Morphology and Thermomechanical Properties of Organic−Inorganic Hybrid Composites Involving Epoxy Resin and an Incompletely Condensed Polyhedral Oligomeric Silsesquioxane

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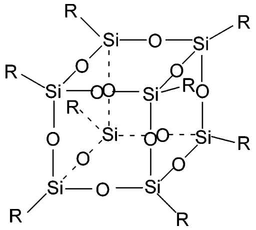
ABSTRACT: Epoxy was modified by an incompletely condensed polyhedral oligomeric silsesquioxane (POSS), and the phenyltrisilanol POSS [$Ph_7Si_7O_9(OH)_3$, POSS-triol] was incorporated into the epoxy networks with the content of POSS up to 30 wt %. The organic−inorganic hybrid composites were prepared via in situ polymerization of epoxy monomers in the presence of POSS-triol, which started from the homogeneous solutions of POSS-triol and epoxy monomers. The nanocomposites of epoxy with POSS-triol can be prepared with the metal complex, aluminum triacetylacetonate ([Al]) being used as the catalyst for the reaction between POSS-triol and diglycidyl ether of bisphenol A (DGEBA). Otherwise, the phase separation induced by polymerization occurred, and the fine phase-separated structures were obtained, in which the spherical POSS-triol particles (0.3−0.5 μm in diameter) were dispersed in the continuous epoxy matrices. The hybrid composites with the different morphological structures displayed quite different thermomechanical properties. The phase-separated composites possessed the higher glass transition temperatures (T_g's) than the nanocomposites while the nanocomposites displayed the higher storage modulus of glassy state in light of dynamic mechanical analysis (DMA). In terms of thermogravimetric analysis, the nanocomposites displayed the higher initial thermal decomposition temperatures (T_d's). The improvement in thermomechanical properties has been ascribed to the nanodispersion of POSS moieties.

Introduction

The properties of organic−inorganic hybrid composites greatly depend on interactions between reinforcing agents and polymer matrices.[1−4] The nanoscaled distribution of reinforcing agents can optimize the intercomponent interactions and affords the materials with improved properties. Recently, polymers reinforced by well-defined nanosized inorganic clusters are being attracted considerable interest due to the potential application of this class of polymer nanocomposites. Polyhedral oligomeric silsesquioxane (POSS) reagents, monomers, and polymers are emerging as a new chemical technology for preparing nanoreinforced organic−inorganic hybrids and are becoming the focus of many studies due to the excellent comprehensive properties of POSS-containing hybrid nanocomposites and the simplicity in processing of materials.[5−17] A typical POSS molecule possesses the structure of cube-octameric frameworks represented by the formula ($R_8Si_8O_{12}$) with an inorganic silica-like core (Si_8O_{12}) surrounded by eight organic corner groups, one or more of which is reactive or polymerizable (Scheme 1). Generally, POSS cages can be incorporated into polymers via copolymerization and physical blending. Copolymerization is an efficient approach to POSS-containing nanocomposites due to the formation of chemical bonds between POSS cages and polymer matrices. Relatively, the nanocomposites prepared via physical blending was less reported due possibly to the unfavorable miscibility (or solubility) of silsesquioxanes with polymers.[18]

Scheme 1. Structure of a Completely Condensed Polyhedral Oligomeric Silsesquioxane (POSS)



Epoxy resins are among the most commercially successful materials known, especially as adhesives and matrices of composite materials, etc.[19,20] The extensive applications of epoxy resins motivate to prepare the organic−inorganic nanocomposites with improved properties. There have been some reports on the inorganic−organic nanocomposites involving epoxy resin and polyhedral oligomeric silsesquioxanes during the past years.[21−34] Lee and Lichtenhan[21,22] investigated the thermal and viscoelastic properties of cyclohexyl (and/or cyclopentyl) POSS glycidyl-reinforced epoxy resin of bisphenol A and found that the molecular level reinforcement provided by the POSS cages can significantly retard the physical aging process in the glassy state. Laine et al.[23−28] reported the modifications of epoxy resin by a series of octasilsesquioxanes with R being various reactive groups such as aminophenyl and dimethylsiloxypropylglycidyl ether groups. The dynamic mechanical properties, fracture toughness, and thermal stability of the epoxy hybrids were addressed in terms of the types of R groups, tether structures between

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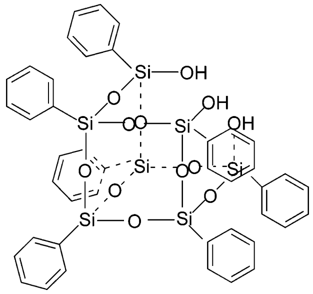
Scheme 2. Structure of Phenyltrisilanol Polyhedral Oligomeric Silsesquioxane (POSS-Triol)



epoxy matrices and POSS cages, and the defects in silsesquioxane cages, etc. Williams et al.[29] investigated the phase behavior of isobutyl POSS glycidyl-containing epoxy resin, and they observed a primary liquid−liquid phase separation occurred at the time of adding epoxy to the POSS-diamine precursors due to the incompatibility between epoxy and isobutyl POSS glycidyl. In our previous studies, we reported that depending on the functionalities of POSS molecules the hybrid composites can displayed different morphological structures, which result in different properties.[31] More recently, Matejka et al.[32,33] investigated the structure and properties of epoxy networks reinforced with POSS, and the effects of POSS−POSS interactions on properties were addressed.

In the previous studies, the most of POSS molecules used in POSS-containing nanocomposites are completely condensed POSS frameworks (e.g., $R_8Si_8O_{12}$) while incompletely condensed POSS frameworks have received little attention.[35,36] Lee et al.[34] reported that phenyltrisilanol POSS (POSS-triol) has a significant catalytic effect on the curing of epoxy with amine, and only a very small amount of POSS-triol (<1.0 wt %) was used and the catalytic activity has been ascribed to the acidity of the POSS silanol.[37,38] To the best of our knowledge, there has been no precedent report on the nanocomposites of epoxy with a large mass fraction of POSS-triol. In the present work, we reported the preparation of epoxy nanocomposites with phenyltrisilanol POSS [$Ph_7Si_7O_9(OH)_3$, POSS-triol] (see Scheme 2). POSS-triol was incorporated into epoxy networks via the formation of covalent bonds, which was mediated by the metal complex, aluminum triacetylacetonate ([Al]).[39,40] For comparison, the phase-separated hybrid composites were also obtained. The morphology and thermomechanical properties of the two types of inorganic−organic hybrid composites are comparatively investigated on the basis of scanning electronic microscopy (SEM), transmission electronic microscopy (TEM), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA).

Experimental Section

Materials. The epoxy monomer used, diglycidyl ether of bisphenol A (DGEBA) with epoxide equivalent weight of 185, was purchased from Shanghai Resin Co., China. 4,4′-Diaminodiphenylmethane (DDM) was used as the curing agent, obtained from Shanghai Reagent Co., China. Phenyl glycidyl ether (PGE) is of chemically pure grade, supplied by Shanghai Reagent Co., China. Phenyltrisilanol polyhedral oligomeric silsesquioxane (denoted POSS-triol) (Scheme 2) was purchased from Hybrid Plastics, CA. FTIR (KBr pellet, cm^{-1}): 3440 (−OH), 500−1700 (H−C, aromatic ring), 1132 (Si−OH), 1090 (Si−O−Si). ^1H NMR (chloroform-*d*, ppm): 6−8 (*m*, O−**H**, protons of aromatic rings). ^{29}Si CP/MAS NMR (ppm): 77.9, 76.7, 67.7.

Reaction of Model Compounds. To investigate the reaction between silanol and DGEBA catalyzed by metal complex, aluminum triacetylacetonate ([Al]), the reaction of model compounds was carried out. The stoichiometric phenyl glycidyl ether (PGE) (7.5 g, 0.05 mol) and POSS-triol (15.53 g, 0.017 mol) were dissolved with chloroform, and the solutions without or with [Al] (0.6 wt % of PGE) were cast onto KBr windows, respectively. The majority of solvent was removed at ambient temperature, and the residual solvent was eliminated by drying in a vacuum oven at room temperature for 30 min. The reactions were allowed to perform at 120 °C for 30 min. The reacted specimens were subjected to FTIR measurements.

Preparation of Hybrid Composites. The epoxy monomer, diglycidyl ether of bisphenol A (DGEBA), was first mixed with desired amount of POSS-triol at 50 °C with continuously stirring until the homogeneous and transparent solutions were obtained. For the formulation of reaction with the latent catalyst, aluminum triacetylacetonate (0.6 wt % of DGEBA) was added at 120 °C with vigorous stirring for 30 min, and finally the stoichiometric 4,4-diaminodiphenylmethane (DDM) was added to the above mixtures. The mixture was cured at 80 °C for 2 h plus 160 °C for 2 h. To access complete curing reaction, the samples were postcured at 180 °C for 2 h.

Measurement and Techniques. a. Fourier Transform Infrared Spectroscopy (FTIR). The FTIR measurements were conducted on a Perkin-Elmer Paragon 1000 Fourier transform spectrometer at room temperature (25 °C). The samples of hybrids were granulated, and the powder was mixed with KBr pellets to press into the small flakes for measurements. The specimens were sufficiently thin to be within a range where the Beer−Lambert law is obeyed. In all cases 64 scans at a resolution of 2 cm^{-1} were used to record the spectra.

b. Nuclear Magnetic Resonance Spectroscopy (NMR). The ^1H NMR and ^{13}C NMR measurements were carried out on a Varian Mercury Plus 400 MHz NMR spectrometer at 25 °C. The samples were dissolved with deuterated chloroform, and the solutions were measured with tetramethylsilane (TMS) as the internal reference. The high-resolution solid ^{29}Si NMR spectra were obtained using the cross-polarization (CP)/magic angle spinning (MAS) together with the high-power dipolar decoupling (DD) technique. The 90° pulse width of 4.1 μs was employed with free induction decay (FID) signal accumulation, and the CP Hartmann−Hahn contact time was set at 3.5 ms for all experiments. The rate of MAS was 4.0 kHz for measuring the spectra. The Hartmann−Hahn CP matching and dipolar decoupling field was 57 kHz. The chemical shifts of all ^{29}Si spectra were determined by taking the silicon of solid Q_8M_8 relative to TMS as an external reference standard.

c. Scanning Electronic Microscopy (SEM). To observe the phase structure of POSS-containing epoxy hybrids, the samples were fractured under cryogenic condition using liquid nitrogen. The fractured surfaces so obtained were immersed in dichloromethane at room temperature for 30 min. The POSS phases could be preferentially etched by the solvent while epoxy matrix phase remains unaffected. The etched specimens were dried to remove the solvents. The fracture surfaces were coated with thin layers of gold of about 100 Å. All specimens were examined with a Hitachi S210 scanning electron microscope (SEM) at an activation voltage of 25 kV.

d. Transmission Electronic Microscopy (TEM). Transmission electron microscopy (TEM) was performed on a JEOL JEM-2010 high-resolution transmission electron microscope at an acceleration voltage of 200 kV. The samples were trimmed using a ultramicrotome machine, and ultrathin sections (ca. 70 nm in thickness) were placed in 200 mesh copper grids for observations.

e. Differential Scanning Calorimetry (DSC). The glass-transition temperatures (T_g's) of the samples were determined using a Perkin-Elmer Pyris 1 thermal analysis apparatus at a heating rate of 20 °C/min in the temperature range between 50 and 200 °C in a nitrogen atmosphere. In all the measurements, the glass transition temperature (T_g) was taken from the second scans.

f. Dynamic Mechanical Thermal Analysis (DMTA). The dynamic mechanical tests were carried out on a dynamic mechanical thermal analyzer (DMTA) (MKIII, Rheometric Scientific, Ltd. Co., UK) with the temperature range from −150 to 270 °C. The frequency used is 1.0 Hz and the heating rate 3.0 °C/min. The specimen dimension was $25 \times 5.0 \times 2.0$ mm^3. The experiments were carried out from −150 °C until the samples became too soft to be tested.

g. Thermal Gravimetric Analysis (TGA). A Perkin-Elmer thermal gravimetric analyzer (TGA-7) was used to investigate the thermal stability of hybrid composites. The samples (about 10 mg) were heated from ambient temperature to 900 °C in an air atmosphere, and the heating rate of 10 °C/min was used in all cases.

Results and Discussion

Morphology of Hybrid Composites. Octaphenyl POSS ($Ph_8Si_8O_{12}$) was found to be insoluble in DGEBA.[31] However, phenyltrisilanol POSS (POSS-triol) can form the homogeneous and transparent mixtures with DGEBA and DDM, indicative of the miscibility (or solubility) of all the monomers. The miscibility could be due to the formation of intermolecular specific interactions (e.g., hydrogen bonding) between POSS-triol and DGEBA (and/or DDM). The homogeneous and transparent mixtures with the contents of POSS-triol up to 30 wt % were cured at the elevated temperatures to in situ prepare the organic−inorganic hybrid composites. It was observed that with the curing reaction proceeding the initially transparent solutions gradually became cloudy, implying the occurrence of phase separation induced by polymerization. However, after a small amount of aluminum triacetylacetonate ([Al]) was added to the mixtures, the resulting composites were homogeneous and transparent; i.e., no discernible phase separation occurred on the scale exceeding the wavelength of visible light.

The morphology of the organic−inorganic hybrid composites was investigated by means of scanning electronic microscopy (SEM). Shown in Figure 1A−C are the SEM micrographs of the phase-separated hybrid composites. After etched with dichloromethane, the composites displayed the heterogeneous morphology. The dispersed particles are attributed to POSS-triol phase since POSS-triol can be rinsed by dichloromethane whereas epoxy matrix remained unaffected. The spherical particles of POSS-triol (<0.5 μm in diameter) were uniformly dispersed the continuous epoxy matrices, which is some of the familiar morphology characteristic of phase separation induced by polymerization.[41,42] It is noted that the sizes of the POSS particles decreased with increasing the concentration of POSS-triol. In marked contrast to the phase-separated hybrid composites, the transparent composites cured with [Al] catalysis exhibited the featureless morphology, and no discernible phase separation was detected (see Figure 2). Transmission electronic microscopy (TEM) allows the morphological analysis of the composites at the higher magnification. Figure 3 presents the TEM micrograph of the transparent composites containing 10 wt % of POSS-triol. The TEM result shows that the microphase separation occurred at the nanoscale. According to the difference in transmitted electronic density between organic epoxy polymer and inorganic POSS component, it is assumed that the dark area is assigned to the POSS domains whereas the white region to epoxy matrix. The interconnected microphase-separated morphology with uniform domain size is some of the familiar characteristics of self-assembly structures. It is proposed that the POSS−POSS interactions formed the POSS domains.

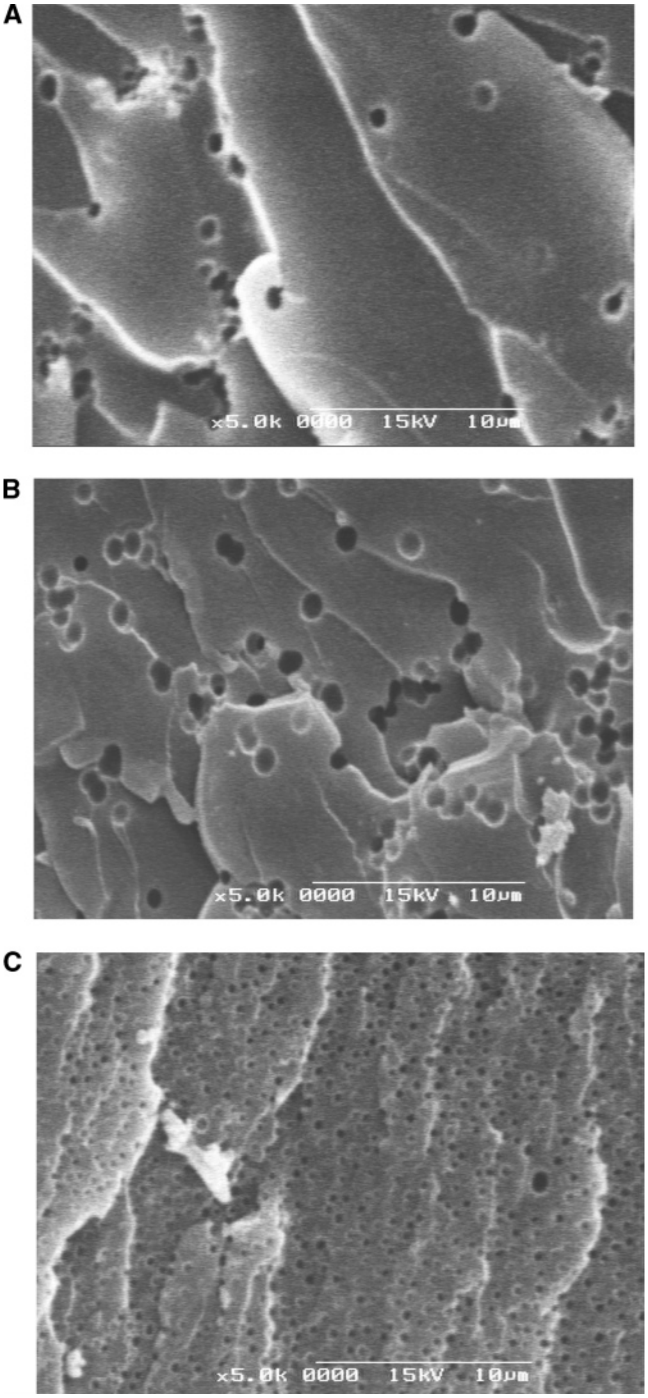


Figure 1. SEM micrographs of the hybrid composites cured without [Al] catalysis containing POSS-triol: (A) 5, (B) 10, and (C) 20 wt %. All the samples were etched with dichloromethane for 30 min.

It is interesting to note that the nanocomposites of epoxy with POSS-triol were successfully prepared via [Al] catalysis. This observation suggested that the additional reaction between POSS-triol and epoxy occurred, which could be mediated by the metal complex, aluminum triacetylacetonate. This intercomponent reaction resulted in the formation of the epoxy nanocomposites with POSS-triol.

Reaction of DGEBA and POSS-Triol. It is proposed that several types of kinetics could be involved

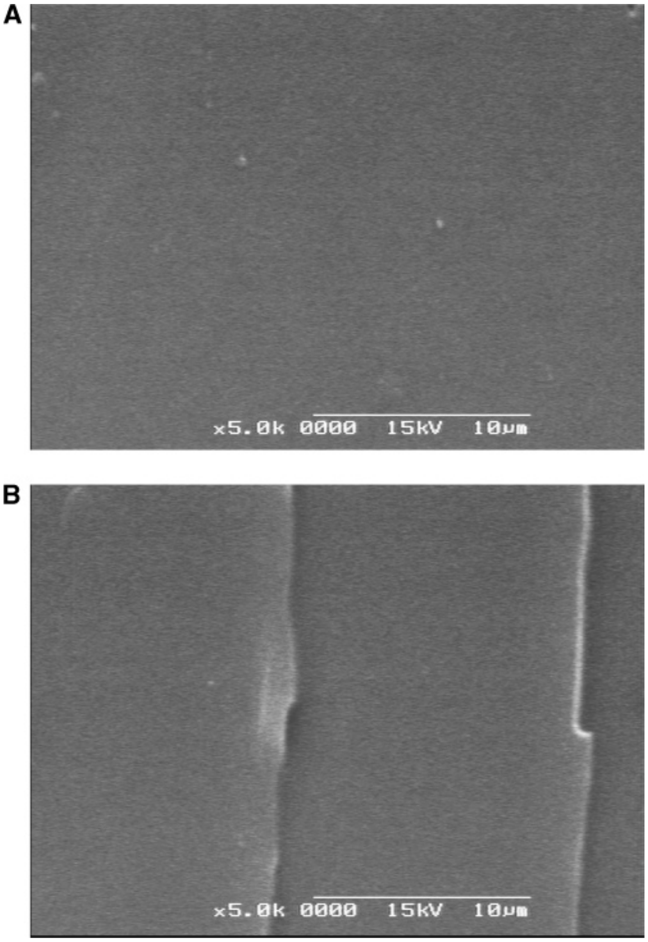


Figure 2. SEM micrographs of the control epoxy (A) and hybrid composites cured with [Al] catalysis containing 10 wt % of POSS-triol (B). All the samples were etched with dichloromethane for 30 min.

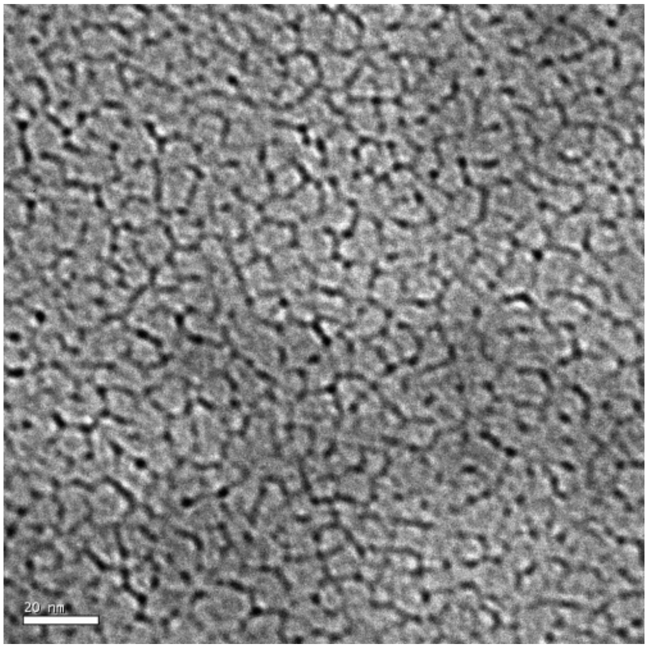


Figure 3. TEM micrograph of epoxy-POSS nanocomposites containing 10 wt % of POSS-triol.

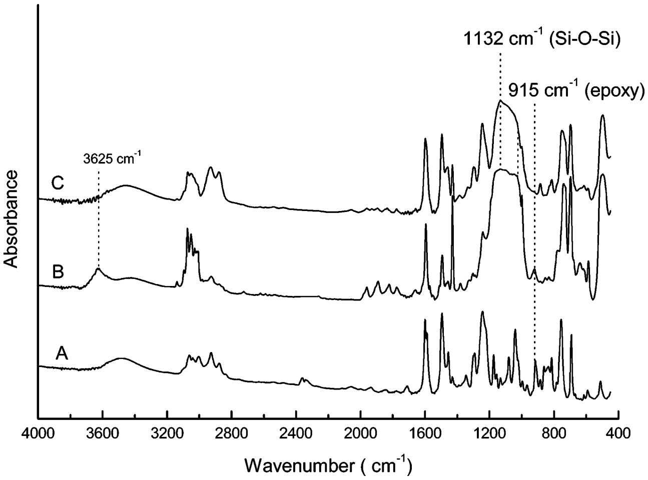


Figure 4. FTIR spectra of PGE and its stoichiometric mixture with POSS-triol with (and/or without) the catalysis of [Al].

with the preparation of the epoxy hybrids with POSS-triol. The first one is concerned with the cross-linking reaction between DGEBA and DDM, which was carried out under the standard curing condition and afforded the densely cross-linked epoxy networks. In the case that the system contains POSS-triol, the phase separation induced by polymerization could occur as the curing reaction proceeds. The driving force for the demixing is the decreased contribution of mixing entropy (ΔS_m) to mixing free energy (ΔG_m). With the curing reaction proceeding, the systems underwent chain growth, branching, gelation, and vitrification in success. The increased molecular weight of the systems will result in the decrease of entropic contribution to miscibility, and thus phase separation took place. In addition to the phase separation induced by polymerization, there could be the intercomponent reaction between POSS-triol and DGEBA although the reaction generally occurs at the higher temperature. Nonetheless, this reaction can be significantly accelerated by the metal complexes, e.g., aluminum triacetylacetonate.[39,40]

The above kinetic processes are competitive and intercoupled, which provides the potentials to control kinetically the morphology of the hybrids. It is proposed that for the hybrid systems without [Al] catalysis the formation of the heterogeneous morphology is responsible for the kinetic competition between phase separation and the reaction of POSS-triol with DGEBA; i.e., the rate of phase separation induced by the reaction of epoxy with amine is much faster than that of the reaction of DGEBA with POSS-triol. It is expected that while the reaction of POSS-triol with DGEBA is accelerated until it is faster than that of phase separation induced by polymerization, the nanocomposites will be obtained. In the present work, the reaction of DGEBA with POSS-triol was accelerated by adding a small amount of aluminum triacetylacetonate ([Al]), which acts as the catalyst of the reaction.[39,40] The homogeneity of the hybrid composites has been verified by the morphological observation by means of SEM and TEM. To confirm the reaction between the silanol hydroxyl groups of POSS-triol and epoxide groups, the reaction of stoichiometric model compounds (viz. POSS-triol and phenyl glycidyl ether) was allowed to carry out at 120 °C for 30 min. Shown in Figure 4 are the FTIR spectra of PGE and its stoichiometric mixture with POSS-triol with (and/or without) the catalysis of [Al]. It can be seen that within a short time (30 min) the band at 915 cm^{-1} characteristic of stretching vibration of epoxide group virtually disappeared for the PGE/POSS-triol mixture

Scheme 3. Reaction between DGEBA and POSS-Triol Mediated by Aluminum Triacetylacetonate

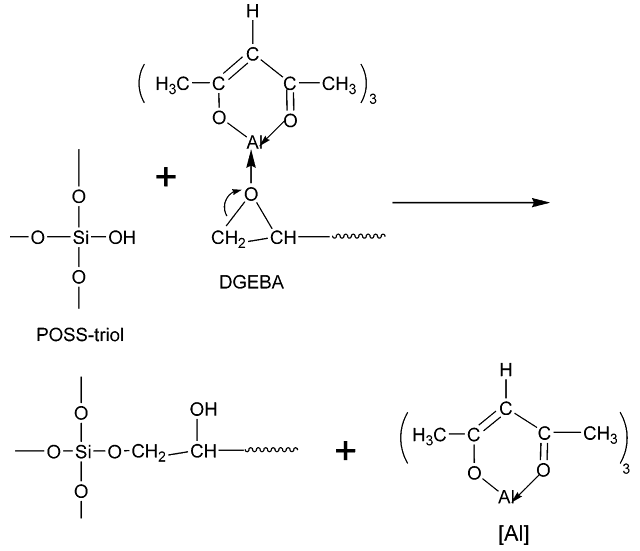


Table 1. Glass Transition Temperatures of the Control Epoxy and Its Composites with POSS-triol

POSS-triol (wt %)	phase-separated composites (°C) [a]	nanocomposites (°C)[a]
0	174	174
5	173	167
10	173	166
15	170	166
20	168	165
30	167	168

[a] All the values of T_g were taken as the second DSC scan at 20 °C/min.

Table 2. Thermal Stability of Epoxy Hybrid Composites Containing POSS-Triol

POSS (wt %)	T_d (°C)[a] phase-separated composites	T_d (°C)[a] nano-composites	ceramic yield (wt %)[b] phase-separated composites	ceramic yield (wt %)[b] nano-composites
0	394	394	0.07	0.07
5	352	361	2.6	1.2
10	345	375	3.6	3.4
20	351	369	9.3	6.0
30	377	369	11.6	9.0

[a] Temperature at mass loss of 5 wt % under air atmosphere. [b] Ceramic yield at 900 °C in air atmosphere.

(see curve C) while the band almost remained unaffected for the mixture without [Al] catalysis (see curve B). It is noted that the intensity of the band at ca. 1027 cm^{-1} assigned to the stretching vibration of Si−OH for POSS-triol was significantly decreased. Moreover, the stretching vibration band of free silanol hydroxyl groups for POSS-triol at 3625 cm^{-1} became indiscernible for the mixture with [Al] catalysis. The FTIR results indicate that the intercomponent reaction between silanol hydroxyl and epoxide groups can be significantly facilitated with the catalysis of [Al]. In terms of the above observation, the possible reactions involved in the reaction of silanol hydroxyls and epoxides are proposed in Scheme 3. The reactions are initiated by the formation of complex between an oxirane of DGEBA and an aluminum atom of aluminum triacetylacetonate, which activates the oxirane. The formation of complex will facilitate the attack of silanol hydroxyls of POSS-triol and afford the hydroxyl ether structural units, and aluminum triacetylacetonate is released.

It is interesting to note that the observation of the [Al] catalysis effect coincides with the previous studies of aluminum *sec*-butoxide [Al(OBu^s)$_3$] effect on cross-linking glycidylpropyltriethoxysilane.[43−45] Spiess et al.[43] proposed that the organic side aluminum acts mainly as a catalyst for the oxirane ring-opening reactions with methanol, water, and another epoxy ring. In the present case, aluminum triacetylacetonate catalyzed the ring-opening reaction of epoxy group with the silanol hydroxyls of POSS-triol.

Thermomechanical Properties. a. Glass Transition Behavior. The POSS-containing hybrid composites were subjected to thermal analysis. In the experimental temperature range (50−200 °C), the DSC thermograms of all the samples displayed single glass rubber transition temperatures. The single glass transitions are attributed to the epoxy matrices since the T_g's of POSS-rich phases cannot be detected due to the high rigidity of POSS monomers. The values of glass transition temperature of the control epoxy and its hybrid composites with POSS-triol are summarized in Table 1. The glass transition of the control epoxy occurred at 174 °C. It is noted that all the hybrid composites displayed the decreased T_g's in comparison with the control epoxy. Apart from the composite containing 30 wt % of POSS-triol, the T_g's of the phase-separated composites are significantly higher than those of the nanocomposites. For the phase-separated composites, the T_g's slightly decreased with increasing the content of POSS while those of the nanocomposites did not monotonically decrease with increasing concentration of POSS-triol. It has been proposed that the depression of glass transition temperatures could result from the incomplete curing reaction due to the inclusion of POSS monomers.[30] In the present cases, glass transition behavior reminded us of examining the curing degree of epoxy. Figures 5 and 6 present the FTIR spectra of the control epoxy and its composites with POSS-triol. Under the identical curing condition, the epoxide bands at 915 cm^{-1} for the two composite systems virtually disappeared as in the control epoxy, suggesting that the curing reactions of epoxy occurred to completion. Therefore, in these present cases the depression of glass transition temperatures (T_g's) will not be ascribed to the incomplete curing reactions resulting from the incorporation of POSS in the hybrid composites. For the phase-separated hybrid composites, the depression in T_g's could be attributed to incomplete phase separation; i.e., a small portion of POSS-triol was dissolved in epoxy matrix. For the nanocomposites prepared via [Al] catalysis, the depression in T_g's could be associated with the reaction between POSS-triol and epoxy.

The depression in T_g's has been found in octaaminophenyl POSS- and octanitrophenyl POSS-modified epoxy.[31] It has been proposed that the decreased T_g could be responsible for the increase in free volume of the system due to the inclusion of a part of bulky POSS cages at the nanoscale level, and the effect could be comparable to internal plasticization effect of low molecular weight compounds, which were copolymerized into polymer matrix. Nonetheless, the depression of T_g's for POSS-containing composites are quite different from the plasticization of low molecular weight compounds. In low molecular weight plasticization systems, the more T_g's will depress the higher the concentration of plasticizer. However, it is noted that the T_g's of the nanocomposites did not monotonically decease with increasing the concentration of POSS-triol, and the T_g's

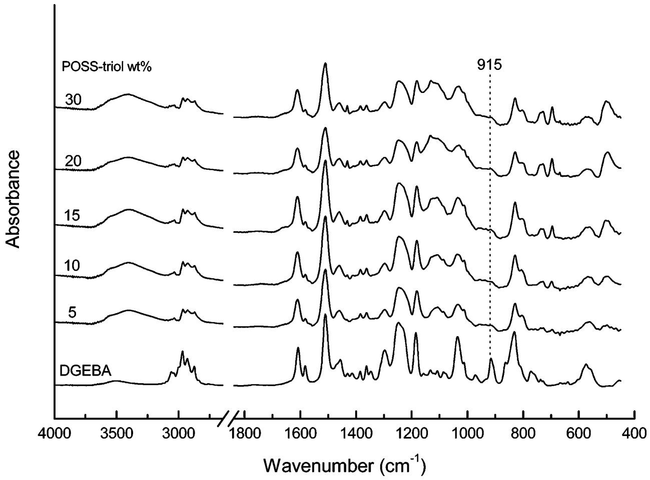


Figure 5. FTIR spectra of the control epoxy and the phase-separated composites.

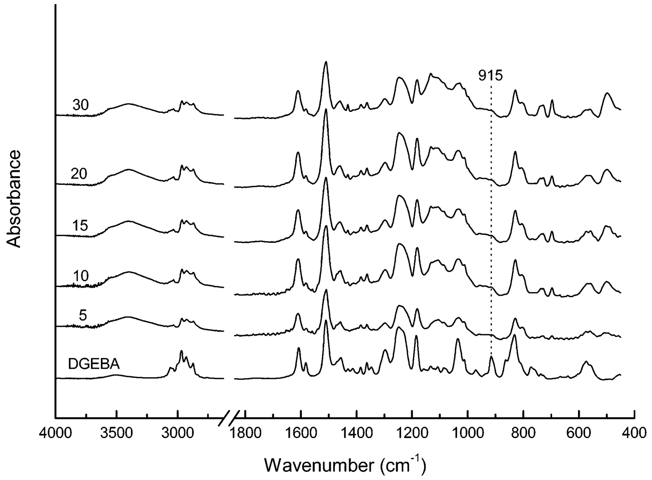


Figure 6. FTIR spectra of the control epoxy and the nanocomposites.

of the nanocomposites almost remain invariant with the contents of POSS-triol. It is plausible to propose that in POSS-containing nanocomposites there are two competitive factors to affect the glass transition temperatures. On one hand, the restriction effect of POSS cages on polymer chain motions will enhance glass transition temperature. In the present case, POSS cages were chemically bonded onto the cross-linking networks, which could contribute the inhabitation effect of POSS cages on the molecular motion. On the other hand, the inclusion of the bulky POSS group could give rise to the increase in free volume of the system, which will result in the depression of T_g's. Depending on the nature of the interactions of POSS cages with matrices of polymers (e.g., functionalities of POSS, types of polymer matrices, and organic groups in POSS vertexes, etc.), the POSS-containing nanocomposites can display increased[21,46,47−50] or decreased[16,29] T_g's in comparison with apparent polymers. The behavior of glass transition of the POSS-containing hybrids could be the comprehensive embodiment of the above two factors. In the present case, it is seen that although the glass transition temperatures of the POSS hybrids were lower than that of the control epoxy they did not significantly vary with increasing the concentration of POSS, indicating the presence of the nanoreinforcement of POSS on the epoxy matrix. In addition to the above factors, the depression of T_g's for the nanocomposites should be due to the co-cross-linking reactions among DGEBA, POSS-triol, and DDM. The POSS-triol reacted with DGEBA, catalyzed by the [Al] agent, and a part of epoxide groups of DGEBA will be consumed by the silanol hydroxyls of POSS-triol. Nonetheless, the curing agent (DDM) was added only with respect of the stoichiometry of DGEBA, and thus amino groups of DDM will be partially excess and existed in the form of free ends, which will introduce the free volume to the systems[50] and give the decreased T_g's.

b. Dynamic Mechanical Properties. Shown in Figures 7 and 8 are the dynamic mechanical spectra of the phase-separated hybrid composites and the nanocomposites. In the plots of tan δ as functions of temperature, the major transitions (viz. α-transition) at ca. 175 °C are assigned to the glass−rubber transition of the materials. It is seen that the T_g's of all the hybrid composites are lower than that of the control epoxy; the T_g's of the POSS-containing nanocomposites are lower than those of the phase-separated hybrid composites when the content of POSS-triol is the same. The results are in a good agreement with those obtained by means of DSC. Apart from the α transitions, all the materials exhibited the secondary transitions (viz. β-relaxation) at the lower temperature (∼−50 °C). The β transition is attributed predominantly to the motion of hydroxyl ether structural units [$CH_2-CH(OH)-CH_2-O-$] and diphenyl groups in amine-cross-linked epoxy.[52−54] The β-relaxation temperatures (T_β's) of the phase-separated hybrid composites almost remained invariant in comparison with the control epoxy, implying that the epoxy matrix were not nearly affected by the dispersed domains. However, the T_β's of the nanocomposites are found to shift to the lower temperatures, implying that the free volume of systems were increased with POSS-triol being incorporating into the cross-linked networks, which facilitates the motion of the hydroxyether structural units and diphenyl groups. This observation is in a good agreement with the result that the nanocomposites displayed the lower glass transition temperatures than the control epoxy.

From Figures 7 and 8, it is noted that with the inclusion of POSS-triol all the hybrid composites displayed the lower storage moduli of glassy and rubbery states than the control epoxy, which is in marked contrast to the epoxy modified by completely condensed POSS.[31] This result could be related to the particulate shape of POSS-triol that is different from the cube-octameric frameworks of completely condensed POSS. Nonetheless, there is the significant difference in dynamic mechanic properties between the phase-separated hybrid composites and the nanocomposites. Figure 9 presents the comparison of dynamic mechanical storage modulus for the two hybrid composite systems. It is seen that with the same content of POSS-triol the nanocomposites possessed the higher modulus of glassy state than the phase-separated hybrid composites. This observation can be interpreted in terms of the interactions between POSS blocks and the epoxy matrices, which are closely associated with the dispersion degree of POSS molecules in the epoxy matrices. For the phase-separated composites, POSS-triol was physically mixed with epoxy and the phase separation induced by polymerization took place. The spherical POSS-triol particles with diameters ranging from 0.3 to 0.5 μm were dispersed in the continuous epoxy matrices. For the

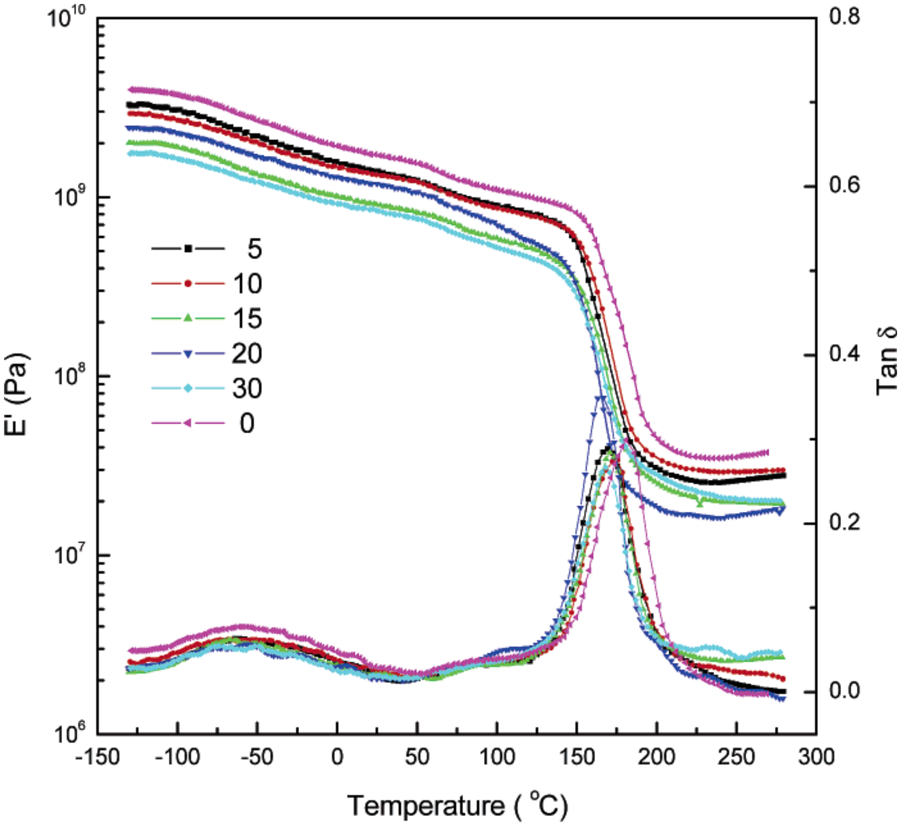


Figure 7. Dynamic mechanical spectra of the phase-separated hybrid composites.

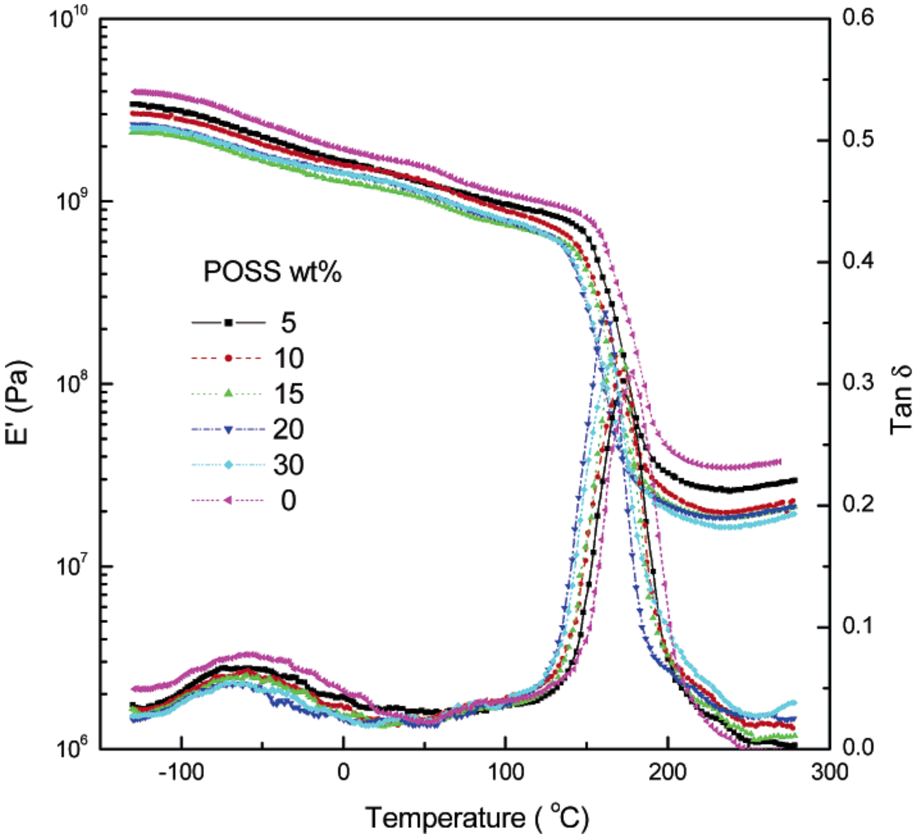


Figure 8. Dynamic mechanical spectra of the nanocomposites.

nanocomposites, the POSS-triol was covalently bonded to the epoxy networks via the reaction between silanol hydroxyls of POSS-triol and epoxide groups of DGEBA, and the POSS blocks were homogeneously dispersed in epoxy matrix at the nanoscale. Therefore, the increased storage moduli for the nanocomposites could be attributed to the efficient nanoreinforcement of POSS cages on the epoxy matrices; i.e., the incorporation of

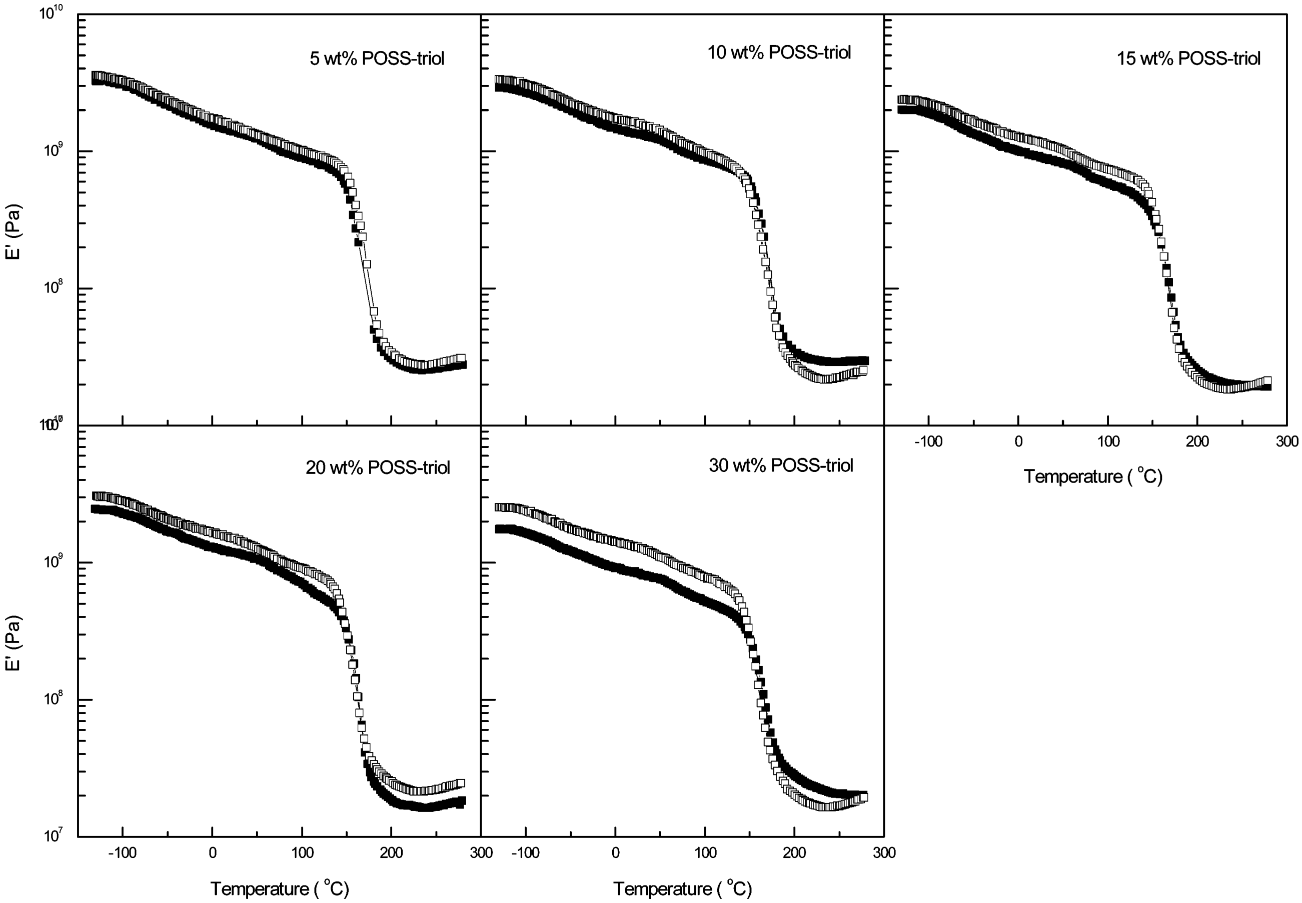


Figure 9. Comparison of dynamic mechanical storage moduli for the of hybrid composites: (□) phase-separated composites; (■) nanocomposites.

the compact nanometer-sized POSS blocks in the cross-linked networks brings about the significant reinforcement of local chains. In addition to the nanoreinforcement of POSS cages, Lichtenhan et al.[55] proposed that the POSS−POSS interactions have a dominant role in controlling the resulting physical properties of modified system. It has been proposed that the POSS−POSS interactions are important in the hybrid systems with chemically grafted POSS.[32] In the present case, the POSS molecules were grafted onto the epoxy networks with the corner trisilanol hydroxyls, and thus the POSS blocks are the dangling units of the epoxy networks. The POSS−POSS interactions formed the POSS domains, which has been proved by the result of high-resolution TEM (see Figure 3). The nanosized POSS domains could act as the physical cross-linking sites and reinforce the networks. It is worth pointing out that the aggregation of POSS moieties unnecessarily purports the enhancement of T_g's since the aggregation of POSS moieties is not required for slowing polymer chain relaxation in terms of the results of theoretical simulation.[56]

It is proposed that that the physical cross-linking sites are stable at the lower temperature (e.g., in glassy state). When the samples were heated to elevated temperature (e.g., in rubbery state), the POSS domains could be destroyed by the thermal motion of molecular chains and thus will contribute less to the modulus of materials. In fact, it is seen that the storage moduli of rubbery states for the nanocomposites were not always higher than those of the control epoxy and the phase-separated composites although there exist the nanoreinforcement of POSS on epoxy networks. In this case, the decrease in cross-linking densities of the matrices could give rise to the decrease in moduli in the rubbery state for the nanocomposites. The decreased cross-linking densities of the matrices result from the reaction of POSS-triol with DGEBA instead of a part of DDM.

c. Thermal Stability. The thermal stability of the hybrid composites was investigated with thermogravimetric analysis (TGA). Figures 10 and 11 showed the TGA curves of the materials, recorded in an air atmosphere. The improvement in thermal stability for epoxy networks by incorporating POSS molecules into the systems was observed for the two composite systems in terms of both rates of weight loss from segmental decomposition and ceramic yields. The initial thermal decomposition temperature (T_d) is defined as the temperature at which the mass loss of 5 wt % occurs. It is worth noticing that, except for the samples containing 30 wt % of POSS-triol, the nanocomposites exhibited the higher initial T_d than the phase-separated composites. This result could be ascribed to the formation of the nanocomposites. It is assumed that the nanoscaled dispersion of POSS-triol molecules in the matrices and their covalent bonding onto the network contributed to the enhancement of the initial decomposition temperature. In addition, the increased T_d for the nanocomposites could result from the increased chain spacing, which gives rise to a lower thermal conductivity. This case is similar to the effect of nanoscaled dispersion of POSS moiety on the glass transition temperature (T_g) and the modulus (E') of materials. It should be pointed out that the higher T_d for the phase-separated composite containing 30 wt % of POSS-triol could be related to the

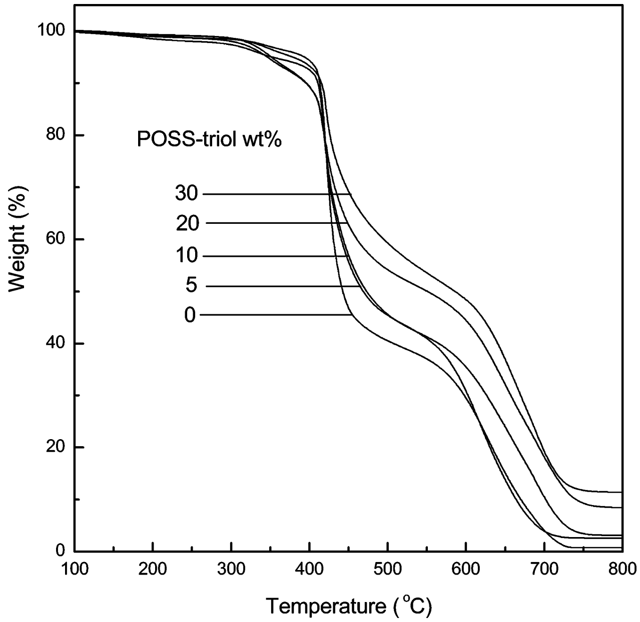


Figure 10. TGA curves of the control epoxy and the phase-separated composites.

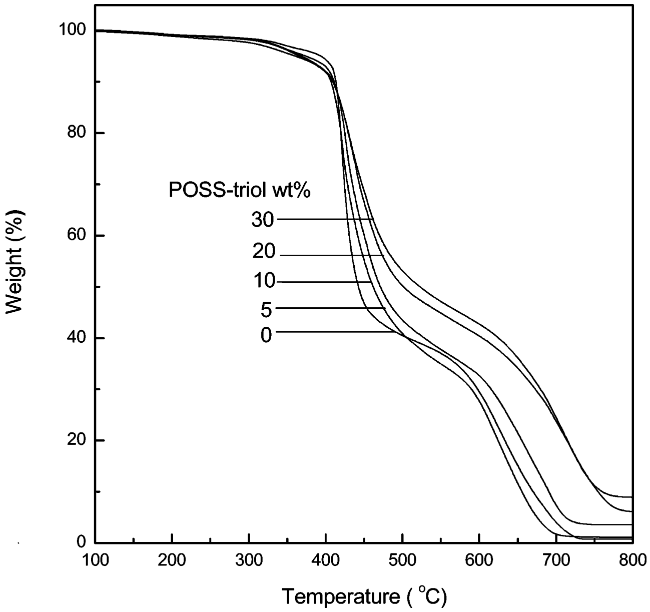


Figure 11. TGA curves of the control epoxy and the nanocomposites.

particulate morphology, in which POSS-triol began to form continuous phase. On the other hand, it is noted that the ceramic yields of the phase-separated composites are significantly higher than those of the nanocomposites. The observation can be interpreted in terms of the condensation of POSS-triol molecules during heating. For the phase-separated hybrid composites, the POSS-triol molecules in the dispersed phase could be converted into the silica particles via the condensation reaction among the silanol hydroxyls of POSS-triol at elevated temperatures. The silica particles are quite stable in the system until the mass loss from segmental decomposition of organic component undergo to completion. For the nanocomposites, however, POSS-triol molecules were covalently bonded with epoxy networks via the reaction of silanol hydroxyls with epoxide groups; the POSS blocks were dispersed into the epoxy network at the nanoscale. It is expected that no significant condensation among the POSS blocks occurred at elevated temperature. Therefore, the molecular POSS blocks could form the volatile portion and be lost during the mass loss of segmental decomposition of organic component.

Conclusions

Epoxy resin was modified by an incompletely condensed polyhedral oligomeric silsesquioxane (POSS). Phenyltrisilanol POSS [$Ph_7Si_7O_9(OH)_3$, POSS-triol] was incorporated into the epoxy networks with the content of POSS up to 30 wt %. The phase separation of POSS-triol induced by reaction occurred, and the heterogeneous morphology was obtained for the hybrid composites. In the hybrid composites the spherical POSS-triol particles with diameter ranging from 0.3 to 0.5 μm were dispersed in the continuous epoxy matrices. Nonetheless, the nanocomposites of epoxy with POSS-triol can be prepared when the metal complex, aluminum triacetylacetonate ([Al]), was used, which could accelerate the reaction between silanol hydroxyls of POSS-triol with epoxide groups of diglycidyl ether of bisphenol A (DGEBA). The hybrid composites with the different microstructure displayed quite different thermomechanical properties. At the same composition the phase-separated composites possessed the higher glass transition temperatures (T_g's) than the nanocomposites while the nanocomposites displayed the higher storage modulus of glassy states. In terms of thermogravimetric analysis, the nanocomposites displayed the higher initial thermal decomposition temperatures (T_d's). The improvement in thermomechanical properties has been ascribed to the nanoscaled dispersion of POSS blocks in the materials.

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