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Injection moulding of self-reinforcing polymers and polymer blends

C. LEKAKOU, J. COWLEY, C. E. DICKINSON
Department of Materials Science and Engineering, University of Surrey, Guildford, Surrey GU2 5XH, UK

In this study it is investigated how to improve the self-reinforcing nature of a liquid crystalline polymer, Vectra, and blends of nylon 6,6 and Vectra processed by injection moulding. Firstly, experiments were conducted on the effect of processing conditions on the mechanical properties of injection moulded Vectra specimens and an optimum injection pressure and melt temperature was specified. Blends of nylon 6,6 with Vectra were then injection moulded under the previously specified optimum processing conditions. During microstructural studies it was observed that the skin contained highly oriented fibrillar domains of Vectra, the density and texture of which changed with blend composition which was varied between 20–30 vol% Vectra. A 25 vol% composition of Vectra displayed the best reinforcing properties and at this composition the fibrils in the skin were arranged into thick bundles. Above a 25 vol% Vectra content the start of fibril coalescence was observed which reduced the self-reinforcing character of the blend.

1. Introduction

Liquid crystalline polymers (LCP's) have the potential to exhibit superior mechanical properties to traditional polymers in preferential directions that depend on the morphology and rigid unit orientation [1–3]. Main chain thermotropic LCP's form nematic domains while they are melt processed by conventional methods such as injection moulding. LCP's can be used in small quantities to enhance the properties of isotropic thermoplastics creating new opportunities for producing molecular composites through blends of flexible and rigid rod like units [1]. Polyblends of such nature are usually immiscible, with structures depending on the nature of the polymer, the composition and the processing technique and processing conditions. LCP's and their blends with other polymers are often referred to as self-reinforcing polymers because of the presence of the nematic domains in their morphology which act as layers of meltable reinforcing fibres. The literature suggests that such molecular composites are easier to process and have lower viscosities than those of the parent polymers [4–8]. The problems of wear of processing equipment due to abrasion and the difficulties in compounding which are encountered in discontinuous glass fibre polymer composites are overcome in LCP blends [9].

In injection moulded specimens of LCP's or two-phase polymer blends containing an LCP, the morphology varies through the cross-section of the component where a skin/core microstructure is usually observed. This is the result of a combination of "fountain flow" at the flow front and shear flow near the walls of the mould [10, 11]. As nematic domains reach the flow front during filling, they are elongated in the fountain type of flow (see Fig. 1) forming fibrillar structures [12]. They then reach the mould walls and are aligned parallel to the wall. If they do not solidify rapidly they are further sheared in the highly shear stress region. The core region, on the other hand, is a low shear stress region and as a result there is no trend of deformation and orientation of the dispersed nematic domains in this region.

Zulle *et al.* [13] have examined the mechanical properties of injection moulded specimens made from Vectra and how these properties were related to processing conditions. They concluded that the tensile modulus and strength were better at low values of injection pressure and injection rate. Hedmark *et al.* [14] carried out extensive microstructural studies of injection moulded specimens made of liquid crystalline co-polymers. They observed that the skin thickness of specimens appeared to be insensitive to melt temperature. The thickness of intermediate layers and core, however, was significantly influenced by both temperature and distance from the mould gate.

Published reviews of polyblends containing LCP's include the works of Wiess *et al.* [15] and Brostow [16]. Beery *et al.* [4] observed the microstructure development during capillary flow of polyblends containing an aromatic LCP as a minor constituent and a conventional thermoplastic as a matrix. Three thermoplastics were tested, namely polycarbonate (PC), poly(butylene terephthalate) (PBT) and nylon 6. They concluded that the ratio of polymer viscosities affects the microstructure. If, in the processing, the LCP had a higher viscosity than the thermoplastic matrix (PC, amorphous nylon) a fibrillar structure developed under shearing. Otherwise very high shear rates were

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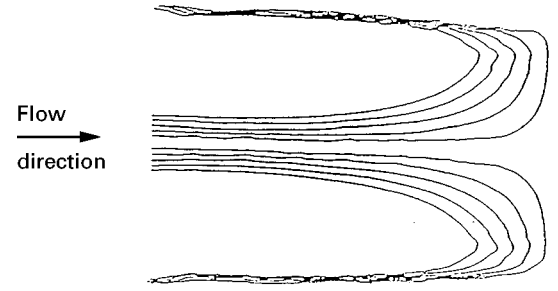

Figure 1 A diagram of flow streamlines relative to the moving melt front during filling in injection moulding.

required for the development of fibrillar structures. It is noted that the polymers viscosity depends on temperature and shear rate.

In another study, Beery *et al.* [17] processed the polyblends by injection moulding at 290 °C. The resultant components had a distinct skin/core morphology, where elongated fibrous or ellipsoidal LCP domains comprised the skin layer in PC/LCP and PBT/LCP blends and spherical and ellipsoidal domains comprised the core section. Nylon 6/LCP blends, on the other hand, contained mainly spherical LCP particles in the skin region and only few elongated LCP particles. The tensile modulus and strength were raised as the LCP content was increased in acrylonitrile (AN), PC and PBT matrices. On the other hand, the modulus and strength decreased as LCP was added up to 20 wt% in nylon-6.

Siegmann *et al.* [5] recorded the mechanical tensile properties of LCP/amorphous polyamide blends of various compositions up to 25% LCP. Both elastic modulus and tensile strength first increased linearly with increasing LCP content up to 10%, and continued to increase at a lower rate thereafter. Simultaneously the elongation at break sharply decreased for compositions up to 10% LCP and very slowly thereafter. Their mechanical behaviour was similar to that of fibre composites with respect to fibre fraction. A layered structure (skin/core) was observed at the fracture surfaces. The blends two-phase morphology depended on their composition, changing from particular (10% LCP) to longer ellipsoids (25% LCP) and finally fibrillar (50% LCP).

Chung [18] studied the morphology and mechanical properties of thermotropic LCP/nylon 12 blends. The morphology of the fracture surface of extruded rods varied from a spiny structure (nylon 12 enriched) to a fibrilar structure (LCP enriched). Besides, the LCP enriched rods displayed a skin/core structure with more nylon in the skin than in the core. The mechanical properties improved with an increase in LCP content up to 70 wt% and then dropped remarkably. The melt viscosity of the blend reached a minimum at 10 wt% LCP, a maximum at 20 wt% LCP and then fluctuated with increasing LCP.

Blizard and Baird [6] studied the morphology and rheology of blends of nylon 6,6 and a copolyester of 60 mol% p-hydroxybenzoic acid 40 mol% PET. Lack of fibrilar formation was observed at 10 wt% LCP. Fibril formation was mostly developed at 30 wt% LCP. Blends of 30 wt% LCP also showed minimum viscosity.

The scope of the present study is to investigate how to improve the self-reinforcing nature of an injection moulded LCP and blends of the LCP with an isotropic thermoplastic. The study comprises two main parts. The first part focuses on the injection moulding of an LCP, commercially known as Vectra, and examines the effect of changes of the injection pressure and melt temperature on the mechanical properties of moulded specimens. As a result, an optimum set of processing conditions is determined corresponding to the best self-reinforcing behaviour of LCP while processability is maintained. The second part considers a blend consisting of a thermoplastic polyamide (nylon 6,6) and Vectra which is injection moulded under the optimum processing conditions for Vectra. The aim is to optimize the blend composition with respect to mechanical properties and carry out microstructural studies to elucidate the effects of different compositions on the self-reinforcing behavior of blends.

2. Experimental procedure

2.1. Materials, specimen preparation and testing

The parent polymer materials used in this study were Vectra A900, a thermotropic liquid crystalline copolyester supplied by Hoechst Celanese, and nylon 6,6 "Maranyl" supplied by ICI Plastics Division. The two polymers have similar melting points, 265 and 280 °C for nylon and Vectra respectively. Blends of the two polymers were prepared with compositions of 20, 25 and 30 vol% Vectra.

Specimens from Vectra and from the blends were processed by injection moulding. Just before the melt processing, granules of Vectra or mixtures of granules of the two polymers were dried for a minimum of 4 h at 160 °C in a tumble drier to prevent possible hydrolytic degradation during melting. The tumble drier also assisted in the mixing process. The material was processed in a Boy 15/2000 injection moulding machine.

For the pure Vectra, the processing conditions were varied in order to study their effect on the mechanical properties. The injection pressure was varied within the range of 50–100 MPa; two melt nozzle temperatures were employed: 290 and 300 °C. The optimized processing conditions for Vectra were then used as a guide in the processing of blends since they were considered to yield the best fibrillar morphology of nematic domains in the skin region. For the blends, the processing temperatures were 200, 230 and 300 °C at the back screw zone, middle screw zone and nozzle, respectively. The injection pressure was set at 50 MPa. Beery *et al.* [4] found that the viscosity of blends of nylon-6 and LCP up to 20% was lower than that of each component at 260 °C. The general impression from the present studies was that the blends of all three compositions were much easier to process by injection moulding than either nylon or Vectra A900 alone.

Tensile test specimens were produced by injection moulding. All specimens were dried under vacuum prior to testing for 48 h at 50 °C to remove moisture

absorbed during storage. Tensile tests up to fracture were carried out on an Instron 1195 at a constant crosshead speed of 2 mm per min. All strains were measured using an extensometer. Fracture surfaces were sputter coated with gold and examined under the scanning electron microscope (SEM). The fracture surface was observed at various positions across the thickness of the specimens.

3. Results and discussion

3.1. Effects of processing conditions on properties of LCP specimens

In the parametric studies of processing of Vectra changes were imposed on the injection pressure and melt temperature which, in turn, affected the mechanical properties. Both side gated and end centrally gated specimens (see Fig. 2(a and b)) were tested.

Figs. 3 and 4 illustrate the effect of changes in injection pressure on the Young's modulus and tensile strength, respectively. Both properties are best at low injection pressures (about 50 MPa), then they display a rapid decrease with increasing pressure up to about 65 MPa and a much slower decrease thereafter. These results agree qualitatively with similar conclusions by Zulle *et al.* [13]. Figs. 5–7 illustrate the effect of melt temperature on the Young's modulus, tensile strength and strain to failure. Only two temperatures, 290 and 300 °C, were tried: due to the occurrence of short-shots and flash, it was not possible to change the melt temperature within a wider range. In general, there were very small changes in the mechanical properties as the melt temperature was varied. A slight improvement of properties may be detected at the melt temperature of 300 °C.

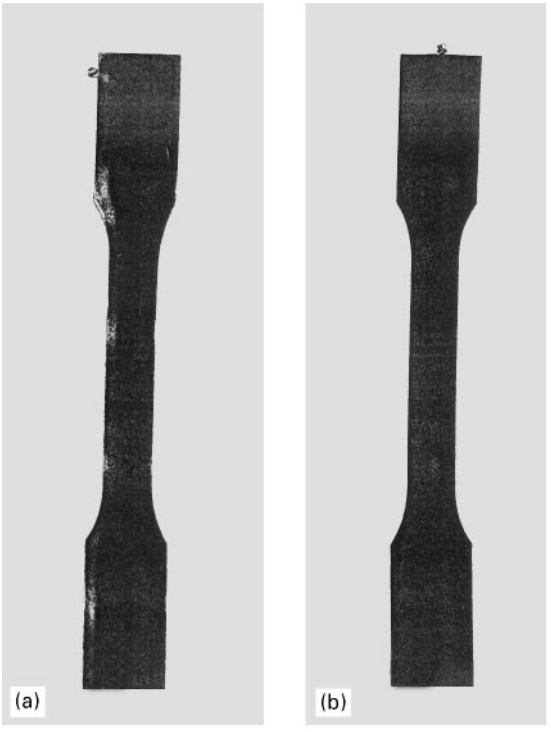

Figure 2 The two types of mechanically tested specimens: (a) side gated specimen and (b) end centrally gated specimen.

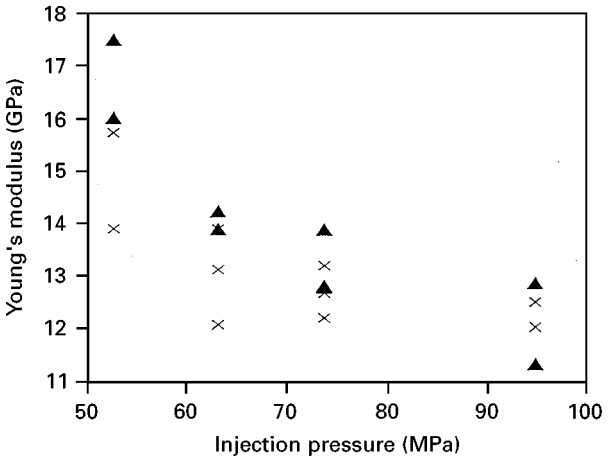

Figure 3 The effect of injection pressure on the Young's modulus in; (▲) side-gated and (×) end-gated Vectra specimens. The injection temperature was 300 °C and the flow rate was 5.6 cc s^{-1}.

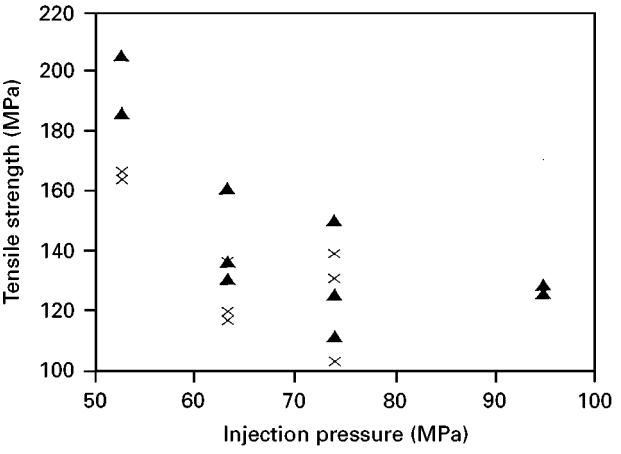

Figure 4 The effect of injection pressure on the tensile strength in; (▲) side-gated and (×) end-gated Vectra specimens. The injection temperature was 300 °C and the flow rate was 5.6 cc s^{-1}.

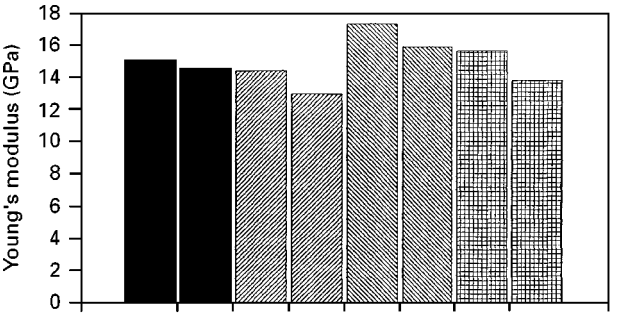

Figure 5 The effect of nozzle melt temperature on the Young's modulus in: (■) side-gated and (▨) end-gated Vectra specimens at 290 °C and (■) side gated and (▦) end-gated Vectra specimens at 300 °C. The injection pressure was 53 MPa and the flow rate was 5.6 cc s^{-1}.

The optimum conditions specified in this section were used for the injection moulding of Maranyl nylon 6,6/Vectra blends in the hope that they would lead to the formation and good alignment of LCP fibrillar domains.

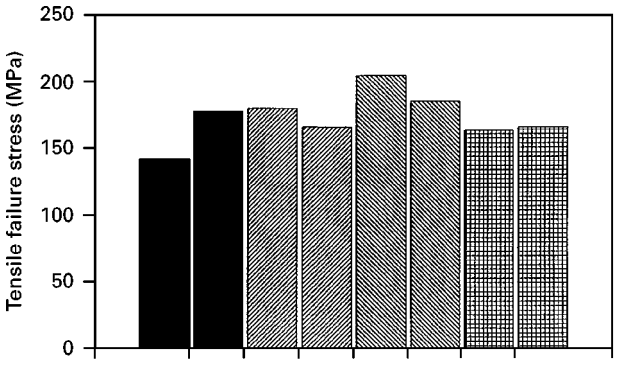

Figure 6 The effect of nozzle melt temperature on the tensile strength in; (■) side-gated and (▨) end-gated Vectra specimens at 290 °C and (■) side gated and (▦) end-gated Vectra specimens at 300 °C. The injection pressure was 53 MPa and the flow rate was 5.6 cc s^{-1}.

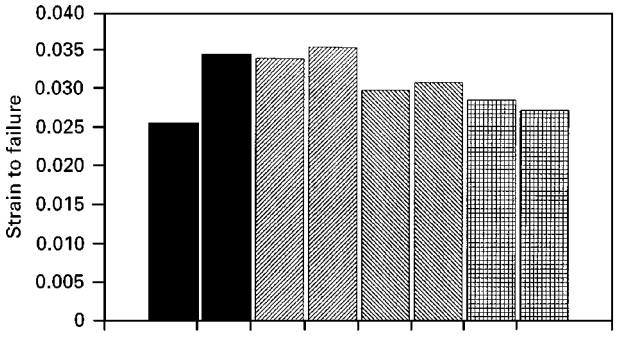

Figure 7 The effect of nozzle melt temperature on the strain to failure in; (■) side-gated and (▨) end-gated Vectra specimens at 290 °C and (■) side gated and (▦) end-gated Vectra specimens at 300 °C. The injection pressure was 53 MPa and the flow rate was 5.6 cc s^{-1}.

3.2. Mechanical testing of Maranyl nylon 6,6/Vectra blends

Stress–strain data were obtained from the mechanical testing of specimens of various compositions. Young's modulus, tensile strength and elongation to break were examined and the results for the three blends are listed in Table 1. Considering these results in combination with the microstructural studies in section 3.3, it was concluded that the LCP displayed in general reinforcing behaviour. As the LCP content increased in the blend, the Young's modulus and tensile strength passed through a maximum. These trends may be due to differences in the volume fraction, size and orientation distributions of the reinforcing phase between the three blends that were examined in the microstructural study.

The three blends displayed non-linear behaviour in tensile tests, as is displayed in Fig. 8, which is similar to that observed in short-fibre reinforced composites. A significant reduction in elongation to break was observed between 20–25 vol% Vectra, followed by an increase between 25–30 vol% Vectra.

If the blends were considered as micro-composites, an improvement in the mechanical properties should be expected in cases in which fibrils were present in the direction of tensile stress. In the absence of elongated LCP domains or in cases where these domains are oriented perpendicularly to the tensile stress direction,

TABLE I Mechanical properties of nylon Maranyl/Vectra A900 blends

Blends	Young's modulus (GPa)	Tensile strength (MPa)	Strain to failure (%)
20% LCP	2.9	48	20
25% LCP	6.3	68	5
30% LCP	3	45	20

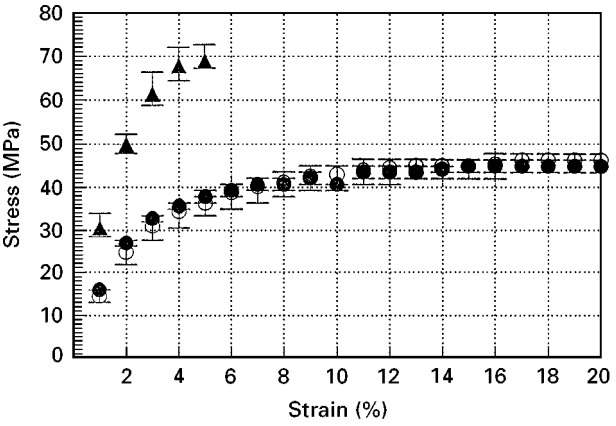

Figure 8 Stress–strain data for Nylon 6,6 Maranyl/Vectra A900 blends of composition: (○) 20% Vectra, (▲) 25% Vectra and (●) 30% Vectra.

low tensile strength is expected. Injection moulding is a process which usually produces a sandwich morphology with high molecular orientation in the skin regions and low orientation in the core. Orientation at the centre tends to be perpendicular to the tensile stress direction due to previous diverging polymer flow at the gate of the moulding.

3.3. Microstructural studies of Maranyl nylon 6,6/vectra blends

SEM micrographs of the fractured surfaces were obtained from both the skin and core regions from each type of specimen. In general, a distinctive fibril formation was observed in the blend where the fibrils seemed to be present in large quantities in the skin region. The fibrils were essentially oriented in the flow direction (longitudinal direction) in the skin. In all cases, Vectra was the minor component found in suspension whereas nylon 6,6 was the major matrix component.

Fig. 9(a–c) presents micrographs from the skin region at various Vectra contents. The skin appeared to be approximately 600 μm deep in all types of specimens and corresponding blend compositions.

It is the size and nature of fibrilar domains that changes with blend composition. The 20 vol% Vectra specimen displays a large amount of oriented fibrils, the orientation of which must have been enhanced during drawing in the tensile testing. The fibrils have a diameter of the order of 1 μm. The 25 vol% Vectra specimen displays clearly a much higher amount of fibrils adhered into thick bundles which are dispersed in the nylon matrix. The much higher content of fibrils justifies the increase in tensile modulus and strength

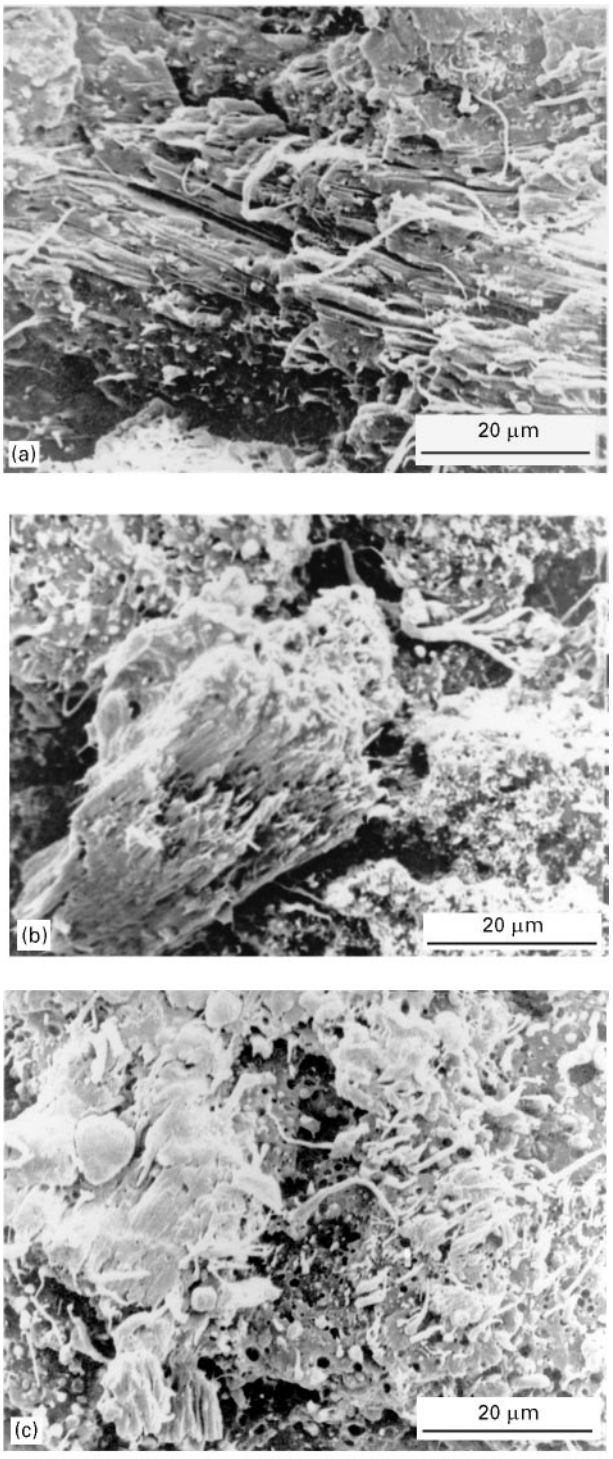

Figure 9 SEM micrographs obtained from the skin region of the fractured surface of Nylon 6,6 Maranyl/Vectra A900 blends (a) 20 vol% Vectra; (b) 25 vol% Vectra; (c) 30 vol% Vectra.

and also the reduction in the elongation to break. This specimen seems to have a larger amount of LCP in the skin region than the other specimen of 20 vol% Vectra. As the Vectra content is raised to 30 vol%, the thin fibrils are not so well distinguishable but seem to coalesce with each other inside the bundles. This tends to yield thicker fibres of irregular cross-section and smaller aspect ratio. As a result the tensile modulus drops.

The matrix becomes continuously depleted of long oriented fibrils as one moves further from the surface until roughly 900–1000 μm from the edge, where the core region begins. Fig. 10 shows an example of a micrograph from the core region. The core shows

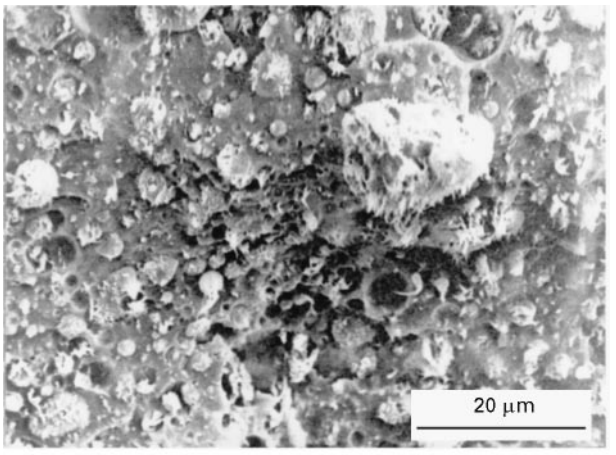

Figure 10 SEM micrograph obtained from the core region of the fractured surface of the 25/75 vol% Vectra/Maranyl blend.

approximately spherical regions of Vectra within the nylon matrix. These regions increase in number and size, from around 2–8 μm, with increasing Vectra content, appearing to sit in cavities and some more freely on the surface. Their shape is attributed to the low shear stresses in the central region during processing which do not result in any deformation or orientation of LCP domains. They are generally hairy containing very short fibrils irregularly oriented which contribute little to reinforcing the matrix.

Fig. 11(a and b) presents the difference between the fracture of a Vectra A900 injection moulded specimen and a blend specimen of 20 vol% Vectra. A lamellar structure is developed during the processing of Vectra A900 which consists of layers of nematic domains of different orientation with poor adhesion between the layers (see also reference [14]). This leads to delamination of the layers parallel to the tensile stress which is clearly visible at the fracture surface of the Vectra A900 specimen in Fig. 11a. The presence of isotropic nylon 6,6 in the blended specimen seems to improve adhesion between layers and contributes to significant reduction of delamination and layer separation (see Fig. 11b). Individual fibrils of the Vectra phase are clearly visible in the skin region of the blended specimen and their formation at high volume fractions leads to an increase in tensile modulus.

4. Conclusions

Tensile specimens from pure Vectra and from blends of nylon 6,6 with Vectra were prepared by injection moulding. Low injection pressures led to a better Young's modulus and tensile strength in Vectra specimens whereas melt temperature changes in the range of 290–300 °C had small effects on the above mechanical properties. As a result, the optimum processing conditions in terms of self-reinforcing behaviour of Vectra were specified as an injection pressure of 50 MPa and a nozzle melt temperature of 300 °C, which were also employed in the injection moulding of nylon 6,6/Vectra blends.

The addition of an LCP to nylon appeared to reduce the viscosity of nylon and ease processing. The blends had a two-phase morphology and exhibited

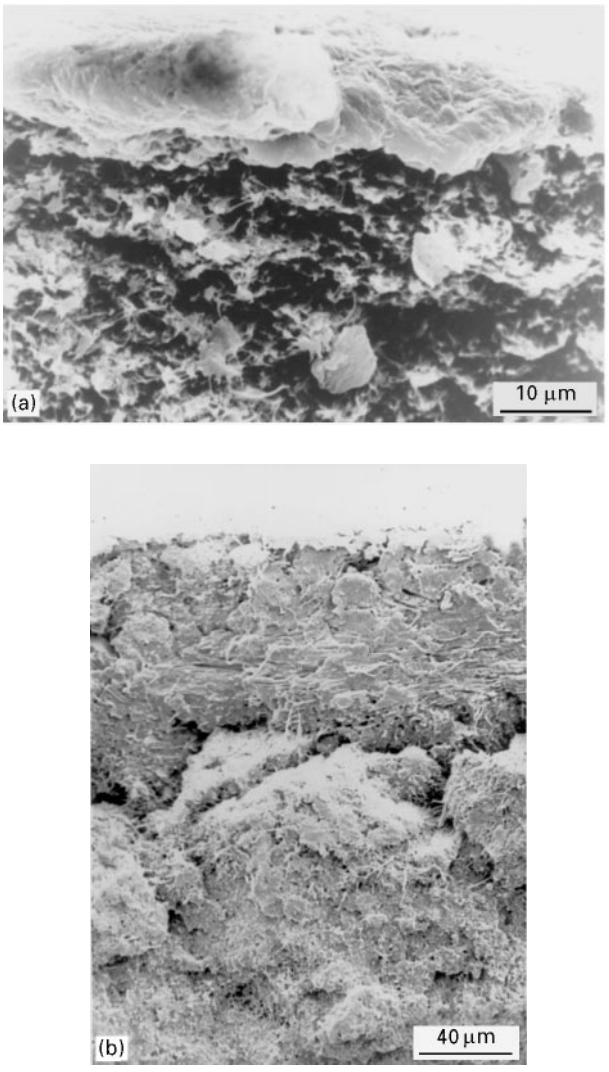

Figure 11 A comparison between the fracture surfaces of Vectra A900 and the 20/80% Vectra/Maranyl blend.

mechanical behaviour similar to that of composite materials. The presence of the isotropic matrix seemed to improve adhesion between the nematic domains of LCP and contribute to the reduction of delamination at fracture, in agreement with previous findings in the literature. The injection moulded specimens displayed a skin and a core region with the skin greatly affecting the mechanical properties. Changes in the blend composition affected the density and structure of the oriented fibrilar domains in the skin, and hence, the self-reinforcing behaviour.

In previous studies of injection moulded LCP/nylon blends [5, 6, 17] it was reported that the skin contained mainly spherical nematic domains at low LCP concentrations up to 10%, fibrillar nematic domains at high LCP concentrations of 30–50% and ellipsoidal nematic domains at intermediate LCP concentrations. Under the processing conditions specified in this study, fibrillar nematic domains were observed in the skin region at 20 vol% LCP. As the LCP content was increased the concentration of fibrillar nematic domains in the skin region also increased. A composition of 25 vol%. Vectra seemed to give the highest Young's modulus and tensile strength and the lowest strain to failure. Microstructural studies revealed that at that composition the skin contained the largest amount of fibrillar nematic domains arranged in thick bundles. Above this concentration of Vectra the fibrils started coalescing into thicker fibres of irregular cross-section and smaller aspect ratio which resulted in a reduction of the Young's modulus and strength.

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