Viscoelastic Responses of Polyhedral Oligosilsesquioxane Reinforced Epoxy Systems

Andre Lee*,† **and Joseph D. Lichtenhan‡**

Department of Material Science and Mechanics, Michigan State University,
East Lansing, Michigan 48824-1226, and Air Force Research Laboratory, Propulsion Sciences and
Advanced Concepts Directorate, Edwards AFB, California 93524-7680

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ABSTRACT: The properties of nanostructured plastics are determined by complex relationships between the type and size of the nanoreinforcement, the interface, and the chemical interaction between the nanoreinforcement and the polymeric chain, along with macroscopic processing and microstructural effects. Recently, families of mono- and difunctionalized polyhedral oligomeric silsesquioxane (POSS) macromers bearing epoxide groups have been developed. This paper presents an investigation of the thermal and viscoelastic property enhancements in commonly used model epoxy resins reinforced with monofunctional POSS-epoxy macromers. The glass transitions of these POSS-epoxy nanocomposites were studied using differential scanning calorimetry. Small-strain stress relaxations under uniaxial deformation were examined to provide insight into the time-dependent viscoelastic behavior of these nanocomposites. The POSS-epoxy macromers utilized in this study were monofunctional and hence occupied chain terminus points within the network. Nevertheless, they were effective at hindering the molecular motion of the epoxy network junctions. Thus the glass transition temperature, T_g, was observed to increase with increasing weight fraction of the monofunctional POSS-epoxy. The viscoelastic response at temperatures below T_g was examined and was found to correlate to a stretched exponential relaxation function. Time−aging time-superposition was found to be applicable to the data under all test conditions and for all of the materials used in this study. Surprisingly, the instantaneous modulus was not observed to be affected by incorporation of the POSS nanoreinforcement. This suggests that while POSS cages influence polymer chain motions, including the motion of the molecular junctions, these nanoreinforcements did not participate in the overall deformation of the chains. Experiments performed under identical thermodynamic states, revealed that the molecular level reinforcement provided by the POSS cages also retarded the physical aging process in the glassy state. Therefore, the time required to reach structural equilibrium was longer for samples reinforced with POSS-epoxy than for those of the neat resins.

Introduction

The development of macromolecules containing inorganic or organometallic segments promises to yield plastics with a variety of new and improved properties.[1] Polyhedral oligomeric silsesquioxane (POSS) reagents, monomers, and polymers are emerging as a new chemical feedstock technology for the preparation of nanoreinforced plastics. The establishment of broad chemical trees of monomeric POSS reagents and resins based on well-defined POSS cages affords new chemical feedstocks for the modification of properties in nearly all traditional organic polymeric materials.[2]

POSS reagents combine a hybrid inorganic−organic composition with nanosized cage structures having dimensions comparable to those of most polymeric segments or coils.[2] Hence incorporation of POSS reagents into linear thermoplastics or thermoset networks can be used to modify the composition, local structure, and chain mobility in polymeric systems. These modifications can ultimately affect the thermal, oxidative, and dimensional stability of many polymeric resins, thus upgrading their properties for numerous high-performance engineering applications.

Epoxy resins are by far the most commonly used engineering thermosets, in part due to their excellent engineering performance upon curing and ease of processing prior to curing. In this paper, we report the viscoelastic performance and physical aging response of cured epoxy networks containing monofunctional POSS-epoxy nanoreinforcements at various temperatures below the glass transition temperature.

The specific focus of this work was to examine the dimensional stability of the resulting network glasses utilizing small-strain stress relaxation techniques and to gain insight into how the nanoscopic inorganic cages affect the structural recovery process of the epoxy network glasses during physical aging at temperatures below the glass transition temperature.

Experimental Section

Synthesis of Epoxide POSS Macromers. $[(c\text{-}C_6H_{11})_7Si_8O_{12}CH_2CHCH_2O]$. *m*-Chloroperbenzoic acid (MCPBA) (0.68 g, 3.9 mmol) was added to a solution of $(c\text{-}C_6H_{11})_7Si_8O_{12}CH_2CH{=}CH_2$ (2.1 g, 2.01 mmol) in methylene chloride (25 mL) and stirred at 23 °C for 3 days. The methylene chloride was removed from the reaction mixture by rotary evaporation, and the resulting solid was placed into methanol (1 L) and stirred for 24 h. The POSS-epoxide product, which is insoluble in methanol, was collected by vacuum filtration, washed with methanol, and dried under vacuum to give 1.26 g (59%) of monofunctional POSS-epoxide. Characterization data for this and related monofunctional POSS-epoxides have been described elsewhere.[3]

Materials Preparation. The nanoreinforced epoxy network glasses used in this study contained 5 and 9 wt % fractions of the monofunctional POSS-epoxide described above. The conventional epoxy resins used in this study were two different difunctional epoxies (diglycidyl ether of Bisphenol A,

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* Corresponding author.
† Michigan State University.
‡ Air Force Research Laboratory.

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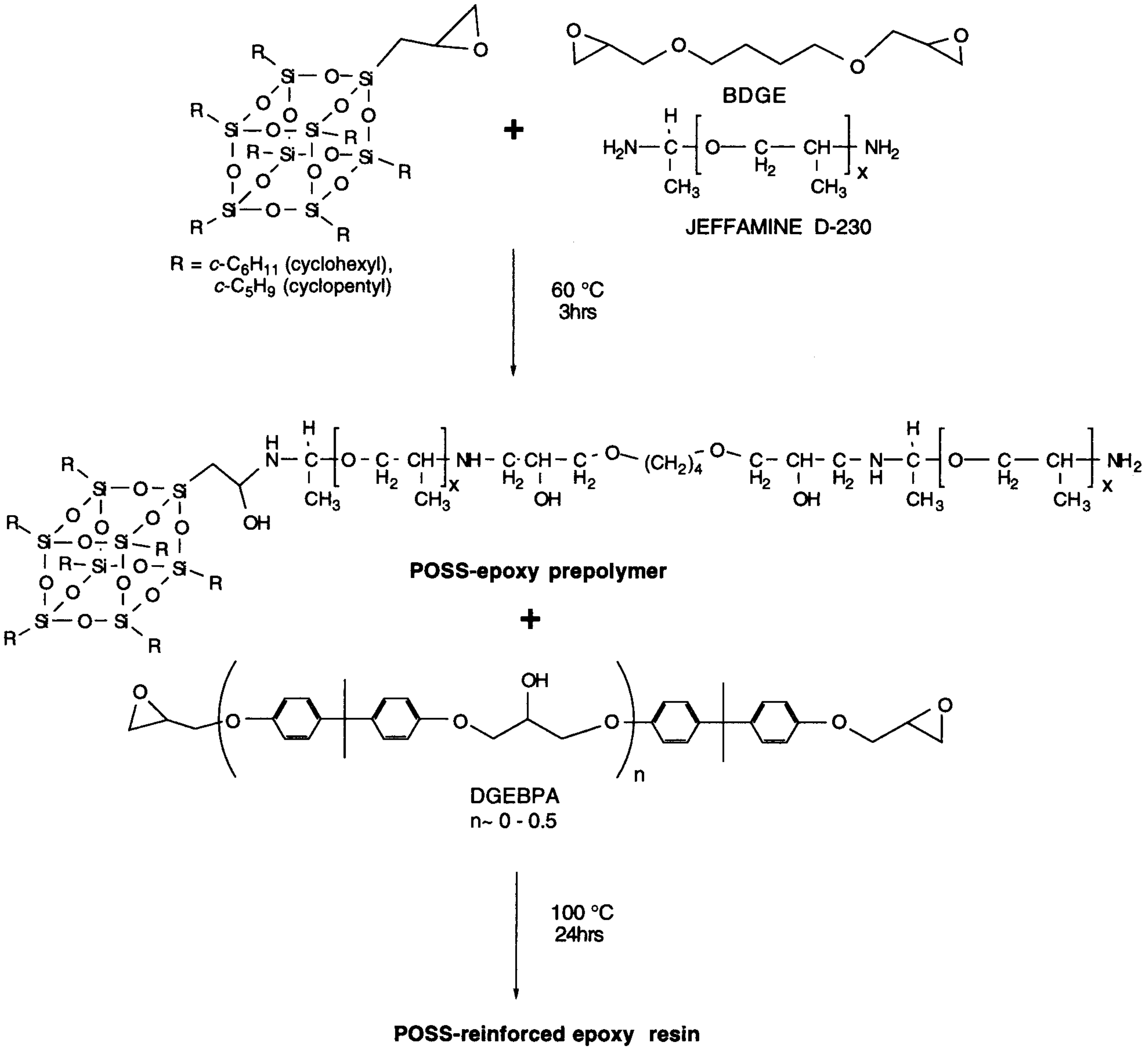

Figure 1. Schematic of the curing cycle of the POSS-epoxy system.

DGEBA, (Dow Chemical DER332, 15.3 g, 0.09 mol of [epoxide]), and 1,4-butanediol diglycidyl ether, BDGE (Shell Chemical Heloxy 67, 1.12 g, 0.01 mol of [epoxide])). The curing agent used was the diamine-terminated poly(propylene oxide), Jeffamine D230; Huntsman Chemical (5.75 g, 0.1 mol of [H]). It is important to note here that the molar ratio of epoxide (the contribution from DER332, Heloxy 67, and functional POSS) and hydrogen (from the Jeffamine D230) was equal to 1 for all epoxy networks investigated in this study. The DGEBA epoxide monomer was first preheated at 60 °C for 2 h to melt any crystals present. First, POSS-epoxide/Heloxy 67/D230 was mixed together and stirred by hand. The mixture was heated at 60 °C for 3 h to promote the reaction between the amines and epoxide functionalities. The preheated DER332 was then added to the mixture and stirred by hand. The mixture was then degassed in a vacuum for 10 min at room temperature. This resin mixture was then poured into a glass tube with a diameter of 12.7 mm (0.5 in.), cured in an air oven at 100 °C for 24 h, and then slowly cooled in an oven overnight to room temperature. A schematic of this curing procedure is depicted in Figure 1.

Cylindrical specimens were machined out of the cured resin rods. The overall length of the specimens was 98 mm, with the diameter of the central portion (at 49 mm) reduced to 3.4 mm. All specimens were vacuum-dried at 90 °C for 24 h to remove any moisture that may have been absorbed during specimen preparation and were subsequently placed in a sealed desiccator until the mechanical experiments were performed. The weights of each sample were then recorded and verified prior to commencement of the mechanical testing.

The glass transition temperature of the cured samples was determined using a Mettler-Toledo 821e/400 differential scanning calorimeter. The sample was first heated to 160 °C and held for 10 min to remove any prior thermal history. The sample was then cooled to 5 °C at a rate of 20 °C/min and then heated back up to 120 °C at a rate of 20 °C/min. The glass transition temperature, T_g, was determined as the inflection point of the glass transition region on the DSC thermograph.

Small-Strain Stress Relaxation. Mechanical tests were performed using a computer-controlled servo-hydraulic testing machine (Instron model 1321) equipped with an oven for temperature control. Temperature measurements taken at the top and bottom surfaces of the samples showed a gradient of less than 0.3 °C. Oven stability was observed to be better than ±0.2 °C during each experiment. The tensile test specimens were first annealed for 30 min at 105 °C to erase any aging that occurred during storage and were then placed in the testing machine at the testing temperature, and the samples were then monitored as they aged.

All mechanical tests were carried out in uniaxial extension under stress relaxation conditions. A small strain was applied periodically at aging time, t_a, that doubled with each test; i.e., t_a = 30 min, 60 min, 120 min, etc. The duration, t_d, of the

Table 1. Differential Scanning Calorimetry Results of Epoxy Glasses

sample	onset of transition (°C)	midpoint of transition (°C)	end of transition (°C)
neat	66.9	71.2	75.3
5 wt % POSS	67.2	74.8	80.3
10 wt % POSS	67.2	78.9	83.4

deformation was varied so that the ratio of t_d/t_a was constant throughout the aging experiment. The value of t_d/t_a in this study was 0.05. A short duration time was used so that the changes that occurred in polymer structures during the mechanical experiment would be minimal and hence would not influence the measurements. The small-strain stress relaxation technique was used to examine the effect of POSS cages on the viscoelastic response of polymeric glasses during physical aging. The applied strain used here was 0.001 and was measured with a full scale of 0.1 strain (Instron extensometer of a 10 mm gauge length). The relaxation modulus was then calculated at $\sigma(t)/\epsilon$, where ϵ was the applied strain.

Results and Discussion

Differential Scanning Calorimetry. Calorimetric (DSC) measurements were performed for network glasses containing 5 and 9 wt % of a monofunctional POSS-epoxy nanoreinforcement. Measurements of the glass transition are routinely used as part of resinous material characterization and provide direct insight into the mobility of polymer chains. The glass transition temperature for this study was taken as the midpoint in the specific heat transition. While the DSC results are summarized in Table 1, the following observations were made:

1. The glass transition temperature, T_g, determined by DSC increases with increased loading of POSS-epoxy into the network. This observation suggests that the presence of POSS cages, due to their nanoscopic size and due to their chemical incorporation directly into the polymer chains, effectively hinder the motion of network junctions, thus the T_g of the network increases.

2. The width of the endothermic transition was not affected with the addition of monofunctional POSS epoxy. This suggests that these POSS cages are completely incorporated within the network and do not form macroscopic phase-separated domains.[4]

Isothermal Aging. Stress Relaxation Experiments. The relaxation modulus curves displayed in Figure 2 are representative of the results obtained with the epoxy network glass aged at a temperatures below T_g. They correspond to aging times of 0.5, 1, 2, and up to 64 h, as indicated. In general, for a given sample, it is always possible to shift the relaxation curve obtained at different aging times horizontally along the time axis to form a time−aging time master curve, as shown in Figure 2. To compare the relaxation modulus curves obtained at different temperatures and between the various epoxy compositions, the relaxation modulus curve was fitted with a stretched exponential Kohlrausch−William−Watts (KWW) type function:[5,6]

$$E(t) = E_0\left\{\exp\left[-\left(\frac{t}{\tau_s}\right)^{\beta_s}\right]\right\} \quad (1)$$

where E_o is the zero-time tensile modulus, τ_s is the characteristic relaxation time, and β_s is the shape parameter related to the breadth of the stress relaxation modulus curve. The numerical analysis for the curve fits at each experimental condition was performed using the Kalidagraph nonlinear least-squares data analysis software on a personal computer. We found that the value of β_s and E_o remained constant despite the differing amounts of monofunctional POSS-epoxy that had been added into the glassy network. Furthermore, it is interesting to note that when tested at different aging temperatures, the value of β_s ($\beta_s = 0.32$) was again not affected by the amount of monofunctional POSS-epoxy present.

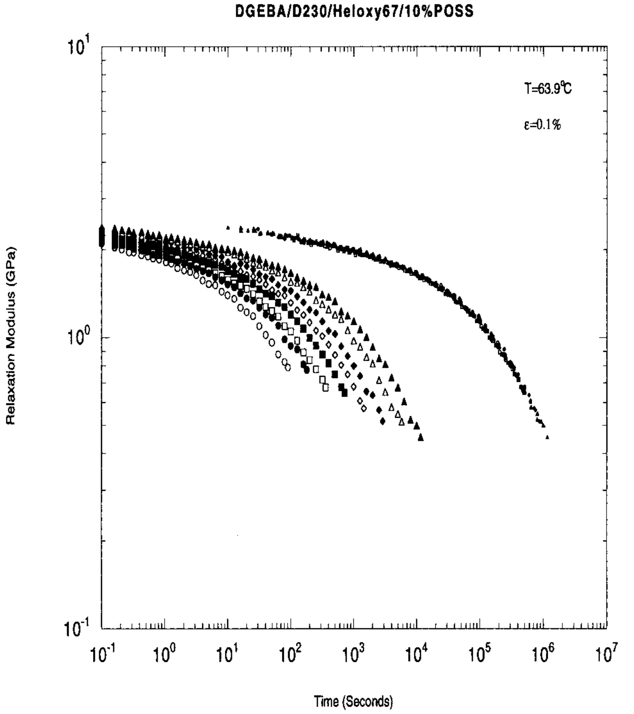

Figure 2. Small-strain stress relaxation modulus curves for DGEBA/D230/Heloxy67/9 wt % POSS-epoxy glass at an aging temperature of 63.9 °C. The applied strain is 0.001. Aging time in hours: (○) 0.5; (●) 1; (□) 2; (■) 4; (◇) 8; (◆) 16; (△) 32, (▲) 64. Master curves offset by an arbitrary shift for clarity.

In Figure 3, we depict the relaxation modulus curves for different loadings of POSS-epoxy monomers after 64 h of isothermal aging at a temperature of 63.9 °C. It is clear that these relaxation curves can be superimposed with only horizontal shifts along the time axis. Furthermore, it is interesting to point out that the value of E_o is not affected by the presence of the nanoreinforcement. This may be in part a reflection the monofunctional nature in POSS epoxy monomers used in this study. Despite the ability of the POSS cages to hinder the relaxation motion of network junctions from a chain terminus location within the network, they do not contribute to the overall deformation process of such glassy networks from this position. Interestingly, such monofunctional POSS-epoxide may be useful for enhancing glass transition without increasing cross-link density and potentially detracting from the desirable mechanical properties of such epoxy networks.

The characteristic relaxation time, τ_s, of the networks was also obtained using eq 1 from the data of the stress relaxation experiments. From Figure 2, we have shown that, as the isothermal aging time increases, the value of τ_s also increases. This is a common phenomenon of glass-forming materials in the nonequilibrium glassy state.[7−9] As the material gradually relaxes toward its equilibrium state, the molecular mobility is decreased. Hence, the characteristic relaxation time is expected to increase with increased isothermal aging time until the

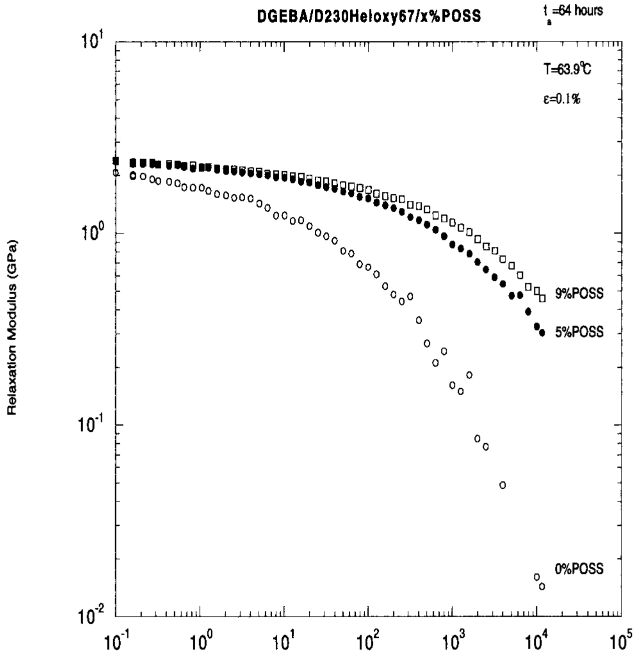

Figure 3. Small-strain stress relaxation modulus curves for DGEBA/D230/Heloxy67/*x* wt % POSS-epoxy glass after 64 h the isothermal aging at a of temperature 63.9 °C. The applied strain is 0.001. Weight fraction of POSS-epoxy: (○) neat resin with no POSS-epoxy; (●) 5 wt %; (□) 9 wt %.

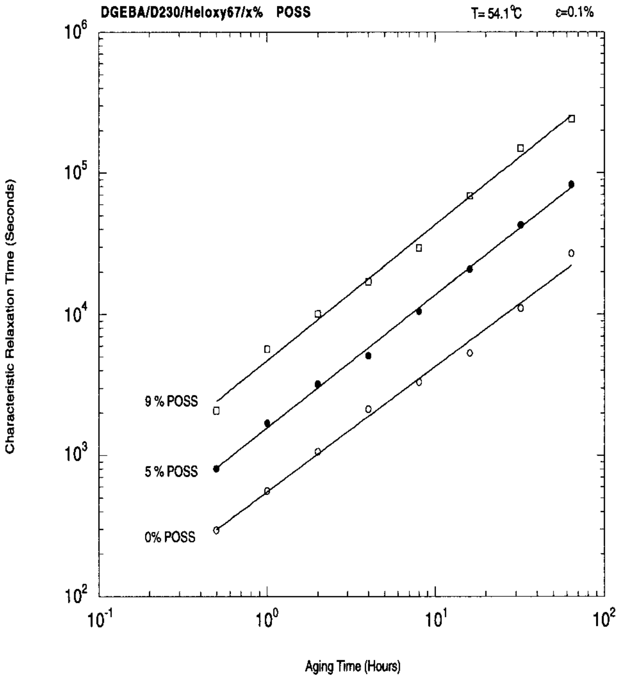

Figure 4. Characteristic relaxation time, τ_s, versus aging time for DGEBA/D230/Heloxy67/*x* wt % POSS-epoxy glass at a testing temperature of 54.1 °C. The applied strain is 0.001. Weight fraction of POSS-epoxy: (○) neat resin with no POSS-epoxy; (●) 5 wt %; (□) 9 wt %.

material reaches its structural equilibrium state. Therefore, the rate of change in τ_s is used as a measure for how a glassy system approaches its structural equilibrium state. In Figure 4, we constructed a double-logarithmic plot of τ_s versus aging time, t_a, at a given testing temperature for the epoxy glasses containing different loadings of the POSS nanoreinforcement. Similar plots but at different testing temperatures are shown in Figures 5 and 6. For aging temperatures well below T_g, the double logarithmic rate of change in the characteristic relaxation time does not appear to be affected by the presence of POSS cages. However, at any given aging time, networks containing higher loadings of the POSS nanoreinforcements have higher characteristic relaxation time values. Increased relax-

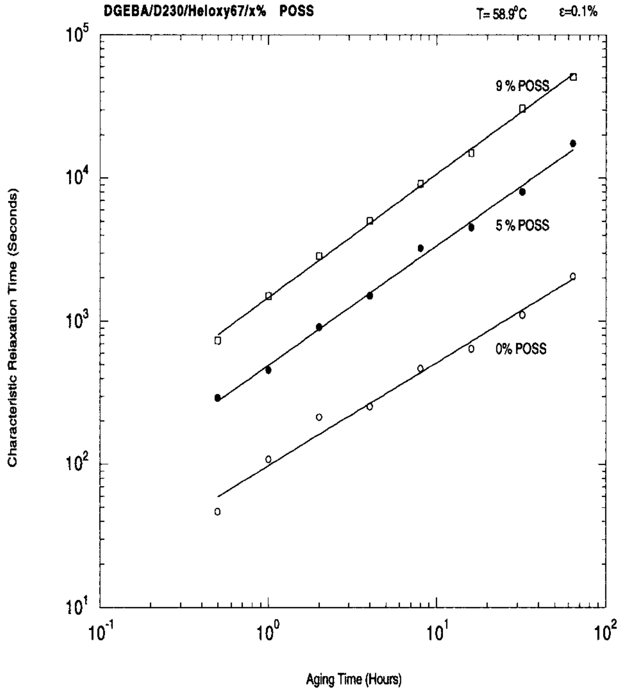

Figure 5. Characteristic relaxation time, τ_s, versus aging time for DGEBA/D230/Heloxy67/*x* wt % POSS-epoxy glass at testing temperature of 58.9 °C. The applied strain is 0.001. Weight fraction of POSS-epoxy: (○) neat resin with no POSS-epoxy; (●) 5 wt %; (□) 9 wt %.

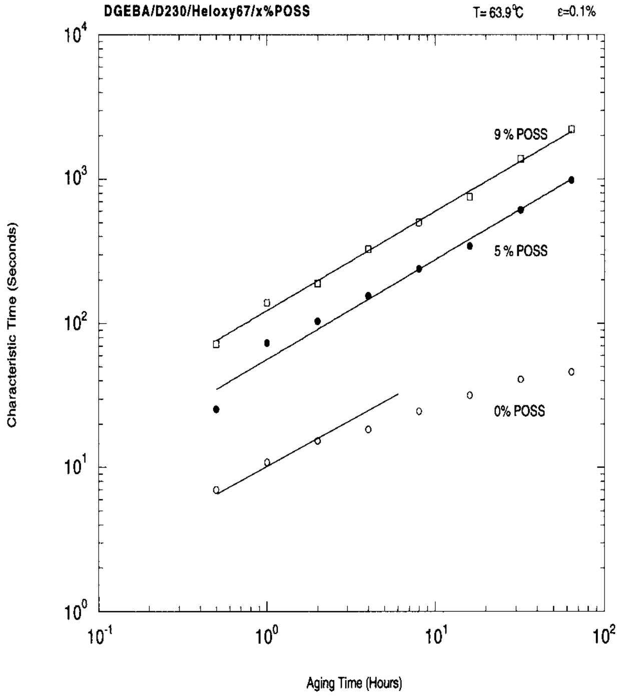

Figure 6. Characteristic relaxation time, τ_s, versus aging time for DGEBA/D230/Heloxy67/*x* wt % POSS-epoxy glass at testing temperature of 63.9 °C. The applied strain is 0.001. Weight fraction of POSS-epoxy: (○) neat resin with no POSS-epoxy; (●) 5 wt %; (□) 9 wt %.

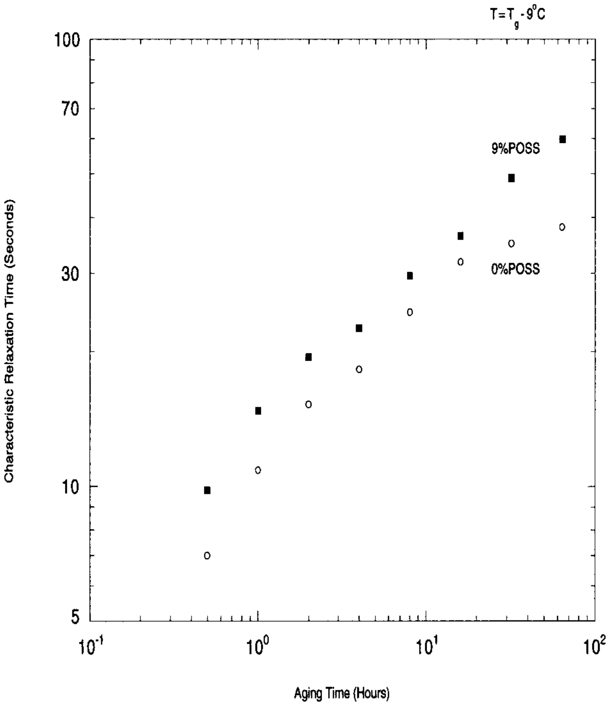

Figure 7. Characteristic relaxation time, τ_s, versus aging time for DGEBA/D230/Heloxy67/*x* wt % POSS-epoxy glass at testing temperature of 9 °C below its T_g. The applied strain is 0.001. Weight fraction of POSS-epoxy: (○) neat resin with no POSS-epoxy and testing temperature 63.9 °C; (■) 9 wt % and testing temperature 69.1 °C.

ation times are also to be expected given the fact that the POSS-reinforced networks show higher T_g values.

To examine the effect of POSS cages on the molecular mobility, it is necessary for the system to be in the same thermodynamic state; i.e., the difference between the aging temperature and the T_g is the same.[9-11] In Figure 7, we show a double logarithmic plot of characteristic relaxation time versus aging time for stress relaxation experiments performed at a temperature of 9 °C below the respective T_g. For the neat resin sample, we observed a change in the slope of the characteristic relaxation time versus aging time after 32 h. This is an indication that the sample is close to its final structural equilibrium. However, for the sample with 9 wt % of POSS-epoxy, the relaxation modulus curve continued to shift to longer times, i.e., no change in the slope of characteristic relaxation time versus aging time. After 64 h of isothermal aging, the sample had not yet reached its structural equilibrium point. From this observation, we proposed that the presence of POSS cages provides topological constraints to the network junctions, which prevent or severely retard the process of the network reaching structural equilibrium. Given that the physical size of POSS cages approaches that of most polymer dimensions (segments)[2], the inability of such a network to relax can be anticipated. Therefore, the time needed to reach structural equilibrium is longer for a sample with POSS cages attached to the network chains.

Conclusions

Commonly used DGEBA epoxy resins were formulated with monofunctional POSS-epoxy nanoreinforcements and subsequently cured into transparent nanoreinforced polymeric networks using common amine-terminated agents. Differential scanning calorimetry was used to measure the glass transition of networks containing different weight fractions of monofunctional POSS-epoxy. The glass transition temperature was observed to increase and broaden with increased loading of the monofunctional POSS epoxy into the network. The increased glass transition occurred without increasing the degree of cross-linking within the network. This may be due to the nanoscopic size of these POSS cages and their ability to hinder the motion of the molecular chains and network junctions.

These networks were subjected to thermal quenching and aging experiments at temperatures below T_g. At a constant temperature below the T_g of the system, it is possible to age these glassy networks to the point where they reach a structural equilibrium. However, the topological constraints provided by the presence of POSS-reinforcements slows down the motion of the network junctions and hence the time needed to reach structural equilibrium is dramatically increased relative to that for nonnanoreinforced networks. This is consistent with the observation of increase in T_g due to the presence of POSS cages.

Small-strain stress relaxation experiments were used to probe the viscoelastic responses of these networks during isothermal aging. The superimposed time–aging time-relaxation modulus curves was accomplished for all network glasses by using only horizontal shifts along the time axis and were fitted with a KWW stretched exponential function. Analysis of these curves revealed that the parameter β_s (the shape factor) associated with the breadth of the relaxation curve remained constant with increases in the weight fraction of POSS-epoxy incorporated into the networks. Furthermore, the value of E_0, the zero time modulus, is also unaffected by the presence of POSS-epoxy. This observation leads one to suggest that the addition of monofunctional POSS-epoxy nanoreinforcements to such networks does not alter the shape of the viscoelastic spectrum despite their ability to shift it to higher temperatures. Therefore, the monofunctional POSS-epoxy nanoreinforcement does not contribute to the deformation process of the network while enhancing its thermal properties.

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