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Polyhedral Oligomeric Silsesquioxane (POSS) Particles in a Polysiloxane Melt and Elastomer. Dependence of the Dispersion of the POSS on its Dissolution and the Constraining Effects of a Network Structure

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Polysiloxane composites containing particles of polyhedral oligomeric silsesquioxane (POSS) were prepared by melt blending, and investigated with regard to their morphologies. Unexpectedly, the POSS crystallites were found to dissolve in the polysiloxane at temperatures that were elevated (but far below the POSS melting points).

X-ray diffraction, differential scanning calorimetry, and polarizing optical microscopy were used to document changes in the dispersions from this dissolution and from the subsequent recrystallization precipitation occurring upon cooling. Quenching was found to give finer POSS dispersions. Cross linking the polysiloxane caused changes in POSS solubility that enhanced the phase separation, but the cross links caused constraints that decreased the domain sizes of the precipitated phases. These decreases in POSS domain size provide an interesting parallel to the decreases in solvent crystallite sizes in thermoporosimetry, and the decreases in ceramic particle sizes in sol-gel technologies.

Keywords: crystallization; morphology; polysiloxanes; polyhedral oligomeric silsesquioxanes; POSS

1 Introduction

There is increasing interest in preparing nanocomposites in which unusual filler particles incorporated into a polymer matrix can vastly improve its mechanical properties. Some of the most impressive examples involve particles of a polyhedral oligomeric silsesquioxane (POSS), which is a structurally well-defined cage-like molecule represented by formula $(RSiO_{1.5})_n$. The most studied structure of this type consists of a cube having eight Si atoms at the corners and alternating with O atoms, with an organic R group at each Si. In some cases, some of the R groups are chosen to be reactive, to permit bonding onto or into the backbone of a polymer chain. In other cases, the R groups are unreactive, and chosen primarily to increase miscibility with a particular polymer matrix.

One complication results from the fact that POSS molecules tend to crystallize at room temperature, resulting in phase separation. Even for POSS particles containing reactive functional groups, very small POSS domains often form as aggregates instead of bonding to the polymer backbones or otherwise dispersing into the polymer matrix (1–3). Nonetheless, incorporation of POSS cages into chain backbones can give dramatic improvements in polymer properties, as has been shown for a wide range of thermoplastics and also for a few thermosets (4–10).

Polyolefins provide some illustrative examples. In one example, Fina et al. (11). reported POSS with different chain lengths that were melt mixed with polypropylene (PP) in a Brabender internal mixer. The POSS influenced the crystallization by acting as a nucleating agent or by inducing PP polymorphism. The nonisothermal crystallization of high density polyethylene/POSS composites prepared on a twin screw extruder was studied by Joshi et al. (12). Similarly, Fu et al. (13) reported crystallization studies at quiescent

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and shear states in isotactic polypropylene (iPP) containing nanostructured POSS molecules introduced by melt mixing. Finally, ethylene-propylene (EP) copolymer/POSS nanocomposites were prepared by melt-mixing (14). The results showed that the POSS caused physical gelation and increased the Young's modulus as well as the glass transition temperature T_g of the EP copolymer.

Because good compatibility between the POSS and the polymer of interest is a key to achieving well-dispersed composites, the present study focuses on POSS/polysiloxane (silicone) blends with as fine a state of dispersion as possible. In this investigation, the matrix was a polysiloxane consisting of mostly methyl side groups (along with a small molar content of vinyl side groups). The dimethyl polymer itself, $[\text{-Si(CH}_3)_2\text{O-}]$, has a backbone composed of alternating silicon and oxygen atoms, and this composition and structure makes it very similar to POSS itself. This suggests good miscibility of the two components.

The present work focuses on revealing the morphologies and extents of crystallization in POSS/silicone rubber blends. The dispersion of the POSS macromers in this elastomeric matrix was investigated using a wide variety of characterization techniques (15). Also of interest was the possible solubility of POSS crystallites in the silicone rubber and the likely effects from cross links when the silicone material was cured. It was obviously important to determine how these circumstances might influence the properties of these POSS nanocomposites.

2 Experimental

2.1 *Materials*

A sample of silicone rubber having 0.15% vinyl substituents and a molecular weight of 640,000 g/mol was purchased from the Second Chemical Factory of Beijing. The POSS used in this study was octaisobutyl-POSS ($C_{32}H_{72}O_{12}Si_8$), which was supplied by the Hybrid Plastics Company, Fountain Valley, CA. This type of POSS molecule consists of a polyhedral silicone-oxygen nanostructured cage, surrounded by eight isobutyl organic R groups on the eight silicon atoms.

2.2 *Preparation of POSS/Polysiloxane Nanocomposites*

POSS/polysiloxane blends were prepared in a Haake Banbury mixer (American Thermo Corporation) at a rotational speed 80r/min, mixing time of 30 min, using various blending temperatures and POSS loadings. Further details, including sample designations, are given in Table 1, and are described in detail elsewhere (15). The curing agent was (2,5-bistert-butyl-2,5-dimethylhexane peroxide), and the blend was vulcanized on a hot press at 160°C and a pressure of 150kgf/cm^2 for the optimal cure time (t_{90}), which had been determined earlier in a torque rheometer (15).

2.3 *Characterization*

Differential scanning calorimetry (DSC) measurements were made using a NETZSCH DSC204F1 instrument under a flow of nitrogen at a heating rate of 10 C/min. X-ray diffraction (XRD) analyses were carried out on a Rigaku D/Max 2500VBZC/PC X-ray diffractometer with Cu K_α radiation. It was difficult to use scanning electron microscopy on POSS/polysiloxane blends before vulcanization since they were very viscous fluids. For this reason, the morphologies of the POSS/polysiloxane blends were examined using a polarizing optical microscope (Olympus BX-51, Japan).

3 Results and Discussion

Because of the high melting point of POSS, elevated mixing temperatures were preferred for the processing. During mixing, it was observed that the blends in the chamber of the Haake mixer at low mixing temperatures were opaque, as mentioned in Table 1. This indicated that the POSS crystallites were poorly dispersed in the polysiloxane matrix. However, the blend gradually became transparent as the processing temperature was increased to 160°C. This temperature was far below the melting point of POSS, which was 268°C, as determined from the DSC results presented later. The transparency was an approximate

Table 1. Characteristics of various POSS/polysiloxane blends

POSS content (wt%)	Polysiloxane content (wt%)	Mixing temperature (°C)	Designation	Transparency of blend during mixing
0	100		SiR	Transparent
5	95	40	P5-40	Opaque
5	95	80	P5-80	Opaque
5	95	120	P5-120	Opaque
5	95	160	P5-160	Transparent
0.5	99.5	180	P0.5-180	Transparent
5	95	180	P5-180	Transparent
10	90	180	P10-180	Transparent
20	80	180	P20-180	Opaque

indication of the good quality of the POSS dispersions in the polysiloxane (15).

Figure 1 depicts the XRD patterns of blends prepared at different mixing temperatures. Three major peaks occurred. The first was very broad diffraction peak appearing at $2\theta = 11.7°$, corresponding to the amorphous structure peak of the polysiloxane. The other two sharp peaks occurred at $2\theta = 7.9°$ and $8.8°$, which corresponded to the POSS crystalline characteristic peaks (9). These peaks indicated that the POSS existed in the matrix as crystallites.

The DSC results are presented in Figure 2 and show that the POSS had a melting peak at 268°C, and that there wasn't any thermal transition up to 300°C for the polysiloxane. It was peculiar that all blends didn't show melting peak of POSS crystals at 268°C, indicative of no POSS crystals existence, which was very contradictory with XRD results.

The optical microscopy results are illustrated by the photographs shown in Figure 3. Part A of the figure shows that the crystallite size of the pure POSS was quite large, about 350 μm. Parts B and C show some large agglomerates of sizes up to 100 μm in the blends prepared at low mixing temperatures. The POSS crystallites became smaller during processing, suggesting that the original POSS aggregates were broken up by the shearing stresses. At a mixing temperature of 120°C, the POSS crystallite size suddenly became as small as approximately 20 μm, and the crystallite shapes seemed quite regular (part D). Also interesting was the fact that at higher mixing temperatures, the shape of the POSS crystallites became hexahedral or flake-like (parts E and G). The microscopy results were consistent with those from the XRD and proved that the POSS existed in crystalline form in all the blends prepared at the temperatures mentioned. Also, it was obvious that the mixing temperature had considerable effects on the shape of the POSS crystallites. It was speculated that POSS crystallites were firstly highly dispersed in polysiloxane matrix as molecules and then recrystallized to form new crystallites when the mixture was cooled. Considering the high melting point of POSS, it should not have been melting that gave this molecular dispersion.

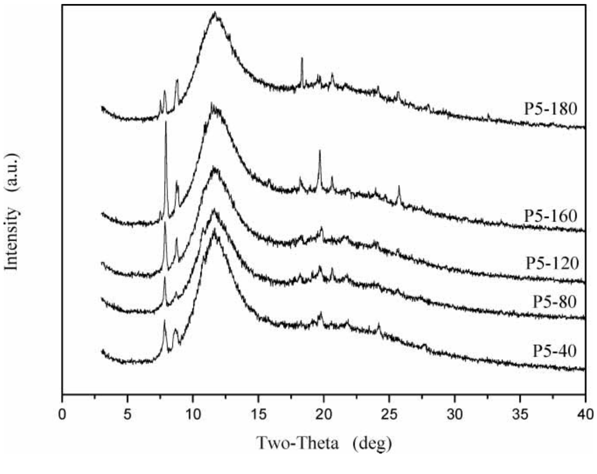


Fig. 1. X-ray diffraction patterns of POSS/polysiloxane blends prepared at various temperatures.

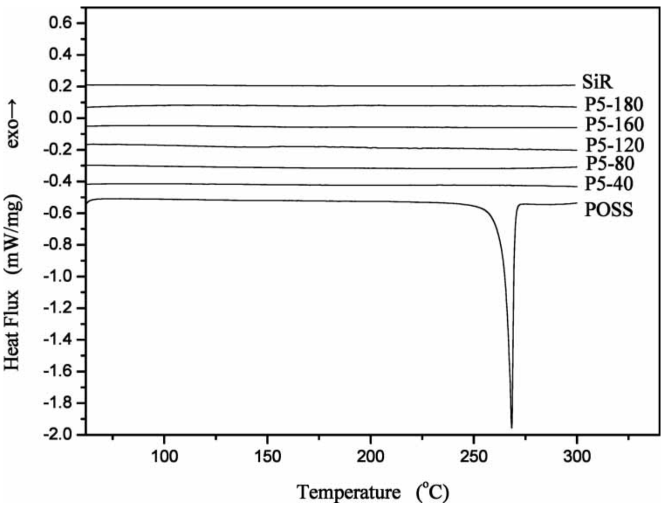
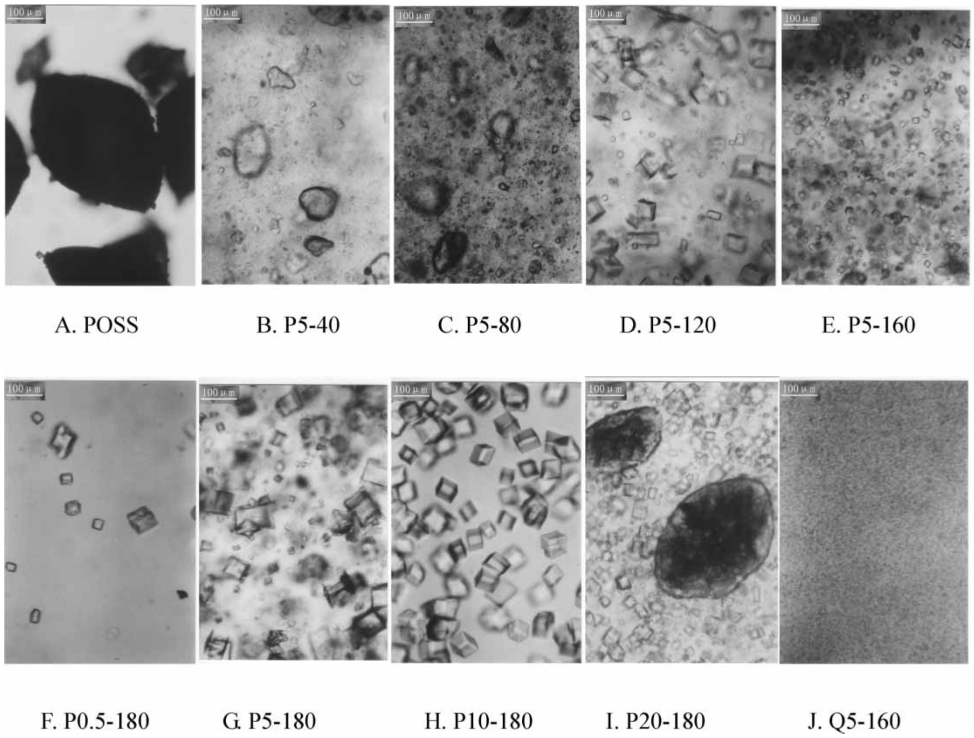


Fig. 2. DSC curves for POSS, the polysiloxane, and the POSS/polysiloxane blends prepared at various mixing temperatures.

In order to test this speculation, a part of the POSS/silicone rubber blend P5-40 (Table 1) was placed between two glass plates. It was heated to 160°C from 40°C (with a heating rate of 10°C/min), kept at this higher temperature for 3 min, and then cooled to 40°C (at 10°C/min). The morphology evolvement of the sample as recoded using the polarizing optical microscope, is shown in Figure 4. (Dark spots in the background were artifacts from the instrument, rather than from the sample). The original crystallites of POSS in sample P5-40 had an irregular shape (as is shown in part A of the figure), and with heating their number gradually decreased. Since the temperature was far below the melting temperature of the POSS crystallites and no shear force was exerted on the blend, this strongly suggested that the POSS crystallites dissolved in the silicone rubber matrix (presumably because of structural similarities between these two components, leading to good compatibility between the POSS and the silicone rubber). The POSS crystallites completely disappeared at 160°C (part B), which implied that the POSS was now totally dissolved in the silicone matrix. Cooling caused the expected decrease in POSS solubility, with POSS precipitating out as hexahedral or flake-like crystallites. Microscopy observations confirmed that the dispersion of POSS crystallites wasn't simply controlled by melting and mechanical breakups but by the described solubility and recrystallization. This explained why no melting peak was observed by DSC for the POSS/polysiloxane blends.

Figure 1 demonstrates that the intensity and breadth of the POSS characteristic peaks changed with mixing temperature, because of changes in POSS solubility. When the blends were prepared at lower mixing temperatures (40 and 80°C), the dispersion of POSS in the polysiloxane matrix was poor, and much of the POSS existed in

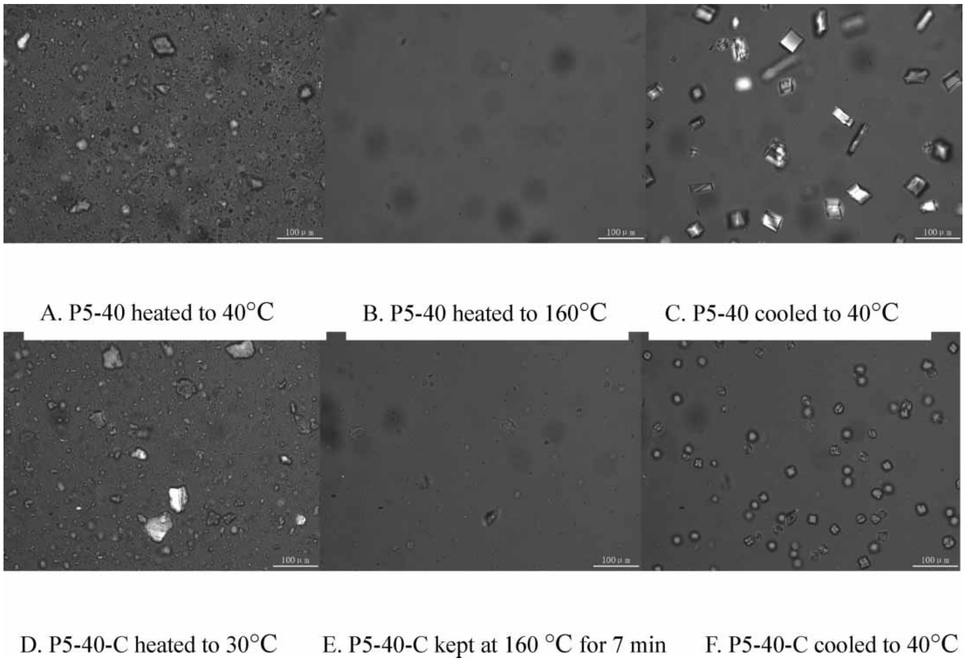


A. POSS B. P5-40 C. P5-80 D. P5-120 E. P5-160

F. P0.5-180 G. P5-180 H. P10-180 I. P20-180 J. Q5-160

Fig. 3. Micrographs showing the morphologies of POSS and POSS/polysiloxane blends prepared under various conditions.

large crystallite aggregates. With increased mixing temperatures (120 and 160°C), the POSS characteristic peaks became more pronounced and sharper. These peaks corresponded to recrystallized POSS from the polysiloxane matrix during cooling, with fewer defects and more regularity existing in the crystallites. Moreover, a new peak at $2\theta = 7.6^\circ$ appeared in the spectra of P5-160 and P5-180 (Table 1), indicating changes in the POSS crystal structure (15). This peak could be attributed to POSS different crystalline forms from the recrystallization. But



A. P5-40 heated to 40°C B. P5-40 heated to 160°C C. P5-40 cooled to 40°C

D. P5-40-C heated to 30°C E. P5-40-C kept at 160 °C for 7 min F. P5-40-C cooled to 40°C

Fig. 4. Polarizing microscopy images of samples P5-40 and P5-40-C (P5-40 containing curing agent) for various heating and cooling processes.

when the mixing temperature was increased to 180°C, the intensities of the POSS characteristic peaks suddenly decreased. At the high blending temperatures, the dispersed POSS molecules could interact with the polysiloxane chains due to increasing thermal energies and motions. This presumably interfered with the recrystallization of POSS from the polysiloxane matrix (leading to the lower crystallinity) (15).

Parts F-I of Figure 3 present the photographs of the blends with different POSS loadings prepared at the same blending temperature, 180°C. Even for the blend P0.5-180 (Table 1), there were also crystallites with hexahedral or flake-like structures, which suggested that the POSS crystallites weren't dissolved in the polysiloxane at room temperature. The number of recrystallized POSS crystallites increased with increasing POSS loadings, but large POSS aggregations up to 300 μm in size with irregular shapes were observed in the P20-180 blend. For this sample, the material still remained opaque during melt blending. This illustrated that the polysiloxane had a solubility limit with isobutyl-POSS, even at high temperatures.

As already mentioned, POSS crystallites could dissolve in the polysiloxane matrix due to the similar chemical compositions of these two components. According to the "like dissolve like" rule, substances with similar solubility parameter δ are likely to be miscible. The literature value of the solubility parameter of the poly(dimethylsiloxane) (PDMS) is 15.5 $(\mathrm{J/cm^3})^{1/2}$ (16). The δ value of isobutyl-POSS could be determined from the group molar attraction constants of the groups, which constitute the macromer and the equation:

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} = \frac{F}{V} = \frac{\sum Fi}{V} = \frac{\rho \sum Fi}{M_0} \tag{1}$$

where ρ, F, and M_0 represent the density, the molar attraction constant, and the mer molecular weight, respectively (17, 18). Group molar attraction constants were obtained from the literature (16). The F values adopted were CH_3:303.4; CH_2:269; CH:176 $(\mathrm{J\cdot cm^3})^{1/2}/\mathrm{mol}$. The F value of SiO was calculated to be 342 $(\mathrm{J\cdot cm^3})^{1/2}/\mathrm{mol}$ using PDMS, with $\rho = 0.98\ \mathrm{g/cm^3}$ (13) and $M_0 = 60\ \mathrm{g/mol}$. The density of POSS was 1.1 $\mathrm{g/cm^3}$, according to information supplied by the Hybrid Plastics Corporation. By using the above information, the solubility parameter of isobutyl-POSS was estimated as $\delta = 15.8\ (\mathrm{J/cm^3})^{1/2}$, which is very close to the value of the PDMS, as expected.

When the blend prepared at high temperature of 160°C was rapidly put into liquid nitrogen for quenching (designated Q5-160), crystallite growth was prevented and a blend with the finer POSS dispersion could be attained. This is shown in part J of Figure 3.

Cross linking is very important in the case of elastomeric polymers in order to obtain the desirable mechanical properties, in particular, recoverability. It was therefore, very important to determine the effects of cross linking on the dissolution, crystallization, and recrystallization of POSS in the polysiloxane. The required curing process was carried out using peroxide thermolysis, as described above and elsewhere (15). Specifically, blend P5-40 containing this curing agent (designated P5-40-C) was heated from 30 to 160°C at a heating rate of 100°C/min, held at this temperature for the optimal cure time (7 min), and then cooled to 40°C at a rate of 10°C/min. The morphology evolvement of sample was observed by microscopy, with the results shown in parts D-F of Figure 4. In the rapidly-increasing temperature process, POSS crystallite aggregates already started dissolving. In the curing process, the dissolution continued but leveled off after 3 min. The solubility was obviously decreased by the network formation, to the extent that the POSS crystallites couldn't be completely dissolved (part E of Figure 4). During cooling, the recrystallized POSS crystallites grew into roughly spherical shapes. In the uncured blends, the POSS crystallites readily grew into nearly perfect hexahedral or flake-like crystallites. In contrast, in the cured blends the crystallite growth was constrained by the polymer network and tended to give spherical particles of relatively small size. These decreases in POSS domain size provide an interesting parallel to the decreases in solvent crystallite size in thermoporosimetry, in which a solvent held in the "pores" of a network structure shows lowered crystallization temperatures (19–21). This is due to the fact that the solvent crystallite size is suppressed by the solvent being constrained by the network strands. It is also an intriguing parallel to the decreases in ceramic particle size in sol-gel technology, in which for example silica particles are grown within an elastomer, and their sizes are again constrained by the polymer strands making up the network structure (22, 23).

4 Conclusions

In POSS/polysiloxane blends prepared by melt blending, the dispersion states of the POSS crystallites in the polysiloxane matrix were controlled by the POSS solubility which, in turn, was strongly affected by the processing conditions. POSS crystallites couldn't dissolve in the polysiloxane at room temperature, but the solubility increased with increasing temperature. POSS crystallites could be entirely dissolved in the polysiloxane at high blending temperatures (around 160°C), but subsequent cooling led to phase separation in which the new POSS crystallites had hexahedral or flake-like structures. Quenching could prevent recrystallization, yielding finer POSS dispersions. There was a solubility limit to isobutyl-POSS in the polysiloxane even at a high temperature of 180°C, which gave loadings of 10 to 20 wt%. The solubility was obviously decreased by cross linking, with the corresponding network structure constraining the POSS crystallites to roughly spherical shapes of relatively small size.

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