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# Amine-cured ω-epoxy fatty acid triglycerides: Fundamental structure–property relationships

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**Abstract**

Several triacyl glycerides (**2**), having terminal epoxy functionalities on aliphatic residues of varying chain length, were allowed to react with either 4,4′-methylenedianiline or phthalic anhydride to give a new group of glassy network polymers with glass transition temperatures ($T_g$s) of 48–133 °C. Although cured **2** have substantially lower moduli than do conventional epoxy thermosets based on bisphenol A-diglycidyl ether (BADGE), the crosslinked triglycerides adhere strongly to steel and aluminum and are much more ductile and considerably tougher than commercial epoxy systems. In addition to a comparison of thermal and mechanical properties of thermosets based on **2**, BADGE and common epoxidized linseed oil, reactivity differences among these epoxy resins are briefly discussed.

*Keywords:* Triglycerides; Thermosetting polymers; Mechanical properties

## 1. Introduction

The past decade has witnessed steadily increasing interest in the potential of renewable resources as alternatives to conventional petrochemicals for the manufacture of organic chemicals and polymers. Fatty acids, fatty acid esters and related vegetable oils have received particular attention as raw materials, owing to their abundance, availability in relatively high purity, and their carboxyl and olefinic functionalities that enable a variety of transformations to a broad range of synthetically useful species [1]. Among such materials, commercially available epoxidized linseed and soybean oils, often used as plasticizers and acid scavengers, recently have been shown to yield robust network polymers when allowed to cure with amines [2], acids [3] and anhydrides [4–6] or when crosslinked *via* photolytically initiated cationic polymerizations [7].

Epoxidized oils, such as epoxidized linseed oil (nominal structure **1**), formed directly from naturally occurring oils, contain only oxirane functionalities that are hindered at both carbons and experience the effects of two electron-injecting alkyl groups; consequently, these epoxides polymerize readily upon cationic attack and ring opening [7], but react sluggishly with nucleophilic curing agents [8–10] in the stoichiometrically balanced polymerizations often utilized in the formation of epoxy composites and coatings [11]. We reasoned that triglycerides with terminal epoxy groups (*e.g.*, **2**), which have a carbon readily accessible to nucleophilic attack, would be considerably more reactive with commonly used amine and anhydride curing agents [11], thus offering more efficient processing conditions to the ultimate fabricator. Also, although a step removed from epoxides prepared directly from natural precursors such as unmodified vegetable oils, triglycerides **2** can still be derived from renewable materials; for example,

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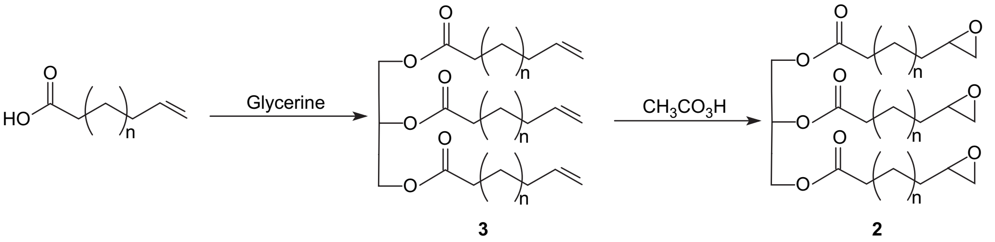
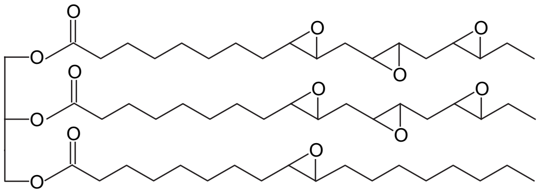
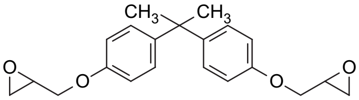


Scheme 1. Preparation of triglycerides **2** from ω-unsaturated fatty acids.

10-undecenic acid, itself a derivative of castor oil [1], leads to the terminally epoxidized, trifunctional triglyceride, **2a**, through the reaction sequence of Scheme 1 (see also Table 1). Consequently, we undertook a study of trisepoxides **2** in which we briefly examined their general curing behavior with 4,4′-methylenedianiline (MDA) and phthalic anhydride (PA) and focused on the fundamental thermal, mechanical and adhesive properties of the resulting network polymers. This paper describes how the property envelopes of the cured **2** vary with chain length of the fatty acid residues ($n = 0–6$) in these resins as well as how the characteristics of these new network polymers compare with those of analogously cured **1**. Comparison is also made between cured **1** and **2** and networks formed from conventional epoxides based on bisphenol A-diglycidyl ether (BADGE).



**1**



BADGE

## 2. Experimental

### 2.1. Materials and methods

Epoxidized linseed oil (Flexol Plasticizer LOE) was obtained from the Union Carbide Corporation and was used as received. 4,4′-Methylenedianiline (MDA), phthalic anhydride (PA), tetrabutylammonium bromide (TBAB), stannous octoate, ω-unsaturated fatty acids and other reagents and solvents were obtained from the Aldrich Chemical Company and other commercial sources and generally were used as received.

Infrared analyses of cured **1** and **2** were performed with a Bio-Rad model FTS-40 spectrometer equipped with a Harrick Split Beam attenuated total reflectance accessory and MCT detector. Spectra were obtained for samples mounted on the silicon reflection element and were collected at a resolution of 4 wave numbers. Proton nuclear magnetic resonance spectra ($^1H$ NMR) were recorded on a Bruker model AC250 operating at 250 MHz; resonances are reported relative to tetramethylsilane.

Table 1
Epoxy equivalent weights (eew[a]) of triglycerides **1** and **2**

| No. | $n$ | eew (calculated) | eew (experimental) |
|---|---|---|---|
| **1** | | | 168 |
| **2a** | 6 | 213 | 217 |
| **2b** | 5 | 200 | 211 |
| **2c** | 2 | 157 | 182 |
| **2d** | 0 | 129 | 132 |

[a] Determined according to ASTM D1652.

### 2.2. Synthesis of triglycerides 2

Triglycerides **2** were prepared by the reaction path of Scheme 1; the following is the procedure for the synthesis of **2d**.

A mixture of 4-pentenoic acid (964 g, 9.64 mol), glycerol (240 g, 2.61 mol), *p*-toluenesulfonic acid monohydrate (15.7 g, 0.08 mol) and toluene (520 g) was allowed to stir at reflux for 12 h in a 2-L round bottom flask equipped with a Dean–Stark trap for continuous removal of water. The solution then was allowed to cool to room temperature, and triethylamine (148 g, 1.46 mol) was added at a rate that maintained the temperature at about 25 °C; the resulting mixture was washed repeatedly with water until the washings had a pH of about 6–7. The organic phase was separated and toluene was removed *in vacuo*. The resulting oil was filtered to give 4-pentenoic acid triglyceride as a clear yellow liquid (875 g, 99%). IR: 1735 $cm^{-1}$ (ester C=O), 1640 $cm^{-1}$ (C=C). $^1H$ NMR ($CDCl_3$): 5.95–5.74 (m, 3H, $-CH=CH_2$), 5.36–5.23 (m, 1H, $CH(CH_2O)_2O-$), 5.17–5.02 (t, 6H, $-CH=CH_2$) 4.38–4.17 (m, 4H, $CH(CH_2O)_2O-$), 2.42 (m, 12H, $-O_2C-CH_2CH_2CH=$) ppm. A solution of a portion of this oil (145 g, 0.43 mol) in chloroform (652 g) in a jacketed reactor was cooled to 10 °C. Peracetic acid (32% in water; 337 g, 1.42 mol) containing sodium acetate (10 g) was added at a rate that maintained a reaction temperature below 20 °C. The resulting stirred mixture then was heated at 35 °C for 15.5 h, after which it was again cooled to 10 °C and sodium sulfite (10%) was added to decompose the remaining peracetic acid. The organic layer was separated and washed repeatedly with a saturated solution of sodium bicarbonate and then with water until the washings had a pH of about 6. The organic phase was separated, dried over magnesium sulfate, and filtered. The solvent was removed *in vacuo* to give **2d** as a yellow liquid (144 g, 87%). Flash chromatography of the **2d** in ethyl acetate/hexanes over silica gel gave the product with an epoxy equivalent weight of 132 g/eq (theory 129 g/eq), determined according to ASTM D1652. $^1$H NMR ($CDCl_3$): 5.36–5.23 (m, 1H, $CH(CH_2O)_2O-$), 4.41–4.12 (m, 4H, $CH(CH_2O)_2O-$), 2.79 (m, 3H, $CH_2OCH$), 2.60–2.37 (m, 6H, $CH_2OCH$), 2.14–1.93 (m, 6H, $CH_2CO_2$), 1.85–1.66 (m, 6H, $-CH_2-CH_2-CO_2$) ppm.

### 2.3. Cure studies of triglycerides 2

Curing behavior of **1** and **2a** was examined using differential scanning calorimetry (see Figs. 1–3) with 10 mg of samples pre-mixed with curing agent and catalyst, using a TA Instruments model DSC 2920.

### 2.4. Mechanical evaluation of 1, 2 and BADGE cured with MDA and PA

Castings of the triglycerides and BADGE were prepared by the following general procedure. The resin (typically about 80 g), contained in a glass vessel, was heated while stirring on a hot plate to the initial temperature used in the cure schedule for each experiment (see Tables 2 and 7), after which an equivalent amount of either 4,4′-methylenedianiline (MDA) or phthalic anhydride (PA) was added and stirring was continued until the curing agent had completely dissolved. The resulting solution was allowed to cool to 80–110 °C, and, when utilized, stannous octoate (3 pph based on weight of **1** or **2**) or TBAB (2 wt% based on weight of **1** or **2** and PA) was added. The mixture then was degassed in a bell jar, poured into a polished aluminum mold with an internal thickness of 127 mm held between molded plates covered with a Teflon™ release film and heated according to the schedules outlined in Tables 2 and 7. After the mold had cooled to room temperature, the resulting casting was cut and mechanically tested according to ASTM methods

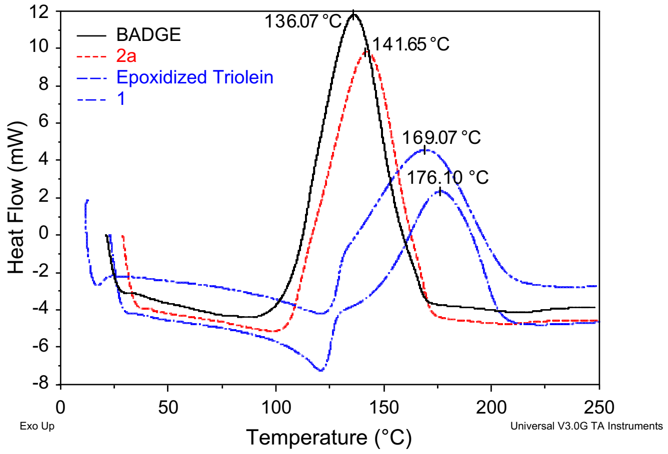


Fig. 1. DSC traces for curing reactions of **1**, **2a**, BADGE and epoxidized triolein with equivalent amounts of phthalic anhydride in the presence of tetrabutylammonium bromide.

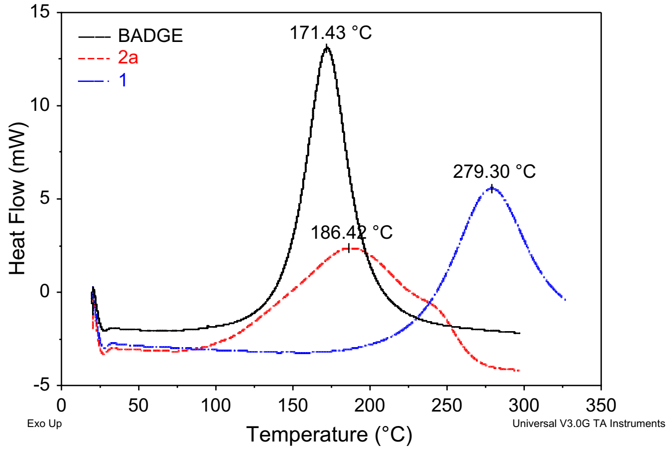


Fig. 2. DSC traces for curing reactions of **1**, **2a** and BADGE with equivalent amounts of MDA.

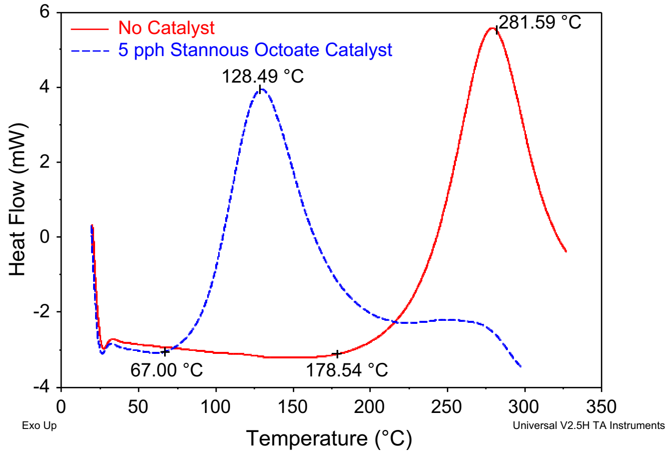


Fig. 3. DSC traces of catalyzed and uncatalyzed cure reactions of **1** with an equivalent amount of MDA.

Table 2
Thermal and flexural properties[a] of various epoxides cured with an equivalent of MDA

| Resin no. | Cure conditions[b] (°C) | $T_g$[c] (°C) | Flexural strength (MPa) | Strain[e] (%) | Flexural modulus (GPa) |
|---|---|---|---|---|---|
| **1** | 120–200[d] | 54 (59) | 56 | 15 | 1.5 |
| **2a** | 120–180 | 56 (55) | 36 | 7.5 | 1.1 |
| **2a** | 120–180[d] | 54–56 | 35 | 8 | 1.0 |
| **2b** | 90–180[d] | 48 | 39 | 17 | 1.1 |
| **2c** | 120–180 | 68 | 72 | 18 | 1.9 |
| **2d** | 120 | 133 (112) | 119 | 6.5 | 3.2 |
| BADGE | 120–180 | 184 (188) | 105 | 13 | 2.4 |

[a] Determined using ASTM method D-790.

[b] Cure temperature of the castings was increased about 25 °C every 2 h until the specimens reached final temperature, at which they were allowed to remain for an additional 2 h.

[c] Values were measured using DSC with a heating rate of 10 °C/min over a range of −50 to 300 °C; values shown in parentheses were determined using DMS at 1 Hz with a heating rate of 3 °C/min over a range of −100 to 250 °C.

[d] Formulations contained stannous octoate (3 pph based on the weight of epoxy resin).

[e] Only specimens of cured **2b** broke at the strains indicated.

D-638 and D-790. Glass transition temperatures of the cured materials were determined with differential scanning calorimetry (DSC) and dynamic mechanical spectroscopy (DMS); for DSC, the heating rate was 10 °C/min over a range of −50 to 300 °C and for DMS, the heating rate was 3 °C/min over a range of −100 to 250 °C at a frequency of 1 Hz. A Rheometrics RMS800 dynamic mechanical spectrometer was utilized in rectangular torsion geometry. In the case of **2d**, a cured sample was heated from −75 to 180 °C also at 3 °C/min and at a frequency of 1 Hz and exhibited an initial loss in storage modulus at 112 °C ($T_g$, Table 2); a second scan over the same temperature range produced initial modulus loss at only 74 °C, and the sample began to undergo flow at 150 °C. The resulting liquid residue was soluble in THF and yielded an IR spectrum (neat) with a strong carbonyl absorption at 1776 $cm^{-1}$.

### 2.5. Thin film toughness testing of **1**, **2** and BADGE cured with 4,4′-methylenedianiline

BADGE, **1** or **2** (4 g), an equivalent of MDA and stannous octoate (0.11 g when utilized) were taken up in a mixture of dimethylformamide (6.6 g) and tetrahydrofuran (2.4 g). The resulting solution was passed through a 0.45-μm filter and cast onto a tin-plated steel sheet using a Gardco adjustable Microm film applicator. The castings were maintained at room temperature for 30 min, 120 °C for 2 h, 150 °C for 2 h and finally at 180 °C for 2 h. The resulting films were floated from the plate with mercury. Films then were evaluated for toughness in terms of energy release rate at break ($J^*$) using a single edge notch film fracture test. Films were cut into 12.7 mm wide strips, and cracks were introduced with a surgical knife. The samples were tested using an Instron model 4507 tensile tester equipped with a Series IX Automated Materials Testing System for instrument control. A cross-head speed of 12.7 mm/min and a gauge length of 25.4 mm were utilized. The values presented are the mean of at least five determinations (see Table 4). The value, $J^*$, was calculated using the formula:

$$J^* = \mathrm{DT}/(w - L)t$$

where DT is the total energy released to break the specimen and is determined as the area under the stress–strain curve, $w$ is the film width, $L$ is the initial crack length and $t$ is the specimen thickness.

### 2.6. Adhesion testing of **1**, **2** and BADGE cured with MDA

BADGE, **1** or **2** (14 g), mixed at room temperature with fumed silica (Cabosil TS 720; 0.84 g) and micro-glass beads (Cataphote 5A; 0.42 g) to provide rheology control during cure, was heated to 120 °C, 1 equiv of MDA was added, and the resulting mixture was maintained at 115 °C until the amine had completely dissolved. The mixture then was either allowed to cool to room temperature or, if stannous octoate (0.34 g) was used, cooled to 100 °C and kept at that temperature only long enough to dissolve the catalyst (after which the mixture was allowed to cool to room temperature as in the case of uncatalyzed formulations). The formulations were applied to strips (1.54 mm × 25.4 mm × 101.6 mm) of either cold rolled steel or aluminum 2024T3, and the entire assembly was clipped together throughout the curing process; strip overlap in the assembly was 12.7 mm and bond line thickness was controlled with micro-glass beads at 0.127 mm. The steel substrates were cleaned with acetone immediately prior to adhesive application, and aluminum substrates were grit blasted to generate a fresh oxide layer and then cleaned with an acetone spray immediately prior to adhesive application. Lap shear strengths were determined with the Instron tensile tester at a cross-head speed of 254 mm/min and the values shown in Table 5 are the mean for at least four determinations.

For T-peel determinations, substrates (0.81 mm × 25.4 mm × 152.4 mm; cleaned as described above) were prebent to an L shape prior to specimen testing. The bonded area was 101.6 mm and the bond line thickness was 0.127 mm. Peel strengths were determined using the tensile tester at a cross-head speed 254 mm/min and the values shown in Table 5 are the mean of at least four determinations.

## 3. Results and discussion

### 3.1. Preparation of triglycerides **2**

Trisepoxides **2** ($n = 0$–6; Table 1) were synthesized by the straightforward reaction sequence outlined in Scheme 1. Acid-catalyzed esterification of the corresponding fatty acids with glycerine in refluxing toluene with continuous water removal afforded intermediate triglycerides **3** in virtually quantitative yield; triglyceride formation was confirmed by the infrared (IR) spectra of the intermediates which display a single, strong ester band at about 1735 $cm^{-1}$ in the carbonyl region along with a characteristic C=C stretching frequency at 1640 $cm^{-1}$; absence of a H–O stretching band in the product spectrum indicates complete consumption of the starting acid. In addition, proton NMR spectra ($^1$H NMR) of the materials exhibit the expected ratio of vinylic protons absorbing at 5.95–5.74 and 5.17–5.02 ppm to the methine (5.36–5.23 ppm) and methylene (4.38–4.17 ppm) protons associated the glyceride portion of the molecules. Treatment of **3** in chloroform with aqueous peracetic acid at 10–35 °C produced trifunctional epoxides **2** in 80–90% yield. Complete oxidation of intermediates **3** was verified by $^1$H NMR spectra of the final products which show loss of the vinylic absorptions noted above along with the appearance of peaks corresponding to terminal epoxy methylene and methane protons at 2.60–2.37 and 2.79 ppm, respectively; again, integration of these absorptions with those of the methylene and methine protons of the glyceride linkage supports the structures of **2** shown in Scheme 1. In addition, the epoxy equivalent weights (eew) of **2a**, **2b**, and **2d** [determined titrimetrically (ASTM D1652)], are quite close to those calculated for the structures indicated (Table 1); eew also provide the absolute information necessary to determine stoichiometric equivalence for the cure studies of **2** with

4,4′-methylenedianiline (MDA) and phthalic anhydride (PA) discussed below.

In the case of **2c**, there is significant disparity between the calculated and experimentally determined eew of the resin (157 *versus* 182; Table 1). Evidently, in the single instance **2c** was prepared, oxidation was accompanied by a side reaction, possibly epoxy–epoxy coupling initiated by carboxylic acid that is formed as a by-product in reduction of the peracid. Why this is so only for **2c** is not clear; repeated preparations of other **2** using Scheme 1 were quite reliable and uncomplicated by side reactions.

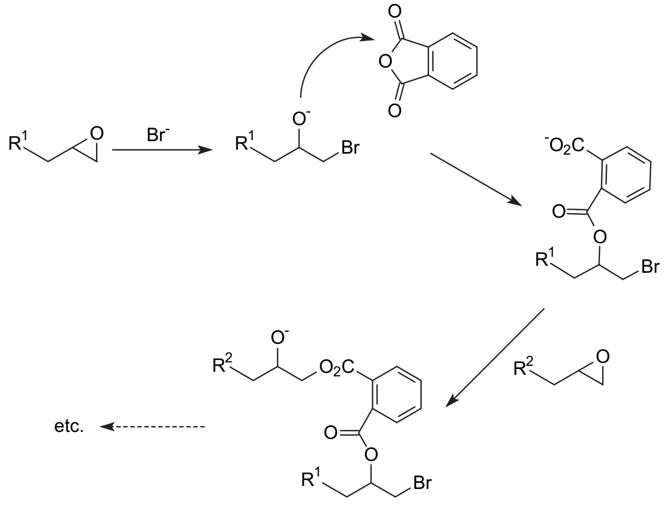
### 3.2. Cure characteristics of triglycerides *1* and *2*

Differential scanning calorimetry (DSC) confirms that, as expected, terminally epoxidized triglycerides **2** are more labile to nucleophilic attack by common curing agents than are the hindered epoxide moieties in commercial epoxidized oils. Fig. 1 indicates that **2a** in the presence of an equivalent of phthalic anhydride (PA) with tetrabutylammonium bromide (TBAB) as an initiator exhibits a thermal profile with an exothermic onset of about 100 °C and a peak temperature ($T_p$) of around 141 °C. These values, which are similar to those observed for conventional BADGE cured identically, suggest that **2** form networks with anhydrides *via* the familiar anhydride or acid initiation–propagation sequence of Scheme 2 [12,13] and clearly contrast with those of less-reactive **1** or epoxidized triolein, which requires higher temperatures to instigate cure and show exothermic $T_p$ of 169–176 °C (Fig. 1). Similarly, the beginning of exothermic activity in the DSC scan of an equivalent mixture of **1** and MDA is above 175 °C, while stoichiometrically identical mixtures of BADGE or **2a** with MDA show exothermic onsets well below 150 °C (Fig. 2). As reported by Proops and Fowler [8,9], tin compounds are effective Lewis acid catalysts for reactions of MDA and **1**, and the DSC scan in Fig. 3 shows a vigorous exotherm beginning at 67 °C for the reactants cured in the presence of stannous octoate, which also decreases the $T_p$ of the reaction to 128 °C from 281 °C. Consequently, specimens of MDA-cured **1** (with an ultimate $T_g$ of 55 °C) used for the mechanical evaluations described below were prepared with 3–5 pph of tin octoate (see Table 3); in the absence of a catalyst, a $T_g$ of not more than 32 °C can be obtained for these reactants even after heating for several days. Kinetically, network formation from reactions of **2d** with MDA, which almost certainly proceed *via* the sequence of Scheme 3 [11–13], benefits less dramatically from catalytic amounts of tin octoate; in DSC scans of mixtures of the reactants, exothermic onsets drop from 88 to 54 °C and $T_p$ decreases from 175 to 136 °C when the catalyst concentration is raised from 0 to 3 pph (based on triglyceride). However, for **2** and MDA, ultimate tensile and flexural properties can be realized with or

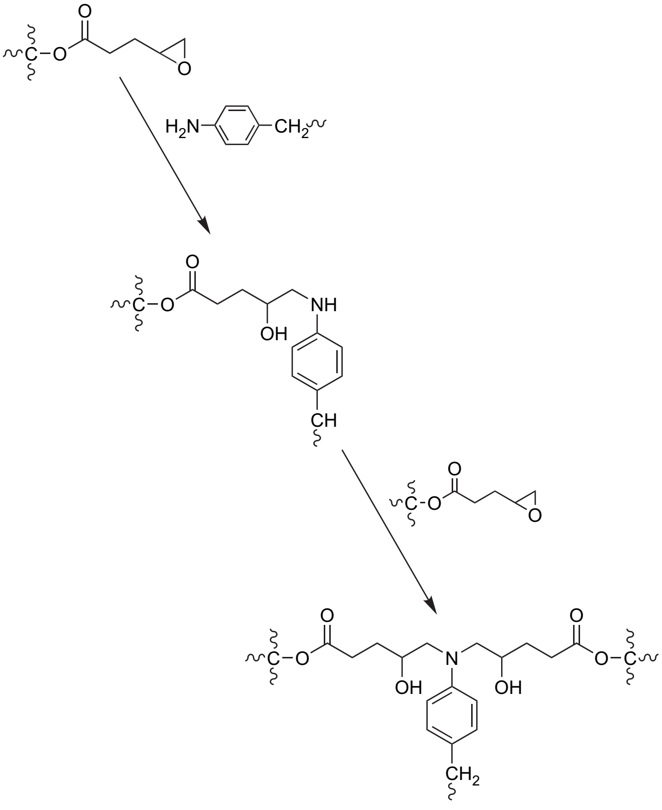
Table 3
Tensile properties[a] of **1**, **2a** and BADGE cured with an equivalent of MDA[b]

| Resin no. | Tensile yield[c] (MPa) | Tensile modulus (GPa) | Elongation at break (%) |
|---|---|---|---|
| **1** | 41 (28) | 1.5 | >30 |
| **2a** | 27 (23) | 1.1 | 15 |
| BADGE | 74[d] | 2.6 | 6[d] |

[a] Determined using ASTM method D-638.
[b] See cure schedules outlined in Table 2.
[c] Break strength is shown in parenthesis.
[d] Specimen did not yield.



Scheme 2. Proposed initiation and propagation sequence for the network polymerization of triglycerides **2** with phthalic anhydride with tetrabutylammonium bromide as an initiator.



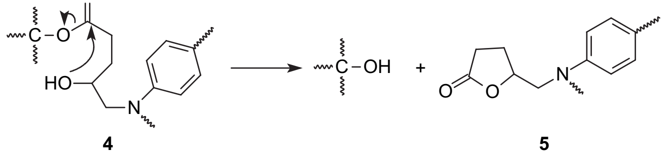
Scheme 3. Idealized network formation during reaction of **2d** with MDA.

without catalyst (*vide infra*). Note also that for MDA-cured **1** or **2**, we saw no evidence (IR) for aminolysis of the ester linkages in these triglycerides.

In this study, we made no attempt to exploit the relatively high reactivity of **2** for developing an optimized cure regimen for these materials. Rather, for preparation of specimens destined for physical evaluations, we exhaustively cured **1**, **2**, and BADGE in order to maximize cure and thus allow a meaningful comparison of their ultimate properties, regardless of differences in cure efficiencies. However, as a part of our screening of crosslinking conditions for **2** with MDA, we discovered that at temperatures above 130 °C, short-chain triglyceride **2d** yields only an incoherent gel, the IR spectrum of which exhibits, along with the expected ester band at 1733 $\text{cm}^{-1}$ [14], a strong absorption at 1776 $\text{cm}^{-1}$ suggesting that network formation is accompanied by the thermodynamically reasonable cyclization of hydroxy-intermediate **4** to the five-membered lactone **5** [15] (Scheme 4) – a pathway unfavorable for other **2** which show no evidence for similar behavior. In a DMS experiment (see Section 2), we found that **2d**, a glassy polymer when cured with MDA at 120 °C (see Table 2 below), can be thermally converted above 150 °C to an oily residue that is completely *soluble* in tetrahydrofuran, indicating that the polymer network can be totally disassembled at elevated temperatures. Based on the lactone-like absorption in the IR spectra of the oil (which was not characterized further), it appears that thermal decomposition of the crosslinked resin is more complicated than simple regeneration of its original monomeric constituents; therefore, cured **2d** does not truly represent a thermoset that is *recyclable* in the strictest sense of the term. Nevertheless, one can speculate that the controlled breakdown of crosslinked **2d** to a tractable species might be utilized to cleanly separate the material from a coated substrate or, in a composite, from reinforcing fibers.

### 3.3. Properties of network polymers based on triglycerides *1* and *2* cured with 4,4′-methylenedianiline

Triglyceride **2a**, cured with an equivalent of MDA at 180 °C according to the schedule outlined in Table 2, yields a glassy polymer with a $T_g$ of 56 °C (DSC) in the absence of the catalyst, stannous octoate; incorporation of catalyst during cure produces a network with virtually the same $T_g$. Not surprisingly, these values are considerably lower than that of a BADGE/MDA composition ($T_g = 184$ °C) and reflect the mobility of the alkylene chains in cured **2a** compared with the rigid bisphenol A nucleus that dominates the structure of the BADGE-based network. Within the series **2**, $T_g$ climbs with decreasing aliphatic chain length and decreasing eew, reaching a value of 133 °C for the short-chain triglyceride, **2d** (Table 2), an expected consequence of relatively high crosslink density and low molecular mobility in networks formed from **2** containing short aliphatic chains. Like **2**, epoxidized linseed oil (**1**), which to a first approximation has functionality (eew = 168) similar to that of **2d** (eew = 132; Table 1), cures with MDA to give a rigid glass. However, the $T_g$ of this material (54 °C) is closer to those of the less tightly crosslinked **2a** and **2b**.



Scheme 4. Possible thermal decomposition pathway for MDA-cured **2d**.

Mechanical behavior of **2** cured with MDA follows a trend analogous to the inverse relationship between $T_g$ and carbon chain length noted above; flexural modulus of the materials increases from 1.1 to 3.2 GPa as the carbon residues shorten within the series (Table 2), a consequence of the stiffness gained in the networks with higher crosslink density. By the same token, flexural strength of these network polymers increases from 36 to 119 MPa. In fact, Table 2 reveals that the composition derived from **2d** actually has higher modulus and strength than does MDA-cured BADGE, but other **2** form materials with mechanical properties that resemble those of crosslinked **1**. Since most specimens were not stressed to the breaking point, flexural strain values found for the epoxides listed in Table 2 are not especially revealing. However, tensile tests for MDA-cured **1** and **2a** indicate that these crosslinked glasses actually exhibit ductile failure, yielding at 41 and 27 MPa, respectively, with elongations of 30 and 15% (Table 3); the less molecularly mobile BADGE/MDA matrix, as expected, breaks without yielding at 6% strain. The tensile moduli range from 1.1 to 2.6 GPa for crosslinked **1**, **2a**, and BADGE (Table 3) paralleling the flexural behavior of these materials. Also, like their flexural strengths, break strengths of cured **1** (28 MPa) and **2a** (23 MPa) are considerably lower than that of crosslinked BADGE (74 MPa; Table 3). Note also that the tensile strength and modulus measured for MDA-cured **1** during this study are about twice those previously reported for the triglyceride crosslinked under similar conditions [10]; purity variations between the starting epoxidized oil are the likely explanation for the performance difference we observed.

Consistent with the relatively high ductility of crosslinked **1** and **2a**, fracture toughness ($J^*$) measurements of thin films (see Section 2) of these epoxides and of **2d** (1.7–4.8 $\text{kJ/m}^2$; Table 4) are considerably higher than that of MDA-cured BADGE (0.7 $\text{kJ/m}^2$), an observation that again demonstrates physical manifestation of the molecularly mobile matrix in the oil-based thermosets indicated by their $T_g$ and mechanical properties.

Conventional epoxy resins based on BADGE are known for their tenacious adhesion to metals and other active surfaces presumably owing to interactions of polar functionalities of such substrates with the hydroxyl groups formed when BADGE is cured [11,16]. Crosslinked, oil-based thermosets, which also are characterized by free hydroxy moieties (see Scheme 3), behave similarly. Thus, MDA-cured **1** and **2a** (filled with fumed silica and glass micro-beads; see Section 2) exhibit lap shear strengths with both steel and aluminum

Table 4
Fracture toughness of thin films[a] of various epoxy resins cured with an equivalent of MDA[b]

| Resin no. | Toughness or $J^*$ (kJ/m$^2$) |
|---|---|
| **1** | 4.8 |
| **2a** | 3.6 |
| **2d** | 1.7 |
| BADGE | 0.7 |

[a] Determined using the method detailed in Section 2.
[b] See cure schedules outlined in Table 2.

of about 18–23 MPa, values that compare favorably with those of a BADGE-based thermoset (18.6 and 16.7 MPa; Table 5). Peel strengths for cured **1** and **2a** bonded to aluminum (510–560 N/m) also are comparable with those of crosslinked BADGE, but both oil-based thermosets show peel strengths (890–930 N/m) to steel that are about 75% higher than that of the conventional epoxy (Table 5).

While we made no effort to develop optimum formulations for amine-cured seed oil compositions, we briefly examined the effects of non-equivalent stoichiometries during crosslinking of **1** and **2a** with MDA and made the predictable observation that use of less than equivalent amounts of the amine degrades properties of the polymer networks. Table 6 shows that $T_g$ of the cured oils drop 26–27 °C when the availability of MDA is adjusted from an equivalent ratio to 0.8 —NH—/epoxy and complete network formation is prevented; this decrease in $T_g$ is of course accompanied by the precipitous loss of flexural modulus and flexural strength noted in Table 6.

### 3.4. Properties of network polymers based on triglycerides *1* and *2* cured with phthalic anhydride

A cursory examination of reactions of triglycerides **1** and **2** with phthalic anhydride (PA), initiated with TBAB as described above, demonstrated that as one would expect, property variations among these materials generally follow trends observed for the triglycerides cured with MDA. Thus, an equivalent of PA reacts with short-chain **2d** to give a network with substantially higher $T_g$ (98 °C) than can be realized with the more mobile **2a** ($T_g = 65$ °C). Of course, neither of these values approach the high $T_g$ (162 °C) obtained for the highly rigid network derived from BADGE cured analogously, and the flexural modulus and flexural strengths of the PA/**2a** composition, as well as those of PA-cured **1**, are far lower than those observed for the BADGE-based network (Table 7).

Table 5
Adhesive properties of **1**, **2a** and BADGE cured with an equivalent of MDA[a] onto steel and aluminum substrates[b]

| Resin no. | Peel strength – steel (N/m) | Lap shear strength – steel (MPa) | Peel strength – aluminum (N/m) | Lap shear strength – aluminum (MPa) |
|---|---|---|---|---|
| **1** | 930 | 22.8 | 510 | 19.3 |
| **2a** | 890 | 19.3 | 560 | 17.9 |
| BADGE | 520 | 18.6 | 510 | 16.7 |

[a] See cure schedule of Table 2.
[b] Data shown are for samples filled with fumed silica and glass micro-beads; see Section 2 for details.

Table 6
Effect of stoichiometry on the properties of **1** and **2a** cured with MDA in the presence of stannous octoate[a]

| Resin no. | MDA equivalency | $T_g$[b] (°C) | Flexural strength[c] (MPa) | Flexural modulus[c] (GPa) |
|---|---|---|---|---|
| **1** | 1.0 | 59 | 56 | 1.5 |
| | 0.9 | 42 | 37 | 0.9 |
| | 0.8 | 32 | 4 | <0.1 |
| **2a** | 1.0 | 55 | 35 | 1.0 |
| | 0.9 | 47 | 30 | 0.7 |
| | 0.8 | 24 | 2 | <0.1 |

[a] Cure conditions are described in Table 2.
[b] Determined by DMS as noted in Table 2.
[c] Determined as described in Table 2.

Table 7
Thermal and flexural properties[a] of various epoxides cured with an equivalent of phthalic anhydride in the presence of TBAB (2 wt% based on epoxy component)

| Resin no. | Cure schedule | $T_g$[b] (°C) | Flexural strength (MPa) | Strain at break (%) | Flexural modulus (GPa) |
|---|---|---|---|---|---|
| **1** | 4 h at 130 °C<br>1 h at 180 °C | 90 | 81 | 6 | 2.1 |
| **2a** | 1 h at 120 °C<br>4 h at 130 °C<br>1 h at 180 °C | 65 | 77 | 9[e] | 2.0 |
| **2d**[c] | 4 h at 130 °C | 98[d] | | | |
| BADGE | 1 h at 120 °C<br>4 h at 130 °C | 162 | 161 | 5 | 3.7 |

[a] Determined using ASTM method D-790.
[b] Determined using DMS as described in Table 2.
[c] Mechanical properties were not evaluated.
[d] Determined using DSC as described in Table 2.
[e] Specimens showed no break.

## 4. Conclusions

Reactions of triglycerides **2** with MDA yield a group of glassy polymers that have adhesive characteristics similar to those of conventional thermosets based on BADGE. While the cured **2** lack the heat resistance and modulus of MDA/BADGE or PA/BADGE compositions, networks obtained from the triglycerides are tougher and more ductile than are the crosslinked BADGE. In terms of mechanical and adhesive properties, network polymers formed from **2** appear to offer little advantage over similarly cured materials prepared from readily available epoxidized linseed (**1**) or soybean oils. However, triglycerides **2**, with their terminal epoxy moieties, clearly are more reactive than are the commercial epoxidized oils, a factor that may provide advantages in formulated systems intended for fabrication of composites or structural parts cured at elevated temperatures.

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