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LETTER

Poly(ethylene terephthalate) and polyhedral oligomeric silsesquioxane nanohybrids and their physical characteristics

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Introduction

Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic polyester with a variety of applications such as fiber, bottles, films, and engineering plastics in automobiles and electronics because of its low cost and high performance [1, 2], whereas polyhedral oligomeric silsesquioxane (POSS) nanostructured chemicals, with their organic–inorganic hybrid nature, well-defined three-dimensional nanoscopic architecture, and monodisperse particle size, are the subject of intense research interest. Silsesquioxane is the term used for all structures with the formula $(RSiO_{1.5})_n$, where R is hydrogen or any alkyl, alkylene, aryl, arylene, or organofunctional derivative or alkyl, alkylene, aryl, or arylene group [3]. Silsesquioxanes may form ladder, cage, partial cage, and polymer structures [4, 5]. Among the various types of silsesquioxanes, the POSS cage consists of 8, 10, or 12 Si atoms, with an Si:O ratio of 2:3, Si–Si diameter of 0.54 nm and Si–C bond length in the range of 1.83–2.03 Å [3]. The cage can be functionalized with a wide range of organic substituents [6–8]. If the polymerizable R groups are selected properly [9–11], 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. Over the past decade, much of the research effort into POSS molecules has centered on the synthesis of homo- and block-copolymers with POSS as an integral part of the polymer chain [12–14], with fewer studies of POSS/melt blended nanocomposites being conducted [15, 16]. They reported that the incorporation of POSS could lead to substantial improvements in the polymer properties including increases in the operation temperature, oxidation resistance, surface hardening, and mechanical properties, as well as reductions in the flammability, heat evolution, and viscosity during processing [12–18]. Especially, Yoon et al. [17] reported that the tensile strength and modulus of the PET nanohybrids containing epoxy-functionalized POSS showed slightly higher values than PET despite the relatively small amounts (1 wt%) of POSS used. In addition, Kim et al. [18] studied the rheological behavior of PET/POSS nanohybrids prepared by the in situ polymerization. They reported that the observation of a plateau region of nanohybrids containing 1 wt% of POSS in the plot of G' versus log G'' indicates strong interfacial interactions between PET and POSS.

While much effort has been focused on the development of new POSS-containing nanohybrids, the thermodynamic interaction between the POSS and polymer matrix has never been studied. Therefore, in this study, we report the thermodynamic interaction of the binary components in nanohybrids, in which a few percent of POSS nanoparticles functionalized with octamethyl-, octaisobutyl-, or octaphenyl groups were incorporated into the PET matrix using the thermodynamic solubility parameter. The thermodynamic solubility parameters of PET and the functionalized POSS were evaluated, in order to derive the Flory–Huggins interaction parameter based on the method of Hoftyzer and van Krevelen [19]. We also analyzed the thermal and mechanical properties of the PET/POSS nanohybrids experimentally, in order to correlate them with the theoretical results.

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Experimental

PET ($M_w = 50000$ g/mol) was purchased from Aldrich Chemical Co. The POSS nanoparticles, octamethyl-POSS ($C_8H_{24}O_{12}Si_8$, Fw = 536.96, denoted as OM), octaisobutyl-POSS ($C_{32}H_{72}O_{12}Si_8$, Fw = 873.60, denoted as OB), and octaphenyl-POSS ($C_{48}H_{40}O_{12}Si_8$, Fw = 1033.53, denoted as OP), were purchased from Hybrid Plastics Inc. The nanohybrids of the PET and POSS derivatives were prepared by the melt mixing method. Initially, PET was introduced into a torque rheometer (Plastograph EC, Brabender) and melted at 255 °C for 10 min with a rotary speed of 60 rpm. POSS was then added to the melted PET and compounded for 15 min to the concentrations of 0.5, 1, and 2 wt%. The thermal stability was measured using a TGA (Q50, TA Instruments), by heating to 700 °C at a heating rate of 20 °C/min with air purging. In order to measure the mechanical properties, the PET/POSS nanohybrid films were subjected to uniaxial elongation at room temperature using a UTM (Hounsfiled Test Equipment, UK), with a typical sample dimension of 10 mm (wide) × 50 mm (length) × 0.1 mm (thickness).

Results and discussion

The PET nanohybrids were characterized on the nanometer scale using a FE-TEM. As shown in Fig. 1, the FE-TEM images of both PET/OB-POSS and PET/OP-POSS nanohybrids showed dark zones that coincided with the POSS-rich zones due to the higher electron density of silicon atoms. A uniform and fine dispersion of POSS in the PET matrix was also observed.

The determination of the thermodynamic interaction parameter between polymer and nanoparticles is crucial to understand their compatibility in polymer nanohybrids. Of the several methods which can be used to measure the thermodynamic interaction parameter [19, 20], the solubility parameter, δ, which is the square root of the cohesive energy density (the energy of vaporization per unit volume), was used to predict the thermodynamic interaction between the PET and POSS derivatives in this study. Since it is not possible to obtain their molar vaporization energies, calculations based on group contributions are used for the solubility parameters of the polymer.

In general, the Small and Hoy method is used to calculate the solubility parameter due to its simplicity. However, it assumes that no specific forces such as the dispersion force, polar force, and hydrogen bonding are active between the structural units of the substances involved. Therefore, the Small and Hoy method is not suitable for crystalline polymers. In this study, we calculated the solubility parameters of the PET and POSS-derivatives on the basis of Eqs. 1 and 2, using the Hoftyzer and van Krevelen method [19].

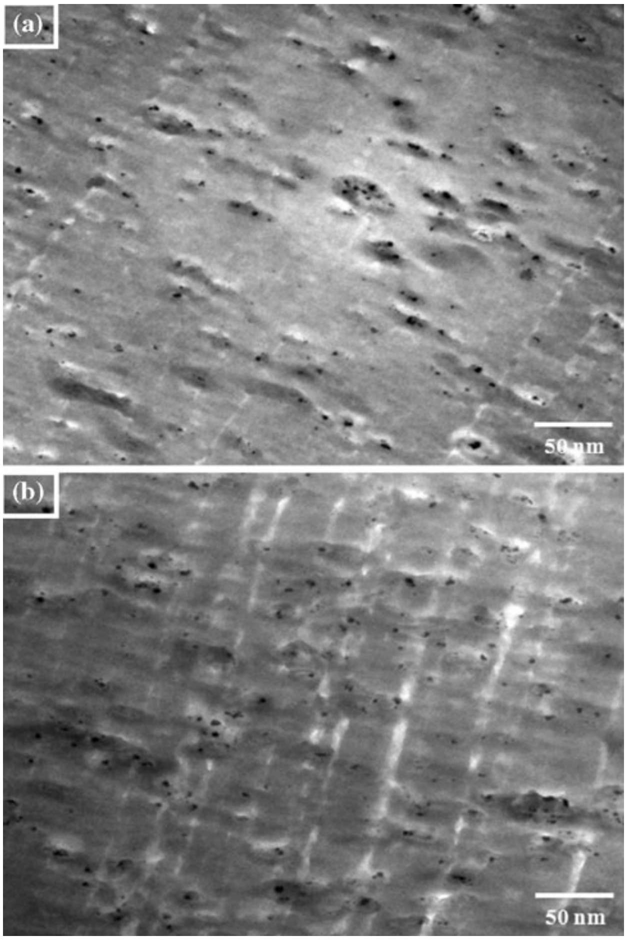

Fig. 1 FE-TEM images of **a** PET/OB-POSS and **b** PET/OP-POSS nanohybrids. The POSS content was fixed at 0.5 wt%

$$\delta_d = \frac{\sum F_{di}}{V}, \quad \delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V}, \quad \delta_h = \sqrt{\frac{\sum E_{hi}}{V}} \tag{1}$$

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{2}$$

where δ_d, δ_p, and δ_h are the dispersion, polar, and hydrogen bonding components of the solubility parameter, respectively. F_{di} and F_{pi} are the dispersion and polar portions of the molar attraction constant, respectively. The F-method is not applicable to the calculation of δ_h. It has already been stated by Hansen that the hydrogen bonding energy E_{hi} per structural group is approximately constant. This leads to the form of Eq. 1 presented above. To calculate the solubility parameters of the PET and POSS by the Hoftyzer and van Krevelen method, two assumptions were made. POSS is inherently an organic/inorganic hybrid, and it is commonly believed that the inorganic part of POSS does not react completely with the organic material. Thus, it is assumed that the functional group in the outer part of POSS

Table 1 Thermodynamic solubility parameters of PET and POSS-derivatives

	F_d ($J^{1/2}$ $cm^{3/2}$/mol)	F_p ($J^{1/2}$ $cm^{3/2}$/mol)	E_h (J/mol)	V (cm^3/mol)	δ_d	δ_p	δ_h	δ ($J^{1/2}/cm^{3/2}$)
PET	390	490	7000	23.7	16.46	20.68	17.19	17.91
OM	420	0	0	21.55	19.49	0	0	19.49
OB	1190	0	0	68.21	17.45	0	0	17.45
OP	1430	110	0	74.52	19.19	1.48	0	19.25

dominates the solubility parameter and, consequently, the inorganic part including the siloxane bonding of POSS is excluded from the calculation of the solubility parameter.

The calculated solubility parameters for the PET and POSS-derivatives are shown in Table 1. It can be seen in Table 1 that for the PET and POSS derivatives in this study, the maximum difference in the solubility parameters ($\delta_A - \delta_B$) showed the lowest value in the case of POSS functionalized with the isobutyl group. This can be explained by Eq. 3, which interrelates the Flory–Huggins parameter terms [19, 21]. The Flory–Huggins interaction parameter has been one of the most widely used quantities, since it can characterize a variety of polymer/solvent, polymer/polymer, and polymer/nanoparticle interactions [22].

$$\chi_{AB} = \frac{V_r}{RT}(\delta_A - \delta_B)^2 \qquad (3)$$

where χ_{AB} is the Flory–Huggins interaction parameter of polymer A and POSS B, R and T are the gas constant and temperature, respectively, and V_r is the reference volume, which is the molar volume of the smallest repeat unit.

The maximum difference in the solubility parameters between PET and OB-POSS was calculated to be 0.46 $J^{1/2}/cm^{3/2}$, which was much smaller than that for PET/OM-POSS (1.58 $J^{1/2}/cm^{3/2}$) and PET/OP-POSS (1.34 $J^{1/2}/cm^{3/2}$). Hence, the interaction between PET and OB-POSS is expected to be more thermodynamically favorable than the others. In addition, it can be also noted that the interfacial interaction between POSS and PET is considered to be a physical interaction of van der Waals attractive force which is more strongly related to the dispersion bonding component in Table 1.

We also analyzed the thermal and mechanical properties of the PET/POSS nanohybrids experimentally, in order to correlate the theoretical and experimental results. The thermal degradation of the neat PET and PET/POSS nanohybrids containing 0.5 wt% of POSS-derivatives is illustrated in the TGA curves in Fig. 2.

Figure 2 clearly shows that there is a moderate increase in the thermal stability of the PET/POSS nanohybrids compared to the neat PET. Interestingly, the TGA trace recorded for the PET/OB-POSS nanohybrids shows that the onset of degradation is about 10 °C higher than that of the neat PET. This may be due to the fact that the oxidation of the long alkyl-substituted POSS in air takes place on the organic chains and leads to the cross-linking of the cage, producing a ceramic silica-like phase [23–25].

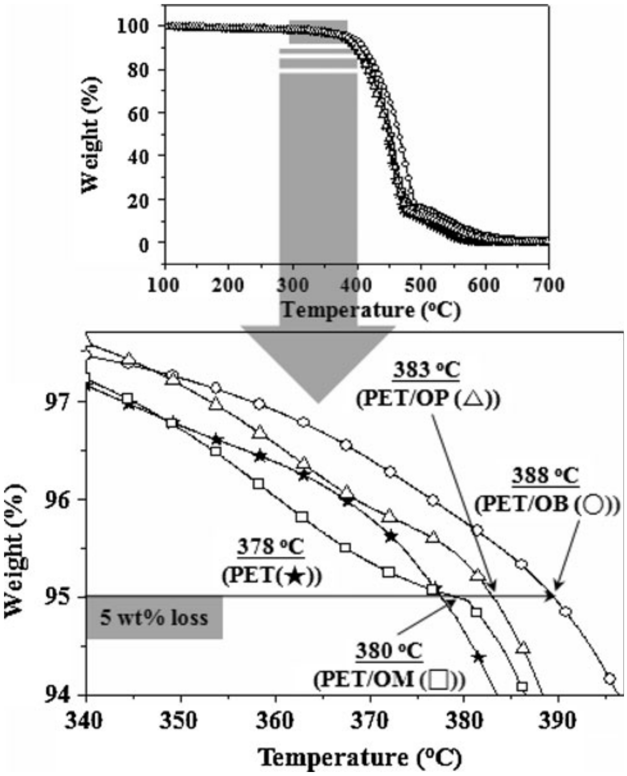

Fig. 2 TGA thermograms of the neat PET and PET/POSS nanohybrids. The POSS content was fixed at 0.5 wt%

In addition, we measured the mechanical properties, such as the tensile strength and elongation at break, of the PET/POSS nanohybrids. Being independent of the type of POSS, the mechanical properties of the nanohybrids were higher than those of the neat PET, as shown in Figs. 3 and 4. These results show that the proper incorporation of POSS can effectively enhance the mechanical properties of PET resin [26, 27]. In addition, we observed that the maximum tensile strength and elongation at break were obtained in the case of the PET/OB-POSS nanohybrid, indicating that the interaction between PET and the long alkyl-substituted POSS is more favorable than that in PET/OM-POSS and PET/OP-POSS. These results corresponded

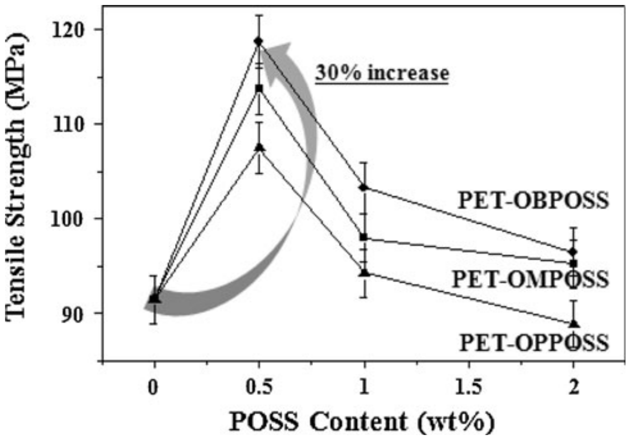

Fig. 3 Tensile strength of the neat PET and PET/POSS nanohybrids

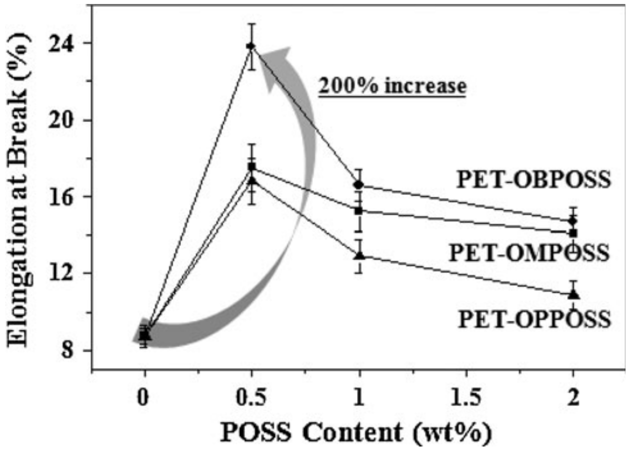

Fig. 4 Elongation at break of the neat PET and PET/POSS nanohybrids

well with the results based on the thermodynamic solubility parameters.

Conclusions

PET nanohybrids containing three different POSS (OM-POSS, OB-POSS, and OP-POSS) were fabricated via a melt mixing method, and their physical properties were investigated. Maximum difference of solubility parameter values were calculated to be 1.58, 0.46, and 1.34 $J^{1/2}/cm^{3/2}$ for PET/OM-POSS, PET/OB-POSS, and PET/OP-POSS, respectively, suggesting that thermodynamic interaction between PET and OB-POSS was the most favorable. Thermal and mechanical properties of the PET/POSS nanohybrids match with corresponding thermodynamic solubility parameters.

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