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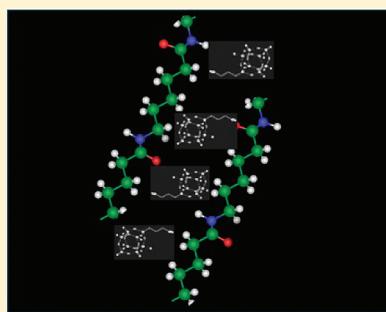
## Structure Property Relationships and the Role of Processing in the Reinforcement of Nylon 6-POSS Blends

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 Supporting Information

**ABSTRACT:** A series of melt-blends were prepared from nylon 6 and a polyhedral oligomeric silsesquioxane (aminopropylisobutyl POSS) in order to develop an understanding of the role of processing in polymer property enhancement. Injection molded samples of the blends show decreases in mechanical properties, while melt-spun composite fibers of the same composition show improvements in modulus and strength, with the maximum increases occurring in the compositions containing 2.5 wt % POSS (and subsequent decreases in properties above that concentration). Dynamic mechanical analysis implies that there are POSS-polymer interactions on the molecular scale, and perhaps there is some level of molecularly dispersed POSS. The maximum property enhancement occurs 2.5%, coinciding with the maximum concentration before POSS phase separation occurs. Raman spectroscopy has been employed to characterize the specific interactions which are taking place between the POSS and polymer. Hypotheses to explain the specific mechanism of reinforcement from fiber spinning are discussed.



### INTRODUCTION

In recent years polyhedral oligomeric silsesquioxanes (POSS) additives have been incorporated into a number of polymers as copolymers, grafts, or as melt blends.<sup>1–6</sup> The advantages gained from using POSS come from its hybrid organic–inorganic nature whose inorganic core potentially provides molecular reinforcement, while its variety of functionalization schemes allows for reaction or compatibilization with the host polymer. Previous work has shown the ability of POSS to enhance polymer properties when incorporated through grafting<sup>7</sup> or copolymerization,<sup>8–11</sup> but there is a lack of understanding of how to obtain successful “enhancement of properties” when using POSS as an drop-in additive. One hypothesis is that a high degree of POSS-polymer interactions are necessary which promote a pseudografted structure yielding results similar to that of a grafted system.<sup>12,13</sup> A problem arises though because very often in melt-blended systems a high degree of POSS aggregation is noted which results in decreased mechanical properties.<sup>14,15</sup> Ideally a high degree of dispersion would be obtained which would indicate a high degree of POSS-polymer interaction. Recent work has shown that the degree of POSS-polymer interactions is the major driving force for reinforcement and can be measured using Hansen solubility parameters.<sup>16</sup> In this work it was noted that nylon 6 and aminopropylisobutyl POSS are predicted to be strongly interacting which was evidenced by others working in the field.<sup>17,18</sup> In that work reinforcement was gained at low concentrations of POSS but does not take into account the role of polymer processing.

The role of POSS in blends and composites is very complex as it can affect the rheological properties of the melt as well as the final solid state structure. In some cases POSS can act as a

rheological modifier.<sup>19</sup> Other recent work by Jana et al. shows that by using a ternary system containing isotactic polypropylene (PP), a dibenzylidene sorbitol (DBS) nucleating agent, and trisilanol phenyl POSS, property enhancements can be gained in melt-spun fiber systems.<sup>20,21</sup> In their works, it was determined that the DBS and POSS formed a stoichiometric complex which influenced the crystallization of PP during melt-spinning. It was also determined, as well as by others in the literature, that the incorporation of POSS leads to a large decrease in melt-viscosity. Most POSS grades are crystalline in nature and have melting points in the range common to the processing temperature of many polymers. The presence of liquid phase POSS is then the likely reason for this decrease in viscosity and results in more facile processing of blends. This enablement of processing is in stark contrast to more traditional polymer-inorganic composites in which orders of magnitude increases in viscosity can be noted with the incorporation of even small amounts of inorganic fillers.<sup>22,23</sup> If property enhancement can be gained while also decreasing melt-viscosity (more facile processing) this would be a great gain in the field of blends/composites.

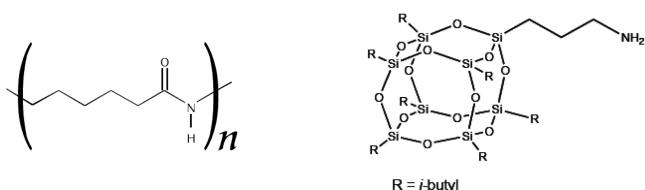
The present study looks to understand the role of polymer-POSS interactions and role of processing in the enhancement of nylon 6 properties. Nylon 6 is a semicrystalline thermoplastic polymer whose interesting properties come from its morphology and hydrogen bonded structures. It thus offers opportunity for a great number of applications. In the hopes of accessing the hydrogen bonding ability of nylon, aminopropylisobutyl POSS

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(AM0265) was chosen as the additive of interest; the presence of a primary amine in the aminopropyl group could reasonably be expected to lead to a high degree of POSS-polymer interactions.<sup>16</sup> As noted previously though strong POSS-polymer interactions are not always sufficient to provide reinforcement and the role of processing must be evaluated. Initial work with this nylon 6-aminopropylisobutyl POSS pair (Figure 1) showed a phase separated morphology (as will be



**Figure 1.** Chemical structures of nylon 6 and aminopropylisobutyl POSS.

discussed later) which was not expected and led to a decrease in properties when the blends were injection molded. Unexpectedly, when the same blends were melt-spun into fibers though, significant increases in mechanical properties were noted. For these reasons, a detailed study of the structure–property relationships and the role of processing was carried out and is presented herein.

## EXPERIMENTAL SECTION

**Materials.** Polyamide 6 resin (Grilon FG-40NL) was obtained from EMS-Grivory and dried under vacuum at 60 °C for 24 h prior to processing. All materials were dried in a similar fashion before each subsequent processing step and before characterization of samples. Aminopropylisobutyl POSS (AM0265) was acquired from Hybrid Plastics Inc. and used as received.

**Blend Preparation.** Initially a 10 wt % master batch of AM0265 and nylon 6 was prepared by twin-screw melt blending in a Haake Fisons Rheodrive 9000 extruder (~500 g capacity) with a screw speed of 22 rpm and a temperature profile of: (Feed) 180 - 220 - 240 - 250 - 240 (Die). The master batch was then diluted with varying amounts of neat polyamide to produce final composite concentrations ranging from 1 to 10% by weight; the blends were then run through the extruder a second time to ensure complete mixing.

Injection molding was carried out on a Boy model 22S with a barrel temperature of 250 °C, mold temperature of 100 °C, and injection pressure of 17.2 MPa (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.

Nylon 6/POSS blend fibers were produced using a Melvern Instruments ROSAND RH7 advanced capillary rheometer fitted with a rotating drum collecting the fiber. The draw down ratio (DDR) of the process was controlled by varying the plunger speed, die diameter, and take-up velocity (drum RPM). In this study, the DDR was held constant at 950 using a die diameter of 2 mm, a plunger speed of 0.5 mm/min, and a drum speed of 100 rpm.

**Characterization.** Injection molded samples were tested on a MTS Insight load frame in tension mode using a 5kN load cell and a strain rate of 100%/min. For each blend composition ten samples were tested. For the fiber samples tensile testing was carried out on an Instron Model 1130 (refit by Instru-Met Corp.) using a 44.5 N load cell and a strain rate of 100%/minute. For each composition ten individual fibers ( $n = 10$ ) were tested.

Scanning electron microscopy (SEM) imaging was carried out on an Environmental Dual-Beam System FEI Quanta 200 3D with an accelerating voltage of 5.0 kV. Prior to imaging, injection molded samples were freeze fractured in liquid nitrogen. To prepare fiber samples for imaging, bundles of 10–15 fibers were embedded in epoxy

and microtomed (room temperature) to produce a sample surface revealing a cross-section of multiple fibers. All samples were sputter coated with a 5 nm film of palladium prior to imaging.

2D wide-angle X-ray scattering (2D WAXS) measurements were carried out for the fiber samples using Micromax 002+ X-ray generator (Rigaku, Woodlands, TX) operated at 45 kV and 0.88 mA producing a highly focused parallel beam of monochromatic CuK $\alpha$  radiation ( $\lambda = 0.154$  nm). 2D WAXS patterns were collected on a magnetic imaging plate by aligning the incident X-ray beam perpendicular to the fiber direction. Imaging plates were processed using a Fujifilm PLA700 image reader after 4 h of exposure. The collimated X-ray beam size used was 0.3 mm, the sample-to-detector distance was 150 mm, and the diffraction angle was calibrated using a CaF<sub>2</sub> standard.

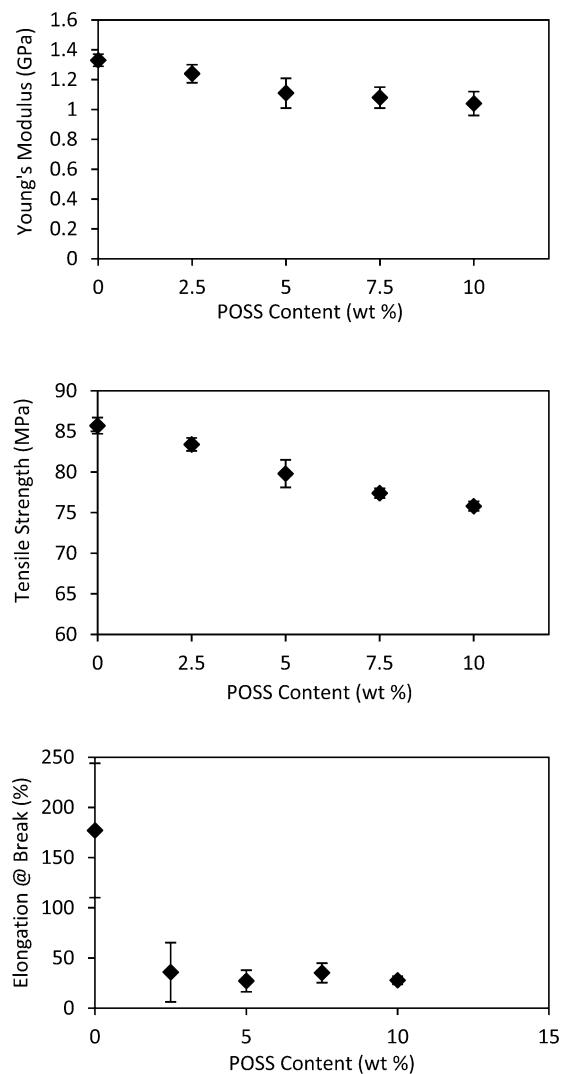
Differential scanning calorimetry (DSC) was performed using a TA Instruments Q100 DSC scanning from 0 to 290 °C at a temperature ramp rate of 10 °C/min; first and second heating curves were obtained. Percent crystallinity was determined through integration of melting endotherms on first heating using the heat of fusion,  $\Delta H_f$ , of 188 J/g for nylon 6.<sup>24</sup> Dynamic mechanical analysis was carried out using a film tension clamp on a TA Q800 DMA ramping from 0 to 150 °C at a rate of 5 °C/minute with an amplitude of 100  $\mu\text{m}$  at 1 Hz frequency, preload force of 0.001N, and force track of 100%, after determining that these conditions are within the linear viscoelastic limit through strain sweep.

MicroRaman scattering studies were performed at room temperature with a Horiba Jobin Yvon LabRam HR800 spectrometer equipped with a charge coupled detector and two grating systems (600 and 1800 lines/mm). A He–Ne laser ( $\lambda = 632.8$  nm) was focused on the sample with an Olympus microscope at an optical power of 17 mW and a spot size of 1  $\mu\text{m}^2$ . Raman shifts were calibrated with a silicon wafer using the 520  $\text{cm}^{-1}$  line.

## RESULTS AND DISCUSSION

**Injection Molded Samples.** Results for tensile testing of the injection molded blends show a stepwise decrease in modulus and tensile strength while results for elongation at break show a sharp decrease with the addition of POSS (Figure 2). DSC thermograms of these blends show minimal changes in percent crystallinity and little to no change in the melting behavior of the nylon ( $T_g$  was not apparent in the DSC; Table 1). These initial results suggest that there is in fact not a high degree of POSS-polymer interactions and that the POSS is actually phase separated into micrometer sized aggregates. SEM images for these blends confirm this hypothesis and show that the POSS is not dispersed in the matrix but rather aggregated into large domains (Figure 3). It is the presence of these aggregates which cause the decrease in mechanical properties and have little to no effect on the thermal properties. While not a positive result in terms of reinforcement, the injection molded blends will serve as a baseline comparison to the melt-spun fiber blends. The only difference between the injection molded and melt-spun fiber blends is the manner in which they were processed. While injection molding can induce some orientation it does so to a very small degree as compared to the conditions in which the fibers were processed (draw-down ratio of ~1000). This work will highlight how reinforcement by POSS is not only affected by POSS-polymer interactions and polymer–filler concentrations but also the manner in which they are processed.

**Melt-Spun Fibers.** Results for tensile testing of the melt-spun fiber blends show a significantly different trend from that of the injection molded samples (Figure 4). For the fiber blends there is an increase in tensile modulus and strength of ca. 50% up to the 2.5% POSS composition and then a decrease with further addition of POSS. The stepwise decrease (similar to that of the injection molded samples) is present except in the



**Figure 2.** Results for tensile testing of injection molded blends.

**Table 1.** Percent Crystallinity As a Function of POSS Content in Nylon (by DSC)

POSS content (weight %)	% crystallinity
0	29.8%
2.5%	31.1%
5.0%	30.7%
7.5%	29.1%
10%	30.2%

1–3% range where significant improvements are seen. The first hypothesis was that due to the rheological conditions during elongational flow (high draw down melt-spinning) a different POSS morphology or structure could be present which was causing the reinforcement. In order for reinforcement to occur, one or more of the following must happen. First, the morphology of the POSS could be altered during fiber spinning resulting in high modulus, high aspect ratio POSS domains. Next the presence of a low concentration of POSS could alter the intrinsic properties of the nylon during fiber spinning (change in crystal form or crystal orientation). An alternative scenario could be that through fiber spinning, a higher degree of POSS-polymer interaction is achieved, resulting in some mode of reinforcement. The remaining results will be examined

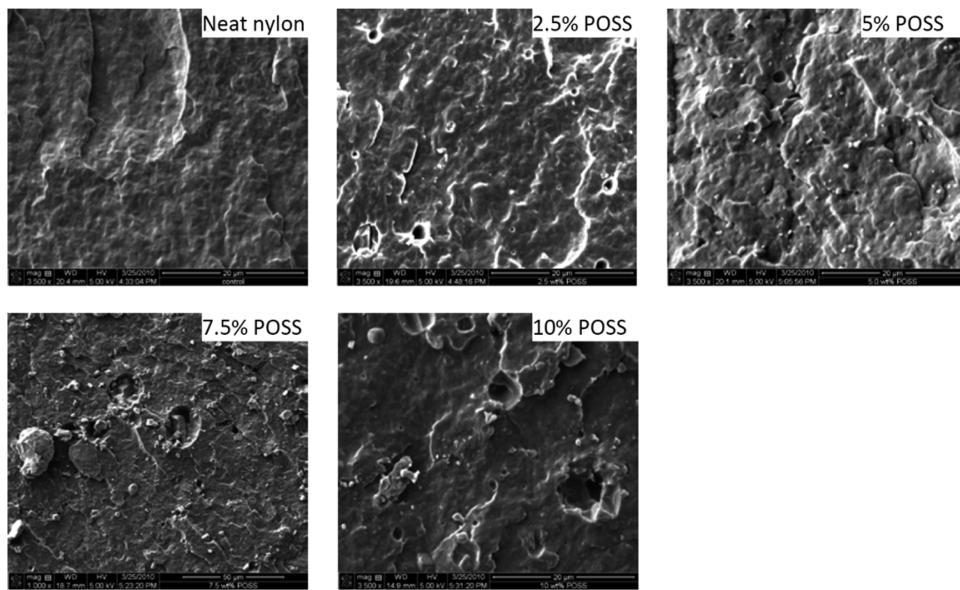
in terms of these possible hypotheses to determine the cause of reinforcement for melt-spun fiber blends containing low concentrations of POSS.

SEM images of the fiber cross sections were taken and indeed show a different POSS domain geometry for samples exhibiting enhanced mechanical properties (SI 1). For the blends with less than 5% loading, the POSS is present in elongated domains, while in the blends with greater than 5% loading the POSS domains are spherical in shape. This result appears to support the hypothesis that the “reinforcement” was due to a change in aspect ratio of the POSS domains. At the same time though, it was known that the intrinsic mechanical properties of POSS domains are very low. If the POSS domains possessed high modulus properties even the injection molded blends should show some improvement in mechanical properties. In order for this to be a simple physical reinforcement (along the lines of a traditional composite) the POSS domains would need to exhibit a dramatic increase in mechanical properties in the fiber blends. The composite fibers were then analyzed by DSC to determine if any change in POSS morphology had occurred in the fiber samples and perhaps the POSS domains in the injection molded samples were simply amorphous aggregates while in the fiber samples perhaps they exist in highly crystalline domains. This DSC analysis should also yield information about the crystalline nature of nylon 6. If there is any change in crystal structure ( $\alpha$  to  $\gamma$ ) the shape and splitting of the nylon melting peak should be altered.

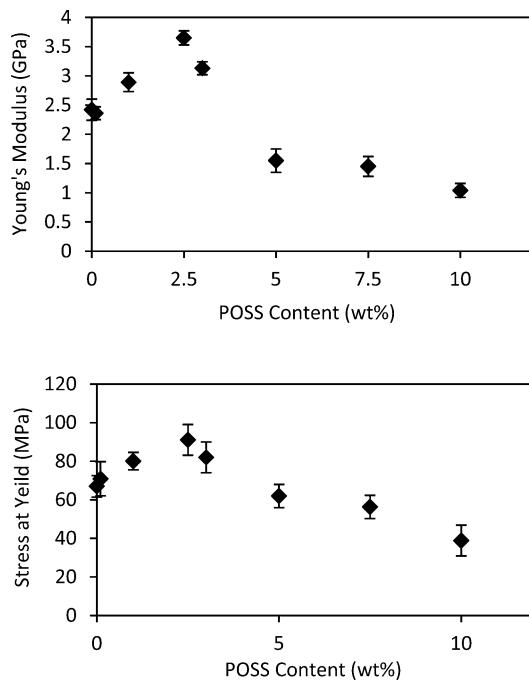
The crystalline nature of POSS in itself is an interesting topic. Figure 5 shows the second heating curve from DSC which indicates that this grade of POSS contains two distinct endothermic transitions upon heating, one at 50 °C and the other at 270 °C. These transitions are also present as crystallization peaks during cooling and do not diminish after multiple heating and cooling cycles. While the exact nature of these transitions is not known, it is known that the POSS remains a solid after the low temperature transition and does not become a liquid until it has passed through the higher temperature transition. It is this liquid state which the POSS is in during processing (resulting in dramatic decreases in viscosity). Whatever the nature of these thermal transitions, if the POSS in the blends exists in a crystalline morphology these peaks should be present in the DSC traces for the blends (DSC of the injection molded samples show no additional peaks).

Thermal analysis of the POSS blend fibers show that indeed there is no change in the melting behavior of the nylon as well as no occurrence of any peaks which would be due to the presence of crystalline POSS (no additional peaks at 50 or 270 °C) (Figure 6). Additionally, integration of the nylon melting peaks shows relatively little difference as a function of POSS loadings (Table 2). From these results it would appear that there is no change in POSS morphology as a function of concentration in the blends. These DSC results show there is a lack of any significant amount of crystalline POSS which is the same result seen in the injection molded samples. Moreover these results indicate that there is no change in the nylon morphology. Together these results would indicate that the POSS is present in amorphous aggregates and that the nylon crystal morphology is remaining constant, leaving molecular interactions as the implied cause for reinforcement, though this will be described in greater detail later.

To further probe the effect of POSS and nylon on the reinforcement of these blends, 2D-wide-angle X-ray diffraction

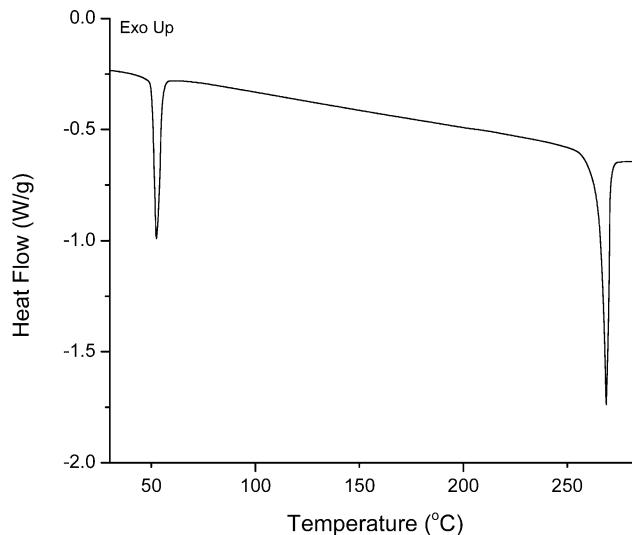


**Figure 3.** SEM images of injection molded POSS blends.



**Figure 4.** Tensile testing results for melt-spun nylon-POSS blends.

was employed. X-ray diffraction studies should yield information about the crystal structure of the POSS as well as for the nylon. Results from WAXD are plotted from an integration of the 2-D images and plotted in SI 2 (original 2D images are shown in SI 3). From this data it is clear that the diffraction patterns for as received and amorphous POSS are significantly different, though they both share a strong peak at  $6.28\text{q}$ , corresponding to a  $d$ -spacing of 1 nm (approximate diameter of a POSS molecule). The fact that even the amorphous POSS shows several reflections can be explained by the symmetry of the molecule. Previous X-ray studies of POSS have shown that depending on the symmetry of the POSS molecules they can cause molecular scattering even in the absence of any long-range crystal ordering.<sup>25,26</sup> Depending on the molecular environment of a POSS molecule distortions



**Figure 5.** DSC thermogram for pure aminopropylisobutyl POSS.

of the cubic shape can take place which will affect the nature of its scattering behavior. This behavior then could explain why several peaks are present in the POSS blends which are not apparent in either the crystalline or amorphous POSS. The X-ray data also confirm that there is no change in the morphology or orientation of the nylon crystals. The results from X-ray diffraction now also support the hypothesis that the POSS is not simply acting as a high modulus, high aspect ratio filler, but rather that some type of molecular interaction must be taking place.

To validate the interaction hypothesis, calculations were carried out using the Halpin-Tsai composite model. The Halpin-Tsai model works best when the composite consists of well dispersed filler particles with uniform geometry and was chosen here because of its use of a geometric factor (aspect ratio).<sup>27</sup> The Halpin-Tsai equation is as follows

$$\frac{M}{M_m} = \frac{1 + \xi \eta c_f}{1 - \eta c_f}$$

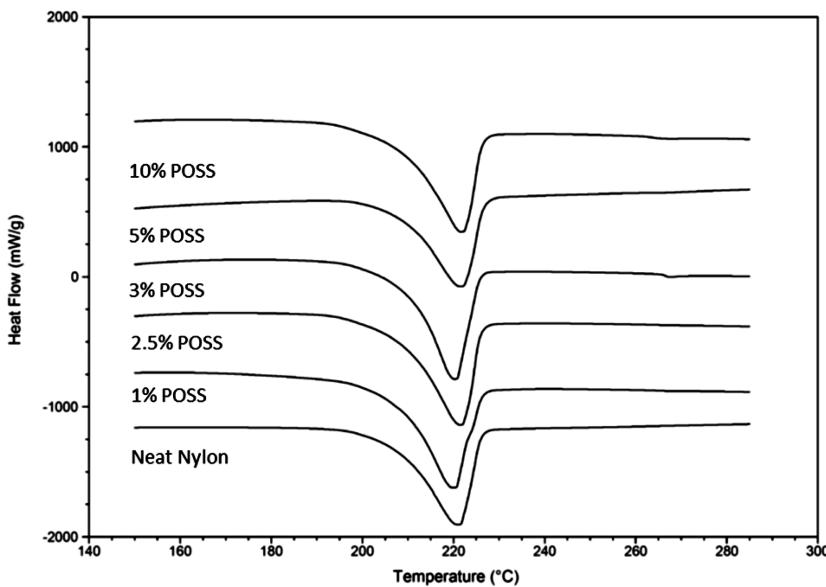


Figure 6. DSC data for series of POSS blend fibers.

**Table 2. Percent Crystallinity Calculated from DSC Melting Peak of Nylon-POSS Blends**

POSS content (weight %)	% crystallinity
0	54.7
1.0%	56.7
2.5%	58.3
3.0%	56.7
5.0%	55.3
10%	56.3

Where

$$\eta = \frac{\frac{M_f}{M_m} - 1}{\frac{M_f}{M_m} + \xi}$$

In this equation  $M$  is the composite modulus,  $M_m$  is the modulus of the matrix,  $M_f$  is the modulus of the filler,  $c_f$  is the volume fraction of filler, and  $\xi$  is a geometric factor which is most often represented by the aspect ratio of the filler; calculations for composite modulus can be carried out and compared to the measured values, as well as calculations for the filler modulus. For a comparison to the injection molded samples the values for matrix modulus ( $M_m$ ) filler volume fraction of filler ( $c_f$ ) (though the exact density of POSS is unknown it is very close to and assumed to be  $1 \text{ g/cm}^3$  and so weight fraction is equivalent to volume fraction) and aspect ratio ( $\xi$ ) are known. Using these values and assuming a POSS filler modulus of zero (0.001 in the model to avoid 0 division) the calculation of composite modulus can be carried out and compared to the measured values. These values are listed in Table 3 and shown graphically in Figure 7. The comparison between the model and measured values shows very good agreement, and so the assumption that the modulus of the POSS in those blends is essentially zero is confirmed. This results support the correctness of the choice of word, blend rather than composite, for the nylon/POSS systems. In the case of the melt-spun fibers similar calculations can be carried out. For the 2.5% POSS blend fiber (maximum measured improvement in modulus), using a matrix modulus of 2.4

**Table 3. Halpin-Tsai Model Results for Injection Molded Blends**

	2.5% POSS	5% POSS	7.5% POSS	10% POSS
matrix modulus ( $M_m$ ) (GPa)	1.33	1.33	1.33	1.33
filler modulus ( $M_f$ ) (GPa)	0.001	0.001	0.001	0.001
filler volume fraction ( $c_f$ )	0.025	0.05	0.075	0.1
filler aspect ratio ( $\xi$ )	1	1	1	1
calcd composite modulus ( $M$ ) (GPa)	<b>1.27</b>	<b>1.20</b>	<b>1.14</b>	<b>1.09</b>
measd composite modulus (GPa)	<b>1.24</b>	<b>1.11</b>	<b>1.08</b>	<b>1.04</b>

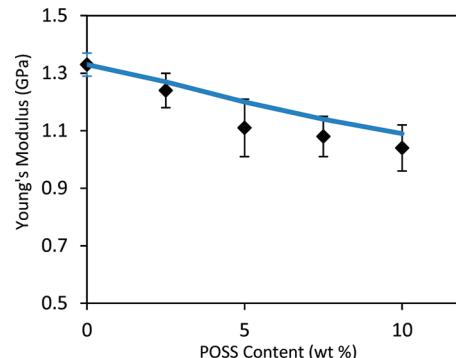


Figure 7. Halpin-Tsai model (line) compared to measured values (points) for injection molded POSS blends.

GPa (measured value for neat nylon), a volume fraction of 0.025 and an aspect ratio of 25 (estimated from SEM images) the calculations show that in order for measured level of reinforcement the modulus of the filler would need to be  $\sim 200$  GPa. In order for the POSS domains to exhibit that level of modulus improvement (0–200 GPa) there would need to be a drastic change in morphology which is simply not apparent in any of the techniques presented here.

From the use of this model it can be seen that in order for the POSS domains to be reinforcing the blend fibers in a traditional mechanical sense the POSS would need to exhibit a

morphological change which would allow for a several orders of magnitude increase in modulus. Results from X-ray and DSC analyses show that no such transformation is present, and so this theory is definitively refuted. Also apparent from the DSC and X-ray analyses is that there is no transformation in the total crystallinity or crystalline morphology of the nylon matrix. This then leaves molecular interaction and reinforcement as the probable cause for the mechanical property reinforcement seen in the composite fibers.

Dynamic mechanical analysis results for storage modulus ( $E'$ ) of the blend fibers show trends similar to those found from tensile testing, which exhibit increased modulus for the blends containing 2.5% POSS and lower concentrations at room temperature (Figure 8a). Above  $T_g$  in the rubbery plateau

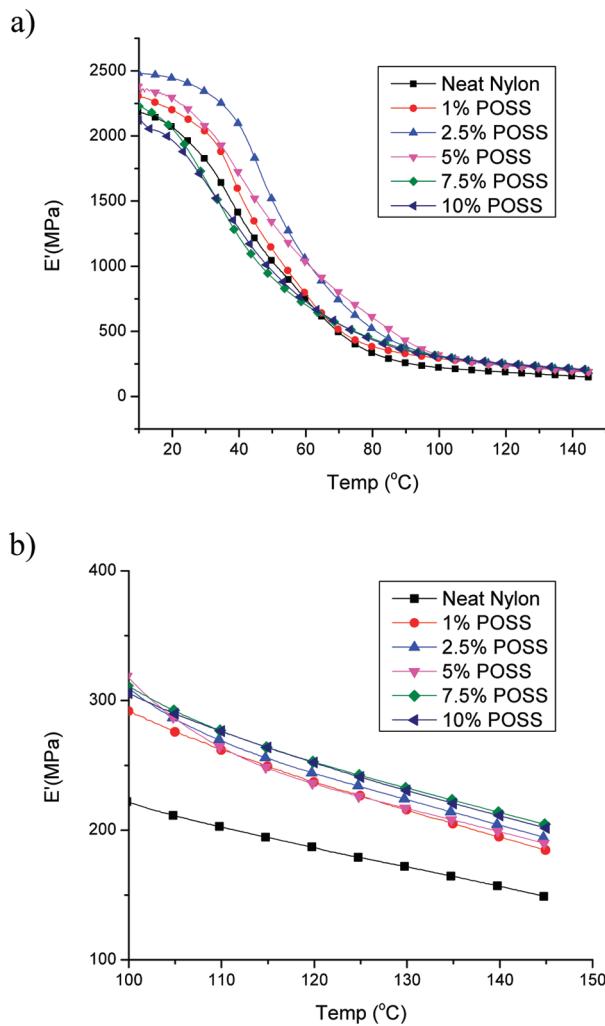


Figure 8. DMA storage modulus (a) full trace and (b) rubbery plateau.

region though (Figure 8b) it can be noted that there is a significant increase in modulus for all of the blend samples. It is observed that after the initial increase at 1% POSS no additional increase is found with increasing POSS concentration. Results for tan  $\delta$  measurements of these fibers show similar results (Figure 9a). With the addition of 1% POSS there is an initial dampening of the tan  $\delta$  value. At 2.5% POSS the dampening is even more pronounced, but with additional POSS loading no additional change is noted. First of all, this increase in rubbery plateau (Figure 9b) is evidence of strong

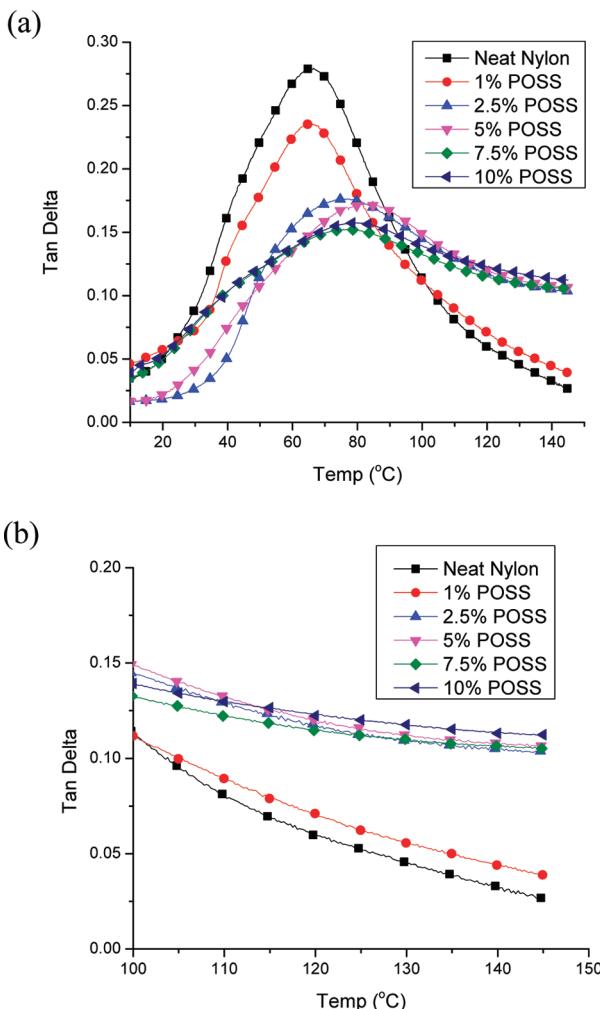
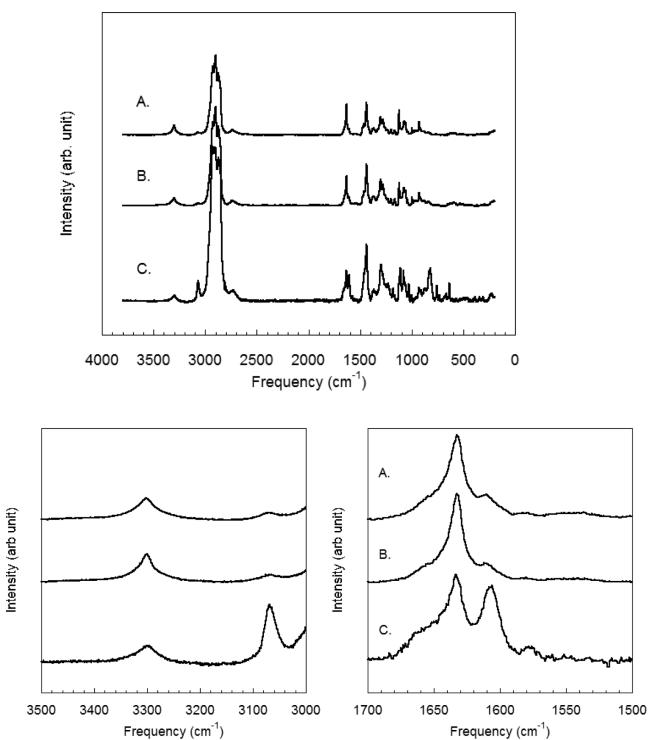


Figure 9. DMA tan delta (a) full trace and b) rubbery plateau.

POSS-polymer interaction which results in a decrease in segmental mobility which in itself can produce reinforcement. Also apparent is a large initial increase in  $T_g$  from 65 °C in the unfilled system, up to 80 °C for the fibers containing 2.5% POSS of more. This result would suggest that the POSS is acting as a physical cross-link in the amorphous domains of the nylon. The dampening of tan  $\delta$  value is also evidence for these strong interactions on the chain segment size scale. The additional information that can be gathered from these data though is that after the initial increase in modulus (and dampening of tan  $\delta$  value) up to 2.5% POSS there is no additional gain from adding additional POSS, suggesting that there is a solubility limit for dispersed POSS. In the samples containing less than 2.5% POSS the maximum benefit from this dispersed POSS is realized, and any additional loading after that point only adds phase separated POSS domains which are detrimental to mechanical properties. The cause for the elongation of POSS domains could then be due to an increased melt strength in the blends containing a lower concentration of POSS.

Additional experiments were carried out to determine what type of molecular interactions were taking place. As already stated previously it was assumed that there should be a significant amount of hydrogen bonding in this system. To probe these interactions Raman spectroscopy was carried out, which indeed show that there are significant differences

between the injection molded and fiber spun samples (Figure 10). The Raman spectra show no difference between the



**Figure 10.** Raman spectra of (a) neat nylon pellet, (b) 2.5% POSS injection molded, and (c) 2.5% POSS fiber.

unprocessed (a) nylon and the 2.5 wt % injection molded sample (b). The 2.5% fiber sample (c) however shows a higher intensity N–H stretch at  $3070\text{ cm}^{-1}$  with Fermi resonance (interaction with overtone from lower fundamental frequencies), while the amide I stretch is shifted to a much lower frequency at  $1607\text{ cm}^{-1}$ . This shift seen in only the fiber samples is sufficient evidence for hydrogen bonding interactions and confirms the hypothesis that it is indeed molecular interactions which are responsible for the reinforcement of the fiber samples.

This hydrogen bonding could be from either the primary amine group on the single corner of the POSS cage or from the siloxane core itself. In order for there to be this type of physical cross-link a multipart hydrogen bonding scheme may be necessary. It is possible that the siloxane core is the main contributor to hydrogen bonding, while the propyl amine assists with solubility. Another possible explanation is that the POSS is acting to retard the relaxation of the amorphous nylon during cooling. The strong POSS-polymer interactions may be causing there to be a more oriented amorphous morphology leading to reinforcement which would only take place in the highly oriented fiber system and not in the injection molded samples. In either case a more detailed study in this area is planned. Also planned for future work is a complete study on the rheology of the system. While it is apparent that the difference in processing of the blends is the cause for the different results for injection moldings vs fibers, the specific mechanism of fiber property enhancements is not fully understood. It is possible that it is simply the high degree of shear during elongational flow which allows for the solubility of POSS. It could also be due to the POSS acting as an anchor to

the amorphous regions resulting in a more oriented amorphous component. This work highlights how the macroscale morphology of a blend of this type might not truly indicate the structure property relationships yielding reinforcement. Initially it was believed that the micrometer sized elongated POSS domains were the *reason* for the macro scale improvements in properties, but it is now hypothesized that these elongated domains are in fact a *result of* molecular scale interactions.

## CONCLUSIONS

A series of melt-blended aminopropylisobutyl POSS-nylon blends were prepared containing between 1 and 10% POSS by weight. Once prepared, two different processing techniques were used, injection molding and fiber melt-spinning. The injection molded blends exhibited decreases in mechanical properties, while thermal properties were left unchanged. These results were attributed to the POSS phase separating and aggregating into micrometer-sized aggregates. In the case of melt-spun fibers though, a dramatic increase in mechanical properties was noted for blends containing up to 2.5% POSS. In the fibers which did show polymer property enhancements, the POSS domains had been elongated into high aspect ratio domains; at higher POSS concentrations the domains had collapsed into spherical morphologies. This result initially led to the hypothesis that the perhaps melt-spinning had induced the crystallization of POSS into a high modulus filler and that the fibers were being reinforced as in a traditional composite sense. DSC and X-ray diffraction studies, as well as Halpin-Tsai calculations however, did not support this hypothesis. Also from DSC and WAXD it was apparent that there was no change in the nylon crystal morphology.

Dynamic mechanical analysis revealed that above the glass transition temperature the rubbery modulus for the blends was significantly higher than that of the neat nylon. This would indicate there must be some level of molecularly dispersed POSS which is acting as a physical cross-link between polymer chains. This is also evidenced by a dampening of  $\tan \delta$  value at  $T_g$  and subsequent increase in  $\tan \delta$  value after  $T_g$  for the blend fibers containing POSS. Also noted from these values is that after the initial increase at 1% POSS and additional increase at 2.5% there is no additional increase with increasing POSS content. This would seem to indicate that there is a solubility limit of this type of POSS in nylon, above which the POSS phase separates. In this system the maximum benefit from dispersed POSS occurs at 2.5%.

Preliminary experiments using Raman spectroscopy indicated the interactions which are causing the physical cross-linking and subsequent property improvements. Shifts in the peaks from the nylon amide group would seem to suggest that hydrogen bonding is the main mode of interaction leading to a molecular based reinforcement mechanism.

## ASSOCIATED CONTENT

### S Supporting Information

SI 1–SI 3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

- (1) Kim, J. K.; Yoon, K. H.; Bang, D. S.; Park, Y.; Kim, H.; Bang, Y. *J. Appl. Polym. Sci.* **2007**, *107*, 272.
- (2) Li, B.; Zhang, Y.; Wang, S.; Ji, J. *Eur. Polym. J.* **2009**, *45*, 2202.
- (3) Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* **2010**, *110*, 2081.
- (4) Gnanasekaran, D.; Madhavan, K.; Reddy, B. S. *J. Sci. Ind. Res.* **2009**, *68*, 437.
- (5) Constable, G. S.; Lesser, A. J.; Coughlin, E. B. *Macromolecules* **2004**, *37*, 1276.
- (6) Seurer, B.; Coughlin, E. B. *Macromol. Chem. Phys.* **2008**, *209*, 1198.
- (7) Zheng, L.; Farris, R. J.; Coughlin, E. B. *Macromolecules* **2001**, *34*, 8034.
- (8) Zheng, L.; Waddon, A. J.; Farris, R. J.; Coughlin, E. B. *Macromolecules* **2002**, *35*, 2375.
- (9) Zheng, L.; Kasi, R. M.; Farris, R. J.; Coughlin, E. B. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 885.
- (10) Fu, B. X.; Namani, M.; Lee, A. *Polymer* **2003**, *44*, 7739.
- (11) Iacono, S. T.; Budy, S. M.; Mabry, J. M.; Smith, D. W. *Macromolecules* **2007**, *40*, 9517.
- (12) Iyer, S.; Schiraldi, D. A. *Macromolecules* **2007**, *40*, 4942.
- (13) Lim, S.; Hong, E.; Song, Y.; Choi, H. J.; Chin, I. *J. Mater. Sci.* **2010**, *45*, 5984.
- (14) Sanchez-Soto, M.; Illescas, S.; Milliman, H.; Schiraldi, D. A.; Arostegui, A. *Macromol. Mater. Eng.* **2010**, *295*, 846.
- (15) Illescas, S.; Sanchez-Soto, M.; Milliman, H.; Schiraldi, D. A.; Arostegui, A. *High Perform. Polym.* **2011**, *23*, 457.
- (16) Milliman, H.; Boris, D.; Schiraldi, D. *Macromolecules* **2012**, *45*, 1931.
- (17) Lim, S.; Hong, E.; Song, Y.; Choi, H. J.; Chin, I. *J. Mater. Sci.* **2012**, *47*, 308.
- (18) Misra, R.; Fu, B.; Plagge, A.; Morgan, S. *J. Polym. Sci., Part B: Polym. Phys.* **2009**, *47*, 1088.
- (19) Joshi, M.; Butola, B.; Simon, G.; Kukaleva, N. *Macromolecules* **2006**, *39*, 1839.
- (20) Roy, S.; Scionti, V.; Jana, S. C.; Wesdemiotis, C.; Pischera, A. M.; Espe, M. *Macromolecules* **2011**, *44*, 8064.
- (21) Perilla, J. E.; Lee, B.; Jana, S. C. *J. Rheol.* **2010**, *54*, 761.
- (22) Lagaly, G. *Appl. Clay Sci.* **1999**, *15*, 1.
- (23) Jancar, J.; Douglas, J. F.; Starr, F. W.; Kumar, S. K.; Cassagnau, P.; Lesser, A. J.; Sternstein, S. S. *Polymer* **2010**, *51*, 3321.
- (24) Inoune, M. *J. Polym. Sci., Part A: Gen. Pap.* **1963**, *1*, 2697.
- (25) Takamura, N.; Viculis, L.; Zhang, C.; Laine, R. M. *Polym. Int.* **2007**, *56*, 1378.
- (26) Waddon, A. J.; Coughlin, E. B. *Chem. Mater.* **2003**, *15*, 4555.
- (27) Halpin, J. C.; Kardos, J. L. *Polym. Eng. Sci.* **1976**, *16*, 344.