

# Miscibility and viscoelastic properties of blends of a liquid-crystalline polymer and poly(ethylene terephthalate)

Y. G. Lin, H. W. Lee and H. H. Winter\*

Chemical Engineering Department, University of Massachusetts, Amherst, MA 01003, USA

and S. Dashevsky and K. S. Kim

Akzo Corporate Research America Inc., Livingstone Avenue, Dobbs Ferry, NY 10522, USA

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A thermotropic liquid-crystalline polymer (LCP) was found to be miscible with poly(ethylene terephthalate) (PET) for LCP contents up to 35 wt% and immiscible at higher LCP contents. The melts of the miscible blends are isotropic under the polarizing microscope. They crystallize with a single transition during rheological cooling measurements. In the solid state, the miscible blends showed a single glass transition, as represented by a single peak of loss modulus  $G''$  versus temperature, which decreased linearly with LCP content. Addition of a small quantity of LCP has a dramatic effect on rheology. For example, addition of 2 wt% LCP reduces the viscosity by about 60%. This effect is most pronounced for PET of higher molar masses. The melt viscosity decreases exponentially with the LCP content in the range of composition where the blends are miscible, but there is no significant further reduction of viscosity when the LCP content exceeds 50 wt% as the phase separation appeared. Addition of LCP also changes the distribution of the relaxation times of PET and broadens the zero-shear viscosity regime.

(Keywords: liquid-crystalline polymer; poly(ethylene terephthalate); miscibility)

## INTRODUCTION

Novel properties have been found when blending conventional thermoplastics with a liquid-crystalline polymer (LCP). Addition of small amounts of LCP may result in a biphasic morphology, decreased melt viscosity<sup>1-9</sup> during processing and improved mechanical properties<sup>6-9</sup> in the solid state after processing. As an alternative, a 'molecular-composite' concept has been attempted where the LCP molecules are individually dispersed with the expectation that reinforcement takes effect at the molecular level<sup>10-14</sup>. Such polymers can be processed in the isotropic phase and quenched with the objective of avoiding the biphasic part of the phase diagram.

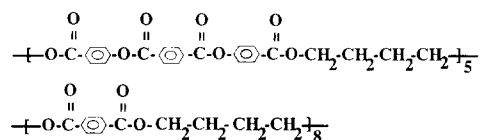
Stein *et al.*<sup>15</sup> showed evidence for a stable molecular composite comprising polyamides and vinyl polymers. The molecular composites were prepared in two different ways: (1) polymerization of the solvent in an isotropic solution of LCP; and (2) solvent evaporation from an isotropic solution of an LCP blend with a flexible polymer.

In the present study, a new liquid-crystalline segmented block copolyester was synthesized in order to blend it with poly(ethylene terephthalate) (PET) and thus alter the viscoelastic properties of the PET.

## EXPERIMENTS

The liquid-crystalline polymer (LCP) is a segmented block copolyester synthesized in Akzo<sup>16</sup>, having the

chemical structure shown and an average molar mass of 11 500 g mol<sup>-1</sup>.



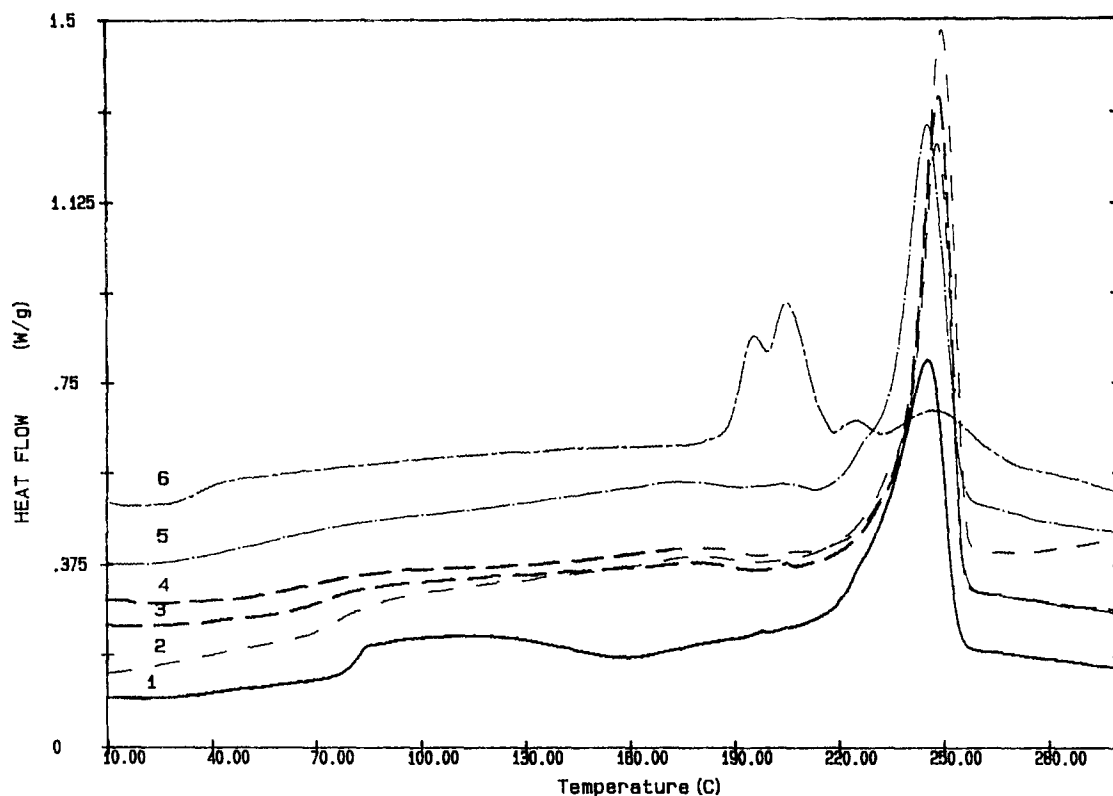
For blending, a poly(ethylene terephthalate) (PET) of 'Tire Yarn Grade' was chosen. It is a commercial product of Akzo with an average molar mass of about 50 000 g mol<sup>-1</sup>. LCP/PET blends of various LCP contents were prepared by melt mixing, in a CSI Mixing Extruder at temperatures between 235 and 280°C, depending on the blend composition. Samples were vacuum dried for 16 h prior to rheological and morphological measurements.

Dynamic mechanical measurements were performed on a Rheometrics Dynamic Spectrometer (RDS 7700) and steady flow measurements on a Rheometrics Mechanical Spectrometer (RMS 800). The use of heated nitrogen gas in the rheometer oven prevented oxidation of the sample. Optical studies were made by using a polarizing microscope (Zeiss Corp.). Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7 in a nitrogen atmosphere and at a heating rate of 20 K min<sup>-1</sup>.

## EXPERIMENTAL RESULTS

### LCP characterization

In d.s.c. heating scans (Figure 1), the pure LCP

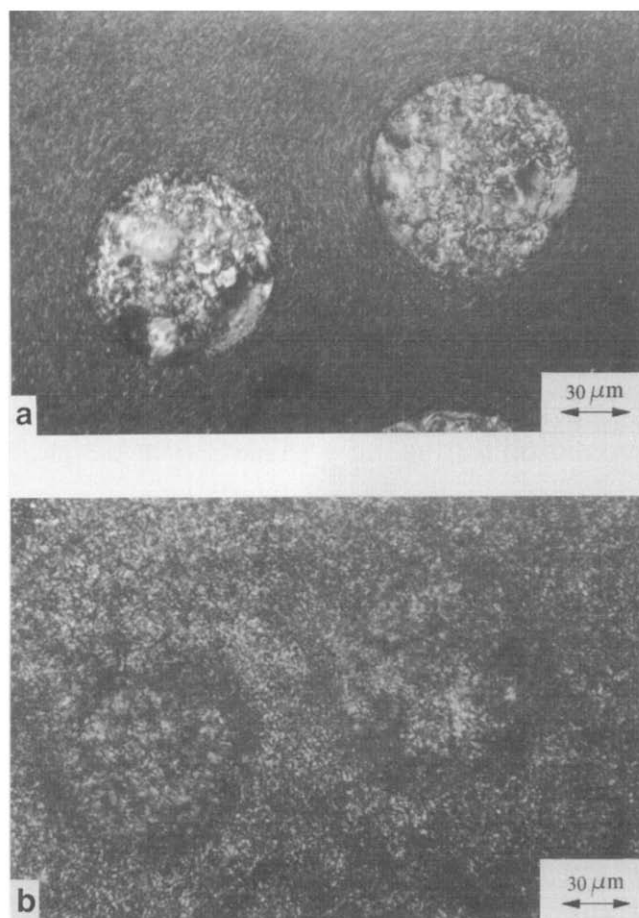


**Figure 1** D.s.c. heating thermograms of PET, LCP and blends at a heating rate of  $20 \text{ K min}^{-1}$ : 1, PET; 2, PET/LCP (90:10); 3, PET/LCP (80:20); 4, PET/LCP (65:35); 5, PET/LCP (50:50); 6, LCP

underwent a glass transition at about  $36^\circ\text{C}$  and a broad melting transition with the highest melting rate at about  $204^\circ\text{C}$ . Polarizing microscopy showed that the LCP morphology is biphasic in the molten state. Above  $260^\circ\text{C}$ , highly birefringent (nematic) domains with a diameter of about  $50 \mu\text{m}$  appeared in a dark (isotropic) continuous matrix with clear phase boundaries (Figure 2a). These highly birefringent domains shrank as the temperature was increased beyond  $290^\circ\text{C}$ , but did not completely disappear even up to  $350^\circ\text{C}$ . Phase separation persisted when solidifying. While a sample was cooled from  $280^\circ\text{C}$  (for 2 min) at a constant rate of  $5 \text{ K min}^{-1}$ , the continuous matrix phase became bright near  $250^\circ\text{C}$  under the cross-polars condition, indicating that the matrix phase underwent a phase transition from the isotropic state to the nematic state. This suggests that the endothermic peak in the d.s.c. heating scan at about  $245^\circ\text{C}$  (Figure 1) may be due to the nematic-isotropic transition of the matrix phase. It was difficult to identify the domain boundary after the LCP had crystallized at  $200^\circ\text{C}$  (Figure 2b).

At  $280^\circ\text{C}$ , the loss modulus  $G''$  is about 5 times as high as the storage modulus  $G'$ ; both  $G'$  and  $G''$  increase with the frequency  $\omega$  in a power law,  $G'(\omega) \sim G''(\omega) \sim \omega^{0.88}$  (Figure 3). Within the accessible frequency window, the LCP melt behaves as an extremely soft gel<sup>17</sup>. The self-similar relaxation behaviour seems to extend beyond the experimental window, but its range is not known. A cut-off (terminal relaxation time) is expected at low frequencies since the sample is believed to be still in the liquid state. At high frequencies, a dynamically induced glass transition is expected to alter the behaviour as is typical for polymeric materials (liquids as well as solids).

During cooling from  $280^\circ\text{C}$  at a constant rate of



**Figure 2** A sample was first heated to  $280^\circ\text{C}$ , then cooled at a constant rate of  $5 \text{ K min}^{-1}$ ; the polarizing micrographs were taken at (a)  $260^\circ\text{C}$  and (b)  $200^\circ\text{C}$

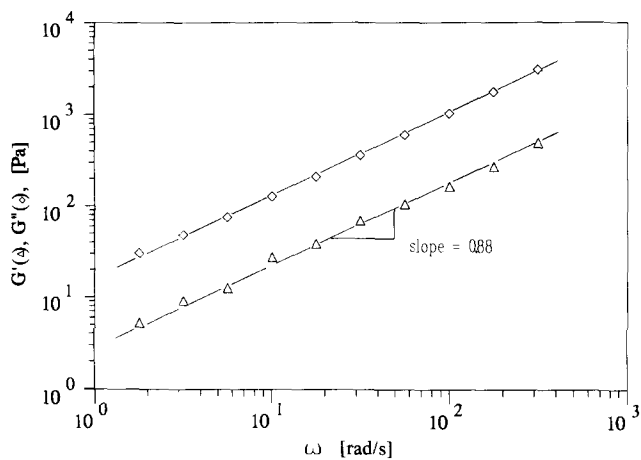


Figure 3 Frequency sweep of LCP at 280°C and strain amplitude  $\gamma_0 = 0.15$  shear units

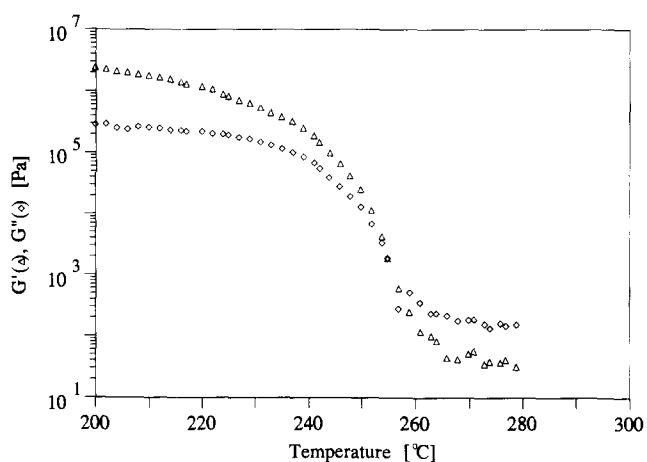


Figure 4 Dynamic moduli of LCP measured at  $10 \text{ rad s}^{-1}$ , during cooling from 280°C at a rate of  $1 \text{ K min}^{-1}$

$1 \text{ K min}^{-1}$ , the dynamic moduli increased sharply at about 255°C (Figure 4). This is where the isotropic–nematic transition of the LCP matrix phase occurs. The modulus increase may be caused by microphase separation of the mesogen segments, which are able to associate and thus act as physical crosslinks for the flexible spacer segments. The same phenomenon is typically observed for main-chain LCPs with long flexible chain segments<sup>18</sup>. The opposite behaviour has been reported for LCPs with very short or without any flexible spacers. Those LCPs are usually characterized by a decrease in the viscoelastic properties at the transition from the isotropic to the nematic state<sup>19</sup>.

When a sample was cooled from 280°C to 250°C and held there for 15 min,  $G'$  was higher than  $G''$  at the accessible frequencies (Figure 5), indicating an elasticity domination at small-amplitude deformations. However, the upper strain limit of the linear viscoelastic regime is only 0.003 shear units; beyond this limit the dynamic moduli decay dramatically with increasing strain amplitude (Figure 6). It should be noted that the relation of Cox and Merz<sup>20</sup>:

$$\eta(\dot{\gamma}) = \eta^*(\omega)|_{\omega = \dot{\gamma}}$$

does not apply to the LCP melt at 250°C. Instead, if we

define an average shear rate<sup>18</sup>:

$$\bar{\dot{\gamma}}_d = 2\omega\gamma_0/\pi$$

where  $\omega$  and  $\gamma_0$  are frequency and strain amplitude, respectively, the complex viscosity matches fairly well with the steady shear viscosity at corresponding shear rates (Figure 7). Both the oscillatory and the steady shear flow measurements evidence the shear-thinning behaviour of the LCP melt.

#### LCP/PET blends

##### Crystallization and isotropic–nematic transition.

Crystallization and isotropic–nematic transition of the blends of various compositions were observed while the samples were cooled from 280°C at a constant rate of  $1 \text{ K min}^{-1}$  (Figure 8). Pure PET crystallizes at about 225°C as shown by the rapid increase in the dynamic moduli. The blends containing 35 wt% or less LCP undergo a single crystallization. The crystallization temperature shifts with the LCP content and reaches a maximum of about 235°C with 10 wt%

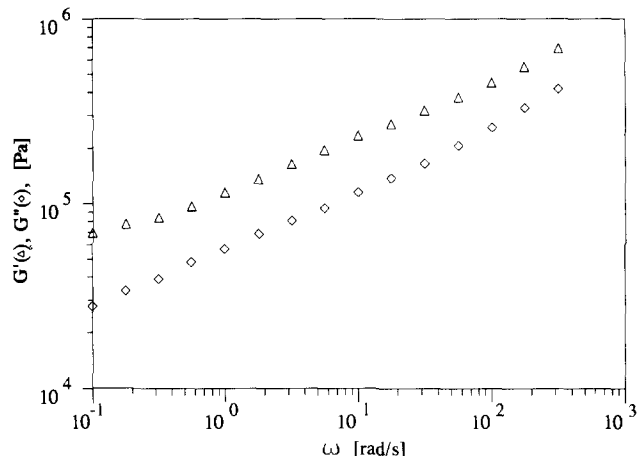


Figure 5 Frequency sweep of LCP at 250°C and strain amplitude  $\gamma_0 = 0.003$  shear units. The sample was first heated to 280°C, then cooled to 250°C and held there for 15 min prior to the measurement

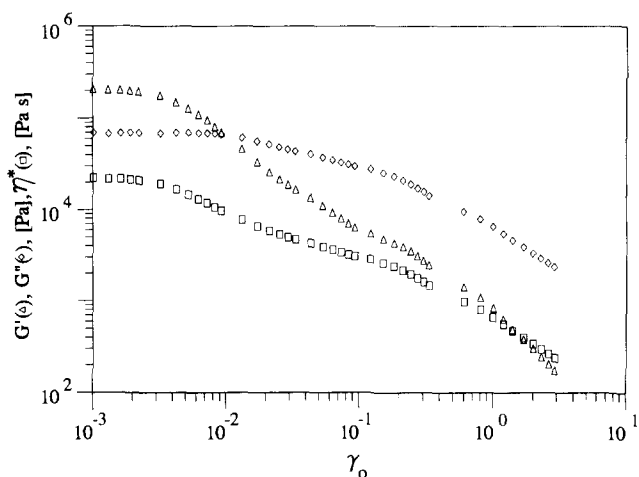


Figure 6 Dynamic moduli of LCP measured at 250°C and  $10 \text{ rad s}^{-1}$  with increasing strain amplitude. The thermal history of the sample is the same as indicated in Figure 5

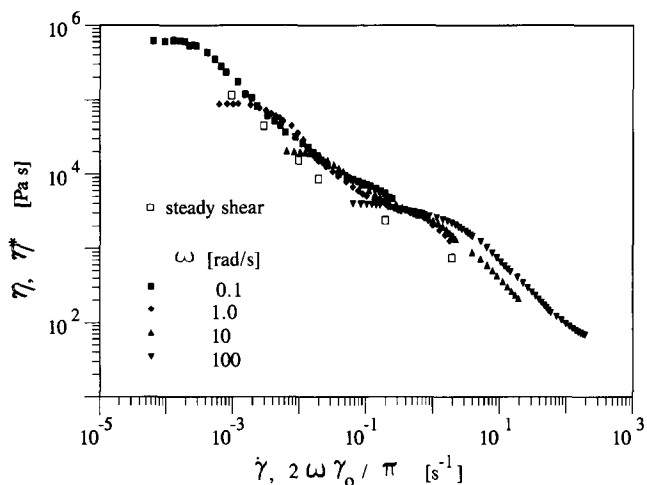


Figure 7 Steady shear viscosity and complex viscosity of LCP at 250°C. The thermal history of each sample was the same as presented in Figure 5

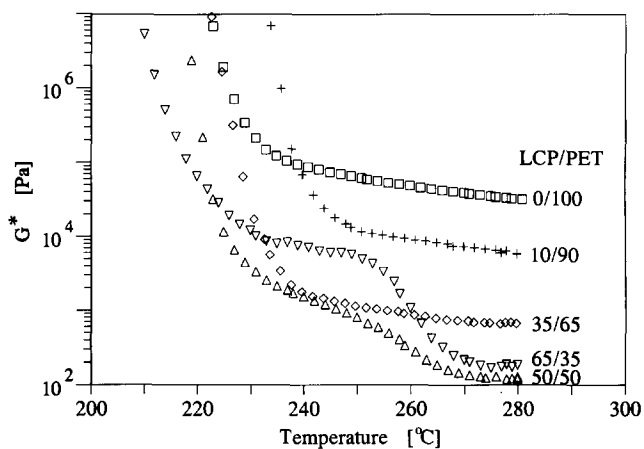


Figure 8 Complex modulus of PET and blends measured at 10 rad s<sup>-1</sup>, during cooling from 280°C at a rate of 1 K min<sup>-1</sup>

LCP. However, the blends containing 50 wt% or more LCP display an additional phase transition at about 255°C, corresponding to the isotropic–nematic transition of LCP (compare with Figure 3). This phase transition becomes emphasized as the LCP content increases, but it keeps its transition temperature constant.

**Glass transition.** The glass transitions of the blends were measured by both d.s.c. and oscillatory torsion techniques. In d.s.c. measurements, a single glass transition was observed for the blends in the whole range of composition (Figure 1). The blends with higher LCP contents exhibit a somewhat broader transition unlike the PET and LCP. The glass transition temperature of the blend decreases linearly with increasing LCP content up to 35 wt%. In dynamic torsion tests,  $G'$  and  $G''$  of a sample were measured at 1 rad s<sup>-1</sup> while heating at a constant rate of 1 K min<sup>-1</sup>. At the glass transition zone,  $G'$  decreased gradually with increasing temperature while  $G''$  displayed the typical peak (Figure 9). The  $G''$  peak temperature has often been defined as a glass transition temperature,  $T_g$ . Pure PET has a single  $G''$  peak at 82°C. Blends containing 35 wt% or less LCP also show a single  $G''$  peak, although their peak is broadened and shifted to lower temperatures in comparison with pure PET.

However, for the blend containing 50 wt% LCP an additional small  $G''$  peak appears at about 40°C. The blends of higher LCP contents were not testable below 50°C owing to their brittleness. The major  $T_g$  decreases linearly with the LCP content (Figure 10). Extrapolation of the data in Figure 10 gives an estimated  $T_g$  value for pure LCP at about 42°C, very close to the temperature at which the small peak appears in the  $G''$  curve of the blend which 50 wt% of LCP.

**Polarizing microscopy.** The pure PET is completely isotropic in the molten state. When a sample was cooled from 280°C at a constant rate of 5 K min<sup>-1</sup>, small crystalline regions appeared at about 230°C. The most rapid growth of the crystalline region was observed at about 220°C. At the same temperature conditions, the blend with 10 wt% LCP is also completely isotropic and single-phased in the molten state. During cooling, crystals appeared and grew very quickly at about 230°C. The size of the crystalline regions is more uniform and finer in the fully crystallized blend (at 220°C) than in pure PET (Figure 11). However, the molten blends of 50 and 65 wt% had a biphasic structure with dispersed nematic domains in an isotropic matrix. The size of the nematic domains increases with the LCP content (Figure 12). The isotropic matrix crystallizes at about 225°C.

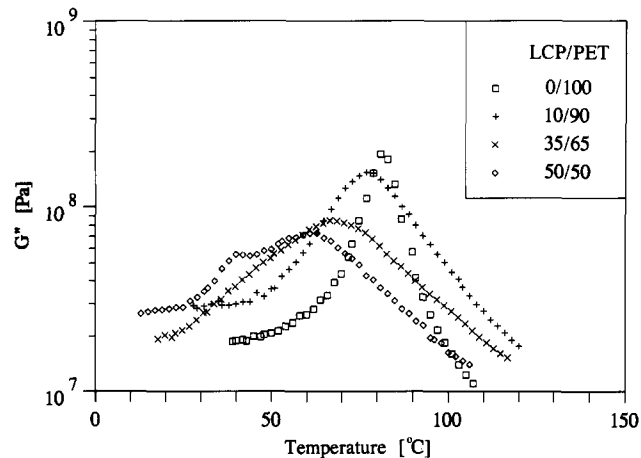


Figure 9 Loss modulus of PET and blends measured at 1 rad s<sup>-1</sup>, during heating at a rate of 1 K min<sup>-1</sup>

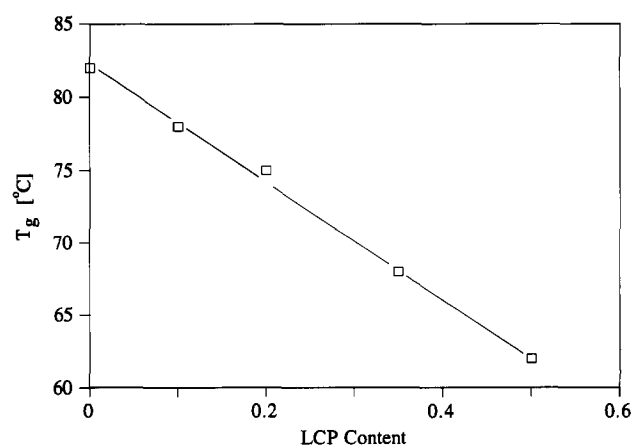
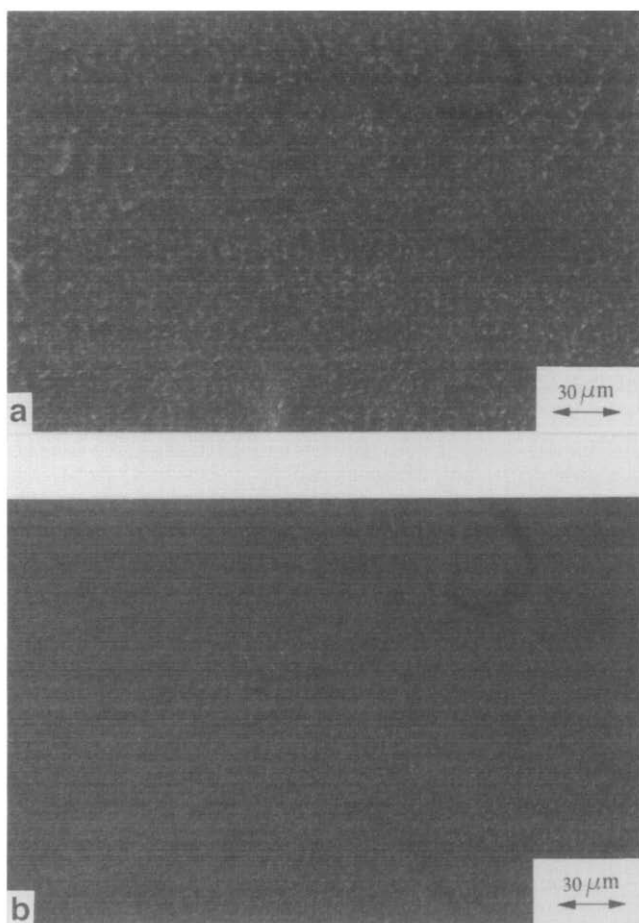


Figure 10 Glass transition temperature of blends versus LCP content.  $T_g$  was taken at the major  $G''$  peak as shown in Figure 9



**Figure 11** Polarizing micrographs of (a) PET and (b) blend of 10 wt% LCP, taken at 220°C after cooling from 280°C at a rate of 5 K min<sup>-1</sup>

*Viscoelastic properties of the blends.* After a temporary preheating to 300°C,  $G'$  and  $G''$  data were taken in the temperature range from 230 to 300°C. Time-temperature superposition applies for PET and its blends with up to 35 wt% LCP in the molten state and the supercooled molten state. The master curves shown in *Figure 13* were obtained without any vertical shifting. The temperature shifting factor  $a_T$  decreases as the LCP content increases (*Figure 14*). It is interesting to note that the master curves of the blends have the same shape over a wide range of LCP content, 2–35 wt%, and hence single  $G'$  and  $G''$  master curves can be obtained by applying a composition shifting factor  $a_C$  along the frequency axis (*Figure 13b*). However, the  $G'$  and  $G''$  master curves of the blends cannot be superimposed on those of the pure PET owing to their difference in shape. This phenomenon implies that the addition of small amounts of LCP already changes the relaxation-time spectrum of PET in a fundamental way.

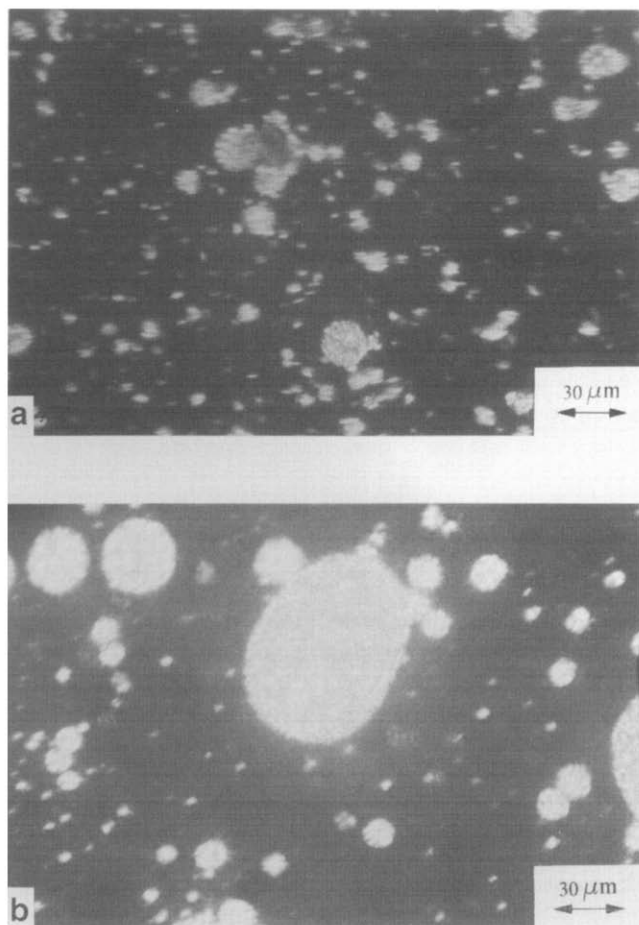
Addition of a small quantity of LCP causes a significant decrease in the melt viscosity of PET. For instance, 2 wt% LCP reduces the viscosity by about 60%. The complex viscosity decreases exponentially (straight line in semi-logarithmic plot) with the LCP content over the range 2–35 wt%. Beyond 50 wt%, the further addition of LCP has little effect (*Figure 15*). The  $G'$  and  $G''$  data can be replotted in the form of the complex viscosity (see *Figure 16*). This shows that the addition of LCP not only lowers the viscosity, but also broadens the zero-shear viscosity regime.

*Effect of PET molar mass.* A small amount (2 wt%) of the same LCP has been blended with two other PETs of different molar masses. For an injection-moulding grade of PET that has a 38% lower molar mass, the blend with 2 wt% of LCP has practically the same melt viscosity as the neat PET (*Figure 17a*). The other PET has a 30% higher molar mass; addition of 2 wt% of LCP reduces its melt viscosity by about 75% (*Figure 17b*). The reduction of melt viscosity was found to be most effective for PET of high molar mass.

## DISCUSSION

### *Biphasic structure of pure LCP*

Polarizing microscopy shows that the pure LCP is not uniform but forms a morphology with two distinct phases, both of them being liquid-crystalline. Biphasic structures have often been observed for thermotropic LCPs that contain flexible sequences as a disordering component. For instance, the first known thermotropic LCPs, a series of copolyesters whose backbone chains consisted of linear PET and *p*-hydroxybenzoic acid residue<sup>21</sup>, form biphasic structures over wide ranges of composition and of temperature<sup>22</sup>. The origin of phase separation for these LCPs is their irregular comonomer distribution<sup>22</sup>. This effect may also account for phase separation in our LCP. Since the dispersed domains have a higher disordering transition temperature, they are assumed to consist of molecular chains that have more and/or longer mesogen



**Figure 12** Polarizing micrographs of blends of (a) 50 wt% and (b) 65 wt% LCP, taken at 240°C after cooling from 280°C at a rate of 5 K min<sup>-1</sup>

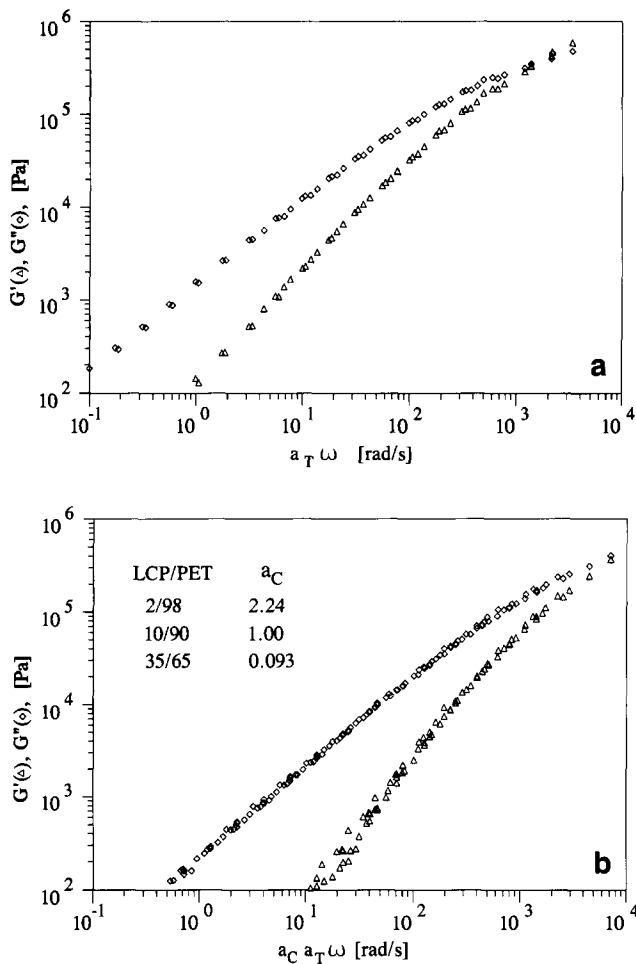


Figure 13 The  $G'$  and  $G''$  master curves of (a) PET and (b) blends at a reference temperature of 300°C, without any vertical shifting.  $a_T$  = temperature shift factor,  $a_C$  = composition shift factor (see table in b)

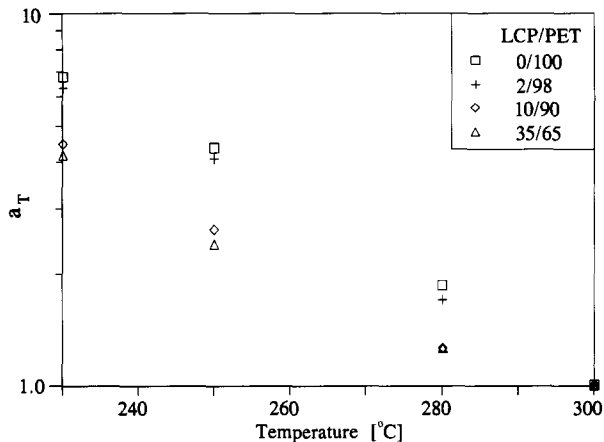


Figure 14 Temperature shift factors applied for Figure 13

sequences. Further studies are needed to confirm this hypothesis. Worthy of note is that the matrix phase, which contains fewer and/or shorter mesogen sequences, also has a nematic state. This implies that our LCP has a relatively narrow distribution of comonomer sequences. For most other biphasic LCPs, only the mesogen-rich phase is able to reach a liquid-crystalline state.

The rheological behaviour of LCP is essentially dominated by the phase state of the matrix phase. Shear thinning, one of the most typical phenomena of nematic

melts, is observed only when the matrix is in the nematic state.

Miscibility

The molten blends with 35 wt% LCP or less exhibit isotropic single-phase structure under the polarizing microscope, and a single crystallization temperature in rheological measurements. This indicates a good miscibility of our LCP in the PET in the molten state. The shifting of crystallization temperature with varying LCP content can also be attributed to the good miscibility, since macroscopic mixing of an immiscible polymer pair would not be able to change the phase transition temperatures of the individual components. In the present case, a small quantity of LCP leads to higher crystallization temperature and finer crystals, implying that LCP may nucleate the PET crystallization. However, since addition of LCP reduces PET concentration, the crystallization temperature does not increase monotonically with LCP content, but shows a maximum with about 10 wt% LCP.

Glass transition provides another test for the miscibility of the non-crystallized fraction of a blend. For a miscible blend, a single new  $T_g$  appears between those of the pure components. A simple empirical equation of

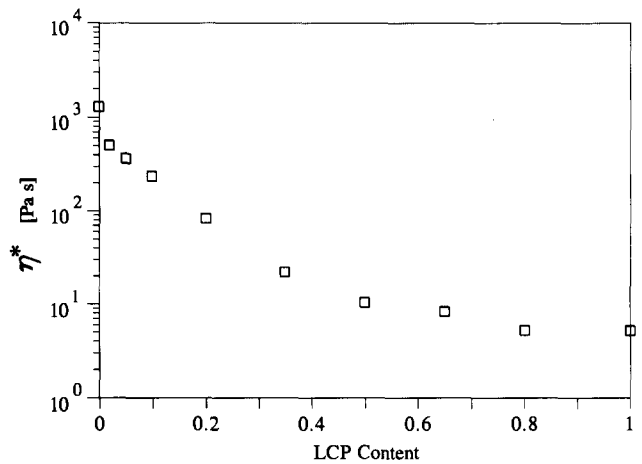


Figure 15 Complex viscosity of blends versus LCP content, measured at 300°C and 10 rad s<sup>-1</sup>

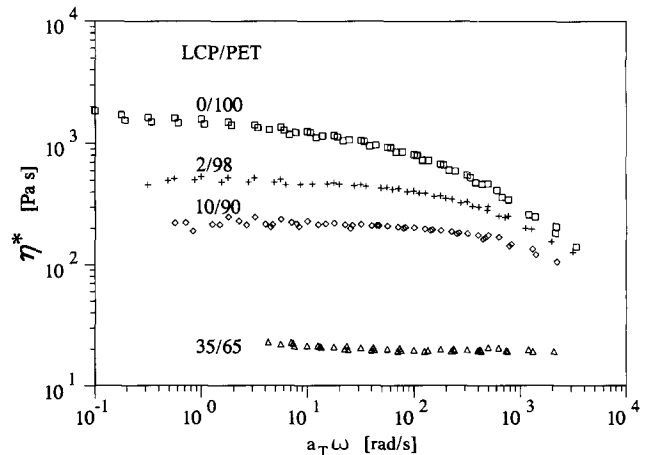
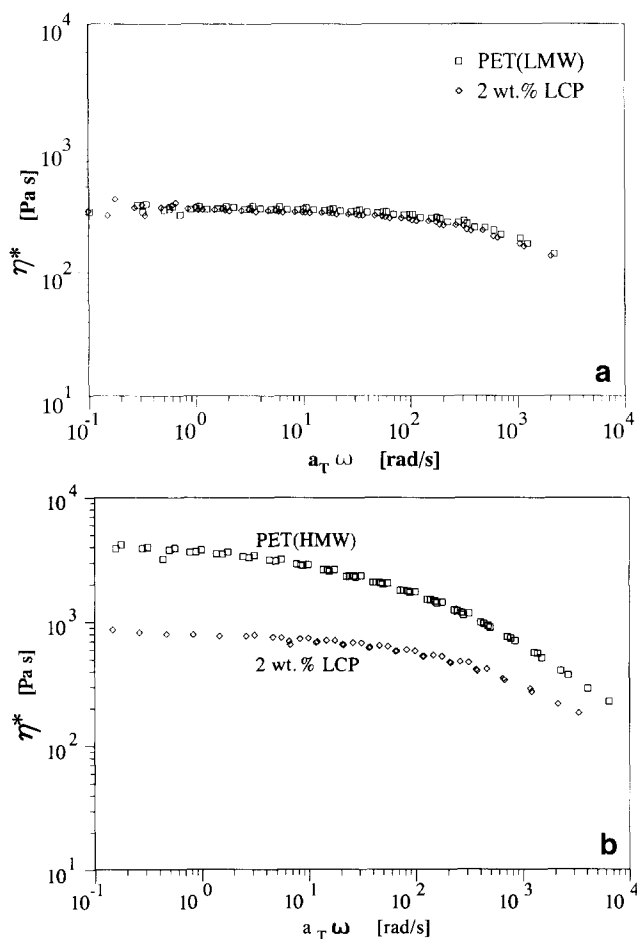


Figure 16 Dependence of complex viscosity on frequency at 300°C. Data points were taken from Figure 13



**Figure 17** Dependence of complex viscosity on frequency at 300°C for: (a) injection-moulding grade of PET (low molar mass) and the blend with 2 wt% of LCP; (b) high-molar-mass PET and the blend with 2 wt% of LCP

Fox<sup>23</sup>:

$$1/T_g = w_a/T_{ga} + w_b/T_{gb}$$

is widely used to predict the blend  $T_g$ , where  $w_i$  and  $T_{gi}$  are the weight fraction and the glass transition temperature (in kelvins) of the  $i$ th component. In the present case, the observed linear interpolation of  $T_g$  versus the LCP content (Figure 10) is very close to the Fox equation with a maximum deviation less than 1 K, if we use  $T_{gPET} = 82^\circ\text{C}$  and  $T_{gLCP} = 42^\circ\text{C}$ . This is further evidence for the good miscibility of 35 wt% or less LCP in PET.

Phase separation takes place when the LCP content exceeds a value between 35 and 50 wt%. The isotropic-nematic transition temperature and the glass transition temperature of the LCP phase in the blends are identical with those of the pure LCP. This lets us conclude that the LCP is well phase-separated or, if some mixing occurs, that the concentration of PET in the LCP phase has to be very low.

#### Effect of LCP on PET melt viscosity

Addition of small quantities of LCP dramatically reduces the melt viscosity of PET. The literature shows most commonly that, when a thermoplastic polymer, such as polycarbonate<sup>1,2,5</sup>, polystyrene<sup>2</sup>, PET<sup>2</sup>, chlorinated poly(vinyl chloride)<sup>3</sup>, nylon-6<sup>4</sup> and polyamide<sup>6</sup>, is blended with 20 wt% of a thermotropic liquid-crystalline polymer, the melt viscosity is reduced by 50–70%. In the present case, addition of only 2 wt% of the studied LCP

produces a similar effect, and the effect is most pronounced for PET with the highest molar mass.

The origin of the observed phenomenon is not yet understood. In some other cases, the reduction of melt viscosity of polymer blends containing an LCP is attributed to phase separation and interfacial flow<sup>4,7</sup>. However, this does not account for the present experimental observations owing to the absence of phase separation at low LCP contents. One hypothesis we made and try to prove by further studies is that the rigid LCP molecular chains might reduce the density of molecular entanglements of PET chains.

## CONCLUSIONS

The newly synthesized LCP by itself has biphasic structure where both phases can become nematic but have different isotropic transition temperatures. This LCP has a good miscibility with PET when the LCP content is at 35 wt% or below. The miscible blends are isotropic and single-phased, without showing any nematic characteristics. The good miscibility between LCP and PET may have a potential for developing molecular composites. On the other hand, the addition of very small quantities of LCP changes the shape of the relaxation-time spectrum of PET and it dramatically reduces the melt viscosity.

## ACKNOWLEDGEMENT

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