Processing and Characterization of Liquid Crystalline Copoly-(ethylene terephthalate-*co*-2(3)-chloro-1,4-phenylene terephthalate)/Polycarbonate Blends

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Abstract: Liquid crystalline (LC) poly(ethylene terephthalate-*co*-2(3)-chloro-1,4-phenylene terephthalate) (50/50, mole/mole) [PECPT] was synthesized and blended with polycarbonate (PC). LC properties of PECPT and thermal, morphological, and rheological behaviors of the PECPT/PC blend were studied. PECPT showed the nematic LC phase and much longer relaxation time than poly(ethylene terephthalate) (PET). The apparent melt viscosity of PECPT was one third of that of PET. An abrupt torque change was observed during the blending process due to the orientation of LC domains. For the blends containing 10~30 wt% of PECPT, the complex viscosities were higher than that of PC. As PECPT content increases above 40 wt%, shear thinning was observed. The lowest complex viscosity was obtained at 40~50 wt%. Transesterification of PECPT and PC was confirmed by the selective chemical degradation of carbonate groups in PC.

Keywords: PECPT, PC, Rheological property, Blend, Morphology, Transesterification

Introduction

The main disadvantage of high-performance polymers is the high melting point arising from their chain stiffness, which sometimes prevents processing in normal condition. Various modifications are attempted to improve the processibility by blending or introducing some flexible spacers, kinked or substituted monomers into the main chain. Especially, polymer blends containing liquid crystalline (LC) components have attracting numerous scientific and industrial interests [1-6]. As a matrix for various thermotropic liquid crystalline polymers (TLCPs), polycarbonate (PC) has been commonly used due to its good physical properties, thermal stability, remarkable electrical property, and good miscibility with TLCPs[7-12]. In the case of thermotropic LC polyester/PC blends, morphology, miscibility, and transesterification have been the subjects of several investigations. Miscibility or adhesion between components is a critical factor to develop good TLCP-reinforced composites. Transesterfication takes place during the blending process of polyester blends near or above their melting temperatures, resulting in block or random copolymers, which can act as compatabilizers [13-17]. Eventually, miscibility of polyester blends is enhanced.

In our previous study[13], LC poly(ethylene terephthalate-*co*-2(3)-chloro-1,4-phenylene terephthalate) [PECPT] having PET units as flexible spacers and chlorohydroquinone units as rigid ones was synthesized and its thermal properties and crystalline structure were investigated. Schaefgen[14] first

synthesized PECPT and melt spun from its anisotropic melt. The fibers obtained exhibited high orientation and high initial modulus. TLCPs having poly(ethylene terephthalate) (PET) units as flexible spacers were usually blended with PC because they exhibited good miscibility and processability [18-22].

In this study, PECPT (50/50. mole/mole) was synthesized and melt blended with PC. Properties of PECPT were studied using a rheological method and compared with those of PET. Thermal, morphological, and rheological behaviors of the PECPT/PC blend were also investigated.

Experimental

Synthesis of PECPT

A mixture of the same monomeric mole% of PET (η_{inh}: 0.58 dl/g, [η]: 0.61 dl/g, bright, Samyang Co.), chlorohydroquinone diacetate (CHQDA), and terephthalic acid (TPA), which were completely dried at 60°C under reduced pressure, was placed in a round flask equipped with a mechanical stirrer, a nitrogen inlet, and a receiver for vacuum application. Where, CHQDA was prepared in advance by refluxing chlorohydroquinone and acetic anhydride with sulfuric acid as a catalyst at 140°C for 2 h. The mixture of PET, CHQDA, and TPA was heated to 280°C at a heating rate of 10°C/min under the nitrogen atmosphere. As the temperature increased, acetic acid formed by the reactions of CHQDA with TPA and PET was vigorously evolved. After 1 h, the reaction temperature was increased to 290°C *in vacuo* (0.1 Torr) and maintained for different times to obtain PECPTs of various molecular weights at that temperature.

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Preparation of PECPT/PC Blend

Various feed ratio of synthesized PECPT (T_m: 224°C, T_g: 70°C, η_{inh}: 0.83 dl/g) and a commercial PC (T_m: 233°C, T_g: 151°C, $[\eta]$: 0.56 dl/g, Samyang Co.) were used for the preparation of PECPT/PC blends. Both polymers, dried at 150°C for 5 h, were mechanically blended using a Brabender plasticorder at a rotation speed of 90 rpm for 10 min (heating from 150°C to 290°C: 2 min, maintaining at 290°C: 8 min.). The blend samples were immediately quenched in a dry ice bath and dried completely for further analysis. Blend samples were coded based on the feed ratio of PECPT to PC. For example, PECPT/PC (10/90) indicates the blend prepared with 10 wt% of PECPT and 90 wt% of PC.

For the study of transesterification, PC and PECPT were dissolved in dichloromethane and phenol/tetrachloroethane (60/40, v/v), respectively, and then precipitated with methanol. The precipitates were ground to powders and their homogeneous physical mixture (50/50, w/w) was used for transesterification reaction at 250°C. After transesterification reaction, unreacted PC units were chemically degraded with piperidine. 1 g of reacted blend was chemically degraded for 1 h with 25 ml dichloromethane solution containing 0.01 mole of piperidine.

Measurements

Viscosity of 0.5 wt% copolymer solution in 100 ml phenol/tetrachloroethane (60/40, v/v) was measured using an Ubbelohde viscometer at 20 ± 0.01°C. The flowing temperature (T_f), at which the polymer melt begins to flow, and the apparent melt viscosity (η_{melt}) of PECPT were measured on a Koka type flow tester. The nozzle diameter (R) and length (L) were 0.25 mm and 1.0 mm, respectively. The load (P) used was 80 kg. T_f was measured at a heating rate of 6°C/min. η_{melt} was determined from the efflux (Q), which was obtained after melting the samples for 10 min at a given temperature, using the following equation:

$$\eta_{melt} = \frac{(PR/2L)}{(4Q/R^3)} \quad (1)$$

A Perkin-Elmer differential scanning calorimeter (DSC-4) was used to determine the glass transition temperature (T_g) and the melting temperature (T_m). A heating rate of 20°C/min was used and the DSC sample cell was purged with nitrogen gas. Rheological properties of the blend were measured on a Rheometrics Dynamic Spectrometer (RDS-

7700, cone and plate type) under the dry nitrogen atmosphere. All the samples were dried before measurement in a vacuum oven at 150°C for 5 h. The morphology of fracture surfaces of PECPT and the blend was studied using scanning electron microscope (SEM, Stereoscan 360, Cambridge Instrument Co.), in which all samples were prepared using a Brabender plasticorder at a rotation speed of 90 rpm, followed by quenching into liquid nitrogen. IR spectra were obtained on a Bruker IFS-66 FTIR spectrometer with a KBr pellet at 4 cm^{-1} resolution and 32 scans were averaged.

Results and Discussion

LC Properties of PECPT

As reported in previous study[13], the content of chloro-1,4-phenylene terephthalate (CPT) units in PECPT, 47.4 mole%, is very close to the feed ratio of CHQDA and TPA, 50 mole%. In general, alignment of LC units in the direction of flow is usually maintained in the solid state and consequently affects physical properties of injection-molded specimens and fibers. Baird[23] reported that a LC copolyester prepared from 40 mole% of PET and 60 mole% of *p*-hydroxybenzoic acid (PHB/PET (60/40)) takes a few seconds for the stress relaxation and a few minutes for the relaxation of molecular orientation. Jerman and Baird[24] reported that ompared with PET PHB/PET shows very small die swell, indicating that LC polymers are aligned during the flow and the alignment is maintained during the spinning. Relaxation times of PET and PECPT determined using the method of Wissbrun and Griffin[25] are listed in Table 1. PECPT shows much longer relaxation time than PET. Relaxation time of PECPT is relatively shorter at higher shear rate and slightly dependent on the temperature. These results indicate that PECPT has nematic LC phase at these temperatures. PET (η_{inh}: 0.58 dl/g) starts to flow at 263°C, but PECPT having similar inherent viscosity as PET begins to flow at lower than 240°C and shows similar flow temperature at quite higher viscosity of *ca.* 1.0 dl/g because LC units are sensitive to shear stress and can easily align along the flow direction (Figure 1). Shear alignment of LC polymers is easily confirmed by polarized microscopy. The nematic LC phase of PECPT was observed by a polarized microscope after shearing a glass plate with a tweezer (Figure 2). Figure 3 shows η_{melt}s of PET and PECPT. η_{melt} of PECPT is one third of that of PET when compared on the basis of their

Table 1. Relaxation times of PET and PECPT

Shear rate (rad/sec)	Relaxation time ×10^{-3} (sec)		PECPT (η_{inh}: 0.83 dl/g)		
	PET (η_{inh}: 0.58 dl/g, 280°C)	PECPT (η_{inh}: 0.61 dl/g, 280°C)	280°C	290°C	300°C
10	3.13	46.4	84.7	76.8	66.5
100	1.64	3.52	8.59	7.94	6.84
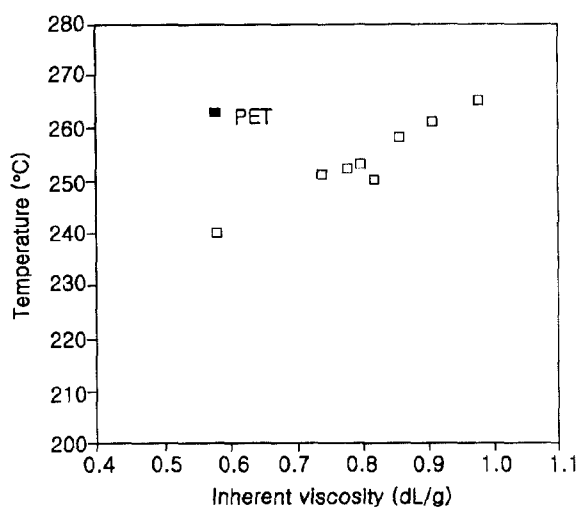
Figure 1. Flowing temperatures of PET and PECPT.
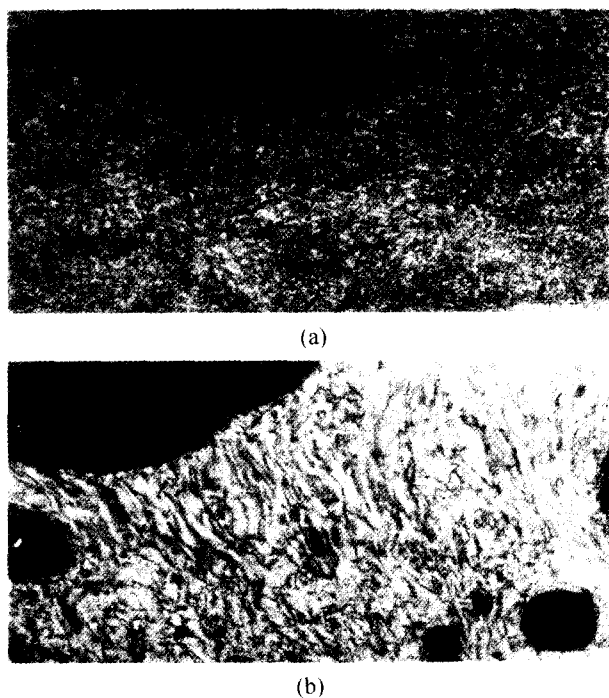

(a)

(b)

Figure 2. Polarized micrographs of PECPT at 280°C (×100): (a) normal state, (b) with shear stress.

solution viscosities. η_{melt} of PECPT decreases with increasing temperature.

Blend Processing

Figure 4 shows changes of torque on a Brabender plasticorder for PC, PECPT, and PECPT/PC blends with time at 290°C. The values of torque are 9 Nm and 1.5 Nm for PC and PECPT, respectively. As the blend ratio of PECPT increases, the torques are gradually decreased. For
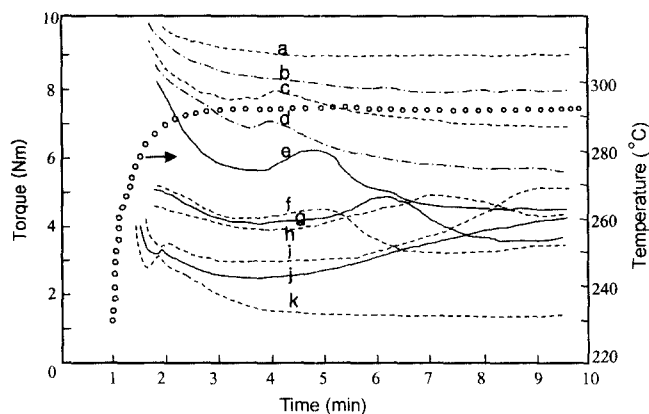

Figure 3. Apparent melt viscosities of PET and PECPT: (a) PET (n), (b) PECPT at 280°C (□), (c) PECPT at 290°C (△), (d) PECPT at 300°C (▲).

Figure 4. Variations of torque with time for PC, PECPT/PC blends, and PECPT at 290°C: (a) PC, (b) PECPT/PC (10/90), (c) PECPT/PC (20/80), (d) PECPT/PC (30/70), (e) PECPT/PC (40/60), (f) PECPT/PC (50/50), (g) PECPT/PC (60/40), (h) PECPT/PC (70/30), (i) PECPT/PC (80/20), (j) PECPT/PC (90/10), and (k) PECPT.

PECPT/PC blends containing 20~70 wt% of PECPT, an abrupt torque change is observed and it is delayed as the blend ratio of PECPT increases. Above 80 wt% of PECPT, the torque change is observed in the very early stage of the blend processing. These torque changes are dependent on the blend ratio. Baird and Viola[26] observed a high stress peak in the very early stage and other peak after 4 seconds during the torque measurement of PHB/PET (60/40) at 260°C. They concluded that the former is attributed to the orientation of LC domains in the matrix and the latter to homogenization of the matrix. Similarly, it is considered that the abrupt torque changes are due to the orientation of LC domains in the matrix and influenced by the blend ratio.
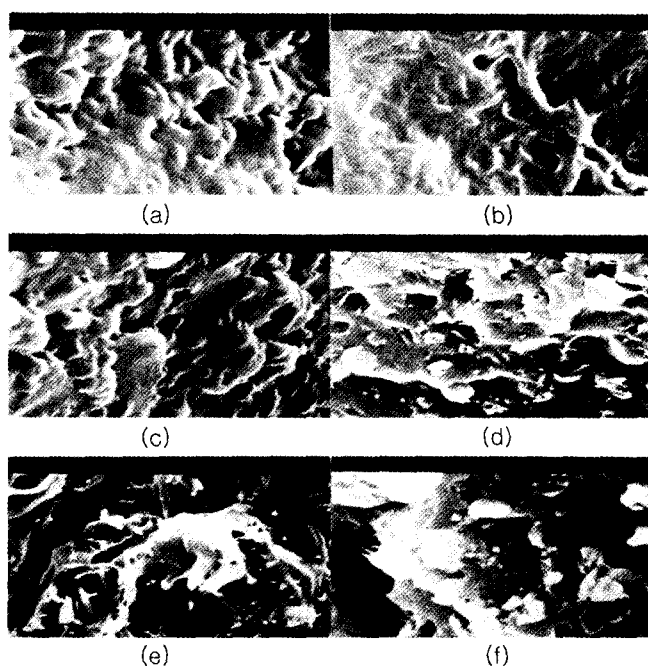
Figure 5. Scanning electron micrographs of fracture surfaces of PECPT/PC blends: (a) PECPT/PC (10/90), (b) PECPT/PC (20/80), (c) PECPT/PC (50/50), (d) PECPT/PC (60/40), (e) PECPT/PC (90/10), and (f) PECPT. The specimens were shadowed with platinum.

Figure 6. Shear rate dependence of complex viscosities of PECPT/PC blends: (a) PC (n), (b) PECPT/PC (30/70) (○), (c) PECPT/PC(40/60) (△), (d) PECPT/PC (50/50) (●), (f) PECPT/PC (70/30) (□), and (g) PECPT (▲).

Thermal and Morphological Analysis

As most of polymer blends are immiscible, they form multiphase domains. The resultant properties of immiscible blends are dependent on the degree of dispersity, size, shape of these domains[27]. Thermal transitions of PC, PECPT, and PECPT/PC blends were analyzed. T_g of PC was clearly determined to be 151°C at the inflection point but that of PECPT was barely determined to be 70°C. T_g of PC was gradually decreased with increasing PECPT content in the blend. However, the T_g change of PECPT could not be traced obviously after blending. Figure 5 shows fracture surfaces of PECPT/PC blends. A spherical domain of PECPT is observed up to 50 wt% of PECPT but the matrix of the PECPT/PC blend is changed to PC from 60 wt% of PECPT. Fracture surface analysis revealed that PECPT/PC blends are not miscible for the blend compositions investigated.

Rheological Properties

Figure 6 shows changes of complex viscosities of PECPT/PC blends with the shear rate. PC shows the Newtonian behavior, while PECPT shows shear thinning. At lower shear rates, PECPT shows higher melt viscosity than that of PC as can be expected from its higher solution viscosity. When the blend ratio of PECPT is less than 30 wt%, the blend shows the Newtonian behavior, but above 40 wt% of PECPT, shear thinning is observed. Figure 7 shows changes of the complex viscosity with the blend ratio for various
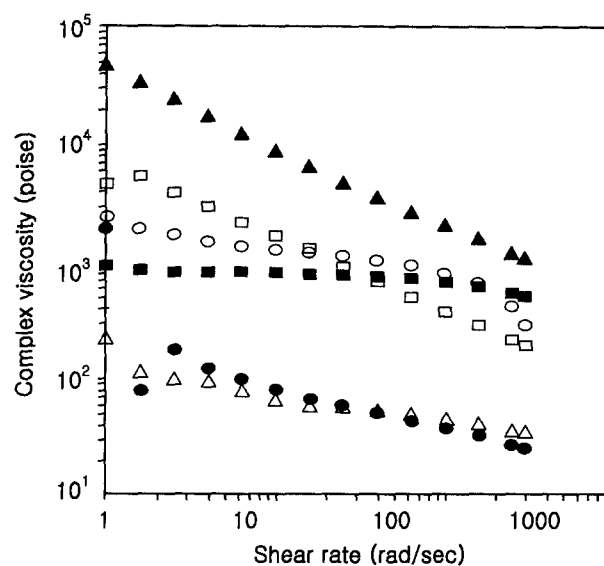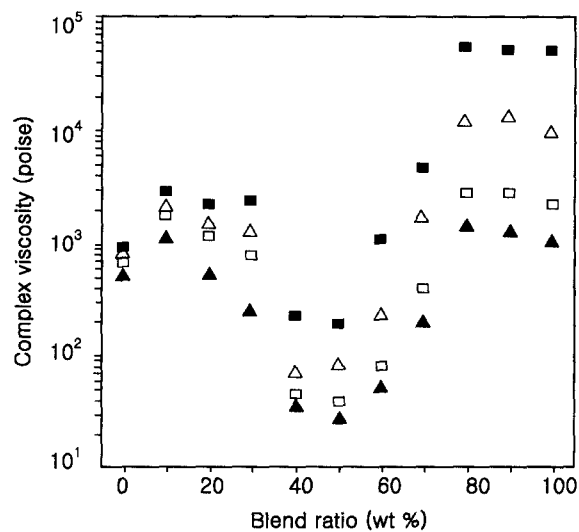

Figure 7. Complex viscosities of PECPT/PC blends at various shear rates: (a) 1 rad/sec (n), (b) 10 rad/sec (△), (c) 100 rad/sec (□), and (d) 1000 rad/sec (▲).

shear rates. Blizard and Baird[28] suggested that the melt viscosity of thermoplastic can be reduced by adding 10~30 wt% of PHB/PET. Siegmann *et al.*[29] reduced the melt viscosity of polyimide by adding just 5% of a LC polymer and Acierno and Amendola[30] observed a drop in the melt viscosity of PC by adding less than 10 wt% of a LC polymer. However, for 10~30 wt% of PECPT, the complex viscosity of the blend is higher than that of PC. The lowest complex

Table 2. Inherent viscosity of the remaining polymer after the selective degradation of PC in the PECPT/PC blend at room temperature: initial η_{inh} of PECPT is 0.83 dl/g

Blending time (min)	3	5	10	20	40	70
η_{inh} [1)	0.68	0.82	0.98	1.08	0.87	0.52
η_{inh} [2)	0.52	0.47	0.45	0.40	0.37	0.24

[1) After the selective degradation for 1 h.
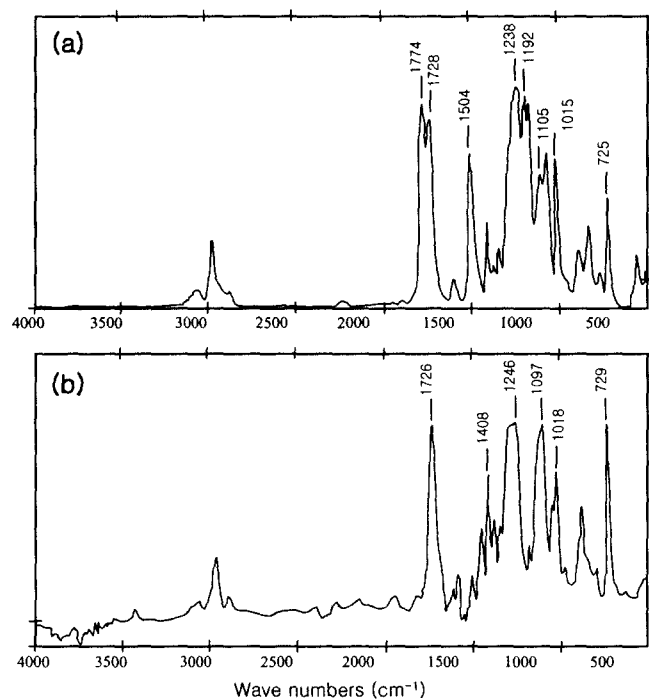[2) After the selective degradation for 48 h.

Figure 8. IR spectra of the PECPT/PC blend (a) before and (b) after selective degradation of PC by piperidine.

viscosity was obtained at 40~50 wt% of PECPT. This is probably due to the high melt viscosity of PECPT and a large difference in solution viscosities of the two.

Transesterification

Transesterification between PECPT and PC was investigated using the selective degradation method of carbonate groups in PC. After transesterification between PECPT and PC powders (50/50, w/w) at 250°C, unreacted PC units were chemically degraded by piperidine, which can selectively degrade carbonate groups in a polyester/PC blend[31]. Figure 8 shows IR spectrum of a PECPT/PC (50/50) blend before and after the selective degradation of PC. An absorbance peak at 1780 cm⁻¹ almost disappears after the selective degradation, which corresponds to the carbonate absorbance band. Viscosity of the remaining polymer after

the selective degradation was measured and listed in Table 2. After the selective degradation for 1 h, viscosity of the remaining polymer is higher than those of the starting PECPT and PC up to 20 min. Pilati *et al.*[31] observed similar phenomenon in a PET/PC blend and suggested that block copolymers such as PET-PC-PET, produced from the reaction between hydroxyl end groups in PET and carbonate groups in PC, can be protected by two long PET chains from selective degradation. In this study, we chose another selective degradation time of 48 h, which would be enough time to overcome the protection of PET block chains. Their suggestion is confirmed by the fact that the viscosity of the remaining polymer after the selective degradation for 48 h decreases with increasing the transesterification time, as shown in Table 2. This result indicates that PET block chain length is decreased with the increase of transesterification time. Also, it is expected that block and random copolymers of PECPT and PC formed by transesterfication would enhance the miscibility of the PECPT/PC blend.

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