8686 *Macromolecules* **2001,** *34,* 8686−8693

Viscoelastic and Mechanical Properties of Epoxy/Multifunctional Polyhedral Oligomeric Silsesquioxane Nanocomposites and Epoxy/Ladderlike Polyphenylsilsesquioxane Blends

Gui Zhi Li,[†] Lichang Wang,[†] H. Toghiani,[‡] Tyrone L. Daulton,[§]
Kiyohito Koyama,[⊥] and Charles U. Pittman, Jr.*[,†]

Department of Chemistry, Mississippi State University, Mississippi 39762; Department of Chemical Engineering, Mississippi State University, Mississippi 39762; Naval Research Laboratory, Marine Geosciences Division, Stennis Space Center, Mississippi 39529-5004; and Venture Business Laboratory, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan

Received June 29, 2001

ABSTRACT: Aliphatic epoxy composites with multifunctional polyhedral oligomeric silsesquioxane (POSS) $((C_6H_5CHCHO)_4(Si_8O_{12})(CH{=}CHC_6H_5)_4)$ nanophases (epoxy/POSS 95/5 and 75/25) and epoxy blends with the prepolymer of ladderlike polyphenylsilsesquioxane (PPSQ) (95/5, 90/10, and 85/15) were prepared by solution casting and then curing. These composites and blends were studied by dynamic mechanical thermal analysis (DMTA) and mechanical testing. The POSS units incorporated into the epoxy network are well dispersed in the composite, probably on the molecular scale, even at high POSS content (25 wt %) based on TEM observations. However, the aliphatic epoxy/PPSQ blends exhibit good miscibility only at low PPSQ content ($\leq$10 wt %). Phase separation was clearly observed when the PPSQ content was 15%. Incorporation of the POSS macromer into this epoxy network by curing at upper temperatures of 120 and 150 °C broadened the temperature range of glass transition of the resulting composites but has almost no influence on their T_g (the tan δ peak temperature). The T_g of epoxy/PPSQ blends containing $\leq$10 wt % PPSQ increased slightly with increasing PPSQ content. However, the T_g of epoxy/PPSQ 85/15 is lower than that of the neat epoxy resin because cross-linking density is reduced in the blend. Inclusion of PPSQ into the epoxy resin has no effect on the width of their glass transition range. The storage moduli E' of both epoxy/POSS composites and epoxy/PPSQ blends at $T > T_g$ are higher than those of neat epoxy resin and increase with the POSS or PPSQ content, improving their thermal dimensional stability. The flexural modulus of the epoxy resin is raised by POSS incorporation or PPSQ addition. Modification of the epoxy resin's flexural modulus is larger for composites with molecularly dispersed POSS than for those containing PPSQ. The magnitude of this increase goes up as more POSS or PPSQ was added. But, the flexural strengths of epoxy/POSS nanocomposites and epoxy/PPSQ blends are lower than that of neat epoxy.

Introduction

The development of polymer−inorganic nanocomposites with improved properties has attracted much research interest in the past few years.[1] Polyhedral oligomeric silsesquioxane (POSS) reagents offer a unique opportunity in this area for preparing truly molecularly dispersed nanocomposites. They combine a hybrid inorganic−organic composition, $R_n(SiO_{1.5})_n$, with nanosized cage structures having dimensions comparable to those of most polymeric segments or coils.[2] POSS chemical reagents are nanostructured with sizes of 1−3 nm and can be thought of as the smallest particles of silica possible. However, unlike silica, silicones, or fillers, each POSS molecule may contain nonreactive organic substituents that make the POSS nanostructure compatible with polymers or monomers. On the other hand, POSS molecules have been prepared which contain one or more covalently bonded reactive functionalities suitable for polymerization or grafting.[2] Hence, nanostructured POSS chemicals are easily incorporated into common plastics via copolymerization, grafting, or blending.[3]

The incorporation of POSS into polymeric materials often results in dramatic improvements in polymer properties which include, but are not limited to, increases in use temperature, oxidation resistance, surface hardening, and improved mechanical properties as well as reductions in flammability and heat evolution. These enhancements have been shown to apply to a wide range of thermoplastic and a few thermoset systems, i.e., methacrylates,[4] styrenics,[5,6] norborenes,[7,8] ethylenes,[9] epoxies,[10,11] etc. Therefore, many nanocomposites may be designed on the basis of using POSS with traditional plastics and resins. In ref 10, the monofunctional epoxy-substituted POSS monomer, $[(c\text{-}C_6H_{11})_7SiO_{12}(CH_2\overline{CHCH_2O})]$ (shown in Scheme 1), was incorporated into an epoxy resin network composed of the two difuctional epoxies, diglycidyl ether of bisphenol A (DGEBA) and 1,4-butanediol diglycidyl ether (BDGE) (DGEBA/BDGE 9/1 mole ratio). The diamine-terminated poly(propylene oxide), Jeffamine D230 with an average of 38 propylene oxide residues and a M_w of 2248, was employed as the curing agent in an amount which gave a 1:1 equivalent of epoxy to amine functions.[10] The glass transition region was observed (by DSC) to broaden with an increase in weight percent of the POSS

[†] Department of Chemistry, Mississippi State University.

[‡] Department of Chemical Engineering, Mississippi State University.

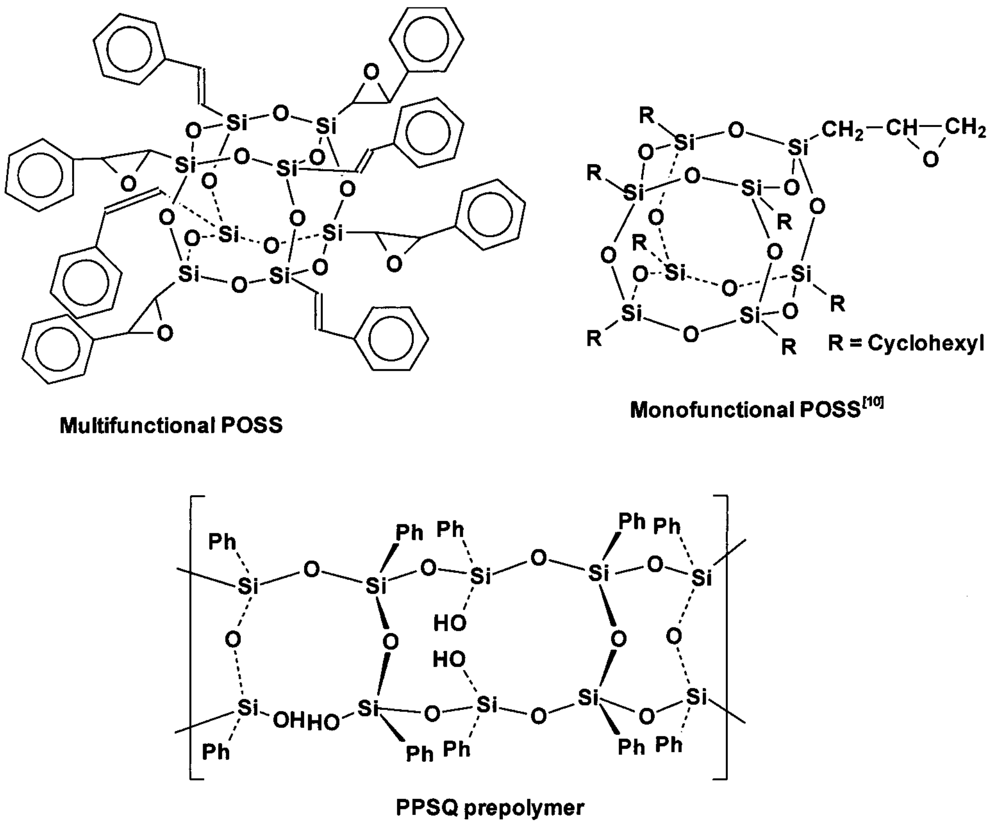
[§] Naval Research Laboratory.

[⊥] Yamagata University.

* Corresponding author. Tel +1-662-3257616; Fax +1-662-3257611; e-mail cpittman@ra.msstate.edu.

10.1021/ma011117q CCC: $20.00

Scheme 1. Structures of Two POSS Monomers and PPSQ Prepolymer



Multifunctional POSS

Monofunctional POSS[10]

PPSQ prepolymer

monomer (≤10 wt %) while there is no change on the onset temperature of the glass transition range.[10]

The POSS-containing epoxy networks described above were subjected to thermal quenching and aging experiments at temperatures below T_g.[10] The topological constraints provided by the presence of POSS reinforcements slow the motion of the network junctions. Therefore, the time needed to reach structural equilibrium is dramatically increased relative to that for non-nanoreinforced networks. Stress relaxation experiments at small strains were used to probe the viscoelastic responses of these networks during isothermal aging.[10] However, very little research has appeared on the use of multifunctional POSS monomers in thermoset systems, and we are unaware of any reports on the incorporation of multifunctional POSS macromers into epoxy resins.

Polyphenylsilsesquioxane (PPSQ) is a ladderlike polymer, composed of two $-Si-O-$ main chains bridged by oxygens. The chemical stoichiomery of PPSQ main chains, $(SiO_{1.5})_n$, is quite similar to that of the core of POSS. Each silicone atom is bonded to three oxygens and one organic group. The special double-chain structure of PPSQ is quite rigid, leading to many outstanding properties such as good thermal and oxidative stability (withstands 400−500 °C), electrical insulating properties, and selective permeability to gases.[12] Moreover, PPSQ is easily dissolved in common solvents, such as tetrahydrofuran (THF), toluene, benzene, and chloroform, etc., allowing the preparation of binary blends of PPSQ with other linear polymers, including polystyrene (PS),[13,14] polycarbonate (PC),[15] poly(ethylene terethalate) (PET),[16] poly(vinyl chloride) (PVC),[17] and poly(methyl methacrylate) (PMMA),[18] by solution-casting or in-situ polymerization. Previous research indicated that the mechanical and thermal properties of PS could be improved by blending a small amount of PPSQ.[14] No reports have appeared on the properties of PPSQ/epoxy blends.

In this paper, the multifunctional POSS monomer, $[(C_6H_5\overline{CHCHO})_4(Si_8O_{12})(CH{=}CHC_6H_5)_4]$, with eight functional groups, including four β-substituted styrenes and four epoxidized styrenes, was blended with a low-viscosity liquid aliphatic epoxy resin and cured. Epoxy/POSS composites with compositions of 95/5 and 75/25 wt/wt were prepared. Epoxy/PPSQ blends at a series of compositions also were made and cured. The PPSQ employed was a prepolymer with a weight-average molecular weight of 4636. The viscoelastic and mechanical properties of the epoxy/multifunctional POSS composites and the epoxy/PPSQ blends have been studied.

Experimental Section

Specimen Preparation. Epoxy 9000 from Clearstream Products, Inc., was employed. It is composed of a proprietary mixture of aliphatic diepoxides of low viscosity. The aliphatic diamine curing agent mixture (proprietary) was also purchased from this company. Multifunctional POSS macromer, $[(C_6H_5\overline{CHCHO})_4(Si_8O_{12})(CH{=}CHC_6H_5)_4]$ (shown in Scheme 1 together with the monofunctional epoxy-POSS macromer in ref 10), with eight functional groups including four epoxidized styrenes and four styrenes, was synthesized by R. L. Blanski at the Air Force Research Laboratory, Edwards AFB, and provided to us. Its chemical structure has been demonstrated by ^1H NMR (($CDCl_3$): δ 2.52 ppm (1H), 4.06 ppm (1H), 6.27 ppm (1H), and 7.35 ppm (11H)). DYTEREP diamine ($C_2H_5CHNH_2CH_2CH_2NH_2$) used for curing multifunctional POSS was purchased from Aldrich Chemical Co., Inc. PPSQ was synthesized as previously reported.[19,20] The prepolymer of PPSQ (M_w = 4636) with an imperfect ladderlike structure (shown in Scheme 1) contains some residual −OH groups that enhance its compatibility with the epoxy system.

Multifunctional POSS was dissolved in tetrahydrofuran (THF), giving a transparent solution (0.552 g/mL). Then, the liquid epoxy components were also dissolved in the THF solution. The resulting solution was put in a vacuum oven (400−450 mmHg) at 30−40 °C for 12 h to remove THF. Then the curing agent for the aliphatic epoxy resin and the diamine ($C_2H_5CHNH_2CH_2CH_2NH_2$) for POSS were added to the POSS/epoxy resin blend. One equivalent of amino groups was employed per equivalent of the sum of the epoxy groups in POSS and the aliphatic epoxy resin. This mixture was cured in mold as follows: room temperature (22−25 °C)/22 h, 80 °C/325 psi (2.24 MPa)/1 h, 120 °C/325 psi (2.24 MPa)/2 h, and 120 °C/23 h. Postcuring at higher temperature of 150 °C was also employed with several samples because the high-temperature curing can enhance the cross-linking of residual epoxy groups in POSS. Three compositions were prepared: epoxy/POSS 100/0, 95/5, and 75/25 (wt).

Epoxy/PPSQ blends were prepared by dissolving both epoxy resin components and PPSQ into a single THF solution followed by evaporation of THF. Then the samples were cured by the same method used for the epoxy/POSS composites. When the percent of PPSQ ($M_w = 4636$) reaches 20 wt %, some PPSQ precipitated after the THF evaporated. Thus, epoxy/PPSQ blends at high PPSQ contents (≥20%) could not be obtained. Attempts were made to prepare epoxy blends with higher molecular weight PPSQ (M_w = 17 000). This higher molecular weight PPSQ has a perfect ladderlike structure. However, poor miscibility between the epoxy resin and this higher molecular weight PPSQ resulted in PPSQ precipitation upon evaporation of THF. This occurred even at low PPSQ content (≤2.3 wt %). Therefore, only epoxy/PPSQ ($M_w = 4636$) blends with epoxy/PPSQ compositions of 95/5, 90/10, and 85/15 were made.

Measurements. The dynamic storage modulus E' and loss factor (tan δ) were determined in the bending mode using a Polymer Laboratories DMTA MK3 instrument. A dual-level bending mode was employed. Small-amplitude bending oscillations (both 1 and 10 Hz) were used at a gap setting of 8.00 mm. The measurements were carried out from 30 to 45 °C to 115−150 °C for all samples. The temperature was raised at a rate of 2 °C/min. The test samples were approximately 3.0−4.0 mm thick, 4.5−5.5 mm wide, and 38 mm long.

Flexural strengths and flexural moduli of both epoxy/POSS composites and epoxy/PPSQ blends were determined according to ASTM D-790-92 using a Zwick materials testing machine (1435). The specimens sizes employed were 38 mm (length) × 10 mm (width) × 3−4 mm (thick). Based on ASTM D790-92, the flexural strength (FS) is defined as the strength when the specimen fails in the three point bending test. The FS value is calculated according to eq 1:

$$\mathrm{FS} = \frac{3PL}{2Wt^2} \tag{1}$$

where P is the breaking force of the specimen, L the support span, W the width, and t the thickness. The flexural modulus (FM) is calculated from the tangent to the steepest initial straight-line portion of the load-deflection curve and using eq 2:

$$\mathrm{FM} = \frac{L^3M}{4Wt^3} \tag{2}$$

where L is the support span, M the tangent of the initial straight-line portion of the load-deflection curve, W the width, and t the thickness.

Results and Discussion

Viscoelastic Properties of Epoxy/POSS Composites. DMTA curves of the neat epoxy resin and the epoxy/POSS 95/5 and 75/25 composites are given in Figures 1 and 2. Figure 1 clearly shows that the bending storage moduli (E') of epoxy/POSS 95/5 are slightly higher than those of the neat epoxy resin while the E' of epoxy/POSS 75/25 are lower than those of the neat epoxy at $T < T_g$. For example, the E' values of neat epoxy, epoxy/POSS 95/5, and 75/25 at 50 °C are 1152, 1384, and 1082 MPa, respectively. At $T > T_g$, the E' values of epoxy/POSS 95/5 and 75/25 are substantially higher than those of the neat epoxy. The E' of neat epoxy, epoxy/POSS 95/5, and 75/25 composites at 115 °C are 7.91, 8.91, and 15.93 MPa, respectively. The E' values of these composites at $T > T_g$ increase with an increase in POSS content. Thus, epoxy/POSS composites have much higher dimensional thermal stability than the neat epoxy resin. Figure 2 shows that the epoxy/POSS 75/25 composite has much broader and lower intensity tan δ peak in the glass transition range than either the neat epoxy resin or epoxy/POSS 95/5.

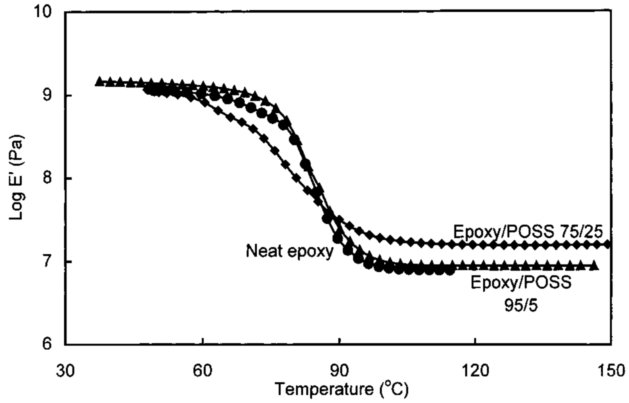


Figure 1. Bending modulus (E') vs temperature curves at 1 Hz (from DMTA) for an aliphatic epoxy resin and its epoxy/POSS 95/5 and 75/25 (wt/wt) composites after final curing at 120 °C/25 h.

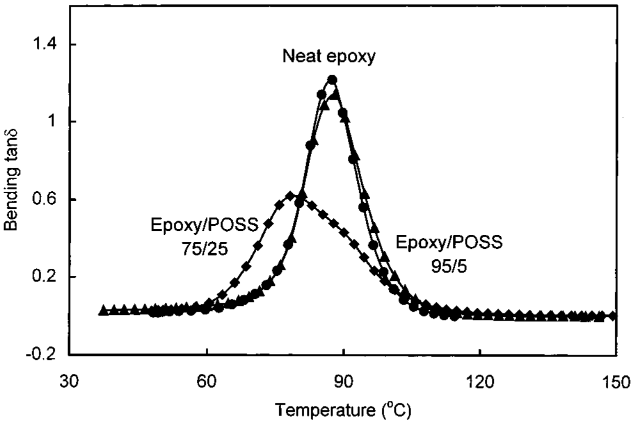


Figure 2. Bending tan δ vs temperature curves at 1 Hz (from DMTA) of an aliphatic epoxy resin and its epoxy/POSS 95/5 and 75/25 (wt/wt) composites after final curing at 120 °C/25 h.

The glass transition temperature (T_g) is defined, herein, as the tan δ peak temperature. Thus, the T_g values of the neat epoxy, epoxy/POSS 95/5, and 75/25 samples are 87.4, 87.9, and 78.7 °C, respectively. The lower T_g of the epoxy/POSS 75/25 composite vs the T_g values of the neat epoxy and epoxy/POSS 95/5 composite may be attributed to some unreacted functional groups that lowered the cross-linking density in this sample. This was due to the low upper curing temperature (120 °C) employed. At higher POSS content (25 wt %), the volume fraction of POSS in the resin is substantial. If the four epoxy functions in the POSS macromer cure

Table 1. T_g Values of Epoxy/POSS Composites

no.	cure temp/time	epoxy/POSS 100/0 T_g(°C)	epoxy/POSS 95/5 T_g(°C)	epoxy/POSS 75/25 T_g(°C)
1	120 °C/25 h	87.4	87.9	78.7
2	120 °C/25 h, 150 °C/2 h	87.8	87.5	85.0
3	120 °C/25 h, 150 °C/6 h	87.1	87.6	86.9
4	120 °C/25 h, 150 °C/10 h	87.8	86.3	87.4

less efficiently than those of the Clearstream resin epoxy functions, then cross-linking density would drop. The epoxy groups in this POSS macromer are disubstituted with a large phenyl ring on one carbon and an extremely bulky corner $-(SiO_{1.5})_8$-POSS cage on the other carbon. Thus, S_N2 substitution by amine functions at either carbon, with epoxy ring-opening, should be slower than the same reaction on the Clearstream epoxy molecules. Therefore, during thermal curing, the epoxy groups in POSS are certainly less reactive than those in the Clearstream resin components. This could lead to a smaller fraction of the POSS epoxy groups participating in the cure. As a result, the cross-linking density in epoxy/POSS 75/25 is less than that in neat epoxy.

This lowered cross-link density can also explain why epoxy/POSS 75/25 has low E' at $T < T_g$. If this correct, curing at high temperature may increase the fraction of POSS epoxy groups that cure, thereby increasing the cross-linking density in the vicinity of the POSS cages. This would raise the T_g of the epoxy/POSS 75/25 sample close to, or higher than, the neat epoxy resin cured at the same temperature. This, as shown later, actually occurred upon postcuring at 150 °C. POSS moieties incorporated into the epoxy network will retard segmental motion due to their high mass and large volume. Even at high temperature ($> T_g$), the segmental motion will be restricted for those segments with POSS bound into the resin by only one chemical bond. This could account for the higher E' values of epoxy/POSS 75/25 at temperatures $T > T_g$.

Since the epoxy/POSS 75/25 sample exhibited a lower T_g value than the neat epoxy resin, these samples were postcured at 150 °C to drive the curing reaction of unreacted epoxy groups in POSS. Upon curing the epoxy/POSS 75/25, neat epoxy, and epoxy/POSS 95/5 samples at 150 °C for 2, 6, and 10 h, respectively, the T_g values of the epoxy/POSS 75/25 sample increased more than those of the others (shown in Table 1). Postcuring at 150 °C for various times has little influence on the T_g values of the neat epoxy resin and epoxy/POSS 95/5 composite. In contrast, T_g of the epoxy/POSS 75/25 composite increases from 78.7 to 85 °C after 2 h of 150 °C postcuring, and it increases more to 87.4 °C when the postcuring is continued for 10 h. The DMTA curves of the neat epoxy resin and two epoxy/POSS composites after curing at 150 °C/10 h are given in Figures 3 and 4.

The bending E' values of the epoxy/POSS composites after postcuring at 150 °C/10 h are now higher than those of neat epoxy over the entire temperature range examined. For an example, the E' values of neat epoxy, epoxy/POSS 95/5, and 75/25 composites at 50 °C ($T < T_g$) are 1262, 1525, and 1521 MPa, respectively, while their E' values at 115 °C ($T > T_g$) are 7.53, 9.38, and 18.81 MPa. This represents increases in the bending modulus E' at 50 °C for the neat epoxy, epoxy/POSS 95/5, and 75/25 samples of 9.5%, 10.2%, and 40.3%, respectively, over the storage moduli exhibited when the samples were only cured at 120 °C/25 h. The E' values at 115 °C for the epoxy/POSS 95/5 and 75/25 composites cured at 150 °C/10 h are greater by 5.2% and 18.1% than those cured at 120 °C for 23 h. The E' value at 115 °C for the neat epoxy decreases slightly (4.8%) vs that of the sample cured at 120 °C. The T_g values of the neat epoxy resin and epoxy/POSS 95/5 and 75/25 samples after curing at 150 °C for 10 h (Figure 4) are 87.8, 86.3, and 87.4 °C, respectively. The T_g of the epoxy/POSS 75/25 composite increased by 8.7 °C when subjected to 150 °C postcuring for 10 h vs the T_g of the sample cured only to 120 °C/25 h. Little change occurred in the T_g values of the neat epoxy resin and epoxy/POSS 95/5 samples after the 150 °C postcuring. Figure 5 illustrates clearly the improvement in both E' and T_g which occur

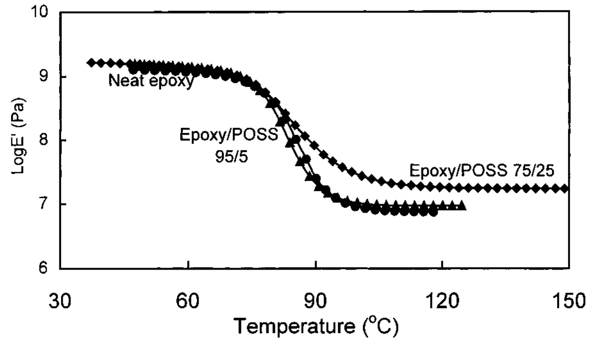


Figure 3. Bending modulus (E') vs temperature curves at 1 Hz (from DMTA) of an aliphatic epoxy resin and its epoxy/POSS 95/5 and 75/25 (wt/wt) composites after curing 150 °C/10 h.

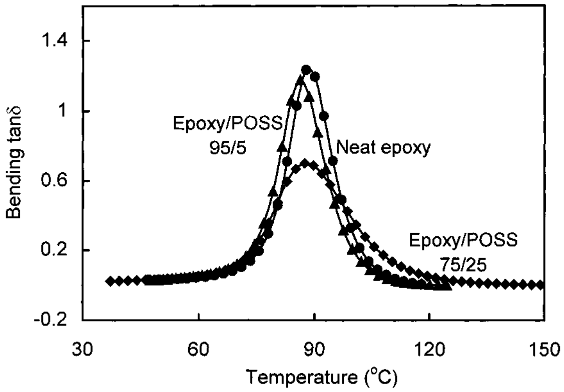


Figure 4. Bending tan δ vs temperature curves at 1 Hz (from DMTA) of an aliphatic epoxy resin and epoxy/POSS 95/5 and 75/25 (wt/wt) composites after curing 150 °C/10 h.

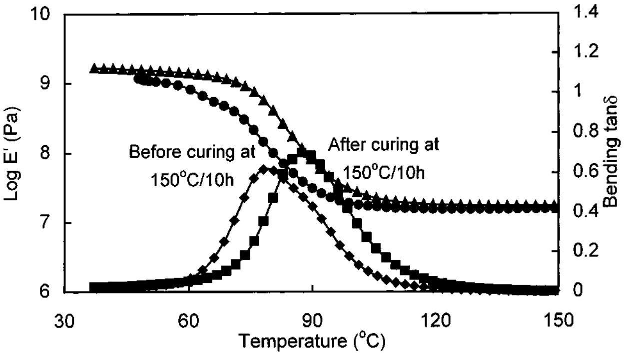


Figure 5. Bending modulus (E') and tan δ vs temperature curves at 1 Hz (from DMTA) of epoxy/POSS 75/25 (wt/wt) composite before and after curing at 150 °C/10 h.

on curing epoxy/POSS 75/25 at 150 °C for 10 h. However, the width of its glass transition region remains broad after curing at 150 °C/10 h.

The changes in bending storage moduli and T_g values indicate that many of the epoxide functions in POSS, which remained unreacted after curing at 120 °C, proceed to react with the curing agent at a higher temperature (150 °C), thereby increasing the composite's cross-linking density. Since the epoxy/POSS 75/25 composite has 5 times more POSS than the 95/5 sample, curing at 150 °C gives more prominent increases in both T_g and E' for the former vs those for the latter. Heating at 150 °C for 10 h could increase segmental entanglements between two cross-linking points in the neat epoxy resin or in the epoxy/POSS 95/5 composite, resulting in a small increase in E' but little change in T_g.

The tan δ peak of the epoxy/POSS 75/25 composite (Figure 4) is less intense and broader than that for the neat epoxy resin. The temperature at the end of this glass transition region for the epoxy/POSS 75/25 sample is higher than that of the neat epoxy although their onset temperatures of the transition are about the same. Lee and Lichtenhan[10] studied the glass transition behavior of monofunctional POSS/epoxy composites using differential scanning calorimetry (DSC). The onset and end temperatures of the glass transition region for the neat aromatic epoxy resin they used and the monofunctional POSS/epoxy 5/95 and 10/90 composites are 66.9−75.3, 67.2−80.3, and 67.2−83.4 °C, respectively. The onset glass transition temperatures of the two monofuntional POSS/epoxy composites were about the same as that of neat epoxy resin, but the glass transition region broadened with an increase of the POSS weight percentage in their compositions.[10] Lee and Lichtenhan's results are similar to our findings in the multifunctional POSS/epoxy composites described here (shown in Figure 4). The incorporation of the multifunctional POSS macromer into the epoxy network causes a retardation of segmental motion in the segments between cross-links that have chemical links to the POSS structure. Therefore, a higher temperature is required to induce these motions. Other segments without a bond to POSS exhibit segmental motion that is essentially the same as the distribution of motions induced in the neat aliphatic epoxy resin. Therefore, the glass state of the epoxy/POSS samples shows about the same onset temperature into the glass transition region, but they have a higher final T_g region temperature than that of the neat epoxy resin. Using the tan δ peak temperature to define T_g, there is little difference in T_g of epoxy/POSS composites (up to 25 wt % POSS).

In summary, the incorporation of multifunctional POSS into the aliphatic epoxy network broadens the glass transition region, increases E' at both low ($<T_g$) and high ($>T_g$) temperatures, thereby increasing the thermal dimensional stability, and exerts only a small effect on the tan δ peak temperature. Clearly using tan δ as a measure for T_g may not accurately characterize the softening points of composites with nanosized POSS phases bound only to a portion of the chain segments between cross-links. This view is further supported by the higher values of the storage modulus, E, at temperatures above T_g. The tetraepoxy multifunctional POSS was cured with short chain diamines at high (150, 175, and 190 °C) temperatures. In these preliminary experiments the T_g was very high and difficult to detect since the POSS unit is present as part of every chain. Experiments with longer chain diamines have not yet been performed, but amine chain segmental motion may be detectable at low temperatures. If so, this would demonstrate T_g could be of little relevance to the softening point or use temperature of such materials.

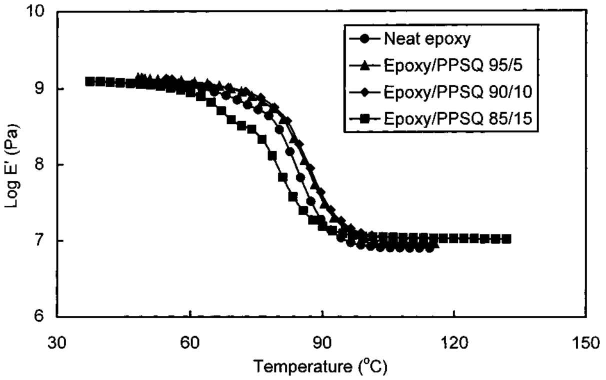


Figure 6. Bending modulus (E') vs temperature curves at 1 Hz (from DMTA) of an aliphatic epoxy resin and its epoxy/PPSQ 95/5, 90/10, and 85/15 (wt/wt) blends after curing at 120 °C/25 h.

Viscoelastic Properties of Epoxy/PPSQ Blends. Epoxy/poly(phenylsilsesquioxane) (PPSQ) blends have several similarities to the epoxy/multifunctional POSS composites. First, the main-chain structure of PPSQ is quite similar to that of the POSS. The PPSQ used in this work has some Si−OH present which might have some reactivity with the aliphatic epoxides of the epoxy resin. However, this PPSQ has no other functional groups that can react with components of the epoxy system during curing. Finally, PPSQ (M_w = 4636) molecules are substantially larger than the multifunctional POSS, which has a molecular weight of 1305.84. Thus, the volume of their microphases would be larger than those of POSS even when the PPSQ is completely compatible and molecularly dispersed in the epoxy. The epoxy/PPSQ 95/5 blend is transparent, but the 90/10 blend is slightly translucent. In contrast, the epoxy/PPSQ 85/15 blend is opaque, and some phase separation has certainly occurred in this blend. Some PPSQ precipitated within liquid resin mixtures after all THF solvent had evaporated during the preparation of blends with higher PPSQ amounts (≥20%).

The bending storage modulus, E', curves of the epoxy/PPSQ 100/0, 95/5, 90/10, and 85/15 blends measured at 1 Hz appear in Figure 6. The E' values of the blends with lower amounts of PPSQ (e.g., epoxy/PPSQ 95/5 and 90/10) are higher than those of the neat epoxy resin over the entire temperature range, and E' increases slightly with the PPSQ content. However, the epoxy/PPSQ 85/15 blend exhibits lower E' values than the neat epoxy resin at $T < T_g$ and higher E' values than the epoxy resin at $T > T_g$. Furthermore, at $T > T_g$, the values of E' for the 85/15 blend are about the same as those of the 90/10 sample.

The tan δ curves of the epoxy/PPSQ blends measured at 1 Hz are shown in Figure 7. The T_g values (peak temperatures of tan δ curves) for the 100/0, 95/5, 90/10, and 85/15 systems are 87.4, 88.2, 89.6, and 83.7 °C, respectively. When the PPSQ content is 10 wt % or less, the T_g values increase slightly with the PPSQ content. Interpenetration of PPSQ molecules into the epoxy network occurs due to the good PPSQ/epoxy miscibility when the PPSQ contents are ≤10%. Epoxy resin seg-

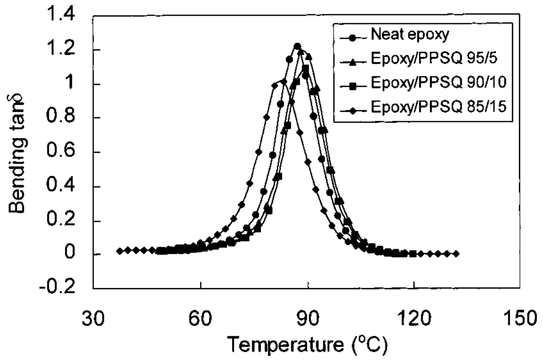


Figure 7. Bending tan δ vs temperature curves at 1 Hz (from DMTA) of an aliphatic epoxy resin and its epoxy/PPSQ 95/5, 90/10, and 85/15 (wt/wt) blends after curing at 120 °C/25 h.

ments may interact with blended PPSQ molecules in several ways. Hydroxyl groups, which formed during epoxide ring-opening during the cure, exist throughout the epoxy network. These hydroxyls in the epoxy resin could hydrogen-bond to oxygens on PPSQ and retard segmental motion. N−H groups are also present in the resin that may form hydrogen bonds in a similar fashion. The Si−OH functions that exist in the PPSQ polymer are quite acidic since each silicon atom is bound to three oxygens. These hydroxyl groups in PPSQ can hydrogen bond to both amine and hydroxyl functions of the epoxy resin. Thus, at low PPSQ loadings the blends are compatible. Finally, it may be possible that a small number of PPSQ hydroxyl groups, though not very nucleophilic, may have participated in epoxy ring-opening reaction during curing. These factors can inhibit some segmental motions in the epoxy network, leading to higher T_g and E' values at low PPSQ content ($\leq$10 wt %).

As the PPSQ content is raised, all the PPSQ cannot be molecularly dispersed and a separate PPSQ-rich phase appears. The epoxy/PPSQ 85/15 blend is opaque, which indicates that phase separation obviously occurred in this blend and PPSQ particles were formed. Epoxy components in the interphase region around these PPSQ particles may cure somewhat differently than the neat epoxy, perhaps leading to lower cross-linking density. Lowering the density of cross-links will lower T_g and lower E' of the blend with 15 wt % PPSQ at $T < T_g$ vs those of the neat epoxy. Conversely, at $T > T_g$, the PPSQ particles present in the 85/15 blend act as hard fillers which tend to increase the values of E' relative to that of the neat epoxy resin. Nobody has reported the T_g of high molecular weight PPSQ with the completed ladderlike structure.[12] Our previous studies[17] could not find a glass transition for the high-M_w PPSQ, and its modulus was almost unchanged from room temperature to 380 °C according to torsional braid analysis (TBA). However, the prepolymer of PPSQ (M_w = 2180) exhibited a T_g of 170 °C by TBA.[18] The PPSQ (M_w = 4636) used for epoxy/PPSQ blends in this paper should have an even higher T_g. Thus, in the temperature range from 83.7 °C (T_g) to 132 °C, the PPSQ particles in the epoxy/PPSQ 85/15 blend would remain in the glassey state and have a higher modulus than the epoxy resin. Therefore, the PPSQ particles present in the 85/15 blend act as hard fillers which tend to increase E' values relative to that of the neat epoxy. However, the magnitude of the increase in E' caused by these PPSQ particles on the E' is less than that of well-dispersed PPSQ molecules. Thus, the E' values of the epoxy/PPSQ 85/15 blend remain almost the same as those of the 90/10 blend.

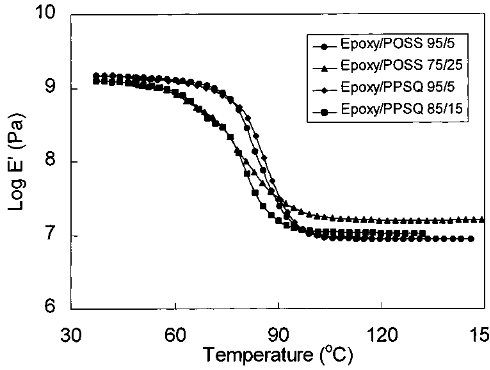


Figure 8. Bending modulus (E') vs temperature curves at 1 Hz (from DMTA) of epoxy/POSS 95/5 and 75/25 composites and epoxy/PPSQ 95/5 and 85/15 blends after curing at 120 °C/25 h.

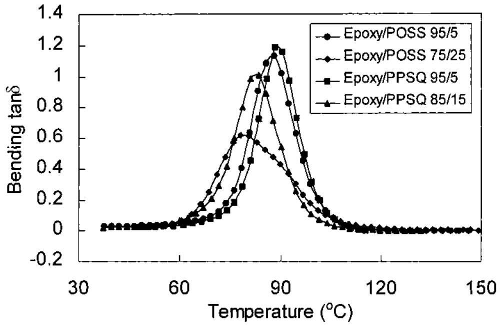


Figure 9. Bending tan δ vs temperature curves at 1 Hz (from DMTA) of epoxy/POSS 95/5 and 75/25 composites and epoxy/PPSQ 95/5 and 85/15 blends after curing at 120 °C/25 h.

The viscoelastic properties of epoxy/POSS composites (cured at 120 °C) can be compared with those of the epoxy/PPSQ blends (cured at 120 °C) in Figure 8 (bending storage moduli, E') and Figure 9 (tan δ curves). The bending storage moduli, E', of the epoxy/POSS 95/5 and epoxy/PPSQ 95/5 samples are quite similar over the entire measured temperature range (see Figure 8), except that the T_g value of the epoxy/POSS sample is somewhat lower. The bending storage moduli, E', of the epoxy/POSS 75/25 composite and epoxy/PPSQ 85/15 blend are very similar at $T < T_g$. At $T > T_g$, epoxy/POSS 75/25 composite has a higher bending E' (15.63 MPa at 120 °C) than epoxy/PPSQ 85/15 (10.56 MPa at 120 °C). This difference in E' values at $T > T_g$ are probably due to the molecular dispersion of the multifunctional POSS and to the chemical bonds that it forms to the epoxy resin during curing. When cured at 150 °C, the E' values of the epoxy/POSS 75/25 composite at 115 °C increase another 18% due to the formation of more chemical bonds between the epoxy resin and the multifunctional POSS macromers which increase cross-linking density. This cannot occur in the epoxy/PPSQ blends.

The opaque nature of the epoxy/PPSQ 85/15 blend indicates that the PPSQ has aggregated to form PPSQ-rich particles. The transparency of the epoxy/POSS 75/25 composite, in contrast, demonstrates that the miscibility between epoxy and POSS is very good. No phase separation could be observed in epoxy/POSS 75/25 sample by TEM at the ultrahigh magnification of ×800 000 using a JEM 3010 transmission electron microscope (TEM). This demonstrates that POSS is dispersed in the epoxy resin very well, probably at the

Table 2. Flexural Strengths (FS) and Flexural Moduli (FM) of Epoxy/POSS Composites and Epoxy/PPSQ Blends

samples	FS (MPa)	FM (MPa)
epoxy[a]	153.31	1548.11
epoxy/POSS 95/5[a]	138.26	1786.17
epoxy/POSS 75/25[a]	135.68	2014.80
epoxy	161.45	1349.87
epoxy/PPSQ 95/5	144.01	1346.11
epoxy/PPSQ 90/10	129.73	1781.95
epoxy/PPSQ 85/15	85.34	1993.88

[a] Samples after curing 150 °C/10 h.

molecular scale. The multifunctional POSS molecule has a diameter of about 1.3−1.4 nm. Clusters of a size formed from only a few of these molecules would be easily observed.

The tan δ peak of the epoxy/POSS 75/25 sample is much broader than those of either the epoxy/PPSQ 95/5 or 85/15 sample (shown in Figure 9). The widths of the tan δ peaks for the epoxy/PPSQ 95/5 and 85/15 composites are quite similar to that of the neat epoxy resin. The inclusion of PPSQ into epoxy resin should have little tendency to broaden of the glass transition region of epoxy/PPSQ blends as long as no chemical bonding between PPSQ and the epoxy resin occurred. The incorporation of the POSS macromer into the epoxy network, on the other hand, could broaden the glass transition region of epoxy/POSS composites. POSS did form chemical bonds into the network, more when cured at 150 °C than at 120 °C. The aliphatic amine curing agents and amine functions present in the aliphatic epoxy resin react with epoxy functions of the POSS moieties to form chemical bonds to the resin. A distribution of from one to four chemical bonds between POSS and the epoxy resin can form. The T_g of the epoxy/PPSQ 85/15 sample is 83.2 °C after curing at 150 °C (10 h), nearly the same with that (83.7 °C) before the 150 °C cure. However, the 150 °C cure treatment induces an increase of 8.7 °C in the T_g of the epoxy/POSS 75/25 sample. These results also indicate that high-temperature curing (150 °C) enhanced cross-linking between the residual POSS epoxy groups and the epoxy resin network, but no enhanced bonding occurred between PPSQ and the resin.

In summary, the T_g of epoxy systems are slightly improved by including small amounts of PPSQ ($\leq$10 wt %) although this has no effect on the width of the glass transition region for epoxy/PPSQ blends. The epoxy/PPSQ 85/15 sample has a lower T_g than the neat epoxy, which might due to hindrance of epoxy cross-linking caused by PPSQ-rich particle phases. The inclusion of PPSQ improves the thermal dimensional stability of epoxy resins as did multifunctional POSS incorporation.

Mechanical Properties. The flexural strengths and moduli of both the epoxy/multifunctional POSS composites and the epoxy/PPSQ blends are shown in Table 2. The flexural strengths of epoxy/POSS 95/5 and 75/25 samples are somewhat lower than that of the neat epoxy resin, but their flexural moduli are much higher than that of the epoxy resin. These moduli increase with an increase in POSS content. For an example, the flexural modulus of the epoxy/POSS 75/25 composites is 30.1% higher than that of the neat epoxy resin while its flexural strength is about 11.5% smaller. The epoxy becomes harder and more brittle upon incorporation of POSS.

The flexural strengths of the epoxy/PPSQ 95/5, 90/10, and 85/15 blends are lower than that of neat epoxy resin and their flexural strengths decrease sharply with an increase in PPSQ content. The sharp drop in flexural strength of the epoxy/PPSQ 85/15 blend suggests that the adhesion between the resin and PPSQ phase is not strong. This is in accord with a low chemical bond density connecting these phases. The flexural moduli of epoxy/PPSQ blends are higher than that of neat epoxy resin except for the 95/5 sample. The flexural modulus of the epoxy/PPSQ 90/10 blend increases about 32.4% vs that of the neat epoxy resin, while its flexural strength decreases 19.6%. The flexural modulus of the opaque, phase-separated epoxy/PPSQ 85/15 blend only increases 47.1%, but its flexural strength decreases about 47.7% vs the neat epoxy resin. So, like the epoxy/POSS composites, blending PPSQ into the epoxy resin makes the resin harder and more brittle. POSS seems to be more efficient in modifying the modulus although more studies are needed.

Conclusions

Multifunctional POSS units are dispersed in epoxy matrix very well, probably on the molecular scale, even at a POSS weight percent of 25%. This molecular dispersion is a result of (1) the mixture of two different corner substituents which enhances the POSS derivative's solubility, (2) the ability of epoxy groups to chemically bond to the epoxy resin's matrix as it cures, and (3) the low tendency for POSS molecules to aggregate[21] when they are originally well dispersed. The miscibility between PPSQ and the aliphatic epoxy resin is good only at low PPSQ content ($\leq$10 wt %). Phase separation is clearly observed as the PPSQ percent is raised to 15%. High-temperature curing (150 °C) enhanced cross-linking reactions between residual epoxy functions of the POSS macromer and amine groups, increasing the cross-linking density, thereby increasing the T_g and E' values of epoxy/POSS 75/25 sample. The incorporation POSS into the epoxy network broadens the glass transition region but has almost no influence on the T_g values. The T_g values of epoxy/PPSQ blends at PPSQ $\leq$10 wt % increase slightly with the PPSQ content. However, the T_g of epoxy/PPSQ 85/15 is lower than that of neat epoxy probably due to hindrance of epoxy resin cross-linking caused by hard PPSQ-rich particles resulting from phase separation. Nevertheless, the inclusion of PPSQ into epoxy has no effect on the width of the glass transition region of these blends. The storage moduli E' of epoxy/POSS composites and epoxy/PPSQ blends at $T > T_g$ are higher than those of neat epoxy. Therefore, thermal dimensional stability of epoxy is increased either by the incorporation of POSS or by the inclusion of PPSQ. The broadening of the T_g region toward higher temperatures and the increase in E' when POSS is incorporated into the epoxy resin corresponds to rheological results reported recently[22] for poly(dimethylsiloxane). Chemically bonding only 5 wt % POSS to PDMS gave a 1 order of magnitude slowing of the characteristic relaxation time.[22] The flexural modulus and hardness of epoxy resins are improved by incorporating either the multifunctional POSS or PPSQ. The flexural strengths of both epoxy/POSS composites and epoxy/PPSQ blends are lower than that of neat epoxy resin.

Acknowledgment. This work was supported by a grant from the Air Force Office of Scientific Research (No. F49620-99-1-0191).

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MA011117Q