

Communication

Properties of Thermosets Derived from Chemically Modified Triglycerides and Bio-Based Comonomers

Evan S. Beach ¹, Zheng Cui ¹, Paul T. Anastas ^{1,*}, Mingjiang Zhan ² and Richard P. Wool ^{2,**}

¹ Center for Green Chemistry and Green Engineering, Yale University, 225 Prospect St, New Haven, CT 06520-8107, USA; E-Mails: evan.beach@yale.edu (E.S.B.); greenchemistry@yale.edu (Z.C.)

² Center for Composite Materials and Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716-3144, USA; E-Mail: zhan@udel.edu

* Authors to whom correspondence should be addressed; E-Mails: paul.anastas@yale.edu (P.T.A.); wool@udel.edu (R.P.W.); Tel.: +1-203-432-5215 (P.T.A.); Fax: +1-203-436-8574 (P.T.A.); Tel.: +1-302-831-3312 (R.P.W.); Fax: +1-302-831-8525 (R.P.W.).

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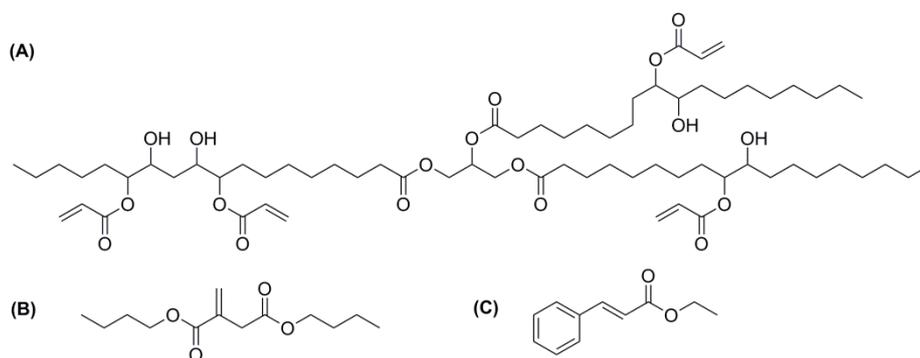
Abstract: A series of materials was prepared by curing acrylated epoxidized soybean oil (AESO) and dibutyl itaconate (DBI) or ethyl cinnamate (EC) comonomers to provide examples of thermosets with a high proportion of bio-based carbon, in accordance with the principles of green chemistry. The comonomers, representative of cellulose-derived (DBI) or potentially lignin-derived (EC) raw materials, were tested at levels of 25%, 33%, and 50% by mass and the resulting products were characterized by infrared spectroscopy, thermogravimetric analysis, and dynamic mechanical analysis. Both DBI and EC were incorporated into the thermosets to a high extent (>90%) at all concentrations tested. The AESO-DBI and AESO-EC blends showed substantial degradation at 390–400 °C, similar to pure AESO. Glass transition temperatures decreased as comonomer content increased; the highest T_g of 41.4 °C was observed for AESO-EC (3:1) and the lowest T_g of 1.4 °C was observed for AESO-DBI (1:1). Accordingly, at 30 °C the storage modulus values were highest for AESO-EC (3:1, 37.0 MPa) and lowest for AESO-DBI (1:1, 1.5 MPa).

Keywords: thermoset; polymer; bio-based; green chemistry

1. Introduction

The reactivity of olefins found in natural oils has been widely exploited as a means of preparing novel polymers with a high proportion of the carbon derived from renewable resources. Besides well-known drying oil technologies [1], various chemical modifications of triglycerides have been explored in order to improve reactivity and access a wider range of materials with desirable properties and functional performance. One strategy has been to apply catalytic isomerization to increase conjugation of polyunsaturated fatty chains. For example Larock *et al.* have developed a Rh-catalyzed process that yields raw materials that are well suited for free radical and ring-opening metathesis polymerizations [2,3]. Unsaturated fatty chains may also be converted to epoxides, which may be used in curing chemistries directly or further modified with reactive maleic or acrylic functionality [4]. The latter, in the form of acrylated epoxidized soybean oil (AESO, representative structure shown in Figure 1A) has been extensively developed as the foundation for a range of bio-based polymer and composite materials: AESO has been copolymerized with numerous petroleum-derived monomers such as alkyl acrylates and methacrylates, vinyl alcohol, vinyl acetate, acrylic acid, and styrene, in thermosetting reactions promoted by free radical initiators. The resulting materials vary widely depending on the blending ratios, cure cycles, and properties of the comonomer [5]. The 12 Principles of Green Chemistry call for use of renewable resources whenever practicable [6,7], therefore recent work has focused on maximizing the bio-based content in triglyceride-derived polymer systems. Prospective biorefinery products from carbohydrates [8,9] and lignin [10] are interesting as potential feedstocks for further development of AESO chemistry. For example, Wool *et al.* have shown that lignin model compounds with reactive functionality can provide similar properties and functional performance as styrene in thermosetting systems [11,12]. Rosin acids have also been explored as potential alternatives to styrene or divinylbenzene [13].

Figure 1. (A) Representative structure of acrylated epoxidized soybean oil (AESO); (B) dibutyl itaconate; (C) ethyl cinnamate.



In this study, we polymerized AESO with bio-based comonomers to produce novel thermoset materials. Dibutyl itaconate (Figure 1B) was selected as one of the comonomers due to its structural similarity to acrylates and methacrylates, lower toxicity, and the status of itaconic acid as one of the US DOE “Top 10” chemical opportunities from biomass [9]. As itaconic acid is readily derived from carbohydrates *via* fungal fermentation, it has been successfully used in a variety of polymer applications [14]. These include as a dienophile for Diels-Alder chemistry in modification of fatty

acids [15], grafting of polyitaconic acid onto other polymers [16], and incorporation into epoxy resins [17]. We also studied ethyl cinnamate (Figure 1C) as a lignin model compound, to determine whether the cinnamyl moieties found in native or isolated lignins (and potentially in bio-oils as well) are reactive with AESO. Dibutyl itaconate and ethyl cinnamate were incorporated into thermoset materials with AESO at various ratios and we report the resulting spectral, thermal, and mechanical properties.

2. Experimental Section

2.1. General

Acrylated epoxidized soybean oil was purchased from Sigma-Aldrich (St. Louis, MO, USA) (3.4 acrylate groups per triglyceride, average molecular weight approx. 1200 g/mol). Dibutyl itaconate (>95%) was purchased from TCI America (Portland, OR, USA). Ethyl cinnamate (>98%) and *tert*-butyl peroxybenzoate (98%) was purchased from Alfa Aesar (Ward Hill, MA, USA). All chemicals were used as received. Gel permeation chromatography was performed using a Shimadzu Prominence Series HPLC (LC-20AD) system (Columbia, MD, USA) with column oven (CTO-20A) and refractive index detector (RID-10A) both maintained at 40 °C. Two Phenogel columns (Phenomenex, Torrance, CA, USA; 5 µm, 300 × 7.8 mm) were placed in series, one with 50 Å and one with 100 Å pore size. The system was calibrated with polystyrene standards purchased from Sigma-Aldrich (St. Louis, MO, USA). Chromatography was performed with injections on a 200 µL sample loop and 1 mL/min flow rate of tetrahydrofuran (Fisher Chemical, HPLC grade, Waltham, MA, USA). Infrared spectra were recorded using a Nicolet 6700 FT-IR spectrometer equipped with a diamond ATR accessory (Thermo Scientific, Waltham, MA, USA). Spectra were acquired in the range 500–4000 cm⁻¹. Thermal analysis on pre-extracted samples (see Section 2.4 below) was performed with a Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA). The TGA samples were pre-dried in a vacuum oven at 45 °C for 24 h, and further exposed to a stream of dry N₂ gas at 50 °C for 1 h prior to analysis (50–700 °C, 10 °C/min). Mechanical and viscoelastic properties were characterized with a Q800 dynamic mechanical analyzer (TA Instruments, New Castle, DE, USA).

2.2. Synthesis of Homopolymers

Poly(dibutyl itaconate) was prepared and purified based on a previously published procedure, which was modified to use *t*-butylperoxybenzoate as the initiator [18]. Similarly, poly(ethyl cinnamate) was prepared and purified according to the literature but using the *t*-butylperoxybenzoate initiator [19].

2.3. Representative Procedure for Copolymerization of the Bio-Based Resins

AESO and comonomer in the desired ratio, with *t*-butyl peroxybenzoate initiator (2 wt. % of the total mixture) were mechanically blended for at least 5 min using an overhead stirrer. To prevent oxygen free radical inhibition, the mixture was then purged with nitrogen gas for 5 min and placed under vacuum to remove gas bubbles. The purge/vacuum cycle was repeated 3 times. The resin was then poured into a silicone mold between two steel plates and cured by the application of heat. The curing process for all resins was 90 °C for 2 h with postcure at 120 °C for 2 h based on previously

demonstrated conditions for curing of AESO resins [20,21]. The polymer samples were allowed to cool to room temperature and were polished with fine sandpaper prior to further analysis.

2.4. Determination of Extractable Content in the Bio-Based Resins

Samples (1 g) were fragmented and extracted overnight in 15 mL dichloromethane. The insoluble material was placed in a desiccator under continuous vacuum for a further 24 h prior to weighing.

3. Results and Discussion

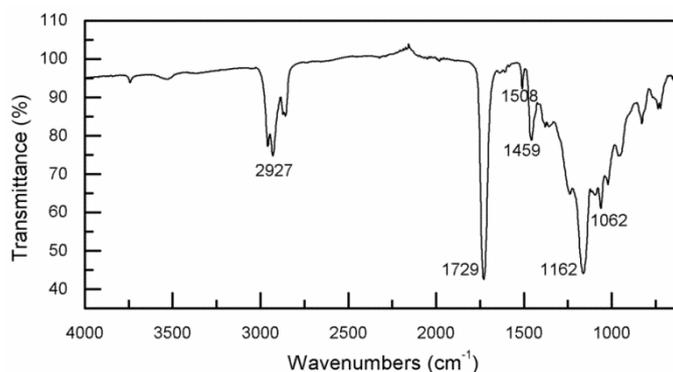
3.1. Degree of Incorporation of Bio-Based Monomers

Thermosets were prepared with AESO-DBI or AESO-EC mixtures with mass ratios of 3:1, 2:1, and 1:1 (for clarity, samples will be discussed according to these mass ratios unless otherwise noted). The corresponding molar ratios of reactive functionalities are 2.1:1, 1.4:1, and 0.7:1 for the DBI series and 1.5:1, 1.0:1, and 0.5:1, comparable to previous studies of comonomer blends. Initiator and thermal curing cycles were similarly based on earlier studies of AESO reactivity [5,20,21]. Extraction with dichloromethane gave >99% recovery of insoluble material for the AESO-DBI series. For the AESO-EC series, >99% recovery was obtained for the 3:1 blend but was 95% for the 2:1 ratio and 90% for the 1:1 ratio. Further exploration of initiator and curing conditions would be necessary to improve the incorporation levels of EC. The mass recovery observations were in good agreement with infrared spectroscopic analysis.

3.2. Infrared Spectroscopy

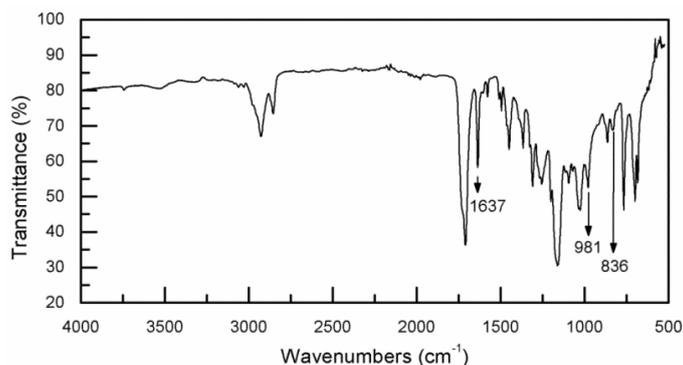
Infrared spectra were measured for each of the AESO-DBI and AESO-EC mixtures. A representative spectrum for AESO-DBI (1:1) is shown in Figure 2; the spectrum was not significantly different at lower levels of DBI. Pure AESO has a C=C stretch at 1635 cm^{-1} , and pure DBI has a C=C stretch at 1642 cm^{-1} ; neither of these is apparent in the spectrum of the copolymer, indicating high degree of polymerization of the C=C functionality. The broad, strong C=O stretching frequencies centered around 1729 cm^{-1} are apparent, characteristic of fatty ester functionality in the triglyceride backbone as well as acrylate and itaconate ester moieties. Corresponding C–O stretches are observed at 1162 and 1062 cm^{-1} .

Figure 2. Infrared spectrum of AESO-DBI (1:1) thermoset.



In contrast, the AESO-EC spectra showed evidence of unreacted starting material. Pure EC has a C=C stretch at 1639 cm^{-1} and the copolymer shows a distinct peak at 1637 cm^{-1} (Figure 3). Peaks seen at 981 and 836 cm^{-1} are also consistent with pure EC. Other signals are consistent with polymerized AESO as discussed above.

Figure 3. Infrared spectrum of AESO-EC (1:1) thermoset.



3.3. Thermal Stability

The thermal stability of the polymers was studied by thermogravimetric analysis (TGA). Results for DBI homopolymer and AESO-DBI thermosets are shown in Figure 4, and T_5 , T_{10} , T_{50} , and char yield values are shown in Table 1.

Figure 4. Thermogravimetric curves for poly(DBI) and AESO-DBI thermosets. Black traces correspond to mass loss vs. temperature; gray traces are the corresponding derivative plots.

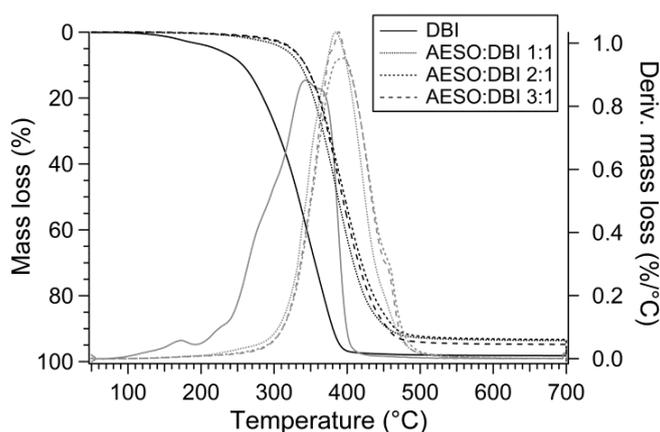


Table 1. Thermogravimetric data for DBI and EC homopolymers, AESO-DBI, and AESO-EC resins. T_5 , T_{10} , and T_{50} temperatures correspond to mass loss of 5%, 10%, and 50% respectively. Char yield is based on residue at 700 °C.

Sample	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	Char yield
DBI homopolymer	220	257	333	1.74%
AESO:DBI 1:1	313	336	387	6.34%
AESO:DBI 2:1	324	343	397	6.66%

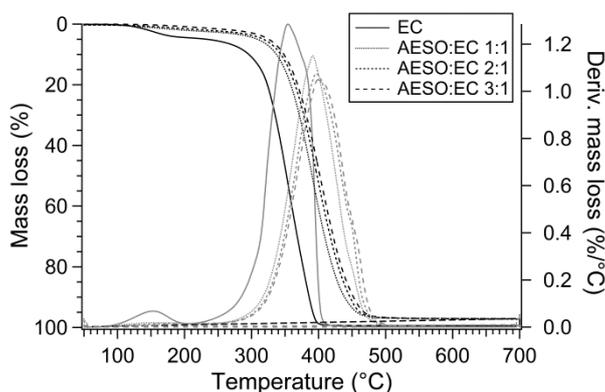
Table 1. Cont.

Sample	T_5 (°C)	T_{10} (°C)	T_{50} (°C)	Char yield
AESO:DBI 3:1	325	343	393	5.16%
EC homopolymer	233	296	352	0.53%
AESO:EC 1:1	309	337	390	2.86%
AESO:EC 2:1	318	344	398	2.42%
AESO:EC 3:1	326	348	402	2.84%

For the AESO-DBI blends, the TGA data show that the major degradation process has an onset around 300 °C, and the maximum rate of degradation occurs at 385–390 °C, apparently independent of the DBI content. The T_{50} values are very similar to that of pure AESO thermoset (398 °C) [13], for which the major thermal transformation is decomposition of the crosslinked polymer network and random scission of the linear chains [22]. In the case of DBI homopolymer, the sample shows loss of mass in the 150–200 °C range. GPC data showed that the purified DBI homopolymer still contained residual DBI monomer (<5%), therefore we attribute the lower-temperature mass loss to the monomer, which was not present in the AESO resins.

EC homopolymer (Figure 5) showed two major degradation stages centered at 153 °C and 355 °C. TGA of EC monomer showed sharp mass loss centered at 165 °C; therefore it is likely that the EC homopolymer contained a small amount of unreacted EC. The AESO-EC samples show that unreacted EC was removed by the solvent extraction pre-treatment. Consumption of EC via thermal [2 + 2] dimerization during the cure was not expected due to the higher temperatures (>200 °C) that would be required [23]. T_5 , T_{10} , and T_{50} values for the two series of thermosets are comparable. The values for AESO-EC are slightly higher than those for the DBI series, suggesting that the aromatic content in EC may provide limited stability, but in general the T_{50} values are not significantly different than the T_{50} of AESO alone. Char values are low for all materials tested, in agreement with the literature on thermal stability of AESO and AESO blends [13].

Figure 5. Thermogravimetric curves for poly(EC) and AESO-EC thermosets.



The AESO blends were further characterized by dynamic mechanical analysis (DMA). Representative traces of storage modulus as a function of temperature for AESO-EC blends are shown in Figure 6. $\tan \delta$ curves as a function of temperature (Figures 7 and 8) were used to determine T_g for AESO-DBI and AESO-EC materials. The results are summarized in Table 2.

Figure 6. Storage modulus as a function of temperature for AESO-EC thermosets.

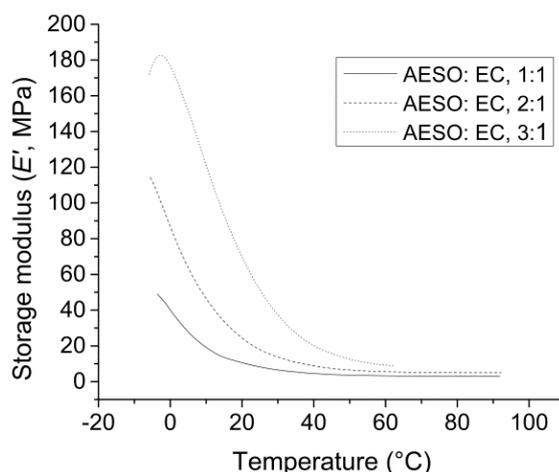


Figure 7. Tan δ as a function of temperature for AESO-DBI thermosets.

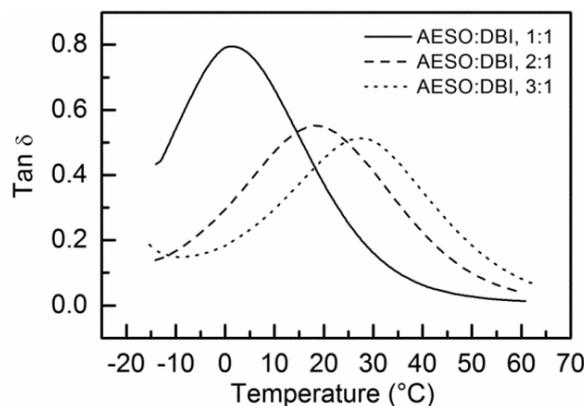


Figure 8. Tan δ as a function of temperature for AESO-EC thermosets.

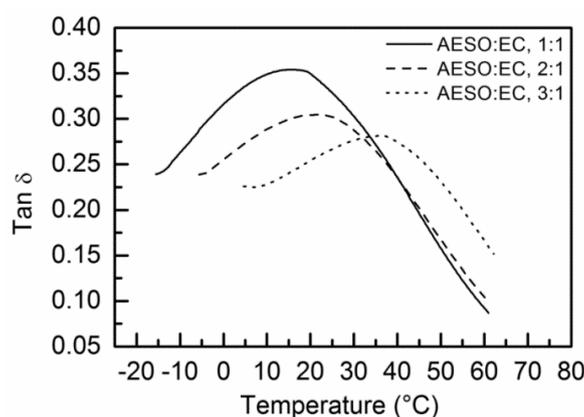


Table 2. Glass transition and viscoelastic properties of AESO blends (Each measurement was made on two different samples).

Sample	AESO: EC, 1:1	AESO: EC, 2:1	AESO: EC, 3:1	AESO: DBI, 1:1	AESO: DBI, 2:1	AESO: DBI, 3:1
T_g (as Tan δ peak, °C)	14.2, 15.6	21.0, 21.1	41.4, 36.3	1.4, 2.5	18.4, 19.2	27.3, 25.4
Storage modulus E' (at 30 °C, MPa)	6.5, 9.1	16.6, 13.7	35.2, 37.0	1.5, 1.6	6.6, 7.1	17.8, 10.2

The T_g of AESO homopolymer depends on the degree of acrylation; a typical value is about 47 °C [5]. In this study, lower values were observed as the amount of EC or DBI increases; this can be attributed to lower cross-link density as both DBI and EC can only serve as linear chain extenders. The T_g of DBI homopolymer is 14.7 °C [24]. Since we observe T_g values as low as 1–2 °C for AESO-DBI polymers, lower than the T_g of DBI or AESO homopolymers, the copolymer shows a strong plasticizing effect. Interestingly, this is the opposite of the effect reported in an AESO-methyl methacrylate system [25]. In the case of the 1:1 AESO-EC blend, the presence of unreacted liquid EC is likely reducing the glass transition temperature. However, in all cases the observed T_g values are slightly higher than those seen for the AESO-DBI blends, suggesting that the aromatic content of the copolymer provides some rigidity. The experimental results are in good agreement with the Twinkling Fractal Theory of the glass transition, which has been extensively used to model the properties of polymers based on acrylated oils [26,27].

Storage modulus (E') values for both AESO-DBI and AESO-EC samples were substantially lower than that of pure AESO which is about 320 MPa at 30 °C. This is consistent with the rubbery nature of the materials which are above or near the glass transition point at room temperature. The modulus values decrease with decreasing AESO content due to the lower crosslink density. In other studies of AESO blends, decreased E' values have been seen for comonomers such as methacrylated lauric acid (100 MPa at 30 °C), whereas styrene blends provide significant increases (typically >1 GPa at 30 °C) [21]. Based on the known properties of related thermoset systems, triglyceride-based copolymers with DBI and EC could be obtained with higher T_g and modulus values through two strategies. First, increasing crosslink density could be achieved by working with starting oils having a higher degree of unsaturation (for example, linseed oil), leading to a higher proportion of reactive acrylate groups after derivatization. Crosslink density can also be increased through maleic anhydride modification of residual OH groups, so the resulting monomers (MAESO) have additional reactive sites [5]. Second, incorporation of fibers into AESO-based resins is known to improve mechanical performance. Renewable resources such as keratin, chicken feathers, and sisal have been recently reported for such a purpose [28–30].

4. Conclusions

We have shown that DBI and EC can be copolymerized with AESO to produce thermoset materials. DBI is readily incorporated into the polymer matrix with AESO at levels of 25%–50% by mass. The glass transition temperature decreases rapidly with increasing amounts of DBI, decreasing below even the T_g for DBI homopolymer. Under the cure conditions investigated, unreacted EC was detected when the starting blend was 33%–50% EC by mass, although it is apparent that the major portion of the added EC did react with AESO. The thermal behavior of the systems are similar to poly(AESO) but the storage modulus is much lower, suggesting that alternative approaches such as fiber reinforcement might be necessary to provide performance comparable to petroleum-derived comonomer systems. Our findings suggest that itaconic acid, as a promising biomass platform chemical, may be interesting as a potential replacement for petroleum-based acrylates in AESO-comonomer systems. Also, since we have demonstrated that the cinnamate functionality is reactive, lignin-derived bio-oils containing high

levels of cinnamate functionality may similarly be useful in thermosets. Altogether, this suggests directions for future development of bio-based thermoset systems based on modified triglycerides.

Conflicts of Interest

The authors declare no conflict of interest.

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