Fracture Toughness and Morphology of Phenolphthalein Poly(ether sulfone)-Thermotropic Liquid Crystalline Polymer Blends

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SYNOPSIS

Blends of a new phenolphthalein poly(ether sulfone) (PES-C) and a thermotropic liquid crystalline polymer (LCP) were prepared by melt-blending in a twin-screw extruder. Rheological properties, fracture toughness, K_{IC}, and morphology of the blends were studied. It was found that the addition of LCP could reduce the melting viscosity and improve the fracture toughness of the PES-C matrix. The morphology of the LCP phase for the fractured section changed with increasing LCP content in the blend from dropletlike to fibrillar and layered structure. Strong interfacial adhesion could be observed at a lower content of LCP. The toughening mechanisms by blending LCP were also discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends containing a thermotropic liquid crystalline polymer (LCP) have received considerable attention in the past decade.[1-12] Because of its lower viscosity, the LCP phase in these blends forms fibers in the thermoplastic polymer matrix, leading to the formation of the so-called self-reinforced or *in situ* composites. Many researchers have found that the discrete LCP phase in the blends functions both as a processing aid and as a solid-state reinforcement even when the content of LCP is lower.[4-8] The size, shape, and distribution of the LCP domains in the polymer matrix depend on the viscosity ratio of the two components, the LCP content, and processing conditions. The interfacial adhesion between the two phases, similar to the particulate-filled or fiber-reinforced polymer composites, is of great importance in the reinforcing effect.[1-3,7,9] However, these articles have been focused mainly on the rheology, morphology, and reinforcement of general mechanical properties such as tensile or flexural strength, modulus, and elongation at break. Another important parameter, toughness, and the toughening effect by blending LCP, has seldom been considered.

Linear elastic fracture mechanics (LEFM), often expressing the results in terms of the stress intensity factor, have been widely used in characterizing the fracture properties for brittle polymers.[13] It was found that the lower content of the LCP phase can also improve fracture toughness of epoxy resins.[5] Reasonable toughness can also be obtained even with weak interfacial adhesion because such LCP fibers tend to be mechanically gripped by the matrix, thereby negating the need for strong adhesions.[9]

Phenolphthalein poly(ether sulfone) (PES-C) is a novel high-performance thermoplastic polymer developed in this Institute in 1985.[14] The repeat unit of PES-C is as follows:
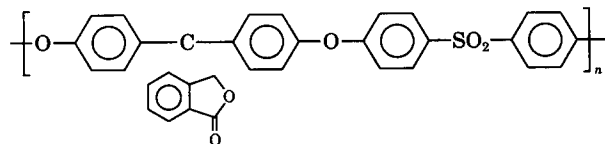
Its glass transition temperature is about 244°C by DSC. It is an amorphous polymer with excellent mechanical properties and exceptional thermal-resistance properties. Its flexural modulus is 2.8 GPa;

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tensile strength, 100 MPa; and heat-distortion temperature, about 220°C. However, its processing temperature region is limited to the range of 340–360°C. Below this range, it is impossible to process due to its extremely high viscosity. On the other hand, the cross-linking reaction can occur if the processing temperature is higher than 360°C.

Another disadvantage of this material is its brittleness. As a promising structural material, its poor resistance to fracture must be improved for efficient utilization. Hence, investigating its fracture properties and improving its toughness are necessary and meaningful.

Previous work in our laboratory[12] demonstrated the feasibility of adding an LCP to the PES-C in order to improve processability and to form an *in situ* reinforcing phase. Interestingly, a small amount of LCP (2.5%) can improve significantly the mechanical properties of the PES-C matrix. Tensile strength and modulus increase about 5% and the unnotched impact strength increases about 150%. In this work, we studied the fracture toughness and the morphology of the fractured surface of PES-C/LCP blends. The mechanisms of toughening by blending LCP are discussed.

EXPERIMENTAL

The PES-C material used in this study was supplied by Xuzhou Engineering Plastic Co. (China). Its reduced viscosity in chloroform at a temperature of 25°C is 0.45 dL/g. LCP is a copolymer of p-hydroxybenzoic acid with ethylene terephthalate (PHB–PET), which was kindly supplied by Rhone-Poulenc (France) marked as RHODESTER. The temperature range of its liquid crystalline state is within 301–419°C.

Powders of LCP and PES-C were mechanically mixed and then extruded in a SHJ-30 twin-screw extruder (Nanjing Rubber and Plastic Machinery Co., China). Blends were prepared with compositions ranging from 2.5 to 50 wt % of LCP in the PES-C matrix. They will be referred to as PES-C/LCP2.5, PES-C/LCP5, and so on, in which the number indicates the LCP percentage in the blends.

Rheological characteristics of PES-C/LCP blends were studied in a nitrogen atmosphere using a cone-and-plate rheometer, CP-400 (Switzerland). The cone has an angle of 2° and a diameter of 20 mm. The scanning rate of the temperature was 6°C/min. A 10^{-2}–10 S^{-1} shear rate was used.

Test specimens were injection-molded in a JSW-17SA injection-molding machine (Japan) with bar-

rel temperatures of 345–358°C; mold temperature, 80°C; injection pressure, 100–120 MPa; and injection speed, 5–6 g/s. Fracture toughness bars of dimensions 6 × 13 × 63 mm were prepared.

Three-point bend tests, carried out in an Instron 1121 tester, were used to determine the plane strain fracture toughness (abbreviated to fracture toughness), K_{IC}, in accordance with ASTM E399 test procedure at room temperature. A sharp precrack (about 7 mm) was made with a fresh razor. The fracture was carried out under static loading with the initial precrack and crack growth perpendicular to the injection-mold direction. The 5 mm/min crosshead speed and 52 mm span were used.

In the case of LEFM,[13] the fracture energy G_{IC} is directly equivalent to the critical J-integral value J_{IC}, which can be determined in accordance with ASTM E813-81. Thus, the fracture energy G_{IC} defined as the energy criterion for fracture can be evaluated from eq. (1):

$$G_{IC} = 2U_c/B(W - a) \qquad (1)$$

where B, W, and a are the thickness, depth, and precrack length of the sample, respectively. U_c is the energy absorbed appropriate to the onset of crack propagation. Fractured surfaces were sputter-coated with gold to examine the morphology of the blends using a scanning electron microscope (SEM) (Model JAX-840).

RESULTS AND DISCUSSION

Rheological Properties

Figure 1 shows the flow curves of PES-C/LCP blends at 340°C. The LCP used in these studies showed extremely low viscosity; therefore, its flow curve is not given here. As shown in Figure 1, PES-C and its blends exhibited a dramatic non-Newtonian behavior. A pseudo-Newtonian plateau at low shear rates and a non-Newtonian region appearing at high shear rates can be observed. A tendency for shear thinning occurred in both PES-C and PES-C/LCP blends. There is a marked reduction in the viscosity with increasing shear rate or LCP concentration. The influence of the LCP content on the viscosity of the blends is clearly shown in Figure 2. Most remarkable is the reduction of flow viscosity that can be observed at LCP content of less than 10% by weight. Beyond this, only a slight change can be seen.

The reduction in viscosity of blends with LCP has been reported by many researchers[6–11] and at-
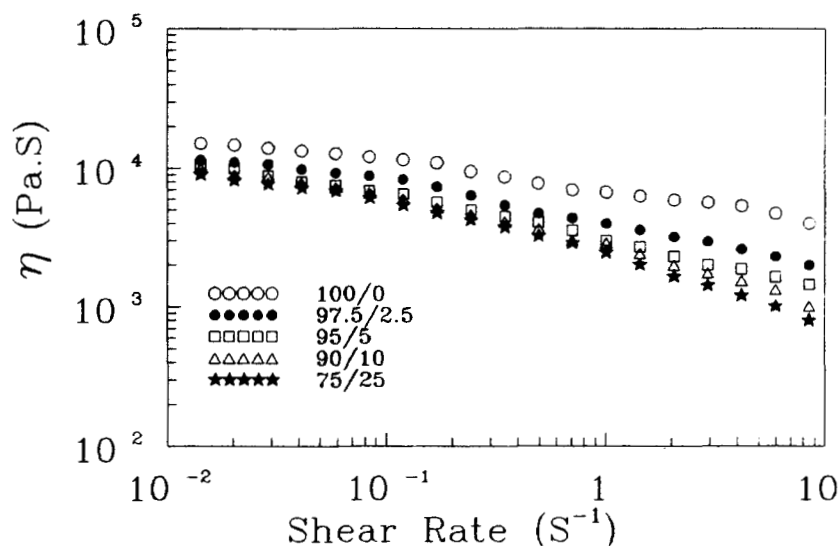
Figure 1 Viscosity vs. shear rate for PES-C/LCP blends at 340°C.

tributed to different reasons, namely: (a) incompatibility between the isotropic thermoplastic polymer and LCP: therefore, lack of adhesion between the two phases; (b) the chains within the polymer blend become stiffer, thus preventing entanglement; and (c) the formation of elongated fibrils in the LCP phase that tend to lubricate the melt and introduce interfacial slippage between the polymers.

The addition of LCP to the PES-C matrix results in a significant reduction in viscosity and therefore leads to improvement in processability. This feature would be reflected in the processing parameters, such as the extruder temperature, torque, melt pressure, and injection pressure. In fact, by addition of a small

amount of LCP, the processing temperature of PES-C can be lowered by about 10–15°C.

Fracture Toughness

Fracture toughness, K_{IC}, defined as the stress intensity factor at crack initiation, was measured at room temperature. According to the ASTM E399 recommendation, the critical load for evaluating a valid K_{IC} value is determined from the load displacement plots by the secant line with a slope of 0.95 times the initial tangent slope. Instead of this procedure, the maximum load is utilized in our cal-
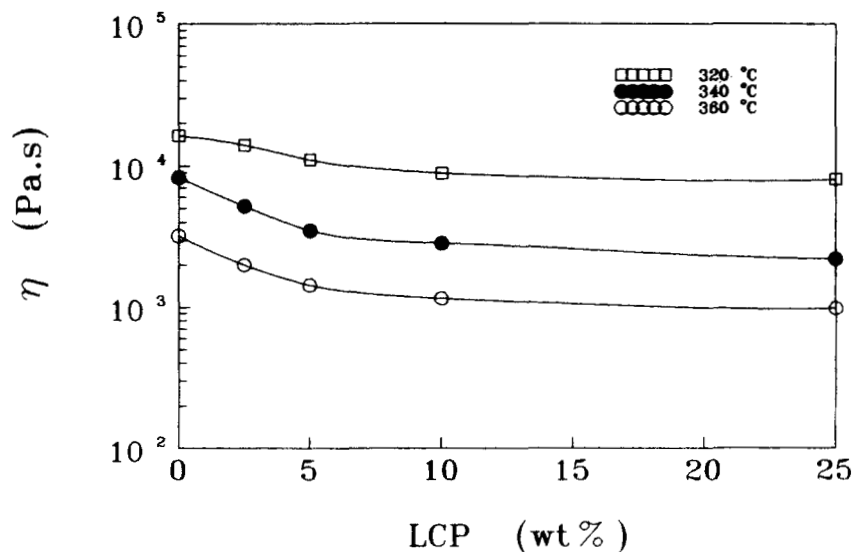

Figure 2 Viscosity of PES-C/LCP blends vs. LCP concentrations at a shear of 1 S^{-1}.
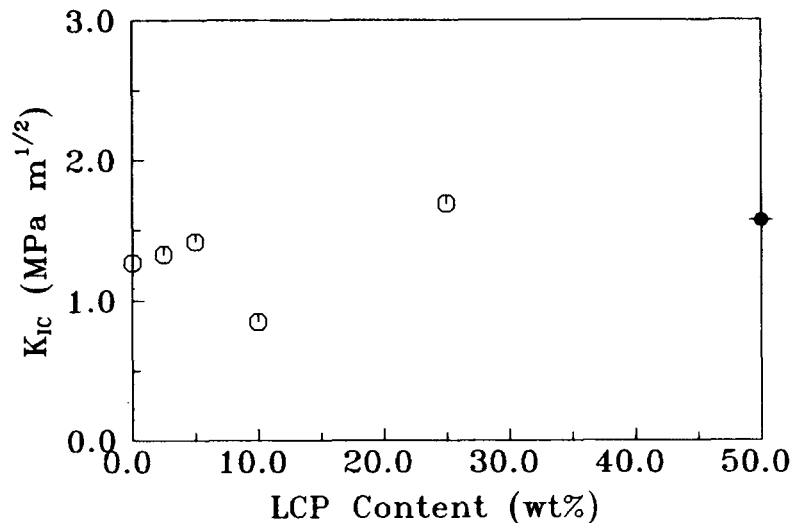
Figure 3 Effect of LCP content on fracture toughness K_{IC} of PES-C/LCP blends at room temperature.

culation because the PES-C and its blends with LCP fractured in a more brittle manner.

The fracture toughness of PES-C/LCP blends are shown in Figure 3. The K_{IC} of the pure PES-C is 1.27 ± 0.09 MPa-m$^{1/2}$. As can be seen from Figure 3, a small content of LCP increases the fracture toughness of the PES-C matrix. This result is similar to that of Ref. 5. The addition of only 5% by weight of LCP to the PES-C matrix increases the fracture toughness by about 10%. As shown later in the SEM micrographs [Fig. 5(a)], this improvement in toughness is without any fiber formation. The fracture toughness exhibits a distinct minimum at an

LCP content of 10%. This unexpected minimum was also observed by Crevecoeur and Groevinck x[11] and was considered to be the result of the difference in ductility between the matrix and the LCP phase. In our opinion, the lower tensile strength, poor adhesion between the two phases, and lack of a high enough aspect ratio of the LCP fibers [as shown in Fig. 5(b)] may cause this unexpected minimum. The blend of PES-C/LCP25 shows the maximum value of K_{IC}. It is noted that the K_{IC} of the blend PES-C/LCP50 can only be considered a qualitative comparison because of the difficulty of making a sharp precrack due to its layered structure.
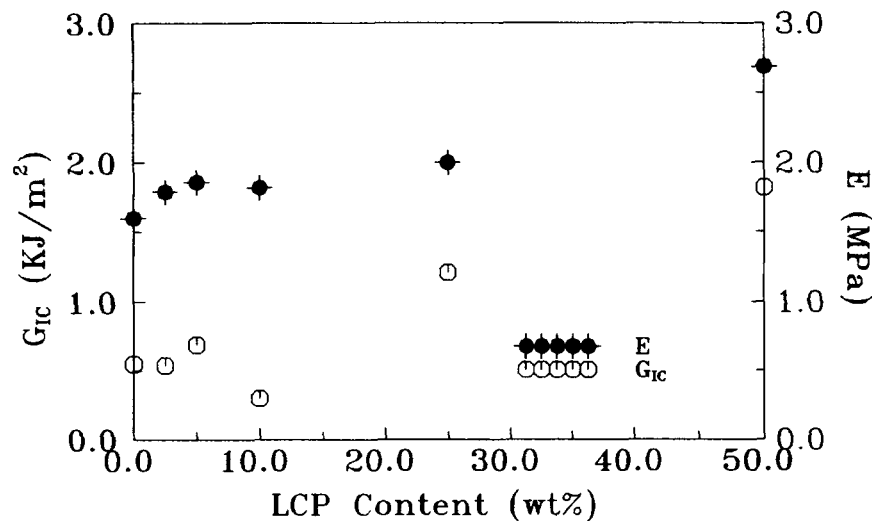

Figure 4 Effect of LCP content on fracture energy G_{IC} and Young's modulus E of PES-C/LCP blends at room temperature.
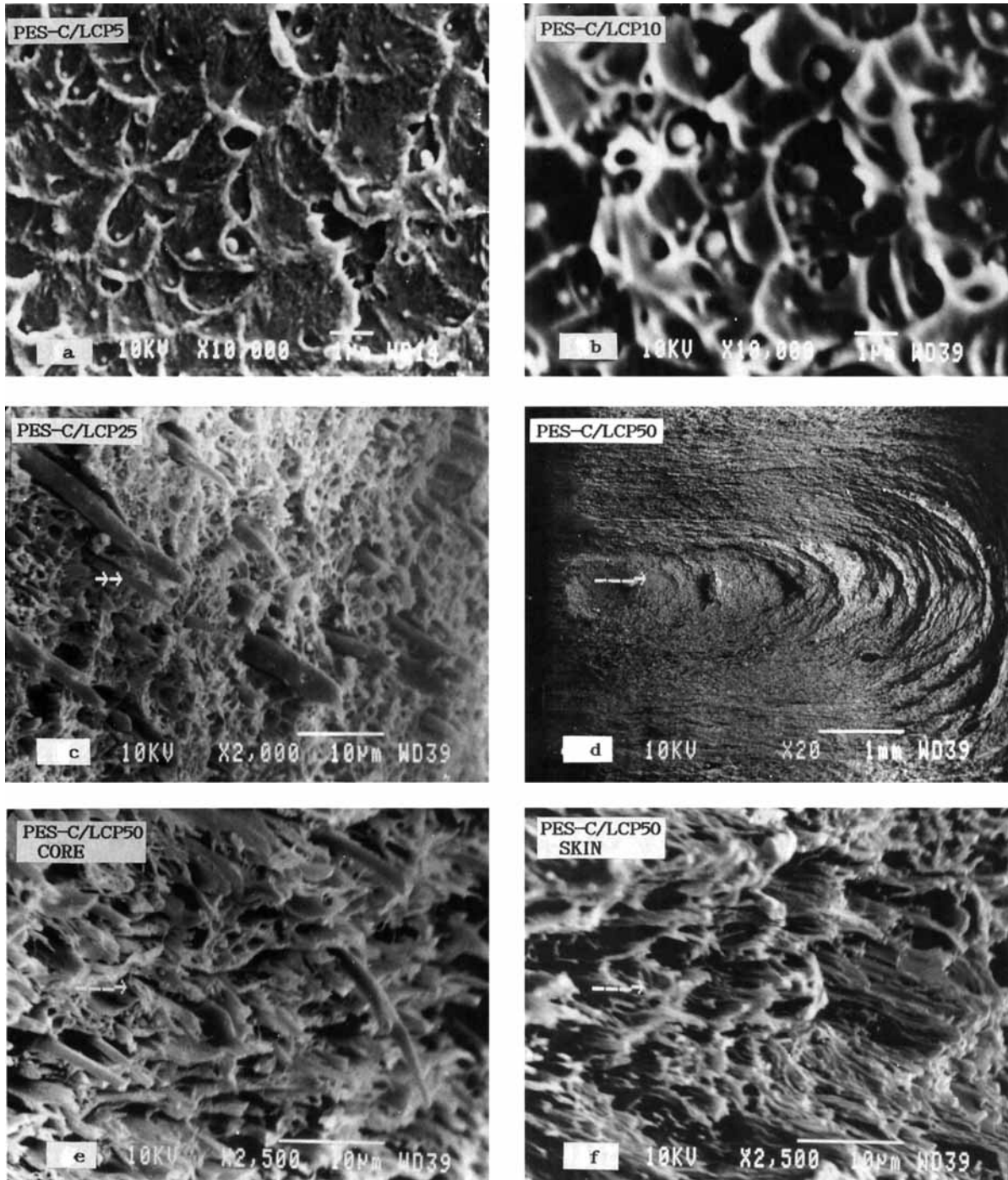
Figure 5   SEM micrographs of PES-C/LCP blends with various LCP contents as indicated; (a), (b), and (d) are micrographs of fractured surface obtained from the transverse direction, and (c), (e), and (f) are the longitudinal direction. The arrow shows the direction of crack propagation.

The effect of the addition of LCP on the fracture energy G_{IC} and Young's modulus E of PES-C are shown in Figure 4. The addition of 5% by weight of LCP to the PES-C matrix increases the fracture en-ergy about 15%. It appears that with increasing LCP content the change in trends of G_{IC} and E are similar to the parameter K_{IC}. This is, of course, in the case of LEFM under plane-strain conditions, because the

load-based toughness K_{IC} combines both the energy-based toughness G_{IC} and the modulus of the material.[13]

Morphological Studies

As many other researchers have reported, blends of LCPs and thermoplastics consist of two phases since the two polymers are generally immiscible. The size, shape, and distribution of the LCP domains in the matrix depend on the LCP content.[1-8]

Figure 5 shows SEM micrographs of fractured surfaces of PES-C/LCP blends tested by the three-point bend method. At a small content of LCP, the dropletlike liquid crystalline domains embedded in the PES-C matrix are revealed by Figure 5(a). It appears that the interfacial adhesion between the two phases is quite strong. The improvement of fracture toughness could be attributed to the strong interfacial adhesion and higher modulus LCP domains dispersed in the matrix.

Some smaller aspect ratio LCP fibers are formed in the matrix at a 10% content of LCP [Fig. 5(b)]. However, poor interfacial adhesion can be observed. As shown in Figure 5(b), holes and open circles around the LCP fibers appear. It is postulated that the unexpectedly lower K_{IC} may correspond to these defects and from not forming a high enough aspect ratio of the LCP fibers.

On the other hand, Figure 5(c) (relative to the 25% content of LCP) clearly shows the higher aspect ratio LCP fibers coming out from the matrix. Different diameter and aspect ratio fibers also can be found. It seems that the PES-C matrix deformation is more ductile here than for the other blends. This can be tentatively explained by these fibers acting as stress concentrators at the crack tip, causing the matrix to deform by means of ductile flow. Local yielding may occur at the crack tip and cause higher fracture energy G_{IC} (as shown in Fig. 4). Moreover, when the stress moving through the matrix reaches the high modulus fiber, it transmits throughout the fiber instantaneously and is thus dispersed over its entire length. The large aspect ratio LCP fibers would produce greater dispersion of the stress beyond the local area at the crack tip and act as crack stoppers. On the other hand, Williams[9] mentioned that reasonable toughness could be obtained due to higher aspect ratio LCP fibers that tended to be mechanically gripped by the matrix, thereby negating the need for strong adhesion. Therefore, higher fracture toughness at a larger content of LCP may be attributed to the higher aspect ratio LCP fibers

that can act as crack stoppers[5] and local yielding of the matrix around these fibers at the crack tip.

For PES-C/LCP50, a layered structure in the thickness direction can be seen from Figure 5(d). Higher aspect ratio LCP fibers can also form in the core region [Fig. 5(e)]. In the skin region [Fig. 5(f)], the PES-C matrix shows a networklike morphology.

Thus, the PES-C/LCP blends consist of two phases: The morphological structure of the LCP phase is composition-dependent and changes gradually from dropletlike particles to fibrillar structure. These observations are similar to those thermoplastics/LCP blends such as PEEK/LCP[2,6] and PA/LCP.[7] It is interesting to note that the reinforcement in toughness of the thermoplastics/LCP blends is similar to the rigid particulate-filled polymers at a lower content of LCP and short fiber-reinforced composites at higher LCP content. In general, for these composites,[13,15] good particle/matrix adhesion or high enough aspect ratio fibers are needed for improving the strength and toughness of polymers. As shown in our results and Ref. 5 and 9, strong interfacial adhesion at lower contents of LCP or a high enough aspect ratio of LCP fibers at higher content are necessary for toughening the polymer matrix.

The above results suggest that a small content of LCP can improve toughness of the polymer matrix together with improving mechanical and rheological properties. It is well known that improved toughness, as well as strength or modulus, of a polymer can be obtained by adding particulate fillers and/or short fibers owing to the mechanisms of multiple deformation and reinforcing agents.[13,15] But addition of these additives results in an increase of melt viscosity and abrasion of screws and barrels. These shortcomings could be overcome if the reinforcement were developed *in situ* during processing. Therefore, since processing is eased and toughness, strength, or modulus is improved by blending in a low content of LCP, this molecular composite can be considered as a promising engineering material.

CONCLUSIONS

The PHB-PET thermotropic liquid crystalline polymer (LCP) can be used as toughening agent as well as reinforcement for a PES-C matrix. The addition of a small amount of LCP to the PES-C matrix results in a significant increase in fracture toughness and a reduction in flow viscosity.

PES-C/LCP blends containing up to 50% LCP are multiphase systems. The morphology of the LCP domains in the blends changes from dropletlike to a fibrillar and layered structure with increasing LCP content. Strong interfacial adhesion at lower contents of LCP or a high enough aspect ratio of LCP fibers at higher content are necessary for toughening the polymer matrix.

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