4942 *Macromolecules* **2007,** *40,* 4942−4952

Role of Specific Interactions and Solubility in the Reinforcement of Bisphenol A Polymers with Polyhedral Oligomeric Silsesquioxanes

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Received May 26, 2006; Revised Manuscript Received May 9, 2007

ABSTRACT: Polycarbonate (PC) and phenoxy resin (PKFE) have similar structures derived from bisphenol A. PKFE resin possesses pendant hydroxyl groups along its backbone; instead of the carbonate carbonyl groups found in polycarbonate, PKFE contains 2-hydroxypropyl groups instead. This difference in structure significantly influences thermomechanical properties when these materials are blended with phenyltrisilanol polyhedral oligomeric silsesquioxanes (POSS). While POSS exhibits some level of solubility in the each of the polymer matrixes tested, the glass transition temperatures of phenoxy composites increase with incorporation of POSS, while the glass transition temperatures of polycarbonate composites decrease significantly. Addition of POSS to PC also results in embrittlement of the composites; POSS thus serves as an antiplasticizer in the PC/POSS system. In the case of PKFE/POSS composites, significant interactions are evidenced by the change in the shape of the infrared spectra for the C−H phenyl stretch. While nuclear magnetic resonance spectroscopy shows definite reactions occurring between polycarbonate and POSS, no reactions were detected with the phenoxy resins. The POSS nanoscale filler can act as a plasticizer or as a reinforcing agent, depending upon the availability of filler−polymer interactions within the system.

Introduction

Polyhedral oligomeric silsesquioxanes (POSS) are versatile nanomaterials, which can be used as additives during blending or as monomers for the production as copolymers. Because of their hybrid inorganic−organic nature, the inorganic core of POSS grades can act to provide molecular reinforcement, while the organic groups can act to increase compatibility with polymers. POSS has been widely used to make copolymers with polyurethanes,[1] polyethylenes,[2] polystyrene,[3] poly(methyl methacrylate),[4] and thermosets.[5] While the mechanism of reinforcement in these copolymers is reasonably well understood, very little systematic work has been reported about reinforcement effects in polymer/POSS physical composites. No clear predictive theory which describes reinforcement of polymers using POSS as nanofillers has been put forth, to the best of our knowledge.

The POSS composites of two related polymers, polycarbonate (PC) and phenoxy resin (PKFE), are described in the current work. The two polymers of interest possess similar structures derived from bisphenol A. Phenoxy resin contains 2-hydroxypropyl groups, while polycarbonate contains carbonyl functionalities. Because of this difference in functional groups within the repeat unit, phenoxy resins are capable of reacting to form thermosets and are also capable of hydrogen bonding, two modes of action not typically available to polycarbonates. Phenoxy resins are tough and ductile thermoplastic materials having high cohesive strength and good impact resistance. The backbone ether linkages and pendant hydroxyl groups promote wetting and bonding to polar substrates and fillers. Phenoxy resins have excellent compatibility with polar materials and surfaces like polyurethanes, polyesters, and nylons.[6] These materials can therefore be used in masterbatch compositions to deliver reinforcing agents and other fillers into a range of polymers. Bisphenol A polycarbonate is a well-known amorphous polymer commonly utilized for its high clarity and high impact properties; enhancement of polycarbonate thermal and mechanical properties is of interest in a wide range of potential applications.

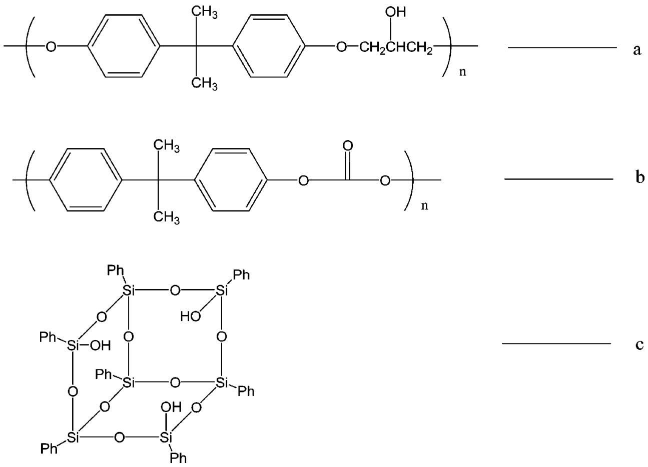

Figure 1. Structures of (a) PKFE phenoxy resin, (b) polycarbonate, and (c) phenyltrisilanol POSS.

Experimental Section

PKFE phenoxy resin was obtained from InChem Resins Inc. (Rock Hill, SC), with reported number-average and weight-average molecular weights of 16 000 and 60 000 g/mol, respectively. Polycarbonate (Makrolon 2205) with a reported melt index of 35 was obtained from Bayer Material Sciences. Both polymers were used as received. Phenyltrisilanol POSS (Hybrid Plastics) was used as received. The structures of the starting components are listed in Figure 1.

The polymers were dried in a vacuum oven for 24 h at 100 °C prior to extrusion. Composites with different weight percentages of phenyltrisilanol POSS were prepared on a DACA microextruder (model 2000) with corotating screws turning at 100 rpm and

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10.1021/ma061180l CCC: $37.00 © 2007 American Chemical Society
Published on Web 06/14/2007

Table 1. Appearance of Compression-Molded PKFE/POSS and PC/POSS Films and Corresponding Glass Transition Temperatures[a]

			method A		method B		method C	
polymer composition	PKFE appearance	polycarbonate appearance	PKFE T_g (°C)	PC T_g (°C)	PKFE T_g (°C)	PC T_g (°C)	PKFE T_g (°C)	PC T_g (°C)
0% phenyl TPOSS	clear	clear	108.1	158.5	91.0	141.9	86.7	141.6
5% phenyl TPOSS	clear	clear	109.0	152.5	97.1	140.8	89.9	138.4
10% phenyl TPOSS	clear	clear	109.4		97.4	135.6	89.3	133.6
15% phenyl TPOSS	slightly hazy	clear	110.9		98.4	129.5	89.0	130.8
20% phenyl TPOSS	hazy	slightly hazy	109.7		89.8	128.0	87.9	126.4
25% phenyl TPOSS	hazy		109.0		89.7		87.3	

[a] Method A: DMA tan δ. Method B: DSC 10 °C/min. Method C: DSC 3 °C/min.

residence times of 5 min. Polycarbonate was processed at 260 °C while phenoxy resin was processed at 230 °C. Extruded samples were then compression-molded on a Carver press (model C) into films of ~0.3 mm thickness. These films were then used for characterization of materials.

Characterization. Dynamic mechanical analyses (DMA) of the materials were carried out on a Thermal Analysis (TA) Q800 dynamic mechanical analyzer. Samples measuring 5 mm in width and 15 mm in length were heated from 25 to 180 °C for polycarbonates (135 °C for PKFE) at 3 °C/min in the tension mode at 1 Hz and amplitude of 20 μm. Differential scanning calorimetry (DSC) was carried out on a Mettler Toledo DSC model 822e/700. Samples were heated at two different ramp rates of 10 and 3 °C/min to separate the kinetic and thermodynamic effects and to relate to the results from the DMA. The data reported are the second heating cycles. Infrared spectroscopy (IR) was carried out in the attenuated total reflection mode (ATR-IR) on a TravelIR (Sensir Technologies). ATR-IR samples were scanned from 650 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. All the data from the IR were normalized relative to the pure polymers. ^1H and ^{13}C nuclear magnetic resonance (NMR) of PKFE/POSS and PC/POSS composites were carried out on a Varian 600 MHz machine to probe hydrogen bonding within the system and possible reactions occurring during melt blending. Samples for NMR titration experiments were prepared as follows: two solutions were prepared in deuterated chloroform, one containing 0.05 M polymer and the other solution containing 0.05 M polymer and 0.1 M POSS. The molarities of the polymer solutions were calculated on the basis of molecular weight of the repeat unit and were kept constant to probe the effect of addition of POSS. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) with a Varian Prostar model 210 solvent-delivery module, model 350 refractive-index detector, model 320 ultraviolet−visible detector, PSS Wingpc compact v6.20 software, and a PSS SDV 5 linear column with tetrahydrofuran (THF) as an eluent and calibrated with polystyrene (PS) standards. Sample solutions with concentration of 5 mg/mL were dissolved in THF to obtain a clear solution. These sample solutions were filtered to remove any particulates from solution prior to analysis. Composite morphology was examined by a Philips XL30 environmental scanning electron microscope (ESEM). Samples were also analyzed by energy dispersive X-ray analysis (EDAX) to identify elemental composition in the bulk as well as in the filler. Samples for SEM and EDAX were prepared by fracturing films in liquid nitrogen and imaging the fractured surfaces. Samples were sputter-coated with palladium prior to analysis. Positron annihilation lifetime spectroscopy (PALS) was performed using the fast−fast coincident method with a time resolution of 230 ps, at a count rate of ~10^6 counts/h.[7,8] A 30 μCi ^{22}NaCl positron source was sandwiched in between two compression-molded films, each with thickness of 1 mm and 1 × 1 cm^2 area. All samples were run at room temperature. The positron lifetime spectrum was determined by PATFIT software. The spectra were fitted to three exponentially decaying lifetime components. The average free volume hole radius (r_h) was calculated from the o-Ps lifetime (τ_3) using the semiempirical equation[9,10]

$$\tau_3\ (\text{ns}) = 0.5\left[1 - \frac{r_h}{r_h + \delta r} + \frac{1}{2\pi}\sin\left(\frac{2\pi r_h}{r_h + \delta r}\right)\right]^{-1}$$

where δr has been empirically determined to be $\delta r = 0.1656$ nm by fitting above equation to the o-Ps annihilation data for molecular solids of known pore size.[10] The uncertainty in r_h based on 10 spectra was ±0.03 Å.

Table 2. Concentration of Different Solutions of PKFC/POSS Blends Prepared for NMR Titration

solution label (refer to Figure 13)	concentration of POSS (M)	concentration of polymer (M)
a	0	0.05
b	0.0093	0.05
c	0.0186	0.05
d	0.0279	0.05
e	0.0372	0.05
f	0.0465	0.05
g	0.0558	0.05
h	0.0651	0.05
i	0.0744	0.05
j	0.0837	0.05
k	0.0930	0.05
l	0.102	0.05

Results

The use of trisilanol POSS is critical in the present study to illustrate the effect of interactions between POSS and the polymer. When a completely condensed POSS cage (octaphenyl POSS) was used to blend with phenoxy and polycarbonate, it was found that the POSS was insoluble in either polymer and the resultant composites were opaque. The POSS domains aggregated into large particles in the composites. This lead to the use of incomplete cage structures (“T7”) for the preparation of the composites. As will be demonstrated through EDAX and SEM, the silanols in the incomplete POSS cage play a crucial role in determining the solubility of POSS in both polymers.

Appearance. Samples of PKFE composites with varying percentages of phenyltrisilanol POSS appeared to be optically transparent up to 15 wt % filler and translucent up to a 25 wt % level. The polycarbonate composites remained transparent up to 20 wt % POSS in the composites. These results indicate either that the POSS is dispersed on the nanoscale in the composites or that POSS is soluble with both polymers up to 15−20 wt %. These results are listed in Table 1 and will be further discussed in this paper using a combination of SEM and EDAX.

Dynamic Mechanical Analysis. An increase of up to 50% in the room temperature modulus and as much as 200% in the rubbery modulus of PKFE was observed with increasing levels of POSS filler. The glass transition temperature of the composites were also observed to increase slightly with a maximum increase in the glass transition temperature of 3 °C in the 15 wt % composite system (Table 1). The elastic modulus responses of PKFE and polycarbonate composites with different weight percentages of phenyltrisilanol POSS are provided as Supporting Information, as are the tan δ responses of the PKFE/POSS and PC/POSS composites.

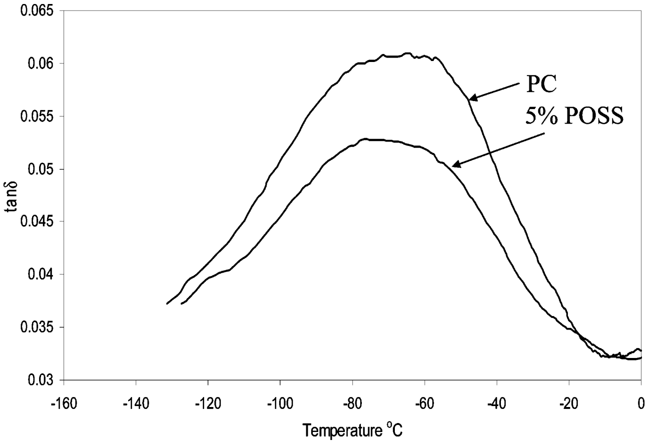

Figure 2. Low-temperature tan δ curves for PC/POSS composites.

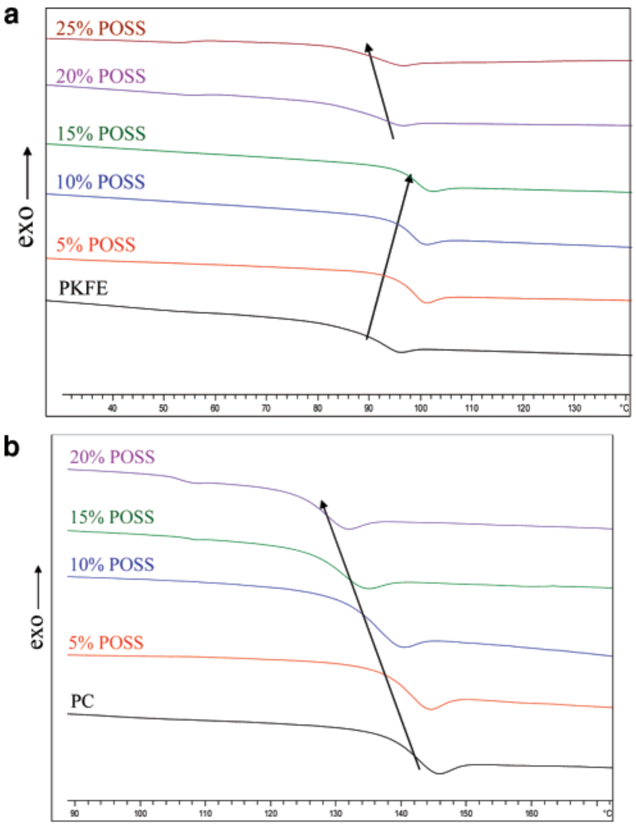

Figure 3. (a) DSC second heating curves at 10 °C for PKFE/POSS composites. (b) DSC second heating curves at 10 °C for polycarbonate/POSS composites.

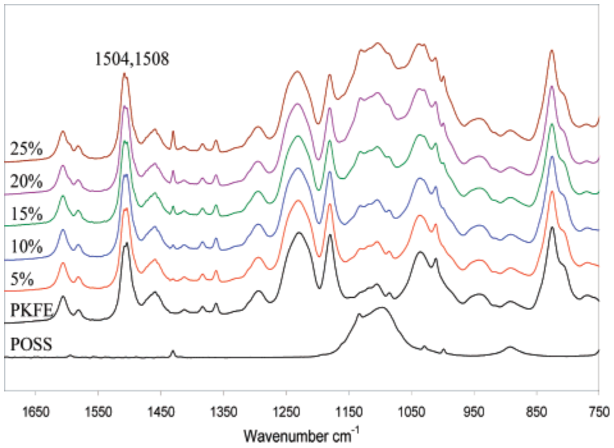

Figure 4. ATR-IR spectra of PKFE/POSS composites.

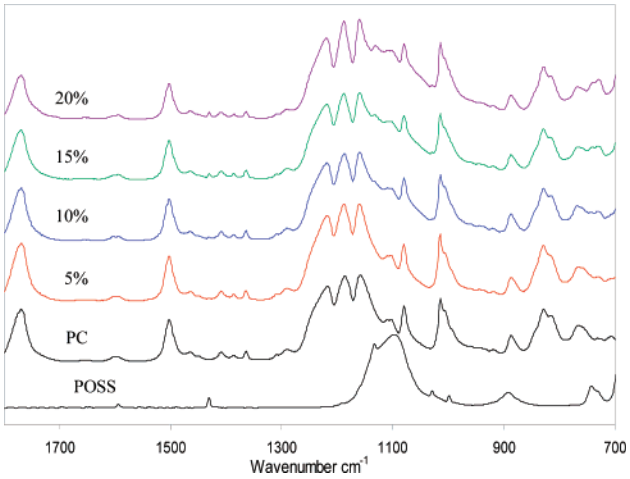

Figure 5. ATR-IR spectra of PC/POSS composites.

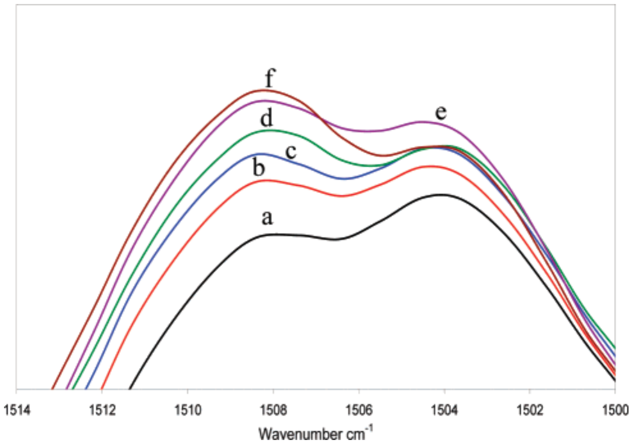

Figure 6. ATR-IR spectra of the C−C stretch region in (a) PKFE, (b) 5% POSS, (c) 10% POSS, (d) 15% POSS, (e) 20% POSS, and (f) 25% POSS.

The DMA curves for PC/POSS composites are drastically different from those of the PKFE/POSS composites. Neither the room temperature modulus nor the rubbery modulus of polycarbonate increased upon incorporation of POSS. On the contrary, a significant reduction in the glass transition temperature of polycarbonate was observed with as little as 5 wt % POSS incorporation. Samples containing greater than 5 wt % POSS in polycarbonates were too brittle to test using the DMA. The glass transition temperatures were taken as the peak of the tan δ curves and are reported in Table 1. Low-temperature DMA scans on PC with and without 5 wt % POSS demonstrated that the transition observed at ca. −70 °C was substantially retarded by the presence of POSS (Figure 2).

Thermal Analysis. Differential scanning calorimetry (DSC) second heating curves of PKFE/POSS and PC/POSS composites are reported in parts a and b of Figure 3, respectively, heated at 10 °C/min. The glass transition temperatures obtained from these curves are listed in Table 1. For PKFE composites there is first an increase in the glass transition temperature followed by a reduction as the weight percentage of phenyltrisilanol POSS increases. In the case of polycarbonate composites, however, there is a clear plasticization effect with the incorporation of POSS, leading to a monotonic decrease in T_g with level of filler added. The glass transition temperature of PC was observed to decrease as much as 16 °C for the composites containing 20 wt % POSS.

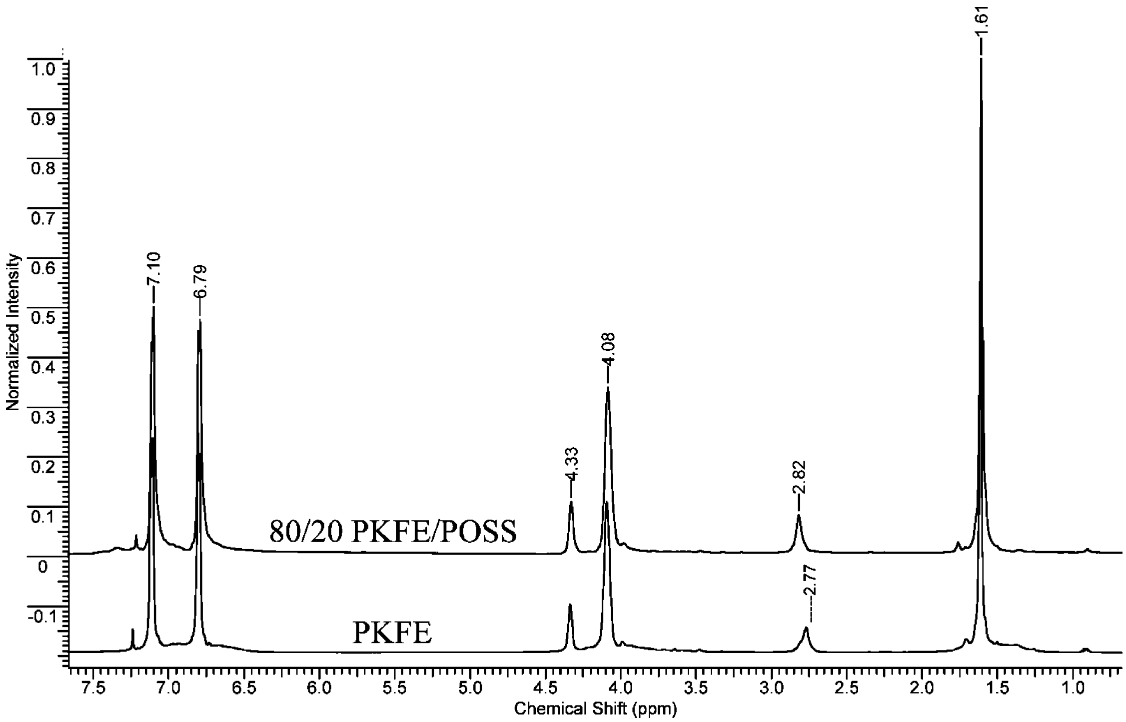

Figure 7. ^{1}H NMR spectra of PKFE and 80:20 PKFE:POSS composite.

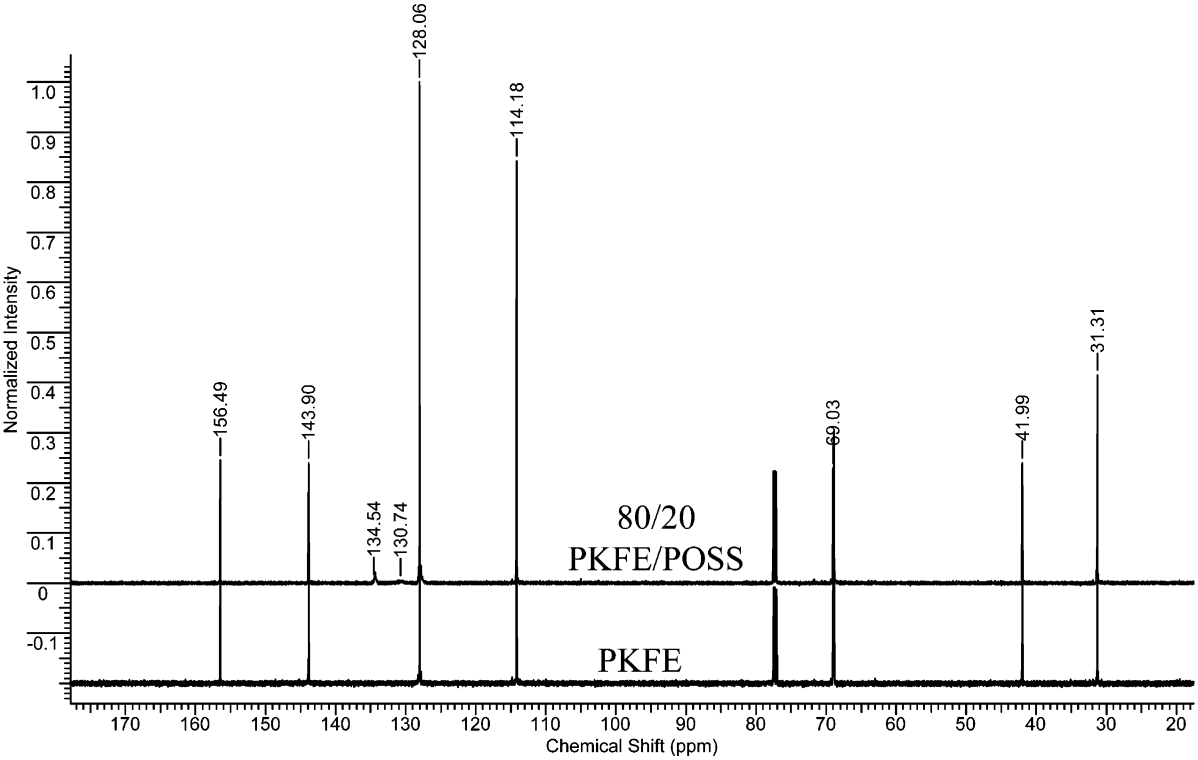

Figure 8. ^{13}C NMR spectra of PKFE and 80:20 PKFE:POSS composite.

In order to separate thermodynamics from any kinetic effects, the samples were retested at 3 °C/min scan rates. If the mixing of POSS is governed by thermodynamics, then the glass transition temperature should change by the same extent irrespective of the heating rate of the sample. This scan rate also allows for a better comparison between the results obtained from the DMA and the DSC. The trends observed at this lower scan rate were consistent with those at 10 °C/min. While the magnitude of change in the polycarbonate systems remained relatively unchanged, the effect of filler is diminished in PKFE/POSS composites interrogated at the lower rate. The data obtained from the lower cooling rate compare well with the data obtained from the DMA for PKFE/POSS composites; these thermograms are provided as Supporting Information, and the values are also listed in Table 1.

It is also interesting to note that while phenyltrisilanol POSS is a crystalline solid and has a melting peak of ~208 °C, both the phenoxy and the polycarbonate composites do not show a melting peak for the POSS in the DSC scans. A similar observation has been made before with PC/POSS composites and is consistent with nanoscale or molecular-scale distribution of the filler within the matrix polymers.[11]

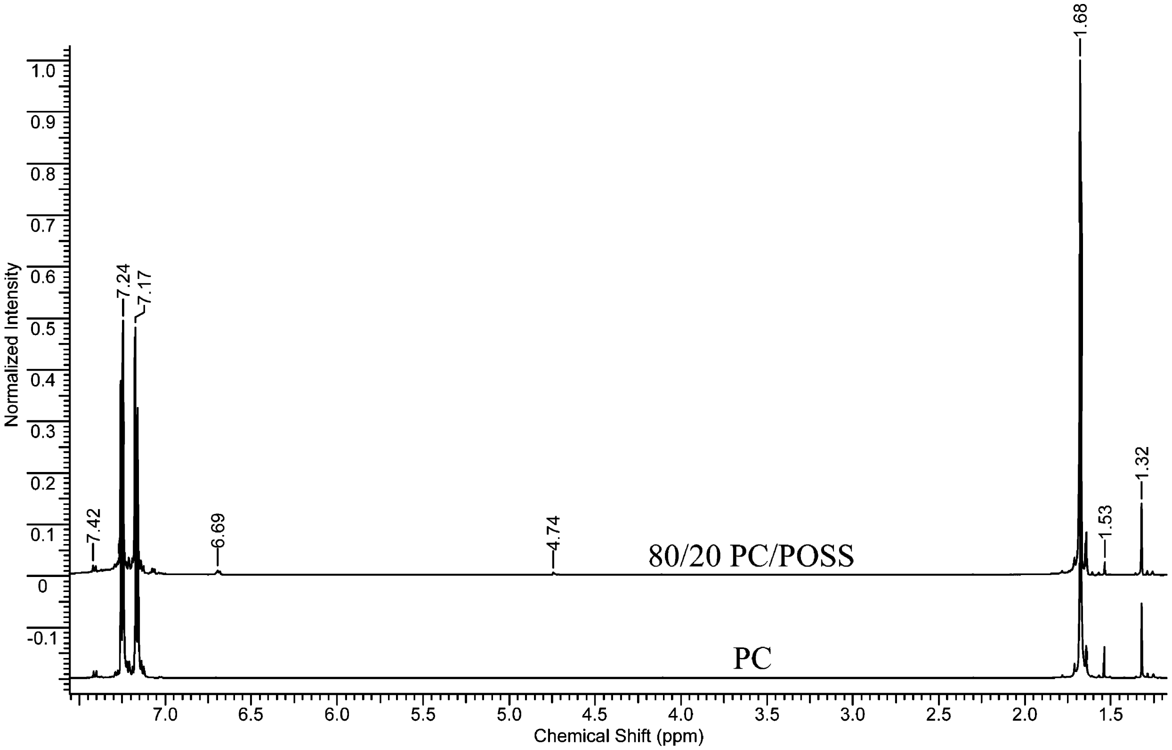

Figure 9. ^{1}H NMR spectra of PC and 80:20 PC:POSS composite.

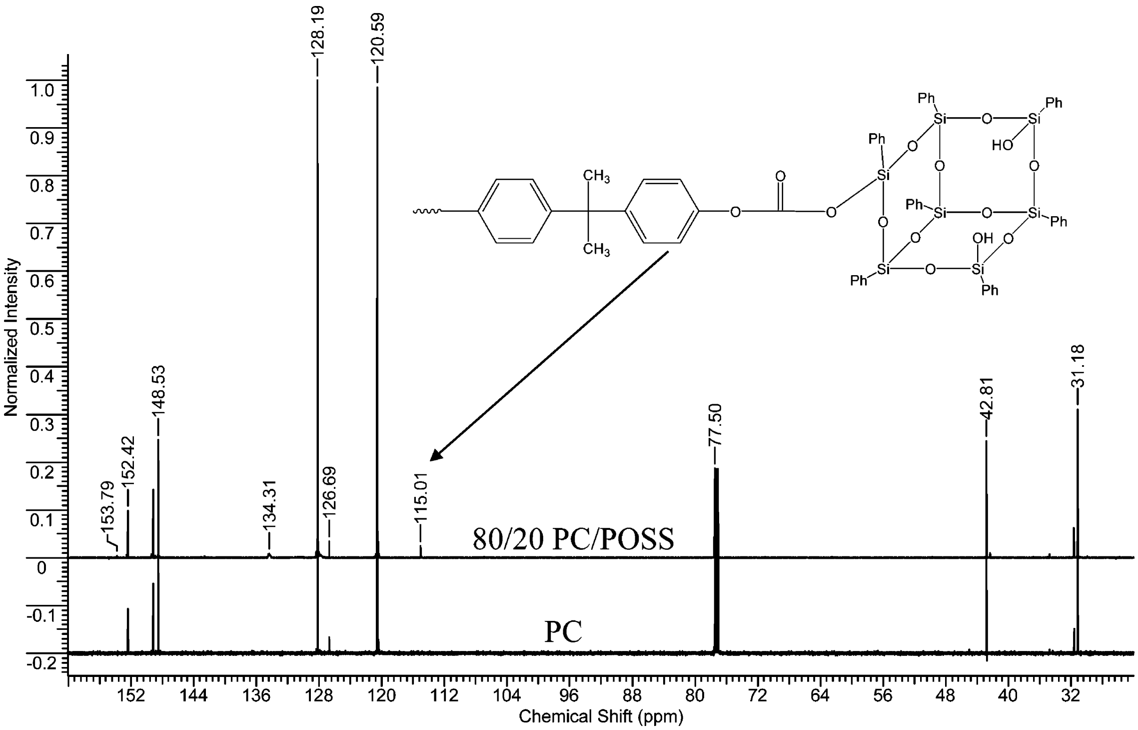

Figure 10. ^{13}C NMR spectra of PC and 80:20 PC:POSS composite.

Infrared Spectroscopy. FT-IR spectroscopy is a powerful tool for elucidation of structural information, wherein the position, intensity, and shape of vibrational bands are useful in clarifying conformational and environmental changes of polymers at the molecular level. Interactions in composites can lead to considerable differences between the spectra of a polymer within a composite and that of the starting matrix material.

Figures 4 and 5 present the fingerprint regions of the attenuated total reflectance infrared spectra (ATR-IR) of PKFE/POSS composites and PC/POSS composites, respectively. In the case of PC/POSS composites, there is no evidence of interactions between the carbonyl group (1770 cm^{-1} band) and the hydroxyl group from the POSS, as there is no shift in peak position or broadening of the carbonyl peak. The expanded region between 1503 and 1508 cm^{-1} for the PKFE/POSS composites is shown in Figure 6; this region corresponds to the carbon−carbon stretch of the para-substituted benzene in bisphenol A.[12] The shape of this doublet changes as the weight percentage of POSS in the composites increases. Similar changes in the peak shape have been observed by other researchers in

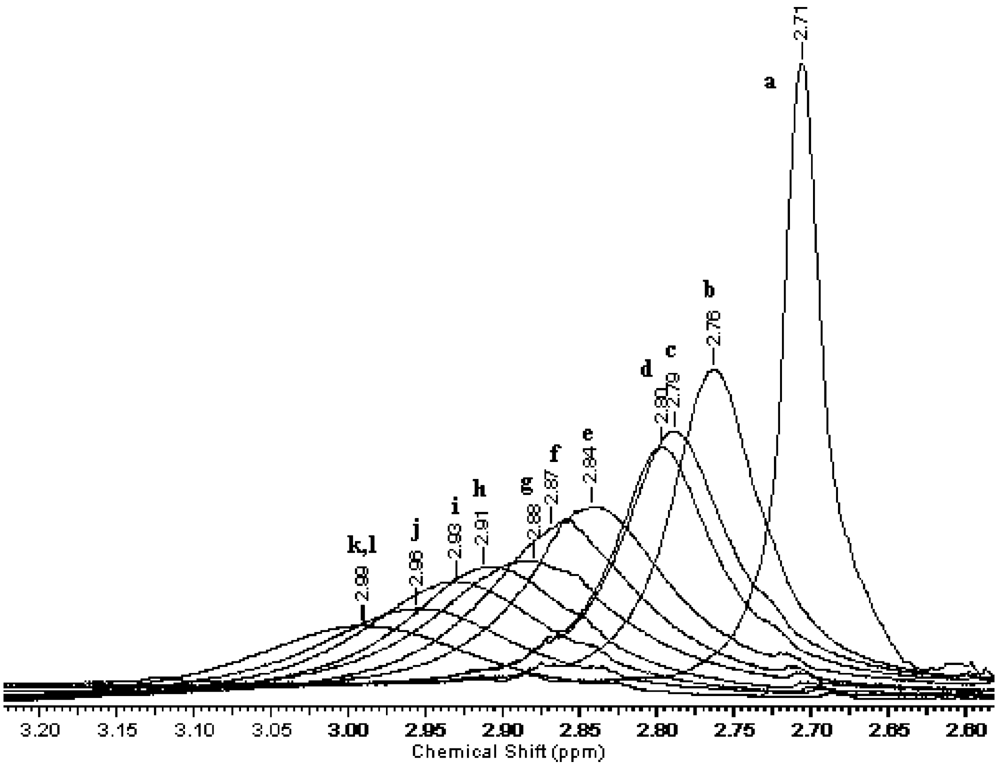

Figure 11. ^1H NMR for various concentrations of POSS in 0.05 M PKFE. The hydroxyl proton region is shown. Labels correspond to the labels in Table 2.

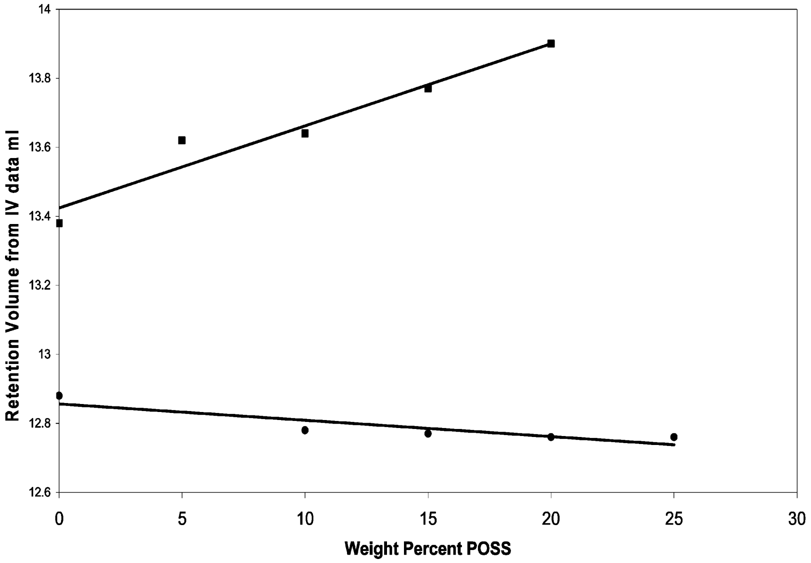

Figure 12. GPC retention volume vs concentration of PC/POSS (■) blends and PKFE/POSS (●) blends.

interacting polymer systems,[13,14] and it has been pointed out in these systems that the peak changes correspond to interactions between two phases.

Nuclear Magnetic Resonance Spectroscopy. The ^1H and ^{13}C NMR spectra for the various polymer/POSS composites examined in this study are shown in Figures 7−10. The spectra presented are for the 80 wt % polymer and 20 wt % POSS composites. In the case of PKFE/POSS composites, there is a significant chemical shift of the hydroxyl region of PKFE in the presence of POSS. This change in chemical shift could result from either hydrogen bonding with POSS or a dilution effect in the polymer. In order to confirm and differentiate these results, a series of concentrations of POSS in PKFE were prepared, and ^1H NMR spectra were obtained for these samples. The ^1H NMR spectra for the various concentrations of POSS in PKFE listed in Table 2 are shown in Figure 11. The peak at 2.71 ppm corresponds to the free hydroxyl group in the pure PKFE resin. As the concentration of POSS is slowly increased, there is a steady shift and broadening effect of the hydroxyl peak in the polymer. It has been well demonstrated that hydrogen bonding leads to a downfield shift and broadening of the free hydroxyl proton in polymers. The ^1H NMR for PC/POSS composites does not show a significant chemical shift for any of the peaks. However, the ^{13}C NMR spectra of 20 wt % POSS show the presence of a new peak at 115 ppm (Figure 10). These results will be discussed in greater detail later.

Gel Permeation Chromatography. Figure 12 shows the GPC traces for PC/POSS and PKFE/POSS composites. The data are plotted as the retention volume obtained from intrinsic viscosity measurements vs concentration of POSS in the blend.

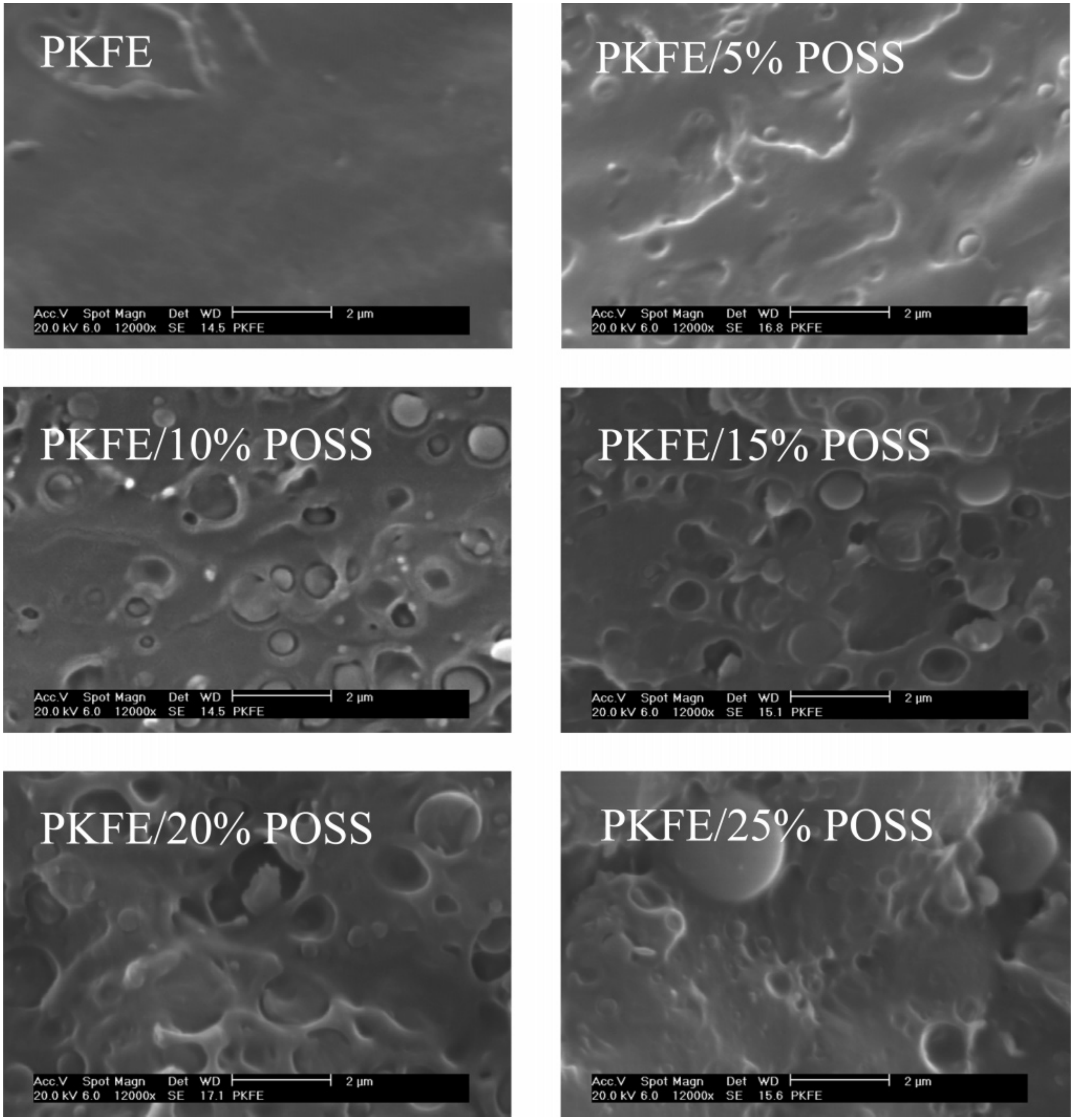

Figure 13. SEM micrographs of PKFE/POSS composites.

Retention volume of PC/POSS composites increases with increasing amount of POSS, indicating a decrease in the molecular weight of the polymer. An opposite effect is seen in the case of PKFE/POSS blends. The retention volume of the composites decreases with increase in molecular weight, indicating a slight increase in the molecular weight of PKFE with increasing amounts of POSS. Results from GPC indicate that POSS can have drastically different behaviors in the presence of carbonyl and hydroxyl groups in a polymer.

Scanning Electron Microscopy. SEM images for the various polymer/POSS compositions are shown in Figures 13 and 14. As can be seen from the images, both polymers exhibit submicron size inclusions with increasing percentages of POSS added. There is, however, a significantly higher dispersion of visible in the PKFE/POSS systems compared to the PC/POSS systems.

In the PKFE/POSS composites, POSS appears to be uniformly distributed in the matrix—there is, however, formation of significant void spaces in the interphase region, indicating incompatibility in these systems. Nonetheless, EDAX of these systems indicates the presence of significant amount of silicon in the matrix, indicating miscibility in these systems. The resolution of the EDAX measurements was around 0.2 μm. Similar observations of miscibility have been reported by other groups.[15] As particles can be seen even in the 5 wt % composites, it seems that the solubility limit for POSS in PKFE is lower than 5 wt % or that the system would need more time to equilibrate. The term equilibrate refers to the time necessary for full dispersion of POSS in PKFE, recognizing that there is a kinetic factor governing the dispersion of POSS in the polymer. There is also a large excluded volume between the interphase of the polymer and filler particles.

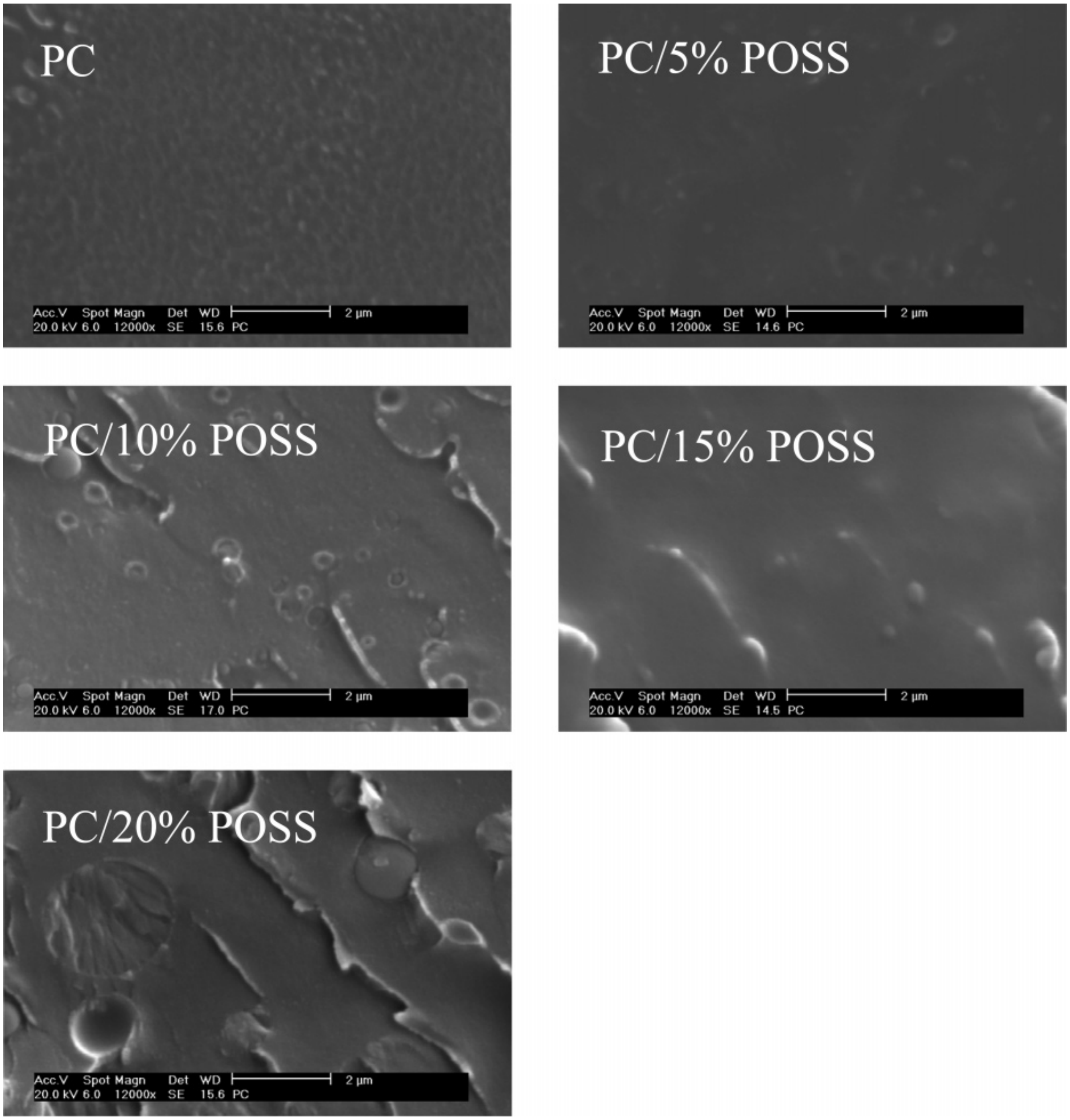

Figure 14. SEM micrographs of PC/POSS composites.

In contrast to the PKFE/POSS composite systems, the morphology of the PC/POSS composites is significantly different. At 5 wt % POSS in PC, very few particle-like inclusions are seen in the SEM. EDAX also shows almost equal concentrations of silicon atoms within these particles as well as in the matrix in PC/POSS composites. At higher percentages of POSS (>10 wt %) a second POSS phase can be seen being formed in the material. There is also little excluded volume formed between the particle and the polymer. These observations hint at significantly higher solubility and adhesion between the filler and the polymer in the case of PC composites.

Positron Annihilation Lifetime Spectroscopy (PALS). In order to further probe and understand the morphology differences between the two composites and to explain the different thermomechanical behavior in the two systems, free volume measurements were made. The PALS data obtained for the size of holes, the concentration of holes, and the fractional free volume for PKFE/POSS and PC/POSS composites are given in Figures 15−17. The results demonstrate an increase in the free volume radius as well as concentration of holes in PKFE composites with increasing percentage of POSS. However, in the PC/POSS systems, the size of the holes remains constant while the concentration of holes increases with POSS loading.

Discussion

The thermomechanical data obtained from the DMA and DSC experiments in this study demonstrate that the hydroxyl groups in phenoxy resin strongly influence the properties of PKFE/POSS composites, whereas the properties of the carbonyl analogue to this polymer, PC, change in the opposite direction. Decreases in composite T_g values accompanied by embrittlement of PC/POSS composites suggest antiplasticization behavior. Antiplasticization in glassy polymers, especially in polycarbonates, has been studied in great detail and is believed to occur due to suppression of the low-temperature β transition of the material. The low-temperature β transition in polycarbonate (∼−100 °C) is caused by the flipping motion of the bisphenol A segment as shown in Figure 18, which is also responsible for the high impact strength of the material.[16,17] Our low-temperature DMA scans on the polycarbonate composites with 5 wt

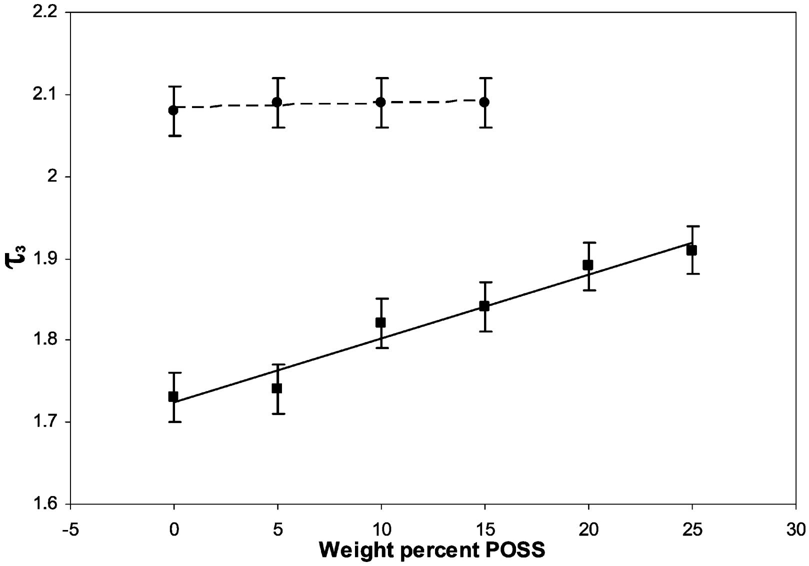

Figure 15. PALS data for lifetime of positron in (■) PKFE/POSS and (●) PC/POSS composites.

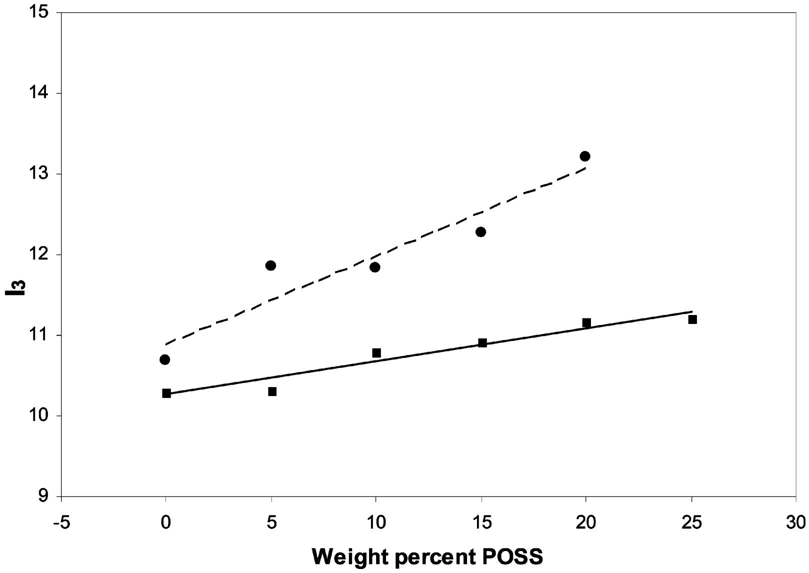

Figure 16. PALS data for the concentration of holes in (■) PKFE/POSS and (●) PC/POSS composites.

% POSS indeed demonstrate significant lowering of the intensity of this low-temperature tan δ peak (Figure 2). The addition of POSS inhibits the motion of the phenylene ring π-flip, thus limiting movement and reducing the toughness of the material. Similar effects of antiplasticization have been seen in compatible polycaprolactone/polycarbonate blends.[18] These systems were reported to exhibit lowering of glass transition temperature and at the same time embrittlement of polycarbonate with increasing addition of polycaprolactone. It was also recently reported by Cohen and co-workers that miscible POSS grades in poly(methyl methacrylate) and poly(vinyl chloride) gave clear composites along with a high degree of plasticization.[15,19] The SEM images along with EDAX of the PC/POSS composites reveal limited solubility (around 5 wt %) of trisilanolphenyl POSS in polycarbonates, above which the POSS phase separates from the polymer. However, there is still good adhesion at the interphase between the polycarbonate and POSS at high concentrations of POSS. Results from ^{1}H and ^{13}C NMR also demonstrate that there is formation of a new species during melt extrusion of polycarbonate/POSS blends; the NMR spectra are consistent with the product which would result from a nucleophilic attack of the carbonyl carbon by the silanol groups, as shown in Figure 19. Similar chain scission of PC has been seen in the presence of amine-terminated silanes.[20] The inhibition in chain motion is perhaps also facilitated by the reaction of POSS with polycarbonate seen through ^{13}C NMR experiments on the composites (Figure 10). Analysis of the ^{13}C NMR data indicates chain scission of PC resulting from the nucleophilic attack of the silanols on the carbonyl group of PC, as shown in Figure 19. Results from GPC also support a reaction as there is significant increase in the retention volume of the composites, indicating a decrease in the molecular weight of PC/POSS composites. While the results from DSC and DMA studies reveal significant loss in chain motion leading to a stiff material, the increase in the number of o-Ps annihilations with the addition of POSS indicates an increase in the free volume. The increase in free volume is known to be indication of material plasticization. An increase in free volume with significant antiplasticization of the polymer is one of the new findings of our research. The present PC/POSS composites studied along with the work done by Cohen et al. demonstrate that with soluble POSS grades, wherein little to no interactions between the polymer and POSS exists, there is consistent lowering of the glass transition temperature of the polymer. Thus, POSS acts as an internal

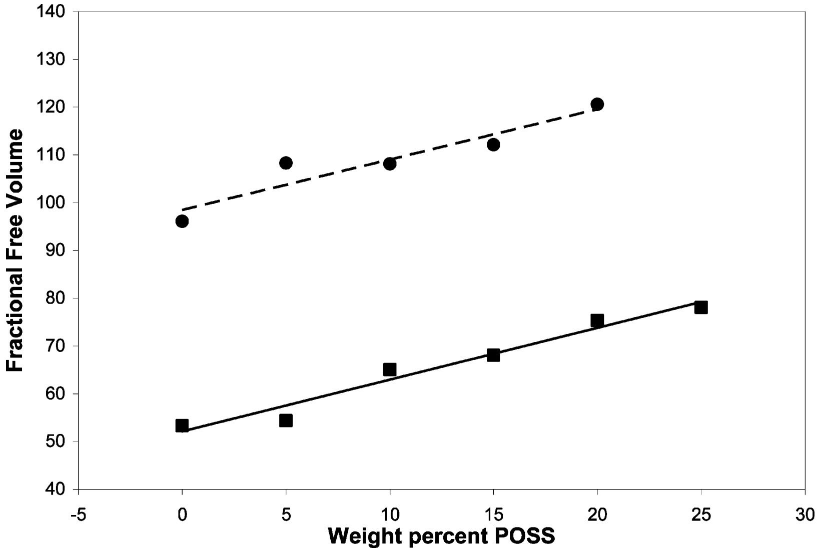

Figure 17. Fractional free volume calculated as $\tau_3{}^3I_3$ for (■) PKFE/POSS and (●) PC/POSS composites.

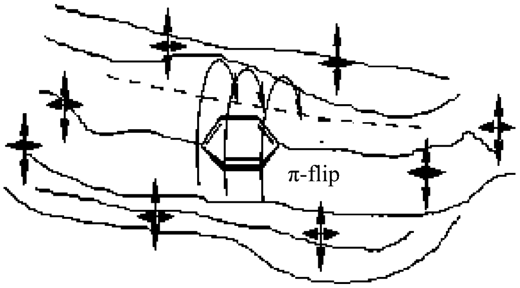

Figure 18. Phenylene ring π-flip and chain motion in polycarbonate below T_g.

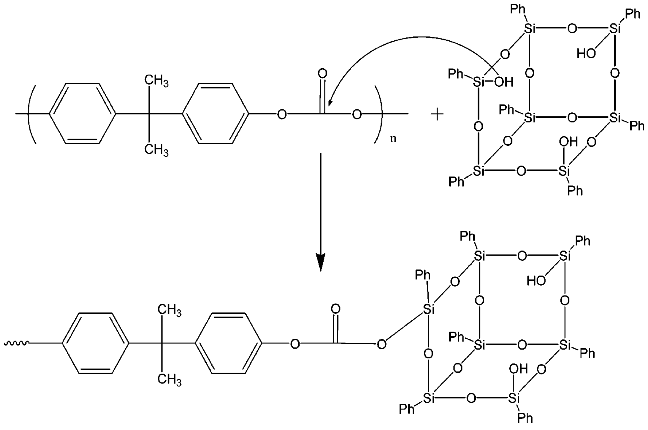

Figure 19. Proposed reaction of PC with phenyltrisilanol phenyl POSS.

molecular lubricant in these systems. Depending on whether the polymers have significant low-temperature transitions (ductile−brittle transition), soluble POSS can act as either a plasticizer or an antiplasticizer in the polymer.

In the case of PKFE/POSS composites, the opposite effect to that of polycarbonate is observed—the addition of POSS enhances the mechanical performance of the material. While poor compatibility between POSS and PKFE is observed by SEM (increased void spacing between the two phases and higher concentration of particles), EDAX demonstrates there is some solubility in the system. Infrared spectroscopy demonstrates significant interactions between the phenoxy resin and the POSS particles. Lu et al.[13] and Garcia[14] studied similar interactions in miscible and immiscible composites of polystyrene and poly(vinyl methyl ether) by FT-IR spectroscopy. These authors separately reported that the miscible PS/PVME composites showed strong evidence for molecular interaction, whereas no interaction was detected for the phase-separated PS/PVME composites. They reported on the infrared spectra of composites of polystyrene/poly(vinyl methyl ether) (PS/PVME); it was observed that PVME has a strong doublet at 1085 and 1107 cm^{-1} with a shoulder at 1132 cm^{-1}, and the relative intensity of this doublet varies considerably when the composite sample is cooled or heated. From the data, these authors concluded that the relative intensity of this doublet was sensitive to the interactions of the PS/PVME composites, indicating that the intensity of the 1085 cm^{-1} peak was greater than that of the 1107 cm^{-1} peak for the miscible composite. Similar results are reported in the present study of the PKFE/POSS system, wherein interactions between the polymer and filler particles change the shape of the doublet at 1508 cm^{-1}. These increased interactions between PKFE and POSS could be caused by preferential stacking of phenyl rings, possibly facilitated by hydrogen bonding between the hydroxyls groups between the polymer and POSS. The NMR titration data shown in Figure 11 further support this hypothesis. While no reaction products were detected by NMR between phenoxy and POSS, we cannot rule out a low level of such a reaction. The reaction is also difficult to monitor using NMR since the chemical shifts for the reacted material would be similar to that of the unreacted material. Results from the GPC indicate there could be small reactions occurring leading to an increase in the molecular weight of PKFE with increasing amount of POSS in the composites.

Low-temperature DMA scans of PKFE and its composites with POSS also exhibits a low-temperature phenylene π-flip motion, similar to that observed in PC. In PKFE composites, however, unlike the case with PC composites, there is no suppression of this phenylene π-flip motion. In the case of PKFE composites, it appears that the majority of POSS molecules that are soluble in the matrix are anchored to the phenoxy chain via hydrogen bonding and $\pi-\pi$ stacking.

The addition of POSS does not affect the free volume hole size within polycarbonate composites. Addition of POSS to PKFE does increase the hole size within PKFE/POSS composites. The complicated variation of free volume hole fractions in immiscible/partially miscible composites observed by the PALS technique is a result of the high sensitivity of the o-Ps particle not only to free volume holes but also to any interfacial spaces, such as those created between boundaries of two phases.[21] Since a higher percentage of free volume is created by the interphase region in PKFE/POSS composites, as compared to PC/POSS composites, there is an increase in the overall free volume as well. The reasons for the constant free volume in PC/POSS composites could be due to significant solubility of POSS in polycarbonate and/or improved adhesion between phases. In the case of PKFE/POSS composites, the possible increase in free volume could be caused by the higher excluded volume between the phases. Thus, while the significant polymer/filler interactions (hydrogen bonding and phenyl stacking) in PKFE/POSS composites act to improve the thermomechanical performance of the composite by increasing its glass transition, the increase in free volume of the composites due to incorporation of POSS tends to decrease the glass transition temperature of the composites. Up to 15 wt % loading of POSS in PKFE, hydrogen-bonding and $\pi-\pi$ stacking interactions dominate the thermal behavior of the system, whereas above 15 wt % the thermal behavior is controlled by the free volume of the composite.

Conclusions

Polycarbonate (PC) and phenoxy resin (PKFE) exhibit drastically different behaviors when blended with phenyltrisilanol POSS. The addition of POSS into PKFE results in improvement in thermomechanical properties whereas polycarbonate is antiplasticized. While POSS exhibits some level of solubility in the each of the polymer matrixes tested, the glass transition temperatures of phenoxy composites increase with incorporation of POSS, while the glass transition temperatures of polycarbonate composites decrease significantly. Addition of POSS to PC also results in embrittlement of the composites and acts as an antiplasticizer in the PC/POSS system. In the case of PKFE/POSS composites, significant interactions are evidenced by the change in the shape of the infrared spectra for the carbon−carbon phenyl stretch and the shift in chemical shift of the hydroxyls on the polymer. Nuclear magnetic resonance spectroscopy also shows possible reactions occurring in the PC in the presence of an open cage POSS which is miscible at low percentages. POSS nanoscale filler can act as a plasticizer or as a reinforcing agent, depending upon the availability of filler−polymer interactions within the system. In order to improve thermomechanical performance of polymers using POSS as filler, the presence of interactions is critical and necessary.

Supporting Information Available: Elastic modulus responses of PKFE and polycarbonate composites with different weight percentages of phenyltrisilanol POSS and tan δ responses of the PKFE/POSS and PC/POSS composites (Figures S1 and S2); thermograms for PKFE/POSS and PC/POSS composites (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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MA061180L