Toughening Anhydride-Cured Epoxy Resins Using Fatty Alkyl-Anhydride-Grafted Epoxidized Soybean Oil

Santosh K. Yadav,† Fengshuo Hu,† John J. La Scala,‡ and Giuseppe R. Palmese*†‡

†Department of Chemical & Biological Engineering, Drexel University, Philadelphia, Pennsylvania 19104, United States
‡Army Research Laboratory, 4600 Deer Creek Loop, Aberdeen Proving Ground, Aberdeen, Maryland 21005-5069, United States

ABSTRACT: The aim of this work is to develop a series of advanced biobased tougheners for thermosetting epoxy resins suitable for high-performance applications. These bio-rubber (BR) tougheners were prepared via a one-step chemical modification of epoxidized soybean oil using biobased hexanoic anhydride. To investigate their toughening performance, these BR tougheners were blended with diglycidyl ether of bisphenol A epoxy monomers at various weight fractions and cured with anhydride hardeners. Significant improvements in fracture toughness properties, as well as minimal reductions in glass transition temperature ($T_g$), were observed. When 20 wt % of a BR toughener was utilized, the critical stress intensity factor and critical strain energy release rate of a thermosetting matrix were enhanced by >200 and >500%, respectively, whereas the $T_g$ was reduced by only 20 °C. The phase-separated domains were evenly dispersed across the fracture surfaces as observed through scanning electron microscopy and atomic force microscopy. Moreover, domain sizes were demonstrated to be tunable within the micrometer range by altering the toughener molecular structure and weight fractions. These BR tougheners demonstrate the possibility of achieving toughness while having the thermal properties of standard bisphenol epoxy thermosetting resins.

1. INTRODUCTION

Epoxy resins are one of the most versatile thermosetting materials with a broad range of industrial applications.1,2 Epoxy–anhydride resins are used in high-performance fiber-reinforced composites, electric insulation, casting, potting, encapsulation, and chemical resistance applications.3 Generally, the requirements for these applications are high glass transition temperatures and high fracture strength.3

Epoxy resins are intrinsically brittle and have poor resistance to crack propagation due to their high cross-link density.4 Therefore, toughening such systems to broaden their applications and improve their durability for existing applications has been a challenging topic to both academia and industry. Introducing a secondary phase into the matrix is one of the major strategies of toughening epoxy resins. By this method, liquid rubber5–8 and thermoplastic9–10 components are introduced in the formulation and subsequent phase separation produces morphologies that contribute to the toughening effects.11–14 However, this strategy tends to result in significant reduction in mechanical and thermal properties.15 Others have also examined the use of micro- and nanocomposites for toughening epoxy using clay,16 carbon nanotubes,17 and graphene,2 but these negatively affect the processing ease, especially when applied in the manufacture of continuous-fiber polymer matrix composites.18,19 In addition, although particulate additives generally improve the modulus, there are conflicting results regarding the magnitude of toughening, with various reports of small toughening effect (≤40%).20 Polymer matrix toughening could be used in conjunction with particulate additives to provide additional improvement of the material properties.

An important challenge is to toughen an epoxy resin without compromising the overall thermal and mechanical properties, such as strength, modulus, and glass transition temperature. Recently, a considerable amount of research has been carried out to toughen epoxy resins using various biobased materials, among which vegetable oils are considered promising candidates because they are sustainable.21–27 Epoxidized soybean oil (ESO) has attracted great interest due to its moderate viscosity, good miscibility with epoxy resins, easy availability, and low cost. ESO is produced by the conversion of the double bonds of soybean oils into secondary oxiranes to obtain materials with an average of 4 to 4.4 epoxy groups per triglyceride.24,28–30 Altuna and co-workers studied various anhydride-cured ESO/diglycidyl ether of bisphenol A (DGEBA) systems and reported that the optimum property composition was DGEBA with 40 wt % ESO, an impact strength increase of 38% and a $T_g$ reduction of 11 °C.31

Received: December 21, 2017
Accepted: February 21, 2018
Published: March 6, 2018

© 2018 American Chemical Society

DOI: 10.1021/acsomega.7b02042
ACS Omega 2018, 3, 2641–2651
Miyagawa and co-workers evaluated the fracture behaviors of anhydride-cured epoxy networks modified with ESO and epoxidized linseed oil (ELO) and found that the fracture toughness was not affected by adding ELO, but was significantly improved by blending 30 wt % ESO. A heterogeneous polymer network is developed during curing process due to the large difference in the reactivity of secondary epoxy in ESO and terminal epoxy in DGEBA, which leads to phase-separated network structure. The epoxy ring opening reaction has been employed to obtain ESO grafted with various chemical moieties including, diamine, azide, fatty acids (FAs), allyl group, acrylates, diester, ketals, and others.

An epoxy toughener superior to that of ESO is needed to significantly improve the fracture properties while maintaining processing ease and thermal properties. Literature suggests that a very high content (30−40 wt %) of ESO is required to observe the distinguishable toughening effect in the epoxy matrix. Furthermore, the largest improvements in fracture properties using ESO were small (≤40%). Other methodologies for toughening resulted in moderate effects or significant lowering of the glass transition temperature and/or increase in the resin viscosity. An epoxy toughener can be developed that increases the fracture properties by a factor of 2 or more, while having no more than 10% effect on the viscosity and glass transition temperature.

In previous work, FA of various chain lengths were grafted on ESO via an esterification reaction to prepare the bio-rubber (BR) tougheners. These BR tougheners were used to toughen the epoxy−amine systems as well as vinyl esters resins. The FA-grafted ESO tougheners were used with epoxy−anhydride systems but phase separation did not occur because of the hydroxyl groups (OH) generated during grafting. The hydroxyl groups on tougheners further react with anhydride curing agents and plasticize the network, which prevents the phase separation. Therefore, in this work, a grafting methodology was applied that avoided the OH generation on the BR. A series of BR tougheners were prepared by grafting different molar ratios of fatty alkyl anhydrides to ESO, which results in the diester derivatives of ESO without the OH groups. These BR tougheners were formulated with Epon 828 as well as a mixture of Epon 828 and 1001F (high-molecular-weight epoxy) at various weight fractions and cured with anhydride hardeners. The structure−property relationships of BR-toughened epoxy−anhydride systems were evaluated with the goal of producing a series of modified ESO tougheners with significantly improved properties compared to pure ESO. The effects of BR on thermomechanical properties and fracture toughness of the prepared epoxy resin systems were discussed and related to the polymer morphologies observed through scanning electron microscopy (SEM) and atomic force microscopy (AFM) (Figure 1).

### 2. RESULTS AND DISCUSSION

#### 2.1. Preparation of Anhydride-Modified ESO

A method was explored for the preparation of ESO-based BR that eliminates the formation of hydroxyl groups on the BR tougheners. The ESO was modified via hexanoic anhydride in the presence of boron trifluoride etherate in an anhydrous solvent, which results in FA diester derivatives of ESO (Scheme 1). Boron trifluoride etherate is used as a catalyst to simultaneously open the oxirane and activate the hexanoic anhydride (Scheme 2). The prepared BR were characterized using different techniques such as mid-IR, epoxy titration (ASTM D1652-97), and rheometry. The Fourier transform
infrared (FTIR) spectra of pure ESO and synthesized bio-rubbers (A-HEX-1, A-HEX-2, and A-HEX-3) are shown in Figure 2.

The extent of epoxy ring opening was determined from the intensity ratio of the epoxy peak at 842 and 823 cm$^{-1}$ in the mid-IR spectra (Figure 2). The epoxy peak decreased in intensity from ESO to A-HEX-1, A-HEX-2, and finally to A-HEX-3 due to the increase in ester functionalities in the structure. In the case of A-HEX-3, the largest number of ESO epoxy groups was converted to diester derivatives of hexanoic anhydride by the ring-opening reaction. It was also supported by the increase in peak intensity ratio of the peak at 1375 cm$^{-1}$ relative to the peak at 1461 cm$^{-1}$, confirming the formation of diester derivatives of hexanoic anhydride. The FTIR spectra of all of these samples, ESO, and hexanoic derivatives have a peak at 1740 cm$^{-1}$, which is caused by the triglyceride carbonyl stretching, a peak at 1461 cm$^{-1}$ for CH$_2$ bending vibration, a peak at 1375 cm$^{-1}$ for CH$_3$ symmetrical bending vibration, and peaks at 1240, 1158, and 1100 cm$^{-1}$ due to the stretching vibrations of C–O group in esters.

The evaluation of epoxy equivalent weight (EEW) of ESO and BR was carried out via ASTM D1652-97 method, and the theoretical value of EEW was calculated using the chemical structures and ratio of reactants used (Table 1). The values of EEW and molecular weight of BR increased with increased hexanoic ester functionality, both theoretically and experimentally. There are some differences between the experimental and theoretical values that are likely due to homopolymerization of epoxy. The viscosity of the ESO and BR was measured using an AR2000 ex rheometer (TA Instruments). The modifications of ESO do not alter the viscosity (>50 Pa s) much, although it does increase some with increasing FA ester functionality (Table 1).

2.2. Extent of Cure. The cure mechanism of the epoxy with the anhydride as detailed by Thomas et al. is shown in Scheme 3. The dimethyl benzyl amine serves as a catalyst in the ring opening of the anhydride to form a reactive anionic species that initiates polymerization. The oxygen anions react with the epoxy group as well as with the anhydride to form a cross-linked structure.

The near-IR spectra of cured samples are plotted in Figure 3, including the spectrum of the unreacted mixture for Epon 828/BR/ECA100NC. The epoxy peak was observed at 4530 cm$^{-1}$ in the precured sample, whereas this peak clearly disappeared after curing, indicating complete reaction in the cured samples within the limits of infrared spectroscopy measurements.

2.3. Thermal–Mechanical Properties of BR-Toughened Thermosetting Polymers. Dynamic mechanical analysis (DMA) was used to investigate the stiffness and damping characteristics of the modified thermosetting polymers. The dynamic mechanical properties were measured from 25 to 200 °C. The change in storage modulus and loss modulus of representative samples are shown in Figure 4 and tabulated in Table 2 with additional data from other systems. Figure 4a shows DMA traces for systems of increasing BR content and Figure 4b shows DMA traces for systems modified with BR having different degree of grafting.

### Table 1. EEW and Viscosity Data of ESO and BR

| samples     | theoretical EEW (g/equiv) | experimental EEW (g/equiv) | viscosity (Pa s) at 25 °C |
|-------------|---------------------------|---------------------------|---------------------------|
| ESO         | 250                       | 249                       | 0.3                       |
| A-HEX-1     | 352                       | 610                       | 0.25                      |
| A-HEX-2     | 635                       | 870                       | 0.37                      |
| A-HEX-3     | 1484                      | 1217                      | 0.43                      |
The storage for all of the samples at room temperature are in the range of 1.75 to 2.00 GPa. In general, the storage moduli of blend samples was lower than those of the neat epoxy system. This may be due to the incorporation of less stiff BR toughener. However, there were a few cases where the BR samples had a higher room temperature modulus, such as in the case of 10%A-HEX-3−90%Epon 828-EC.

All of the samples had narrow loss modulus peaks. The loss modulus peak shifted to a lower temperature with increasing amount of BR, indicating a gradual decrease in $T_g$ as the rigid Epon 828 network became more flexible with the introduction of the BR chains allowing a higher chain mobility. Similarly, $T_g$ also decreased with the incorporation of unmodified ESO, and generally, samples with ESO had similar $T_g$’s as samples with A-HEX-1 for the same BR/ESO content. The $T_g$ was found to decrease as the level of fatty ester modification of the BR increased. For example, the incorporation of 10 wt % A-HEX-1, A-HEX-2, and A-HEX-3 has $T_g$ in a decreasing order of 135, 131, and 123 °C, respectively. The higher molecular weight of the toughener may also play a role in reducing the $T_g$ of the A-HEX-2 and A-HEX-3 series compared with A-HEX-1.

Another curing agent, methylhexahydrophthalic anhydride (MHHPA), was also used to determine whether the thermomechanical property trends were sensitive to the specific curing agent used. Samples were prepared with Epon 828 and 20 wt % of modified ESO and cured with MHHPA (Table 3 and Figure S1).

Similar results were observed when compared with that of the ECA100NC. The neat Epon 828 cured with MHHPA had a $T_g$ at 138 °C and, after the incorporation of 20 wt % of ESO, $T_g$ of A-HEX-1, A-HEX-2, and A-HEX-3 decreased to 115, 117, 115, and 109 °C, respectively. Furthermore, the magnitude of $T_g$ reduction for the MHHPA-cured samples upon addition of 20 wt % ESO or BR is very similar to that of the ECA100NC.
addition of BR, whereas the addition of ESO had no significant effect until 25 wt % was added to the resin (Table 2 and Figure S1). These samples also followed the toughness values. Among all of the samples, the one with 20 wt % A-HEX-1 followed by A-HEX-3, then ESO, and A-HEX-2. The magnitude of the toughness reduction for the samples with EPON1001F as a function of BR/ESO was similar to that for Epon 828 samples.

2.4. Fracture Properties of BR-Toughened Thermosetting Polymer. Fracture toughness test was carried out to measure the toughening effects of the BR in Epon 828 anhydride-cured system. Tables 2, 3, and Figures S2, S3 show the fracture toughness of the Epon 828 with various amounts of ESO and BR. The critical stress intensity factor ($K_{IC}$) and the critical strain energy release rate ($G_{IC}$) were improved with the addition of BR, whereas the addition of ESO had no significant effect until 25 wt % was added to the resin (Table 2 and Figure S2). Furthermore, the toughness values generally increased as the BR content in the resin increased. The level of epoxidation of the BR may have an effect on the toughness values, but differences among the samples were generally insignificant because of the sizeable error bars, which are typical for these measurements. Moreover, it appears that increasing the BR content from 20 to 25 wt % does not have a significant effect on the toughness values. Among all of the samples, the one with 20 wt % A-HEX-2 demonstrated the highest toughening effect with a >200% increase in $K_{IC}$ and >500% increase in $G_{IC}$ with respect to neat Epon 828 cured with ECA100NC. Furthermore, this improvement resulted in only a 20 °C reduction in the $T_g$ values.

For Epon 828 samples cured with MHHPA, 20 wt % BR again significantly improved the toughness values, as $K_{IC}$ (1.26 ± 0.31 MPa m$^{1/2}$) and $G_{IC}$ (0.76 ± 0.38 kJ/m$^2$) were much higher than those for the Epon 828 MHHPA sample with and without the ESO additive (Table 3 and Figure S3).

To verify the impact of the toughener on a higher-molecular-weight polymer, the epoxy blend system was prepared with 15

| sample code$^{a}$ | $E'$ at 25 °C (GPa) | $T_g$ (°C) | $K_{IC}$ (MPa m$^{1/2}$) | $G_{IC}$ (kJ/m$^2$) |
|-------------------|--------------------|-----------|-----------------|-----------------|
| 100%Epon 828-EC   | 2.03               | 136       | 0.65 ± 0.04     | 0.20 ± 0.03     |
| 10%ESO–90%Epon 828-EC | 2.06           | 125       | 0.67 ± 0.13     | 0.20 ± 0.08     |
| 10%A-HEX-1–90%Epon 828-EC | 1.88      | 126       | 0.90 ± 0.10     | 0.38 ± 0.09     |
| 10%A-HEX-2–90%Epon 828-EC | 2.07      | 121       | 0.91 ± 0.14     | 0.38 ± 0.11     |
| 10%A-HEX-3–90%Epon 828-EC | 2.32      | 112       | 0.97 ± 0.13     | 0.44 ± 0.11     |
| 15%ESO–85%Epon 828-EC | 2.04      | 122       | 0.64 ± 0.09     | 0.18 ± 0.05     |
| 15%A-HEX-1–85%Epon 828-EC | 1.90     | 120       | 1.11 ± 0.10     | 0.56 ± 0.09     |
| 15%A-HEX-2–85%Epon 828-EC | 2.00     | 117       | 1.26 ± 0.24     | 0.75 ± 0.32     |
| 15%A-HEX-3–85%Epon 828-EC | 1.91     | 115       | 0.98 ± 0.20     | 0.48 ± 0.22     |
| 20%ESO–80%Epon 828-EC | 1.98     | 115       | 0.56 ± 0.06     | 0.15 ± 0.03     |
| 20%A-HEX-1–80%Epon 828-EC | 1.78     | 118       | 1.03 ± 0.16     | 0.55 ± 0.18     |
| 20%A-HEX-2–80%Epon 828-EC | 1.86     | 116       | 1.41 ± 0.18     | 1.15 ± 0.29     |
| 20%A-HEX-3–80%Epon 828-EC | 1.87     | 112       | 1.14 ± 0.15     | 0.67 ± 0.27     |
| 25%ESO–75%Epon 828-EC | 1.85     | 116       | 1.02 ± 0.24     | 0.62 ± 0.27     |
| 25%A-HEX-1–75%Epon 828-EC | 1.83     | 116       | 1.20 ± 0.07     | 0.67 ± 0.08     |
| 25%A-HEX-2–75%Epon 828-EC | 1.78     | 107       | 1.24 ± 0.09     | 0.78 ± 0.11     |
| 25%A-HEX-3–75%Epon 828-EC | 1.83     | 105       | 1.24 ± 0.11     | 0.79 ± 0.26     |

“$T_g$ taken as peak of loss modulus ($E''$).”

Table 3. Storage Modulus at Room Temperature, $T_g$, $K_{IC}$, and $G_{IC}$ for Untoughened and Toughened Samples of Epon 828 Cured with MHHPA and Epon 828 with 15 wt % 1001F Cured with MHHPA and ECA100NC

| sample code$^{a}$ | $E'$ at 25 °C (GPa) | $T_g$ (°C) | $K_{IC}$ (MPa m$^{1/2}$) | $G_{IC}$ (kJ/m$^2$) |
|-------------------|--------------------|-----------|-----------------|-----------------|
| 100%Epon 828–MHHPA | 2.12 | 138       | 0.54 ± 0.10     | 0.14 ± 0.05     |
| 20%ESO–MHHPA       | 1.99 | 115       | 0.53 ± 0.08     | 0.13 ± 0.04     |
| 20%A-HEX-1–MHHPA   | 1.81 | 117       | 1.02 ± 0.07     | 0.47 ± 0.07     |
| 20%A-HEX-2–MHHPA   | 1.74 | 115       | 1.26 ± 0.31     | 0.76 ± 0.38     |
| 20%A-HEX-3–MHHPA   | 2.11 | 109       | 1.09 ± 0.13     | 0.51 ± 0.11     |
| 15%1001F–MHHPA     | 1.97 | 139       | 0.81 ± 0.09     | 0.29 ± 0.09     |
| 20%ESO–15%1001F–MHHPA | 1.84 | 116       | 0.85 ± 0.31     | 0.37 ± 0.21     |
| 20%A-HEX-1–15%1001F–MHHPA | 1.62 | 120       | 1.12 ± 0.12     | 0.63 ± 0.14     |
| 20%A-HEX-2–15%1001F–MHHPA | 1.64 | 113       | 1.10 ± 0.068    | 0.59 ± 0.07     |
| 20%A-HEX-3–15%1001F–MHHPA | 1.69 | 108       | 1.12 ± 0.169    | 0.62 ± 0.19     |
| 15%1001F–ECA       | 1.81 | 134       | 0.74 ± 0.310    | 0.32 ± 0.28     |
| 20%ESO–15%1001F–ECA | 1.91 | 117       | 0.72 ± 0.171    | 0.31 ± 0.14     |
| 20%A-HEX-1–15%1001F–ECA | 1.76 | 121       | 1.25 ± 0.228    | 0.83 ± 0.32     |
| 20%A-HEX-2–15%1001F–ECA | 1.72 | 113       | 1.21 ± 0.122    | 0.84 ± 0.17     |
| 20%A-HEX-3–15%1001F–ECA | 2.08 | 110       | 1.11 ± 0.097    | 0.710 ± 0.12    |

“$T_g$ taken as peak of loss modulus ($E''$).”

cured samples. The epoxy blend system with 15 wt % of EPON1001F and 85 wt % Epon 828 was prepared to verify the impact of the toughener on a higher-molecular-weight epoxy system (Table 3 and Figure S1). These samples also followed the same trend as the other samples, with the nontoughened sample having the highest $T_g$ followed by A-HEX-1, then ESO, and A-HEX-3. The magnitude of the toughness reduction for the samples with EPON1001F as a function of BR/ESO was similar to that for Epon 828 samples.
wt % of EPON1001F and 85 wt % Epon 828. The toughener (20 wt % of ESO, A-HEX-1, A-HEX-2, and A-HEX-3) was incorporated into the prepared high-molecular epoxy system of Epon 828/1001F and cured with ECA100NC and MHHPA. Similarly, 20 wt % BR produced a high fracture toughness, whereas 20 wt % ESO did not. The two anhydride curing agents produced similar fracture properties for common sample formulations. Although the EPON1001F blend system has a higher molecular weight compared to the Epon 828 resin, the $K_I$ value for the 20%A-HEX-2–15% 1001F-EC (1.21 ± 0.12 MPa m$^{1/2}$) was lower than the 20%A-HEX-2–Epon 828-EC system (1.41 ± 0.18 MPa m$^{1/2}$). This may be due to the presence of hydroxyl groups on the DGEBA oligomers in EPON100F, which may react with the remaining epoxy groups on BR and become a part of the network chain, which further suppresses the toughening effect (Table 3 and Figure S2).

Although fracture behavior was not examined in detail to explain the observed toughening effects, it is likely that shear localization was enhanced due to BR particles serving as stress concentrators. Pearson and co-workers have explained that the two main factors responsible for toughening in rubber-toughened systems are cavitation and the generation of shear bands.

**2.5. Fracture Surface Analysis of BR-Toughened Thermosetting Polymers.** Evaluation of fracture morphology is important to investigate the secondary phase network and the particle size of BR in the polymer matrix. The fracture morphology of the toughened epoxy system was investigated by

---

**Figure 5.** SEM images of fracture surfaces of epoxy–anhydride thermosetting polymers as a function of FA ester modification relative to the neat resin. (a) 20%ESO–Epon 828-EC, (b) 20%A-HEX-1–80%Epon 828-EC, (c) 20%A-HEX-2–80%Epon 828-EC, and (d) 20%A-HEX-3–80%Epon 828-EC.

**Figure 6.** SEM images of the fracture surfaces of epoxy–anhydride thermosetting polymers for different loadings of A-HEX-2 BR (a) 10%A-HEX-2–90%Epon 828-EC, (b) 15%A-HEX-2–85%Epon 828-EC, (c) 20%A-HEX-2–80%Epon 828-EC, and (d) 25%A-HEX-2–75%Epon 828-EC.
SEM. In the case of 20 wt % ESO (Figures 5 and 6), the brittleness of the sample can be observed by the presence of smooth glassy fracture surface with cracks in different planes. Thus, it is not surprising that this material displayed weak resistance to crack propagation.

The lack of any significant morphology suggests that the ESO fully reacted into the system and became part of the network. Interestingly, the samples were clear and transparent, and macroscopic phase separation was not observed at even higher loadings of up to 20 wt % of ESO (Figure S4). Opacity is only observed at 25 wt % ESO upon which the fracture toughness improves significantly. On the other hand, the BR samples with only 10 wt % BR were opaque and cloudy. The SEM image of BR-toughened epoxies (20% A-HEX-1, A-HEX-2, and A-HEX-3 cured with ECA100NC) clearly indicates the microstructure of the evenly distributed particles of the sub-micron size (Figures 5 and 6). In addition, the volume fraction of phase-separated domains increases as the BR content increases. The average particle diameter of the BR domain increased with BR concentration: 10%A-HEX-2 (195 nm), 15%A-HEX-2 (207 nm), 20%A-HEX-2 (315 nm), and 25%A-HEX-2 (332 nm). However, the average particles diameter of BR domain was not affected much by the functionality on the BR: 20%A-HEX-1 (310 nm), 20%A-HEX-2 (315 nm), and 20%A-HEX-3 (308 nm). The area of rubbery domains for all of the compositions was found to be less than the added volume fraction (vol %) of BR. The samples 10%H-2 (11.0 vol %), 15%H-2 (16.5 vol %), 20%HEX-2 (21.4 vol %), and 25%HEX-2 (27.3 vol %) have rubbery domains of 4.4, 5.2, 9.7, and 19.4%, respectively, which is less than the corresponding volume fractions of BR in the resin system. The difference was smaller for the high-volume-fraction BR samples compared with the low-volume-fraction samples. These results indicate that there is BR in the primary phase that should reduce the $T_g$ and modulus of the primary phase relative to the untoughened epoxy–anhydride resin.

As per Tables 2 and 3, all of the compositions using BR exhibited a higher fracture toughness than the neat Epon 828. Thus, there is a clear correlation between the 2nd phase morphology and the fracture toughness measured (Tables 2 and 3). These dispersed particles likely played a key role as the center of dissipation of mechanical energy through shear yielding. Therefore, it can also be concluded that the neat ESO in Epon 828 resin systems had a lower toughness because they did not exhibit phase separation. These results indicate that the BR molecular structure creates a larger driving force for phase separation versus ESO. From a thermodynamic point of view, as described often by the Flory–Huggins relation, the increase in phase separation could be due to both and increase in unfavorable enthalpic interactions between the BR and epoxy resulting from the addition of more aliphatic chains to the BR (higher $\chi$) and reduction in the entropy of mixing due to the higher molecular weight. It should be noted that the degree of phase separation is also probably influenced by significant diffusion limitations linked to the reaction and resulting gelation, and vitrification that kinetically trap structures at a smaller size.

The anhydride-curing molecule on the interface in the primary and secondary phases could react with both the epoxy groups of the Epon 828 resin and the unreacted epoxy groups of the ESO and BR and form chemical bonds between the rigid matrix and the rubbery particles. Another factor in the phase separation behavior is likely that the ESO has too many reactive functionalities, which cause a significant reaction with the growing polymers that prevent aggregation of the ESO into sizeable domains. This could be tested with the use of epoxidized plant oils with a lower degree of epoxidation similar to that of A-HEX-1 to assess whether it is simply a reaction effect or also a molecular-weight effect. We suspect that both
factors affect the phase separation behavior. Note, non-epoxidized plant oils phase separate on a much larger scale and generally form polymers with a high content of the unreacted resin (the plant oils) on the surface. The plant oil is thus excluded from the network because it cannot react into the network. Thus, the reactive functionality is necessary to ensure compatibility of the BR with the network and limit the 2nd phase domain size.

AFM is an excellent technique for observing the micron and sub-micron domains in polymer networks. Morphology of the BR-toughened epoxy samples was evaluated using AFM on the fracture surfaces of the samples (Figure 7). The craterlike architectures are observed in the three-dimensional AFM images of the fracture surface. These craters result from the rubbery particles being pulled out or breaking apart from the matrix in which particle residuals can be clearly observed as a hole. Small deformation of the matrix was observed near the holes. Such a deformation occurs due to the optimal bonding between the BR particles and the adjacent matrix. The collected images revealed that the BR particles size increased with increase in the content of BR in the epoxy matrix.

Figure 8 shows the Derjaguin–Muller–Toropov modulus map of samples via AFM. There are two distinct phases showing different Derjaguin–Muller–Toropov moduli, with the holes/2nd phase domain having significantly lower modulus values. It is expected that the BR would have a much lower modulus than the Epon 828 resin itself based on its aliphatic chemical structure and the reduction in modulus and glass transition temperature observed in Tables 2 and 3. Thus, we can conclude that the BR are phase separating into these smaller domains. These modulus values are relative, so it would be difficult to directly correlate them with the actual modulus properties of materials. However, such maps can be successfully used to identify and characterize the composition of multiphase materials.

3. CONCLUSIONS

The ESO-based BR epoxy toughening agent was prepared via one-step chemical modification of ESO with hexanoic anhydrides. The BR were incorporated into epoxy Epon 828-based matrices and cured with anhydride hardeners. A two-phase thermosetting network was developed that consisted of a rigid Epon 828 matrix and evenly distributed small rubbery particles of BR. The fracture toughness and the critical energy release rate of the anhydride-cured epoxy were greatly improved with the addition of BR with only a small reduction in $T_g$. In particular, the sample 20%A-HEX-2–80%Epon 828-EC had the highest fracture toughness ($K_{IC} = 1.41 \pm 0.18 \text{ MPa m}^{-1/2}$) and energy release rate ($G_{IC} = 1.15 \pm 0.29 \text{ kJ/m}^2$), which was improved by >200 and >500%, respectively, compared with 100% for Epon 828 cured with anhydride with only a 20 °C reduction in $T_g$. The morphology of the anhydride-cured Epon 828/BR confirmed that the improvement in both the impact strength and the fracture toughness was the result of the phase separation of the BR into rubbery domains. These systems could be useful for high-performance resins and composites applications.

4. EXPERIMENTAL SECTION

4.1. Materials. Drapex 6.8, supplied by Galata Chemicals from Louisiana, was the ESO used. The EEW of ESO (250 g/eq) is listed in Table 1. Boron trifluoride diethyl etherate, dimethyl benzyl amine, and hexanoic anhydride (97%) were obtained from Sigma-Aldrich, whereas sodium chloride and sodium bicarbonate were obtained from Fisher Scientific, and used as received. Epon 828 (epoxy equivalent weight, EEW 185–192 g/eq) is Hexion technical data sheet of Epon 828 issued September 2005) and EPON1001F (EEW 525–550 g/eq. Hexion technical data sheet of EPON1001F issued September 2005) epoxy resins, containing diglycidyl ether of bisphenol A and oligomers were purchased from Miller Stephenson. Methylhexahydrophthalic anhydride (MHHPA)
and ECA100NC curing agent were obtained from Dixie Chemical, Pasadena, TX. ECA100NC curing agent is composed of three different anhydride molecules hexahydromphthalic anhydride (HHPA > 10%), MHHPA, and methyltetrahydrophthalic anhydride. The same batch of ECA100NC was used for all of the experiments to prevent batch-to-batch variation in the results described in this work. The molecular structures of various key molecules used in this work are shown in Figure 1. The anhydride equivalent weight of the anhydrides were provided by the manufacturer (epoxy curing agent ECA100NC and MHHP technical data sheet, Dixie Chemical): 165 g equiv for ECA100NC and 168 g equiv for MHHPA.

4.2. Fatty Anhydride-Modified ESO (Bio-Rubber). The modification of ESO to prepare the BR tougheners was carried out via acylation reaction (Scheme 1).37 The ESO modified with 1, 2, and 3 equivalents of hexanoic anhydride were named A-HEX-1, A-HEX-2, and A-HEX-3, respectively. A-HEX-1 was prepared by adding 12.5 g of ESO (50 mmol of epoxy groups) and 2.678 g of hexanoic anhydride (12.5 mmol, 4:1 mol equiv) in 100 mL of dichloromethane to a 250 mL round-bottomed flask fitted with a condenser. The catalyst boron trifluoride etherate (0.125 g, 0.95 mmol) was charged via syringe into the reaction mixture and the reaction was allowed to stir for 3 h under inert atmosphere (0.125 g, 0.95 mmol) was charged via syringe into the reaction mixture and the reaction was allowed to stir for 3 h under inert (N2) condition. After the completion of the reaction, the reaction mixture was washed 3–4 times each with 100 mL of 5% sodium bicarbonate solution and 100 mL of sodium chloride solution. The reaction solution was dried over MgSO4 overnight. The solvent dichloromethane was evaporated by rotary evaporation at 30 °C in vacuum. A-HEX-2 and A-HEX-3 were also prepared with 2 and 3 equivalents, respectively, of hexanoic anhydride, following the procedure mentioned above. The yield was 80–85% for all the bio-rubbers systems.

4.3. Monomer Characterization. Epoxy titration was carried out on the Epon 828 resins and the BR using ASTM D1652-90, Procedure B. FTIR (Mid-IR) was used to track the functional groups of these BR tougheners on a Thermo Nicolet Nexus 870 FTIR spectrometer in a dry air atmosphere (32 scans, 8 cm−1 resolution, transmission mode). All of the cured epoxy samples were sanded to a standard size and shape (nominally 38 mm × 13 mm × 5.5 mm) with 600 grit paper and averaged with a SEPS sander. The densities of cured resin samples were measured using a high-speed density gradient column as described in the ImageJ software. The AFM images were acquired using a Bruker Dimension Icon AFM equipped with a tapping mode. The critical strain energy release rate (Gic) and critical stress intensity factor (Kit) values of samples were measured at 25 °C using a servo-hydraulic INSTRON model 8872 apparatus following ASTM D5045-99, method E 399. The Gic was calculated by Kit using the storage modulus values. Five to seven compact tension specimens with a dimension of 16 mm × 13 mm × 5.5 mm were prepared and tested for each composition. A sharp precrack was introduced at the bottom of 8 mm notch of the each sample before testing with a 1.0 mm/min crosshead speed. The density of cured Epon 828 (1.2038 g/cm3) and ESO (1.0739 g/cm3) with ECA100NC was measured via a density gradient column as described in ASTM D1505. The density of ESO cured with ECA100NC was taken as an estimated density for BR to calculate the volume fraction of BR in the resin system.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b02042.

DMA graphs (Figure S1), fracture toughness data (Figures S2 and S3), and photograph (Figure S4) of the untoughened, ESO-toughened, and BR-toughened polymers with various weight percents of tougheners (PDF).

AUTHOR INFORMATION

Corresponding Author

*E-mail: grp27@drexel.edu.
ACKNOWLEDGMENTS

We would like to acknowledge the National Science Foundation as well as support from the Strategic Environmental Research and Development Program (SERDP) under project WP-1758.

REFERENCES

(1) Auvergne, R.; Caillol, S.; David, G.; Bouteven, B.; Pascault, J.-P. A Process for Preparing Epoxy Resins. Chem. Rev. 2013, 114, 1082–1115.
(2) Liu, M.; Yeh, Y.-J.; La Scala, J. J.; Sadler, J. M.; Palmese, G. R. Preparation and Characterization of Fully Furan-Based Renewable Thermosetting Epoxy-amine Systems. Macromol. Chem. Phys. 2015, 216, 1441–1446.
(3) Lee, H.; Neville, K. Handbook of Epoxy Resins; McGraw-Hill: New York, 1967.
(4) Liu, W.; Zhou, R.; Goh, H. L. S.; Huang, S.; Lu, X. From Waste to Functional Additive: Toughening Epoxy Resin with Lignin. ACS Appl. Mater. Interfaces 2014, 6, 5810–5817.
(5) Thomas, R.; Yumei, D.; Yuelong, H.; Le, Y.; Moldenaers, P.; Weim, Y.; Czajany, T.; Thomas, S. Miscibility, morphology, thermal, and mechanical properties of a DGEBA based epoxy resin toughened with a liquid rubber. Polymer 2008, 49, 279–289.
(6) Chukhi, N.; Fellahi, S.; Bakar, M. Modification of epoxy resin using reactive liquid (ATBN) rubber. Eur. Polym. J. 2002, 38, 251–264.
(7) Ratna, D. Phase separation in liquid rubber modified epoxy mixture. Relationship between curing conditions, morphology and ultimate behavior. Polymer 2001, 42, 4209–4218.
(8) Pearson, R. A.; Yee, A. F. Toughening mechanisms in thermoplastic-modified epoxies: 1. Modification using poly(phenylene oxide) diacrylates. Polymer 1993, 34, 3658–3670.
(9) Hodgkin, J. H.; Simon, G. P.; Varley, R. J. Thermoplastic toughening of epoxy resins: a critical review. Polym. Adv. Technol. 1998, 9, 3–10.
(10) Mimura, K.; Ito, H.; Fujisaka, H. Toughening of epoxy resin modified with in situ polymerized thermoplastic polymers. Polymer 2001, 42, 9223–9233.
(11) Palmese, G. R.; La Scala, J. J.; Sands, J. M.; Geng, X. Toughening Cross-linked Thermosets. U.S. Patent 14/791057, 2015.
(12) Wise, C. W.; Cook, W. D.; Goodwin, A. A. CTBN rubber phase precipitation in model epoxy resins. Polymer 2000, 41, 4625–4633.
(13) Ni, Y.; Zheng, S.; Nie, K. Morphology and thermal properties of inorganic-organic hybrids involving epoxy resin and polyhedral oligomeric silsesquioxanes. Polymer 2004, 45, 5557–5568.
(14) Elks, O.; Gao, J.; Shojae, S. A.; Thomas, A.; Chow, P.; Bartolucci, S. F.; Lucca, D. A.; Koratkar, N. Epoxy Nanocomposites with Two-Dimensional Transition Metal Dichalcogenide Additives. ACS Nano 2014, 8, 5282–5289.
(15) Bagheri, R.; Marouf, B. T.; Pearson, R. A. Rubber-Toughened Epoxies: A Critical Review. Rev. Polym. Sci. 2009, 49, 201–225.
(16) Wang, K.; Chen, L.; Wu, J.; Toh, M. L.; Ho, C.; Yee, A. F. Epoxy Nanocomposites with Highly Exfoliated Clay: Mechanical Properties and Fracture Mechanisms. Macromolecules 2005, 38, 788–800.
(17) Throckmorton, J. A.; Watters, A. L.; Geng, X.; Palmese, G. R. Room temperature ionic liquids for epoxy nanocomposite synthesis: Direct dispersion and cure. Compos. Sci. Technol. 2013, 86, 38–44.
(18) Wong, D. W. Y.; Lin, L.; McGrail, P. T.; Pejs, T.; Hogg, P. J. Improved fracture toughness of carbon fibre/epoxy composite laminates using dissolvable thermoplastic fibres. Composites, Part A 2010, 41, 759–767.
(19) Chen, W.; Yu, Y.; Li, P.; Wang, C.; Zhou, T.; Yang, X. Effect of new epoxy matrix for T800 carbon fiber/epoxy filament wound composites. Compos. Sci. Technol. 2007, 67, 2261–2270.
(20) Domun, N.; Hadavinia, H.; Zhang, T.; Sainsbury, T.; Liaghat, G. H.; Vahid, S. Improving the fracture toughness and the strength of epoxy using nanomaterials - a review of the current status. Nanoscale 2015, 7, 10294–10329.
(21) Xia, Y.; Larocch, R. C. Vegetable oil-based polymeric materials: synthesis, properties, and applications. Green Chem. 2010, 12, 1893–1909.
(22) Ronda, J. C.; Lligadas, G.; Gali, M.; Cadiz, V. Vegetable oils as platform chemicals for polymer synthesis. Eur. J. Lipid Sci. Technol. 2011, 113, 46–58.
(23) Tan, S. G.; Chow, W. S. Biobased Epoxidized Vegetable Oils and Its Greener Epoxy Blends: A Review. Polym.-Plast. Technol. Eng. 2010, 49, 1581–1590.
(24) Baroncini, E. A.; Kumar Yadav, S.; Palmese, G. R.; Stanzione, J. F. Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. J. Appl. Polym. Sci. 2016, 133, No. 44103.
(25) Yadav, S. K.; Schmalbach, K. M.; Kinaci, E.; Stanzione, J. F.; Palmese, G. R. Recent advances in plant-based vinyl ester resins and reactive diluents. Eur. Polym. J. 2018, 98, 199–215.
(26) Karger-Kocis, J.; Grischuk, S.; Sorochynska, L.; Rong, M. Z. Curing, gelling, thermomechanical, and thermal decomposition behaviors of anhydride-cured epoxy (DGEBA)/epoxidized soybean oil composites. Polymer. Eng. Sci. 2014, 54, 747–755.
(27) Wang, R.; Schuman, T. P. Vegetable oil-derived epoxy monomers and polymer blends: A comparative study with review. eXPRESS Polym. Lett. 2013, 7, 272–292.
(28) Gupta, A. P.; Ahmad, S.; Dev, A. Modification of novel bio-based resin-epoxidized soybean oil by conventional epoxy resin. Polym. Eng. Sci. 2011, 51, 1087–1091.
(29) Huang, K.; Zhang, P.; Zhang, J.; Li, S.; Li, M.; Xia, J.; Zhou, Y. Preparation of biobased epoxies using tung oil fatty acid-derived C21 diacid and C22 triacid and study of epoxy properties. Green Chem. 2013, 15, 2466–2475.
(30) Li, S.; Huang, K.; Yang, X.; Li, M.; Xia, J. Design, preparation and characterization of novel toughened epoxy asphalt based on a vegetable oil derivative for bridge deck paving. RSC Adv. 2014, 4, 44741–44749.
(31) Altuna, F. I.; Espósito, L. H.; Ruseckaite, R. A.; Stefani, P. M. Thermal and mechanical properties of anhydride-cured epoxy resins with different contents of biobased epoxidized soybean oil. J. Appl. Polym. Sci. 2011, 120, 789–798.
(32) Miyagawa, H.; Misra, M.; Dral, L. T.; Mohanty, A. K. Fracture toughness and impact strength of anhydride-cured biobased epoxy. Polym. Eng. Sci. 2005, 45, 487–495.
(33) Biswas, A.; Adhivaryu, A.; Gordon, S. H.; Erhan, S. Z.; Willett, J. L. Synthesis of Diethylamine-Functionalized Soybean Oils. J. Agric. Food Chem. 2005, 53, 9485–9490.
(34) Biswas, A.; Sharma, B. K.; Willett, J. L.; Advaryu, A.; Erhan, S. Z.; Cheng, H. N. Azide Derivatives of Soybean Oil and Fatty Esters. J. Agric. Food Chem. 2008, 56, 5611–5616.
(35) Luo, Q.; Liu, M.; Xu, Y.; Ionescu, M.; Petrović, Z. S. Thermosetting Allyl Resins Derived from Soybean Oil. Macromolecules 2011, 44, 7149–7157.
(36) Zhang, P.; Xin, J.; Zhang, J. Effects of Catalyst Type and Reaction Parameters on One-Step Acrylation of Soybean Oil. ACS Sustainable Chem. Eng. 2014, 2, 181–187.
(37) Sharma, B. K.; Liu, Z.; Advaryu, A.; Erhan, S. Z. One-Pot Synthesis of Chemically Modified Vegetable Oils. J. Agric. Food Chem. 2008, 56, 3049–3056.
(38) Doll, K. M.; Erhan, S. Z. Synthesis of cyclic acetics (ketals) from oleochemicals using a solvent free method. Green Chem. 2008, 10, 712–717.
(39) Biswas, A.; Sharma, B. K.; Vermillion, K.; Willett, J. L.; Cheng, H. N. Preparation of Acetonides from Soybean Oil, Methyl Soylate, and Fatty Esters. *J. Agric. Food Chem.* 2011, 59, 3066−3070.

(40) Hwang, H.-S.; Erhan, S. Modification of epoxidized soybean oil for lubricant formulations with improved oxidative stability and low pour point. *J. Am. Oil Chem. Soc.* 2001, 78, 1179−1184.

(41) Erhan, S. Z.; Sharma, B. K.; Liu, Z.; Adhvaryu, A. Lubricant Base Stock Potential of Chemically Modified Vegetable Oils. *J. Agric. Food Chem.* 2008, 56, 8919−8925.

(42) Varley, R. J. Toughening of epoxy resin systems using low-viscosity additives. *Polym. Int.* 2004, 53, 78−84.

(43) Palmese, G. R.; Yadav, S. K.; Hu, F. Toughening of Anhydride Cured Thermosetting Epoxy. U.S. Patent 20160075872, 2016.

(44) Thomas, R.; Durix, S.; Sinturel, C.; Omonov, T.; Goossens, S.; Groenincks, G.; Moldenaers, P.; Thomas, S. Cure kinetics, morphology and miscibility of modified DGEBA-based epoxy resin−Effects of a liquid rubber inclusion. *Polymer* 2007, 48, 1695−1710.

(45) Mauck, J. R.; Yadav, S. K.; Sadler, J. M.; La Scala, J. J.; Palmese, G. R.; Schmalbach, K. M.; Stanzione, J. F. Preparation and Characterization of Highly Bio-Based Epoxy Amine Thermosets Derived from Lignocellulosics. *Macromol. Chem. Phys.* 2017, 218, No. 170013.

(46) Chen, Y.; Yang, L.; Wu, J.; Ma, L.; Finlow, D.; Lin, S.; Song, K. Thermal and mechanical properties of epoxy resin toughened with epoxidized soybean oil. *J. Therm. Anal. Calorim.* 2013, 113, 939−945.

(47) Kargarzadeh, H.; Ahmad, I.; Abdullah, I.; Thomas, R.; Dufresne, A.; Thomas, S.; Hassan, A. Functionalized liquid natural rubber and liquid epoxidized natural rubber: A promising green toughening agent for polyester. *J. Appl. Polym. Sci.* 2015, 132, No. 41292.

(48) Mathew, V. S.; George, S. C.; Parameswaranpillai, J.; Thomas, S. Epoxidized natural rubber/epoxy blends: Phase morphology and thermomechanical properties. *J. Appl. Polym. Sci.* 2014, 131, No. 39906.

(49) Qian, J. Y.; Pearson, R. A.; Dimonie, V. L.; Shaffer, O. L.; El-Aasser, M. S. The role of dispersed phase morphology on toughening of epoxies. *Polymer* 1997, 38, 21−30.

(50) Xu, S.-A. Miscibility and Phase Separation of Epoxy/Rubber Blends. In *Handbook of Epoxy Blends*; Parameswaranpillai, J., Hameed, N., Pionteck, J., Woo, E. M., Eds.; Springer International Publishing: Cham, 2016; pp 1−32.

(51) Marieta, C.; Remiro, P.; Garmendia, G.; Harismendy, I.; Mondragon, I. AFM approach toward understanding morphologies in toughened thermosetting matrices. *Eur. Polym. J.* 2003, 39, 1965−1973.

(52) VanLandingham, M.; McKnight, S.; Palmese, G.; Elings, J.; Huang, X.; Bogetti, T.; Eduljee, R.; Gillespie, J., Jr. Nanoscale indentation of polymer systems using the atomic force microscope. *J. Adhes.* 1997, 64, 31−59.