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Poly(butylene terephthalate)/organoclay nanocomposites prepared by in situ interlayer polymerization and its fiber (II)

Jin-Hae Chang[a,*], Yeong Uk An[a], Sung Jong Kim[a], Seungsoon Im[b]

[a]*Department of Polymer Science and Engineering, Kumoh National University of Technology, Kumi 730-701, South Korea*
[b]*Department of Fiber and Polymer Engineering, Hanyang University, Seoul 133-791, South Korea*

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Abstract

Intercalated nanocomposites with poly(butylene terephthalate) (PBT) incorporated between the montmorillonite layers were synthesized from dimethyl terephthalate and 1,4-butane diol by using an in situ interlayer polymerization. The PBT nanocomposites were melt-spun at different organoclay contents to produce monofilaments. The samples were characterized by using wide angle X-ray diffraction, electron microscopy, thermal analysis, and tensile testing. The extent of the clay layer in the PBT was confirmed by using X-ray diffraction and electron microscopy, and the clay layer was found to be highly dispersed on a nanometer scale. The addition of only a small amount of organoclay was enough to improve the thermo-mechanical properties of the PBT hybrid fibers. The hybrids were extruded with various draw ratios (DRs) to examine the tensile mechanical property of the fibers. At DR = 1, the ultimate tensile strength of the hybrid fibers increased with the addition of clay up to a critical content and then decreased. However, the initial modulus monotonically increased with increasing amount of organoclay in the PBT matrix. When the DR was increased from 1 to 6, for example, the strength and the initial modulus values of the hybrids containing 3 wt% organoclay decreased linearly.

Keywords: PBT nanocomposite fibers; In situ interlayer polymerization; Organoclay

1. Introduction

Although Blumstein [1] demonstrated polymerization of vinyl monomers intercalated into montmorillonite clay as early as 1961, numerous methods to prepare polymer/clay nanocomposites have recently been developed by several groups [2–5]. To overcome problems of macro- and micro-phase separation between organic polymers and inorganic clays, organic/inorganic polymer hybrids have mostly been synthesized by using three methods: solution intercalation [6,7], melt intercalation [8,9], and in situ polymerization intercalation [3,10,11]. Additionally, other approaches, such as the sol–gel process [12,13] and monomer/polymer grafting to clay layers [14,15], have resulted in organic/inorganic polymer hybrids. Among these, melt intercalation and in situ intercalation are the two techniques most commonly used to prepare polymer/clay nanocomposites.

In the process of melt intercalation [16,17], the layered silicate is mixed with a molten polymer matrix. If the silicate surfaces are sufficiently compatible with the chosen polymer, then the polymer can enter the interlayer space and form an intercalated or an exfoliated nanocomposite. Ha et al. [18] prepared PBT nanocomposites via melt intercalation with organoclays. They observed good nanoparticle dispersion of the organoclay in the polymer matrix. Otherwise, in situ intercalation polymerization is a method based on the use of one or more monomers that may be in situ linearly polymerized or crosslinked and was the first method used to synthesized polymer-layered silicate nanocomposites based on polyamide 6 [10]. The in situ intercalation method relies on the swelling of the organoclay due to by the monomer, followed by in situ polymerization initiated thermally or by the addition of a suitable compound. The chain growth in the clay galleries triggers clay exfoliation and nanocomposite formation. Thus, an advantage of the in situ method is the preparation of polymer hybrids without physical or chemical interactions between the organic polymer and the inorganic material [3,10,11,19,20].

* Corresponding author. Tel.: +82-54-467-4292; fax: +82-42-483-6155.
E-mail address: changjinhae@hanmail.net (J.H. Chang).

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When thermoplastic polymer nanocomposites are prepared, 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, interlayer cations, such as Na^+, Ca^+, and K^+, are replaced with alkyl ammonium cations and enhance the dispersibility. Since the thermal stability of these kinds of organoclays has been a problem, i.e. thermal degradation in polyesters being processed at temperatures of 250 °C or more, much attention has been directed toward the preparation of high-temperature stable organoclays [21–23].

The objective of this study was to evaluate the effect of the organoclay in poly(butylene terephthalate) (PBT) composites, as a hybrid system, as a function of the amount of organoclay. In this paper, we describe a method for making PBT nanocomposites by using in situ interlayer polymerization. We also report the thermo-mechanical properties and the morphologies of PBT hybrid fibers with different organoclay contents and different draw ratios (DRs).

2. Experimental

2.1. Materials

The reagents were purchased from TCI, Junsei Chemical Co. and Aldrich Chemical Co. Commercially available solvents were purified by distillation. Common reagents were used without further purification. The organically modified montmorillonite used in this study was kindly supplied by NC Technology, Co. and had been synthesized by using an ion-exchange reaction between Na^+-montmorillonite (Na^+-MMT) and alkyl ammonium (NCT) chloride. The chemical structure of NCT-MMT is as follows:

2.2. Preparation of PBT/NCT-MMT hybrids

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 preparation of nanocomposites containing 2 wt% organoclay, is given. In a polymerization tube, 100 g of 1,4-butane diol (BD) (1.1 mol) and 2.2 g of NCT-MMT were placed; the mixture was stirred for 30 min at room temperature. In a separate tube, 97 g of dimethyl terephthalate (DMT) (0.5 mol) and 60 mg (2.1×10^{-4} mol) of isopropyl titanate were mixed; this mixture was added to the organoclay–BD system and was mechanically stirred to obtain a homogeneously dispersed system. This mixture was then heated for 1 h at 190 °C under a steady stream of N_2 gas. Next, the temperature was raised to 230 °C and was maintained there for 2 h under a steady stream of N_2 gas. During this period, continuous generation of methanol was observed. Finally, the system was heated for 3 h at 260 °C at a pressure of 1 Torr. The product formed was cooled to room temperature, repeatedly washed with water, and dried under vacuum at 70 °C for 1 day to obtain the nanocomposites. A schematic illustration of the composite synthesis is shown in Fig. 1.

2.3. Extrusion

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

2.4. 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 measurements were performed at room temperature by using a Rigaku (D/Max-IIIB) X-ray diffractometer with Ni-filtered Co Kα radiation. d-Spacing experimental

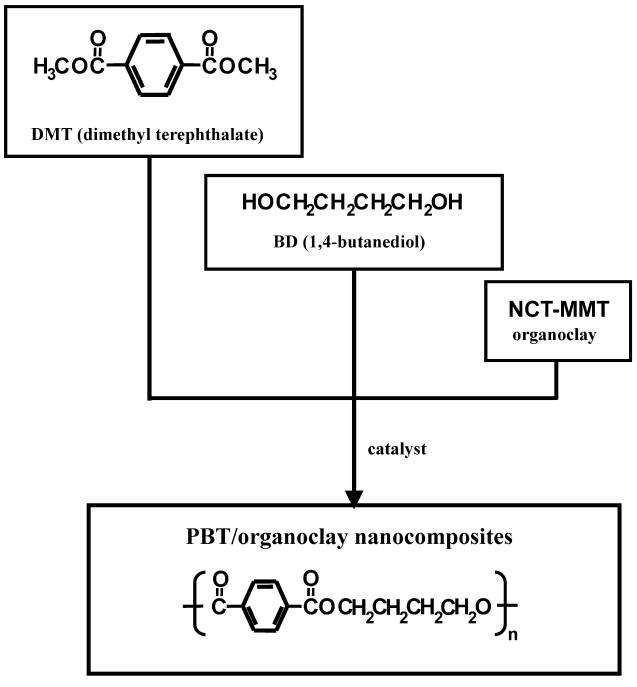

Fig. 1. Schematic representation of the preparation of PBT hybrids.

standard uncertainty was ±1.2 Å. 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 specimens were prepared by cutting strips 5 mm wide by 70 mm long. 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 morphologies of the fractured surfaces of the extruded fibers were investigated using a Hitachi S-2400 scanning electron microscope (SEM). An SPI sputter coater was used to sputter-coat the fractured surfaces with gold for enhanced conductivity. 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 h in vacuum. After that, the cured epoxies containing the PBT hybrids for TEM observation were microtomed into 90 nm 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.

3. Results and discussion

3.1. Dispersibility of organoclay in PBT

Fig. 2 illustrates the XRD patterns of pristine clay and organoclay. The characteristic peak for pristine clay, Na^+-MMT, appears at $2\theta = 8.56°$ ($d = 11.99$ Å). For Na^+-MMT reacted with alkylamine, NCT-MMT, this peak is broadened and shifted to $2\theta = 3.98°$ ($d = 25.75$ Å), suggesting that the clay is swollen to the range of the d spacing. In general, a greater interlayer spacing should be advantageous in the intercalation of polymer chains [24–27]. It should also lead to easier dissociation of the clay, which should result in hybrids with better dispersions of clay. In addition to the main diffraction peak, an additional small peak is observed at $2\theta = 7.13°$ ($d = 14.38$ Å). This secondary peak may be related to the XRD spectra of the organoclay itself.

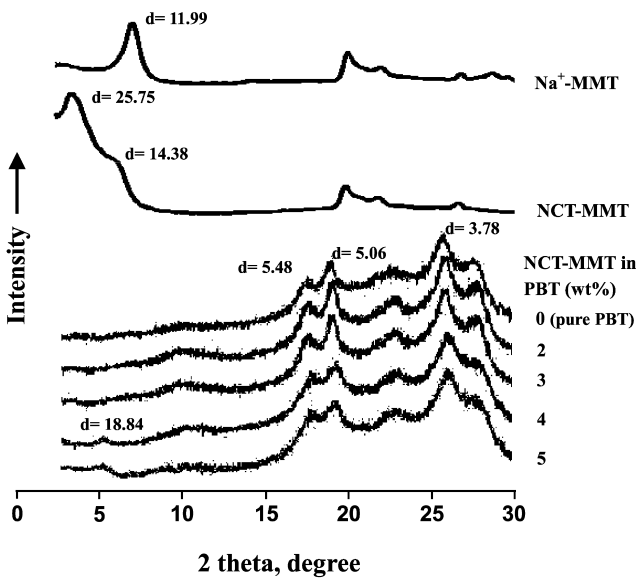

Fig. 2. XRD patterns for clay, organoclay, and PBT hybrid fibers with various organoclay contents.

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

XRD is most useful for the measurement of the d-spacing of ordered immiscible and ordered intercalated polymer nanocomposites with clay, but it may be insufficient for the measurement of disordered and exfoliated materials that give no peak. The organoclay dispersion in PBT was crosschecked further by using the SEM and TEM data, as discussed in the next section.

3.2. Morphology

It is well known that XRD information alone is not sufficient to characterize a nanocomposite. The XRD results noted above give useful information on the state of the nanocomposites, but do not provide a complete picture; thus, electron microscopic measurements (SEM and TEM) are required.

SEM micrographs of the fractured surfaces of PBT hybrid fibers prepared with different clay contents are compared in Fig. 3. The micrographs of the pure PBT (Fig. 3(a)) and the PBT hybrid fiber containing 3 wt% NCT-MMT (Fig. 3(b)) show smooth surfaces due to better dispersed clay particles. Conversely, Fig. 3(c) and (d) show voids and some deformed regions that may result from the coarseness of the fractured 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 [28,29]. More direct evidence for the formation of a true nano-scaled composite was provided by TEM analysis of an ultra-microtomed section.

The TEM micrographs are presented in Fig. 4. 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. 4(a) and (b) show individual dispersion of delaminated sheets in the matrix, as well as regions where the regular stacking arrangement is

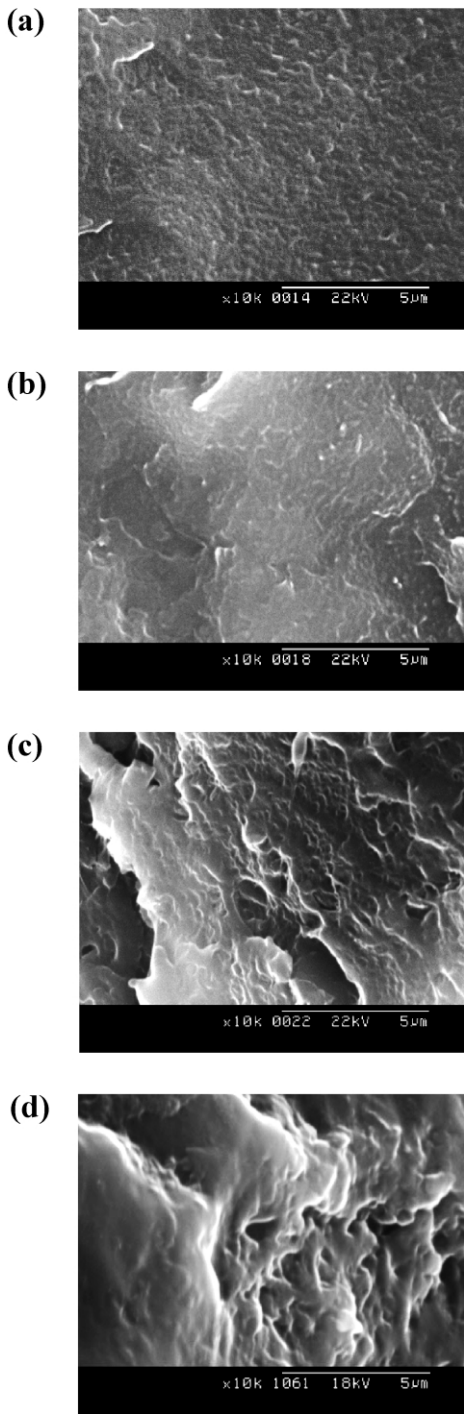

Fig. 3. SEM photomicrographs of (a) 0% (pure PBT), (b) 3%, (c) 4%, and (d) 5% NCT-MMT in PBT hybrid fibers at DR = 1.

maintained with a layer of polymer between the sheets. Although a face-to-face layer morphology is retained, the layers are irregularly separated by ~4–10 nm of polymer. For the 4 and the 5 wt% organoclay-loaded PBT hybrid fibers (Fig. 4(b) and (c)), however, some of the clay is well dispersed in the PBT matrix, and some of it is agglomerated to a size of approximately 4-8 nm. This is consistent with the XRD results shown in Fig. 2.

From the results of XRD and electron micrographs, the morphology at a low organoclay content (<3 wt%) presents a mixture of intercalated and partially exfoliated features. The dispersion is better at a lower organoclay loading than at a high organoclay loading.

3.3. Thermal properties

The thermal properties of PBT hybrids with different contents of organoclay are listed in Table 1. A mixed solvent of phenol/tetrachloroethane was used in measuring the solution viscosities. The solution viscosity values were reasonably high, 0.84–1.16. The glass transition temperatures (T_g) of the PBT hybrids increased from 27 to 33 °C with increasing clay loading from 0 to 2 wt% and then remained fairly constant up to 5 wt% organoclay. The increase in the T_g of these hybrids may be the result of two factors [30–33]. First, the effect of a small amount of dispersion of the clays on the free volume of PBT is significant and has an influence on the glass transition temperature of the PBT hybrids. Second, confinement of intercalated polymer chains within the clay galleries prevents segmental motions of the polymer chains.

The endothermic peak of pure PBT appears at 222 °C and corresponds to the melting temperature (T_m). Similar to the result for T_g, the DSC thermograms show that the value of T_m increases from 222 to 230 °C with increasing organoclay content up to 2 wt%, and then remained constant for additional organoclay loading up to 5 wt% (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 interaction between the organoclay and PBT molecular chains [34,35].

The thermal stabilities determined from TGA analyses of PBT/NCT-MMT are shown in Table 1 and Fig. 5. In addition to having a higher glass transition temperature and melting temperature, thermal degradation properties of PBT hybrids also exhibit more thermal stability than pure PBT. The initial decomposition temperature (T_D^i) of the hybrid clearly increases with increasing NCT-MMT up to 2 wt% and then remains constant, regardless of the organoclay loading. At a 2% weight loss of PBT/NCT-MMT in the TGA curves, the values of T_D^i for the hybrid increased from

Table 1
General properties of PBT nanocomposite fibers

Clay (wt%)	I.V.[a]	T_g (°C)	T_m (°C)	T_D^i[b] (°C)	W_R^{600c} (%)
0 (pure PBT)	0.84	27	222	371	1
2	1.16	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 weight-loss temperature.
[c] Weight percent of residue at 600 °C.

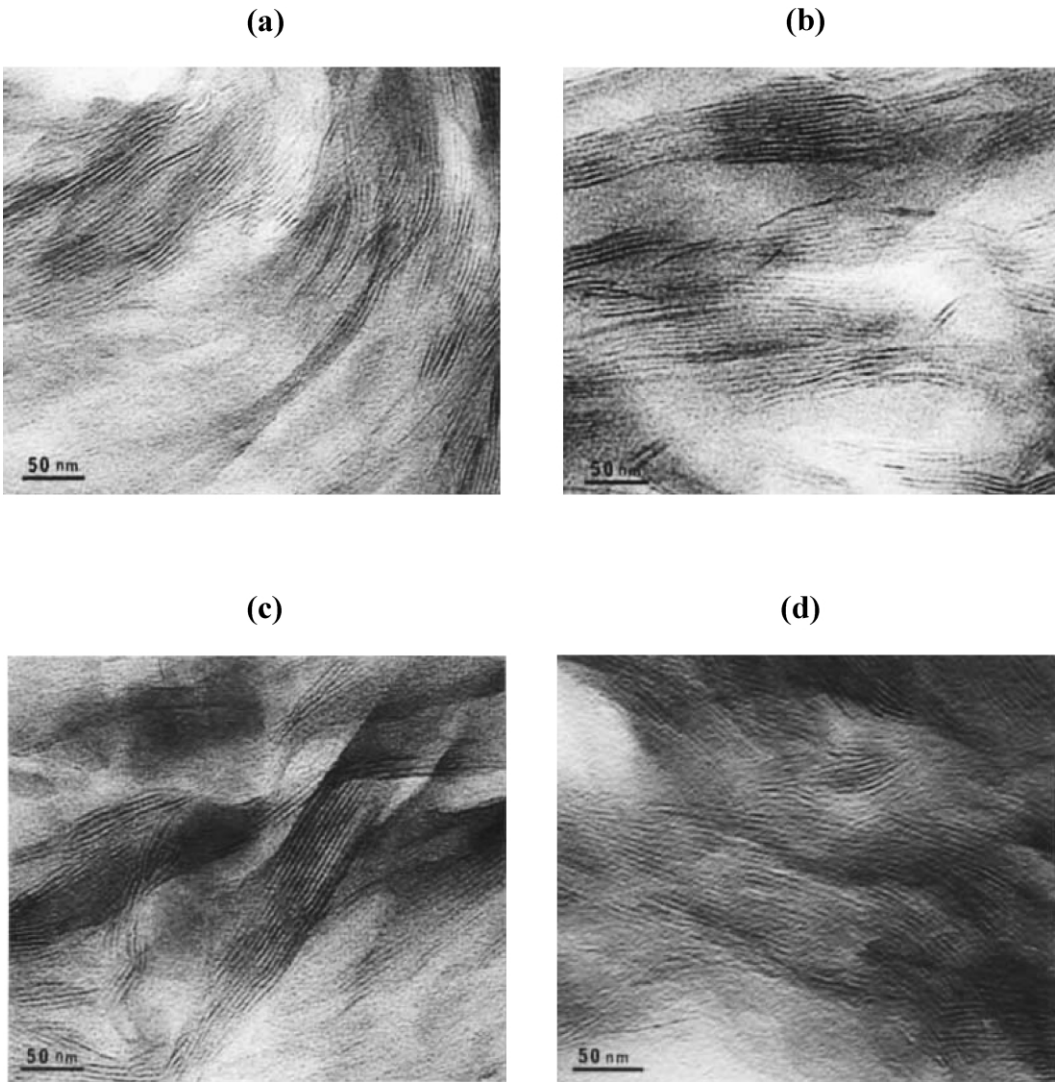

Fig. 4. TEM photomicrographs of (a) 2%, (b) 3%, (c) 4%, and (d) 5% NCT-MMT in PBT hybrid fibers at DR = 1.

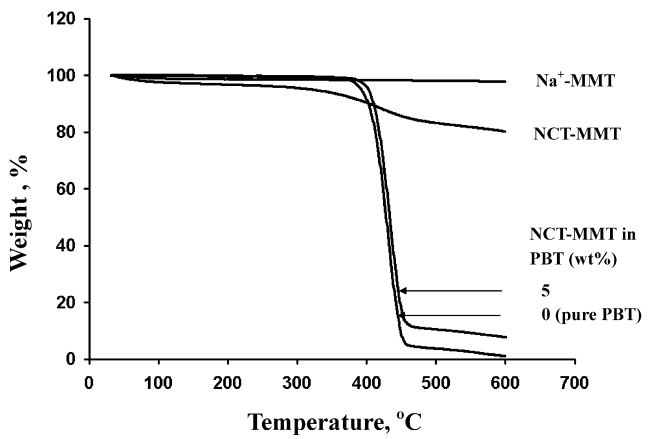

Fig. 5. TGA thermograms of clay, organoclay, and PBT hybrid fibers with various organoclay contents.

388 to 390 °C with increasing clay content from 2 to 5 wt%. The weight loss due to the decomposition of PBT and its hybrids was nearly the same until a temperature of 350 °C (Fig. 5). Above 350 °C, 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 as a mass-transport barrier to the volatile products generated during decomposition. This kind of improvement in thermal stability has also been observed in many systems of hybrids [36–39]. The weight of the residue at 600 °C increased with increasing clay loading from 0 to 5%, ranging from 1 to 9%. This enhancement of the char formation is ascribed to the high heat resistance due to the clay itself.

Considering the above results, we find it consistently believable that the introduction of an inorganic clay component into an organic polymer can improve polymer's thermal properties due to the good thermal stability of the clay. However, in this hybrid system the maximum effect on

the thermal properties was seen at an organoclay loading of 2 wt%.

3.4. Mechanical properties

The pure PBT and the PBT hybrids were extruded through a capillary die with different DRs to examine the tensile strength and 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 hybrids are given in Table 2. At DR = 1, the ultimate tensile strength of the PBT/NCT-MMT 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 3 wt% PBT hybrid fibers is 60 MPa, which is about 50% higher than that of pure PBT (41 MPa). When the amount of organoclay in PBT reaches to 5 wt%, the strength has decreased again to 49 MPa. This suggests that the NCT-MMT domains are more agglomerated above a 3 wt% organoclay content in the PBT matrix [34,40,41]. Evidence for clay agglomeration in the PBT matrix polymer was also provided by XRD, SEM, and TEM, as shown in Figs. 2–4.

However, the initial modulus monotonically increased with increasing organoclay content in the PBT matrix (Table 2). The value of the initial modulus increased constantly 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 [42]. The percent elongations at the break of all the hybrids were 6–7%. These values remained constant for organoclay loadings from 2 to 5 wt%.

On the basis of the aforementioned results, the enhancement of the mechanical properties can be directly attributed to the reinforcement provided by the intercalation of PBT in clay galleries, as well as by the fine dispersion of clay particles in the polymer matrix. The amount of increase in the tensile properties caused by the clay layers depends on the interactions between rigid, rod-shaped polyester molecules and layered clay, as well as the rigid nature of the clay layers.

The hybrids were extruded with increasing DRs to examine the tensile mechanical properties of fibers of the 3 wt% hybrid. As Table 3 shows, the values of the strength and the initial modulus for pure PBT fibers were enhanced with increasing DR. However, as expected for the case of a flexible coil polymer, the increases in the tensile strength and the modulus with increasing DR were insignificant for pure PBT. Table 3 shows that for pure PBT, the strength and the modulus values increased slightly from 41 to 52 MPa and from 1.37 to 1.52 GPa, respectively, with increasing DR from 1 to 6. On the other hand, the values of the strength and the initial modulus of the hybrid fibers decreased with increasing DR. For the hybrid with 3 wt% organoclay, for example, when the DR was increased from 1 to 6, the ultimate strength and the initial modulus decreased from 60 to 29 MPa and from 1.76 to 1.39 GPa, respectively. These trends with increasing DR were observed in all our systems containing 2–5 wt% organoclay. This declination in the tensile properties seems to be the result of debonding between the organoclay and the PBT and the presence of many micro-sized voids due to excess stretching of the fibers. Similar trends have been observed by researchers studying other polymer hybrids [43–45]. Those researchers reported that an imperfect incursion/matrix interface cannot sustain the large interfacial shear stress that develops as a result of an applied strain. This usually causes yielding or debonding, or both, to occur at or near the interface. Because of imperfect bonding, debonding occurs at the interface, giving rise to a constant interfacial shear stress when strain is applied to the composite. The effects of debonding and voids on the mechanical properties of our system of different DRs will be pursued in a future work.

These observations supported two facts. Better dispersion of the clay layer in the polymer and a strong interaction between the polymer and the clay layer are essential for achieving higher tensile properties in polymer nanocomposites.

Table 2
Mechanical properties at DR = 1 of PBT nanocomposite fibers

Clay (wt%)	Ult. Str. (MPa)	Ini. Mod. (GPa)	E.B.[a] (%)
0 (pure PBT)	41	1.37	5
2	50	1.66	7
3	60	1.76	6
4	53	1.80	7
5	49	1.86	7

[a] Elongation percent at break.

Table 3
Effect of the DR on the tensile properties of PBT nanocomposite fibers

Clay (wt%)	Ult. Str. (MPa)			Ini. Mod. (GPa)		
	DR = 1	DR = 3	DR = 6	DR = 1	DR = 3	DR = 6
0 (pure PBT)	41	50	52	1.37	1.49	1.52
3	60	35	29	1.76	1.46	1.39

4. Conclusion

We prepared PBT nanocomposites, in which organoclay is dispersed at the nanometer-scale level, via an in situ interlayer polymerization approach. Hybrids of different organoclay (NCT-MMT) contents were extruded with different DRs from a capillary rheometer to investigate the thermo-mechanical properties and the morphology of the hybrids. We found that a small added amount of NCT-MMT

was enough to improve the properties of the PBT matrix polymer. The thermal behaviors (T_g, T_m, and T_D^i) of the hybrid fibers were shown to be better than those of pure PBT fibers and were unchanged by the organoclay loading (2–5 wt%). The ultimate tensile strength of the PBT/NCT-MMT hybrid fibers increased with the addition of organoclay up to a critical organoclay content (3 wt%) and then decreased. However, the initial modulus monotonically increased with increasing amount of organoclay in the PBT matrix.

On the other hand, the values of the ultimate strength and the initial modulus of the 3 wt% organoclay-loaded hybrid fibers decreased significantly as the DR was increased from 1 to 6. Further studies of the relationships between the mechanical properties and the DR for hybrid fibers are currently being conducted.

Acknowledgements

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