

# Curing and Mechanical Characterization of a Soy-Based Epoxy Resin System

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**ABSTRACT:** A potentially inexpensive alternative epoxy resin system based on soybean oil has been developed for polymer composite applications. Epoxidized methyl soyate (EMS) and epoxidized allyl soyate (EAS) have been synthesized at the University of Missouri–Rolla. These materials consist of mixtures of epoxidized fatty acid esters. The epoxidized soy-based resins provide better intermolecular crosslinking and yield materials that are stronger than materials obtained with commercially available epoxidized soybean oil (ESO). The curing behavior and glass transition have been monitored with differential scanning calorimetry.

Neat resin test samples have been fabricated from resin systems containing various amounts of EMS, EAS, and ESO. Standardized tests have shown that the addition of EAS enhances the tensile and flexural properties of the base epoxy resin system. Therefore, epoxidized soy ester additives hold great potential for environmentally friendly and lower cost raw materials for the fabrication of epoxy composites for structural applications. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3513–3518, 2004

**Key words:** resins; composites; soybean

## INTRODUCTION

With the depletion of earth's limited petroleum reserves, the use of renewable resources as replacement materials for industrial products is attracting great interest. Triglyceride vegetable oils represent a major class of such resources and are being used in an increasing number of industrial applications, in addition to being a food source for human beings.<sup>1</sup> These renewable natural resources also hold additional beneficial characteristics, being nontoxic, biodegradable, and, therefore, environmentally friendly. The main components of these triglyceride oils are saturated and unsaturated fatty acids. They can be polymerized to form elastomeric networks and are promising as alternative material resources to petrochemical-derived resins.<sup>2</sup> Emerging applications directly using these fatty acids or their derivatives from some chemical modifications include painting, coating, varnishes, cosmetics, and, more recently, polymers and composites. Of the available plant oils, soybean oil appears to be the most attractive alternative resource because of its very low price and abundant supply, being the

second largest cash crop in the United States of America. The largest category of industrial soybean oil use includes plastics and resins. Epoxidized soybean oil (ESO) is currently mainly used as a plasticizer or stabilizer to modify the properties of plastic resins such as PVC. ESO can be used as a reactive modifier or diluent of epoxy resin systems.<sup>3</sup> ESO also shows potential use as an efficient toughener when large-particle second-phase rubber is formed for epoxy applications.<sup>4,5</sup> Several researchers have investigated the curing and conversion of soybean oil into flexible, semiflexible, and rigid crosslinked polyesters with various approaches.<sup>6–9</sup> These studies show the potential for the synthesis of new polymers derived from renewable soybean oil. More recently, researchers have begun to explore the feasibility of manufacturing polymer composites from ESO. Crivello et al.<sup>10</sup> reported the fabrication and mechanical characterization of glass-fiber-reinforced and ultraviolet-cured composites from epoxidized vegetable oils. So far, widespread structural applications of ESO have been limited because of its low crosslinking density and mechanical performance. The development of soy-based resins for structural applications is still a challenge for the polymer and composite industries.

The goal of this research is the development of inexpensive but enhanced soy-based epoxy resins, namely, epoxidized methyl soyate (EMS) and epoxidized allyl soyate (EAS), from unsaturated soybean oil. We expect that these modified soy-based epoxy

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resins will possess higher reactivity and, therefore, provide denser intermolecular crosslinking and yield materials that are stronger than materials obtained from commercially available unmodified ESO. As a long-term target, using a high content of a soyate coresin will create inexpensive but still high-performance fiber-reinforced composite materials from renewable sources. In this work, the curing behavior and thermal properties of three ESOs were investigated and compared by thermal analysis. Coresin systems with conventional epoxy were developed, and the effects of the soy-based resins on the mechanical properties were extensively studied.

## EXPERIMENTAL

### Materials

Shell Epon 9500 and Epicure 9550 (Shell Chemical Co., Houston, TX) were selected as the base epoxy resins. Epon 9500 was specifically designed for pultruding composites, and it can be processed at high line speeds with low pull loads and good quality. Commercial ESO was obtained from Witco Corp. (Oakland, NJ). Modified soy-based resins (EMS and EAS) were synthesized with a laboratory-scale two-step process from food-grade soybean oil. First, large molecular triglycerides were transesterified to yield fatty acid methyl ester and allyl ester with methyl alcohol and allyl alcohol, respectively. Second, the fatty acid esters were epoxidized to yield soyate epoxy resins. The epoxidation of the carbon-carbon double bond of the unsaturated vegetable oil proceeded without molecular rearrangement (some procedures have been developed for the epoxidation of unsaturated fatty acid esters and vegetable oils<sup>11-14</sup>). *m*-Chloroperoxybenzoic acid was selected as an epoxidizing agent.

### Preparation of the coresin system

In this work, soy-based coresin systems were prepared with two kinds of curing methods. In the initial experiment, all coresin formulations were prepared by the direct mixing of three kinds of epoxidized soyate resins into the base Epon resin and one-step curing. The following weight ratios of Epon epoxy to epoxidized soyate resin were used: 100%/0%, 90%/10%, 80%/20%, and 70%/30%. Then, a hardening agent was added at a ratio of 100/33, mixed well, and degassed for a few minutes. For the glass-transition temperature ( $T_g$ ) and mechanical testing, resin mixtures were poured into a preheated mold, which was first treated with a Chemlease 41 mold-release compound (Howell, MI). The cure reaction was performed in an oven with hot-air circulation. The resin mixtures were kept at 177°F for 1 h; then, the temperature was

ramped to 350°F, and the curing process was held for 1.5 h.

For the two-step curing method, the prepolymer was first prepared from ESO, EAS, and EMS by the reaction of these epoxidized soyate resins with the highly reactive curing agent para-amine cyclohexylmethane (PACM) (Air Products, Lehigh Valley, PA) with a weight ratio of 10/4 at 320°F for around 1 h. The curing temperature and time were carefully controlled and adjusted for each type of soyate resin so that the resin was kept in the gelation state. A relatively shorter heating time and a relatively lower temperature were used for the EAS prepolymer preparation. These prepolymers were still soluble in the base Epon epoxy mixture.

### Differential scanning calorimetry (DSC) analysis

DSC was used to study the curing characteristics and thermal transition properties for the neat soy-based resin and Epon coresin on a thermal analyzer (DSC 2010, TA Instrument, New Castle, DE). A nonisothermal process was run to investigate the reactivity of ESO, EAS, and EMS with the amine curing agent. A temperature program from 25 to 250°C at a heating rate of 10°C/min was used. The measurement of  $T_g$  by DSC was carried out over a temperature range from -50 to 200°C at a heating rate of 5°C/min.

### Mechanical testing of the cured neat resin

The mechanical properties were tested on thermosets cured from the soyate-based coresin system. Five specimens were tested for each set of resin formulations. Tensile tests were performed on an Instron 4204 test machine (Canton, MA) in accordance with ASTM D 638. It was equipped with an extensometer for the determination of the longitudinal strain. IBM 4500 PC interface series IX software (Armonk, NY) was installed for data acquisition. Each coupon specimen was tested to failure at 23°C at a crosshead speed of 10 mm/min. Flexural strength and modulus tests were performed on an Instron 4204 test machine with a three-point flexure jig according to ASTM D 790. The support span length was 5 cm. The head speed was 5 mm/min.

## RESULTS AND DISCUSSION

### Curing reactivity of the soy-based resins

The ESO molecule contains an epoxy functionality group. When ESO reacts with the curing agent, epoxide rings are opened and form new chemical chains with amine molecules; therefore, a crosslinked polymer network can be formed. For an epoxidized soyate resin, the degree of epoxidation controls the polymer-

ization process. Only with enough epoxide group functionalities is the crosslinking reaction possible. The current conversion of unsaturated soybean oil fatty acids into epoxidized soyate resin is around 85%. Two possible reasons are assumed: (1) terminal carbon-carbon double bonds are relatively difficult to epoxidize, and (2) some of the epoxide rings might be opened again by residual acid during the last separation and washing step. At low epoxidation degrees below 65%, neat EMS and EAS are very hard to cure.

The curing agent also plays an important role in the curing of ESO because of the internal epoxy groups and low reactivity. Several kinds of curing agents were selected to investigate the curing of ESO: PACM, tetraethylene pentamine (TEPA), Ancamine K54, Epicure 9550, and Epicure 9551. The catalyst was EMI-24. The multifunctional amine PACM was selected as a curing agent because of its high reactivity with ESOs.

Nonisothermal DSC was run to investigate the curing reactivity of ESO, EAS, and EMS with the amine curing agent. Table I compares the curing processes by DSC. The resin formulation is represented by the weight content with different concentrations of epoxidized soy-based resins (10–30%). The results prove that the reactivity of soy-based epoxy resins increases through the transesterification of large-molecule ESO into short-chain esters and the addition of more epoxide functional groups. EAS possesses the highest reactivity, and a more exothermic curing reaction occurs. For EMS, no apparent improvement has been observed over ESO because of the very low degree of epoxidation achieved so far. Moreover, there are 15% nonreactive palmitic and stearic structures and 20% monofunctional oleic structures.

### Measurement of $T_g$

Pure epoxidized soyate resins

$T_g$  gives an indication about the crosslinking density of a polymer. The literature generally shows that ESO

**TABLE I**  
Curing Reactivity of Coresin Systems as a Function of Resin Components

Resin formulation	Heat of reaction (J/g)	Exothermic peak (°C)	Time to peak (min)
Epon epoxy	356	128	9.70
10 wt % ESO	354	129	10.28
20 wt % ESO	334	132	10.71
30 wt % ESO	265	134	10.86
10 wt % EAS	360	125	10.00
20 wt % EAS	347	128	9.60
30 wt % EAS	276	132	9.49
10 wt % EMS	358	129	10.05
20 wt % EMS	310	130	10.38
30 wt % EMS	257	134	10.65

**TABLE II**  
Comparison of  $T_g$  Values for Various Resin Formulations

Resin formulation	One-step-curing $T_g$ (°C)	Two-step-curing $T_g$ (°C)
Epon epoxy	74.8	74.8
10 wt % ESO	69.1	72.3
20 wt % ESO	61.2	67.0
30 wt % ESO	54.2	61.9
10 wt % EAS	72.5	75.1
20 wt % EAS	63.0	69.2
30 wt % EAS	58.4	65.0
10 wt % EMS	64.0	68.0
20 wt % EMS	54.2	63.3
30 wt % EMS	47.1	55.3

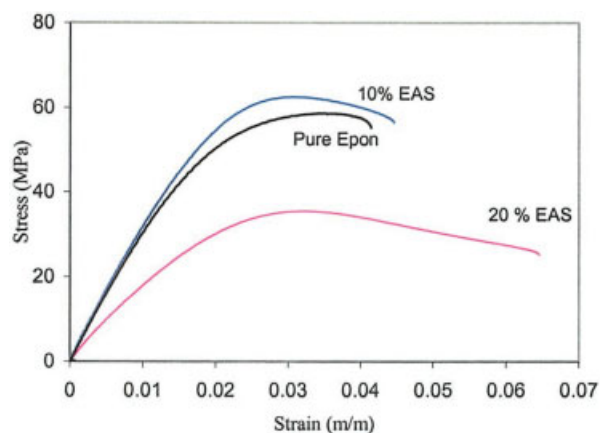
reacts with commercial diamines to form elastomers at room temperature that have fairly low  $T_g$  values in the range of  $-70$  to  $0^\circ\text{C}$ .<sup>4</sup> ESO reacts very slowly with the Epicure 9550 curing agent because of the low reactivity of the internal epoxy.  $T_g$  of Witco ESO cured with Epicure 9550 was very low (only  $-20^\circ\text{C}$ ). EMS was not cured at all and remained in the liquid state. EAS cured with Epicure 9550 had a slightly higher  $T_g$  at  $-5^\circ\text{C}$ . PACM was found to be a much more reactive curing agent for Witco ESO, EAS, and EMS. As expected, EAS cured by PACM had the highest crosslinking density and the highest  $T_g$  value ( $20^\circ\text{C}$ ). The final thermosets were relatively rigid polymers, whereas Witco ESO had a  $T_g$  of only  $12.5^\circ\text{C}$ , and EMS had a  $T_g$  of  $2.6^\circ\text{C}$ . Pure EAS cured by PACM was stiffer and rigid than Witco ESO.

Soyate resin/epon epoxy copolymer: one-step curing

To evaluate the effect of a soy-based resin additive on the crosslinking density of a epoxy matrix, we conducted a series of  $T_g$  measurements on various coresin formulations. First, samples from direct one-step curing were investigated. The DSC results for all the formulations showed a single glass-transition region, indicating that Epon epoxy and ESO, EMS, and EAS were molecularly miscible and formed copolymers with a curing agent. The direct mixing of ESO, EMS, and EAS with Epon epoxy led to a decrease in  $T_g$  of the final cured thermosets, as shown in Table II. The decrease in  $T_g$  was lowest for EAS-containing formulations, indicating higher crosslinking density. EMS formulations showed the maximum  $T_g$  decrease because of the lowest degree of epoxidation. The results were not unexpected because EMS contains methyl stearate and methyl palmitate, which are devoid of oxirane functionalities and do not react with the curing agents. These EMS components merely act as plasticizers. It was reasonable to believe that ESO partially reacted with the curing agent and that the unreacted portion plasticized the base Epon resin.

### Soyate resin/epoxy copolymer: two-step curing

According to the  $T_g$  results for the thermosets cured with one-step curing, ESOs had fairly low crosslinking with the base Epon 9500/9550 system as a result of the reduction of the transition temperature. Only partial soyate resins appeared to participate in the epoxy polymer network. Directly blending the soy-based resins into the base epoxy system limited their utilization at low content levels of only 20 wt % without much sacrifice of thermal properties. Because of the big reactivity difference between epoxidized soyate and Epon epoxy, a two-step curing process was developed to increase the incorporation of epoxidized soyate resins into the epoxy matrix structure network. The multifunctional amine-curing agent PACM has a primary amine to react with the epoxy ring of the soyate resin and has another hydrogen-forming secondary amine. This secondary amine is still active and can continue to react with the base epoxy resin and form a crosslinked structure. In this way, soyate resins are expected to participate in the crosslinking reaction more easily and thoroughly and, therefore, can form interpenetrating copolymer networks with the base Epon epoxy and contribute to the strength of the whole resin matrix. A higher crosslinking density can, therefore, be obtained. Table II compares  $T_g$  values from the one-step and two-step curing methods. All soyate resin formulations using the two-step curing method showed significant improvements in  $T_g$ . For example,  $T_g$  increased 7.8°C for the 30 wt % ESO formulation in comparison with one-step curing. Low levels of soyate resins (10 wt %) had a very minor effect on  $T_g$  of the final cured thermosets. As expected, the EAS formulation offered the highest crosslinking density and  $T_g$ . Only a 9°C reduction of  $T_g$  was observed for the 30 wt % EAS formulation. This was because EAS possessed more epoxide groups at the



**Figure 1** Ductility behavior of soyate coresins from one-step curing.

**TABLE III**  
Tensile Properties of Neat Resins from One-Step Curing

Resin formulation	Young's modulus (MPa)	Peak strength (MPa)	Peak strain (%)
Epon epoxy	3041	58	3.9
10 wt % ESO	3145	59	4.3
20 wt % ESO	2807	51	10.9
30 wt % ESO	2434	36	28
10 wt % EAS	3193	60	4.4
20 wt % EAS	2972	53	4.1
30 wt % EAS	2979	41	5.1
10 wt % EMS	2952	54	1.7
20 wt % EMS	2890	45	2.4
30 wt % EMS	2621	31	1.0

terminal position and higher reactivity; as a result, the copolymer crosslinking density increased.

### Mechanical properties of the thermosets from the soyate coresins

Generally, two-phase toughening by ESO<sup>4</sup> can result in a dramatic decay of the tensile strength with a higher content of vegetable oil. The modulus was reduced almost by half with 30 wt % ESO rubbers. In this work, with enhanced soy-based resin formulations, the reduction of the mechanical properties was less pronounced, and this indicated at least some of the soyate resin participated in the crosslinking reaction, rather than acting only as a plasticizer or toughening agent. With the Epon 9500/9550 system and a new batch of soy-based epoxy resins with a higher degree of epoxidation, neat resin panels with up to 30 wt % soyate resin were fabricated successfully. A series of tensile and flexural tests were performed to study the effects of soy-based resins. All specimens with soyate resins showed large yields before breaking. The higher proportion of epoxidized soyate resins resulted in a more ductile behavior with the one-step curing process. High elongation (up to nearly 50%) was observed with only 20 wt % ESO; 36% was observed with 30 wt % EAS. Figure 1 compares the ductility behavior of the EAS formulation and the base epoxy resin. Obviously, these flexibility properties in the resin matrix were the result of larger molecular weight soybean oil. As shown in Table III, these increases in the ductility were accompanied by corresponding decreases in the ultimate strength and modulus. For the EMS formulation, a relatively brittle matrix was obtained because of the small molecule and low epoxidation degree. Witco ESO formulations gave the highest tensile strain and flexibilized final thermosets.

Tables III and IV present the tensile and flexural properties for various formulations. The highest modulus and strength were observed for the EAS formu-

**TABLE IV**  
Flexural Properties of Neat Resins from One-Step Curing

Resin formulation	Flexural modulus (MPa)	Flexural strength (MPa)
Epon epoxy	3021	110
10 wt % ESO	3117	106
20 wt % ESO	2841	93
30 wt % ESO	2641	79
10 wt % EAS	3214	112
20 wt % EAS	2959	100
30 wt % EAS	2579	89
10 wt % EMS	3310	107
20 wt % EMS	2917	88
30 wt % EMS	2510	70

**TABLE V**  
Tensile Properties of Neat Resins from Two-Step Curing

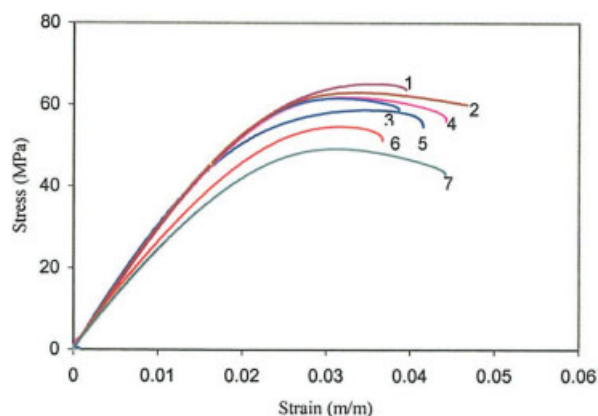
Resin formulation	Young's modulus (MPa)	Peak stress (MPa)	Peak strain (%)
Epon epoxy	3041	58	3.9
10 wt % ESO	3076	63	5.4
20 wt % ESO	3034	60	4.5
30 wt % ESO	2738	50	4.7
10 wt % EAS	3359	63	3.9
20 wt % EAS	3207	58	3.6
30 wt % EAS	2945	54	3.4
10 wt % EMS	3483	53	1.9
20 wt % EMS	3234	46	3.1
30 wt % EMS	3131	45	2.7

lation. With a 10 wt % content of all the soyate resins, the modulus and strength were even improved somewhat over those of the base Epon epoxy system. However, the properties degraded dramatically with an increase in the soyate resin content up to 30 wt %. For the one-step curing process, the direct mixing of the soyate resins with the base epoxy prevented the soyate resins from fully participating in the crosslinking because of the low reactivity. Therefore, the resulting crosslinked thermosets were plasticized by only partially reacted soyate resins at high contents. For the one-step curing process, the use of these soyate resins was limited to 20 wt % without much degradation of the mechanical strength.

With the two-step curing process, significant property improvements were obtained. All the formulations with epoxidized soyate resins at low contents showed improvements over the mechanical properties of the base epoxy resin, especially the flexural modulus and yield strength, as shown in Tables V and VI. With the two-step curing process, soyate resins formed prepolymers with the highly reactive curing agent PACM first. The primary amine in PACM re-

acted with the epoxide groups in the soyate resins and formed secondary amine. The unreacted secondary amine continued to react with the Epon epoxy resin during the second step of the curing process; consequently, a copolymer network could form among the epoxidized soyate resins, base epoxy resin, and amine curing agent. By the two-stage curing method, most ESO could be incorporated into the polymer structure. When copolymerization was achieved, soyate resins could contribute more to the strength. At higher soy-based resin contents (up to 30 wt %), the tensile properties began to decrease but were much less pronounced. As a matter of fact, the flexural properties did not show any degradation at 20 wt %. This result shows that the potential exists for adding more soy-based resins as supplements for epoxy resins when a further improved epoxidation degree is achieved.

EAS afforded higher glass transitions and higher stiffness and strength. These thermal and mechanical improvements were attributed to the modified fatty acid compositions with a greater epoxy functionality of oils. The intermolecular bond was easily formed between the epoxy and curing agent. With increasing functionalities and reactivity, the resulting networks were more densely crosslinked, and this resulted in higher glass transitions, strength, and stiffness than



**Figure 2** Stress-strain curves of various coresin systems (1: 10% EAS; 2: 10% ESO; 3: 20% EAS; 4: 20% ESO; 5: neat Epon; 6: 30% EAS; 7: 30% ESO).

**TABLE VI**  
Flexural Properties of Neat Resins from Two-Step Curing

Resin formulation	Flexural modulus (MPa)	Flexural strength (MPa)
Epon epoxy	3021	110
10 wt % ESO	3234	119
20 wt % ESO	3090	111
30 wt % ESO	2910	99
10 wt % EAS	3503	127
20 wt % EAS	3359	123
30 wt % EAS	2979	103
10 wt % EMS	3214	115
20 wt % EMS	3083	110
30 wt % EMS	2841	98

for unmodified ESO. Conversely, the use of lower molecular weight EMS may have stiffened the matrix but reduced the strength dramatically because EMS had a low epoxidation degree at this stage and few sites reacted with the curing agent. Therefore, some portion of the curing agent probably was not consumed and made the final cured panel relatively brittle with high modulus and low strength. Also, EMS had palmitic and stearic fatty acids, which had no epoxy functionality and had no capacity for crosslinking. These nonreactive parts existed as dangling structures and plasticized the resin.

### CONCLUSIONS

Two novel families of epoxidized soy-based resins for epoxy composites were developed from modified natural soybean oil. The materials were synthesized through a two-step process. The additives possessed functional epoxy groups, which could form flexible crosslinked structures with a suitable curing agent. Because of the increased intermolecular reactivity, these materials offered distinct advantages in curing over ESO. The resulting networks were more densely crosslinked, and this resulted in higher glass transitions, strength, and modulus. When copolymerization was achieved, the addition of EMS and EAS to a commercial epoxy resin yielded a viable low-cost, high-performance thermoset product. The results showed that the addition of EAS improved the mechanical properties; the EAS-augmented materials ex-

hibited the highest  $T_g$ 's, greater stiffness, and superior strength. EAS offers the greatest potential for the synthesis of new polymers derived from renewable soybean oil. This research promises innovative methods for developing inexpensive polymer materials from renewable soybean oil for composite applications with enhanced strength and modulus.

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