Fibres from polypropylene and liquid crystal polymer (LCP) blends: 1. Effect of LCP concentration

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Polypropylene (PP) resin and a thermotropic liquid crystal polymer (LCP) were mixed and coextruded on a screw extruder. The LCP was found to exist in fibril form above a PP/LCP (wt/wt) ratio of 100/5 and a PP/LCP ratio of 100/15 the LCP existed in a network structure. For the as-spun fibre, both the initial modulus and the yield stress increased with the increase in the LCP concentration. In the drawn fibres, however, the LCP fibrils were found to be split into short fragments. A two-stage drawing process was used in order to reduce the extent of fracture of the LCP fibrils. The drawn fibres were found to contain more long fibrils from the two-stage process and as a result, there were significant increases in both the tensile strength and initial modulus of the two-stage drawn fibres.

(Keywords: polypropylene; liquid crystal polymer; polyblend fibre; melt extrusion)

INTRODUCTION

The process of making fibres from polymer blends has attracted much scientific and industrial interest[1,2]. By mixing two or more polymers, polyblend fibres can be produced with properties that are not obtainable with the individual polymers. The fibre properties can be tailored to suit specific needs by adjusting the blend composition and phase morphology, thus producing cost effectiveness. A number of polyblend fibres have achieved commercial successes[2]. For example, a 70/30 mixture of nylon 6 and poly(ethylene terephthalate) (PET) was used to produce non-flatspotting nylon tyre yarn, taking advantage of the high glass transition temperature and modulus of the PET component[3].

In recent years, liquid crystal polymers (LCPs) have attracted a great deal of attention. These polymers usually consist of rigid rod-like molecular chains and can be shaped into highly oriented structures using conventional processing conditions[4]. There have been a number of attempts to blend LCPs with conventional polymers[5–8]. This process can be beneficial in two ways. First, as LCPs usually have low solution or melt viscosities, there can be an improved processibility for the polyblend. Second, mechanical properties such as the strength and modulus can be enhanced due to the inherited high strength and modulus of the LCPs.

The structures of the polyblend fibres are affected by the chemical structures of the individual components and the processing conditions in general[1]. Most polymer/polymer blends are incompatible and the individual components exist in separate phases. According to Hersh[2], the minor component usually exists in three different forms, i.e. particles, fibrils and an interpenetrating network. In a polyblend of LCP and conventional polymers, the LCP would preferably exist in thin fibrils of large aspect ratios to achieve reinforcement. There are many experimental parameters affecting the LCP phase morphology, such as the viscosity ratio of the two-component polymers, the degree of shearing, etc.[9–16].

In this paper, we report a process for producing fibres from blends of polypropylene (PP) and a LCP. We found that in an appropriate range of LCP contents, reinforcing fibrils could be formed within a PP matrix, thus producing *in situ* composite fibres.

EXPERIMENTAL

Materials

The thermotropic LCP, Vectra A900, was supplied by Hoechst Celanese Corporation. It is an aromatic copolyester based on 6-hydroxy-2-naphthoic acid and *p*-hydroxybenzoic acid and has a melting point of 280°C. The PP resin, Appryl, has a melt flow index of 3.

Melt extrusion and hot-stretching

Melt extrusion was carried out on a 25 mm single screw Labspin extruder (Extrusion Systems Ltd) with a 2.5 cm³ metering pump. The die head was equipped with a single hole spinneret ($d = 0.5$ mm).

PP granules and LCP chips of various proportions were tumble-mixed before they were loaded onto the extruder. The temperature profile was 230/285/285/285/280/280°C which represents the temperatures of three barrel zones, the metering pump and two heating zones in the die head. Normally, the pump speed was 1.6 rev min⁻¹ which is equivalent to an extrusion rate of 20 m min⁻¹. Unless otherwise indicated, a take-up speed of 60 m min⁻¹ was used.

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The as-spun fibres were hot-stretched on a small-scale drawing unit consisting of two pairs of advancing rollers and a hot plate. In one-stage drawing, the as-spun fibre was fed at $6\,m\,min^{-1}$ and was drawn to the maximum ratio at 150°C. In two-stage drawing, the fibre was partially drawn at 130°C before it was stretched to the maximum extent at 160°C.

Tensile testing

Tensile properties were obtained on a Nene tensile tester. The test was carried out at 20°C, 65% relative humidity with a gauge length of 20 mm and an extension rate of $20\,mm\,min^{-1}$ except where otherwise indicated. The fibre thickness was measured in tex which is the weight in grams of 1000 m of fibre. The fibre tenacity was expressed in Newton tex^{-1}. The figures quoted are the average of 10 tests, with the standard deviation being generally < 5%.

Hot-stage microscopy

The LCP phase was observed on a Leitz hot-stage microscope. A piece of the fibre was heated to 185°C and it was pressed vertically between two glass slides to form a thin film. The LCP phase was then observed at a magnification of × 400.

RESULTS AND DISCUSSION

Figure 1 shows the hot-stage photomicrographs of three samples of the polyblend fibres with PP/LCP (wt/wt) ratios of 100/2.5, 100/5 and 100/15. It can be seen that within the as-spun fibres, the LCP and PP exist in separate phases. The LCP phase exists mainly in particles and short fibrils at a PP/LCP ratio of 100/2.5. At a ratio of 100/5, long fibrils can be observed. Further increase in the LCP concentration to 100/15 leads to the formation of a network structure as shown in *Figure 1c*. In fact, beyond this critical concentration, the as-spun fibre became very brittle. It was not possible to collect the 100/20 sample as frequent fractures of the as-spun fibre occurred during winding.

In the literature, the formation of LCP fibrils in *in situ* composites has been well documented[6,8]. Weiss et al.[17] reported that when an extensional component is present during processing of the melt, the LCP component of the blend forms an elongated, fibrous phase that orients in the direction of flow. Because of the long relaxation times of the LCP, the fibrous nature of the dispersed phase may be preserved even in cases where the extensional flow is followed by a simple shear flow. Paul[1] pointed out that at the spinneret hole entrance, a rapid acceleration begins, which produces an elongational flow that deforms the dispersed phase into fibril form. Tsuruta et al.[18] found that when LCP powder and polysulphone are blended, the microstructure is dependent on both the particle size and the LCP content. The appropriate proportion of the LCP lies between 1% and 80% and preferably between 5 wt% and 70 wt% on the basis of the total weight of the matrix resin and the LCP. If the LCP is employed in an amount below 1%, the mechanical properties of the final products would not be improved to any appreciable extent. On the other hand, if the LCP is employed in a proportion of > 80%, the fibres of the LCP in the matrix would tend to coalesce into a sheet-like structure, resulting in poor reinforcement.

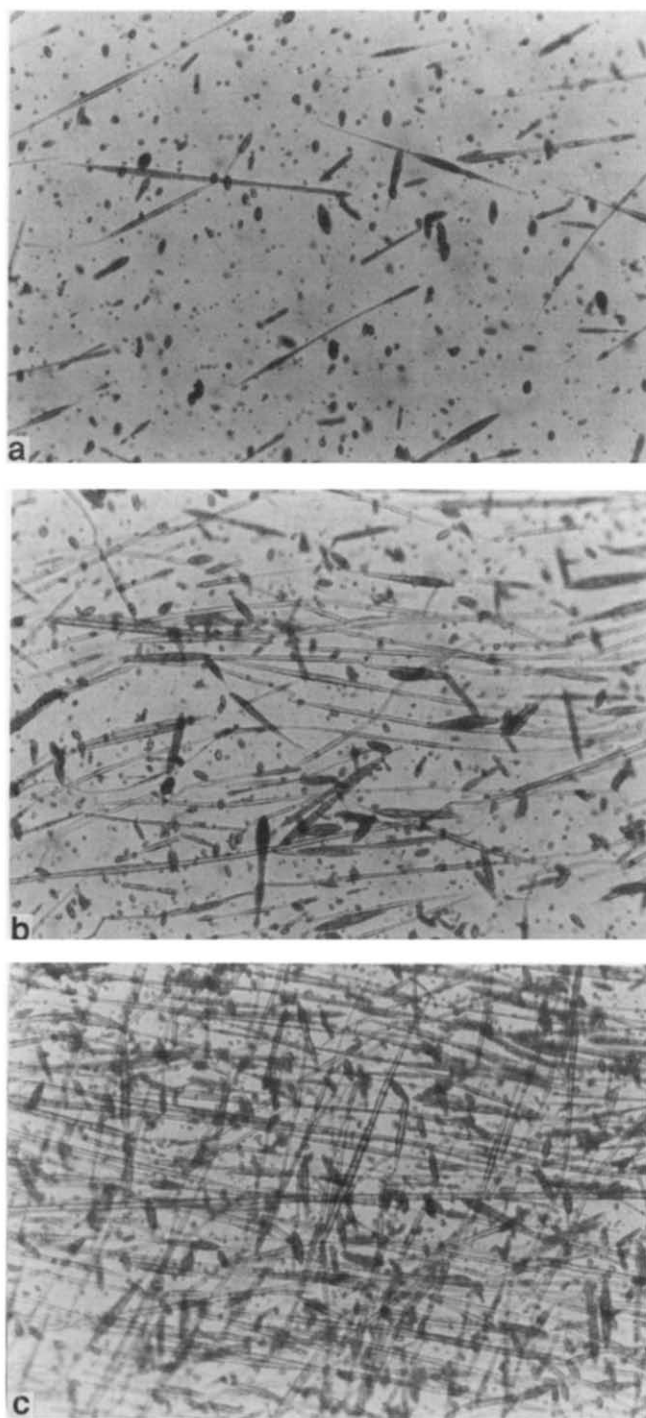In this work, the transformation of the LCP into fibrils

Figure 1 Hot-stage photomicrographs (× 267) of PP/Vectra A900 blends (wt/wt): (a) 100/2.5; (b) 100/5; (c) 100/15

may take place in three stages. First, when the PP/LCP blend passes through the screw, the metering pump and the filtering materials, a certain degree of shear and elongational strain is applied to the polymer melt. Second, there is an elongational flow at the spinneret hole entrance where deformation can take place. Third, there exists an elongational strain below the spinneret which can deform the LCP phase.

Figure 2 shows the LCP phases at extrusion rates of 16.2 and $37.5\,m\,min^{-1}$. It is clear that the LCP fibrils are thinner at a higher extrusion rate, indicating the effect of the degree of shearing involved. Similarly, thin LCP
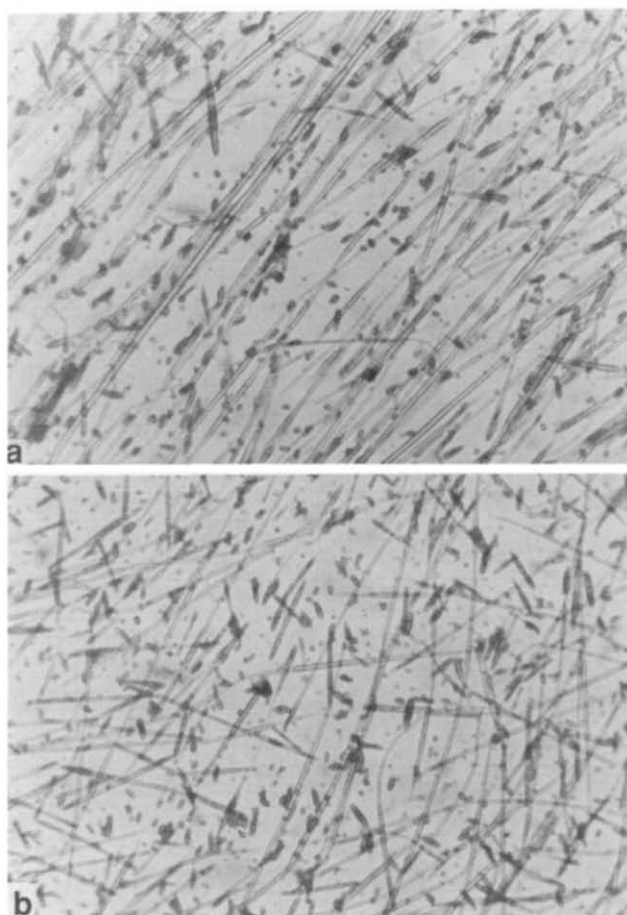
Figure 2 LCP phases ($\times 267$) at extrusion rates of : (a) $16.2 \, \mathrm{m \, min^{-1}}$; (b) $37.5 \, \mathrm{m \, min^{-1}}$, pp/LCP (wt/wt) ratio 100/10
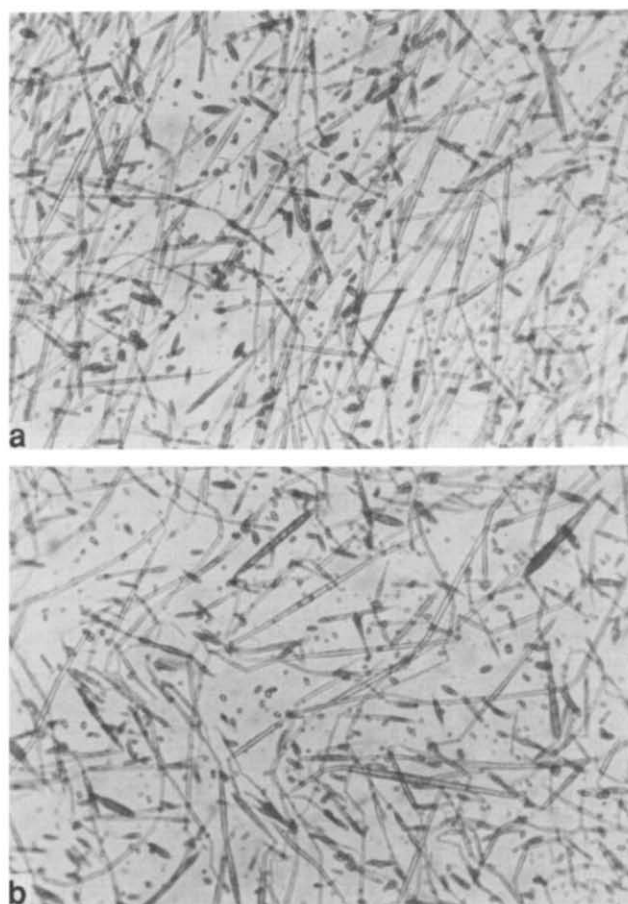
Figure 3 LCP phases ($\times 267$) at take-up speeds of: (a) $150 \, \mathrm{m \, min^{-1}}$; (b) $75 \, \mathrm{m \, min^{-1}}$, PP/LCP (wt/wt) ratio 100/10

fibrils were observed when a high take-up speed was used. *Figure 3a* shows the LCP fibrils at a take-up speed of $150 \, \mathrm{m \, min^{-1}}$, while in *Figure 3b* a take-up speed of $75 \, \mathrm{m \, min^{-1}}$ was used. It can be seen that at a low take-up speed, the LCP fibrils exist in a coiled structure.

Table 1 shows the tensile properties of the as-spun fibres tested with a gauge length of 20 mm and an extension rate of $2 \, \mathrm{mm \, min^{-1}}$. Both the initial modulus and yield stress showed increases with increase in LCP concentration, indicating the reinforcement of the LCP fibrils. Compared to the pure PP fibre, the 100/15 sample showed a 54.0% increase in initial modulus and a 60.0% increase in yield stress. The load–extension curves of the as-spun PP and polyblend fibres are shown in *Figure 4*. It is interesting to note that while the pure PP fibre and the PP/LCP polyblend fibres containing < 12.5% LCP showed clear yield points and ductile fractures, the sample containing 15% LCP did not yield and gave a brittle fracture.

The tensile properties of the fibres drawn at 150°C are shown in *Table 2*. It can be seen that although the initial moduli showed improvement in some cases, the tenacities of the polyblend fibres were generally poorer than that of the pure PP fibre. *Figure 5* shows the hot-stage photomicrograph of a drawn polyblend fibre. It is clear that after drawing the LCP fibrils were split into short fragments. These fragments have aspect ratios of ~10 which is very low; it has been suggested[19] that the aspect ratio should be above 40 to achieve effective reinforcement.
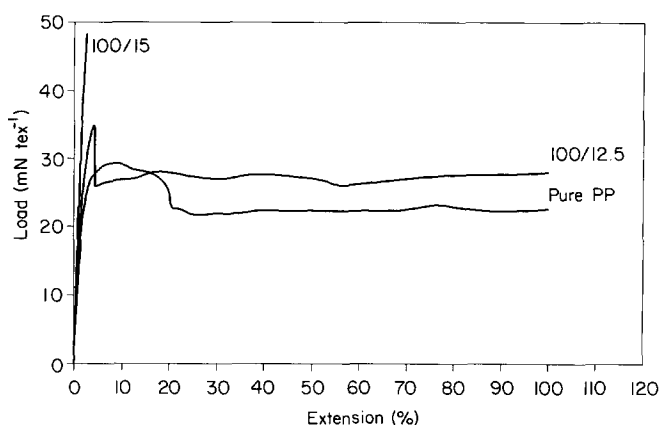

Figure 4 Load–extension curves of the as-spun fibres

Table 1 Effect of LCP concentration on specific modulus and yield stress of the as-spun fibres[a]

PP/LCP (wt/wt) ratio	Tex	Specific modulus (N tex^{-1})	Increase over PP (%)	Yield stress (mN tex^{-1})	Increase over PP (%)
100/0	44.87	0.927		28.5	
100/2.5	47.36	0.974	+5.1	30.0	+ 5.2
100/5	47.61	1.108	+19.5	35.6	+24.9
100/10	47.00	1.071	+15.5	32.9	+15.4
100/12.5	47.20	1.205	+30.0	38.9	+36.4
100/15	48.14	1.428	+54.0	45.6[b]	+60.0

[a] Testing conditions: gauge length, 20 mm; extension rate, $2 \, \mathrm{mm \, min^{-1}}$
[b] Breaking stress

The fracture of the LCP fibrils can be attributed to the distinct differences in the extensibility of the as-spun PP and Vectra A900 fibres. While the pure as-spun PP fibre consists of a random molecular structure with little orientation and is hence very extensible, the as-spun Vectra A900 fibre has an extension at break of <5%. Fracture of the LCP fibrils during hot-stretching is therefore unavoidable. Similar problems have been reported where polyblend fibres of conventional polymers were processed[2].

It is interesting to note that although a number of studies have claimed improved mechanical properties from polyblends of conventional polymers and LCPs, most of them are involved with either injection moulded products or thick extruded strands[5-9]. In these cases, the improvement of the initial modulus and breaking load is similar to the improvement of the initial modulus and the yield stress obtained for the as-spun fibres in this

Figure 5 Hot-stage photomicrograph (×267) of a drawn sample [PP/LCP (wt/wt) ratio 100/10]

Table 2 Draw ratios and fibre properties from one-stage drawing at 150°C

PP/LCP (wt/wt) ratio	Tex	Draw ratio	Tenacity (N tex^{-1})	Elongation (%)	Modulus (N tex^{-1})
100/0	3.70	12.13	0.960	23.6	8.32
100/2.5	3.99	11.86	0.817	21.6	8.20
100/5	3.99	11.92	0.709	16.9	8.33
100/7.5	3.87	12.19	0.719	15.5	8.99
100/12.5	3.93	12.01	0.701	15.4	8.81
100/15	4.80	10.03	0.627	23.5	6.34

work. There can be two reasons for this improvement. First, in the as-made state, the LCP exists in a well preserved fibril structure, thereby giving an effective reinforcement. Second, the properties of the conventional polymers are usually poor in the as-made state while the LCPs often have outstanding properties even without drawing. Therefore, when the LCPs are introduced into the as-made structure, there can be a good improvement in the mechanical properties of the polyblend.

For a number of reasons, the LCP can only be a minor component when fibres from PP and Vectra A900 are produced. Therefore, the PP consists of the bulk of the polyblend fibre and it is essential to draw the as-spun fibres to produce molecular orientation for the PP matrix. Fracture of the LCP fibrils is unavoidable, and to improve the properties of the polyblend fibres it is essential that a good length of the LCP fibrils should be preserved.

A two-stage drawing process was used to see if longer lengths of the LCP fibrils would be preserved. It has been reported that when a polyblend fibre is drawn, the fibril component is broken to a smaller extent at a lower draw ratio[20]. Further, it is assumed that in the first-stage drawing of a lower ratio at a lower temperature, the PP matrix would withstand more stress and give less fracture of the LCP fibrils. Once they are imbedded in a partially drawn PP matrix, the second-stage drawing at a high temperature would produce little destruction as the fibrils would then have a high degree of mobility. *Table 3* shows the draw ratios and the fibre properties from two-stage drawing at 130 and 160°C. The overall draw ratios were much higher in the two-stage process than those obtained from one-stage drawing (*Table 2*). For the pure PP sample, the tenacity value showed little change over that from one-stage drawing, while the initial modulus was increased by 32%. For the polyblend fibres, both the tenacities and initial moduli were improved in the two-stage drawing. The 100/7.5 sample had a 19% increase in tenacity and a 39% increase in initial modulus. In addition, it is clear that although the tenacities of the polyblend fibres were slightly lower than that of the pure PP fibre, the initial moduli showed improvement with increase in the LCP concentration up to a PP/LCP (wt/wt) ratio of 100/12.5. For the 100/7.5 sample, there was a 14% increase in the initial modulus as compared to that of the pure PP sample. The poor fibre properties of the 100/15 sample can be the result of limited drawing due to resistance from the LCP network.

The effect of LCP concentration on the tenacities and initial moduli of the polyblend fibres from one- and two-stage drawings can be seen in *Figures 6* and *7*.

Figure 8 shows the LCP phases of a one-stage fully drawn sample, a partially drawn sample and a two-stage
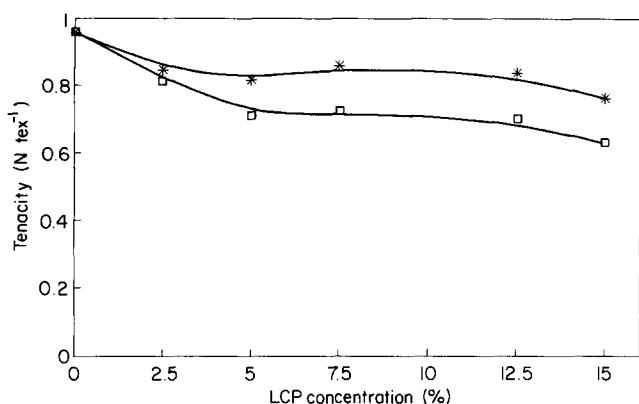
Table 3 Draw ratios and fibre properties from two-stage drawing at 130 and 160°C

PP/LCP (wt/wt) ratio	Draw ratio[a]			Tex	Tenacity (N tex^{-1})	Elongation (%)	Modulus (N tex^{-1})
	r_1(130)	r_2(160)	r				
100/0	7.29	1.93	14.0	3.18	0.958	17.3	10.99
100/2.5	7.37	2.00	14.7	3.20	0.845	14.5	11.15
100/5	7.55	1.98	14.9	3.18	0.816	13.1	11.35
100/7.5	7.63	2.06	15.7	3.00	0.858	11.9	12.54
100/12.5	8.11	2.01	16.3	2.88	0.837	12.0	12.59
100/15	6.73	2.16	14.5	3.30	0.762	13.4	11.31

[a] r_1(130), first-stage draw ratio at 130°C; r_2(160), second-stage draw ratio at 160°C; r, overall draw ratio

Figure 6 Effect of LCP concentration on fibre tenacity: (□) one-stage drawing; (∗) two-stage drawing
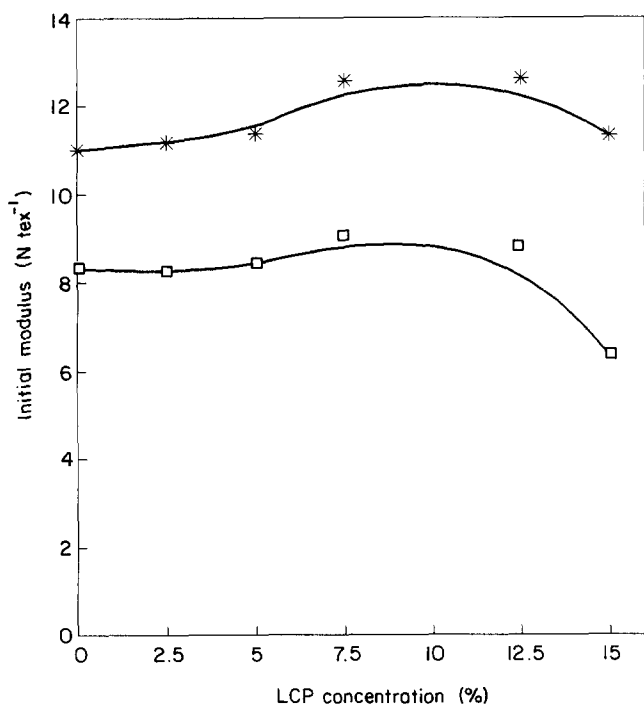

Figure 7 Effect of LCP concentration on initial modulus. Symbols as in *Figure 6*

fully drawn sample. It is clear that the LCP fibrils were split to a much smaller extent in the two-stage drawing, thereby giving more effective reinforcement.

CONCLUSIONS

1. In the polyblend fibre of PP and Vectra A900, the two polymers exist in two separate phases. The morphology of the LCP phase can be particles, fibrils or a network structure depending on the LCP concentration.
2. The morphology of the LCP phase is also related to the processing conditions. Thin fibrils can be obtained at a high extrusion rate and a high draw-down ratio.
3. The LCP fibrils produced a significant reinforcement in the as-spun fibres. As these fibrils were split into short fragments, the reinforcement in the one-stage drawn sample was not fulfilled.
4. The two-stage drawing process reduced the extent of splitting of the LCP fibrils. As a result, both the
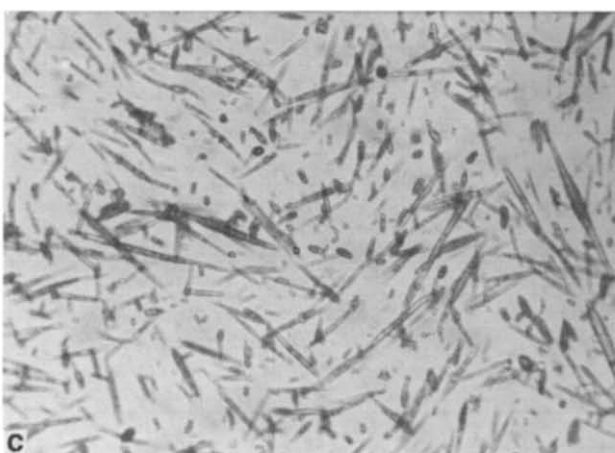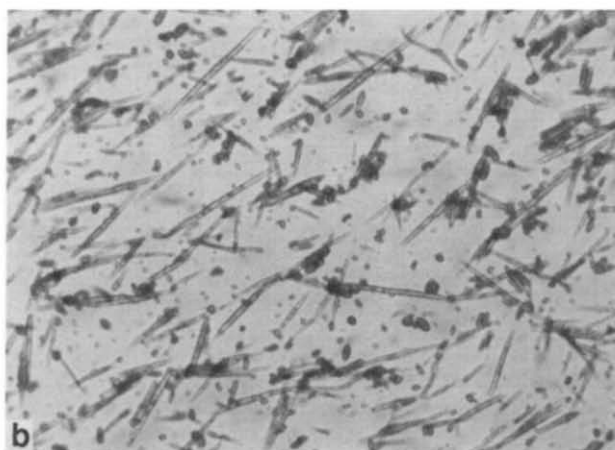

Figure 8 Hot-stage photomicrographs (× 267) of the polyblend fibres: (a) one-stage fully drawn; (b) partially drawn; (c) two-stage fully drawn, PP/LCP (wt/wt) ratio 100/10

initial modulus and the tensile strength were improved from the polyblend fibres in the two-stage drawing. Although the tensile strength of the polyblend fibres is slightly lower than that of the pure PP fibre, the initial modulus showed a good improvement.

ACKNOWLEDGEMENTS

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