

Liquid Crystal Polymers (LCP) as Processing Aids and Reinforcing Agents. A Study of Nylon 6 / LCP Blends

Liquid crystal polymers (LCPs) are a new class of polymeric materials that present very interesting chemical and physical properties.¹⁻³ In particular, low viscosity and long range molecular orientation are their most important features. Among physical properties, the values of modulus and stiffness are very impressive.⁴⁻⁶

An interesting use of these polymers is to blend them with conventional thermoplastic materials in order to achieve blends easily processable and with improved mechanical properties.⁷⁻¹⁰ Indeed, some authors⁷⁻⁹ noticed that the adding of small amount of LCPs gives rise not only to an improvement of the main mechanical properties, but also to a reduction of the viscosity and then of the energy necessary to the processing with respect to the neat polymer.

In this work the effect of small amounts of a commercial thermotropic copolyesteramide, made from Celanese, on the mechanical and processing characteristics of a polyamide 6 is studied. In particular, the energy necessary to extrude these blends is considered.

EXPERIMENTAL

The materials used in this work were a polyamide (nylon 6) and an all-aromatic copolyesteramide. The polyamide was kindly supplied by SNIA (Italy) and is commercially known as ADS 40. The melt flow index is 4.60 following ASTM D1238 cond. R.

The copolyesteramide was purchased from Celanese (U.S.A.) and is commercially known as Vectra B950. This liquid crystal polymer is synthesized from hydroxynaphtic acid (60%), aminophenol (20%), and terephthalic acid (20%). The chemistry and the properties of these types of copolyesters have been reviewed by Calundann and Jaffe¹¹ and by Chung.¹²

Both materials were carefully dried at $T = 120^{\circ}\text{C}$ under vacuum for at least 24 h, and then blended using a laboratory single screw extruder ($D = 19$ mm, $L/D = 25$) Brabender equipped with a die assembly for ribbon.

Two thermal profiles were used for all the investigated materials:

- (a) 200, 220, 240, and 260°C ;
- (b) 200, 240, 280, and 290°C .

During extrusion the torque was continuously recorded and the flow rate determined by direct weighing. The content of Vectra in the blends, ϕ , was 1, 2.5, 3.5, 5, 10, and 20% wt/wt. A few tests were performed, for comparison, using glass fibers as reinforcing agents at a concentration ϕ of 5 and 10% wt/wt. The extrusion of these latter materials were carried out only with the lower thermal history.

Strips of 0.5 cm were cut out from the ribbon in order to determine the mechanical properties. Stress-strain curves were determined using an Instron model 1122 at an elongational rate of 1.66 min^{-1} . All the results are average of at least seven measurements.

Rheological measurements were carried out using a capillary viscometer Rheoscope 1000 (CEAST, Italy), at 260 and 290°C . The capillary was 1 mm in diameter with length to diameter ratio of 40.

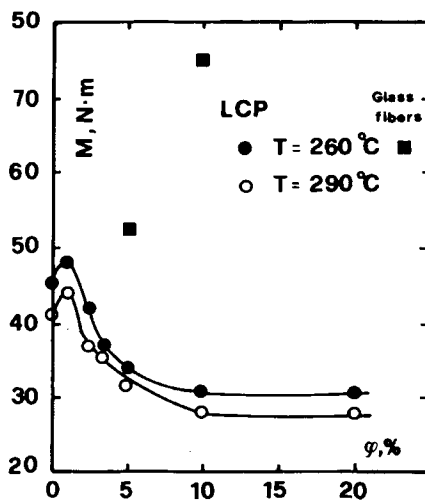


Fig. 1. Torque vs. composition.

RESULTS AND DISCUSSION

The torque M recorded during extrusion is reported in Figure 1 versus the content of Vectra for the runs performed at the two thermal profiles. In both cases the torque necessary to extrude the blends is smaller than that recorded for the pure nylon except for the sample with the lowest LCP content, which shows a slight rise. As the concentration of the liquid crystal polymer increases, the torque decreases continuously until the content of Vectra reaches about 10%; then the torque-composition curve flattens, and the torque remains almost unchanged in the 10–20% composition range. The two samples of nylon with glass fibers show, on the contrary, a dramatic increase of the torque.

The output flow rate Q is reported in Figure 2. Also in this case a slight maximum is seen in both curves at $\phi = 1\%$. A decrease of the flow rate, on the contrary, occurs for all other compositions, though being remarkable only for the extrusions carried out at the lower temperature. As for the samples with glass fibers, the output flow rate does not vary appreciably in the investigated range.

Since the addition of the LCP gives rise to two contrasting effects, namely, an increase followed by a reduction of both torque and flow rate, in Figure 3 the torque necessary to extrude 1 g/min of material, M/Q , is plotted as a function of the composition. For both extrusion temperatures a reduction of this parameter is observed for all the blends with Vectra, whereas a marked rise is observed for the glass-fiber-reinforced nylon. This means that the extrusion energy decreases on addition of the liquid crystal polymer to nylon, this reduction being more significant at the higher

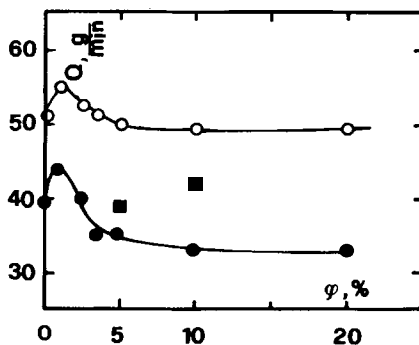


Fig. 2. Output flow rate vs. composition. Key of symbols as in Figure 1.

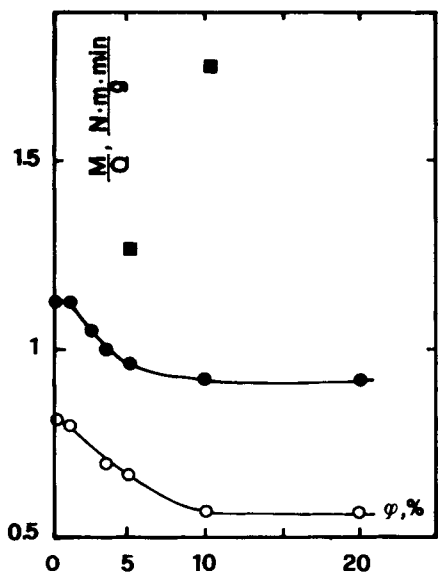


Fig. 3. M/Q (see text) vs. composition. Key of symbols as in Figure 1.

extrusion temperature, and that, on the contrary, it increase markedly on short glass fibers addition.

In order to better understand the working mechanism of the LCP, the dimensionless values \bar{M} and \bar{Q} (i.e., the ratios of the torque and of the output flow rate of the blends, divided by those of the neat nylon) are reported in Figures 4 and 5, respectively, as a function of the die temperature for all the investigated compositions. Furthermore, the viscosity at two fixed shear rates is reported vs. the composition at $T = 260$ and 290°C in Figures 6(a) and 6(b). For all compositions, \bar{M} decreases as the die temperature rises. The plot of the dimensionless flow rate is more complicated. Indeed, on increasing the extrusion temperature, \bar{Q} decreases for $\varphi = 1\%$, remains almost unchanged for $\varphi = 2.5\%$, and increases for higher values.

As far as the shear viscosity is concerned, the presence of the liquid crystal polymer reduces significantly the viscosity of nylon: this reduction is more remarkable at higher temperatures. The reduction of the viscosity is noticeable also at very low content of Vectra. An obvious conclusion can be drawn from all these results.

The liquid crystal copolyester is insoluble in the nylon matrix⁷ and has a larger density; it migrates in the zone of transport of solids, towards the polymer-metal interphase, decreasing the friction factor between polymer and metal, thus reducing the apparent viscosity of the material. This hypothesis is confirmed, not only by the reduction of the dimensionless torque with the temperature, but also by the increase of the flow rate.

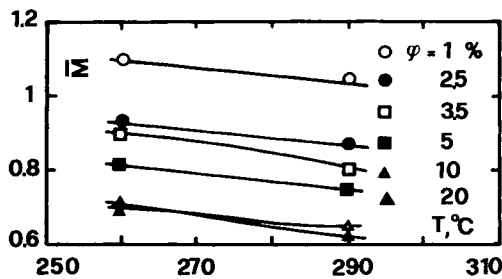


Fig. 4. Dimensionless torque vs. die temperature.

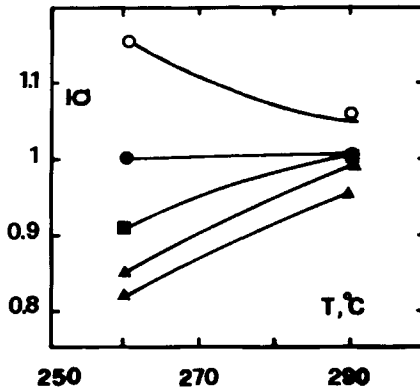


Fig. 5. Dimensionless output flow rate vs. die temperature. Key of symbols as in Figure 4.

As for the blend with $\varphi = 1\%$, the slight rise of the torque can be attributed to the very low concentration of LCP which is not sufficient to reduce the friction factor in the zone of transport of solids of the extruder. In this case the dispersion of a "solid" component gives rise to an increase of the extrusion energy. However, because of the remarkable drop of the viscosity at higher temperature, the dimensionless torque decreases with temperature also for this blend.

Another confirmation of this model is given by the plot of \bar{Q} . Indeed \bar{Q} is less than unity at low temperature when the smaller friction factor in the zone of transport of solids reduces the feeding of the polymer. At high temperature \bar{Q} increases because of the lower viscosity of the material. On the contrary, the output flow rate of the sample with $\varphi = 1\%$ is larger because of the low viscosity of the blend but especially because the pressure generated in the extruder is not reduced by the decrease of the friction factor. At the higher temperature, the reduction of the viscosity is larger (see Fig. 6) and the flow rate rises.

As far as the mechanical properties are concerned, elastic modulus, tensile strength, and elongation at break are reported in Figures 7–9, respectively, as a function of the composition for the samples extruded at the die temperature of 260°C. Both elastic modulus and tensile strength increase with increasing LCP content, although the rise of the tensile strength is not particularly remarkable. The elongation at break decreases as the LCP content increases, but, contrary to previous results of others,^{7,8,10} it remains relatively large even for blends with a high content of liquid crystal polymer: All the investigated samples showed a ductile behavior.

In the same figures the results obtained for the glass-fiber-filled nylon are reported for comparison. It is evident that, at the same composition, the elastic modulus and the tensile

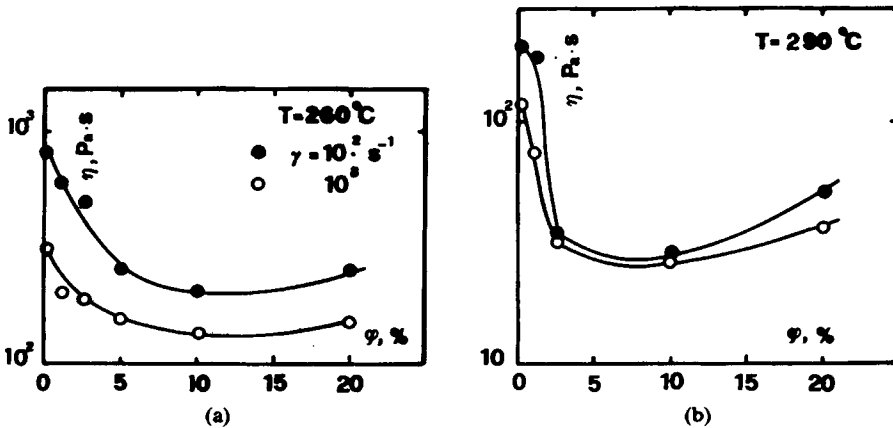


Fig. 6. Viscosity vs. composition at fixed shear rates: (a) $T = 260^\circ\text{C}$; (b) $T = 290^\circ\text{C}$.

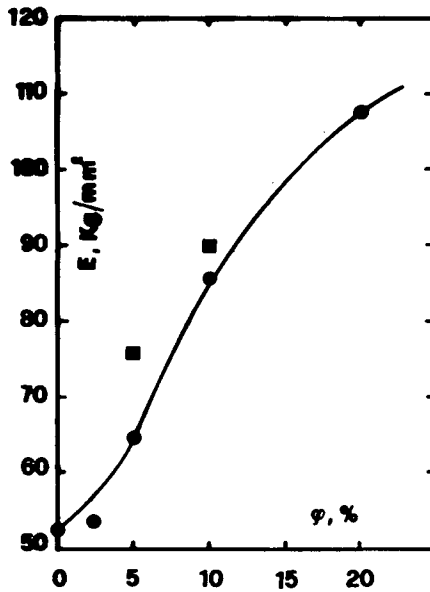


Fig. 7. Elastic modulus vs. composition. Key of symbols as in Figure 1.

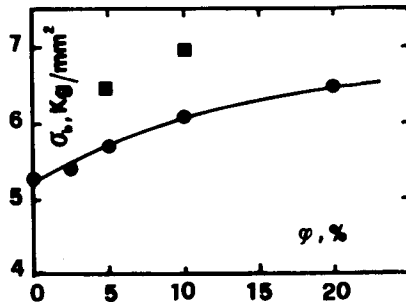


Fig. 8. Tensile strength vs. composition. Key of symbols as in Figure 1.

strength of the glass-fiber-reinforced nylon are only slightly larger than those of the LCP-filled polymer, whereas the elongation at break is significantly lower. Thus in spite of the incompatibility of nylon and Vectra, this latter polymer acts as a reinforcing agent of good effectiveness.

CONCLUSIONS

The results discussed in the present article lead to the two main conclusions: First, small additions of LCP to nylon reduce the extrusion energy; second, the mechanical properties of the blends are significantly improved with respect to the neat polymer.

As for the first effect, this had already been noticed by other authors for blends of LCP with polyamides. In fact, Siegman et al.⁷ found a 60–80% decrease of the viscosity at shear rates of 54 and 540 s^{-1} , respectively, on blending an amorphous polyamide with 10% LCP. Kiss⁸ obtained a 95% reduction of the torque on processing a 30% LCP nylon blend at 300°C. Chung¹⁰ found a maximum reduction of 80–90% (depending on shear rate) for blends of nylon 12 with 10% Vectra. These literature data are in fair agreement with ours, considering that the systems studied by different researchers are not the same.

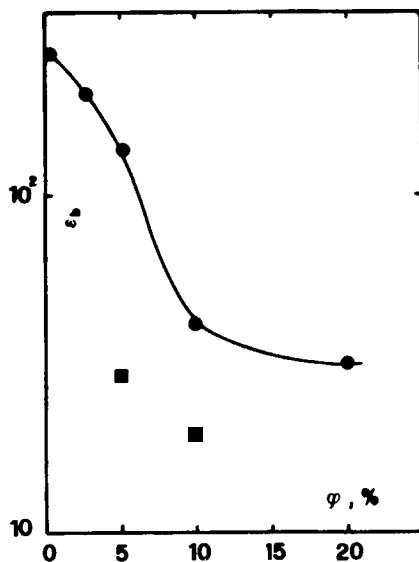


Fig. 9. Elongation at break vs. composition. Key of symbols as in Figure 1.

The evidences obtained in the present study indicate that the reduction of the extrusion energy can be interpreted as being due to the reduction of both friction factor in the zone of transport of solids of the extruder and viscosity, although the decrease of viscosity tends to reduce the output flow rate too.

As for the reinforcing effect of the LCP, the 60% increase of the modulus and the 20% increase in the tenacity, for a 10% LCP content, seem to be in reasonable agreement with the data obtained by Siegman et al.⁷ and by Kiss⁸ for nylon with 30% LCP. On the contrary, the improvements found by us appear rather large than those recorded by Chung¹⁰ for nylon 12 with HNA/HBA liquid crystal copolymer. The differences in the LCP and in sample processing can probably account for this discrepancy.

It is worth noticing that, contrary to previous findings by other workers, we found that the nylon 6/Vectra B blends display a ductile behavior over the entire composition range investigated. This point seems of interest and justifies further studies on the phase interactions in these blends.

Finally, a comparison of the investigated blends with samples of short-glass-fiber-reinforced nylon has shown that the extrusion energy required by the formers are about half of that necessary for the latter, whereas the mechanical properties are almost alike.

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