Morphological Studies of Blends Containing Liquid Crystalline Polymers with Poly(ethylene Terephthalate)

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Synopsis

The investigation involved the structure–property behavior of extruded cast films prepared from blends of thermotropic liquid crystalline copolyesters with poly(ethylene terephthalate) (PET). Data were obtained which showed not only the temperature dependence of the moduli and stress–strain behavior but also the orientation effects that must be prevalent in order to explain the differences between the moduli measured parallel and perpendicular to the extrusion direction. Only at high liquid crystal polymer (LCP) composition is the modulus particularly increased. The modulus enhancement with lower LCP content and utilization of process variables are discussed with respect to the induced morphological textures and nature of the process equipment. Specifically, the process variable extruder gear pump speed did not enhance Young's modulus at the same LCP content as extensively as did the process variable of extruder screw speed.

INTRODUCTION

In the last decade, there has been a continual increase in interest with respect to the utilization of liquid crystalline polymers as a means of obtaining high strength-high modulus materials.[1-10] Clearly it has been demonstrated that when these systems are employed in their pure form and processed appropriately, such high strength-high modulus characteristics can be well achieved and in fact have been commercialized. Even before the development of the liquid crystalline polymers, and in particular the more recent thermotropic systems, there has been also a desire to tailor-make properties of polymeric systems through the use of blending of two or more polymeric systems to alter mechanical, barrier, surface, etc. characteristics accordingly.[11,12] It then comes as no surprise that there has been very recent interest in attempts of utilizing a thermotropic liquid crystalline polymer as a blending agent for flexible chain materials in hopes of again achieving many of the characteristics of a pure liquid crystalline polymer but at a lower expense. It is recognized, however, that the final morphological texture of the blend will dictate the final properties.[13,14] In particular, is the lower volume fraction the dispersed phase or does it form the continuous matrix? What are the shapes and sizes of the dispersed phase if indeed cocontinuity of the two components does not occur? How does the viscosity ratio of the two components alter the final material? Finally, how does the morphology relate to process variables of

technological importance such as screw design, screw speed, gear pump speed, actual process equipment, etc?

The majority of reported work on blend systems has been focused on blends of flexible–flexible chain conformation polymers. However, some discussion of blends of flexible and the rodlike liquid crystalline polymers have also been appearing in the last few years.[15-19] In fact, several publications concerned with blends of the thermotropic liquid crystalline copolyester of parahydroxy benzoic acid with poly(ethylene terephthalate) (PHB/PET), a polymer originally pioneered through the work of Jackson and Kuhfuss of Tennessee Eastman, have been provided from this laboratory.[18-20] Not only have these publications discussed many of the characteristics of this liquid crystal polymer and how it responds to process variables,[19] but also how it influences the flow characteristics and final properties when blended with PET homopolymers and utilized in a sandwich injection-molded process.[20] In fact, this earlier study demonstrated that as little as 35 wt % PHB/PET could be added as a blending agent and still achieve properties nearly equivalent to the pure liquid crystal polymer—at least in terms of flexural modulus behavior. This was accounted for by skin core morphological features where an oriented liquid crystalline skin resulted in this specific process. In addition, Joseph[18] carried out initial studies of blends of PHB/PET with PET and reported that the liquid crystalline materials served as a reinforcing agent for the homopolymer. He found that, among the different blend ratios studied, there was an influence of a composition of the PET comonomer in the liquid crystalline polymer upon the final properties of the system and in particular upon the ease of processability.

Recently, Celanese Corporation has introduced a new thermotropic liquid crystalline polymer denoted in this paper as LCP 2000. We have utilized this system in the present study as a means of investigating its influence on final morphology and properties when employed as a blending agent for PET during extrusion processing. Although many of our investigations are of a qualitative or at best semiquantitative nature, we believe the results help to illustrate the influence of specific processing conditions which may well be optimized to achieve good properties from such blends.

MATERIALS

The liquid crystalline polymer for this work was obtained from Celanese company and is based on *p*-hydroxybenzoic acid and 2-hydroxyl-6-naphthoic acid,[10] and is denoted in this paper as LCP 2000.

Sample Preparation

Dry Blended and Extruded Films

The LCP 2000 polymer was first dry-blended with PET in pellet form, dried in a vacuum oven at 120°C overnight, and then mixed within an extruder. Extrusion was carried out in a Wayne 2.54 cm single screw extruder. The blend was extruded through a slit die at 280–288°C and quenched onto a chill roll at ambient temperature. The die dimensions were 23.0 × 0.0127 cm and approximate shear rate at the die was 1.5×10^3 s^{-1}. The screw speed was

kept constant at 20 rpm. The extruded film of 0.15–0.25 mm thickness was removed from the quench roll and characterized. Materials were prepared with different levels of LCP content, specifically being—20, 40, 60, and 80 wt % LCP 2000 blended with PET.

Films Produced by Systematic Variation of the Process Conditions

Specific process parameters that were varied to produce the films were extruder screw speed and gear pump speed.

For the samples that were prepared by systematic variation in the screw speed, the samples were first dry-blended in pellet form, and then dried at 150°C in a hot air oven for 48 h. Again, extrusion was done at 280–288°C with a Wayne 1-in. extruder where the screw speed was controlled from 10 to 70 rpm. The extrudate was quenched into water at room temperature. (There was no gear pump to regulate speed; therefore, extruder residence time can be viewed as inversely proportional to screw speed.)

For the samples that were prepared by systematic variation in the gear pump speed, extrusion was done at 285–290°C in a small 1.9 cm laboratory extruder equipped with a gear pump to regulate extrusion rate. The screw speed was kept constant at low rates, but the screw speed had to be increased with the gear pump speed at high rates. The extrudates having thicknesses of 0.08–0.38 mm were quenched onto a chill roll and taken up with little or no stretching. The nomenclature for different screw speed and gear pump speed along with the calculated shear rates at the die are given in Table I.

EXPERIMENTAL

Preferential Component Solvation. Trifluoroacetic acid (TFA) solvates PET readily whereas it does not solvate the LCP 2000 polymer utilized in this study. The PET phase could thus be preferentially removed and followed by direct SEM investigation of the remaining LCP solid phase. The procedure used was as follows: The samples were placed between fine screens in a Petri dish and completely immersed in the liquid agent, and the dissolution was carried out at room temperature for 8 h for a 0.38 mm thick sample. A fine screen (100 mesh) was used to keep the nonsolvated LCP component in one place in the liquid medium and to prevent the sample from being oriented when the sample is being removed after extraction. Subsequently, the screens with sample were removed from the Petri dish, and, after removing the sample from the screens, the samples were dried. These specimens were sputter-coated with gold and observed in a ISI super III-A scanning electron microscope.

Wide Angle X-Ray Scattering (WAXS). For these investigations, a Phillips PW 1720 table top X-ray generator equipped with Warhus cameras was utilized. Diffraction patterns were recorded photographically at a distance of 7.8 cm from the sample.

Mechanical Properties. Mechanical response was investigated by use of a Model 1122 Instron testing machine operated at a crosshead speed of 10 mm/min on 10.0 × 2.7 mm specimens. In order to observe the stress–strain behavior at high temperatures, a thermal chamber with a proportional con-

TABLE I
Nomenclature of the Various Process Variable and Different Liquid Crystal Polymer Samples

	Volume rate (cc/min)	Shear rate (1000/s)
LCP 2000-30-SS, 30% LCP 2000, 70% PET		
LCP 2000-30-SS[a]-10	19	14.7
LCP 2000-30-SS-20	36	27.5
LCP 2000-30-SS-30	50	38.0
LCP 2000-30-SS-50	76	57.4
LCP 2000-30-SS-70	88	66.4
LCP 2000-30-GPS, 30% LCP 2000, 70% PET		
LCP 2000-30-GPS[b]-5	2.5	1.59
LCP 2000-30-GPS-8	4	2.54
LCP 2000-30-GPS-17	8.5	5.42
LCP 2000-30-GPS-27	13.5	8.61
LCP 2000-30-GPS-52	26	16.6
LCP 2000-30-GPS-78	39	24.9
LCP 2000-30-GPS-105	52.5	33.2
LCP 2000-40-GPS, 40% LCP 2000, 60% PET		
LCP 2000-40-GPS-10	5	3.18
LCP 2000-40-GPS-17	8.5	5.42
LCP 2000-40-GPS-27	13.5	8.61
LCP 2000-40-GPS-52	26	16.6
LCP 2000-40-GPS-78	39	24.9
LCP 2000-40-GPS-105	52.5	33.2

[a] SS = screw speed (rpm).
[b] GPS = gear pump speed (rpm).

troller was utilized for maintaining the environment temperature in the range of 80–120°C. The environment temperature was controlled within ±2.0°C.

Melt Viscosity. The rheological behavior of the resins was studied using an Instron Capillary Rheometer, Model 3211. Four length to diameter ratios were used for the capillaries: 15.22, 37.11, 75.11, and 110.22. In each case the die had a diameter of 0.069 cm. Measurements were taken at 285°C, which is the average processing temperature used in this study.

Thermal Mechanical Analysis (TMA). A Perkin-Elmer TMA device was used in the penetration mode with a 100 g load for selected samples. The atmosphere was air and the heating rate was 20°C/min.

RESULTS AND DISCUSSION

The results of this study are presented in two sections. The first section of this paper concerns the investigation of structure–property behavior of extruded cast films prepared from blends of thermotropic liquid crystalline copolyesters with PET. The second section of this paper concerns modulus enhancement with lower LCP content and the effect of the process variables such as the extruder screw speed and gear pump speed and how such variables can greatly influence the final structure of the processed material.

Mechanical Studies

To investigate the potential of LCP/PET blends as molecular composites and the structure–property relationships of the various compositions, the tensile properties of the blends were determined. As shown in Figure 1, these data clearly present not only the temperature dependence of the behavior but also the orientation effects of the LCP 2000 phase that must play a role in the differences between the moduli measured with the draw axis parallel to the extrusion direction ($E_{\parallel}$) and those determined perpendicular to the extrusion axis ($E_{\perp}$). The data also reflect the fact that only at high LCP composition (greater than 60% LCP) is the modulus particularly enhanced in the extruded cast film. If indeed phase inversion occurred, as might have been expected in the range of 40–60% LCP, the modulus would be expected to rise much faster than is shown in Figure 1.

Due to the fact that the PET component was later determined to be amorphous in the initial stress–strain behavior, samples of the same blends were annealed in an unstrained state for 1 h at 160°C under vacuum for
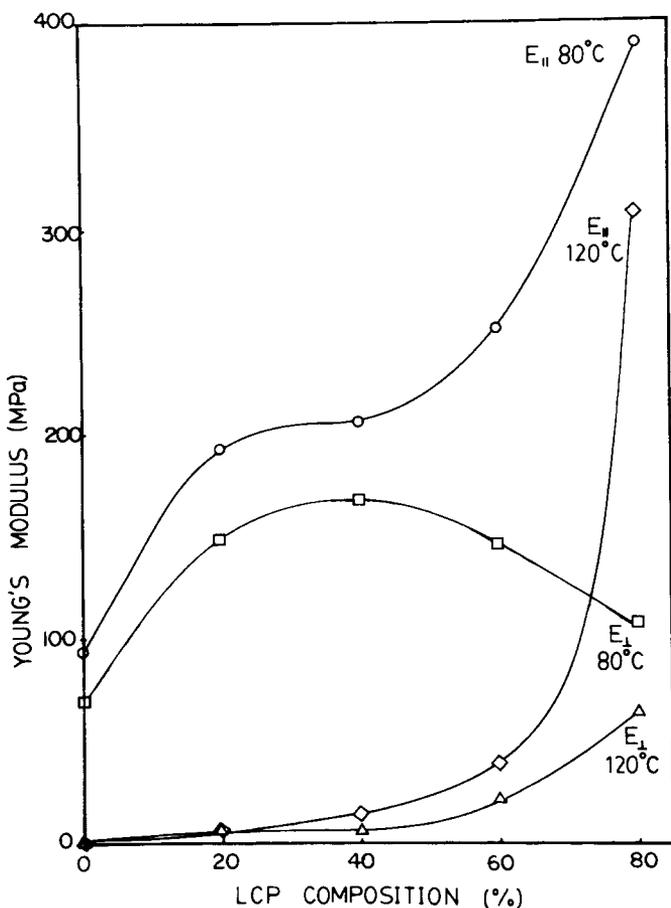

Fig. 1. Young's modulus of various LCP 2000 compositions. Measurements were made perpendicular and parallel to the flow direction.
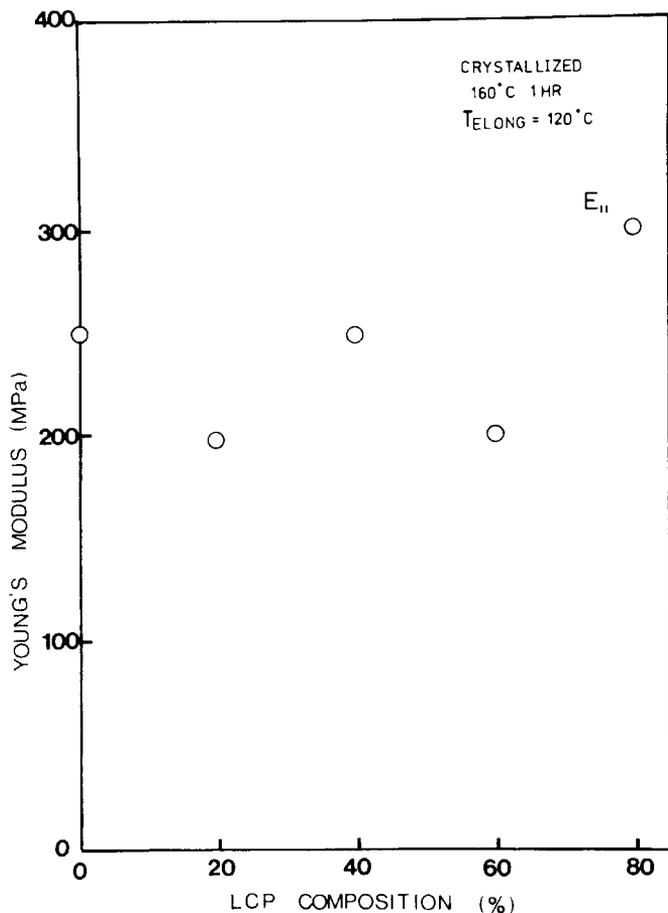
Fig. 2. Modulus of various LCP 2000 compositions that were first annealed at 160°C for 1 h. Samples were drawn at 120°C parallel to the film flow direction.

purposes of promoting the crystallization of the PET component. The stress–strain behavior was determined only at 120°C (above the T_g of PET). From these data, the value of Young's modulus was determined as shown in Figure 2. Here it is clear that the values are considerably higher than those presented in Figure 1 and show little dependence on LCP composition up to 80% where the modulus then increases, clearly suggesting some continuity of the LCP phase. When these data are compared with those in Figure 1 obtained at the same draw temperature, it is seen that, for the lower LCP contents, there is a enhancement in moduli of a factor of 5, which clearly results from PET crystallinity.

As a final indication of the LCP component on general film stiffness, the TMA results for the initially extruded cast films of varying LCP contents are shown in Figure 3. Here, of course, the penetration probe is normal to the film plane. As the data illustrate, increasing the LCP content leads to a lower degree of softening at the T_g range of PET (ca. 70°C). Yet it is to be noted that this relative level of softening is particularly decreased at the 80% LCP content. This is in line with the earlier modulus result which implied that it
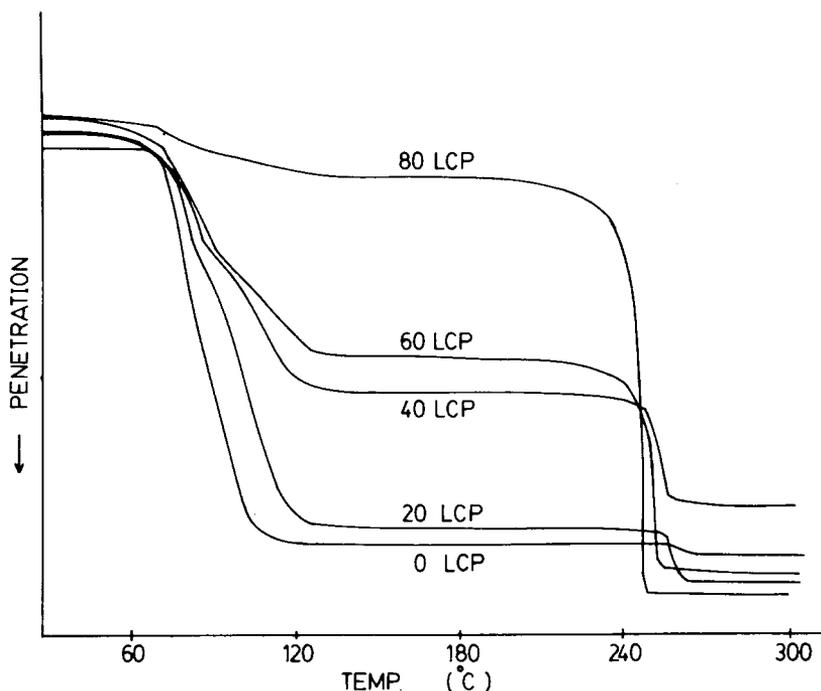
Fig. 3.   TMA results of extruded cast films of various LCP 2000 compositions.

takes this level of LCP to generate a continuous LCP phase in the blend. The shoulder in the softening curves in the range of 5–120°C is due to the crystallization of PET. The higher softening point at ca. 250°C is due to the flow of the LCP component under the 100 g load.

SEM Studies of Fracture Surfaces

The morphological features of the samples discussed above were investigated. Fracture surfaces were prepared by "snapping" the materials after cooling in liquid nitrogen. The SEM micrographs of the resulting surfaces are presented in Figures 4(I)–4(V), where the associated a and b figures presents a parallel as well as a perpendicular fracture with respect to the extrusion axis.

Figures 4(Ia) and 4(Ib) show the pure PET material to be homogeneous as expected while Figures 4(II)–4(V) clearly display a two-phase morphological texture where the dispersed phase represents the LCP component. It is noted in Figures 4(II)–4(IV) that the relative size of the dispersed phase, i.e., the LCP component, tends to increase in size with increasing LCP content in the blend from 20 to 60%. However, the droplet size might be expected to decrease if a more intensive mixing had occurred as, for example, by a twin screw device. While there is a distinct two-phase morphology and discrete fracture of the matrix around the particles, there is also the observation that the dispersed LCP component shows a somewhat "fuzzy" surface, implying that there is some signs of adhesion of the LCP with the matrix polymer. This good interfacial interaction can be seen more clearly on the close up photomicrograph of the interfacial region in Figure 4(VI). If there was no adhesion
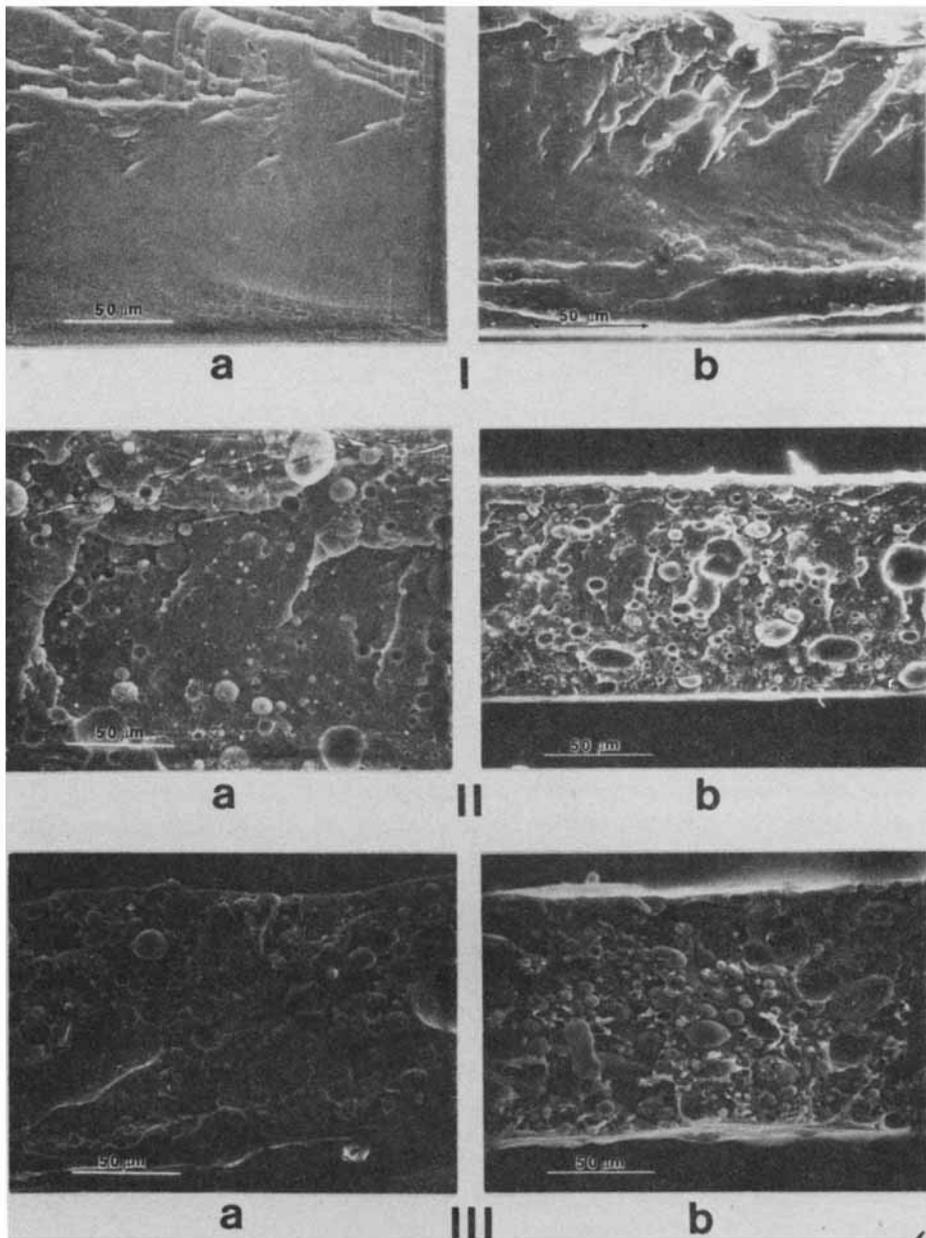
Figs. 4(I)–(VI).   Fracture surfaces of 0% (I), 20% (II), 40% (III), 60% (IV), and 80% (V) LCP 2000 film samples: (a) samples fractured perpendicular to the film flow direction; (b) samples fractured parallel to the film flow direction. Close-up photomicrograph of the interfacial region (VI).

between the LCP with the matrix polymer, then the LCP inclusions would be "loose" in the holes of the matrix. Good interfacial interaction, of course, is important from the point of view of stress transfer between phases and the relative effects on mechanical behavior. This feature will have to be considered in more detail as LCP materials are considered as potential blending
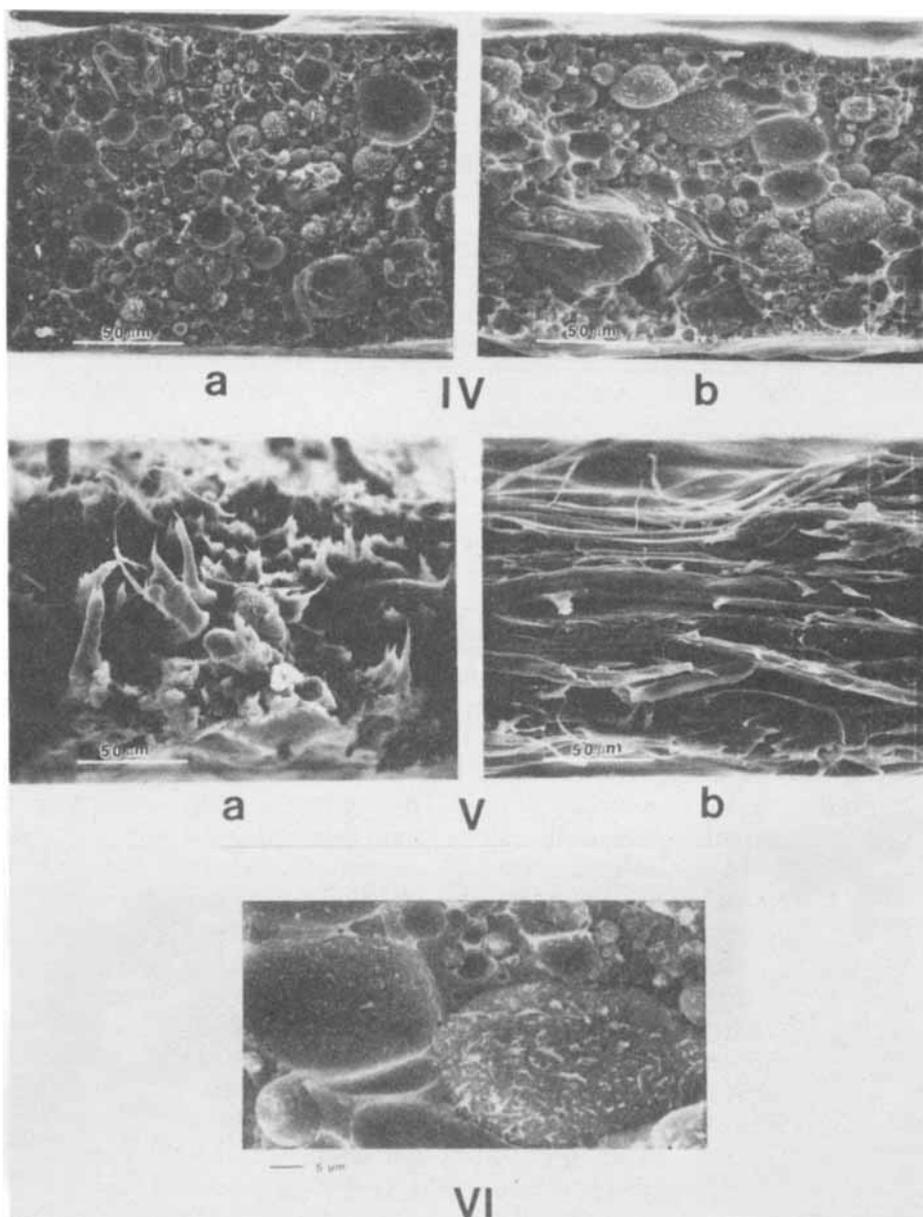
Fig. 4. *(Continued from the previous page.)*

agents with other thermoplastics. Another observation is that, in observing the parallel and perpendicular fracture surfaces, it is clear that the micrograph which depicts the fracture parallel to the extrusion axes shows signs of an oriented dispersed phase yet not highly fibrillated as would be desired for uniaxial systems. This is in contrast to what is observed when the fracture is perpendicular to the extrusion axis. In the first case, the LCP component is in the form of elliptically shaped dispersed particles whereas in the fracture surface perpendicular to the extrusion axis, an "end on" view of these ellipsoidal particles is displayed. Observation of only the latter photos could
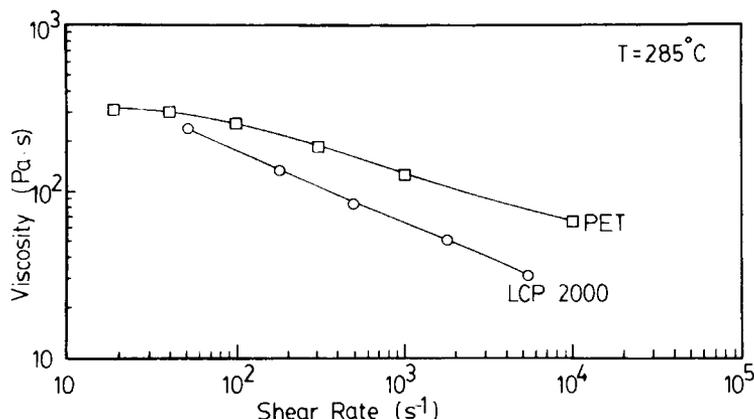
Fig. 5.   Shear rate dependence of the viscosity of LCP 2000 and PET at 285°C.

have led one to erroneously interpret that these were spherical particles and hence not oriented.

Interestingly, once an 80% LCP content is achieved, the nature of the morphological texture becomes drastically different, as shown in Figures 4(V). Here the fracture surface perpendicular to the extrusion axis tends to display more continuity for the LCP component which takes on a distinct fibril-like structure. This is clearly confirmed from the fracture surface parallel to the extrusion axis where one can easily view the LCP component now showing continuity and a fibrous-like texture. These textures clearly show how the moduli values and corresponding stress-strain behavior begin to be dominated by the LCP component at the 80% LCP content. The fact that this particular component does not display continuity until high weight percent content may well result from the difference in the melt viscosity of the two blend components. The differences in melt rheological behavior are shown in the shear dependence of the melt viscosity (Fig. 5). A somewhat stronger shear dependence is exhibited by the pure LCP 2000 relative to PET, and the viscosity of the LCP component is distinctly below that of PET. Jerman and Baird[19] and Jackson and Kuhfuss[1] also found that the PHB/PET thermotropic copolymers exhibited lower values of viscosity than the PET homopolymer. The lower viscosity commonly displayed at high shear rates by the thermotropic liquid crystalline polymers is due to the facilitated flow of the domains of semirodlike molecules which have a common orientation. During flow, these domains act somewhat as the flow unit rather than the individual molecules. The stiffer or more rodlike molecules slide smoothly over each other dissipating less energy than randomly oriented and entangled coil molecules.

The parameters needed for determining the extent of deformation[21] are expressed by the ratio of the relative viscosities η'_0/η_0 and the dimensionless group $W = \eta_0\dot{\gamma}a/\sigma$, where η'_0 and η_0 are the zero shear viscosity of the dispersed phase and the matrix, $\dot{\gamma}$ is the shear rate, a is the diameter of the particle, and σ is the interfacial tension. Since the above equation can be expressed by $W = \tau a/\sigma$, where τ is the shear stress of the medium, the droplet or fibril formation would depend on the ratio of the shear stress to the interfacial tension and the ratio of the viscosities of the two phases. However,

other authors[22,23] have reported that the initial particle size, ratio of elasticity, and extrusion temperature[22] as well as the flow field conditions and mixing mode[23] determine the morphology of the blends.

The reason for the lack of fibrillation below 80% LCP for the blend studied is that, without the coalescence of droplets in the matrix, the surface energy of the smaller particles is too large for deformation to occur, according to hydrodynamic stability theory.[24] Therefore, the formation of a fibrillar structure for a given set of flow conditions depends on the viscosity ratio and critical shear stress that promotes coalescence of the disperse phase.[25] A complete investigation of viscosity versus composition of LCP 2000 in the blend might well help explain this behavior, but this was not carried out due to limited quantities of materials.

Wide Angle X-Ray Scattering Studies (WAXS)

Noting that the strong support of the morphological features lead to the observed mechanical behavior, one additional technique was utilized for purposes of giving further support to the above analysis. Specifically, WAXS patterns of the extruded films were taken with the X-ray beam normal to the plane of the film and the extrusion axis oriented vertically. These WAXS
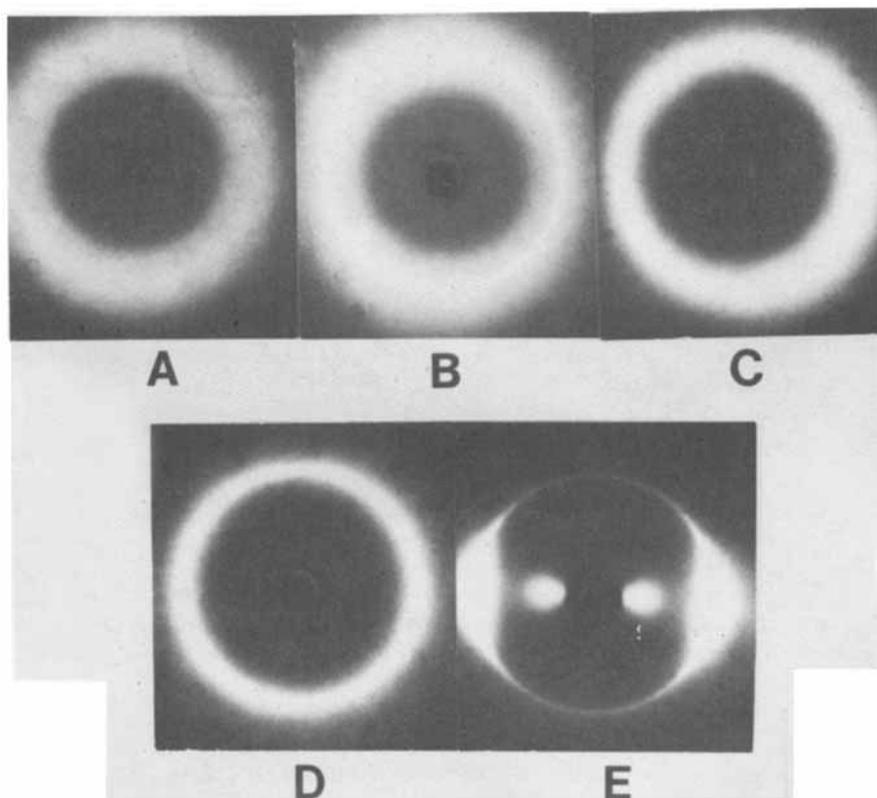
Figs. 6(A)–(E).   WAXS patterns of 0% (A), 20% (B), 40% (C), 60% (D), and 80% (E) LCP 2000 film samples. The extrusion axis is vertical.
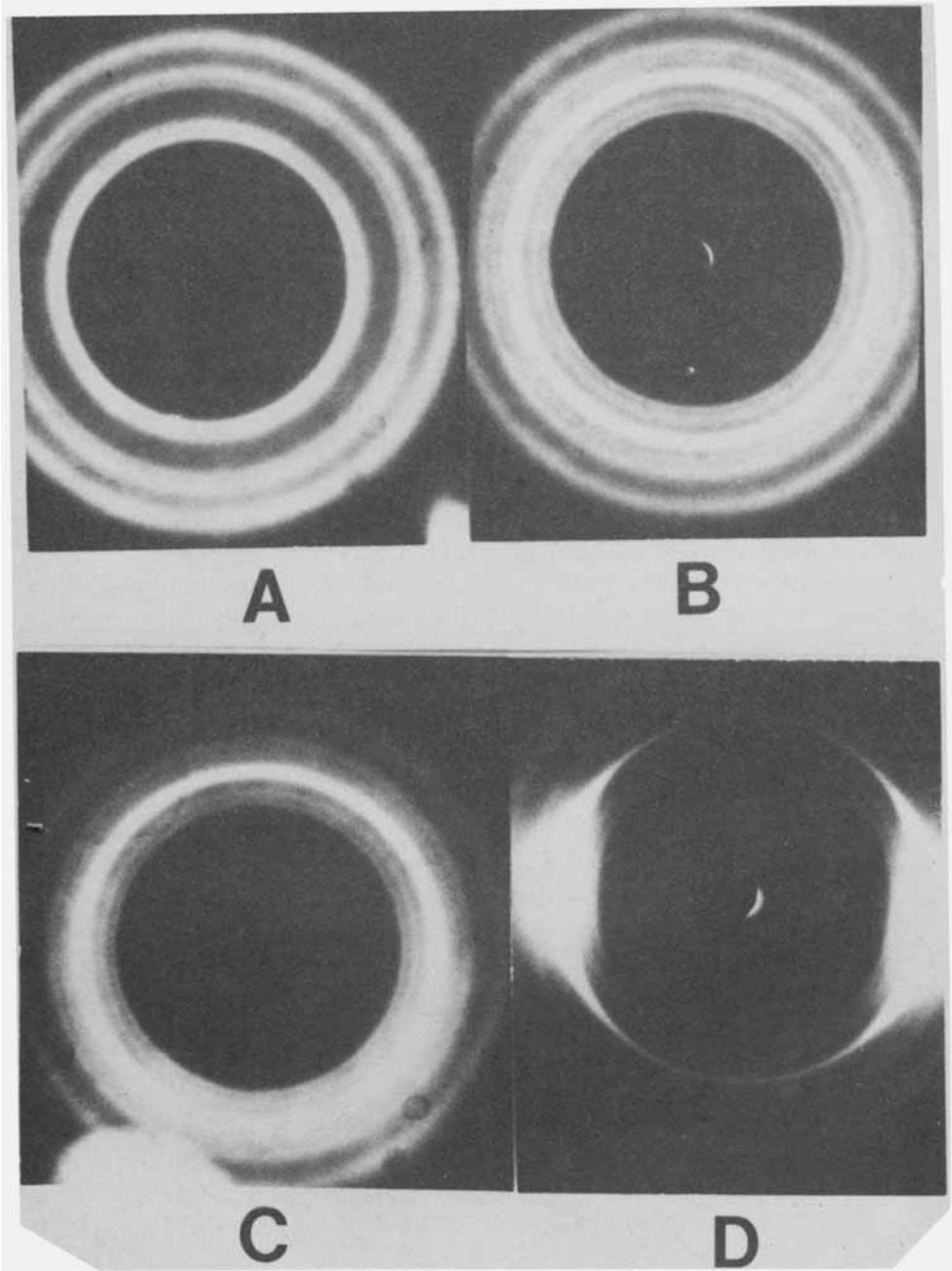
Figs. 7(A)–(D).   WAXS patterns of 0% (A), 40% (B), 60% (C), and 80% (D) LCP 2000 film samples which were annealed at 160°C for 1 h. The extrusion direction is vertical.

patterns are shown in Figures 6(A)–6(E) for the corresponding 0, 20, 40, 60, and 80% LCP/PET blends. No sign of PET crystallinity nor significant orientation of the LCP component is displayed in the first four WAXS patterns, although there is some variability due to the differences in the scattering behavior of the two components. However, in the final WAXS patterns, i.e., the 80% LCP blend, a very distinct orientation of the LCP phase occurs, and this helps to account particularly for the much greater modulus observed from the stress–strain behavior. This is directly in agreement with the observed fracture surfaces of the SEM micrographs [Figs. 4(V)].

To illustrate the effect of the 160°C annealing treatment on the initial films to produce a semicrystalline PET phase, Figures 7(A)–7(D) present WAXS patterns for four of these materials showing that a 1-h annealing converts the PET phase to a semicrystalline phase. This is very clear from the WAXS patterns, and it also demonstrates that in those systems which show significant signs of orientation of the LCP component, the effect of annealing does not strongly alter its orientation.

THE EFFECT OF PROCESS VARIABLES ON THE MORPHOLOGICAL TEXTURES BLENDS OF PET WITH THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTERS—LCP 2000

Based on the observations that direct dry blending and sheet extrusion under conventional conditions did not produce signs of a continuous LCP phase in low content LCP blends, some qualitative but useful investigations were made as to the effect of two particular process variables on the relative dispersability of the LCP component. The specific aim was to influence the morphology of the blend and improve the film's mechanical properties. Some range of composition was also investigated. The two process variables that were utilized for this study were the speed of the exturder screw (which alters extruder mixing shear stress and rate), which will be simply referred to as screw speed (SS), and gear pump speed (GPS) (which influences shear rate). The nomenclature for different screw speed and gear pump speed samples are given in Table I. For these studies, dry pellet blends of the materials were also made of PET with LCP 2000.

Effect of Extruder Screw Speed (SS)

SEM Studies Following Preferential Dissolution of PET

SEM dual magnification micrographs of blends of 30% LCP 2000 with PET, are given in Figures 8(A)–8(E). The effect of variable screw speed is clearly indicated. The samples have been prepared by first solvating and extracting the PET component with TFA thereby leaving the LCP phase. As is clear from Figures 8(A)–8(E), it is obvious that increasing the value of SS has a very pronounced effect on the general texture of the LCP component and its dispersability and fibrillation as seen by the progression from a distinct particulate to a continuous strandlike fibrous network. For example, in sample LCP 2000-30-SS-10, the screw speed of 10 rpm is the lowest, and while there are some strandlike LCP phases, there are many globular or distinct particu-
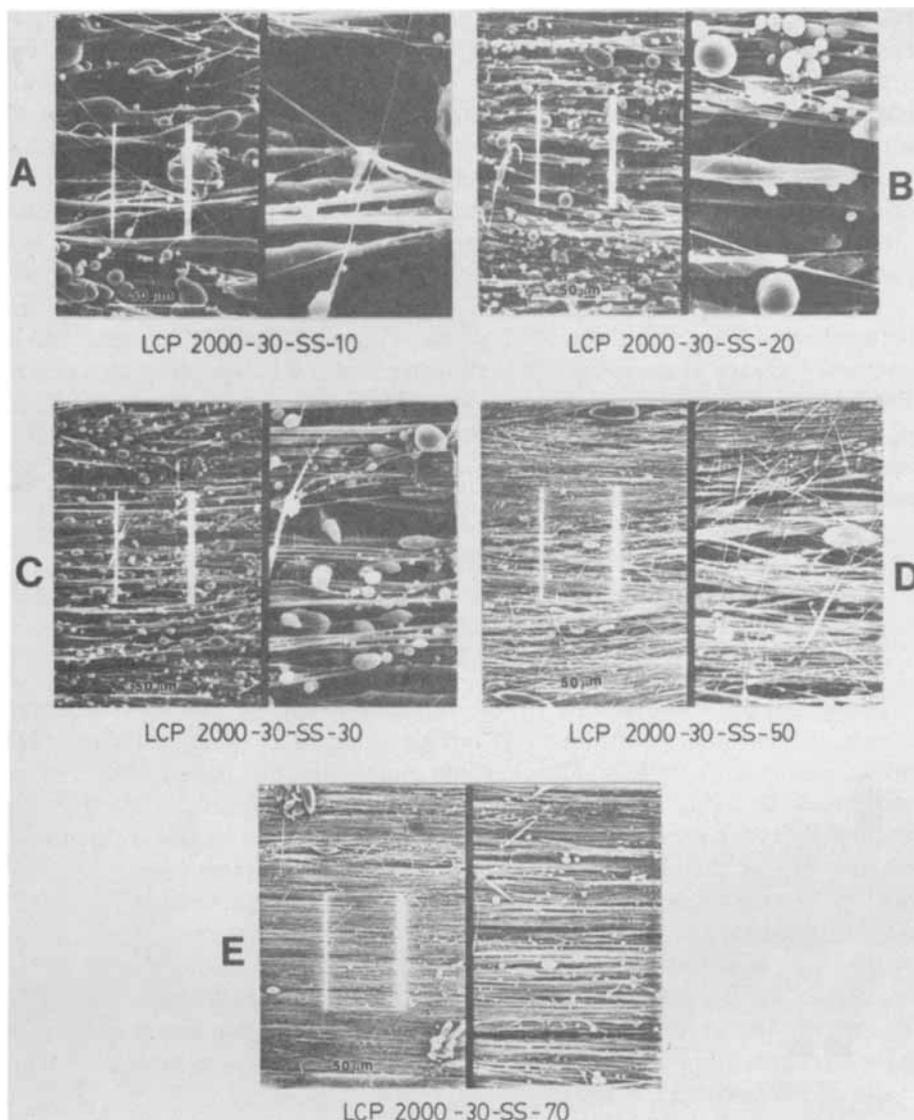
Fig. 8. SEM micrographs of trifluoroacetic acid treated 30% LCP 2000 blends, the highest extruder screw speed being 70 rpm.

late components as well. However, at the highest screw speed represented by sample LCP 2000-30-SS-70, there is a very highly pronounced fibrous texture which also is highly aligned along the extrusion axis for the same extrusion die following the extrusion process. This is confirmed by the distinct azimuthal dependent WAXS patterns shown in Figures 9(A)–(E). Clearly the effect of screw speed plays a very important role on the general dispersability of these systems, all of which have 30% of the LCP 2000 component. This suggests that this process variable is very influential for this blend. Recall the earlier statement that the morphology in a molten polyblend is a result of the components' viscosity ratio, elasticity, particle size, and shape, which are
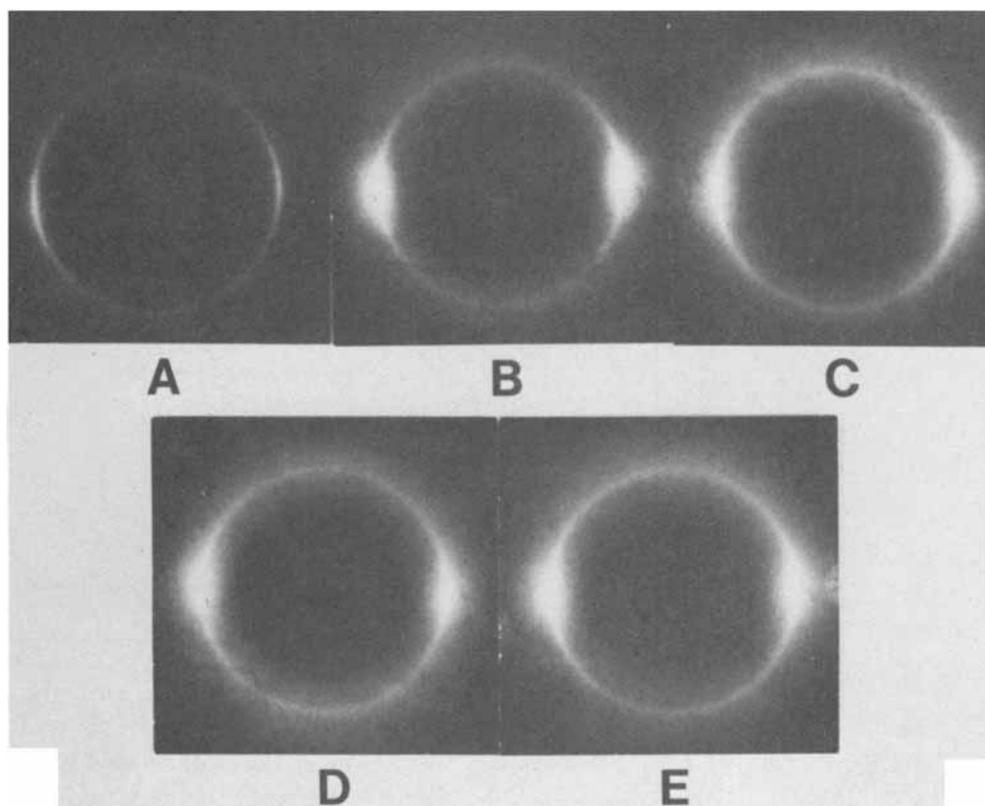
Figs. 9(A)–(E). WAXS patterns of 30% LCP 2000 blends. Extruder screw speeds (rpm): (A) 10; (B) 20; (C) 30; (D) 50; and (E) 70. The extrusion axis is vertical.

obviously dependent on the level of shear stress or shear rate level as well as on the initial size of the component phase. Specifically, the ratio of melt viscosities determined at a specific shear rate, temperature, and residence time for the polyblend components influences the phase grain size (droplet, rod) as mentioned before.

Mechanical Studies

Figure 10 shows the values of Young's modulus determined for the films produced after utilizing different screw speeds. The moduli values shown are those that were determined at 80°C. While there is some scatter in the data, it is clear that producing a more continuous or fibrous-like network structure in the LCP component has promoted a much higher modulus (800 MPa) than was observed in comparable LCP content containing films (200 MPa) produced through "conventional" extrusion conditions as discussed earlier. The basic point is therefore that a much more enhanced modulus can be obtained with lower LCP content by utilizing the appropriate process variables to alter the dispersability and fibrillar behavior of the LCP component for purposes of promoting a more continuous or fiber reenforcing phase. One major drawback to this approach, however, is that while the modulus can be increased greatly
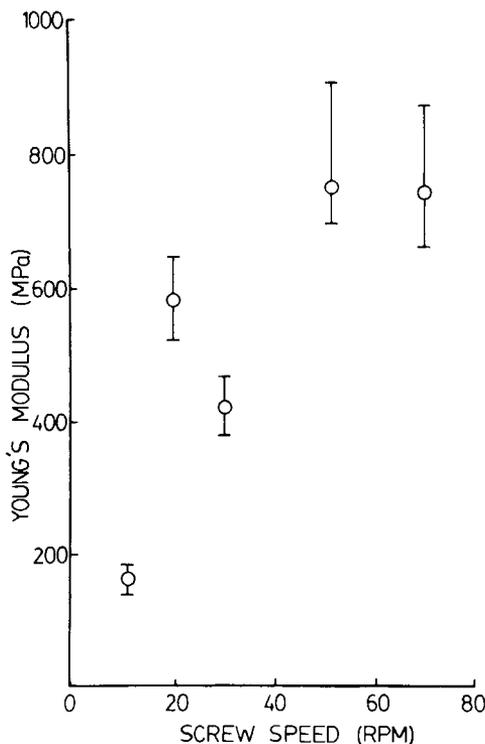
Fig. 10.   Modulus of 30% LCP 2000 blends at 80°C with increasing extruder screw speed left to right.

in the extrusion direction, the same films displayed very poor properties in the transverse direction due to the fact that there was little continuity of the LCP component in this direction. Recall that a transverse modulus of only 120 MPa was obtained for the 80% LCP 2000 blend in the earlier study.

Effect of Extruder Gear Pump Speed (GPS)

SEM Studies Following Preferential Dissolution of PET

Figures 11(A)–11(D) illustrate the effect of gear pump speed on the structure of the LCP 2000/PET blends containing 30 wt % LCP. These display the morphological features observed following TFA extraction of the PET component. In particular, Figure 11(A) shows a particulate texture which results from the fact that the PET component was the continuous phase. Therefore, following extraction with TFA, only the particulate LCP 2000 remained. This LCP material in general shows little sign of orientation except for sample LCP 2000-30-GPS-52, which is from an intermediate gear pump speed. However, at higher gear pump speeds, some strand or fiberlike formation of the LCP component is clearly produced [see Figs. 11(C) and 11(D)]. WAXS patterns (not shown) also indicated orientation of the LCP component. Hence, it can be concluded that there is a strong dependence on the process variable of gear pump speed, especially at higher gear pump speeds as might be expected due
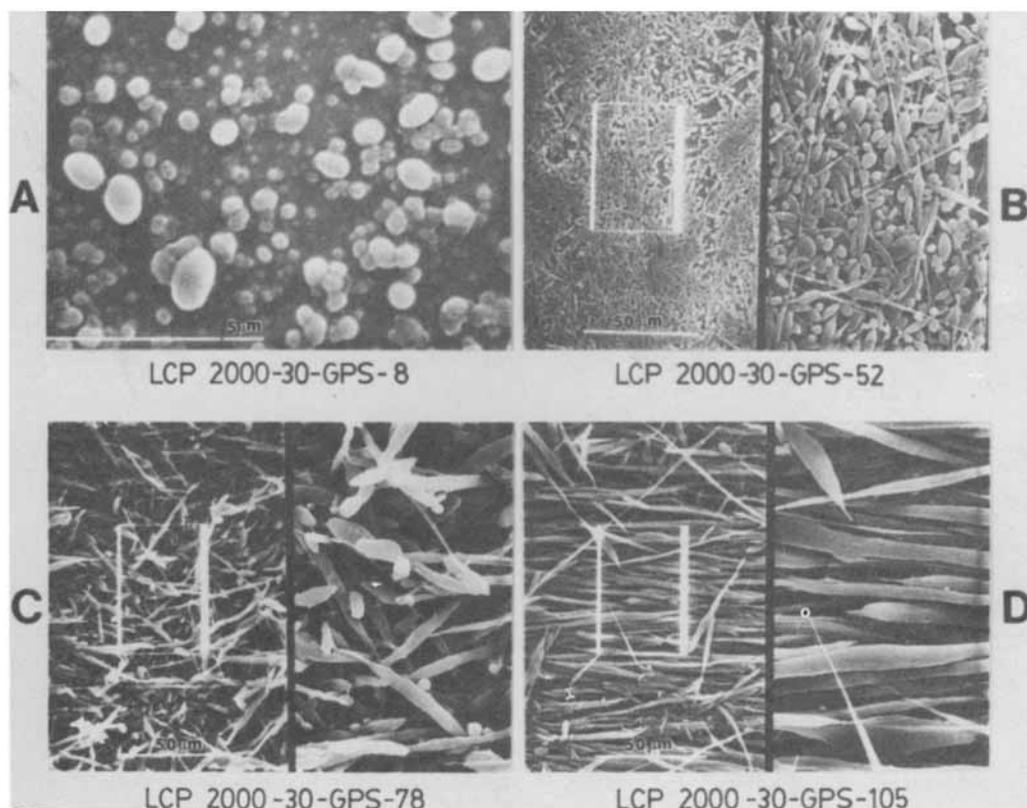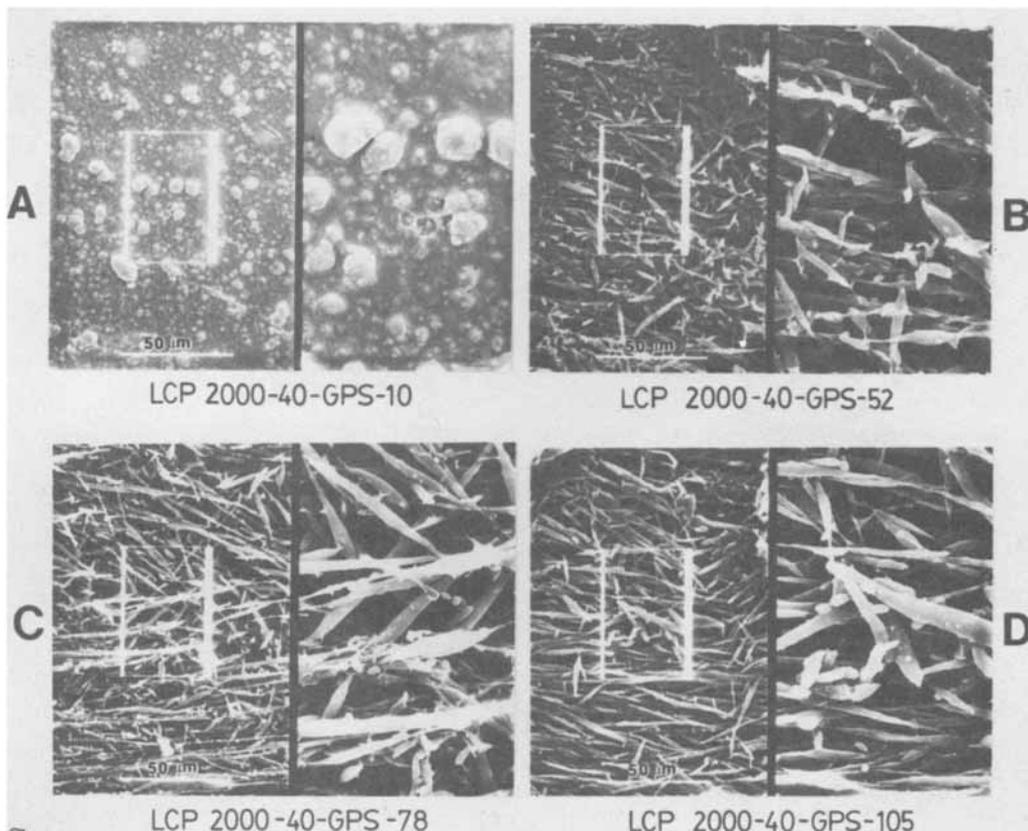
Figs. 11(A)–(D).   SEM micrographs of trifluoroacetic acid treated 30% LCP 2000 blends. The gear pump speed increases in the order of 8, 52, 78, and 105, the highest gear pump speed being 105 rpm.

to the higher shear rate effects in the film die. Any extensional flow components are also likely enhanced by this same process variable.

To note the effect of LCP composition, a 40% blend of LCP 2000 was also investigated for the effects of gear pump speed. The results are shown in Figures 12(A)–12(D), which again illustrate a very similar behavior as was shown in the last series of micrographs. Specifically as gear pump speed goes from lower to higher values, the LCP phase is transformed from a particulate to a partially oriented particulate phase to that of continuous fibrouslike structures.

Mechanical Studies

The general trend was that the effect of gear pump speed did not strongly enhance Young's modulus in the extrusion direction at the same LCP content as extensively as did the effect of screw speed. Although the morphological textures show the formation of LCP 2000 strands at high GPS, their formation did not greatly improve the mechanical properties in the extrusion direction—see Figure 13.

Figs. 12(A)–(D). SEM micrographs of trifluoroacetic-acid-treated 40% LCP 2000 blends. The gear pump speed increases in the order of 10, 52, 78, and 105, the highest gear pump speed being 105 rpm.

However, the GPS samples has to be compared with the SS samples on the basis of the same shear rates. In this respect, Figure 14 provides a plot of modulus determined at 80°C against the shear rate at the die for both the LCP-30-SS and LCP-30-GPS series. Clearly, the difference between the effect of varying screw speed and gear pump speed is not as dramatic when compared on the basis of equal shear rates. There was still some differences between the SS and GPS series, however. Morphologically, the LCP in the SS series seems to have a bimodal distribution of aspect ratios. Specifically, there seem to be a population of spheres and ellipsoids and another population of long fibers existing in the same sample as revealed in Figure 8. On the other hand, the GPS series tends to have only one population of elongated ellipsoids, as revealed in Figures 11 and 12. This difference may explain why the modulus values for the SS series were slightly higher than the GPS series, especially at the higher shear rates. The highly stretched LCP fibers, even though at lower counts, reinforced the film more effectively than the elongated ellipsoids at higher counts, as one would expect.
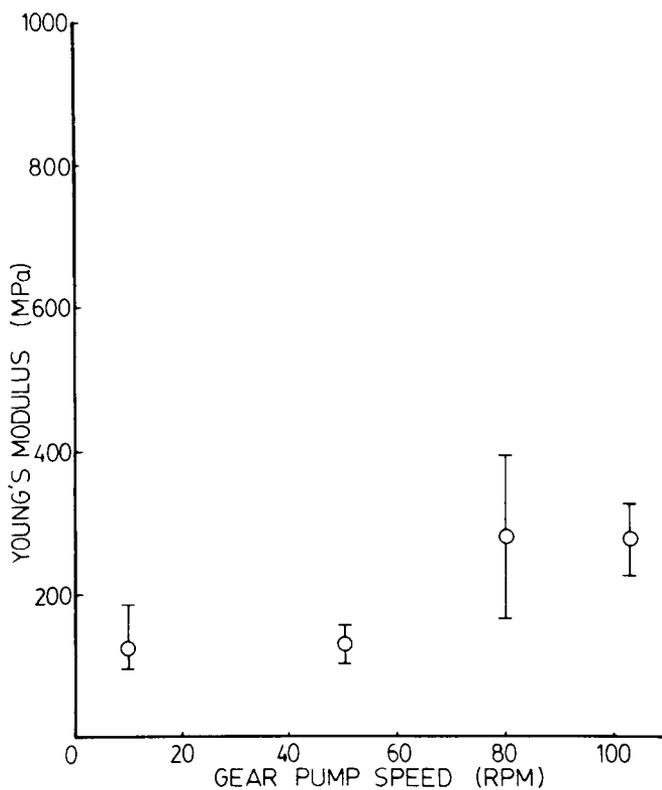
Fig. 13.   Modulus of 30% LCP 2000 blends at 80°C with increasing gear pump speed from left to right.
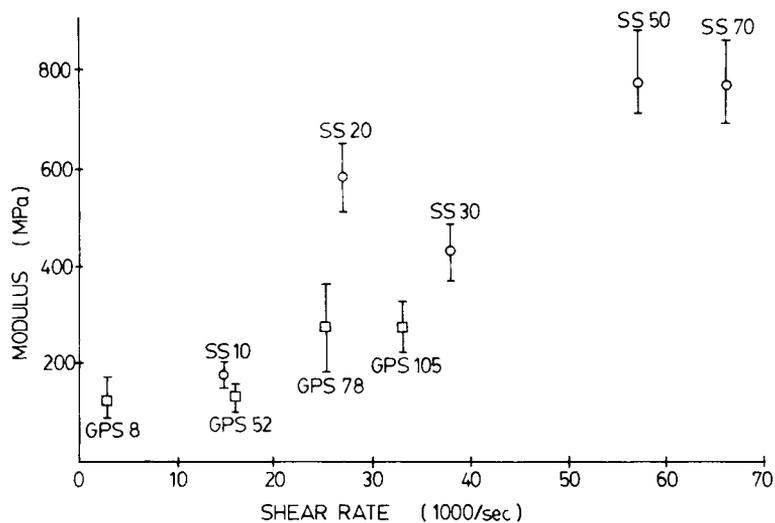

Fig. 14.   Modulus ($E_{\parallel}$) plotted against shear rate at the die wall for LCP-30-SS and LCP-30-GPS materials.

CONCLUSIONS

The goal of this study was to correlate observed mechanical properties, as determined above ambient temperatures, to the morphological features of blends of PET and LCP. From this study, the following highlights were denoted.

1. The technique of selective chemical dissolution is very useful for studying the morphological textures of blends of PET and LCP 2000. Specifically, using trifluoroacetic acid, PET-rich regions can be selectively dissolved away.

2. Preferential dissolution on these blended samples show that at low LCP 2000 levels, PET is the continuous phase. The PET-rich phase remains the continuous phase until the LCP 2000 content reaches 80 wt % in the blend. In the 80% LCP 2000, however, it is the LCP-2000-rich phase that is the continuous phase, and PET is the dispersed phase. At this higher content of the liquid crystal polymer, LCP 2000 provides high strength through orientation. These studies indicate that the thermotropic copolyester system does not reach continuous fiberlike structure until 80% LCP 2000. This is due to among other factors, the ratio of the shear stress to the interfacial tension, the ratios of viscosity and elasticity of these two components, incoming drop size, flow field conditions, and mixing mode. Presently more detailed studies of these variables are being investigated at this laboratory.

3. Scanning electron microscopy studies on the 20, 40, and 60% LCP 2000 fracture surface shows the presence of LCP 2000 ball shapes which are in the 5–25 μm size range. The balls, however, are deformed forming ellipsoidal shapes in the extrusion direction. At 80% LCP 2000, the morphological texture appears to be more fiberlike due to the near continuity developed by the LCP phase.

4. The fibril-like structures which were obtained by incorporating 80% of LCP 2000 into the blend with PET with conventional extrusion can also be obtained at lower contents of LCP 2000 by varying the screw speed and gear pump speed which influences melt mixing through melt shear stress and shear rate as well as likely influencing extensional flow behavior. These effects were studied using a blend of 30% LCP 2000 and 70% PET. Specifically, for the sample LCP 2000-30-SS-70, the modulus in the extrusion direction at 80°C is 800 MPa vs. for the sample with 80% LCP 2000 in the blend with PET, the modulus of which is 400 MPa determined under same conditions.

5. The modulus in the extrusion direction can be enhanced considerably at the low content of LCP 2000 polymer (30%) in the blend by increasing screw speed from 10 to 70 rpm. However, the gear pump speed does not enhance the mechanical properties in the extrusion direction as well as screw speed at the same composition of LCP 2000. Even at higher (40%) LCP 2000 content, varying gear pump speed alone does not greatly improve mechanical properties in the extrusion direction. However, the screw speed samples were extruded at higher shear rates through a smaller slit.

6. Through further studies of different viscosity of the components—as could be controlled by temperature and/or molecular weight—it is expected that, in conjunction with other process variables, further optimization of properties through morphological control could be obtained at possibly even lower LCP contents.

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