Polyblends containing a liquid crystalline polymer

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Polyblends of a liquid crystalline thermotropic polymer (LCP) and an amorphous polyamide (PA) were prepared by melt blending. The blends' rheological behaviour was found to be very different from that of the individual components and very significant viscosity reductions were observed for blends consisting of only 5% LCP. The blends viscosity was always much lower than that of the parent polymers. The tensile mechanical behaviour of LCP/PA blends is very similar to that of polymeric composites. The blends' two phase morphology was found to be affected by their compositions. The LCP phase changed gradually with increasing LCP content from ellipsoidal particles to rod-like and fibrillar structure. A good interphase adhesion was observed.

(Keywords: blend; thermoplastic; thermotropic; rheology; structure; properties)

INTRODUCTION

Multicomponent polymeric systems, called polyblends, have recently attracted both scientific and industrial curiosity. They have been found to be the main route for the preparation of better cost effective plastics having the desired technological properties, especially for engineering purposes. Most polyblends are composed of immiscible polymers forming multiphase systems. In addition to the properties of the individual polymeric components the blends behaviour is affected mainly by the mode of dispersion, the size shape and orientation of the phases and their interaction. Furthermore, the blend morphology is strongly affected by the mode of mixing used for their preparation. Most of the reported work and commercial developments of polyblends is concerned with conventional flexible chain type molecules. However, with the newly emerging polymers composed of rigid, rod-like molecules such as wholly aromatic polyamides and thermotropic liquid crystalline polymers[1-3], new opportunities exist for producing molecular composites through blends of flexible and rigid rod-like chains[4].

Consequently, the present study deals with a unique system composed of an amorphous thermoplastic polyamide (PA) matrix and a liquid crystalline thermotropic polymer (LCP). As mentioned earlier, such a system should have the potential of forming a polymer/polymer thermoplastic composite material. The objectives of this paper are to report preliminary results related to rheological behaviour of thermoplastic/thermotropic blends, their resulting mechanical properties and morphology. As will be shown, the rheology of such blends systems is rather unique and their mechanical properties and structure are interesting.

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EXPERIMENTAL

Two resins were used throughout this study: Amorphous polyamide (Trogamide T-Dynamite Nobel, West Germany) served as a thermoplastic matrix; liquid crystalline aromatic copolyester based on 6-hydroxy-2-naphthoic acid (HNA) and p-hydroxybenzoic acid (HBA) was used as the reinforcing polymer (Celanese Corp., U.S.A.).

The blending of the two polymers was carried out in the molten state. Moulding was performed using an Arburg 220/150 machine and an appropriate mould producing ASTM testing specimens. The blend was injected at 295°–300°C (above the melting temperature of the LCP) into a mould which was kept at a constant temperature of 70°C.
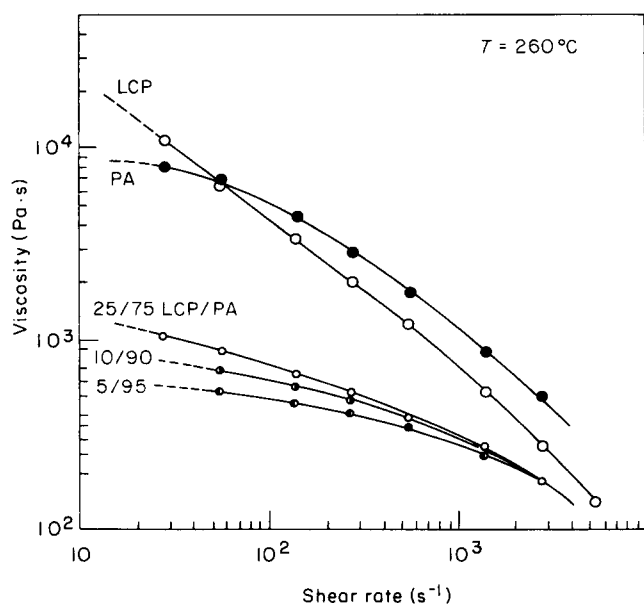
The mechanical properties of ASTM specimens (10 cm gauge length) were determined with an Instron Testing Machine operated at either 0.5 or 5 cm min⁻¹ cross-head speed. All strains were measured using an extensometer. The rheological behaviour of the resins and their blends was studied using a capillary rheometer (type MCR) attached to the Instron testing machine. The capillary used covered a wide range of shear rates and had a length to diameter (L/D) ratio of 33. Measurements were taken at 260°C (below the LCP melting).

To study the blends morphology the specimens surface was etched with a selective solvent namely concentrated sulphuric acid, which dissolves the polyamide matrix without affecting the LCP. The samples were immersed in the acid at room temperature and shaken for 20 min followed by additional 5 min immersion in a fresh reagent ultrasonic bath. Subsequently, the sample was washed in a mixture of 2 parts sulphuric acid and 7 parts water, rinsed in water and dried. These specimens were sputter coated with gold and observed in a Joel T200 scanning electron microscope. Wide angle X-ray diffraction (WAXD) patterns of LCP (ground powder), PA and their blends
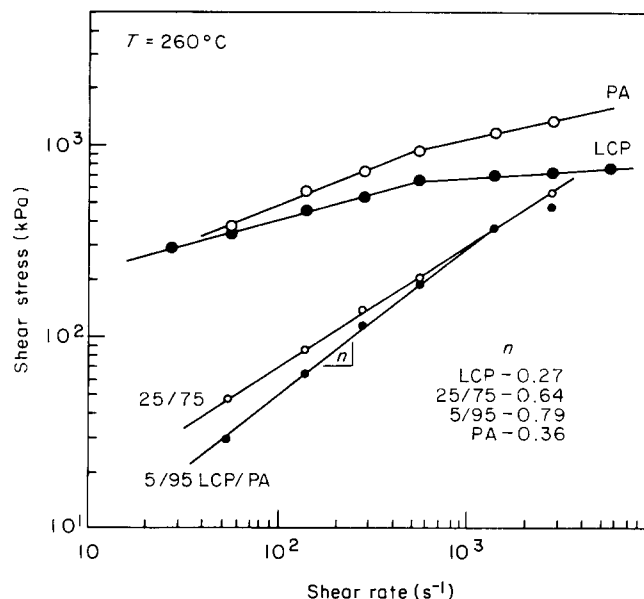
**Figure 1** Flow curves of LCP, PA and two of their blends measured at 260°C using a capillary of $L/D=33$

for the blend containing only 5% LCP. The very large differences in rheological behaviour are shown in the shear dependence of the melt viscosity (*Figure 2*). The strongest shear dependence is exhibited by the pure LCP. Its viscosity continues to be shear dependent even at the lower studied shear rates whereas the PA viscosity tends to level off when the shear rate and stress are decreased to $10 \mathrm{s}^{-1}$ and 2×10^6 dyne cm^{-2}, respectively. Moreover, the viscosity of all blends are much lower and their shear sensitivity approaches that of the parent components only at the upper part of the studied shear range. The most dramatic presentation of the data is the viscosity at constant shear rate or stress as a function of the LCP content. *Figure 3* describes such a presentation at constant shear rate; the plots at constant shear stresses are very similar in nature. The viscosities of the parent polymers are quite the same in the shear rate range of 54–2700 s^{-1}. However, the viscosity attains a minimum at 5% LCP content; up to about 20–25 times lower than that of the PA. Upon further addition of LCP (up to 25%) the blends' viscosity slightly increases.

Figure 2 Shear rate dependence of the viscosity of LCP, PA and three of their blends ($T = 260°C$)
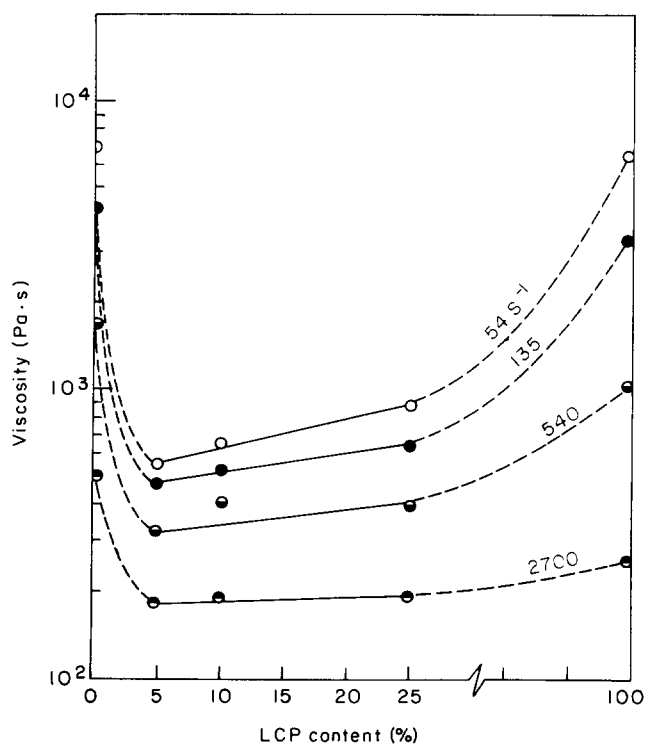
Figure 3 Composition dependence of the viscosity of LCP/PA blends as a function of shear rate ($T = 260°C$)

were obtained in the reflection mode using a Phillips diffractometer and CuKα source.

RESULTS AND DISCUSSION

The flow curves of the two parent polymers and of two representative blends (at 260°C) are shown in *Figure 1*. All the melts exhibited a non-Newtonian flow behaviour in the shear range studied. Their behaviour can be described by the Power Law expression, though the Power n remains constant only in a limited shear range. It should be noted that first, the large difference between the shear stresses required for the flow of the blends and that of the constituents, especially at the lower rates; secondly, the much steeper flow curves of the blends compared to those of the parent polymers. The highest n value was measured

Table 1 Mechanical tensile properties of some injection moulded LCP/PA blends

Composition LCP/PA	Sample thickness (mm)	Ultimate strength (kg cm^{-2})	Elastic modulus ($10^4 \times$ kg cm^{-2})	Elongation (%)
10/90	3.4[a]	810	3.96	14
10/90	2.4[b]	760	3.06	58
15/85	3.4	1120	4.38	8
15/85	2.4	910	3.15	8
25/75	3.4	1010	4.34	7
25/75	2.4	930	4.17	6

[a] Thickness of injection moulded specimen
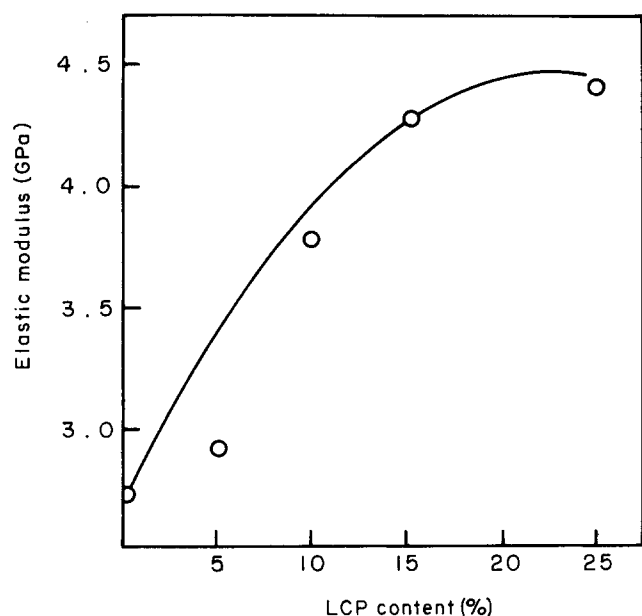[b] Thickness after outer layer removal

Figure 4 Composition dependence of the elastic modulus of injection moulded LCP/PA blends
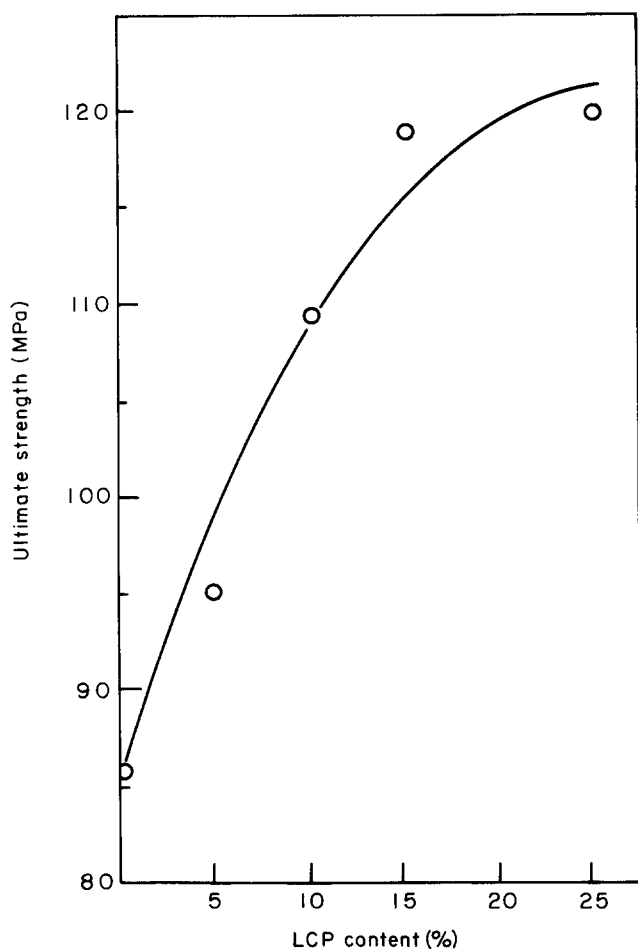
Figure 5 Composition dependence of the maximum tensile strength of injection moulded LCP/PA blends

The intriguing rheological behaviour, unpredictable by all available models for blends, should first be compared with blends rheology described in literature. Most $\eta(\dot{\gamma})$ data were obtained for various blends of polyolefins (see refs. 5–8) Plochocki has studied[9] the flow behaviour of PE/PP blends in the whole range of composition. The blends' viscosity (measured in a capillary viscometer) was

found to change gradually between the values for PE and PP when a capillary of $L/D = 66$ was used. However, using a capillary of $L/D = 33$ (the same as used in the present study) resulted in a sigmoid shape of the viscosity vs. composition curve having minimum and maximum viscosities at about 20 and 80% PE blends, respectively. In addition, the values of n, the power law exponent, was reported to change with composition exhibiting a minimum and a sigmoid shape curve when determined by using capillaries of L/D ratios of 66 and 33, respectively.
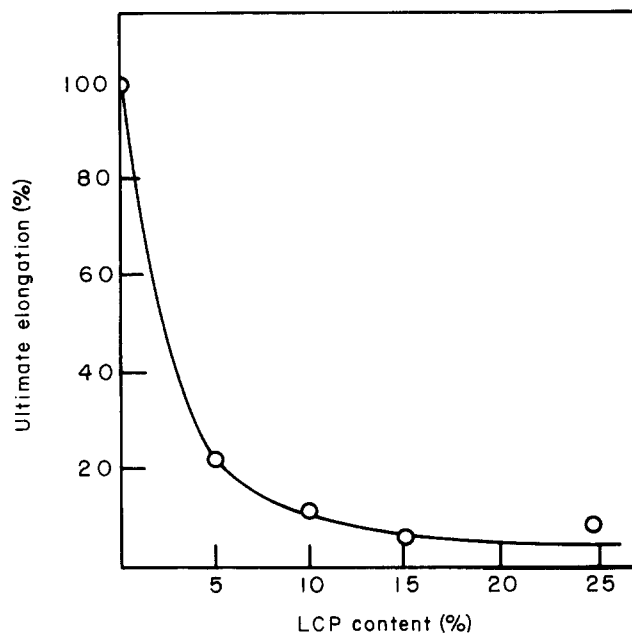
Figure 6 Composition dependence of the ultimate elongation of injection moulded LCP/PA blends
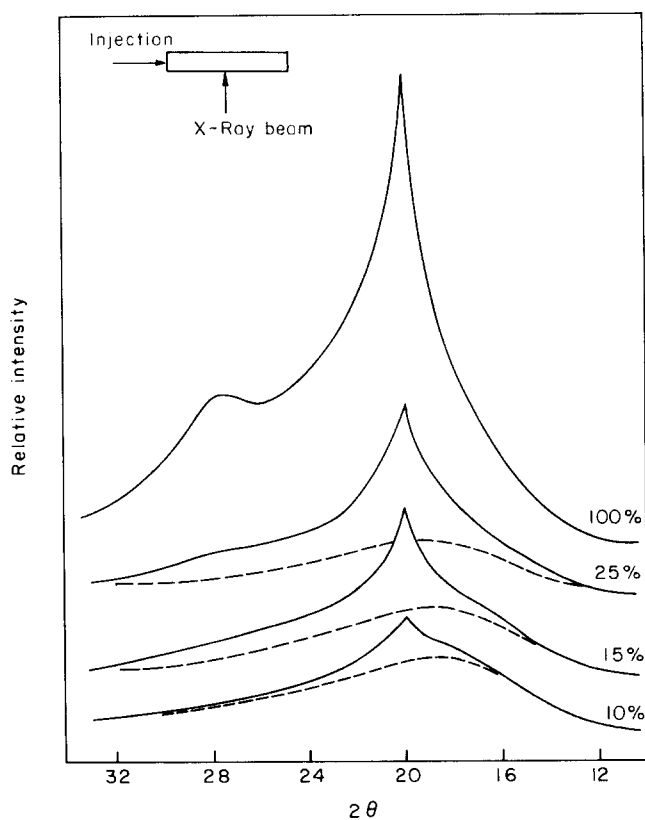
Figure 7 Wide angle X-ray diffractograms of LCP powder and three injection moulded LCP/PA blends. Diffractograms of PA are drawn in (— — — line)
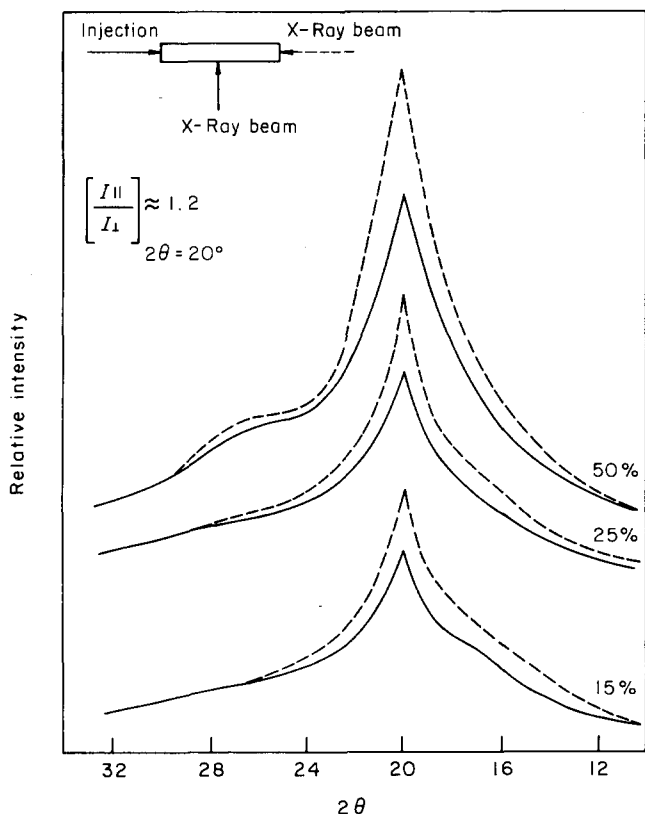
Figure 8   Wide angle X-ray diffraction of three injection moulded LCP/PA blends with the beam parallel (– – –) and perpendicular (——) to the injection flow direction
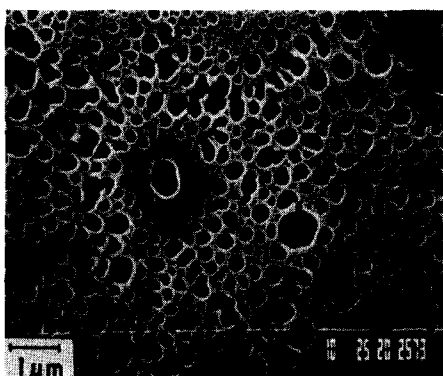

Figure 9   Etched PA surface

Without being able to explain this behaviour, Plochocki has compared it with a particulate flow which is characterized also by a lower melt viscosity[9]. Utracki and coworkers[10] have studied PET/polyamide-6,6 blends. They have observed a shallow minimum of the viscosity at about 5–10% polyamide level in the blend. The depth of this minimum has increased with decreasing shear rate and increasing melt temperature. Vinogradov and coworkers[11] have studied blends of POM and copolyamides. They have observed dramatic changes in the blends viscosity depending on blend composition. At lower shear stresses the viscosity went through a maximum whereas at higher stresses through a minimum, though at the same composition. Recently various LCP's were also claimed as efficient processing aids for melt processable polymers[12].

As reviewed by Van Oene[13], polyblends rheology is influenced by the melt structure. The latter strongly depend on the characteristics of the phases such as viscosity ratio, on their interaction, on the flow conditions and mixing mode. Droplets, ribbons and fibrils are the typical morphological units found in polyblends. They may change from one type to another depending on blends composition and flow conditions. Most authors suggest that the observed rheology of polyblends stems from melt structural changes. However, they still do not account for such phenomenon as blend viscosity being lower than that of the parent components.

To investigate the potential of LCP/PA blends as molecular composites and the structure–property relationships, blends of various compositions were injection moulded. The mechanical tensile properties of the blends are shown in *Figures 4–6*. Both the elastic modulus and ultimate tensile strength first increase linearly with increasing LCP content and then continue to increase at a lower rate; simultaneously, the ultimate elongation sharply decreases. This behaviour is characteristic of polymeric composites. The higher modulus LCP particles dispersed in the PA matrix act as reinforcing components. Some interesting observations were made by determining the tensile properties of specimens following removal of their outer layer (0.5 mm thick). In all the blends studied, the core sections have a lower modulus and strength and a higher elongation than those of the whole specimens; the differences increased with decreasing LCP content (see *Table 1*). A layered structure (core-shell) is observed with all the fracture surfaces. These results could be accounted for by higher orientation in the outer layer due to the fountain flow phenomenon[14].
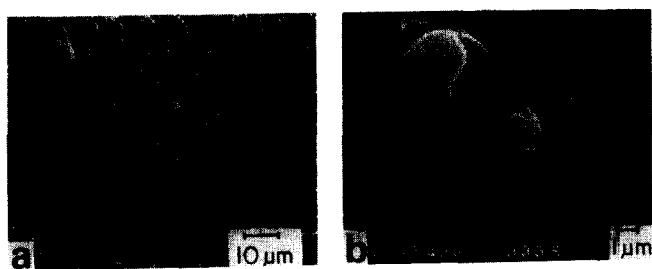

Figure 10   Etched surface of a 10% LCP blend: (a) 1000×, (b) 5000×, (c) 5000×

Figure 11 Fracture surface of a 10% LCP blend: (a) 1500 × , (b) 5400 ×

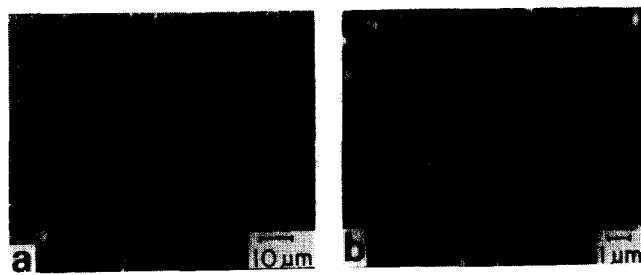**Figure 12** Fracture surface of a 15% LCP blend: (a) 1500 × , (b) 10 000 ×

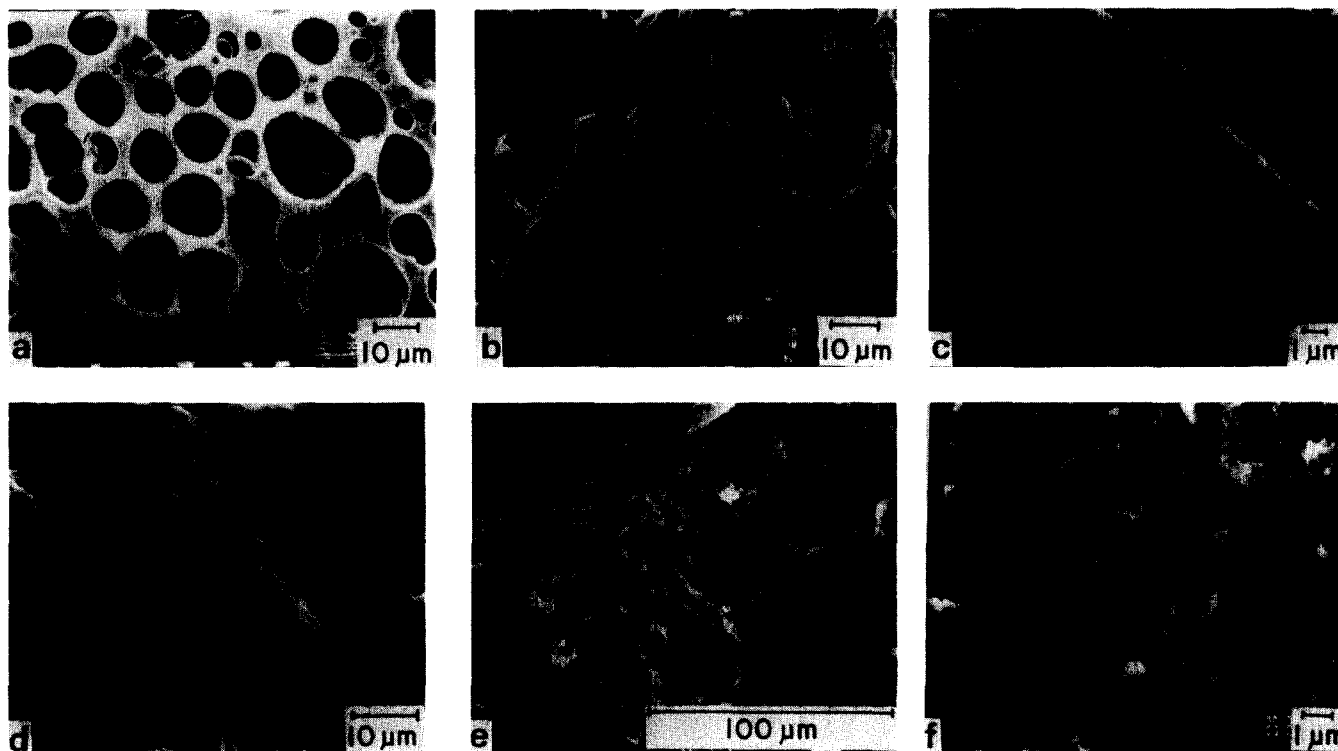**Figure 13** Etched surface of a 25% LCP blend: (a) 1500 × , (b) 1500 × , (c) 4800 × , (d) 2000 × , (e) 500 × , (f) fracture surface. 10 000 ×

Wide angle X-ray diffraction patterns of LCP and its blends are shown in *Figure 7*. The diffractogram of the PA is indeed typical for an amorphous polymer whereas that of LCP consists of two broad peaks. The diffractograms of the blends increase in their intensity and sharpness with increasing LCP content. The diffraction patterns of the PA were drawn onto those of the blends at intensities proportional to the blend compositions. The remaining major peak intensity (above the broken line) is approximately proportional to the LCP content. Thus, one may conclude that the LCP is dispersed as a separate phase having the parent polymer structure. Diffraction patterns were obtained with the beam parallel and perpendicular to the injection direction (see *Figure 8*). For all compositions, up to 50% LCP, the intensity ratio of the major peak (at 20°) obtained in both directions was about 1.2. Thus, the LCP is slightly oriented in the flow direction and moreover, the degree of orientation is independent of composition.

The morphology of the LCP/PA blends was studied by scanning electron microscopy of fracture surfaces and

etched surfaces; both of injection moulded specimens. The interpretation of the micrographs obtained from etched surfaces has to be very cautious. The etched surface of PA, as seen in *Figure 9*, illustrates the very uneven etching process. The acid etching causes the formation of holes of various sizes and shapes resulting in the formation of a network-like surface.

The etched surface of a 10/90 LCP/PA blend reveals ellipsoidal LCP domains embedded in the PA matrix (see *Figure 10a*). These domains are few microns in size. Most of them appear to sit in cavities (see *Figure 10b*) and some more freely on the surface (see *Figure 10c*). The micrographs obtained from fracture surface of this blend confirm the above described morphology. The LCP particles seen in *Figure 11a* are distributed quite evenly on the surface. Higher magnification (*Figure 11b*) reveals the shape of the LCP particles; some quite elongated. It appears that the adhesion between the two phases is quite strong.

The etched surface of a 15/85 LCP/PA blend (not shown here) seems to be similar to that of the 10/90 blend.
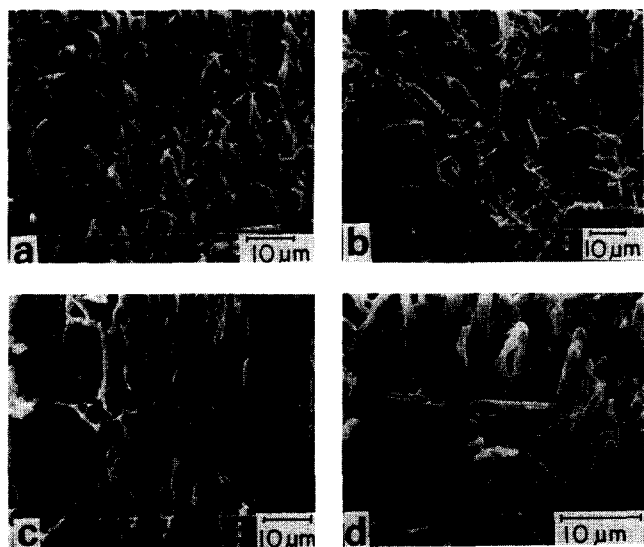
Figure 14 Etched surface of a 50% LCP blend: (a) 2000 ×, (b) 1500 ×, (c) 2000 ×, (d) 3500 ×

Figure 15 Fracture surface of a 50% LCP blend: (a) 1500 ×, (b) 10 000 ×

However, the fracture surface (*Figure 12*) clearly shows the higher content of LCP. Moreover, some of the LCP particles are elongated emerging from the matrix and broken at their edges. Most of the particles are still adhered to the matrix and no major pullout has taken place.

The morphology of the 25/75 LCP/PA blend included both particulate and fabrillar LCP structures. LCP particles and the residual PA voids matrix is seen in *Figure 13a*. Various entangled fibrils (*Figure 13b*) or rod like structures (*Figure 13b,c*) are another characteristic LCP morphology in this blend. There are also regions where the LCP has formed some kind of a network. As seen in *Figure 13e* this network is not isotropic hence the surface etching seems first directional. The fracture surface of this blend includes also both particulate and fibrillar LCP structures (*Figure 13f*).

The etched surface of a 50/50 LCP/PA blend reveals rod-like (*Figure 14a*) or fibrillar (*Figure 14b*) structures. Some of these LCP structures still seem to be either heavily (*Figure 14c*) or lightly (*Figure 14d*) coated with the matrix polymer. Fracture surface of the 50/50 blend reveals also the same morphology, showing the broken edges of the LCP structures emerging from the surface (*Figure 15*). These micrographs illustrate again the very good adhesion between the two phases.

Thus, the LCP/PA blends consist of two phases, the structure of which is composition dependent. At low LCP content the LCP is dispersed as ellipsoidal particles and at high content as fibrils or rodlike structures. There is a gradual change from one type of morphology to the other as both can be seen in the intermediate 25/75 LCP/PP blend. Good interphase adhesion is characteristic of all the blends studies. It should be noticed that the morphology observed in the injection moulded specimens is not necessarily the structure of the melt prior to its solidification. It has been shown recently[13] that there is a structural break-down upon cooling and that the cooling rate affects the final structure.

The work presented above includes preliminary studies of the rheological and mechanical behaviour of blends consisting of a liquid crystalline polymer dispersed in an amorphous polymeric matrix and their morphology. The
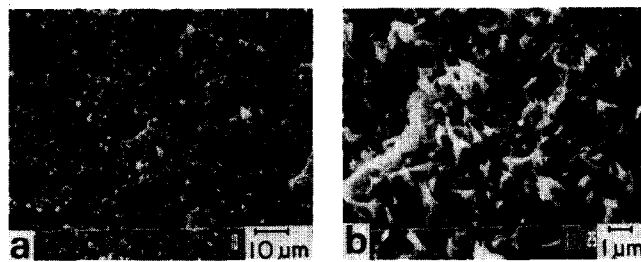
results were found intriguing however, a lot more has to be done to shed light on the uniqueness of the studied system as to the contribution of the anisotropic liquid crystalline additive to its behaviour.

CONCLUSIONS

(1) LCP/PA blends containing up to 50% LCP are multiphase systems.
(2) The addition of LCP results in marked changes in the rheological behaviour of PA.
(3) The addition of just 5% LCP results in a dramatic reduction in the viscosity (a factor of 20–25).
(4) The viscosity of all blends is much lower than that of both parent polymers.
(5) Injection moulded blends exhibit mechanical behaviour similar to that of composite materials.
(6) The blends two phase morphology depends on their composition, changing from particular to fibrillar with increasing LCP content.
(7) Though not compatible the blends exhibit good interphase adhesion.
(8) The blends rheological behaviour cannot be explained either by their unique melt structure or by any available model. It may be altered by a non-uniform LCP distribution in the melt.

ACKNOWLEDGEMENTS

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