

Liquid Crystalline Polymer Laminates

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SYNOPSIS

On the basis of a poly(ethylene terephthalate) copolyester containing 60 mol % *p*-hydroxybenzoic acid, thin liquid crystalline films (160 μm thick) are obtained by melting the polymer at 300°C and chilling at 0°C. The undrawn films obtained have a high degree of orientation as evidenced by X-ray measurements. Due to molecular orientation, these films are characterized by their excellent mechanical properties. In order to avoid losses in the mechanical strength due to increase in their thickness, laminates are prepared using thin liquid crystalline films. Lamination is carried out by annealing under pressure at 170°C for 6 h, resulting in samples with excellent mechanical properties regardless of their thickness. A method is proposed that makes it possible to combine the unique mechanical properties of thin films of liquid crystalline polymers with a lamination process in order to obtain thick and very strong materials.

INTRODUCTION

During the last two decades numerous investigations have been carried out with the intention of developing high-performance liquid crystalline polymers.¹⁻⁷ It has been found that aromatic polyesters have liquid crystalline character and are capable of providing injection-molded shapes with much higher modulus values in one direction, i.e., with anisotropic properties due to orientation of the polymer chains during molding.^{4,5} Nowadays work on liquid crystalline aromatic polyesters is shifting toward the development of new and innovative processing techniques, so as to achieve shapes that take advantage of the unique mechanical properties and melt processability of these materials.⁷

The liquid crystalline polymer melt can be highly oriented through injection molding and the molecular orientation achieved can be frozen after cooling. This orientation of rigid molecules reinforces the material, increasing its tensile strength, stiffness, and impact strength.^{5,8}

The molecular orientation of a liquid crystalline polymer depends strongly on the specimen's thick-

ness. On the other hand, mechanical properties depend on the degree of orientation. It has been found that the flexural modulus depends exponentially on the specimen's thickness: the higher the latter, the greater the loss of the excellent mechanical properties of the material.^{5,8}

The purpose of the present study was to find an approach to the processing of liquid crystalline polymers by preserving their high mechanical properties regardless of the thickness of the final product. An attempt was made to combine the unique mechanical properties of thin films of liquid crystalline polymers with a lamination process in order to obtain thick and very strong materials.

EXPERIMENTAL

Commercial copolyester of poly(ethylene terephthalate) (PET) and 60 mol % *p*-hydroxybenzoic acid (PHBA) (Eastman Chemical Products, Inc., Tennessee) was melted at 300°C in a 1-oz plunger-type injection molding machine. The melt was extruded through a die with a flow rate of 16 g/min and the extrudate was passed between metal rolls at 0°C (ice-water bath). The resulting films were 0.5 cm wide and 160 μm thick.⁹

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The copolyester films were annealed with free or fixed ends at 210°C for 6 h in a vacuum oven. The mechanical properties of annealed and unannealed samples of PET/PHBA copolyester were tested on a Zwick 1464 machine. The structure of the samples was studied qualitatively by wide-angle X-ray scattering (WAXS) (Siemens, Kristalloflex, flat camera, Ni-filtered Cu-K α -radiation) and by differential scanning calorimetry (DSC) (Mettler TA 3000).

Laminates of the copolyester films were prepared as follows. Previously annealed with free ends, strips of PET/PHBA copolyester, 5 cm long and 0.5 cm wide, were overlapped and pressed in a drill press vise placed in a vacuum oven. Annealing was carried out at 170°C for 6 h. The mechanical strength of the laminates obtained was tested on a Zwick 1464 machine.

RESULTS AND DISCUSSION

The stress-strain curves of PET copolyester containing 60 mol % PHBA, unannealed and annealed with free or fixed ends at 210°C for 6 h are shown in Figure 1. Thermal treatment with free ends leads to a significant increase of the tensile modulus [from 2324 to 8962 N/mm², Fig. 1, curves (a) and (b)].

Annealing with fixed ends results in intermediate values of the tensile modulus [Fig. 1, curve (c)]. The tensile strength changes from 57 to 101 N/mm² [Fig. 1, curves (a) and (b)]. Both annealed and unannealed copolyester films show a very low relative elongation (from 0.9 to 1.9%).

The changes in the mechanical properties observed can be explained taking into account that the PET/PHBA copolyester studied had rigid macromolecules. It is known that during thermal treatment with free ends such polymers undergo spontaneous arrangement of the macrochains related with elongation and improvement of the tensile modulus of the specimen, its tensile strength remaining practically the same.¹⁰

The very limited drawability of the undrawn material can be explained by the results of the WAXS measurements. WAXS patterns of undrawn samples of PET/PHBA copolyester, unannealed and annealed with free or fixed ends, are shown in Figures 2(a), (b), and (c). The film obtained by quenching of the liquid crystalline polymer melt is highly oriented without additional drawing [Fig. 2(a)]. The rigid macromolecules of PET/PHBA copolyester are highly oriented by extrusion of the melt through the narrow die, and this orientation is frozen after quenching of the melt. Additional improvement of

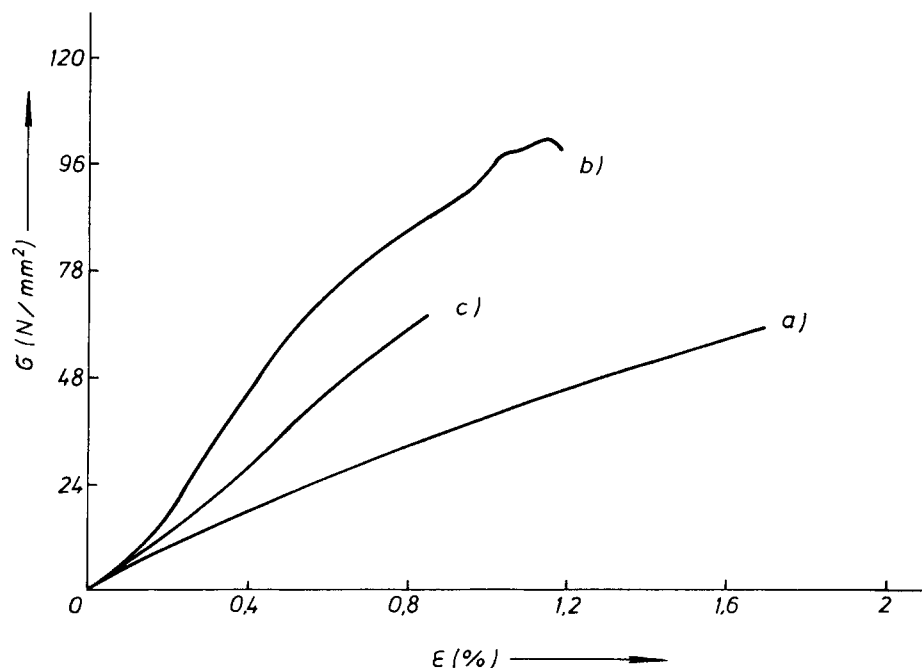


Figure 1 Stress-strain curves of liquid crystalline PET copolyester films containing 60 mol % PHBA: (a) unannealed, (b) annealed at 210°C for 6 h with free ends, (c) annealed at 210°C for 6 h with fixed ends.

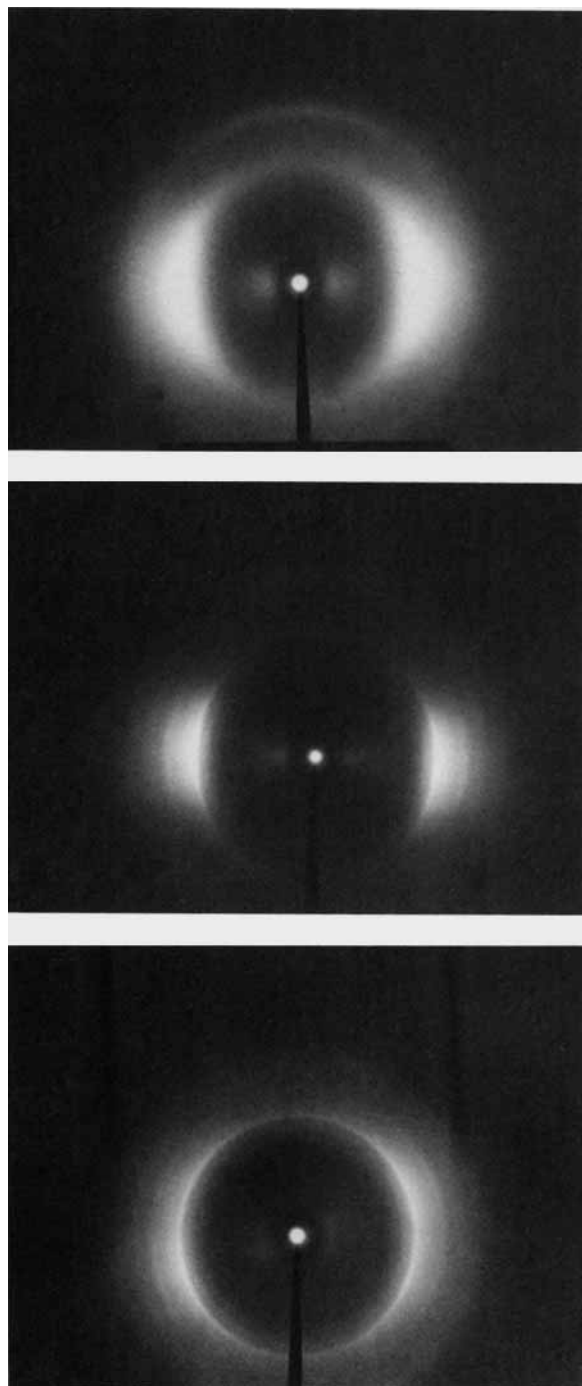


Figure 2 WAXS patterns of liquid crystalline PET copolyester films containing 60 mol % PHBA: (a) unannealed, (b) annealed at 210°C for 6 h with free ends, (c) annealed at 210°C for 6 h with fixed ends.

the orientation by drawing is practically impossible. The linear nature of the chains would yield a continuous oriented phase and a discontinuous glassy

phase so that heating above T_g would not result in a disastrous loss in the mechanical properties.⁷ Annealing with free ends at 210°C leads to an improvement of the crystal structure, preserving the degree of orientation whereas thermal treatment with fixed ends at the same temperature leads to some losses in the orientation [Figs. 2(a), (b), (c)]. Evidently, arrangement of the rigid PET/PHBA macromolecules is easier when annealing is performed with free ends. Unlike the case of polymers with flexible macromolecules annealing of PET/PHBA copolyester is related with elongation, and improvement of the ordering can be achieved when sample is with free ends.

The DSC measurements confirm the WAXS results. DSC curves of undrawn samples, unannealed and annealed at 210°C for 6 h as well as those of laminates obtained at 170°C by pressing for 6 h, are shown in Figure 3. It appears that all curves have the same heat deflection temperatures at about 60 and 230°C. The first one can be attributed to PET segments. It should be noted that the second deflection temperature has not been observed earlier at 230°C with the same material.⁵ Most likely, this difference is due to the polymer processing. Our material is thinner by about one order of magnitude than that discussed in Ref. 5. Since our samples are highly oriented and the macrochain interactions are enhanced, some molecular motions of the rigid chains could take place only at temperatures higher than 230°C. Once again, this fact demonstrates the strong influence of processing on the polymer properties.

In Figure 3, curves (b) and (c), a small endothermal peak is observed at about 210°C with the samples annealed at 210°C with fixed as well as with free ends. The same peak appears also in the case of laminates undergone heating at 170°C [Fig. 3, curve (d)]; its position corresponds to that of the peak observed with samples annealed with free ends [Fig. 3 curve (c)]. Hence, lamination conditions (temperature and pressure applied) do not lead to any further changes in the polymer structure, as evidenced by DSC data.

The high mechanical properties of the liquid crystalline PET/PHBA copolyester films along the melt flow are due to the high degree of orientation and self-reinforcement by their rigid molecules. These properties are lost, however, upon increasing the thickness of the samples, as observed by Jackson and Kuhfuss.⁵ Their sample, 1.3 cm thick, has the same mechanical properties both along and across the flow, i.e., it is isotropic (Fig. 4).

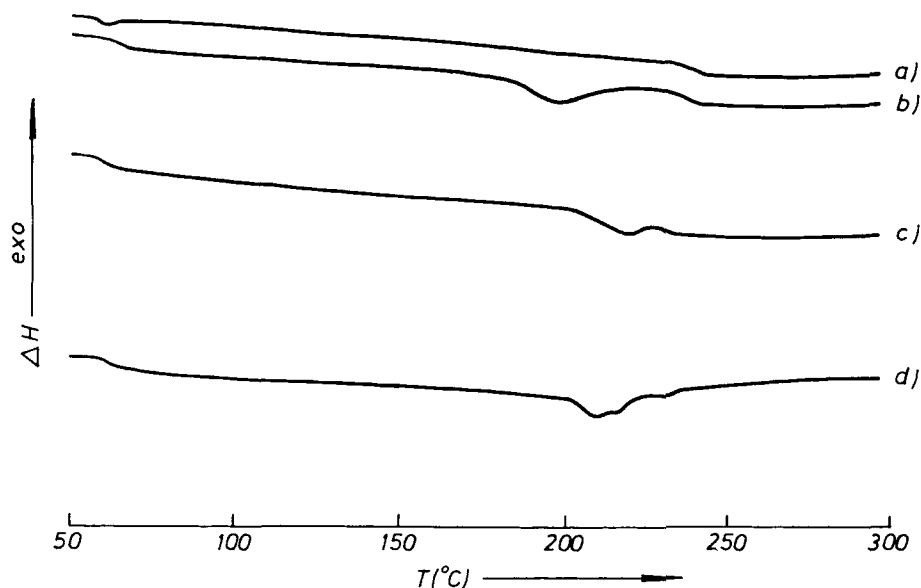


Figure 3 DSC curves of liquid crystalline PET copolyester films containing 60 mol % PHBA: (a) unannealed, (b) annealed at 210°C for 6 h with fixed ends, (c) annealed at 210°C for 6 h with free ends, (d) after lamination under pressure at 170°C for 6 h.

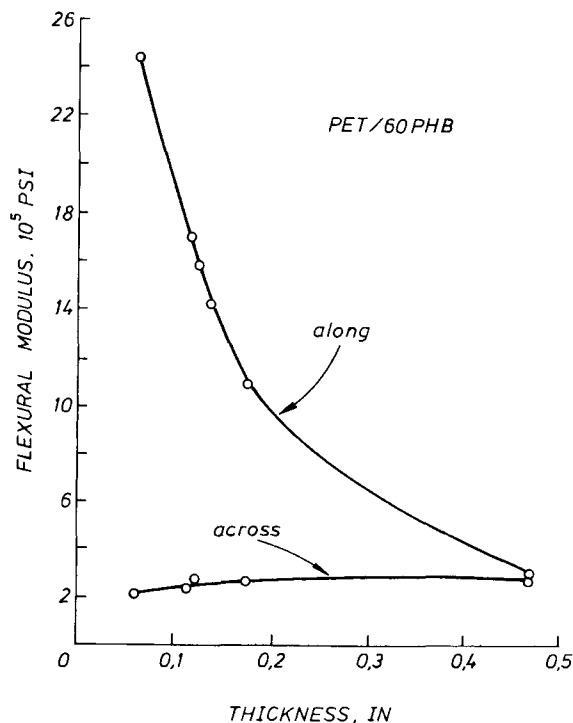


Figure 4 Effect of thickness on along- and across-the-flow flexural modulus of PET modified with 60 mol % PHBA.⁵

In order to avoid this negative effect, the rise in the thickness of the samples was achieved by lamination of thin films. The resulting material, 0.5 cm thick, has a tensile modulus of 8900 N/mm², this value being higher by an order of magnitude than that of the material of the same thickness obtained directly by injection molding (870 N/mm²).

Lamination is carried out by heating in vacuum at high temperature (170°C) and application of pressure. Under these conditions exchange (*trans*) reactions take place between ester groups of polyester macromolecules on the contact surfaces of the layers.¹¹⁻¹³ Thus lamination is achieved by the formation of new chemical bonds between the layers in the solid state. As a result of this treatment a material of desired thickness is prepared, characterized by both high orientation of the macrochains and excellent mechanical properties.

The lamination temperature (170°C) is chosen to be high enough for the occurrence of chemical reactions. The further increase of this temperature leads to a significant drop of the elasticity modulus (Fig. 5). The loss of the high mechanical properties of liquid crystalline polymer laminates obtained at 250°C can be explained with our WAXS results (Fig. 6). It is seen that the initial orientation (Fig. 2) is almost destroyed. This fact demonstrates once again

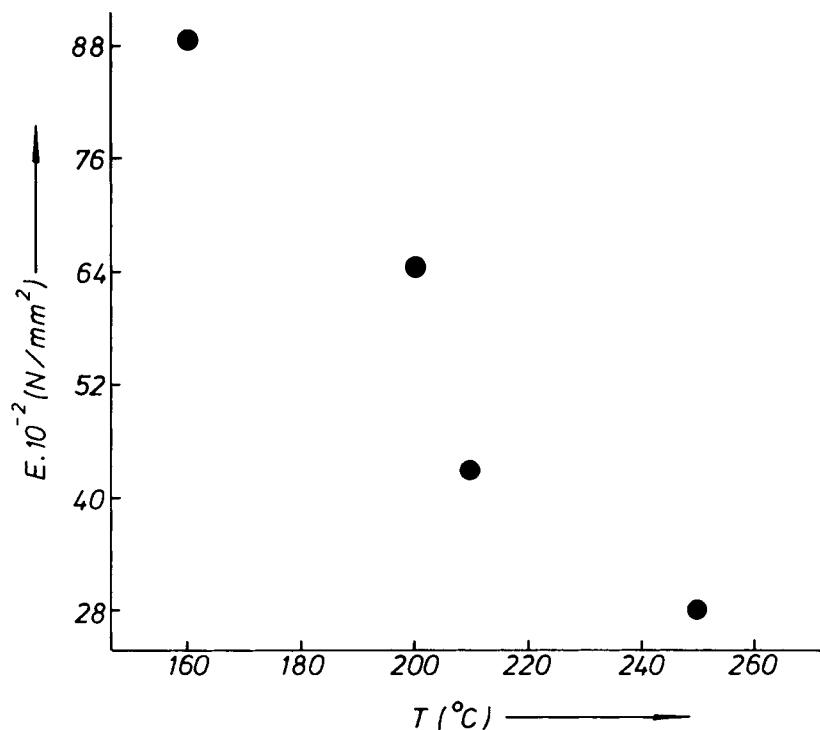


Figure 5 Dependence of elasticity modulus on the temperature of lamination of PET copolyester films containing 60 mol % PHBA.

that processing conditions of liquid crystalline polymers are of particular importance.

The principal advantage of the proposed method over those found in the patent literature^{14,15} consists of lower temperature of lamination (100°C below the softening temperature), while the cited patents teach an excess of 20–30°C of the melting temperature resulting in a decrease of orientation and loss

of mechanical properties of the laminates up to three times.¹⁵ In the present study the mechanical properties of laminates are even improved if compared with those of the initial films. Welding is a result of chemical reactions on the contact surfaces of layers rather than of melting.

This approach enables the obtaining of a liquid crystalline polymer material characterized by both isotropy and high mechanical properties when lamination is carried out by cross-plying of the starting films.

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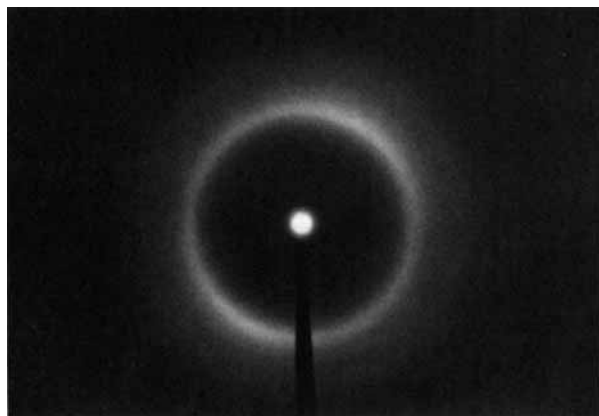


Figure 6 WAXS patterns of laminate obtained at 250°C from PET copolyester film containing 60 mol % PHBA.

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