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Structure formation and miscibility of sheets from PBT and LCP blends

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Sheets from blends containing poly(butylene terephthalate) (PBT) and liquid crystalline polymer (LCP) were prepared using a twin-screw extruder. The LCP used is a copolymer composed of 20 mol % ethylene terephalate (PET) and 80 mol % p-hydroxybenzoic acid (PHB). Thermal behavior, viscoelastic properties, and structure of the sheets of various compositions were investigated by using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), microwave orientation analysis (MOA), and wide angle x-ray diffraction (WAXD). X-ray diffractograms of extruded sheets from PBT, LCP, and their blends show a high degree of orientation along extrusion direction. The orientation is mainly due to the high crystallization rate of PBT, although crystallization and orientation of PBT in the PBT and LCP blends could also be induced by adding LCP. In the PBT and LCP blends, the thermal properties of the constituents are slightly changed indicating that PBT and LCP are partially miscible. DSC measurements show that as the amount of LCP added to the blend increased, the melting point T_m of PBT in the blends decreased. The single glass transition temperature T_g for the PBT and LCP was observed by DMA. Furthermore, no evidence of transesterification in PBT and LCP blends was observed by WAXD.

1. Introduction

Over the last decades, blends containing thermotropic liquid crystalline polymers (LCPs) and thermoplastics have attracted much attention, and they sustain still now significant scientific and industrial interests [1–5]. An area of special interest has been the use of LCPs in isotropic polymer blends. The main advantage of properties of LCP in polymer blends is the potential to obtain fine and uniform microfibrillation of the LCP with a large aspect ratio in thermoplastics. Elongated rod-like structures in the nematic phase during processing are developed due to the inherent nature of thermotropic LCP [1]. Two major advantages in adding a small amount of LCP to thermoplastics are an improvement of proccesability and an enhancement of mechanical properties, especially for modulus and tensile strength.

Poly(butylene terephthalate), PBT, is an aromatic polyester with a rapid crystallization rate that finds uses as an engineering material in its attractive mechanical properties, electrical insulation properties, good mouldability, and dimensional stability [6–8]. A considerable amount of research literatures on PBT blends with different types of LCP are found, also with much controversy in their results and interpretations [9–11].

Several parameters affect the final properties of the products obtained by 'in-situ' reinforced thermoplastics, with interphase adhesion and morphology of the dispersed LCP phase playing two of the most important roles. Both of these aspects depend on the chemical nature of the two polymers and the processing conditions [12–18]. Therefore, for the effective use of LCP, several factors, such as LCP concentration, miscibility between LCP and thermoplastics, and processing parameters should be taken into account.

The LCP used in this study is a copolymer composed of 20 mol % ethylene terephalate (PET) and 80 mol % *p*-hydroxybenzoic acid (PHB). The sheets of blends based on LCP and PBT were extruded with a twin-screw extruder. The dynamic mechanical properties and the structure development of blends which cover the complete composition range were investigated using such methods as wide angle x-ray diffraction (WAXD), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and molecular orientation analysis (MOA). The orientation and crystallization of LCP and PBT in the blend sheets were also investigated.

2. Experimental

2.1. Materials

Commercial engineering-grade polymer LCP (Rodran LC5000, Unitika Ltd., Japan) and PBT (Duranex 2000,

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Polyplastics Co, Japan) were dried in an oven under vacuum at 80°C for 24 hours prior to use. These parent polymers were mixed with the following composition ratios in weight: 90/10, 80/20, 70/30, 60/40, 40/60, and 20/80.

2.2. Sheet processing

Sheets were extruded on a twin-screw lab extruder (LABO PLASTOMILL, Toyoseiki Co.) through a coat-hanger T-die attached. The temperature profile setting for the extruder was 230, 280, and 295°C. The T die was controlled at 290°C. The screw rotation speed was fixed at 30 rpm. Extruded sheets through the T-die were cooled at 50°C by a set of chill rollers.

2.3. Characterization

Differential scanning calorimetry (DSC) experiments were performed on a thermoanalyser (Thermo plus DSC 8230, Rigaku Co.) under a constant flow of dry nitrogen. The weight of samples was kept approximately constant (~10 mg) throughout the study. The heating scans were made with the rate of 20°C/min.

Dynamic mechanical analysis (DMA) of the sheets was conducted as a function of temperature by using a non-resonant forced-vibration type apparatus, Orientec Model DDV-25FP automatic dynamic viscoelastometer. Measurements were made at a heating rate of 3°C/min between 20 and 300°C.

Dielectric measurements at microwave frequencies were carried out by means of a microwave molecular orientation analyzer (MOA-3020A, New Oji Paper Co., Ltd.). Information on the orientation in the sheet plane could be obtained.

Wide angle X-ray diffraction (WAXD) experiments were carried out by using a Ni-filtered Cu K_α radiation (40 kV, 40 mA). WAXD profiles were recorded along the equatorial and meridional directions by using a fiber-specimen attachment equipped with a scintillation counter and a pulse-height analyzer.

3. Results and discussion

3.1. Dynamic mechanical behavior

The curves of loss tangent (tan δ) as a function of the temperature for PBT, LCP, and their blends, respectively, are shown in Fig. 1. The temperature corresponding to the maximum of the peak or shoulder in the tan δ or E″ versus temperature curves is assumed to be the α relaxation temperature: glass transition (T_g). The T_g and the height of tan δ peaks for pure PBT, pure LCP, and their blends, respectively, are shown in Table I. PBT (in Fig. 1) presents an intense relaxation with the maximum at 69°C attributed to the glass transition. LCP presents a relaxation at 83°C related to the glass transition relaxation. For the PBT and LCP blends, a single glass transition lies at the temperature between 69°C and 87°C, the T_g of the two components. The relaxation intensities show a blend composition dependence on the rise of LCP concentration.

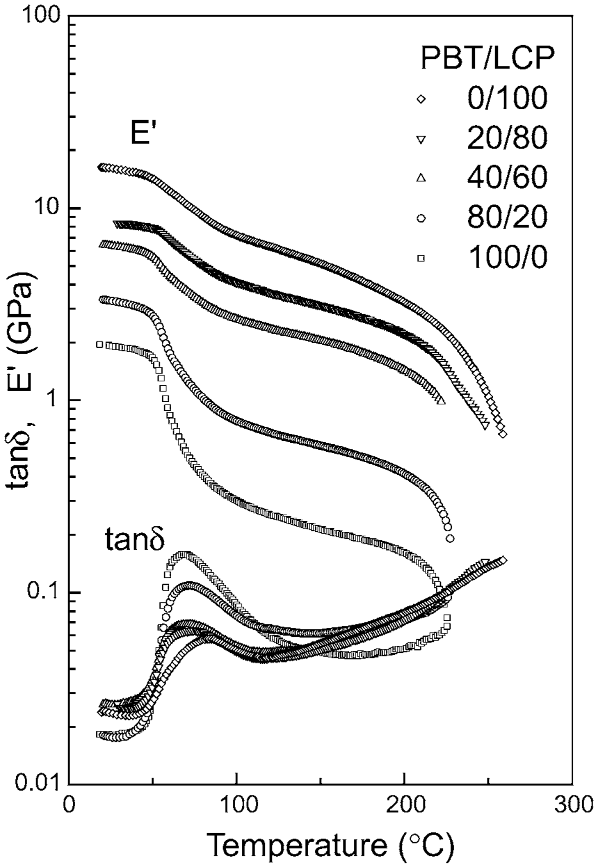

Figure 1 Temperature dependence of storage modulus, E′, and tan δ, of PBT, LCP, and their blends. Ratios between PBT and LCP are shown in figure. Frequency: 10 Hz.

The storage moduli (E′) as a function of the temperature for PBT, LCP, and the blends, are also shown in Fig. 1. The E′ for PBT drops at 69°C due to the glass transition process followed by dispersion: at about 250°C due to the melting of the crystalline region. A

TABLE I Comparison of the dynamic mechanical behavior of PBT, LCP and blends

PBT/LCP	Peak value of tan δ	T_g (°C) (tan δ)	T_g (°C) (E″)	E′(GPa) at 25°C	E′(GPa) at 150°C
100/0	0.159	69.6	60.3	1.92	0.21
90/10	0.158	69.6	60.5	1.84	0.26
80/20	0.109	72	61.7	3.3	0.58
70/30	0.108	73	62.4	3.94	0.72
60/40	0.079	71.1	61.6	4.51	1.52
40/60	0.068	72	61.7	6.39	2.04
20/80	0.063	74.4	63.2	8.41	3.12
0/100	0.057	83.8	71.9	16.2	5.12

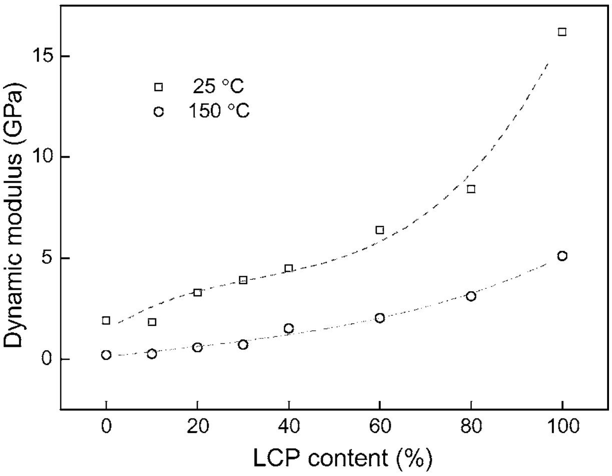

Figure 2 Changes of storage moduli, E′, of sheets at 25 and 150°C with LCP content. Frequency: 10 Hz.

similar profile is observed in LCP, but in this case the T_g occurs at 87°C and T_{iso} at 275°C, and the drop of the E′ value between T_g and T_m is more pronounced in pure PBT than in LCP due to the higher degree of rigidity of the LCP, which acts as a reinforcement. The E′ values as a function of the blends composition at 25°C and at 150°C for the pure polymers and the blends are shown in Table I and Fig. 2. Basically we can analyze the influence of two factors on the E′: the crystallinity of PBT and the amount of stiff LCP. Blends with LCP exhibit nearly the same degree of crystallinity as the corresponding PBT, as can be seen later; as a consequence, the moduli of blends with a higher LCP content are higher for the former one. At the temperatures below the T_g (at 25 °C), for lower concentrations of LCP, the E′ versus composition curves for blends exhibit a minimum, and the mechanical behavior of the blends is governed by the PBT crystalline phase. However, for higher concentrations of LCP, the mechanical behavior can be attributed to the high stiffness of the LCP chains and their orientation that make the repetition processes in the material more difficult. In the region between T_g and T_m (at 150°C), the behavior of E' is governed by both the crystallinity of PBT and the content of LCP. The modulus increased with the increase of LCP content.

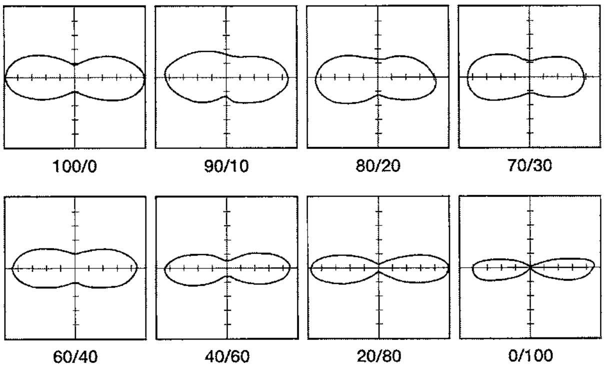

Figure 3 MOR patterns of sheets from PBT, LCP and their blends. Blends compositions of PBT and LCP are shown in figure.

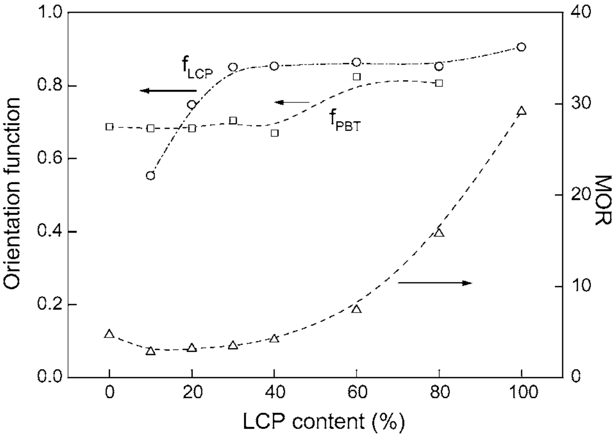

Figure 4 Orientation function of PBT and LCP, and MOR value for sheets versus LCP content.

3.2. Orientation and crystallinity

The as-extruded sheets for pure PBT, LCP, and their blends show a clear orientation. Microwave orientation analysis (MOR) is a simple way to investigate qualitatively the orientation behaviors of films and sheet samples. The principle of the measurement can be found in other literatures [19, 20]. Polarized microwaves were irradiated perpendicularly to the plane of a sheet sample inserted in a cavity resonator system. The sample was rotated around its central axis normal to the sheet plane. The transmitted microwave intensity was detected during the rotation of the sample. The angular dependence of the transmitted microwave intensity is called orientation pattern, which corresponds to the orientation distribution of molecule in the film plane. From the measurement, orientation patterns are generated. Circle pattern was given by an unoriented sample, while an ellipsoid pattern corresponds to the orientated sample. A value MOR, the ratio between the long axis and the short axis, hence can serve as a relative measure for the molecular orientation. Fig. 3 shows some typical patterns of PBT, LCP, and their blends. Fig. 4 shows the change of MOR with LCP content. It is clear that the orientation of the sheets increase as the LCP content increases.

It should be noted that the MOR data show the overall crystalline and amorphous orientation of LCP and PBT. For a better understanding the orientation and crystallization of LCP and PBT, WAXD of homo polymer and their blends were observed. In Fig. 5 WAXD patterns of pure PBT and pure LCP sheets clearly show an anisotropic distribution of the crystal in the sheets plane.

Equatorial and meridional diffractograms for pure LCP are shown in Fig. 6. The difference of the two WAXD traces shows a high degree of molecular orientation existing in the LCP sheet. The profiles show a diffraction peak at $2\theta = 20.10°$ for the equatorial scan and ones at $2\theta = 27.94°$ and 43.50° for the meridional scan. The scans in Fig. 6 reveal an increased diffraction intensity of certain planes in the respective directions relative to the other crystal reflection. The crystals are preferentially oriented with their c axis parallel to the extrusion direction.

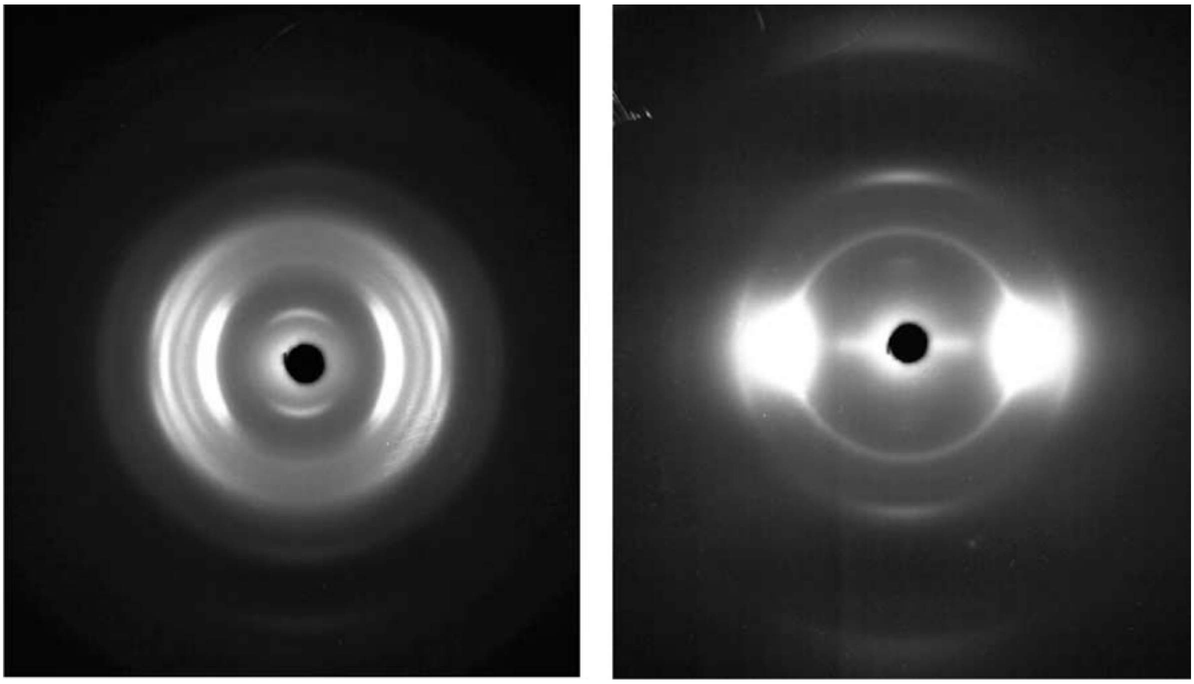

Figure 5 WAXD patterns of pure PBT (left) and pure LCP (right) sheets.

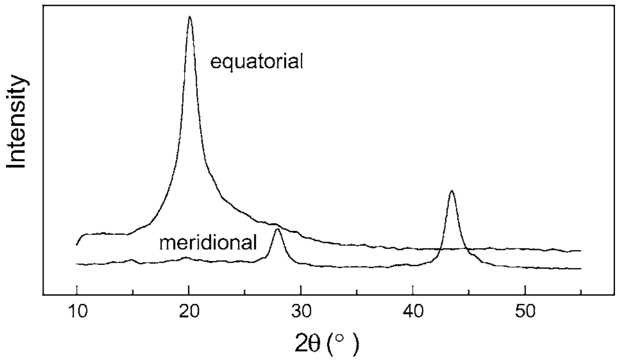

Figure 6 WAXD intensity profiles of LCP.

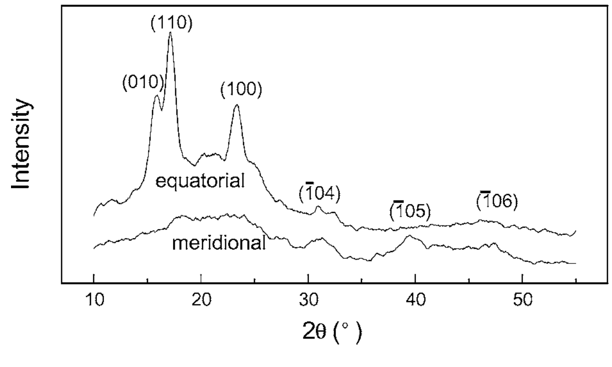

Figure 7 WAXD intensity profiles of PBT.

WAXD profiles of PBT are shown in Fig. 7. The equatorial and meridional scans for PBT show a difference. PBT crystallites have two kinds of modification, α and β forms [21, 22]. A unit cell of α form PBT is a triclinic system [7] with parameters $a = 0.596$ nm, $b = 0.483$ nm, $c = 1.162$ nm, $\alpha = 115.2^\circ$, $\beta = 99.9^\circ$, and $\gamma = 111.3^\circ$. The intensity distributions in Fig. 7 indicate that there is a high degree of crystalline anisotropy existing in the sheet. The peaks at $2\theta = 17.32^\circ$, 21.86°, and 23.6° attributed to 010, 110, and 100 reflections appeared in the equatorial scan. In the meridional scan the intensity of these peaks is very low. But at higher angles, other reflections [21] at $2\theta = 31.4^\circ$, 39.4°, and 47.3° assigned to $\bar{1}04$, $\bar{1}05$, and $\bar{1}06$ reflections were observed. The disappearance of peaks in the meridional scan at $2\theta = 17.32^\circ$, 21.86°, and 23.6° indicates that the 010, 110, and 100 planes are lying parallel to extrusion direction.

The equatorial and meridional scan profiles for blends are shown in Fig. 8. The reflection peaks of PBT and LCP coexist for all compositions. The PBT crystals in pure or in blends are believed to be in the α form according to the crystallographic data reported in the literature.

Orientation distribution of the crystallite phase PBT and LCP can be quantitatively measured independently. The molecular orientation is more often characterized by the Hermans [23] orientation function in the form of

$$f = (3\,\langle \cos^2 \Phi \rangle - 1)/2$$

Where Φ is the angle between the machine direction and the chain axis. A perfect orientation along the machine direction corresponds to $f = 1$, while a perfect perpendicular orientation gives $f = -0.5$; random orientation or no macroscopic orientation results in $f = 0$. The orientation measurement of a different blend component is made possible through the use of WAXD. This method allows for the determination of the orientation function through

$$f = (1 - \beta/180)$$

where β is the peak width at a half maximum. Fig. 4 also shows the orientation function of PBT and LCP, f_{PBT} and f_{LCP}, in the pure state and their blends, which are obtained by azimuthal scans of the equatorial peak at

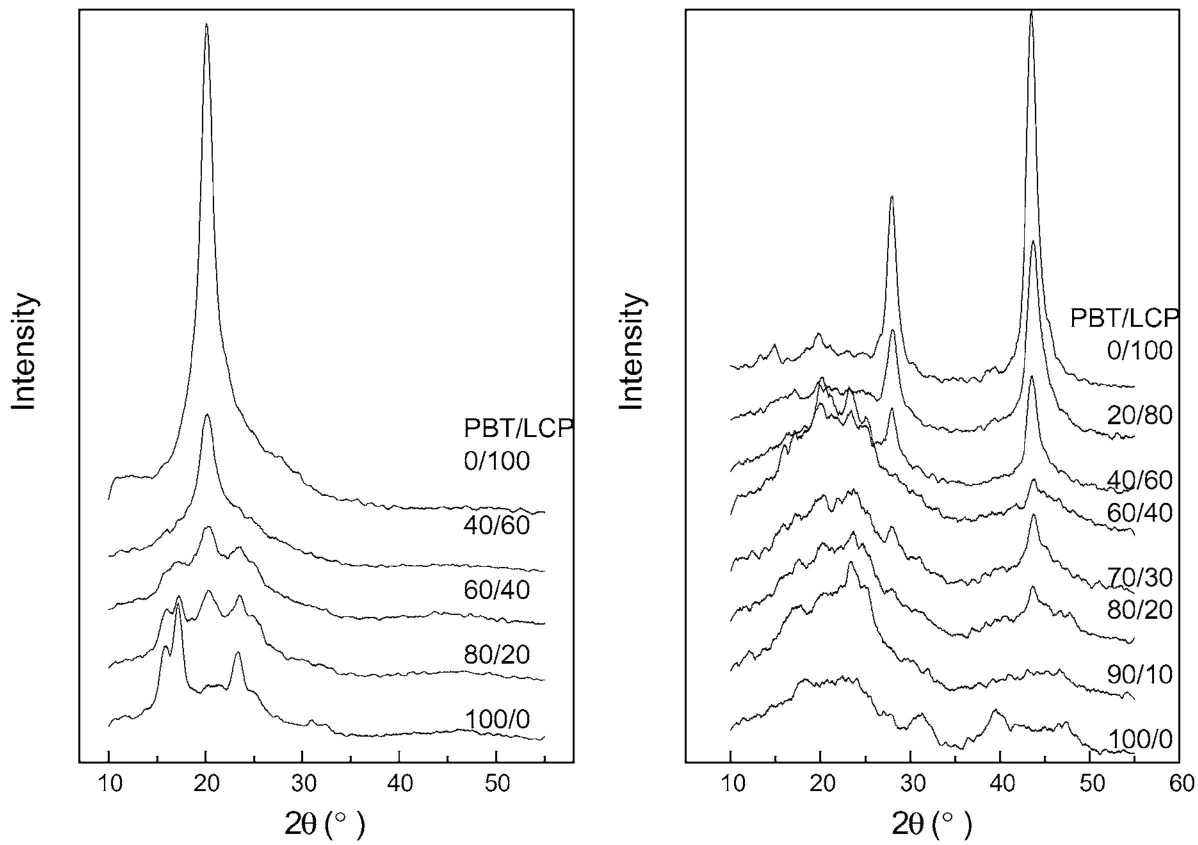

Figure 8 WAXD intensity profiles of PBT, LCP, and their blends in equatorial (left) and meridional (right) directions. Composition ratios are shown in figure.

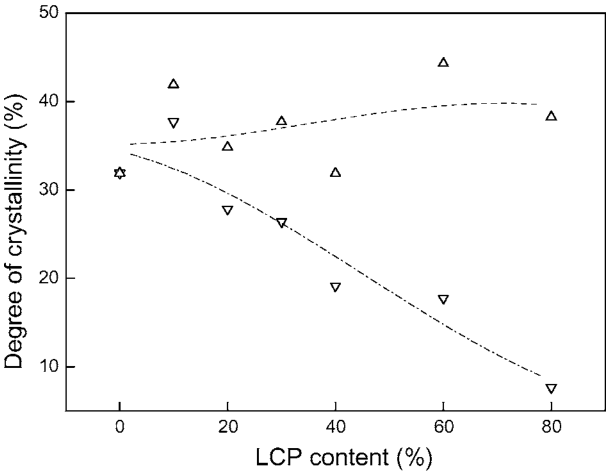

Figure 9 Crystallinity of PBT (up triangle) and PBT and LCP blends (down triangle) calculated from DSC data as a function of LCP content.

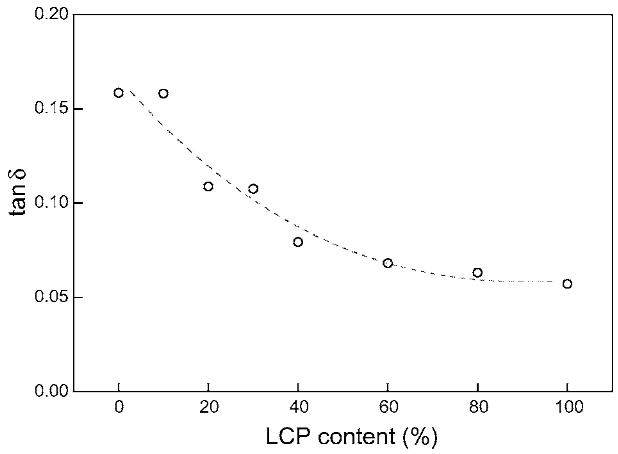

Figure 10 Plot of tan δ peak value as a function of LCP content.

the diffraction angles of 17.30° and 20.10°, separately. It can be seen that the degree of crystalline orientation of PBT and LCP increased with the increase of LCP content.

Percent crystallinity of PBT was calculated from the heat of fusion using the value of 140 J/g for perfect crystals [24]. It is noted that as the LCP content increases, the crystallinity values of blends decreases (Fig. 9). Whereas, if the heat of fusion normalized to PBT weight content is used, the crystallinity values of PBT will increase slightly with the increase of LCP content.

The tan δ peak at about 70°C corresponds to the glass transition of the amorphous phase. So, the height of the loss peak depends on the mass fraction of the amorphous phase. It is interesting to note that as the crystallinity increases, the tan δ value decreases (Fig. 10). The value of crystallinity of PBT and the blends measured by DSC are in line with those of DMA data.

Generally speaking, the orientation state of sheets from pure PBT, LCP, and their blends are very high. A main reason is due to the extrusion method. A higher orientation of the molecular chain in melting state easily forms in the extension and shear stress field of the extrusion process. Since PBT is a semicrystalline polyester with a high crystallization rate [8], a higher molecular orientation frozen in cooling-down state should be expected, leading to an oriented sheet. On the other hand,

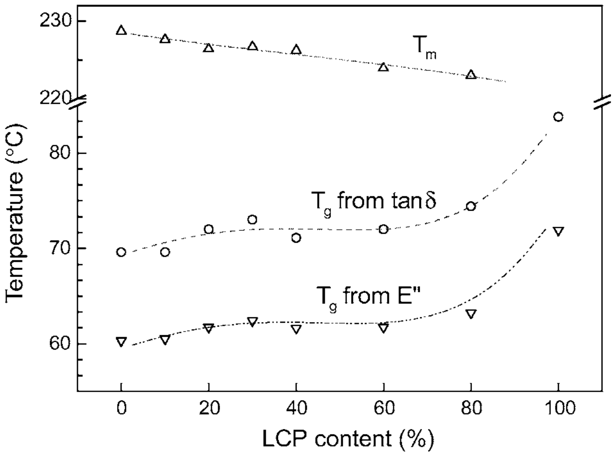

Figure 11 Melting temperature of PBT, T_m, and glass transition temperature of blends, T_g, as a function of LCP content.

the LCP also induces and aids the orientation of the PBT.

3.3. Miscibility in PBT and LCP blends

The determination of changes of T_g with LCP contents could help to assess the miscibility in the PBT and LCP blends. For the semi-crystal polymer PBT and its blends, it is very difficult to get the T_g from DSC measurement, due to the poor sensitivity and low intensity of the glass transition compared with the melting peak. Fig. 11 shows T_g, which is observed in the peak of tan δ in DMA curves.

Fig. 1 shows the plots of tan δ versus temperature for the PBT and LCP blends. It is apparent that all the curves exhibit only one peak or one glass transition temperature T_g. The thermal properties of the PBT and LCP blends are presented in Table I. The T_g values of PBT and LCP are 67 and 87°C, respectively. The PBT and LCP blends exhibit a single T_g between the T_g of PBT and the T_g of LCP, which indicates that PBT and LCP are miscible in all compositions. Moreover, the peaks of T_g tend to shift towards higher temperatures with increasing LCP content (Table I and Fig. 11). The LCP, as a copolyester, is known to form partially miscible blends with various thermoplastic polyesters. This partial miscibility could be attributed to intermolecular π-electron interaction between terephthalate residues of LCP and PBT [6].

The miscibility between the PBT and LCP of a polymer melt blend has some effect on its mechanical properties. Generally, a miscible blend exhibits a poor mechanical strength because of the loss of reinforcement of a polymer component. This point could be seen clearly in Fig. 2, that modulus at the room temperature does not increase linearly with increasing of LCP content in PBT and LCP blends.

The variation of ΔH_m and hence of the degree of crystallinity stays rather constant for PBT with decreasing LCP content (Fig. 9). We can conclude that there are some interactions between LCP and PBT when PBT crystallizes. And the interaction is in favor of the crystallization of PBT.

The melting temperatures, T_m, from DSC measurement also showed a depression trends with the increase of LCP contents. Fig. 11 also shows the T_m of PBT in the PBT and LCP blends measured at the maximum of the melting endothermic peak. The T_m of PBT decreased from 228 to 223°C with the increase of LCP content. These observations mean that either the components are miscible in the melt at the melting point of PBT as shown above or that the interaction parameter χ has a considerably large value. This is a further evidence of the partially miscible blend of PBT and LCP.

It is also possible to conclude that transesterification may occur between PBT and LCP. The crystal reflection peaks of PBT and LCP coexist with all compositions as shown in Fig. 8. The WAXD profiles of the blends are very similar to the combination WAXD profiles of pure PBT and pure LCP, without any visible shift of the peak position and appearance of any other characteristic peak, suggesting that the crystalline structure of the PBT in the blends is not altered in the presence of LCP. Hence, therefore, there is no sign of other supports for transesterification that could be drawn from WAXD profiles.

4. General discussion

This study shows that the orientation degree of extruded sheets of pure PBT and PBT and LCP blends is relatively high. This is because the crystallization rate of PBT is very high. Hence, the thermal relaxation process, which is competing with the chain orientation process, becomes less pronounced. The molecular orientation of melting polymer, which is induced by elongation and shear stress in the extrusion process, could be kept in solid state.

The DMA results confirmed that PBT and LCP blends are partially miscible. By this technique the detection of the glass transition relaxations, which were not observed by DSC, was also possible. The analysis of the glass transition made the attribution to the amorphous and amorphous-crystalline phase possible. Both of crystalline phases of PBT and LCP act as reinforcement on the mechanical properties as shown by the storage modulus dependence on the blends composition. DSC and DMA examination shows that PBT and LCP blends are miscible over the whole composition range. The transesterification between PBT and LCP is negligibly small to give any changes in the PBT crystal reflections in WAXD.

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