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# Morphology and mechanical properties of PET by incorporation of amine-polyhedral oligomeric silsesquioxane

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ABSTRACT

Amine-polyhedral oligomeric silsesquioxane(AM-POSS)/poly (ethylene terephthalate) (PET) nanocomposites were prepared using in situ polymerization. The thermal decomposition temperatures of the composites, measured at a 5 wt.% weight loss, were 5–10 °C higher than those of PET. There was no significant change in the other thermal properties. The SEM observations suggest that there was an obvious phase separation in the POSS/PET composites. The nanocomposites that contained 1 wt.% of aminoisobutyl-POSS (AM-POSS-1) showed fine dispersions of POSS (less than 80 nm in diameter), which arose from the strong interfacial interactions between POSS and PET during the polymerization. The nanocomposite that contained liquid aminoisooctyl-POSS (AM-POSS-2) showed both the particles that arose from the reaction and the liquid drops that did not react during the polymerization. The viscosity of the composites increased with the addition of POSS, except for the AM-POSS-2/PET composites at high concentrations. In the nanocomposite film that contained 1 wt.% of AM-POSS-1 and AM-POSS-2, the tensile strength increased by 63% and 35%, respectively, and the modulus, by 300% and 280%, respectively. The storage modulus retention at 120 °C kept 45% for the AM-POSS-2/PET composite fiber at 1 wt.% loading.



## 1. Introduction

Silicon-based organic/inorganic hybrid nanocompounds have been studied for the development of new materials with the properties of both organic and inorganic materials. Polyhedral oligomeric silsesquioxanes (POSS), the formula of which is $[RSiO_{1.5}]_n$, are being studied for the preparation of truly molecularly dispersed composites. POSS reagents can be incorporated into polymer chains to modify the local structure and chain mobility of polymeric materials, which eventually show enhanced properties such as mechanical, thermal, and other physical properties compared to those of pristine polymer systems. Unlike silica, silicones, and fillers, however, each POSS molecule contains a non-reactive organic substituent and one or more covalently bonded reactive functionalities suitable for grafting, polymerizing, or blending with common organic polymers. Furthermore, if the polymerizable R groups are selected properly [1–5], the organic components can be varied to control the cross-linking density about the cube, the segment distances between the cross-links, the packing of individual cubes with respect to one another, and the stability of the cube-organic bond.

The incorporation of POSS reagents that contain reactive groups into organic polymer systems creates the possibility of nanoscale reinforcement, with POSS bound to the polymer chain with chemical bonds. A number of recent literature describe POSS/polymer covalent composites, including POSS/HDPE [6], POSS/polypropylene [7], POSS/epoxy [8–11], POSS/PMMA [12–15], POSS/polyurethane [16,17], POSS/PET [18–20] and POSS/polycarbonate [21]. Recently, Zheng et al. [8–11,16] reported that the morphology of the resulting hybrids was quite dependent on the types of substituents R on the POSS monomers, and that the dynamic moduli of the hybrids was significantly higher than those of control epoxy and polyurethane. Cohen et al. [13] investigated the thermomechanical properties of PMMA by blending two types of acrylic-POSS (unmodified and hydrogenated) with PMMA. They found that both POSS species have a plasticizing effect on PMMA by lowering the glass transition temperature and decreasing the melt-state viscoelastic moduli measured in a small-amplitude oscillatory shear flow. Schiraldi et al. [19] studied PET composite fibers made with three types of POSS additives. Significant increases in the tensile modulus and strength were achieved with non-reactive POSS. The high-temperature moduli of the PET/POSS nanocomposite fibers were found to be rather variable, likely due to the modest compatibility between the filler and the polymers, which can lead to structural anisotropy within the composite.

In this study, monofunctional POSS (aminopropyl isobutyl and aminopropyl isooctyl-POSS) were incorporated into PET with in situ polymerization. The dispersion of the POSS molecules into the PET matrix through the reaction between the amine group on

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POSS and the amine group on PET was investigated by analyzing the morphology and the thermal, rheological, and mechanical properties.

## 2. Experimental

### 2.1. Materials

Two kinds of amine-POSS-aminopropyl isobutyl (AM-POSS-1) and aminopropyl isooctyl (AM-POSS-2) were used. They were purchased from Hybrid Plastics, Inc. (Hattiesburg, MS). AM-POSS-1 consisted of white powders and AM-POSS-2, of viscous liquid. The chemical structures of the two AM-POSS's are shown in Fig. 1. Dimethyl terephthalate (DMT) and ethylene glycol (EG) were obtained from SK Chemicals Co. (Korea) and Daejung Co. (Korea), respectively.

### 2.2. Preparation of POSS/PET nanocomposites

To prepare the POSS/PET nanocomposites, the POSS molecules were dispersed in EG using an ultrasonic homogenizer for better dispersion. The dispersed EG solution was found to have been slightly unclear due to POSS. The EG solution with the dispersed POSS and DMT were mixed in a polymerization vessel at a molar ratio of 2:1. A manganese (Mn) catalyst was used for the esterification, and the reaction was performed at 230 °C for 5 h to obtain methanol with a similar theoretical value. Thereafter, a small amount of TMP catalyst as a thermal stabilizing agent was added, after which an antimony (Sb) catalyst was added to perform polycondensation in a vacuum at 280 °C for 2 h to obtain POSS/PET nanocomposites. The polycondensation time became shorter than with pure PET. This was caused by the characteristics of POSS. The POSS/PET nanocomposites that were obtained from the addition of 1, 3, and 5 wt.% of POSS based on the total weight of the polymers were dried in a vacuum oven at 70 °C, which was the same as the crystallization temperature, for 24 h. The composites were hot-pressed to a thickness of about 200 μm. The film that was obtained was cut into a rectangle that was 80 mm long and 15 mm wide. The specimens were extended four times in a hot chamber equipped with an Instron instrument. The POSS/PET nanocomposite fiber was prepared with a capillary rheometer (Capillary Rheometer Model 8052, KAYENESS Inc, USA) at 265 °C and quenching at room temperature. This fiber was sufficiently stretched in an oil bath in a passive mode, washed with carbon tetrachloride, and then dried at a normal temperature.

### 2.3. Measurements

The thermal stability of POSS was evaluated as follows. A thermogravimetric analysis (TGA) was performed to examine the thermal stability of POSS and the POSS/PET nanocomposites. Before the TGA analysis, all the samples were sufficiently dried in a vacuum oven at 40 °C. The mass loss was traced as the samples were heated at a rate of 10 °C/min from 30 °C to 800 °C under nitrogen.

The thermal behavior of the POSS/PET nanocomposites was measured using DuPont 910 differential scanning calorimetry (DSC). The glass transition, melting, and crystallization temperature were determined at the heating and cooling rate of 20 °C/min.

The dispersion and morphology of the POSS/PET nanocomposites were analyzed with field emission scanning electron microscopy (FE-SEM, JSM-6700F, Jeol Co., Japan). The samples were prepared at 280 °C through compression molding, and fractured at cryogenic temperature after immersion in liquid nitrogen.

To study the reaction between POSS and PET, a 500 MHz FT-NMR spectrometer (Bruker AMX-500) was used. The mixed solvents that were used were deuterated trifluoroacetic acid/chloroform (70/30, v/v). The inherent viscosity of PET and the POSS/PET nanocomposites was measured with a mixed solvent of phenol/tetrachloroethane (60/40, v/v) at 35 °C. The inherent viscosity of the samples was 0.55–0.72 dL/g.

The storage modulus and $\tan\delta$ of the nanocomposite fiber were measured with a dynamic mechanical analyzer (DMA, DMA7e, Perkin Elmer) that was connected to an intra-cooler cooled by He gas. The measuring temperature range was 30–180 °C at the heating rate of 5 °C/min. The static force, dynamic force, and frequency were 50 mN, 30 mN, and 1 Hz, respectively.

The mechanical properties of the nanocomposite films were measured using an Instron model 4467 universal instrument. The measurements were made at room temperature at a constant crosshead speed of 2 mm/min. Data were taken as averages of at least five measurements.

Dynamic rheological measurements were performed using a rotational rheometer (PHYSICA Rheo-Lab MC120). The measurements were carried out in an oscillatory shear mode using parallel plate geometry. Prior to any measurement, all the samples were allowed to relax at the measuring temperature for 2 min, and then sheared at a low shear rate ($0.01\ s^{-1}$) for 3 min under a nitrogen atmosphere. Frequency sweeps were performed from 0.1 to 100 rad/s.

Wide-angle X-ray diffraction measurements were performed with a Rigaku (D/Max-IIIB) X-ray diffractometer, using Ni-filtered Cu Kα radiation.

## 3. Results and discussion

### 3.1. Characterization of POSS/PET nanocomposites

A series of POSS/PET nanocomposites that contained small amounts of two AM-POSS was prepared through in situ polymerization. The $^1$H NMR spectra of PET and the AM-POSS/PET nanocom-

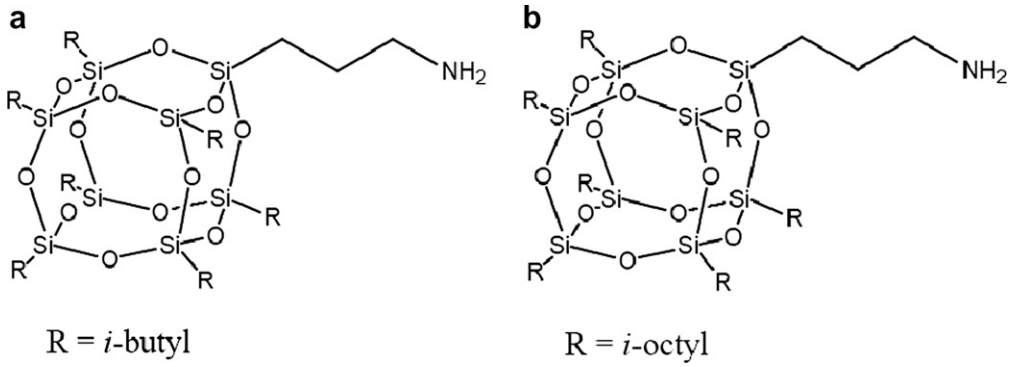


**Fig. 1.** Typical chemical structures of POSS molecules: (a) aminopropyl isobutyl-POSS and (b) aminopropyl isooctyl-POSS.