

THERMAL ANALYSIS AND STRUCTURE STUDIES ON THE BLENDS OF LIQUID CRYSTALLINE COPOLYESTERS AND PET, PBT

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ABSTRACT

The apparent uniform blends of liquid crystalline aromatic copolyesters and semiflexible polyesters PET or PBT were obtained by mechanical mixing in the molten state within certain range of composition.

The effects of blending with liquid crystalline components on the structure of homopolyester matrix were examined by thermal analysis and X-ray diffraction. These results suggest that the LC component in the blend may possibly be acting as a nucleating agent, or it may induce axial orientation of molecules promoting the local ordering of matrix. For the blends of PET, these influences mainly display in narrowing the width of cold crystalline peak and enhancing the main peak of x-ray diffraction; and for the blends of PBT, the pre-melting crystalline peak was enhanced.

In recent years the thermotropic liquid crystalline copolyesters, consisting of aromatic units, have attracted widespread attention. In the early investigation on the thermotropic liquid crystalline copolyesters, we studied a polymer system based on chlorohydroquinone (diacetate) (CHQ), 4,4'-oxydiphenol diacetate (ODP), terephthalic acid (TPA) and isophthalic acid (IPA)^[1]. The four-component-copolyesters (within certain range of composition) exhibit strong striae, nematic optical texture. They show lower melting temperatures and stable nematic phase within a broad temperature range.

With the newly emerging thermotropic liquid crystalline polymers as the reinforcing materials and the common thermoplastic polymers as the matrix, there exist new opportunities for producing new type of composites with improved properties.

The present study deals with a unique system composed of two kinds of polyesters: thermotropic liquid crystalline copolyesters as mentioned above and the common homopolyesters PET or PBT. The LC component and matrix were blended by mechanical mixing in molten state. The effect of blending with a liquid crystalline component on the structure of the homopolyester matrix have been examined by thermal analysis and X-ray diffraction.

A few similar works based on the blends of 60% PHB (p-hydroxybenzoic acid) 40% PET copolymer (LC polymer) and poly (ethylene terephthalate) homopolymer (PET) and PBT were presented in literatures.^[2,3] The authors of these papers considered that the liquid crystal polymer acts as a nucleating agent for the crystallization of PET and also increases the level of PET crystallinity.

EXPERIMENTAL

Preparation of samples

LC copolyesters were prepared in our laboratory. Their compositions and some thermal data are shown in Table 1. The blends of LC polymer and PET or PBT were obtained by mechanical mixing in molten state. A small amount of sample was placed between two pieces of metal plates on

Table 1 Composition and T_g , T_m of LC copolyesters

Number of sample	Composition (mole%)				T_g (°C)	T_m (°C)
	CHQ	ODP	IPA	TPA		
LC-1	70	30	10	90	102.2	289.1
LC-2	70	30	15	85	107.2	266.9
LC-3	70	30	25	75	107.0	254.7

an oven which had been preheated to the temperature above the melting point of the sample. and pressed into film, then rapidly cooled in cold water, so quenched film was obtained, some of them were annealed at 200°C for 7 hr under nitrogen atmosphere.

Thermal analysis

DSC measurements were performed with a Du Pont model 1090 Thermal Analyzer at heating rate of 10°C/min under nitrogen atmosphere, amount of sample is about 3–5mg. After the first scan, if needed (for PBT and its blends), the sample was cooled to room temperature in DSC cell, then the second scan was repeated.

X-ray diffraction

X-ray diffraction spectra were obtained with a model 3014 diffractometer (Japan Physical Electrical Machine Company), by powder method with $\text{CuK}\alpha$ radiation source.

RESULTS AND DISCUSSION

Thermal analysis of blends of PET and LC copolyesters

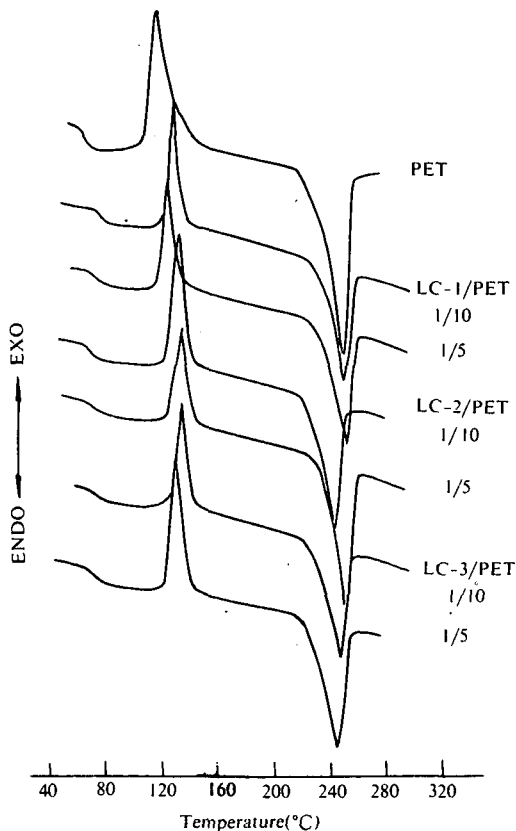


Fig. 1 DSC curves of blends of several LC/PET

The blends of LC/PET with ratio 1/5, 1/10 and 1/20 were prepared by mechanically mixing in molten state for 10–20 minutes until uniform in appearance. Figure 1 shows the DSC curves of several blends with different compositions, while Table 2 summarizes the parameters of interest obtained from the curves. The transitions of blends are believed to be due to those from the matrix PET. A single T_g , T_{cc} and T_m appeared in order. The T_g and T_{cc} of the blends are a little higher than those of pure PET, but the T_g and T_{cc} are lowered with increasing content of LC component. We also noticed that the cold crystalline peak of the blends is narrower than that of pure PET. As we know the cold crystalline peak could be attributed to the local ordering of the segments, so narrower cold crystalline peak could be suggested that the addition of LC component may promote the local ordering of the matrix.

Table 2 T_g , T_{cc} , T_m of polymers and blends with different composition*

Number of LC	Mixing ratio LC PET	T_g (°C)	T_{cc} (°C)	T_m (°C)
LC-1	0 100%	68.6	120.7	250.2
	1 20	77.3	130.4	252.0
	1 10	75.3	124.7	248.8
	1 5	73.7	122.4	249.8
LC-2	100% 0	102.2	121.2	289.1
	1 10	71.6	133.9	245.1
	1 5	71.5	132.9	249.4
LC-3	100% 0	107.2	127.3	266.9
	1 10	74.7	136.2	249.4
	1 5	73.5	132.8	247.8
	100% 0	109.4	133.3	251.4

* All data obtained from quenched films

Figure 2 shows the DSC curves of annealed samples with different compositions. Twin melting peaks appeared as the same as that of pure PET, but the front peak shifts to high temperature (see Table 3). According to the theoretical explanation about twin peaks^[4], this indicated that LC component would create improvement of metastable crystals.

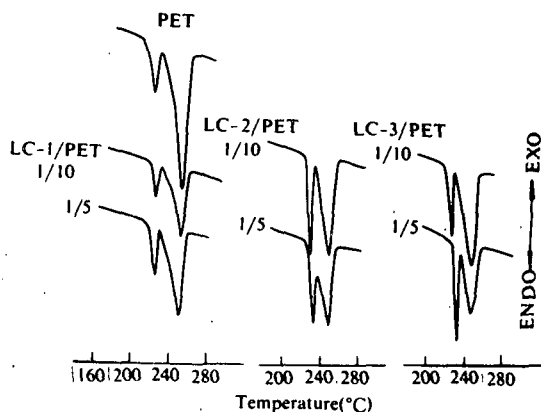


Fig. 2 DSC curves of annealed samples of blends LC/PET

Table 3 Twin melting peak of annealed samples*

Components	Mixing ratio	$T_1(^{\circ}\text{C})$	$T_2(^{\circ}\text{C})$	$\Delta T(^{\circ}\text{C})$
pure PET		220	251	31
LC-1/PET	1/10	223	250	27
	1/5	225	250	25
LC-2/PET	1/10	227	246	19
	1/5	228	245	17
LC-3/PET	1/10	223	245	22
	1/5	226	245	19

* 200°C, 6 hours

Thermal Analysis of blends of PBT and LC copolyesters

For the melt-compressed and quenched sample of pure PBT, a normal melting peak was shown on the DSC curve. After the first scan, the molten sample was slowly cooled down in the DSC cell, then the second scan was repeated, so that a small pre-melting exothermic peak appeared. But for the quenched blends B-7 and B-8 with LC-1/PBT ratio of 1/5 and 1/10 respectively, in the first scan, the pre-melting exothermic peak has already appeared, in the second scan, this peak became more pronounced (Fig.3). This observation suggests a possible explanation as follows: PBT is a easy-crystallizing polymer, when the melt was slowly cooled in DSC cell, dispersed and ungrown metastable nuclei may be created in the amorphous part, at the moment of melting, these metastable nuclei may induce moveable molecular rearrangement into crystal lattice. So it could be called as pre-melting crystallization. The rigid moiety in the blend may possibly be acting as nucleating agent and make this premelting crystalline tendency enhanced. Since this behavior may be relative with the rearrangement of molecular chain in amorphous part, so it should be influenced by the heating rate (Fig.4). As the heating rate is 5°C/min, this peak appears before melting, but at 20°C/min this peak appears after melting-started.

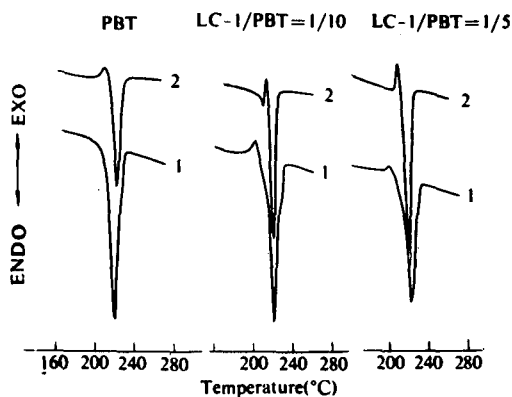


Fig. 3 DSC curves of PBT and blends for twice heating
1. first scan; 2. second scan

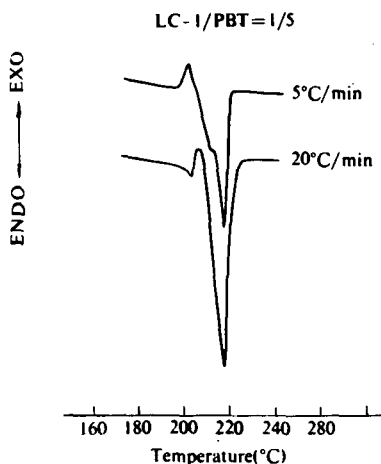


Fig.4 DSC curves of blends LC/PBT with different heating rates

X-ray diffraction

Fig.5 shows the X-ray diffraction curves of annealed samples of PET and its blends. The positions of several diffraction peaks of blends are almost the same as that of pure PET, this implies the parameters of unit cell of matrix are almost unchanged. It should be noticed that the

main diffraction peak of blends are enhanced apparently. This may suggest that axial orientation of the molecules in the blends increased. For easy-crystallizing PBT, addition of LC component did not result in enhancing the crystallization level. (Fig.6)

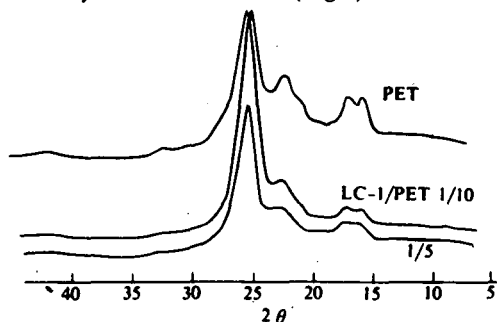


Fig.5 X-ray diffraction curves of annealed samples (200°C, 7hr) of PET and its blends

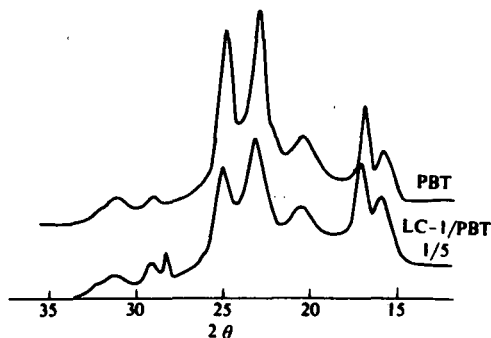


Fig.6 X-ray diffraction curves of annealed samples (200°C, 7hr) of PBT and its blends

Keywords:

Thermotropic Liquid Crystalline; Blend; Local ordering; Pre-melting Crystallization

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