

Polyester nanocomposite fibers: comparison of their properties with poly(ethylene terephthalate) and poly(trimethylene terephthalate) (II)

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Received: 30 March 2004 / Revised version: 8 July 2004 / Accepted: 23 July 2004

Summary

Two polyester nanocomposites were synthesized, one with poly(ethylene terephthalate) (PET) and the other with poly(trimethylene terephthalate) (PTT), by using organoclay. The in-situ interlayer polymerization method was used to disperse the organoclay in polyesters at different organoclay contents and at different draw ratios to produce monofilaments. The thermal stability and tensile mechanical properties increased with increasing organoclay content at a DR=1. However, the values of the tensile mechanical properties of the hybrid fibers decreased with increasing DR. The reinforcing effects of the organoclay of the PET hybrid fibers were higher than those of the PTT hybrid fibers.

Introduction

Nanocomposites are a class of composites derived from ultrafine inorganic particles with sizes on the order of nanometers that are homogeneously dispersed in a polymer matrix. Because of their nanometer sizes, nanocomposites possess properties that are superior to those of conventional composites because of interfacial adhesion being maximized. Recently, nano-scale composites of polymers with organoclays have been studied extensively [1,2]. When linear aromatic polyester nanocomposites are prepared, elevated temperatures to, at least, above 260°C are required for in-situ intercalation and bulk processing. If the processing temperature is higher than the thermal stability of the organoclay, decomposition will occur. Since the thermal stability of these kinds of organoclays with alkyl ammonium cations has been a problem, i.e., thermal degradation in the processing of polyesters such as PET and PTT above 260°C, much research has been directed toward the preparation of organoclays that are thermally stable at high processing temperatures [3-5].

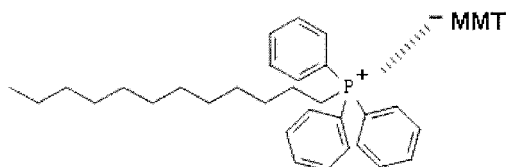
Among the several methods to obtain polymer nanocomposites by using organoclays, in-situ interlayer polymerization relies on swelling of the organoclay by a monomer, followed by in-situ polymerization initiated thermally or by addition of a suitable compound. The chain growth in the clay galleries accelerates clay exfoliation and nanocomposite formation [6-8]. In this study, dodecyltriphenyl-phosphonium-montmorillonite (C₁₂PPh-MMT) was used as a thermally stable organoclay for the PET and the PTT nanocomposites. This paper deals with the influences of matrix

polymers, such as PET and PTT, on the thermal stability, the tensile mechanical property, and the morphology. These properties of PET/ C_{12} PPh-MMT hybrid fibers are compared with those of similar fibers prepared from PTT and the properties of polyester hybrid fibers as functions of the organoclay content and the draw ratio (DR) are described.

Experimental

Materials

All reagents were purchased from TCI, Junsei Chemical Co., and Aldrich Chemical Co. Commercially available solvents were purified using distillation. 1,3-Propanediol (PDO) was supplied by Huvis Co. (Korea). The organically modified montmorillonite (C_{12} PPh-MMT) used in this study was synthesized using an ion exchange reaction between Na^+ -montmorillonite (Na^+ -MMT) and dodecyltriphenyl-phosphonium chloride (C_{12} PPh-Cl) (in the same way as described in our previous paper [5]). The chemical structure of C_{12} PPh-MMT is as follows:



Preparation of C_{12} PPh-MMT/polyester nanocomposites

All of the samples were prepared as melts. Since the synthetic procedures for all of the hybrids were almost the same, only a representative example, the procedure for the preparation of PTT nanocomposites containing 2 wt% organoclay, is given here. In a polymerization tube, 76 g of 1,3-Propanediol (PDO) (1.0 mole) and 2.08 g of C_{12} PPh-MMT were placed. In a separate tube, 97 g of dimethyl terephthalate (DMT) (0.5 mole) and a few drops (1.2×10^{-4} mole) of isopropyl titanate were placed and this mixture was added to the organoclay-PDO system. This mixture was heated first for 1 hr at $190^\circ C$ under a steady stream of N_2 gas. Then, the temperature of the reaction mixture was raised to $230^\circ C$ for 2 hrs under a N_2 gas. Finally, the mixture was heated for 2 hrs at $265^\circ C$ at a pressure of 1 Torr. The product was cooled to room temperature, repeatedly washed with water, and dried under a vacuum at $70^\circ C$ for 1 day to obtain the PTT hybrids. PET nanocomposites were obtained through a similar multi-step process [5].

Extrusion

The composites were extruded through the die of a capillary rheometer (INSTRON 5460) at $270^\circ C$ for PET and at $250^\circ C$ for PTT and were immediately drawn at the constant speed of the take-up machine to form fibers with different DRs. The mean residence time in the capillary rheometer was ~ 3 -4 min.

Characterization

The thermal behavior was studied by using a Du Pont model 910 (differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA)) at a heating rate of 20°C/min under a N₂ flow. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature by using a Rigaku (D/Max-III B) X-ray diffractometer with Ni-filtered Co-K α radiation. The scanning rate was 2°/min over a range of $2\theta = 2$ -10°. 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 samples for the transmission electron microscope (TEM) were prepared by putting polyester hybrid fibers into epoxy capsules and then curing the epoxy at 70°C for 24 hrs in vacuum. TEM photographs of ultrathin sections of the polyester/organoclay hybrid fibers were taken on a EM 912 OMEGA TEM using 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 $2\theta = 8.56^\circ$ ($d = 11.99\text{\AA}$). For C₁₂PPh-MMT, this peak is broadened and shifted to $2\theta = 2.86^\circ$ ($d = 36.08\text{\AA}$), suggesting that the clay had swollen to the range of the d spacing. In addition to the main diffraction peak, an additional small peak is observed near $2\theta = 5.65^\circ$ ($d = 18.20\text{\AA}$), which correlates to the 002 plane of the clay layers.

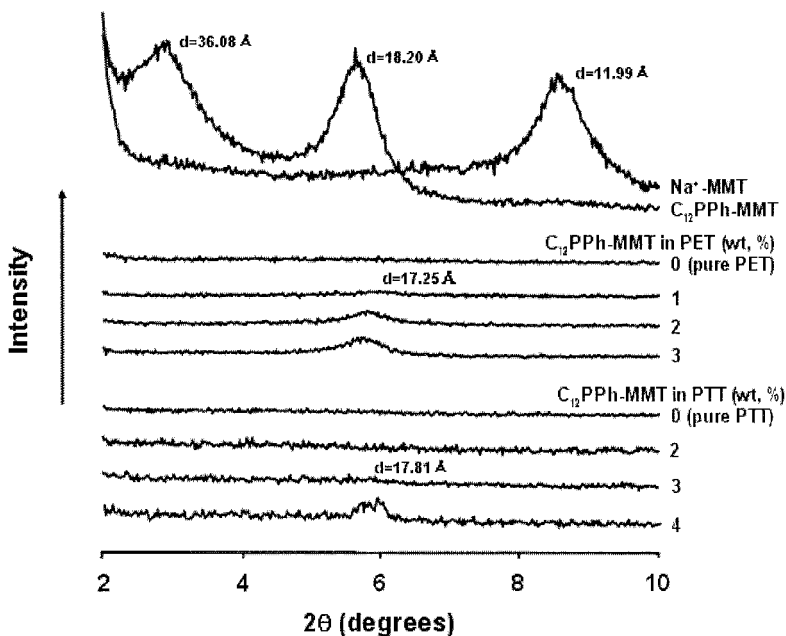


Figure 1. XRD patterns for clay, organoclay, and polyester fibers with various organoclay contents.

For PET containing a 1 wt % organoclay content, only a slight peak at $d = 17.25 \text{ \AA}$ existed in the XRD results for the extrudate fibers. Substantial increases in the intensities of the XRD peaks were observed for clay loadings from 1 to 3 wt %, which suggested that the organoclay became an agglomeration easily at a higher clay loading. Dispersion was also better at a lower clay loading than at a higher clay loading.

Figure 1 also shows the XRD curves of pure PTT and of PTT hybrids with 2 - 4 wt% organoclay loadings. However, in the cases of the 2 wt% PTT hybrids, the curves show no characteristic organoclay peaks in the range of the $2\theta = 5 - 7^\circ$; that is, the peak corresponding to the basal spacing has disappeared. In the cases of the PTT hybrids with 3 and 4 wt% organoclay loadings, however, a peak is observed at $2\theta = 5.76^\circ$ ($d = 17.81 \text{ \AA}$). This indicates that agglomeration of a small part of the clay does occur in PTT. From the above results, substantial increases were observed in the intensities of the XRD peaks with clay loading up to 4 wt%, which suggests that perfect exfoliation of the clay layer structure of the organoclay does not occur in either of the of the two hybrids.

Figure 2 shows the XRD results for the PET nanocomposites containing 3 wt % C_{12} PPh-MMT at various DRs. When the DR was increased from 3 to 16, no obvious clay peaks appeared. This absence of peaks is an indication that the clay layers were exfoliated and dispersed homogeneously in the PET matrix [6], is direct evidence that the C_{12} PPh-MMT/PET systems formed exfoliated nanocomposites, and suggests that higher stretching of the fiber during the extrusion leads to better dispersion of the clay and a more delamination morphology. Figure 2 also shows the XRD results for the PTT nanocomposites containing 4 wt % C_{12} PPh-MMT at various DRs. For PTT containing a 4 wt % organoclay content, a very small peak at $d = 17.81 \text{ \AA}$ existed in the XRD results for the extrudate fibers at DR=1. As opposed to the PET hybrids, significant decreases in the intensities of the XRD peaks in PTT hybrids were not

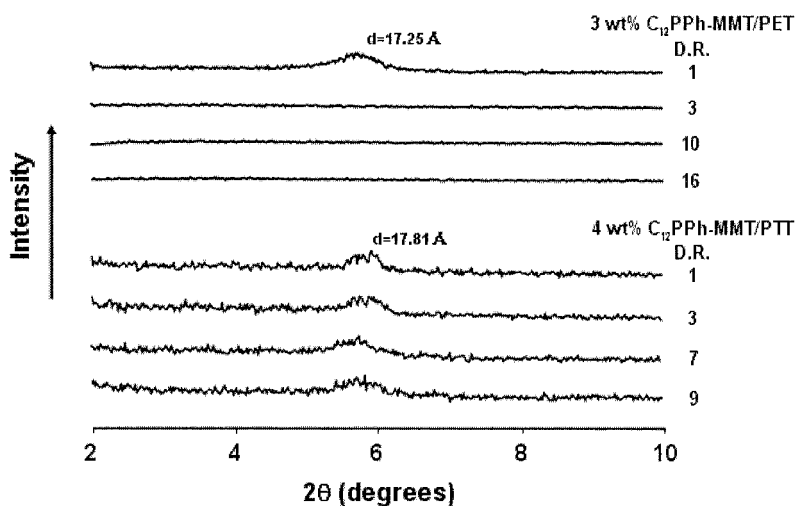


Figure 2. XRD patterns of C_{12} PPh-MMT/polyester hybrid fibers with different draw ratios.

observed for increasing DRs from 1 to 9, which suggests that higher stretching of the fiber during the extrusion was not effective for good dispersion of the clay in a polymer matrix. A decrease of the peak intensity in XRD with increasing DR is usually observed in coil-like polymers. However, PTT have several outstanding properties such as the resilience, softness, and elastic recovery. The constant XRD peak intensities of PTT in Figure 2 are thought to attribute to these advantageous properties.

TEM micrographs are presented in Figure 3. Some of the clay layers of the PET hybrid fiber in Fig. 3 (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. A similar morphology is also seen for the 4 wt% PTT hybrid in Fig. 3 (b). In a word, the morphologies of the two samples showed mixtures of intercalated and partially exfoliated features.

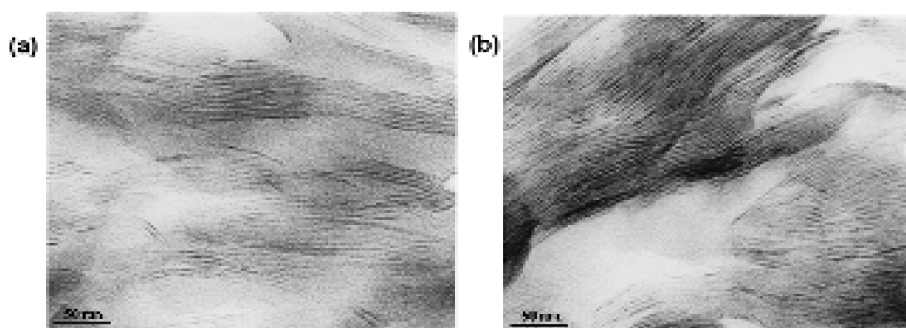


Figure 3. TEM micrographs of hybrid fibers containing (a) 3 wt% organoclay in PET and (b) 4 wt% organoclay in PTT.

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 (0.98-1.26 for PET and 0.81-0.86 for PTT) prior to the study. The endothermic melting (T_m) peak of the pure PET appears at 245 °C. Compared with pure PET, the maximum transition peaks of the PET hybrid fibers containing different clay contents were virtually unchanged in the DSC thermograms regardless of the organoclay loading. However, the hybrids showed improved thermal degradation properties. Table 1 shows that the initial thermal degradation temperature (T_D^i) of the C_{12} PPH-MMT/PET hybrid fibers increased with the amount of organoclay. T_D^i at a 2% weight loss was observed at 370-386 °C for clay compositions from 0 to 3 wt % in the PET hybrids, with a maximum increase of 16 °C in the case of the 3 wt % C_{12} PPH-MMT/PET as compared to that for pure PET.

Table 1. Thermal properties of polyester hybrid fibers

organoclay wt, %	PET				PTT			
	I.V. ^a	T _m °C	T _D ^{ib} °C	wt _R ^{600c} %	I.V.	T _m °C	T _D ⁱ °C	wt _R ⁶⁰⁰ %
0	1.02	245	370	1	0.84	228	362	1
1	1.26	247	375	8				
2	0.98	245	384	15	0.86	227	371	10
3	1.23	246	386	21	0.83	228	370	11
4					0.81	227	371	13

^aInherent viscosity. ^bInitial weight reduction onset temperature. ^cWeight percent of residue at 600 °C.

In the case of PTT, the melting endothermic peak of the pure PTT appears at 228 °C and the maximum transition peaks of the PTT hybrids containing different clay contents were about the same (227 - 228 °C) regardless the organoclay content from 2 to 4 wt% (see Table 1). However, T_Dⁱ of the PTT hybrids was observed to increase from 362 to 371 °C as the clay content in the hybrid was increased from 0 to 2 wt% and then remained constant regardless of the clay content. The addition of clay enhanced the performance by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition. The weight of the residue at 600 °C of the PET hybrids increased with clay loading from 0 to 3%, ranging from 1 to 21%. In the case of PTT hybrid fibers, the weight of the residue at 600 °C increased with clay loading from 0 to 4 %, ranging from 1 to 13%. 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 introduction of inorganic components into organic polymers can improve their thermal stabilities. For the two hybrid fibers, PET and PTT, the overall thermal properties did not change with increasing DRs (not shown here).

The ultimate tensile strength of the C₁₂PPh-MMT/PET hybrid fibers increased linearly with increasing the addition of clay from 1 to 3 wt% (see Table 2). For example, the value of the ultimate strength of the hybrid fiber containing 3 wt % C₁₂PPh-MMT (71 MPa) was 1.5 times higher than that of a pure PET fiber (46 MPa) at DR=1. The same kind of behavior was observed for the initial moduli. When the organoclay in PET reached 3 wt %, the modulus had increased about 1.9 fold (4.10 GPa) over that of pure PET (2.21 GPa).

The tensile properties of PTT hybrid fibers also increased with increasing amount of organoclay. When the organoclay was increased from 0 to 4 wt % in hybrids at DR = 1, the value of the ultimate strength of PTT hybrid fiber containing 4 wt % C₁₂PPh-MMT (48 MPa) was 1.5 times higher than that of a pure PTT fiber (32 MPa). The value of the initial modulus also monotonically increased from 1.77 to 3.08 GPa with increasing organoclay content up to 4 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 [5].

As Table 2 shows, the values of the ultimate strength and the initial modulus of the hybrid fibers decreased markedly with increasing DR for PET hybrids. For 1 wt % of organoclay in the hybrid fiber, for example, when the DR was increased from 1 to 16, the tensile strength and the initial modulus values decreased from 58 to 48 MPa and from 2.88 to 2.47 GPa, respectively. Similar trends were observed for 2 and 3 wt % of C₁₂PPh-MMT in the PET hybrid fibers. The values of the ultimate strength with increasing DR from 1 to 9 were also observed decrease in PTT hybrids containing 2 – 4 wt% organoclay. This declination in the tensile ultimate strength seems to be the result of debonding between the organoclay and the matrix polymer and the presence of many nano-sized voids due to excess stretching of the fibers. Many researchers [9-11] have reported that an imperfect incursion/matrix interface cannot sustain the large interfacial shear stress that develops as a result of an applied strain. In addition to having the lower ultimate tensile strength change, the initial modulus of the PTT hybrid fibers showed nearly constant values for increasing DR. The percent elongations at break of all the samples were 2 - 3%. These values remained constant regardless of the organoclay loading and the DR.

Table 2. Tensile properties of polyester hybrid fibers

or organoclay wt, %	PET				PTT			
	D.R. ^a	Ult. Str. MPa	Ini. Mod. GPa	E. B. ^b %	D.R.	Ult. Str. MPa	Ini. Mod. GPa	E. B. %
	0	1	46	2.21	3	1	32	1.77
	3	47	2.24	3	3	35	1.85	2
	10	51	2.28	3	7	35	1.94	2
	16	51	2.39	2	9	34	2.02	3
1	1	58	2.88	3				
	3	56	2.80	3				
	10	50	2.63	3				
	16	48	2.47	3				
2	1	68	3.31	3	1	43	2.61	2
	3	55	2.63	3	3	40	2.58	2
	10	54	2.51	3	7	41	2.54	2
	16	51	2.29	3	9	41	2.57	2
3	1	71	4.10	3	1	45	2.76	3
	3	66	3.40	3	3	45	2.74	2
	10	62	3.12	2	7	38	2.77	2
	16	55	3.08	3	9	38	2.77	2
4					1	48	3.08	2
					3	46	3.10	3
					7	40	3.09	3
					9	41	3.04	2

^a Draw ratio. ^b Elongation percent at break.

Conclusions

We prepared the linear aromatic polyester nanocomposites, such as PET and PTT, in which organoclay was dispersed at the nanometer-scale level, via an in-situ interlayer polymerization approach. Hybrids of different organoclay (C₁₂PPh-MMT) contents

were extruded with different DRs from a capillary rheometer to investigate the thermo-mechanical properties and the morphology. We found that a small added amount of C₁₂PPh-MMT was enough to improve the properties of the polyester matrix polymer. The thermal stability of the hybrid fibers were shown to be better than those of pure polyester fibers and increased with organoclay loading (1 - 4 wt%). The tensile mechanical properties of the C₁₂PPh-MMT/polyester hybrid fibers monotonically increased with increasing amount of organoclay in the polyester matrix at DR=1. On the other hand, the values of the ultimate strength and the initial modulus of the organoclay-loaded polyester hybrid fibers decreased with increasing DR.

Acknowledgements. This work was supported by grant No. R05-2003-000-10438-0 from the Korea Science & Engineering Foundation.

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