Cross-linkers Control the Viscoelastic Properties of Soybean Oil-Based Biomaterials

Jingyuan Xu[a,*], **Zengshe Liu**[b], **Sevim Z. Erhan**[b], **and Craig J. Carriere**[a]

[a]Cereal Products and Food Science Research and [b]Food and Industrial Oil Research, NCAUR, ARS, USDA, Peoria, Illinois 61604

ABSTRACT: Because of environmental concerns, biodegradable materials have been of increasing research interest over the last several years. Previously, we reported on a biobased material developed from epoxidized soybean oil (ESO) that displayed viscoelastic behavior similar to synthetic rubbers or plastics. In this work, the viscoelastic properties of several biomaterials made from ESO cross-linked by different amounts of two different cross-linking agents were investigated. The composites exhibited different glass transition temperatures and viscoelastic behaviors depending on the type and amount of cross-linker used. Higher glass transition temperatures and stronger viscoelastic properties of the materials were found with a greater amount of cross-linker. Comparing agent triethylene glycol diamine (TGD) with agent triethylenetriamine (TETA), we found that the material cross-linked by TETA had a higher glass transition temperature and stronger viscoelastic solid properties than the material cross-linked by the agent TGD.

Paper no. J10766 in *JAOCS 81*, 813–816 (August 2004).

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

Because of environmental concerns, such as the need to reduce recycling, the commercial utilization of biodegradable polymers has attracted the interest of scientists over the past few decades (1–4). Many biological polymers have potential advantages compared with synthetic petroleum polymers because of their biodegradable properties. Since soy-based composites contain FA residues that can be readily attacked by lipase-secreting bacteria, this family of materials is generally regarded as biodegradable. Annually, the United States produces about 450 thousand tons of soybean oil in excess of current commercial need. Thus, developing new materials from soybean oil has become highly desirable. These new materials can open needed new markets for this important crop.

Soybean oil is a mixture of TG, which are esters of glycerol with saturated and unsaturated FA. The double bonds in unsaturated FA can be converted into an epoxidized soybean oil (ESO) by reaction with peroxide compounds. Wool and colleagues (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 cross-linked with curing agent triethylene glycol diamine (TGD). The viscoelastic properties of this material were reported in an earlier work (8).

In this paper, the viscoelastic properties of polymerized ESO with two different curing agents (cross-linkers) were investigated. We discovered that by adopting different curing agents or altering the amount of cross-linker, the material exhibited different thermal and rheological properties. This work shows us potential opportunities for developing more rubber-like biomaterials that have different thermal and rheological behaviors.

MATERIALS AND METHODS

Materials. ESO was obtained from Elf Atochem Inc. (Philadelphia, PA) and used as received. TGD (brand name: Jeffamine EDR-148) was obtained from Huntsman Corporation (Houston, TX), and triethylenetriamine (TETA) was purchased from Aldrich Chemical Inc. (Milwaukee, WI). The structures of the two curing agents used are as follows:

$$H_2N–CH_2–CH_2–O–CH_2–CH_2–O–CH_2–CH_2–NH_2 \quad [1]$$

TGD

$$H_2N–CH_2–CH_2–NH–CH_2–CH_2–NH–CH_2–CH_2–NH_2 \quad [2]$$

TETA

The thixotropic agent Aerosil R805 was obtained from Degussa Corp. (Ridgefield Park, NJ).

Sample preparation. ESO was mixed with Aerosil R805 in a ratio of 13 g/100 g ESO. The mixture was degassed in a vacuum system at 55°C for 30 min. The mixture was then removed from the vacuum oven and cooled to room temperature. The material produced possessed an oil-like appearance. The desired curing agent was added to the mixture in the ratio of 1:1.08 or 1:1.8 of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent). The sample was agitated manually with a spatula to ensure extensive mixing and then poured into a plate. The plate was placed in an oven at a constant temperature of 140°C for 48 h. The rubber-like material was then cut into about 15 × 10 × 12 mm (length × width × thickness) rectangular bars for measurement. Four materials were produced using two curing agents at two different ratios. The sample materials were designated as follows: (i) material

---

*To whom correspondence should be addressed at Cereal Products and Food Science Research, National Center for Agricultural and Utilization Research, Agricultural Research Service, USDA, 1815 N. University St., Peoria, IL 61604. E-mail: xuj@ncaur.usda.gov

1: ESO cross-linked by TGD in a 1:1.08 ratio of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent); (ii) material 2: ESO cross-linked by TGD in a 1:1.8 ratio of (epoxy group of ESO)/(hydrogen of the amino group in curing agent); (iii) material 3: ESO cross-linked by TETA in a 1:1.08 ratio of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent); (iv) material 4: ESO cross-linked by TETA in a 1:1.8 ratio of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent).

Measurements. A strain-controlled Rheometric ARES Series IV rheometer (TA Instruments, Inc., New Castle, DE) was used to perform the rheology studies. Torsion rectangular geometry was used. The temperature was controlled by an air convection oven to within ± 0.1°C. Linear viscoelastic measurements were conducted for the cross-linked ESO composites. To ensure that all the measurements for the cross-linked materials were made within the linear viscoelastic range, a strain-sweep experiment was initially conducted at different temperatures from –65 to 35°C. An applied shear strain in the linear range was used for the other viscoelastic property measurements for the same material; new samples were used for each experiment. Each measurement was repeated four to five times with a different sample. Temperature ramp measurements were made over a range of –60 to 35°C with small shear strain less than 0.5%, which was within the linear range for all the samples measured. The temperature was increased by a rate of 1°C/min. Small-amplitude oscillatory shear experiments were conducted over a frequency (ω) range of 0.1–100.0 rad/s, yielding the shear storage (G') and loss (G'') moduli. The storage modulus represents the nondissipative component of mechanical properties. The loss modulus represents the dissipative component of the mechanical properties and is characteristic of viscous flow. The complex modulus, G^*, was expressed as $G^* = G' + iG''$, where G^* is a complex number with G' as its real part and G'' as its imaginary part, respectively. The magnitude of the complex modulus, abbreviated as $|G^*|$, measures the material's resistance to an oscillatory deformation, and $|G^*| = (G'^2 + G''^2)^{1/2}$. The phase shift or phase angle (δ) is defined by $\delta = \tan^{-1}(G''/G')$ and indicates whether a material is solid with perfect elasticity ($\delta = 0°$), liquid with pure viscosity ($\delta = 90°$), or something in between. The glass transition temperature was determined as the midpoint of the change in slope in the $|G^*|$ vs. T curve. The statistical data shown here are the means, and the errors are ±SD of the means of at least four to five replicates.

RESULTS AND DISCUSSION

The hydrogen on the amino group of the curing agents can react chemically with the epoxy group of the ESO at elevated temperatures. Therefore, the curing agents 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, the properties of ESO are similar to soybean oil and behave as a viscous Newtonian fluid (8). TGD (Jeffamine EDR-148) has four acting sites on the two ends and a chain backbone. TETA has the same four acting sites on the two ends as TGD, but has two additional acting sites in the middle of the chain. TETA and TGD have almost identical lengths of the backbone chain. Because TETA has two more acting sites in the middle of the chain, TETA behaves as a "short-armed" cross-linker compared with the "long-armed" TGD.

Figure 1 displays the temperature ramp measurements for materials 1 and 2, in which TGD was used as the cross-linker. The glass transition temperature (T_g) of material 1 was −20.8 ± 0.5°C. When a larger amount of curing agent (1:1.8 ratio of epoxy/hydrogen) was used in the production of the material, a higher T_g was obtained, namely, −12.8 ± 0.4°C for material 2 (Fig. 1). Apparently, a larger amount of curing agent made the chemical reaction between the hydrogen on the amino group of the cross-linker and the epoxy group on the ESO more efficient. The same tendency was observed for the samples using TETA as the cross-linker (Fig. 2). A lower T_g of 12.0 ± 0.6°C was obtained for the material produced using a smaller amount of TETA (1:1.08 ratio of epoxy/hydrogen). A higher T_g, 15.5 ± 0.5°C, was obtained for the material using a greater amount of TETA (1:1.8 ratio of epoxy/hydrogen) as the curing agent (Fig. 2).

The different cross-linkers also produced materials with different properties (Figs. 1, 2). For the same ratio of epoxy group/hydrogen, the ESO cross-linked with TGD and TETA exhibited large differences in T_g. The material cross-linked with TGD had T_g much lower than 0°C, e.g., −20.8 and −12.8°C, respectively (Fig. 1). However, the material cross-linked by TETA had T_g close to room temperature, e.g., 12.0 and 15.5°C, respectively. Therefore, at room temperature the composite made with TETA was more rigid or harder than the material made with TGD. Because the distance between acting

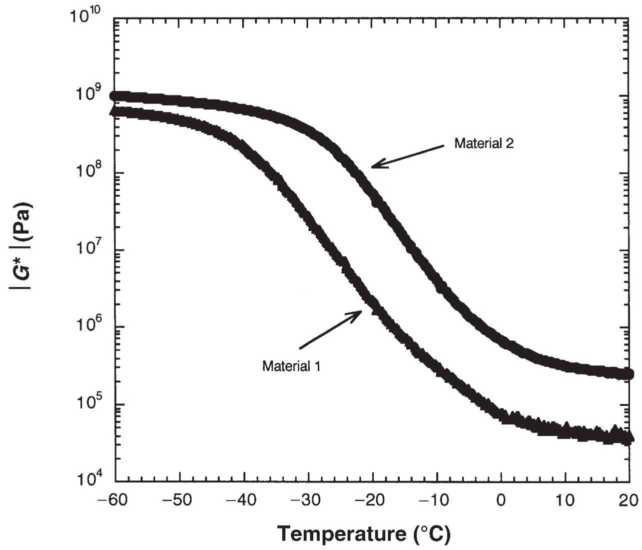

FIG. 1. The viscoelastic properties of epoxidized soybean oil (ESO) cross-linked by triethylene glycol diamine (TGD) during the temperature ramp measurement. (▲): Material 1 [1:1.08 of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent)]; (●): material 2 [1:1.8 of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent)].

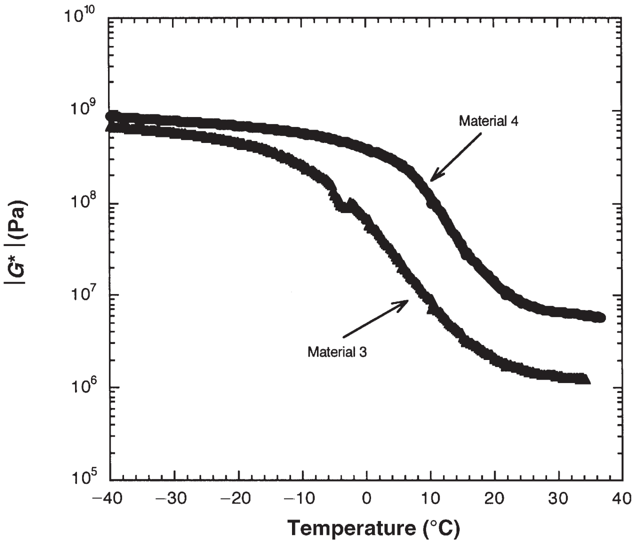

FIG. 2. The viscoelastic properties of ESO cross-linked by triethylenetriamine (TETA) during the temperature ramp measurement. (▲): Material 3 [1:1.08 of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent)]; (●): material 4 [1:1.8 of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent)]. For other abbreviations see Figure 1.

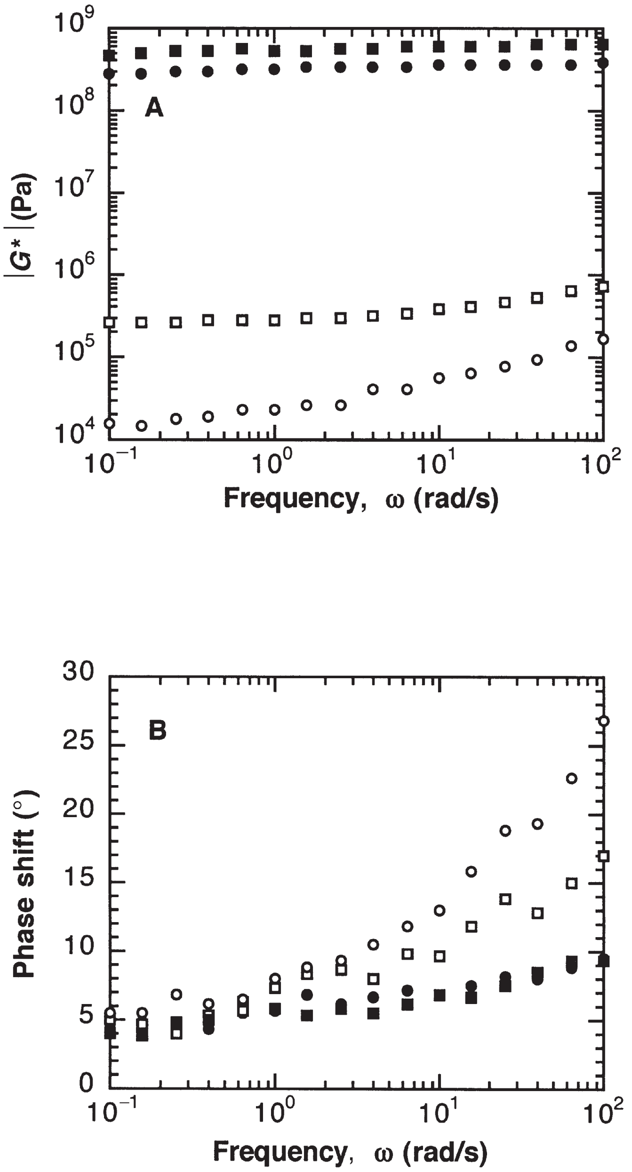

FIG. 3. Linear viscoelastic properties of ESO cross-linked by TGD at −45 and 35°C, respectively. (A) Magnitude of the complex modulus, |G*|. (B) Phase shift, δ. Filled symbols, −45°C; open symbols, 35°C. (●,○): Material 1 [1:1.08 of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent)]; (■,□): material 2 [1:1.8 of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent)]. For abbreviations see Figure 1.

sites on TETA is much shorter than that on TGD, one can posit that the networks cross-linked with TGD and TETA would have different cross-linking density. In addition, we used the same ratios of epoxy/hydrogen for both TGD and TETA with ESO. Thus, for the same amount of ESO, the total amount of TGD used was even greater than that for TETA. The structure of the cross-linker was the key factor controlling the properties of the material in this case.

To further understand the structure–function relationship, we studied the linear viscoelastic properties of the biomaterials made from ESO. We measured the magnitudes of the complex modulus ($|G^*|$) and the phase shift (δ) of these materials at temperatures lower and higher than T_g for the materials. At temperatures lower than T_g, the ESO materials cross-linked with TGD and TETA all exhibited very strong viscoelastic solid behavior (Figs. 3, 4). At –45°C, the shape of $|G^*|$ for all four materials was independent of the frequency. The samples made with more cross-linker had slightly higher $|G^*|$, so they had slightly stronger viscoelastic properties than those made with less cross-linker (Figs. 3A, 4A). The materials using TETA as a cross-linker (materials 3 and 4) had higher values of $|G^*|$ than those using TGD (materials 1 and 2) (Figs. 3A, 4A). At –45°C, the $|G^*|$ for materials 1 and 2 were 3.2×10^8 and 5.3×10^8 Pa, respectively, at a frequency of 1 rad/s (Fig. 3A), whereas the $|G^*|$ for materials 3 and 4 were 4.2×10^9 and 4.9×10^9 Pa, respectively, at a frequency of 1 rad/s (Figs. 3A, 4A). The phase shifts were all within 4–10° (Figs. 3B, 4B). However, at 35°C, which is higher than T_g for the samples using TGD as the cross-linker, the $|G^*|$ of the material became lower, at 2.2×10^4 and 2.8×10^5 Pa, respectively, for materials 1 and 2 at a frequency of 1 rad/s. The shapes of the $|G^*|$ for these two materials still exhibited viscoelastic solid behavior and had a long plateau at 35°C, but the one using a lower amount of cross-linker (material 1) showed the $|G^*|$ to be slightly dependent on the frequency at higher frequencies (Fig. 3A). The phase shifts for these two materials at 35°C were higher (5–27°) than those at −45°C, especially for material 1 (Fig. 3B). Figures 4A and 4B display the $|G^*|$ and phase shift for materials 3 and 4 at 35°C, which is higher than the T_g for the materials using TETA as the cross-linker. Materials 3 and 4 had $|G^*|$ values of 1.2×10^6 and 5.5×10^6 Pa, respectively, at 35°C and a frequency of 1 rad/s, which were much higher than

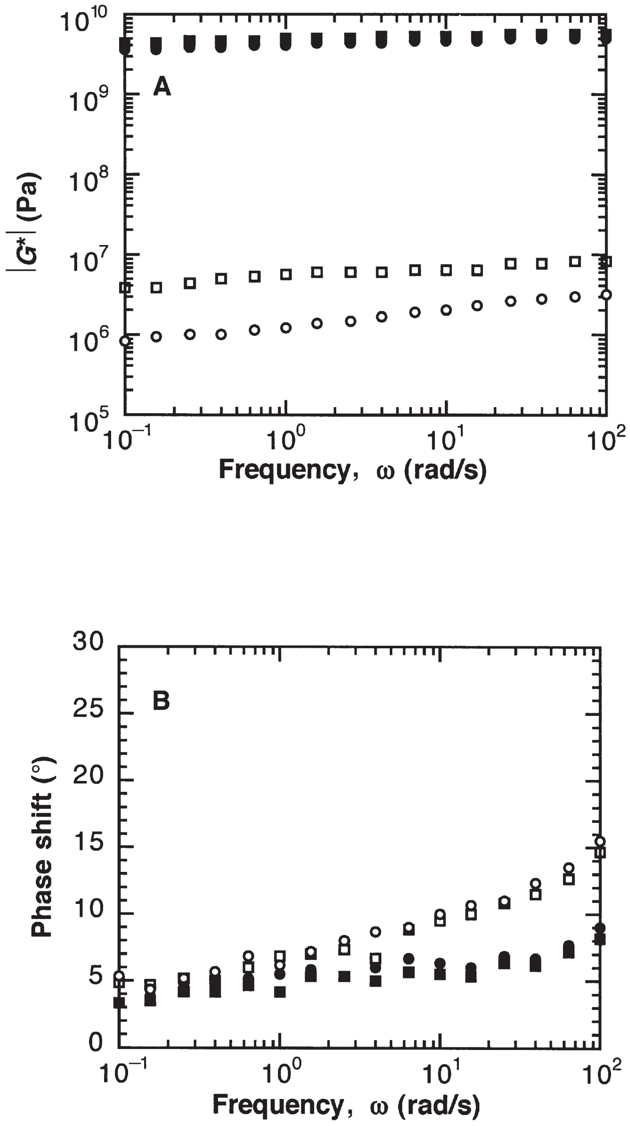

FIG. 4. Linear viscoelastic properties of ESO cross-linked by TETA at −45 and 35°C, respectively. (A) Magnitude of the complex modulus, $|G^*|$. (B) Phase shift, δ. Filled symbols, −45°C; open symbols, 35°C. (●,○): Material 3 [1:1.08 of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent)]; (■,□): material 4 (1:1.8 of (epoxy group of ESO)/(hydrogen of the amino group in the curing agent)]. For abbreviations see Figures 1 and 2.

those of materials 1 and 2 at 35°C. The phase shifts for materials 3 and 4 were 5–16°, which were smaller than those for materials 1 and 2 at 35°C. Therefore, materials 3 and 4 had stronger viscoelastic solid properties and smaller phase shifts than those for materials 1 and 2 at 35°C. These results were consistent with the foregoing results of the T_g for these materials. Although the total amount of TETA used was less than that of TGD for the same amount of ESO, TETA, as a short-armed cross-linker, made the samples relatively more brittle, whereas TGD, as a long-armed cross-linker, made the composites relatively more flexible and softer. Therefore, the long- or short-armed cross-linker was the crucial factor controlling the viscoelastic properties of the materials. One can use different curing agents and adjust the amount of curing agent to produce materials with different properties. A curing agent such as TETA can be used to make more brittle rubber-like material, whereas a curing agent such as TGD can be used to make more flexible rubber-like material.

Because of the biodegradable behavior of these materials (7), controlling the cross-linkers to make these biomaterials provides us more opportunities to produce materials with different thermal and viscoelastic properties. The viscoelastic properties of the materials we obtained from this work are very close to the viscoelastic properties of some synthetic rubbers such as polyisoprene, polyvinyl ethylene, and polybutadiene (9). Using the method of our earlier work (8), we estimated that the M.W. of the materials we used in this work were on the order of 10^4 to 10^5 g/mol, which are also close to those of some synthetic rubbers such as polystyrene, polyethylene, and polymethyl acrylate (9). Therefore, these biodegradable materials made from vegetable oil have the potential to replace some of the synthetic rubbers or plastics.

ACKNOWLEDGMENTS

The expert technical assistance of Andrew J. Thomas in the completion of this work is acknowledged with gratitude. This work was financially supported by the U.S. Department of Agriculture, Agricultural Research Service.

REFERENCES

1. Mishra, D.P., and P.A. Mahanwar, Advances in Bioplastic Materials, *Pop. Plast. Packag. 45*:68–76 (2000).
2. Schroeter, J., Biodegradable Plastic Materials, *Kunststoffe 90*:64–66, 68–70 (2000).
3. Fomin, V.A., and V.V. Guzeev, Biodegradable Polymers: Status and Prospects, *Plast. Massy 2*:42–48 (2001).
4. Wool, R.P., Development of Affordable Soy-Based Plastics, Resins, and Adhesives, *Chemtech 29*:44–48 (1999).
5. Wool, R.P., S.H. Kusefoglu, S.N. Khot, R. Zhao, G. Palmese, A. Boyd, C. Fisher, S. Bandypadhyay, A. Paesano, P. Dhurjati, *et al.,* Affordable Composites from Renewable Sources (ACRES), *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 39*:90 (1998).
6. Wool, R.P., S.H. Kusefoglu, R. Zhao, G. Palmese, A. Boyd, C. Fisher, S. Bandypadhyay, A. Paesano, S. Ranade, P. Dhurjati, *et al.*, Affordable Composites from Renewable Sources (ACRES), 216th American Chemical Society National Meeting, Boston, August 23–27, 1998.
7. Liu, Z.S., S.Z. Erhan, J. Xu, and P.D. Calvert, Development of Soybean Oil-Based Composites by a Solid Freeform Fabrication Method: Epoxidized Soybean Oil with Bis or Polyalkyleneamine Curing Agents System, *J. Appl. Polym. Sci. 85*:2100–2107 (2002).
8. Xu, J., Z.S. Liu, S.Z. Erhan, and C.J. Carriere, A Potential Biodegradable Rubber—Viscoelastic Properties of a Soybean Oil-Based Composite, *J. Am. Oil Chem. Soc. 79*:593–596 (2002).
9. Wen J., Some Mechanical Properties of Typical Polymer-Based Composites, in *Physical Properties of Polymers Handbook*, edited by J.E. Mark, American Institute of Physics, Woodbury, NY, 1996, pp. 371–377.

[Received December 15, 2003; accepted July 5, 2004]