Rubber-Toughening Epoxy Thermosets with Epoxidized Crambe Oil

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ABSTRACT: Epoxidized crambe oil and rapeseed oil were synthesized by reaction of the oils with *m*-chloroperoxybenzoic acid. Formulating the neat epoxidized oils with epoxy-amine systems gave two-phase thermosets with epoxidized crambe oil, but not with epoxidized rapeseed oil. Glass transition temperature, mechanical properties, and fracture toughness of the epoxidized crambe oil thermoset specimen were measured. Fracture toughness values of the epoxy thermosets were increased approximately 100% by both 5 and 10% epoxidized crambe oil. Glass transition temperature and mechanical properties were affected only modestly.

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KEY WORDS: Epoxidized crambe oil, epoxy resin, fracture toughness, rubber toughening, structural applications, thermosets.

Combinations of epoxy resin chemistries and curing agents can be formulated to meet a wide variety of market demands. Epoxy resins are similar to other engineering resins in that they are either brittle, notch-sensitive, or both. For load-bearing purposes, this means that the product may be subject to catastrophic failure. Toughness is a measure of a material's resistance to failure. Numerous methods of defining "toughness" are known, but the most reliable for engineering structural parts are the critical stress intensity factor, K_{IC}, or fracture energy, G_{IC} (1). A major effort over the years focused on improving the toughness of epoxy structural systems. As a result, epoxy resins have been used for structural applications, such as adhesives, encapsulation of electronic devices, and composites, such as electrical laminates, aerospace parts and automotive parts.

Four methods of toughening brittle epoxy resins are known: Type 1—chemically modify with a more flexible backbone; Type 2—increase molecular weight of the epoxy backbone resin; Type 3—decrease crosslink density of the matrix; Type 4—incorporate a dispersed toughener phase in the epoxy matrix.

Sue *et al.* (2) have recently reviewed rubber-toughening of epoxy resins. This method has been most effective and can improve toughness substantially. Sultan and McGarry (3) showed that an epoxy matrix can be toughened by the introduction of a carboxyl-terminated butadiene–acrylonitrile copolymer (CTBN). CTBN forms a separate phase in the epoxy matrix, which terminates cracks and reduces crack propagation, thus preventing catastrophic failure of the plastic part. Qureshi *et al.* (4) reported that the use of 25% epoxidized crambe oil as reactive diluent in bisphenol A and cycloaliphatic epoxy compounds gave improvements in resistance to fatigue crack propagation without significant sacrifice in tensile or impact strength and Young's modulus. Frischinger and Dirlikov (5) showed that epoxidized vegetable oil rubbers would phase-separate from cured or partially cured epoxy/4,4′-diaminodiphenylmethane (DDM) mixtures, and they proposed that the rubbery particles will dissipate part of the impact energy, leading to rubber-toughened epoxy resins. Epoxidized soybean oil (ESO) and vernonia oil (VO), a naturally occurring epoxidized vegetable oil triglyceride based on C_{18} fatty acids, result in one-phase epoxy thermosets—the rubbery prepolymers are necessary to achieve phase separation.

Crambe oil and rapeseed oil have a unique composition compared to most vegetable oils. They have high (45–60%) levels of erucic acid ($C_{22:1}$) (6):

$$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$$
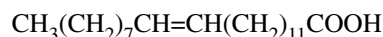
The higher molecular weight of epoxidized crambe oil (ECO) and epoxidized rapeseed oil (ERO) was proposed by Dirlikov *et al.* (7) to make them less miscible than ESO, resulting in phase separation and possible direct substitution for CTBN in rubber-toughening of epoxy matrices without preliminary preparation of the liquid rubbers. This paper reports phase separation in thermoset matrices of diglycidyl ether bisphenol (DGEBA)-DDM-ECO and significant improvements in toughness (K_{IC}) of the epoxy matrices.

EXPERIMENTAL PROCEDURES

Materials. ESO and epoxidized linseed oil (ELO) were obtained from Elf Atochem, Inc. and used as received. Samples of crambe and rapeseed oils were obtained from the United States Department of Agriculture and used as received. Diglycidyl ether bisphenol A epoxy resins were obtained

from Shell Chemical Co. (Houston, TX). DGEBA1 is Epon™ 825 and DGEBA2 is Epon 828. DGEBA1 contains almost pure diglycidyl ether bisphenol A monomer, while DGEBA2 contains about 85% diglycidyl ether bisphenol A monomer and 15% higher oligomers. The amine curing agents used were a modified isophorone diamine adduct (Epotuf™ 37601; Reichhold Chemicals, Research Triangle Park, NC) and DDM (Aldrich Chemical Co., Milwaukee, WI). Carboxyl-terminated butadiene-acrylonitrile copolymer, Hycar™ CTBN 1300x8, was obtained from B.G. Goodrich (Brecksville, OH).

Preparation of epoxidized vegetable oils. Crambe and rapeseed oils were epoxidized by reaction with *m*-chloroperoxybenzoic acid (Aldrich Chemical) by the procedure reported by Chang (6). The degree of epoxidation was determined by iodine and oxirane values by using ASTM D1959-85 and ASTM D1652-87, respectively.

Epoxy resin thermosets. Epoxy resin thermoset panels were prepared from a 1:0.55 stoichiometric mixture of DGEBA2 and DDM in a $7 \times 7 \times 0.125$-in. mold at 70°C. DDM was dissolved in the DGEBA2 at 70°C, and the mixture was poured into the heated molds. Vacuum was applied to remove the majority of air bubbles. The plates contained some bubbles. The cure schedule was 1 h at 75°C, then 48 h at 150°C.

Epoxy resin-CTBN thermoset. A 10% CTBN-epoxy adduct was prepared by blending 10% by weight of CTBN rubber with 90% by weight of DGEBA2 at 71°C and heating the mixture to 150 ± 5°C for 3.5 h with constant stirring under a dry nitrogen purge (8,9). The mixture was cooled to room temperature and stored under a nitrogen blanket. The epoxy equivalent weight (EEW) of the adduct was determined by using ASTM D 1652. The adduct was mixed with a 1:1 stoichiometric amount of modified isophorone diamine adduct curing agent with stirring, and panels were prepared as above.

Epoxy resin–5 and 10% ECO thermoset. The EEW of fully ECO was determined. Then it was blended with DGEBA2 at 70°C, and the resulting resin was mixed with a 1:0.55 stoichiometric amount of the curing agent DDM for the 5% ECO formulation and at 1:0.5 for the 10% ECO formulation. Panels were prepared as described above.

Morphology. Homogeneous formulations (Table 1) of DGEBA1-DDM-ECO with 0, 5, 10, 20, and 30% ECO were cured in test tubes at 75°C for 1 h, and then at 150°C for 48 h. The morphology of the fracture surface of the epoxy thermosets was examined by an Amray Model 1000B (Bedford,

MA) scanning electron microscope after the samples were sputter-coated with gold. The electron micrographs were examined to determine the particle size where two phases existed.

Mechanical testing of the thermosets. The following test properties were evaluated on sets of 8–10 test specimens in an Instron Model 4502 with Series II automated materials testing system v4.05e (Instron Corp., Canton, MA) at the University of Michigan, Materials Science and Engineering Department.

Tensile test. The tensile strength and modulus testing of the thermosets was performed in accordance with ASTM D 638 in the Instron. Test specimens (dogbones) were machined from the molded plates at the instrument shop at the University of Michigan. The dimensions of the test were: width of narrow portion = 0.25 in.; thickness of narrow portion = 1/8 in.; length = 2.5 in. Cross head speed, 0.2 in./min; sample rate, 25 pts/s; temperature, 73°F; humidity, 50%. The width and thickness of the specimens of each type of material was measured. The gauge length of all specimens was set at 0.5 in. Samples were maintained at the environmental conditions for 24 h before testing.

Fracture toughness test. The fracture toughness of the thermosets was measured in terms of the K_{IC} (10). The test was performed with an Instron instrument. Test specimens were machined from the molded plates at the instrument shop at the University of Michigan to the following approximate dimensions: width = 0.5 in.; thickness = 0.125 in.; length = 6 in. Three cracks were made on each specimen bar such that the distance between two adjacent cracks was 1.5 in. The length of the cracks ranged from 0.45 to 0.55 times the width of the specimen. Test type: 3-point bend K_{IC} test. Cross head speed, 0.1 in./s (152.4 mm/min); support span, 2 in. The width, thickness and crack length of each of the specimens was measured.

Glass transition temperature (T_g). The T_g of the thermosets was determined by differential scanning calorimetry (DSC) on a Dupont Thermal Analyzer (Wilmington, DE) 2100 with DSC Model 2920 or by modulating DSC on a TA 2920 DSC.

RESULTS AND DISCUSSION

Epoxidation. The procedure used for the epoxidation of crambe oil and rapeseed oil gave yields of 58 to 95%. Smaller batch sizes of 20–50 g gave higher yields than 100-g batch sizes. The conversion of vegetable oil unsaturation to oxirane was 98%, as shown by the iodine results. The average iodine values for epoxidized crambe and rapeseed oils were 1.6 and 1.98, respectively; the iodine values of the starting oils were 91.3 and 96.8, respectively. The average oxirane values for the epoxidized crambe and rapeseed oils were 373 and 278, also indicating a high level of conversion to the epoxy groups.

Thermoset morphology. Five DGEBA1-DDM-ECO homogeneous formulations were prepared according to Table 1 and used for thermoset preparation. Because DDM has a much higher reactivity with DGEBA than with ECO, it reacts first with DGEBA and forms a rigid DGEBA-DDM phase at 70°C. The ECO, or mixtures with DGEBA, and curing agent sepa-

TABLE 1
DGEBA1-DDM-ECO Formulations for Morphology Tests[a]

ECO (%)	DGEBA (g)	DDM (g)	ECO (g)
0	2.02	1.17	0.00
5	1.91	1.13	0.10
10	1.8	1.11	0.21
20	1.6	1.04	0.41
30	1.42	1.01	0.62

[a]Abbreviations: DGEBA, diglycidyl ether bisphenol A; DDM, 4,4′-diaminodiphenylmethane; ECO, epoxidized crambe oil.
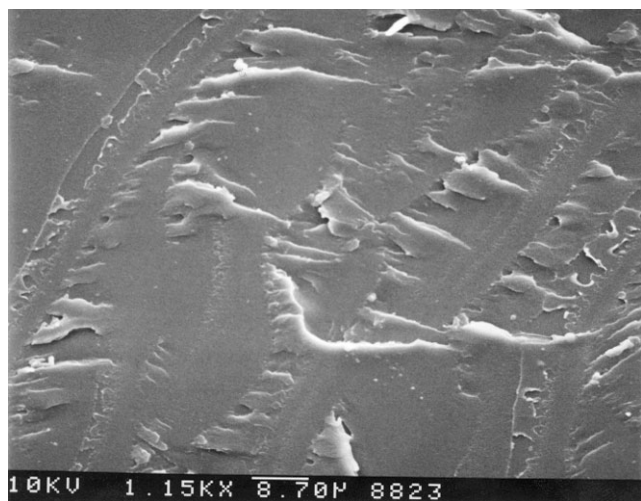
FIG. 1. Scanning electron microscope (SEM) photomicrograph of the fracture surface of diglycidyl ether bisphenol A monomer/4,4'-diamin-odiphenylmethane (DGEBA/DDM).
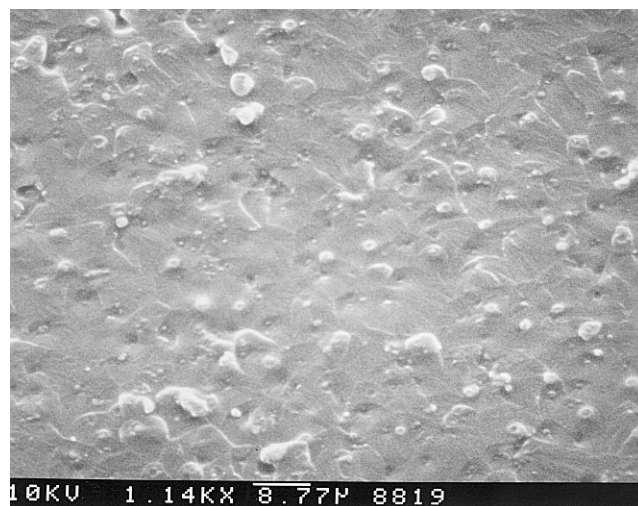
FIG. 3. SEM photomicrograph of the fracture surface of DGEBA/DDM/10% epoxidized crambe oil (ECO). See Figure 1 for other abbreviations.

rates at this stage as a second liquid phase. Montarnal *et al.* (11) discuss the controlling factors in rubber-toughening of epoxy networks, including the cure process, transitions, and morphology. ECO cures at the higher temperature (150ºC) with the unreacted DDM amino groups and crosslinks with the formation of two-phase epoxy thermosets. Scanning electron microscopy shows that the epoxy thermoset without ECO forms a homogeneous one-phase thermoset (Fig. 1), while incorporation of 10% CTBN gives randomly distributed particles about 0.5 micrometers in diameter (Fig. 2).

Phase separation is observed for DDM and diamin-odiphenylsulfone formulations that contain ECO. Table 2 gives a summary of the morphology and particle size distribution for this system. Figures 3 and 4 show electron micrographs of DGEBA-DDM-ECO thermosets with 10% ECO

content. These two-phase thermosets consist of a rigid DGEBA-DDM-ECO epoxy matrix and randomly distributed particles (about 1–2 microns) of presumably DDM-ECO. Craters left by debonded "crambe" particles are clearly distinguished. The amount of craters increases with increasing ECO content. The volume fraction of these ECO particles in formulations with less than 30 wt% ECO is significantly lower than the actual ECO content. This is evidence that ECO is partially soluble in the epoxy-curing agent mixture.

The ECO particles observed in the 30 wt% ECO formulation are much more disparate and include particles up to 1000 microns. These larger particles indicate the beginning of phase inversion.

ECO/DGEBA/DDM formulations that contain 5 and 10 wt% ECO form two-phase thermosets with a continuous rigid
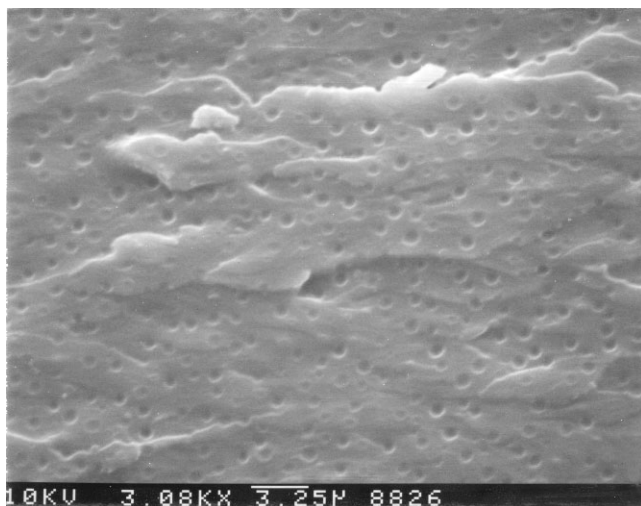
FIG. 2. SEM photomicrograph of the fracture surface of DGEBA/isophorone diamine adduct/10% carboxyl-terminated butadiene-acrylonitrile (CTBN). See Figure 1 for other abbreviations.

FIG. 4. SEM photomicrograph of the fracture surface of DGEBA/DDM/10% ECO. See Figures 1 and 3 for abbreviations.

TABLE 2
Morphology and Particle Size Distribution for DGEBA/DDM/ECO Thermosets[a]

Formulation	Morphology	Dispersed phase	Particle size
DGEBA/DDM	Homogeneous	—	—
5% ECO	Mostly homogeneous	Crambe	2–3 µm
	Some particles		
10% ECO	Two-phase	Crambe	0.9–3.0 µm
20% ECO	Two-phase	Crambe phase	2–40 µm
		Inversion starts	0.1 mm to 1.0 mm
30% ECO	Two-phase	Crambe phase	10 µm to 50 µm
		Inversion	0.25 mm to 0.5 mm

[a]See Table 1 for abbreviations.

DGEBA/DDM matrix and randomly distributed small, spherical, ECO particles of 1–3 µm in size. Particles at the fracture surface of the 5 and 10% ECO systems have undergone partial or complete cavitation, with formation of voids observed as dark circles within the particles or at the particle matrix interface. Once formed, these voids grow on application of stress and dissipate energy. The remaining cavitated rubber is distinctly observed as a lining on their walls. The cavitation phenomenon increases with increasing rubber content. It can greatly enhance the shear yielding process and is the main epoxy-toughening mechanism (12). The matrix surrounding the particles is characterized by a rippled fracture surface with striations. It appears to exhibit plastic shear deformation. During fracture, ejection or debonding of rubbery particles is not observed under the shear deformation. The diamine molecules on the interface react with epoxy groups of both DGEBA and ECO to form chemical bonds between the two phases.

At 20 wt% ECO, particles of 0.25 mm to 1.0 mm are formed. A different morphology is observed with 20 and 30% ECO. These thermosets are characterized by a bimodal particle size distribution. This indicates the beginning of the phase inversion phenomenon.

Epoxidized rapeseed formulations that contained from 5 to 30% ERO formed homogeneous thermosets. All electron photomicrographs of the rapeseed formulations were devoid of any indication of a second phase. No rubbery particles were seen. These thermosets were not examined any further. The epoxidized rapeseed appears to dissolve and plasticize the rigid DGEBA matrix, just as VO and ESO do. Miscibility of epoxidized vegetable oil with DGEBA appears to be related to the molecular weight of the epoxidized oil.

T_g. The T_g of the thermosets are given in Table 3. The T_g declined 5°C (6%) for the 5% epoxidized crambe system, indicating that at least some of the epoxidized oil is compatible with the epoxy and does not precipitate. Table 4 gives the glass transition points of other systems for comparative purposes. The T_g did not decline for the 10% CTBN thermoset. The differential scanning calorimeter results indicate that epoxidized vegetable oils act as relatively miscible flexibilizers for DGEBA/DDM thermosets.

Tensile test. The mean values of the tensile strength and modulus data obtained for samples in this study are compared

in Table 5. The addition of 5–10% ECO and 10% CTBN gave useful tensile strength and tensile modulus values. Table 6 gives tensile test data from the literature for comparison.

Fracture toughness tests. The value of the load at failure, obtained from the three-point bend test, is used in the calculation of the K_{IC}, which is given (10) by

$$K_{IC} = Y P_f \frac{6}{4} \frac{S a^{1/2}}{t w^2} \qquad [1]$$

where K_{IC} = critical stress intensity factor, Y = shape factor, P_f = load at failure, S = length of span, a = crack length, w = specimen width, t = specimen thickness.

The shape factor Y has the form:

$$Y = 1.93 - 3.07\left(\frac{a}{w}\right) + 14.53\left(\frac{a}{w}\right)^2 - 25.11\left(\frac{a}{w}\right)^3 + 25.8\left(\frac{a}{w}\right)^4 \quad [2]$$

The mean values of K_{IC} obtained in this study are compared in Table 7. The toughness of ECO/DGEBA2/DDM formulations was increased approximately 100% for both 5 and 10% ECO thermosets. Half of the 5% ECO test panels had K_{IC} values of 1.8. Comparative studies showed that a 10% CTBN modification increased the Epotuf 37601 thermoset toughness by 149% to a value of 1.89 (Table 8). The 10% ELO rubber increased toughness by 45%.

In conclusion, homogeneous formulations of epoxy resin, DDM, and ECO form two-phase epoxy thermosets. At ECO content below 20 wt%, these thermosets consist of a rigid DGEBA-DDM matrix and randomly distributed ECO particles. Phase inversion starts at about 20 wt% ECO content. Thermosets with 10% ECO were observed to have a signifi-

TABLE 3
Glass Transition Temperature of ECO and ERO Thermosets

Thermoset	ECO, T_g (°C)[a]	ERO, T_g (°C)
0 wt% Epoxy oil/DGEBA2/DDM	86.2	84.5
5 wt% Epoxy oil/DGEBA2/DDM	80.9	83.2
10 wt% Epoxy oil/DGEBA2/DDM	73.9	74.3
20 wt% Epoxy oil/DGEBA2/DDM	65.2	67.3
30 wt% Epoxy oil/DGEBA2/DDM	60.1	61.8
Epoxy oil/DDM	7.4	4.8

[a]Determined on a Dupont Thermal Analyzer 2100, DSC Model 2920. ERO, epoxidized rapeseed oil; T_g, glass transition temperature. See Table 1 for other abbreviations.

TABLE 4
Glass Transition Temperatures of Comparable Thermosets[a]

Thermoset	T_g (°C)[b]
DGEBA2-Epotuf 37601	79.89
10% CTBN	−36.2, 89.06
10% ELSOR	64.93
20% ELSOR	54.14

[a]ELSOR, epoxidized linseed oil rubber; CTBN, carboxyl-terminated butadiene-acrylonitrile. See Tables 1 and 3 for other abbreviations.
[b]Determined on TA 2929 modulating differential scanning calorimeter.

TABLE 5
Tensile Test Results ECO—Epoxy Resin Thermoset

Material	Tensile strength (MPa)	Tensile modulus (MPa)
DGEBA2-DDM (1:0.55)	93.4[a]	3930
5% ECO-DGEBA2-DDM (1:0.55)	75.4	3853
10% ECO-DGEBA2-DDM (1:0.5)	79.3	3619

[a]Average of only three values. See Table 1 for abbreviations.

TABLE 6
Reference Tensile Data for Comparison[a]

Material	Tensile strength (MPa)	Tensile modulus (MPa)
DGEBA2-Epotuf 37-601	67.27	3663
10% CTBN	59.84	3114
10% ELSOR	69.53	3687
10% ESOR	67.67	3701
20% ELSOR	64.14	3112
20% ESOR	52.95	2970
DGEBA1-DDM (13)		2840
20% ESOR		1950
DGEBA1-DDS (13)		3420
10% ESOR		2810
20% ESOR		2100
DGEBA2 - CTBN (12) Clear casting, diethanolamine	57.5	2813
DGEBA2 - CTBN (12) (filled potting compound) diethanolamine	39.8	3577
DGEBA2- Epon Z (10) (filled potting compound)	42.3	2896
DGEBA2-Epon Z -CTBN (10) (filled potting compound)	36.5	3309

[a]See Tables 1 and 4 for abbreviations.

TABLE 7
Fracture Toughness Test ECO—Epoxy Resin Thermoset[a]

Material	K_{IC} (MPa m$^{1/2}$)	Increase (%)
DGEBA2-DDM 1:0.55 DDM	0.76	—
5% ECO-DGEBA2-DDM 1:0.55 DDM	1.51	99
10% ECO-DGEBA2-DDM 1:0.50 DDM	1.64	116

[a]See Table 1 for abbreviations.

TABLE 8
Comparative Fracture Toughness Measurements[a]

Material	K_{IC} (MPa m$^{1/2}$)	Increase (%)
DGEBA2 - Epotuf 37-601 1:1 thermoset	0.75	—
10% CTBN	1.89	152
10% ELSOR	0.91	21
20% ELSOR	1.02	36
DGEBA1 (DDM cured) thermoset (13)	0.75	
20% ESOR	1.33	77
DGEBA1 (DDS cured) thermoset (13)	0.75	
10% ESOR	1.09	45
20% ESOR	1.19	59

[a]ESOR, epoxidized soybean oil rubber (rubbery reaction product of ESBO and amine). See Table 4 for other abbreviation.

lecular weight than ESO and VO, and its phase separation does not require preliminary preparation of a crambe liquid rubber (soluble ECO/DDM prepolymers). ESO and VO have lower molecular weights, and phase separation of their DGEBA-DDM formulations is only observed if their prepolymer rubbers are used for thermoset preparation. The cost of ECO is projected to be less than 1/3 that of CTBN.

ACKNOWLEDGMENTS

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cant increase of 111% in K_{IC} compared to 149% for 10% CTBN, and 45% for ELO rubber. Physical properties, such as T_g and tensile strength, remain acceptable for many applications. Thermosets with only 5% ECO gave a 95% increase in toughness with even less effect on physical properties of the thermoset.

ECO epoxy formulations have an advantage over formulations based on CTBN, ESO, and VO. ECO has a higher mo-

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