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# Blending thermotropic liquid crystal and thermoplastic polymers for microreinforcement

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A new process to obtain fibrous shaped thermotropic liquid crystal domains in bulk forms by proper blend processing with engineering thermoplastic polymer systems is presented. Normally, unless such a blend has experienced high elongational flow, the liquid crystalline domains are globular in shape and provide little or no improvement in tensile mechanical properties. One solution to this dilemma was to make the liquid crystalline domains small enough so that their size approaches that of microvoids in the thermoplastic polymer system. Preliminary investigations were made to demonstrate the process. It was then successfully applied to a thermoplastic polymer for use in aircraft interior panels. Besides the tensile mechanical property improvement, several other properties were greatly improved. One of these was fracture toughness, which doubled in value. © 1998 Elsevier Science Ltd. All rights reserved.

**(Keywords: liquid crystal; Vectra; thermoplastics)**

## INTRODUCTION

The use of thermoplastic resins as matrix materials for fibre reinforced composites has had success in aerospace applications. However, the inherent high melt viscosity of engineering thermoplastic polymers inhibits flow into fibrous mats and therefore precludes low cost manufacturing processes such as resin transfer moulding (RTM) for structural composites. One could use thermotropic liquid crystalline polymers (TLCP), but the low viscosity in the temperature range above the crystalline-to-nematic transition temperature $T_{CN}$, and below the nematic-to-isotropic transition temperature $T_{NI}$, results in very high orientation of the TLCP molecules upon flow. When used as a matrix polymer in continuous filament mats, very low mechanical properties transverse to the composite fibres are observed. Another approach is to use a blend of TLCP and engineering thermoplastic as a chopped fibre composite. If the use-temperature of such a composite is below $T_{CN}$, the elongated TLCP domains can be viewed as reinforcing, "fibres". Such composites being completely thermally processable would be recyclable. The reinforcing fibre or elongated TLCP domains would be formed when the processing temperature was between $T_{CN}$ and $T_{NI}$ of the TLCP. The thermoplastic resin must also be a melt in this temperature range. Later, we show how this concept is successfully applied to form aircraft interior panels which are tough at −40°C and have enhanced properties at room and elevated temperatures.

Siegmann *et. al.*[1] were among the first to publish work related to TLCP/flexible chain polymer blends where the TLCP formed reinforcing fibres during processing. They studied blends of a naphtholic acid based TLCP with an amorphous polyamide (nylon). They reported a significant reduction in viscosity of the blends when compared with the viscosity of the neat polymers. A minimum in viscosity was reached with the addition of as low as 5% by weight of the TLCP. Reduction of viscosity upon addition of LCP is also described in the patent literature[2,3]. A common problem when extruding blends of TLCP and thermoplastics is that a sheath-core morphology results. An increase in the TLCP content coincides with a change from droplet to fibrillar morphology of the TLCP phase. However, the sheath-core morphology associated with increasing the TLCP content has prevented further development. More recently, Isayev and Modic[4] studied blends of polycarbonate (PC) with two naphtholic acid based TCLPs. Their results, however, showed that the fibrillar morphology was only achievable at low (10%) concentrations of the TCLP phase. At higher levels, the TCLP assumed a droplet form resulting in thermoplastic composites with poor mechanical properties. It was also shown that a reduction in impact strength (notched Izod) of the TCLP reinforced PC was observed in comparison to glass fibre reinforced PC.

Kiss[5] reported on the results of his investigation of several flexible chain polymers such as polyetherimide (PEI), polyethersulfone (PES), polyetheretherketone (PEEK), polyacetal (PA), and polycarbonate (PC) blended with TCLPs containing naphthalene moieties along the backbone. At 30 weight percent of TCLP (30/70 weight per weight composition) he found a significant improvement (100–300%) in the tensile modulus and strength of the blends when compared with neat matrix resin properties. However, Izod impact and elongation-at-break properties suffered in comparison. Even though Kiss reports improved mechanical properties, he says nothing specific about the TLCP chemical composition or the processing conditions.

Joseph *et. al.*[6] studied blends of TLCP60 with PET. The morphology of injection moulded plaques exhibited a

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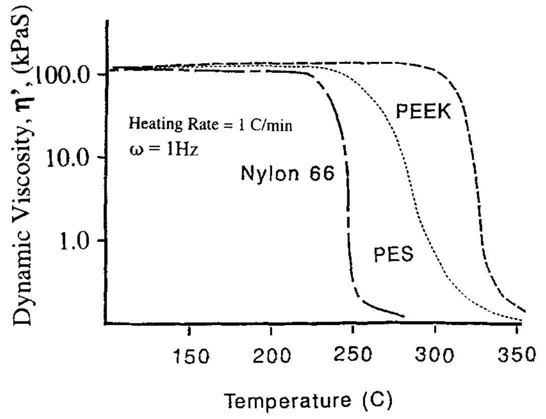

**Figure 1** Rationale for choosing Nylon 6-6, PES, and PEEK as matrix polymers

sheath-core structure where the skin exhibited fibrils of the TLCP phase and the core showed droplets of the TLCP. The processing conditions were not investigated and although compatibility (miscibility) was alluded to as a basis for selecting PET, no attempt was made to elaborate on this factor.

More recently, Zhuang *et al.*[7] studied blends of hydrobenzoic acid based TLCP (TLCP60) with polycarbonate (PC), polyethylene terephthalate (PET) and polystyrene (PS). On the basis of calorimetry, dielectric, and dynamic mechanical analysis, a claim was made that PS was totally immiscible, PC partially miscible, and PET completely miscible with the PET component of the TLCP. They found improvements in tensile properties and the presence of TLCP fibrils, but no effort was made to explain the reason for that morphology.

In all these examples, the reinforcing fibres (TLCP) were generated in an elongational flow field. Once the temperature is lowered below $T_{CN}$, it is the fibrous shape (formed during post extrusion elongational flow) of the TLCP regions that provides reinforcement to the matrix polymer.

While attempting to disperse individual rigid rod molecules in thermoplastic and thermoset matrices, one constantly tries to minimize phase separation[8,9]. With this background in mind, we focused on forming micro- to nano-size TLCP domains. That is, we wanted to approach the size of microvoids in the thermoplastic polymer matrix. The shapes would be fibrous and form a microsize mesh. In an effort to achieve this type of morphology, the well-known dispersive and distributive concepts of polymer mixing were considered[10]. To achieve this goal, Vectra B900 was elected as the TLCP. This required mixing temperatures between $T_{CN} = 285°C$ and $T_{NI} = 350°C$ for the nematic range of Vectra B900 and a thermoplastic matrix polymer with a relatively high melt viscosity in this temperature range, i.e. at 1 Hz, $\eta_{matrix}'/\eta_{TLCP}' \geq 10^3$.

Rheological investigations led us to consider three matrix polymers to investigate the concept. These matrix polymers were polyamide (Nylon 6-6), $T_m = 245°C$, polyethersulfone (PES), $T_{flow} = 287°C$, and polyetheretherketone (PEEK), $T_m = 347°C$ (see *Figure 1*). It has been observed that once Vectra has been above $T_{CN}$ in an extruder, it retains its low LC viscosity to cooler temperatures (25°C lower)[11,12]. This would make Nylon 6-6 a good matrix-resin candidate for commercial use if the TLCP was extruded prior to mixing with the engineering thermoplastic resin.

## EXPERIMENTAL

### *Materials*

The thermotropic liquid crystal polymers (TLCP) used in this study were Vectra B900, and a research sample RD501, both products of Hoechst Celanese Corporation. Preliminary studies used Victrex PEEK 450G and Victrex PES 3600G both by ICI and Zytel 42 (Nylon 6-6) by DuPont Chemical Company. The matrix polymer used for aircraft interior panels was Mindel S1000, a polysulfone alloy by Amoco Chemical Company.

### *Processing*

The extruder used for processing the TLCP/engineering thermoplastic blends was a single screw Brabender extruder, Model PLV-300. The screw used was a 24 to 1 ratio plastics screw with an approximately 2 inch section with mixing pins. The extruder has three temperature controlled zones with zone 1 being nearest to the input hopper and zone 3 being closest to the exit die (*Figure 2*). At the exit to the extruder we attached a half-inch stainless steel mixer made by Liquid Control Corporation. The actual inside diameter of the tube, or outside of the stainless steel static mixers was 1/4 inch. There were 10 platelets in the approximately 6 inch long tube. *Figure 2* also shows a temperature controlled return flow tube and switching valve attachment which provided a cycling capability for successive passes through the static mixer. Once an optimum amount of mixing was determined, this return flow system was removed and if, for example, two passes were optimum, two 1/2-inch static mixers were added to the end of the extruder.

For the aircraft interior panels, the extrudate was cut into 1/2-inch-long fibres and were compression moulded into

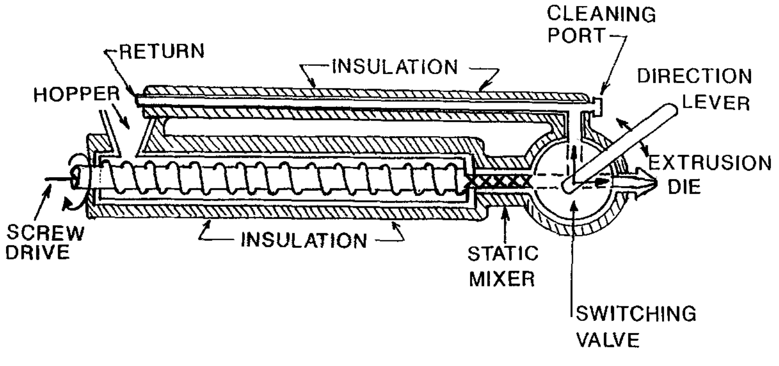

**Figure 2** Processing system used to disperse and distribute TLCP in engineering thermoplastics

15.2 cm × 45.7 cm × 0.32 cm panels using a TMP Inc. vacuum hydraulic press.

Control samples were prepared by grinding sequenced blend compositions of Vectra/Nylon 6-6, Vectra/PES, and Vectra/PEEK in a condux Grinder cooled with dry ice. These powdered blends were then fed into a Brabender extruder having a screw with a pin section for further mixing.

### *Measurement of blend properties*

Mechanical property measurements were made with a Model 4208 Instron Tensile Tester. Thermomechanical properties were measured using a Rheometrics Dynamic Mechanical Thermal Analyzer (DMTA). Thermal characterization was achieved using a Perkins-Elmer Model 2C Differential Scanning Calorimeter (DSC). The morphology of the processed test specimens was determined with a JOEL Model JSM-35 scanning electron microscope. Rheological parameters were determined with a Bohlin VOR rheometer using the 25 mm parallel plate geometry.

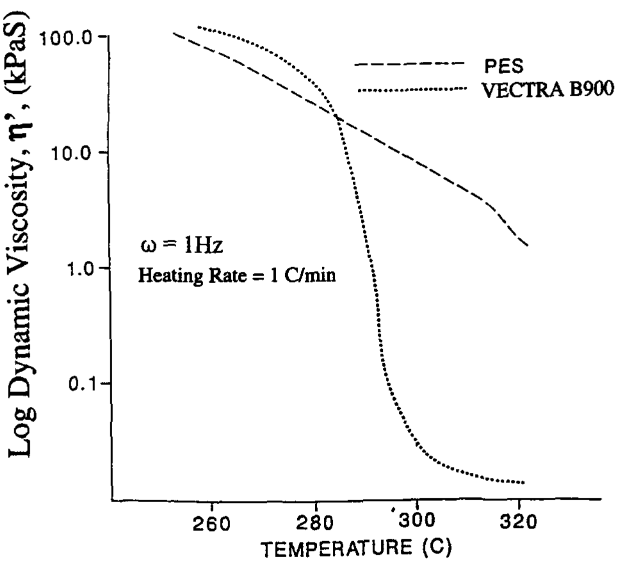

**Figure 3** Viscosities of PES and Vectra B900 as function of temperature (1 kPaS = $10^4$ poise)

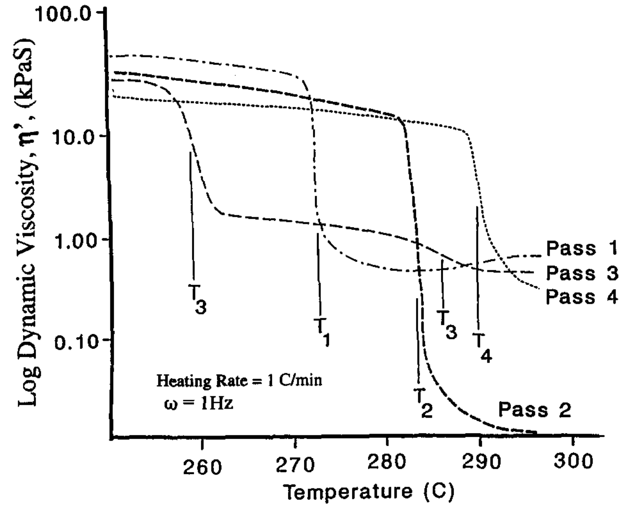

**Figure 4** Viscosities of (10/90) Vectra B900/PES blend for various number of passes through the extruder–static-mixer system

## RESULTS AND DISCUSSION

The best mechanical properties of the control samples in terms of modulus were obtained from a 40/60 Vectra B900/PES blend. Its tensile modulus, strength, and percentage elongation-at-break were 6.1 GPa, 42.0 Mpa, and 1.8%, respectively, while the tensile modulus of neat PES was 0.76 GPa. In order to avoid any contribution of crystallite formation in PEEK affecting the mechanical properties of the composite, we focused our attention on the amorphous polymer PES.

To establish a temperature for extruding Vectra B900/PES blends using the extruder/static-mixer configuration presented in *Figure 2*, a viscosity *versus* temperature plot of superimposed neat Vectra B900 and PES results is shown in *Figure 3*. We see that at about 300°C and at 1 Hz, the dynamic viscosity ratio, $\eta_{\mathrm{PES}}'/\eta_{\mathrm{Vectra}}' \sim 10^3$. *Figure 4* presents viscosities of a 10/90 blend of Vectra B900/PES,

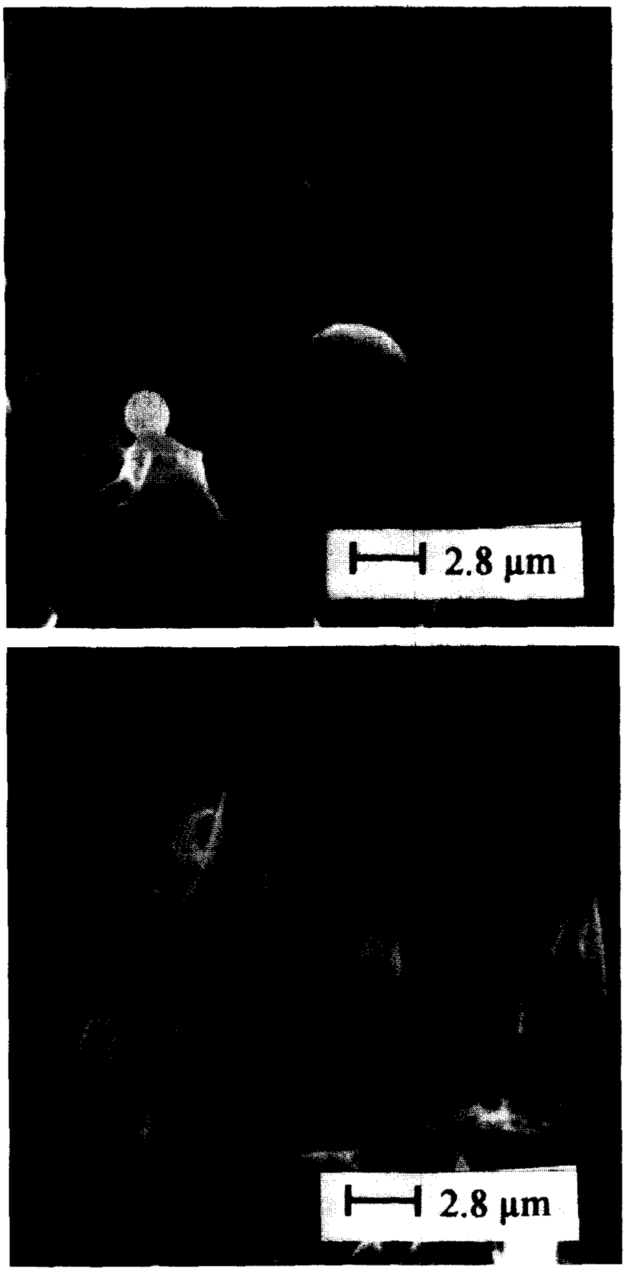

**Figure 5** SEM photomicrograph of a (10/90) Vectra B900/PES blend from (a) pass 1, and (b) pass 2. These tapered and rod-like domains were from pass 2, 5, and 6

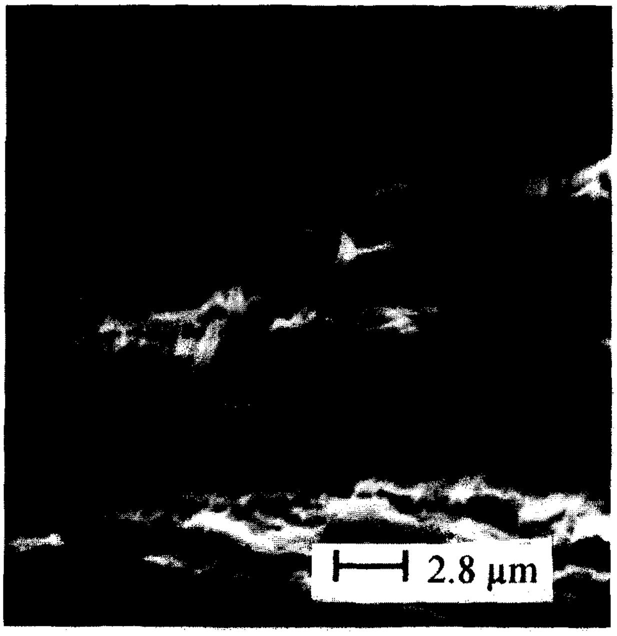

**Figure 6** SEM photomicrograph of a (10/90) Vectra B900/PES blend sample from pass 5. Note the fine fibrous strands of the small domains. This type was also found in samples from pass 2, pass 3, and pass 4, but not in those from pass 1

extruded at 300°C after successive passes through the static mixer. The results for pass number 3 showed a lower $T_g$ than those of other passes. Since the test sample was very small, (0.3 mm thick × 25 mm diameter) it may be an artifact of non-uniformity. The experiment was not repeated. The shift of the softening temperature with the number of passes was interpreted as more intimate mixing being achieved at each pass, i.e. obtaining a finer dispersion of TLCP domains.

Scanning electron micrographs (*Figure 5*) show that after two passes elongated domains are being formed. *Figure 6* shows that an enhanced fibre dispersion was gained by further passes through the static mixer. The fibrils have diameters of 0.2 μm to 0.5 μm (200–500 nm).

Dynamic mechanical properties were determined for a 30/70 Vectra B900/PES blend (see *Figure 7*). Pass number 4 showed the greatest increase in storage modulus, $E'$. *Figure 8* presents a scanning electron micrograph of a freeze-fractured cross section of an extrudate after pass number 4. Here the liquid crystalline domains are definitely fibrillar and have a diameter of 200 to 500 nm.

**Table 1** Mechanical properties of a Vectra RD501/resin (Mindel S 1000, Firebrake, FSA) blend

| | Composition | |
|---|---|---|
| Properties | 0/100 | 5/95 |
| Moulding temperature (°C) | 280 | 260 |
| Tensile modulus (GPa) | 2.55 | 2.75 |
| Tensile strength (MPa) | 41.30 | 42.70 |
| Flexural modulus (GPa) | 2.55 | 2.75 |
| Flexural strength (Mpa) | 71.60 | 81.30 |
| Izod impact (J/m crack) at −40°C | 29.90 | 58.20 |

To apply this concept to a real application, we added four static mixers in series to the end of the Brabender extruder. This was the equivalent of four passes in the previous system. The extrusion was performed at 30 to 80 rpm and the material was forced through a die at the end of the static mixers to provide a strand. The heating profile was: zone 1, 230°C; zone 2, 250°C; zone 3, 270°C, and static mixer, 290°C. The strands were hand ground and dried before melt compression moulding into 15.2 cm × 45.7 cm × cm test sheets at 47 000 N under vacuum. The liquid crystalline polymer was Vectra RD 501. The matrix resin was Mindel S1000 a polysulfone alloy from Amoco. The material tested contained zinc borate (Firebrake XPI 187), a flame retardant additive, and small particle PTFE (FSA, Fluoromist). The 100% resin contained 94 parts Mindel S1000, 5 parts Firebrake and one part FSA by weight. A (5/95) composition of Vectra RD501/resin contained 5 parts Vectra RD501, 89 parts Mindel S1000, 5 parts Firebrake, and one part FSA by weight.

The mechanical properties are presented in *Table 1*. There is an improvement in modulus and strength properties for both tensile and flexural modes of measurement. If we use equations applied to short-fibre reinforced composites[8,9], insight can be gained as to the equivalent fibre length or average aspect ratio of the dispersed LCP nanoscale domains. The tensile modulus of the Vectra B900 was measured as 11.0 GPa. From *Table 1* the matrix

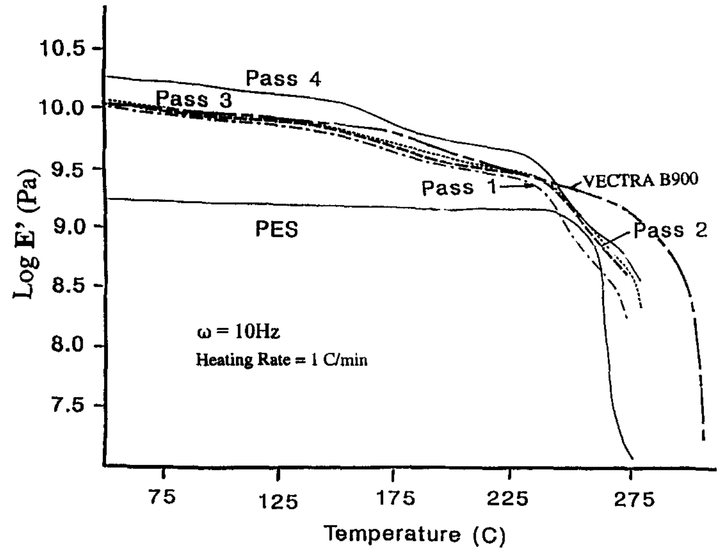

**Figure 7** DMTA results for a (30/70) Vectra B900/PES blend from passes 1, 2, 3, and 4 through the single screw/static mixer processing system

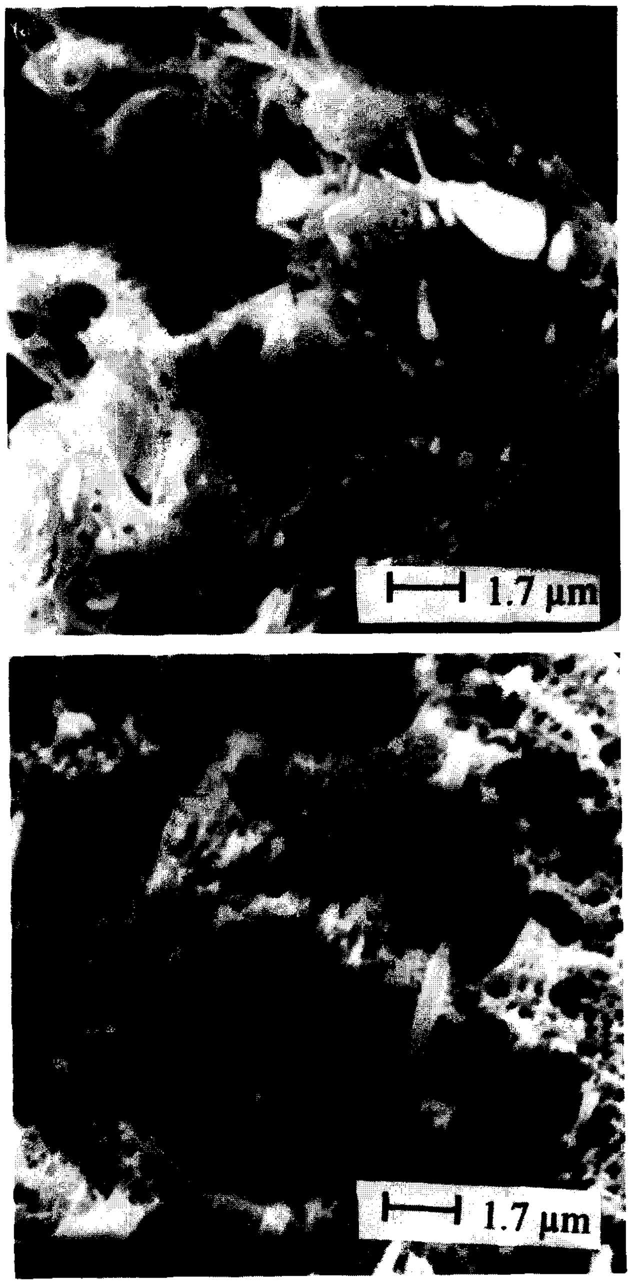

**Figure 8** Fracture surface at two different cross sections of a (30/70) Vectra B900/PES blend extrudate

tensile modulus is 2.55 GPa and the isotropic tensile modulus of a 5/95 blend is 2.75 GPa. Using the equations given by Wiff and Lenke[8] and Wiff *et al.*[9], the average aspect ratio is 0.25. Taking the diameter of the LCP to be approximately 300 nm (typical for the 10/90 blend results shown in *Figure 6* and the 30/70 blend results shown in *Figure 8b*) the length of the typical LCP reinforcement domain is about 74 nm. This is much too small and implies the reinforcements are not needle- or fibre-shaped, but rather form a nanoscale disk or platelet. In addition to the enhancement of modulus, the surprising finding was that the Izod impact at −40°C doubled in value. This is something which should be further investigated. Again a possible explanation is that the LCP domains are not globular or needle-like, but form an interconnecting network of nanoscale platelets.

## CONCLUSION

Special processing techniques applied during blending of a TLCP (Vectra RD501) with polysulfones and polysulfone copolymers produced blends with improved isotropic mechanical properties (flexural and tensile modulus and strengths, and low-temperature impact strengths). The unique characteristic of these materials is that their properties are isotropic, i.e. one can make bulk forms other than fibres. Scanning electron micrographs of the TLCP/thermoplastic blends indicate that the improved properties are the result of nanoscale fibrous TLCP domains. The uniform dispersion and small size were achieved through the use of static mixers at temperatures where the TLCP is in the nematic state and the thermoplastic is a melt.

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