A thermo-rheological study on the structure property relationships in the reinforcement of nylon 6–POSS blends

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**A B S T R A C T**

Blends of nylon 6 and a silsesquioxane additive, aminopropyl isobutyl POSS (APOSS) were prepared containing 0–5% POSS by weight. APOSS was previously demonstrated by us to be an ineffectual additive at concentrations of more than approximately 3% by weight, lacking solubility and favorable interactions with the polymer matrix. Significant reinforcement was only obtained under the extreme confinement and orientation conditions induced by melt-spinning, under which it was suggested the APOSS might undergo forced-assembly into elongated, rebar-like reinforcement structures.

In the present work, we show that while the structure–property relationships of these systems, measured by WAXS, DSC and Raman spectroscopy revealed there are no major changes in the chemical structure induced by molecular interactions, rheological and SEM investigations on the APOSS-polymer systems suggest that at temperatures above the APOSS melting point, solubility and dispersion is slightly enhanced. We also show that two conditions seem to be necessary for improvement of properties: i) A sufficient concentration of APOSS needs to exist in the system to diffuse in significant quantities into the matrix upon re-melting; ii) The remaining non-diffused APOSS agglomerates need to be below a critical size around 4 μm in diameter, which does not happen for concentrations above approximately 3%.

**1. Introduction**

The reinforcement of polymers has attracted considerable interest in recent years, with several attempts to combine the advantageous processing properties of polymers with the desired characteristics of specific fillers, ending with dramatic improvements, such as mechanical, barrier, electrical and thermal properties, using a relatively low amount of fillers [1]. These improvements can be achieved more easily as the filler size is decreased to the micro- and nano-scale, which takes advantage of enhanced surface properties and increased interfacial interactions [1]. However, as filler sizes are reduced to the nano-scale, the surface energy effects become more significant, which can lead to aggregation of nanoparticles in order to reduce the overall surface energy. The capability of fillers to disperse within a polymer matrix is extremely important to the final composite properties, which have been pursued with approaches to increase the quality of dispersions, such as the incorporation of dispersants, grafting onto polymer chains or even copolymerizing fillers directly into the desired polymer chains [1,2].

Polyhedral oligomeric silsesquioxane (POSS) additives have been incorporated into a number of polymers as copolymers, grafts, or as melt blends over the past two decades [3–8]. POSS, a hybrid material (organic-inorganic), contains a basic polyhedral silicone-oxygen nanostructured skeleton or cage. POSS chemistry is very versatile, and it is possible to attach different functional organic groups (−R) to the corner Si atoms to enhance interactions with a matrix material. The POSS molecule can thus be synthetically modified to contain functional groups which allow copolymerization, light sensitization, and improved solubility in organic solvents, distinguishing it from other nanofillers. 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 reaction or compatibilization with the host polymer. The incorporation of POSS cages into polymeric materials may potentially result in dramatic improvements in polymer properties, including increase in upper use temperature, oxidative resistance, and surface hardening, leading to improved mechanical properties as well as a reduction in flammability [9].
While incorporation of POSS by copolymerization or through grafting is well known [10,11], preparation of polymer–POSS systems by melt blending has attracted significant research efforts only in recent years [12,13]. Compared to in situ polymerization methods, melt blending presents several advantages, being inexpensive, fast, versatile and easily upscalable technology. Indeed, standard equipment used for polymer compounding, such as twin-screw extruders, is generally suitable for processing of nanostructured polymers. Extrusion is usually a very fast method, with blending times of the order of minutes, so that high throughput is possible with relatively small equipment. Moreover, no organic solvents are normally used during melt blending, which results in a relatively low environmental impact. Successful nano-composite melt blending requires very careful design of the processing conditions, however, to obtain a proper dispersion and distribution of nanoparticles. Variables to be optimized include equipment parameters such as temperature, time, and shear forces, as well as the choice of proper compatibilization agents and nanoparticle functionalization.

A key design element in the preparation of polymer–POSS melt blends is the chemical–physical interaction between POSS and the matrix. The unique feature of POSS having a precisely controlled chemical structure with organic groups covalently attached to the Si–O framework allows for tunable miscibility into organic polymers. Strong self-interactions between geometrical regularly regular POSS cages often results in POSS aggregation, however, which has to be carefully taken into account when aiming at POSS molecular dispersion into polymers.

Molecular scale, or at least nanosized cluster of POSS is a necessary condition in order to properly exploit POSS properties. Aggregation of POSS into microparticles does not allow one to take advantage of the nanoscale POSS features and would result in properties that can be obtained with other filler microparticles, thus making the use of POSS unjustified because of their higher cost.

The role of POSS in blends and composites is very complex as it can affect the rheological properties of the melt and the final solid-state structure. In some cases POSS can act as a rheological modifier [14]. Recently, Jana et al. showed 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 [15,16]. That effort determined that the DBS and POSS form a stoichiometric complex which influences the crystallization of PP during melt-spinning. Incorporation of POSS leads to a large decrease in melt viscosity, as reported by Jana and others in the literature. Most POSS materials are crystalline solids with melting points in the range common to the processing temperature of many polymers. The presence of POSS’s liquid phase induces a decrease in viscosity and is supposed to facilitate blends processing. This enablement is in stark contrast to more traditional polymer-inorganic composites, with orders of magnitude increase in viscosity with the incorporation of even small amounts of inorganic fillers [17,18].

That the degree of POSS – polymer interactions is plays a major role in determining property enhancements was recently reported; this interaction can be measured using Hansen solubility parameters [19]. Nylon 6 and aminopropyl isobutyl (APOSS) were anticipated to be strongly interacting, due to the hydrogen bonding ability of nylon, as evidenced by others working in the field [20,21]. With this aim, APOSS was chosen as the additive of interest, with the goal achieving a high degree of POSS-polymer interactions with the primary amine in the aminopropyl group. Reinforcement was seen at low concentrations of POSS, but the role of processing was not taken into account.

The reinforcement of melt-spun fibers of APOSS/polyamide (nylon 6) blends was recently reported by our group [22]. It was observed that there exists an optimal loading in terms of POSS solubility at a low 2.5–3.0 wt%, where a significant increase in the Young’s modulus and yield stress occurs. This improvement in mechanical properties was seen to only occur in highly elongated melt-spun fibers, and not in bulk injection molded samples. At low POSS concentrations, small, elongated aggregates were formed in the axial direction, although there was also the presence of individually dispersed POSS molecules. As the concentration of POSS was increased past this window, larger spherical aggregates began to form, resulting in POSS acting primarily as a processing aid and a decrease in the blend’s mechanical properties [22]. As was suggested in the previous work [22], a combination of different possibilities, including the solubility of the POSS in the matrix due to shear during the fiber melt-spinning, and POSS acting as an anchor to the amorphous regions of the nylon 6, resulting in a more oriented amorphous phase could be at work in that system. An answer from among these suggestions and the hypothesis that the “elongated domains observed are in fact a result of molecular scale interactions”, was never confirmed.

A more detailed study, especially of the rheology of those systems, is necessary to better understand their complexity. The present study looks to fill this gap and understand the dynamics of POSS AM0265-nylon 6 interactions by performing a full spectrum of thermal, chemical and viscoelastic studies, with the focus on the thermo-rheological behavior of the blends. A study the solubility of the POSS in the nylon 6 with temperature, and their molecular interactions, and a clear mechanism of reinforcement occurring at a 2.5% w/w incorporation content of POSS in the nylon 6 matrix are presented herein.

2. Experimental

2.1. Materials

Polyamide 6 (nylon 6) resin (Grilon® FG40-NL) was obtained in the form of pellets from EMS-Grivory with MVR 20 g/10 min (ISO 1133), density 1.14 g/cm3 (ISO 1183). Aminopropyl isobutyl-POSS (APOSS, AM0265) was acquired from Hybrid Plastics Inc. in the form of a white powder and was used as received. Fig. 1(A–B) presents the chemical structures of nylon 6 and APOSS, respectively.

2.2. Preparation of POSS blends

All materials were dried in a vacuum oven at 100 °C for 24 h prior to blending. APOSS-polymer compositions were weighed and dry-mixed prior to blending. The blend consisted of nylon 6 blended with 0–5 wt% APOSS. Blend compositions were selected for optimal solubility in their respective polymers as determined previously [19]. Mixtures were melt-blended using a Haake Rheodrive 5000 counter rotating conical twin-screw extruder, with average screw diameter 2.54 cm and l:D ratio 13:1, at 240 °C at a rotor speed of 20 rpm. The extrudate was collected and pelletized in preparation for further analysis.

2.3. Image analysis

The morphology of the APOSS-polymer blends was observed edge-on by scanning electron microscopy (SEM) using a JOEL JSM-6510 scanning electron microscope. In order to acquire edge-on images, samples were freeze-fractured in liquid nitrogen. All samples were spatter coated with a 5 nm thin layer of gold prior to imaging.
2.4. Thermal analysis

The thermal behavior of the APOSS-polymer blends was investigated by differential scanning calorimetry (DSC) using a Mettler Toledo DSC200 calorimeter under continuous nitrogen purge, at a flow rate of 50 ml/min. The thermal properties such as melting temperature ($T_m$), glass transition temperature ($T_g$), and enthalpy change ($\Delta H_m$) in melting were determined at a heating rate of 10 °C/min from 0 to 290 °C.

2.5. Rheological analysis

A MARS III rheometer (Thermo Fisher Scientific), operated with a 25 mm parallel plate setup was used to measure the rheological dynamic properties of the nylon 6 and nylon 6/APOSS blends. Disk-shaped specimens of 25 mm diameter and 1 mm thickness were molded at 240 °C in a compression molder. The specimens were subject to 240 °C for 5 min during molding. The polymer compound in the rheometer was first heated and kept at the desired temperature for 2 min to reach equilibrium. All rheological experiments were performed under a nitrogen atmosphere. Prior to the experiments, all samples were vacuum dried for 12 h at 80 °C.

Time sweeps at constant temperatures of 225 and 285 °C were performed in order to analyze the dynamic modulus over time. Frequency sweeps at constant temperatures of 225 and 265 °C with oscillatory shear frequency between 1 and 100 rad/s was carried out. Temperature sweep experiments were also conducted, from 225 to 285 °C. A second experiment, a cooling temperature sweep, with a fresh sample, was performed from 285 to 225 °C. These experiments were performed at constant frequency at 1 Hz. Storage modulus ($G'$), loss modulus ($G''$), and damping factor (tan δ) were measured in all rheological experiments described above. All experiments were performed in the linear viscoelastic regime, which was independently confirmed by stress sweeps under the relevant conditions.

2.6. WAXS analysis

Wide-angle X-ray scattering data was acquired at the Advanced Polymers Beamline X27C at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). A 2D MAR CCD X-ray detector (MARUSA) was employed for detection of 2D-WAXS images having a resolution of 1024 × 1024 pixels (pixel size = 158.44 μm). The X27C X-ray wavelength, $\lambda$, was 1.371 Å, monochromatized using a double multilayer (silicon/tungsten) monochromator. The relative X-ray intensity was measured before ($I_b$) and after ($I_f$) the sample by using proportional counters. Scattering data are expressed as intensity vs. $q$, where $q = (4\pi \sin(\theta))/\lambda$.

2.7. Raman spectroscopy

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 μm [2]. Raman shifts were calibrated with a silicon wafer using the 520 cm$^{-1}$ line.

3. Results and discussion

Nylon 6 and APOSS were melt blended, varying POSS weight percentage from 0 to 5%, and these samples were characterized as a function of POSS concentration; representative data in this section. SEM images of polymer blends cross-sections show APOSS forms large, spherical, phase-separated aggregates (Fig. 2) which increase with increasing APOSS concentration, suggesting that the additive is not compatible with the polymer matrix at high concentrations. Thermal analysis of the nylon 6/APOSS samples shows non-covalently interaction between them, since there is little change in the nylon 6 melting behavior (Fig. 3). From our previous work [22], it is known that this grade of POSS contains two distinct endothermic transitions upon heating, one at 50 °C and other at approximately 270 °C. It is also known that the APOSS remains a solid after the first transition and becomes a liquid after the second transition. For concentrations above 1%, it is possible to observe a residual peak that increases with the APOSS concentration around 267 °C, appearing to be the second endothermic transition of APOSS (Fig. 3). This additional peak was not observed on the previous work in both injection and fiber samples, probably due to the multiple heating and cooling processes that they were submitted to, as well as the multiple shear processes, leading the APOSS to amorphous state. This observation will be analyzed and further discussed below.

Results from Wide-Angle X-ray Scattering (WAXS) yield information about the crystal structure of APOSS and nylon 6. 2D images were integrated to give relative scattering intensities of each crystal face. Neat nylon 6 shows two sharp characteristic peaks at 20.3° and 23.4°, which are assigned to the (200) and (002)/(202) plane reflections of the α-form, respectively [23]. From this data (Fig. 4) it is possible to observe the presence of APOSS crystals in the blends via a small peak (due to the high signal from the equipment) around 7q, which has been previously reported [22]. The diffraction patterns for the nylon 6/APOSS blends are similar to those of neat nylon 6, and it is evident from the figure that the basic nature of the diffraction pattern does not change in the presence of APOSS; moreover, the pattern is isotropic, indicating no orientation effects due to processing (Fig. 5).

Fig. 1. Molecular structures of A) nylon 6; B) APOSS.
From the structure–property relationships of APOSS within melt spun nylon 6 fibers it was previously shown to exist a significant amount of hydrogen bonding [22]. Raman spectroscopy was used in order to probe and analyze if there were any molecular interactions taking place between the APOSS molecules and nylon 6 in the extruded blends. The results displayed in Fig. 6 show there is no significant shift in hydrogen bonding taking place among the different systems examined in the present study, suggesting there is no significant level of hydrogen bonding between these materials upon melt compounding.

That the solubility of the POSS could be influenced by the high degree of deformation during elongational flow, which could increase significantly the temperature via viscous dissipation, was previously suggested, but not tested [22]. In the present work we will study how temperature can influence the solubility of the POSS in the matrix, especially at temperatures above the POSS second endothermic transition, and how that affects the morphology/structure of the blend.

Rheological experiments were conducted in order to analyze the blends’ viscoelastic properties at different temperatures. First, the stability of the nylon 6 was studied at different temperatures (Fig. 7) to determine the time interval for the frequency sweeps, since the polymer is very sensitive to temperature. At 225 °C, the material shows nearly constant behavior; by contrast, at 285 °C a significant change in the dynamic modulus is observed over time. Using an increase of 10% in both $G'$ and $G''$ as the (arbitrary) upper limit for the duration of an experiment, the maximum potential duration of the experiment was 7 min at 225 °C, 6 min at 265 °C and...
4 min at 285 °C. In keeping with these findings, all the rheological temperature sweeps were performed by heating the samples from 225 to 285 °C, i.e., above the melting point of both the nylon 6 and APOSS, at 10 °C per minute, and frequency sweeps were performed at temperatures no higher than 265 °C and over no more than 6 min.

SEM images were taken before and after the temperature sweeps, which were performed under Small Amplitude Oscillatory Shear at 1 Hz frequency, i.e., in quasi-quiescent conditions. Fig. 8 shows the SEM image of a nylon 6/0.5% APOSS blend before and after heating, and it is clear that there are no significant morphological differences at this sub-micron scale, with the APOSS
domains dispersed uniformly in the matrix. This structural consistency is also confirmed by the particle area distribution histograms in Fig. 9, in which the average area of agglomerates for this particular blend is identical before and after heating.

At the other end of the APOSS content spectrum, the SEM images and histograms of the nylon 6/5% APOSS blend are shown for the same conditions as above in Figs. 10 and 11 respectively. A smaller average APOSS agglomerate size is clearly observed upon cooling, with the largest aggregates decreasing in diameter from approximately 11 µm prior to heating to 6 µm after cooling. This change in domain size distribution strongly suggests that some APOSS is diffused from the agglomerates into the matrix upon melting above 267 °C.

In order to ascertain whether this phenomenon can explain the optimal loading of 2.5% POSS concentration observed in our previous work [22], this analysis was also carried out for the nylon 6/2.5% APOSS blend. In Figs. 12 and 13, a similar effect to that seen for 5% loading is observed, but with smaller overall APOSS
The largest aggregates now have a diameter reduction from almost 10 µm before heating, to approximately 4 µm after cooling, which, again, suggests that for 2.5% concentration most APOSS is diffused from the agglomerates in matrix upon melting above 267 °C. Interestingly, these are also the dimensions of the biggest final aggregates in the nylon 6/0.5% APOSS blend after cooling, suggesting there are limits to the solubility of APOSS in the nylon 6 matrix.

The rheological data collected during the temperature sweeps is shown in Fig. 14, demonstrating that there is clearly an increase in the storage modulus with increasing APOSS concentration as well as the formation of a plateau at high temperatures for concentrations above 1%, evidence of a polymer network after APOSS melting. It is important to point out how tan δ is sensitive to the onset of POSS melting point (second endothermic transition) around 267 °C, which is in agreement with the DSC measurements. At this temperature, there is a noticeable decrease in the slope of the tan δ curve for APOSS contents equal or higher than 1%, suggesting the melting of the APOSS particles is changing the physical structure blend and, consequently, its viscoelasticity.

In order to confirm that no chemical changes occurred in the blends upon heating, WAXS and Raman tests were performed before (Figs. 5 and 6) and after (Figs. 15 and 16) the rheological temperature sweeps. Again, there are no significant changes between them, confirming that the chemical structure of the blends is unchanged as a result of the heating cycle.

It was shown previously that a concentration of approximately 2.5% APOSS was the “sweet spot” for maximum properties reinforcement upon fiber-spinning [22]. Results presented so far in the present work show a clear influence of temperature on the morphology of the blends, especially when they are submitted to temperatures above the APOSS melting temperature, even for short periods of time, but no significant change in the chemical structure. These results also suggest that there is a critical size for the agglomerates (approximately 4 µm in diameter), above which the remaining aggregates will behave as structural defects and lead to a decrease in mechanical properties. This behavior will only happen, however, if there are weak or non-existent interactions between the APOSS agglomerates and the nylon 6 matrix below the APOSS melting temperature (if the interactions were strong, the APOSS aggregates would probably reinforce the matrix, which is not observed). Thus, in order to probe the level of interactions between the APOSS and the nylon 6 matrix prior to APOSS melting, further rheological testing was performed at different temperatures.

The variation of $G'$, $G''$ and tan δ as a function of frequency at 225 and 265 °C, are shown in Fig. 17a and b for nylon 6 and nylon 6/ APOSS, respectively (it was not possible to perform experiments at 285 °C because of matrix degradation before a meaningful set of data points could be collected). At 225 °C, only a very small, if any, influence of APOSS content can be detected (Fig. 17a). As temperatures increase to 265 °C (Fig. 17b), the presence of APOSS is more evident, bringing about a decrease in the loss modulus for nylon 6/APOSS samples at concentrations lower than 3%, and an increase thereafter. The storage modulus is barely sensitive to the presence of the APOSS phase, but tan δ becomes clearly smaller as APOSS content increases, indicating a more pronounced viscoelastic behavior with increasing

![Fig. 11. Histogram representing the evolution of average agglomerates area for the nylon 6/5% APOSS blend.](image1)

![Fig. 12. SEM image of nylon 6/2.5% APOSS polymer blend a) before temperature sweep and b) after the temperature sweep test.](image2)
APOSS concentration. When analyzed together with the SEM results (Fig. 2), these results indicate a variable, but real degree of adhesion between the nylon 6 and the APOSS agglomerates. Relatively large APOSS aggregates appear to be necessary in order to significantly influence $G'$ and $G''$, but the significant combined viscoelastic effect in $\tan \delta$ indicates that interactions, most likely weak van der Waals forces, do occur. Such interactions could lead to a decrease in chain entanglement and more free volume in the melt, resulting in lower viscosity at lower APOSS concentrations when the impact on the viscosity of having a solid filler in the system is not yet relevant. For higher concentrations (>3%), the increased storage modulus (elasticity) results in the presence of a well-known pronounced plateau at low frequencies [24].

The rheological data was used to further analyze the compatibility of nylon 6/APOSS blends by using the criteria proposed by Han and Chang [25,26]; miscible (compatible)/immiscible (incompatible) polymer pairs showed that $G'$ vs. $G''$ plots give (a) a temperature-independent correlation for both compatible and
incompatible blend systems, (b) a composition-independent correlation for immiscible blends, and (c) a composition-dependent correlation for miscible blends. Fig. 18 shows a temperature-independent correlation for neat nylon 6, as expected. The correlation for the blends, however, is temperature dependent, and much more pronounced for higher concentrations of APOSS, which can be related with a change in internal morphology (but not in chemical structure given the lack of differences in the Raman spectra and the x-ray patterns). This change occurs for concentrations at 1% APOSS and above, which seem to be the minimum detectable APOSS concentration.

3.1. Mechanical reinforcement hypothesis

Prior work [22] taught that the maximum reinforcement in melt-spun fibers of nylon 6/APOSS occurs at 2.5% loading. The present study demonstrates that two conditions appear to be necessary for good mechanical improvement of nylon 6/APOSS blends:

1. It is necessary to heat the blend above the melting temperature of APOSS for a brief period (short enough to avoid matrix degradation) in order for APOSS to diffuse into the matrix. It is this diffused APOSS that probably will posteriorly be highly elongated upon melt-spinning and form the elongated domains previously hypothesized, providing the reinforcement ability reported.

2. The more APOSS that diffuses into the matrix, the higher this reinforcement will be, suggesting that the more APOSS initially present, the better. However, because the interactions between the APOSS aggregates and the matrix are weak, and there are limits to the solubility, the remaining APOSS domains will tend to act as structural defects if they are too large and will eventually decrease the mechanical properties. Thus, there is a maximum acceptable size for the remaining APOSS domains; judging from the SEM data and from our previous work [24], this seems to be on the order of 4 μm, which is the maximum domain size in all the blends with 2.5% or less of APOSS.

4. Conclusions

Previous work had suggested that under extreme confinement and orientation conditions, such as in melt-spun fibers, the APOSS would undergo forced-assembly into elongated, rebar-like reinforcement structures, and that the maximum reinforcement occurred for loadings of approximately 2.5%, but a clear explanation for this optimal loading was not presented.

In this work we attempted to explain this behavior by melt-compounding a series of nylon 6/APOSS blends containing between 0 and 5% POSS by weight, and studying their rheological behavior in the melt, below and above the melting temperature of APOSS. WAXS, DSC and Raman revealed there are no major changes...
Fig. 17. Frequency sweep data for nylon 6 and nylon 6/APOSS blends at a) 225 °C, b) 265 °C.
in the chemical structure induced by molecular interactions in the blends, but rheology and SEM showed clear physical changes.

The present results show APOSS existing as large, phase-separated aggregates, with only weak interactions with the matrix below the APOSS melting temperature of 267 °C. However, above this point, the APOSS melts and becomes partially soluble in the nylon 6 matrix, leading to smaller domains upon posterior cooling. The maximum acceptable size for these domains seems to be of the order of 4 μm in diameter, a value that is observed for all blends with APOSS content equal or lower than 2.5%.

Based on these results, a mechanism for optimal reinforcement at approximately 2.5% APOSS loading can be postulated. It is under this loading that both conditions necessary for properties improvement are met: i) sufficient APOSS exists in the system to diffuse in significant quantities into the matrix upon re-melting; ii) the remaining non-diffused APOSS agglomerates are below the critical size of approximately 4 μm in diameter, so as not to negatively impact the mechanical properties.

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References