

Morphology and Rheological Behaviors of Poly(ethylene terephthalate) Nanocomposites Containing Polyhedral Oligomeric Silsesquioxanes

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ABSTRACT: Poly(ethylene terephthalate) (PET)/polyhedral oligomeric silsesquioxane (POSS) nanocomposites were prepared by *in situ* polymerization. Light scattering measurement suggested that there is significant change in molecular weight arising from gel formation by chemical crosslinking during polymerization. The thermal decomposition temperatures of the composites measured at 5 wt % weight loss were 5–10°C higher than that of PET. There is no significant change in other thermal properties. Scanning electron microscopy observations suggest that there is obvious phase separation in PET/POSS composites, composites containing 1 wt % of disilanolisobutyl and trisilanolisobutyl-POSS show fine dispersions of POSS (30–40 nm in diameter), which arise from

strong interfacial interactions between POSS and PET during polymerization. The viscosity of the composites increased with the addition of POSS. The observation of a plateau region of composites containing 1 wt % of POSS in the plot of $\log G'$ vs. $\log G''$ indicates strong interfacial interactions between POSS and PET. Sixty-three percent and 41% increase in tensile strength and 300 and 380% increase in modulus were achieved in the composites containing 1 wt % of disilanol- and trisilanol-POSS, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 272–279, 2008

Key words: polyesters; reinforcement; nanotechnology; rheology; mechanical properties

INTRODUCTION

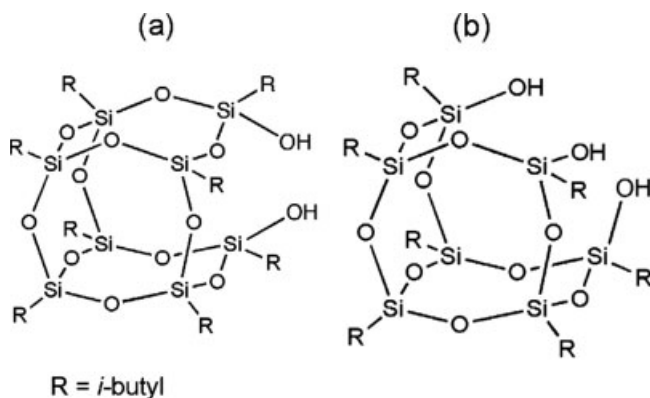
Organic/inorganic hybrid materials have recently received considerable attention, because they offer the opportunity to develop composite materials with properties that differ significantly from those predicted, applying the rule of mixtures to the component phases. One family of inorganic phases that is being combined with an increasingly broad range of polymers is polyhedral oligomeric silsesquioxanes, $(\text{RSiO}_{1.5})_n$, where R may be a wide variety of functional groups.^{1–5} The functionality, solubility, and reactivity of these molecules can be easily changed through modifying the R with a variety of organic substituents. Octameric polyhedral silsesquioxanes have a SiO cage structure very similar to that of silica particles with eight vertices. Each vertex may be functionalized for specific applications.

The incorporation of polyhedral oligomeric silsesquioxane (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. There are a number of recent papers that describe polymer/POSS covalent composites, including epoxy/POSS,^{6–9} polyurethane/POSS,^{10,11} PMMA/POSS,^{12–15} polypropylene/POSS,¹⁶ HDPE/POSS,¹⁷ PET/POSS,^{18,19} and polycarbonate/POSS.²⁰ Recently, Zheng and coworkers^{6–10} have reported that the morphology of the resulting hybrids were quite dependent on the types of substituents R on the POSS monomers, and the dynamic moduli of the hybrids was significantly higher than those of control epoxy and polyurethane. By blending two types of acrylic-POSS (unmodified and hydrogenated) with PMMA, Cohen and coworkers¹³ investigated the thermomechanical properties of PMMA. It was 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 small amplitude oscillatory shear flow. Schiraldi and coworkers¹⁹ studied poly(ethylene terephthalate) (PET)

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Scheme 1 Typical chemical structures of POSS molecules: (a) disilanol POSS; (b) trisilanol POSS when R = butyl.

composite fibers made with three types of POSS additives. Significant increases in tensile moduli and strengths were achieved with nonreactive POSS. The high-temperature moduli of PET/POSS nanocomposite fibers were found to be rather variable, likely because of the modest compatibility between filler and polymers, which can lead to structural anisotropy within the composite.

In this study, two types of POSS (disilanolisobutyl-POSS and trisilanolisobutyl-POSS) were incorporated into PET by *in situ* polymerization. The chemical structures of POSS are shown in Scheme 1. The dispersion of POSS molecules into the PET matrix through the reaction between the hydroxyl groups on POSS and PET was investigated by analyzing the morphology, thermal, rheological, and tensile properties.

EXPERIMENTAL

Materials

POSS derivatives used in this work were supplied by Hybrid Plastics (Hattiesburg, MA) and used as received. Dimethyl terephthalate (DMT) and ethylene glycol (EG) were obtained from SK Chemical Co. (Korea) and DaeJung Co. (Korea), respectively. The catalyst used was titanium isopropoxide.

Preparation of PET/POSS composites

PET/POSS composites were prepared by *in situ* polymerization. POSS derivatives were first mixed with EG in a 100 mL beaker and sonicated for dispersion. In a small scale batch reactor, 100 g of DMT and 65 g of EG mixture containing 1–5 g of POSS and catalyst were mixed. The mole ratio of DMT to EG was 1.0/2.0. This mixture was first heated to 190°C under nitrogen in a silicone oil bath. This temperature was maintained for 2 h. The

temperature was then increased to 210°C, where it was maintained for 2 h. The reaction temperature was progressively increased to 280°C. Then the pressure was reduced to 0.1 Torr and maintained for 0.5–1 h. The pure PET was also prepared by the same method for comparison.

Measurements

To study the reaction between PET and POSS additives, a 500 MHz FT-NMR spectrometer (Bruker AMX-500) was used. The mixed solvents used were deuterated trifluoroacetic acid/chloroform (70/30, v/v). The inherent viscosity of PET and PET/POSS composites was measured by mixed solvent of phenol/tetrachloroethane (60/40, v/v) at 35°C. To measure the apparent weight-average molecular weight (M_w) and the hydrodynamic radius (R_H), a commercial laser light scattering spectrometer (Brookhaven BI-200SM detector system, BI-9000AT digital correlator) was used with a He-Ne laser (Spectra Physics model 127, operated at $\lambda_0 = 632.8$ nm and 35 mW). The thermal behaviors of the PET/POSS composites were measured using a DuPont 910 differential scanning calorimetry. The glass transition, melting, and crystallization temperature were determined at heating and cooling rates of 20°C min⁻¹. The thermal stability of the samples was measured by thermogravimetric analysis (TGA) using a TA Instruments 2950 thermogravimetric analyzer. Mass loss was traced when samples were heated at a rate of 10°C min⁻¹ from room temperature to 700°C under nitrogen. Morphology of PET/POSS composites was examined by scanning electron microscopy (SEM, S-4300, Hitachi). Samples were prepared at 280°C by compression molding, and fractured at cryogenic temperature after immersion in liquid nitrogen. Mechanical properties were measured using an Instron model 4467 universal instrument. The composites were hot-pressed to the thickness of about 200 μ m. The film obtained was cut into a rectangle shape of 80-mm long and 15-mm wide. These specimens were extended four times in hot chamber equipped with Instron instrument. Measurements were made at room temperature at a constant crosshead speed of 2 mm min⁻¹. 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 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 0.1–100 rad s⁻¹.

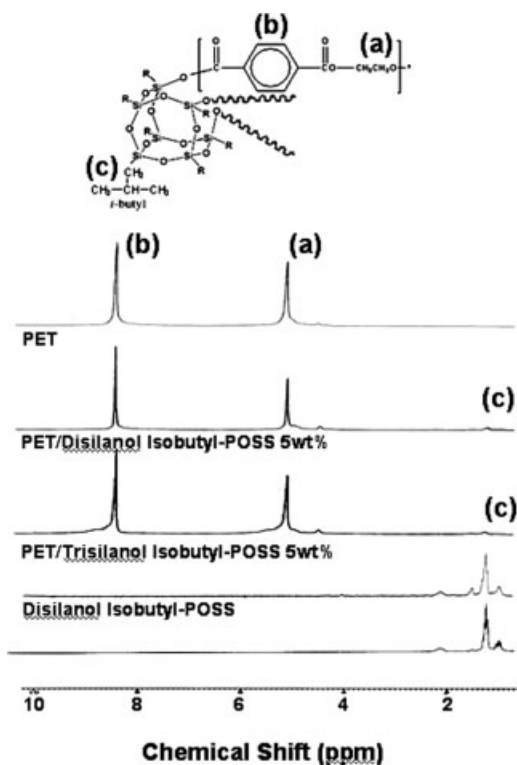


Figure 1 The ^1H NMR spectra of PET, PET/disilanol-POSS composite, PET/trisilanol-POSS composite, disilanol-POSS, and trisilanol-POSS.

RESULTS AND DISCUSSION

Characterization of PET/POSS composites

A series of PET/POSS composites containing small amounts of disilanol-POSS or trisilanol-POSS were prepared by *in situ* polymerization. ^1H NMR spectra of PET and PET/POSS composites are shown in Figure 1. Two main peaks are shown for PET: one for the ethylene unit (4.9 ppm) and the other for the aromatic unit (8.2 ppm). In addition to the aforementioned two peaks, PET/POSS composites containing 5 wt % of disilanol- and trisilanol-POSS showed a new peak at 1.1 ppm. This arises from the side R group (isobutyl groups) in POSS. It is not positive proof that the reaction between POSS and PET occurred during polymerization, because it may result from unreacted POSS.

The molecular weights and radii of gyration of PET/POSS composites are measured by light scattering and are listed in Table I. During polycondensation, we tried to control the molecular weight by monitoring the torque meter attached to the reactor. Thus, the inherent viscosity of the samples was in the range of 0.55–0.72 dL g $^{-1}$. The weight-average molecular weight measured by light scattering, however, showed large deviations compared to the viscosity. Especially, the molecular weights of 3 and 5 wt % trisilanol-POSS composites are far from real-

istic. The trisilanol-POSS has three functional groups. The incorporation of a small amount of branching agent may lead to the formation of long-chain branches. If the amount of the branching agent exceeds about 1 wt %, a crosslinked structure may be obtained. Hence, the PET/trisilanol-POSS composite could be branched or crosslinked. Because of the higher segment density, branched macromolecules have a smaller radius of gyration than linear macromolecules of the same molecular weight. However, the radius of gyration of PET/trisilanol-POSS composites containing 3 and 5 wt % of trisilanol-POSS are larger than those of PET and PET/disilanol-POSS composites. So large molecular weight of PET/trisilanol-POSS composites may be due to the fact that POSS reacted with PET are strongly aggregated, resulting in gel formation. Hsiao and co-workers²¹ demonstrated that physical crosslinking in molten ethylene-propylene copolymers may be induced by addition of POSS molecules. The physical gelation can be a contribution to two factors: the interaction between the POSS aggregates and the interaction between the POSS and the polymer matrix. The latter may be more important in the chemically crosslinking POSS/polymer composites. The large molecular weight of the composites measured by light scattering may be attributed to the interaction between trisilanol-POSS and PET by chemical crosslinking.

Thermal properties of PET/POSS composites

Disilanol-POSS and trisilanol-POSS are white crystalline powders at room temperatures, with melting temperatures of 87 and 142°C, respectively. They are mixed in a molten state during polymerization. The melting, glass transition, and crystallization temperatures determined from heating and cooling scans of PET and PET/POSS composites are listed in Table II. The composite T_g values decrease slightly with increases in POSS concentration. It was found that

TABLE I
Characteristics of PET and PET/POSS Composites

| PET/POSS samples | M_w^a (g mol $^{-1}$) | Radius of gyration (nm) |
|-------------------------|-----------------------------|-------------------------|
| PET | 75,000 | 33 |
| Disilanolisobutyl-POSS | | |
| 1 wt % | 135,000 | 45 |
| 3 wt % | 139,000 | 34 |
| 5 wt % | 1,180,000 | 118 |
| Trisilanolisobutyl-POSS | | |
| 1 wt % | 24,000 | 12 |
| 3 wt % | 13,440,000 | 480 |
| 5 wt % | 16,500,000 | 543 |

^a Values measured by light scattering.

TABLE II
Thermal Properties of PET and PET/POSS Composites

| PET/POSS samples | T_g (°C) | T_m (°C) | T_c^a (°C) | T_d^b (°C) |
|-------------------------|------------|------------|--------------|--------------|
| PET | 80 | 248 | 176 | 396 |
| Disilanolisobutyl-POSS | | | | |
| 1 wt % | 72 | 249 | 173 | 406 |
| 3 wt % | 75 | 245 | 169 | 404 |
| 5 wt % | 70 | 244 | 187 | 403 |
| Trisilanolisobutyl-POSS | | | | |
| 1 wt % | 75 | 247 | 165 | 405 |
| 3 wt % | 72 | 248 | 189 | 404 |
| 5 wt % | 60 | 244 | 182 | 401 |

^a Crystallization peak temperature at a cooling rate of 20°C min⁻¹.

^b Values measured at 5 wt % of weight loss.

the incorporation of small amounts of less than 3–4 mol % POSS acts as an inert diluent, and actually reduces the glass transition temperature.²² Five weight percent of POSS used in this work corresponds to 0.5 mol %. The melting temperatures of the composites were very close to that of pure PET, and decrease slightly with POSS content. The PET crystallization temperature decreases up to 3 wt % disilanol-POSS and 1 wt % of trisilanol-POSS, and increases at 5 wt % disilanol-POSS and more than 3 wt % trisilanol-POSS. Very small amounts of POSS molecules incorporated into PET react with PET, resulting in decreases in the crystallization temperature due to the copolymerization effect. However, at higher concentrations, POSS molecules start to agglomerate and act as nucleating sites, so that the composite crystallization temperatures increase although the reaction between POSS molecules and PET occurs. As shown in Figure 2, the thermal stabilities are almost identical for both PET and PET/POSS composites. However, the decomposition

temperatures listed in Table II indicated a moderate increase in the thermal stability of the composites, with 5% weight loss of decomposition temperature increasing 5–10°C for all of the PET/POSS composites relative to PET. Schiraldi and coworkers²³ reported that heating trisilanol isooctyl-POSS to the PET processing temperature of 280°C under nitrogen results in production of a resinous organosilicate material, but no differences in thermomechanical properties of POSS-polymer composite are observed. Therefore, the slight increase in decomposition temperature under nitrogen may be due to the reaction between POSS molecules and PET.

Morphology

Figures 3 and 4 show the morphologies of PET/disilanol-POSS and PET/trisilanol-POSS composites with the POSS contents, respectively. The composites displayed heterogeneous morphology. The dispersed particles are attributed to POSS phases. PET/disilanol-POSS composite containing 1 wt % of disilanol-POSS showed uniform dispersion of disilanol-POSS, with sizes ranging from 30 to 40 nm. As for the 3 wt % disilanol composite, the sizes of POSS were almost the same as 1 wt % of POSS, but particles larger than 100 nm were also observed. At 5 wt % POSS loading, micron-sized rather than nanosized POSS particles were observed mainly because of agglomeration. In the case of the PET/trisilanol-POSS composite shown in Figure 4, a similar morphology was observed. POSS molecules tend to agglomerate in the polymer matrix due to POSS-POSS interactions, whose sizes range from a few hundreds of nanometers to a few microns. However, the size of the POSS particles in the composites containing 1 and 3 wt % POSS shown in Figures 3 and 4 are relatively

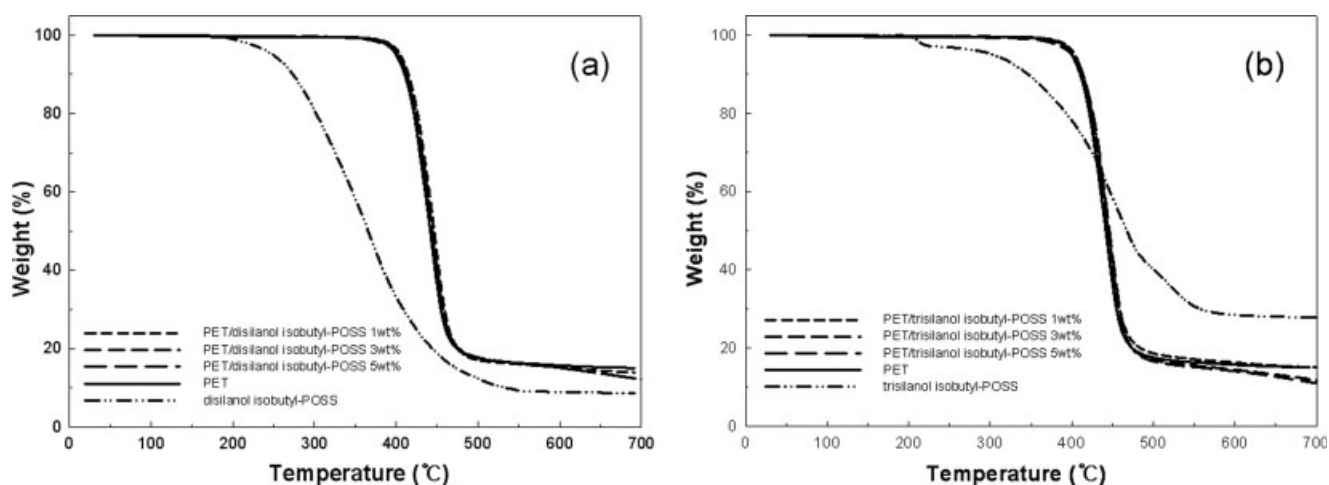


Figure 2 TGA curves of (a) disilanol-POSS and its composites and (b) trisilanol-POSS and its composites.

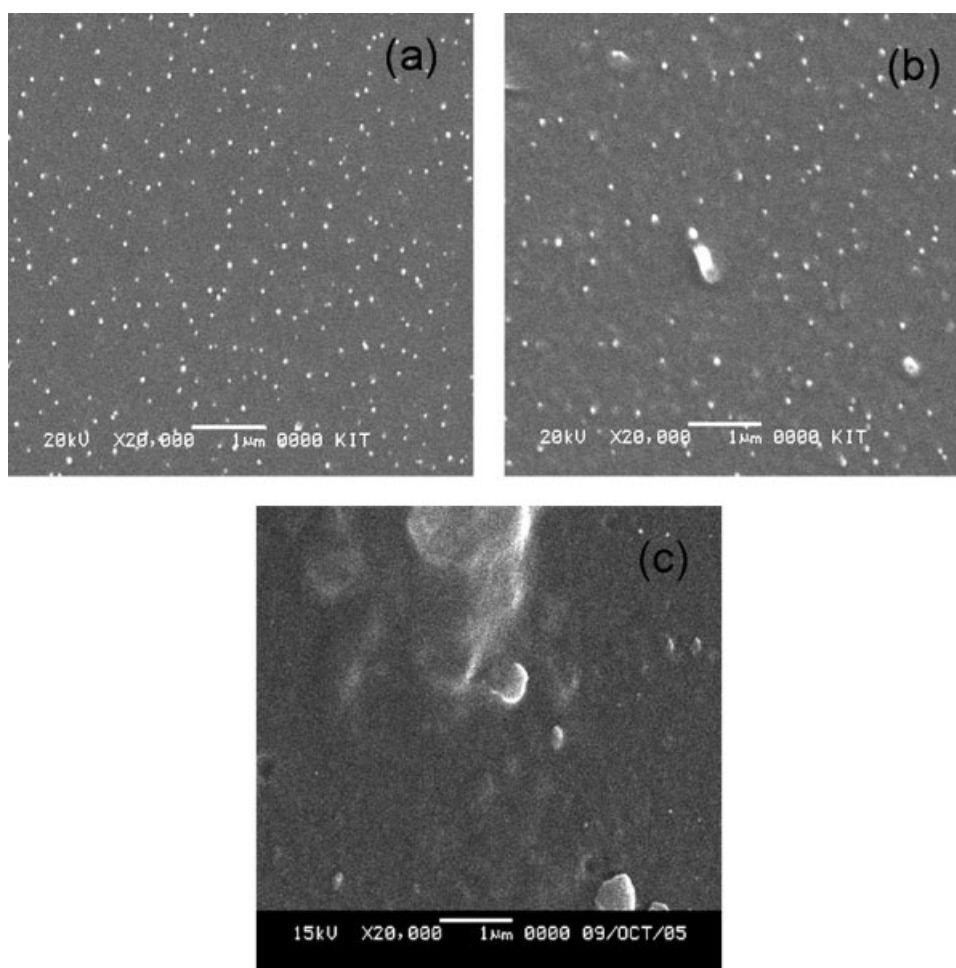


Figure 3 SEM micrographs of PET/disilanol-POSS composites containing (a) 1 wt %, (b) 3 wt %, and (c) 5 wt % of disilanol-POSS.

small. POSS used in this work has two and three hydroxyl groups in their structures, which react with PET. Therefore, it is believed that the small POSS particles in composites result from the reaction between hydroxyl groups in POSS and PET.

Rheological behavior of PET/POSS composites

The frequency dependence of complex viscosity and the plot of shear storage modulus G' vs. loss modulus G'' for PET/POSS composites are shown in Figures 5 and 6, respectively. The values were measured at 280°C. In terms of PET/disilanol-POSS composite, the incorporation of POSS leads to increases in complex viscosity, with increases in POSS content at low frequencies. However, the relative effect diminishes with increasing frequency due to shear thinning. The complex viscosity of PET/trisilanol-POSS composite shows similar behavior, although there was a slight difference in viscosity with POSS content.

It is well known that the interconnected structures of anisometric fillers result in a plateau region in $\log G'$ vs. $\log G''$ plots at low frequencies. Only composites containing 1 wt % disilanol- or trisilanol-POSS shows a plateau region (Fig. 6), which indicates strong interfacial interactions between PET and POSS. The rheological compatibility of polymer blends proposed by Han et al.²⁴ can be obtained by the plot of $\log G'$ vs. $\log G''$, which shows the composition-independent correlation for compatible systems. Figure 6 shows the composition-dependent correlation for PET/POSS composites, resulting in heterogeneous morphology, and the deviation from the compatibility increases with POSS content. The result is in agreement with the morphology, indicating fine dispersion for PET/POSS composites containing 1 wt % of POSS.

Tensile properties of PET/POSS composites

The tensile strength and modulus of PET and PET/POSS composites are shown in Figure 7. The

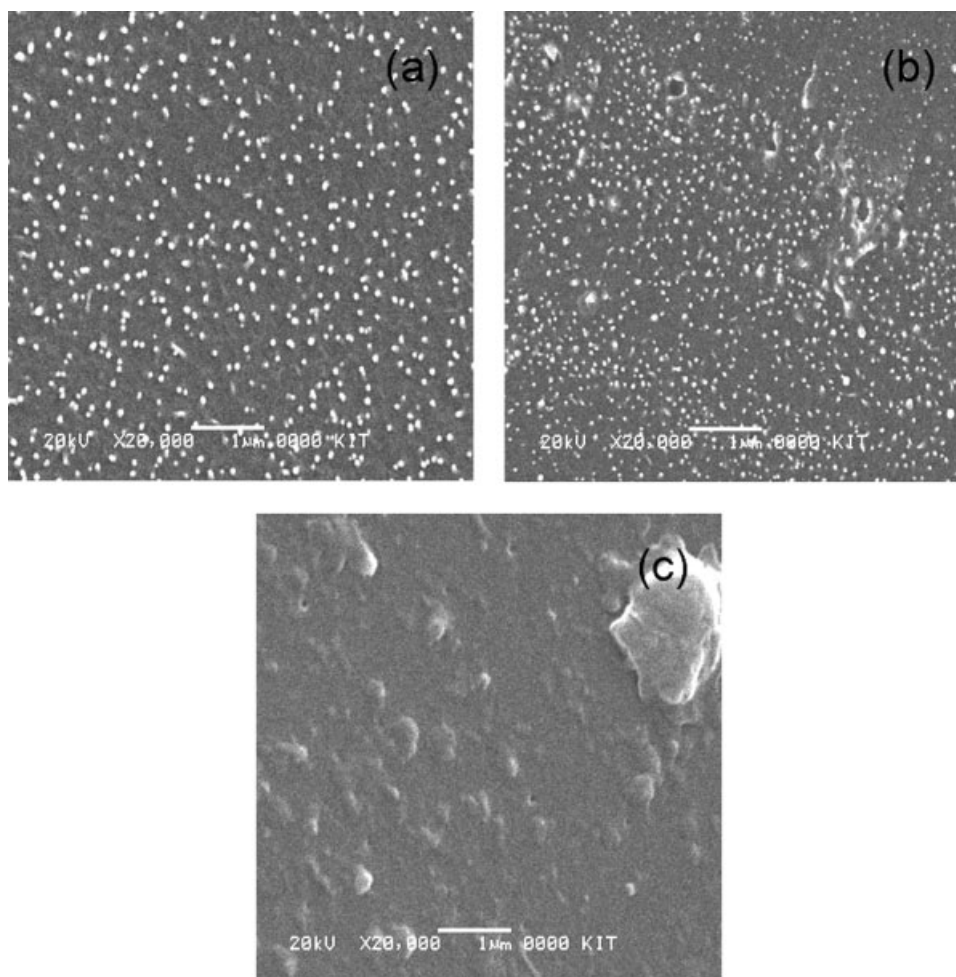


Figure 4 SEM micrographs of PET/trisilanol-POSS composites containing (a) 1 wt %, (b) 3 wt %, and (c) 5 wt % of trisilanol-POSS.

strength of PET/disilanol-POSS composites showed a 63% increase at 1 wt %, 18% increase at 3 wt %, and 82% decrease at 5 wt % as compared to PET.

The strength of PET/trisilanol-POSS composites showed a 41% increase at 1 wt %, 44% decrease at 3 wt %, and 85% decrease at 5 wt %. The modulus

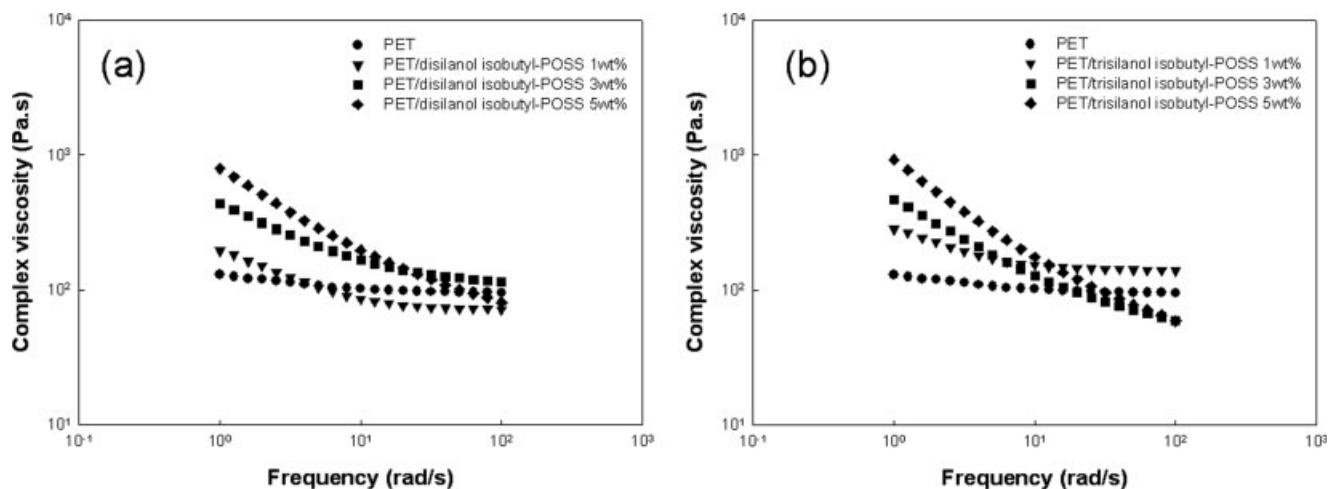


Figure 5 Complex viscosities of (a) PET and PET/disilanol-POSS composites and (b) PET and PET/trisilanol-POSS composites.

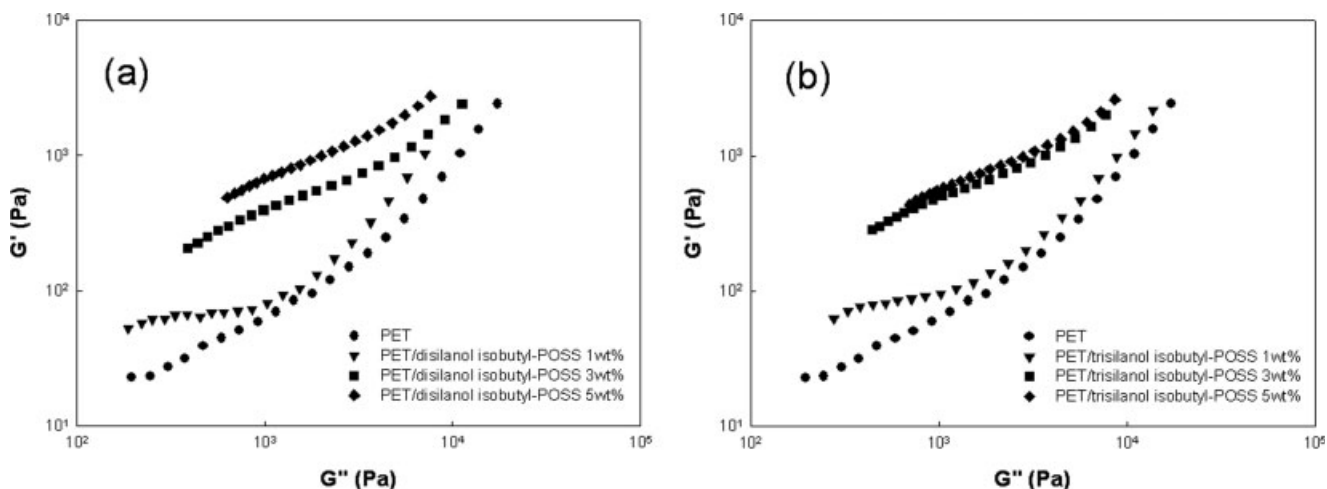


Figure 6 (a) G' vs. G'' for PET and PET/disilanol-POSS composites. (b) G' vs. G'' for PET and PET/trisilanol-POSS composites.

of PET/disilanol-POSS composites showed about 300% increase at 1 and 3 wt %, and 84% decrease at 5 wt % as compared to PET. The modulus of PET/trisilanol-POSS composites showed a 380% increase at 1 wt %, 36% increase at 3 wt %, and 40% decrease at 5 wt %. The modulus at 5 wt % becomes significantly smaller as larger POSS crystallites significantly weaken the material. The PET/POSS composites at 1 wt % loading of POSS showed the largest tensile strength and modulus because of the dominance of phase-separated crystallites with relatively small diameters ($d < 50$ nm).

CONCLUSIONS

In this study, the PET/POSS composites containing disilanol- and trisilanol-POSS were prepared by *in*

situ polymerization. Light scattering measurement of composites containing trisilanol-POSS showed a large radius of gyration, resulting from the gel formation by chemical crosslinking. The thermal properties of the composites were not different from that of PET, but the thermal decomposition temperature of the composites measured at 5 wt % weight loss showed an increase of 5–10°C. The morphology of the composites containing 1 wt % of disilanol- and trisilanol-POSS indicated fine dispersions of POSS, with sizes ranging from 30 to 40 nm, owing to the strong interfacial interaction between POSS and PET during polymerization. At higher concentrations of POSS, aggregates were observed. The morphology of 1 wt % PET/POSS composites was confirmed by rheological analysis, which showed a plateau region in the plot of $\log G'$ vs. $\log G''$, suggesting a strong

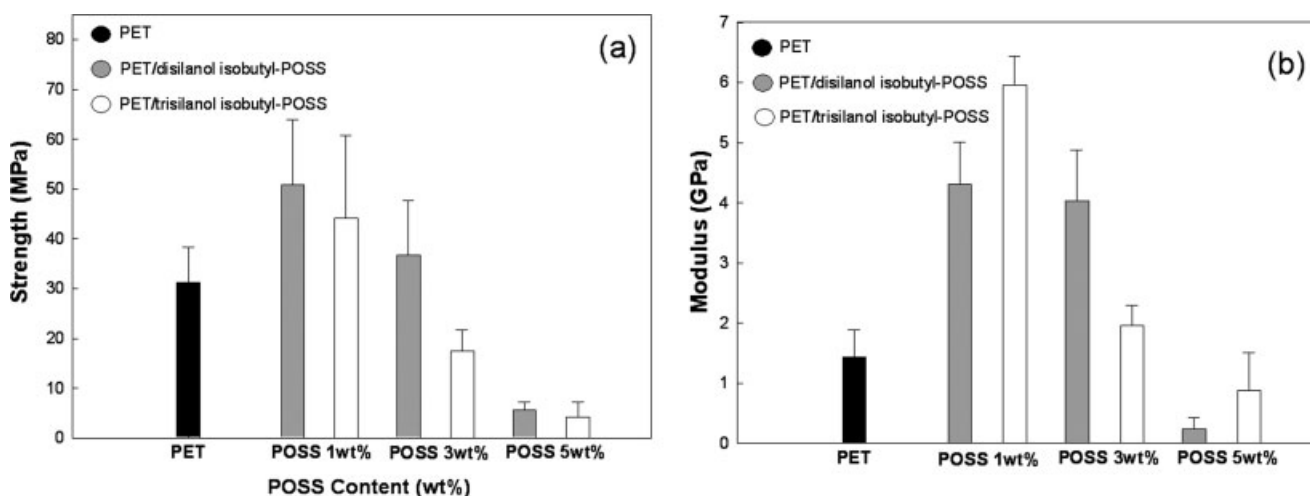


Figure 7 (a) Tensile strengths of PET and PET/POSS composites and (b) tensile moduli of PET and PET/POSS composites with increasing POSS content.

interfacial interaction between POSS and PET. Sixty-three percent and 41% increases in tensile strength and 300 and 380% increase in modulus were achieved in the composites containing 1 wt % of disilanol- and trisilanol-POSS, respectively.

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