

# Synthesis and Characterization of Poly(butylene terephthalate)/Mica Nanocomposite Fibers via *In Situ* Interlayer Polymerization

Jin-Hae Chang,<sup>1</sup> Mu Kyung Mun,<sup>1</sup> Jeong-Cheol Kim<sup>2</sup>

<sup>1</sup>Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi 730-701, Korea

<sup>2</sup>Gwangju R&D Center, Korea Institute of Industrial Technology, Gwangju 500-460, Korea

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**ABSTRACT:** Intercalated nanocomposites consisting of poly(butylene terephthalate) (PBT) incorporated between mica layers were synthesized from dimethyl terephthalate (DMT) and 1,4-butanediol (BD) by *in situ* interlayer polymerization. PBT nanocomposites of varying organoclay content were melt-spun to produce monofilaments. The samples were characterized using wide angle X-ray diffraction, electron microscopy, thermal analysis, and tensile testing. Some of the clay particles were found to be well dispersed in the PBT matrix, but other clay particles were agglomerated at a size level greater than approximately 20 nm. The glass transition temperatures ( $T_g$ ) and the thermal degradation properties ( $T_D^i$ ) of undrawn PBT hybrid fibers were found to improve with increases in

the clay content. At draw ratio (DR) = 1, the ultimate tensile strengths of the hybrid fibers increased with the addition of clay up to a critical content and then decreased. However, the initial moduli monotonically increased with increases in the amount of organoclay in the PBT matrix. The ultimate strengths were found to decrease linearly with increases in DR from 1 to 18. In contrast to the trend for the tensile strengths, the initial moduli of the hybrid fibers increased only slightly with increases in DR up to 18. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1248–1255, 2007

**Key words:** PBT; nanocomposite; fiber; *in situ* interlayer polymerization; organoclay

## INTRODUCTION

Poly(butylene terephthalate) (PBT) is an engineering thermoplastic with good thermal stability, good chemical resistance, excellent flow properties, a fast re-crystallization rate, a poor impact strength, and a low heat distortion temperature. Many attempts<sup>1–3</sup> have been made to overcome the drawbacks of PBT by blending with fillers. Unfortunately, the existence of the fillers often decreased other properties of PBT, such as its tensile property and thermal stability.

Organic–inorganic nanometer-scaled blended composites, called nano-composites or organic–inorganic hybrids, have attracted great interest from many researchers because they often exhibit unexpected hybrid properties synergistically derived from the two components.<sup>4–8</sup> The fabrication of organic/inorganic hybrids can produce materials with excellent ther-

momechanical and gas barrier properties, and that have far less inorganic content than conventionally filled polymer composites; it has been found that the higher the degree of delamination in polymer/clay nanocomposites, the greater the enhancement of these properties.<sup>9–13</sup>

Clays have sandwich-type structures that typically consist of one octahedral Al sheet and two tetrahedral Si sheets, a so-called phlo-silicate structure. There are many types of phlo-silicates: kaolinite, montmorillonite (MMT), hectorite, saponite, synthetic mica, etc. MMT and synthetic mica (Mica) were chosen in our study of the synthesis of clay/polymer nanocomposites. MMT and Mica consist of stacked silicate sheets with lengths of about 220 and 1230 nm respectively.<sup>14,15</sup> They have the same sheet thickness of 1 nm. MMT has a high swelling capacity, which is essential for efficient intercalation of the polymer, and is composed of stacked silicate sheets that provide good thermal, tensile, and molecular barrier properties, as do its hybrid materials with polymers. Mica is a different kind of clay that has been widely used as a reinforcing filler in polymeric matrices because of its excellent mechanical, electrical and thermal properties. Pristine mica-type layered silicates usually contain hydrated  $\text{Na}^+$  or  $\text{K}^+$ . Micas also have the highest layer charge density among

Correspondence to: J.-H. Chang (changjinhae@hanmail.net).

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the clays. Although naturally occurring micas are nonswelling, synthetic micas, which swell in water, can be prepared by hydrothermal, solid-state, and topotactic exchange methods.

To overcome the problems of macro- and micro-phase separation of organic polymers and inorganic clays, organic/inorganic polymer hybrids have mostly been synthesized using three methods<sup>6,16–20</sup>: solution intercalation, melt intercalation, and *in situ* polymerization intercalation. Among these methods, melt intercalation and *in situ* intercalation are the techniques most commonly used to prepare polymer/clay nanocomposites. The *in situ* intercalation method relies on swelling the organoclay with the monomer, followed by *in situ* polymerization initiated thermally or by the addition of a suitable compound. Chain growth in the clay galleries then triggers clay exfoliation and nanocomposite formation. An advantage of the *in situ* method is thus the preparation of polymer hybrids without physical or chemical interactions between the organic polymer and the inorganic material.<sup>19–21</sup>

Elevated temperatures are required for the melt intercalation and bulk processing used in the preparation of thermoplastic polymer nanocomposites. 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<sup>+</sup>, Ca<sup>+</sup>, and K<sup>+</sup>, are replaced with alkyl ammonium cations to enhance the dispersibility. Since the thermal stability of these kinds of organoclays is a problem, because thermal degradation occurs in polyesters processed at temperatures of 250°C or more, much attention has been directed toward the preparation of organoclays that are stable at high temperatures.<sup>22–25</sup>

The objective of the present study was to evaluate the effects of varying the organoclay content of the PBT nanocomposite fibers on their properties. To obtain nanocomposites without producing thermal degradation during processing, we used the thermally stable organoclays C<sub>12</sub>PPh-Mica. In this paper, we describe a method for fabricating PBT nanocomposites by using *in situ* interlayer polymerization. We also report the variations of the thermomechanical properties and morphologies of the PBT hybrid fibers with organoclay content and DR.

## EXPERIMENTAL

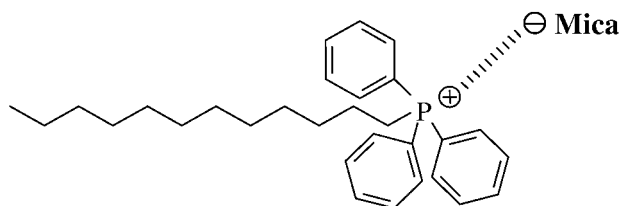
### Materials

Na<sup>+</sup>-type fluorinated synthetic mica (Na<sup>+</sup>-Mica) with the free OH group of the mica replaced by fluorine was supplied by CO-OP Ltd. (Tokyo, Japan). Its

cationic exchange capacity was found to be in the 70–80 mequiv./100 g range. All reagents were purchased from TCI (Tokyo, Japan), Junsei Chemical Co. (Tokyo, Japan), and Aldrich Chemical Co. (Seoul, Korea). Commercially available solvents were purified using distillation.

### Preparation of the organoclay: C<sub>12</sub>PPh-Mica

Dispersions of Na<sup>+</sup>-Mica were added to solutions of the phosphonium salt of dodecyltriphenyl (C<sub>12</sub>PPh<sup>-</sup>). The organophilic clay was obtained through a multi-step process with the same methods as described in our previous paper,<sup>25</sup> and is denoted C<sub>12</sub>PPh-Mica. The chemical structure of C<sub>12</sub>PPh-Mica is as shown:



### *In situ* polymerization

Dimethyl terephthalate (DMT, 99%) and C<sub>12</sub>PPh-Mica were dried at 80°C overnight under vacuum prior to use. The samples were obtained by melt polymerization method. Since the syntheses of the hybrids were very similar, only a representative example, the procedure for the preparation of the nanocomposite containing 2 wt % organoclay is described here. An amount of 90.1 g of 1,4-butanediol (BD) (1.0 mol) and 2.24 g of C<sub>12</sub>PPh-Mica were placed in a polymerization tube, and the mixture was stirred for 30 min at room temperature. 97 g of DMT (0.5 mol) and 0.034 mg (1.2 × 10<sup>-4</sup> mol) of isopropyl titanate were placed in a separate tube, and the organoclay/BD system was added to this mixture. Mechanical stirring was used to obtain a homogeneously dispersed system. This mixture was heated for 1 h at 190°C under a steady stream of N<sub>2</sub> gas. The temperature of the reaction mixture was then raised to 230°C and maintained there for 2 h under a steady stream of N<sub>2</sub> gas. During this period, continuous generation of methanol was observed. Finally, the mixture was heated for 2 h at 260°C at a pressure of 1 Torr. The product was cooled to room temperature and repeatedly washed with water. It was dried under vacuum at 70°C for 1 day to obtain the nanocomposite. Inherent viscosities were measured at 30°C by using 0.1 g/100 mL solutions in a phenol/1,1,2,2-tetrachloroethane (w/w = 50/50) mixture. The inherent solution viscosity numbers (see Table I) range from 0.81 to 0.91.

We tried to synthesize PBT hybrids containing more than 3 wt % organoclay using the *in situ* inter-

**TABLE I**  
**Thermal Properties of PBT Hybrid Fibers**

Organoclay (wt %)	D.R.	I.V. <sup>a</sup>	$T_g$ (°C)	$T_m$ (°C)	$T_d^b$ (°C)	wt <sub>R</sub> <sup>600c</sup> (%)
0 (Pure PBT)	1	0.91	27	222	366	1
1	1	0.89	33	223	371	2
2	1	0.83	32	222	373	3
3	1	0.81	33	223	375	7
	12		33	222	374	7
	18		34	223	375	7

<sup>a</sup> Inherent viscosities were measured at 30°C by using 0.1 g/100 mL solutions in a phenol/1,1,2,2-tetrachloroethane (w/w = 50/50) mixture.

<sup>b</sup> Initial weight-loss temperature.

<sup>c</sup> Weight percent of residue at 600°C.

layer approach. However, repeated attempts to polymerize the 4 wt % C<sub>12</sub>PPh-Mica/PBT hybrid failed due to bubbles produced in the polymerization reactor during the transesterification of DMT and BD. The problem of how to produce a high molecular weight polymer hybrid with a high organoclay content without the formation of bubbles remains unresolved. The solution of this problem is one objective of our future research.

### Characterization

Thermal behavior of the hybrid was studied with a Du Pont model 910 differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) at a heating rate of 20°C/min under a N<sub>2</sub> flow. Wide-angle X-ray diffraction measurements were performed at room temperature with an X'Pert PRO-MRD X-ray diffractometer using Ni-filtered Cu-K $\alpha$  radiation. The scanning rate was 2°/min over a range of  $2\theta = 2\text{--}15^\circ$ .

The tensile properties of the fibers were determined at room temperature using an Instron mechanical tester (Model 5564) at a crosshead speed of 20 mm/min. These properties were determined from the average of at least 10 individual determinations.

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 were prepared for transmission electron microscopy (TEM) by placing the PBT hybrid fibers into epoxy capsules and then curing the epoxy at 70°C for 24 h in vacuum. The cured epoxies containing the PBT hybrids were then microtomed into 90 nm thick slices, and a layer of carbon, about 3 nm thick, was deposited onto each slice on a mesh 200 copper net. TEM photographs of ultrathin sections of the polymer/organoclay hybrid samples were obtained with an EM 912 OMEGA transmission electron microscope using an acceleration voltage of 120 kV.

### Extrusion

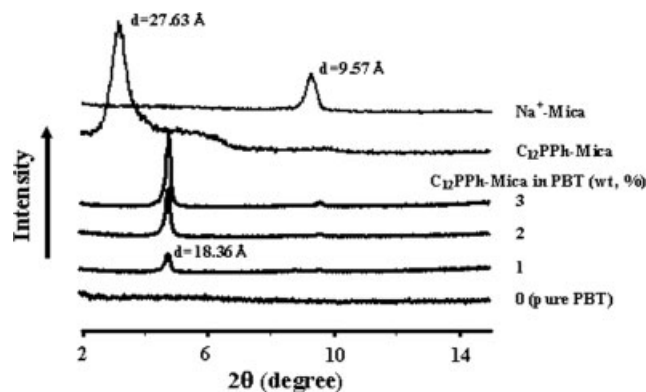
The composites were pressed at 235°C, 2500 kg/cm<sup>2</sup>, for 2–3 min on a hot press. The resulting ~ 0.5 mm thick films were dried in a vacuum oven at 80°C for 24 h; the hot extrudates were then extruded through the die of a capillary rheometer (INSTRON 5460) at 240°C and immediately drawn at the constant speed of the take-up machine to form fibers with various DRs. Pure PBT was also extruded into fibers with various DRs through a capillary die, and the thermal and tensile mechanical properties of all the extrudates were then examined. The standard die diameter (DR = 1) was 0.75 mm.

When the concentration of the organoclay was in the range 0 to 3 wt %, the fibers obtained from the capillary rheometer were found to be bright yellow. The DR was calculated from the ratio of the velocity of extrusion to the take-up speed. The mean residence time in the capillary rheometer was ~ 2–3 min.

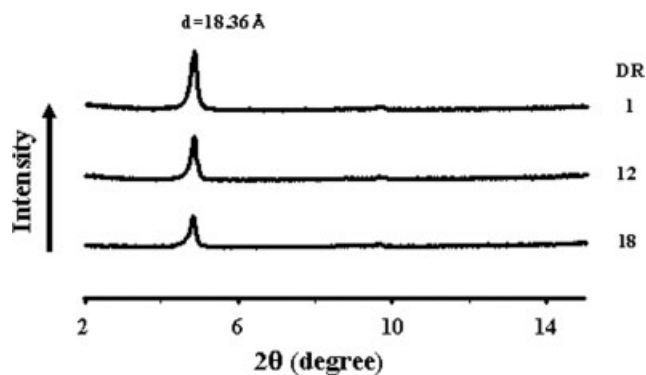
## RESULTS AND DISCUSSION

### Wide angle X-ray diffraction

The XRD results for the C<sub>12</sub>PPh-Mica/PBT nanocomposites are shown in Figure 1. The  $d_{001}$  reflection for



**Figure 1** XRD patterns of clay, organoclay, and PBT hybrid fibers with various organoclay contents.



**Figure 2** XRD patterns of 2 wt %  $C_{12}$ PPh-Mica/PBT hybrid fibers with various DRs.

$Na^+$ -Mica was found at  $2\theta = 9.23^\circ$ , which corresponds to an interlayer distance of 9.57 Å. The XRD peak for the surface-modified clay,  $C_{12}$ PPh-Mica, was found at  $2\theta = 3.20^\circ$ , corresponding to an interlayer distance of 27.63 Å. As expected, ion exchange between  $Na^+$ -Mica and dodecyltriphenylphosphonium chloride ( $C_{12}$ PPh- $Cl^-$ ) results in an increase in its basal interlayer spacing over that of pristine  $Na^+$ -Mica, and in a big shift of the diffraction peak toward lower values of  $2\theta$ . In general, a larger interlayer spacing should be advantageous in the intercalation of polymer chains.<sup>26–28</sup> It should also lead to easier dissociation of the clay, and thus result in hybrids with better clay dispersion.

Only a small peak at  $d = 18.36$  Å ( $2\theta = 4.81^\circ$ ) was found in the XRD results for the PBT extrudate fibers with 1 wt % organoclay content. This indicates that agglomeration of a small part of the clay has occurred in the PBT matrix. Substantial increases in the intensities of the XRD peaks were observed as the clay loading was increased from 1 to 3 wt %, suggesting that dispersion is more effective for lower clay loadings than for higher clay loadings. Higher clay loadings are expected to result in increased agglomeration of some portion of the clay within the PBT matrix. The  $d_{001}$  reflection of  $Na^+$ -Mica at  $2\theta = 9.23^\circ$  is also seen in the modified clay ( $C_{12}$ PPh-Mica), as well as in the hybrids. This means that pristine mica is present in the final materials, as well as in the PBT/ $C_{12}$ PPh-Mica hybrids, for  $C_{12}$ PPh-Mica contents up to 3 wt %. The presence of the organoclay was found, however, to have no effect on the location of the peak, which indicates that exfoliation of the layer structure of the organoclay does not occur in PBT.<sup>29</sup> The level of organoclay dispersion in PBT was cross-checked further using the TEM data, which are discussed in the next section.

For PBT hybrids, the disappearance of the main peak at  $2\theta = 3.20^\circ$  is thought to be due to the peak of the swollen organoclay inserted as polymer chains having a lower diffraction peak than  $2^\circ$ . Figure 2

shows the XRD curves for PBT nanocomposites containing 2 wt % organoclay with various DRs. A peak at  $d = 18.36$  Å was found in the XRD results for the extrudate fibers with DR = 1. As DR was increased from 1 to 18, the intensity of this peak was found to decrease gradually. It has previously been suggested that increasing the stretching of fibers during extrusion results in disordered clay/polymer matrix crystalline structures.<sup>25</sup>

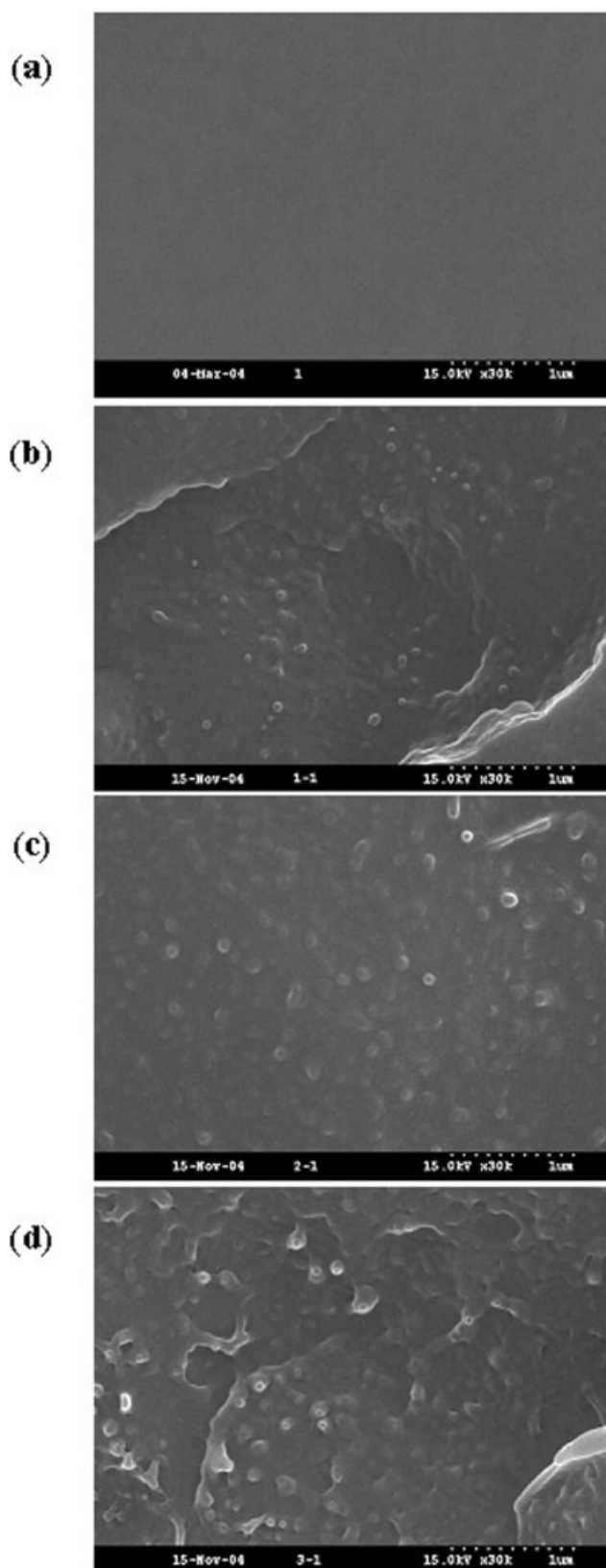
## Morphology

The morphologies of the extruded fibers obtained from hybrid systems with up to 3 wt %  $C_{12}$ PPh-Mica in the PBT matrix were examined by observing their fracture surfaces with an SEM, and the results are shown in Figures 3 and 4. The PBT hybrid fibers with 0–3 wt %  $C_{12}$ PPh-Mica have morphologies consisting of clay domains, 100–250 nm in size, in the PBT phase (see Fig. 3). Figure 4 shows micrographs of the 2 wt %  $C_{12}$ PPh-Mica/PBT hybrid fibers obtained for various DRs in the range 1–18. The 2 wt % hybrid fiber with DR = 12 contains fine clay phases that are 100–200 nm in diameter [see Fig. 4(b)]. The hybrid fiber with DR = 18 also contains pull-out particles with domain sizes of 100–150 nm [see Fig. 4(c)]. The average particle sizes of clays were decreased slightly with increasing DR, which is consistent with the XRD observations shown in Figure 2.

It is well known that SEM information alone is not sufficient to characterize nanocomposites. 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 qualitative understanding of internal structures through direct observation. Figure 5 shows TEM photographs of 2 wt % hybrid fibers. The dark lines are the cross sections of 1 nm thick sheet layers. In Figure 5, the organoclay can be seen to be well dispersed in the polymer matrix at all magnification levels, although some of the clay particles are agglomerated at size levels greater than approximately 20 nm. The presence of peaks in the XRD patterns of these samples is attributed to these agglomerated layers (see Fig. 1).

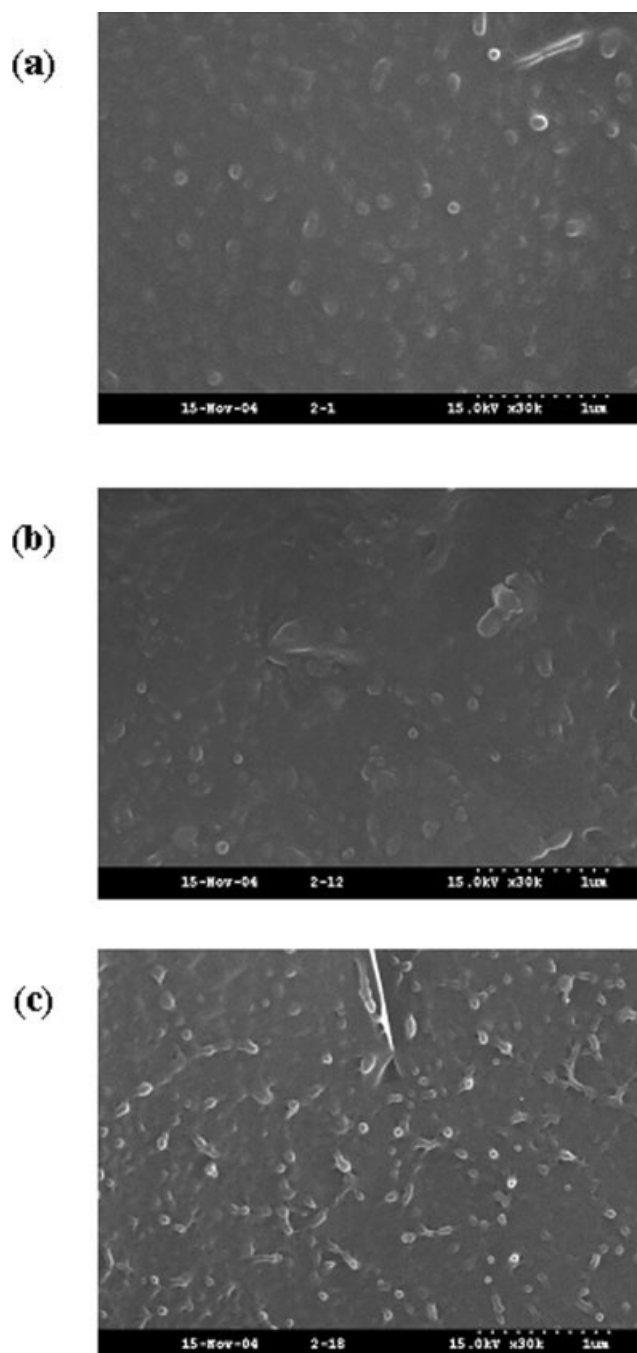
## Thermal behavior

The thermal properties of PBT hybrids with various organoclay contents are listed in Table I. A mixed solvent consisting of phenol and tetrachloroethane was used in measuring the solution viscosities. The inherent viscosities of the samples were maintained nearly the same (0.81–0.91) prior to the study. The glass transition temperatures ( $T_g$ ) of the PBT hybrids increase from 27 to 33°C with increase in the clay

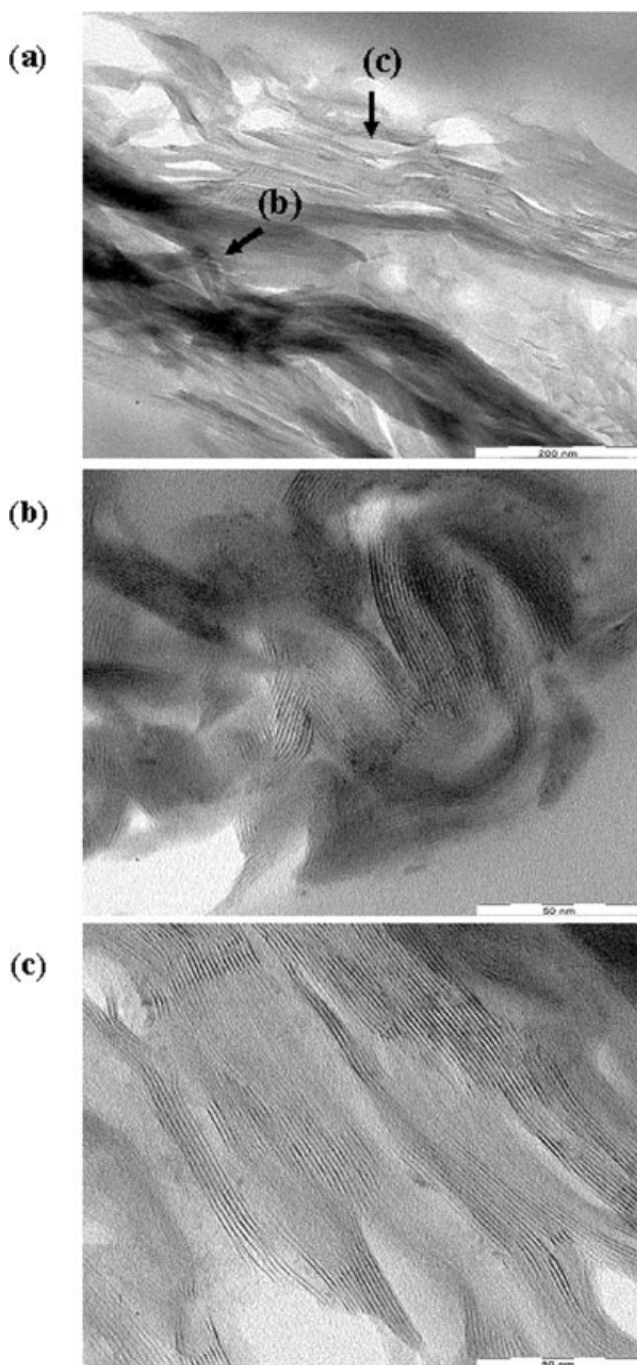


**Figure 3** SEM micrographs of  $C_{12}PPh$ -Mica/PBT hybrid fibers with various organoclay contents: (a) 0 wt % (pure PBT), (b) 1 wt %, (c) 2 wt %, and (d) 3 wt %.

loading from 0 to 1 wt %, and then remain fairly constant up to 3 wt % organoclay. The increase in the  $T_g$  of these hybrids with clay loading may be the result of two distinct factors.<sup>30</sup> First, the effect of a small amount of dispersion of the clays on the free volume of PBT is significant, and this has an influence on the glass transition temperature of the PBT hybrids. Second, the confinement of the intercalated polymer chains within the clay galleries prevents segmental motion of the polymer chains.



**Figure 4** SEM micrographs of 2 wt %  $C_{12}PPh$ -Mica/PBT hybrid fibers for various DRs: (a) 1, (b) 12, and (c) 18.



**Figure 5** TEM micrographs of 2 wt %  $C_{12}PPh$ -Mica/PBT hybrid fibers; the magnification level increases from (a) to (b) to (c).

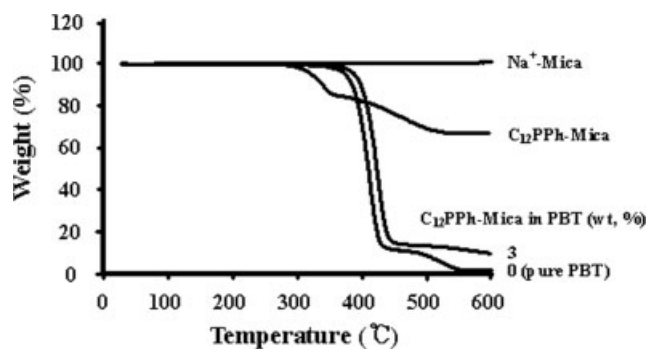
The endothermic peak of pure PBT appears at  $222^{\circ}C$ , which corresponds to the melting transition temperature ( $T_m$ ). The maximum transition peaks in the DSC thermograms of PBT hybrid fibers with various clay contents were found to be virtually unchanged from this value, for organoclay loadings in the range 1 to 3 wt %. This implies that varying the clay content does not result in improvements in

the insulation of the PBT matrix, as is evident in Table I.<sup>31,32</sup>

In contrast to the results for  $T_m$ , the PBT hybrids were found to exhibit improved thermal degradation properties. The thermal stabilities obtained from the TGA analyses of the PBT hybrids are shown in Table I and Figure 6. Table I shows that the initial thermal degradation temperatures ( $T_D^i$ ) of the PBT hybrid fibers increase with increases in the amount of organoclay. The  $T_D^i$  at 2% weight loss were found to be in the range  $366$ – $375^{\circ}C$  for clay compositions of the PBT hybrids of 0–3 wt %, with a maximum increase of  $9^{\circ}C$  in the case of 3 wt %  $C_{12}PPh$ -Mica/PBT with respect to that of pure PBT. The thermal stabilities of PBT hybrids with various clay loadings are plotted in Figure 6.

The weight loss due to the decomposition of PBT and its hybrids is nearly independent of the organoclay content for temperatures below  $350^{\circ}C$  (see Fig. 6). Above  $350^{\circ}C$ ,  $T_D^i$  is influenced by variation in the organoclay loading of the hybrids. Thus the introduction of inorganic components into organic polymers can improve their thermal degradation stabilities; clays provide good thermal stability to the nanocomposites because of the heat insulation effects of the clay layers and the mass transport barrier they provide to the volatile products generated during thermal decomposition. This kind of improvement in thermal stability has previously been observed in many hybrid systems.<sup>30,33–36</sup> The weight of the residue at  $600^{\circ}C$  increases with increases in the clay loading from 0 to 3%, ranging from 1 to 7%. This enhancement of char formation is ascribed to the high heat resistance of the clay itself. For the PBT hybrid fibers with 3 wt % organoclay, the overall thermal properties of the PBT hybrid fibers were found to be unchanged for DRs in the range 1–18 (see Table I).

The above results confirm that the introduction of an inorganic clay component into an organic polymer can improve the polymer's thermal properties,



**Figure 6** TGA thermograms of clay, organoclay, and PBT hybrid fibers with various organoclay contents.

**TABLE II**  
Tensile Properties of PBT Hybrid Fibers

Organoclay (wt %)	D.R. <sup>a</sup>	Ult. Str. (MPa)	Ini. Mod. (GPa)	E.B. <sup>b</sup> (%)
0 (Pure PBT)	1	41	1.37	3
	12	43	1.69	3
	18	46	1.77	3
1	1	48	2.21	4
	12	44	2.25	3
	18	42	2.28	3
2	1	50	2.61	3
	12	41	2.62	2
	18	41	2.67	2
3	1	47	2.80	3
	12	45	2.80	2
	18	44	2.87	2

<sup>a</sup> Draw ratio.

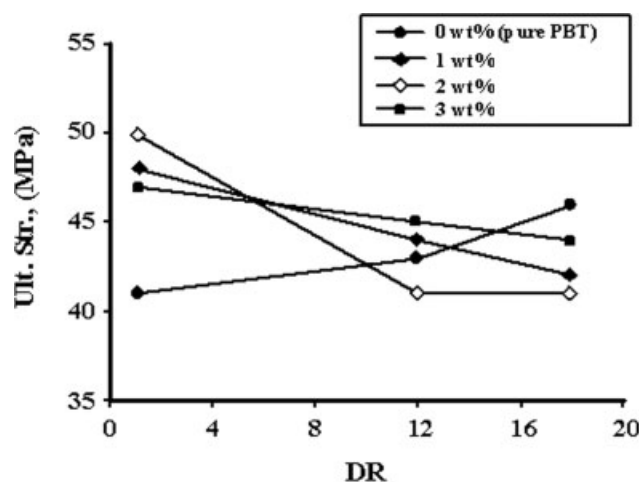
<sup>b</sup> Elongation percent at break.

and that these improvements are due to the thermal stability of the clay.

### Mechanical properties

Pure PBT and the PBT hybrids were extruded through a capillary die with various DRs to determine the tensile strengths and moduli of the extrudates. The tensile mechanical properties of PBT and its hybrids are given in Table II. At DR = 1, the ultimate tensile strength of the C<sub>12</sub>PPH-Mica 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 2 wt % PBT hybrid fibers is 50 MPa, which is about 22% higher than that of pure PBT (41 MPa). When the amount of organoclay in PBT reaches 3 wt %, the strength decreases to 47 MPa. This decrease in ultimate strength is mainly due to the agglomeration of clay particles above the critical clay loading, as we have previously reported.<sup>37,38</sup> Unlike the tensile strength, the initial modulus values were found to increase significantly with increase in the organoclay content. For a organoclay content of 3 wt %, the modulus of the hybrid was found to be 2.80 GPa, about 2.0 times that of pure PBT (1.37 GPa).

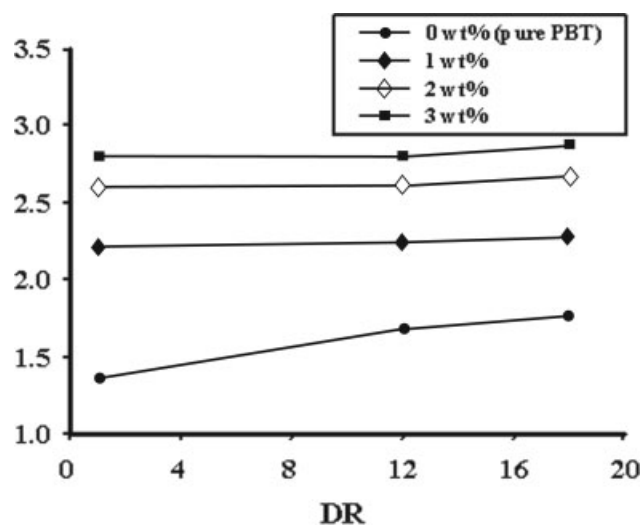
This large improvement in the tensile properties of Ini. Mod. (GPa) the hybrid fibers with respect to those of pure PBT is due to the presence of the organoclay, and can be explained as follows. Note that the improvements in the tensile properties depend on the interactions between the PBT molecules and the layered organoclays, and on the rigid nature of the clay layers. Moreover, the clay is much more rigid than, and so does not deform or relax as much as, the PBT molecules. Thus, the improvements arise because the organoclay layers are dispersed and intercalated within the PBT matrix. This is consistent



**Figure 7** Effects of DR on the ultimate tensile strengths of organoclay contents.

with the general observation that the introduction of an organoclay into a matrix polymer increases its strength and modulus.<sup>21,39</sup> The percent elongations at break of all the hybrids were 2–4%. These values remained constant for increases in the organoclay loading in the range 1 to 3 wt %.

As Table II shows, the variations in the tensile strength and the initial modulus with DR were found to be insignificant for pure PBT, as is usually the case for flexible coil-like polymers. For pure PBT, the strength and the modulus were found to increase as the draw ratio (DR) was increased from 1 to 18, from 41 to 46 MPa and 1.37 to 1.77 GPa respectively, as shown in Table II. For PBT hybrid fibers, the ultimate strengths of the hybrid fibers decreased with increase in DR, as can also be seen in Table II. For example, for a hybrid fiber with an organoclay content of 1 wt %, increase in DR from 1 to 18 resulted



**Figure 8** Effects of DR on the initial tensile moduli of organoclay contents.

in decreases in the tensile strength from 48 to 42 MPa. Similar trends were observed for hybrid fibers with organoclay contents of 2 and 3 wt %.

An increase in the tensile strength with increases in DR is very common for engineering plastics and is usually observed for flexible coil-like polymers.<sup>40,41</sup> However, our system did not follow this trend. The observed decline in the tensile properties seems to be due to debonding between the organoclay and the matrix polymer, and to the presence of the many nanosized voids that result from excess stretching of the fibers. This indicates that hydrostatic elongation during the extrusion and compression molding operations results in debonding in the polymer chain as well as in void formation around the polymer–clay interfaces.<sup>42–44</sup> The variations of the ultimate strengths with DR are shown in Figure 7. In contrast to the decrease in tensile strength values, the initial moduli were found to increase slightly with increase in DR for each clay content, as shown in Table II and Figure 8. This enhancement of the modulus could be the result of two different factors: the high resistance of the clay, and the orientation and the aspect ratio of the clay layers. Further, increasing the clay content increases the constraints on polymer chain mobility, which also increases the modulus.<sup>21,39</sup>

## CONCLUSIONS

We prepared a series of PBT hybrids consisting of monomers and organoclay via the *in situ* interlayer polymerization method. Hybrids with various organoclay (C<sub>12</sub>PPH-Mica) contents were extruded with various DRs from a capillary rheometer to investigate their thermomechanical properties and morphologies.

Overall, the addition of only a small amount of organoclay was found to be sufficient to improve the thermal and tensile mechanical properties of the PBT hybrid fibers at DR = 1. Further, when DR was increased from 1 to 18, the presence of the organoclay in the PBT matrix resulted in linear decreases in the ultimate tensile strengths of the hybrids due to debonding around the polymer–clay interfaces and void formation. There were, however, slight increases in the initial modulus with increases in DR.

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