

# A Potential Biodegradable Rubber—Viscoelastic Properties of a Soybean Oil-Based Composite

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**ABSTRACT:** Scientists are more and more interested in biodegradable materials owing to their environmental advantage. We investigated viscoelastic properties of a newly developed biomaterial made from epoxidized soybean oil (ESO). ESO cross-linked by triethylene glycol diamine exhibited viscoelastic solid properties. The storage modulus ( $G'$ ) was  $2 \times 10^4$  Pa over four frequency decades. The phase angles were 14–18°. Stress relaxation measurements showed that there was no relaxation up to 500 s. From the plateau modulus we estimated that the M.W. of this cross-linked soybean oil was on the order of  $10^5$ . The composites of cross-linked ESO with three different fibers had 50 times higher elasticity ( $G'$ ) than those without fiber. Phase shifts were the same as those of cross-linked oil without fibers, but the linear range of rheological properties was much narrower than that of the material without fibers. All these results indicated that this new biopolymer made from soybean oil exhibited strong viscoelastic solid properties similar to synthetic rubbers. These rheological properties implied that this biomaterial has high potential to replace some of the synthetic rubber and/or plastics.

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**KEY WORDS:** Biodegradable material, rheology, soybean oil, viscoelastic properties.

Because of environmental concerns, the commercial utilization of biological polymers has become an active research area during the past few decades (1–3). Biopolymers have potential advantages compared with synthetic petroleum polymers owing to their biodegradable properties and, in many cases, lower cost. Since soy-based composites contain FA residues that can be readily attacked by lipase-secreting bacteria, the family of materials is generally regarded as biodegradable. Annually, the United States produces about one billion pounds of soybean oils in excess of current commercial demand. This excess capacity has resulted in lower prices for soybean oils as well as other agricultural commodities. New fields of use for these materials need to be developed and exploited. In recent years, polymer scientists have shown increased interest in research in this field (4).

Soybean oil is composed of TG with structures of double bonds. By reacting with peroxide compounds, soybean oil can be converted into epoxidized soybean oil (ESO). Wool *et al.* (5,6) reported that epoxy-containing soybean oil could be synthesized into new polymers suitable for liquid molding. Liu *et al.* (7) recently developed a new polymer using ESO. ESO was cross-linked into a polymer by thermal polymeriza-

tion with triethylene glycol diamine (TGD). This new composite behaves as a rubber-like elastomer. In order to develop its usage and application, its mechanical and rheological properties need to be investigated.

In this paper, the viscoelastic properties of TGD-polymerized ESO with and without fibrous fillers are studied. The rheological properties of this new biopolymer indicate that it behaves largely as a rubber-like material.

## MATERIALS AND METHODS

**Materials.** ESO was obtained from Elf Atochem Inc. (Philadelphia, PA) and used as received. Triethylene glycol diamine (brand name Jeffamine EDR-148) was obtained from Huntsman Corporation (Houston, TX). Thixotropic agent Aerosil R805 was obtained from Degussa Corp. (Ridgefield Park, NJ). Franklin fiber H-45 was provided by the United States Gypsum Company (Chicago, IL). Wollastonite mineral fiber is a surface-modified wollastonite, an inorganic mineral reinforcement, and was obtained from Intercorp Inc. (Milwaukee, WI). Milled E-glass (electric glass) fiber with a nominal length of 1/32 inch and diameter of 10  $\mu\text{m}$  was purchased from Sigma Chemical Company (St. Louis, MO).

**Composite preparations.** ESO with or without fibrous filler was mixed with Aerosil R805 in the ratio of 13 g/100 g ESO. The mixture was degassed in a vacuum system at 55°C for 30 min. The mixture was removed from the vacuum oven and cooled to room temperature. The fiber mixture had a slurry-like appearance. The mixture produced without fiber possessed an oil-like appearance. TGD (Jeffamine EDR-148) was added to the mixture in the ratio of 37 g/100 g ESO and agitated manually with a spatula to ensure extensive mixing. The sample was placed on the plate fixture of the rheometer and the measurements were taken directly.

**Measurements.** A strain-controlled Rheometric ARES rheometer (Rheometric Scientific, Inc., Piscataway, NJ) was used to perform the rheology studies. A 25- or 50-mm diameter cone and plate geometry was adopted. The cone angle was 0.04 rad. The temperature was controlled at  $150 \pm 0.1^\circ\text{C}$  by an air convection oven or at  $25 \pm 0.1^\circ\text{C}$  by a water circulation system. A steady shear experiment was performed on the ESO. Linear viscoelastic measurements were conducted for the cross-linked ESO with and without fibers. To ensure that all the measurements for the cross-linked materials were made within the linear viscoelastic range, a strain-sweep experiment was conducted initially. The sample was incubated in the rheometer at 150°C for more than 24 h prior to the start of the experiments. A strain-sweep measurement was made

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first. An applied shear strain valued in the linear range was adopted for the other viscoelastic property measurements for the same material; fresh samples were used for each experiment. Linear viscoelasticity indicates that the measured parameters are independent of applied shear strain. Time-sweep experiments were conducted to monitor the gelation process with time. Small-amplitude oscillatory shear experiments were conducted over a frequency ( $\omega$ ) range of 0.01–100 rad/s, yielding the shear storage ( $G'$ ) and loss ( $G''$ ) moduli. The storage modulus represents the nondissipative component of mechanical properties. The elastic or “rubber-like” behavior is suggested if the  $G'$  spectrum is independent of frequency and greater than the loss modulus over a certain range of frequency. The loss modulus represents the dissipative component of the mechanical properties and is characteristic of viscous flow. The phase shift or phase angle ( $\delta$ ) is defined by  $\delta = \tan^{-1}(G''/G')$ , and indicates whether a material is solid with perfect elasticity ( $\delta = 0^\circ$ ), or liquid with pure viscosity ( $\delta = 90^\circ$ ), or something in between. Stress relaxation experiments measured the stress relaxation with time after the material was subjected to a step increase in shear strain. The plateau modulus, obtained using the method of Xu *et al.* (8), indicates that the measured stress relaxation modulus is nearly constant over a measured range of time.

The density of the composite without fiber was measured using the method of Rabek (9).

## RESULTS AND DISCUSSION

TGD (Jeffamine EDR-148) can react chemically with the epoxy group of ESO at high temperature, which will cross-link small ESO molecules into a 3-D thermoset network (7). The structure of ESO is analogous to that of soybean oil; thus, properties of ESO are similar to soybean oil. ESO itself behaved as a viscous Newtonian fluid (Fig. 1). Its viscosity was  $374 \pm 3$  cP at  $25^\circ\text{C}$ , and  $6.0 \pm 0.5$  cP at  $150^\circ\text{C}$ . Owing to the low viscosity of ESO at  $150^\circ\text{C}$ , data at low shear rates could not be accurately measured (Fig. 1). The viscosity of ESO was independent of shear rate at both 25 and  $150^\circ\text{C}$ . When ESO was mixed with TGD (Jeffamine EDR-148), the material gradually showed viscoelastic behavior as the chemical cross-linking reaction progressed (Fig. 2). At the beginning,  $G'$  data were noisy and not reliable due to the sensitivity of the rheometer. After about 6 h,  $G'$  quickly increased. The  $G'$  value became stable after more than 20 h, which means that the chemical reaction of ESO and TGD (Jeffamine EDR-148) requires a fair amount of time to achieve full cure. According to Liu *et al.* (7), this reaction is temperature dependent. The higher the temperature, the faster the reaction will be. At the equilibrium temperature of  $150^\circ\text{C}$ , the material exhibited viscoelastic solid properties (Fig. 3). The  $G'$  curve had a plateau of  $2 \times 10^4$  Pa over four frequency decades. The  $G''$  also had a plateau on the order of  $5 \times 10^3$  Pa. The phase shifts were  $14$ – $18^\circ$ . The shapes of  $G'$  and  $G''$  curves were very similar to those of rubber (10). At room temperature, the  $G'$  value is expected to be higher than that at  $150^\circ\text{C}$ . According to Liu *et al.* (7), the dynamic mechanical analysis of this cross-linked

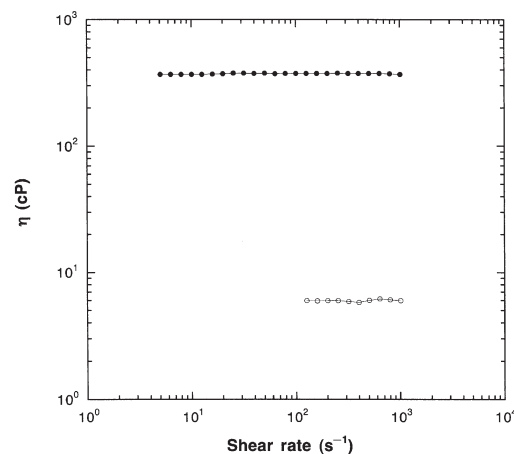


FIG. 1. The viscosity of epoxidized soybean oil at  $25^\circ\text{C}$  (filled symbols) and  $150^\circ\text{C}$  (open symbols).

ESO composite had a modulus on the order of  $5 \times 10^6$  Pa. The  $G'$  and phase angle of highly cross-linked rubber are approximately  $10^7$  Pa and  $11^\circ$ , respectively. The viscoelastic properties of this material made by cross-linking ESO are very close to the properties of other highly cross-linked thermoset rubbers (11). The stress relaxation measurements showed that there was no relaxation for up to several hundred seconds (Fig. 4). The plateau modulus ( $G_e$ ) was  $2.2 \times 10^4$  Pa. This result further supported the theory that the material was not only a viscoelastic solid but also tightly cross-linked. In addition, the stress relaxation data showed almost no differences from 0.05 to 2% initial step strain, implying that the linear range of the properties was wide. The strain sweep experiment of cross-linked ESO is displayed in Figure 5. The linear range was up to 70% of strain, indicating that the material is quite solid-like and tightly cross-linked.

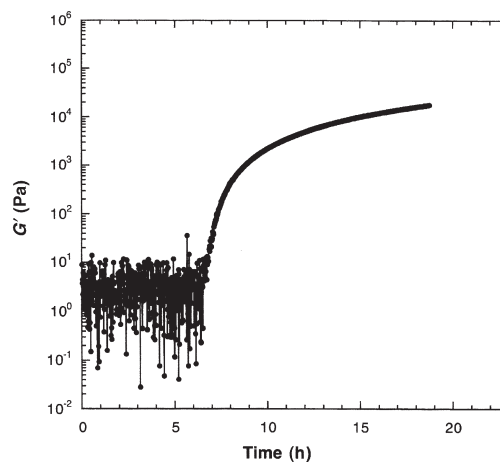


FIG. 2. The storage modulus ( $G'$ ) of the material during chemical reaction occurring between epoxidized soybean oil and triethylene glycol diamine (Jeffamine EDR-148; Huntsman Corp., Houston, TX).

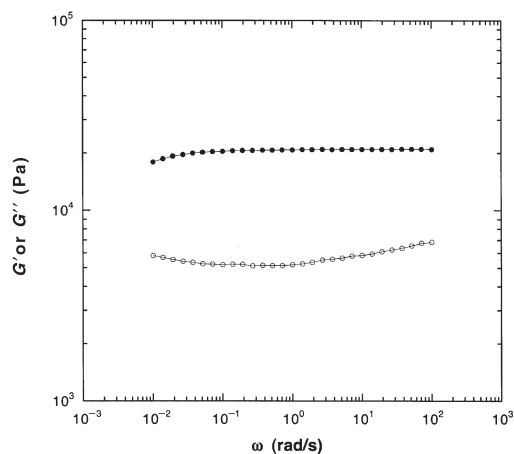


FIG. 3. The linear viscoelastic properties of the cross-linked epoxidized soybean oil at 150°C. Filled symbols,  $G'$ ; open symbols,  $G''$ .

An estimate of the M.W. for the cross-linked material can be obtained from the equation  $G_e = \rho RT/M$  (12), in which  $G_e$ ,  $\rho$ , and  $M$  are the plateau modulus, density, and M.W., respectively. The density of this cross-linked ESO composite was measured at room temperature to be 1.474 g/cm<sup>3</sup>. Assuming that the density was not changed much at 150°C, one estimates that the M.W. between cross-links for the ESO thermoset was in the order of 10<sup>5</sup> g/mol. This M.W. is much greater than that of oil itself (*ca.* 50 g/mol). In addition, some of the synthetic rubbers, such as polyisoprene, polyvinyl ethylene, and polybutadiene, have M.W. in this order (11). These results imply that there may be a high potential for using this new kind of composite to replace synthetic rubber and/or plastics.

When ESO was polymerized in the presence of some fibers, the material exhibited a somewhat different behavior (Figs. 6–8). A time-sweep measurement of ESO with E-glass fiber is illustrated in Figure 6. At the beginning of the cross-linking reaction, material with glass fiber already had viscoelastic properties. Apparently, this is due to the fiber's solid

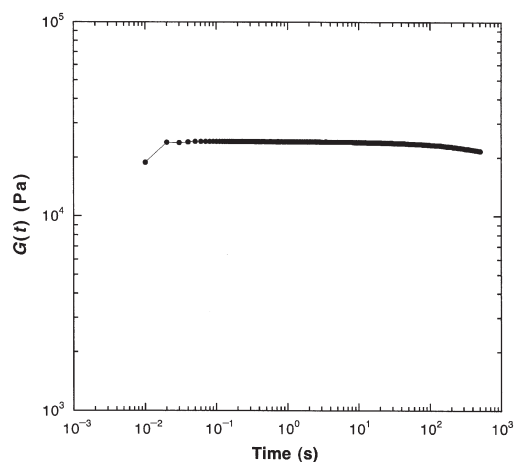


FIG. 4. Stress relaxation measurement of the cross-linked epoxidized soybean oil at 150°C. The initial step strain was 0.1%.

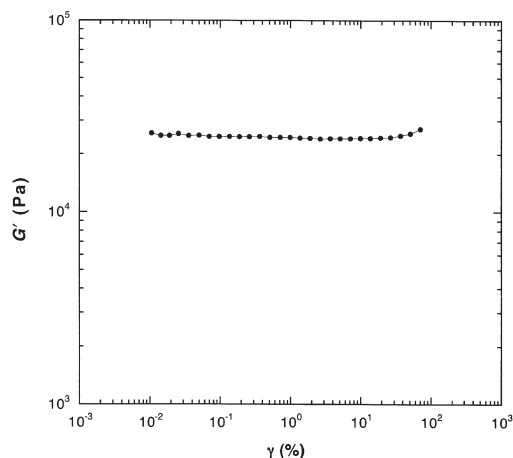


FIG. 5. Strain-sweep experiment of the cross-linked epoxidized soybean oil at 150°C.

behavior. For the fiber-filled system, it also took about 20 h for  $G'$  and  $G''$  to reach equilibrium. The cross-linked ESO with Franklin fiber and Wollastonite mineral fiber had properties identical to the ESO with E-glass fiber (data not shown). Both  $G'$  and  $G''$  of all three materials with different fibers were greater than those of material without fibers as expected. The plateau storage modulus of cross-linked ESO with all three fibers was on the order of 10<sup>6</sup> Pa, which was 50 times greater than that of cross-linked ESO without fibers (Fig. 7). The phase shifts of the materials with the three different fibers were 14–18°, which were the same as the cross-linked ESO without fibers. This implied that the viscoelastic properties of this material were mainly controlled by cross-linked ESO. Fibers functioned only as fillers, which were not cross-linked together with ESO molecules. The strain-sweep measurements of cross-linked ESO with two different fibers are presented in Figure 8. The linear range was below 0.05%

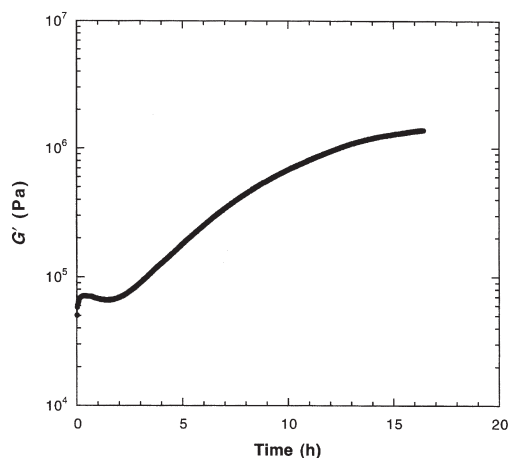
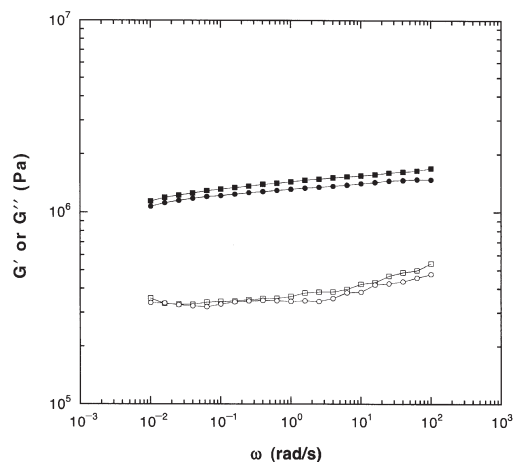


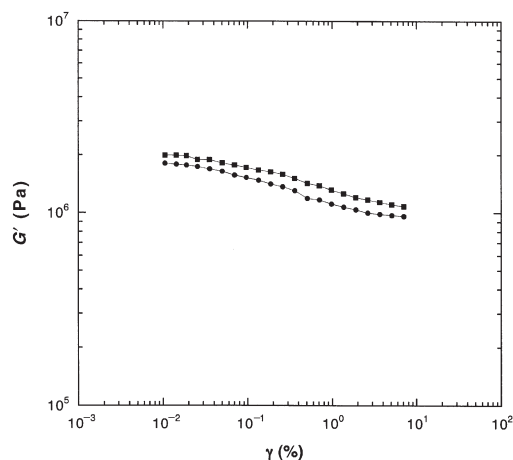
FIG. 6. The storage modulus ( $G'$ ) of the material during the chemical reaction occurring between epoxidized soybean oil and triethylene glycol diamine (Jeffamine EDR-148) when epoxidized soybean oil was mixed together with E-glass fiber.



**FIG. 7.** The linear viscoelastic properties of the cross-linked epoxidized soybean oil with two different fibers at 150°C. Square symbols, ESO with Wollastonite mineral fiber; circle symbols, ESO with E-glass fiber. Filled symbols,  $G'$ ; open symbols,  $G''$ .

of the shear strain. The rheometer could not test this material at 150°C above 10% of shear strain due to the torque range of the instrument. But it was clear that the linear range of cross-linked ESO with fibers was much smaller than that of the material without fiber. The glass fillers contributed markedly to the measured viscoelastic properties of the cross-linked ESO materials. For instance, the elastic modulus of E-glass fiber is on the order of  $10^9$  Pa at room temperature (13). However, molecularly, fibers only physically interacted with oil molecules but were not chemically cross-linked with them. Therefore, the macro properties of cross-linked ESO with fibers showed stronger viscoelastic properties than those without fibers, but the linear range became much smaller.

In summary, ESO cross-linked by TGD exhibited strong viscoelastic solid properties.  $G'$  was independent of frequency over four frequency decades and was equal to  $2 \times 10^4$



**FIG. 8.** Strain-sweep experiment of the cross-linked epoxidized soybean oil with two different fibers at 150°C. Square symbols, ESO with Wollastonite mineral fiber; circle symbols, ESO with E-glass fiber.

Pa. The phase angles were 14–18°. The cross-linked ESO composites with three different fibers yielded a 50 times higher modulus. Phase shifts for the ESO composite with fibers were comparable to the cross-linked ESO without fibers. The linear range of rheological properties was much narrower for the composites with fibers than for the cross-linked ESO material. The viscoelastic properties of this kind of new biodegradable material were close to the behavior of highly cross-linked rubber.

#### ACKNOWLEDGMENT

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