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

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ABSTRACT

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].

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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 an 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 nanocomposite 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 compatiblization 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 geometrically 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/cm^3 (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-bended using a Haake Rheodrive 5000 counter rotating conical twin-screw extruder, with average screw diameter 2.54 cm and L:D ration 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 sputter coated with a 5 nm thin layer of gold prior to imaging.