Drawing Behavior of Polyblend Fibers from Polypropylene and Liquid Crystal Polymers

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SYNOPSIS

Polyblend fibers were made from mixtures of polypropylene (PP) and thermotropic liquid crystal polymers (LCPs). The as-spun fibers were drawn to produce the oriented structure for the PP matrix. The LCPs were found to exist in thin and long fibrils in the as-spun fibers; after drawing, they were split into short fragments. From a simplified model whereby a single LCP fibril is embedded in a PP matrix fiber, it was calculated out that the length of the LCP fibril in the drawn fiber is directly proportional to the fibril diameter and tenacity, and is reversely proportional to the compressional stress on the fibril and the friction coefficient between the fibril and the surrounding matrix. With regard to the drawing conditions, it was found that a long length of the LCP fibrils can be preserved by increasing the drawing temperature, or by reducing the draw rate. The effect of two-stage drawing on the LCP phase morphology was also studied in the present work. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyblend fibers made from mixtures of two or more polymers may exhibit a combination of the properties of the component polymers.[1,2] In this respect, the fiber properties of one polymer may be modified by introducing a second polymer with contrary properties. For example, the difficulty in dyeing polypropylene (PP) fibers can be largely improved by blending PP with polymers containing functional dye sites, such as polyvinylpyrrolidone. Mechanical properties of polymers can also be modified by means of blending, typical examples being rubber toughened plastics and polystyrene reinforced rubbers.

Liquid crystal polymers (LCPs) are a relatively new class of materials that, due to their rigid rod-like molecular chains and the mesophase structure, are capable of forming a high degree of molecular orientation even in the as-made state.[3] Fibers with exceptionally high strength/modulus have been developed in recent years, such as Kevlar and Vectran

fibers. However, LCPs are quite expensive at present and their applications are limited in a few specialized areas such as high strength/modulus fibers. Blending of LCPs with conventional polymers is one way to dilute the cost and widen their applications. In addition, as LCPs usually have low solution or melt viscosities, processibility of the blend can be improved by reducing the blend viscosity. A number of researchers have found that by blending LCPs into conventional thermal plastic polymers, the tensile mechanical properties of the conventional polymers can be improved due to the inherited high strength/modulus of the LCPs.[4-8]

In a recent article, Qin et al.[9] found that in a PP/Vectra A900 blend, thin and long microfibrils of the LCP can be produced at an appropriate range of LCP concentration, and there were remarkable increases in the initial moduli of the as-spun fibers. However, these fibrils were split into short fragments during drawing, which reduces the capacity of the LCP as the reinforcing component. It was found that long LCP fibrils can be preserved by partially drawing the as-spun fiber at a low temperature, and then drawing the fiber again at a higher temperature to the maximum extent.[10]

The result of further studies on the drawing behavior of PP/LCP polyblend fibers is reported in

this study. It is among the objectives of the present work to study the effect of drawing conditions on the morphology of the LCP phase. Various drawing parameters such as drawing temperature and speed, draw ratio, and the effect of the structure and properties of the LCP fibrils on the fibril length in the drawn fiber were studied.

EXPERIMENTAL

Materials

Two thermotropic liquid crystal polymers were used in this work. These were Vectra A900, which is an aromatic copolyester of 1,4-hydroxybenzoic acid and 2,6-hydroxynaphthoic acid, and Vectra B950, which is composed of 2,6-hydroxynaphthoic acid, 4-aminophenol, and terephthalic acid. Both polymers were supplied by Hoechst Celanese and have the same melting point of 280°C. The PP used (Appryl) has a melt flow index of 3 and a melting temperature of 165°C.

Fiber Preparation

The polyblend fibers were prepared in two ways. One PP/Vectra B950 blend (wt/wt ratio 100/10) was extruded on a piston and cylinder type extruder with a single hole spinnerette plate ($D = 0.5$ mm, entrance angle $= 120$°C, capillary $L/D = 1$). The extrusion rate was roughly 4 m min^{-1} and the take-up speed was 36 m min^{-1}. In this method, the PP and LCP were precompounded on a single screw melt extruder. The temperature for extrusion and compounding was 300°C.

PP/Vectra A900 and PP/Vectra B950 polyblend fibers (PP/LCP wt/wt ratio 100/10) were made on a 25-mm single screw melt extruder with the same single hole spinnerette plate. The temperature profiles were 230/285/285/285/280/280 and 230/300/300/300/290/290°C for PP/Vectra A900 and pp/Vectra B950, respectively, which represent the temperatures of three barrel zones, the metering pump, and the two heating zones in the die head. The extrusion rate and take-up speed were 25 and 100 m min^{-1}, respectively, which were the same for the two polyblend fibers.

Cold Drawing

Cold drawing was carried out on a laboratory scale drawing unit consisting of two pairs of advancing rollers and a hot plate. The temperatures and speeds

will be mentioned in the Results Section. The fibers were either drawn one stage to a fixed draw ratio or alternatively, the partially drawn fibers can be fed into the feeding rollers for a second stage drawing at a higher temperature.

Characterization Methods

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

RESULTS AND DISCUSSION

Figure 1 shows typical hot-stage micrographs of a PP/Vectra A900 polyblend fiber before and after drawing. In the as-spun fibers [Fig. 1(a)], the LCP exists in thin and long microfibrils; after drawing [Fig. 1(b,c)], the fibrils can be seen split into short fragments. Previous studies have indicated the effect of drawing conditions on the LCP phase morphology in the drawn fibers.[9,10] It was found that by partially drawing the as-spun fibers at a relatively low temperature and then drawing the fibers again at a higher temperature, more long LCP fibrils exist in the drawn fibers than from a one-stage fully drawn fibers [Fig. 1(b,c)]. This has been found to be due to the fact that the LCP fibrils partially break in the first stage; the second stage drawing at a higher temperature preserves the long length of the LCP fibrils because of the higher degree of mobility of the LCP fibrils at a higher temperature.

Figure 2 shows a simplified model of the polyblend fiber, where a single LCP fibril is embedded in a matrix fiber. Assuming the fibril has a round and smooth surface, the axial tension during drawing was passed to the LCP fibril through friction between the fibril and the surrounding matrix. For a given length of the fibril, the axial tension T is related to the friction coefficient and fibril diameter in the following equation:
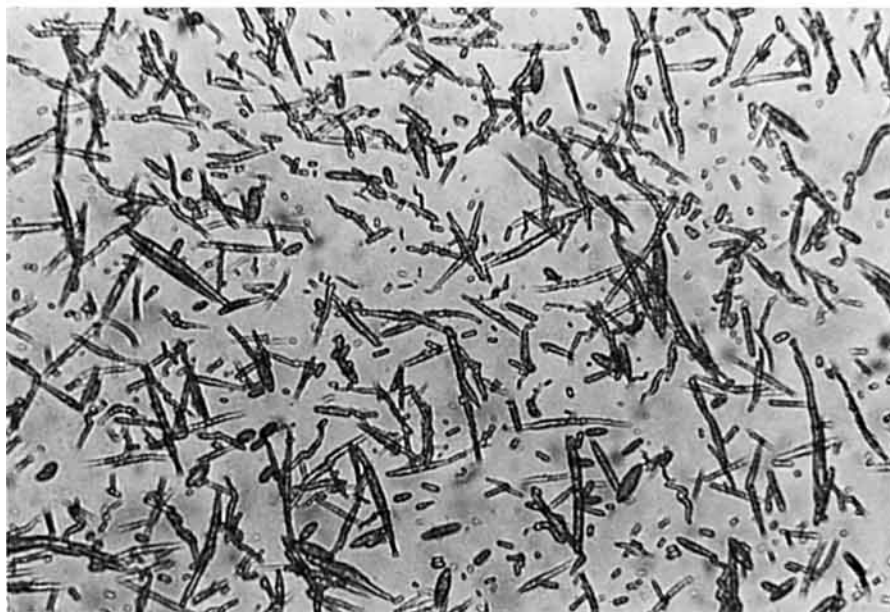
$$T = \pi D L f F \tag{1}$$

where T = axial tension on the microfibril in Newtons; D = fibril diameter in meters; L = fibril length in meters; f = friction coefficient; and F = compressional force in Newtons. The breaking strength of the fibril is related to the fibril tenacity in the following equation:
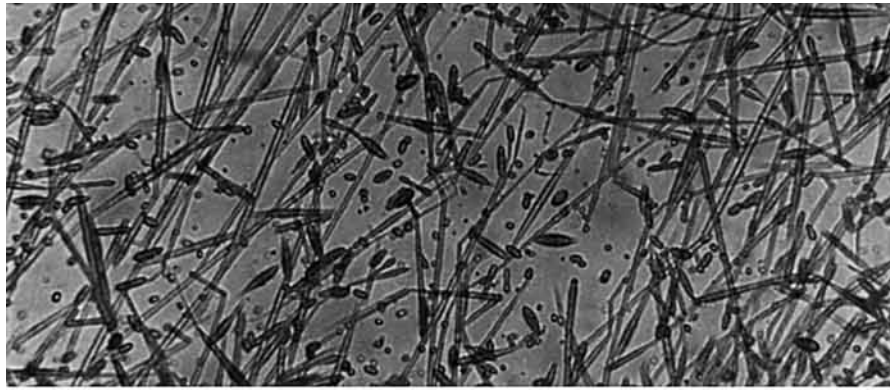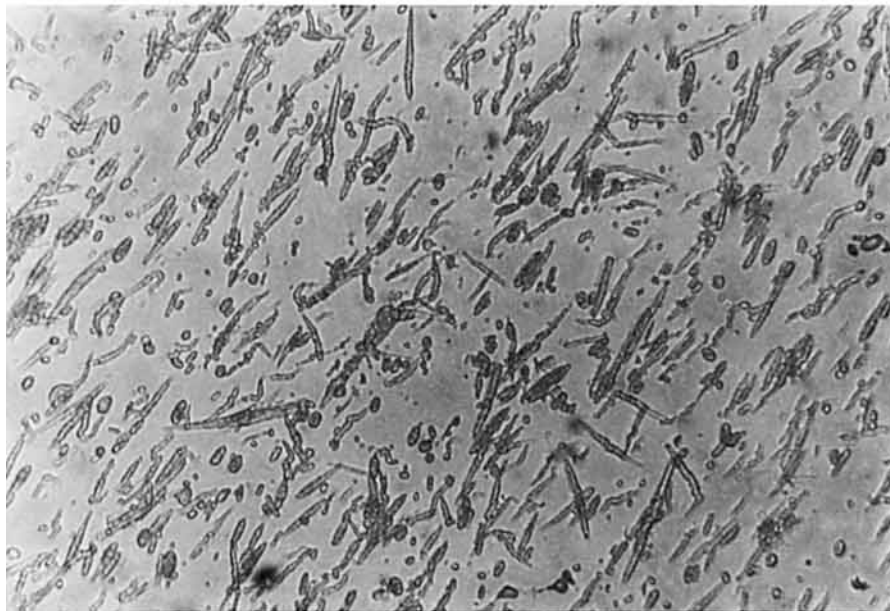
Figure 1 Hot-stage photomicrographs (400×) of PP/Vectra A900 (wt/wt ratio 100/10) polyblend fibers: (a) as-spun fibers; (b) one-stage fully drawn at 150°C; (c) two-stage fully drawn at 120 and 165°C.

(a)   **(b)**

Figure 2 Schematic representation of an LCP microfibril embedded in a PP matrix fiber; (a) as-spun fiber and (b) drawn fiber.

$$S = \pi D^2 \delta / 4 \qquad (2)$$

where S = fibril breaking strength in Newtons and δ = fibril tenacity in Newton meters^{-2}. The microfibril breaks when the tension T exceeds the breaking strength, that is, it breaks when $T > S$, or

$$DLfF > \pi D^2 \delta / 4. \qquad (3)$$

Thus, the critical fibril length is

$$L = D\delta / 4fF \qquad (4)$$

or the aspect ratio

$$L/D = \delta / 4fF. \qquad (5)$$

It can be seen from eq. (4) that the length of the LCP fibril in the drawn fiber is directly proportional to the diameter and strength of the LCP fibril, and is reversely proportional to the interfacial adhesion between the fibril and the matrix. In composite theory, there are several types of interfacial adhesion on the fiber–matrix interface, such as adsorption and wetting, interdiffusion, electrostatic attraction, chemical bonding, and mechanical adhesion. The friction coefficient is therefore a complex of various sources. Because PP and the LCPs are of distinctively different chemical composition, and from the smooth and round surface structure of the LCP fibrils in the hot-stage micrographs, it can be reasonably assumed that the interfacial adhesion in terms of interdiffusion, chemical bonding, and electrostatic attraction are minimum. The primary bonding is therefore mainly adsorption and wetting, and mechanical bonding.

A large length of the LCP fibril can be preserved when the fibril diameter is large and the fibril tenacity is high, or when the friction coefficient and the compressional force are low [eq. (4)]. In the case of PP and the LCP blends, as the storage and drawing temperatures were much lower than the melting point of the LCPs, it can be reasonably assumed that both the fibril diameter and the fibril tenacity remain roughly constant during drawing;

they are the result of the extrusion process and they are influenced mainly by the extrusion conditions. The length of the LCP fibrils is therefore influenced by variations in the friction coefficient and the compressional forces. In order to preserve a long length of the LCP fibrils in the drawn fiber, it is important to reduce these two factors.

As pointed out earlier, the main interfacial adhesion between the PP matrix and the LCP fibril is through adsorption and wetting, and mechanical adhesion, which can be reduced by increasing the drawing temperature. At a high temperature, it is obvious that the high mobility and short relaxation time of the matrix polymer reduced the friction coefficient. Additionally, the interfacial adhesion can decrease upon the increases in the drawing temperature through the differential thermal expansion coefficients of PP and LCP. Because LCPs tend to have a higher degree of axial orientation than conventional thermoplastics, in the cross sectional direction, the LCP fibrils would expand to a smaller extent than the PP matrix. Because the LCP fibrils are embedded in the PP matrix, this differential expansion should deteriorate the interfacial adhesion. Figure 3 shows the hot-stage micrograph of the PP/Vectra A900 blend drawn at 120 and 150°C to similar draw ratios. It can be seen that with the increase in draw temperature, there followed a remarkable increase in the fibril length in the drawn fibers.

Figure 4 shows the LCP phase of the PP/Vectra A900 blend drawn at 150°C to two higher draw ratios than in Figure 3(b), that is, 9 and 11. With the increase in draw ratio, the fibril length decreased sharply. In the neck zone of the fiber (Fig. 5), an increase in draw ratio is accompanied by a more rapid deformation of the matrix polymer (the feeding speed was fixed for the three samples). This leads to an increase in the compressional force. As a result, more severe fracture of the LCP fibrils were produced.

Figure 6 shows the LCP phase in the PP/Vectra B950 blend made from the piston and cylinder extruder. In this extruder, there is a low degree of shear and extensional strains as compared to the screw extruder. The fibrils were therefore coarser and there
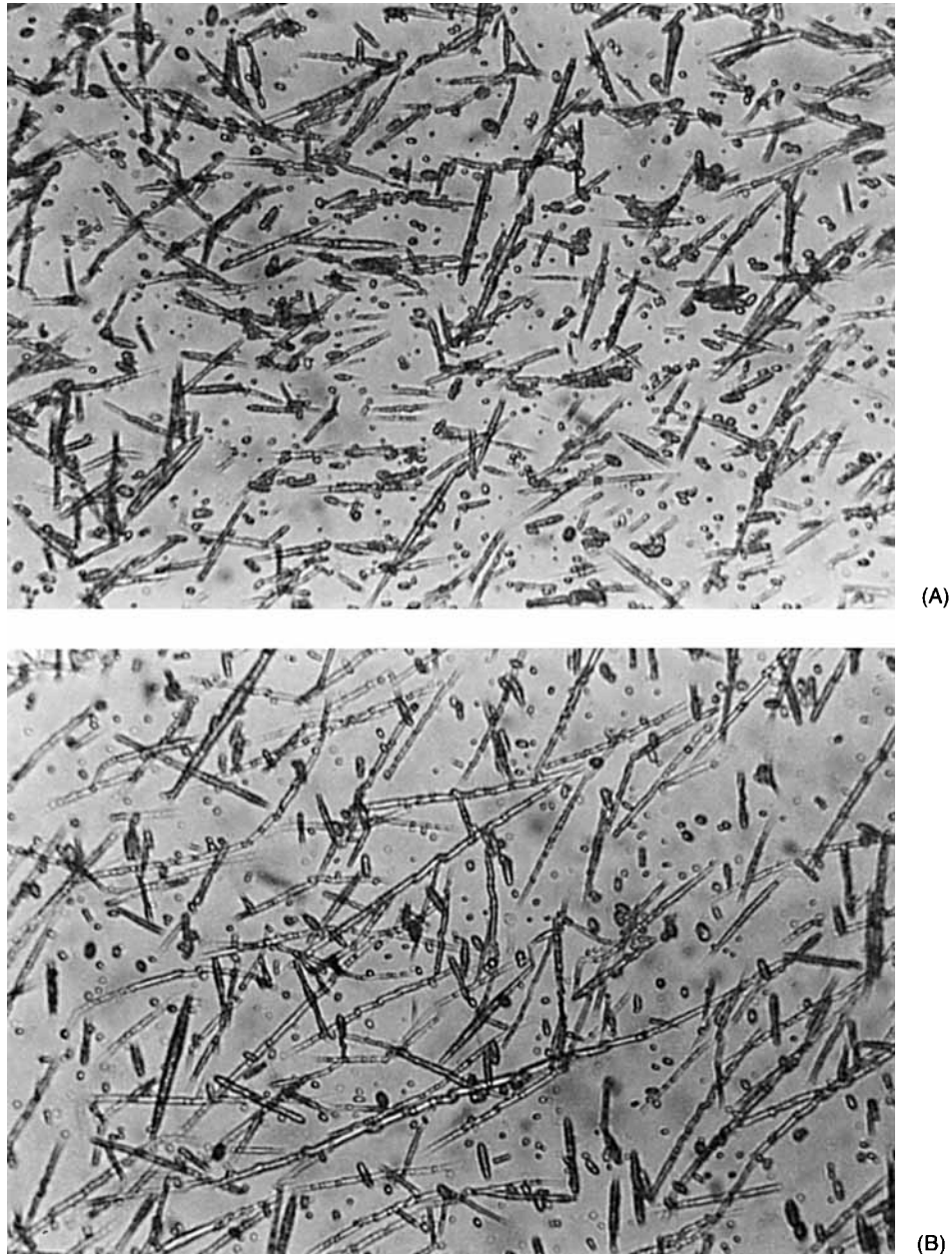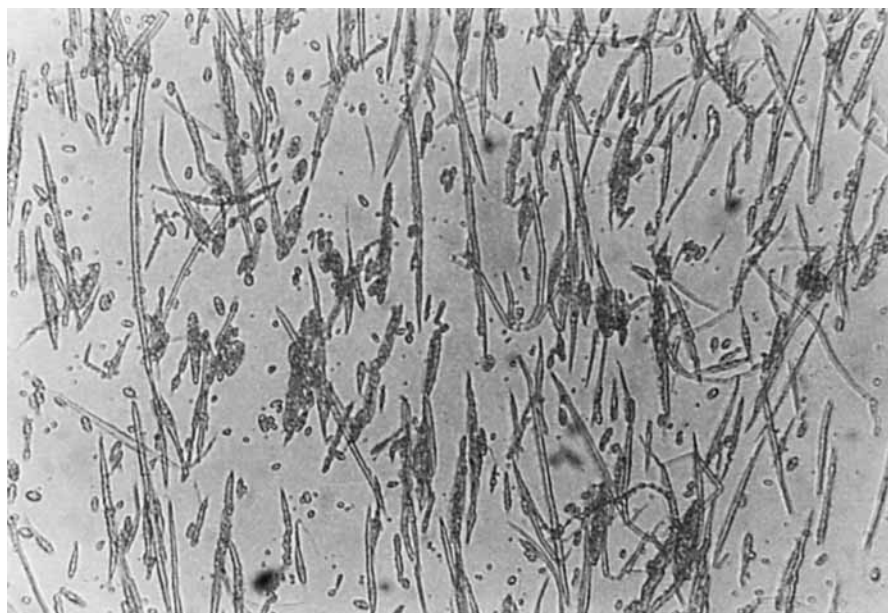
Figure 3   Hot-stage photomicrographs (400×) of one-stage drawn PP / Vectra A900 (wt / wt ratio 100/10) polyblend fibers (draw ratio = 6) ; (a) drawn at 120°C and (b) at 150°C.

is also a wider distribution of the diameter of the LCP fibrils. The LCP phase of a one-stage fully drawn fiber is shown in Figure 6(b). It can be seen that long and thick fragments were evident in the drawn fiber, which confirmed the view that the length of LCP fibril in the drawn fiber is proportional to the fibril diameter.

Figure 7 shows the LCP fibrils of the PP/Vectra A900 in the two-stage drawn fibers [first stage as in Fig. 3(b)]. The second-stage drawing was carried out at 165°C, a temperature much higher than the temperature used in the first-stage drawing. It is clear, by comparing Figures 7 and 3(b), that the LCP fibrils in the partially drawn fiber fractured further in the second-stage drawing. It is worth noting that in the as-spun fiber, the fibrils are embedded in a random unoriented structure; in the partially drawn fiber, the PP matrix is oriented along the fibril direction. Therefore, there is an increase in the interfacial adhesion and frictional coefficient in
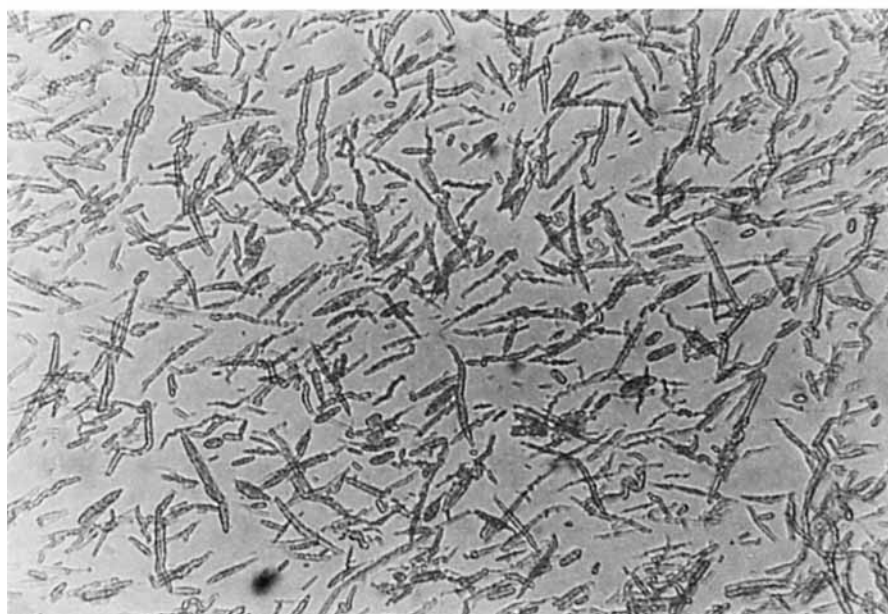
Figure 4   Hot-stage photomicrographs (400×) of one-stage drawn PP/Vectra A900 (wt/wt ratio 100/10) polyblend fibers (drawn at 150°C); (a) at a draw ratio of 9 and (b) at 11.
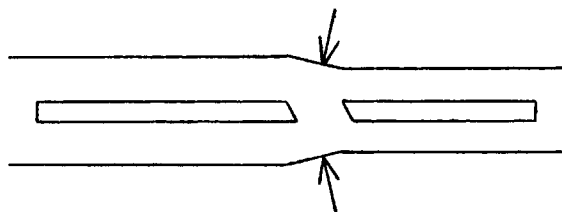

Figure 5   Schematic representation of the neck zone during cold drawing of the PP/LCP polyblend fiber.

the second-stage drawing as compared to the first-stage drawing. The fracture of the LCP fibrils in the second-stage drawing could be caused by both increased compressional pressure and increased frictional coefficient due to the high draw line tension and improved interfacial adhesion between the LCP fibril and the PP matrix. The interfacial adhesion can be reduced by increasing the second-stage drawing temperature. This can be confirmed by results
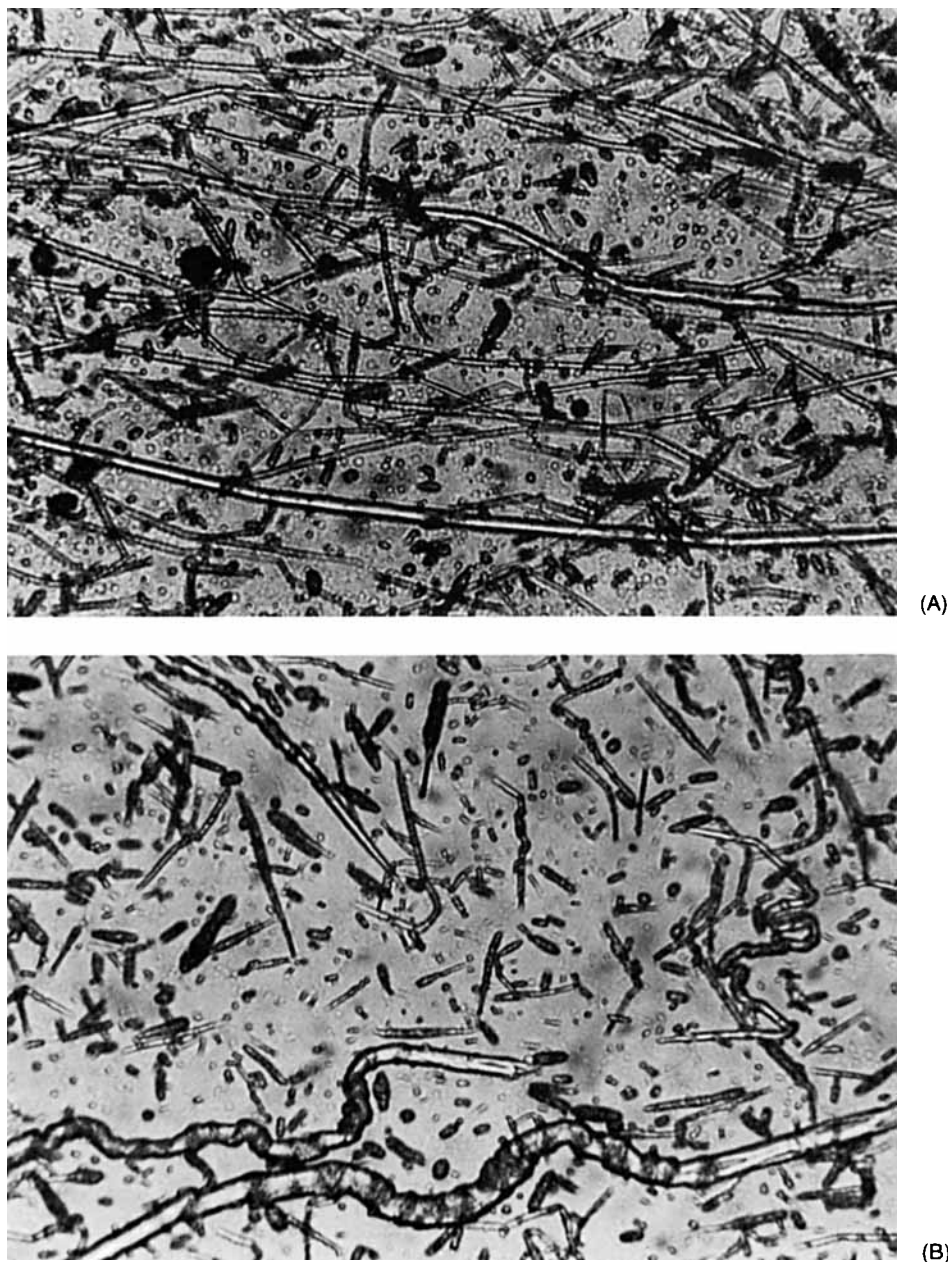
Figure 6   Hot-stage photomicrographs (400×) of PP/Vectra B950 (wt/wt ratio 100/ 10) polyblend fiber made on the piston and cylinder extruder; (a) as-spun fiber and (b) one-stage fully drawn at 150°C.

published previously[10] where in the PP/Vectra A900 blend, an increase in the second-stage drawing temperature reduced the extent of fracture of the LCP fibrils.

It is interesting to note that when the LCP fibril is fractured, the splitting of the fibril created voids between the neighboring fragments (Fig. 2). It is therefore possible that during the second-stage drawing at a higher temperature, these voids may be partially healed by the softening of the matrix polymer. This can be supported by the results pub-

lished earlier[9] where PP/Vectra A900 polyblend fibers produced remarkable increases in the initial modulus of the two-stage drawn fibers as compared to the one-stage fully drawn fibers.

CONCLUSIONS

This study has shown that during the cold drawing of polyblend fibers of PP and thermotropic LCPs, the fracture of the LCP fibrils are affected by the
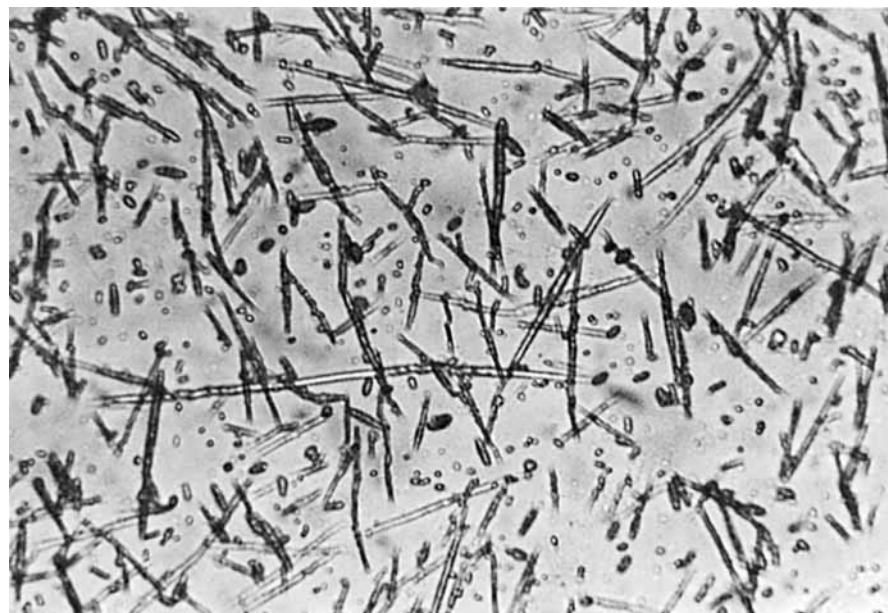
Figure 7   Hot-stage photomicrograph (400×) of PP/Vectra A900 (wt/wt ratio 100/10) polyblend fiber after two stage drawing at 120 and 165°C (draw ratios 6 and 2.5, respectively).

drawing conditions such as draw ratio and drawing temperature. The aspect ratio of the LCP fibrils in the drawn fiber is directly proportional to the fibril tenacity and reversely proportional to the frictional coefficient between the LCP fibrils and PP matrix. A long length of the LCP fibrils can be preserved by reducing interfacial adhesion, such as by increasing the drawing temperature, or by reducing the compressional force on the fibril during drawing, such as at a low draw rate.

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