

High-Modulus Poly(ethylene terephthalate)/Expandable Fluorine Mica Nanocomposites with a Novel Reactive Compatibilizer

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One of the major advantages of polymeric materials over inorganic ones such as metals or ceramics is their lower specific gravity. Substitution of the latter by the former is promoted not only by economic reasons but also from an environmental point of view. To improve the inferior mechanical and thermal properties of the polymeric materials, compounding with inorganic fillers and fibers has been carried out.¹ However, when the inorganic additives were increased, the specific gravity also increased while better performance could be achieved. Compounding on the order of nanometers, so-called *nanocomposites*, is expected to avoid such a conflict. Many studies on polymer–clay nanocomposites have demonstrated that the low inorganic content of a few weight percent can result in significant improvements in stiffness, strength, thermal stability, and gas barrier properties and fire retardance.^{2–6}

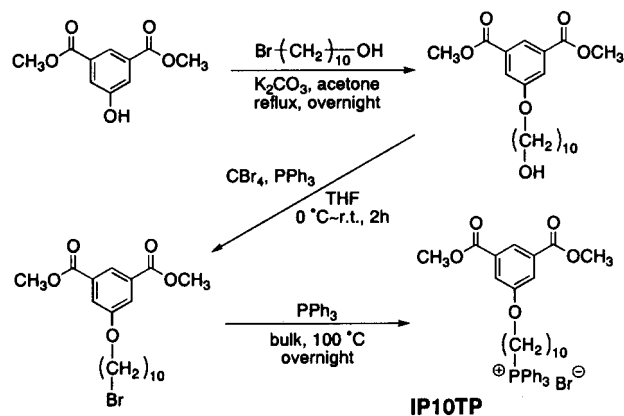
Poly(ethylene terephthalate) (PET) has found a variety of applications such as fibers, bottles, films, and engineering plastics for automobiles and electronics because of its low cost and high performance.⁷ The primary objective of the development of PET–clay nanocomposites was to improve the gas barrier property that is required for beverage and food packagings.⁸ Another expectation for PET–clay nanocomposites is to be an alternative to the glass-fiber reinforced PET. Recently, several researchers reported PET–clay nanocomposites. Ke et al. dispersed organically modified

montmorillonite in PET.⁹ Complete delamination was not achieved, but the tensile modulus of the nanocomposites increased as much as 3 times over that of pure PET. Tsai et al. reported nanocomposites of PET and clay by utilizing an amphoteric surfactant and an antimony acetate catalyst.^{10,11} Their nanocomposites showed higher flexural strength and modulus than pure PET with 3 wt % loading of the silicate.

It has been traditionally recognized that stress transfer from the matrix to the reinforcement is essential for accomplishing high stiffness in composite materials.¹² Likewise, to accomplish high mechanical performance using nanocomposites, both sufficient exfoliation of the clay and strong adhesion of the polymer matrix to the layered silicate must be achieved. In the case of nylon–clay nanocomposites, nylon can strongly adhere to the silicates through ionic and hydrogen bonds.² Compared to this, PET is less polar and cannot be expected to have an interaction like nylon. Therefore, the PET main chain must be tethered in some sense to the silicate layer to achieve a high mechanical performance. In this study, we developed a novel compatibilizer that connects PET through covalent bonds and the layered silicates through ionic bonds. To design the compatibilizer suitable for the PET–clay nanocomposites, we set the following conditions: (1) It possesses functional groups that can react with PET by transesterification. (2) It possesses a cationic group that can interact with the negatively charged silicate layer. (3) It should be stable at the polymerization temperature of PET (275 °C). To satisfy condition (1), we chose the dimethyl isophthalate group, and for conditions (2) and (3), the triphenylphosphonium group was selected. Expandable fluorine mica (ME)¹³ was used as the layered silicate. The two-dimensional size of ME was about 6 μm and the cation-exchange capacity of ME was 1.2 mmol/g.

The synthetic route of the designed reactive compatibilizer, 10-[3,5-bis(methoxycarbonyl)phenoxy]decyltriphenylphosphonium bromide, which is abbreviated as IP10TP hereafter, is shown in Scheme 1.¹⁴ The inter-

Scheme 1



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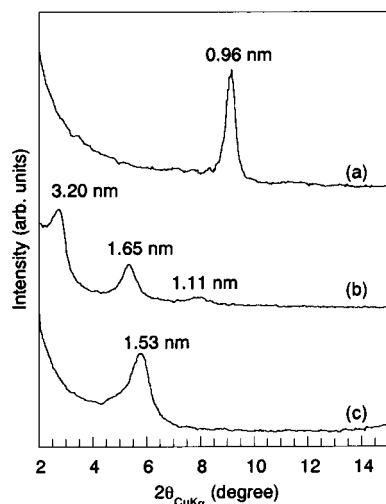


Figure 1. X-ray diffraction patterns: (a) completely dried expandable fluorine mica (ME); (b) IP10TP/ME cation-exchanged compound (IP10TP/ME = 1.2 mmol/g); (c) PET/IP10TP/ME nanocomposite (ME/BHET = 2/100 (w/w) and IP10TP/ME = 1.2 mmol/g).

calation of IP10TP into ME with various proportions of IP10TP was carried out by the cation-exchange reaction. To the solution of IP10TP (0.12–1.20 mmol) in a methanol–water mixture (67 and 100 mL, respectively) was added a 1 wt % ME dispersion in water (100 g). The resulting mixture was stirred at room temperature for 1 day, followed by centrifugation (6000 rpm, 20 min) and drying under vacuum. The thermogravimetric analysis of the silicate contents of the IP10TP/ME compounds indicated that the cation-exchange reaction took place as quantitatively as expected from the feed ratio of IP10TP to ME. In the X-ray diffraction (XRD) patterns (Figure 1), it was observed that the peak corresponding to the basal spacing of 0.96 nm for unmodified ME (1a) completely disappeared in the fully cation-exchanged compounds (1b). The reflections for the fully cation-exchanged compound produced the series of 00/ lines at 3.20, 1.65, and 1.11 nm, and an average basal spacing was 3.28 nm. According to the molecular modeling of IP10TP, and assuming a double molecular layer in the interlayer, the basal spacing of the fully cation-exchanged compound was estimated to be 4.8 nm. The observed value was shorter than the estimated one. It is considered that the IP10TP in the interlayer is tilted from the ideal model structure. The details of the structure of the IP10TP/ME intercalation compounds will be discussed separately.¹⁵ At least, it can be said that the cation-exchange reaction took place, and the compatibilizer was intercalated in the interlayer of the layered silicates.

PET/IP10TP/ME nanocomposites were prepared by the polymerization of bis(2-hydroxyethyl)terephthalate (BHET) in the presence of the IP10TP/ME intercalation compounds. The mixture of BHET and IP10TP/ME compounds were reacted in the presence of Sb_2O_3 (0.025 mol % to BHET) at 275 °C under vacuum (<0.1 Torr) for 3 h. A typical XRD pattern of the PET/IP10TP/ME composites is shown in Figure 1c. In all the samples,

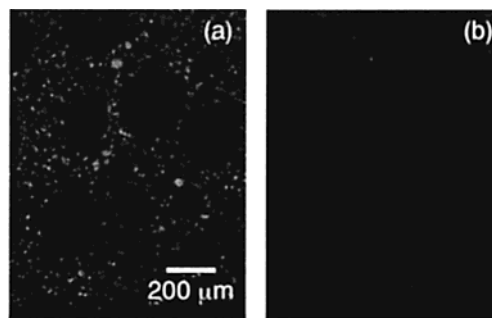


Figure 2. Images observed using a polarization microscope at 280 °C under cross nicol conditions (magnification $\times 100$): (a) PET/ME: ME/BHET = 2/100 (w/w); (b) PET/IP10TP/ME: ME/BHET = 2/100 (w/w) and IP10TP/ME = 1.2 mmol/g.

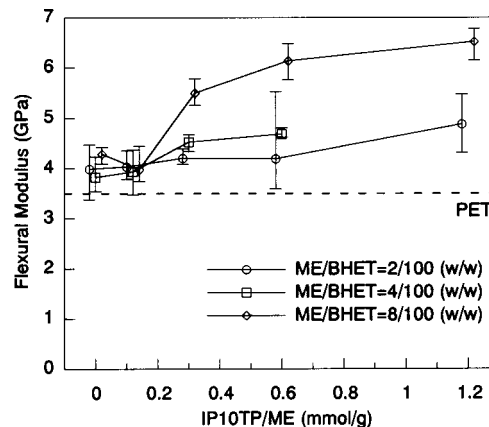


Figure 3. Flexural modulus of PET/ME and PET/IP10TP/ME composites as a function of the amount of IP10TP in the starting IP10TP/ME intercalation compounds with the changing ME contents.

the peak around 1.5–1.6 nm was still observed. Unfortunately, the exfoliation of the silicate layer in the PET matrix seemed to be unsatisfactory under the present reaction conditions. However, on the basis of the observations using a polarization microscope, it was confirmed that the dispersibility of ME in the PET matrix was improved by the utilization of IP10TP (Figure 2). In the PET/ME composite without IP10TP, many particles of layered silicates were observed. On the other hand, no particles could be observed in PET/IP10TP/ME, suggesting that the number of stacks of the silicate layers decreased as a result of the delamination. To confirm the reaction between IP10TP and BHET, solid-state ^{13}C NMR (CP/MAS) measurement was carried out. The mixture of BHET (0.88 g, 3.46 mmol), IP10TP/ME compound (1.2 mmol/g, 0.50 g, 3.46 mmol equivalent of IP10TP), and Sb_2O_3 (2 mol % to BHET) was heated at 250 °C for 3 h, and ^{13}C NMR spectra before and after the reaction were compared to each other. After the reaction, peaks corresponding to the methyl group of IP10TP (53 ppm) and the hydroxyethyl group of BHET (61 and 68 ppm) disappeared, and a new peak of the ethylene unit of PET (64 ppm) was observed.¹⁶ It was confirmed that the covalent bonds between IP10TP and BHET were actually formed by the reaction between IP10TP/ME compound and BHET. The flexural moduli of the PET/IP10TP/ME composites are plotted in Figure 3 versus the IP10TP/ME ratio with changing ME/BHET

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ratio. The flexural modulus of PET itself is also shown as a dotted line. The flexural moduli of the PET/ME composites without IP10TP were about 10% higher than that of PET. There was only a slight effect of the ME content on the flexural moduli in the absence of IP10TP. In this case, the dispersibility of ME in PET is quite low and there is no strong interaction between PET and the silicate layer. Therefore, only a small reinforcement effect can be obtained. In contrast, the reinforcement was remarkably improved by employing IP10TP as the compatibilizing agent. With an increasing amount of IP10TP in the starting cation-exchanged compounds, the flexural moduli of the composites increased up to about 170% of PET at its maximum. These observations supported the fact that both the better dispersion of the silicate layer in PET and the strong interaction between PET and the silicate layer are essential for achieving such high modulus PET/layered silicate nanocomposites.

In summary, we have demonstrated that the employment of the novel reactive compatibilizer gave PET/layered silicate nanocomposites with a high modulus. Not only the dispersibility of the layered silicates but the interaction between the polymeric matrix and the

layered silicate is crucial for improving the mechanical properties of the nanocomposites. Efforts to clarify the effect of the structure of the compatibilizer on the mechanical, thermal, and other properties of the composites as well as to develop a better process to achieve further dispersion of ME in PET are in progress.

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Supporting Information Available: Experimental procedures for the synthesis of IP10TP and details of the measurements, the solid-state ^{13}C NMR spectra of the mixture of BHET, IP10TP/ME compound, and Sb_2O_3 before and after the heating at 250 °C (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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