Fibres from polypropylene and liquid crystal polymer blends: 3. A comparison of polyblend fibres containing Vectra A900, Vectra B950 and Rodrun LC3000

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Polyblend fibres were made of polypropylene (PP) and three thermotropic liquid crystal polymers (LCPs). The LCPs were found to exist in different morphological structures; the Vectra A900 and Vectra B950 LCPs existed mainly as fibrils, while the Rodrun LC3000 existed as short elongated ribbons. The tensile properties of the as-spun fibres were improved on addition of the LCPs, with the properties of the drawn polyblend fibres varying with the drawing procedure. In one-stage drawing, the polyblend fibres gave poorer tensile properties than the pure PP fibre. However in two-stage drawing, the Vectra A900 blend showed an increase in initial modulus over that of the pure PP fibre, while the Rodrun LC3000 blend produced an improvement in fibre tenacity.

(Keywords: polypropylene; liquid crystal polymer; polyblend fibre; drawing)

INTRODUCTION

A number of thermotropic liquid crystal polymers (LCPs) are commercially available, with the majority of these being modified aromatic copolyesters. To blend them into polypropylene (PP) fibres, it is preferable that the melting point of the LCP be less than 290°C, as severe thermal degradation of PP occurs above this temperature. Most thermotropic liquid crystal polymers have melting temperatures higher than 300°C, because of their chain rigidity, and only a few commercially available LCPs have melting points below 290°C. The Vectra A900 and Vectra B950 LCPs, from Hoechst Celanese Corporation, have melting points of 280°C and the Rodrun LC3000 LCP, from Unitika, has a melting point of ~220°C. In parts 1 and 2 of this series[1,2], we studied the effect of the LCP (i.e. Vectra A900) concentration, the extrusion conditions and the drawing conditions on the structure and properties of PP/LCP polyblend fibres. In part 3 we now examine the extrusion processes and fibre properties of polyblend fibres produced from PP and Vectra A900, Vectra B950 and Rodrun LC3000. We found that apart from the different fibre structures that can be obtained from blends containing different LCPs, the properties of the polyblend fibres also showed considerable differences.

EXPERIMENTAL

Materials

Three thermotropic liquid crystal polymers were used in these experiments. The Vectra A900 is a copolyester of 2,6-hydroxynaphthoic acid and *p*-hydroxybenzoic acid. The Vectra B950 is synthesized from 2,6-hydroxynaphthoic acid (60 wt%), 4-aminophenol (20 wt%), and terephthalic acid (20 wt%). Both polymers were supplied by Hoechst Celanese Corporation and have the same melting point of ~280°C. The Rodrun LC3000 was supplied by Unitika and is a copolymer of *p*-hydroxybenzoic acid and poly(ethylene terephthalate). The PP resin used in this study has a melt flow index (MFI) of 3.

Melt extrusion and hot stretching

Melt extrusion was carried out on a 25 mm single screw extruder (Labspin extruder, Extrusion Systems Ltd) with a single-hole spinneret plate ($D = 0.5$ mm; $L/D = 1$; entrance angle = 120°). The pure PP sample was produced using a temperature profile of 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, respectively. The extrusion rate was 20 m min^{-1}, and the take-up speed was 60 m min^{-1}.

All three blends used the same PP/LCP wt/wt ratio of 100/10. For the blend containing Vectra A900, the temperature profile was 230/285/285/285/280/280°C, while the extrusion rate was 25 m min^{-1} and the take-up speed was 100 m min^{-1}. The blend containing Vectra B950 was extruded using the same extrusion rate and take-up speed but with a slightly different temperature profile, i.e. 230/300/300/300/290/290°C. The blend with Rodrun LC3000 was extruded at 20 m min^{-1} and taken up at 70 m min^{-1}; the temperature profile in this case was 200/270/270/270/270/260°C.

All the PP and PP/LCP polyblend fibres were subjected to the same drawing procedures. In one-stage drawing, the fibre was fed at 6 m min^{-1} and was drawn at 150°C to its maximum extent before fracture occurred. In two-stage drawing, the fibre was fed at 6 m min^{-1} and was drawn in the first stage at 120°C, using a drawing

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speed of 38 m min^{-1}. The partially drawn sample was then drawn again at 165°C to its maximum extent. The draw ratios were determined from the thicknesses of the original and the drawn fibres.

Tensile testing

Tensile properties were measured on a Nene tensile tester. The as-spun fibres were tested with a gauge length of 20 mm and an extension rate of 2 mm min^{-1}, while the drawn fibres were tested with a gauge length of 20 mm and an extension rate of 20 mm min^{-1}. All tests were carried out at 20°C, at 65% relative humidity and the figures quoted were the average of ten tests, with a standard deviation generally less than 5%.

Hot-stage microscopy

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

Differential scanning calorimetry (d.s.c.)

D.s.c. was carried out on a Dupont 910 differential scanning calorimeter, with a Model 2000 monitoring unit, employing a heating rate of 10°C min^{-1}.

Wide-angle X-ray diffraction

X-ray diffraction studies were carried out with a Hilger and Watts Y90 generator and a sealed-off type X-ray tube, employing an exposure time of 5 h.

RESULTS AND DISCUSSION

Melt extrusion

The melting temperature of Vectra A900 and Vectra B950 is 280°C which should be the minimum extrusion temperature for the PP/Vectra A900 and PP/Vectra B950 blends. This temperature is considerably higher than the melting temperature of PP, which is ~165°C. Preliminary work showed that at temperatures above 280°C it was difficult to extrude fibre-grade polypropylene because of its low melt strength. Tape-grade polypropylene with low MFI showed good spinnability at high temperatures. It was found that PP with a MFI of 3 gave optimum fibre tenacity at an extrusion temperature of 290°C, and therefore, this PP sample was used as the matrix polymer.

Results, previously reported in part 1 of these studies[1], showed that the LCP phase exhibits a fibrillar structure at PP/LCP wt/wt ratios preferably between 100/5 and 100/15, and on the basis of this finding, a PP/LCP wt/wt ratio of 100/10 was used in this present study. For the PP/Vectra A900 and PP/Vectra B950 blends, the extrusion rate and take-up speed were 25 m min^{-1} and 100 m min^{-1}, respectively; these were found to be the optimum extrusion conditions, as reported in part 2 of this series of papers[2]. Both the PP/Vectra A900 and PP/Vectra B950 blends can be easily extruded and wound-up. In contrast, the PP/Rodrun LC3000 blend showed a poorer spinnability than the Vectra blends, and it was found that melt fracture frequently occurred, and the draw-down ratio was limited to 4.

As-spun fibres

Figures 1a and *1b* show the hot-stage photomicrographs of the as-spun PP/Vectra A900 and PP/Vectra B950 polyblend fibres. It can be seen that in both blends, the LCPs exist mainly in fibrillar form. The fibrils vary in diameter and length and in general show a smooth surface structure. Some small particles and droplets of the LCPs can also be observed. A photomicrograph of the LCP phase in the PP/Rodrun LC3000 polyblend fibre is shown in *Figure 2*. The Rodrun LC3000 blend shows a different structure to the Vectra blends, both in terms of the shape and distribution of the LCP. In general, the LCP phase in the Rodrun LC3000 blend is composed mainly of short elongated ribbons. The PP/LCP interface is not clearly revealed, which indicates that Rodrun LC3000 is more

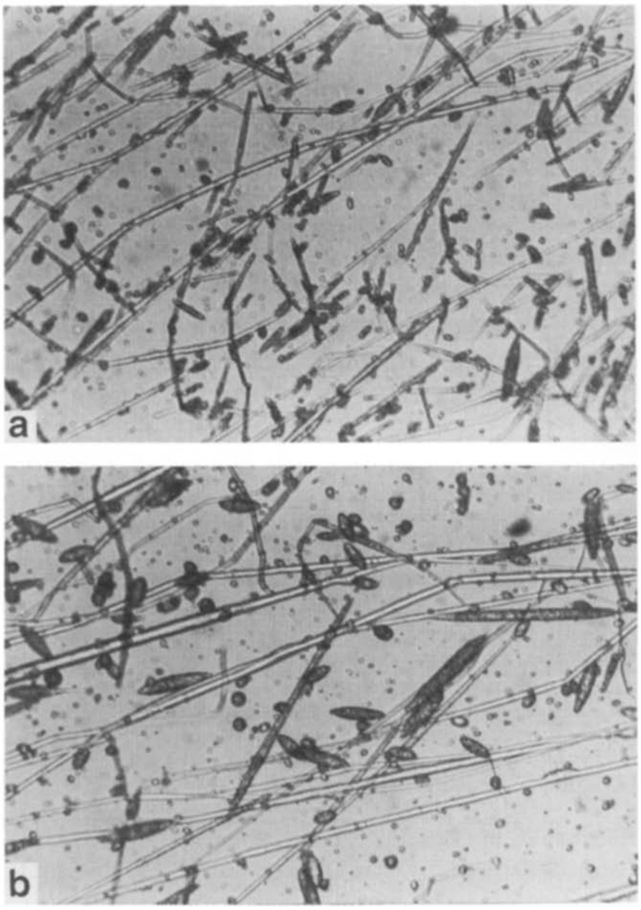

Figure 1 Hot-stage photomicrographs (×260) of the as-spun fibres: (a) PP/Vectra A900 (100/10) and; (b) PP/Vectra B950 (100/10)

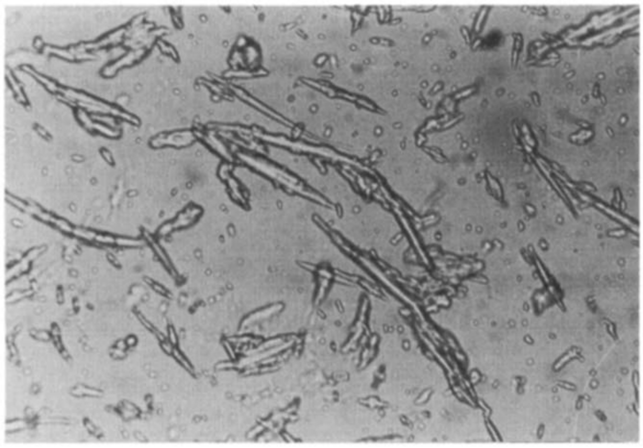

Figure 2 Hot-stage photomicrograph (×260) of the as-spun PP/Rodrun LC3000 (100/10) polyblend fibre

Table 1 Fibre thicknesses and initial moduli of the as-spun fibres

	System			
Property	PP	PP/Vectra A	PP/Vectra B	PP/Rodrun LC
Fibre thickness (tex)	44.90	36.52	38.80	43.41
Initial modulus (N tex^{-1})	1.08	1.18	1.80	1.21
Increase in modulus[a] (%)		9.2	66.6	12.0

[a] With respect to PP

Table 2 Maximum draw ratios and other properties of the fibres obtained from a one-stage drawing process carried out at 150°C

	System			
Property	PP	PP/Vectra A	PP/Vectra B	PP/Rodrun LC
Maximum draw ratio	12.32	10.47	9.70	11.85
Fibre thickness (tex)	3.64	3.49	4.00	3.66
Tenacity (N tex^{-1})	0.931	0.812	0.610	0.866
Initial modulus (N tex^{-1})	8.74	7.84	6.53	7.41
Elongation (%)	26.8	19.6	18.2	26.5

compatible with PP (when compared to Vectra LCPs). From the shape of the LCP phase in the Rodrun LC3000 blend, the process of drop forming and breakup is clear, which agrees with the proposed mechanism of fibril formation in polymer blends[3].

The structural differences of the LCP phases in the Vectra A900, Vectra B950 and Rodrun LC3000 blends can be attributed to differences in the chemical composition of the various LCPs. The Vectra polymers are composed mainly of rigid aromatic segments, while Rodrun LC3000 is a semi-flexible chain copolymer containing 40 wt% PET. As PET contains a high proportion of $-CH_2-CH_2-$ units, it can act as a compatibilizing agent for the polyblend. The ill-defined interface between the PP and the Rodrun LC3000 indicates that the latter LCP is more compatible with PP than the two Vectra LCPs. Baird and Ramanathan[3] have pointed out that LCP fibrils can be more readily produced when the polyblend has either a poorer miscibility or a poorer interfacial adhesion. A similar conclusion can be drawn from these observations of the blends of PP with Vectra A900, Vectra B950 and Rodrun LC3000; it is found that the less compatible Vectra polymers gave better developed fibrillar structures.

Table 1 shows the fibre thickness and initial modulus of the as-spun fibres, where it can be seen that all of the polyblend fibres had higher initial moduli than the pure PP fibre sample. A significant reinforcement was observed for the PP/Vectra B950 blend where the initial modulus showed a 66.6% increase over that of the pure PP sample. The load–extension curves (see *Figure 3*) showed that the polyblend fibres had higher yield stresses and lower yield strains than the pure PP fibre.

This improvement in the mechanical properties of the as-spun fibres, on the addition of a LCP component, agrees with the results of other workers[4–9]. Many have reported improved mechanical properties in injection moulded and extruded products upon the inclusion of a LCP component to the matrix polymer. It is interesting to note that while the improvements derived from the addition of Vectra A900 and Rodrun LC3000 were modest, the Vectra B950 blends showed an outstanding increase in the initial modulus. Two factors are clear: first, pure Vectra B950 gave the highest mechanical properties of all the three LCPs; secondly, the Vectra B950 fibrils are thicker and longer than the other two LCPs, as can be seen from *Figures 1* and *2*.

Drawn fibres

One-stage drawing. Table 2 shows the maximum draw ratios and other properties of the fibres that were obtained from a one-stage drawing process at 150°C, where it can be seen that the pure PP sample showed both the highest draw ratios and the best fibre properties. The low draw ratios obtained for the polyblend fibres could be the result of the resistance towards drawing from the LCP fibrils. This is supported by the fact that the draw ratio of 11.85 for the Rodrun LC3000 blend, where the LCP exists in short elongated ribbons, is considerably higher than the value of 9.70 for the Vectra B950 blend, where the LCP is present in well developed fibrils. *Figure 4* shows the LCP phases in one-stage drawn samples of the three polyblend systems. The LCP fibrils in the Vectra A900 and Vectra B950 blends were split into short fragments during the drawing process, while in the Rodrun LC300 blend, the LCP phase changed from relatively smooth-surfaced ribbons to a rough-surfaced sheet-like structure.

The poor tensile properties of the drawn PP/LCP polyblend fibres can be attributed to two factors. First,

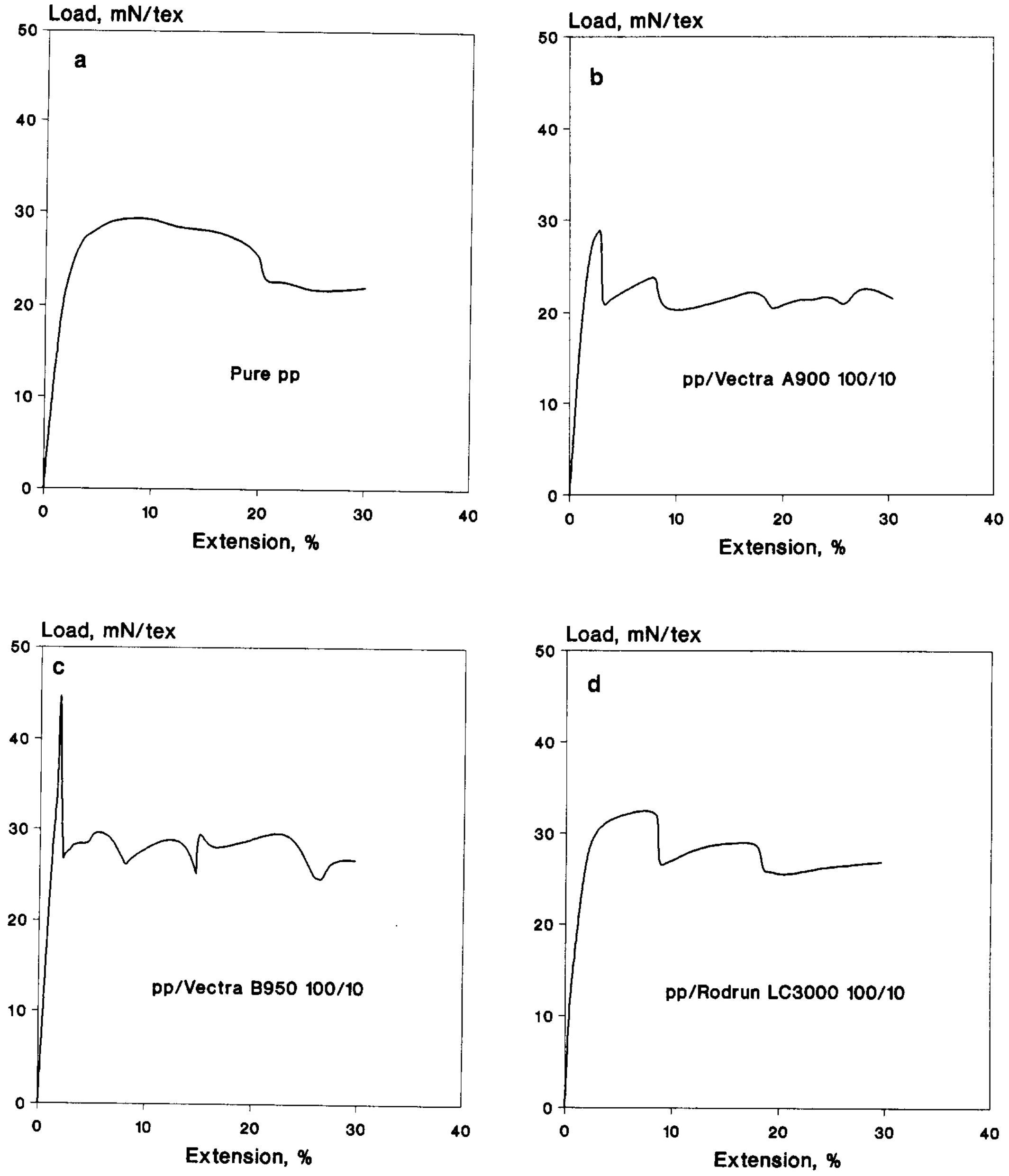

Figure 3 Load–extension curves of the as-spun fibres: (a) PP; (b) PP/Vectra A900 (100/10); (c) PP/Vectra B950 (100/10) and; (d) PP/Rodrun LC3000 (100/10)

the maximum draw ratios were lower for the polyblend fibres than for the pure PP fibres. As the pure PP matrix consists of the bulk of the fibre, a weak matrix, such as can be expected from a low draw ratio, can cause a reduction in the overall fibre properties. In fact, the Vectra B950 blend had the lowest draw ratio and also showed the lowest tensile properties. Secondly, the LCP fibrils in the Vectra A900 and B950 blends split into short fragments during the drawing process. Hot-stage photomicrographs (see *Figures 1* and *4*) have also revealed a smooth surface structure for the LCP phase in the Vectra A900 and B950 blends, indicating poor interfacial adhesion. The Rodrun LC3000 blend showed the best fibre tenacity of the polyblend fibres, which could be due to the fact that it exists in short ribbons in the as-spun fibre, and hence gives less resistance towards drawing, therefore resulting in a strong PP matrix. In addition, the PP–LCP interfacial adhesion appeared to be better in the Rodrun LC3000 blend than in the Vectra blends, as can be observed from the hot-stage photomicrographs (see *Figures 2* and *4c*).

Two-stage drawing. As reported previously[2], a two-stage drawing process can reduce the extent of fracture of the LCP fibrils. In *Table 3*, the drawing conditions and various fibre properties are shown for PP and the three polyblend fibre systems obtained by a two-stage drawing treatment. The first-stage drawing process was carried out at 120°C, with the draw ratio r_1, set at ~ 6, while in the second-stage of drawing, the draw ratio r_2 was the maximum that could be used before fracture occurred. The latter drawing was carried out at 165°C, i.e. at a temperature slightly higher than used previously. As can be seen from the table, the overall draw ratios showed considerable increases over those obtained from the one-stage drawing process. For the pure PP, in addition to a large increase in the initial modulus, the fibre tenacity showed a slight increase, when compared

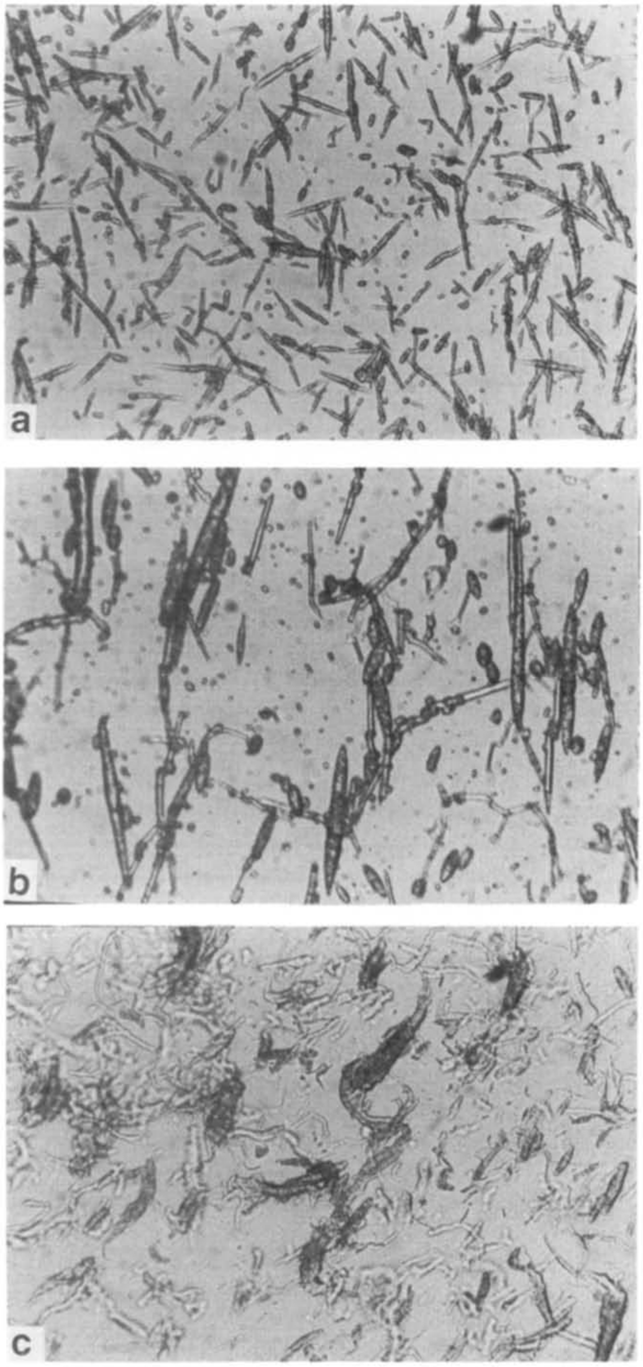

Figure 4 Hot-stage photomicrographs (×260) of the (fully drawn) fibres obtained from a one-stage drawing process at 150°C: (a) PP/Vectra A900 (100/10); (b) PP/Vectra B950 (100/10) and; (c) PP/Rodrun LC3000 (100/10)

to the results obtained for the one-stage drawing treatment. For the polyblend fibres, however, both the fibre tenacity and initial modulus showed significant increases over those reported from one-stage drawing, results which confirm the findings reported earlier[1,2].

When comparing the properties of the PP and polyblend fibres, it can be seen that the Vectra A900 polyblend has a similar tenacity to the pure PP fibres, while the initial modulus shows a slight increase (~4%). The Rodrun LC3000 polyblend shows an improvement in tenacity of 5.4% over the pure PP fibres, although its initial modulus was much lower than the latter. Overall, the Vectra B950 polyblend has the poorest properties of all of the three polyblend fibre systems.

Figures 5 and *6* show, respectively, the hot-stage photomicrographs of the partially drawn and fully drawn polyblend fibres. It is noteworthy that although the mechanical properties of the Vectra B950 blend were poorer than those of the Vectra A900 blend, the fibrils in the drawn samples were longer in the Vectra B950 blend. The Rodrun LC3000 blend showed particularly interesting results. The Rodrun LC3000 component exists in a flat sheet-like structure, similar to the structure found in the one-stage drawn samples. In this structure the flat sheets seem to have formed a network across the drawn fibres. As mentioned above, the rough surface of the LCP phase may improve the interfacial adhesion.

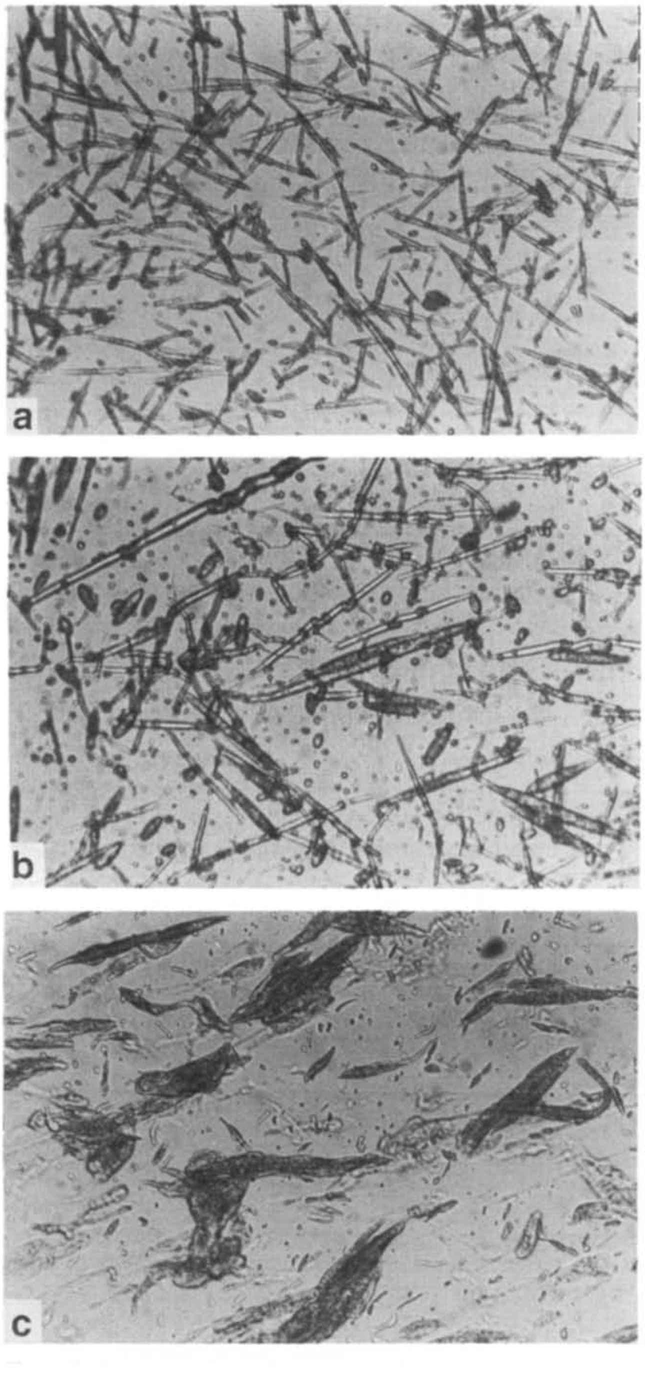

Figure 5 Hot-stage photomicrographs (×260) of the partially drawn fibres: (a) PP/Vectra A900 (100/10); (b) PP/Vectra B950 (100/10) and; (c) PP/Rodrun LC3000 (100/10)

Table 3 Draw ratios and other properties of the fibres obtained from a two-stage drawing process carried out at 120 and 165°C

	System			
Property	PP	PP/Vectra A	PP/Vectra B	PP/Rodrun LC
r_1[a]	6.02	5.65	5.93	6.20
r_2[b]	2.50	2.60	2.45	2.41
r[c]	15.09	14.70	14.56	14.96
Fibre thickness (tex)	2.97	2.48	2.66	2.90
Tenacity (N tex^{-1})	0.986	0.974	0.808	1.04
Initial modulus (N tex^{-1})	13.49	14.01	12.77	10.52
Elongation (%)	16.6	14.2	11.4	22.7

[a] First-stage draw ratio, at 120°C
[b] Second-stage draw ratio, at 165°C
[c] Overall

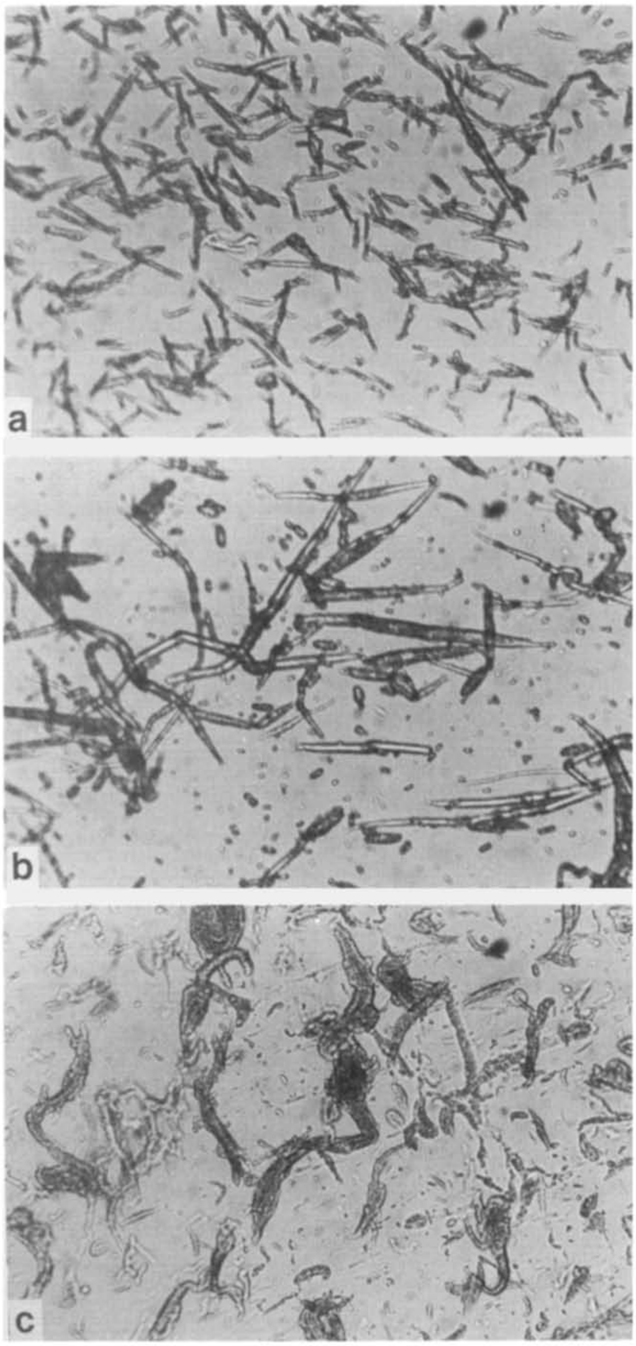

Figure 6 Hot-stage photomicrographs (×260) of the two-stage fully drawn fibres: (a) PP/Vectra A900 (100/10); (b) PP/Vectra B950 (100/10) and; (c) PP/Rodrun LC3000 (100/10)

D.s.c. and wide-angle X-ray diffraction studies

Figure 7 shows the d.s.c. curves obtained for PP and polyblend fibres, both for as-spun and drawn samples. In general, both types of treatment produce highly crystalline fibres. For pure PP the as-spun fibre has a degree of crystallization (DC, based on the d.s.c. endotherm) of 52.1%, with a corresponding value for the fully drawn fibre of 70.6%. The PP fraction in the polyblend fibres showed a similar DC to the pure PP fibres (see *Table 4*). All of the two-stage fully drawn samples had two distinct melting peaks, indicating formation of two different types of crystal, with the melting temperature showing a slight increase as the fibre orientation increased (see *Table 5*). There is no evidence from the d.s.c. measurements of any melting of the LCP component in either of the three polyblend fibre systems.

Wide-angle X-ray diffraction patterns (shown in *Figure 8*) confirmed that both the pure PP and the PP/Vectra A900 polyblend fibres are highly crystalline and highly oriented; similar diffraction patterns are obtained for both of these systems, with only a minor effect from the LCP component, possibly due to its relatively low concentration.

CONCLUSIONS

1. The structure of the LCP phase in these polyblend fibres is affected by the molecular structure of the LCPs and their compatibility with PP. The more compatible Rodrun LC3000 formed elongated micro-ribbons in the polyblend fibres, whilst the less compatible and more rigid Vectra polymers gave fibrillar structures.
2. The inclusion of a strong reinforcing component in the as-spun materials reduced the drawability of the polyblend fibres, thus limiting the ultimate properties of the PP matrix.
3. The importance of two-stage drawing was demonstrated for all three types of polyblend fibres. The properties of PP/Vectra A900, PP/Vectra B950 and PP/Rodrun

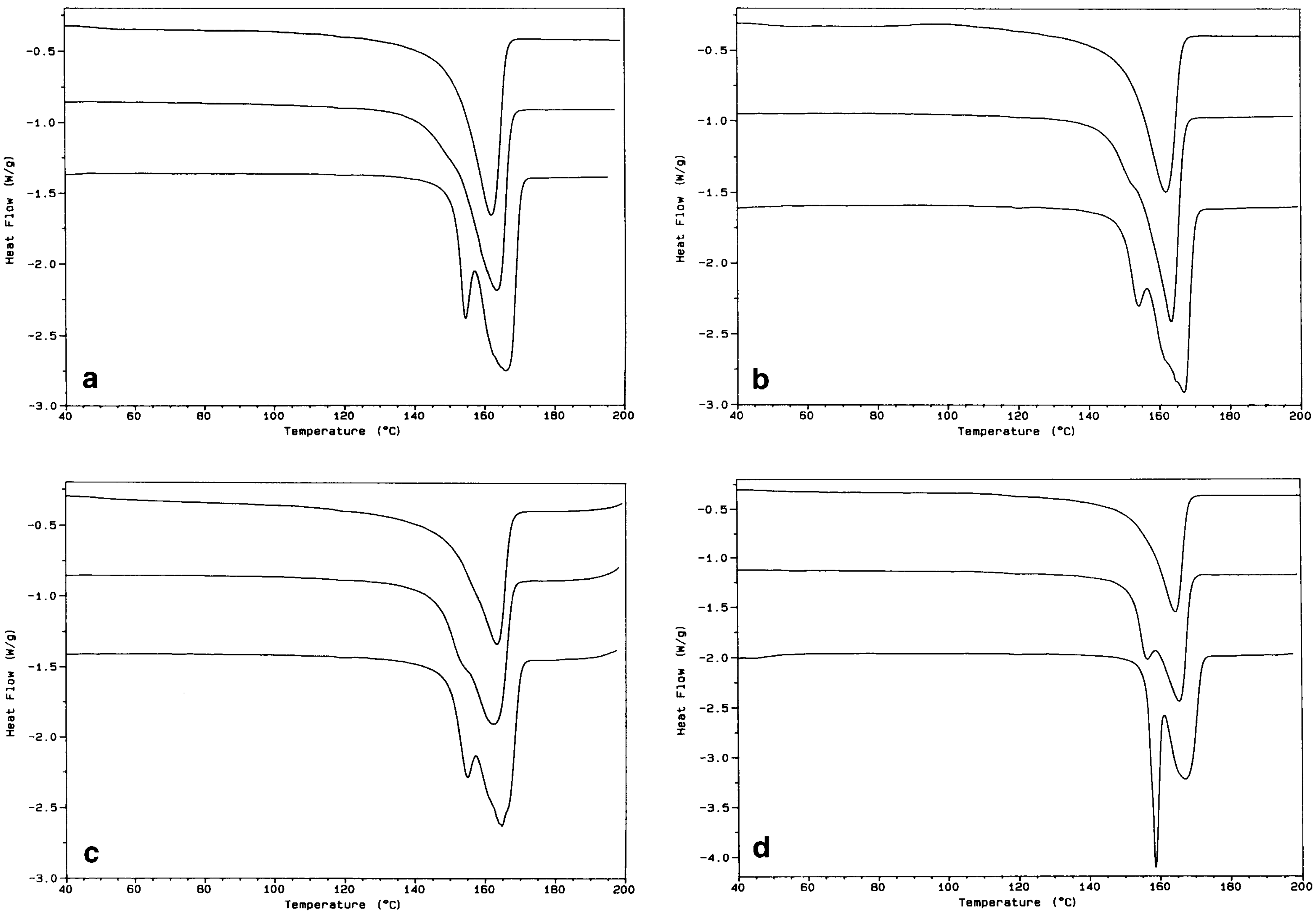

Figure 7 D.s.c. curves (top to bottom: as-spun, partially drawn and two-stage fully drawn fibres, respectively): (a) PP; (b) PP/Vectra A900 (100/10); (c) PP/Vectra B950 (100/10) and; (d) PP/Rodrun LC3000 (100/10)

Table 4 Degree of crystallinity (PP fraction) of the as-spun and drawn fibres

	System			
Type of fibre	PP	PP/Vectra A	PP/Vectra B	PP/Rodrun LC
As-spun	52.1	54.4	49.6	52.4
Partially drawn	61.8	64.9	60.4	57.7
Fully drawn	70.6	70.2	69.0	69.3

Table 5 Melting points of the as-spun and drawn fibres

	System							
	PP		PP/Vectra A		PP/Vectra B		PP/Rodrun LC	
Type of fibre	T_{m_1}	T_{m_2}	T_{m_1}	T_{m_2}	T_{m_1}	T_{m_2}	T_{m_1}	T_{m_2}
As-spun		161.9		161.8		163.3		164.4
Partially drawn		163.5		163.4		162.2	155.7	166.4
Fully drawn	154.4	165.9	153.7	166.8	154.9	164.8	158.6	167.1

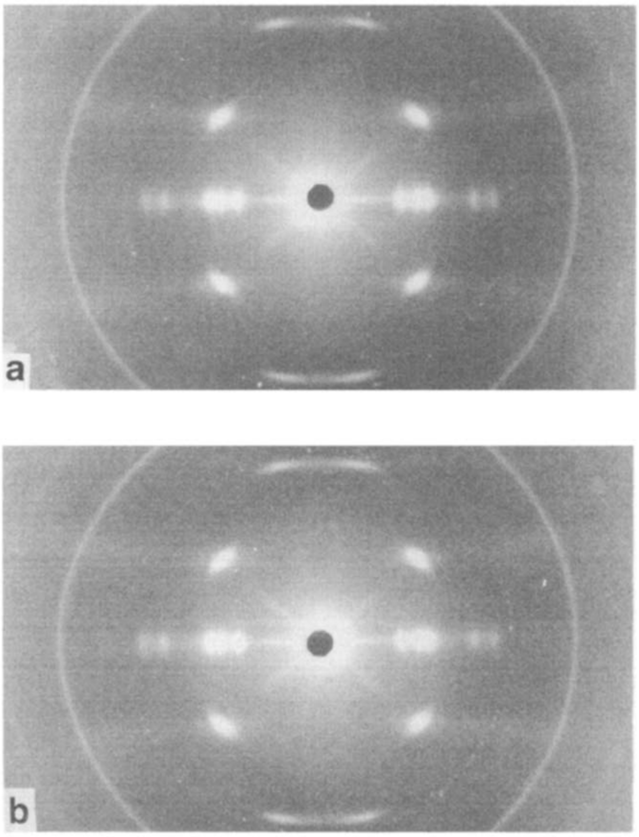

Figure 8 Wide-angle X-ray diffraction patterns of two-stage fully drawn fibres: (a) PP and; (b) PP/Vectra A900 (100/10)

LC3000 polyblend fibres were significantly improved by using a two-stage drawing process, as compared to one-stage drawing, with higher draw ratios being possible for the former. For the Vectra polymers, the fracture of the LCP fibrils was reduced to a low level, while the LCP phase was deformed into a network structure in the case of the Rodrun LC3000 polyblend.

4. The PP/Rodrun LC3000 polyblend showed a 5.4% increase in fibre tenacity over that of pure PP while the initial modulus of the fibre increased by 4% in the case of the Vectra A900 polyblend. This showed the importance of careful selection of the most suitable polymers for modifying specific fibre properties.

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