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Synthesis of Poly(butylene terephthalate) Nanocomposite by *In-situ* Interlayer Polymerization and Characterization of Its Fiber (I)

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Summary

The nanocomposites with poly(butylene terephthalate) (PBT) incorporated between the montmorillonite (MMT) layers were synthesized from dimethyl terephthalate (DMT) and butane diol (BD) by using an in-situ interlayer polymerization approach. The PBT nanocomposites were melt spun at different organoclay contents to produce monofilaments. The existence of clay layers in the PBT was confirmed by using X-ray diffraction and transmission electron microscopy, and those layers were found to be disperse on a nanometer scale. The thermal properties of the layered structures of the hybrids were found to be more stable than those of pure PBT. These improved thermal properties of the nanocomposites might arise from an extensive and strongly bonded interface between the organic and the inorganic components. Moreover, the addition of only a small amount of organoclay was enough to improve the mechanical properties of the PBT hybrid fibers.

Introduction

The several methods of nanocomposite preparation have been mainly divided into three groups[1-3] based on the starting materials and the processing techniques: solution intercalation, melt intercalation, and in-situ polymerization intercalation. Additionally, other approaches, such as the sol-gel process[4] and monomer/polymer grafting to clay layers, have resulted in polymer-clay hybrids.[5] Among them, in-situ polymerization intercalation is a method based on the use of one or more monomers that may be in-situ linearly polymerized or cross-linked and was the first method used to synthesized polymer-layered silicate nanocomposites based on polyamide 6.[6] This technique is particularly attractive due to its versatility and processing compatibility and is beginning to be used for commercial applications. Also, it is still widely used in many studies, especially those on thermosetting polymer-layered silicate nanocomposites. Quite a number of polymers, such as polystyrene,[7] poly(methyl methacrylate),[8] and poly(ε-caprolactone),[3] have been in-situ intercalated into clays, predominantly into layered silicates that have been modified by organoclays.

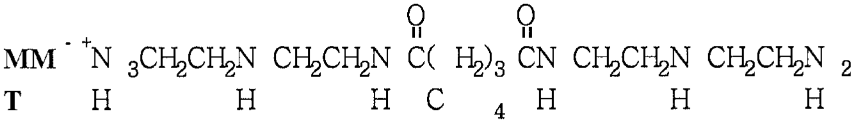
When preparing thermoplastic polymer nanocomposites, elevated temperatures are required for melt intercalation and bulk processing. If the processing temperature is higher than the thermal stability of the organoclay, decomposition will occur, altering the interface between the filler and the matrix polymer. In real processes with organophilic polymers, the interlayer cations are replaced with primary alkyl ammonium cations and quaternary alkyl ammonium cations to enhance the dispersibility. Since the thermal stability of these kinds of organoclays has been a problem, i.e., thermal degradation in the processing of polyesters above 250 °C, much attention has been directed toward the preparation of high-temperature stable organoclays.[9]

The objective of this study is to evaluate the effect of an organoclay filler in poly(butylene terephthalate) (PBT) composites, as a hybrid system, as a function of the amount of organoclay. To obtain the hybrids without thermal degradation during the processing, we introduced a new thermally stable organoclay. In this paper, we also describe a method for forming PBT nanocomposites by in-situ interlayer polymerization. Also, the thermal and the mechanical properties of PBT hybrid fibers are reported for various organoclay contents, together with some results on the morphology of the insertion polymer.

Experimental

Materials

All reagents were purchased from Junsei Chemical Co., TCI, and Aldrich Chemical Co. The organically modified montmorillonite (NCT-MMT) used in this study was kindly supplied from Nano Composite Technology, Co. (Korea). The chemical structure of NCT-MMT is as follows:



$$\begin{array}{l} \mathrm{MM}^{-}\ {}^{+}\mathrm{N}\ {}_{3}\mathrm{CH_2CH_2N}\ \mathrm{CH_2CH_2N}\ \overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}(\ \mathrm{H_2)_3}\ \overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{N}\ \mathrm{CH_2CH_2N}\ \mathrm{CH_2CH_2N}\ {}_{2} \\ \mathrm{T}\quad \mathrm{H}\qquad\qquad \mathrm{H}\qquad\qquad \mathrm{H}\ \ \mathrm{C}\ \ {}_{4}\ \mathrm{H}\qquad\qquad \mathrm{H}\qquad\qquad \mathrm{H} \end{array}$$

Preparation of NCT-MMT/PBT nanocomposites

All of the samples were prepared as melts. Since the synthesis procedures for all of the hybrids were about the same, only a representative example, the procedure for the preparation of the nanocomposites containing 2wt% organoclay, is given. In a polymerization tube were placed 100 g of 1,4-butane diol (BD) (1.1 mole) and 2.0 g of NCT-MMT; the mixture was stirred for 30 min at room temperature. In a separate tube were placed 97 g of dimethyl terephthalate (DMT) (0.5 mole) and 60 mg (2.1×10^{-4} mole) of isopropyl titanate, and to this mixture was added the organoclay/BD system. Mechanical stirring was used to obtain a homogeneously dispersed system. First, this mixture was heated for 1 hr at 190 °C under a steady stream of N_2 gas. Then, the temperature of the reaction mixture was raised to and maintained at 230 °C for 2 hrs under a steady stream of N_2 gas. During this period, continuous generation of methanol was observed. Finally, the mixture was heated for 3 hrs at 260 °C at a pressure of 1 Torr. The product formed was cooled to room temperature and repeatedly washed with water. It was dried under vacuum at 70 °C for 1 day to obtain the nanocomposites.

Extrusion

The composites were pressed at 220 °C, 2500 kg/cm^2 for 2 - 3 min on a hot press. The obtained films, ~ 0.5 mm thick, were dried in a vacuum oven at 110 °C for 24 hrs and were then extruded through the die of a capillary rheometer. The hot extrudates were immediately drawn at constant speed on a take-up machine to form fibers with a draw ratio (DR) of 1. The mean residence time in the capillary rheometer was ~ 3 - 4 min.

Characterization

The thermal behavior was studied by using a DuPont model 910 differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) at a heating rate of 20 °C/min under a N_2 flow. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature by using a Rigaku (D/Max-IIIB) X-ray diffractometer with Ni-filtered Co-Kα radiation. The scanning rate was 2°/min over a range of $2\theta = 2 - 30°$.

The tensile properties of the fibers were determined using an Instron Mechanical Tester (Model 5564) at a crosshead speed of 20 mm/min at room temperature. The experimental uncertainties in the tensile strength and the modulus were ± 1 MPa and ± 0.05 GPa, respectively. An average of at least ten individual determinations was obtained.

The samples for transmission electron microscope (TEM) measurements were prepared by putting PBT hybrid fibers into epoxy capsules and then curing the epoxy at 70 °C for 24 hrs in vacuum. After that, the cured epoxies containing the PBT hybrids for TEM observation were microtomed into 9-mm-thick slices, and a layer of carbon, about 3-nm thick, was deposited on each slice on a mesh 200 copper net. TEM photographs of ultrathin sections of the polymer/organoclay hybrid samples were taken on a EM 912 OMEGA TEM operating at an acceleration voltage of 120 kV.

Results and Discussion

Figure 1 illustrates the XRD patterns of the pristine clay, of the organoclay, and of the hybrid samples that were fabricated with different organoclay contents via in-situ interlayer polymerization. The characteristic peak for the pristine clay, Na^+-MMT, appears at $2\theta = 8.56^\circ$ (d = 11.99Å). For NCT-MMT, this peak is broadened and shifted to $2\theta = 3.98^\circ$ (d = 25.75Å), suggesting that the clay had swollen to the range of the d spacing. In general,[10] a larger interlayer spacing should be advantageous in the intercalation of polymer chains. It should also lead to easier dissociation of the clay, which should result in hybrids with better dispersions of the clay. In addition to the main diffraction peak, an additional small peak is observed near $2\theta = 7.13^\circ$ (d = 14.38Å). This suggests that this secondary peak might be related to the organoclay itself.

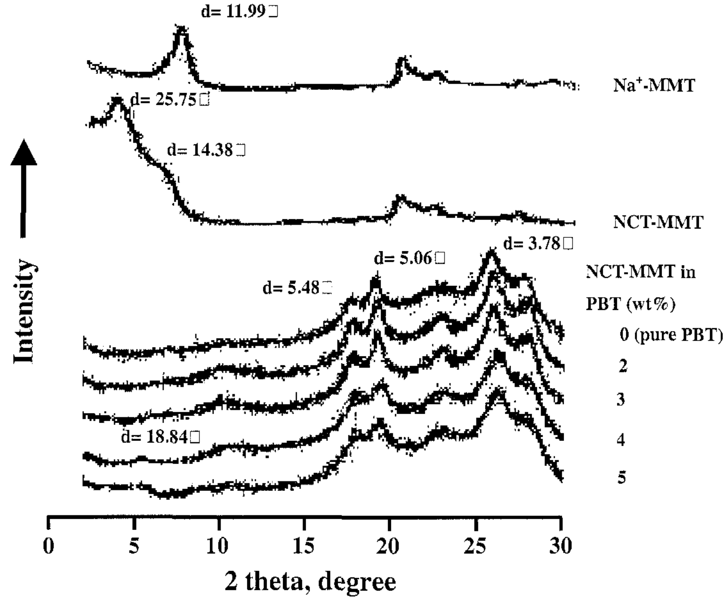


Figure 1. XRD patterns of clay, organoclay, and PBT hybrids.

Figure 1 also shows the XRD curves of pure PBT and of PBT hybrids with 2 - 5 wt% organoclay loadings. Pure PBT synthesized in an MMT interlayer exhibits its usual XRD peaks. However, in the cases of the 2 - 3 wt% PBT hybrids, the curves show no characteristic organoclay peaks in the range of the $2\theta = 2 - 8^\circ$; that is, the peak corresponding to the basal spacing has disappeared. In the cases of the PBT hybrids with 4 - 5 wt% organoclay loadings, however, a small peak is observed at $2\theta = 5.44^\circ$ (d = 18.84 Å). This indicates that agglomeration of a small part of the clay in PBT does occur.

The XRD results provided the first clues as to the nature of the nanocomposites. Since the formation of an exfoliated structure usually results in complete loss of registry between the clay layers, no peak was observed in the XRD pattern. It is well known that XRD information alone is not sufficient to characterize a nanocomposite. The XRD results noted above gave useful information on the state of the nanocomposites, but did not provide a complete picture. Thus, electron microscopic measurements were required. More direct evidence for the formation of a true nano-scaled composite was provided by TEM analysis of an ultramicrotomed section. TEM and XRD become complimentary techniques, filling in gaps of information that other technique cannot obtain.

The TEM micrographs are presented in Figure 2. The dark lines are the intersections of 1-nm-thick clay sheets, and the spaces between the dark lines are the interlayer spaces. Some of the clay layers of Fig. 2 (a) show individual dispersion of completely delaminated sheets in the matrix; also, regions are seen in which the regular stacking arrangement is maintained with a layer of polymer between the sheets. For the 5 wt% PBT hybrid in Fig. 2 (b), some of the clay also dispersed well in the PBT matrix, and some of it is agglomerated to a size of approximately ~ 10 nm. In a word, the morphology at clay content from 2 to 5 wt% present mixture of intercalated and partially exfoliated features.

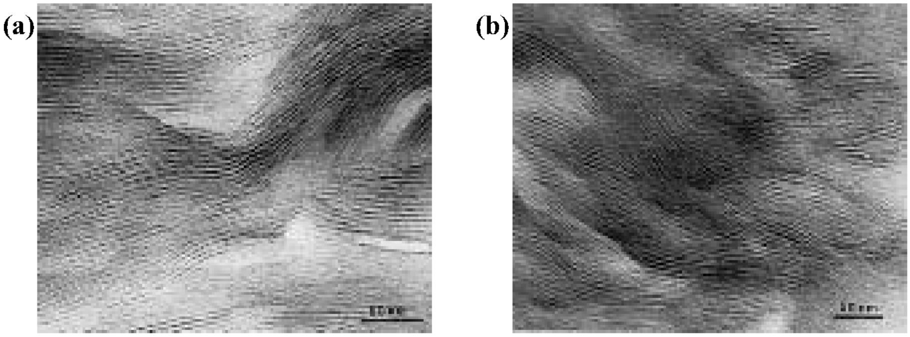


Figure 2. TEM photomicrographs of PBT/NCT-MMT hybrid fibers containing (a) 3 and (b) 5 wt% NCT-MMT. The arrows indicate the agglomerated regions of the nanocomposites.

None of the hybrids was soluble in common solvents, so a mixed solvent of phenol/ tetrachloroethane was used in the measurement of solution viscosities. The solution viscosity numbers were reasonably constant (0.84 - 1.06). The thermal properties of PBT hybrids with different organoclay contents are listed in Table 1. The glass transition temperatures (T_g) of the PBT hybrids increased from 27 to 33 °C when the clay loading was increased from 0 to 2 wt% and leveled off for organoclay contents larger than 2 wt%. The increase in the T_g of these hybrids may be the result of two factors.[11] First, the effect of small amounts of dispersed clay layers on the free volume of PBT is significant and does have an influence on the glass transition temperatures of the PBT hybrids. Second, the confinement of the intercalated polymer chains within the clay galleries prevents segmental motions of the polymer chains.

The endothermic peak of the pure PBT appears at 222 °C and corresponds with the melt transition temperature (T_m). In the DSC thermograms, the maximum transition peaks of the PBT hybrids containing different clay contents slightly increased to 229 – 231 °C (see Table 1). This increase in the thermal behavior of the hybrids may result from the heat insulation effect of the clay layer structure, as well as from the strong interaction between the organoclay and the PBT molecular chains.[12,13]

The thermal stabilities determined from a thermogravimetric analysis (TGA) of PBT/NCT-MMT are shown in Table 1 and Fig. 3. In addition to having a higher melting point, the PBT hybrids also have improved thermal degradation properties. The initial decomposition temperature ($T_D{}^i$) of the

Table 1. General properties of PBT nanocomposite fibers by in-situ interlayer polymerization

Clay wt %	I.V.^{a}	T_g °C	T_m °C	$T_D^{i\ b}$ °C	$wt_R^{600\ c}$ %
0	0.84	27	222	371	1
2	1.06	33	230	390	6
3	0.77	34	230	388	7
4	0.88	33	229	390	7
5	0.86	33	231	389	9

[a] Inherent viscosity was measured at 30 °C at a concentration of 0.1 g/dL in a phenol/tetrachloroethane =50/50 (W/W) mixture. [b] Initial decomposition temperature at a 2% weight loss. [c] Weight percent of residue at 600 °C.

hybrid clearly increases with increasing organoclay content up to 2 wt% of NCT-MMT, after which the value remains constant, regardless of the organoclay loading. At a 2% weight loss of PBT/NCT-MMT in the TGA curves, for example, T_D^i was observed to increase from 371 to 390 °C as the clay content in the hybrid was increased from 0 to 2 wt% and then remained constant regardless of the clay content. In the TGA thermograms (see Fig. 3), the weight loss due to the decomposition of PBT and its hybrids was nearly the same until a temperature of 350 °C. After that, T_D^i was influenced by the organoclay loading in the hybrids. The addition of clay enhanced the performance by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition. This kind of improvement in the thermal stability has also been observed in many systems of hybrids.[14,15]

The weight of the residue at 600 °C increased with clay loading from 0 to 5%, ranging from 1 to 9%. This enhancement of the char formation is ascribed to the high heat resistance exerted by the clay itself.[16]

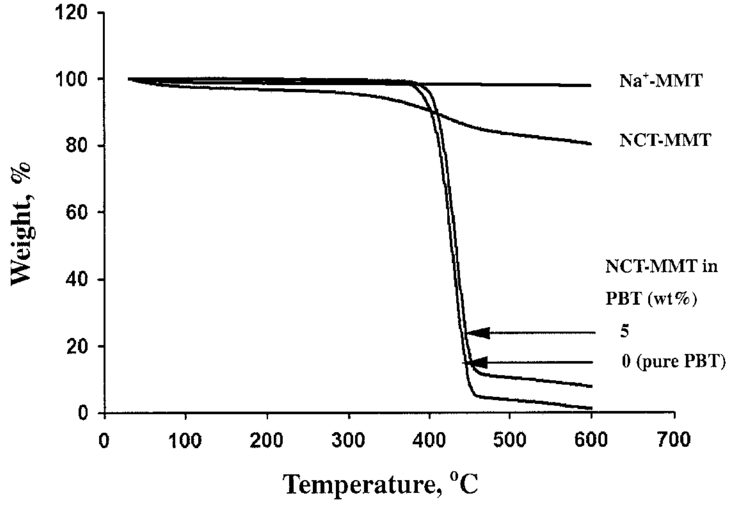


Figure 3. TGA thermograms of clay, organoclay, and PBT hybrids.

Considering the above results, it is easily to conclude that introduction of inorganic components into organic polymers can improve their thermal stabilities. However, in this hybrid system, the maximum effect on the thermal properties occurred when the NCT-MMT was loaded at 2 wt%.

The pure PBT and the PBT hybrid fibers were extruded through a capillary die with a DR = 1 to examine the tensile strength and the modulus of the extrudates. The DR was calculated from the ratio of the diameter of the drawn extrudate to that of the extruder die. The tensile mechanical properties of PBT and its hybrid fibers are given in Table 2. The ultimate tensile strength of the PBT/NCT-MMT hybrid fibers increases with the addition of clay and then decreases at an organoclay content corresponding to the critical weight percent. For example, the strength of 3 wt% NCT-MMT is 60 MPa, which is about 50% higher than the strength of pure PBT (41 MPa). However, when the organoclay in PBT reaches 5 wt%, the strength is only 49 MPa. This suggests that the 5% NCT-MMT domains may be more poorly dispersed in the PBT matrix than the 3% NCT-MMT domains. In a word, a high organoclay content leads to an agglomeration of MMT particles, which reduces the value of tensile strength.[10] Evidence for this organoclay agglomeration in PBT was cross checked by using XRD and TEM (see Figs. 1 and 2).

The initial modulus monotonically increased with increasing amount of organoclay in the PBT matrix (see Table 2). The value of the initial modulus increased from 1.37 to 1.86 GPa with increasing NCT-MMT content up to 5 wt%. This enhancement of the modulus is ascribed to the high resistance exerted by the clay itself. Additionally, the stretching resistance of the oriented backbone of the polymer chain in the gallery contributes to the enhancement of the modulus.[17] The percent elongations at break of all the samples were 5 - 7%. These values remained constant regardless of the organoclay loading.

Table 2. Mechanical properties of PBT nanocomposite fibers by in-situ interlayer polymerization

clay wt %	Ult. Str. MPa	Ini. Mod. GPa	E. B.* %
0	41	1.37	5
2	50	1.66	7
3	60	1.76	6
4	53	1.80	7
5	49	1.86	7

*Elongation percent at break.

Conclusions

On the basis of the aforementioned results, the enhancement of the thermal properties and tensile properties can be directly attributed to a fine dispersion of clay particles in the polymer matrix, as well as to the interactions between the polyester molecules and the layered clay. From the ultimate tensile strength, the PBT/NCT-MMT hybrid shows a critical content of organoclay to attain the more increased property. The dispersion is better at a lower clay loading than at a high clay loading. This suggests that the MMT domains can more agglomerate above 4wt% of organoclay content in the PBT matrix. Further studies of the tensile properties for different values of the DR in this material are currently being conducted.

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