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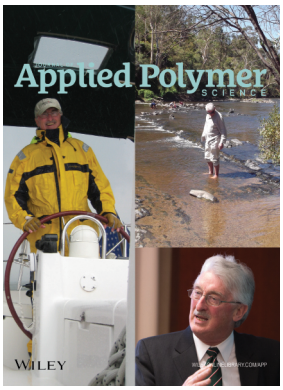
Special Issue: Sustainable Polymers and Polymer Science Dedicated to the Life and Work of Richard P. Wool

Guest Editors: Dr Joseph F. Stanzione III (Rowan University, U.S.A.)
and Dr John J. La Scala (U.S. Army Research Laboratory, U.S.A.)



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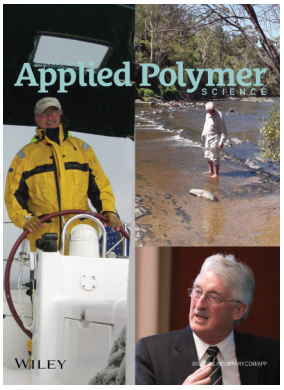

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Bio-based hydrophobic epoxy-amine networks derived from renewable terpenoids

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ABSTRACT: Carvacrol and *p*-cymene are sustainable and versatile starting materials for the preparation of hydrophobic monomers. These molecules can be readily derived from pine resin or produced from other sustainable feedstocks via a biosynthetic approach. A hydrophobic epoxy monomer [bis(2-isopropyl-5-methyl-4-(oxiran-2-ylmethoxy)phenyl)methane, **3**] with methyl and isopropyl substituents on the aromatic rings was synthesized from carvacrol. A bisaniline [4,4′-methylenebis(5-isopropyl-2-methylaniline, 4] was then synthesized from *p*-cymene. Using a cured epoxy-amine network prepared from the diglycidyl ether of bisphenol A (**DGEBA**) and 4,4′-methylenedianiline (**MDA**) as a baseline system, three additional networks were prepared from **DGEBA:4**, **3:MDA**, and **3:4**. The cured epoxy-amine networks were tested for moisture uptake as well as changes in thermomechanical properties after exposure to boiling water for several days. Incorporation of the bio-based monomers resulted in up to 53% lower water uptake compared to the baseline system. The bio-based resins also showed greater resistance to degradation under hot-wet conditions, with wet-T_G knockdowns as low as 8% as compared to a 19% decrease for the baseline system. These results show that the unique functionality of the renewable bisphenol and aniline used in this study can result in materials with improved hot/wet performance as compared to conventional thermosetting resins. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43621.

KEYWORDS: biopolymers and renewable polymers; differential scanning calorimetry; glass transition; thermogravimetric analysis; thermosets

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INTRODUCTION

Despite enormous reserves, the world supply of petroleum and other nonsustainable carbon-based feedstocks is limited. This realization, coupled with the increasing demand for petroleum-derived fuels and chemicals as the world population grows, has made the discovery and utilization of sustainable feedstocks of vital importance. Polymer synthesis and consumption account for ~7% of petroleum use and thus represent a significant opportunity for researchers to develop new sustainable chemistry.[1–3] In light of the abundance of bisphenol A derived polymers in use today, researchers have begun developing novel polymers and composite materials based on bisphenols derived from biomass sources including lignin,[4–12] resveratrol,[13] anethole,[14] diphenolic acid,[15,16] canalol,[17] and cardanol.[18] In large part, these studies have shown that polymers prepared from renewable bisphenols have similar properties to those derived from petroleum and in some cases offer unique advantages over conventional polymers. In addition to material properties, a few studies have specifically focused on finding less toxic alternatives to bisphenol A.[19–22] By combining these approaches, the use of renewable phenols from biomass sources may allow for the development of high performance materials while utilizing less toxic monomer precursors.

In stark contrast to the development of renewable bisphenols, the preparation of bisanilines from sustainable feedstocks has been largely ignored. 4,4′-methylenedianiline (**MDA**) is a widely used commercial bisaniline with applications in polyurethanes, adhesives, high temperature polyimides, and thermosetting epoxy resins. Unfortunately, MDA is a liver toxin, confirmed animal carcinogen, and suspected human carcinogen.[23] The occupational exposure limit for MDA is only 10 ppb averaged over an 8 h workday.[24] Synthesis of MDA replacements from renewable feedstocks offers the potential to both improve sustainability and reduce the toxicity of paints, coatings, thermoplastics, and thermosetting monomers.

Terpenoids are sustainable hydrocarbons that can potentially be used to replace significant quantities of petroleum-based phenols and anilines. While less abundant than lignin, ~350,000 tons

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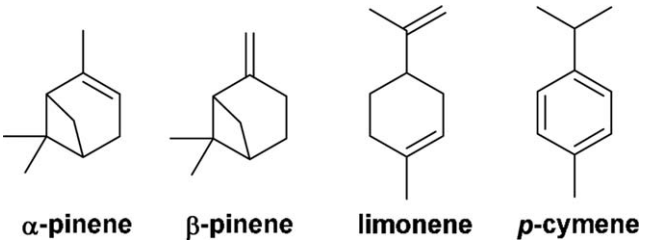

Figure 1. Structures of common cyclic monoterpenes.

of turpentine are produced each year from pine resin, which is a rich source of cyclic terpenes[2,25,26] (Figure 1). Several methods have been developed for the polymerization of cyclic terpenes, specifically α-pinene, β-pinene, and limonene, via cationic, radical, or ring-opening metathesis polymerization of carbon–carbon double bonds.[25–29] However, few studies have focused on the development of polymers from *p*-cymene, an aromatic component of turpentine, which can also be readily synthesized by dehydrogenation of α-pinene, β-pinene, limonene, and other terpenes.[30–35] A phenolic terpenoid, 2-methyl-5-isopropylphenol (carvacrol), can be isolated from thyme and oregano essential oils[36–38] or can be synthesized from a variety of turpentine components including *p*-cymene.[39–46] A recent study by our laboratory demonstrated the conversion of carvacrol into a bisphenol that was subsequently used to make polycarbonates and a hydrophobic cyanate ester monomer.[46] Therefore, *p*-cymene and carvacrol represent two sustainable molecules with potential as precursors to epoxy monomers after chemical modification.

Epoxy monomers cured with amines are versatile materials used commercially in the adhesive, aerospace composite, and microelectronics industries. The key advantages of epoxies are high strength-to-weight ratios, low dielectric constants, and excellent processability. However, epoxy-amine cured networks can absorb significant quantities of water, typically several percent by mass. The absorbed moisture is problematic because it causes material swelling and plasticization of the polymer chains, which results in a lower glass transition temperature as well as degradation of adhesive and mechanical properties.[47–52] Several studies over the past three decades have focused on the mechanism of water absorption in epoxy networks.[53–70] A few of these studies have focused on nanovoids or network free volume in the material as the source of moisture uptake.[61–70] The primary conclusion from these studies is that larger voids in the network will result in increased moisture uptake due to the increased open space that can accommodate water. Alternately, other studies have shown that the polarity and functional groups of the network play an important role in moisture uptake.[53–60] Despite the numerous studies on moisture uptake in epoxy networks, very few reports have focused on developing an approach to prevent this problem. One potential route involves addition of "antiplasticizing" chemicals to the epoxy-amine formulation, which causes nanoscale phase separation of the network that in turn reduces moisture uptake.[71–73] A more straightforward technique focuses on blocking the polar groups in the network by placing substituents on the phenyl rings *ortho* to the polar groups (Figure 2). This approach has been demonstrated in cyanate esters and modified epoxy systems.[74–78] In

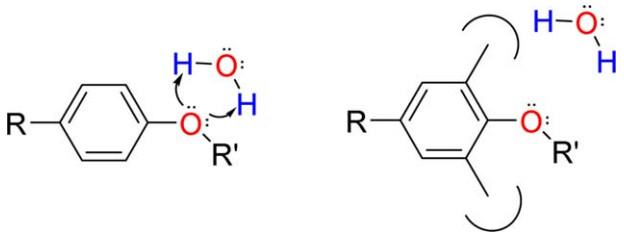

Figure 2. *ortho*-Methylation has been shown to effectively reduce moisture uptake by blocking access to polar functionality in cyanate ester and modified epoxy networks.[74–78] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the cyanate ester networks, *ortho* substituents were able to decrease moisture uptake by up to 50% as compared to unsubstituted systems.[78] Thus, monomers with *ortho* substituents may have the potential to mitigate the problem of moisture uptake in epoxy-amine cured networks.

This article focuses on the use of carvacrol and *p*-cymene as sustainable precursors to epoxy monomers and amine curing agents. The bisphenolate derived from carvacrol is converted to an epoxy monomer via a reaction with epichlorohydrin, while *p*-cymene is converted into a bisaniline after nitration, hydrogenation, and coupling with formaldehyde. The resulting epoxy and amine monomers are then cured with each other as well as the diglycidyl ether of bisphenol A (**DGEBA**) and 4,4′-methylenedianiline (**MDA**) in combinations to prepare four different epoxy-amine cured networks. Characterization of the networks allows for a comparison of the relative effects of the isopropyl and *ortho*-methyl substituents on the thermomechanical properties and hydrophobicity of the epoxy-amine thermosets.

EXPERIMENTAL

General

4,4′-methylenebis(5-isopropyl-2-methylphenol) was available from a previous study[46] and was a mixture of *para*, *para* and *para*, *ortho* isomers in a 97:3 ratio by mass. All solvents and chemicals were purchased from Sigma Aldrich and used as received except for HNO_3, HCl, and H_2SO_4, which were purchased from Fisher Scientific. Synthetic schemes for new compounds can be found in Figure 3. NMR spectra were collected with a Bruker Avance II 300 MHz NMR spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported versus the deuterated solvent peak [$CDCl_3$: δ 7.27 (^{1}H), 77.36 (^{13}C)]. Gas chromatography was carried out on an Agilent 6890N GC using a Restek Rxi-5ms 20 m × 0.18 mm i.d. capillary column with a 0.18 μm coating of Crossbond 5% diphenyl/95% dimethyl polysiloxane. The GC was programmed to ramp from 40 to 300 °C at 20 °C/min. The GC detector was an Agilent 5973N mass selective detector (MSD). Elemental analysis was performed by Atlantic Microlabs Inc. Norcross, GA.

Bis[2-isopropyl-5-methyl-4-(oxiran-2-ylmethoxy)phenyl]Methane (3)

Method 1: To a solution of potassium tert-butoxide (4.5 g, 40 mmol) in ethylene glycol dimethyl ether (EGDE, 25 mL) cooled to 0 °C, a solution of 4,4′-methylenebis(5-isopropyl-2-methylphenol) (5.0 g, 16 mmol) in EGDE (50 mL) was added

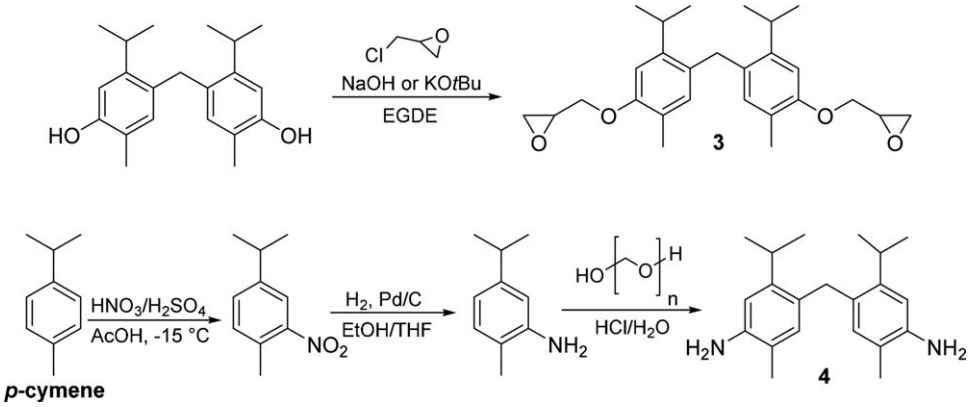

Figure 3. Synthetic scheme for preparation of renewable, hydrophobic monomers.

dropwise. The solution turned light green. Epichlorohydrin (14.8 g, 160 mmol) was added to the stirred solution, which was allowed to warm to room temperature and then heated to 70 °C for 4 h. A white solid began precipitating after 1 h. Diethyl ether (100 mL) was added to dilute the reaction mixture, which was then washed with 2 × 100 mL deionized water and 100 mL of brine. The organic fraction was dried over $MgSO_4$, and the volatiles were removed at 100 °C under reduced pressure (5 torr) to yield the product as a white powder upon cooling (5.24 g, 77.2%). mp = 92–95 °C. ^{1}H NMR ($CDCl_3$) δ: 6.80 (s, 2H, Ph), 6.66 (s, 2H, Ph), 4.26 (dd, J = 11.0 Hz, 3.3 Hz, 2H, CH_2), 4.04 (dd, J = 11.0 Hz, 5.4 Hz, 2H, CH_2), 3.90 (s, 2H, CH_2), 3.44–3.39 (m, 2H, CH), 3.11 (sept, J = 6.8 Hz, 2H, CH), 2.94 (dd, J = 5.0 Hz, 4.2 Hz, 2H, CH_2), 2.82 (dd, J = 5.0 Hz, 2.7 Hz, 2H, CH_2), 2.16 (s, 6H, CH_3), 1.22 (d, J = 6.8 Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 155.7, 145.7, 132.5, 130.3, 124.5, 109.1, 69.4, 50.8, 45.2, 34.0, 29.4, 24.13, 24.11, 16.1. Anal. Calcd for $C_{27}H_{36}O_4$: C, 76.38; H, 8.55; O, 15.07. Found: C, 76.21; H, 8.60. GC/MS: major peak (95%) 424 (M^+), minor peak (4%) 424 (M^+), minor peak (1%) 206 (M^+).

Method 2: A second synthetic method was created by modification of the typical laboratory procedure.[79] 4,4′-methylenebis (5-isopropyl-2-methylphenol) (3.10 g, 10 mmol) was dissolved in a solution of EGDE (3.0 mL) and epichlorohydrin (8.0 mL). NaOH (1.00 g, 25 mmol) was added to the solution, which was heated to 70 °C for 4 h. The solution turned dark purple upon addition of the NaOH, and a white precipitate began to form within 1 h. Diethyl ether (50 mL) was added to dilute the reaction mixture, which was then washed with 2 × 50 mL deionized water and 50 mL of brine. The organic fraction was dried over $MgSO_4$ and the volatiles were removed at 100 °C under reduced pressure (5 torr) to yield the product as a white powder upon cooling (3.52 g, 83.8%).

4-Isopropyl-1-Methyl-2-Nitrobenzene

To a mixture of concentrated H_2SO_4 (42.6 g, 160 mmol) and glacial acetic acid (13.6 g, 227 mmol) chilled to −15 °C in a dry ice/brine bath, *p*-cymene (21.5 g, 160 mmol) was added dropwise while stirring the solution vigorously with a mechanical stirrer. In a separate round-bottomed flask containing concentrated H_2SO_4 (42.6 g, 160 mmol) chilled to 0 °C, concentrated HNO_3 (70%, 15.5 g, 247 mmol) was added dropwise. The HNO_3/H_2SO_4 mixture was transferred to an addition funnel chilled to 0 °C and then added dropwise over a 1 h period to the vigorously stirred emulsified *p*-cymene mixture. The mixture changed color from yellow to orange during the addition of the nitrating agent. The contents of the flask were poured over 150 g of ice with 50 g water and stirred carefully for 1 h. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 40 mL). The combined organic layers were washed with water (60 mL) followed by brine (60 mL), dried over $MgSO_4$, and the solvent was then removed under reduced pressure. Fractional distillation of the residue at 110–117 °C under reduced pressure (5 torr) yielded the product as a bright yellow liquid (18.23 g, 63.5% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.83 (d, J = 1.9 Hz, 1H, Ph), 7.37 (dd, J = 8.1 Hz, 1.9 Hz, 1H, Ph), 7.26 (d, J = 8.1 Hz, 1H, Ph), 2.97 (sept, J = 6.9 Hz, 1H, CH), 2.56 (s, 3H, CH_3), 1.27 (d, J = 6.9 Hz, 6H, CH_3).

5-Isopropyl-2-Methylaniline

4-Isopropyl-1-methyl-2-nitrobenzene (22.2 g, 124 mmol) was dissolved in 85 mL THF and 15 mL EtOH and transferred to a thick-walled glass reactor. 1.4 g of 10% Pd/C was then added to the solution. The mixture was placed under 50 psi H_2 and mechanically shaken until H_2 was no longer consumed (1.5 h). The mixture was then filtered through a pad of Celite 545, and the solvent was removed under reduced pressure. Fractional distillation at 116–122 °C under reduced pressure (15 torr) yielded the product as a colorless liquid (15.4 g, 83.4% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.00 (d, J = 7.6 Hz, 1H, Ph), 6.62 (dd, J = 7.6 Hz, 1.8 Hz, 1H, Ph), 6.59 (d, J = 1.8 Hz, 1H, Ph), 3.59 (bs, 2H, NH_2), 2.82 (sept, J = 6.9 Hz, 1H, CH), 2.16 (s, 3H, CH_3), 1.24 (d, J = 6.9 Hz, 6H, CH_3).

4,4′-Methylenebis(5-isopropyl-2-methylaniline) (4)

An HCl solution (30 mL, 3.8*M*) was added dropwise to 5-isopropyl-2-methylaniline (10.0 g, 67 mmol) while stirring. The hydrochloride salt of the aniline precipitated out of solution. The solution was heated to 80 °C and stirred until the salt completely redissolved. Paraformaldehyde (1.00 g, 33 mmol) was added to the solution, which was then stirred for 3 h. The dihydrochloride salt of 4,4′-methylenebis(5-isopropyl-2-methylaniline) precipitated out of solution and was collected by filtration. The solid was rinsed with cold acetonitrile, dissolved in water

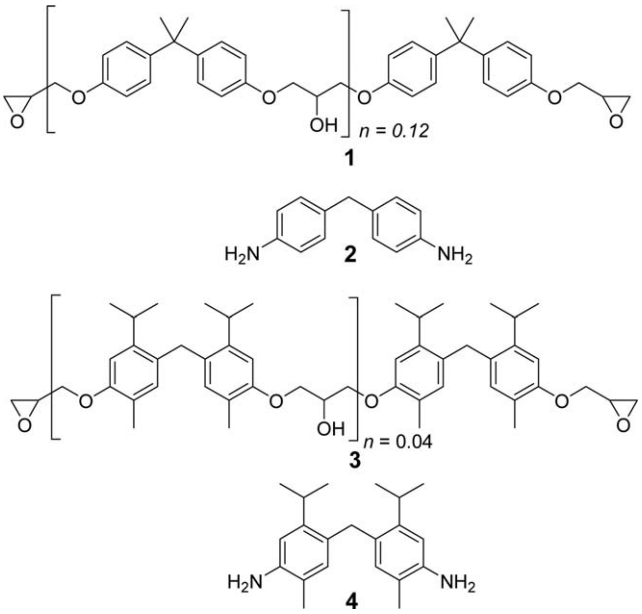

Figure 4. Chemical structures of compounds **1–4**.

(220 mL), and then a NaOH solution (40 mL, 6.3*M*) was added dropwise to the stirred solution at 0 °C. The solution was extracted with ethyl acetate (3 × 50 mL), and the combined organic fractions were washed with water (50 mL) and brine (50 mL) and then dried over $MgSO_4$. The solvent was removed under reduced pressure to obtain the product as a light tan powder (6.18 g, 59.4% yield). mp = 120–125 °C. ^{1}H NMR ($CDCl_3$) δ: 6.65 (s, 2H, Ph), 6.58 (s, 2H, Ph), 3.83 (s, 2H, CH_2), 3.51 (bs, 4H, NH_2), 3.05 (sept, J = 6.9 Hz, CH, 2H), 2.06 (s, 6H, CH_3), 1.18 (d, J = 6.9 Hz, 12H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 145.8, 142.9, 132.1, 128.5, 120.1, 112.4, 33.7, 28.9, 24.0, 22.7, 17.2. Anal. Calcd for $C_{21}H_{30}N_2$: C, 81.24; H, 9.74; N, 9.01. Found: C, 81.52; H, 9.72; N, 8.85. GC/MS: major peak (99%) 310 (M^+), two minor peaks (combined 1%) 334 (M^+), 322 (M^+).

Preparation of Networks

The four monomers used in this study can be found in Figure 4. Epoxy **1** is the diglycidyl ether of bisphenol A (**DGEBA**) and was purchased from Momentive Specialty Chemicals under the trade name Epon 828. Amine **2** is 4,4′-methylenedianiline (**MDA**) and was purchased from Sigma Aldrich. Networks **A–D** were prepared from combinations of monomers **1–4** as described in Table I.

Table I. Composition of Mixtures Used to Prepare Networks A–D

Network	Epoxy	Curing agent	Epoxy (Mass %)	Curing agent (Mass %)
A	Epon 828	MDA	79.1	20.9
B	Epon 828	**4**	70.7	29.3
C	**3**	MDA	81.0	19.0
D	**3**	**4**	73.2	26.8

A standard sample preparation process for all epoxy-amine combinations was unobtainable due to the different melting points, viscosities, and curing behaviors of the epoxy monomers and amines. Individual curing protocols were developed based on the melting points of the monomers and initial DSC scans. The epoxy-amine solutions were comprised of one epoxy component and one amine curing agent. The epoxy monomer and amine curing agent were mixed in a 1:1 mole ratio of epoxy functional group to amine hydrogen. The mass ratio for mixing was determined using the epoxy equivalent weight (EEW) and amine hydrogen equivalent weight (AHEW) in the parts per hundred resin (phr) formula (see Supporting Information). All samples were cured under a nitrogen atmosphere to prevent oxidation. Samples prepared for water immersion testing were cast into 0.35 mL aluminum weigh dishes obtained from Cole-Parmer. To prepare cured bars for TMA analysis, aluminum molds were stamped from heavy duty aluminum foil pressed into silicone molds.

In a typical sample preparation, the epoxy monomer and amine curing agent were heated separately and degassed at 90–125 °C during melting of the material. In the liquid state, the components were added together and mixed thoroughly to ensure homogeneity of the solution, and the solution was then poured into the aluminum weigh dishes and/or molds. The samples were placed in the curing oven where they were degassed and cured. For Networks **A–C**, the samples were degassed for 30 min at 100 °C and then cured under N_2 for 12 h at 100 °C, 2 h at 130 °C, 2 h at 170 °C, and 24 h at 200 °C. For Network **D**, the samples were degassed for 30 min at 135 °C and then cured under N_2 for 12 h at 135 °C, 2 h at 155 °C, 2 h at 175 °C, and 24 h at 200 °C.

Samples were also prepared with solvent to improve processability by decreasing the solution viscosity and slowing down the curing reaction. Additional studies were performed on these samples to determine the effects of solvent on the thermomechanical properties and cure chemistry of the networks. In the processing studies, the epoxy-amine solutions contained one epoxy component and one amine curing agent mixed in the same ratio as the neat samples with xylenes comprising 20% of the mixture by mass. Higher temperatures were required to process the samples based on shifted exotherms in the DSC scans and to remove solvent during cure. Network **A** was processed in solvent using the following cure protocol: 30 min at 100 °C (vacuum); 6 h at 100 °C (N_2); 12 h at 170 °C (N_2); 4 h at 240 °C (N_2). Networks **B** and **C** were processed in solvent as follows: 30 min at 130 °C (vacuum); 6 h at 130 °C (N_2); 12 h at 190 °C (N_2); 4 h at 240 °C (N_2). For Network **D**, the samples were degassed for 30 min at 130 °C then cured under N_2 for 6 h at 170 °C, 12 h at 240 °C, and 4 h at 260 °C.

CHARACTERIZATION OF NETWORKS

Differential Scanning Calorimetry (DSC)

All DSC studies were performed on a TA Instruments Q100 differential scanning calorimeter. Samples were contained in hermetically sealed, aluminum pans under a N_2 atmosphere. High purity indium was used to calibrate the calorimeter. The samples were heated from 0 °C to either 300 °C or 350 °C at

10 °C/min. Two heating cycles were performed on each sample to determine if curing was complete. The initial DSC studies were used to create optimal curing programs for each reaction mixture and to determine the enthalpy of cure.

The neat DSC samples were prepared using a modified protocol from Wisanrakkit.[80] To ensure effective mixing with minimal curing before measurement, the epoxy monomer and amine curing agent were heated separately and degassed at 90–125 °C to melt all the material. After cooling to 100 °C, the components were added together, mixed thoroughly, and then quickly cooled back to room temperature within 5 min to minimize the curing reaction. DSC scans were performed on 5–10 mg samples.

Dynamic-Mode TMA

Dynamic-mode TMA was performed using a TA Instruments Q400-0537 analyzer under 100 mL/min N_2. The bars were placed in contact with a flexural probe under a force of 0.10 N. Samples were cooled to 0 °C then heated at 5 °C/min to 200 °C. The force was modulated ±0.04 N at a frequency of 0.05 Hz during the cycle. The TMA studies were used to determine the glass transition temperature of the epoxy-amine networks, which is reported as the average loss peak with standard deviation values determined from three separate runs.

Thermogravimetric Analysis (TGA)

All TGA studies were performed on a TA Instruments Q5000 thermogravimetric analyzer in a standard, aluminum pan under a nitrogen or air atmosphere. Sample sizes were between 5 and 10 mg, and the samples were heated from 50 to 600 °C at 10 °C/min. The TGA studies were used to determine the decomposition temperature (T_d) of the epoxy-amine networks under nitrogen and air, which are reported as the average temperature at which 5% weight loss was observed from three separate runs.

Water Uptake

Moisture uptake samples consisted of 200–500 mg pucks. The dry pucks were weighed on a Mettler AE-160 analytical balance, which has a sensitivity of ±0.1 mg. Three samples were tested concurrently in three separate 250 mL round-bottomed flasks. 100 mL of deionized H_2O was added to each flask and the contents were heated to reflux for four days. The samples were then blotted dry and the wet mass was obtained. Moisture uptake was calculated as follows:

$$\text{Moisture Uptake} = \frac{\text{Wet Mass} - \text{Dry Mass}}{\text{Dry Mass}} * 100\%$$

The moisture uptake was calculated for each sample tested, and the reported value was obtained from the average of the three samples.

Density

Density measurements were obtained on a Micrometrics Accupyc 1330 gas pycnometer using helium gas. The instrument was calibrated using a 0.718527 cm^3 metal ball bearing standard. Samples used for density measurements were pucks prepared in the same manner as the water immersion testing samples. The samples were weighed to ±0.1 mg. Two samples of each epoxy-amine network were tested to ensure sample consistency. Ten measurements were obtained for each network.

RESULTS AND DISCUSSION

The experimental strategy focused on the synthesis of substituted epoxy and amine monomers from a carvacrol-derived bisphenol and *p*-cymene (Figure 3), respectively. These monomers were used to prepare various epoxy-amine networks, which were then compared with a baseline system derived from DGEBA (**1**) and MDA (**2**). The difference between the substituted monomers and unsubstituted monomers are the methyl groups adjacent to the polar functional groups and the isopropyl substituents adjacent to the methylene carbon bridging between the aromatic rings. The methyl groups can potentially block water from absorbing at the polar sites in the network as shown by previous studies.[74–78] Thus, preparation and characterization of network **B** from **1** and **4** allows comparison with network **A** to determine the effect of the aliphatic substituents when they are present on the amine component. Similarly, preparation and characterization of network **C** from **3** and **2** allows one to determine the effect of the aliphatic substituents when they are present on the epoxy component. Lastly, preparation of network **D** from **3** and **4** allows for an evaluation of the substituent effects when they are present on both network components and could show whether the effects are additive, synergistic, or neither.

Monomer **3** was readily synthesized by reaction of 4,4′-methylenebis(5-isopropyl-2-methylphenol) with epichlorohydrin using potassium *tert*-butoxide or NaOH as the base (Figure 3). 4,4′-methylenebis(5-isopropyl-2-methylphenol) was available from a previous study[46] and was synthesized by coupling carvacrol with 1,3,5-trioxane in water and HCl. GC/MS analysis of monomer **3** showed two bis(epoxides) due to the formation of *para*, *para* (*p,p*), and *para*, *ortho* (*p,o*) isomers during the coupling of carvacrol. The ratio of the *p,p* to the *p,o* isomer was ~19:1 with no formation of the *o,o* isomer, which reflects the favorability of the coupling reaction at the position *para* to the hydoxy group due to steric hindrance caused by the methyl and isopropyl substituents. Monomer **3** was obtained as a white powder with yields of 77.2% and 83.8% when using potassium *tert*-butoxide and sodium hydroxide, respectively. These yields are higher than the typical yield (60%) for similarly substituted epoxies.[22] Initially, potassium *tert*-butoxide was used as the base because of its excellent solubility in organic solvents. However, similar yields were obtained with both reagents, so NaOH is the preferred base for this reaction due to its lower cost. The ^{1}H NMR spectrum (Figure S2, Supporting Information) was typical for a bis(epoxide) and showed four doublets of doublets, representing the diastereomeric epoxide protons. The melting point of monomer **3** was 92–95 °C and is much higher than monomer **1**, which is a viscous liquid at room temperature. The higher melting point of monomer **3** did not result in significant processing challenges because the melting point was similar to that of monomer **2** (88–92 °C). ^{1}H NMR analysis of monomer **3** showed a degree of polymerization of 1.04 based off the ratio of aromatic protons to terminal epoxide protons, which was much lower than the degree of polymerization for monomer **1** (1.12).

Monomer **4** was synthesized from *p*-cymene in three steps (Figure 3). The first step involved nitration of *p*-cymene at low

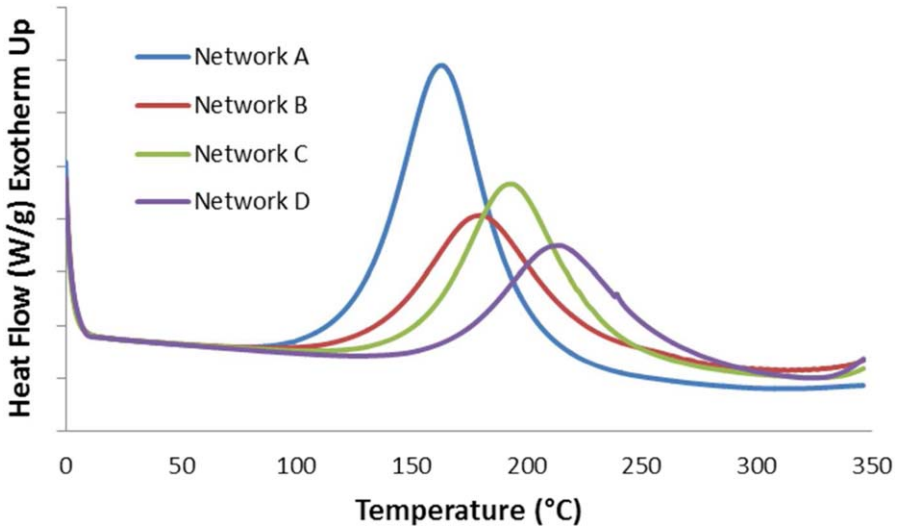

Figure 5. DSC data for formation of networks **A–D**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature to obtain 4-isopropyl-1-methyl-2-nitrobenzene. The nitration reaction has been optimized previously by Kobe and Langworthy to obtain yields as high as 89% when performed at −15 °C.[81] However, we were only able to obtain a maximum yield of 63.5% after fractional distillation due to less specialized scale-up equipment, which made temperature control more difficult and resulted in the formation of more side-products. 4-Isopropyl-1-methyl-2-nitrobenzene was then reduced using 10% Pd/C under 50 psi H_2. The reaction was facile, and 5-isopropyl-2-methylaniline was obtained in 83.4% yield after fractional distillation. Monomer **4** was obtained after coupling 5-isopropyl-2-methylaniline with paraformaldehyde in HCl solution at 80 °C. The dihydrochloride salt of monomer **4** precipitated out of solution readily during the coupling reaction and was easily isolated by filtration and purified by rinsing with cold acetonitrile. The dihydrochloride salt was then converted to monomer **4** by reaction with NaOH followed by extraction and removal of the volatiles under reduced pressure. The product was 99% pure based on GC/MS data with about 1% of the mono- and di-imines of monomer **4** formed by condensation of formaldehyde with the amino groups. Extremely high purity bisaniline could be obtained by recrystallization from hot toluene/heptane solutions. The melting point of crystalline monomer **4** was 120–125 °C and is much higher than monomer **2**, which impacted the processability of the corresponding networks. A similar bisaniline, 4,4′-methylene-bis[2-isopropyl-6-methylaniline] (**MIPA**), with isopropyl and methyl groups in the *ortho* positions, has been investigated as a component of epoxy-amine[82] and bismaleimide[83] networks. Interestingly, **MIPA** has a melting point of only 70–73 °C, ∼50 °C lower than monomer **4**. The higher melting point of monomer **4** is likely a result of increased intermolecular hydrogen bonding as compared to **MIPA** due to decreased steric hindrance around the amines.

The higher melting points of monomers **3** and **4** as compared to their unsubstituted counterparts required higher temperatures to form homogenous solutions before casting samples for use in polymerization reactions. However, the processing windows for networks **B-D** were still comparable with unsubstituted network **A** because the substituents on monomers **3** and **4** delay the onset of cure in their respective networks due to steric hindrance near the reactive sites. This delayed onset was observed when comparing the DSC scans for formation of networks **A–D** (Figure 5). The *ortho*-methyl substituent on the amine was expected to cause a more significant curing onset delay as compared to the case when the substituent was on the epoxy because the amino functionality is in closer proximity to the substituent and should be more effectively shielded by the methyl group. Pascault and Eloundou have studied the kinetics of epoxy polymerization with DGEBA and 4,4′-methylene-bis[2,6-diethylaniline] (MDEA),[84,85] which has ethyl groups in all four *ortho* positions. Because of the steric hindrance of the ethyl groups, the reactivity of MDEA at 135 °C, as measured by the gelation time, was an order of magnitude lower than that for MDA. Although a similar effect was observed for network **B**, the aliphatic groups cause a comparable delay in onset temperature regardless of whether they are on the epoxy component (network **C**) or the amine component (network **B**). This result is surprising, but a likely explanation is that the *ortho*-methyl group does not have a significant impact on the kinetics of the chain growth reaction. Instead, the delayed onset of cure is due to a dilution of reactive groups in the epoxy-amine solution. In line with this theory, Network **D**, which has the most dilute reactive solution, exhibits the longest curing onset delay.

To determine the relative degree of cure for each network, the enthalpy of reaction per mole of epoxide (ΔH_{cure}, Table II) was obtained from the DSC results. The widely accepted value for ΔH_{cure} is 107 kJ/mol, but this value was derived from studies that used an excess of amine, which allowed all of the epoxide functional groups to fully react.[86,87] ΔH_{cure} is typically lower when stoichiometric epoxy-amine mixtures are used because chain motion becomes limited as curing progresses, which restricts the remaining functional groups from coming into close proximity to each other at the end of cure.[87] The literature value for stoichiometric epoxy-amine mixtures has been reported as 23.5 kcal/mol

Table II. Properties of Networks **A**, **B**, **C**, and **D**.

Network	ΔH_{cure} (kJ/mol epoxide)	T_d [N_2/Air (°C)]	Moisture uptake (wt %)	Normalized moisture uptake*	Density (g/cm^3)
A	98.8 (1.1)	376/375	2.87 (0.03)	63.7 (0.8)	1.198 (0.001)
B	83.3 (0.4)	378/371	2.20 (0.06)	54.6 (1.5)	1.132 (0.001)
C	94.9 (1.1)	367/368	1.76 (0.05)	46.4 (0.4)	1.107 (0.002)
D	76.7 (0.1)	363/360	1.35 (0.07)	40 (2)	1.067 (0.001)

Standard deviations are included in parentheses.
*Reported in mmol H_2O/mol HBS.

(98.3 kJ/mol) by Riccardi,[88] and this value is consistent with the value obtained for network **A** in this study (98.8 kJ/mol). Network **B** and network **C** had ΔH_{cure} values of 83.3 and 94.9 kJ/mol, respectively. Comparing these values with ΔH_{cure} for network **A** showed that having the aliphatic groups on the epoxy resulted in a 3.9% decrease in conversion of the epoxy groups, whereas when the substituents were on the amine, a 15.7% decrease in epoxy group conversion was realized. The decreases in functional group conversion are likely due to the *ortho*-methyl groups, which sterically hinder the epoxy and amine groups that are responsible for chain growth and crosslinking. The crosslinking reaction is more likely to be affected because the secondary amine formed in the polymer is more sterically hindered than the primary amine in the bisaniline monomer. In addition, the degree of cure was lower in network **B** as compared to network **C**. This result was expected because having the methyl group adjacent to the amine imparts a greater steric hindrance to polymerization compared to when the methyl group is on the epoxy monomer and several bonds away from the site of polymerization. Network **D,** which has substituents on both the epoxy and amine components, had a ΔH_{cure} of only 76.7 kJ/mol, 22.4% lower than the unsubstituted network **A**. This result was in line with expectations based on the results from networks **B** and **C**.

After examining the cure chemistry of the networks, their thermal stability was probed by TGA. The substituted networks had similar decomposition temperatures (T_d, defined as 5% weight loss) in N_2 and air compared to network **A**, with all networks having a T_d at or above 360 °C. However, the degree of cure and substitution of the networks had a subtle effect on the thermal stability of the substituted networks in air. As substitution increased and the degree of cure decreased, the onset of decomposition of the networks shifted to lower temperature as shown by the 2.5% decrease in the mass of network **D** between 280 °C and 325 °C (Figure 6). This small mass decrease between 280 °C and 325 °C was not observed in network **A** but was observed in networks **B** and **C** with mass losses of 1.5% and 1.6%, respectively (Figures S6 and S7, Supporting Information). This loss was likely the result of an increase in unreacted functional groups in the substituted networks.

To determine the effect of the aliphatic substitution of the monomers on the hydrophobicity of the resulting networks, the moisture uptakes of the four epoxy-amine networks were measured (Table II). Network **A** absorbed 2.87% water by mass over the 96 h immersion period, which is fairly consistent with the literature value of 2.54% reported by Bellenger and Verdu,[53] considering they immersed their samples for only 48 h. Networks **B**-**D** have reduced moisture uptake with increasing substitution on the epoxy monomer and amine curing agents. Network **B** absorbed 23% less water by mass than network **A**, while Network **C** absorbed 39% less water by mass than network **A**. On the basis of these results, functionalization of the epoxy component of the network has more of an effect than when the substituents are on the amine. Alternatively, the reduced moisture uptake may not necessarily be due to efficient blocking of water by the substituents on the epoxy, but may instead be artificial because there are more hydrophobic groups in the network. Network **D** which has aliphatic substituents on both components of the network had a water uptake of only 1.35%, which is 53% lower than network **A**.

To examine the impact of the substituted monomers on a polar group basis, the normalized moisture uptake was calculated for each network (Figure 7). The normalized moisture uptake is based on the number of hydrogen bonding sites (HBS) per unit mass in the network, which includes lone pairs on oxygen and nitrogen as well as hydrogens attached to oxygen and nitrogen. The value was calculated directly from the measured moisture uptake (see Supporting Information). The results confirm that the isopropyl and *ortho*-methyl substituents effectively block water from the polar hydrogen bonding sites when incorporated into either the epoxy monomer or the amine curing agent. Previous studies on *ortho*-methylated cyanate ester networks showed the same trend on a polar group basis when comparing moisture uptake with network crosslink density,[76–78] which supports the hypothesis that the *ortho*-methyl substituents are the

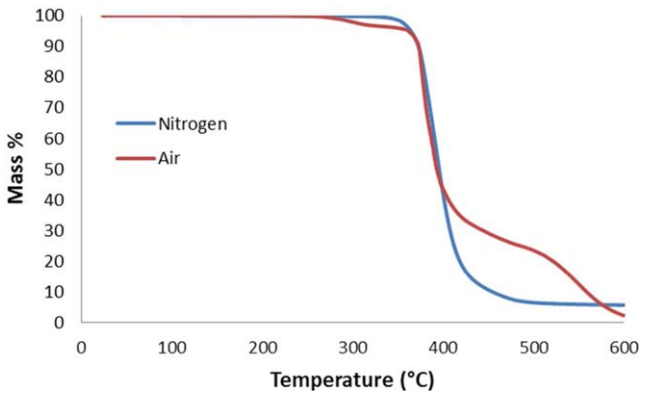

Figure 6. TGA data for network **D**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

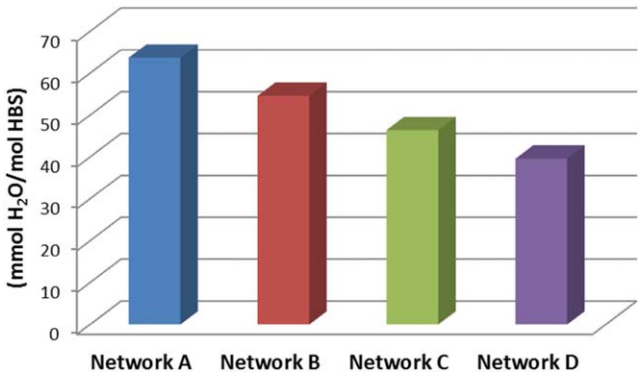

Figure 7. Normalized moisture uptake of networks **A–D**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

key contributors to increased hydrophobicity instead of the distant isopropyl groups. Another interesting finding from the normalized moisture uptake data is that *ortho*-substitution on the epoxy component appears to be nearly twice as effective at blocking water as *ortho*-substitution on the amine component. The use of substituted epoxy and amine monomers led to decreases in normalized moisture uptake of 27% and 14%, respectively, based on comparisons of networks **C** and **B** with network **A**. The higher normalized moisture uptake reduction observed when the epoxy is substituted implies that the epoxy component and corresponding polar group domains are more involved in moisture uptake in epoxy-amine networks than the amine curing agent. On the basis of purely theoretical considerations, oxygen is more electronegative than nitrogen, so the oxygen-bound hydrogens are expected to form stronger hydrogen bonds than the hydrogens on nitrogen. Also, the nitrogens and ether oxygens in these networks are both adjacent to an aromatic ring, which makes the lone pairs less nucleophilic because of delocalization of the electrons into the adjacent conjugated network. However, the ether oxygen has two lone pairs, so one lone pair can be delocalized into the aromatic ring whereas the other can participate in hydrogen bonding. The nitrogen lone pair becomes much less nucleophilic after delocalization and thus becomes a less effective hydrogen bonding site for water. This last point has been confirmed experimentally in previous studies on epoxy-amine networks.[53,89] Interestingly, *ortho*-methylation on both the epoxy and amine components revealed an additive effect compared to the reduction in moisture uptake from substitution on the epoxy or amine alone. Substitution on both components resulted in a reduction in normalized moisture uptake of 38% compared to network **A**, which is close to the sum of the reductions (41%) observed from substitution on either the epoxy component (27%) or the amine component (14%) individually.

The T_Gs of the networks were also examined to determine the ultimate use temperatures of the bio-based networks compared to the baseline network and are provided in Table III and Figure 8. The fully-cured T_Gs obtained from DSC correlated well with the degree of cure inferred from ΔH_{cure}. Network **A** had the highest T_G followed by networks **C** and **B**, while network **D** had the lowest T_G. The T_G for network **B** as measured by DSC (154 °C) was similar to the predicted fully cured T_G for a network prepared from MDEA and DGEBA (165 °C).[85] For comparison, the T_G of the networks was also measured via TMA and is reported as the peak loss temperature. The same trend between T_G and ΔH_{cure} was observed when comparing the TMA T_Gs for the networks, which shows consistency between the two thermal methods. However, the smaller difference in peak loss T_G between networks **B** (147.4 °C) and **C** (149.4 °C) was unexpected due to the modestly higher ΔH_{cure} of network **C**. Because loss is based on the viscosity of the networks, the smaller difference likely reflects the similarities in viscosity of networks **B** and **C** at elevated temperature. Overall, the glass transition temperatures from both DSC and TMA were consistent with ΔH_{cure} values and the inferred degree of cure for the networks.

In addition to differences in degree of cure, the cure independent effects of increased aliphatic character on the crosslink density and T_G of the thermosets were also considered. Substituents can prevent polymer chains from packing tightly, which disrupts intermolecular interactions and lowers the T_G.[90] This principle is important in networks that can form strong secondary interactions between chains. However, substituents along a polymer chain can also limit rotational motion along the backbone, which makes the chain more rigid and raises the T_G.[87] Previous work on a cyanate ester containing the *p*-cymene moiety revealed a substantial decrease in T_G as compared to a cyanate ester derived from bisphenol A, despite a similar degree of cure for both monomers.[46] The greater aliphatic character of the *p*-cymene derived cyanate ester resin resulted in a significantly lower volumetric crosslink density, which imparted a lower glass transition temperature. In contrast, the aliphatic groups in the current system impact both the degree of cure as measured by

Table III. T_G Data for Networks **A–D**

Network	ΔH_{cure} (kJ/mol epoxide)	T_G (°C) DSC[a]	T_G (°C) Peak loss TMA	"Wet" T_G (°C) peak loss TMA
A	98.8 (1.1)	178.6 (0.2)	170.9 (0.6)	138.6 (0.6)
B	83.3 (0.4)	154.0 (0.4)	147.4 (1.2)	127 (2)
C	94.9 (1.1)	161 (2)	149.4 (1.3)	136.3 (0.9)
D	76.7 (0.1)	142.9 (0.7)	134.2 (0.6)	124 (2)

Standard deviations are reported in parentheses.
[a] From DSC scans on fully-cured samples using the indicated protocols.

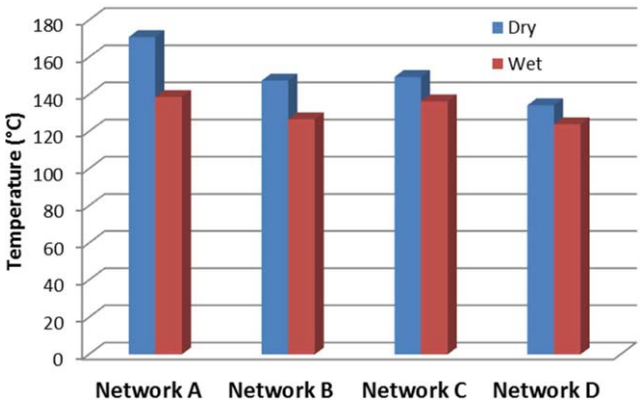

Figure 8. Dry and "wet" T_Gs of the fully-cured epoxy-amine networks (based on the peak loss value from TMA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ΔH_{cure} and the crosslink density of the thermoset networks due to the lower density of the aliphatic groups compared to the aromatic rings. For example, network C has a lower density than network B due to its greater aliphatic character. However, network C also cures more completely, which allows it to overcome its lower density, resulting in a modestly higher T_G. The epoxy monomer degree of polymerization would also be expected to impact the T_G because higher n values will result in lower crosslink densities and more flexibility in the network. However, network **A** showed the highest T_G despite its preparation from monomer **1**, which had a higher degree of polymerization compared to monomer **3**. Thus it appears that the degree of cure is the most important factor for determining the T_G of these networks, although the maximal T_Gs for networks **B–D** at an equivalent ΔH_{cure} are presumed to be lower than that of network A because of lower achievable volumetric crosslink densities.

The "wet" T_Gs of moisture-saturated samples were also determined to understand the effects that moisture uptake had on the thermomechanical properties of the networks. Network **A** had the most significant decrease in T_G (32.3 °C), which is consistent with the value reported by Bellenger and Verdu for the same system (36 °C).[53] The significant decrease in T_G for network **A** corresponds to having the most water absorbed of all the networks characterized. Networks **B** and **C** had wet T_G knockdowns of 20.7 °C and 13.1 °C, respectively, which correlated with the moisture uptake trend of these samples (2.20% in network **B** and 1.78% in network **C**). The T_G knockdown of network **C** is similar to the value reported by Bellinger and Verdu in their study using a network comprised of DGEBA cured with MDEA, which had a T_G knockdown of 13 °C and absorbed 1.81% water by mass.[53] The "wet" T_G of network **C** is roughly the same as the baseline system, which shows that this system has similar thermomechanical performance in wet environments with much lower moisture uptake. Finally, network **D** had the lowest wet T_G knockdown (10.2 °C). Thus, the lower moisture uptake in the substituted epoxy-amine networks resulted in reduced "wet" T_G knockdowns.

In an effort to improve the processability of networks **A–D**, these mixtures were prepared using 20% xylenes by mass. These studies were performed to assess the suitability of the bio-based epoxy-amine networks for incorporation into composite materials, which can typically require up to 50% solvent by mass for improved processing.[91] The networks prepared in xylenes were easier to handle due to their lower viscosities. The properties of these networks are summarized in Table IV. In general, the properties were similar to the networks that were cured without solvent, except both the dry and wet T_Gs were lower than observed in the solvent free system. The lower T_Gs likely resulted from the networks being less fully cured due to a lower concentration of reactive groups during curing as well as residual solvent remaining in the networks after curing was complete. Overall, the moisture uptake and "wet" T_G knockdowns in the networks processed in solvent were consistent with the corresponding properties in the networks prepared without solvent, which shows that solvent processing is a viable approach for fabricating composite materials with these thermosetting resins.

CONCLUSIONS

Carvacrol and *p*-cymene are versatile and sustainable starting materials for the synthesis of hydrophobic epoxy monomers and curing agents. In this study, an epoxy monomer was synthesized from a carvacrol-derived bisphenol in a single step, and a hydrophobic aniline was synthesized from *p*-cymene in three steps with modest yields and high purity. The monomers had higher melting points than their unsubstituted analogues (DGEBA and MDA), but there was no significant decrease in processability due to the delayed onset of cure in the networks containing the synthesized monomers. The aliphatic substituents in the hydrophobic monomers resulted in lower degrees of cure

Table IV. Properties of Networks **A**, **B**, **C**, and **D** Processed in Xylenes

Network	Fully-cured T_g (°C)*	Fully-cured "wet" T_g (°C)[a]	Moisture uptake (wt %)	Normalized moisture uptake[b]	Density (g/cm^3)
A	156 (4)	121 (4)	2.66 (0.06)	59.2 (1.0)	1.190 (0.004)
B	122 (6)	107 (6)	2.02 (0.05)	50.3 (1.1)	1.133 (0.002)
C	134 (8)	123 (5)	1.59 (0.02)	41.9 (0.6)	1.112 (0.004)
D	120 (3)	114 (2)	1.38 (0.04)	40.4 (1.3)	1.067 (0.001)

Standard deviations are included in parentheses.
[a] The glass transition temperatures were determined as the average loss peak over three trials.
[b] Reported in mmol H_2O/mol HBS.

based on DSC enthalpy data but also decreased moisture uptake per functional group as compared to the unsubstituted baseline network. The *ortho*-methyl substituent is believed to be the primary contributor to the lower degree of cure and higher moisture resistance observed in the bio-based systems because it is located adjacent to the curing functionality in both monomers, the likely sites of moisture uptake. As has been seen in previous studies, the hydrophobic epoxy was more effective at blocking water absorption, which implicates the polar groups generated from the epoxy monomer as the key contributor to moisture uptake in epoxy-amine networks. Lastly, the lower moisture uptakes observed for the bio-based networks resulted in less significant decreases in performance under wet conditions as shown by decreased "wet" T_G knockdowns. The results of this study show the unique advantages of monomers derived from renewable terpenoids over commonly-used epoxy resins and curing agents.

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REFERENCES

1. Wilbon, P. A.; Chu, F.; Tang, C. *Macromol. Rapid Commun.* **2013**, *34*, 8.
2. Gandini, A. *Green Chem.* **2011**, *13*, 1061.
3. Auvergne, R.; Caillol, S.; David, G.; Boutevin, B.; Pascault, J.-P. *Chem. Rev.* **2014**, *114*, 1082.
4. Harvey, B. G.; Guenthner, A. J.; Lai, W. W.; Meylemans, H. A.; Davis, M. C.; Cambrea, L. R.; Reams, J. T.; Lamison, K. R. *Macromolecules* **2015**, *48*, 3173.
5. Harvey, B. G.; Guenthner, A. J.; Meylemans, H. A.; Haines, S. R. L.; Lamison, K. R.; Groshens, T. J.; Cambrea, L. R.; Davis, M. C.; Lai, W. W. *Green Chem.* **2015**, *17*, 1249.
6. Meylemans, H. A.; Groshens, T. J.; Harvey, B. G. *ChemSusChem* **2012**, *5*, 206.
7. Meylemans, H. A.; Harvey, B. G.; Reams, J. T.; Guenthner, A. J.; Cambrea, L. R.; Groshens, T. J.; Baldwin, L. C.; Garrison, M. D.; Mabry, J. M. *Biomacromolecules* **2013**, *14*, 771.
8. Fache, M.; Boutevin, B.; Caillol, S. *Eur. Polym. J.* **2015**, *68*, 488.
9. Davis, M. C.; Parrish, D. A.; Harvey, B. G. *Org. Prep. Proc. Intern.* **2013**, *45*, 304.
10. Harvey, B. G.; Guenthner, A. J.; Yandek, G. R.; Cambrea, L. R.; Meylemans, H. A.; Baldwin, L. C.; Reams, J. T. *Polymer* **2014**, *55*, 5073.
11. Harvey, B. G.; Sahagun, C. M.; Guenthner, A. J.; Groshens, T. J.; Cambrea, L. R.; Reams, J. T.; Mabry, J. M. *ChemSusChem.* **2014**, *7*, 1964.
12. Schutyser, W.; Koelewijn, S. F.; Dusselier, M.; Van de Vyver, S.; Thomas, J.; Yu, F.; Carbone, M. J.; Smet, M.; Van Puyvelde, P.; Dehaen, W.; Sels, B. F. *Green Chem.* **2014**, *16*, 1999.
13. Cash, J. J.; Davis, M. C.; Ford, M. D.; Groshens, T. J.; Guenthner, A. J.; Harvey, B. G.; Lamison, K. R.; Mabry, J. M.; Meylemans, H. A.; Reams, J. T. *Polym. Chem.* **2013**, *4*, 3859.
14. Davis, M. C.; Guenthner, A. J.; Groshens, T. J.; Reams, J. T.; Mabry, J. M. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 4127.
15. Van de Vyver, S.; Geboers, J.; Helsen, S.; Yu, F.; Thomas, J.; Smet, M.; Dehaen, W.; Sels, B. F. *Chem. Commun.* **2012**, *48*, 3497.
16. Zúñiga, C.; Larrechi, M. S.; Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz, V. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1219.
17. Morley, K. L.; Grosse, S.; Leisch, H.; Lau, P. C. K. *Green Chem.* **2013**, *15*, 3312.
18. Voirin, C.; Caillol, S.; Sadavarte, N. V.; Tawade, B. V.; Boutevin, B.; Wadgaonkar, P. P. *Polym. Chem.* **2014**, *5*, 3142.
19. Staples, C. A.; Dome, P. B.; Klecka, G. M.; Oblock, S. T.; Harris, L. R. *Chemosphere* **1998**, *36*, 2149.
20. Tyl, R. W.; Myers, C. B.; Marr, M. C.; Thomas, B. F.; Keimowitz, A. R.; Brine, D. R.; Veselica, M. M.; Fail, P. A.; Chang, T. Y.; Seely, J. C.; Joiner, R. L.; Butala, J. H.; Dimond, S. S.; Cagen, S. Z.; Shiotsuka, R. N.; Stropp, G. D.; Waechter, J. M. *Toxicol. Sci.* **2002**, *68*, 121.
21. Chen, M. Y.; Ike, M.; Fujita, M. *Environ. Toxicol.* **2002**, *17*, 80.
22. Niederst, J.; Evans, R. H.; O'Brien, R. M.; Romagnoli, K.; Von Maier, M. S. U.S. Patent Application 2013/0316109, (**2013**).
23. Zhang, X.; Lambert, J. C.; Doll, M. A.; Walraven, J. M.; Arteel, G. E.; Heln, D. W. *J. Pharmacol. Experiment. Therap* **2006**, *316*, 289.
24. Weiss, T.; Schuster, H.; Müller, J.; Schaller, K.-H.; Drexler, H.; Angerer, J.; Käfferlein, H. U. *Ann. Occup. Hyg.* **2011**, *55*, 886–892.
25. Erman, W. F. Chemistry of Monoterpenes; Marcel Dekker: New York, **1985**.
26. Belgacem, M. N.; Gandini, A. Monomers, Polymers and Composites from Renewable Resources; Elsevier: Amsterdam, **2008**.
27. Lu, J.; Kamigaito, M.; Sawamoto, M.; Higashimura, T.; Deng, Y. X. *Macromolecules* **1997**, *30*, 27.
28. Mathers, R. T.; Damodaran, K.; Rendos, M. G.; Lavrich, M. S. *Macromolecules* **2009**, *42*, 1512.
29. Satoh, K.; Matsuda, M.; Nagai, K.; Kamigato, M. *J. Am. Chem. Soc.* **2010**, *132*, 10003.
30. Martin-Luengo, M. A.; Yates, M.; Domingo, M. J. M.; Casal, B.; Iglesias, M.; Esteban, M.; Ruiz-Hitsky, E. R. *Appl. Catal. B: Environ.* **2008**, *81*, 218.
31. Martin-Luengo, M. A.; Yates, M.; Rojo, E. S.; Arribus, D. H.; Aguilar, D.; Hitzky, E. R. *Appl. Catal. A: Gen.* **2010**, *387*, 141.

32. Kamitsou, M.; Panagiotou, G. D.; Triantafyllidis, K. S.; Bourikas, K.; Lycourghiotis, A.; Kordulis, C. *Appl. Catal. A: Gen.* **2014**, *474*, 224.
33. Meylemans, H. A.; Quintana, R. L.; Rex, M. L.; Harvey, B. G. *J. Chem. Technol. Biotechnol.* **2014**, *89*, 957.
34. Leita, B. A.; Warden, A. C.; Burke, N.; O'Shea, M. S.; Trimm, D. *Green Chem.* **2010**, *12*, 70.
35. Harvey, B. G.; Wright, M. E.; Quintana, R. L. *Energy Fuels* **2010**, *24*, 267.
36. Fachini-Queiroz, F. C.; Kummer, R.; Estevão-Silva, C. F.; de Barros Carvalho, M. D.; Cunha, J. M.; Grespan, R.; Aparecida, B.-A.; Cuman, R. K. N. *Evid Based Complement. Alternat. Med.* **2012**, *2012*, 10. DOI: 10.1155/2012/657026
37. De Falco, E.; Mancini, E.; Roscigno, G.; Mignola, E.; Taglialatela-Scafati, O.; Senatore, F. *Molecules* **2013**, *18*, 14948.
38. Sökmen, M.; Serkedjieva, J.; Daferera, D.; Gulluce, M.; Polissiou, M.; Tepe, B.; Akpulat, H. A.; Sahin, F.; Sokmen, A. *J. Agric. Food Chem.* **2004**, *52*, 3309.
39. Gibbs, H. D.; Phillips, M. J. *Ind. Eng. Chem.* **1920**, *12*, 145.
40. Singh, B.; Patial, J.; Sharma, P.; Chandra, S.; Kaul, P.; Maity, S. *Ind. J. Chem. Technol.* **2011**, *18*, 21.
41. Royals, E. E.; Horne, S. E. *J. Am. Chem. Soc.* **1951**, *73*, 5856.
42. Rothenberger, O. S.; Krasnoff, S. B.; Rollins, R. B. *J. Chem. Educ.* **1980**, *57*, 741.
43. Maksimchuk, N. V.; Kovalenko, K. A.; Fedin, V. P.; Kholdeeva, O. A. *Adv. Synth. Catal.* **2010**, *352*, 2943.
44. Costa, V. V.; da Silva Rocha, K. A.; Kozhevnikov, I. V.; Kozhevnikova, E. F.; Gusevskaya, E. V. *Catal. Sci. Technol.* **2013**, *3*, 244.
45. Wallach, O. *Justus. Leibigs. Ann. Der. Chemie.* **1895**, *286*, 90.
46. Harvey, B. G.; Guenthner, A. J.; Koontz, T. A.; Storch, P. J.; Reams, J. T.; Groshens, T. J. *Green Chem.* **2016**, DOI: 10.1039/C5GC02893K
47. Zhou, J.; Lucas, J. P. *Polymer* **1999**, *40*, 5513.
48. Frigione, M.; Lettieri, M. *J. Polym. Sci. Part B: Polym. Phys.* **2008**, *46*, 1320.
49. Luo, S.; Leisen, J.; Wong, C. P. *J. Appl. Polym. Sci.* **2002**, *85*, 1.
50. Ito, S.; Hashimoto, M.; Wadgaonkar, B.; Svizero, N.; Carvalho, R. M.; Yiu, C.; Rueggeberg, F. A.; Foulger, S.; Saito, T.; Nishitani, Y.; Yoshiyama, M.; Tay, F. R.; Pashley, D. H. *Biomaterials* **2005**, *26*, 6449.
51. Choi, S.; Phantu, A.; Douglas, E. P. *J. Appl. Polym. Sci.* **2012**, *125*, 3778.
52. Colombini, D.; Martinez-Vega, J. J.; Merle, G. *Polymer* **2002**, *43*, 4479.
53. Bellenger, V.; Verdu, J. *J. Mater. Sci.* **1989**, *24*, 63.
54. Mensitieri, G.; Lavorgna, M.; Musto, P.; Ragosta, G. *Polymer* **2006**, *47*, 8326.
55. Li, L.; Liu, M.; Li, S. *Polymer* **2004**, *45*, 2837.
56. Nie, L.; Burgess, A.; Ryan, A. *Macromol. Chem. Phys.* **2013**, *214*, 225.
57. Frank, K.; Wiggins, J. *J. Appl. Polym. Sci.* **2013**, *130*, 264.
58. Grave, C.; McEwan, I.; Pethrick, I. A. *J. Appl. Polym. Sci* **1998**, *69*, 2369.
59. Diamant, Y.; Marom, G.; Broutman, L. J. *J. Appl. Polym. Sci.* **1981**, *26*, 3015.
60. Li, L.; Yu, Y.; Wu, Q.; Zhan, G.; Li, S. *Corros. Sci.* **2009**, *51*, 3000.
61. Soles, C. L.; Chang, F. T.; Gidley, D. W.; Yee, A. F. *J. Polym. Sci. Part B: Polym. Phys.* **2000**, *38*, 776.
62. Soles, C. L.; Yee, A. F. *J. Polym. Sci. Part B: Polym. Phys.* **2000**, *38*, 792.
63. Soles, C. L.; Chang, F. T.; Bolan, B. A.; Hristov, H. A.; Gidley, D. W.; Yee, A. F. *J. Polym. Sci. Part B: Polym. Phys.* **1998**, *36*, 3035.
64. Frank, K.; Childers, C.; Dutta, D.; Gidley, D.; Jackson, M.; Ward, S.; Maskell, R.; Wiggins, J. *Polymer* **2013**, *54*, 403.
65. Maxwell, I. D.; Pethrick, R. A. *J. Appl. Polym. Sci* **1983**, *28*, 2363.
66. Enns, J. B.; Gillham, J. K. *J. Appl. Polym. Sci.* **1983**, *28*, 2831.
67. Dang, D. N.; Cohendoz, S.; Mallarino, S.; Feaugas, X.; Touzain, S. *J. Appl. Polym. Sci.* **2013**, *129*, 2451.
68. Cotugno, S.; Mensitieri, G.; Musto, P.; Sanguigno, L. *Macromolecules* **2005**, *38*, 801.
69. Jackson, M.; Kaushik, M.; Nazarenko, S.; Ward, S.; Maskell, R.; Wiggins, J. *Polymer* **2011**, *52*, 4528.
70. Tai, H. J.; Wang, J. B.; Chen, J. H.; Chou, H. L. *J. Appl. Polym. Sci.* **2001**, *79*, 652.
71. Sauvant, V.; Halary, J. L. *J. Appl. Polym. Sci.* **2001**, *82*, 759.
72. Sauvant, V.; Halary, J. L. *Compos. Sci. Technol.* **2002**, *62*, 481.
73. Chateauminois, A.; Sauvant, V.; Halary, J. L. *Polym. Int.* **2003**, *52*, 507.
74. Liu, M.; Ding, Y.; Wang, M.; Li, S.; Liu, W.; Wang, B. *J. Polym. Sci. Part B: Polym. Phys.* **2003**, *41*, 1135.
75. Ding, Y.; Liu, M.; Li, S.; Zhang, S.; Zhou, W. F.; Wang, B. *Macromol. Chem. Phys.* **2001**, *202*, 2681.
76. Shimp, D. A. *Polym. Mater. Sci. Eng.* **1986**, *54*, 107.
77. Shimp, D. A. U.S. Pat. 4,604,452 (**1986**).
78. Guenthner, A. J.; Wright, M. E.; Chafin, A. P.; Reams, J. T.; Lamison, K. R.; Ford, M. D.; Kirby, S. P. J.; Zavala, J. J.; Mabry, J. M. *Macromolecules* **2014**, *47*, 7691.
79. Kroschwitz, J. I., Ed. Encyclopedia of Polymer Science and Engineering, Vol. *6*; Wiley: New York, **1986**; Epoxy Resins, 326.
80. Wisanrakkit, G.; Gillham, J. K. *J. Appl. Polym. Sci.* **1990**, *41*, 2885.
81. Kobe, K. A.; Langworthy, E. M. *Indus. Eng. Chem.* **1957**, *49*, 801.
82. Karkanas, P. I.; Partridge, I. K. *J. Appl. Polym. Sci.* **2000**, *77*, 1419.
83. Hardt, P.; Völker, T. U.S. Pat 5,286,874 (**1994**).
84. Girard-Reydet, E.; Riccardi, C. C.; Sautereau, H.; Pascault, J. P. *Macromolecules* **1995**, *28*, 7599.

85. Eloundou, J. P.; Ayina, O.; Nga, H. N.; Gerard, J. F.; Pascault, J. P.; Boiteux, G.; Seytre, G. *J. Polym. Sci. Part B: Polym. Phys.* **1998**, *36*, 2911.
86. Prime, R. B. In Thermal Characterization of Polymeric Materials, 2nd ed.; Turi, E. A. Ed.; Academic Press: San Diego, **1997**; p 1379.
87. Prime, R. B. In Thermal Analysis of Polymers; Menczel, J. D. Ed.; Wiley: Hoboken, NJ, **2009**; p 7.
88. Riccardi, C. C.; Adabbo, H. E.; Williams, R. J. J. *J. Appl. Polym. Sci.* **1984**, *29*, 2481.
89. Morel, E.; Bellenger, V.; Verdu, J. *Polymer* **1985**, *26*, 1719.
90. Odian, G. Principles of Polymerization, 4th ed.; Wiley: Hoboken, NJ, **2004**; p 24.
91. Chawla, K. K. Composite Materials: Science and Engineering, 3th ed.; Springer: New York, **2012**; p 137.