW of the Epon 828 used was 186 g/equiv as per the certificate of analysis. In this study, Epon 828 was cured with Epikure W using the same procedure as the E-OCP for the primary purpose of producing comparative fracture test specimens.

**Polymer Properties.** The extent of cure for the cured resins was measured using a Nicolet iS50 Fourier transform infrared (FTIR) spectrometer operating in the near-IR range. Method details and calculation information can be found in the SI. Thermogravimetric analysis (TGA) of the cured resins was performed on a TA Instruments Discovery TGA 550. Thermal analysis was performed using a TA Instruments Discovery

2500 DSC. The viscoelastic properties of the polymers were characterized using a TA Instruments Q800 DMA. Fracture testing was performed in accordance with ASTM D5045 using an Instron 5966 with a 1 N load cell and a three-point bend flexure fixture at a cross-head speed of 10 mm/min.<sup>33</sup> Test specimens were scored with a fresh razor to produce the initial crack.<sup>33</sup>

## RESULTS AND DISCUSSION

**Characterization of the OCP and E-OCP.** The OCP formed during the synthesis of BG is a highly viscous, dark amber liquid, proposed to be a low-molecular-weight novolac containing both vanillyl alcohol- and guaiacol-derived segments. A novolac is defined as being the product of an acid-catalyzed reaction under an excess of phenol.<sup>7,34</sup> In the synthesis of BG, Amberlyst 15, the ion exchange resin used, performs acid catalysis, while the five molar excess of guaiacol behaves as an excess of phenol. The most popular and simplest novolac produced is bisphenol-F (BPF). BPF can be considered the “most difficult bisphenol to obtain” as the reaction tends to result in oligomerization and, thus, formation of higher-molecular-weight novolacs.<sup>34</sup> The synthesis routes are also similar in that BPF is synthesized under an excess of phenol, while BG was synthesized under an excess of guaiacol, a substituted phenol, and both form multiple isomers.<sup>34</sup> Given this information, the OCP produced during the synthesis of BG is proposed to be a low-molecular-weight novolac, with the lower molecular weight being associated with the lower temperature at which the reaction was performed. As determined by APC,  $M_n$ ,  $M_w$ , and  $\bar{D}$  values for the OCP were determined to be  $643 \pm 104\text{ Da}$ ,  $663 \pm 103\text{ Da}$ , and  $1.03 \pm 0.02$ , respectively. These results demonstrate that the chemistry in producing the OCP is relatively consistent and, thus, produces structurally similar molecules. By  $^1\text{H}$  NMR, it was estimated that there are five hydroxyl groups per OCP molecule on average. Figure 1 shows a representative spectrum of a spiked sample with the proposed chemical structure of



OCP isomers and the chemical structure of cyclohexane (12 protons at  $\sim 1.4$  ppm).

Based on the known novolac chemistry, the APC data, and the estimated hydroxyl number obtained via  $^1\text{H}$  NMR, an estimated average OCP structure was constructed. The averaged proposed structure shown in Figure 1 represents the structure that is predicted to be present most often. Occasionally, an OCP molecule could contain an extra hydroxymethyl group, an additional ring or one less ring; however, given the consistently low  $\bar{D}$ , it is expected that deviations from this averaged structure would be rare. It is important to note the isomeric nature of this coproduct. As with BG, it would be expected to see isomeric differences based on the various locations in which the methylene bridging can occur. Given that the hydroxymethyl group of vanillyl alcohol is *para* to the aromatic hydroxyl group, each bridge will have one attachment *para* to an hydroxyl. Hydroxyl and methoxy groups are both *para* directing with an hydroxyl being a stronger director than a methoxy.<sup>35</sup> Therefore, the most common methylene bridging occurrence would be *para* to the hydroxyl group. Furthermore, slightly less common bridging would be *para* to the methoxy group; thus, *meta* to the hydroxyl. Variations between bridging sites are possible for each bridging connection between aromatic rings. As a result, a high number of isomers present in the OCP are expected. As a case in point, the novolac glycidyl ether (NOGE) related to BPF has 27 isomers for a novolac containing four rings.<sup>36</sup> While the OCP has five phenolics, methoxy groups are expected to reduce the number of isomers compared to a BPF-based novolac structure.

The OCP was successfully epoxidized via a widely used epoxidation process, which employs the reaction of a molar excess of epichlorohydrin with a phenolic compound and sodium hydroxide, resulting in a liquid novolac-based epoxy resin.<sup>20</sup> The molar excess of epichlorohydrin allows for the elimination of additional solvents, as the epichlorohydrin acts as both a solvent and a reactant. The excess also typically reduces the amount of high-molecular-weight oligomers formed as well as reduces branching caused by the reaction of hydroxyl groups with epoxide groups.<sup>20</sup> Confirmation of successful epoxidation was determined via  $^1\text{H}$  NMR (see Figure S2). The EEW of the E-OCP was calculated to be  $204 \pm 11$  g/equiv.<sup>32</sup> Based on the predicted structure of the OCP (shown in Figure 1), if all five hydroxyl groups were successfully epoxidized, the EEW is estimated to be 190 g/equiv. The slightly higher experimental EEW value would be expected as some oligomerization is expected to occur during epoxidation. Full epoxidation was verified by increasing the amount of epichlorohydrin used in the synthesis from 15 equiv (relative to OCP) to 30 equiv. Table S1 compares experimental EEW values and APC data for the E-OCP synthesized. The increase in epichlorohydrin equivalency did not result in a significant difference in EEW values, indicating that 15 equiv is sufficient to convert all hydroxyls to glycidyl ethers. However, a slight reduction in oligomerization during epoxidation was observed. Finally, the primary structural difference between the E-OCP (Figure 1) and Epon 164 (Figure S1) is that Epon 164 contains methyl moieties, while the E-OCP possesses methoxy moieties; hence, the rationale to directly compare cured epoxy resins that contain these similar epoxy components.

**Extent of Cure.** Near-IR spectra of the resins were obtained before and after the curing process (see Figure S2).

Within the limits of near-IR, the cured resin containing the E-OCP exhibited a  $98.7 \pm 1\%$  extent of the cure, while the cured Epon 164 resin showed a  $77.8 \pm 2\%$  extent of cure. The lower extent of cure observed for the Epon 164 resin system is likely due to the postcure temperature falling below the  $T_g$  of the system and the difficulty in properly curing a high-melting-point epoxy resin; however, for comparative purposes, the curing schedules after mixing for both resins were kept identical.

**Polymer Properties.** TGA data is summarized in Table 1 with representative TGA thermograms for the cured resins in

**Table 1. TGA Data for the Cured Resins in  $\text{N}_2$  (10  $^\circ\text{C}/\text{min}$  Heating Rate)<sup>a</sup>**

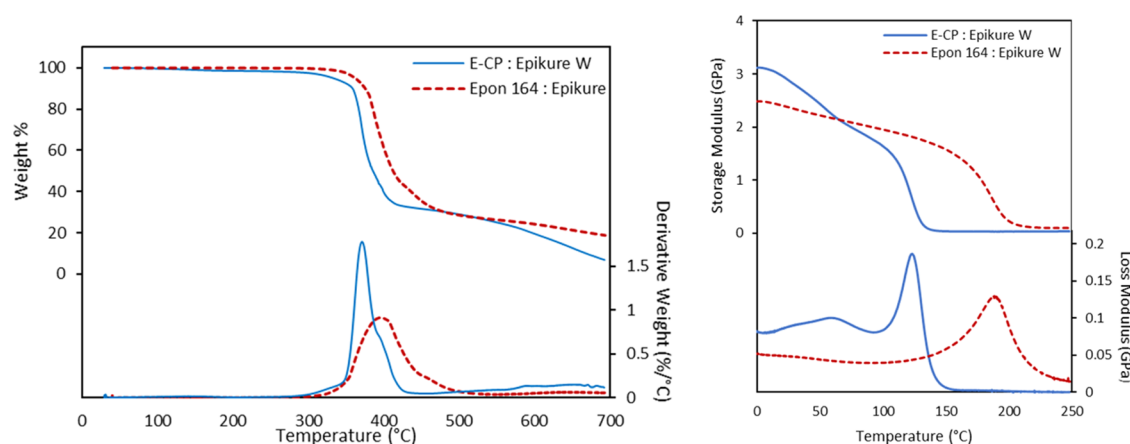
| cured resin         | IDT ( $^\circ\text{C}$ ) | $T_{50}$ ( $^\circ\text{C}$ ) | $T_{\text{max}}$ ( $^\circ\text{C}$ ) | char content <sup>b</sup> (wt %) |
|---------------------|--------------------------|-------------------------------|---------------------------------------|----------------------------------|
| E-OCP: Epikure W    | $336 \pm 5$              | $382 \pm 4$                   | $353 \pm 4$                           | $9.0 \pm 3$                      |
| Epon 164: Epikure W | $362 \pm 1$              | $414 \pm 3$                   | $367 \pm 3$                           | $20 \pm 1$                       |

<sup>a</sup>IDT = the initial decomposition temperature (taken at 5% weight loss);  $T_{50}$  = temperature at 50% weight loss; and  $T_{\text{max}}$  = temperature at maximum decomposition rate. <sup>b</sup>Char content at 700  $^\circ\text{C}$ .

$\text{N}_2$  shown in Figure 2 (Left) (see Table S2 and Figure S3 for corresponding TGA data in air). The cured E-OCP resin showed promising thermal stability, exhibiting IDT,  $T_{50\%}$ , and  $T_{\text{max}}$  values of 336, 382, and 353  $^\circ\text{C}$ , respectively. The cured Epon 164 resin exhibited IDT,  $T_{50\%}$ , and  $T_{\text{max}}$  values of 362, 414, and 367  $^\circ\text{C}$ , respectively. In comparison, the cured E-OCP resin showed a slightly lower thermal stability. This is believed to be a result of the methoxy groups present in the cured E-OCP resin, which have the propensity to cleave off of the main structure upon heating.<sup>37</sup> This behavior is also believed to result in the lower char content observed for the cured E-OCP resin.

Polymer properties of the cured resins were further analyzed via DMA. Samples were prepared in accordance with McAninch et al. to uniform dimensions of  $35 \times 11 \times 2.5$  mm<sup>3</sup>, see Table 2 and Figure 2 (Right) as well as Figure S4.<sup>38</sup> As seen in Figure 2 (Right), the  $E''$  shows  $\beta$  relaxations for the cured E-OCP resin around 50  $^\circ\text{C}$ . These relaxations represent the small chain motions of side groups, believed to be a result of the methoxy groups that are hydrogen bonded to the hydroxyl group present in the system that were formed upon the epoxy-amine reaction relaxing upon heating.<sup>20</sup> When compared to the cured Epon 164 and Epon 828 resins, there is a slight increase in  $E'$  at 25  $^\circ\text{C}$  for the cured E-OCP resin (Table 2). This increase could be attributed to the methoxy groups present in the cured E-OCP resin, which have hydrogen bonded with the present hydroxyl groups. Glassy moduli are related to chain packing and chemical structure.<sup>20</sup> Moreover, increases in density can be a result of greater chain packing. The cured E-OCP resin exhibited a higher density compared to the cured Epon 164 and Epon 828 resins, suggesting higher chain packing, thus the higher  $E'$  value at 25  $^\circ\text{C}$ .<sup>20,39</sup> The highest  $T_g$  values were observed for the cured Epon 164 resin. It has been observed that methoxy substituents can result in lower  $T_g$  values.<sup>20</sup> Regardless, the cured E-OCP resin displayed promising thermomechanical properties when compared to the commercial epoxy resins.

Fracture testing was performed in accordance with ASTM D5045.<sup>33</sup> Table 3 below summarizes the critical strain energy release rate,  $G_{1C}$ , and the plane strain fracture toughness,  $K_{1C}$ ,



**Figure 2.** (Left) Representative TGA thermograms of the cured resins in  $N_2$ ; (Right) representative dynamic mechanical analysis (DMA) storage modulus and loss modulus thermograms for the cured resins.

**Table 2. Thermomechanical and Gravimetric Properties of the Cured Resins<sup>a</sup>**

| cured resin         | $E' @ 25\text{ °C}$ (GPa) | $T_g$ via $E''$ (°C) | $T_g$ via $\tan \delta$ (°C) | $\rho$ (g/cm <sup>3</sup> ) |
|---------------------|---------------------------|----------------------|------------------------------|-----------------------------|
| E-OCP: Epikure W    | $2.8 \pm 0.4$             | $133 \pm 10$         | $143 \pm 10$                 | $1.24 \pm 0.012$            |
| Epon 164: Epikure W | $2.3 \pm 0.3$             | $177 \pm 11$         | $204 \pm 1$                  | $1.18 \pm 0.012$            |
| Epon 828: Epikure W | $2.1 \pm 0.1$             | $169 \pm 1$          | $180 \pm 2$                  | $1.17 \pm 0.010$            |

<sup>a</sup> $\rho$  = Density at 25 °C.

**Table 3.  $K_{IC}$  and  $G_{IC}$  Values of the Cured E-OCP Resin Compared to the Cured Epon 828 Resin**

| system                          | $K_{IC}$ (MPa m <sup>1/2</sup> ) | $G_{IC}$ (J/m)   |
|---------------------------------|----------------------------------|------------------|
| E-OCP:Epikure W                 | $1.34 \pm 0.22$                  | $448.16 \pm 109$ |
| Epon 828:Epikure W <sup>a</sup> | $0.69 \pm 0.05$                  | $199.78 \pm 58$  |

<sup>a</sup>Data reported by Sweet et al.<sup>40</sup>

of both the cured E-OCP and Epon 828 resins. Epon 828 was used as a commercial comparison rather than Epon 164 due to the increased ease in processing and its dominance in usage in the composite industry. With Epon 164 being a high-melting-point solid, it was difficult to melt the novolac-based epoxy resin and mix it well with Epikure W at a large enough scale to produce fracture test specimens. Higher  $G_{IC}$  and  $K_{IC}$  values were observed for the cured E-OCP resin compared to cured Epon 828 resin. This suggests that tougher cured epoxy resins can be produced with E-OCP. This is likely due to the ability of the methoxy functionalities in the E-OCP to hydrogen bond with the hydroxyls formed during the curing process. While these data show the cured E-OCP resin as having improved toughness, both cured resins still exhibited brittle behavior, demonstrated by the load and deformation increasing linearly up to the point of fracture. This is illustrated in the load–displacement curves found in the SI (Figure S6).

## CONCLUSIONS

This work explored the use of the oligomeric coproduct of the synthesis of bisguaiacol (BG) as the phenolic component in a thermosetting resin. The highly phenolic coproduct was characterized as a low-molecular-weight novolac and was successfully synthesized into an epoxy-amine thermosetting resin showing promising thermal stability and thermomechanical properties. Finding viable applications for the coproduct can increase the overall economic feasibility of the reaction by giving use to both the intended product, BG, and the

coproduct. This work also demonstrates the potential of lignin-inspired phenolics to be used in the synthesis of materials with high-performance attributes. Epoxy-amine thermosetting resins composed of the epoxidized oligomeric coproduct (E-OCP) and Epikure W showed promising thermal properties including good thermal stability and a glass transition-temperature value  $> 120\text{ °C}$ . While the cured E-OCP resin exhibited lower thermal stability and glass transition-temperature values than a thermoset containing a commercial epoxy cresol novolac, Epon 164, the epoxidized coproduct showed improved processability and promoted an increase in glassy modulus. Moreover, the cured E-OCP resin exhibited promising fracture behavior when directly compared to a thermoset containing Epon 828. The ability of the E-OCP to easily create thermosetting resins with the extent of cure values over 95% and promising thermal stability and thermomechanical properties on its own shows promise for its utility in developing more sustainable polymeric systems for a wide variety of applications.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c02799>.

Detailed description of determining the hydroxyl content per mole of oligomeric coproduct (OCP); extent of cure determination details; TGA, DSC, DMA, and fracture testing details; chemical structures of Epon 164, Epon 828, and Epikure W; <sup>1</sup>H NMR of the epoxidized OCP (E-OCP); near-IR spectra of E-OCP: Epikure W; TGA and  $\tan \delta$  thermograms of the cured epoxy resins; and load versus displacement graph of the cured E-OCP: Epikure W resin (PDF)

## AUTHOR INFORMATION

### Corresponding Author

Joseph F. Stanzione, III – Department of Chemical Engineering, Rowan University, Glassboro, New Jersey 08028, United States; [orcid.org/0000-0003-0464-835X](https://orcid.org/0000-0003-0464-835X); Email: [stanzione@rowan.edu](mailto:stanzione@rowan.edu)

### Author

Kelli M. Hambleton – Department of Chemical Engineering, Rowan University, Glassboro, New Jersey 08028, United States

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsomega.1c02799>

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of the U.S. Army Research Laboratory through Cooperative Agreements W911NF-14-2-0086 and W911NF-16-2-0225. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the U.S. Army Research Laboratory or the U.S. government. The authors would also like to thank Joseph R. Mauck (Cardolite Corporation, Bristol, PA, USA) for assisting with the synthesis of bisguaiacol and the oligomeric coproduct as well as for assisting in product separation. Finally, the authors would like to thank Jonathan Foglein of the Chemistry & Biochemistry Department at Rowan University for his aid in the use of their NMR facility.

## REFERENCES

- (1) Pham, H. Q.; Marks, M. J. Epoxy Resins. In *Ullmann's Encyclopedia of Industrial Chemistry*, 2005.
- (2) Hodgkin, J. H.; Simon, G. P.; Varley, R. J. Thermoplastic toughening of epoxy resins: a critical review. *Polym. Adv. Technol.* **1998**, *9*, 3–10.
- (3) Jin, F.-L.; Li, X.; Park, S.-J. Synthesis and application of epoxy resins: A review. *J. Ind. Eng. Chem.* **2015**, *29*, 1–11.
- (4) Kumar, S.; Samal, S. K.; Mohanty, S.; Nayak, S. K. Recent Development of Biobased Epoxy Resins: A Review. *Polym.-Plast. Technol. Eng.* **2018**, *57*, 133–155.
- (5) Ellis, B. *Chemistry and Technology of Epoxy Resins*; Blackie Academic & Professional, 1993.
- (6) May, C. *Epoxy Resins: Chemistry and Technology*, 2nd ed.; CRC Press, 2018.
- (7) Fried, J. R. *Polymer Science and Technology*; Pearson Education: US, 2003.
- (8) Auvergne, R.; Caillol, S.; David, G.; Boutevin, B.; Pascault, J.-P. Biobased Thermosetting Epoxy: Present and Future. *Chem. Rev.* **2014**, *114*, 1082–1115.
- (9) Ritter, S. K. Debating BPA's Toxicity. *ACS Chem. Eng. News* **2011**, 14–19.
- (10) Rubin, B. S. Bisphenol A: An endocrine disruptor with widespread exposure and multiple effects. *J. Steroid Biochem. Mol. Biol.* **2011**, *127*, 27–34.
- (11) Vandenberg, L. N.; Hauser, R.; Marcus, M.; Olea, N.; Welshons, W. V. Human exposure to bisphenol A (BPA). *Reprod. Toxicol.* **2007**, *24*, 139–177.
- (12) Wang, H.; Tucker, M.; Ji, Y. Recent Development in Chemical Depolymerization of Lignin: A Review. *J. Appl. Chem.* **2013**, *2013*, No. 838645.
- (13) Kleinert, M.; Barth, T. Phenols from Lignin. *Chem. Eng. Technol.* **2008**, *31*, 736–745.
- (14) Wang, H.; Pu, Y.; Ragauskas, A.; Yang, B. From lignin to valuable products—strategies, challenges, and prospects. *Bioresour. Technol.* **2019**, *271*, 449–461.
- (15) Calvo-Flores, F. G.; Dobado, J. A. Lignin as Renewable Raw Material. *ChemSusChem* **2010**, *3*, 1227–1235.
- (16) Fache, M.; Boutevin, B.; Caillol, S. Vanillin Production from Lignin and Its Use as a Renewable Chemical. *ACS Sustainable Chem. Eng.* **2016**, *4*, 35–46.
- (17) Lignin. <https://www.acs.org/content/acs/en/molecule-of-the-week/archive/l/lignin.html>.
- (18) Belgacem, M. N.; Gandini, A. *Monomers, Polymers and Composites from Renewable Resources*; Elsevier Science, 2011.
- (19) Stewart, D. Lignin as a base material for materials applications: Chemistry, application and economics. *Ind. Crops Prod.* **2008**, *27*, 202–207.
- (20) Hernandez, E. D.; Bassett, A. W.; Sadler, J. M.; La Scala, J. J.; Stanzione, J. F., III Synthesis and Characterization of Bio-based Epoxy Resins Derived from Vanillyl Alcohol. *ACS Sustainable Chem. Eng.* **2016**, *4*, 4328–4339.
- (21) Bassett, A. W.; Breyta, C. M.; Honnig, A. E.; Reilly, J. H.; Sweet, K. R.; La Scala, J. J.; Stanzione III, J. F. Synthesis and Characterization of Molecularly Hybrid Bisphenols Derived from Lignin and CNSL: Application in Thermosetting Resins. *Eur. Polym. J.* **2019**, *111*, 95–103.
- (22) Fache, M.; Auvergne, R.; Boutevin, B.; Caillol, S. New Vanillin-Derived Diepoxy Monomers for the Synthesis of Biobased Thermosets. *Eur. Polym. J.* **2015**, *67*, 527–538.
- (23) Fache, M.; Darroman, E.; Besse, V.; Auvergne, R.; Caillol, S.; Boutevin, B. Vanillin, a Promising Biobased Building-Block for Monomer Synthesis. *Green Chem.* **2014**, *16*, 1987–1998.
- (24) Mahajan, J. S.; O'Dea, R. M.; Norris, J. B.; Korley, L.T.J.; Epps, T. H., III Aromatics from Lignocellulosic Biomass: A Platform for High-Performance Thermosets. *ACS Sustainable Chem. Eng.* **2020**, *8*, 15072–15096.
- (25) Nicasastro, K. H.; Kloxin, C. J.; Epps, T. H., III Potential Lignin-Derived Alternatives to Bisphenol A in Diamine-Hardened Epoxy Resins. *ACS Sustainable Chem. Eng.* **2018**, *6*, 14812–14819.
- (26) Chen, C.-H.; Tung, S.-H.; Jeng, R.-J.; Abu-Omar, M. M.; Lin, C.-H. A Facile Strategy to Achieve Fully Bio-Based Epoxy Thermosets from Eugenol. *Green Chem.* **2019**, *21*, 4475–4488.
- (27) Zhao, S.; Huang, X.; Whelton, A. J.; Abu-Omar, M. M. Renewable Epoxy Thermosets from Fully Lignin-Derived Triphenols. *ACS Sustainable Chem. Eng.* **2018**, *6*, 7600–7608.
- (28) Fadlallah, S.; Roy, P. S.; Garnier, G.; Saito, K.; Allais, F. Are Lignin-Derived Monomers and Polymers Truly Sustainable? An In-Depth Green Metrics Calculations Approach. *Green Chem.* **2021**, *23*, 1495–1535.
- (29) Peng, Y.; Nicasastro, K. H.; Epps, T. H., III; Wu, C. Evaluation of Estrogenic Activity of Novel Bisphenol A Alternatives, Four Inspired Bisguaiacol F Specimens, by In Vitro Assays. *J. Agric. Food Chem.* **2018**, *66*, 11775–11783.
- (30) Hong, H.; Harvey, B. G.; Palmese, G. R.; Stanzione, J. F., III; Ng, H. W.; Sakkiah, S.; Tong, W.; Sadler, J. M. Experimental Data Extraction and In Silico Prediction of the Estrogenic Activity of Renewable Replacements for Bisphenol A. *Int. J. Environ. Res. Public Health* **2016**, *13*, No. 705.
- (31) Peng, Y.; Nicasastro, K. H.; Epps, T. H., III; Wu, C. Methoxy Groups Reduced the Estrogenic Activity of Lignin-Derivable Replacements Relative to Bisphenol A and Bisphenol F as Studied Through Two In Vitro Assays. *Food Chem.* **2021**, *338*, No. 127656.
- (32) ASTM D1652-11. *Standard Test Method for Epoxy Content of Epoxy Resins*; ASTM International, West Conshohocken, PA, 2011.
- (33) ASTM D5045-14. *Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials*; ASTM International: West Conshohocken, PA, 2014.
- (34) Pilato, L. *Phenolic Resins: A Century of Progress*; Springer: Berlin, Heidelberg, 2010.

- (35) Wade, L. G. *Organic Chemistry*; Pearson, 2013.
- (36) Brem, S.; Grob, K.; Biedermann, M. Method for Determining Novolac Glycidyl Ether (NOGE) and its Chlorohydrins in Oily Canned Foods. *Food Addit. Contam.* **2001**, *18*, 655–672.
- (37) Mauck, J. R. *Synthesis of Novel, Highly Bio-based Monomeric Materials Derived From Lignocellulosic Biomass and Their Respective Epoxy Resins, Polycarbonates, and Polyesters*; Rowan University, 2016.
- (38) McAninch, I.; Palmese, G. R.; Lenhart, J.; Scala, J. J. DMA testing of epoxy resins: The importance of dimensions. *Polym. Eng. Sci.* **2015**, *55*, 2761–2774.
- (39) Palusiak, M.; Grabowski, S. Methoxy group as an acceptor of proton in hydrogen bonds. *J. Mol. Struct.* **2002**, *642*, 97–104.
- (40) Sweet, K. R.; Stanzione, J. F., III Epoxy-functional Thermoplastic Copolymers and Their Incorporation into a Thermosetting Resin. *J. Appl. Polym. Sci.* **2021**, *138*, No. 50608.