# Improvement of the Processability
# of Advanced Polymers

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## Synopsis

The possibility of improving processability of engineering polymers was studied in this work. Low percentages of a thermotropic liquid crystalline polymer supplied by Bayer Co. were added to the polyetherimide Ultem. The thermal and morphological analysis revealed a two phase system. Rheological measurements in shear flow were carried out in the temperature range of the existence of the mesophase. A significant drop of $\sim$ 30% in the Ultem viscosity occurs even with 5% w/w TLCP. The influence of the addition of the thermotropic polymer on the mechanical properties of Ultem was also investigated. Moreover, the morphological analysis of the unfilled polymers and of the blends was performed and related to their rheological and mechanical behavior.

## INTRODUCTION

Engineering polymers represent a new class of materials characterized by high mechanical properties, good flame retardancy, and mostly high continuous-use temperatures with excellent retention of properties at the elevated temperatures. Among these materials, the ones most used are Polysulfone (PS), Polyetherimide (PEI), Polyetheretherketone (PEEK), Polyphenilsulfone (PPS), and Polyimide (PI), whose continuous-use temperatures range from 150°C for PS to about 310°C for PI.[1] In general, however, the high performance polymers are high cost, low impact, and difficult-to-process materials. Improving processability without a consequent decrease in the mechanical properties represents, therefore, a goal in the processing operations of these resins. In this regard, the inclusion of a low viscosity second phase can be a successful procedure to decrease the extrusion temperature of the engineering plastics.

Due to their unique physical properties, the thermotropic liquid crystalline polymers (TLCP) seem to represent the class of materials offering the above-mentioned advantages. These materials, in fact, consist of rigid backbone molecules spaced with flexible groups to make their processing possible. The liquid crystalline structure is based on domains including fairly parallel chain molecules characterized by a "director" that identifies the local molecular orientation.[2,3] In the absence of external constraints, the directors are randomly oriented, yielding an isotropic supramolecular morphology, while if a TLCP is subjected to a flow field at the temperature of the mesophase existence, the directors easily orient along the flow direction. TLCP viscosity values lower

than those measured for the corresponding isotropic polymers are a consequence of this phenomenon. This event was ascribed by Wissburn[4] to the assumption that the rigid rods in TLCP easily line up when sheared, thereby reducing the resistance to flow. Moreover, if a spinning process is performed, a fibrillar material can be easily obtained in the solid state due to the high TLCP relaxation times. As a result, the extruded and melt drawn articles are characterized by a highly anisotropic structure responsible for the measured high rigidity values.[5]

Engineering plastics, therefore, are expected to show an easier processability if a low amount of TLCP is added as a second phase and the processing operations are carried out in the temperature range of mesophase stability. In addition, an improvement in the rigidity of the high performance resins can be obtained if the TLCP molecules, included in the matrix, orient in a fibrillar-like shape during the spinning operations. Blends of traditional thermoplastics, like polystyrene and polycarbonate, with TLCPs are reported in the technical and scientific literature.[6-8] In that case the main objective was the improvement of the rigidity of the matrix to obtain the so called "*in situ* composites," while in this study the main purpose is the processability improvement of engineering plastics.

In particular, the matrix used in this work is the polyetherimide, Ultem, which combines a relatively low production cost with appreciable good physical properties.[1,9] Moreover, it represents, for future years, the engineering plastic with the highest production market increase, and therefore it seems the most attractive material to verify the effect of TLCP's inclusion on the processability.

## EXPERIMENTAL

### Materials

The amorphous matrix used in this work is the polyetherimide Ultem 1000, produced by General Electrics. The thermotropic liquid crystalline polymer utilized is an almost wholly aromatic polyester based on hydroxybenzoic acid, isophthalic acid, terephtalic acid, hydroquinone, and 4,4'-dihydroxybiphenol, kindly provided by Bayer Co. and referred to here as K161.

The materials were vacuum dried at $T = 140°C$ for 10 h before mixing. The blending procedure was performed by means of a Brabender equipped with a mixing chamber at the temperature of 340°C and at 32 rpm. Blends were prepared with compositions ranging from 5 to 30% w/w of TLCP in Ultem. They will be referred as Ultem/K161-95/5 and so forth, where the numbers identify the matrix and the TLCP percentages respectively.

### Methods of Investigations

A differential scanning calorimeter (DSC) Mettler TA3000 system was used to evaluate the transition temperatures of the unfilled polymers and of the blends. The temperature range investigated was 0–500°C at a scanning rate of 10°C/min.

Rheological measurements in shear flow were carried out in the high shear rate region with the aid of a capillary viscometer, CEAST Rheoscope 1000. Flat entry capillaries with $D = 1$ mm and $L/D = 5, 10, 20,$ and 40 were used for the

rheological characterization of the unfilled materials. A capillary of $L/D = 10$ was used for the viscosity measurements of the blends. The shear rate range investigated was $1-10^3$ s$^{-1}$. The end effects (Bagley corrections) were evaluated for the pure polymers. Rabinowitch corrections were performed in all cases.

Spinning of the pure polymers and of the blends was performed by means of the Rheoscope 1000 equipped with a spinning unit, using a die of 1 mm diameter and $L/D = 10$. The temperature used was $T = 370°C$ for the TLCP and $T = 330°C$ for the other materials. The extrusion velocity was 18 cm/min in all cases. The filaments were collected in air at room temperature on a 8 cm diameter bobbin at a distance of about 30 cm from the die exit. The take-up velocity, $V_f$, was varied to obtain $V_f/V_0$ (draw ratio) values ranging from 10 to 250 for the ductile Ultem and for the blends with low TLCP content. In the case of the brittle TLCP and the Ultem/K161-70/30 blend, a maximum draw ratio of 50 could be obtained. Moreover, the true draw ratio values were determined as the ratio between the die and the fiber cross sections ($S_0/S_f$) measured by an optical microscope. Mechanical fibers properties were determined at room temperature with an Instron testing machine equipped with a HP computer, operating with a crosshead velocity of 10 mm/min on samples of 30 mm length prepared following the ASTM D 3379 standards for filaments. The elastic Young modulus was evaluated as a secant modulus at 0.3 and 0.5% strain.

The TLCP morphology was analyzed on samples obtained both through simple extrusion and through spinning by means of a scanning electron microscope (SEM), Hitachi S-2300. The Ultem/K161 blends morphology was investigated by SEM on compression molded and extruded samples. In particular, the effect of the shear rate on the TLCP particles elongation in the extruded blends samples has been also studied. Transversal sections of the samples were obtained by fracturing them in liquid nitrogen.

The morphology of the TLCP phase in the drawn blends was analyzed by dissolving the Ultem matrix with methylene chloride and observing the TLCP remaining phase by an optical microscope Reichert-Jung, Polyvar, under cross polarizers at room temperature.

## RESULTS AND DISCUSSION

### Calorimetry

The DSC thermograms of the as-received TLCP K161 and Ultem are shown in Figure 1. The Bayer thermotropic polymer shows a first solid-mesophasic transition at $T = 118°C$ and a second solid-mesophasic transition at $T = 279°C$. No melting peaks are detectable, while the isotropization starts at $T = 380°C$, with a peak temperature $T = 466°C$. The polyetherimide shows the typical amorphous thermal behavior, i.e. the only detectable thermal transition is the glass transition occurring at $T = 214°C$ ($T_g$). The Ultem processability temperature range reported in literature[9] is $\sim 310-410°C$. Injection-molded parts are, therefore, usually obtained by setting the different extruder zones at temperatures included in this range. It is worthwhile to note that the processing temperature range of Ultem and the mesophasic stability temperature range overlap.
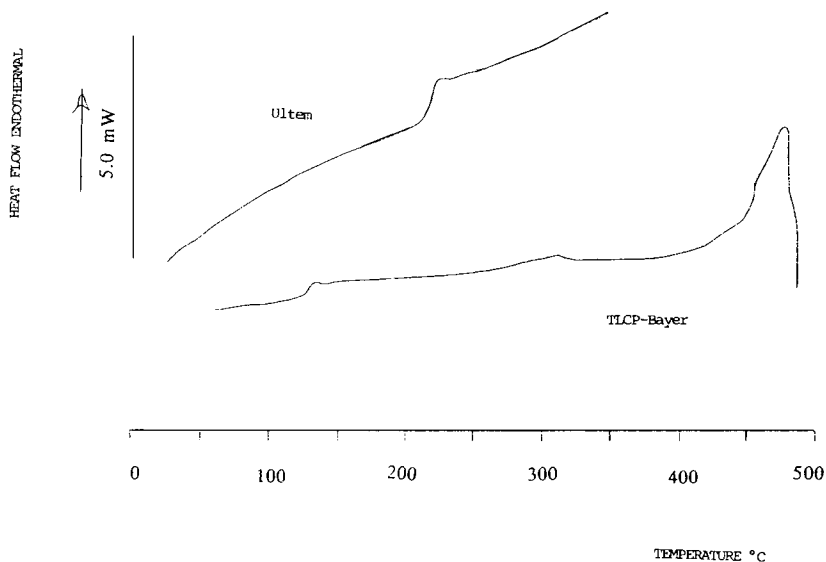
Fig. 1.   DSC thermograms of TLCP 161 and Ultem.

In Figure 2, the DSC thermograms of the Ultem/K161-90/10 and 70/30 w/w blends are shown. In both cases, a slight decrease in the $T_g$ of Ultem is recognizable ($T_g$ = 211°C), showing that a plasticizing effect occurs for the Ultem when blended with the TLCP phase. However, despite the partial interaction between the two phases, the Ultem/K161 system results mostly an incompatible system, as is revealed by the SEM analysis and shown in the morphology session.
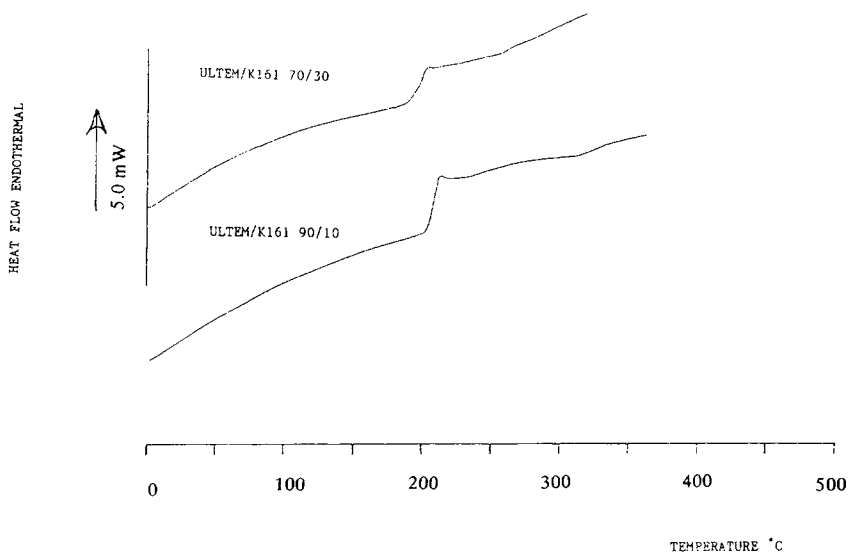


Fig. 2.   DSC thermograms of Ultem/K161-90/10 and 70/30 w/w blends.

## Rheology

The Ultem rheological behavior has been analyzed in the temperature range generally used to process it. Viscosity measurements were, therefore, performed at $T$ = 315, 330, and 350°C. In particular, the temperature of 315°C represents the lowest temperature at which the Ultem could be extruded. Figure 3 shows the Ultem flow curves relative to the different temperatures mentioned above. At the lowest shear rates, the material has a Newtonian behavior, while increasing $\dot{\gamma}$ a shear thinning behavior is shown. A detailed discussion on the Ultem viscosity data will be reported in a separate paper.[10]

Viscosity measurements on the TLCP K161 have been performed at different temperatures chosen in the temperature range of Ultem extrusion processing operations. The TLCP flow curves in Figure 4 refer, therefore, to the temperatures of 315 and 330°C. A continuous viscosity decrease with the shear rate in the whole $\dot{\gamma}$ range investigated is recognizable. In order to understand if a yield stress exists or not for this polymer, measurements in the low shear rate range are being performed and the results will be reported elsewhere.[10]

The effect of the inclusion of a low amount of TLCP on the Ultem processability was investigated by studying the rheology of Ultem/K161-95/5 and 90/10 w/w blends. In Figure 5, the blends viscosity values are compared with the Ultem viscosity values at the temperature of 330°C. For both compositions, the flow curves lie below the Ultem curve. At a shear rate of 140 s$^{-1}$, a significant drop ($\sim$ 30%) in the Ultem viscosity occurs with 5% w/w TLCP, showing that an improvement in the processability of this engineering plastic can be obtained if a low amount of liquid crystal polymer is added. No appreciable difference is recorded between the Ultem/K161-95/5 and 90/10 rheological data. To verify if the presence of a higher TLCP content could modify the general trend of the matrix flow behaviour the Ultem/K161-70/30 blend was studied. The viscosity data are reported in Figure 5, and show that the rheo-
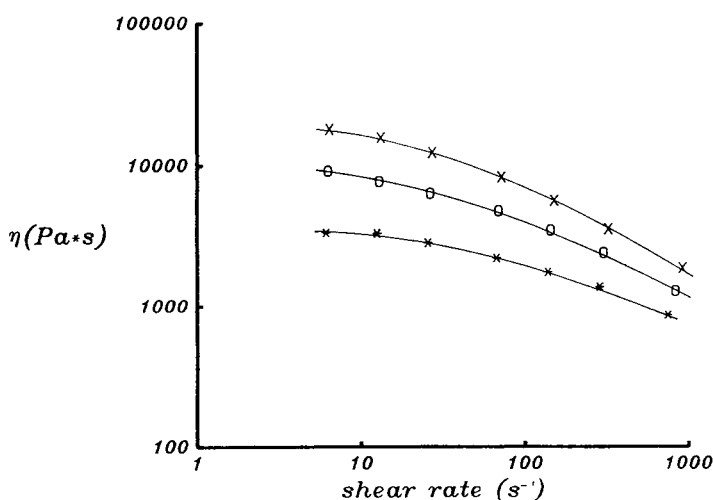


Fig. 3.   Viscosity ($\eta$) $vs.$ shear rate ($\dot{\gamma}$) of Ultem at different temperatures $T$ (°C): ($\times$); 315 (O) 330; ($*$) 350.
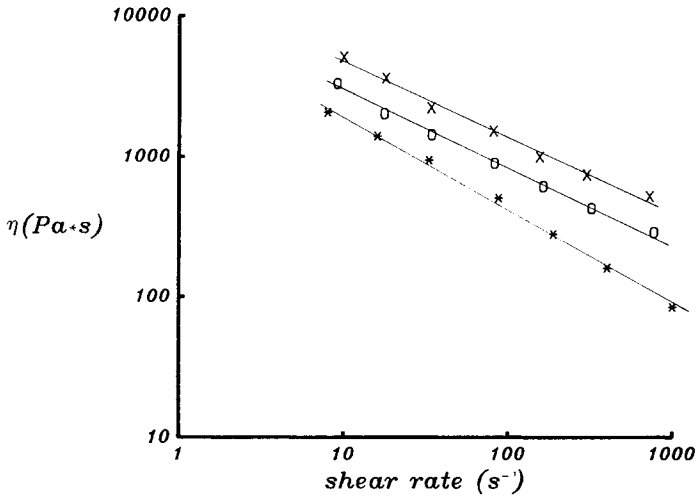
Fig. 4.  Viscosity ($\eta$) vs.-shear rate ($\dot{\gamma}$) of K161 at different temperatures $T$ (°C): ($x$) 300; (○) 315; (∗) 330.

logical properties of this blend are strongly affected by the TLCP presence. In particular, at $\dot{\gamma} = 300$ s$^{-1}$, the viscosity decreases from the 2400 Pa s value of Ultem to the 770 Pa s value of the Ultem/K161-70/30 blend. A similar flow behavior has been observed for data obtained at $T = 315$°C.

## Spinning and Mechanical Properties

Fibers of TLCP K161 were spun at the temperature of 370°C with different draw ratios following the procedure described in the experimental session. In Figure 6, the values of the Young modulus, $E$, versus the draw ratio ($S_0/S_f$)
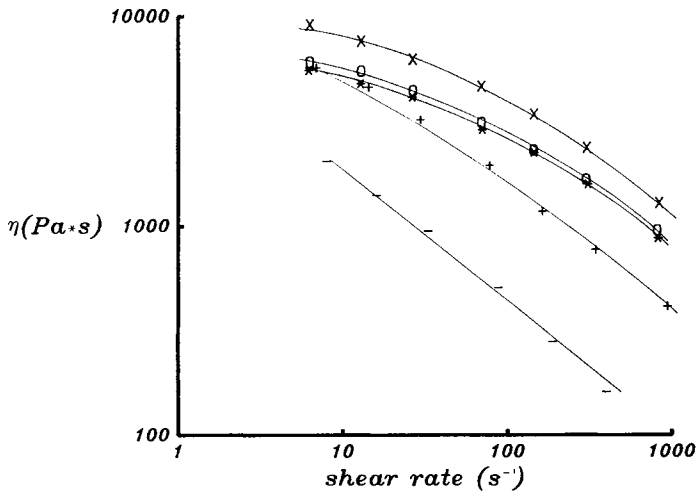


Fig. 5.  Viscosity ($\eta$) vs. shear rate ($\dot{\gamma}$) at $T = 330$°C of: ($x$) Ultem; ($o$) Ultem/K161-95/5; (∗) 90/10; (+) 70/30; (−) K161.
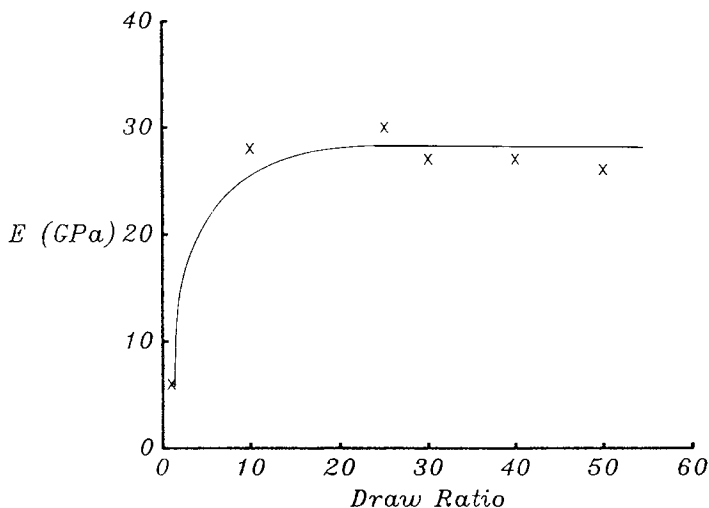
Fig. 6.    Elastic modulus ($E$) vs. draw ratio ($S_0/S_f$) of K161 drawn at $T = 370°C$.

are reported. The modulus sharply increases from the value of 6 GPa for the undrawn polymer to the plateau value of 28 GPa reached at the draw ratio of $\sim 20$. A similar trend has been reported in literature for thermotropic polymers,[11,12] and comparable plateau modulus values have been measured. The sharp increase in modulus with draw ratio has been usually justified taking into account the liquid crystalline nature of the polymer. The directors of the TLCP domains, in fact, randomly distributed in the quiescent state, easily orient along the fiber axis if the polymer is uniaxially drawn at the temperature of the mesophase existence. A fibrillar structure, responsible for the measured high rigidity values, is obtained at low imposed draw ratios. The high relaxation times characteristic of these materials, moreover, allow the retention of the orientation in the solid polymers.[13] In this regard, it can be justified that the modulus value of the undrawn K161 TLCP results is higher than the corresponding PET/PHB60 results ($\sim 2.4$ GPa) as measured in a previous work.[14] The more rigid chemical structure of the K161 may, in fact, produce the retention of most of the flow induced orientation after the material is cooled down to room temperature.

The Young moduli of Ultem/K161-90/10 blends at different draw ratios are compared with those of the matrix in Figure 7. The data refer to a spinning temperature of $330°C$. No appreciable differences between the two materials' data are recognizable, showing that a low amount of TLCP inclusion does not decrease the elastic modulus of the matrix. A similar behavior is shown by the Ultem/K161-95/5 blend. However, if 30% w/w of TLCP is added as a second phase, the blends' mechanical properties significantly differ from the matrix ones. The elastic modulus increases from the value of $\sim 3$ GPa measured for Ultem at a draw ratio of 30 to the value of $\sim 7$ GPa measured for the blend at the same draw ratio. In addition, the material can be drawn to a maximum $S_0/S_f$ value of $\sim 50$, similarly to the K161 case, as it is evident in Figure 8.
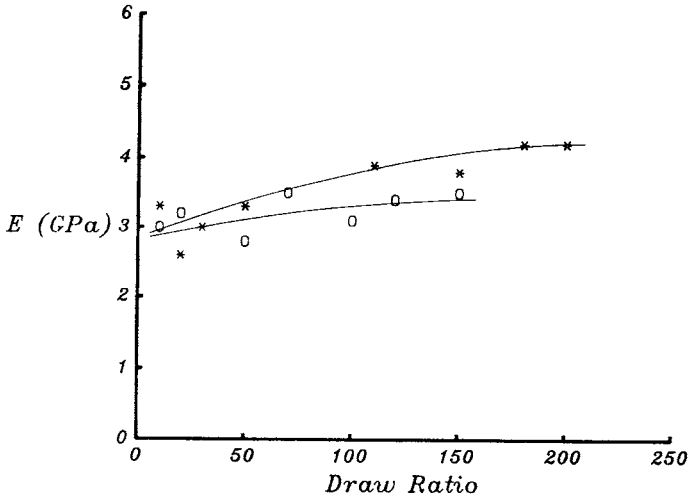
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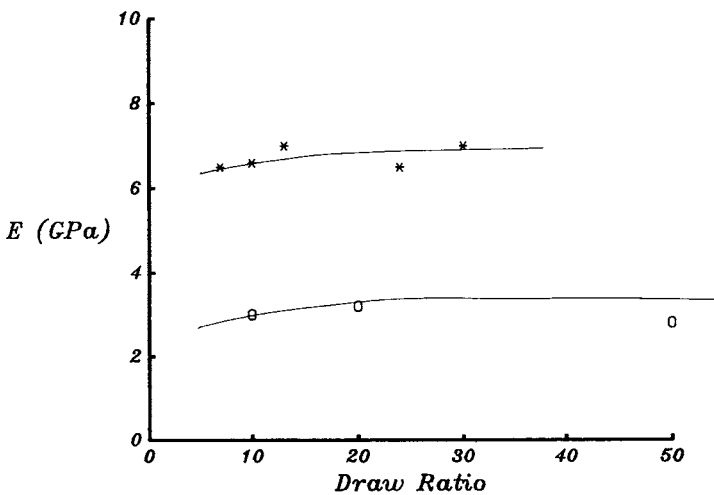


Fig. 7.   Elastic modulus $(E)$ vs. draw ratio $(S_0/S_f)$ of Ultem (O) and of Ultem/K161-90/10 (∗) drawn at $T = 330°C$.

The elongation at break, and the strength of the Ultem/K161-90/10 and of the unfilled Ultem at different draw ratios, are shown in Figures 9 and 10. The elongation at break values, as expected, decreases with $S_0/S_f$ and with the TLCP inclusion, while the strength values show the usual increase with $S_0/S_f$. The blends strength values, however, lie below the Ultem values, due to the poor adhesion between the two phases, as revealed by the morphological analysis.



Fig. 8.   Elastic modulus $(E)$ vs. draw ratio $(S_0/S_f)$ of Ultem (O) and of Ultem/K161-70/30 (∗) drawn at $T = 330°C$.

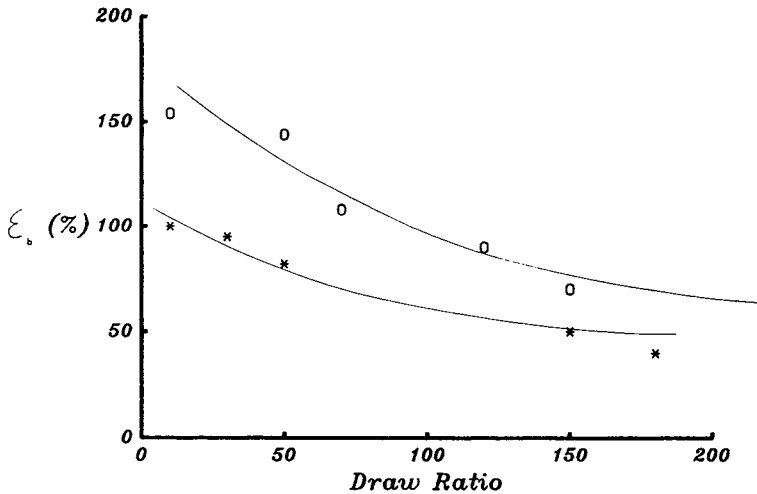Fig. 9. Elongation at break ($\epsilon_b\%$) vs. draw ratio ($S_0/S_f$) of Ultem (O) and of Ultem/K161-90/10 (*) drawn at $T$ = 330°C.

## Morphology

The morphological study of the TLCP K161 is essential to carry out before approaching the blends' morphological analysis. The scanning electron micrograph of the K161 undrawn sample extruded at $T$ = 330°C, $\dot{\gamma}$ = 800 s$^{-1}$, with $L/D$ = 10 is shown in Figure 11. A slightly oriented structure, certainly different from the completely disordered texture seen in PET/PHB60 extruded samples reported in a previous paper,[14] is distinguishable. This observation matches with the mechanical results that showed an elastic modulus of the undrawn K161 polymer higher than the corresponding value measured for the PET/
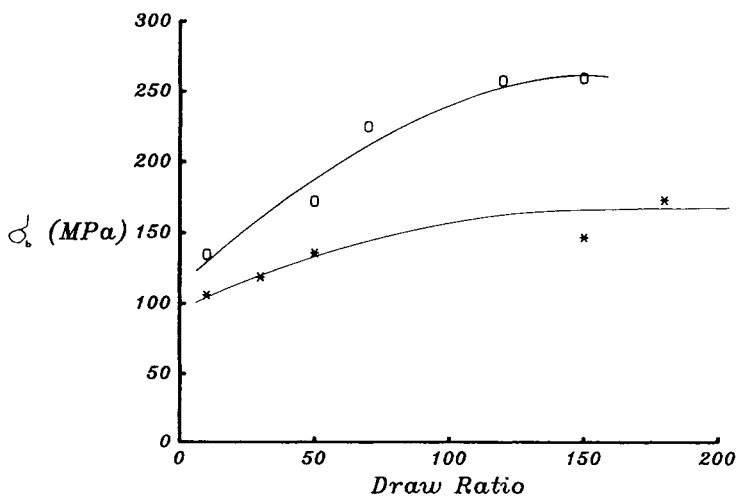


Fig. 10. Strength ($\sigma_b$) vs. draw ratio ($S_0/S_f$) of Ultem (O) and of Ultem/K161-90/10 (*) drawn at $T$ = 330°C.
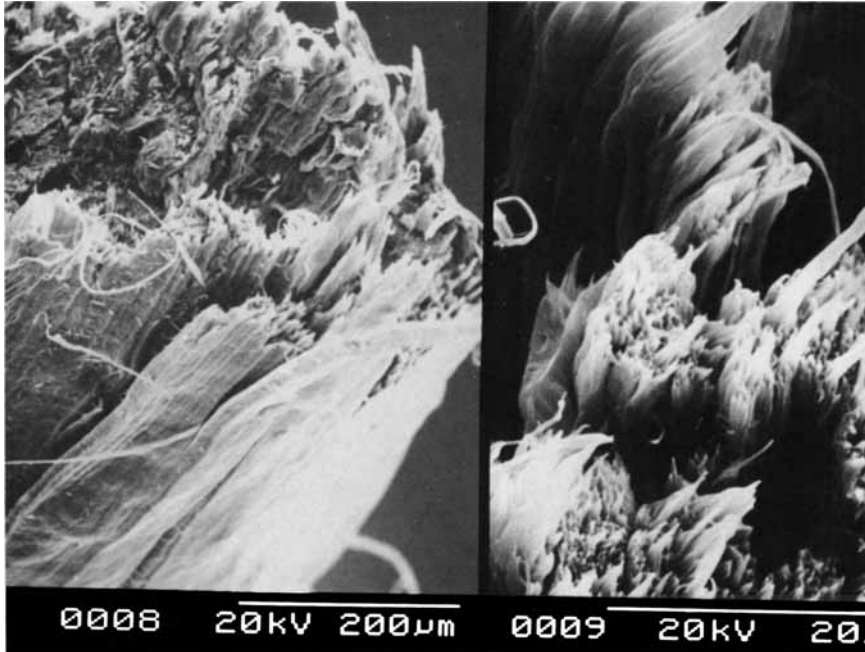
Fig. 11.    SEM micrograph of K161 extruded at $T = 330°C$, $\gamma = 800$ s$^{-1}$, $L/D = 10$.

PHB60.[14] Analogously to what we discussed for the mechanical behavior, the higher degree of orientation can be attributed to the more rigid structure of the K161 polymer compared, to that of the PET/PHB60.

The spinning operation, as expected, enhanced the domain orientation along the fiber axis (i.e., the drawing direction), and a more fibrillar morphology characterized the drawn TLCP sample.

The morphology of the Ultem/K161 extruded and/or drawn blends can be related to their rheological and mechanical behavior. For this purpose, it seemed opportune to start the morphological study with the compression molded blend samples, whose structure is not influenced by flow history. The TLCP phase segregates in the Ultem matrix as spheroidal domains whose size depends on the relative percentages of the two components. Mesophasic domains of $\sim 0.5$ $\mu$m are, in fact, distinguishable in the SEM micrograph of the Ultem/K161-90/10 blend [Fig. 12(a)], while domains of $\sim 1$–2.5 $\mu$m can be observed in the SEM micrograph of the Ultem/K161-70/30 blend [Fig. 12(b)]. The highest TLCP content blends, therefore, show the largest TLCP domains size.

The shear rate effect on the particles shape was also studied. In the case of the low TLCP content blends, the shear rate doesn't seem to modify the initial domain's shape as it is shown in Figure 13 (SEM micrograph of Ultem/K161-90/10 blend extruded at $\dot{\gamma} = 800$ s$^{-1}$, $T = 330°C$, with $L/D = 10$). The micrograph is representative of all the shear rates investigated. Nevertheless, the slight deformability of the TLCP particles, coupled with the low mesophase viscosity, could be responsible for the viscosity decrease of the Ultem/K161-95/5 and 90/10 blends with respect to the viscosity of Ultem. Moreover, the
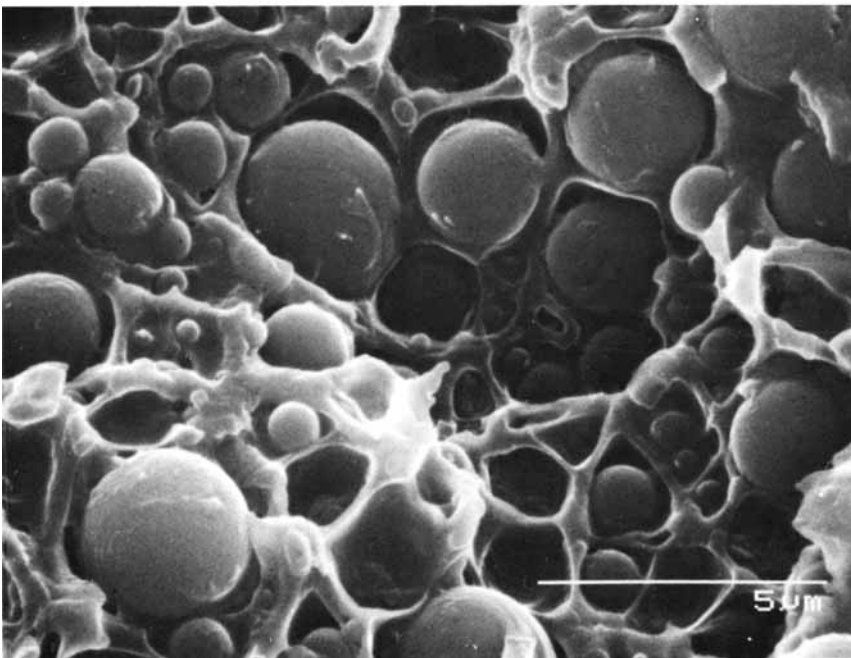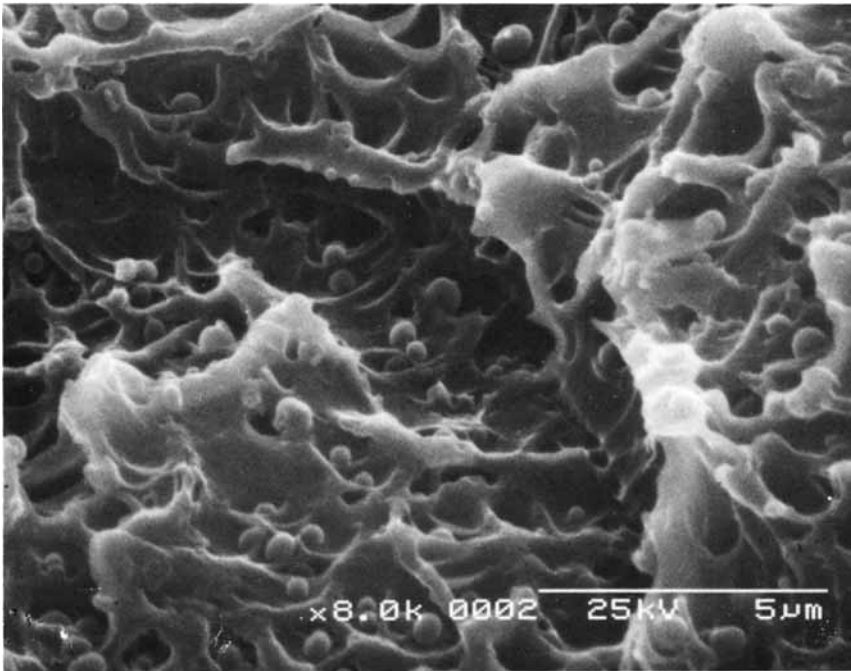
Fig. 12. SEM micrograph of compression molded: (a) Ultem/K161-90/10; (b) Ultem/K161-70/30.
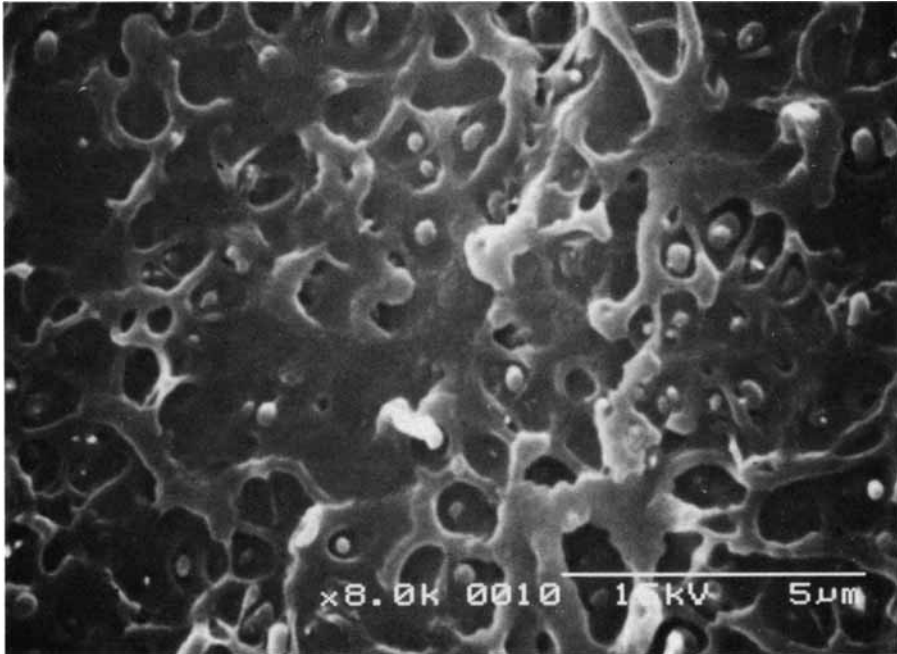
2734      NOBILE ET AL.



Fig. 13.    SEM micrograph of Ultem/K161-90/10 extruded at $T = 330°C$, $\dot{\gamma} = 800$ s$^{-1}$, $L/D$ = 10.

small difference in viscosity data between these two blends can be attributed to their similar morphology in terms of TLCP domains shape and size.

The themotropic phase morphology in the Ultem/K161-70/30 blend, on the other hand, depends significantly on flow history. The mesophasic large initial domains highly deform when the material is subjected to increasing shear rates, as shown in Figures 14(a) and (b) (SEM micrographs of the Ultem/K161-70/30 blend extruded at $T = 330°C$, $L/D = 10$, with $\dot{\gamma} = 12$ s$^{-1}$ and $\dot{\gamma}$ = 800 s$^{-1}$, respectively). The long, threadlike TLCP fibrils well aligned in the flow direction can, therefore, act as lubricant layers for the flow of the Ultem matrix. This effect, combined with the low TLCP viscosity, determines the large viscosity decrease observed in this blend compared to the polyetherimide viscosity.

Optical analysis was performed on the drawn blends in order to investigate the effect of the elongational flow on the TLCP domains shape. It was found that the spinning procedure slightly influences the TLCP morphology in 95/5 and 90/10 w/w blends. The spheroidal droplets, in fact, deform into rods only in same cases; these rods have an aspect ratio of $\sim 10$, as shown in Figure 15(a). Continuous TLCP fibers are, on the other hand, well evident when the Ultem/K161-70/30 is spun with a draw ratio of $\sim 40$ [Fig. 15(b)]. The high modulus ($\sim 7$ GPa) measured for this blend could be, therefore, related to the presence of high aspect ratio TLCP fibers, whose Young modulus ($\sim 28$ GPa) are much higher than the corresponding matrix Young modulus ($\sim 3$ GPa).

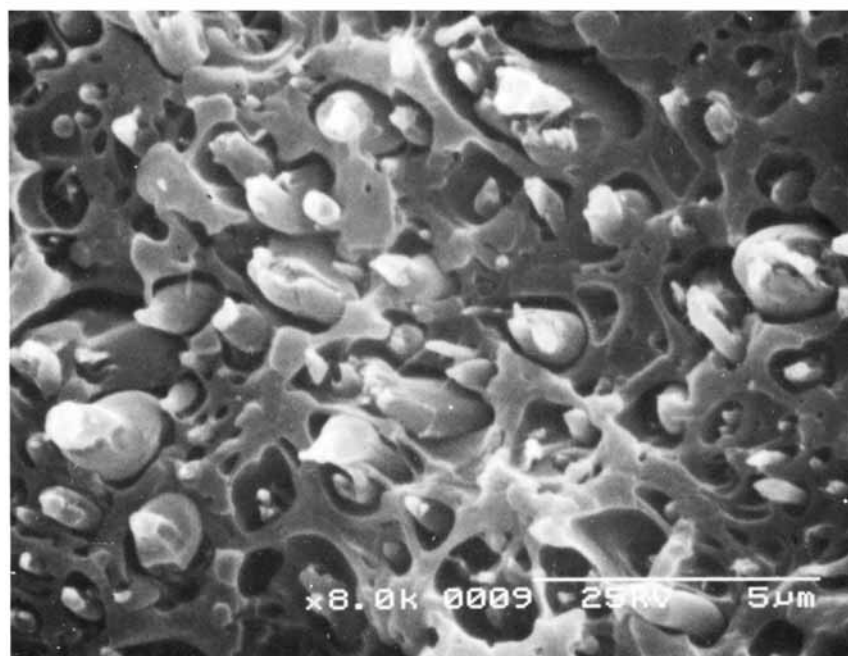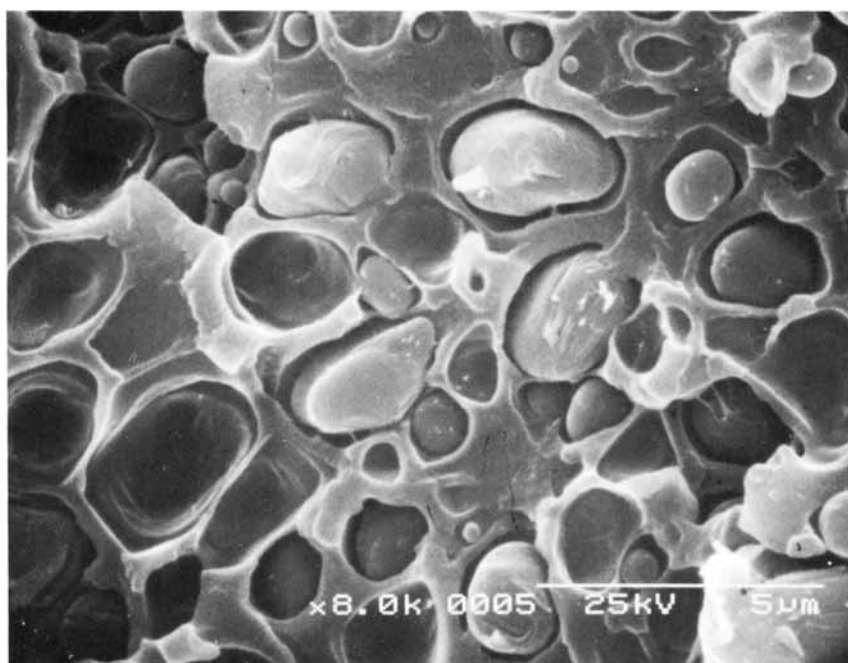Fig. 14. SEM micrographs of Ultem/K161-70/30 extruded at $T = 330°C$, $L/D = 10$ with different shear rates: (a) $\dot{\gamma} = 12$ s$^{-1}$; (b) $\dot{\gamma} = 800$ s$^{-1}$.
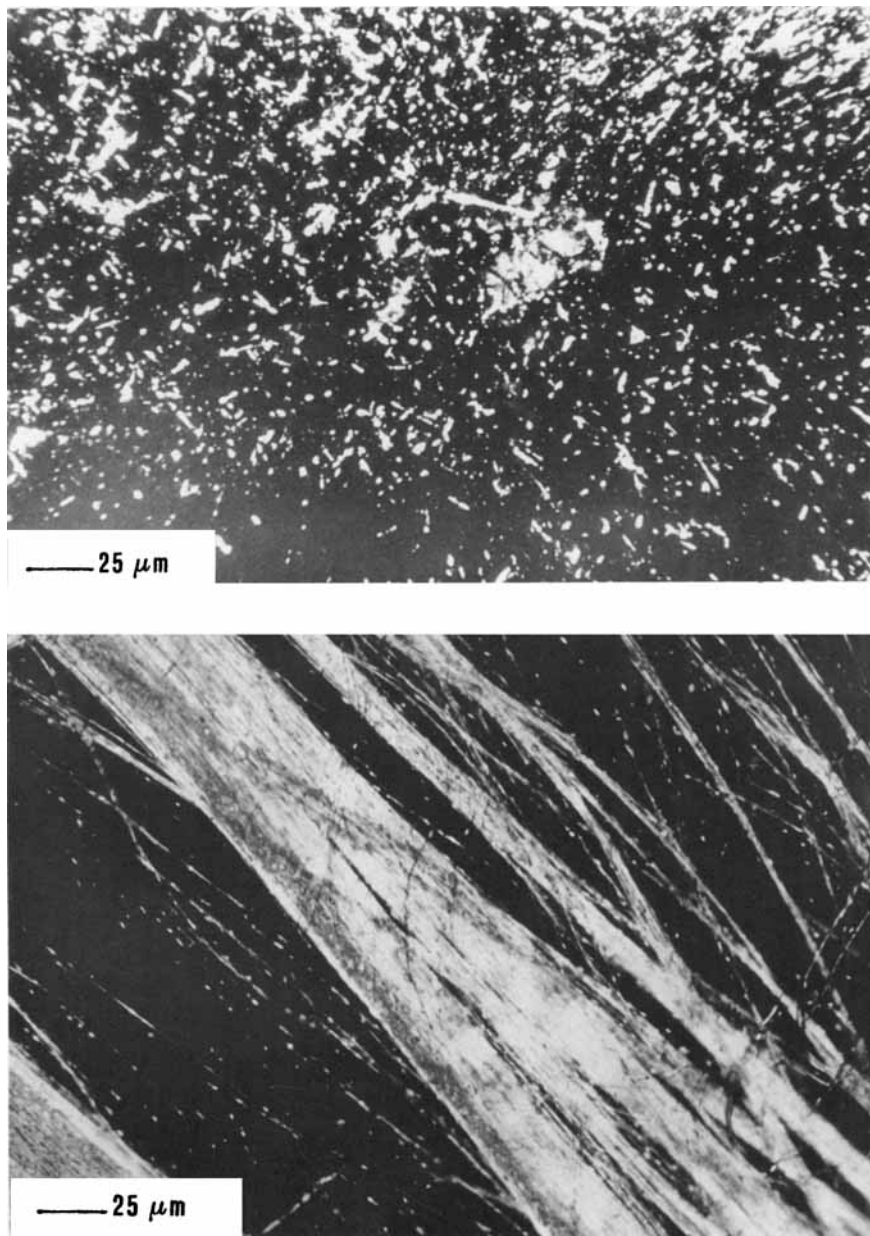
Fig. 15.   Optical micrographs of: (a) Ultem/K161-90/10 and (b) Ultem/K161-70/30 drawn at $T = 330°C$.

## CONCLUSIONS

The polyetherimide Ultem has been blended with a thermotropic liquid crystalline polymer from Bayer Co. to investigate the possibility of improving the processability of engineering polymers. Thermal analysis revealed a slight decrease of the Ultem $T_g$ in the 90/10 and 70/30 w/w blends, i.e., some plasticizing

effect occurs for the Ultem when it is blended with the TLCP. However, the Ultem/K161 is a mostly incompatible system, as is shown by the morphological analysis. The inclusion of 5 and 10% of TLCP in Ultem produces a significant drop of ~ 30% in the matrix viscosity. This was attributed to the low TLCP viscosity coupled to the deformability of the TLCP spheroidal domains. The mechanical analysis showed that the Young modulus values of Ultem are not affected by the inclusion of a low TLCP amount, while the elongation to break and the strength of the matrix decrease. On the other hand, if 30% w/w of TLCP is added, a large decrease in the viscosity as well as a large increase in the fibers Young modulus results. In this case, in fact, the TLCP deform into fibrils acting in the melt state as lubricant layers for the Ultem matrix, while in the solid state they act as reinforcing phase.

In conclusion, improvement of the Ultem processability without reduction of the Young modulus can be realized with the addition of a low percentage of K161 polymer. The enhancement of the Young modulus, on the other hand, can be obtained only if a high percentage of TLCP is included in the Ultem.

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