Synthesis and Characterization of an Adipic Acid–Derived Epoxy Resin

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ABSTRACT: Adipic acid, a highly abundant chemical that can be produced from biomass, was used to prepare an aromatic-free epoxy resin. Synthesis of the diglycidyl adipate was performed by a one-step process using epichlorohydrin and by a two-step process comprising allylation and epoxidation. The viscosity of diglycidyl adipate is 25 mPa·s, which is 99% lower than the diglycidyl ether of bisphenol A (DGEBA). The storage modulus at 25 °C for cured diglycidyl adipate and DGEBA is 2000 and 3200 MPa, respectively. The alpha transition temperature through peak of the loss modulus and the peak of tan(δ), are 77 °C and 90 °C, respectively. Low-viscosity epoxy applications are discussed herein. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, 54, 2625–2631

KEYWORDS: biobased; epoxy resins; glycidyl esters; rheology; sustainable; thermosets; thermoset polymers; viscosity

INTRODUCTION The industrial use of thermoset polymers is rapidly growing worldwide due to their high performance capabilities in demanding environments.[1] Epoxy resins are one of the most versatile thermoset polymers and are prevalent because of their ability to polymerize or "cure" under a wide range of conditions. Epoxy resins also offer good to excellent mechanical properties, high heat deflection temperatures, good electrical insulating properties, excellent adhesion to a wide variety of substrates, and their use is prevalent in a wide range of applications.[2] Additionally, once cured, epoxy resins exhibit excellent chemical resistance, for example, as anticorrosive metal coatings.[3] The three main applications for epoxy resins are coatings, composites, and structural adhesives.[4] Bisphenol A (BPA) is historically the predominant building block used by the epoxy resin and polycarbonate industries due to its ability to deliver superior mechanical and thermal properties relevant to other systems.[5]

However, bisphenol A has received considerable attention worldwide—both from governments and the public, due BPA's ability to disrupt the human endocrine system.[6–8] Public awareness of BPA's effects on the human body is widespread and the public distrusts polymer products that could contain BPA such as food packaging and reusable water bottles.[9] The potential for BPA to disrupt the human endocrine system also implies that it's a contaminant of concern that has sparked numerous researchers to find sustainable and safe alternatives.[10]

Currently, the majority of research on developing new epoxy resins is focused on either aromatic structures or fused cycloaliphatic rings so that corresponding polymers have rigid chain structures.[11] Derivatives of hydroxyl methyl furfural have been studied as renewable aromatic building blocks in epoxy resins.[12–14] Epoxy resins synthesized from diglycidyl isosorbide have excellent thermomechanical properties, but, currently, they are sourced from food based feedstocks.[15–17] Abietic acid, a product from tree rosin, has been epoxidized and corresponding cured epoxy resins exhibit excellent mechanical properties. However, epoxy abietic resins are crystalline solids with relatively high melting points which is undesirable for their processing into cured materials.[18] Eugenol based epoxy resins exhibit excellent thermomechanical properties that are competitive with DGEBA, however, they also exhibit high melting points.[19,20] Issues pertaining to the development of aromatic epoxy resins are that multifunctional aromatic moieties such as bisphenols are relatively expensive. Indeed, Bisphenol A, due to the requirement for the high-purity *para, para* regioisomer, is also a relatively expensive molecule to produce compared to chemicals such as styrene, propylene, and terepthalic acid.[5] The higher cost of epoxy resins relegates their use to higher performance applications and, consequently, epoxy resins must deliver higher performance properties than commodity thermoplastics.[5]

The development of economically viable routes to adipic,[21] succinic,[22] and malonic acids[23] from renewable feedstocks

Additional Supporting Information may be found in the online version of this article.

using engineered microbial production platforms is rapidly progressing such that their manufacturing at commodity production levels is moving toward reality. However, use of these diacid platform chemicals for thermosets is under studied. The earliest peer reviewed report of epoxy resins from multifunctional diacids was by Maerker and coworkers in 1963 who observed high heat deflection temperatures when they were cured with stoichiometric amounts of anhydride crosslinker.[24] The next academic paper on diglycidyl esters was in 2013 when Ma and coworkers synthesized and studied epoxy resins derived from itaconic acid.[25] They reported that the corresponding epoxy resins from itaconic acid when crosslinked with anhydrides and divinyl benzene have excellent mechanical properties.[25] Dai and coworkers demonstrated that triglycidyl citrate epoxy resins are effective reactive plasticizers that improve the flexural strength, flexural elongation, and flexural modulus of polylactide when used in conjunction with microcrystalline cellulose.[26] Although numerous patents have been filed that describing the preparation of epoxy resins from aliphatic acids, these patents and related literature provide little information on their viscosity or corresponding thermomechanical properties.[27–31]

This work examines the synthesis and thermomechanical properties of an epoxy resin derived from adipic acid. One factor that motivated this study is the excellent progress in developing biobased adipic acid.[32,33] Two pathways for the synthesis of diglycidyl adipate were evaluated: (i) the first being by the direct, one pot reaction between adipic acid and epichlorohydrin based on the work by Maerker and coworkers[24] and (ii) the second by adipic acid allylation and epoxidation. Characterization of diglycidyl adipate by Maerker and coworkers was limited to a melting point and physical appearance. Furthermore, characterization of the corresponding epoxy resins prepared from diglycidyl adipate and cured with o-phthalic anhydride are limited to the heat deflection temperature.[24] This work examines whether diglycidyl adipate, when cured with a conventional diamine hardener, meet important criteria that would make it suitable for current epoxy resin applications such as vacuum infusion molding to prepare epoxy composites.

The article describes the relative merits of synthetic routes to diglycidyl adipate and its characterization by nuclear magnetic resonance (NMR), viscosity, and epoxide equivalent weight. Diglycidyl adipate was cured with stoichiometric amounts of isophorone diamine. Studies of corresponding epoxy resin thermomechanical properties such as the storage modulus and glass transition temperature demonstrate they are similar to that of diglycidyl ether of bisphenol A. Furthermore, the low viscosity of the diglycidyl adipate system is ideal for its use in vacuum infusion molding of high filler content composites or as a reactive diluent to lower the viscosity of more viscous systems. Furthermore, the results herein demonstrate that epoxidation of simple aliphatic diacids provides a versatile platform for the development of new and important epoxy resin materials.

EXPERIMENTAL

Materials
Adipic acid, diglycidyl ether of bisphenol A, m-chloroperoxybenzoic acid <77%, sodium hydroxide, epichlorohydrin, allyl alcohol, benzyl trimethylammonium chloride, 0.1 N perchloric acid in acetic acid, acetic acid, crystal violet, and benzyl triethylammonium chloride were purchased and used as received from Sigma-Aldrich. Concentrated hydrochloric acid and isophorone diamine were purchased and used as received from VWR.

Synthesis of Diglycidyl Adipate Through One-Pot Method
The synthesis of diglycidyl adipate using a one-pot method was adapted from Maerker and coworkers.[24] In summary, epichlorohydrin (162 g, 1.75 mol) was charged to a three-neck round-bottom flask equipped with magnetic stirring, heating mantle, Dean-Stark condenser, and two pressure equalizing addition funnels. A disodium adipic acid salt was prepared from adipic acid (17 g, 0.116 mol) in a 250 mL Erlenmeyer flask with H_2O (60 mL), benzyl trimethyl ammonium chloride (7.13 g, 0.038 mol), and NaOH (9.77 g, 0.244 mol). The aqueous disodium adipate salt solution was transferred to one of the addition funnels and 80 mL of epichlorohydrin was transferred to the other addition funnel. Then, the contents of the round bottom flask were brought to reflux with magnetic stirring and addition of the disodium adipate solution was begun. When water and epichlorohydrin were collected through the Dean Stark condenser, addition of epichlorohydrin from the second addition funnel was begun so that the excess of epichlorohydrin in the reaction flask is kept constant. Constant excess of epichlorohydrin was used to mitigate formation of higher oligomers and to favor formation of the monomer. After addition of disodium adipate over 30 min, the reaction was refluxed for an additional 20 min with addition of epichlorohydrin to maintain constant volume and then cooled to room temperature. The reaction mixture was transferred to a separatory funnel to remove water and then the organic phase was washed with 3 M acetic acid (200 mL, 2×), brine (200 mL, 2×), distilled deionized water (200 mL, 2×), and then dried over magnesium sulfate. Excess reactants were then removed by rotary evaporation yielding a viscous light yellow liquid. The liquid was then crystallized in hexanes at −20 °C giving white sticky crystals in about 50% yield. Recrystallization in 10% methanol/90% at −20 °C water gave white powdery crystals in 20–30% yield.

^{1}H NMR (500 MHz, $CDCl_3$): ppm δ 1.68 (t, 4H), 2.38 (t, 4H), 2.64 (dd, J = 4.89 Hz, 2H), 2.84 (observed triplet, J = 4.16 Hz, 2H), 3.20 (m, 2H), 3.90 (dd, J = 12.23 Hz, 2H), 4.40 (dd, J = 12.23 Hz, 2H); ^{13}C NMR (600 MHz, $CDCl_3$): ppm δ 172.8, 64.8, 49.2, 44.5, 33.5, 24.1; melting point 55 °C; epoxide equivalent weight: 132

Synthesis of Diglycidyl Adipate by a Two-Pot Method
Fischer Esterification
Adipic acid (50 g, 0.342 mols), allyl alcohol (300 mL), and concentrated HCl (1 mL) were added to a 500-mL round-

bottom flask equipped with magnetic stirring, heating mantle, and a reflux condenser. The mixture was brought to reflux at 97 °C with magnetic stirring and maintained under these conditions for 24 hours. The reaction mixture was then cooled to room temperature and the majority of allyl alcohol was removed by rotary evaporation. Then, the reaction mixture was dissolved in ethyl acetate (250 mL) and the resulting solution was transferred to a 1 L separatory funnel. The organic phase was washed twice with 200 mL distilled deionized water, twice with 200 mL with sodium bicarbonate and twice with 200 mL distilled deionized water and then was dried over anhydrous magnesium sulfate. Excess reactants and solvents were removed by rotary evaporation until a colorless liquid was obtained.

^{1}H NMR (500 MHz, CDCl$_3$) 1.61 (s, 2H), 2.28 (s, 2H), 4.50 (dd, J = 4.40 Hz, 2H), 5.16 (observed doublet, J = 9.0 Hz, 2H), 5.21 (observed doublet, J = 17.63 Hz, 2H), 5.83 (m, 2H).
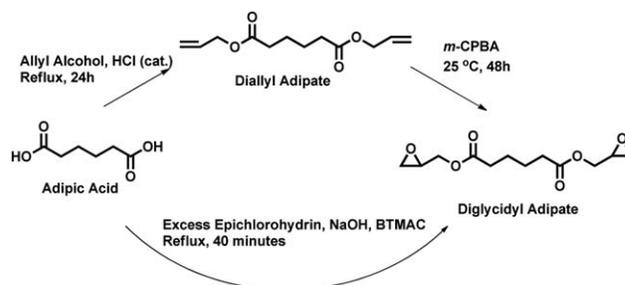
Epoxidation
Diallyl adipate (10 g, 0.044 mol), dichloromethane (250 mL), and m-chloroperoxybenzoic acid (12.7 g, 0.074 mol) were added to a one-neck 500-mL round-bottom flask equipped with a magnetic stir bar. The reaction was protected with an adapter and an argon balloon and stirred for 48 h. Excess m-chloroperoxybenzoic acid was quenched with saturated sodium sulfite, m-chlorobenzoic acid was removed by filtration, and washed with dichloromethane (50 mL). The filtrate was then transferred to a 1 L separatory funnel, washed exhaustively with saturated sodium biocarbonate, dried over magnesium sulfate, and dichloromethane was removed by rotary evaporation to give a crystalline solid. Characterizations of the compound gave almost identical results as those above for diglycidyl adipate prepared by the one-pot method.

Sample Preparation and Curing Procedure
Liquid diglycidyl adipate formed by melting the solid at 60 °C in a disposable aluminum weighing boat. Immediately thereafter, diglycidyl adipate liquid was mixed with a stoichiometric amount of isophorone diamine with a metal spatula for 3 min until a homogenous clear liquid is formed. After transfer of the resin mixture to a syringe, it was degassed in a centrifuge for 3 min at 3000 rpm and 20 °C. Thereafter, the degassed resin mixture was transferred to stainless steel molds equipped with PTFE mold release agent. The samples were immediately cured at 80 °C for 2.5 h and 160 °C for 2.5 h. A similar procedure was performed for the diglycidyl ether of bisphenol A. Dimensions for the molds used for dynamic mechanical analysis (DMA) were 35 mm × 12 mm × 3 mm.

NMR
Proton and ^{13}C NMR spectra of diglycidyl adipate were recorded using a Varian 500 MHz NMR and a Bruxer 600 MHz NMR in CDCl$_3$, respectively.

SCHEME 1 Synthetic routes toward diglycidyl adipate.

Epoxide Equivalent Weight Titration
Epoxide Equivalent Weight's (EEW's) of prepared resins were determined by following the ASTM D1652 method using the perchloric acid and crystal violet as an indicator.

Differential Scanning Calorimetry
Differential scanning calorimetry (DSC) thermograms were recorded using a TA Instruments Model Q2000. The peak melting points (T_m) were determined during the first heating scan from ambient temperature to 100 °C at a rate of 10 °C/min. The melting point is reported as the peak of the endotherm transition.

Rheology
A TA Instruments AR-G2 equipped with 25 mm stainless steel parallel plates was used to determine the viscosity of the resins as a function of shear rate. The shear rate was swept from 2.5 to 1549 1/s at 25 °C and a gap of 1 mm. Viscosity is reported as the average of the Newtonian region.

DMA
A TA Instruments Q800 equipped with a dual cantilever clamp was utilized to determine the temperature dependence of the complex modulus and tan δ. Samples were analyzed over a temperature range of 0 to 200 °C for DGEBA and 0 to 150 °C for diglycidyl adipate.

Thermogravimetric Analysis
Thermal stability studies were performed by Thermogravimetric Analysis (TGA) using a TA Instruments Q50 equipped with an alumina pan. Samples were about 10 mg each. TGA thermograms were recorded by heating samples from ambient conditions to 800 °C at 10 °C/min.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Monomer
The synthesis of diglycidyl adipate by previously reported methods[34] for diphenolate esters with 2-propanol and epichlorohydrin does not yield any significant amounts of the monomer, but only oligomeric products. This is attributed to the poor nucleophilicty of a carboxylate anion in comparison to the sodium phenoxide anion. Therefore, synthesis of the diglycidyl adipate was performed by two different routes (Scheme 1). The first was based on a one-pot method first reported by Maerker and coworkers.[24] The method involved multiple operations and gave a crude yield that ranged from
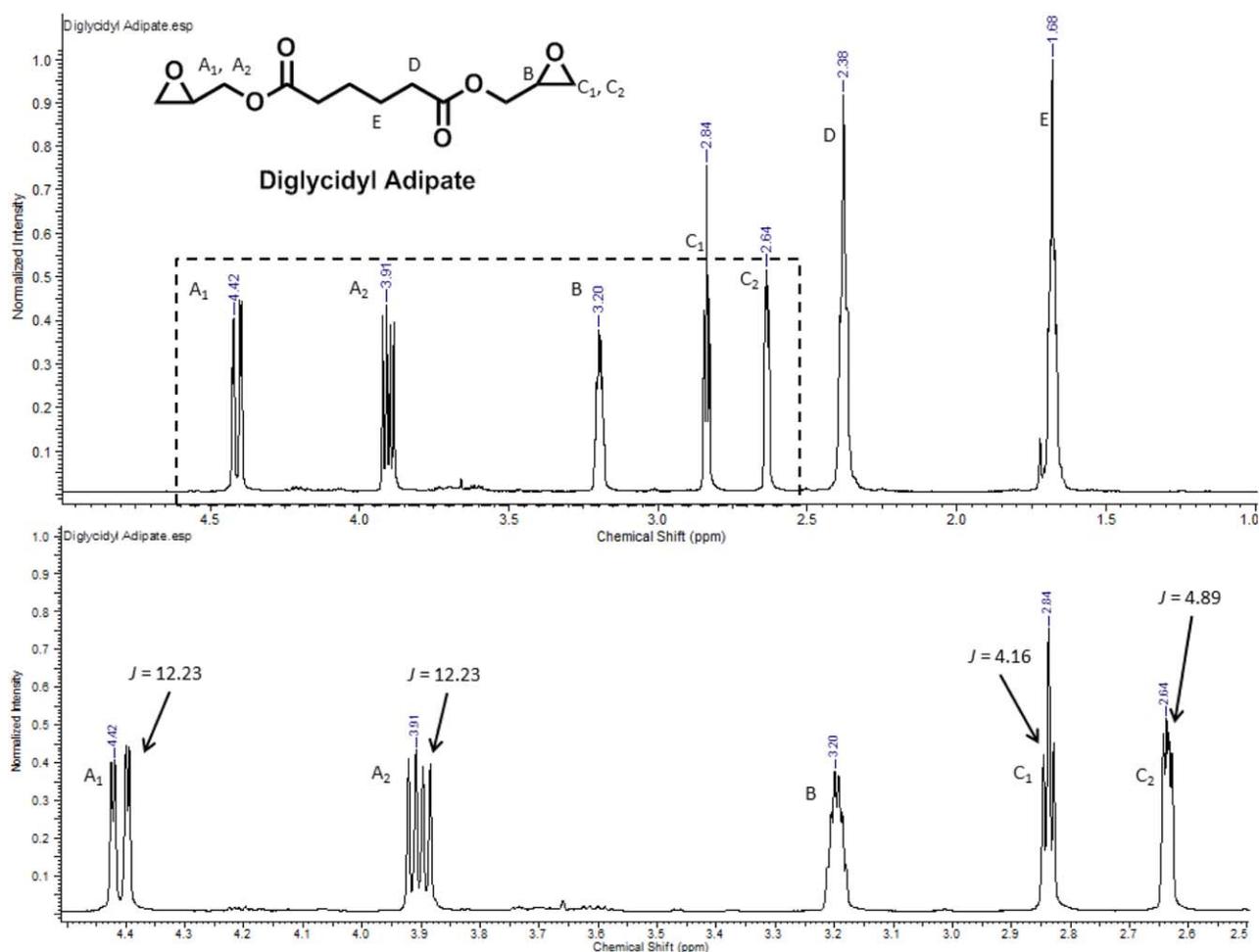
FIGURE 1 ^{1}H NMR spectrum (500 MHz, CDCl$_3$) of diglycidyl adipate prepared by the one-pot reaction of with expanded spectral regions that correspond to protons of the glycidyl ester.

50% to 60% and highly pure monomer after crystallization in 20–30% yield. This purified product, when heated to 60 °C, is a low viscosity liquid that recrystallizes in 10–30 min after being cooled to room temperature and exhibits super cooled liquid behavior on a short time frame in comparison to the diglycidyl ether of bisphenol A. The ^{1}H NMR of the product is displayed in Figure 1(a) with peak assignments. The glycidyl ester proton chemical shifts are at 4.42, 3.91, 3.20, 2.84, and 2.64 ppm, in good agreement with the literature.[25,34] Furthermore, the coupling constants of the doublet of doublets at 4.42 and 3.91 ppm of 12.23 Hz, and the doublet of doublet at 2.64 ppm of 4.89 Hz are in good agreement with previous literature.[25,34] Moreover, relative signal intensities from ^{1}H NMR spectral integrations are within ± 5% of that expected. Titration of the epoxide groups result in an epoxide equivalent weight (EEW) of 132 that is within 6% error of the theoretical value of 129. Work by Ma and coworkers demonstrated higher yields with itaconic acid through a similar adapted process, but required column purification to remove coproducts yielding a mixture of monomer and oligomeric products.[25] The side products from the synthesis of these resins through

the one pot method were primarily oligomeric and are similar to the products characterized by Ma and coworkers. Additionally, saponification of these glycidyl ethers is also possible and is another pathway toward oligomerization. In addition, the multiples steps in the one-pot method reported by Maerker and coworkers[24] appears difficult to scale and, indeed, numerous patents and artciles from 1950 to the present have focused on developing better methodologies toward the synthesis of glycidyl esters.[27–31,35]

The synthesis of diglycidyl adipate by a two-step process consisted of first allylation through esterification with allyl alcohol and then epoxidation utilizing *m*-chloroperoxybenzoic acid was also explored.[18,36] The first step was accomplished in almost quantitative yields (∼95%) and the second step yielded 50–60% product. The yield of the epoxidation step was low relative to results reported by other workers on larger molecules. This is likely due to the partial water solubility of diglycidyl adipate and its propensity to form difficult to separate emulsions during extraction of *m*-chlorobenzoic acid. Further, we anticipate that shorter chain diacids or
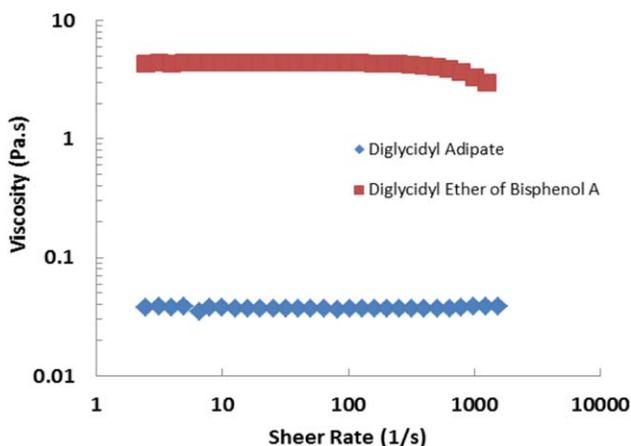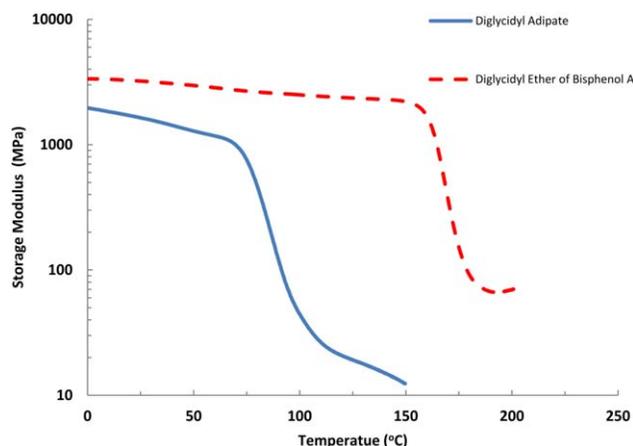
FIGURE 2 Comparing the diglycidyl ether of bisphenol A to diglycidyl adipate viscosities. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

multifunctional acids with higher water solubility than adipic acid will exhibit similar issues. Analysis by ^{1}H NMR spectrum (see SI-1) of this product is similar to that in Figure 1(a) except that small amounts of m-chlorobenzoic acid are still present (<5 mol %). Also, as above, titration of the epoxide groups results in an EEW of 134 that is within 6% error of the theoretical value. The product physically appears as sticky crystals that, on cooling from the melt, crystallize more slowly than the high purity monomer obtained by the one-pot method. The slower propensity of the monomers to crystallize due to impurities is beneficial to epoxy resins where low viscosity liquids are used for composite fabrication. All further work was performed with diglycidyl adipate derived from the one-pot method. Viscosities at 25 °C of monomers from both synthetic routes are 25 mPa·s and the shear rate dependent viscosity is shown in Figure 2 and demonstrates Newtonian behavior. Despite the speed at which diglycidyl adipate crystallizes, no crystallization was observed on the rheometer during testing. The viscosity at higher shear rates is reported and is 99% lower than that of diglycidyl ether of bisphenol A (DGEBA). The low viscosity of diglycidyl adipate combined with that it has two epoxy functionalities indicates that it has excellent potential for incorporation in epoxy resins used for vacuum infusion molding, high solids coatings and as a reactive diluent for epoxy resins with higher viscosity. Typical vacuum infusion epoxy resins have viscosities ranging from 800 to 1000 mPa·s[37] which is typically achieved through formulation of DGEBA with low viscosity reactive diluents such as glycidyl phenol[2] and monofunctional glycidyl esters.[38]

DMA

Diglycidyl adipate and DGEBA were each cured with stoichiometric amounts of isophorone diamine and the thermomechanical properties of these materials was compared by DMA. The glassy phase storage modulus at 25 °C for cured diglycidyl adipate and DGEBA is 2000 and 3200 MPa, respectively (Fig. 3). The diglycidal adipate glassy phase modulus
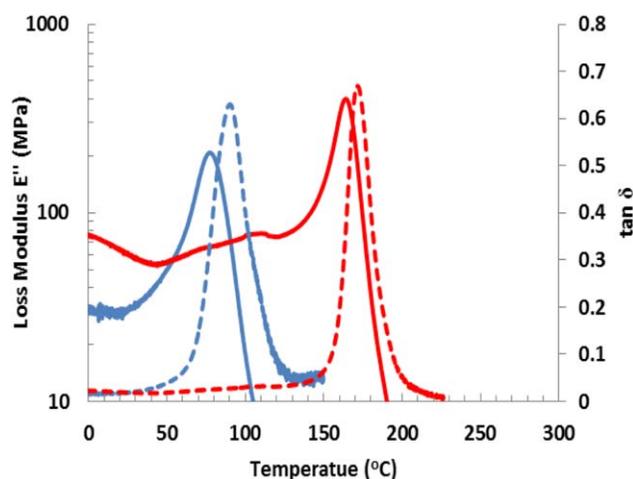

FIGURE 3 Storage modulus (E') as a function of temperature, determined by DMA, of cured diglydicyl adipate and diglycidyl ether bisphenol A resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is 60% lower than DGEBA and is attributed to the lack of aromatic structures. It is similar to cardanol based systems,[39] 4-hydroxy benzoates,[40] and equal or better than some epoxidized fatty acid and triglyceride derivatives.[41–43]

Figure 4 displays Loss modulus (E'') and tan(δ) traces determined by DMA. The alpha transition temperature (T_α) is typically reported either from peaks of the loss modulus or tan δ plots. The T_α is closely related to the glass transition temperature (T_g).

Generally, the peak of the loss modulus is considered as a more conservative representation of T_g. The E'' peak for diglycidyl adipate and DGEBA occur at 77 °C and 160 °C, respectively. In comparison, tan δ peaks for diglycidyl adipate and DGEBA occur at 90 °C and 170 °C, respectively. The

FIGURE 4 Loss modulus (E'') (solid line) and tan(δ) (dashed line) of cured diglydicyl adipate and diglycidyl ether bisphenol A resins as a function of temperature determined by DMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
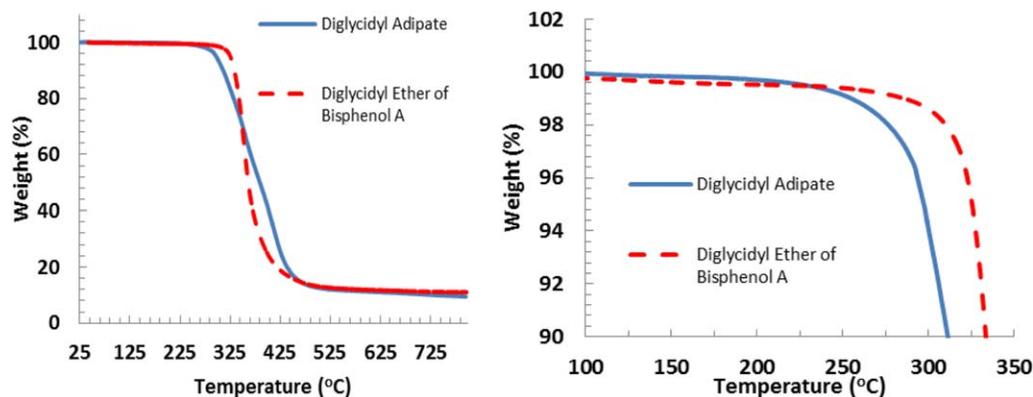
FIGURE 5 TGA thermograms of cured diglycidyl adipate and DGEBA as a function of temperature under constant N_2 flow: (a) y-axis from 0 to 100%, (b) y-axis from 90 to 100%. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

value of cured diglycidyl adipate T_α is relatively high considering that thermoplastics built from adipic acid such as poly[(butylene-succinate)-co-adipate] (PBSA)[44] and Nylon 6,6[45] have T_g's of -36 °C and 70 °C, respectively. The similarity of nylon 6,6 and cured diglycidyl adipate T_g values is likely due to that nylon 6,6 also possess crosslinks, although they are noncovalent, through hydrogen bonding.

Thermogravimetric Analysis

Figure 5 displays TGA thermograms of cured diglycidyl adipate and DGEBA to assess their thermal stability. The weight percent as a function of temperature of both cured diglycidyl adipate and DGEBA show similar profiles. Furthermore, they also have similar percent char when heated above 600 °C. Figure 5(b) is an expansion of the y-axis region for the 90% to 100% weight loss region so that differences between the onset of degradation to 10% weight loss are evident. The onset of thermal degradation at 5% weight loss ($T_{d5\%}$) for cured diglycidyl adipate and DGEBA occur at 297 °C and 325 °C, respectively.

The onset of thermal degradation at 10% weight loss ($T_{d10\%}$) for cured diglycidyl adipate and DGEBA occur at 311 °C and 333 °C, respectively. Hence, $T_{d5\%}$ and $T_{d10\%}$ values for diglycidyl adipate are 8% and 6% lower than those of DGEBA. Values of $T_{d50\%}$ for cured diglycidyl adipate and DGEBA occur at 384 °C and 361 °C, respectively. Values of weight loss percentages, percent char at 800 °C and plots of the derivative of weight loss curves are tabulated in Supporting Information (Fig. S1).

CONCLUSIONS

In conclusion, this article describes the results of diglycidyl adipate synthesis by two routes. The yields of both reactions are relatively low and the processes involve multiple manipulations. Hence, there remains a need for development of an efficient process to prepare diglycidyl adipate in high yields by 1 step. The viscosity of diglycidyl adipate at room temperature is 25 mPa·s., which is $\geq$99% lower than that of DGEBA. When cured with stoichiometric amounts of isophorone diamine, the cured properties of diglycidyl adipate are

higher than expected with respect to both the glassy phase modulus and the T_g without any rigid structures within the resin such as fused or aromatic rings. We attribute the cured properties of the resin to the epoxide equivalent weight (132), which is significantly lower than that of highly pure diglycidyl ether of bisphenol A. This implies that epoxy resins that create cured thermosets with a crosslink density can be utilized in place of rigid epoxy resin structures to reach or move closer to a desired glass transition temperature or glassy phase modulus. Analysis of thermostability by TGA shows that, under inert atmosphere, cured diglycidyl adipate has a similar thermal degradation profile as DGEBA.

The low viscosity of the resin and the thermomechanical properties signify a paradigm shift for researchers exploring biobased epoxy resins and seeking to replace those from bisphenol A. The important role that diglycidyl esters of aliphatic diacids can play is evident given the challenges currently faced in developing epoxy resins from biomass derived aromatic building blocks with suitable purity. Indeed, efforts directed at developing cost-effective aromatic phenolic-based building blocks from biomass sources such as lignin are challenging and are high priority objectives of numerous scientists and engineers in academic, government and industrial laboratories. In contrast, it appears that development of commercial scale processes to produce succinic and adipic acids from biomass is advancing relatively more rapidly. Hence, based on diglycidyl adipate's low viscosity, dual epoxide functionality, and the thermomechanical properties of the cured materials, we believe it is of significant interest for vacuum infusion molding, high solids coatings, and as a reactive diluent for other epoxy resins in those applications.

ACKNOWLEDGMENTS

REFERENCES AND NOTES

1 S. Black, Automotive Composites: Thermosets for the Fast Zone; CompositesWorld, **2015**.

2 H. Q. Pham, M. J. Marks, In Ullmann's Encyclopedia of Industrial Chemistry, Electronic Release; B. Elvers, Ed.; Wiley-VCH: Weinheim, **2012**; pp 155–244.

3 P. A. Sørensen, S. Kiil, K. Dam-Johansen, C. E. Weinell, *J. Coatings Technol. Res.* **2009**, *6*, 135–176.

4 M. M. Green, H. A. Wittcoff, Organic Chemistry Principles and Industrial Practice; Wiley-VCH: Weinheim, **2003**.

5 H. A. Wittcoff, B. G. Reuben, J. S. Plotkin, In Industrial Organic Chemicals; Wiley: Somerset, NJ, **2012**; pp 323–373.

6 H. Okada, T. Tokunaga, X. Liu, S. Takayanagi, A. Matsushima, Y. Shimohigashi, *Environ. Health Perspect.* **2008**, *116*, 32–38.

7 R. Steinmetz, N. G. Brown, D. L. Allen, R. M. Bigsby, N. Ben-Jonathan, *Endocrinology* **1997**, *138*, 1780–1786.

8 M. V. Maffini, B. S. Rubin, C. Sonnenschein, A. M. Soto, *Mol. Cell. Endocrinol.* **2006**, *254*, 179–186.

9 Abrams, R, Facing Consumer Pressure, Companies Start to Seek Safe Alternatives to BPA; New York Times: New York, NY, **2015**.

10 A. M. Nelson, T. E. Long, *Polym. Int.* **2012**, *61*, 1485–1491.

11 R. Auvergne, S. Caillol, G. David, *Chem. Rev.* **2014**, *114*, 1082–1115.

12 F. Hu, J. J. La Scala, J. M. Sadler, G. R. Palmese, *Macromolecules* **2014**, *47*, 3332–3342.

13 S. Ma, X. Liu, Y. Jiang, L. Fan, J. Feng, J. Zhu, *RSC Adv.* **2015**, *5*, 15930–15939.

14 F. Hu, S. K. Yadav, J. J. La Scala, J. M. Sadler, G. R. Palmese, *Macromol. Chem. Phys.* **2015**, *216*, 1441–1446.

15 M. Chrysanthos, J. Galy, J. P. Pascault, *Polymer (Guildf)* **2011**, *52*, 3611–3620.

16 J. Łukaszczyk, B. Janicki, M. Kaczmarek, *Eur. Polym. J.* **2011**, *47*, 1601–1606.

17 J. Hong, D. Radojčić, M. Ionescu, Z. S. Petrović, E. Eastwood, *Polym. Chem.* **2014**, *5*, 5360–5368.

18 C. Mantzaridis, A. L. Brocas, A. Llevot, G. Cendejas, R. Auvergne, S. Caillol, S. Carlotti, H. Cramail, *Green Chem.* **2013**, *15*, 3091–3098.

19 J. Wan, B. Gan, C. Li, J. Molina-Aldareguia, E. N. Kalali, X. Wang, D. Y. A. Wang, *Chem. Eng. J.* **2016**, *284*, 1080–1093.

20 J. Wan, B. Gan, C. Li, J. Molina-Aldareguia, Z. Li, X. Wang, D. Y. Wang, *J. Mater. Chem. A* **2015**, *3*, 21907–21921.

21 A. S. Matharu, C. Ding, P. S. Shuttleworth, J. Clark, S. Makin, *Green Chem.* **2015**, *17*, 4000–4008.

22 Hartman, M, In Bioamber Sarnia Producing High Quality Bio-Succinic Acid at Commercial Scale—Copany Now Shipping Bio-Succinic Acid to Customers; Press Release: Montreal, **2015**.

23 S. Ma, D. C. Webster, *Macromolecules* **2015**, *48*, 7127–7137.

24 G. Maerker, H. A. Monroe, W. S. Port, *J. Appl. Polym. Sci.* **1963**, *7*, 301–307.

25 S. Ma, X. Liu, Y. Jiang, Z. Tang, C. Zhang, J. Zhu, *Green Chem.* **2013**, *15*, 245.

26 X. Dai, Z. Xiong, S. Ma, C. Li, J. Wang, H. Na, J. Zhu, *Ind. Eng. Chem. Res.* **2015**, *54*, 3806–3812.

27 C. L. F. D. Hove, D. Heymans, C. Steinbrecher, A. Kotlweska, R. V. Sand. Glycidyl Esters of Alpha, Alpha Branched Neononanoic Acids, Synthesis and Uses, U.S. Patent 2014/0316030 A1, October 23, **2014**.

28 C. F. Dukes, R. W. Welch. Process for Preparing Glycidyl Esters of Polycarboxylic Acids, 3,859,314, January 7, **1975**.

29 K. Gumlich, R. Merten, M. Henningsen, M. Schaefer, J. H. Teles, B. Mohr. C10 Alkanoic Acid Glycidyl Esters and Use Thereof, U.S. 2010/0180802 A1, June 22, **2010**.

30 G. Maerker, W. S. Port. Synthesis of Glycidyl Esters, 3,053,855 September 11, **1962**.

31 D. R. Smith. Process for the preparation of Glycidyl Esters, 3,334,156, August 8, **1967**.

32 M. M. Bomgardner, *C&EN News* **2015**, *40*, 20.

33 M. Bomgardner, *Chem. Eng. News* 14AD, *92*, 10–14.

34 A. Maiorana, S. Spinella, R. A. Gross, *Biomacromolecules* **2015**, *16*, 1021–1031.

35 G. J. Martin, N. Jack. 2,567,842, September 11, **1951**.

36 J. Qin, M. Woloctt, J. Zhang, *ACS Sustain. Chem. Eng.* **2013**, *2*, 2217–2236.

37 Hexion, In EPIKOTE ™ Resin MGS ® RIMR 235 and EPIKURE ™ Curing Agent RIMH 235-238. Available at: http://hexion.com/Products/TechnicalDataSheets.aspx?id=3510 (accessed on January 17, **2006**).

38 H. Reichwein, P. Langemeier, T. Hasson, M. Schendzielorz, In 10th-Annual SPE® Automotive Composites Conference Exhibition, **2010**, pp 1–20.

39 F. Jaillet, E. Darroman, A. Ratsimihety, R. Auvergne, B. Boutevin, S. Caillol, *Eur. J. Lipid Sci. Technol.* **2014**, *116*, 63–73.

40 D. Fourcade, B. Ritter, P. Walter, *Green Chem.* **2013**, *15*, 910–918.

41 K. Huang, P. Zhang, J. Zhang, S. Li, M. Li, J. Xia, Y. Zhou, *Green Chem.* **2013**, *15*, 2466–2475.

42 J. M. Raquez, M. Deléglise, M. F. Lacrampe, P. Krawczak, *Prog. Polym. Sci.* **2010**, *35*, 487–509.

43 X. Pan, P. Sengupta, D. C. Webster, *Biomacromolecules* **2011**, *12*, 2416–2428.

44 S. S. Ray, J. Bandyopadhyay, M. Bousmina, *Polym. Degrad. Stabil.* **2007**, *92*, 802–812.

45 TA Instruments, Thermal Analysis Application Brief Measurement of Moisture Effects on the Mechanical Properties of 66 Nylon, TA-133A. Available at: www.tainst.com (accessed on May 5, **2016**).