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Novel blends made of ionic naphthalene thermotropic polymer and poly(ethylene terephthalate)

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Abstract

Novel blends made of ionic naphthalene thermotropic polymer (NTP) and poly(ethylene terephthalate) (PET) have been prepared by melt mixing. Homogeneous blends were formed when a small amount (5 wt%) of ionic NTP was blended with PET; but, phase separation occurred at a higher composition of the ionic NTP (10 wt%). Both the stiffness and the strength are enhanced in all the blends studied as compared with PET. A remarkable increase in ductility and toughness is noted during necking in these blends. Enhancement in tensile properties and good homogeneity of the blends at low composition (5 wt%) are attributed to ion–dipole interactions between the ionic groups of the ionic NTP and the dipolar units of the PET. It is suggested that ionic NTP chains not only act as reinforcer in the homogeneous blends, but also serve as a nucleating agent to increase crystallinity and as a good stress transfer agent to ease an inhomogeneous deformation process during necking of the PET matrix under tensile stress.

Keywords: Ionic thermotropic liquid crystalline polymers; Polymer blends; Mechanical properties

1. Introduction

Poly(ethylene terephthalate) (PET), a thermoplastic polymer, is one of the most widely used polyesters for fabricating fibers and films. Blends of PET with commercial main-chain thermotropic liquid crystalline polymers (LCPs) have been reported in the literature [1–4]. Generally, PET and main-chain thermotropic LCPs, including nonionic naphthalene thermotropic polymers (Vectra® type copolyesters) [5], are incompatible [1,6]. The morphological observations of the LCP/PET blends have shown totally separated two-phase structure, indicating that these two types of polymers are immiscible unless significant interchange chemical reactions are present [1,2]. To make high-performance thermoplastic blends, investigations of the phase behavior and the factors for promoting molecular or interfacial adhesion between dissimilar polymer chains are important [1,2,6,7].

Ionic naphthalene thermotropic polymers (NTPs) are novel ion-containing main-chain thermotropic LCPs based wholly on aromatic copolyesters, which have been developed in this laboratory [8–11]. We have demonstrated that ionic NTPs show enhanced tensile and compressive properties compared with nonionic NTPs [11], which are attributed to ionic bonds formed between polymer chains in these polymers. Due to the ionic interactions that ionic NTP can provide, they are also expected to promote miscibility and adhesion with other polymers that contain polar groups (polymer blends). As a first such blend system, we have investigated polymer blends made of ionic thermotropic LCP, an ion-containing rigid polymer and a flexible polar polymer, PET. When melt-processable blends made from these two types of polymers are homogeneous, they are considered as ionic molecular composites, in which an ionic rigid polymer reinforcer is dispersed in the flexible polymer matrix [12–18]. It is expected that the addition of ionic groups to thermotropic LCP will lead to better

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miscibility and a good dispersion of the rigid chains in the PET matrix through ion–dipole interactions between molecules. As observed for "self-reinforced" rigid-rod polymer films [19], performance of the molecular composites can surpass that of a fiber-reinforced composite without having drawbacks that arise from distinct fiber and matrix phases. Again, these beneficial effects are attributed to the favorable ionic interactions between the ionic groups on the ionic NTP chains and the ionic dipoles due to ester moieties of the PET chains. Ion–dipole interactions not only promote miscibility but also provide beneficial effects on other properties, such as enhanced thermal and mechanical properties, of the resulting molecular composites [18]. This is encouraging when we consider the fact that a majority of LCP/thermoplastic blends indicate immiscibility between the components [4].

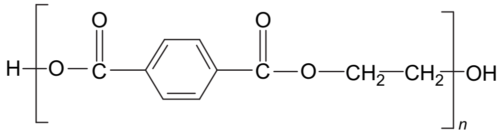
In this study, we present experimental results on the PET/ionic NTP blends, which show various degrees of homogeneity, from a homogeneous molecular composite to a phase-separated mixture. The objective of the present work is to find how thermal and mechanical properties of the blends are influenced by the presence of intermolecular ionic interactions. It may be expected that a rigid ionic LCP reinforcement should increase the strength and modulus of the flexible matrix polymer. However, it is not immediately clear whether it would enhance large-strain properties, such as elongation at break (ductility) and toughness, since the reinforcing polymer is more rigid and brittle than the matrix polymer. The results obtained in this study indicate that the addition of a small amount of ionic NTP to the PET matrix leads to a homogeneous blend (a molecular composite), which shows enhanced strength, larger elongation at break, and greater toughness.

2. Experimental section

2.1. Materials

Poly(ethylene terephthalate) (PET) used in this study was purchased from Scientific Polymer product and used as received. Ionic NTPs were prepared in this laboratory. Table 1 lists the characteristics of the polymers used.

Table 1
Characteristics of polymers



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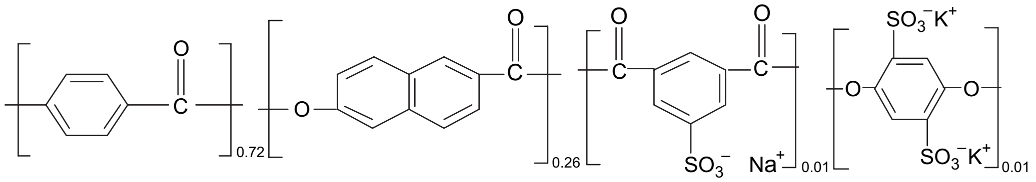

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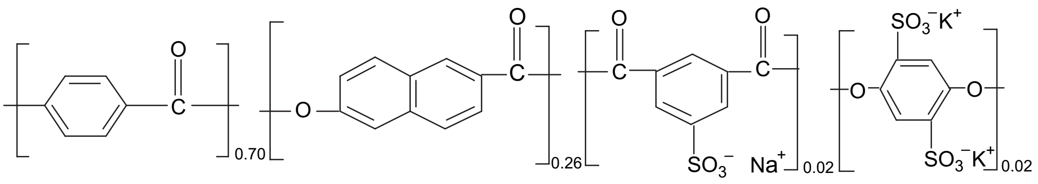

III

Polymer	Chemical structure	Ionic content[a] (mol%)	I.V.[b]	T_g (°C)	T_m (°C)
Poly(ethylene terephthalate) (PET)	**I**	–	0.7	80.1	252
Ionic NTP1	**II**	3 (1 mol% SSI + 1 mol% HQDS)	4.42	–[c]	279
Ionic NTP2	**III**	6 (2 mol% SSI + 2 mol% HQDS)	7.93	–[c]	279

[a] HQDS has 2 ionic groups per repeat unit, whereas SSI has 1 ionic group per repeat unit.

[b] Inherent viscosity (dl/g): the value of PET was provided by the supplier and the values of ionic NTPs were measured with a capillary viscometer at 0.1 wt% concentration in a solvent mixture, pentafluorophenol (PFP)/hexafluoro-2-propanol (HFIP) (50/50 v/v), at 25 °C.

[c] T_g was not detected by DSC.

Table 2
Components and composition of the blends

Blend	Components	Composition (w/w)
PET-B1	PET/ionic NTP1	95:5
PET-B2	PET/ionic NTP2	95:5
PET-B3	PET/ionic NTP1	90:10

2.2. Preparation of ionic NTPs and their blends

Ionic NTPs were synthesized by incorporating *a meta-linked ionic monomer*, sodium 5-sulfoisophthalate (SSI) and *a para-linked ionic monomer*, potassium hydroquinone-2,5-disulfonate (HQDS) to NTP base formulation, i.e., 1,4-hydroxybenzoic acid (HBA) and 6,2-hydroxynaphthoic acid (HNA) [4]. All the ionic NTP samples were prepared according to the method described elsewhere [8–11]. Component polymers (PET, ionic NTP) were dried overnight under vacuum at 100 °C before blending. Blends were prepared by melt mixing on a Haake System 90 mixer for 10 min at 300–310 °C; and, cooled blends were grounded into small chips and dried. The description and composition of the blends are listed in Table 2.

2.3. Tensile tests

Tensile mechanical properties were measured on a Minimat Materials Tester (Polymer Laboratories) by using thin film specimens, according to the ASTM standard (D 882-91). The crosshead speeds used were 0.5 mm/min for an ionic NTP and 2 mm/min for PET and the blends. Films were melt extruded with Micro-Melt extruder (Hoechst Celanese) with a film die of 0.005 in. thickness and 0.250 in. width, cooled at ambient temperature, and then collected with a wind-up roll at a take-up speed of 5 m/min. Film thickness was measured with a micrometer at various points of the film, and an average value was used. At least five specimens were tested for each sample at room temperature and the average values were used for the analysis. Various mechanical properties were obtained as follows: the modulus from the initial slope of the stress–strain curve, yield properties (both the strength and the strain at yield) from a yield point, and the ultimate properties (both strength and strain at break) from a break point of the curve.

2.4. Differential scanning calorimetry (DSC)

Thermal transitions of the component polymers and the blends were studied with DSC using a TA Instrument Thermal Analyst (2100/910). Samples of 5–10 mg, which were made by cutting extruded films, were examined at a heating rate of 20 °C/min, followed by cooling to an ambient temperature under nitrogen atmosphere. The glass transition temperature (T_g), the melting temperature (T_m), and the crystallization temperature (T_c) were determined from DSC thermograms. The T_g value was obtained as a midpoint between the onset and the end point of a step transition region, and T_m and T_c are the peak temperatures of a melting endotherm and a crystallization exotherm, respectively.

2.5. Scanning electron microscopy (SEM)

Tensile fractured specimens of the blends were examined with SEM. Specimens were mounted on a stub with conducting double-sided carbon tape, and coated with platinum for 4 min with a sputter coater (Polaron, SEM coating unit, E 5100). The specimens were then examined with a scanning electron microscope (Amray 1200C) operating at 30 kV, and images were recorded directly on Polaroid 55 films from the cathode ray tube.

3. Results and discussion

3.1. Thermal properties of component polymers and blends

Table 3 lists the transition temperatures (T_m and T_c), the heat of fusion (ΔH_m), and the heat of crystallization (ΔH_c) of ionic NTP polymers, determined from the DSC thermograms (not shown). No glass transitions were detected, and the same melting temperature (279 °C) was obtained for these ionic NTPs despite the difference in ionic content of as large as 3 mol%. This indicates that the ionic bonds do not significantly affect T_m of the ionic thermotropic LCPs, as also known for conventional crystalline ionomers [20]. The T_c of ionic NTP2 of 6 mol% ionic content is lower by 3 °C than that of ionic NTP1 of 3 mol% ionic content. A lower crystallization temperature may be explained by larger supercooling [21]: ionic interactions between chains, which still exist in the melt, increase with an increase in ionic content; and, as a result, melt viscosity increases and segmental mobility of polymer chains for spatial rearrangement during crystallization is reduced [9].

Fig. 1 shows DSC heating curves for extruded film samples of PET and PET/ionic NTP blends. Two glass transitions, a cold-crystallization (exothermal) peak and a melting (endothermal) peak are revealed for each case. Thermal properties obtained from these DSC thermograms are summarized in Table 4. All the extruded films exhibit relatively low degrees of (initial) crystallinity for the PET component, which are determined first by subtracting the heat of cold-crystallization from the heat of fusion and then dividing it by the heat of fusion of 100% crystalline PET (166 J/g) [22,23].

The cold-crystallization temperature T_c of the PET component of all the blends is lower by more than 10 °C as compared with pure PET. It was reported that LCP molecules can serve as a nucleating agent for crystallization of PET in the blends [1,24]. In PET/ionic NTP blends, the nucleating effect of ionic NTP should contribute to the observed reduction of cold-crystallization temperature T_c. This implies that the activation

Table 3
DSC results of ionic NTPs

Sample	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)
Ionic NTP1	279	240	1.04	1.85
Ionic NTP2	279	237	0.67	1.37

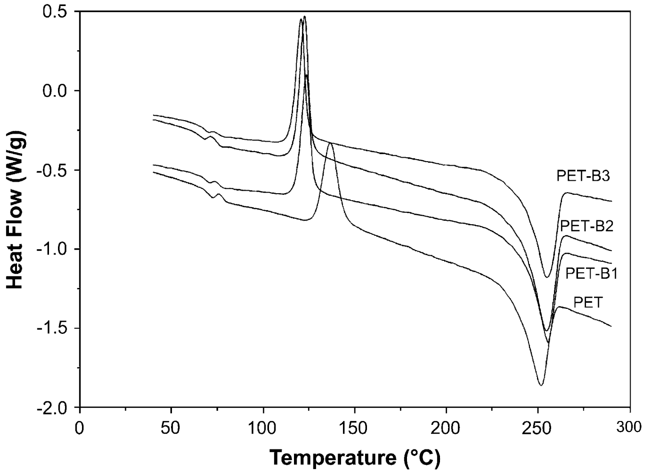

Fig. 1. DSC heating thermograms of extruded PET and PET/ionic NTP blends.

energy for cold-crystallization of PET in the blends is decreased. However, in contrast to a cold-crystallization temperature T_c, the melting temperature T_m of the PET component of all the blends is 3 °C higher than that of the pure PET sample. This is even more significant when we consider the fact that ion–dipole interactions would cause melting temperature depression in miscible blends containing crystallizable and amorphous components, as observed for a miscible blend that contains a semi-crystalline polymer, such as the blend of poly(ethylene oxide) (PEO) and poly(*p*-vinyl phenol) [25]. The elevation of T_m in the blends may result from higher crystallinity and possibly larger crystallite size of the PET component induced by a strong nucleating effect of ionic NTP chains in the blends, since the larger the size of crystallites, the higher the T_m of polymer samples [21].

Strong nucleating effect of an ionic NTP in the blends can be seen in the cooling behavior of the melts under controlled (refrigerated) cooling conditions (Fig. 2): the rate and the degree of crystallization of PET are much higher in the blends than in the pure polymer, and exothermal peaks are much sharper and larger in the blends. PET-B1 and PET-B2 have the same composition of the PET components, and when they form melts, "long range" forces due to ionic (ion–dipole) interactions can be present between segments. Since ionic interactions are stronger in the PET-B2 melt than in the PET-B1 melt due to higher ionic content of PET-B2, there is more hindrance of mobility for PET chains to ordered spatial arrangement, leading to a lower T_c from the melt of PET-B2 than PET-B1.

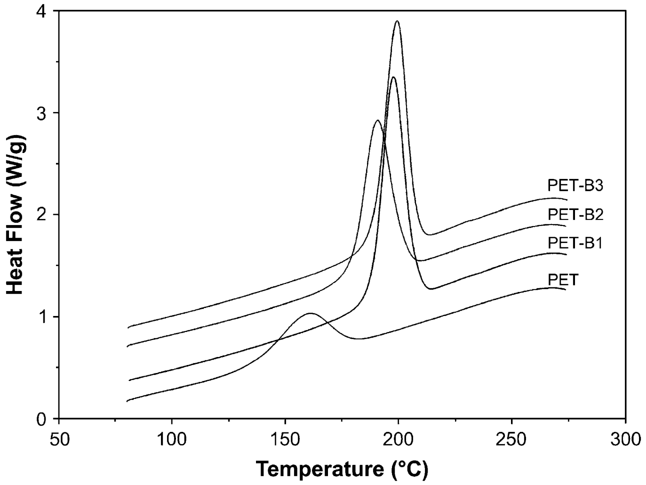

Fig. 2. DSC cooling thermograms of PET and PET/ionic NTP blends after first heating (Fig. 1).

3.2. Possibility of interchange reactions

Because of the functional linkages and end-groups in PET and ionic NTPs, various interchange reactions may occur, as observed for nonionic thermotropic LCP/polyester blends [7]. The extent of interchange reactions depends on the time–temperature history of the blend and the presence of any residual catalysts from the polymerization step. This type of chemical reactions would eventually convert a physical blend into an essentially random copolymer consisting of residues from the two originally different types of chains. Due to dissimilarity of the structural units consisting of the two component polymers, one would expect crystallizability to reduce substantially as such reactions progress [26]. As the studies on PET/polycarbonate (PC) blends have shown, a convenient tool for examining interchange reactions in the blend is to monitor the crystallization by thermal analysis, using carefully controlled procedures [26–28]. For the current PET/ionic NTP system, film samples were obtained by rapid quenching during extrusion and all of them possessed a relatively low degree of crystallinity. A controlled DSC nonisothermal method was used for evaluating their crystallizability (melting enthalpy ΔH_m); i.e., crystallinity from initial scan through cold-crystallization up to melting. If significant interchange reactions had occurred, crystallizability of PET would be reduced substantially in the blends. Instead, based on the thermal analysis data (Table 4), ΔH_m for PET increases in the blends. Kwon and Chung also reported [7] that little interchange reaction occurred for the melt-mixed blends of

Table 4
DSC results for extruded films of PET and PET/ionic NTP blends (from Fig. 1)

Sample	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH^*_{cc} (J/g)	ΔH_m (J/g)	ΔH^*_m (J/g)	$\Delta (\Delta H)$ (J/g)	w_c (%)
PET	70.9, 78.2	137	252	31.2	31.2	45.8	45.8	14.6	8.80
PET-B1	68.9, 75.8	124	255	27.8	29.3	48.4	50.9	21.6	13.0
PET-B2	66.4, 74.7	123	255	32.3	34.0	57.6	60.6	26.6	16.0
PET-B3	68.1, 75.6	121	255	28.8	32.0	51.5	57.2	25.2	15.2

Data from the first run of DSC measurements, film take-up speed: 5 m/min; ΔH_{cc}: heat of cold-crystallization of the blends; ΔH^*_{cc}: heat of cold-crystallization based on the mass of PET in the blends; ΔH_m: heat of fusion of the blends; ΔH^*_m: heat of fusion based on the mass of PET in the blends; $\Delta (\Delta H)$: the difference between ΔH^*_m and ΔH^*_{cc}; w_c: initial crystallinity of the PET component of the blends.

thermotropic LCPs (including a nonionic NTP, Vectra 950A) with a flexible polymer with ester functional moieties under the melt processing conditions similar to that employed in this study. In addition, exchange reactions would incorporate stiffer ionic NTP segments into PET chains, which would result in an increase in the glass transition temperature T_g. However, the T_g values of PET are slightly lower in the blends than in pure PET. Based on these results, one would conclude that no significant interchange reactions between the ionic NTP and the PET chains occurred under the melt processing conditions employed.

3.3. Tensile properties of component polymers and blends

Average tensile properties of ionic NTPs are listed in Table 5. Also listed are the values of nonionic NTPs [9]. It is clear that ionic NTPs develop higher stiffness and strength than nonionic NTPs. This is consistent with our previous results on different ionic NTPs [9,10]: both modulus and strength values are higher in these ionic NTPs, and these values are increased with ionic content. However, the values of ionic NTP2 are lower than those of ionic NTP1 despite higher ionic content of ionic NTP2. This may be due to the difference in the quality of the extruded films that were made under similar processing conditions employed: since the polymer of a high ionic content has higher melt viscosity and more complex flow behavior, ionic NTP2 may have less order than ionic NTP1 during extrusion, leading to poorer mechanical properties than ionic NTP1.

Table 5
Tensile properties of ionic NTPs and nonionic NTP

Sample	Ionic NTP1	Ionic NTP2	Nonionic NTP
Tensile modulus (GPa)	36.9	25.5	13.3
Tensile strength (MPa)	410	294	142
Max. strain (%)	1.25	1.39	1.27

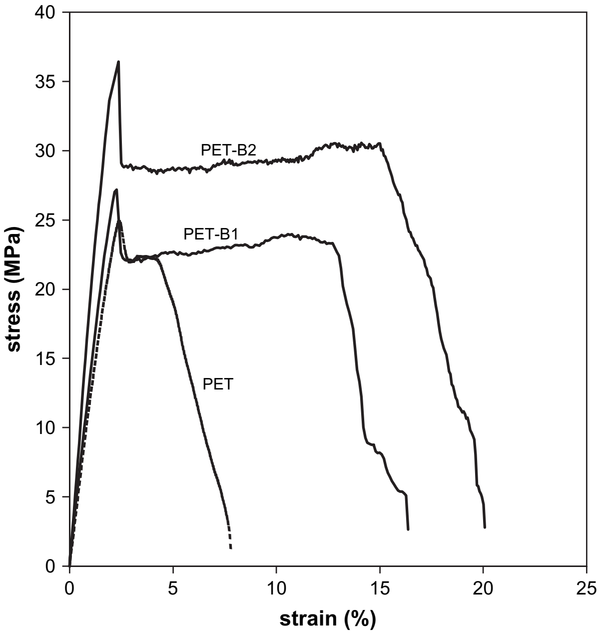

Fig. 3. Typical stress–strain curves for extruded film samples of PET and PET/ionic NTP blends.

Following mechanical testing of the ionic NTP polymers, we studied mechanical properties of polymer blends made of these ionic NTPs and PET. Fig. 3 shows typical stress–strain curves of PET and PET/ionic NTP blends, and Table 6 summarizes their tensile properties. The initial slope of the stress–strain curves increases, reflecting an increase in *tensile modulus* (stiffness), in the order of PET < PET-B1 < PET-B2 (see Fig. 4). The *yield strength* increases in the same order, as also shown in Fig. 4. Improved modulus and yield strength of the blends are due to the effective reinforcement of the PET matrix by rigid ionic NTP molecules, which arises from good dispersion of ionic NTPs in the PET matrix, as noted by SEM (will be shown later). Although both PET-B1 and PET-B2 contain the same amount of ionic NTP, the higher ionic content (6 mol% vs. 3 mol%) provided by the ionic NTP2 in the PET-B2 contributes to stronger intermolecular interactions in the blend, which lead to greater enhancement in mechanical properties. This is similar to what has been reported for the blends of conventional ionomers, where mechanical properties of the blends increase with ionic content of the ionomer component [29,30]. It should be added that the effect of molecular weight is much smaller than that of the effect of ionic content of the ionic NTP polymer [9]. Fig. 3 also shows that the ultimate properties (*tensile strength at break*, *elongation at break*, and *toughness*) are increased in the order PET < PET-B1 < PET-B2. The film becomes stronger and tougher, i.e., more energy is needed to break

Table 6
Tensile properties of PET and blends

Sample	PET	PET-B1	PET-B2	PET-B3
Tensile modulus (GPa)	1.28	1.39	1.82	1.58
Tensile stress at yield (MPa)	25.5	28.5	36.2	35.2
Strain at yield (%)	2.44	2.49	2.47	2.77
Tensile strength (at break) (MPa)	22.3	23.0	29.6	–
Strain at break (%)	4.1	12.5	16.3	–
Toughness (MJ/m^3)	1.2	3.0	4.7	–

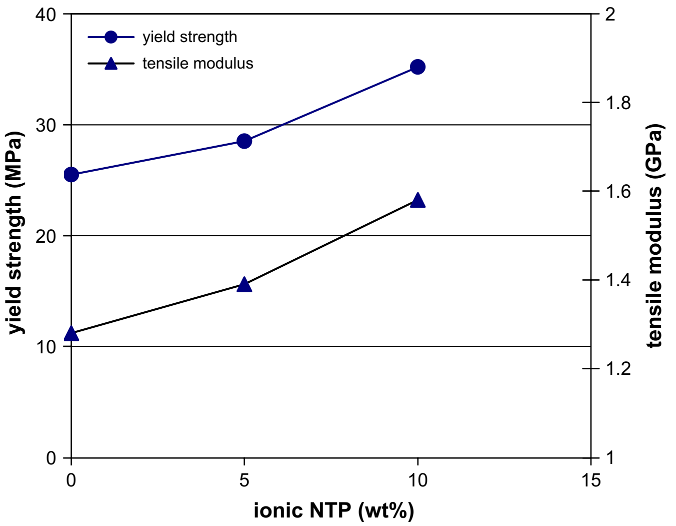

Fig. 4. Yield strength and tensile modulus vs. composition of PET/ionic NTP blends.

the sample, upon blending only 5 wt% of ionic NTP with PET; and further improvements in strength and toughness are achieved by higher ionic content at the same composition of ionic NTPs. Our results clearly demonstrate that ionic NTPs act as a reinforcer for PET. It is expected that ionic NTP chains are well dispersed in the PET matrix and form homogeneous blends (molecular composites) at a low NTP composition: i.e., the PET matrix is reinforced at the molecular level with the ionic NTP. As the ionic content of the ionic NTP increases, enhancement due to ion–dipole interactions can be greater.

Although significant enhancement in mechanical properties is noted for PET/ionic NTP blends at the composition of 5% of ionic NTP, further increase in the ionic NTP component shows a significant drop in mechanical properties. Whereas a ‘‘necking’’, localized reduction in cross-section in a material under tensile stress [31], was observed for PET, PET-B1, and PET-B2, such ductile behavior was not observed for PET-B3 (figure not shown). Instead, PET-B3 ruptured in a brittle fashion: this sample yielded and broke at the same point and necking did not occur. This may be due to ionic aggregation caused by higher content of ionic NTP component (10 wt%), leading to phase separation and development of brittleness in the sample. At a lower composition (5 wt% of ionic NTP component), ionic NTP molecules may be well dispersed in the PET matrix and achieve good mixing, since ion–dipole interactions in the mixture can stabilize molecular dispersion leading to the formation of a miscible blend. To exclude the possibility of chemical cross-linking, a solubility test of film samples was performed. The observation showed that the films from pure PET, PET-B1, and PET-B2 were completely soluble in *o*-chlorophenol. Thus, a melt processing procedure used in this study did not induce cross-linking reaction in PET.

Among enhanced tensile properties, significant enhancement in ductility, a percent elongation at break, is of particular interest: the value of PET-B1 became 3 times (12.5%) and the value of PET-B2 became 4 times (16.3%) as compared with pure PET (4.1%). Murff et al. [26] observed for PET/PC blends that the elongation at break increased as PC was blended with PET. In this case, however, an extruded film of pure PC already shows highly ductile behavior with the elongation at break many times larger than that of PET film under tensile stress [26,32]. In contrast, a reinforcing component, ionic NTP, is rigid and brittle and shows much lower ductility (<1.4%) than PET films (4%). A remarkable increase in the elongation at break upon blending a very small amount (5 wt%) of ionic NTP with PET is indeed a distinguished feature of our blends. Although the cause of this phenomenon is not completely clear, our speculation can be given. Well dispersed ionic NTP molecules serve as a good stress transfer agent in the PET matrix under the predominantly inhomogeneous deformation process after neck formation. Good mechanical properties of the ionic NTP/PET blends reflect favorable interactions between the ionic NTP and the PET molecules. In addition to possible dipole–dipole interactions, ion–dipole interactions can make a major contribution to the enhancement of mechanical properties. In addition, the difference in the degree of crystallization may have some contribution. Since PET-B2 has a higher degree of crystallinity (16%) than PET-B1 (13%), or PET (8.8%) (here, ionic NTP also works as a nucleating agent), and since much of the ductile behavior arises from deformation of a crystalline region, the sample with higher crystallinity may develop larger ductility. However, the enhancement in ductility (3 times and 4 times for PET-B1 and PET-B2, respectively, over PET) is larger than the enhancement in crystallinity (1.5 and 1.8 times). Also, PET-B3 has a degree of crystallization of 15%, yet shows little ductility. Thus, crystallinity cannot be a sole factor. Both increased crystallinity and good interchain interactions, both due to the presence of ionic NTP chains, are responsible for significant enhancement in ductility.

3.4. Fracture surface morphology

Tensile fracture surfaces of the extruded film specimens were investigated for PET and the blends with SEM. Although thorough investigation of the fracture surface morphology was not performed, SEM images of fractured surfaces reveal specific features of the morphology and the deformation mechanisms. Fig. 5a shows the SEM micrograph of pure PET: a relatively smooth fracture surface with aligned traces with certain angles is revealed along the fracture direction. Since films are extruded from molten polymers (at about

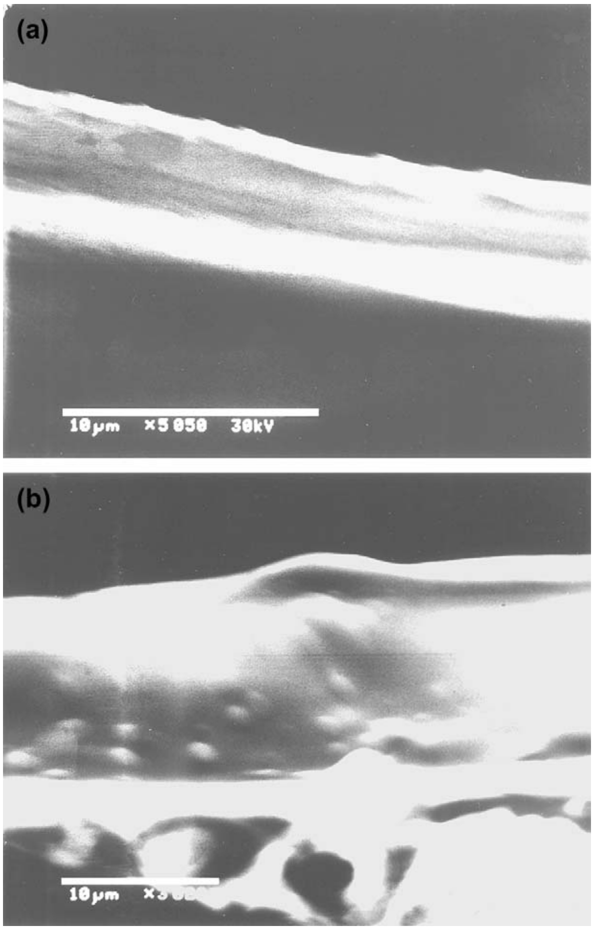

Fig. 5. SEM micrographs of tensile fracture surfaces: (a) PET; (b) PET-B3.

300 °C) through a spinneret directly into air at room temperature, the films are thus rapidly cooled (quenched) and are largely amorphous [33]. PET is a brittle glassy polymer at room temperature. The aligned traces revealed on the fracture surface reflect the deformation history of neck formation and cold drawing (neck extending) due to partially crystalline ($w_c = 8.8\%$) structure. The necking develops the resistance to brittle rupture and adds some ductility.

The SEM micrograph of PET-B3 (Fig. 5b) exhibits a smooth fracture surface, which reflects brittle fracture of the sample, with the presence of distinguishable second phase particles. The brittleness of PET-B3 results from phase separation of the ionic NTP polymer from the PET matrix at the composition of 10 wt% of ionic NTP. Individual ovate domains seen on the micrograph correspond to phase-separated (aggregated) ionic NTP molecules. Phase separation prevents development of any necking process and this leads to a ductile-to-brittle transition, although the PET matrix possesses partially crystalline ($w_c = 15.2\%$) structure in the blend. Although such phase separation leads to brittle fracture, ionic NTP particles present can still act as a reinforcing filler for the PET matrix: the yield strength increases by 38%, the yield strain by 14%, and modulus by 23% over those of pure PET. This suggests the existence of favorable interactions at the interface between the ionic NTP particles and the PET matrix.

Fig. 6 shows SEM micrographs of fracture surfaces of PET-B1 and PET-B2 (both at the same composition of 5 wt% of ionic NTP). The fracture surfaces become rougher than those of pure PET and PET-B3 (already shown in Fig. 5), reflecting greater resistance to fracture. As a result, ultimate properties are greatly enhanced: both PET-B1 and PET-B2 develop ductility and resistance to fracture under tensile stress. There is no evidence of phase-separated ionic NTP phases in these blends: homogeneous appearance on the micrographs indicates that ionic NTP chains are well dispersed in the PET matrix. Although PET, PET-B1, and PET-B2 all exhibit signs of local drawing, PET-B1 and PET-B2 show considerably rougher fracture surfaces than PET (compare Fig. 6a and b with Fig. 5a). This reflects the fact that both PET-B1 and PET-B2 possess higher resistance to failure than pure PET does. For example, Fig. 6b shows that PET-B2 develops extensive local drawing and has a strong tendency to form fibril structure along the tension direction. The degree of interchain ionic interactions in PET-B1 and PET-B2 is expected to be parallel to the order of tensile properties: PET-B1 < PET-B2.

3.5. Comparison with the results on molecular composites containing ionic LCP

It is of interest to compare the current result with previous results on ionic molecular composites. These composites (blends) used ionic poly(*p*-phenylene terephthalamide) (PPTA) as a reinforcer and poly(4-vinylpyridine) (PVP) [15], poly(ethylene oxide) (PEO) [16–18], and other polar polymers [18] as matrix polymers. Since ionic PPTA and PPTA are lyotropic (not thermotropic at least up to 15 mol% ionic content, above which some rigidity is compromised), solution processing was the only way to make the composite: both a reinforcing polymer and a matrix polymer were dissolved in a common solvent, and after precipitation of the composite into a nonsolvent, followed by drying, samples were made by compression molding (a wet process). By contrast, the current composite was made by melt mixing the component polymers, and orienting the reinforcing polymer in the extruder due to thermotropic liquid crystallinity (a *dry process*). Melt processing is much more convenient than the solution processing, especially that from aggressive acids necessary to produce aromatic polyamides. Nevertheless, homogeneous samples were made at low reinforcer compositions (up to 5 wt%), and phase separation (aggregation of ionic polymers) occurred above that composition for both the ionic PPTA and ionic NTP composites. This is a general trend observed for ion–dipole blends, in which more dipoles than ionic groups are needed to achieve good miscibility [34].

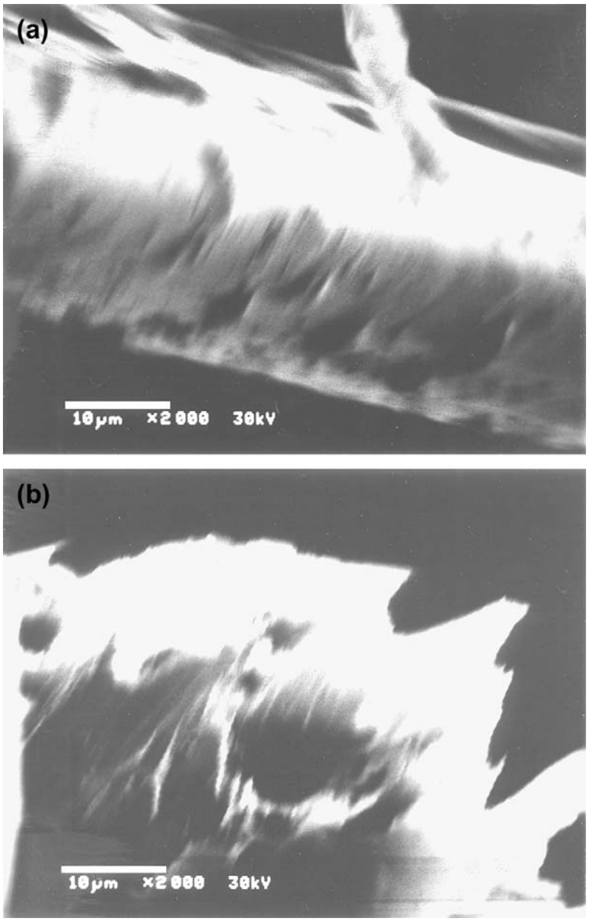

Fig. 6. SEM micrographs of tensile fracture surfaces: (a) PET-B1; (b) PET-B2.

The enhancements in mechanical properties of these molecular composites are classified roughly into two: (i) both modulus/strength and toughness/ductility are enhanced or (ii) modulus/strength is enhanced, but toughness/ductility is reduced. The case (ii) is more common for composites, an example being ionic PPTA/PEO (high MW: 5,000,000), in which small spherulite formation leads to ductile behavior of high MW PEO [35] and its composites. By contrast, the case (i) was observed for rather brittle systems, i.e., ionic PPTA/PVP and ionic PPTA/PEO (low MW: 300,000), in which low MW PEO forms large spherulites, making polymer more brittle (due to easy crack propagation through inter-spherulite boundary [35]). The current ionic NTP/PET system also follows case (ii), although the degree of ductility (showing a yield point and necking) is somewhere between the high value of PEO (low MW) and the low value of PVP or PEO (high MW). Thus, except for highly ductile polymers, ionic rigid polymers seem to enhance *both stiffness/strength and toughness/ductility of the component polymers*. We believe that this is due to the change in the properties of the matrix polymer arising from favorable interactions at the molecular (or nm) level in the amorphous phase of the blends. For the PVP system, we have shown that the deformation mode of the matrix polymer (PVP) changes favorably (from crazing to shear yielding) due to ion–dipole interactions between the component polymers [15]. Also, we have indicated the favorable interactions between the component polymers in the amorphous phase of the matrix polymer due to ion–dipole bonds for ionic PPTA/PEO blends [16]. We believe that such a reinforcing mechanism is also involved in the current system, as already described.

4. Conclusions

We have shown that homogeneous blends are made by incorporating a small amount of ionic NTP to a semi-crystalline polymer, PET. The extent of reinforcement depends on the composition and the ionic content of the reinforcing polymer, ionic NTP. Homogeneous blends (also considered to be molecular composites) are obtained at the composition of 5 wt% of ionic NTP. Phase separation is evident at a higher composition, 10 wt% of ionic NTP. The homogeneous blends show enhanced tensile properties. For example, as compared with pure PET, the values of the PET-B2 blends are higher by: 42% in the modulus, 42% in the yield strength, 34% in the tensile strength, *290% in toughness, and over 300% in the elongation at break*. For homogeneous blends at the same composition, as the ionic content of the ionic NTP component is increased, interchain ionic interactions are increased, the degree of necking becomes larger, and enhancement of the mechanical properties becomes greater. The enhancements in both yield and ultimate properties are attributed to the presence of ionic groups, which develop ion–dipole interactions between ionic groups of the ionic NTP chains and dipoles of the PET molecules, and work as a nucleating agent and as a good stress transfer agent. By contrast, phase-separated blends show little ductility: they do not develop necking and fracture in a brittle fashion.

We have demonstrated that ionic NTPs are effective reinforcer of the PET matrix polymer and their extruded films become more ductile and more resistant to fracture in the longitudinal direction. We may also expect that the mechanical properties in the transverse direction will be enhanced due to interchain ionic interactions, as shown for fibers made from ionic LCPs [9]. Since many engineering polymers contain polar dipole units and since our blends at low compositions are considered to be molecular composites made by a dry process (i.e., no solvent involved), these composites made of ionic NTP and engineering polymers have the potential to be used for advanced materials.

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