

# Structure–Property Evaluation of Trisilanolphenyl POSS<sup>®</sup>/Polysulfone Composites as a Guide to POSS Melt Blending

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Received 9 August 2011; accepted 28 September 2011

DOI 10.1002/app.36229

Published online 31 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A series of polysulfone/phenyl trisilanol POSS nanocomposites were produced by melt blending by twin screw batch mixing. These materials were then injection molded, and their thermal, mechanical, and morphological properties were tested. The tensile properties of polysulfone were moderately compromised by the addition of phenyl TPOSS, because of the formation of large ( $\sim 1 \mu\text{m}$ ) voided POSS aggregates. These domains however did cause the improvement of the impact resistance of the composites as described by the mechanism of crack pinning and bowing. Flexural properties remained essentially unchanged, which is attributed to the formation of an aggregate free-skin layer, which formed in the injection molded parts.

Thermal behavior of the composites also remained largely unchanged due to the lack of POSS-polymer interactions on the molecular/chain segment scale. Initially, it was hypothesized that a high degree of POSS-polymer interactions would be present in these composites based on examination of their chemical structures. This however, was not the case as phase separation was clearly present. This work highlights the need for a better understanding of the prediction of POSS-polymer interaction. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2914–2919, 2012

**Key words:** POSS; polysulfone; nanocomposite; interactions; properties; structure

## INTRODUCTION

Polyhedral oligomeric silsesquioxane (POSS) technology has been studied in recent years as a means to improve the thermal/mechanical properties and rheological/processing of numerous materials including amorphous and semicrystalline thermoplastic polymers and thermosets.<sup>1–3</sup> Many approaches can be taken to incorporate POSS into a given system including melt blending,<sup>4,5</sup> cross-linking<sup>6</sup> copolymerization,<sup>7,8</sup> and grafting.<sup>9</sup> The present study focuses on the “bottom-up” self assembly of POSS into higher order structures (Fig. 1). This bottom-up approach differs from that attempted with other types of nanocomposites such as clay composites that begin with micron sized structures, which are then exfoliated into nanometer scale platelets to some extent. Full exfoliation of top-down nanocom-

posites can be problematic and often produce orders of magnitude increases in viscosity and limiting processability. In the bottom-up approach, 1–3 nm single POSS cages are brought together in larger assemblies dependent on the degree of POSS-POSS and POSS-polymer interaction. In this way the specific chemistry of the pendant organic groups on the POSS cage act as directors of the self assembly while the rigid inorganic core provides reinforcement. By choosing the appropriate grade of POSS coupled with a particular polymer it should be possible to achieve dispersion on the nanometer to micron scale, intermediate between molecular scale solubility and complete phase separation.

Previous work has shown that thermal and mechanical reinforcement can be achieved by blending phenyl trisilanol POSS in phenoxy resin (PKFE).<sup>10</sup> This reinforcement was attributed to the presence of a two mode interaction between the POSS and polymer via  $\pi$ - $\pi$  stacking of the phenyl rings (present in both polymer and POSS) and hydrogen bonding between the hydroxyl groups of the PKFE and silanol groups of the POSS. Phenyl trisilanolphenyl POSS (phenyl TPOSS) was melt blended in the present study with the glassy polymer polysulfone (Fig. 2). Polysulfone is a tough, chemically resistant

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Contract grant sponsor: National Science Foundation, Division of Civil, Materials and Manufacturing Innovation; contract grant number: CMMI-0727231.

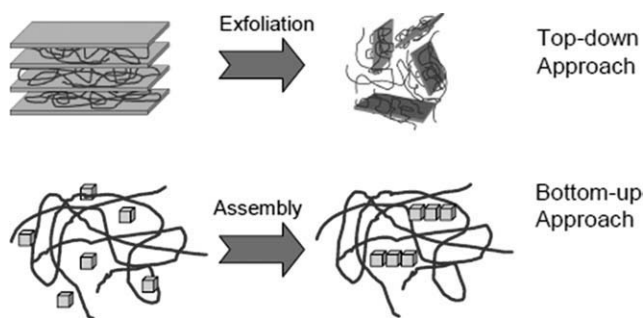


Figure 1 Bottom-up versus top-down approach.

polymer, which finds use in applications including medical devices and purification membranes. It was anticipated that similar types of interactions would be present in a phenyl TPOSS/polysulfone system (both polymers being bisphenol A derivatives differing only by a hydroxyl group in PKFE versus a sulfone group in polysulfone). The effects of POSS on the structure, thermal, and mechanical properties of polysulfone are described herein, along with a hypothesis adding processing conditions to the list of parameters that must be considered when designing a POSS-reinforced nanocomposite material.

## EXPERIMENTAL SECTION

### Materials

Polysulfone was obtained from Solvay Advanced Polymers (Udel P-1700 NT 11) with a reported melt flow index of 6.5 g/10 min at 343°C and 2.16 kg. The polymer was dried under vacuum at 100°C for 24 h before each processing step. Trisilanophenyl POSS<sup>®</sup> was obtained from Hybrid Plastics (Hattiesburg, MS) and used as received.

### Blending and sample preparation

Composites were prepared by melt blending in a twin screw batch mixer (Haake Rheocord Fisons 9000) at a melt temperature of 325°C and a screw speed of 60 rpm. Blends were made with three levels of POSS<sup>®</sup> content, 0% (neat polymer) 5%, and 10% POSS<sup>®</sup> by weight. At each filler content level, three batches of 300 g were prepared. The resulting composites were pressed into plaques of ~ 1 cm thickness while still hot. These plaques were then cut into pieces measuring about 1 cm<sup>3</sup> using a band saw. Once in manageably sized pieces the material was fed into a Haake Rheomex single screw extruder (L/D = 22, 325°C, 12–15 rpm) and fed onto a conveyor to draw it into a strand. This strand was then pelletized such that it could be injection molded.

Injection molding was carried out on a Boy model 22S with a barrel temperature of 330°C, mold tem-

perature of 120°C, and injection pressure of 2500 psi. The mold used produced a tensile bar which conforms to ASTM standard D-683, and a flex bar which can be used for both impact (ASTM D-256) and flexural (ASTM D-790) testing.

### Characterization

Tensile testing was carried out using an Instron model 1011 universal tester with 5 kN load cell at a strain rate of 3.8 mm/min (100%/min). Flexural testing was performed on an Instron model 5565 with a 1 kN load cell and at a strain rate of 5%/min. Izod impact measurements were carried out using a Qualitest QC-639 Universal Impact Tester using notched samples. Dynamic mechanical analysis was carried out using a dual cantilever clamp on a TA Q 800 DMA ramping from -100 to 220°C at 3°C/min with amplitude of 20 μm at 1 Hz frequency. For tensile and Izod testing 20 samples were tested at each composition ( $n = 20$ ).

Thermal gravimetric analysis was done using a Mettler Toledo model SDTA 815 TGA ramping from 50 to 550°C at 10°C/min under nitrogen. Differential scanning calorimetry was performed on a Mettler Toledo model 700e DSC scanning between 25 and 300°C; data presented in this work are from second heating of samples to remove initial heat histories. Microscopy was carried out on freeze fractured samples using a Phillips model XL-30 environmental scanning electron microscope with an accelerating voltage of 15 kV.

## RESULTS AND DISCUSSION

### Thermal properties

Thermogravimetric analysis of the composites shows modest changes in the onset of degradation (6°C for 10 wt % POSS addition; Table I), while DSC analysis shows less than 2°C change in the glass transition temperature measured at all POSS loadings (Fig. 3).

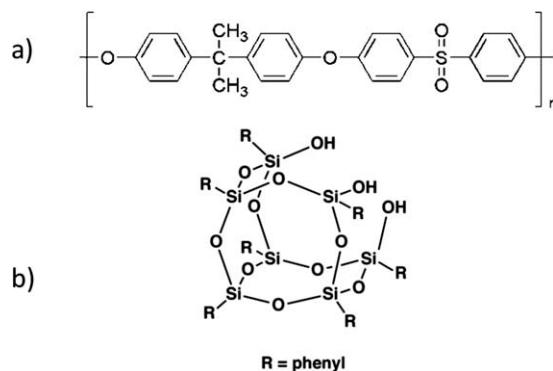


Figure 2 (a) Repeat unit of polysulfone. (b) Phenyl TPOSS (SO1458).

**TABLE I**  
Measured Values for Onset of Thermal Degradation

Composition	Onset degradation 99.5 Mass (°C)
0% POSS	486.0
5% POSS	488.3
10% POSS	492.2

The results from the TGA imply that the POSS has relatively little effect on the degradation behavior of the polymer through any chain scission or molecular scale interaction. The results from DSC similarly suggest that there is little affect on the polymer in terms of free-volume or segmental motion, both of which could be affected by molecularly dispersed POSS.

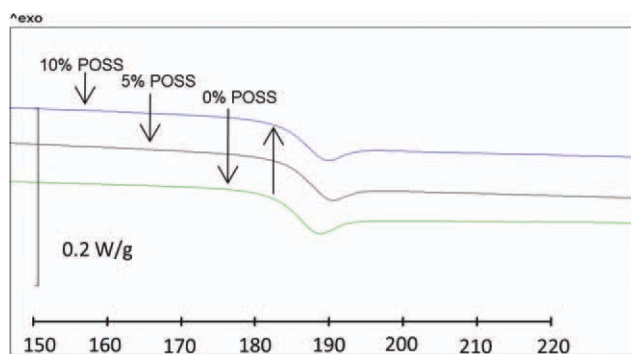
### Thermomechanical properties

Results from dynamic mechanical analysis (DMA) measurements for  $\tan \delta$  again show no more than a 2°C change in the peak value for either of the composites as compared to the pure polymer (Fig. 4). This result is consistent with the DSC in that there was minimal effect (less than 1% change) on the  $T_g$  with increasing phenyl TPOSS content and again may indicate that the POSS filler is not interacting with the polysulfone on the molecular or chain segmental scale.

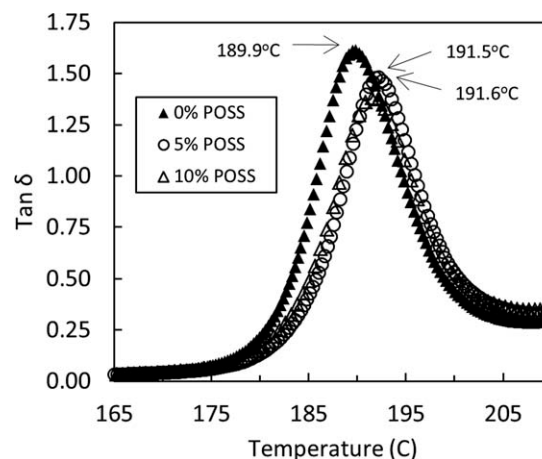
Results from the measurement of storage modulus in DMA shows a decrease in modulus below as well as above  $T_g$  (Fig. 5), which indicates that the incorporation of this grade of POSS has disrupted the solid-state structure of the polymer to some extent; the mechanism of this disruption will be discussed later.

### Mechanical property characterization

The tensile stress–strain behavior of the samples shows a moderate (15%) decrease in tensile modulus



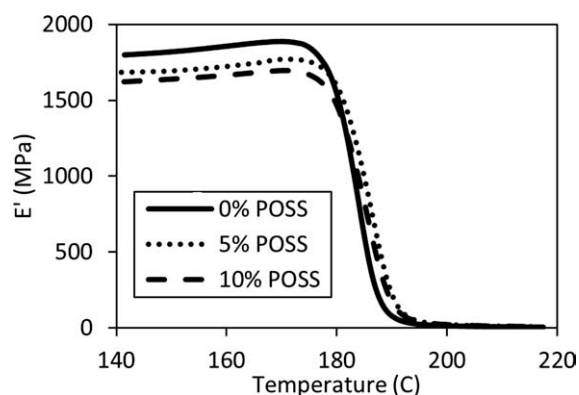
**Figure 3** DSC thermogram from second heating (upward arrow indicating similar onset of  $T_g$ ) [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].



**Figure 4** Measurement of  $\tan \delta$  through  $T_g$ .

and yield stress and a dramatic decrease in the elongation at break ( $\sim 90\%$ ) at the highest POSS loading of 10% by weight (Table II). This decrease in modulus is consistent with the findings from DMA that show that the structure of the composites has been compromised with increasing POSS loading.

While the tensile properties of the polysulfone composites suffered from the addition of POSS, the results from notched Izod impact testing showed a different trend. The addition of phenyl TPOSS at 5% by weight caused an increase in impact strength of 17% over the neat polymer while the addition of 10% POSS resulted in an increase of 25% in impact strength over the pure polysulfone (Fig. 6). This result could be explained if the POSS was present in large fractal aggregates. Aggregates such as this would cause an increase in the amount of energy needed to propagate a crack through the composite and so cause an increase in impact strength as measured by Izod.<sup>11–13</sup> In this model of crack pinning and bowing first established by Lange<sup>14</sup> and Evans<sup>15</sup> when a propagating crack interacts with a second phase dispersion more energy is needed to propagate secondary cracks than needed to propagate



**Figure 5** Measurement of storage modulus in DMA.

**TABLE II**  
Tensile Properties of Phenyl TPOSS-Polysulfone Composites

Composition	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
0% POSS	955 ± 7	87 ± 1	96 ± 45
5% POSS	908 ± 6	82 ± 1	34 ± 19
10% POSS	816 ± 10	74 ± 1	12 ± 2

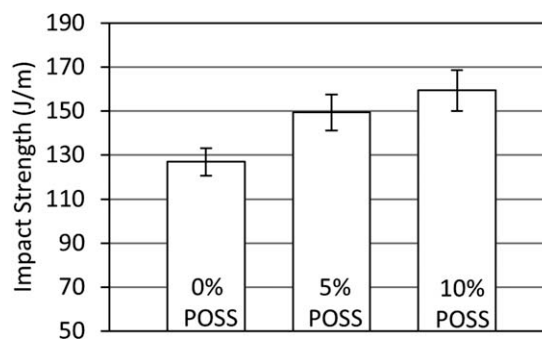
through the neat material. The fracture energy needed to continue the crack with a dispersed second phase is increased as the distance between in homogeneities is decreased. Therefore, as the concentration of POSS in the present system was increased and the distance between the POSS aggregates decreased and the fracture energy and therefore impact strength increased. This result would also agree with the previous findings from thermal and thermomechanical tests, which show no interaction between POSS and the polymers on the molecular scale.

### Microscopy

SEM images from the composites show that indeed the POSS has associated with itself to a high degree, causing the formation of large (~ 1 μm) aggregates (Fig. 7). This morphology explains the loss of tensile properties as the aggregates possess an aspect ratio of one and are highly voided from the matrix. These characteristics however are beneficial in the improvement of impact properties as described by the theory of crack pinning and bowing.

### Three-point bend flexural properties

The results from three point bend tests show a trend that is different from those seen in tensile or impact behaviors. An initial decrease in both flexural-modulus and -strength were observed with the addition of

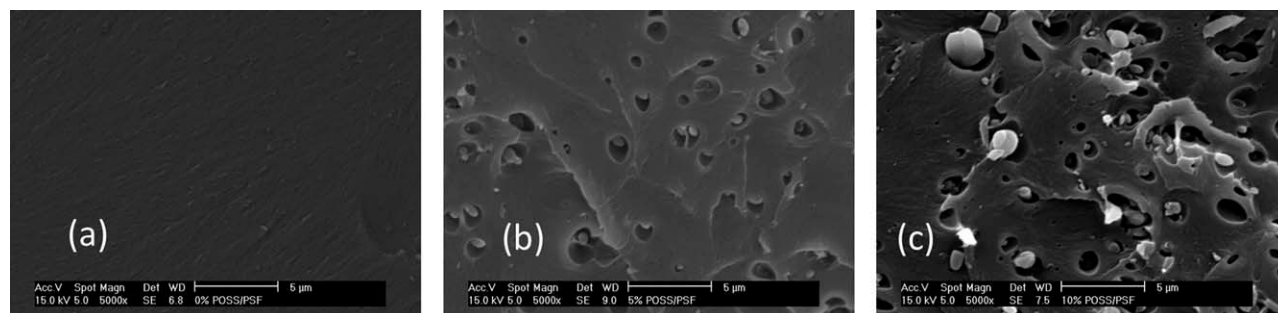


**Figure 6** Measured values for notched Izod impact tests.

5 wt % POSS (Table III). At a POSS loading of 10 wt %; however, the flexural strength of the composite recovered to almost the original value for pure polysulfone and the flexural modulus leveled off to a similar value as the 5% composition.

These flexural data could be explained by the fact that flexural testing concentrates most of the incident forces on the surface (outermost fiber) when experiencing strain.<sup>16</sup> It is possible that the process of injection molding caused the migration of POSS aggregates towards the interior (bulk) portion of the molded parts leaving the outer (skin) layer with a much lower concentration of POSS.<sup>17</sup> This migration could be causing the outermost portion of the flex bar that contributes a more highly weighted component of the flexural properties to maintain its strength while the bulk portions of the parts decreased in strength. For this reason SEM images were taken in the machine direction of the molded parts to see if indeed there was POSS migration (Fig. 8). These SEM images indeed show a migration of POSS aggregates towards the center of the injection molded part, causing the formation of a skin layer. It is the formation of this skin-layer, which explains the relatively smaller changes in flexural properties as compared to the tensile testing results.

It is possible to explain all of the thermal and mechanical properties observed in this system on the basis of the two phase system which is present. The



**Figure 7** SEM images of polysulfone-phenyl TPOSS composites; (a) 0% POSS (neat PSF), (b) 5% POSS, and (c) 10% POSS.

**TABLE III**  
Flexural Properties of POSS/Polysulfone Composites

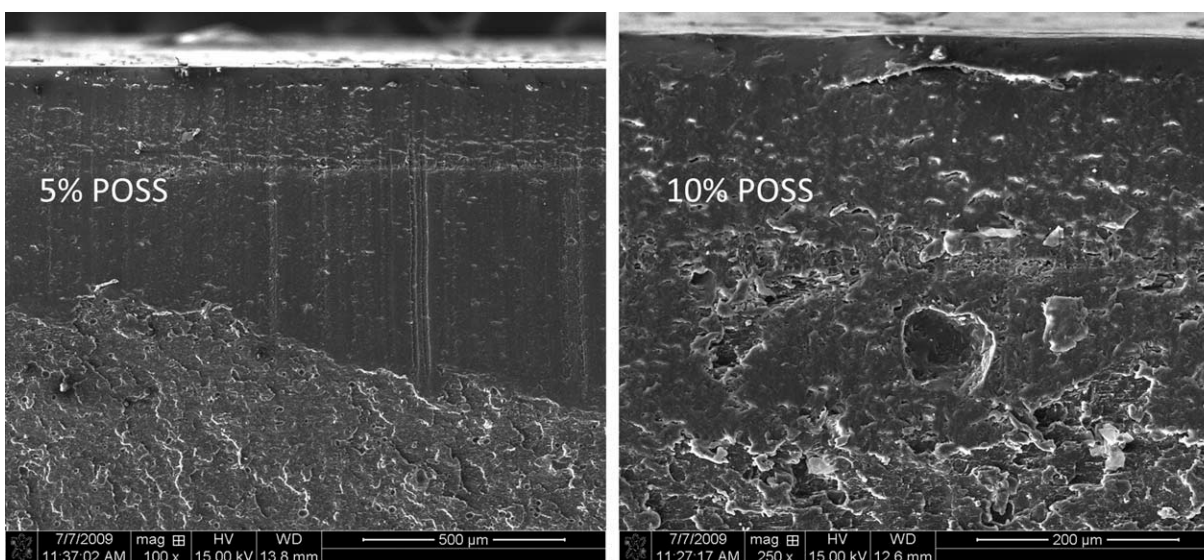
Composition	Flexural modulus (MPa)	Flexural strength (MPa)
0% POSS	3018 ± 21	72.8 ± 0.2
5% POSS	2986 ± 15	72.1 ± 0.3
10% POSS	2992 ± 19	71.6 ± 0.4

question then is of why a two phase system was formed when previous findings had indicated that a large degree of POSS-polymer interaction could be expected. It was anticipated that phenyl TPOSS would interact strongly with the polymer matrix because of polar interactions between the silanol groups of the POSS and sulfone groups on the polymer backbone and  $\pi$ - $\pi$  stacking of the phenyl rings of the POSS and polymer; this however, was not the case. It appears that there was an absence of POSS-polymer interactions but instead the system was dominated by POSS-POSS interaction. One hypothesis is that at the relatively high processing temperature of polysulfone (320–330°C) those interactions were overcome by thermal motion and so the melt existed in two distinct phases (phase separation upon heating). This two phase system was then frozen when injected into the cold mold of the injection molding machine before those interactions could allow for the further dispersion of POSS. Because of the extremely high  $T_g$  of polysulfone (165°C above room temperature) the system had no mobility, which would allow for the inversion of the phase separated behavior.

To test this hypothesis a second DSC experiment was carried out to probe this phase behavior. The

DSC sample was heated to the processing temperature of 325°C and held there for 2 min to ensure fluid behavior. The melt was then cooled at the much lower rate of 1°C/min back to room temperature, upon which a second heating at 10°C/min was recorded. If the hypothesis was correct that phase separation occurred upon heating, then the system should have enough time to equilibrate upon cooling and show some change in the glass transition behavior upon second heating. The results from the DSC experiment however showed no change in the glass transition temperature upon second heating. It was therefore hypothesized that there is no thermal history, which would allow for the miscibility of phenyl TPOSS in polysulfone. This could mean that either the initial hypothesis that this system would exhibit strong POSS-polymer interaction was incorrect or that because of the relatively high  $T_g$  of polysulfone (190°C) with temperatures low enough to allow hydrogen bonding and  $\pi$ - $\pi$  stacking the system simply lacks mobility to allow for the dispersion of POSS.

While not a positive outcome in the sense of reinforcing polysulfone using this grade of POSS this system has brought to attention the importance of phase behavior when designing these melt blended POSS composites. Work from Esker and co-workers<sup>18,19</sup> shows that the phase behavior of these POSS systems can be determined experimentally and used to design systems with desired qualities. Also working towards this theme Morgan et al.<sup>20</sup> have shown that solubility parameters can be calculated for POSS-polymer combinations which have a noted effect on the morphology of the final composite. By using the information gathered in this study and the recent work of others in the field it is



**Figure 8** SEM images showing skin layer containing significantly lower content of POSS aggregates.

possible to develop specific design rules for making reinforced melt-blended POSS composites.

### CONCLUSIONS

The tensile properties of polysulfone were moderately compromised by the addition of phenyl TPOSS because of the formation of large ( $\sim 1 \mu\text{m}$ ) voided POSS aggregates. These domains however, did cause the improvement of the impact resistance of the composites as described by the mechanism of crack pinning and bowing. Flexural properties remained essentially unchanged, which is attributed to the formation of an aggregate free-skin layer, which formed in the injection molded parts. Thermal behavior of the composites also remained largely unchanged because of the lack of POSS-polymer interactions on the molecular/chain segment scale. It is hypothesized that the large POSS aggregate formation was due to phase separated morphology, which was present at the elevated processing temperature and frozen in place through molding. This work highlights the need to be able to better predict POSS-polymer interactions in a more precise manner to avoid these phase separated morphologies that is a detrimental the mechanical properties of these composites.

Many fruitful conversations with Professor Sadhan Jana (University of Akron) are acknowledged.

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