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Poly(butylene terephthalate) Nanocomposites Prepared by in-Situ Polymerization

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Introduction. In our previous research,[1−4] cyclic poly(butylene terephthalate) oligomers, c-PBT, were successfully polymerized to a high molecular weight PBT employing the advantages of the low viscosity (17 cP) of c-PBT oligomers and lack of chemical emissions during polymerization. In this research, we intend to ascertain the possibility of producing high-performance nanocomposites of PBT and organically modified clay, using c-PBT oligomers as low-viscosity precursors. Structurally, two idealized polymer/clay nanocomposites are possible:[5−10] intercalated and exfoliated. Intercalation occurs from a penetration of polymer chains into the silicate layers of the clay and subsequent expansion of the clay interlayers, increasing the *d* spacing[6,8,11−13] of the silicate layers. Exfoliation involves an extensive polymer penetration into the silicate, resulting in a random dispersion of clay layers in the polymer matrix. The random dispersion of clay layers is the key to property enhancement such as better thermal stability, higher mechanical properties, and greater resistance to flammability.[14−17] Whether a mixture of polymer and organoclay produces intercalated or exfoliated nanocomposites depends on the characteristics of the polymer matrix and the organoclay. Here, c-PBT oligomers are successfully intercalated in the clay layers prior to the in-situ polymerization because of their low molecular weight [$M_w = (220)n$, $n = 2−7$]. Subsequent polymerization could result in an exfoliated nanocomposite by tailoring the interactions between c-PBT oligomers, organoclays, and the clay surface. In this work, we produce an exfoliated or intercalated−exfoliated PBT/clay nanocomposite by in-situ polymerization in the presence of cyclic stannoxane catalyst and sodium montmorillonite modified by dimethyl dihydrogenated tallow ammonium ions. In the first instance, we have tried to make PBT/clay nanocomposites by dissolving c-PBT oligomers, organoclay, and catalyst in a suitable solvent so that clay layers would be delaminated prior to the polymerization, resulting in an exfoliated structure. Unlike other systems,[10,18−20] this is a demonstration of in-situ polymerization where the organoclay has been swollen in a catalyst solution first, rather than a monomer (here c-PBT oligomer) solution (usually catalyst/c-PBT (wt/wt) = 2.6/1000), so that catalyst can be intercalated within clay layers for the polymerization reaction to occur inside clay galleries.

Experimental Section. a. Materials. Cyclic oligomers of poly(butylene terephthalate) [molecular weight $M_w = (220)n$, $n = 2−7$][21] (CAS # 24968-12-5) and cyclic stannoxane (I) catalyst were provided by Cyclics Inc.,

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New York.[22] An organophilic clay Cloisite 20A (20A), a sodium montmorillonite modified by dimethyl dihydrogenated tallow ammonium, was purchased from Southern Clay Products.[22] An antioxidant Irganox 1010 [butylated hydroxytoluene, 2,6-di-*tert*-butyl-*p*-cresol] was procured from Aldrich.[22]

(I)
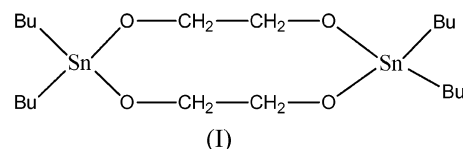
b. Synthesis. *Preparation of Mixture of Oligomer and Clay.* The required amount of organically modified clay, 20A (previously dried in a vacuum oven below 80 °C for 12 h), was swollen under constant stirring for about 20 h at 80 °C in a solution of catalyst cyclic stannoxane and antioxidant, Irganox 1010, in a round-bottom flask equipped with a magnetic stirring bar and sealed with rubber septa. 0.01 g (0.017 mmol) of cyclic stannoxane (0.2 wt % of c-PBT oligomers) and 0.01 g Irganox 1010 were dissolved in toluene at around 80 °C prior to the incorporation of clay into the round-bottom flask. 2 g of c-PBT (previously dried in a vacuum oven below 80 °C for 12 h) was allowed to dissolve in toluene at above 80 °C in a vial and then incorporated into a round-bottom flask, which contained clay and catalyst, under constant stirring. The stirring was continued for another 20 h at above 80 °C. The solution was cooled to room temperature, the solvent was evaporated, and finally the mixture was vacuum-dried at 80 °C. This mixture was ready for the in-situ polymerization. A small amount of this mixture (prior to polymerization) was made into a pellet for XRD measurement to determine any increment in the *d* spacing of the nanoclay layers. Samples are marked as 20A2%M, 20A4%M, and 20A6%M respectively for 2, 4, and 6 wt % modified clay in the mixture.

In-Situ Polymerization of c-PBT. The polymerization of c-PBT was conducted directly on the above dried mixture in a vial at 190 °C for 6 min under sealed conditions. This sample was directly analyzed by XRD and thermal analysis. To investigate the orientation of the clay layers in the polymer matrix in the in-situ polymerization, samples were prepared in a Carver press at 190 °C for 6 min between two Kapton films before being pressed into film (∼0.8−1 mm thick). The press was then cooled to room temperature by circulating tap water through two hot plates. According to the weight percent of the organoclay in the nanocomposites, polymerized samples were marked as 20A2%P, 20A4%P, and 20A6% P.

c. Characterization. *X-ray Diffraction (XRD).* X-ray diffraction data were collected on a D500 Siemens diffractometer using Cu Kα (40 kV, 35 mA) radiation and a nickel filter. The spectra were recorded in the 2θ range from 2° to 40° in steps of 0.1° and a counting time per step of 1 s.

Transmission Electron Microscopy (TEM). To prepare specimens for TEM, a small sample was microtomed using a Leica Ultracut Cryo-ultramicrotome with a Diatome diamond knife at a sample temperature of −60 °C to obtain ultrathin (about 40−100 nm) sections. The
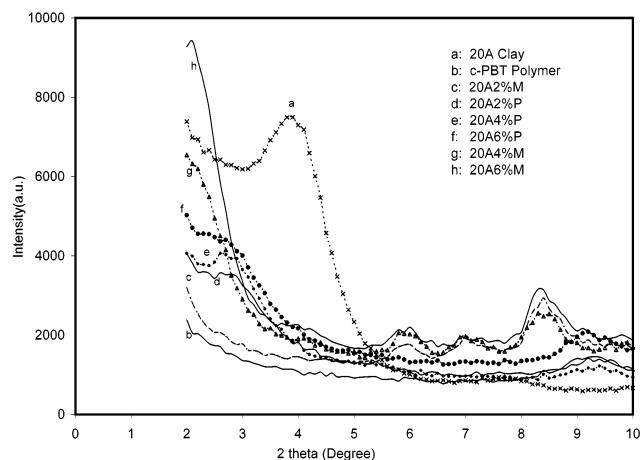
Figure 1. X-ray diffraction patterns of mixtures and composites.

Figure 2. Thermogram of various nanocomposites in a nitrogen atmosphere.

sections were not treated by any staining procedure since there was enough mass thickness contrast between the clay layers and the polymer matrix. Clay layers consisting of silicon atoms appear dark due to less electron scattering whereas the regions corresponding to the polymer matrix look bright relative to the clay layers in TEM micrographs. TEM imaging was performed on a JEOL 100 CX operated at 100 kV accelerating voltage.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis was carried out using a TA Instruments TGA 2050 thermogravimetric analyzer with a heating rate of 20 °C/min from room temperature to 600 °C under a nitrogen atmosphere.

Results and Discussion. The X-ray diffraction curves of the 2–6 wt % organoclay/c-PBT mixtures, both before and after polymerization, are presented in Figure 1. None of the mixtures shows a peak between $2\theta = 2°$ and 10° in comparison with the diffraction peak at $2\theta = 4.7°$ for the 20A clay. This indicates the presence of exfoliated silicate layers of organoclay dispersed in the c-PBT matrix. However, when the mixture is polymerized, a small peak at $2\theta = 2.3°$ appears for the 20A6%P sample, corresponding to a d spacing (d_{001}) of 3.7 nm, which is higher than that of the organoclay 20A ($d_{001} = 2.2$ nm). This implies that a small amount of the organoclay is not exfoliated in the PBT, and it exists in the form of an intercalated layered structure. It is very interesting that intensity of the diffraction peak corresponding to 2θ has drastically been reduced in all ratios of nanocomposites (Figure 1). We also observed that the XRD along the edge of the compressed polymeric film of the 20A6%P does not show the diffraction pattern of a crystalline material, indicating no further orientation of the clay layer but an exfoliated–intercalated structure. Details of the nanostructure can be understood from the TEM micrographs of the respective samples.

The thermogravimetric analysis of nanocomposites (Figure 2) indicates better thermal stability of 20A2%P than its corresponding polymer without clay. There is an almost 8–10 °C increment in the onset temperature of degradation of 20A2%P compared with the c-PBT polymer without any clay. This observation is very much consistent with other reported nanocomposite systems.[15,16] It means that a mere 2 wt % of nanoclay is capable of improving the thermal stability of the PBT. In fact, with the increase of the organoclay percentage
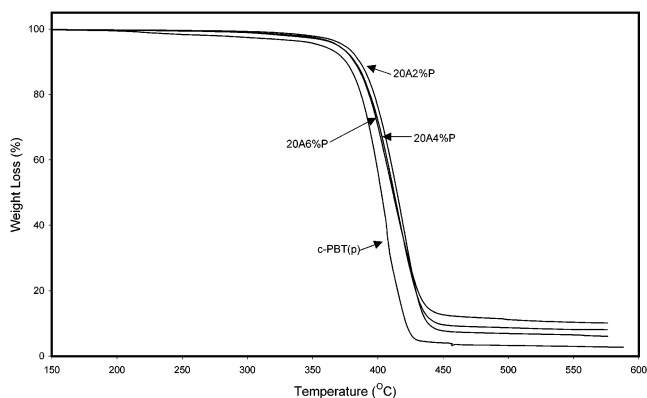
in the nanocomposites the thermal stability decreases slightly (Figure 2) in a nitrogen atmosphere.

Further evidence of the nanometer-scale dispersion of silicate layers in the PBT/clay is provided by the TEM micrographs, as shown in Figure 3a–c. In Figure 3a, we observe a nanoscale pattern of the matrix of c-PBT polymer, which confirms a smooth background of crystals originating from the PBT host. Individual silicate layers, along with two, three, and sometimes more layers stacked together, are observed to be well dispersed in the PBT host matrix (20A6%M) in Figure 3b. Here, the darker lines are clay layers and the polymer matrix is brighter. A few multilayer tactoids also exist; mostly single clay layers are observed, but there are no large, undispersed clay tactoids. This indicates that the 20A organoclay is well dispersed and exfoliated in the c-PBT host before polymerization, and that is why X-ray diffraction shows no peak, 2θ, corresponding to dispersed clay (Figure 1). The individual silicate layers have an original thickness of ∼1 nm and average length of ∼100–150 nm,[23] connected through their edge and changed to an average ∼5 nm thickness and a length of ∼100–200 nm in 20A6%M, exhibiting an orientation in the same direction throughout the matrix (Figure 3b). Figure 3c shows both elements of exfoliation and intercalation of the clay layers of 20A6%P. The clay layers are observed to be better oriented than in 20A6%M. But still, clay stacks are visible in abundance. There are few aggregates but mostly well-dispersed clay layers due to disruption of clay tactoids (originally present in the 20A6%M) located along with polymer matrix in 20A6%P, which is reflected in the X-ray diffraction of the increment of the d spacing in comparison to the original clay (Figure 1). The average thickness of the clay stacks ∼7 nm and the length ∼100–200 nm are observed in the after polymerization case. As a whole, the nanoclay has been dispersed in the polymer matrix with orientation and a few aggregates. Given these observations, they should probably be defined as exfoliated–intercalated nanocomposites.[18]

There are two possible ways of ordering of polymer chains inside the silicate galleries: as the temperature increases near about 160 °C (softening range of c-PBT), c-PBT oligomers tend to melt, and already dispersed clay layers have enough time to aggregate prior to the polymerization. Once the polymerization starts, the movement of clay layers would be restricted, and perhaps, that is the reason for having a few aggregates,
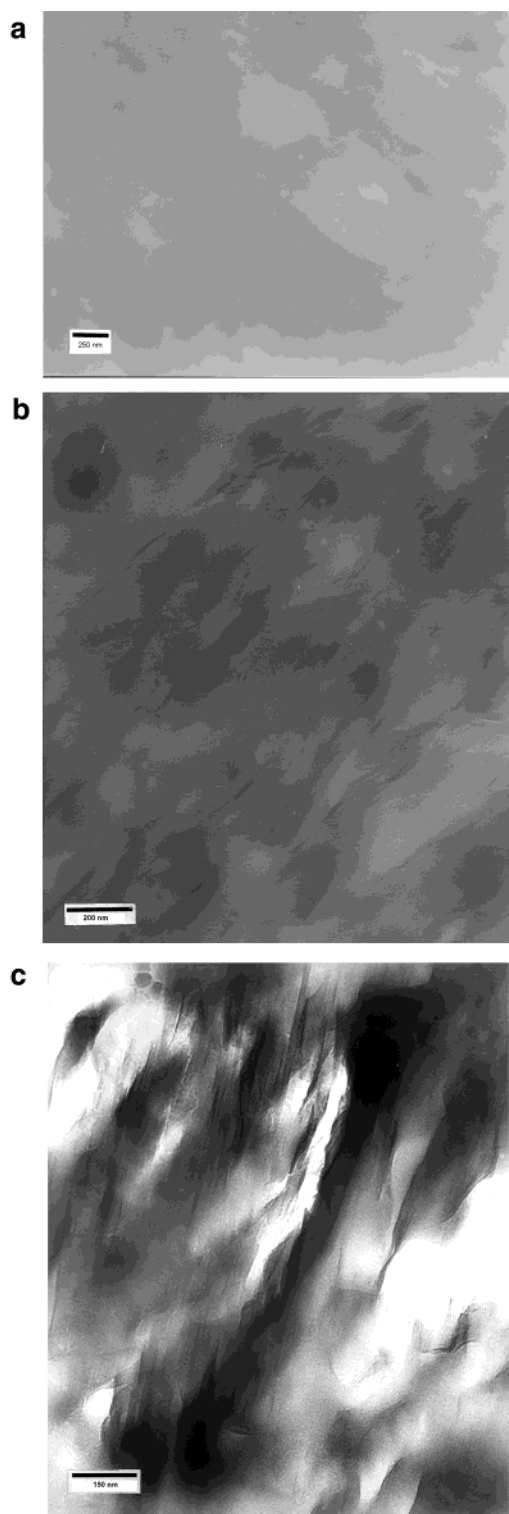
Figure 3. (a) TEM micrograph of c-PBT polymer. (b) TEM micrograph of 20A6%M (before polymerization). (c) TEM micrograph of 20A6%P (after polymerization).

and more and thicker stacks in the 20A6%P than 20A6%M. There is another possibility that the tethered site due to surfactant (dihydrogenated tallow ammonium ions) could be depleted at the temperature of polymerization (190 °C) so that adjacent clay layers have an opportunity for crystalline growth on cooling.

To conclude, we have been able to successfully synthesize PBT/clay nanocomposites using organically modified clay via in-situ polymerization in the solution method. X-ray diffraction suggests an exfoliated nanostructure before polymerization and an intercalation after polymerization. TEM images confirm the intercalated–exfoliated morphology in the ultimate polymer which contains 6 wt % of clay. The thermal stability of the nanocomposites containing 2 wt % of 20A organoclay has been increased at least 8–10 °C in a nitrogen medium.

Note Added after ASAP Posting

This communication was released ASAP on October 25, 2003. The last sentence in the Introduction has been revised. The correct version was posted on 10/31/2003.

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