Blends of a Polyetherimide and a Liquid Crystalline Polymer: Fiber Orientation and Mechanical Properties

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INTRODUCTION

Addition of liquid crystalline polymers (LCPs) can be an outstanding tool to improve processability of engineering thermoplastics without decreasing their mechanical properties. LCPs can reduce the extrusion temperature of the host matrix, due to their low melt viscosity, even if added in low amounts.

Several papers were published on the rheological analysis of blends of LCP with different polymers. Some of us worked in the past on the physical characterization of the blends of a thermoplastic polyetherimide (ULTEM 1000 by GE) and a liquid crystalline polymer (K 161 by Bayer Co.).[1-5]

It has been found that the inclusion of 10% LCP in the matrix causes a drop of viscosity of ULTEM of the order of 30%. This effect was ascribed to the low LCP viscosity. The mechanical analysis evidenced that the values of the tensile modulus of ULTEM were not affected by the inclusion of low amounts of liquid crystalline filler.

On the other hand, if 30% w/w of thermotropic filler is added, a considerable decrease in the viscosity as well as a large increase in the fiber's Young modulus results.

In this article, we propose to relate the mechanical properties with the structure of the blends on the basis of X-ray diffraction patterns of the spun fibers.

EXPERIMENTAL

The amorphous matrix used in this work is the polyetherimide Ultem 1000, produced by General Electric. The LCP utilized is the fully aromatic polyester K161, kindly provided by Bayer Company.

Materials were vacuum dried at 100°C for 10 h before mixing. The Ultem/K161 blends were prepared by means of a Brabender equipped with a mixing chamber at 320°C at 32 rpm. Rheological characterization was carried out in high shear rate range by means of a capillary viscometer (Rheoscope 1000, CEAST).

Spinning was performed by means of the Rheoscope 1000 provided with a melt spinning unit, using a die of 1 mm in diameter, and a L/D ratio of 10. The extrusion rate was approximately 45 cm/min. The filaments were collected in air at room temperature on a bobin at a distance of about 30 cm from the die exit. The take-up velocity was varied to obtain V_f/V_o (draw ratio) values included between 10-100. The true draw ratio values were determined from the ratio of the die and the fiber cross-section (S_o/S_f) measured by an optical microscope.

The X-ray diffraction patterns were obtained using a wide-angle medium pin-hole vacuum camera installed at a Rigaku Denki RV 300 rotating anode generator. Nickel-filtered CuKα X-ray radiation was used.[6]

The diffraction intensity along the principal halo was measured by means of a microphotodensitometer.

Tensile modulus of LCP and the blends was evaluated by means of a dynamometer (INSTRON) according to ASTM D3379-5.

The morphology of the LCPs and of the blends was analyzed by means of an optical microscope under cross-polarizers (Polyvar, Reichert-Jung). The LCP fibers in the blend were previously separated from the matrix by solvent extraction in methylene chloride.

RESULTS AND DISCUSSION

It is well known that the elastic modulus of short fiber-oriented composites can be evaluated by using the Halpin–Tsai theory[7]:

$$E_c/E_m(1 + A \cdot B \cdot \Theta)/(1 - A \cdot B \cdot \Theta), \quad (1)$$

where E_c is composite modulus in the direction of the fibers, E_m the modulus of the matrix, Θ the volume fraction of the filler, A the 2 (L/D), aspect ratio of the fibers, B the $(E_f/E_m - 1)/(E_f/E_m + A)$, and E_f the modulus of the filler.

Equation (1) can be rewritten to make the aspect ratio A explicit as:

$$A = \frac{E_c/E_m[(E_f/E_m)(1 - \Theta) + \Theta] - E_f/E_m}{1 - \Theta + \Theta(E_f/E_m) - (E_c/E_m)}.$$
$$(2)$$

If we assume, for a blend containing 30% LCP, that the modulus of the matrix and the filler are 3 GPa and 28 GPa, respectively (i.e., the plateau values found for the oriented polymers), as inferred from Figures 1 and 2, and a modulus of 7 GPa for the composite, an aspect ratio of the order of 1 results. This value indicates that the liquid crystalline filler should appear as spherical droplets in the host matrix.

However, as results from analysis of the optical micrographs, the LCPs appear as long threadlike fibrils with a long aspect ratio, surrounded by a few small droplets (Fig. 3).[5]

If we suppose that the Halpin–Tsai model can be applied to this kind of composite, and that the quantities E_c and E_m have been correctly measured, the remaining uncertainties consist in the value attributed to E_f and in the volumetric fraction of filler. Let us consider both the quantities.
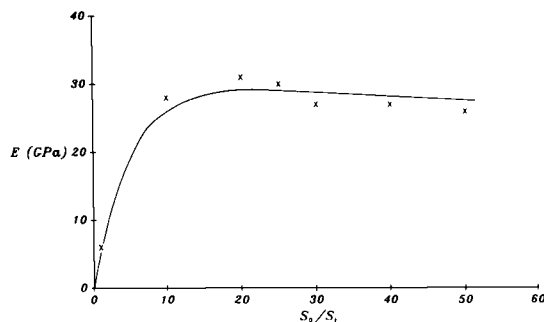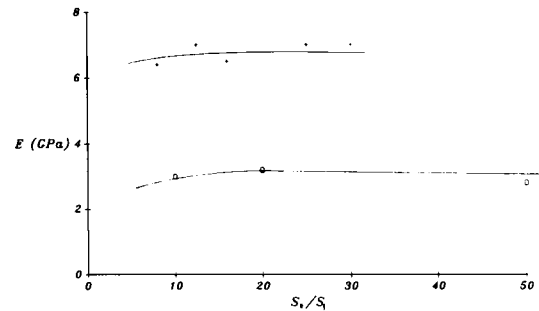

Figure 2   Elastic modulus (E, GPa) vs. draw ratio (S_o/S_f) for pure Ultem (O) and Ultem/K 161 (+) drawn fibers.

To explain why the LCP is present with different geometries, the microrheology of the blend during the processing procedure should be considered.

If we assume that in the molten state the blend is a suspension constituted by a suspending medium (ULTEM) and suspended particles (K 161), the theories of the rheology of suspensions can be successfully applied.

Taylor[8] widely studied the effect of the different parameters on the elongation and then on the burst of droplets in different suspensions. He extended Einstein's theoretical treatment of the viscosity of a suspension of rigid particles to the case of small immiscible fluid spheres.

He found that in simple shear flow of Newtonian fluids an initial droplet can modify its form according to the relationship:

$$\frac{b_3 - b_2}{b_3 + b_2} = \frac{\dot{\gamma} \cdot \eta_0 \cdot b}{\sigma} \cdot \frac{19\delta + 16}{16\delta + 16}, \quad (3)$$
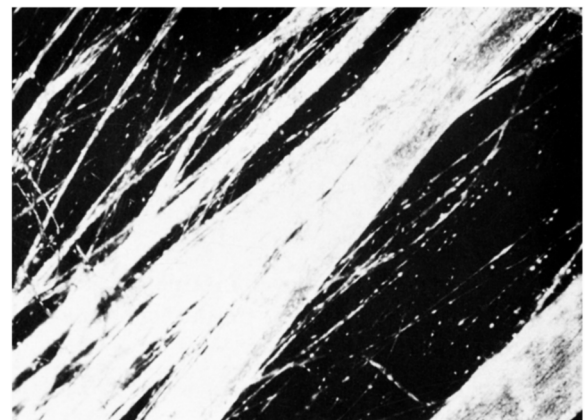
where b_2 and b_3 are the principal semiaxes of the

Figure 1   Elastic modulus (E, GPa) vs. draw ratio (S_o/S_f) for pure K 161 (×) drawn fibers.

Figure 3   Optical micrographs (× 500) of K 161 microfibers extracted from Ultem/K 161 30% w/w blend.

deformed drops, $\dot{\gamma}$ the shear rate, σ the interfacial tension, b the initial diameter of the drop, η_0 the viscosity of the suspending liquid, and δ the ratio between the viscosity of the dispersion and the viscosity of the suspending liquid.

Taylor suggested that, when the maximum value of pressure difference across the interface between a suspending liquid and a dispersion, tending to disrupt the drop, exceeds the force, due to surface tension, which tends to hold it together, the drop will burst. This occurs when:

$$4 \cdot \dot{\gamma} \cdot \eta_0 \frac{19\delta + 16}{16\delta + 16} > 2\sigma/b. \tag{4}$$

If the viscosities of Ultem and LCP are considered,[5] the value of δ is of the order of 0.3 at a shear rate of 10 sec^{-1}. It reduces to about 0.1 if the shear rate is increased to 1,000 sec^{-1} (Fig. 4). This means that the expression (4) can be reasonably simplified to

$$\frac{2 \cdot \dot{\gamma} \cdot \eta_0 \cdot b}{\sigma} > 1, \tag{5}$$

indicating that if the viscosity of the matrix is large enough, with respect to the interfacial tension, the droplets will elongate.

It should be said that eq. (3) is valid for small deformations. As the deformation increases beyond the range of its applicability, distinct modes of behavior are observed: These depend mainly on δ and are illustrated in Figure (5).

With a small value of δ, the droplet will elongate, developing pointed ends from which fragments of disperse phase are released. These fragments will appear as very small microdroplets. The contribution of these small fragments to the elastic modulus of the composite is meaningless for two reasons:
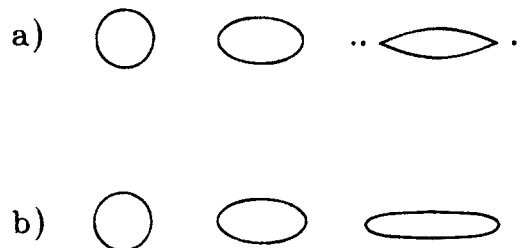
Figure 5 Deformation and burst of droplets.

First, they have an aspect ratio close to one, owing to their spheroidal shape. The second reason concerns the elastic modulus of these fragments. In fact, when they are released from the mother drop, they relax and loose the orientation induced, during shearing, to the initial droplet before bursting. Since the elastic modulus of the quiescent LCP is of the same order of magnitude of Ultem, the contribution of these fragments to the modulus of the composite is very small. This means that the effective volume fraction of dispersion contributing to increase the stiffness of the composite is slightly lower than the amount blended with the matrix.

The X-ray diffraction patterns can reveal the degree of molecular orientation relative to the elongated drops, which are the larger fraction of the liquid crystalline filler in the blend, and, therefore, the congruous value of elastic modulus (E_f) to assign in eq. (2).

In fact, Figures 6 and 7 report the X-ray diffraction patterns for the fibers of K 161 extruded without drawing and for the fibers spun with a draw ratio of 50, respectively.

Figure 6 shows two diffuse spots on the equatorial line, the central positions corresponding to a periodic length of 11.2 and 4.47 Å, respectively. Similar peaks appear in Figure 3.

For both samples, the order parameters (f) were calculated from the azimuthal profile of the more intense equatorial reflection:

$$\langle \cos^2 \beta \rangle = \frac{\displaystyle\int_0^{\pi/2} I(\beta)\sin \beta \cos^2 \beta d\beta}{\displaystyle\int_0^{\pi/2} I(\beta)\sin \beta d\beta}$$

$$f = \tfrac{1}{2}(3\langle \cos^2 \beta \rangle - 1).$$

The value of f found for the drawn fibers was 0.90, higher than the value for the undrawn polymer, which was 0.70.

Furthermore Figure 6 indicates the presence of two sharp and weak peaks along the fiber line (6.07
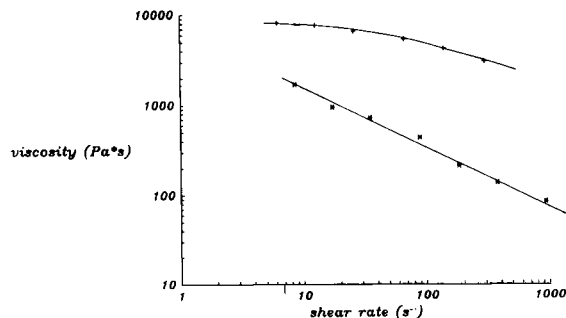
Figure 4 Viscosity (Pa s) vs. shear rate (s^{-1}) of Ultem (+) and K 161 (*).
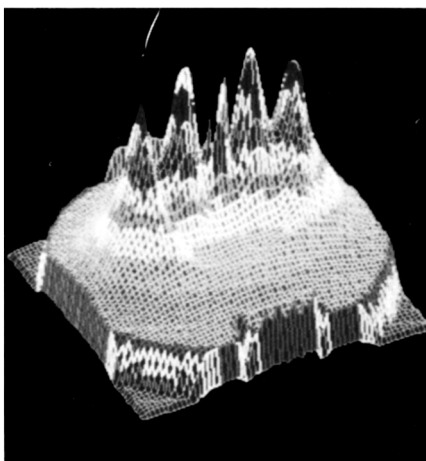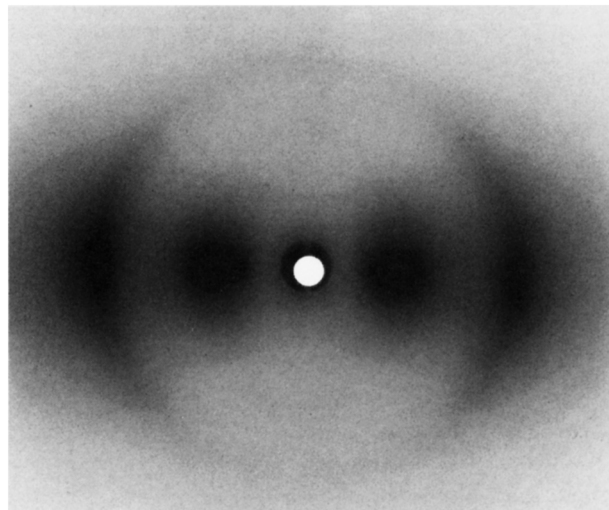
Figure 6   X-ray diffraction pattern of K 161 undrawn extrudate. a, flat-film camera image; b, tridimensional plot.

Since the order parameter is related to the modulus of the polymer, the value of E_f for the LCP in the blend can be reasonably considered lower than that of the drawn fibers of K 161.

The reason for this low level of orientation for the fibers of LCP can be due to shearing that is not sufficient to induce a high level of orientation of the rigid rod macromolecules in the blend. This means that the stresses transmitted from the matrix to the nematic polymer in the capillary can produce only the tumbling of the liquid crystalline domains, and not their orientation along a specific direction. In fact, the viscosity of LCP is very small and can only allow the shearing of the nematic domains that tumble in space and no much molecular orientation takes place. However, it is possible that the interfacial adhesion between filler and matrix, due to the
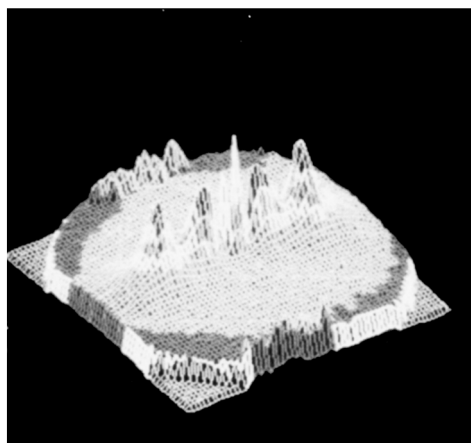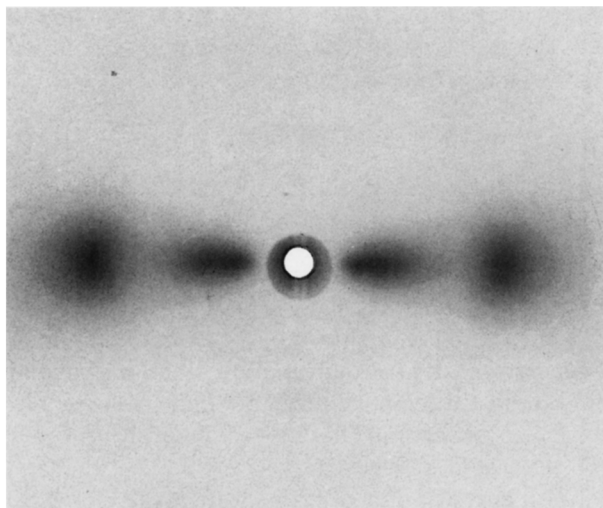

and 3.05 Å). They may correspond to the reflection of repetitive units perpendicular to the fiber direction or may be associated with the presence of impurities. Further investigations will be performed in the near future on this point.

Figure 8 reports the X-ray diffraction pattern for the blend composed of 70% ULTEM and 30% K 161. Besides the amorphous halo of the host matrix, the reflection characteristic of liquid crystalline order is well evident. The order parameter (f) relative to LCP was calculated in this case too after subtracting the background contribution of the amorphous matrix. Its value is 0.75, intermediate between the previous ones, indicating that the degree of orientation of the liquid crystalline macromolecules is far from being as large as that of the completely drawn sample.

Figure 7   X-ray diffraction pattern of K 161 drawn fibers (draw ratio = 50). a, flat-film camera image; b, tridimensional plot.
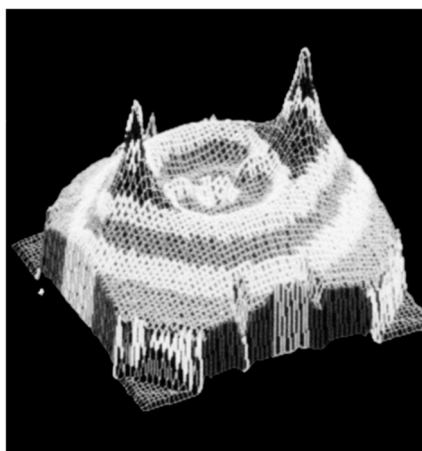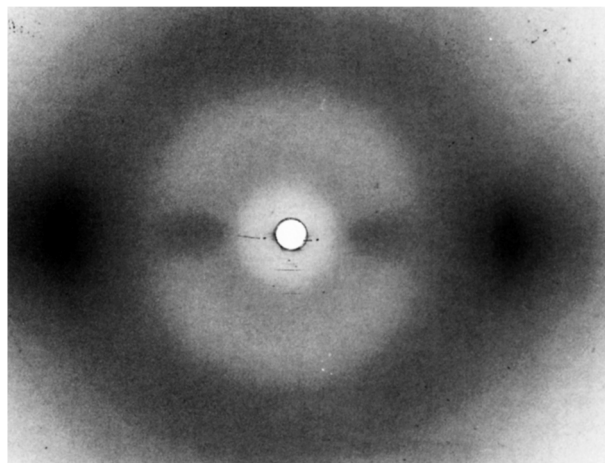
Figure 8 X-ray diffraction pattern of Ultem/K 161 30% drawn fibers (draw ratio = 50). a, flat-film camera image; b, tridimensional plot.

nonbonded interactions, are high enough that the stresses transmitted by Ultem can produce a larger orientation in the outer shell of LCP, the inner core remaining in a less oriented state.

During the blend spinning, the air cooling at the exit of the die increases the viscosity of the outer shell of the composite. The viscosity of the liquid crystalline filler increases too at a higher extent with respect to that of the matrix. In fact, since the LCP has a T_g at 280°C, well 70°C higher than Ultem, during spinning at room temperature of the extrudate, the nematic polymer quickly cools to a temperature close to its T_g, freezing any motion of the rods and not allowing further macromolecular orientation, by spinning.

According to Min et al.,[9,10] it is not possible to deform the suspended droplets when the dispersed phase has a very high viscosity. Undeformed droplets

are observed when δ = 2. Therefore, the maximum level of orientation and of deformation for LCP fibers in the blend is reached only in the capillary.

During fiber spinning, the Ultem is drawn after the die exit, but the LCP fibers quickly stiffen due to the cooling. Thus, the LCP is almost unaffected by the fiber spinning, retaining the degree of molecular orientation reached in the capillary.

At this point a rough evaluation of the aspect ratio of the fibers can be carried out on the basis of these considerations.

From an analysis of the explicit form of the Halpin–Tsai equation, let us put Θ = 0.25 (slightly smaller than 0.30). If the value of E_f = 20 GPa (lower than the maximum value, which is 28 GPa), an aspect ratio L/D = 30 for the fibers of liquid crystalline filler results. This value well matches the form of the fibrils that appear from the optical microscopy.

CONCLUSIONS

In conclusion, from an analysis of the physical characterization of the blends Ultem/K 161, some general considerations can be derived on this class of composites.

If the desired goal is a lower viscosity of the blend with respect to the pure thermoplastic, the stability range of the nematic phase of the LCP must overlap the processing temperature of the thermoplastic.

If, however, a reinforcing effect is also required, attention should be devoted to the ratio of the viscosities between the filler and the matrix.

To obtain a liquid crystalline phase, in the form of fibers with a high aspect ratio, the LCP viscosity should be lower than that of the matrix. However, if it is too much smaller, the deformed droplets will release unelongated fragments and a wide fiber aspect ratio distribution will result.

For what concerns the elastic modulus of the LCP fibers, shearing of the blends does not allow a high level of molecular orientation. Also in the converging zone of the capillary, the elongational flow field is not sufficient to increase the orientation function of the LCP in the blend. However, since a larger elongation can be obtained at the exit of the die during the spinning of the blend, great attention should be paid to the T_g of the LCP. If the LCP T_g is much higher than the T_g of the matrix, cooling will freeze any motion of the rigid rods and no more orientation of LCP will result.

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