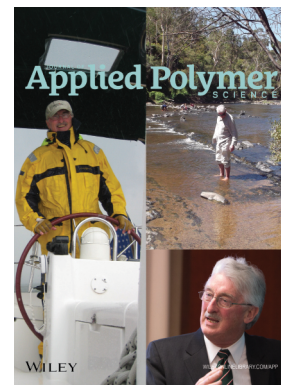## Special Issue: Sustainable Polymers and Polymer Science Dedicated to the Life and Work of Richard P. Wool

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.)

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.)

Structure–property relationships of a bio-based reactive diluent in a bio-based epoxy resin

Anthony Maiorana,[1] Liang Yue,[2] Ica Manas-Zloczower,[2] Richard Gross[1]

[1]New York State Center for Polymer Synthesis, Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180

[2]Department of Macromolecular Science and Engineering, Case Western Reserve University, 2100 Adelbert Road, Kent Hale Smith Bldg, Cleveland, Ohio 44106

Correspondence to: R. A. Gross (E-mail: grossr@rpi.edu)

ABSTRACT: The monofunctional glycidyl ether of eugenol (GE) was used as a reactive diluent for the diglycidyl ether of diphenolate n-pentyl ester (DGEDP-Pe). Viscosities of GE and DGEDP-Pe are 25 mPa s and 11 Pa s, respectively. Compositions GE/DGEDP-Pe epoxy resins with 5, 10, 15, 20, and 30 wt % GE were analyzed for viscosity reductions and, subsequently, cured with isophorone diamine. The glassy modulus of cured GE/DGEDP-Pe epoxy resins remained between 2000 and 3000 MPa. The glass transition temperature decreased linearly, from 92 °C for neat DGEDP-Pe, with progressively higher loadings of GE to 53 °C at the highest GE loading of 30 wt %. The thermal stability decreased as GE loading increased with a maximum of 30 °C loss in the onset of degradation at 5 wt % mass loss. The role of GE as a reactive diluent is discussed and a range of loadings was determined to be suitable for a vacuum infusion epoxy resin system. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43635.

INTRODUCTION

Epoxy resins are one of the most versatile thermosetting polymers that can be designed to function in applications ranging from structural adhesives to composites to protective coatings.[1] When fully cured, epoxy resins exhibit low shrinking, good creep resistance, and the qualities of an engineering polymer with an elastic modulus ranging from 2 to 3 GPa and a high glass transition temperature (typically 120 °C or higher).[2] Because of their physical and chemical properties, the use of epoxy resins as a thermoset composite polymer matrix is expected to grow because of increasing demands from automotive and wind energy industries as high filler content composites can be competitive with metals.[3–5] However, in order to enable composites with filler loadings of 70% or greater, low viscosity epoxy resins are required to infuse continuous fiber mats before significant curing can take place.

Bisphenol A (BPA) based epoxy formulations have shown remarkable versatility in properties to meet the majority of needs by the epoxy resin industry. However, BPA is coming under increasing scrutiny by the federal drug administration (FDA) and the public as a potential toxin to humans and is a contaminant of concern.[6] BPA has been linked to disrupting the human endocrine system,[7] cancer,[8] onset of disease,[9] and the FDA has placed a ban on BPA based products for prenatal women and infants.[10] BPA is also derived from the cumene, which requires large excesses of benzene with propylene and this process is currently sourced from petroleum.[11] Hence, the use of BPA in epoxy resins for growing industries such as new and replacement wind turbines will require increasing extraction and refinement of petroleum.

Petroleum is the basis of the polymer industry.[11,12] With the passing of an era of easy-to-drill oil, we usher in a period where oil is obtained from more challenging locations such as deep water environments that pose environmental and safety risks that are dangerous to workers and create increased potential for catastrophic oil spills. Moreover, since the co-location of oil generation and petroleum refineries is problematic, millions of barrels of oil are transported daily by truck, tankers, pipelines, and railcars. This infrastructure has led to the release of pollutants that endanger waterways, land, and other ecosystems with effects for time periods that we are just beginning to understand. Furthermore, the age of petroleum-derived carbon is linked to climate change that poses serious threats to our planet.

As a result, scientists in academia, industry, and government labs are pursing research to replace petroleum-based polymers with cost-performance competitive bio-based products that preferably are from nonfood-based feedstocks such as ligno-cellulose and plant oils.[13,14] Solvay has recently commercialized a glycerol to epichlorohydrin process,[15] which has the potential to enable sustainable epoxy resins from a wide range of platform chemicals. Many reported cured bio-based epoxy resins are competitive to cured DGEBA with respect to elastic modulus, glass transition temperature, and thermal stability. Qin et al. synthesized and studied the properties of a diglycidyl eugenol prepared by epoxidation of the double bond and glycidylation of the phenolic moiety, which yielded excellent thermomechanical properties when cured with anhydride crosslinkers.[16] Wan et al. synthesized and studied bifunctional eugenol systems incorporating both esters[17] and ethers[18] into the backbone of the polymers and demonstrated using dynamic mechanical analysis (DMA) that modulus and glass transition temperatures are competitive with bisphenol A analogs and exhibit superior flame retardant properties. However, bio-based epoxy resins are often crystalline solids.[16–19] Some notable liquid systems that have been recently reported are based on furfural derivatives,[20] terpenes,[21] gallic acid,[22] and cardanol derivatives.[23–25]

We recently reported sustainable epoxy resins derived from a levulinic acid derivative known as diphenolic acid as an alternative to BPA. The diphenolic acid-based epoxy resin system utilized the functionalization of the carboxylic acid with n-alkyl alcohols easily obtained from bacterial fermentation (C1-C5) where, increasing the length of the n-alkyl chain reduced the resin viscosity and glass transition temperature.[26] However, the lowest viscosity epoxy resin in this series, diglycidyl ether of diphenolate n-pentyl ester (DGEDP-Pe), is still too high (11 Pa s) for vacuum infusion of continuous fibers for composite fabrication. Hence, this article explores the use of a bio-based reactive diluent to reduce DGEDP-Pe viscosity and thereby broaden its use in epoxy resin formulations.

Development of thermoset infusion resins has primarily been the focus of industrial resin development and formulation[27–29] and has received little to no academic attention. Infusion resins for production of high filler content composites require epoxy resins with viscosities below that of neat DGEBA (less than 4 Pa s).[30] The route to development of infusion resins is primarily based in the mixing of DGEBA with low viscosity reactive diluents such as monofunctional aliphatic glycidyl esters[31] and aliphatic[32] or aromatic glycidyl ethers.[1] In addition to reduced epoxy resin viscosity, desirable characteristics of reactive diluents include enabling the fabrication of epoxy resin composites with higher filler loading, improving filler wetting and impregnation. In addition, the diluent should react with the curing agent at approximately the same rate as the resin while being nonreactive with the resin under normal storage conditions. The commercial importance of reactive diluents in epoxy resin formulations is reflected by a corresponding rich patent literature.[31,32] However, because of the scarcity of academic papers on reactive diluent systems, the literature provides little guidance on how reactive diluents function before, during, and after cure. The importance of reactive diluents is closely tied to advances in composite fabrication where lower viscosity thermoset matrices can allow for faster infusion of continuous fillers to make light-weight engineering composites in order to meet demands from the growing composite market for wind turbine blades and automotive parts.[33]

This article describes the synthesis of a monofunctional glycidyl ether reactive diluent from eugenol, an extract from certain essential oils such as clove[34] and nutmeg,[35] its ability to reduce DGEDP-Pe viscosity and thereby broaden its potential utility in epoxy resin formulations. DMA, chemorheology, and thermogravimetric analysis (TGA) were performed to determine how incorporation of the glycidyl ether of eugenol (GE) influences the gel point and the final cured properties (e.g., glassy phase modulus, glass transition temperature) of DGEDP-Pe cured with isophorone diamine. An additional variable considered herein is the relationship between the above property changes and the corresponding increases in the average molecular weight between crosslinks through chain extension. The results of this work show that GE at a wide range of loadings is an effective reactive diluent for DGEDP-Pe that has excellent promise for use in infusion molding systems with high filler content.

EXPERIMENTAL

Materials
Eugenol, tetraethylammonium bromide, isopropanol, and epichlorohydrin was purchased and used as received from Alfa Aesar. Isophorone diamine (IPDA), 0.1 M perchloric acid in acetic acid, sodium hydroxide, crystal violet, and acetic acid was purchased from Sigma Aldrich and used as received. The diglycidyl ether of diphenolate methyl ester (DGEDP-Me) was prepared as previously reported.[26]

Synthesis of Glycidyl Ether of Eugenol
The synthesis of glycidyl eugenol was reported as an intermediate for the synthesis of crown ethers, in a paper focused on the synthesis of crown ethers and no glycidyl ether of eugenol spectral data are reported.[36] The boiling point of this compound was reported in 1958 by Beasley et al. to be 110 °C.[37] A general procedure for the synthesis of aromatic glycidyl ethers was first patented by Shell[38] and was adapted for this work. The isolated product was a light yellow liquid with a yield of 85–90%. *Glycidyl Ether of Eugenol* nuclear magnetic resonance (^{1}H NMR) (500 MHz, CDCl$_3$): ppm δ 2.73 (dd, $J = 4.89$ Hz, 1H), 2.83 (observed triplet, $J = 4.65$ Hz, 1 H), 3.34 (d, 2 H), 3.37 (m, 1H), 3.86 (s, 3H), 4.01 (dd, $J = 11.25$ Hz, 1H), 4.22 (dd, $J = 3.42$ Hz, 1H), 5.07 (m, 1H), 5.10 (t, 1H), 5.96 (m, 1H), 6.71 (s, 1H), 6.73 (d, 1H), 6.86 (d, 1H); High-Resolution Mass Spectrometry (ESI): 238 (220 + NH$_4^+$) m/z.

Synthesis of Diglycidyl Ether of Diphenolate Pentyl Ester
The preparation is described elsewhere.[26] In summary, the product obtained is a viscous light yellow liquid in yields of 85–97%.

Preparation of Cured Epoxy Materials for Testing
Epoxide equivalent weights of the neat resins were taken from previously reported results or determined through titration according to ASTM D1652.[26] Weights of reaction components were calculated by using the epoxide equivalent weight (EEW)
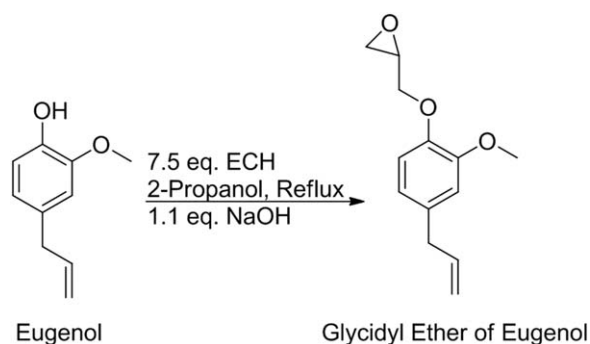
Scheme 1. Synthesis of glycidyl ether of Eugenol

and the amine hydrogen equivalent weight (AHEW), which were calculated by eqs (1) and (2), respectively. Values of EEW and AHEW were placed into eq. (3) to obtain the parts by weight of diamine per hundred parts resin (phr)[1]:

$$EEW \ of \ Mix = \frac{Total \ Weight}{\frac{Weight \ of \ Resin \ A}{EEW \ of \ A} + \frac{Weight \ of \ Resin \ B}{EEW \ of \ Resin \ B}} \quad (1)$$

$$AHEW = \frac{Molecular \ weight \ of \ amine}{number \ of \ active \ hydrogens} \quad (2)$$

$$phr = \frac{AHEW \times 100}{EEW} \quad (3)$$

Epoxy resins were mixed by hand with a metal spatula with the appropriate amount of isophorone diamine (IPDA) until the mixture appeared homogenous. The mixed resins were then transferred to a capped syringe and degassed by centrifugation (3000 rpm, 2 min) to remove air bubbles. The resins were then transferred via syringe into stainless steel molds coated with PTFE mold release agent. The mold geometries used were: rectangular dual cantilever bars (40 mm × 12 mm × 3 mm) and rheology discs (25 mm × 2 mm). The method of resin curing was adapted from a literature procedure.[39] In summary, the resins were maintained under ambient conditions in the molds for 16 h after which they were compression molded for 4 h at 80 °C with 2 metric tons of applied pressure and then 4 h at 160 °C without any release of pressure. For chemorheology, samples were mixed with IPDA as previously described and were then placed on the rheometer to minimize effects of cold curing.

Dynamic Mechanical Analysis
DMA was performed using a Q800 from TA Instruments (New Castle, DE). A dual cantilever mode with an amplitude of 10 μm was used to determine the storage modulus (E') and alpha transition temperature (determined from the peak of the loss modulus) (E'') by scanning at 2 °C/min from 0 °C to 200 °C. All DMA tests were repeated at least five times.

Rheology
The viscosity of the different resins and their mixtures was determined by steady shear experiments at 25 °C using a TA AR-G2 rheometer equipped with 25 mm diameter parallel plates. The shear rate ranged from 1 to 100 s^{-1} under the steady shear flow with an equilibration time of 1 min and a sample gap of 1 mm. The viscosity was reported as an average from the Newtonian region. The average molecular weight between crosslinks was determined using a TA AR-G2 rheome-

ter by a literature method.[26] For chemorheology, dynamic shear experiments were performed using a TA AR-G2 rheometer equipped with 8 mm diameter parallel plates. Temperatures were ramped at 5 °C/min at a frequency of 1 rad/s to the isothermal time sweep. Each isothermal cure was monitored in multifrequency mode from 1 to 15 rad/s with a total of five frequencies operating at 0.1% strain. Gel times are measured as the time from the start of the test till momentary frequency independence of the tan δ.[40]

Thermogravimetric Analysis
The thermal stability of the prepared resins was studied by TGA using a TA Instruments Q50 with an alumina pan. The samples were about 10 mg each and were run from room temperature to 800 °C at a heating rate of 10 °C/min under constant N$_2$ flow.

Nuclear Magnetic Resonance
The ^{1}H NMR was obtained on a Varian 500 MHz in CDCl$_3$.

RESULTS AND DISCUSSION

Synthesis and Characterization of Reactive Diluent
The glycidyl ether of eugenol (GE) was prepared by a single step process depicted in Scheme 1 (for detailed procedures see Experimental Section). The glycidylation reaction was performed with excess epichlorohydrin under alkaline conditions under homogenous conditions. The resulting product was obtained in yields ranging from 85% to 90%. The products was analyzed by ^{1}H NMR and high resolution mass spectrometry (see Experimental) and characterized by epoxide equivalent weight titration and viscosity. The glycidyl ether of eugenol was first characterized by ^{1}H NMR, and the peak positions were assigned based on predicted chemical shift positions using ChemDraw. Further rational for peak assignments was based on published work.[16,26] The GE ^{1}H NMR spectrum along with peak assignments are shown in Figure 1.

Dimeric co-products were observed in the high-resolution mass spectrum, but were not able to be quantified with ^{1}H NMR or epoxide equivalent weight titrations. The epoxide equivalent weight of the GE showed the theoretical value at 220 ± 8 and further indicates that the majority of isolated product was pure. Aside from the purity of GE it was a low viscosity liquid, much lower than that of the prepared DGEDP-Pe epoxy resin. The viscosity of GE was observed to be 25 mPa s and in comparison to DGEDP-Pe (11.5 Pa s) the viscosity is significantly lower and thus would enable the glycidyl ether of eugenol to act as a reactive diluent.

Blending GE with DGEDP-Pe
In order to assess the working range of a reactive diluent system, the viscosity of neat DGEDP-Pe, without addition of crosslinker, was characterized with progressive loadings of GE. The viscosity as a function of GE weight percent loading is shown in Figure 2. The addition of 5, 10, 15, 20, 30, and 50 wt % GE to DGEDP-Pe results in significant decreases in system viscosity. Addition of just 5 wt % GE reduces the viscosity by 38% whereas 10 wt % reduces the viscosity by 70%. A viscosity reduction of 100% is observed at about 20 wt % GE and viscosities less than 1 Pa s result from loadings above 20 wt %. In comparison, a Hexion infusion resin system has a viscosity of 0.7–1.1 Pa s as reported from the manufacturer.[41]
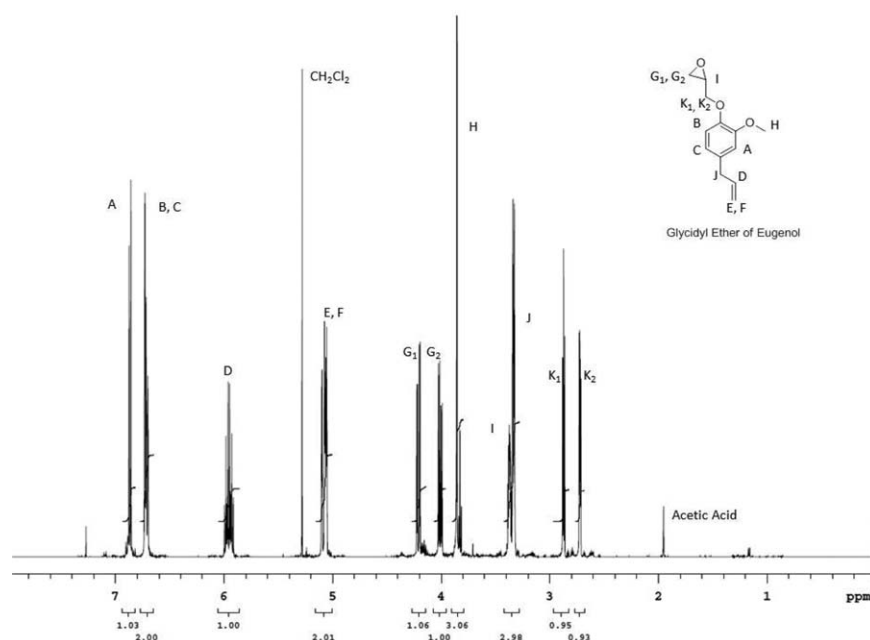
Figure 1. ^{1}H NMR (500 MHz, CDCl$_3$) and assigned peaks of glycidyl ether of eugenol (GE).

Values of both GE wt % and mol % in GE/DGEDP-Pe mixtures along with corresponding values of EEW are listed in Supporting Information Table S1. Thirty wt % GE corresponds to 48 mol % GE which, based on stoichiometry, is almost at the highest possible GE loading that would theoretically change the system from a thermoset to a thermoplastic when utilizing a diamine crosslinker. Furthermore, EEW values range from 230 to 234 over the compositional range of 30 wt % GE in GE/DGEDP-Pe mixtures. Since EEW remains nearly constant, variables that change over this GE/DGEDP-Pe compositional range are viscosity and the extent of chain extension. The latter is a consequence of that, by replacing DGEDP-Pe with GE units, potential crosslink sites are occupied by GE that consequently extends the molecular weight between crosslink points. It fol-

lows that for cured resins, increasing the content of GE in DGEDP-Pe/GE mixtures will extend the molecular weight between crosslinks as well as the onset of network formation (gel time). Studies to assess gel time as a function of the epoxy resin composition are described below.

Dynamic Shear Rheology: Chemorheology for Gelation

Dynamic shear rheology at 80 °C with a 5 °C/min temperature ramp was employed to mimic a realistic simulation for the curing of epoxy resins as curing temperatures are not obtained instantaneously. At the start of curing studies the epoxy resins have stoichiometric amounts of isophorone diamine and have been degassed according to the experimental section. Once the resin compositions reached 80 °C the rheometer was operated in a multifrequency mode to determine the gel point as the momentary frequency independence of the tan δ shown in Figure 3(b).[40] The gel point when measured by the aforementioned method is indicative of the onset of network formation and is the point where the polymer starts to exhibit thermoset like behavior. Figure 3(a) shows the gel time as function of GE content. The gel point is often the end of the processing window for epoxy thermosets so extending the gel point in effect also extends the working time or pot-life of the resin. Additionally, because these tests were conducted at 80 °C, the time to gelation at lower and higher temperatures would require longer and shorter times, respectively.

Small gains in inhibiting the gel time were observed at 10 wt % GE and correspondingly higher times to gelation required larger GE contents. Indeed, at 10 wt % GE, the gel time is extended from 45 to 50 min (an 11% increase). Progressively higher loadings at 15, 20, and 30 wt % GE showed a near linear increase in the gel time to 61, 70, and 84 min, respectively. In other words, to significantly influence gel times at 80 °C, GE contents above 10 wt % are required. For GE contents of ≤ 10% GE's primary affect is to reduce the epoxy resin viscosity. GE contents above
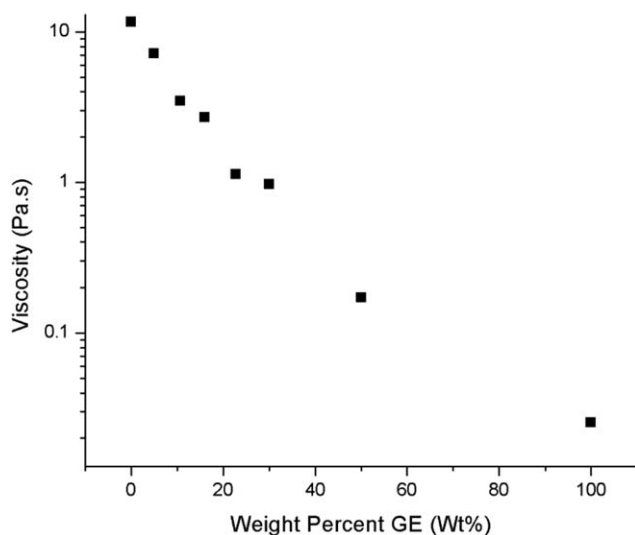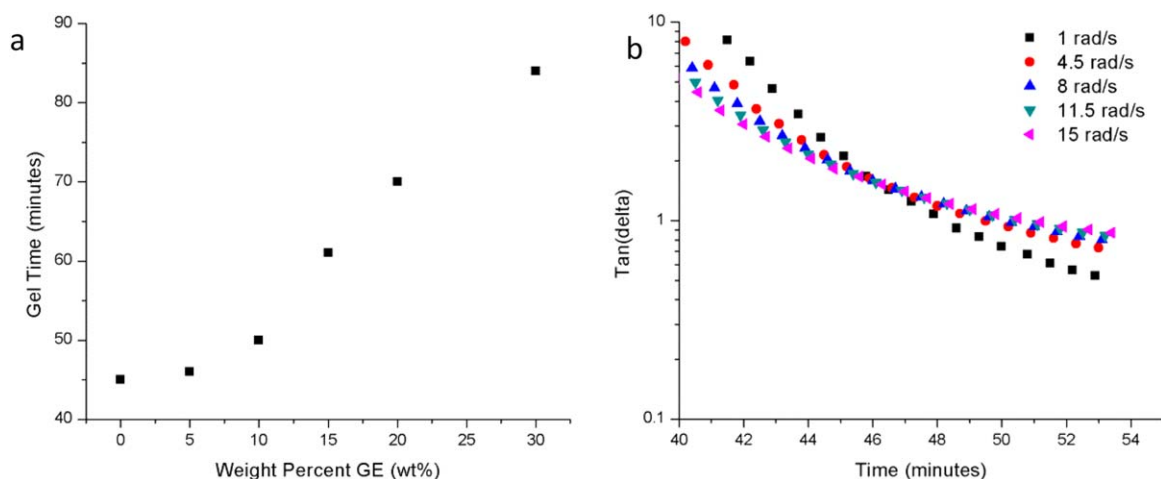

Figure 2. Average of the Newtonian viscosity as a function of percent GE in DGEDP-Pe mixtures at room temperature.

Figure 3. (a) Gel time as a function of the reactive diluent concentration at 80 ∘C and (b) momentary frequency independence of tan δ for the 5 wt % GE composition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

30 wt % did not show a gel point based on measurements by the frequency dependence of tan δ.

Dynamic Mechanical Analysis

DMA was used to determine how increasing the content of GE in DGEDP-Pe/GE mixtures influences the storage modulus and glass transition (T_g) and, correspondingly, how such changes in properties relate to extending the matrix by increasing molecular weight between crosslinks. DMA of the cured resin mixture provided the temperature dependence of the storage modulus (E') and loss modulus (E''). The peak of the loss modulus correlates to the alpha transition temperature (T_α) that is closely related to the glass transition temperature ($T_\alpha \approx T_g$) and is the more conservative value than the peak of the tan δ. The storage modulus at 25 °C was taken to be the glassy modulus of the cured thermosets. Over the range of GE loadings (up to 30 wt %), the glassy modulus remained between 2 and 3 GPa [Figure 4(a)] without any trends that would indicate changes in GE content significantly alters the glassy modulus.

Alternatively, T_∞, which is taken as T_g, exhibits significant changes even at 5 wt % GE [Figure 4(b)] and exhibits a nearly linear trend as a function of GE (slope = −1.36, $R^2 = 0.995$). Thus, in contrast to the similarity of glassy modulus values over a wide range of epoxy resin compositions and the small change in gel time for GE contents ≤ 10%, the T_g of DGEDP-Pe/GE epoxy resin mixtures is highly sensitive to even low GE loadings (i.e., 5 wt %). The effect of decreasing the glass transition temperatures with higher loadings of GE is a significant tradeoff in final material performance to develop a low viscosity epoxy resin system. Composites made from such low T_g resins may only be applicable to nontemperature demanding applications. The decrease of glass transition temperature with increasing monofunctional reactive diluent is a definitive indicator that the molecular weight between crosslinks is indeed increasing. Additionally, the significant changes in T_g are not reflected in the glassy modulus supporting results by Liu et al. who utilized BPA as a chain extender for DGEBA with a trifunctional phenolic crosslinker.[42] Further, Bell,[43] Levita,[44] Pearson and Yee,[45] Crawford and Lesser[46] have also reported that the elastic
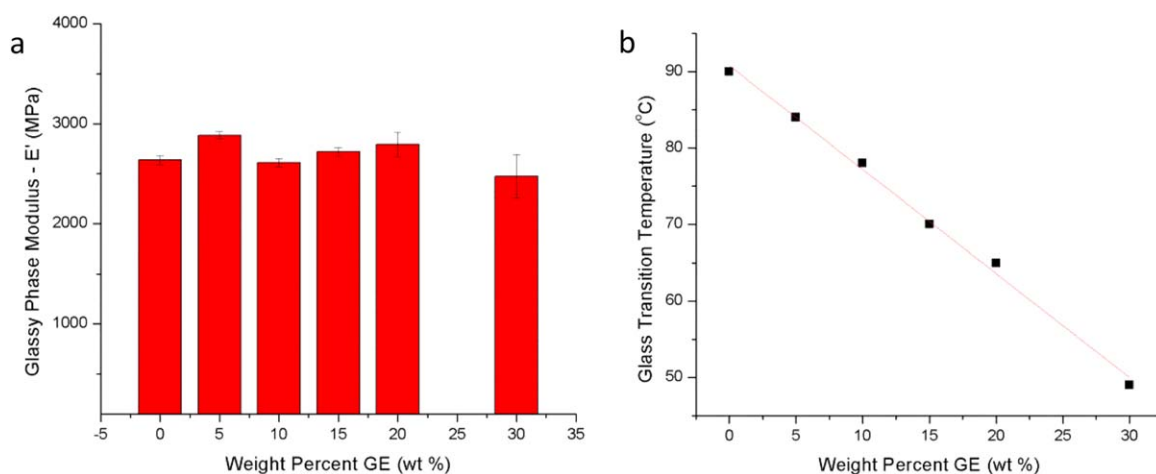
Figure 4. (a) Storage modulus (25 ∘C) and (b) peak of the loss modulus (alpha transition) being related to the glass transition temperature as a function of increasing glycidyl eugenol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
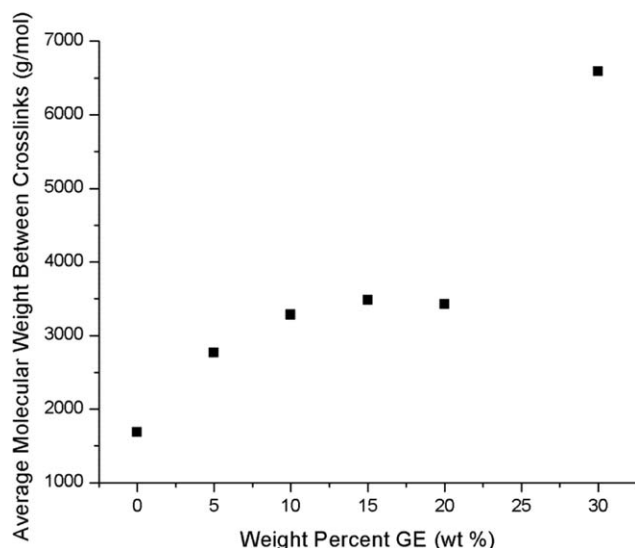
Figure 5. Changes in the average molecular weight between crosslinks (M_x) as a function of GE content determined by parallel plate oscillatory rheology.

modulus of cured epoxy resins does not significantly change with crosslink density, but that the glass transition temperature decreases and fracture toughness increases with decreased crosslink density.

While the glassy phase modulus remains unaffected, it remains to be determined whether this would also be true for the rubbery phase modulus. The rubbery phase modulus was analyzed by measuring the frequency independence of the shear modulus, which is directly related to the average molecular weight between crosslinks according to eq. (4). This method has been employed previously[24,26] and is detailed in the experimental section.

$$M_x = \frac{\rho RT}{G_N} \qquad (4)$$

In eq. (4), M_x is the average molecular weight between crosslinks, ρ is density, R is the universal gas constant, G_N is the shear modulus, and T is the absolute temperature of the rubbery region. The density of the polymers were determined to be about 1 g/cm^3 according to ASTM D792-13 and the temperature for the rubbery region was taken as the peak of tan $\delta + 50\,°C$ in Kelvin.[47] Figure 5 shows changes in M_x as a function of GE content. The magnitude of M_x values is significantly higher than what is realistic. This is because of inherent assumptions during determinations of M_x such as the strain is homogenous throughout the sample, deformation is affine, and steady state conditions are achieved at any strain.[48] Therefore, analysis of this data is limited to determining trends as opposed to quantitative changes in M_x. Some of us have utilized this method to characterize M_x in previous work.[24,26]

Indeed, similar to T_g, M_x values are highly sensitive to small GE contents in DGEDP-Pe/GE epoxy resin mixtures. The addition of 5 wt % GE resulted in a 40% increase in M_x. However, further increases in GE content result in relatively smaller rises in M_x. Indeed, within the range of GE values from 0% to 20%, M_x

values plateau at about 15 wt %. Nevertheless, between 20 and 30 wt % GE, a large increase in M_x occurs. This result was confirmed by repeating the analysis multiple times. Apparently, at 30 wt % GE, the system to may exhibit behavior more like a lightly crosslinked thermoplastic polymer as opposed to a thermoset. However, to better understand this phenomenon, a separate study focused on high loadings of monofunctional reactive diluents would be required. Eugenol also provides an unsaturated bond that could further act as a crosslink site when free radically crosslinked with initiators such as benzoyl peroxide, which has been demonstrated previously in epoxy systems utilizing styrene.[49] Having a bio-based reactive diluent that would allow for reduced viscosity while maintaining high crosslink density could further enhance the potential of many previously studied bio-based epoxy resins that are crystalline solids to be processed as liquid epoxy resin systems.

Thermogravimetric Analysis

Thermal stability of the resins is important to define its suitability for temperature demanding applications. Figure 6 displays weight loss curves as a function of temperature while Supporting Information Table S2 compiles corresponding data on the onset of degradation. As GE increases, the general trend observed is a decrease in onset of degradation temperatures. Neat DGEDP-Pe has an onset of degradation at 5% weight loss ($T_{d5\%}$) of 350 °C, while addition of 30 wt % GE results in a decrease in $T_{d5\%}$ to 321 °C, a 9% decrease. However, for 5 and 10 wt % GE, $T_{d5\%}$ does not significantly change relative to neat DGEMD-Pe. In contrast, at 15 wt % GE, $T_{d5\%}$ decreases by 13 °C, a 4% change. We hypothesized that large increases in M_x relative to neat DGEDP-Pe for DGEMD-Pe/GE mixtures with 5% and 10% GE indicates that a significant expansion of the matrix occurs at these epoxy resin compositions and this would correlate with regular decreases in the thermal degradation temperature. Furthermore, T_g was highly sensitive to GE content in DGEDP-Pe/GE mixtures. However, trends in M_x and T_g do not correlate with the thermal decomposition behavior.
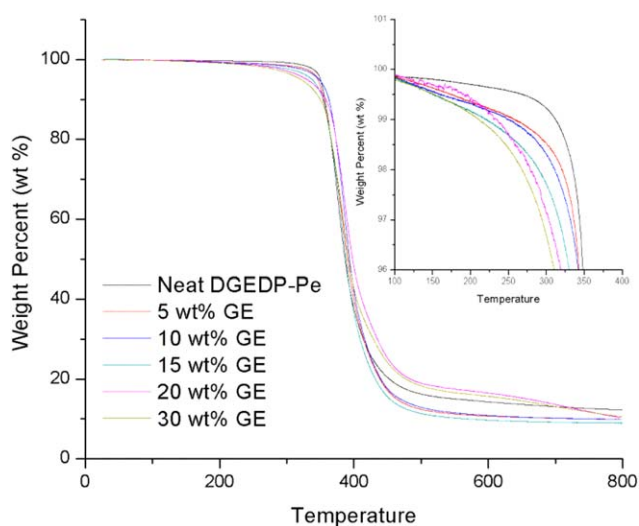
Figure 6. Onset of degradation of prepared formulations by comparing weight loss curves as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Chattopadhyay and Webster discuss the thermal stability and flame retardancy of polyurethanes and cite decreasing crosslink density as a factor for decreased thermal stability.[50] In contrast, incorporation of up to 10% GE units in DGEDP-Pe matrices has little effect on the corresponding cured epoxy resin thermostability. We hypothesize that the retention of thermal stability is because of the methoxy groups present on the glycidyl ether of eugenol. Reano et al. have demonstrated that increasing methoxy moieties adds anti-radical activity for bis and trisphenols derived from ferulic and sinapic acid.[51] Wan et al. have also shown that a eugenol-based epoxy resin exhibits high percentages of char and thermal stability.[18] Indeed, we also observe similar results (Figure 6) but to a lesser extent and without a clear trend as a function of GE loading. The samples containing 20 and 30 wt % GE exhibited slightly higher char yields than that of neat DGEDP-Pe.

CONCLUSIONS

The glycidyl ether of eugenol is an effective reactive diluent that lowers the viscosity of the overall system without changing the glassy phase modulus while also extending the onset of network formation. DGEDP-Pe/GE mixtures with ≥ 15 wt % GE have excellent potential for use in infusion resin systems for continuous composite preparation. However, careful attention should be given to the working temperature of the composites as the glass transition temperature of DGEDP-Pe/GE mixtures with- ≥ 15 wt % GE are significantly lower than that of a traditional infusion system based on bisphenol A. Finally, extension of the molecular weight between crosslinks has been linked to increased fracture toughness by numerous researchers,[42,45,46] however, at 20 and 30 wt % GE the corresponding cured epoxy resins appeared to be more brittle than lower compositions. Future work by our group is expanding on this study to determine effects of GE and other monofunctional reactive diluents on fracture toughness, fatigue life, and their use as infusion resins for continuous fiber composites.

ACKNOWLEDGMENTS

REFERENCES

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

2. Raquez, J. M.; Deléglise, M.; Lacrampe, M. F.; Krawczak, P. Prog. Polym. Sci. 2010, 35, 487.

3. Black, S. CompositesWorld 2015.

4. Noblesville November 2011, p 3.

5. Jacob, G. C.; Hoevel, B.; Pham, H. Q.; Dettloff, M. L.; Verghese, N. E.; Turakhia, R. H.; Hunter, G.; Mandell, J. F.; Samborsky, D. D. In Society for the Advancement of Materials and Process Engineering; DEStech Publications, Inc., 2009.

6. Nelson, A. M.; Long, T. E. Polym. Int. 2012, 61, 1485.

7. Okada, H.; Tokunaga, T.; Liu, X.; Takayanagi, S.; Matsushima, A.; Shimohigashi, Y. Environ. Health Perspect. 2008, 116, 32.

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

9. Steinmetz, R.; Brown, N. G.; Allen, D. L.; Bigsby, R. M.; Ben-Jonathan, N. Endocrinology 1997, 138, 1780.

10. U.S. Government, F.D.A. Indirect Food Additives: Adhesives and components of coatings; United States, 2013; Vol. 78, p 41840.

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

12. Wittcoff, H. A.; Reuben, B. G.; Plotkin, J. S. In Industrial Organic Chemicals; John Wiley and Sons: Somerset, NJ, 2012; p 323.

13. Cheng, H. N.; Smith, P. B.; Gross, R. ACS Symp. Ser. 2013, 1144, 1.

14. Auvergne, R.; Caillol, S.; David, G. Chem. Rev. 2014, 114, 1082.

15. Gilbeau, P.; Balthasart, D. U.S. Patent 8,314,205 B2 (2012).

16. Qin, J.; Liu, H.; Zhang, P.; Wolcott, M.; Zhang, J. Polym. Int. 2014, 63, 760.

17. Wan, J.; Gan, B.; Li, C.; Molina-Aldareguia, J.; Li, Z.; Wang, X.; Wang, D. Y. J. Mater. Chem. A 2015, 3, 21907.

18. Wan, J.; Gan, B.; Li, C.; Molina-Aldareguia, J.; Kalali, E. N.; Wang, X.; Wang, D. Y. Chem. Eng. J. 2016, 284, 1080.

19. Mantzaridis, C.; Brocas, A. L.; Llevot, A.; Cendejas, G.; Auvergne, R.; Caillol, S.; Carlotti, S.; Cramail, H. Green Chem. 2013, 15, 3091.

20. Hu, F.; Yadav, S. K.; La Scala, J. J.; Sadler, J. M.; Palmese, G. R. Macromol. Chem. Phys. 2015, 216, 1441.

21. Park, H. J.; Ryu, C. Y.; Crivello, J. V. J. Polym. Sci. Part A: Polym. Chem. 2013, 51, 109.

22. Aouf, C.; Lecomte, J.; Villeneuve, P.; Dubreucq, E.; Fulcrand, H. Green Chem. 2012, 14, 2328.

23. Kathalewar, M.; Sabnis, A. J. Coatings Technol. Res. 2014, 11, 601.

24. Maiorana, A.; Ren, L.; Lo Re, G.; Spinella, S.; Ryu, C. Y.; Dubois, P.; Gross, R. A. Green Mater. 2015, 3,

25. Liu, R.; Zhu, G.; Li, Z.; Liu, X.; Chen, Z.; Ariyasivam, S. Green Chem. 2015, 17, 3319.

26. Maiorana, A.; Spinella, S.; Gross, R. A. Biomacromolecules 2015, 16, 1021.

27. Younes, U. E. Polyurethane Composites Produced by Vacuum Infusion Process. U.S. Patent 2012/0245286 A1 (2012).

28. Develder, H.; Leroy, A.; Riviere, J.; Ruehle, E. Epoxy Resin Formulations for Textiles, Mats and Other Fibrous Reinforcements for Composite Applications. WO Patent 2013/117308 A1 (2013).

29. Marks, M. J.; Hunter, G. A. U.S. Patent 2011/0163474 A1, (2011).

30. Gardiner, G. Comps. Technol. 2012.

31. Hove, C. L. F. D.; Heymans, D.; Steinbrecher, C.; Kotlweska, A.; Sand, R. V. U.S. Patent 2014/0316030 A1 (**2014**).

32. Hwang, P. Y.; Alto, P.; City, R. U.S. Patent 3488404 (**1973**).

33. Red, C. Wind Turbine Blades: Big and Getting Bigger http://www.compositesworld.com/articles/wind-turbine-blades-big-and-getting-bigger.

34. Alma, M. H.; Ertaş, M.; Nitz, S.; Kollmannsberger, H. *BioResources* **2007**, *2*, 265.

35. Lugemwa, F. N. *Molecules* **2012**, *17*, 9274.

36. Dishong, D. M.; Diamond, C. J.; Cinoman, M. I.; Gokel, G. W. *J. Am. Chem. Soc.* **1983**, *105*, 586.

37. Beasley, Y. M.; Petrow, V.; Stephenson, O. *J. Pharm. Pharmacol.* **1958**, *10*, 103.

38. Long, J. H.; Griffin, L. U.S. Patent 2,848,435 (**1958**).

39. Garcia, F.; Soares, B. *J. Appl. Polym. Sci.* **2007**, *106*, 2047.

40. Holly, E. E.; Venkataraman, S. K.; Chambon, F.; Henning Winter, H. *J. Nonnewton. Fluid Mech.* **1988**, *27*, 17.

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

42. Liu, J. (D.; Sue, H. J.; Thompson, Z. J.; Bates, F. S.; Dettloff, M.; Jacob, G.; Verghese, N.; Pham, H. *Polymer (Guildf)* **2009**, *50*, 4683.

43. Bell, J. *J. Appl. Polym. Sci.* **1970**, *14*, 1901.

44. Levita, G.; Petris, S. D.; ; Marchetti, A.; Lazzeri, A. *J. Mater. Sci.* **1991**, *26*, 2348.

45. Pearson, R. A.; Yee, A. F. *J. Mater. Sci.* **1989**, *24*, 2571.

46. Crawford, E.; Lesser, A. J. *J. Polym. Sci. Part B: Polym. Phys.* **1998**, *36*, 1371.

47. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: New York, NY, **1953**.

48. Mangnus, M. A.; Karjala, T. P.; Gelfer, M. M.; Hahn, S. F. In The XVth International Congress on Rheology, The society of Rheology 80th Annual Meeting; **2008**; p 1399.

49. Chozhan, C. K.; Alagar, M.; Sharmila, R. J.; Gnanasundaram, P. *J. Polym. Res.* **2007**, *14*, 319.

50. Chattopadhyay, D. K.; Webster, D. C. *Prog. Polym. Sci.* **2009**, *34*, 1068.

51. Reano, A. F.; Chérubin, J.; Peru, A. M. M.; Wang, Q.; Clément, T.; Domenek, S.; Allais, F. *ACS Sustain. Chem. Eng.* **2015**, acssuschemeng.5b01281.