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PHYSICAL CHARACTERIZATION OF BLENDS BASED ON LIQUID CRYSTALLINE POLYESTERS AND AMORPHOUS POLYMERS

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Abstract In this work the effect of the inclusion of
low percentages of the liquid crystal polymer PET/PHB60 on
the rheological and mechanical behaviour of Polycarbonate
is described.

INTRODUCTION

In the last few years the interest of the scientific and industrial world for the use of polymer based composites has notably increased. The simple blending of different components, in fact, has been found to be one of the most advantageous methods for obtaining materials with specific characteristics for each particular application.

The mechanical properties of polymers, for example, can be greatly affected by the inclusion of fibrous fillers; in particular the strength and the modulus of a polymer can be improved by adding chopped glass fibers in the polymeric matrix. However, the presence of solid fibers during the processing operations produces difficulties in fabrication of molded parts because of the increase in the viscosity of the

system coupled with the occurring of abrasion phenomena in the surfaces in relative motion in the extruder.

Modification of physical properties of plastics can also be obtained by blending different kinds of polymers. Most of the so-called "polyblends" are composed of immiscible polymers that determine a multiphase system whose characteristics depend on the amount and on the properties of the individual polymeric components as well as on the mode of dispersion, the size, the shape, and the interaction between the phases¹.

The present study deals with polyblend systems composed of amorphous thermoplastic polymers and of thermotropic polymeric liquid crystalline materials. The latter can form fibers when drawn in the molten state. In fact, in absence of external constraints (i.e. electrical or magnetic field) the directors of the liquid crystalline domains are randomly oriented, while they significantly orient along the fiber axis when the polymer is uniaxially stretched. These oriented molecules included in the amorphous matrix may induce to the polyblend improvements in the mechanical properties of the pure thermoplastic material acting as fibrous reinforcements. In addition, amorphous polymers are expected to show an easier processability if low percentages of mesophasic materials are added as a second phase and the processing operation is carried out in the temperature range of the existence of the mesophase.

In this communication the effect of the inclusion of low

percentages of the liquid crystalline polymer (LCP) PET/PHB60 on the rheological and mechanical properties of polycarbonate (PC) will be described.

EXPERIMENTAL

The thermotropic liquid crystalline polymer used in this study has been the polyester composed of 60 mole% p-hydroxybenzoic acid and 40 mole% polyethylene terephthalate (PET/PHB60) first synthesized by W.J. Jackson and H.F. Kuhfuss in 1976 and kindly supplied by Tennessee Eastman Company. The amorphous polymer used as matrix is the polycarbonate (PC) Lexan provided by General Electric Company.

Blends of PC and LCP with composition of 2, 5 and 10% by weight of LCP in PC were prepared by mixing and extruding the materials at 240°C and at 32rpm. Before the mixing operation occurred the materials were dried at 100°C under vacuum for three hours.

Rheological measurements in shear flow were carried out in the high shear rate region with the aid of a capillary viscometer (Rheoscope 1000, CEAST). Flat entry capillaries with $D=1\text{mm}$ and $L/D=5, 10, 20,$ and 40 were used for the rheological characterization of the PC and LCP in order to evaluate the end effects (Bagley corrections). For one type of blend (PC/LCP 90/10) the same procedure has been followed and the end corrections were found to be negligible. For the other blends only the capillary with $L/D=40$ has been used. The rheological measurements were performed at the

temperature of 260°C.

Spinning of the LCP, PC, and PC/LCP 90/10 blend was performed by means of the Rheoscope 1000 provided with a melt spinning unit using a die having a diameter of 1mm and a L/D ratio of 10. Fibers of LCP were spun at the single temperature of 260°C since it was impossible to spin this material at lower temperatures. Fibers of PC and PC/LCP 90/10 blend were obtained both at the temperatures of 260°C and 210°C. The extrusion rate, V_o , was approximately 45cm/min. The filament was extruded in air at room temperature and collected by a 8cm diameter bobbin placed at a distance of approximately 0.3m from the extruder die. The take-up velocity, V_f , was varied in order to obtain V_f/V_o (draw ratio) values included between 10 and 300. The true V_f/V_o values were determined from the ratio between the die and fiber cross section measured by an optical microscope.

The elastic component of the Young modulus, E' , of the fibers was determined using a mechanical spectrometer (Dynastat) working at room temperature and at a frequency of 1Hz.

The morphology of the LCP and of the blends processed under shear and elongational flow conditions have been analyzed by means of Scanning Electron Microscope (SEM) using a Cambridge instrument, Stereoscan 100 model. Transversal sections of the extrudate samples and of the fibers have been obtained by fracturing them in liquid nitrogen.

RESULTS AND DISCUSSION

Flow curves of PC, LCP, and PC/LCP blends extruded at the temperature of 260°C are shown in Fig.1.

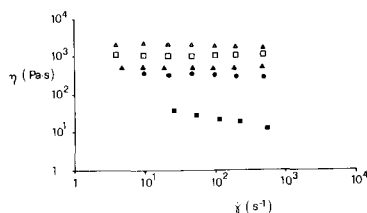


FIGURE 1. Viscosity vs shear rate at $T=260^{\circ}\text{C}$ for PC(▲), PC/LCP 98/2 (□), PC/LCP 95/5 (▲), PC/LCP 90/10 (●), LCP(■).

The polycarbonate extruded at this temperature exhibits a Newtonian behaviour in the range of shear rates studied. The same Newtonian characteristics are shown by the PC/LCP blends tested in this work, while the pure LCP shows a shear thinning behaviour according to the literature data^{2,3,4}. In addition, the viscosity values of all the blends are included within the values of the pure polymers in the full range of shear rates investigated. The viscosity value of $2 \cdot 10^3 \text{Pa}\cdot\text{s}$ for the pure PC, for example, decreases to the value of $9.8 \cdot 10^2 \text{Pa}\cdot\text{s}$ for the PC/LCP 98/2 blend at the shear rate of 10s^{-1} , while more pronounced is the decrease in the viscosity for the case of the PC/LCP 90/10 blend. The flow properties of the polycarbonate are, then, affected by the presence of the LCP even for low percentages of the latter.

The elastic component of the Young modulus, E' , against the draw ratio V_f/V_o is shown in Fig.2a for the liquid crystal polymer and in Fig.2b for the polycarbonate and the blend PC/LCP 90/10 fibers obtained at the extrusion temperature of 260°C.

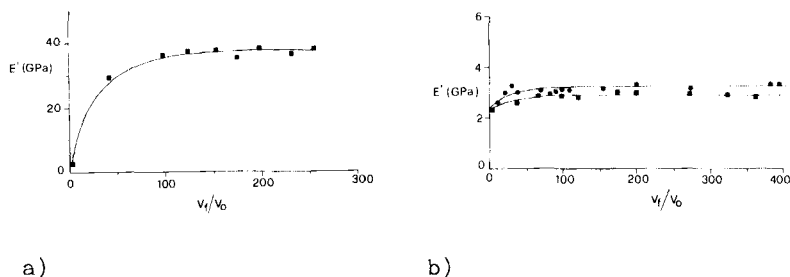


FIGURE 2. Elastic modulus, E' , vs spin draw ratio, V_f/V_o , for LCP (a); PC(■) and PC/LCP 90/10(●) (b).

The E' value for the LCP strongly increases with V_f/V_o changing from the value of 2.4 GPa at $V_f/V_o = 1$ to the value of about 37 GPa at $V_f/V_o = 150$, value comparable to those reported in literature^{5,6,7}.

The morphology of the LCP extruded in the capillary rheometer but not drawn ($V_f/V_o = 1$) is reported in Fig.3a, while the micrograph of the LCP drawn at $V_f/V_o = 200$ is shown in Fig.3b. The sample subjected to the simple shear flow is characterized by a disordered structure showing that the directors of the liquid crystalline domains are randomly oriented. On the other hand, the morphology of the LCP subjected to the elongational flow, that occurs during the drawing

operation, is characterized by a highly oriented structure.

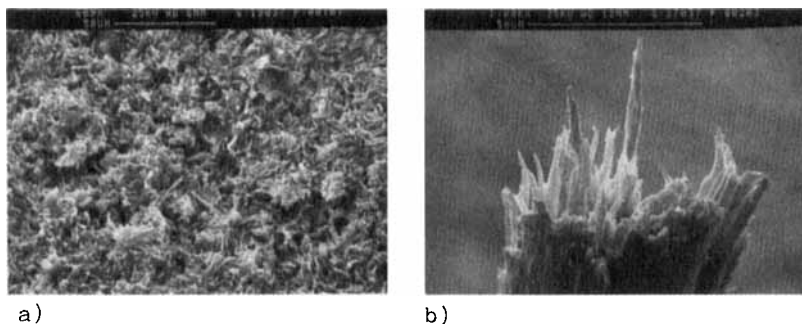


FIGURE 3. Scanning electron micrographs of the fracture surfaces of LCP fibers spun with $L/D=10$ and $V_f/V_o=1$ (a), and $V_f/V_o=200$ (b).

The increase in E' with the draw ratio is, on the other hand, very slight for the polycarbonate (Fig.2b) as expected for amorphous polymers characterized by very small relaxation times. For the blend PC/LCP 90/10 the moduli have been found to be very close to those of the pure PC. In this case, then, the LCP phase doesn't act as a reinforcing agent.

The SEM micrograph of the transversal section of the blend PC/LCP 90/10 extruded but not drawn ($V_f/V_o=1$) is shown in Fig.4a. The morphology results in a two phase system where the continuous phase is the polycarbonate while the LCP is present in a droplet-like structure. The droplets are in a spherical shape and have a diameter of approximately 1μ . The morphology of the same blend drawn at the temperature of 260°C with a draw ratio of 60 is shown in the Fig.4b. The LCP phase is present again as droplets which, in this case,

tend to deviate more from the spherical shape than those showed in the previous figure. During the drawing operation, however, the LCP domains have not formed fibrils and, then, any reinforcing effect on the modulus of the matrix can be expected.

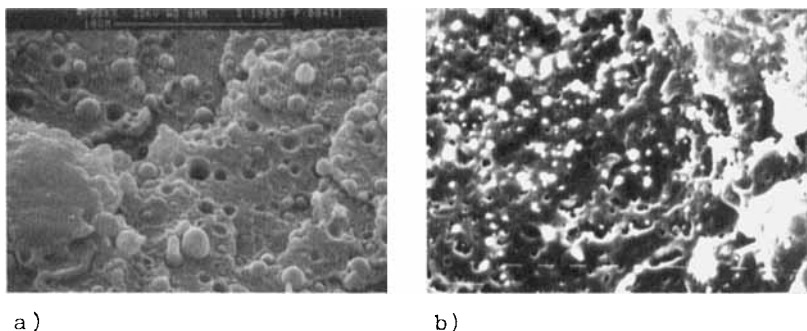


FIGURE 4. Scanning electron micrograph of PC/LCP 90/10 spun with $V_f/V_o=1$ (a), and with $V_f/V_o=60$ at $T=260^\circ\text{C}$ (b).

The values of E' for the pure PC and for the PC/LCP 90/10 fibers obtained at the extrusion temperature of 210°C are shown in Fig.5.

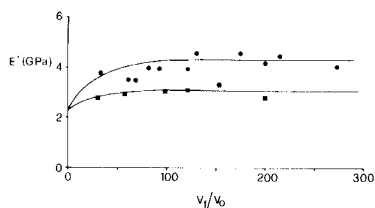


FIGURE 5. Elastic modulus, E' , vs spin draw ratio, V_f/V_o , for PC(■) and PC/LCP 90/10(●) extruded at $T=210^\circ\text{C}$

In this case the tensile modulus for the PC reaches a plateau value of 3.1GPa while the blend's tensile modulus reaches a plateau value of about 4.4GPa. The tensile modulus of the pure PC increased, then, 50% with the addition of a low percentage of the LCP in the amorphous matrix.

The SEM micrograph of the transversal section of the PC/LCP 90/10 blend drawn at $T=210^{\circ}\text{C}$ and at $V_f/V_o=75$ is shown in Fig.6a. From the comparison between the Fig.4b and the Fig.6a it results that the LCP domains form a more oriented structure in the case of the blend drawn at $T=210^{\circ}\text{C}$. A longitudinal section of the same blend is shown in Fig.6b in which is evident the polymer blend fibrillar structure.

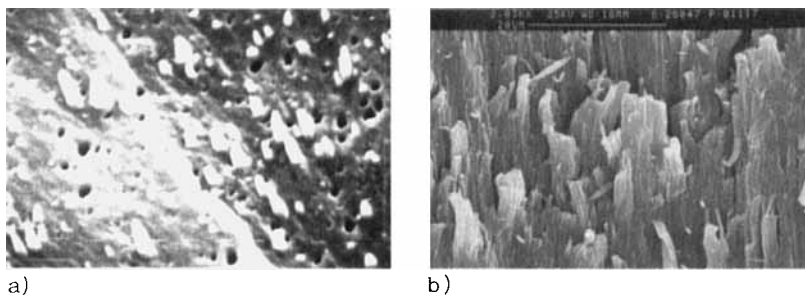


FIGURE 6. Scanning electron micrographs of PC/LCP 90/10 spun with $V_f/V_o=75$ at $T=210^{\circ}\text{C}$, transversal section (a), and longitudinal section (b).

The differences in the mechanical and morphological behaviour shown by the PC/LCP 90/10 blends spun at the temperatures of 210 and 260°C can be attributed to different PC, PC/LCP viscosity ratios obtained in correspondence of the two extrusion temperatures used in this work.

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