

STUDIES ON MISCIBILITY AND MORPHOLOGICAL FEATURES OF BLENDS OF LC COPOLYESTER AND PET

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ABSTRACT

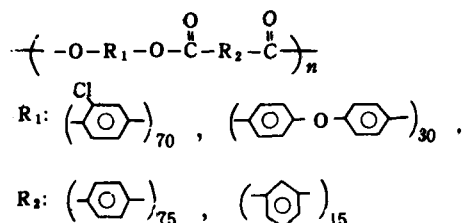
The morphology of a special blend system composed of liquid crystalline aromatic random copolyester (LCP) and semiflexible polyester PET over the whole composition range has been studied by means of polarized microscope, density measurement, DSC, FTIR and SEM. Based on the microscopic observation, it is found that under suitable mechanical mixing condition, LCP may be rather homogeneously dispersed in the PET matrix, with the middle composition range of the contents of LCP at 30–70 wt % the anisotropic and isotropic phase segregation appears. while with LCP contents over 80 wt% the blends exhibit wholly anisotropic. The DSC thermographs of the melt-pressed and quenched films show single T_g , T_{α} and T_m . T_g increases with increasing content of LCP and approaches to the T_g of pure LCP. The experimental results indicate that the two components of this blend system are miscible, there exist some specific interactions between them.

The miscibility of polymer blends is of interest to both industrial application and theoretical studies. The theories and practical examples for this have been shown in numerous publications^[1–4]. Polymeric liquid crystal is a new field of polymeric material science which was rapidly developed over the past decade. This type of polymers has special orientation properties. Blending it with common polymers or some organic materials may introduce some special characteristics into the blends including its molecular orientation, rheological and mechanical properties, and may form some specific functional materials. Takayanagi and others have proposed an idea of molecular composite^[5], e.g. to disperse rigid rod-like molecules in a common polymer matrix on the molecular level, and produce a so-called "molecule reinforcement", which is an ideal and most effective reinforcement. By dispersing a low mass liquid crystalline substance in polymer matrix, Kajiyama et al.^[12] have prepared polymer/liquid crystal composite membranes, which possess selective permeability. The structure and properties of such composites are dependent on the miscibility between the components. In recent years, a few works on blends of thermotropic liquid crystalline polymers have been reported^[6–9]. In a previous paper^[10] we have described the induced orientation of the molecules of matrix PET and enhancement of pre-melting crystalline peak of PBT caused by adding LCP in the blends of LCP/PET or PBT in the composition range of low concentration of LCP (below 20 wt %). The present study deals with the miscibility between the LCP and PET and its influence on the morphological features examined with DSC, polarized microscope, density measurement, Fourier transform infrared spectrography (FTIR) and scanning electron microscope (SEM) over the whole composition range.

EXPERIMENTAL

Materials

Two polyesters were used throughout this study. The liquid crystalline copolyester with the following structures



were prepared by using the procedure of melting polycondensation^[11].

PET is spinning-grade resin in pellet form (Japan).

Preparation of blend samples

Two polymers, grinded into powder in liquid nitrogen, were melt-mixed at 330°C under nitrogen atmosphere for about 20–25 min until uniform in appearance. A small amount of sample was placed between two pieces of metal plates on an oven preheated to 340°C, and pressed into film, then quenched in ice-water.

Characterization of the blends

DSC measurements were performed with a Du Pont model 1090 Thermal Analyzer at heating rate of 10°C/min under nitrogen atmosphere.

Density measurements were made by using a density gradient column made up of carbon tetrachloride/ xylene.

For IR measurements 2–3 μm thick films of pure polymers and blends were melt cast on the salt crystal plate. The FTIR spectra of these thin films and data treatment were obtained using a bruker IFS-113 V model spectragraph.

Morphological observations

For optical microscope studies, a small amount of the blend samples was placed between two pieces of microscope cover glass in an oven, which had been preheated to 350°C. After the sample had melted completely, then the melt film was quenched on a cold metal plate. The optical micrograph was obtained using a microscope equipped with a pair of crossed polarizers.

The samples for SEM observation were obtained from compression mold sheets. The specimen surface was etched with argon ion using IB-3 model etching apparatus. These specimen were coated with platinum and observed with a HITACHI scanning electron microscope.

RESULTS AND DISCUSSION

Blending or mixing is an important approach to improve polymer properties. The properties of the blends are dependent on the chemical structure, aggregate state and dispersing morphological feature, and the latter two depend not only on the molecular structure of the original components, but also on the way of mixing, temperature and miscibility between the components. The mechanical mixing in the molten state is an industrial practicable method for preparing blends. The thermotropic liquid crystalline copolyester may be mixed with common thermoplastic polymer such as PET by mechanical mixing in the melt. The miscibility of the components of the blends is

dependent on the similarity in chemical structure and specific interaction. The present system provides miscible possibility based on the structural consideration.

On the basis of polarized microscope, when the concentrations of LCP are below 20 wt%, optical micrographs display indistinct stars-like pictures on the dark field, it can be concluded that LCP exists in homogeneous dispersion. In the middle composition range (30—70 wt% of LCP), phase segregation appears. When the concentrations of LCP are below 50 wt%, smaller separated anisotropic regions homogeneously disperse in the isotropic continuous phase of matrix (Fig. 1a). With increasing content of LCP, anisotropic regions gradually connect with each other and become continual phase as the contents of LCP were higher than 60 wt% (Fig. 1b). The blend films containing more than 80 wt% of LCP exhibit wholly anisotropic and their optical micrographs display homogeneous optical texture that is special for nematic phase (Fig. 1c) and row-like structure for shearing oriented film (Fig. 1d).

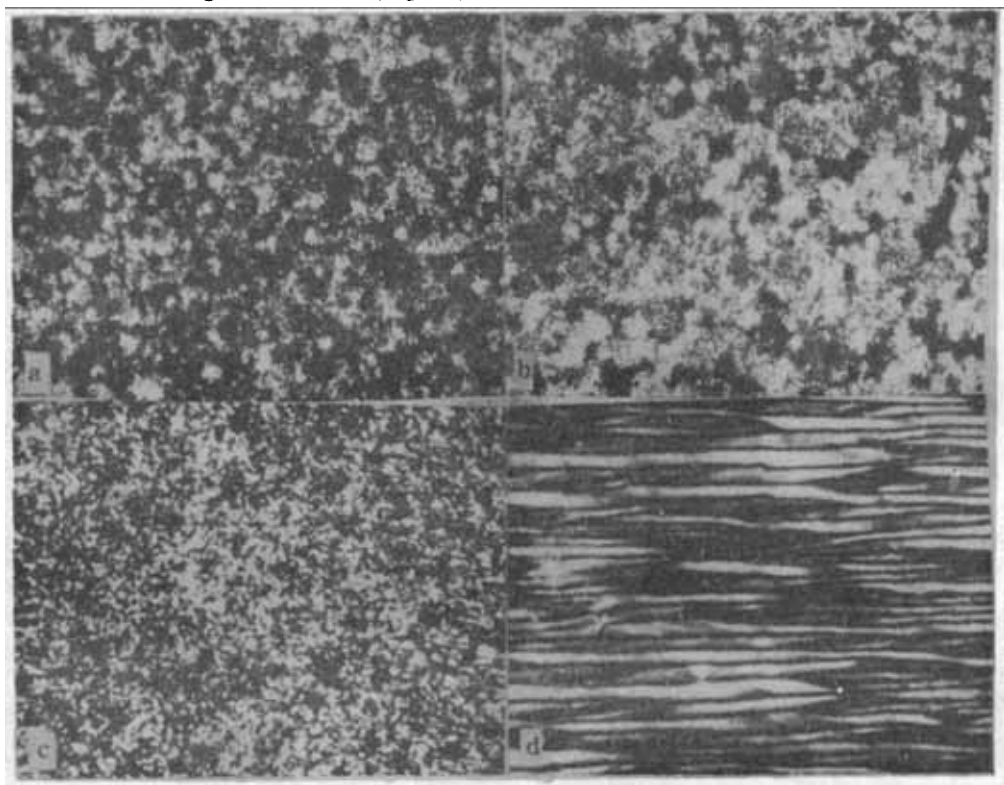


Fig.1 Optical micrographs of blend films (crossed polars)

The DSC thermographs of the melt-pressed and quenched film samples show single T_g , T_{cc} (cold crystallization) and T_m . The data are summarized in Table 1. The T_g , T_{cc} and T_m changed with increasing contents of LCP. For many miscible blends, the relationship between T_g and the composition may be expressed by the simple Fox-equation as follows:

$$\frac{1}{T_{g_b}} = \frac{m_1}{T_{g_1}} + \frac{m_2}{T_{g_2}}$$

where m_i represents the weight fraction of polymer i with glass transition temperature T_{g_i} . Plots of T_g against composition show (Fig.2) that in the range of low concentration of LCP, the T_g values

generally agree with the Fox-relationship. Lower T_g values were detected for the blends with lower concentrations of LCP (below 20 wt%) and almost did not change with the content of LCP, it can be explained as follows, the hindering of the chain segments of matrix from moving and the depressing of viscosity (plasticizing) caused by the addition of LCP may offset each other to some extent. T_g increases with increasing the concentrations of LCP and approaches to the T_g of pure LCP as the contents of LCP are higher than 80 wt% as shown in Fig.2.

* Table 1 T_g , T_{cc} and T_m of pure components and blends of LCP/PET

Compositions wt%		T_g (°C)	T_{cc} (°C)	T_m (°C)
LCP	PET			
0	100	72.1	119.0	254.1
10	90	74.0	133.9	248.3
20	80	74.3	141.0	242.3
30	70	79.4	148.7	226.2
40	60	80.3	159.8	219.6
50	50	83.9	129.5	217.6
60	40	84.6	117.2	193.7
80	20	93.2	128.0	
90	10	95.3	122.4	
100	0	95.1	119.9	

* For the quenched samples

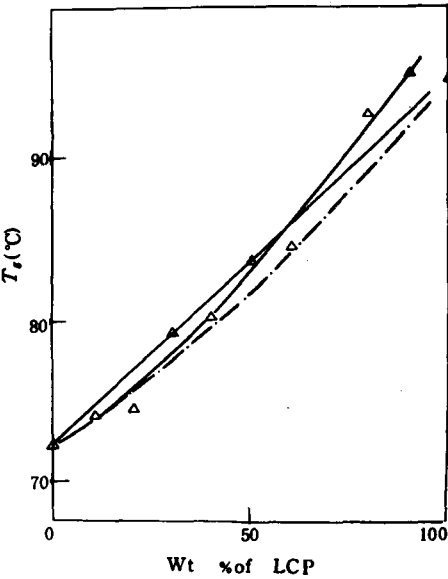


Fig.2 DSC T_g of blends, quenched from 340°C, as a function of composition (—), calc. from Fox equation (---)

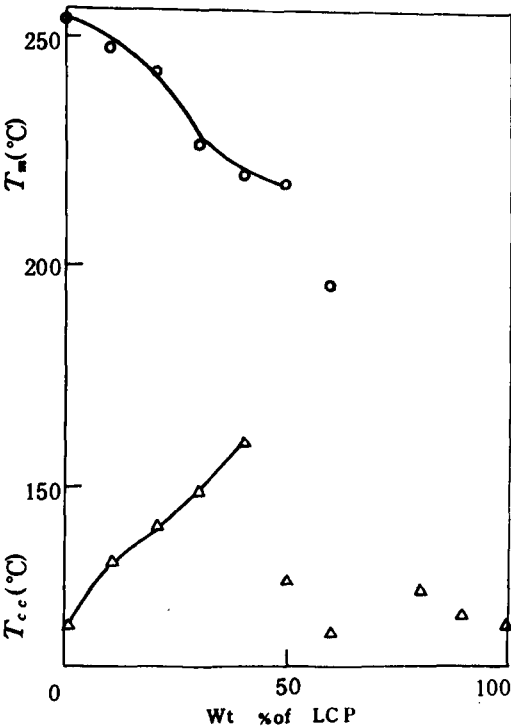


Fig.3 T_{cc} and T_m of blends as a function of composition

Phase segregation, as described by D. R. Paul^[16], may be caused by crystallization of one or more components from a homogeneous melt mixture. A homogeneous amorphous phase upon cooling will eventually become a glass state at a single temperature. This will be so even if phase segregation by crystallization occurs provided that there remains a homogeneous amorphous phase. The above description may also be used to explain our experimental results. In this case phase segregation is caused by liquid crystallization when contents of LCP increase to some extent, but there still exists a homogeneous amorphous phase, and single glass transition is a characteristic of a homogeneous amorphous phase.

On the other hand, the cold crystalline temperature T_{cc} and the melting temperature T_m also changed with the composition as shown in Fig.3. Cold crystallization may be attributed to the local ordering rearrangement of chain segments. The addition of rigid LCP molecules in the PET matrix may hinder the rearrangement of the segments, so T_{cc} 's increase with increasing contents of LCP. But as the LCP contents are close to 50 wt%, T_{cc} 's suddenly decrease and then almost keep at a level. It could be illustrated that because of the easy-orientation tendency of LCP molecules, when LCP is a dominant component of the blends, T_{cc} may become lower, and due to LCP's induced effect to the orientation of PET molecule, PET almost has no effect on T_{cc} , so the levelling may be reached. The T_m decreases with increasing the contents of LCP. The thermographs of the blends with LCP contents higher than 60 wt% just like that for amorphous polymers, T_m can not be detected. In this case the solid phase is a freeze-in mesophase.

It could be concluded that both components coexist in the optical anisotropic and isotropic regions and there is strong specific interaction between them.

The density measurement is an auxiliary method for studying the interaction of components of blend^[13,14]. For the present case a density gradient column is used. The measured densities (d_m) were compared with the calculated densities (d_c), assuming the additivity of specific volume, based on the d -values of the individual polymers: $d_{PET} = 1.374$, $d_{LCP} = 1.41$, and the results are summarized in Fig.4. The measured and calculated densities are generally agree with each other (except one or two points) most measured densities are slightly higher than that of the calculated ones. They are most likely due to the interaction between the two components on a molecular level.

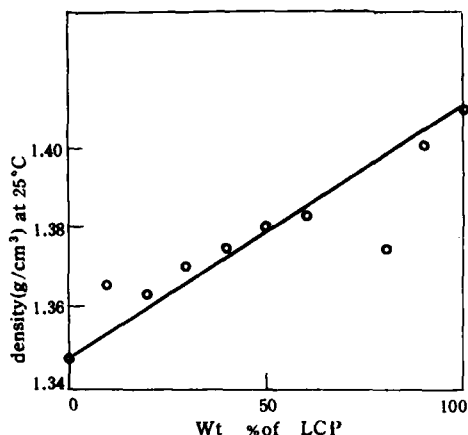


Fig.4 Densities of blends as a function of composition d_m (O), d_c calc. assuming additivity of specific volume (—)

The most direct way of looking at the specific interactions is by using spectroscopic measurement^[13]. In recent years infrared spectroscopy technique has been most commonly used to study blend. It can be approximately assumed^[15] that if two components of the blend are completely incompatible, then the spectrum of the blend must be the simple addition of two original spectrums of the pure components. If the two components of the blend are compatible, so due to interactions between the different molecular chains, when the blend spectrum was compared with additive spectrum, it can be found that for those bands, which are sensitive to structural differences, some frequency shift and intensity change would take place. Fig.5a shows the spectrum of blend with LCP/PET = 1:1 (wt) and Fig.5b shows the spectrum additive based on 1:1 of two original spectrums of pure compounds, it was found that the position and intensity of several bands are different. Selective data are summarized in Table 2. The more apparent frequency shifts are relative to —O—, C=O. The most apparent shift is due to the symmetric stretching vibration of ether bond (C—O—C) in the range of 1060—1130 cm^{-1} , not only the frequency shift, but the number and intensity of bands are also different. Above experimental results indicate that the bands of the ether and the carbonyl bond with strong polarity are more sensitive to the environment.

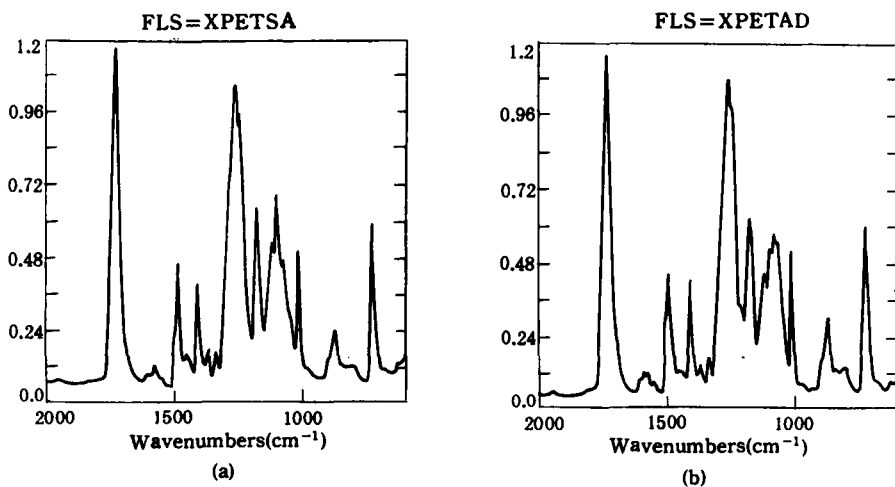


Fig.5 a. IR spectrum of blend with LCP/PET = 1:1 (wt)
b. additive spectrum with composition 1:1

The SEM micrographs of etched surface show (Fig.6) that the two polyesters with different rigid-flexibility can homogeneously disperse in each other, no matter what the concentration is, the regions aggregated from LCP almost homogeneously penetrate in the matrix. In these pictures the bulging parts may be due to the rigid LCP and the etched parts-gorges may be due to the flexible matrix. These results also indicate that the apparent phase segregation observed by polarized microscope is not a real phase separation of the two polymers.

It seems that complete homogeneity may almost be impossible to be achieved by the mechanical mixing of two high molecular weight polymers. The differences in the preparation and the morphology of the samples may lead to some errors, but it is no doubt that these two polymers are miscible and there exist some specific interactions between them.

Table 2 Comparison between the spectrum of the blend (wt 1:1) and additive spectrum based on 1:1 of original spectra of two individual components

Position of bands (cm ⁻¹)		Typical of
Blend	additive	
1726	1734	ν (C=O)
1493	1494	ν (C=C)
1340	1342	ω (CH ₂) (PET)
1264	1265	} ν_{as} (C—O—C)
1245	1247	
1181	1178	ν_{as} (C—O—C) (LC)
1120	1123	} ν_s (C—O—C)
1100	1098	
	1083	
	1070	

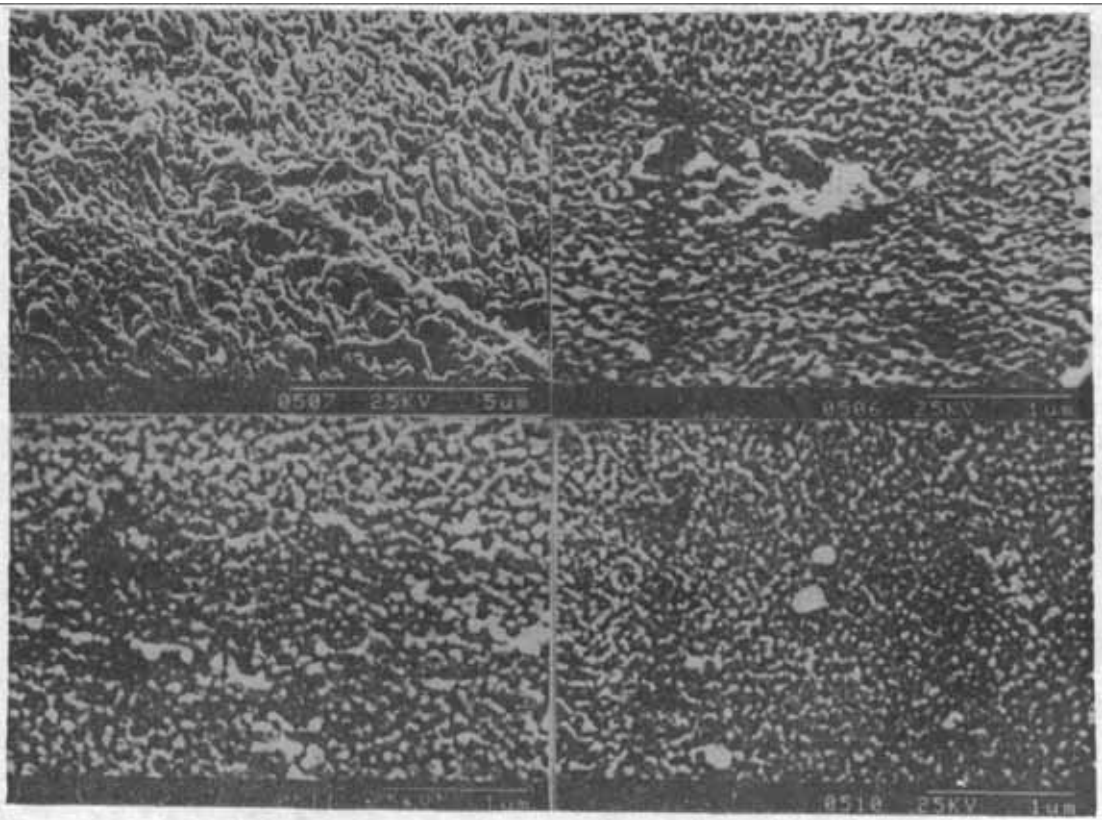


Fig.6 SEM micrographs of etched surface of blend sheets LCP wt%:
a. 20, b. 40, c. 60, d. 80

Keywords:

Blend, Liquid Crystalline Copolyester, PET, Miscibility, Morphological Feature, Phase segregation, Additive spectrum

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