

Blends of Thermotropic Polyester with Poly(phenylene Oxide)

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SYNOPSIS

A thermotropic liquid crystalline polymer (LCP) based on wholly aromatic copolyesters based on hydroxynaphthoic and hydroxybenzoic acid was melt-blended with a thermoplastic poly(phenylene oxide) by corotating twin screw extruder. Rheological properties, temperature transitions, dynamic and mechanical properties, and electron microscopy study have been performed. Rheological study indicated significant viscosity reductions with increasing LCP content leading to ease of processing. From the differential scanning calorimeter (DSC) and dynamic mechanical thermal analyzer results, these blends showed incompatibility for the whole range of concentrations. Mechanical properties were found to be slightly improved at low LCP and dramatically improved at above 50% LCP contents. In addition, impact strength was significantly increased up to two times after adding 10% LCP into the matrix. The morphology of blends was affected by composition. Droplets and stubby fibrils structures caused lower tensile strength, whereas fibrillar structure improved this property.

INTRODUCTION

One of the outstanding tools utilized by polymer scientists and engineers to modify and improve the properties of one or more components is the so-called "polyblend." These approaches have been used as the main methods to prepare the better cost-effective plastics having the desired physical properties. Most polyblends consist of immiscible polymers resulted in multiphase systems. The properties of polymer blends are determined by the amount and properties of the individual polymeric components as well as the mode of the dispersion, size, and shape of the dispersed material, and interaction between phases. Moreover, the mode of blending used for preparation greatly affects morphology of the blends.

An important and general method used nowadays is the addition of fibrous fillers (the most popular being used chopped glass fiber) to a polymer, in order to improve mechanical properties. Glass is rather inexpensive; however, processing and fabrication of

chopped glass composites present some technical difficulties. Wear, owing to abrasion on screw and barrel wall of processing machineries, usually occurs during processing. Viscosity increase of the molten polymer and difficulties in compounding are other consequences.

For these reasons, it would be important to find another approach in which the reinforcing species is not actually present before processing. (However, the reinforcing fiber should be developed during processing.) The self-formation of the reinforcing species has led to the term "self-reinforced composite." Blending of liquid crystalline polymers (LCPs) with less expensive thermoplastics offers the full advantage of using many of the LCP's desirable characteristics with a reduced material cost. Therefore, the growing interest in LCP blends has recently developed. A large number of works have been reported to improve properties in which a LCP phase acts as a processing aid and a self-reinforcing material. The LCP phase at the elevated temperature may present anisotropic phase having low melt viscosity.¹⁻⁵ The LCP phase may be deformed and oriented such that the solidified composite contains a fibrillar LCP phase during processing. The blend-

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ing morphology and properties of such composites are in many respects similar to the conventional glass fiber-filled composites.

Our research is directed toward the investigation of an appropriate and less expensive thermotropic-thermoplastic blending system capable of yielding improvement of mechanical and rheological properties. The present work reports results on the LCP/poly(phenylene oxide) (PPO) blends. The rheological, thermal, and mechanical properties of the blends at various compositions will be illustrated. Furthermore, the explanation of the effects of processing conditions and compositions on the properties related to morphology will be discussed.

EXPERIMENTAL

Materials and Method of Investigation

The thermotropic liquid crystalline polymer used in this study was Vectra A950 supplied by Hoechst Celanese Co. This polymer consists of 25–27 mol % of 2,6-hydroxynaphthoic acid and 75–73 mol % of *p*-hydroxybenzoic acid. Poly(phenylene oxide) 646 supplied by G.E. Plastics was used as the thermoplastic polymer. The pellets of all materials were vacuum dried at 110°C overnight.

All blends were prepared by corotating twin screw extruder ZSK-30 (Werner & Pfleiderer Corp.) with compositions ranging from 2.5 to 90 wt % of LCP in PPO. They will be referred to as 2.5LCP/97.5PPO, 5LCP/95PPO, and so on.

Rheological measurements under shear flow were carried out using Instron Capillary Rheometer. The capillary diameter (D) is 0.00157 m and length to diameter ratio (L/D) is 28.7. The experiments were done at 310°C under shear rate range of 1–10³ s⁻¹.

Blending mixtures were molded using a reciprocating screw injection molding machine (Boy 15 S) with a clamping force of 150 kN and maximum shot size of 3.6 × 10⁻⁵ m³. In general, the injection-molded small tensile bars and impact strips were prepared at a barrel wall temperature of 310°C, mold temperature of 150°C, volumetric flow rate of 4.48 × 10⁻⁵ m³/s, whereas the pure PPO, 2.5LCP/97.5PPO, and 5LCP/95PPO samples were molded at 330°C.

Transition temperatures of blends and homopolymers have been evaluated by the differential scanning calorimeter (DSC DuPont 9900). The temperature range investigated was 25–350°C at a scanning rate of 20°C/min. All data were obtained from the second reheating scans.

A dynamic mechanical thermal analyzer (DMTA) from Polymer Laboratories was employed in flexural mode to investigate the dynamic properties and the transition temperatures in blends. A heating rate of 2°C/min at a frequency of 1 Hz in the temperature range of 35–300°C was used. Measurements were performed by using the middle part of small tensile bars (3.10 × 1.5 × 14 mm). Frame and clamp used were N and C type, respectively.

Monsanto Tensiometer (T-10) was used to measure tensile properties at the speed of 5 mm/min and gage length of 10 mm. Izod notched impact was evaluated by means of Impact Tester (Testing Machines Inc.).

The morphology of the blends was analyzed with the aid of a scanning electron microscope (SEM) (Model SX-40, International Scientific Instruments, Inc.). The study was done after fracturing the small tensile bars in liquid nitrogen. Morphology of the LCP in the blends was also studied by etching the PPO matrix with benzene for 50LCP/50PPO samples.

RESULTS AND DISCUSSION

Rheological Properties

The flow curves at 310°C of the LCP, LCP/PPO blends, and PPO are shown in Figure 1. The coverage of viscosity data range is 3 decades of shear rates from 1 to 10³ s⁻¹. All the melts in the studied range of shear rates exhibited a non-Newtonian flow behavior. It should be noted that the large difference in rheological behavior occurs at the higher shear rates. The dependence of viscosity on the shear rate is much steeper for LCP and blends containing large

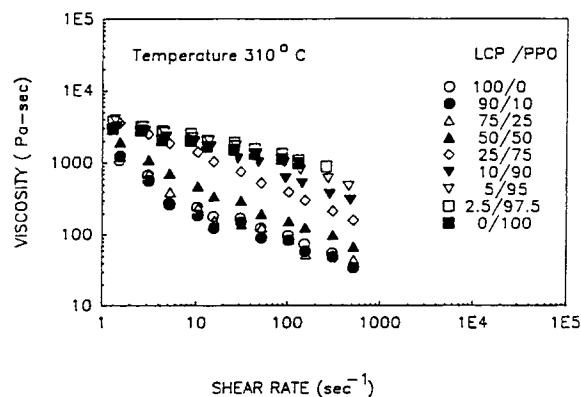


Figure 1 Viscosity as a function of shear rate for LCP-PPO blends at different composition obtained using a capillary rheometer.

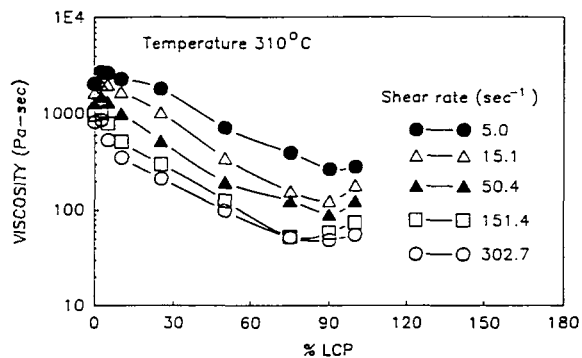


Figure 2 Composition dependence of the viscosity of LCP/PPO blends as a function of shear rate.

amount of LCP than for PPO and low amount of LCP in PPO blends. Viscosity of LCP and most of its blends is lower than that of PPO. This behavior means that the addition of LCP into the PPO aids the processing performance by lowering torque, die head pressure, injection pressure, and so on, particularly at high shear rates.

It can also be observed from Figure 1 that there is no intersection between the PPO and LCP flow curves under the shear rate range and temperature studied. Tsebrenko,⁶ who studied blends of flexible

thermoplastics, suggested that there was a maximum fibrillation occurring during flowing at shear rate corresponding to the intersection point, where the viscosity ratio of the original components was approximately equal to unity. However, in some engineering thermoplastics and LCP systems, for example, PC-LCP^{1,7} and PEI-LCP,⁸ the maximum fibrillation was observed to take place at high shear rates where the viscosity of the thermoplastics is much higher than that of the LCP.

The most dramatic presentation of the data is the viscosity at constant shear rates or stress as a function of the LCP concentration. Figure 2 describes such a presentation at various constant shear rates. The plots at constant shear stresses are similar in nature. The viscosity attains a minimum at about 90% LCP concentration. At this concentration the viscosity of the blend is about 16 times lower than that of PPO.

Thermal Properties

The results of the DSC thermograms of neat polymers and blends are shown in Figure 3. The glass transition temperatures of PPO and LCP are at the temperature of 213 and 100°C, respectively. The

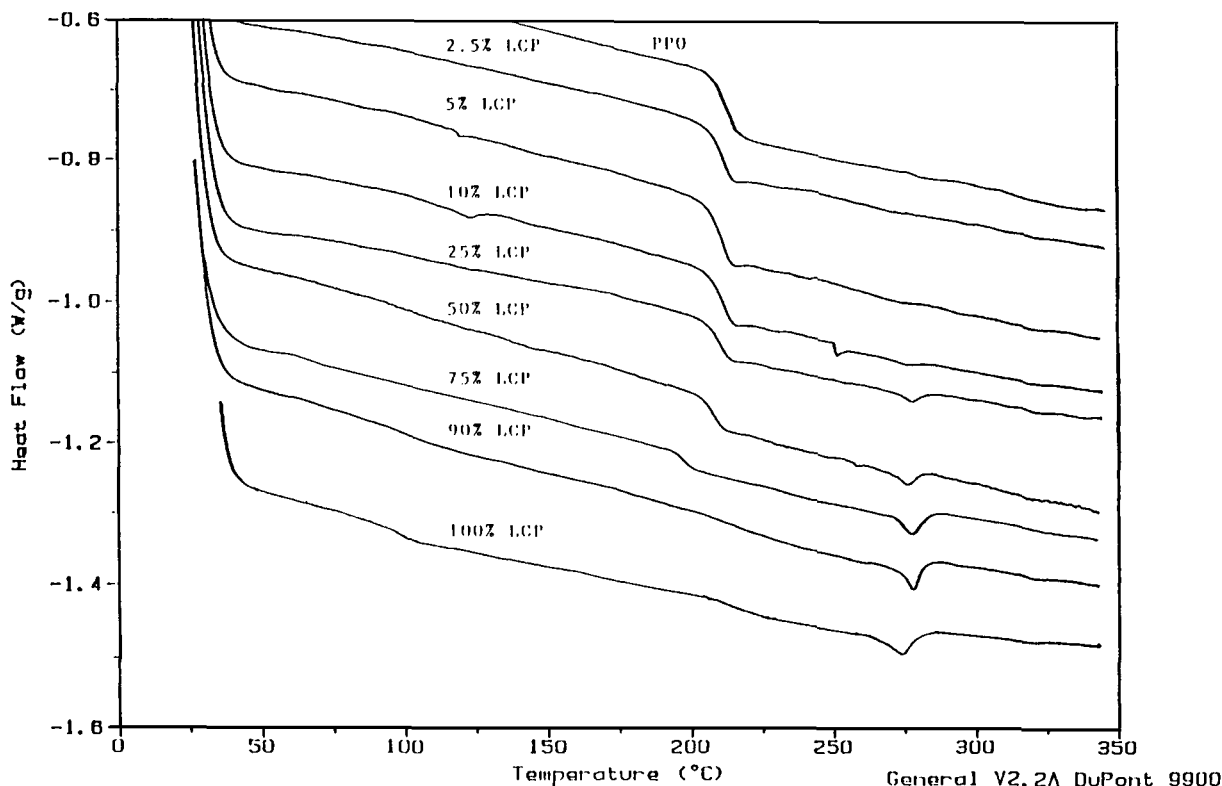


Figure 3 Heat flow as a function of temperature obtained using DSC.

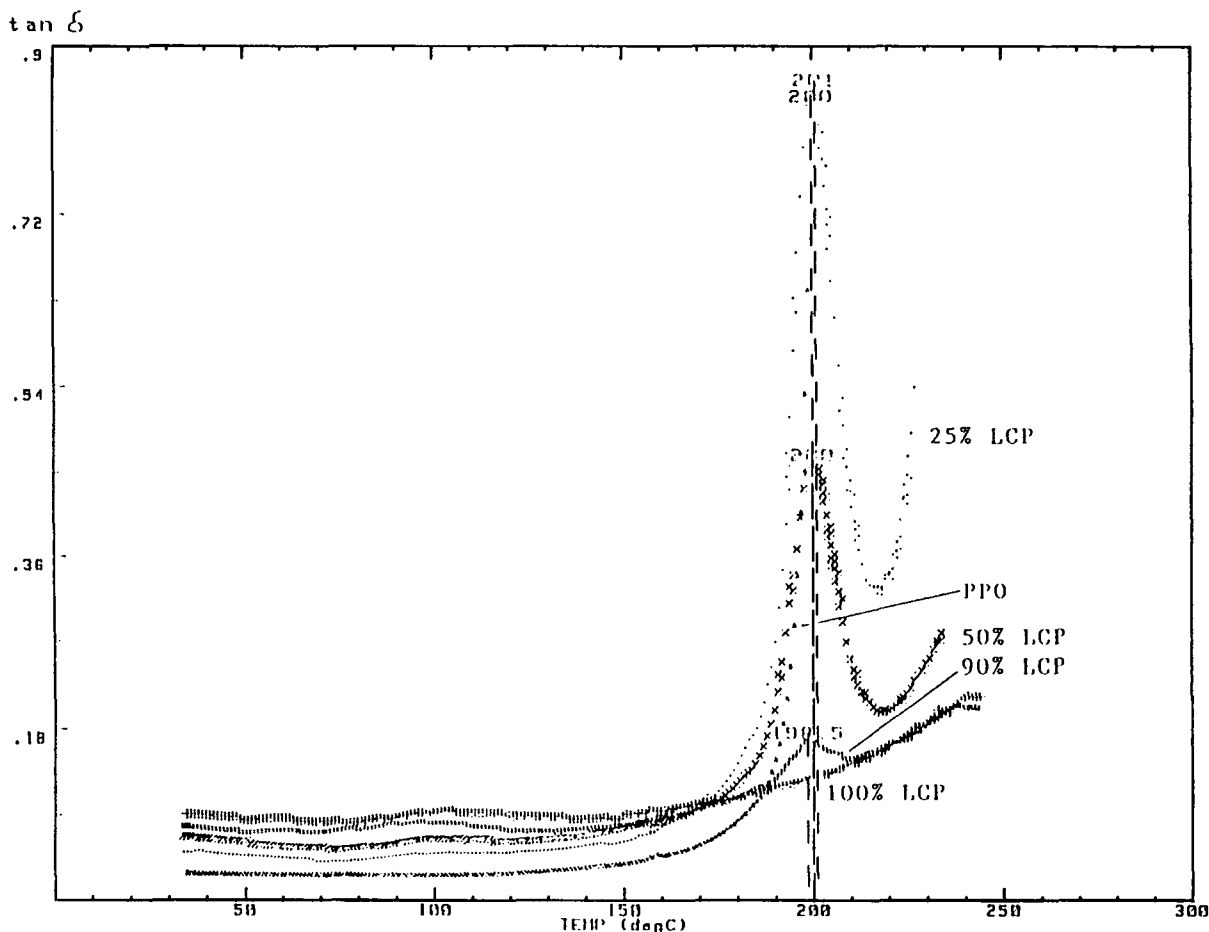


Figure 4 Tan δ as a function of temperature obtained using DMTA.

crystalline to nematic transition for the LCP is about 275°C. This transition temperature of LCP remains almost at the same temperature as for the blends. T_g 's of LCP and PPO are slightly composition dependent; however, it is not clear that this is caused by some miscibility or by phase size.

Tan δ as a function of temperature obtained by means of DMTA is shown in Figure 4. What is evident right away is the presence of two glass transition temperatures indicating that these blends are incompatible. T_g 's of LCP and PPO are 100 and 201°C, respectively. It is evident that T_g of LCP is broad, whereas T_g of PPO is sharp. These positions of T_g 's for PPO component in blends are different from those of DSC results. These might be due to the difference in heating rates used in DSC (20°C/min) and DMTA (2°C/min) experiments.

Mechanical Properties

Dependencies of storage modulus E' of LCP/PPO blends versus concentration of LCP are shown in

Figure 5. Tensile properties of PPO, LCP, and their blends have been determined on injection molded specimens. The secant modulus at 1% strain as a function of LCP content is reported in Figure 6. Samples in both experiments were small tensile bars.

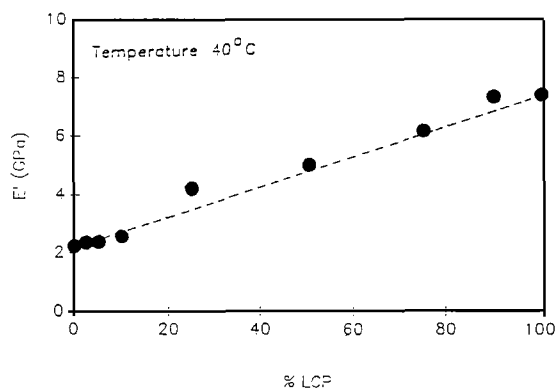


Figure 5 Storage modulus (E') as a function of LCP composition obtained using DMTA. Discontinuous line is drawn according to rules of mixtures.

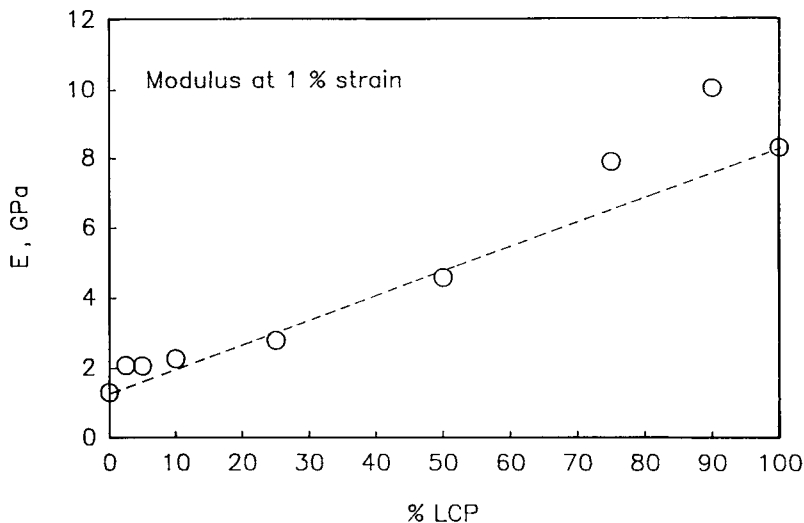


Figure 6 Modulus as a function of LCP composition for PPO-LCP blends obtained using a tensile machine. Discontinuous line is drawn according to rules of mixtures.

The secant modulus, see Figure 6, first slightly increases with increasing LCP content and then stays at a plateau and sharply increases again above 50% LCP contents. The results from storage modulus (Fig. 5) show almost the same tendency, even though both experiments were measured by different modes. The calculated values illustrated in Figures 5 and 6 by discontinuous lines were obtained according to simple composite theory based on the rule of mixture.⁹ It is important to note that most moduli lie above those obtained from the composite theory, especially secant modulus results.

Although LCP is added to PPO, yield stress increases (Fig. 7). For 5% LCP blend, the improve-

ment of yield stress is up to 10%. Figure 8 shows tensile strength as a function of composition for PPO-LCP blends. Elongation at break as a function of composition can also be seen in Figure 9. It is interesting to note that tensile strength of 2.5% LCP blend lies slightly above pure homopolymer PPO. It implies that LCP serves as reinforcing additive in PPO. Beyond 2.5% LCP content, tensile strength begins to fall down and dramatically increase again above 50% LCP concentration. It should also be observed that the modulus and tensile strength of 90% LCP blend lie above those of pure LCP. Increase in modulus and strength is accomplished by the dramatical drop of elongation at break even after adding

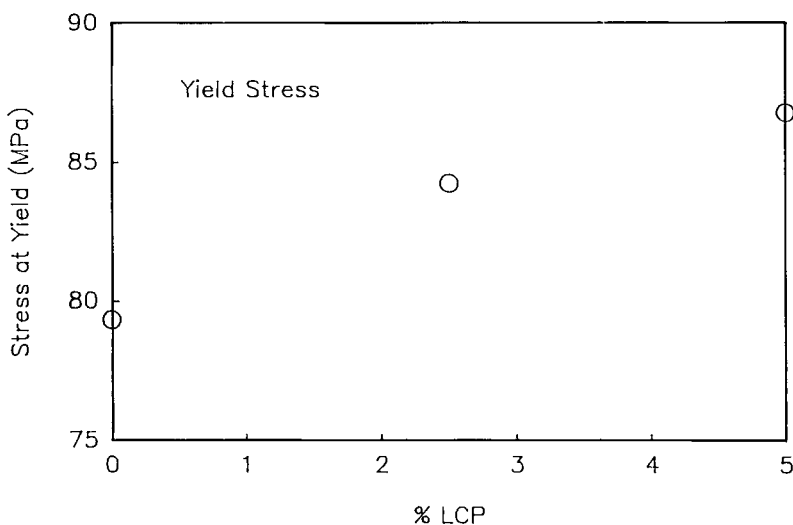


Figure 7 Stress at yield as a function of composition for PPO-LCP blends obtained using a tensile machine.

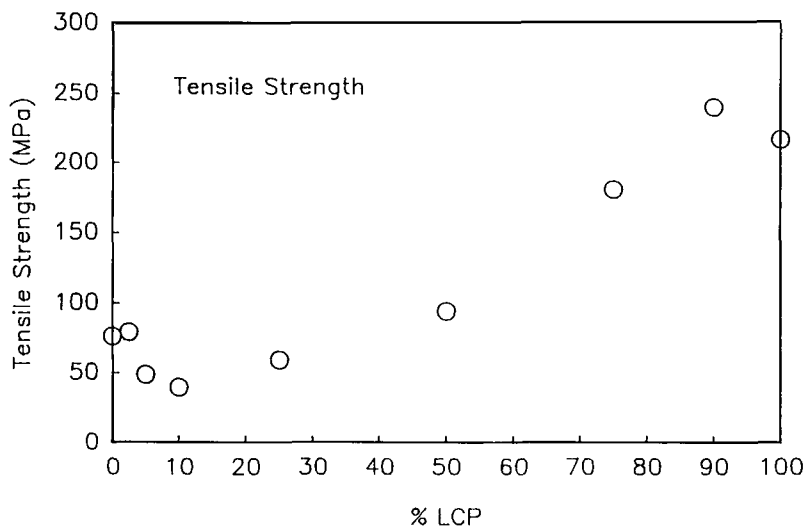


Figure 8 Tensile strength as a function of composition for PPO-LCP blends obtained using a tensile machine.

a small amount of LCP (2.5–5% LCP). The low elongation at break corresponding to high tensile strength and modulus (above 50% LCP content) are typical for fiber-reinforced composites.

The notched Izod impact strength as a function of the LCP content is reported in Figure 10. It can be observed that the impact strength increases at small LCP concentrations, levels off at 25 and 50% LCP, and then suddenly increases at higher concentrations. Figure 11 shows a higher magnification scale plotting of impact strength versus LCP concentrations up to 10%. It can be seen that the impact strength improves about two times at 10% LCP.

Morphological Studies

Finally, morphological studies has been done via scanning electron microscope. Fracture surfaces of samples broken in liquid nitrogen have been investigated. The main purpose of this investigation is to detect the formation of LCP fibers in the PPO matrix and consequently to relate the structure-mechanical property relationships.

The skin surfaces of LCP/PPO blends are shown in Figure 12. At the concentration of 2.5% LCP, the picture [Fig. 12(a)] reveals fibrillar structures of LCP domain embedded in the PPO matrix. These

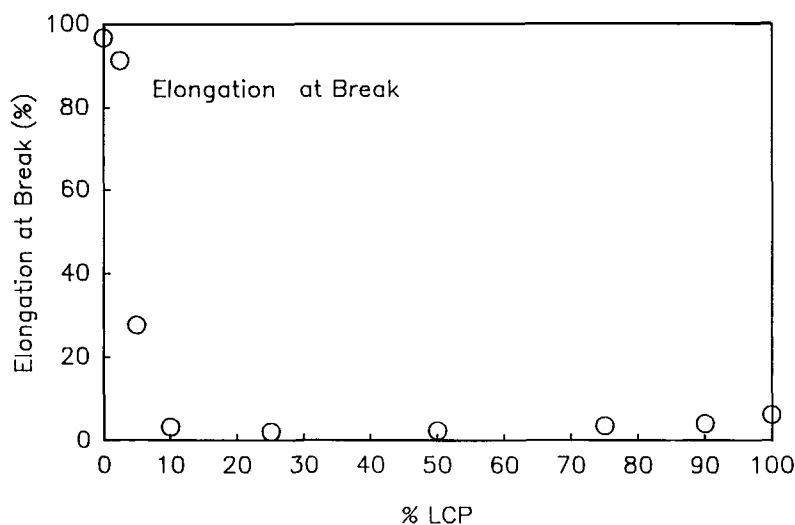


Figure 9 Elongation at break as a function of composition for PPO-LCP blends obtained using a tensile machine.

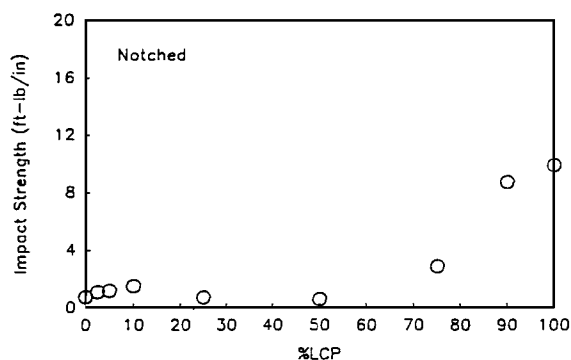


Figure 10 Impact strength as a function of LCP composition for PPO-LCP blends obtained using an Izod impact tester.

domains are a few microns in diameter. They appear to be distributed unevenly in PPO matrix. Most of the fibrils are still adhered to the matrix and no major pullout has taken place. The detachment of the LCP fibrils during deformation is believed to be responsible for the moderate improvement of properties at the low 2.5% LCP concentration.

At concentration of 5% LCP, a smaller size of fibers (about 1.5 μm) are formed in the PPO matrix [Fig. 12(b)]. Furthermore, the bad adhesion between fiber and matrix takes place as observed by holes and open circles around fibers, i.e., there is a major pullout of fibers occurring. This may be responsible for lower tensile properties.

The skin morphology of the 10LCP/90PPO blend includes both stubby fibrils and ellipsoidal droplets [see Fig. 12(c)]. These structures having size around 2 μm . These structures may cause a lower value in tensile properties.

The skin surface of a 50LCP/50PPO blend reveals larger and longer rodlike or fibrillar structures [see Fig. 12(d)]. These LCP structures seem to be heavily coated with the PPO matrix. The etched surface of the 50LCP/50PPO blend [Fig. 12(e)] reveals a better view of this morphology. It can be observed the broken edges of the LCP structures emerging from the surface. At higher LCP concentration the clear forest of LCP fibers is seen as evident from Figure 12(f) for 75LCP/25PPO blend. These micrographs illustrate the very good adhesion between the two phases. That is a reason for improvement of tensile properties of blends above at LCP concentrations beyond 50%. It should be noticed that the morphology observed from these broken minitensile bars does not necessarily represent the structure of the melt prior to its solidification. Van Oene¹⁰ observed the breakdown structure on cooling; therefore, the cooling rate should affect the

final structure. Furthermore, Kiss⁵ observed tensile properties measured from minitensile bars were somewhat higher than those from standard tensile bars.

The core structure begins to form at LCP concentrations above 50% LCP. Below 50% LCP contents [for example, in Fig. 12(g)–(i), the middle part of tensile bars of 2.5–10% LCP contents] the core structure has not formed yet. It can be seen that the random formation of small sizes of fibers, holes, and poor adhesion between fiber and matrix take place as occurring at the skin. Figures 12(j) and (k) reveal the core structure of 75LCP/25PPO and 90LCP/10PPO blends. Morphological studies at the core of injection molded specimens of LCPs have been carried out by many researchers. The reported results can be classified into two groups. The first group^{11–15} observed no preferred orientation in the core, whereas another group^{16–19} observed transverse core orientation. The size and the level of orientation of the layers in the thickness direction of an injection-molded part was observed to be a function of gate and cavity geometries and of the processing conditions.¹⁷ However, in blends of LCP with PPO the LCP melt, having lower viscosity than that of PPO, may migrate to the skin area. This will leave a small amount of LCP fibers at core to be covered with PPO polymer. Therefore, it might be difficult to identify the preferred orientation at core.

CONCLUSION

A thermotropic LCP based on wholly aromatic copolyesters was blended with a thermoplastic PPO. The addition of LCP results in a dramatic reduction in viscosity and improvement in the melt process-

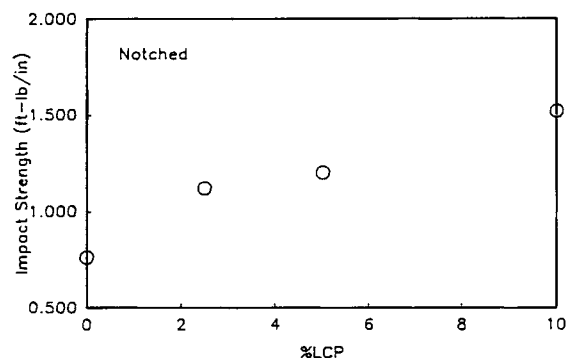
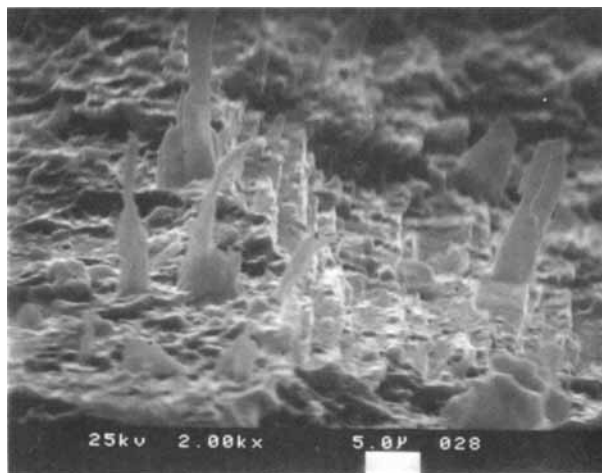
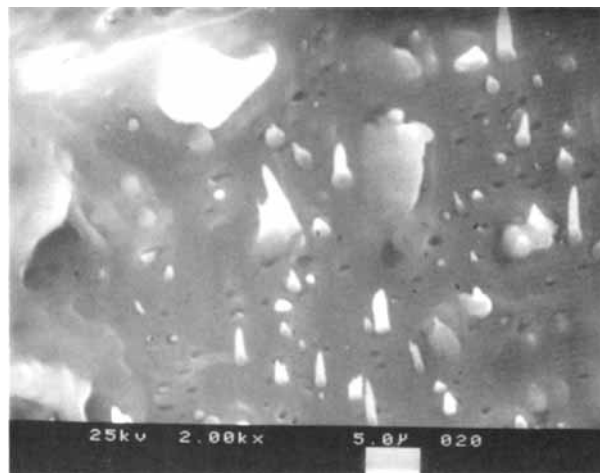


Figure 11 Impact strength as a function of LCP composition for PPO-LCP blends obtained using an Izod impact tester.

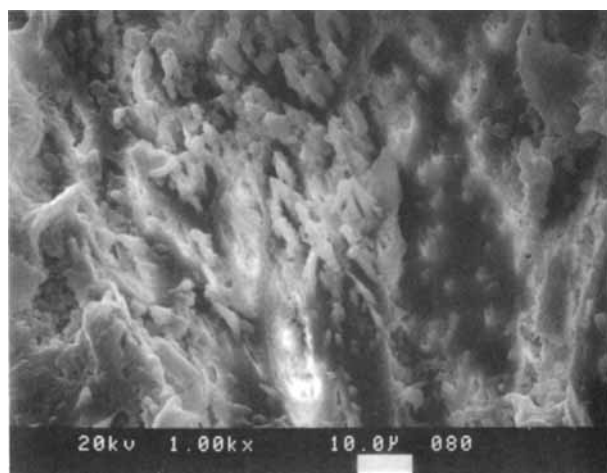
a) 2.5LCP/97.5PP0 (skin)



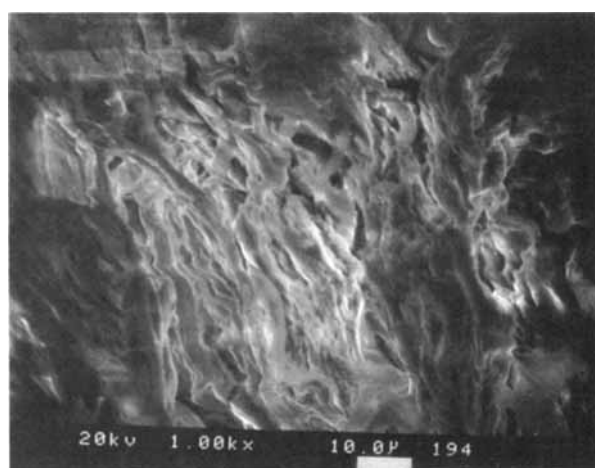
b) 5LCP/95PP0 (skin)



c) 10LCP/90PP0 (skin)



d) 50LCP/50PP0 (skin)



e) 50LCP/50PP0 (skin, etched with benzene)

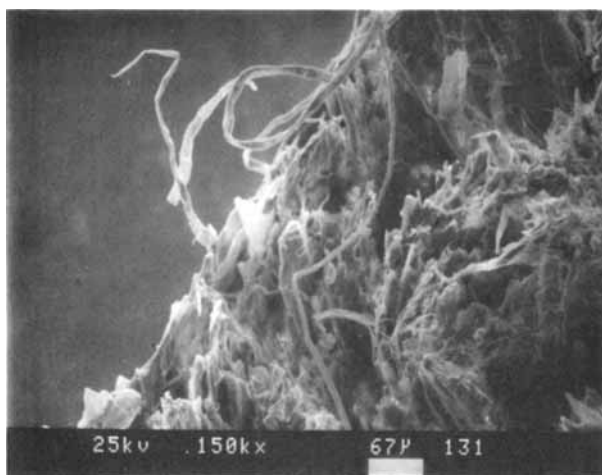
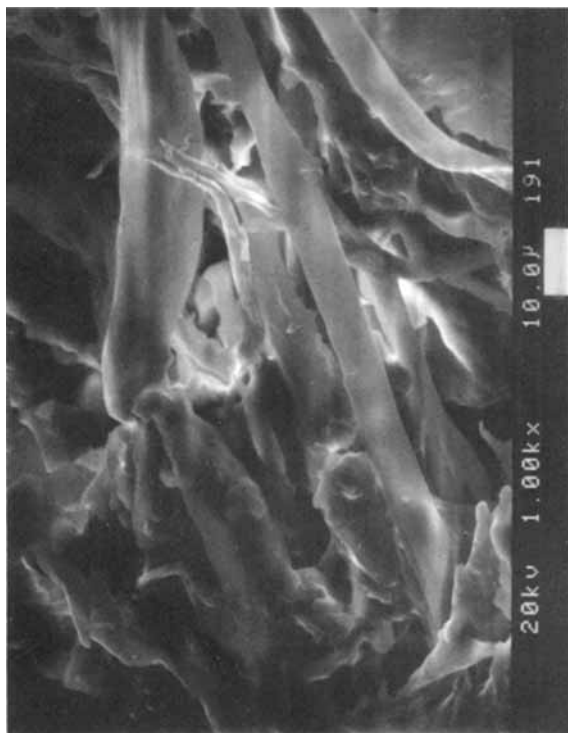
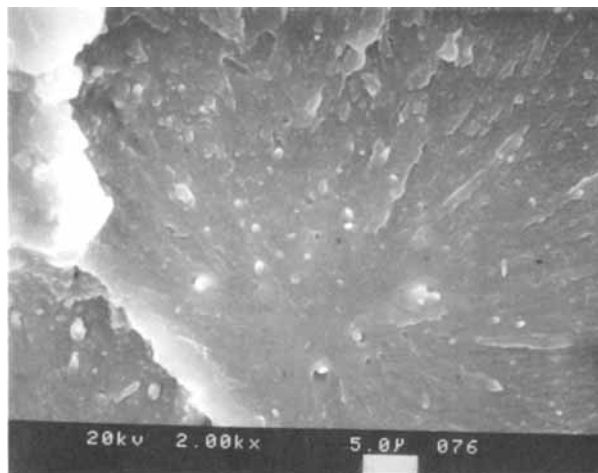


Figure 12 SEM microphotographs of small tensile bar surfaces from twin screw blend with various concentrations after breakage in liquid nitrogen.

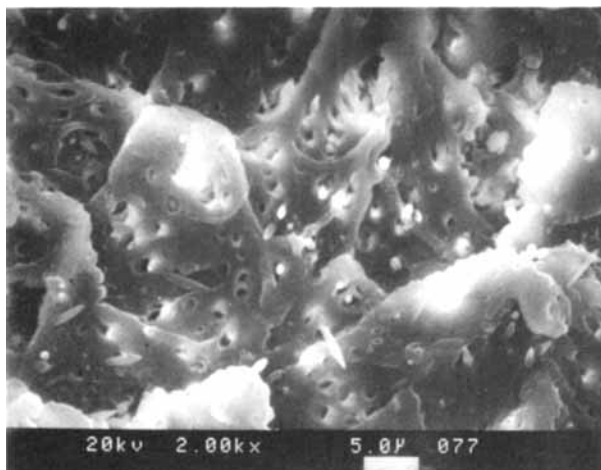
f) 75LCP/25PPO (skin)



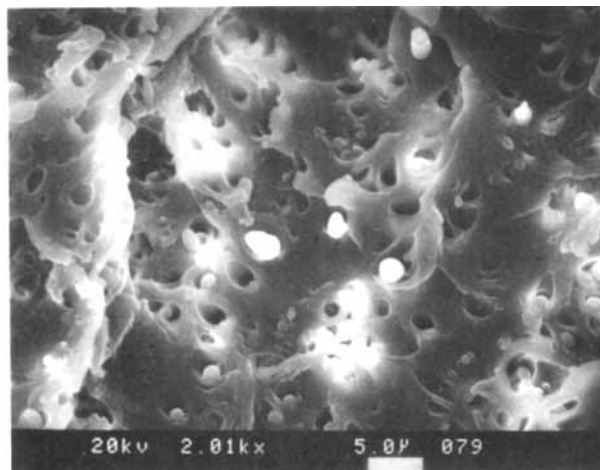
g) 2.5LCP/97.5PPO (core)



h) 5LCP/95PPO (core)



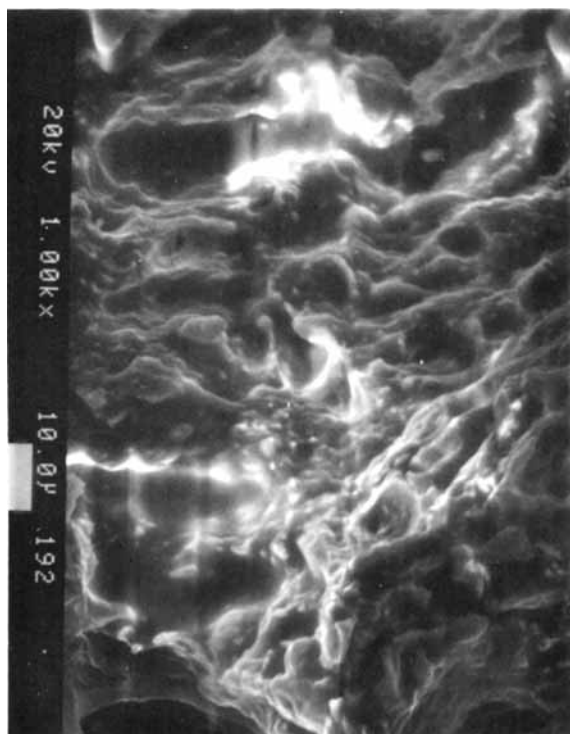
i) 10LCP/90PPO (core)

**Figure 12** (Continued from previous page)

ability of a host PPO. These blends are incompatible. The blends show two-phase morphology dependent on their compositions. Significant improvement in properties of injection-molded blends is achieved at

above 50% LCP concentrations and slightly at low LCP contents. Skin-core structure is detected in injection-molded samples especially evident at concentration of 50% LCP and higher. Impact strength

j) 75LCP/25PPO (core)



k) 90LCP/10PPO (core)

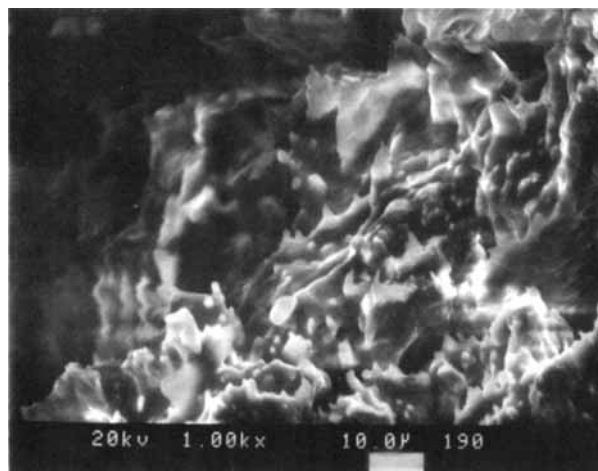


Figure 12 (Continued from previous page)

increases two times after adding 10% LCP into the PPO matrix.

This work is supported by a grant from the Edison Polymer Innovation Corporation (EPIC).

REFERENCES

1. I. Isayev and M. J. Modic, *Polym. Compos.*, **8**, 158 (1987).
2. K. G. Blizard and D. G. Baird, *Polym. Eng. Sci.*, **27**, 653 (1987).
3. R. A. Weiss, W. Huh, and L. Nicolais, *Polym. Eng. Sci.*, **27**, 684 (1987).
4. A. Siegmann, A. Dagan, and S. Kenig, *Polymer*, **26**, 1325 (1985).
5. G. Kiss, *Polym. Eng. Sci.*, **27**, 410 (1987).
6. M. V. Tsebrenko, *Int. J. Polym. Mater.*, **10**, 83 (1983).
7. A. I. Isayev and M. J. Modic, *SPE Tech. Pap.*, **32**, 573 (1986).
8. A. I. Isayev and S. Swaminathan, in *Advanced Composites III: Expanding the Technology*, Conference on Advanced Composites, September 1987, Detroit, MI, ASM, 1987, p. 259.
9. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Dekker, New York, 1974, Vol. 2.
10. H. Van Oene, in *Polymer Blends*, F. R. Paul and S. Newman, Eds., 1, Academic, New York, 1978, Vol. 1, p. 295.
11. E. G. Joseph, G. L. Wilkes, and D. G. Baird, *Polym. Eng. Sci.*, **25**, 377 (1985).
12. E. G. Joseph, G. L. Wilkes, and D. G. Baird, *Polymer*, **26**, 689 (1985).
13. H. Thapar and M. Bevis, *J. Mater. Sci. Lett. Eds.*, **2**, 733 (1983).
14. J. L. White, *Appl. Polym. Symp.*, **41**, 241 (1985).
15. G. G. Viola, D. G. Baird, and G. L. Wilkes, *Polym. Eng. Sci.*, **25**, 888 (1985).
16. L. C. Sawyer and M. Jaffe, *J. Mater. Sci.*, **21**, 1897 (1986).
17. J. J. Duska, *Plast. Eng.*, (Dec.), 39 (1986).
18. Z. Ophir and Y. Ide, *Polym. Eng. Sci.*, **23**, 793 (1983).
19. T. Weng, A. Hiltner, and E. Baer, *J. Mater. Sci.*, **21**, 744 (1986).

Received February 22, 1990

Accepted October 5, 1990