Through-Thickness Distribution of LCP in PPS/LCP Blends

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SYNOPSIS

Through-thickness distribution of liquid crystalline polymer (LCP) of blends containing polyphenylene sulfide (PPS) and LCP was investigated using differential scanning calorimetry and scanning electron microscopy. The effect of the LCP distribution on the mechanical test was checked through bending testing of the various compositions of the injection molded samples. These studies showed a nonuniform distribution of LCP in the PPS-rich region where the LCP content in the skin layer was higher than in the core layer or boundary between the two layers. The LCP component was uniformly distributed in the LCP-rich region. The increase of bending modulus with increasing LCP content was attributed to the reinforcing nature of the LCP fibrils in the skin layer. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Blending of multicomponent polymeric systems has been of academic and commercial interest because it generates excellent physical properties that offer advantages over either of the individual components.[1,2] Blend components selected for various reasons must provide stable and reproducible properties that may involve incorporation of a compatibilizer, a chemical reaction, or high shear mechanical reentanglement.[3] Some of the properties improved by suitable blending include impact resistance, stiffness, heat distortion temperature, chemical resistance, thermal stability, etc.[4-8] Polyphenylene sulfide (PPS) and liquid crystalline polymer (LCP) are high temperature specialty polymers for high performance applications, especially in the electrical and electronic industries. In earlier articles,[9,10] the results of differential scanning calorimetry (DSC) analysis indicated that PPS is immiscible with other polymers over the entire composition range. Recent studies[11] had shown that the presence of LCP in PPS/LCP blends prevents flashing during injection molding of the blends. Thus, the propensity to flash formation depends on the LCP content in the blend. Because the content of LCP through the thickness of the sample can affect the mechanical properties of the blend, the main objective of this work is to study the through-thickness distribution of LCP in the blend using DSC and scanning electron microscopy (SEM). The effect of the distribution on bending properties is also investigated.

EXPERIMENTAL

Materials

The linear PPS homopolymer used was obtained from Idemitsu Petrochemical Company and commercial grade LCP was purchased. The molecular weight of PPS was determined in chloronaphthalene by gel permeation chromatography (GPC) at 207°C. The results were $M_w = 42{,}038$, $M_n = 5782$, $M_z = 82{,}557$ with polydispersities of 7.27 (M_w/M_n) and 1.96 (M_z/M_w). The molecular weight of LCP could not be determined because it was difficult to find a suitable solvent that can dissolve it. The melting temperatures as determined by DSC were: 277°C for PPS and LCP. The structures of PPS and copolyester type LCP are shown in Figure 1.

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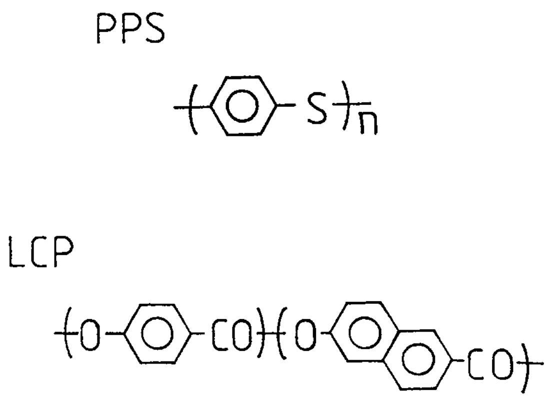


Figure 1 Structures of PPS and LCP.

Blending and Injection Molding

The polymers were mixed to give compositions of (PPS/LCP) 90/10, 75/25, 50/50, and 25/75. Blending was carried out using a Toshiba TEM35B-10/IV double-screw blender. The blends were extruded and pelletized. The pellets were dried for about 24 h at 150°C. The blended samples were predried at 230°C for 6 h before injection molding. The injection molding operation was carried out on Toyo Ti-30F6 injection molding machine. The molding conditions were: cylinder temperature, 300°C; mold temperature, 100°C; and injection pressure 30 kg/cm^2.

DSC

The LCP contents in three regions were evaluated from the heat of fusion (H) obtained from DSC analysis. Samples for DSC analysis were taken from the locations shown in Figure 2. Location 1 corresponds to the skin layer, location 2 was the boundary, and location 3 was the core layer. The samples were annealed at 250°C for 1 h simply to melt away imperfections that may affect the values of H. The sample weight for DSC analysis was 6.0 ± 0.01 mg.

DSC analysis was carried out using a Perkin–Elmer DSC, Model DSC7, fitted with a thermal analysis data station. The sample was heated to 320°C at a heating rate of 20°C/min. The LCP content was calculated from the following relationship

$$\text{LCP content } (\%) = \left(1 - \frac{\Delta H_{\text{pps}}}{\Delta H_{\text{blend}}}\right) \times 100 \qquad (1)$$

where ΔH_{blend} and ΔH_{PPS} are the heat of fusion of the blend and neat PPS, respectively.

The blend crystallinity was computed from[12]

$$X_c = \Delta H_{\text{exp}}/\Delta H^{\circ} \qquad (2)$$

where $\Delta H = \Delta H_{\text{melt}} - \Delta H_{\text{cryst}}$; ΔH° is the heat of fusion of 100% crystalline PPS ($\Delta H = 146\text{J/g}$).

SEM

The morphology of the blends was studied by SEM using a JEOL Model JSM-5200 at 15 kV accelerating voltage. The fracture surface was examined with specific reference to skin and core morphologies. All samples were coated with gold and examined at a magnification of 1000.

Bending Test

The three-point bending test was carried out by using an Instron Tensile Testing Machine, Model 4206. The specimen geometry of the injection molded bar is shown in Figure 3. The bending span was 48 mm and the testing speed was 2.0 mm/min. Experiments were conducted on batches of five or more samples of each blend and the results were averaged.

RESULTS AND DISCUSSION

Through-Thickness Distribution of LCP

The through-thickness LCP contents in blends containing PPS/LCP of 90/10, 75/25, 50/50, and

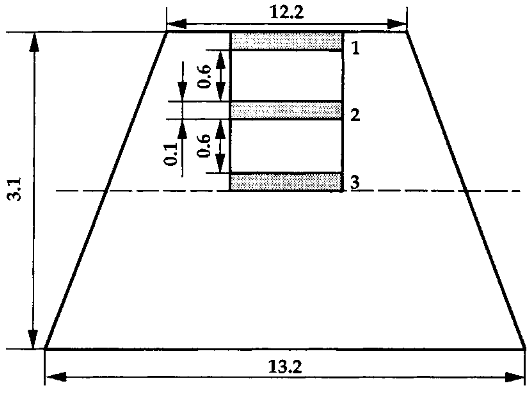


Figure 2 Schematic representation of injection molded PPS/LCP sample; (1) skin layer, (2) boundary, and (3) core layer.

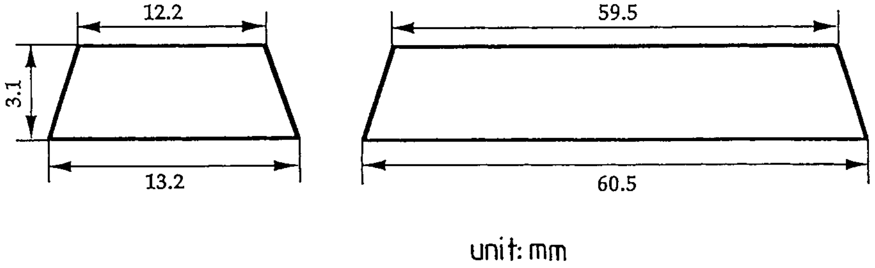


Figure 3 Bending specimen geometry.

25/75 are shown in Table I. In the 90/10 blend, the LCP content in the skin layer was about 15%, 9.27% in the core layer, and 9.38% in the boundary between the two layers. In the 75/25 blend, the skin layer had the highest LCP content and the boundary region had the lowest. Similar observation occurred in the 50/50 blend except that there was no significant difference in LCP distribution between the skin and core layers. Uniform distribution of LCP through-thickness occurred in the 25/75 blend where the content was almost the same irrespective of layers. In the PPS-rich region, the LCP content in the skin layer of the 90/10 blend was about 38% higher than that of the core layer; and in the 75/25 blend, the skin layer LCP content was only 5% higher than the core layer. With the 50/50 and 25/75 blends, the core layer LCP content was higher than the skin layer content. This observation indicates that uniform distribution of LCP in a PPS/LCP blend can only be achieved in an LCP-rich region. A high value of LCP content in the core region of the 75/25 blend was simply due to the large diameter of LCP fibrils and droplets that reduces its tendency to flow into the cavity wall. This reduction however, leads to a low LCP content in the skin layer especially in the 50/50 and 25/75 blends. It seems that the higher the LCP component in the blend, the better the through-thickness distribution.

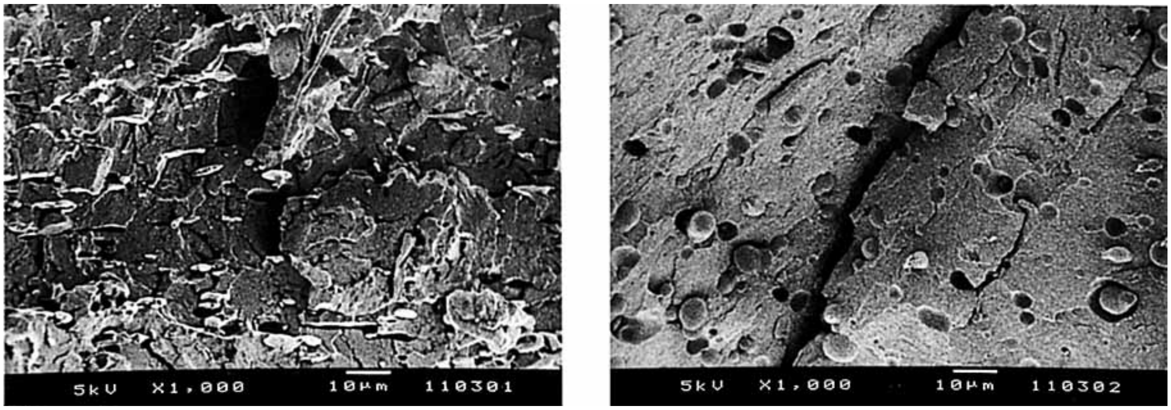
The SEM micrographs of the blends are shown in Figure 4. In the 90/10 blend shown in Figure 4(a), the skin layer contains fibrils of rod-like structures of LCP about 1–3 μm embedded in the PPS matrix. The core region indicates the formation of fine droplets (about 1–2 μm dia.) of the LCP in PPS matrix. The formation of fibrils in the 90/10 sample is in contrast to other investigations[13] in which fibrils were not observed in the blend containing nylon 66 and 10% LCP. In the 75/25 blend shown in Figure 2(a), both the fibrils' diameter in the skin layer and the droplets in the core layer are larger and nonuniform. A similar situation occurred in the 50/50 blend and the structure contains extremely large fibrils with ellipsoids of irregular diameter similar to those observed by Subramanian and Isayev on PPS/LCP blends.[14] The nonuniform distribution of the LCP region may be due to:

1. fibrillation of LCP in the skin layer caused by high shear stress near the cavity wall or
2. low viscosity of LCP.

During injection molding, a high shear flow is developed near the cavity wall (i.e. skin region); in the core region, little or no shear flow occurred. Thus, the component with low viscosity congregates in the region with high shear flow and the component with high viscosity will be housed in the region with low shear flow. In Figure 5, the viscosity of PPS was higher than that of LCP and this was found to reduce with increasing LCP content. Recent studies[15,16] had shown that orientation of the LCP fibrous phase in the flow direction lubricates the polymer melt, thereby reducing the viscosity. An addition of as little as 10% LCP results in about 15% reduction of viscosity from that of the neat PPS. With 25% LCP content, the reduction was 21%; in the 50/50 blend, it was reduced by about 43%; and in the case of the 25/75 blend the viscosity of LCP was about 72% lower than that of pure PPS. Because the viscosity of LCP is lower than that of PPS, the LCP component flowed into the cavity wall well ahead of PPS, thereby causing a high concentration in the skin layer.

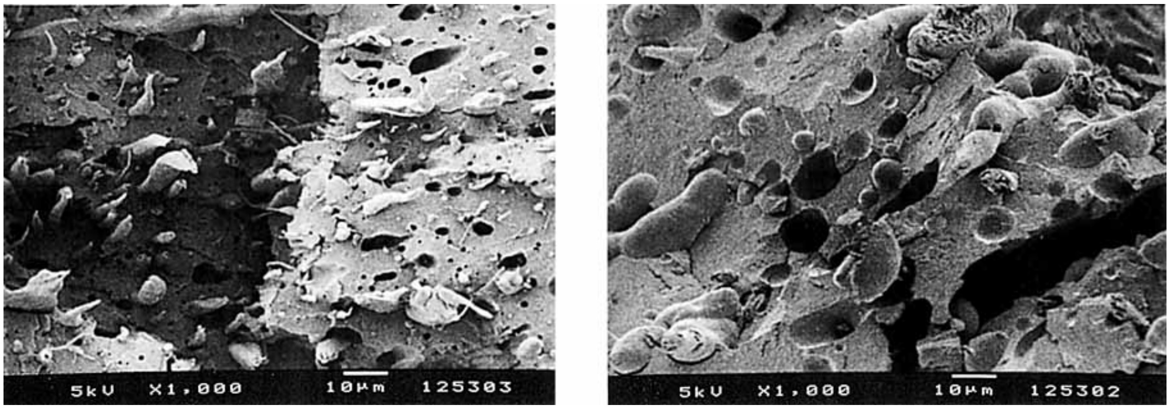
Table I Through-Thickness LCP Content (%) in PPS/LCP Blends

Sample	90/10	75/25	50/50	25/75
Skin	14.99	27.13	55.18	70.45
Boundary	9.38	22.57	52.80	70.83
Core	9.27	25.77	55.95	70.95



(a) (b)

90/10



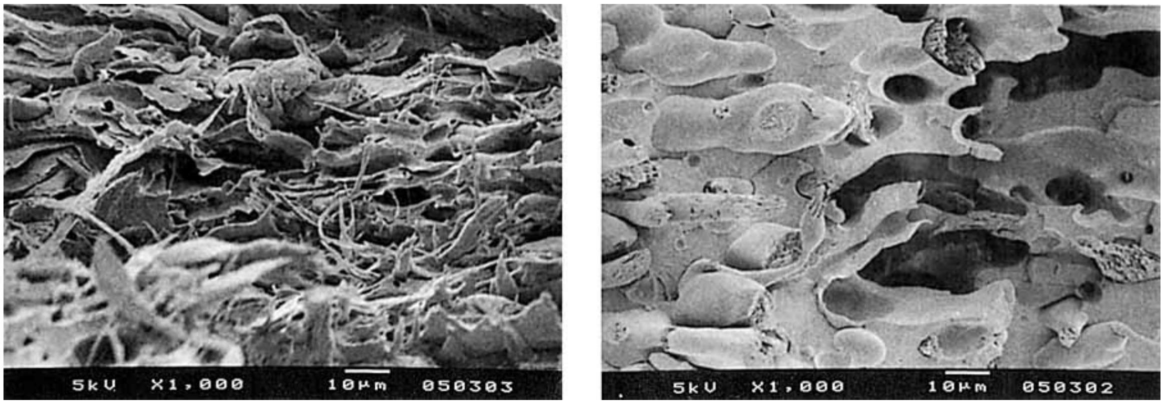
(a) (b)

75/25

Figure 4 SEM micrographs of fractured surface of PPS/LCP blend. (a) skin layer and (b) core layer.

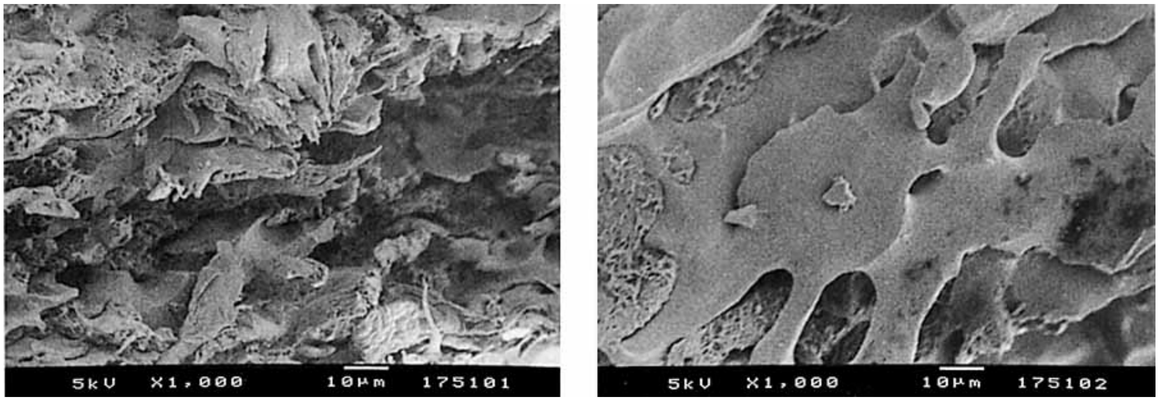
Effect of LCP Distribution on Bending Properties

It is anticipated that the LCP distribution will have a profound effect on bending properties of PPS/LCP blends. The bending modulus as a function of LCP content is shown in Figure 6. It is seen in this figure that the modulus increases with increasing LCP content. However, the bending strength drops (Fig. 7) with increasing LCP content, although both neat LCP and PPS had identical strengths. Kiss[17] reported on LCP blended with polyarylate, polychlorotrifluoroethylene, and polycarbonate; Siegman and coworkers[18] also reported an increase in tensile strength on blending on PA/LCP. The improved bending modulus was attributed to the stiffness of the pure LCP. The skin-core morphology of the LCP, however, is responsible for the increase of modulus and reduction of bending strength as the



(a) (b)

50/50



(a) (b)

25/75

Figure 4 (*Continued from the previous page*)

LCP content increases. It was shown in Figure 4 that the skin contains LCP fibrils and the core region had droplets embedded in the PPS matrix. It is suggested that under short-term loading, the LCP fibrils on the skin layer oriented in a similar way to the traditional reinforcing agents such as glass and carbon fibers. This alignment of LCP fibrils enhances bending modulus. On the other hand, as deformation continues, that is under long-term loading, the droplets in the core were unable to sustain a high load, thereby leading to premature failure as the LCP content increased.

Blend Crystallinity

The degree of crystallinity of the blend as a function of LCP content is shown in Figure 8. As can be seen

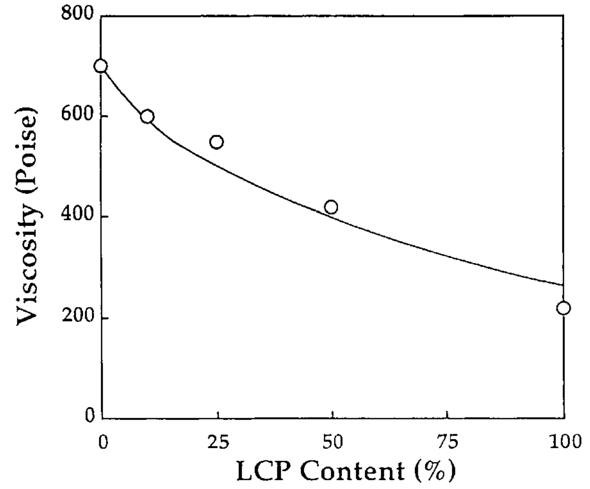


Figure 5 Viscosity as a function of LCP content in PPS/LCP blends.

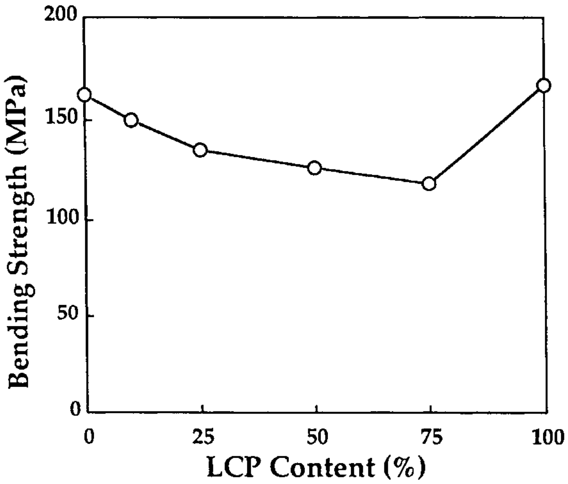


Figure 7 Bending strength vs. LCP content.

in the figure, crystallinity of PPS was not affected by LCP even when the PPS content is as low as 25%. This is in agreement with earlier studies[10] where the PPS retains its crystallinity after blending it with PEI and PSF. However, partial miscibility occurred because the results of viscosity measurements and bending properties indicated that some of the LCP dissolved in the PPS. The partially dissolved LCP component lubricates the PPS matrix, thereby reducing the viscosity of PPS. Further, an increase of bending modulus with increasing LCP component was also due to partial miscibility of the two components.

CONCLUSIONS

The distribution of LCP in the PPS/LCP blend was observed to vary through the thickness of the sample. In a PPS-rich region, the skin layer contained more LCP than either the core layer or the boundary between the two layers; in the LCP-rich region uniform distribution of LCP through the thickness of the sample occurred. The skin layer contained LCP fibrils and the core layer contained droplets of LCP embedded in PPS matrix. The increase of bending modulus with increasing LCP fibrils was attributed to the aligned LCP fibrils in the

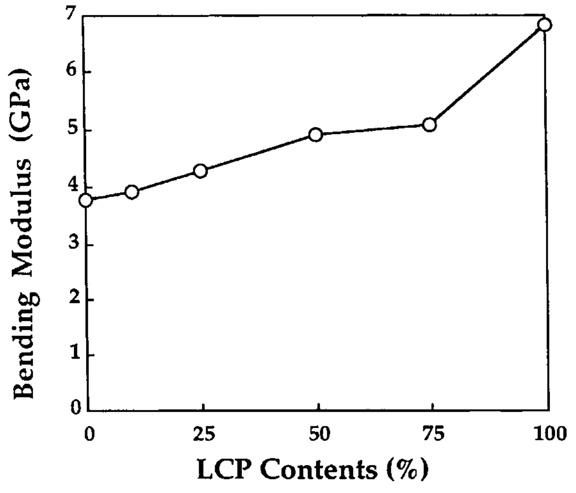


Figure 6 Bending modulus of PPS/LCP blends at various LCP contents.

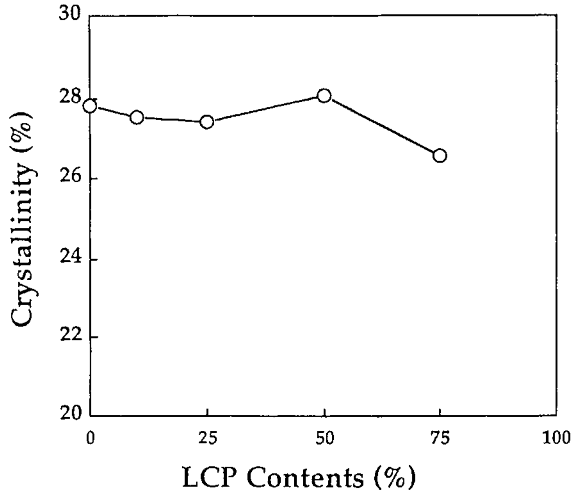


Figure 8 Crystallinity as a function of blend composition.

skin layer. Crystallinity of PPS was not affected by LCP.

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