Thermal and Viscoelastic Property of Epoxy–Clay and Hybrid Inorganic–Organic Epoxy Nanocomposites

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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 chemical interaction between the nanoreinforcement and the polymeric chain, along with macroscopic processing and microstructural effects. In this article, we investigated the thermal and viscoelastic property enhancement on crosslinked epoxy using two types of nanoreinforcement, namely, organoion exchange clay and polymerizable polyhedral oligomeric silsesquioxane (POSS) macromers. Glass transitions of these nanocomposites were studied using differential scanning calorimetry (DSC). Small-strain stress relaxation under uniaxial deformation was examined to provide insights into the time-dependent viscoelastic behavior of these nanocomposites. Since the size of the POSS macromer is comparable to the distance between molecular junctions, as we increase the amount of POSS macromers, the glass transition temperature T_{σ} as observed by DSC, increases. However, for an epoxy network reinforced with clay, we did not observe any effect on the $T_{\scriptscriptstyle g}$ due to the presence of clay reinforcements. In smallstrain stress relaxation experiments, both types of reinforcement provided some enhancement in creep resistance, namely, the characteristic relaxation time, as determined using a stretched exponential relaxation function increased with the addition of reinforcements. However, due to different reinforcement mechanisms, enhancement in the instantaneous modulus was observed for clay-reinforced epoxies, while the instantaneous modulus was not effected in POSS-epoxy nanocomposites. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1993-2001, 1999

Key words: nanocomposites; clay reinforcements; inorganic–organic hybrids; epoxy; stress relaxation; superposition

INTRODUCTION

The major problems in engineering applications of polymer are the low stiffness and strength when compared to metals. Two methods are used to offset these deficiencies as follows: (1) the ingenious use of shape, designing into a component the necessary stiffness and strength by means of ribs or box sections; and (2) the addition of reinforced particles or fibers to the resin to form composite materials. The idea and application of composite materials do not belong solely to either synthetic materials or modern technology since nature is full of examples wherein the ideas of

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composite materials are utilized. Besides the naturally occurring composites, there are many engineering materials that are composites in a very general way and have been in use for a long time, such as mud mixed with straw (chopped-fiber reinforcement) and cement mixed with sand (particulate reinforcement).

In the past 30 years, the demand on lightweight, high-performance materials is so great and diverse that the composite concept is a natural conclusion. Owing to the development of highstrength, lightweight fibers, such as carbon filer and silicon carbide fiber, the fiber-reinforced composites has been more prominent than other types of composites. However, the high cost of these novel fibers and the additional complexity in the manufacturing technologies have restricted their application to mainly high-tech, low-production volume areas. In the past few years, there are considerable interest in the development of highspeed, low-cost composites. There are various materials that consist of structured analogs to the high-strength fibers on the nanometer scale, such as molecular wire imogolite, layered silicates, and zeolites, which are examples of one-, two-, and three-dimensional natural and synthetic microassemblies. This recent development of nanocomposites provides a promising opportunity to apply microassemblies as reinforcement in composite materials.

Nanocomposites are composite materials consisting of building blocks in the nanometer or tens-of-nanometer-size scales. The properties of nanocomposites are determined not only by the bulk properties of each of the components but also by complex interactions between different phase and the interfaces between them. Nanocomposites promise to be the wave of the future, having major implications for industry and technology. The types of nanocomposites can be classified depending on the material used, such as ceramicceramic, metal-ceramic, metal-metal, metalpolymer, and ceramic—polymer. In this study, we investigated two types of newly developed ceramic-polymer nanocomposites. Since the ceramic or inorganic phase is chemically attached to the polymeric or organic phase, these composites can also be refer as hybrid inorganic-organic polymer.^{1,2}

The synthesis of these hybrid inorganic–organic polymers has been achieved over the past 10 years. One approach is the application of sol– gel reaction,^{3–5} in which the inorganic components are formed in situ in the hybrid system

through hydrolysis and condensation of mononuclear species. However, owing to the loss of volatile by-products formed in the hydrolysis-condensation reactions, it is difficult to control sample shrinkage during processing. Another approach for incorporate nanoscopic inorganic cluster into organic polymer is to design well-defined inorganic oligomers with a single polymerization site per cluster.⁶⁻¹⁴ Each oligomeric cluster has an exactly defined degree of polymerization of eight, $(RSiO_{1.5})_8$, or more precisely, $P_1R_7Si_8O_{12}$, where R and P are organic groups. These polyhedral oligomeric silsesquioxane (POSS) macromers have an inorganic silica-like core and are surrounded by eight organic groups, of which seven are inert and jut one is reactive. Further polymerization involving the single reactive P site results in a linear polymer containing monodisperse, nanosize inorganic clusters pendent to an organic polymer backbone. These hybrid inorganic-organic polymers can be processed further like any thermoplastic polymers.

Another type of nanocomposites that have attracted significant attention is the incorporation of the layered inorganic component.¹⁵⁻²⁴ The varieties of layered inorganic available and the established understanding of intercalation chemistry have attributed to this growing interest. The intercalated polymer-clay system is that the organic polymer layers and inorganic silicate layer are alternatively interstratified at the molecular level. Various polymers have been intercalated into clay galleries. To further overcome the binding forces between the clay layers, material chemists have synthesized exfoliated polymer-clay nanocomposites. The exfoliated clay layers about 10 Å in thickness are dispersed inside the polymer matrix. The first exfoliated polymer-clay nanocomposite was the Nylon 6-montmorillonite system reported by Toyota researches.^{16–18} Based on a similar technique, other polymers have also used to produce exfoliated clay nanocomposites.

Epoxy resin, owing to the ease of process and excellent engineering performance upon curing, it is, by far, the most commonly used engineering thermoset.²⁵ In this article, we compare the viscoelastic performance and physical aging behavior of cured epoxy networks containing either monofunctional POSS–epoxy and exfoliated clay reinforcements. Specifically, we use small strain stress relaxation technique to examine the dimensional stability of network glasses containing the nanoscopic inorganic clusters or dispersed layered smectite clay. Moreover, we are interested in the complex interaction between molecular structures of the polymeric host and different nanoscopic inorganic structures, where one can optimize viscoelastic performance of nanocomposites at temperatures below the glass transition temperature.

EXPERIMENTAL

Synthesis of Epoxide POSS Macromers

$[(c - C_6 H_{11})_7 Si_8 O_{12} C H_2 C H C H_2 O]$

Solid *m*-chloroperbenzoic acid (MCPBA) (0.68 g, 3.9 mmol) was added to a solution of POSS- α olefins (2.1 g, 1.93 mmol) in methylene chloride (25 mL). The reaction mixture was stirred for 3 days. The methylene chloride was removed from the reaction mixture by rotary evaporation, and the resulting solid was stirred with methanol for 24 h. The epoxide, which is insoluble in methanol, was collected by vacuum filtration, washed with methanol, and dried under vacuum to give 1.263 g (84%) of monofunctional POSS–epoxide. The detail description in the synthesis of monofunctional POSS epoxide was presented elsewhere.⁶

Preparation of Intercalated Montmorillonite Organoclays

The inorganic cations in the clay gallery, such as Na^+ , provide an environment for water molecule coordination around the cations, and the water molecules may form monolayer or multilayer structures in the clay galleries. The layer spacing is controlled by the total water content. Owing to the cation exchange properties of smectite clays, the clay gallery ions can be replaced by organic cationic species, such as alkylammonium ions. The exchange of the gallery cations changes from inorganic to organic, and the surface property of the clay changes from hydrophilic to hydrophobic.

Montmorillonite from Wyoming were obtained from the Source Clay Mineral Depository, University of Missouri, Columbia. The mineral was purified by sedimentation to exclude particles larger than 2 μ m, followed by removal of carbonates by using pH 5 acetate buffer solution and elimination of iron oxide by using sodium hydrosulfate. Long-chain primary alkylamines CH₃(CH₂)₁₇NH₂ was obtained from Aldrich Chemicals. The cation exchange reaction was carried by mixing 500 mL of 0.05*M* alkylammonium chloride ethanol : water (1 : 1) solution and 2.0 g of clay at 70°C for 24 h. The exchanged clays were washed with ethanol : water (1 : 1) several times until no chloride were detected with $1.0M \text{ AgNO}_3$ solution and then airdried. Finally, the clays were ground, and the particle size fraction of 40 to 50 μ m was collected.

Preparation of POSS Reinforced Epoxy Networks

The epoxy network glasses used here contain various weight fractions of monofunctional POSSepoxide described above. The major component of epoxy resin was a mixture of two different difunctional epoxies (diglycidyl ether of bisphenol A (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 mole of [Epoxide]). The curing agent used was the diamine-terminated polypropylene 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 and Heloxy 67) 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, POSSepoxide—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 amines and POSS-epoxide. The DER332 was then added to the mixture and stirred by hand. This mixture was degassed in a vacuum for 10 min at room temperature. This final mixture was then poured into a glass tube with a diameter of 12.7 mm (0.5 in.) and cured in an air oven at 75°C for 3 h, then at 100°C for an additional 20 h. The samples were slowly cooled in the oven overnight to room temperature.

Preparation of Epoxy-Clay Nanocomposites

The organoion-exchanged, intercalated montmorillonite clays were mixed with diglycidyl ether of bisphenol A epoxy, DGEBA; Dow Chemical DER332. The mixture was stirred at 75°C for 2 h for uniform dispersion and to melt any crystals present. To modify the molecular structure of network, the curing agent was mixture of the diamine-terminated polypropylene oxides, of different molecular weight, Jeffamine D230 and D2000 (Huntsman Chemical). To reduce additional complexity, the molar ratio of epoxide (from DER332) to hydrogen (from the Jeffamine D230 and D2000) was equal to one. We note here that the weight of DGEBA used per sample was 17 g. (0.1 mol of [Epoxide]), the weight of Jeffamine D230 was 5.635 g. (0.098 mol of [Hydrogen]), and the weight of Jeffamine D2000 was 1 g. (0.002 mol of [Hydrogen]). After the addition of diamine curing agent, the mixture was then degassed in a vacuum for 10 min at room temperature. This final mixture was then poured into a glass tube with a diameter of 12.7 mm (0.5 in.) and cured in an air oven at 75°C for 3 h, then at 100°C for an additional 20 h. The cured samples were then slowly cooled in the oven overnight to room temperature.

Thermal Analysis

The glass transition temperature of cured epoxy network glasses was with a Mettler-Toledo 821e/400 differential scanning calorimeter. The sample was first heated to 160°C and held for 10 min to remove previous aging. Sample was then cooled to 5°C at a rate of 20°C per min, then heated back up to 120°C at a rate of 20°C per min. The glass transition temperature T_g , was determined as the inflection point of the glass transition region on the DSC thermograph.

Viscoelastic Experiments

Cylindrical specimens were machined out of the cured resin rods. The overall length of the specimen was 98 mm, with the diameter of the central 49 mm reduced to 3.4 mm. All specimens were vacuum-dried at a temperature of 90°C for 24 h to remove any moisture that may have picked up during specimen preparation. After the weights of each sample were recorded and compared prior to the mechanical testing, they were kept in a sealed desiccator until the mechanical experiments were performed.

Mechanical tests were performed using a computer-controlled servo-hydraulic testing machine (Instron model 1321) equipped with an oven for temperature control. Measurements of the temperature between the top and bottom of the samples showed a gradient of less than 0.3°C. Oven stability was 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 then placed in the testing machine at the testing temperature, where the glass began to age. Since these networks were polymeric glasses prior to viscoelastic experiments, it was necessary to subjected them to similar thermal history and tested at the same isothermal aging time at temperatures below T_g .

The mechanical tests were carried out in uniaxial extension under stress relaxation conditions. Small strain was applied periodically at aging time t_a that doubled with each test, that is, $t_a = 30, 60, \text{ and } 120 \text{ min, etc. The duration } t_d \text{ of }$ the 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. The short duration time was used so that the changes that occurred in polymer structures during the mechanical experiment would be small and not influence the measurements. Since we are interested in the effect of different reinforcements and molecular structures of epoxy network, only small strain is used. The applied strain used here was 0.001 and was measured using a Instron extensometer of a 10 mm gauge length with a full scale of 0.01 strain. the relaxation modulus was then calculated at $\sigma(t)/\varepsilon$, where ε was the applied strain.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

Calorimetric (DSC) measurements were performed on all the network glasses used in this study. These results are used to provide information about the materials in a format commonly used in routine laboratory characterization and are used to establish the reference temperature for the isothermal aging experiments. DSC results are in Table I. (The glass transition temperature for this study is defined as the midpoint in the specified heat transition.) The following observations were made.

- 1. The glass transition temperature T_g , determined by DSC, increases with the increases in amount of POSS–epoxy in the network. This observation suggests that the presence of POSS clusters, due to their nanoscopic size, hinder the motion of network junctions; thus, the T_g of the network increases.
- 2. The width of transition increases with the addition of monofunctional POSS epoxy. However, the onset of transition is not change. This suggests the presence of these POSS nanoclusters slows down the transition from glasslike behavior to rubberlike behavior. Since the onset of transition is governed only by the di-functional epoxy-

Samples	Reinforced with Clay $E_0, \ \beta_s, \ \tau_s, \ T_g$	Reinforced with Poss $E_0, \ \beta_s, \ \tau_s, \ T_g$
Neat resins	2.5 GPa; 530 s; 0.24; 78.9°C	2.45 GPa; 40 s; 0.32; 71.2°C
5 wt % reinforcement	2.8 GPa; 1750 s; 0.24; 78.3°C	2.50 GPa; 950 s; 0.32; 74.8°C
10 wt % reinforcement	3.0 GPa; 2920 s; 0.24; 78.3°C	2.50 GPa; 2200 s; 0.32; 78.9°C

 Table I
 Kohlrausch-Williams-Watts Curve-Fitting Parameters and the Midpoint Glass Transition

 Temperature for the Samples Used in This Study

 T_g reported above is an average of five different samples reading with a standard deviation of ± 0.4 °C or better.

amine junctions, it is not affected by the presence of POSS inorganic clusters.

3. The value of glass transition temperature and the width of transition were affected only by the amount of D2000 diamine in the epoxy network. Unlike the inclusion of inorganic cluster, the presence of exfoliated clays did not affect T_g of the epoxy network glasses.

Viscoelastic Responses

The relaxation modulus curves displayed in Figure 1 are representative of the results obtained with the epoxy network glass aged at a temperature below T_g . They correspond to aging times of 0.5, 1, and 2 h, 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 1. To compare the relaxation modulus curves obtained at different temperatures and between the various compositions, all relaxation modulus curves obtained in this study were fitted with a stretched exponential Kohlrausch-William-Watts (KWW) type function^{26,27} as follows:

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

where E_0 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. Value of KWW parameters for curves depicted in Figures 2 and 3 are summarized in Table I. The numerical analysis for the curve fits at each experimental condition was performed using the KalidagraphTM nonlinear least-squares data analysis software on a desktop computer. We found that the value of β_s and E_0 remained constant despite the differing amounts of monofunctional POSS–epoxy that had been added into the glassy network. Furthermore, it is interesting to point out 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 presence.

The characteristic relaxation time τ_s of the networks upon deformation at different aging times was also obtained using eq. (1). From Figure 1, we show 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 that we often refer to as physical aging.²⁸⁻³² As the material gradually relaxes into its equilibrium state, the molecular mobility is impacted. Hence, the characteristic relaxation time is expected to increase with increased isothermal aging time until the material reaches its structural equilibrium state. Therefore, in comparing the effectiveness of reinforcement, the subsequent thermal history is critical. In the following discussion, we compare those relaxation modulus curves of the same thermal history. In Figure 2, we depict the relaxation modulus curves tested for different loading of POSSepoxy 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. However, it is interesting to point out that the value of E_0 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 crosslink density



DGEBA/D230/Heloxy67/10%POSS

Figure 1 Small-strain stress relaxation modulus curves for DGEBA-D230-Heloxy 67-9 wt % POSS-epoxy glass at an aging temperature of 63.9°C. Applied strain is 0.001. Aging time in h: (\bigcirc) 0.5; (\bigcirc) 1; (\square) 2; (\blacksquare) 4; (\diamondsuit) 8; (\diamondsuit) 16; (\triangle) 32; (\blacktriangle) 64. Master curves are offset by an arbitrary shift for clarity.

and potentially detracting from the desirable mechanical properties of such epoxy networks.

In Figure 3, we depict the relaxation modulus curves tested for different loading of alkylammonium ions exchanged clay reinforced epoxies after 64 h of isothermal aging at a temperature of 64°C. These curves were fitted using the three-parameter stretched exponential function, as shown in eq. (1). The value of β_s , ($\beta_s = 0.24$), remained constant despite the differing amounts of clay that had been added into the glassy network. The value of β_s is different from those reinforced with monofunctional POSS epoxy. This is not a surprise since the amines used were different. It is interesting to point out here that, unlike those reinforced with POSS, we observed an increase in the value of E_0 as the clay content increases. This observation suggests that the clay layers provided some reinforcement effect, which may be due to the platelike shape of clay layers.

CONCLUSIONS

Commonly used DGEBA epoxy resins were formulated with either monofunctional POSS-epoxy at alkylammonium ions exchanged. Montmorillonite clay and subsequently cured into reinforced



Figure 2 Small-strain stress relaxation modulus curves for DGEBA–D230–Heloxy

67-wt % POSS-epoxy glass after 64 h of isothermal aging at a of temperature 63.9°C. Applied strain is 0.001. Weight fraction of POSS-epoxy: (\bigcirc) neat resin with no POSS-epoxy; (\bigcirc) 5 and (\square) 9 wt %.

polymeric networks using common amine-terminated agents. DSC was used to measure the glass transition of these networks containing different weight fraction of monofunctional POSS-epoxy or organo-clay. For networks reinforced with monofunctional POSS-epoxy, the glass transition temperature was observed to increase and broaden with increased loading of the monofunctional POSS-epoxy. The increased glass transition occurred without increasing the degree of crosslinking 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. However, for networks reinforced with organo-clay, the glass transition temperature was not affect by the presence of reinforcement. This is not a surprising result since, upon exfoliation, the spacing between clay layers is expected to be greater than 1000 Å. Hence, the T_g , as measured using DSC, did not expect to change.

It was observed that the topological constraints provided by either the POSS-epoxy or organoclay reinforcements, the motions of the network junctions slow down, and, hence, the characteristic relaxation time in the small strain stress relaxation increased relative to that for non-nanoreinforced networks. For system reinforced with



Figure 3 Small-strain stress relaxation modulus curves for DGEBA-D230-D2000-wt % organo-clay glasses after 64 h of isothermal aging at a of temperature 63.9°C. Applied strain is 0.001. Weight fraction of organo-clay: (\bigcirc) neat resin with no clay; (\bigcirc) 5 and (\square) 10 wt %.

POSS-epoxy, this is consistent with the observation of increase in T_g due to the presence of POSS cages. While for the organo-clay reinforced system, the presence of clay layers not only retarded the motion of relaxation, it also provided some reinforcement effect; thus, the initial modulus increases with the loading of clay.

From the above results, we concluded that to improve thermal, viscoelastic, and mechanical properties, it is necessary to reinforced in both molecular (using the POSS macromer) and microscopic levels (exfoliated clay). The results for sample with both reinforcements are to be reported in the future.

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