

Dynamic Mechanical Characterization of a Soy Based Epoxy Resin System

A. Shabeer,¹ A. Garg,¹ S. Sundararaman,¹ K. Chandrashekhara,¹ V. Flanigan,¹ S. Kapila²

¹ Department of Mechanical and Aerospace Engineering, University of Missouri–Rolla, Rolla, Missouri 65409

² Department of Chemistry, University of Missouri–Rolla, Rolla, Missouri 65409

Received 30 August 2004; accepted 16 February 2005

DOI 10.1002/app.22362

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Epoxidized allyl soyate (EAS), a novel soy based epoxy resin, has been prepared by the process of transesterification and epoxidation of regular food grade soybean oil. Two types of crosslinking agents were employed in this study. The effects of the concentration of EAS and the type of crosslinking agent on the dynamic mechanical behavior of the soy based resin system have been investigated. The room temperature storage moduli (E') and the glass transition temperatures (T_g) increased for the anhydride cured and decreased for the amine cured resins. The loss tangent maximum $(\tan \delta)_{\max}$ decreased for anhydride cured resins and increased for amine cured resins. The effect

of frequency on the storage modulus was also studied. Master curves were constructed by the time-temperature superpositioning technique (TTS) to predict the storage modulus at times and temperatures that are not experimentally feasible. The results indicate that soy based epoxy resins with appropriate concentrations hold great potential as a replacement for petroleum based materials in noise and vibration attenuation applications. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1772–1780, 2005

Key words: dynamic mechanical analysis; soy resin; storage modulus

INTRODUCTION

In recent years, polymeric materials prepared from natural and renewable resources, such as triglyceride vegetable oils, are finding numerous applications. The fatty acid esters derived from the triglyceride vegetable oils are attractive sources of raw materials for polymer synthesis.¹ Among the triglyceride oils, soybean attracts great interest because of its plentiful supply in the United States, low cost, and environmentally benign status. Soybean oil contains 85% unsaturated oleic, linoleic, and linolenic fatty acids. This high degree of unsaturation makes it possible to polymerize it into useful materials.^{2,3}

Polymeric materials are finding extensive use in sound and vibration damping applications because of their inherent damping characteristics.^{4–6} The region of maximum damping is the glass transition region, where the polymer changes from the glassy to the rubbery state. In this region, a broad and intense peak of $\tan \delta$ is expected for polymers used in damping applications because of micro-brownian motion of the polymer chains. However, the loss tangent is low when the temperature is below and above the T_g . This is due to the presence of frozen polymer segments at

temperatures lower than the T_g . At temperatures higher than the T_g , polymer segments provide less resistance and are free to move. The location and the intensity of the loss tangent peak depend on the frequency and temperature of measurement. The glass transition region in polymers can be broadened or shifted depending on end applications by the addition of plasticizers and fillers.⁷

The temperature range for efficient damping ($\tan \delta > 0.3$) for most of the common homopolymers is around 20 to 30°C.⁸ Several researches have been carried out to increase the temperature range for efficient damping by the formation of interpenetrating polymer networks (IPNs), blending, and copolymerization.⁹ IPNs are a mixture of two or more crosslinked polymers with microheterogeneous morphology. The presence of this morphology due to crosslinks results in broad glass transition regions, making a useful damping material. Polymers obtained from blending and copolymerization exhibited a much more intense and narrow loss tangent peak at the glass transition. The narrow and intense peak can be attributed to a lesser degree of crosslinking among the polymers. For most sound and vibration applications, the polymeric material is required to possess high damping over a wide range of temperature and frequency. However, not all polymers can have high and broad loss tangent peaks. When the frequency range of the transition is broad, the damping peak is low; and when the transition is sharp, the damping peak is high. This behav-

Correspondence to: K. Chandrashekhara (chandra@umr.edu).

ior is attributed to the proportionality of the area under the damping peak to the activation energy of the transition. Thus, the shape of the loss tangent curve in the glass transition region and also the area under the curve determines the material's ability to dampen sound and vibration.

Though the performance of any damping material is determined by its application, relative performance evaluation can be obtained from dynamic mechanical analysis (DMA) techniques. Dynamic mechanical analysis has been used to evaluate the damping characteristics of polymers and rubbers. It has proved to be an effective tool in the characterization of viscoelastic materials. It measures the response of a material as it is deformed due to a sinusoidal stress for a wide range of temperatures and frequencies.¹⁰ Specifically, this technique provides information about three important parameters: storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$). Storage modulus is the measure of the maximum energy stored in the material during one cycle, and loss modulus is the measure of the energy that has been dissipated as heat by the sample. Loss tangent is the damping term, which is the ratio of the loss modulus to the storage modulus. Several researchers have used this technique to examine the molecular mechanisms of polymeric materials and rubbers. Li and Larock studied the effect of soybean oil and the nature of the crosslinking agent on the dynamic mechanical properties of soybean oil-styrene-divinylbenzene copolymers.¹¹ Varughese et al. studied the effect of various types of fillers on the dynamic mechanical properties of epoxidized natural rubber.¹² Chern et al. used this technique to study the epoxy/polyurethane interpenetrating polymers.^{13,14}

Dynamic mechanical tests are generally performed in a fixed frequency mode. To predict the long term time dependent properties of resins, TTS is employed. This technique uses a multifrequency data at a variety of temperatures. The data collected at various temperatures can be shifted to a reference temperature using the Williams-Landel-Ferry (WLF) equation. Kuzak and Shanmugam used TTS in constructing the master curves for fiber reinforced phenolics.¹⁵ Simon et al. reported the use of the above technique to model the evolution of dynamic mechanical properties of a commercial epoxy during cure.¹⁶

In previous work, we reported the mechanical characterization of EAS blended with the Shell Epon 9500 resin.¹⁷ Studies on the properties of these resins showed that by varying the concentration of EAS in the base Epon resin, a wide range of polymeric materials have been obtained ranging from soft to brittle plastics. The flexibility of these materials makes them an ideal candidate for damping applications.

In the current study, we report the effect of the soy concentration and the nature of the curing agent on the dynamic mechanical behavior of soy based epoxy

resins. Master curves are also plotted using TTS to predict the storage modulus at times and temperatures that are not experimentally feasible.

EXPERIMENTAL

Materials

Shell Epon 9500 (Shell Chemical Co., Houston, TX) was the base epoxy resin used in this study. Epicure 9550 (Shell Chemical Co., Houston, TX), an aliphatic amine, and phthalic anhydride (Aldrich Chemical Co., Houston, TX) were the two curing agents used. Soy based resin (EAS) was synthesized in a two step laboratory scale process from regular food grade soybean oil. First, the triglyceride molecules in the soybean oil were transesterified with allyl alcohol to yield fatty acid allyl esters. Next, the fatty acid esters were epoxidized to yield soyate epoxy resin.

Preparation of the resin system

In this work, soy resin samples were prepared with two kinds of crosslinking agents. The blends were prepared by mixing the soy epoxy resin with the base Epon resin. The blends chosen for the present work were 10%/90%, 20%/80, and 30%/70% soy epoxy resin/Epon resin. In the first type, Epicure 9550, an amine hardening agent, was used. The ratio of resin to hardener was 100 : 33. The resin and the hardener were mixed well, and the mixture was degassed for few minutes to remove any air bubbles. The mixture was poured into a preheated mold, which was sprayed with a mold release agent Chemlease 41(Howell, MI). Curing was performed in two stages in the oven. First, the mixtures were cured for 1 h at 80°C followed by 1.5 h at 175°C. In the second type, phthalic anhydride was used as the curing agent. The ratio of resin to hardener was 100 : 70. Phthalic anhydride was in the form of flakes and, hence, the mixture was heated up to 130°C to dissolve the flakes. The resultant mixture was cured at 160°C for around 1 h in the oven.

Dynamic mechanical analysis

The dynamic mechanical tests were performed using a Perkin-Elmer DMA Pyris-7e analyzer. The data were collected and analyzed using Pyris software. The specimens were deformed under a three point flexural mode arrangement. Rectangular specimens of 23 mm in length and 5 mm in cross section were used. The DMA tests were carried out in two modes as follows: a fixed frequency mode, in which the frequency was held constant at 1 Hz and the temperature was ramped from -30 to 120°C for amine cured resins and -30 to 200°C for anhydride cured resins at a heating

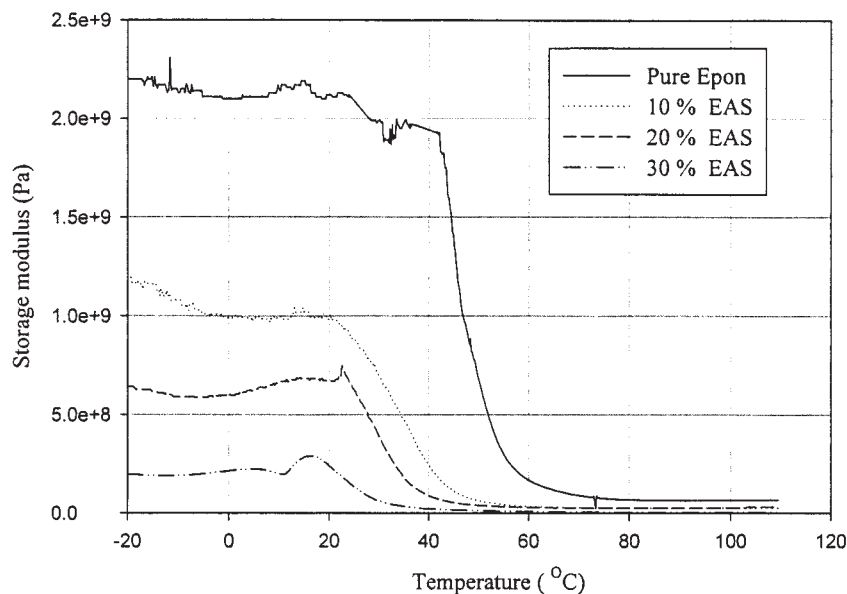


Figure 1 Temperature dependence of E' for the amine cured soy based epoxies at 1 Hz.

rate of $10^{\circ}\text{C}/\text{min}$; and the multifrequency isothermal mode, in which the frequency was varied from 1 to 20 Hz at different temperatures. E' and $\tan \delta$ were plotted as a function of temperatures and frequencies. Master curves were plotted using the Perkin-Elmer Pyris software. The T_g of the resins was obtained from the peaks of the $\tan \delta$ curves.

RESULTS AND DISCUSSION

Effect of different curing agents on the dynamic mechanical properties

Soy based resins were prepared to investigate the effect of different types of curing agents on the dynamic mechanical behavior. Two crosslinking agents were employed in curing the soy resins. Figure 1 shows the temperature dependence of E' for the amine cured soy resins prepared by varying the concentration of EAS. Pure Epon resin exhibited higher storage moduli than the soy based resins. The high storage moduli of the pure Epon resin are attributed to the presence of bulky bisphenol groups in the polymeric networks and a higher degree of crosslinking. The storage modulus remained almost constant at lower temperatures, but showed a sharp drop followed by a rubbery plateau as the temperature was increased. Pure Epon resin showed a storage modulus drop at the highest temperature, whereas the 30% EAS showed a modulus drop at the lowest temperature. Figure 1 indicates that the addition of soy resin resulted in a soft rubbery material at room temperature. The room temperature storage moduli for 10% EAS, 20% EAS, and 30% EAS were 2.7×10^7 Pa, 2.6×10^7 Pa, and 0.5×10^7 Pa, respectively. The crosslinking

density ν_c was obtained from the theory of rubber elasticity from the following equation^{5,7}:

$$E' = 3\nu_c RT$$

where E' is the storage modulus in the rubbery plateau region, R is the gas constant, and T is the absolute temperature. The crosslinking densities of the soy resins were 5.4×10^3 mol/ m^3 , 2.4×10^3 mol/ m^3 , and 0.5×10^3 mol/ m^3 for 10, 20, and 30% EAS, respectively.

Figure 2 shows the temperature dependence of $\tan \delta$ for amine cured soy based resins. The increase in soy concentration increased the loss tangent intensity and also shifted the peak at lower temperatures. This behavior is attributed to the decrease in the crosslinking density of the amine cured soy resins. The loss tangent peak is associated with the molecular movement of polymeric chains within the structure. It is well established that the higher the peak $\tan \delta$ value, the greater the mobility of the polymeric chains.¹⁸ On comparing the peaks in Figure 2, it can be seen that the 30% EAS has the highest value, indicating more molecular mobility because of decreased crosslinking. The T_g obtained from the peak of the $\tan \delta$ curve decreased with the addition of soy resins. Pure Epon had a higher T_g , located at approximately 70°C . The appearance of single relaxation indicated the presence of a single homogenous phase at the molecular level.

Figure 3 shows the temperature dependence of the storage modulus E' for the anhydride cured soy resins. 30% EAS exhibited higher storage moduli than the pure Epon resin. The high storage moduli of the 30% EAS is attributed to the better crosslinking reaction between the soy resin and the anhydride. The reactiv-

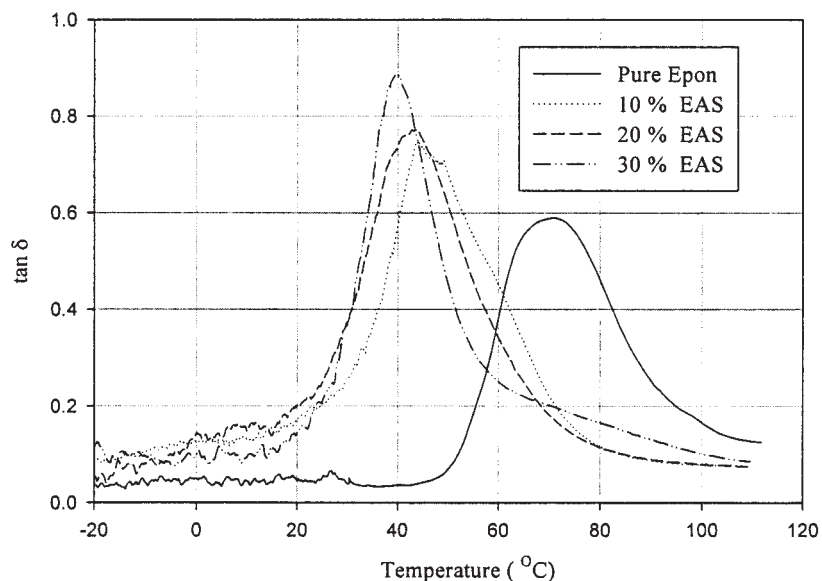


Figure 2 Temperature dependence of $\tan \delta$ for the amine cured soy based epoxies at 1 Hz.

ity of pure Epon is less as compared to soy resin when cured with phthalic anhydride. The anhydride ring must first be opened by active hydrogen, and the crosslinking reaction is carried out either by addition esterification with the carboxyl group or by condensation reactions of pendant hydroxyl groups. The presence of active hydroxyl groups in soy resins is more prominent than the pure Epon resins and, hence, the possibility of forming more crosslinked networks is higher in soy resins than the pure Epon resin. Thus, the increase in the concentration of soy resin increased the room temperature storage modulus of the resins.

30% EAS showed a storage modulus drop at the highest temperature, whereas the pure Epon resin showed a modulus drop at a lower temperature. The room temperature storage moduli for 10% EAS, 20% EAS, and 30% EAS were 8×10^8 Pa, 1.18×10^9 Pa, and 1.47×10^9 Pa, respectively. The crosslinking densities of the soy resins were 7.1×10^3 mol/m³, 8.2×10^3 mol/m³, and 10×10^3 mol/m³ for 10, 20, and 30% EAS, respectively.

Figure 4 shows the temperature dependence of the $\tan \delta$ for anhydride cured soy based resins. The increase in soy concentration decreased the loss tangent

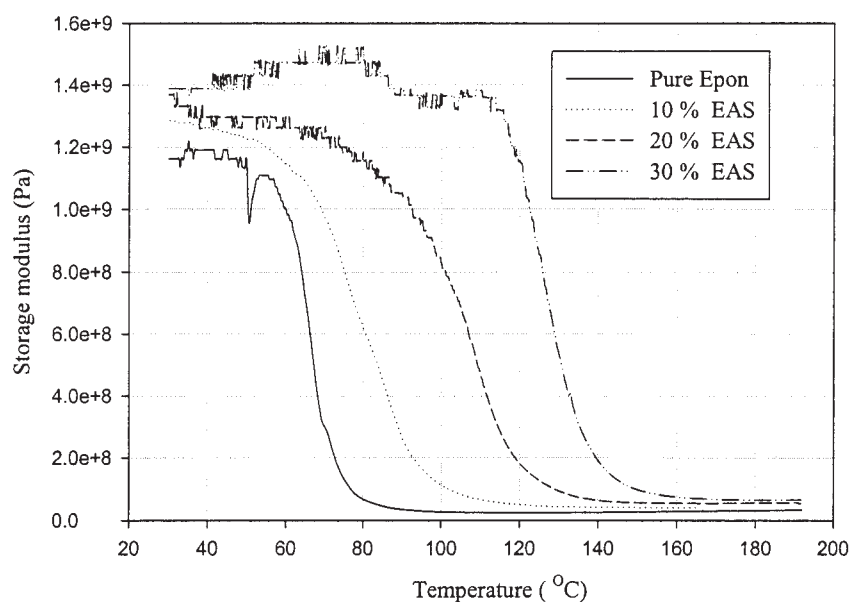


Figure 3 Temperature dependence of E' for the anhydride cured soy based epoxies at 1 Hz.

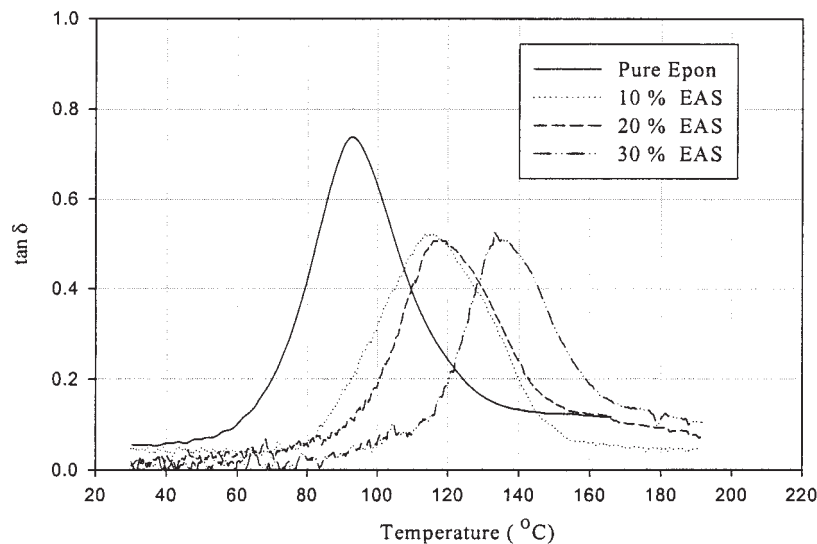


Figure 4 Temperature dependence of $\tan \delta$ for the anhydride cured soy based epoxies at 1 Hz.

intensity and also shifted the peak to higher temperatures. This behavior is attributed to the increase in the crosslinking density of the soy resins. From Figure 4, it can be seen that the 30% EAS has the lowest value, indicating more crosslinking. The T_g obtained from the peak of the $\tan \delta$ curve also increased with the addition of soy resins. 30% EAS had higher T_g , located at approximately 137°C.

Figure 5 shows the T_g of the soy resins prepared with two different curing agents. The T_g decreased for amine cured and increased for anhydride cured resins. This phenomenon can be attributed to better affinity of the soy resin with the anhydride, leading to a highly

crosslinked network, which introduced molecular restrictions on the polymeric chains.

Figure 6 shows that the crosslinking densities of the soy resins increased for anhydride cured and decreased for amine cured resins. The crosslinking density has a direct influence on the $\tan \delta$ of a polymer. It restricts the molecular motion of the chains and, thus, reduces the energy that can be dissipated during the glass transition.

Figure 7 shows the effect of crosslinking density on the loss tangent, $\tan \delta$, of the soy resins. The loss tangent decreased when the crosslinking density of the polymers increased.

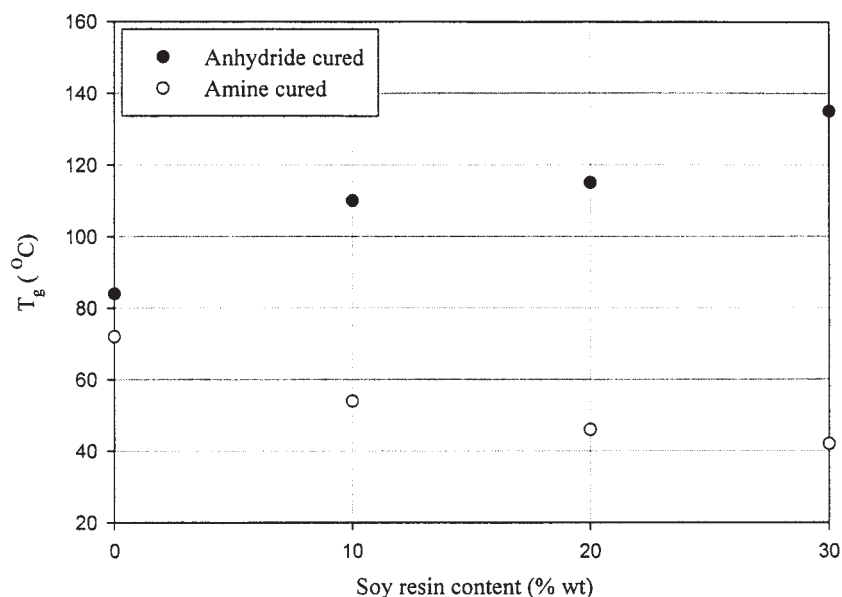


Figure 5 Effect of the soy resin concentration on the T_g .

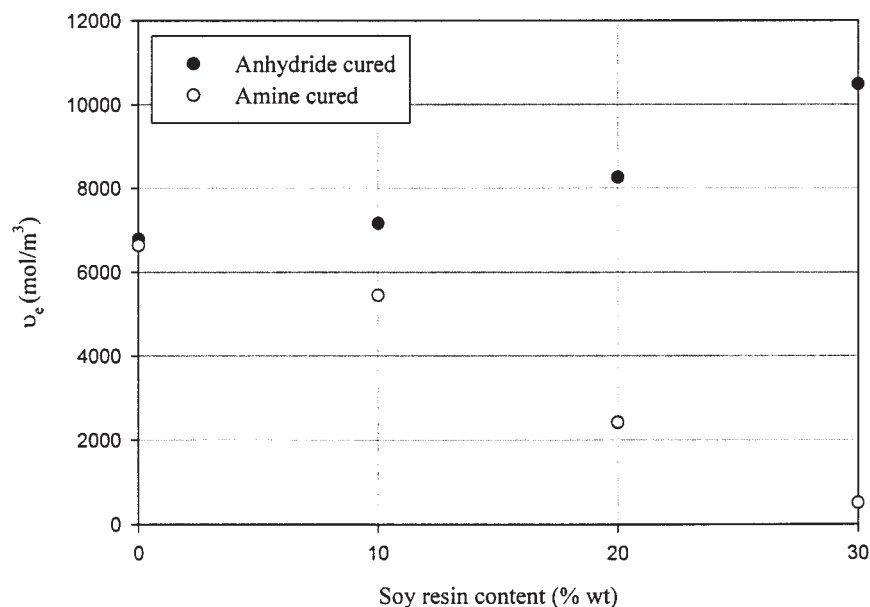


Figure 6 Dependence of the T_g on ν_e .

Figure 8 shows the area under the loss tangent curve for the soy resins. The area under these curves gives an indication of the total amount of energy that can be absorbed during the experiment. The larger area under the curve indicates that the material absorbs and dissipates energy well. The area under the $\tan \delta$ curves for the soy resins decreased with the increase in the crosslinking densities.

Frequency dependence on the dynamic mechanical properties

The dynamic mechanical analyses in this study so far were conducted in fixed frequency mode, in which the

response of the material was studied as a function of temperature only. Since the polymeric materials exhibit viscoelastic behavior that depends on time as well as temperature, the tests were carried out at different frequencies to obtain the time dependent material properties.

Figures 9 and 10 show the effect of frequency on the storage modulus of the amine cured and anhydride cured resins at different temperatures in the region of their glass transition temperatures. The storage modulus of the soy resins increased with the frequency of testing. The decrease in the storage modulus of the soy resins is more pronounced near and above their glass

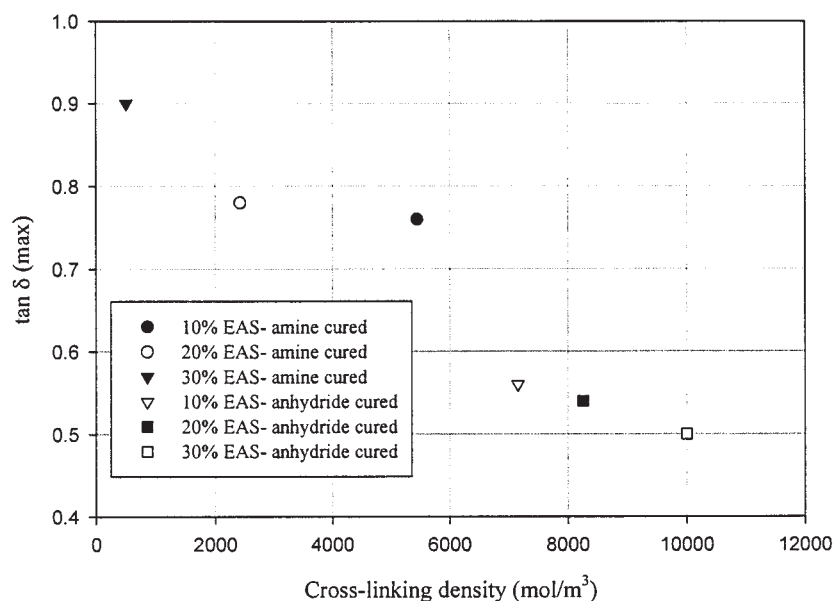


Figure 7 Relationship between $(\tan \delta)_{\max}$ on ν_e of the soy resins.

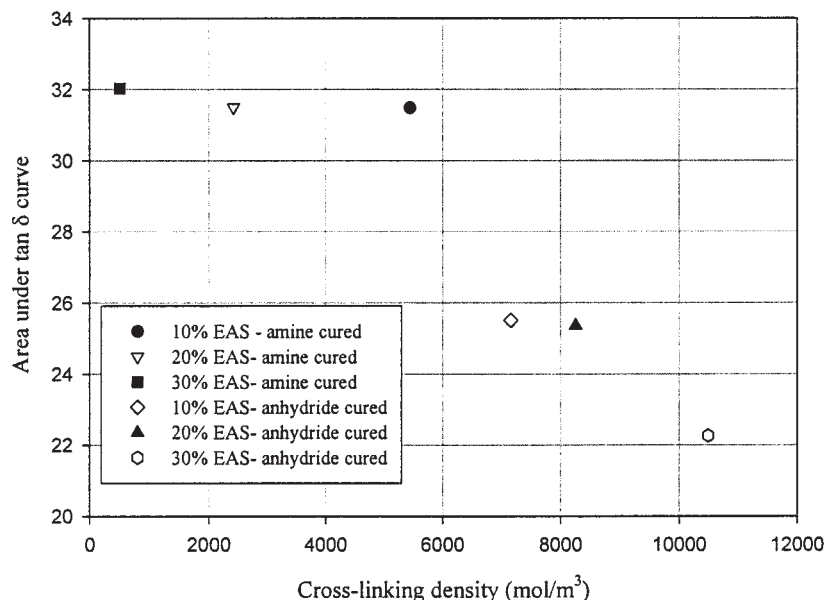


Figure 8 Area under the curve versus ν_e of soy resins.

transition temperatures. Using the above frequency multiplex data and the principle of TTS, storage modulus master curves were constructed that allow long term predictions of the modulus. The shift factors a_t used in the construction of master curves are obtained from the universal WLF equation¹⁹ as follows:

$$\log a_t = -C_1 \frac{T - T_g}{C_2 + T - T_g}$$

where C_1 and C_2 are empirical constants and T is the absolute temperature. The values of C_1 and C_2 used are 17.44 and 51.6, respectively. C_1 and C_2 depend on free volume and expansion coefficient relationships. The T_g of the soy resin was chosen as the reference temperature for the construction of the master curve.

Figure 11 shows the master curve of the storage modulus for 30% EAS cured with amine and anhydride, respectively. The master curves of 30% EAS

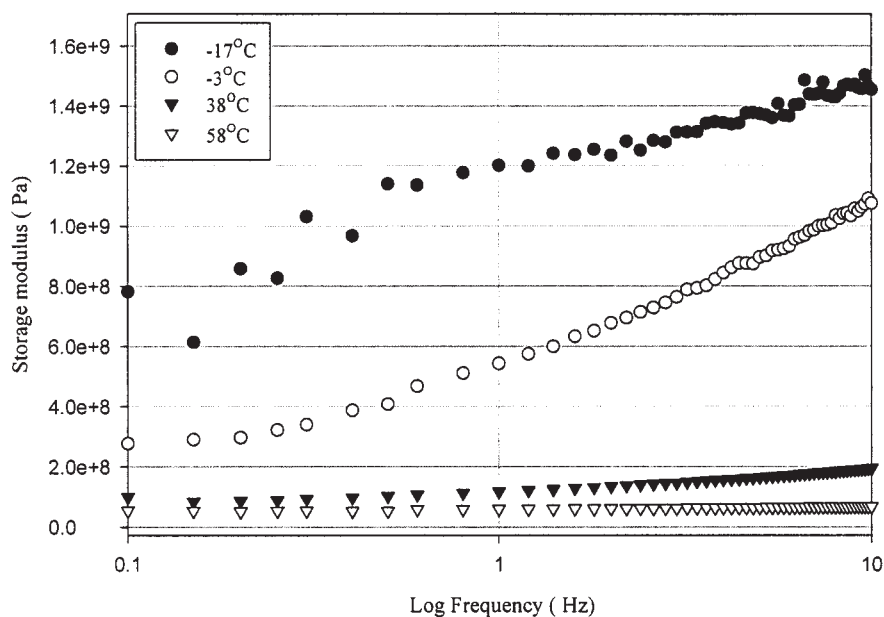


Figure 9 Storage modulus as a function of frequency for 30% EAS-amine cured resin.

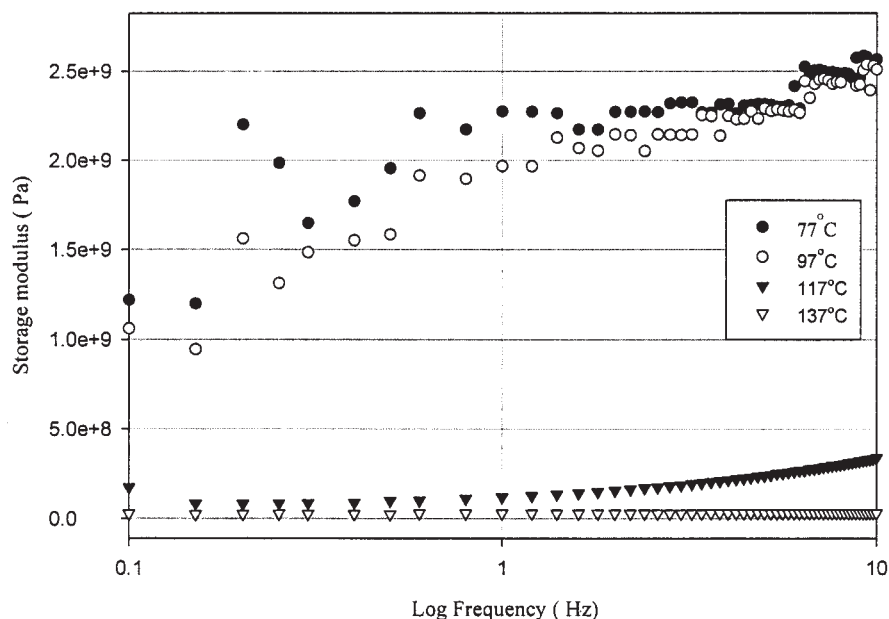


Figure 10 Storage modulus as a function of frequency for 30% EAS-anhydride cured resin.

allowed prediction of the storage modulus for over six decades, whereas the experimental data covered only two decades of frequency. The reference temperature for the construction of master curves for the amine cured and the anhydride cured resins were taken as 38°C and 137°C, respectively.

CONCLUSIONS

Dynamic mechanical behavior of the soy based resins was investigated in terms of the storage modulus and

the loss tangent. Soy resins showed a wide range of room temperature storage moduli ranging from 0.5×10^7 to 1.47×10^9 and T_g 's from 40 to 120°C approximately. The anhydride cured soy resins had higher initial storage modulus. The high modulus was due to the better crosslinking reaction of our soy resins with the anhydride curing agent, resulting in a stronger material. The amine cured resins showed higher $\tan \delta$ values. The high $\tan \delta$ peaks in amine cured resins were attributed to the contribution from long flexible chains of EAS, which did not take part in the crosslink-

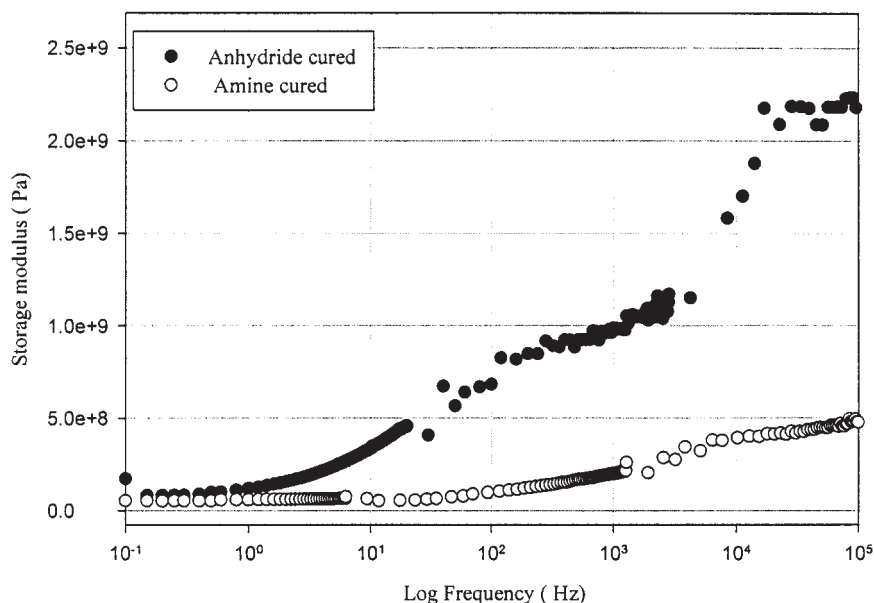


Figure 11 Storage modulus master curves for 30% EAS.

ing reaction. The degree of crosslinking increased for the anhydride cured resins, which in turn restricted the molecular mobility of the chains, resulting in a decrease in the amount of energy that can be dissipated. The peak $\tan \delta$ values and the area under the $\tan \delta$ curves were found to decrease with the increase in the crosslinking densities of the resins. The single relaxation in the loss tangent peaks of the soy resins indicated that the resins exhibited a homogenous phase at the molecular level. The effect of frequency on the storage modulus of the soy resins was also studied. The results showed that soy based resin systems with appropriate concentration and type of curing agent can efficiently dampen vibration for a wide range of temperatures and frequencies.

This project is sponsored by the National Science Foundation (Grant # NSF CMS-0229731) and the U.S. Department of Housing and Urban Development. Partial support from the Missouri Soybean Merchandising Council and the University Transportation Center is gratefully acknowledged.

References

1. Nevin, C. S.; Moser, B. F. *J Appl Polym Sci* 1963, 7, 1853.
2. Kaplan, D. L. *Biopolymers from Renewable Resources*; Springer: New York, 1998.
3. Li, F.; Larock, R. C. *J Appl Polym Sci*, 2000, 78, 1044.
4. Corsaro, R. D.; Sperling, L. H. *Sound and Vibration Damping with Polymers*; ACS Symposium Series 424; American Chemical Society: Washington, DC, 1990.
5. Nielson, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1994; 2nd ed.
6. Klempner, D.; Sperling, L. H.; Utracki, L. A. *Interpenetrating Polymer Networks*; ACS Symposium Series 239; American Chemical Society: Washington, DC, 1994.
7. Murayama, T. *Dynamic Mechanical Analysis of Polymeric Materials*; Elsevier Scientific Publishing: Amsterdam, 1982.
8. Li, F.; Larock, R. C. *Polym Adv Technol* 2002, 13, 436.
9. Li, S. Qiu, Q.; Jarvela, P. *J Appl Polym Sci* 2000, 76, 722.
10. Menard, K. P. *Dynamic Mechanical Analysis—A Practical Introduction*; CRC Press: Boca Raton, FL, 1999.
11. Li, F.; Larock, R. C. *J Polym Sci Part B: Polym Phys* 2000, 38, 2721.
12. Varughese, S.; Tripathy, D. K. *Plast Rubber Compos Process Appl* 1992, 17, 219.
13. Chern, Y. C.; Hsieh, K. H. *J Mater Sci* 1997, 32, 3503.
14. Chern, Y. C.; Tseng, S. M.; Hsieh, K. H. *J Appl Polym Sci* 1999, 74, 328.
15. Kuzak, S. G.; Shanumugam, A. *J Appl Polym Sci* 1999, 73, 649.
16. Simon, S. L.; McKenna, G. B.; Sindt, O. *J Appl Polym Sci* 2000, 76, 495.
17. Zhu, J.; Chandrashekhara, K.; Flanigan, V.; Kapila, S. *J Appl Polym Sci* 2004, 91, 3513.
18. Li, F.; Larock, R. C.; Otaigbe, J. U. *Polymer* 2000, 41, 4849.
19. Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980; 3rd ed.