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Preparation of poly(ethylene terephthalate) nanocomposite fibers incorporating a thermally stable organoclay

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Summary

A series of poly(ethylene terephthalate) (PET) nanocomposites containing organically-modified mica (HB-Mica) were prepared by in-situ interlayer polymerization of dimethyl terephthalate and ethylene glycol. The PET nanocomposites, which contained organoclay loadings of 0 to 2 wt %, were melt-spun to produce monofilaments with various draw ratios. Some of the clay particles appeared well dispersed within the PET matrix, while others were found to form agglomerates with sizes greater than 20 nm. The addition of a small amount of organoclay was sufficient to improve the thermo-mechanical properties of the PET hybrid fibers. Both the thermal stability and the mechanical tensile properties increased with increasing clay content for draw ratios of 1–16.

Introduction

Poly(ethylene terephthalate) (PET) is a widely used low-cost material with good mechanical, and high gas barrier properties. Recently, a new class of materials, PET/clay nanocomposites, has been developed. Compared to pure polymers or conventional composites, these nanocomposites usually possess improved strength, an enhanced modulus, decreased thermal expansion coefficients, increased thermal stability, and reduced gas permeability, due to the nanoscale dispersion of clay in the polymer matrix, the high aspect ratio of clay platelets, and the strong interfacial interaction between the clay and the polymers [1-3] .

Various preparation approaches have been explored to obtain these nanocomposites. Clays can be exfoliated into polymer matrices via in-situ intercalation polymerization. The resulting polymer/clay nanocomposites exhibit improved thermo-mechanical properties compared with those of the clay alone. In-situ intercalation polymerization enables the preparation of polymer nanocomposites with a satisfactory degree of exfoliation, which cannot be achieved by the direct mixing of polymer and clay. This technique is also particularly attractive because of its versatility and compatibility with the use of reactive monomers, and is beginning to be used in commercial applications [4,5].

In this paper, we describe the use of in-situ intercalation polymerization to fabricate PET nanocomposites. The present study evaluates the effects of varying the amount of organoclay and draw ratio (DR) on the properties of the PET hybrid fibers. To obtain nanocomposites without thermal degradation during processing at 280℃, we used a new thermally-stable organoclay: hexadimethrine-Mica (HB-Mica). The effects of HB-Mica on the thermal stability, tensile properties, and morphology of the resulting hybrid fibers were also examined.

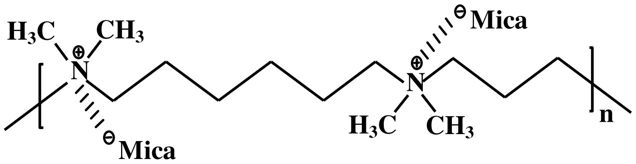
Experimental

Materials

All reagents were purchased from either TCI, Junsei Chemical Co., or Aldrich Chemical Co. Commercially available solvents were purified by distillation.

Preparation of the organoclay: HB-Mica

The organically-modified mica (HB-Mica) used in this study was synthesized using an ion exchange reaction between Na^+-Mica and hexadimethrine bromide ($HB\text{-}Br^-$). Hexadimethrine bromide 6.53 g (0.0175 mol) and 100 mL of de-ionized water were placed in a 500-mL beaker, and the resulting $(HB\text{-}Br)^-$ solution was heated at 80℃ for 1 h. A dispersion of Na^+-Mica (20.0 g) in de-ionized water (200 mL) was then added to the $HB\text{-}Br^-$ solution, and the mixture was stirred vigorously at 80℃ for 3 h. The precipitate was isolated by filtration, placed in a 500 mL-beaker with 300 mL of water and ethanol (50/50=v/v), and stirred for 1 h. The product was then filtered and freeze-dried. The initial thermal degradation temperature (T_D^i) at a 2% weight loss of the HB-Mica was observed at 328℃. This confirms that HB-Mica was thermally stable at 280℃, which is the processing temperature of PET (see Figure 4). The chemical structure of HB-Mica is as follows:



Preparation of HB-Mica/PET nanocomposites

All of the samples were prepared as melts. Since the synthetic procedures for all the hybrids are similar, the procedure for the preparation of PET nanocomposites containing 1 wt% organoclay is given as a representative example. HB-Mica (0.96 g) and ethylene glycol (EG; 62 g) (1.0 mol) were placed in a polymerization tube. To this mixture was added 97 g of dimethyl terephthalate (DMT) (0.5 mol) and a few drops (1.2×10^{-4} mol) of isopropyl titanate. This mixture was heated first for 1 h at 190 ℃ under a steady stream of N_2 gas, and then the temperature was raised to 230 ℃ and the mixture heated for a further 2.5 h under N_2 gas. Finally, the mixture was heated for 1.5 h at 280 ℃ at a pressure of 1 Torr. The product was cooled to room temperature, washed repeatedly with water, and then dried under vacuum at 70℃ for 1 day to obtain the PET hybrids.

Extrusion

The composites were extruded through the die of a capillary rheometer (INSTRON 5460) at 270℃ for PET, and then were immediately drawn at the constant speed of the take-up machine to form fibers with different DRs. The mean residence time within the capillary rheometer was ~ 3-4 min.

Characterization

The thermal behavior of these HB-Mica/PET nanocomposites was studied using a DuPont model 910 differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) at a heating rate of 20℃/min under a N_2 flow. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature using an X'Pert PRO-MRD Multi-Purpose X-ray diffractometer with Ni-filtered Cu-Kα radiation. The scanning rate was 2^o/min over a range of $2\theta = 2\text{-}15^o$. The tensile properties of the fibers were determined using an INSTRON mechanical tester (Model 5564) at a crosshead speed of 5 mm/min at room temperature. The samples for the transmission electron microscope (TEM) were prepared by placing polyester hybrid fibers into epoxy capsules and then curing the epoxy at 70℃ for 24 h under vacuum. TEM photographs of ultrathin sections of the PET hybrid fibers were taken on an EM 912 OMEGA TEM using an acceleration voltage of 120 kV.

Results and discussion

Figure 1 shows the XRD patterns of the pristine clay, organoclay, and the hybrid samples, fabricated with different organoclay contents via in-situ interlayer polymerization. The characteristic peak of the pristine clay (Na^+-Mica) appears at $2\theta = 9.278^o$ (d = 9.52Å). For HB-Mica, this peak is shifted to $2\theta = 6.378^o$ (d = 13.84Å), suggesting that the clay had swollen to the range of the d-spacing. In general, a larger interlayer spacing should be advantageous in the intercalation of polymer chains. It should also lead to easier dissociation of the clay, resulting in hybrids with better clay dispersions [6]. For PET containing a 0.5 wt % organoclay content, only a slight peak at d = 13.84 Å was observed in the XRD results for the extruded fibers. Substantial increases in the intensities of the XRD peaks were observed for clay loadings from 0.5 to 2 wt %, which suggested that the organoclay became an agglomeration easily at a higher clay loading.

The clay dispersion in a PET matrix was cross-checked further by examining electron microscopy data. Electron microscopy and XRD are complimentary techniques that provide valuable information that cannot be obtained by other techniques [7,8]. The morphologies of the extruded fibers obtained from hybrid systems containing up to 2 wt% HB-Mica in a PET matrix were examined by observing their fracture surfaces with SEM (Fig. 2). The micrographs of the PET hybrid fiber containing 0.5 wt % HB-Mica (Fig. 2(b)) show smooth surfaces due to well dispersed clay particles.

Conversely, the fibers containing 1.0 and 2.0 wt % HB-Mica (Figs. 2(c) and (d)) show voids and some deformed regions that may result from the coarseness of the fractured

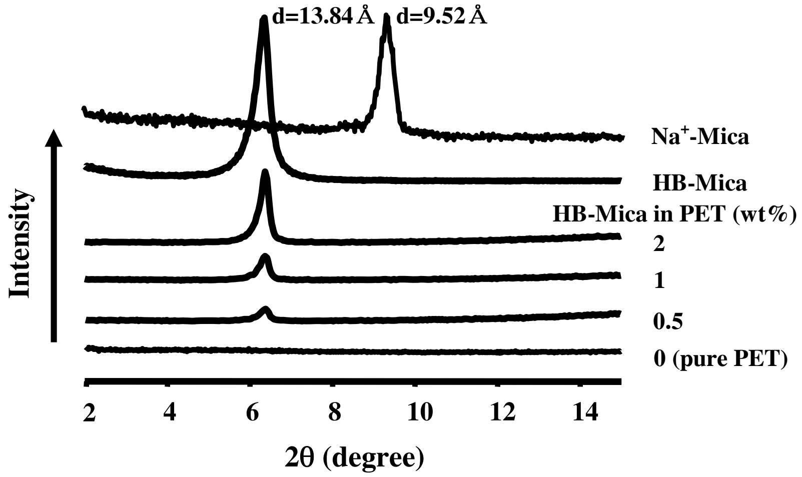


Figure 1. XRD patterns for clay, organoclay, and PET hybrid fibers with various organoclay contents.

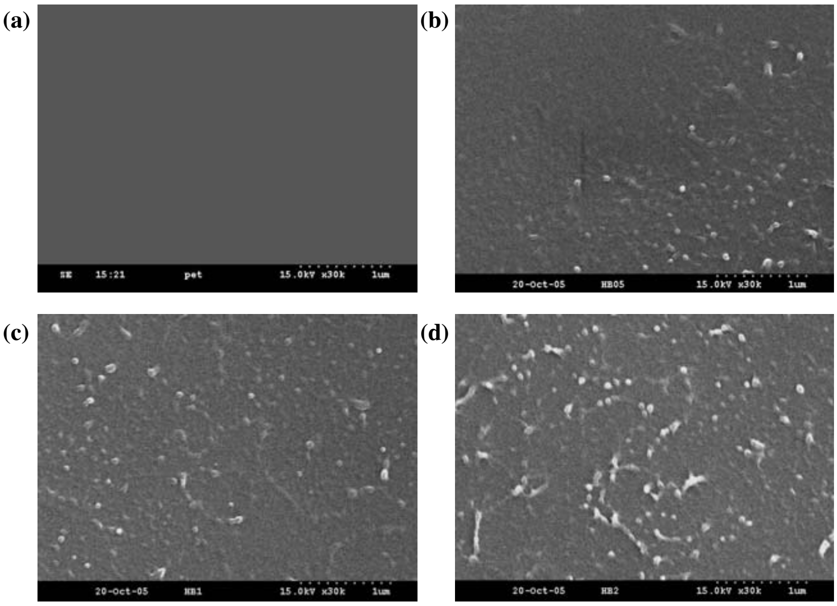


Figure 2. SEM micrographs of (a) 0 (pure PET), (b) 0.5, (c) 1, and (d) 2 wt% HB-Mica in PET hybrid fibers.

surface. However, the fractured surfaces were more deformed when higher contents of organoclay were used in the hybrids. This is probably a consequence of the agglomeration of clay particles. More direct evidence for the formation of a true nano-scaled composite was provided by the TEM analysis of an ultramicrotomed section. TEM can produce a qualitative understanding of internal structures through direct observation.

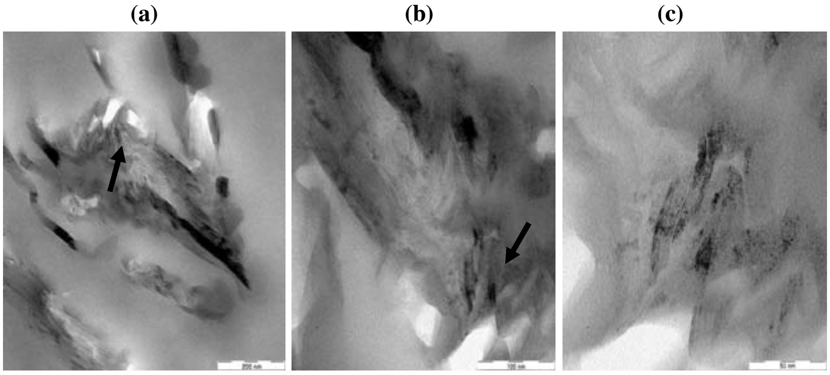


Figure 3. TEM micrographs of 0.5 wt% HB-Mica in PET hybrid fibers. The magnification level increases from (a) to (c).

Figure 3 shows the TEM photographs of 0.5 wt % hybrid fibers. The dark lines are the intersections of 1 nm thick sheet layers. In Figure 3, the organoclay is well dispersed in the polymer matrix at all magnification levels, although some of them are agglomerated at size levels greater than approximately 20 nm. The presence of peaks in the XRD patterns of these samples can be attributed to these agglomerated layers (see Fig. 1).

The thermal properties of hybrids with different organoclay contents are listed in Table 1. The inherent viscosities of the samples were maintained nearly the same (0.90-1.02) prior to this study. The glass transition temperature (T_g) and endothermic melt transition temperature (T_m) of the pure PET appear at 76℃ and 245℃, respectively. Compared with pure PET, the T_g and T_m peaks of the PET hybrid fibers containing various clay contents were virtually unchanged in the DSC thermograms regardless of the organoclay loading. The hybrids showed improved thermal degradation properties. Table 1 shows that the initial thermal degradation temperature ($T_D{}^i$) of the HB-Mica/PET hybrid fibers increased with the amount of organoclay. $T_D{}^i$ at a 2% weight loss was observed at 370-397℃ for clay compositions from 0 to 2 wt % in the PET hybrids, with a maximum increase of 27℃ in the case of the 2 wt % HB-Mica/PET, as compared to that for pure PET. The addition of clay enhanced the performance of the HB-Mica/PET hybrid fibers by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition [9]. The weight of the PET hybrid residue at 600℃ increased with clay loadings from 0 to 2%, ranging from 1 to 19%. This enhancement of char formation is ascribed to the high heat resistance exerted by the clay itself. Considering the above results, it is easy to conclude that the introduction of inorganic components into organic polymers can improve their thermal stabilities. For the PET hybrid fibers, the overall thermal properties did not change with increasing DR (data not shown). The TGA thermograms of the clay, organoclay, and PET hybrid fibers are given in Figure 4.

The tensile mechanical properties of PET and the hybrid fibers are given in Table 2. At DR=1, the ultimate tensile strength of the HB-Mica/PET hybrid fibers increases with the addition of clay up to a critical clay loading, and then decreases above that critical content. For example, the strength of 0.5 wt % HB-Mica/PET hybrid fibers is 57 MPa, which is about 24% higher than that of pure PET (46 MPa). When the amount

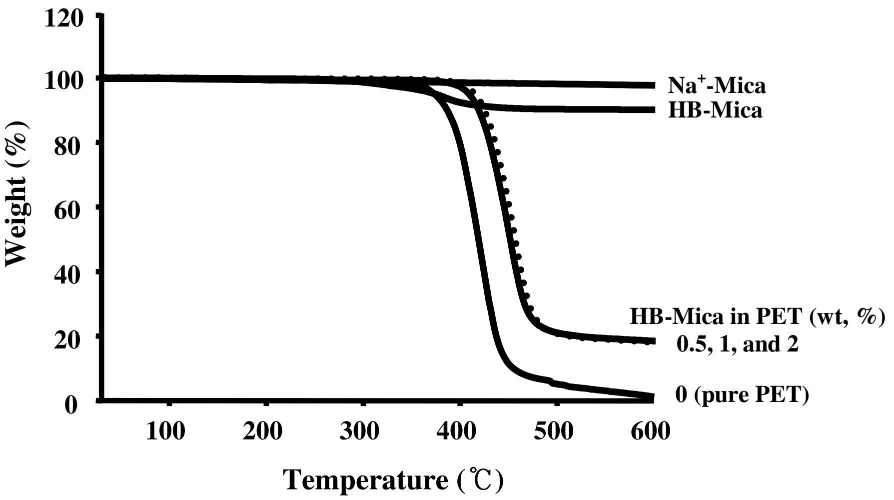


Figure 4. TGA thermograms of clay, organoclay, and PET hybrid fibers with various organoclay contents.

Table 1. Thermal properties of PET hybrid fibers

Organoclay wt, %	I.V. [a]	T_g ℃	T_m ℃	T_D^{i} [b] ℃	wt $_R^{600}$ [c] %
0 (pure PET)	1.02	76	245	370	1
0.5	0.94	75	244	395	18
1	0.91	75	244	396	18
2	0.90	75	245	397	19

[a] Inherent viscosities were measured at 30℃ by using 0.1 g/dL solutions in a phenol/1,1,2,2-tetrachloro-ethane (w/w = 50) mixture.
[b] Initial weight-loss temperature. [c] Weight percent of residue at 600℃.

of organoclay in PET reaches 2 wt %, the strength decreases to 48 MPa. This decrease in ultimate strength is mainly due to the agglomeration of clay particles above critical points of organoclay content [7]. Unlike the tensile strength, the initial modulus values were found to increase linearly with increasing organoclay content. For an organoclay content of 2 wt %, the modulus of the hybrid was found to be 3.33 GPa, about 1.5 times that of pure PET (2.21 GPa).

This improvement in the tensile properties of the hybrid fibers with respect to those of pure PET is due to the presence of the organoclay, and can be explained as follows: the increases in the tensile properties due to the clay layers are largely dependent on the interactions between the PET molecules and the layered organoclays, and on the rigid nature of the clay layers. Moreover, the clay is much more rigid than the PET molecules, and so does not deform or relax as much as the PET molecules. The improvement arises because the organoclay layers are dispersed and intercalated within the PET matrix. This is consistent with the general observation that the introduction of an organoclay into a polymer matrix increases its strength and modulus [10].

Table 2. Tensile properties of PET hybrid fibers

Organoclay wt, %	D.R.[a]	Ult. Str. MPa	Ini. Mod. GPa	E. B.[b] %
0 (pure PET)	1	46	2.21	3
	10	51	2.28	3
	16	51	2.39	2
0.5	1	57	2.47	2
	10	57	2.52	2
	16	58	2.69	3
1	1	47	2.52	2
	10	52	3.21	2
	16	53	3.55	2
2	1	48	3.33	2
	10	51	3.75	2
	16	53	3.92	2

[a] Draw ratio. [b] Elongation percent at break.

As shown in Table 2, the variations in tensile strength and initial modulus with DR were found to be insignificant for pure PET. For pure PET, the mechanical tensile properties were found to increase from 46 to 51 MPa for the ultimate strength and from 2.21 to 2.39 GPa for the initial modulus, respectively, as the DR was increased from 1 to 16. For PET hybrid fibers, the ultimate strength of the hybrid fibers increased linearly with increasing DR. In a previous paper [11], we reported that the values of the ultimate strength and initial modulus of the hybrid fibers decreased markedly with increasing DR. However, this system did not follow the previous results. The increase in strength and modulus might be attributed to the stretching of the fiber leads to a strengthening effect in the hybrids. An increase in the tensile strength with increasing DR is very common for engineering plastics and is usually observed for flexible coil-like polymers. The percent elongations at break of all samples were 2–3%. These values remained constant regardless of the organoclay loading from 0.5 to 2 wt %.and the DR.

Conclusions

Hybrid fibers consisting of PET and newly-synthesized organoclays were prepared via in situ interlayer polymerization for organoclay contents ranging from 0 to 2 wt %.

The thermo-mechanical properties and morphology of the hybrid fibers were examined in detail at various organoclay contents and DRs. Our results show that the thermal degradation stability and mechanical properties of these fibers depend on the organoclay content in the polymer matrix and DR. Each clay displayed well-dispersed individual clay layers in the PET matrix, although some particles appear agglomerated at size levels greater than approximately 20 nm. From this work, the addition of small amounts of clay was found to be sufficient to improve the properties of PET.

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