On the *In Situ* Generation of Reinforcing Fibers

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SYNOPSIS

A study has been made of the formation of the microstructure of a polypropylene (pp) and liquid crystal polymer (LCP) blend. The pp/LCP mixture was fed into a single-screw melt extruder, and polyblend fibers were made by extrusion of the melt through a spinneret plate. Samples of the melt were taken from various sections of the screw barrel, before and after the metering pump, before and after the mesh filter, before and after the die head, and in the as-made fibers. The microstructure of the LCP phase in the blend was studied with a hot-stage microscope. It was found that the dispersion of the LCP phase in the pp matrix was well completed before the metering pump. Planar flow and compressional strain in the metering pump had little influence on the LCP phase structure, but elongational strain in the mesh filter produced fine dispersion of the LCP phase. It was found that the LCP phase existed largely in spherical particles before the die-head entrance. Although the extensional flow in the die entrance deformed the LCP particles into thin droplets, further elongational strain below the die head is essential if thin and long LCP fibrils are required in the polyblend fibers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends made from liquid crystal polymers (LCPs) and conventional polymers have unique structures and properties. In these blends, LCPs are often the minor component, and in most cases they are used as the reinforcing element, producing the so-called molecular composite.[1] In terms of ease of fabrication and interfacial adhesion, this process of making *in-situ*-generated reinforcement in a conventional polymer matrix offers many advantages over the traditional short fiber reinforced composite materials, and an increasing amount of research and development work is being done with these materials.[2] In a recent paper Qin et al.[3] reported the morphological structures of polyblend fibers made from pp and a thermotropic LCP. They found that in the pp/LCP polyblend fibers the LCP existed in particles, short droplets, microfibrils, and an interpenetrating network, depending on the LCP concentra-

tion. The LCP phase morphology was also affected by the extrusion conditions and by the degree of compatibility between the pp and the LCPs.[4,5] For blends of LCPs and conventional thermoplastic polymers, other workers have indicated the importance of LCP concentration,[6–10] the extrusion rate[3] the draw-down ratio,[11–13] and the die-head design[14] in determining the morphological structure of the LCP phase in the final product. In general, fibrillar structures of the LCP that are essential for effective reinforcement can be formed at a high level of LCP content in the blend, a high viscosity ratio of matrix polymer to LCP, a high extrusion rate, and a high draw-down ratio.

LCP phase morphology before extrusion has not been fully studied. Much also remains unknown of the process whereby LCP chips the size of a few millimeters are transformed into microfibrils with diameters of a few microns. It is therefore the aim of this article to study the formation of the LCP phase morphology in pp/LCP fibers. The structure of the LCP phase in various parts of a single-screw extruder is investigated with a hot-stage microscope. The effect of draw-down ratio on the LCP phase morphology is also studied.

EXPERIMENTAL

The thermotropic LCP used in this work was Vectra A900 (Hoechst Celanese), which is an aromatic co-polyester of 1,4-hydroxybenzoic acid and 2,6-hy-droxynaphthoic acid. The polypropylene resin used (Appryl) has a melt-flow index of 3. The two polymers have melting points of 280°C for the LCP and 165°C for the pp.

Melt extrusion was carried out on a 25-mm single-screw extruder equipped with a spinneret plate (37 holes, diameter 0.4 mm). The temperature profile was 200/285/285/285/280/280°C, which represents the temperatures of three barrel zones, the metering pump, and the two heating zones in the die head. The extrusion rate was 3 m min^{-1}, and the extrudate was subjected to three different take-up procedures, i.e., collection of the melt immedi-
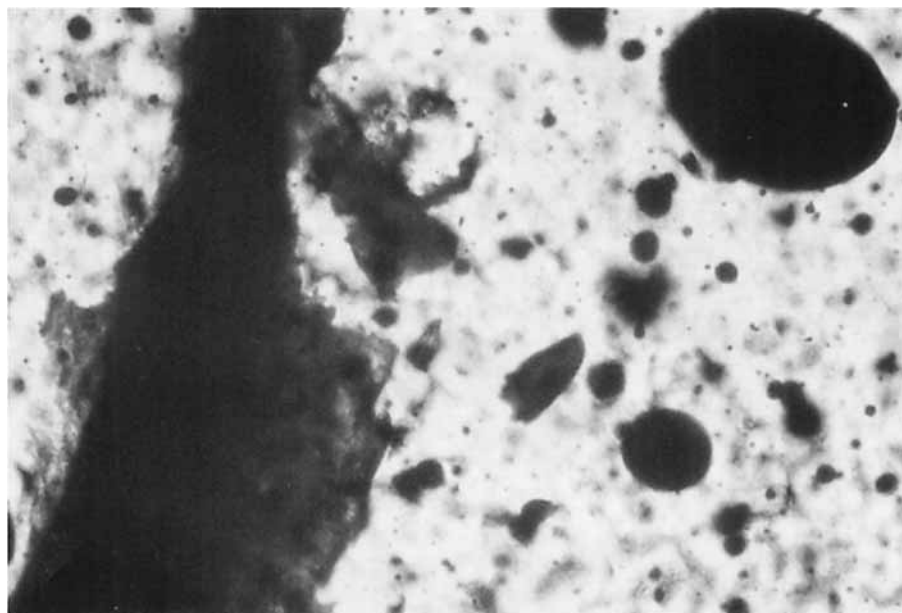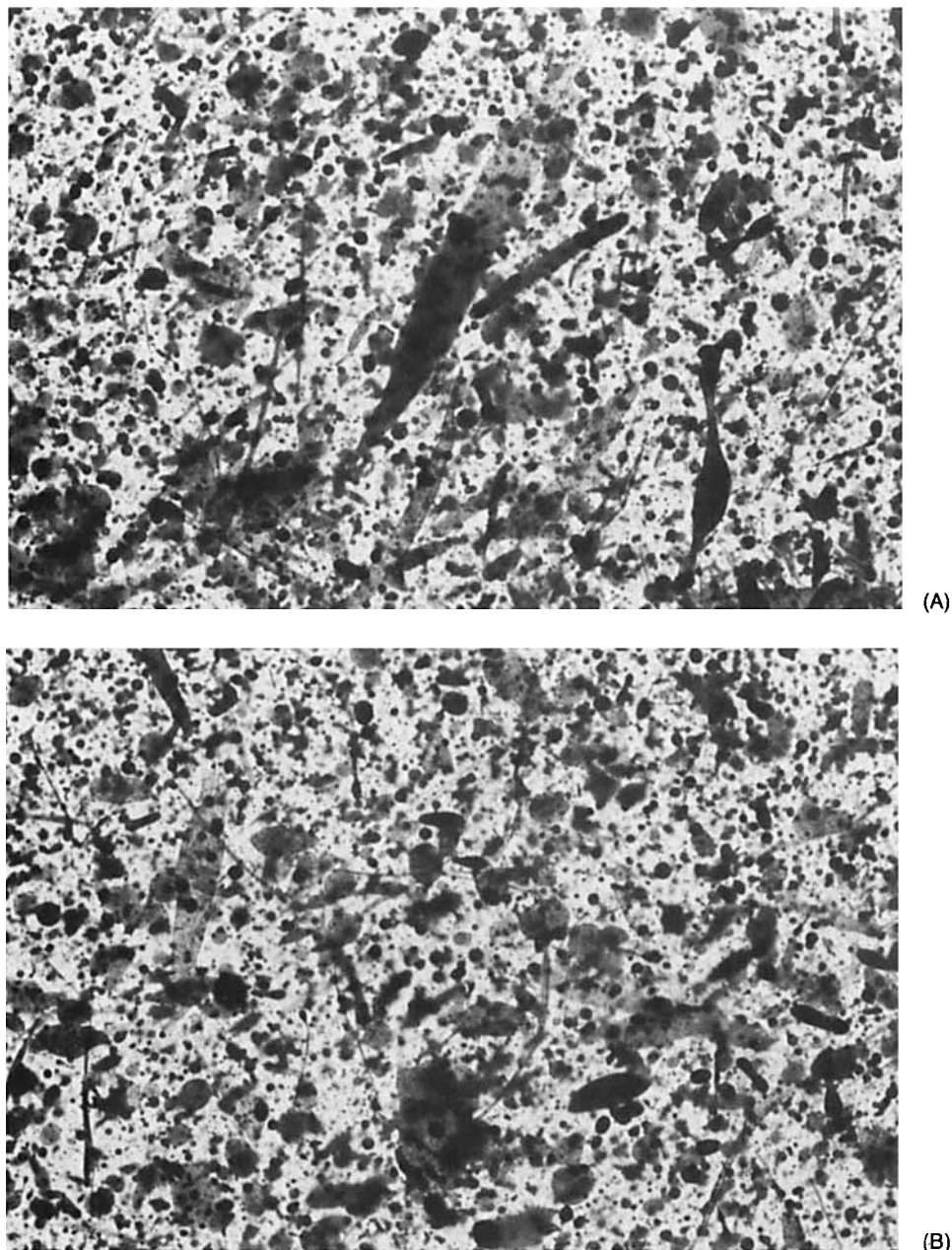

(A)
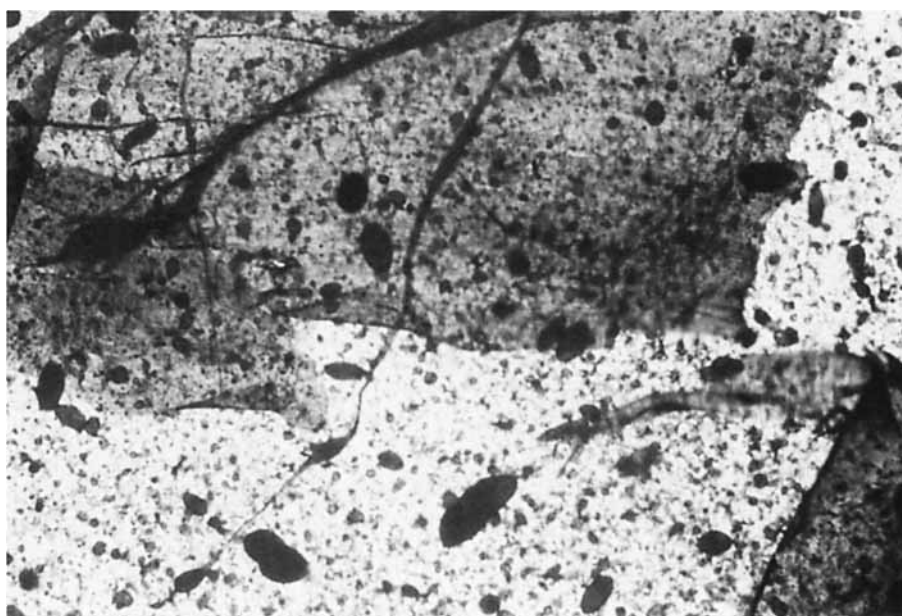
(B)

Figure 1 Hot-stage photomicrographs (×40) of a pp/Vectra A900 (wt/wt ratio 100/10) blend: (a) in the compression zone of a single-screw melt extruder, (b) in the feeding zone.

Figure 2   LCP phase morphology of a pp/Vectra A900 (wt/wt ratio 100/10) blend: (a) before the metering pump, (b) after the metering pump (×100).

ately below the spinneret plate and after the sample free falls onto the ground and collection of the sample on an advancing roller with a draw-down ratio (ratio of take-up speed to extrusion rate) of 20.

Samples of the polymer blend were collected in various parts (feeding, compression, and metering zones) of the screw barrel, before and after the metering pump, before and after the filter pack (mesh filter), before and after the die head, and in the extruded products. A small piece of the blend was

melted on a hot-stage at 185°C and pressed vertically between two glass slides to form a thin film. The LCP phase was then observed with a Leitz microscope.

RESULTS AND DISCUSSION

Figure 1(a) shows a hot-stage micrograph of a sample taken from the compression zone of the screw

barrel. The LCP phase is in the process of being torn apart. As Vectra A900 has a much higher melting point than pp, in the initial feeding zone before the compression zone the Vectra A900 pellets were embedded in a molten-pp matrix. In fact, this promotes a more even distribution of the LCP in the pp. At the end of the feeding zone and in the beginning of the compression zone, the Vectra A900 pellets started melting, and as the pellets softened they were compressed into flat sheets [Fig. 1(b)], which

disintegrated into smaller parts under the shear and extensional stresses in the flow field [Fig. 1(a)].

Thermotropic LCPs consisting of rigid aromatic molecular chains usually have extended chain structure, and their melt viscosity is low because of the low degree of molecular entanglement. The polypropylene used in this work was a tape-grade sample with high molecular weight, and it can be reasonably assumed that in the screw barrel, where the shear rate is relatively low, the polypropylene

(A)

(B)
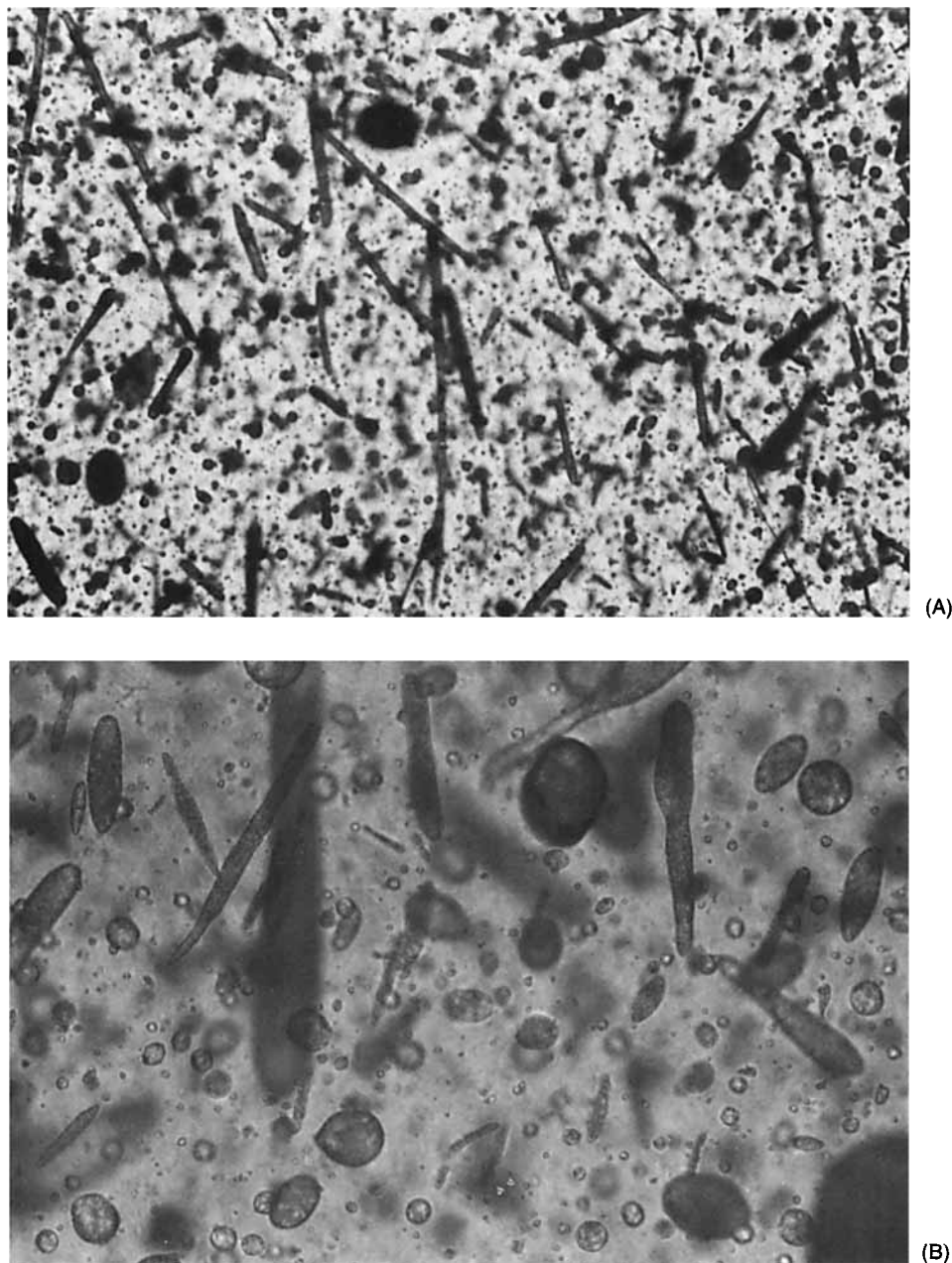
Figure 3   LCP phase morphology of a pp/Vectra A900 (wt/wt ratio 100/10) blend after the melt passes the filtering mesh: (a) ×100, (b) ×400.
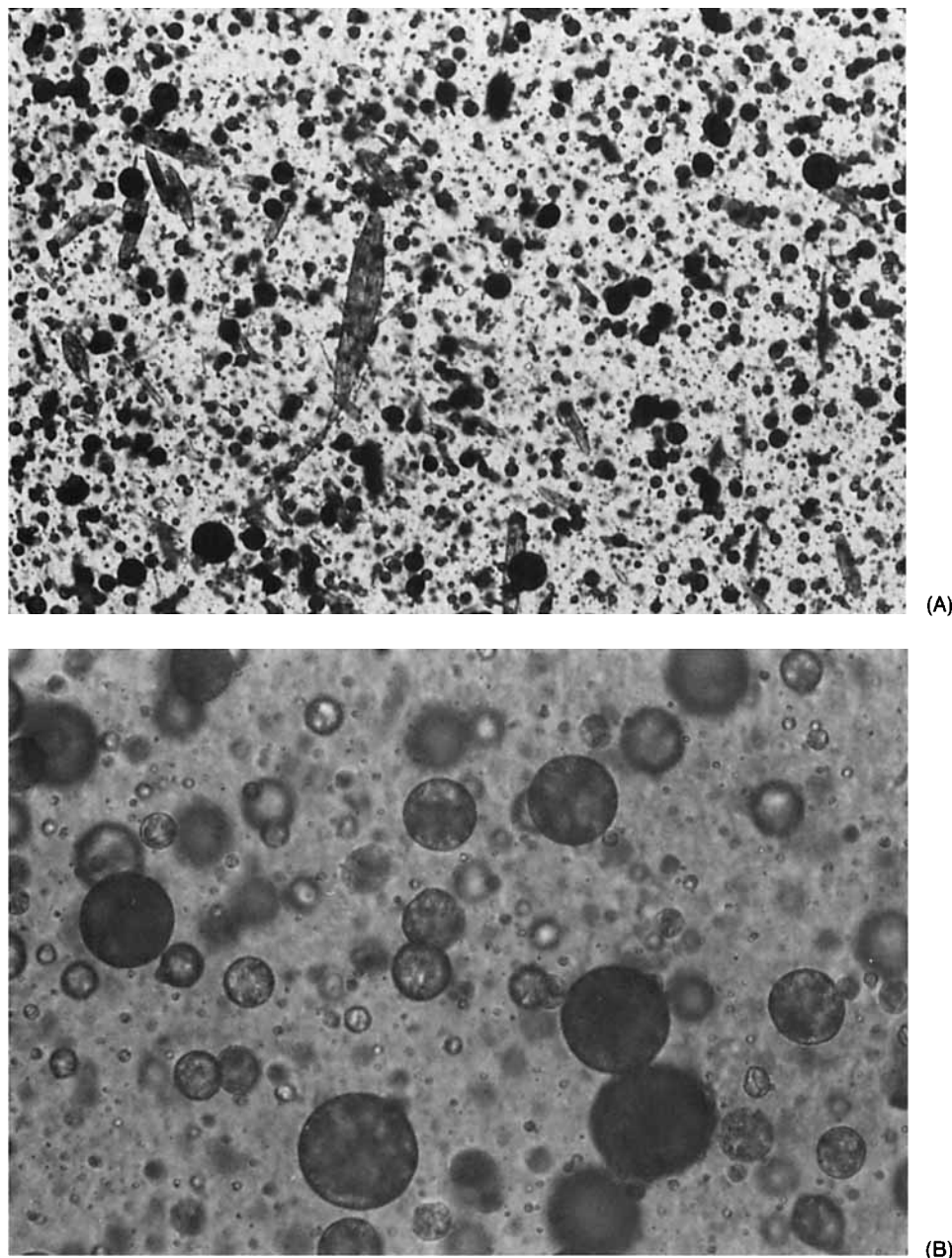
Figure 4 Hot-stage photomicrograph of a pp/Vectra A900 (wt/wt ratio 100/10) blend before the spinneret hole entrance: (a) ×100, (b) ×400.

melt has a higher viscosity than does the Vectra A900. This relatively low viscosity of the LCP favors the disintegration of the LCP phase in the polymer blend. As can be seen from Fig. 2(a), at the end of the screw barrel and before the entrance to the metering pump the LCP has largely broken up into microdomains of various sizes and shapes. Whereas the majority of these pieces were microsheets and elongated particles, the formation of microfibrils of large aspect ratio was also evident. Figure 2(b)

shows the LCP phase of the polymer melt after it passed through the metering pump. It can be seen that here the LCP has similar sizes and shapes to those in Fig. 2(a), indicating that the planar flow and compressional stresses that the polymer melt experienced in passing through the metering pump has a minor influence on the LCP phase morphology.

Figure 3(a) shows the LCP phase of the polymer blend after it has passed through the filtering pack. It is clear that, on passing through the filter, the

large pieces are deformed by the converging force into thin and long droplets. As can be seen from Fig. 3(a), the flat sheet and particles that can be seen in Fig. 2(b) are absent; having been transformed into elongated droplets. At a higher magnification, it was interesting that some droplets were in the process of breaking up, forming a bead-and-string-type structure [Fig. 3(b)]. This phenomenon is similar to those reported for a blend of polycarbonate and ABS rubber, in which the rubber phase forms

a bead-and-string structure, following the interfacial instability mechanism.[15] It is obvious that polypropylene and the Vectra A900 have distinctively different chemical compositions and that a high interfacial tension exists on the pp/LCP interface. In fact, this can be readily confirmed by the clear interfacial boundary between the pp and LCP in the polyblend. On passing through the filtering mesh, the LCP phase experienced a certain extensional flow field, causing deformation of the microdomains

(A)

(B)
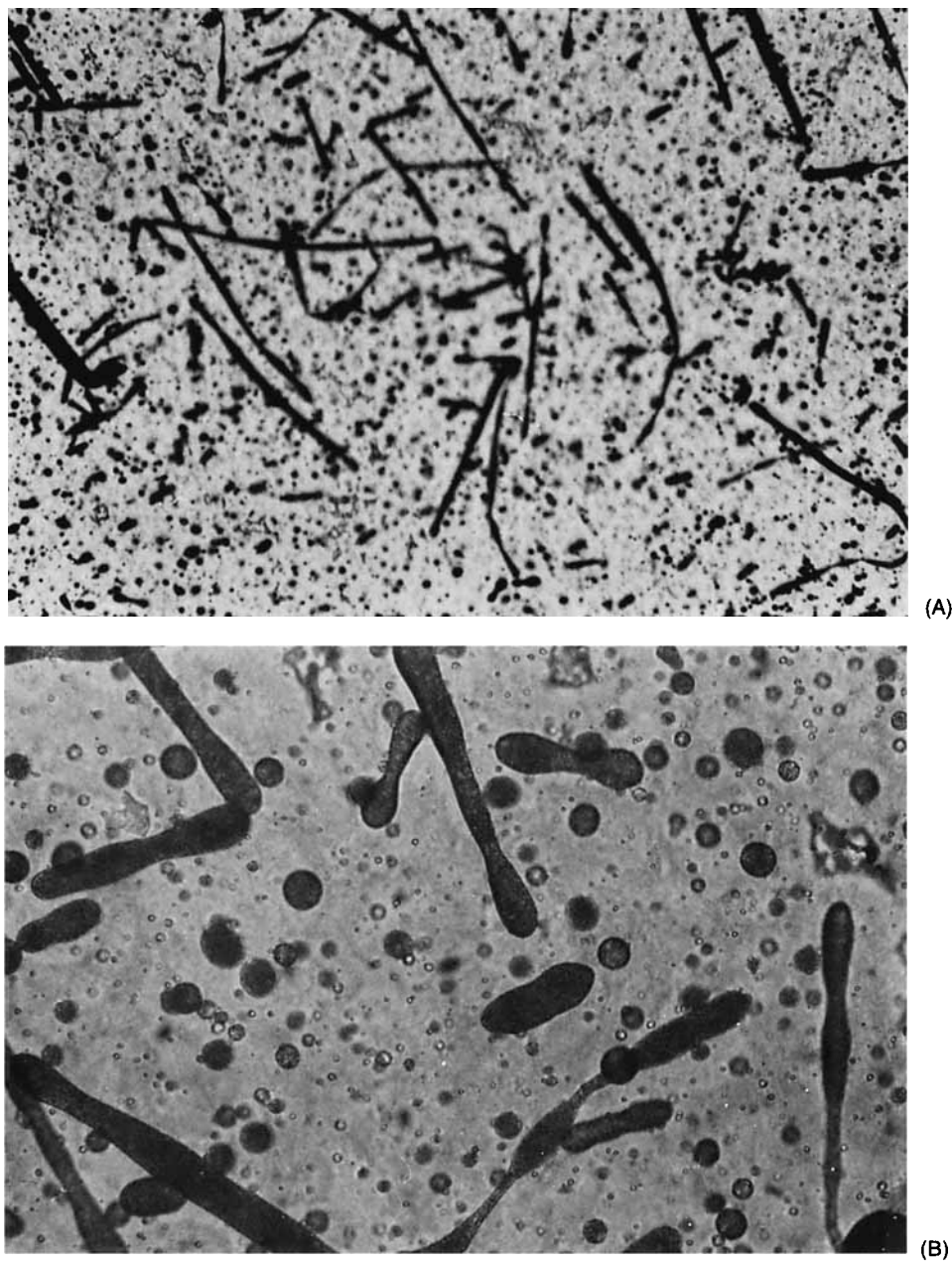
Figure 5 LCP phase morphology of a pp/Vectra A900 (wt/wt ratio 100/10) blend just after extrusion: (a) ×100, (b) ×400.
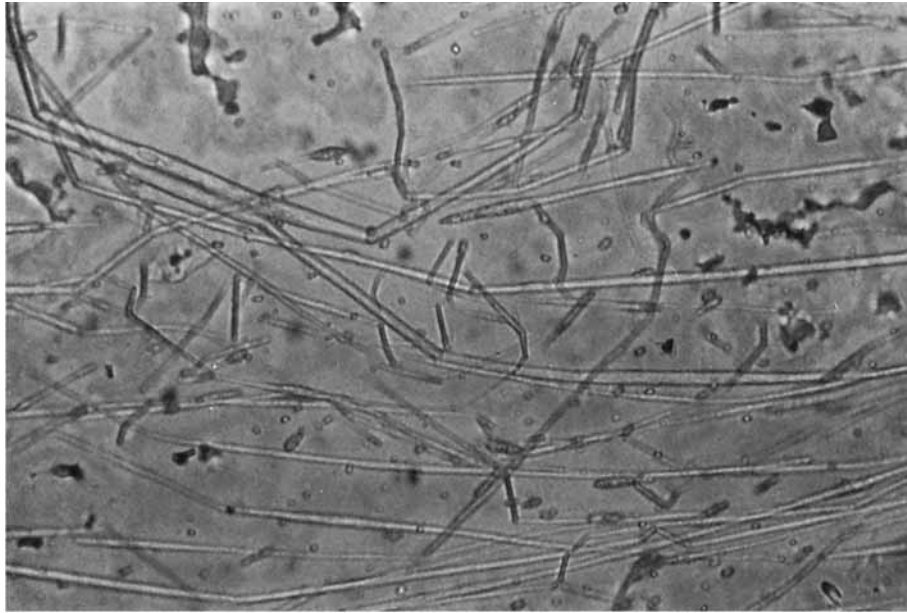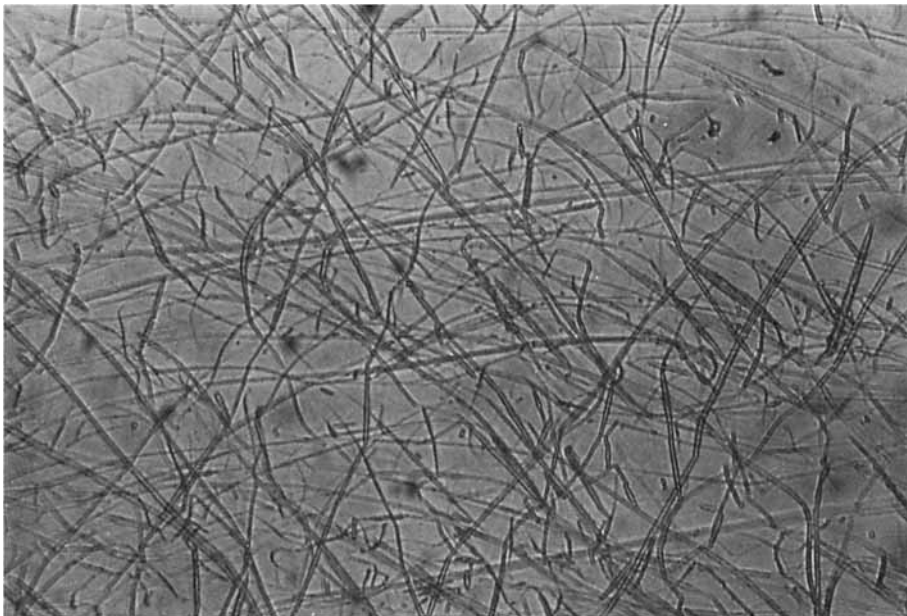
Figure 6 LCP phase morphology of the as-made pp/Vectra A900 (wt/wt ratio 100/10) polyblend fiber: (a) free-falling sample, (b) with a draw-down ratio of 20 (×400).

into elongated droplets, as can be seen from Fig. 3(a). The relaxation of the extended structure on cessation of the extensional flow field and the interfacial tension resulted in the disintegration of the elongated droplets, as can be seen from Fig. 3(b).

Just before the spinneret hole entrance, the LCP phase had largely relaxed and broken up into small particles [Fig. 4(a)]. At a higher magnification [Fig. 4(b)] it can be seen that the particles differ in di-

ameter, but they all resume a round spherical shape, indicating poor compatibility between the two polymers. This spherical structure of the LCP confirmed that in blends of LCP and conventional thermoplastics the fibrillar structure of the LCP is formed after the die entrance, where the converging force promotes the breakup of the spherical structure.

Figure 5(a) shows the LCP phase of the extrudate collected immediately below the spinneret. The par-

ticles that can be observed before the spinneret entrance [Fig. 4(b)] have been largely converted into elongated droplets. This again confirmed the view that the converging forces at the die entrance deform the dispersed particles in polyblend fibers. At a higher magnification [Fig. 5(b)] the droplets can be seen in the process of breakup. This phenomenon is similar to that observed earlier for the LCP on passage through the filter pack, where, on cessation of the extensional flow field, the elongated droplets relaxed and broke up into particles.

The LCP phase of the free-falling sample is shown in Fig. 6(a). It is clear that the droplets have been extended into thin and long fibrils. The effect of extensional strain on the LCP phase morphology is further evidenced in the fiber made with a draw-down ratio of 20 [Fig. 6(b)], for which much thinner LCP fibrils were formed in the polyblend fibers.

CONCLUSIONS

The formation of the LCP phase morphology has been studied for a polypropylene/Vectra A900 blend. The disintegration of the LCP chips in the barrel of a single-screw extruder, resulting in the distribution of small particles of LCP in the pp matrix, was well completed before the melt entered the metering pump. The planar flow and compressional force had little influence on deformation of the LCP phase, whereas effective deformation of the LCP phase into an elongated structure was observed from extensional flow fields, e.g., in the filtering pack and at the die entrance. High interfacial tension and the relaxation of the elongated structure promoted the formation of spherical particles before the spinneret hole entrance. Although the elongated structure of the LCP was formed through the converging force at the spinneret hole entrance, a high draw-down ratio is essential to sustain and develop further the fibrillar structures of the LCP phase.

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