DYNAMIC MECHANICAL CHARACTERIZATION OF SOY BASED EPOXY RESIN SYSTEM

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ABSTRACT

Two novel soy based resin systems namely Epoxidized Allyl Soyate (EAS) and Epoxidized Methyl Soyate (EMS) have been synthesized at the University of Missouri-Rolla. These resins form co-polymers with base epoxy in varied proportions to obtain a family of polymeric networks. The effects of the stoichiometry on the dynamic mechanical properties of the resulting resins were investigated. The results show that the damping ability is enhanced through the introduction of EAS and EMS into the base Epon resin. The good damping in the soy resins is attributed to the presence of long flexible polymer chains in the backbone. The glass transition temperature decreased and the intensity of the loss tangent increased with the addition of soy resins. EMS possessed the highest loss tangent peak and the lowest glass transition temperature among the other co-polymers. The increase in frequency of the loading displaced the loss tangent response to higher temperatures for all the concentrations. Therefore, soy resins are capable of damping the sound and vibration over a wide range of temperatures and frequencies.

KEY WORDS: Dynamic Mechanical Analysis, Soy resins, Damping.

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1. INTRODUCTION

In recent years polymeric materials prepared from natural and renewable resources such as triglyceride vegetable oils are finding numerous applications. Among the triglyceride oils, soybean attracts great interest because of plentiful supply in the United States, low cost and the biodegradability [1-4]. 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.

In previous work, we reported the mechanical characterization of two novel soy resins, Epoxidized Allyl Soyate (EAS) and Epoxidized Methyl Soyate (EMS) mixed with the Shell Epon 9500 [5]. Studies on the properties of these resins showed that by varying the concentration of EAS and EMS in base Epon resin, a wide range of polymeric materials have been obtained ranging from soft to brittle plastics. These materials are comprised of long flexible chains of EAS and EMS crosslinked with pure epoxy. The backbone flexibility of these materials makes it an ideal candidate for damping applications.

Polymeric materials are finding extensive use in sound and vibration damping applications because of their inherent damping characteristics [6-10]. The region of maximum damping is the glass transition region where the polymer changes from glassy to rubbery state. In this region, a broad and intense peak of loss tangent (\(\tan \delta\)) 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 glass transition temperature (\(T_g\)). This is due to the presence of frozen polymer segments at temperatures lower than \(T_g\). At temperatures higher than \(T_g\), polymer segments provide less resistance and are free to move. Also, frozen polymer segments are found to store more energy than the free segments [11-13]. The location and the intensity of 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 [14].

The temperature range for efficient damping (\(\tan \delta>0.3\)) for most of the common homopolymers is around 20 to 30°C [15]. 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 [16]. IPNs are a mixture of two or more crosslinked polymers with microheterogenous morphology. The presence of this morphology due to crosslinks results in broad glass transition regions, making it a useful damping material [17]. Polymers obtained from other techniques exhibited a much more intense and narrow loss tangent peak at the glass transition. The narrow and intense peak can be attributed to lesser degree of crosslinking among the polymers.

Dynamic mechanical analysis (DMA) has been used to evaluate the damping characteristics of polymers and rubbers. Several researchers have used this technique to examine the molecular mechanisms of polymeric materials and rubbers. Li and Larock studied the effect of soy bean oil and the nature of crosslinking agent on dynamic mechanical properties of soybean oil-styrene-divinylbenzene copolymers [18]. It was found that the storage modulus was related to the degree of unsaturation of the soybean oil methyl esters used in the study. Varughese et. al. studied the
effect of various types of fillers on the dynamic mechanical properties of epoxidized natural rubber [19]. It was reported that increasing the filler content decreased the loss tangent peak. This phenomenon in the rubber is attributed to the increased interaction between the filler and the epoxidized natural rubber. Chern et. al. showed the increase in loss tangent peak for epoxy/polyurethane interpenetrating polymers [20-21].

The current study examines the effect of various concentrations of EAS and EMS on the dynamic mechanical behavior of soy resins. The effect of crosslinking on the $T_g$ and the loss tangent peak are also investigated. The results obtained were compared with that of base Epon resin. In this context, it is hoped that the use of EAS and EMS in base epoxy provides better damping properties for the usage of these resins in sound and vibration damping applications.

2. EXPERIMENT

2.1 Materials Epon 9500 a bisphenol-A based epoxy from the Shell Chemical Company was used as the base resin. Epicure 9550 a proprietary aliphatic amine supplied by Shell Chemical Company was used as the curing agent. EAS and EMS were synthesized from regular food grade soybean oil by the process of trans-esterification and epoxidation at the University of Missouri Rolla. The percentage of epoxidation of EAS and EMS was 92% and 85% respectively.

2.2 Resin Preparation EAS and EMS were mixed in percentages of 10%, 20%, and 30% by weight with the base Epon resin. Epicure 9550 was used as curing agent in this process. The ratio of resin to hardener was around 32.6%. The reaction mixture was stirred vigorously until the soy resins coalesced with the base resin. The mixture was poured into a mold and heated for 60 minutes at 80°C, followed by 90 minutes at 177°C in a Blue-M Laboratory oven with hot air circulation.

2.3 Dynamic Mechanical Analysis The dynamic mechanical properties of the soy resins were obtained with a Perkin-Elmer DMA Pyris -7e analyzer in a three point flexural mode. The specimens were 23 mm in length and 5 mm thick with a span of 1.5mm on both sides. The specimens were first cooled to -30°C under liquid nitrogen and then heated at rate of 10°C/min. The frequencies used were 1 Hz, 10Hz and 20 Hz. The storage modulus ($E'$) and the loss tangent ($\tan\delta$) were plotted as a function of temperature. The $T_g$ of the resins was obtained from the peaks of the loss tangent $\tan\delta$ curve. The crosslinking densities ($\nu_e$) of the resins have been obtained from rubber elasticity theory [12, 13, 22]. The dynamic mechanical properties of the soy resins have been evaluated by the $\tan\delta$ maximum.

3. RESULTS AND DISCUSSION

3.1 Damping Properties of EMS/Epon Figure 1 shows the dynamic mechanical properties as a function of temperature for various concentrations of EMS in base Epon resin. The storage modulus ($E'$) varies with the concentrations of EMS. For a given concentration, the storage modulus remained constant at lower temperatures, but showed a sharp drop followed by a plateau as the temperature increased. This region is the transition region where the polymer changes from glassy state to rubbery state. This behavior of the resins was attributed to the segmental mobility of polymer chains in that region. The appearance of the plateau at the higher
temperature indicates that stable crosslinked network exists [15]. The T_g of soy resins decreased with the decrease in concentration of EMS. The room temperature storage modulus (E’) for 10, 20 and 30% EMS were $1.0 \times 10^9$, $1.68 \times 10^8$ and $1.65 \times 10^8$ Pa, respectively. The crosslinking densities of 10, 20 and 30% of EMS determined from the theory of rubber elasticity were $8.2 \times 10^3$, $6.6 \times 10^3$ and $2.7 \times 10^3$ mol/m$^3$ respectively.

Figure 2 shows that the increase in the concentration of EMS decreased the crosslinking density ($\nu_c$) of the resulting resins. Crosslinking hindered the segmental motion of the polymers and thus required high temperature for onset of the motion of polymer chains. Pure epoxy possessed a much higher crosslinking density than the EMS. This is attributed to the fact that the reactivity of EMS is much lower than the pure epoxy. The differences in the storage modulus for the various concentration of EMS are related to the different crosslinking densities.

Figure 3 shows the T_g of soy resins. The T_g determined from the peak of tan$\delta$ curve decreased with the concentration of EMS in pure epoxy. Thus 30% EMS in pure epoxy had the lowest crosslinking density ($\nu_c$), resulting in the lowest T_g and the lowest storage modulus.

Figure 4 shows the temperature dependence of the loss tangent (tan$\delta$) for the soy resins by varying the EMS concentration. The tan$\delta$ value indicates the damping ability of the resins. It is the ratio of mechanical dissipation energy to the stored energy. High tan$\delta$ peak is essential for a good damping material. For the soy based resins, a single loss tangent peak has been observed. These peaks correspond to the T_g of the resins. The increase in EMS concentration shifts the loss tangent peak to lower temperatures and increases the loss tangent intensity. The loss tangent (tan$\delta$) peak for 10%, 20% and 30% EMS were 0.72, 0.83 and 1.1 located at 24, 42, and 52°C, respectively. This increase in intensity of damping peak is due to low crosslinking densities of EMS.

Figure 5 shows the effect of crosslinking density ($\nu_c$) on the tan$\delta$ for EMS. The loss tangent (tan$\delta$) decreased when the logarithmic crosslinking density of the polymers increased. Thus, the results in Figures 1 and 4 showed that the increase in concentration of EMS in pure epoxy increased the tan$\delta$ peak and decreased the T_g.

3.2 Damping Properties of EAS/Epon Figure 6 shows the dynamic mechanical properties as a function of temperature and various concentrations of EAS in pure epoxy. The T_g of soy resins decreased with the concentration of EAS. The storage modulus (E’) at room temperature for 10, 20 and 30% EAS were $8.8 \times 10^8$, $7.66 \times 10^8$ and $1.3 \times 10^8$ Pa respectively. The crosslinking densities of the soy resins were $2.85 \times 10^3$, $2.51 \times 10^3$ and $4.59 \times 10^2$ mol/m$^3$ for 10, 20 and 30% of EAS respectively. The storage modulus for EAS is higher than EMS. This is attributed to the fact that the reactivity of EAS is higher than EMS because of reactive terminal epoxy groups in EAS.

Figure 7 shows that the increase in concentration of EAS in base epoxy leads to decrease in crosslinking density of the resulting resins. The T_g determined from the peak of tan$\delta$ curve decreased with the concentration of EAS. Figure 8 shows that the T_g of EAS based resins is higher than EMS based resins.
Figure 9 shows the temperature dependence of the loss tangent ($\tan\delta$) for the soy resins prepared by varying the EAS concentration. It can be observed that the magnitude of $\tan\delta$ reduces as the concentration of EAS increases. The $\tan\delta$ peak for 10%, 20% and 30% EAS were 0.72, 0.77 and 0.88 located at 45, 42 and 40°C, respectively. Also the single loss factor peak indicated that these resins possessed a single homogenous phase at the molecular level. The increase in the damping peak intensity is lower in EAS than EMS. This is due to more cross linking in EAS than in EMS based resins.

Figure 10 shows the effect of crosslinking density on the loss tangent ($\tan\delta$) for EAS. The loss tangent decreased when the logarithmic crosslinking density of the polymers increased. The increase in height of $\tan\delta$ peak and the decrease in the $T_g$ indicate greater molecular mobility.

### 3.3 Frequency Dependence of the Dynamic Mechanical Properties

The damping property of resins increases with an increase in frequency. An increase in frequency shifts the $\tan\delta$ curve to higher temperatures and also changes the shape of the curve. The amount of shift on changing the frequency depends on the $T_g$ and also on its energy of activation [13].

Figure 11 to 16 shows the loss tangent curves for various concentrations of EMS and EAS in pure epoxy measured at frequencies of 1, 10 and 20 Hz. The $\tan\delta$ increased from 1.1 to 1.3 and 0.88 to 0.95 for 30% EMS and EAS respectively for an increase in frequency.

## 4. CONCLUSIONS

The dynamic mechanical behavior of the soy based resins was investigated as a function of their stoichiometry and the nature of the soy resins. Soy resins used in this study showed a wide range of room temperature storage moduli ranging from $1.3\times10^8$ to $1\times10^9$ and $T_g$’s from 24 to 52°C. Increase in concentration of EAS and EMS in base epoxy (Pure Epon) decreased the $T_g$ and increased the loss tangent peak. EMS possessed higher $\tan\delta$ values than the EAS with the same concentration. The high $\tan\delta$ peaks are attributed to the contribution from long chain flexible EAS and EMS segments in the resins. The crosslinking density ($\nu_e$) of the EAS and EMS calculated from the rubber elasticity theory decreased with their concentration in base Epon resin. Thus the 30% EAS and EMS in base epoxy showed higher $\tan\delta$ peaks because of increased polymer segmental motions due to reduced crosslinking. The single $\alpha$ relaxation in the loss tangent peak indicated that the resins exhibited a single homogenous phase at the molecular level. Increase in frequency of the testing displaced the $\tan\delta$ peaks to higher temperature and also changed the shape of the curve. The results showed that the soy based resin systems with appropriate concentration and the type of curing agent can efficiently dampen the vibration for a wide range of temperatures and frequencies and hence can be a substitute for petroleum based plastics.

## 5. ACKNOWLEDGEMENTS

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6. REFERENCES

Figure 1: Storage modulus vs. temperature of various concentrations of EMS/Pure Epon

Figure 2: Effect of the EMS concentrations on Crosslinking density

Figure 3: Effect of EMS concentrations on Glass Transition Temperature

Figure 4: Loss tangent ($\tan \delta$) vs. temperature of various concentrations of EMS/Pure Epon
**Figure 5** Relationship between Loss Factor (tanδ) and Logarithmic crosslinking density in EMS

**Figure 6** Storage modulus vs. temperature for concentration of EAS/Pure Epon

**Figure 7** Effect of EAS concentration on the crosslinking density.

**Figure 8** Effect of EAS concentration on the Glass Transition Temperature.
Figure 9 Loss tangent ($\tan \delta$) vs. temperature for various concentration of EAS/Pure Epon.

Figure 10 Relationship between loss factor ($\tan \delta$) and Logarithmic crosslinking density in EAS/Pure Epon.

Figure 11 Loss tangent ($\tan \delta$) vs. temperature for 10 %EMS in Pure Epon at different frequencies.

Figure 12 Loss tangent ($\tan \delta$) vs. temperature for 20 %EMS in Pure Epon at different frequencies.
Figure 13 Loss tangent (tan $\delta$) vs. temperature for 30% EMS in Pure Epon at different frequencies

Figure 14 Loss tangent (tan $\delta$) vs. temperature for 10% EAS in Pure Epon at different frequencies

Figure 15 Loss tangent (tan $\delta$) vs. temperature for 20% EAS in Pure Epon at different frequencies

Figure 16 Loss tangent (tan $\delta$) vs. temperature for 30% EAS in Pure Epon at different frequencies