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BLENDS OF A LIQUID CRYSTALLINE COPOLYESTER WITH POLYETHERSULPHONE

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Abstract Examination of the rheological properties of blends of polyethersulphone (PES) and a liquid crystalline polymer (LCP) has shown an approximately fourfold drop in viscosity at low shear rates for the addition of only 2% LCP. Optical microscopy of sections of extruded pellets (cut parallel and perpendicular to the extrusion axis) has been carried out. It is found that the LCP orientation varies significantly across the pellet. When the thin sections are annealed at temperatures ~ 300° C the LCP tries to minimise interfacial contact with the PES suggesting a high surface energy.

INTRODUCTION

Previous work[1,2] has shown that addition of an LCP to a conventional thermoplastic leads not only to a reduction in viscosity but also to the LCP

acting as a reinforcing agent in much the same way as glass fibre, but without the wear and tear on the processing equipment.

With liquid crystalline polymers being relatively expensive at the present time, it is essential to optimise the compositions and processing conditions, to get the required properties from as little LCP as possible. To this end we are making a detailed study of the rheology and morphology of PES blended with a copolyester based on hydroxybenzoic acid and hydroxynaphthoic acid residues. The particular polymers were chosen as they can be processed together, without the danger of degradation of one or the other.

Sample Preparation

The two component polymers in granular form were weighed, to give the required compositions (from 2-90% LCP content), and mixed together before being dried overnight in an air circulating furnace at 150° C. The mixture was then blended, at 340° C, in a single screw extruder, extruded through a 2mm circular die into a waterbath and finally chopped into pellets. These pellets were either sectioned by a sledge microtome fitted with a glass knife, for optical microscopy, or dried overnight before being pressed into plaques 30mm diameter and 3mm thick for rheological measurements.

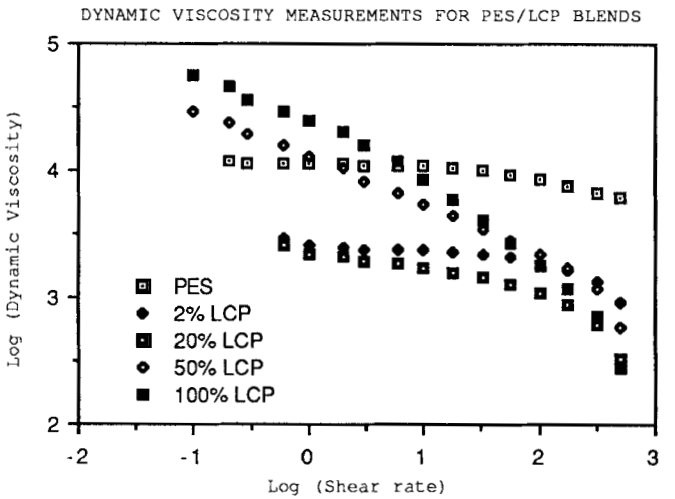

FIGURE 1. Plot of dynamic viscosity against shear rate for PES,2,20,50,100% LCP at 10% strain.

Rheology

The plaques were placed in a Rheometrics Dynamic Spectrometer operating in the parallel plate mode (plate separation of 1mm), under nitrogen at 350° C, and were held for 10 minutes to allow attainment of operating temperature. Measurements of the complex viscosity were made for shear rates from 10^{-1} to 500 rad s^{-1} at 10% strain. At low shear rates some points had to be discarded as the torque on the lower plate was below that specified for accuracy.

Figure 1. is a log-log plot of viscosity against shear rate for the pure polymers and the 2, 20 and 50% LCP blends. The most striking

feature is that the addition of only 2% LCP to PES reduces the viscosity by a factor of 4, even at low shear rates where the viscosity of the LCP is higher than that of PES. The shape of the curve is similar to that of PES, showing Newtonian fluid type behaviour before shear thinning starts to occur at ~ 100 rad s^{-1}. Increasing the concentration of LCP up to 20% gives a further, but slight, decrease in viscosity at low shear rates, with a larger decrease at higher shear rates. The 50% blend gives a viscosity curve of similar shape to that of pure LCP ie. it is very shear sensitive.

Optical Microscopy

Pellets were sectioned, both parallel and perpendicular to the extrusion direction, to a thickness of approximately 5μm. Some samples were sandwiched between slide and coverslip with an immersion oil of the same refractive index as PES and viewed at high magnification using an oil immersion lens. Figure 2a. shows a region near the edge of a 12% LCP/PES pellet cut parallel to the extrusion direction. The LCP can be seen as highly oriented birefringent areas showing the characteristic banded texture[3] of a thermotropic liquid crystalline polymer under shear.

Figure 2b. shows an area close to the centre of the pellet, again sectioned parallel to the flow direction. In this case no elongation of the LCP can be seen. Figure 3. shows an area sectioned perpendicular to the flow direction. The LCP

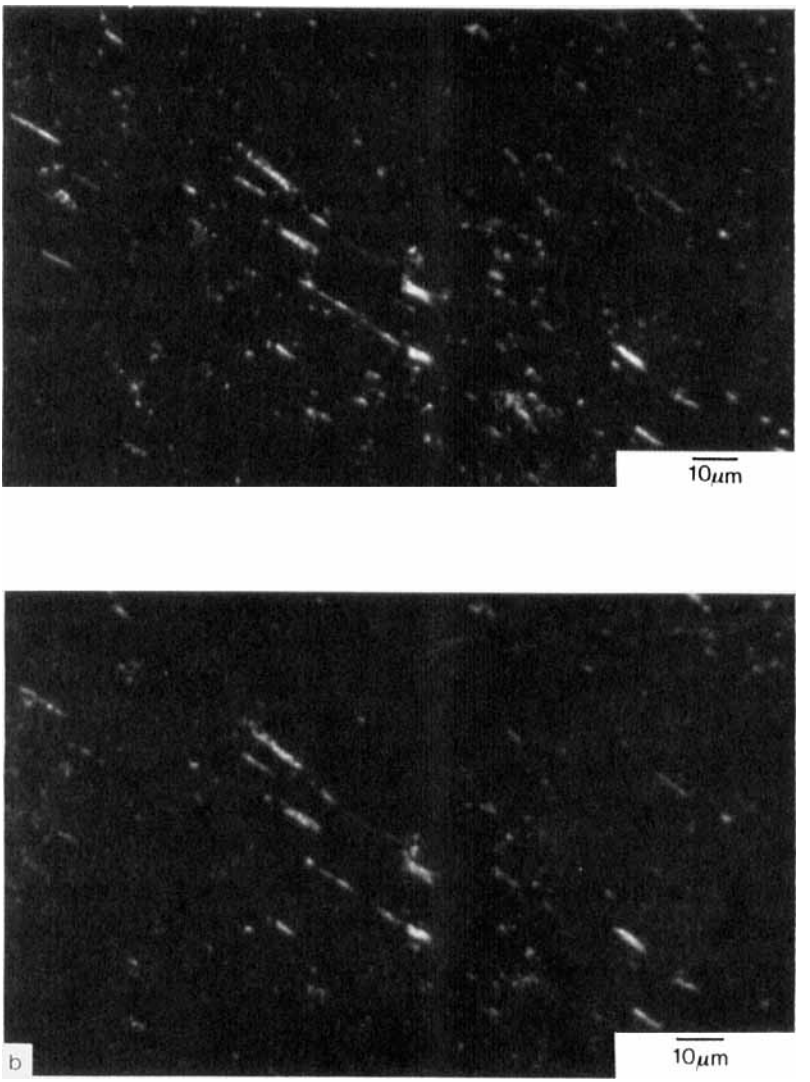

FIGURE 2. Polarised light micrographs of 12% LCP sample microtomed parallel to extrusion direction a) near edge of pellet and b) towards centre of pellet.

regions are similar in shape to those in Figure 2b., having a circular cross section of 1-2μm diameter.

The above suggests that there are two distinct regions in the extruded pellet. In the skin region the elongational flow field produces cylinders of the LCP oriented with their axes parallel to the extrusion direction. In the 12% sample these cylinders are continuous over large distances due to separate LCP regions running into one another. In lower concentration samples the LCP regions are discrete and elongated with an

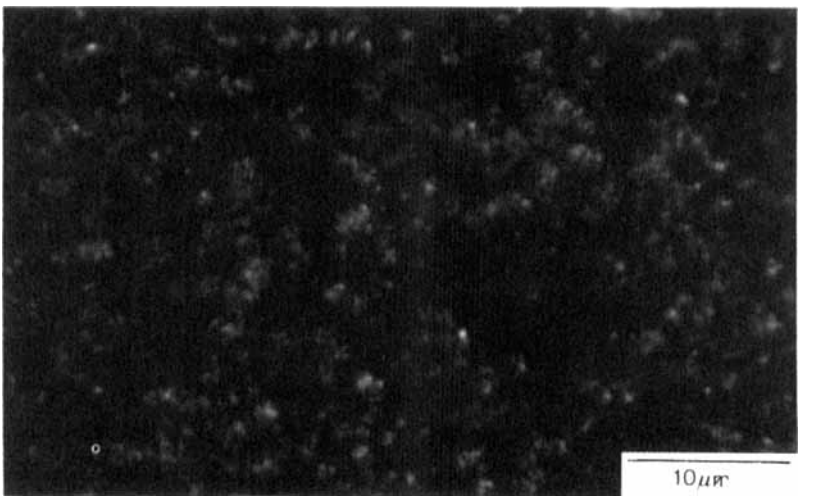

FIGURE 3. Polarised light micrograph of a 12% LCP sample sectioned perpendicular to the flow direction.

axial ratio of about 5:1 (Figure 4a).

In the core region the decelerating flow does not produce any orientation, as evidenced by the

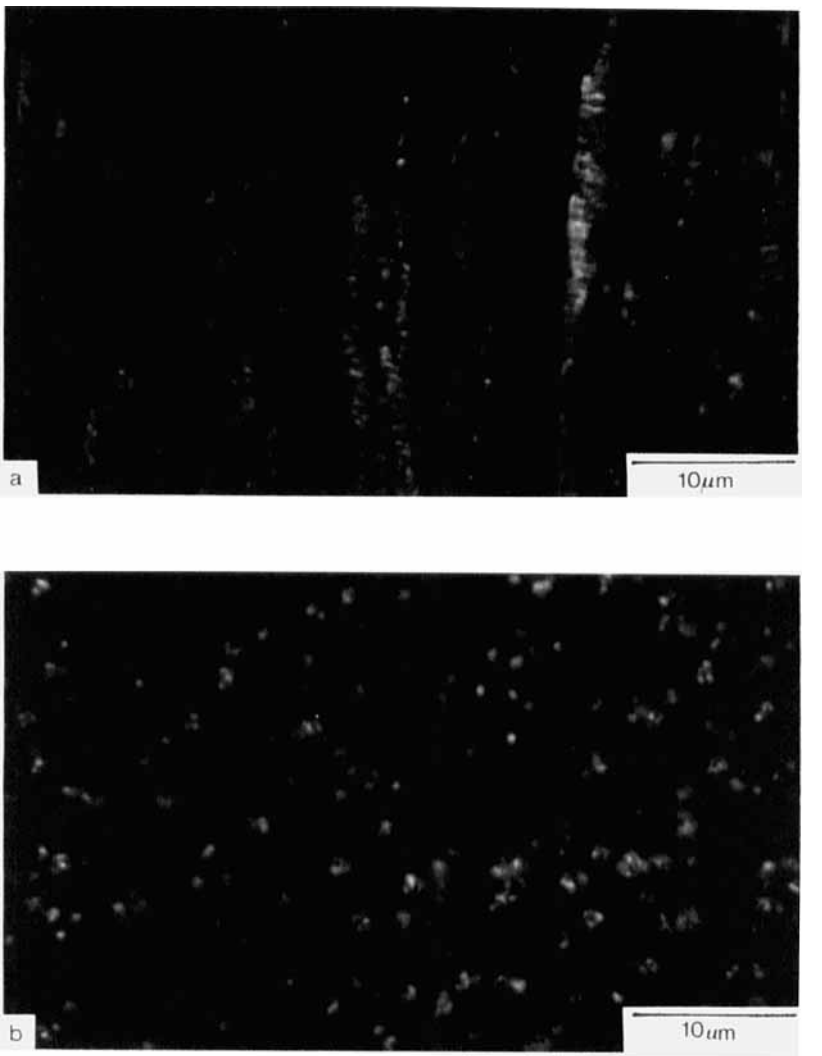

FIGURE 4. Polarised light micrographs of 7% LCP sample microtomed parallel to extrusion direction a) at 290° C and b) at 320° C.

circular cross sections of the LCP when viewed along and perpendicular to the extrusion direction. The exact shape of the internal LCP areas is very sensitive to turbulence in the flow during processing. In one case an expanding gas bubble gave rise to a small amount of elongation in the centre region.

Some sections were sandwiched between cover slips and thermally cycled, in a nitrogen atmosphere (to avoid any possible degradation during long experiments), whilst being viewed in a Carl Zeiss Jenapol polarising microscope. The samples were heated at 10° C per minute from room temperature to 230° C, held for 1 hour, to allow any flow birefringence in the PES matrix to relax away, and then heated to 320° C at 10° C per minute.

Figure 4a. is a micrograph of a 7% LCP sample, microtomed parallel to the extrusion direction, viewed between crossed polars at 290° C. On heating to 320° C (Figure 4b.) the regions of birefringence shrink in length, whilst their width remains approximately constant, and the overall birefringence appears to decrease. The latter is probably associated with the local thickening of the LCP seen when sections are viewed in transmitted light. These observations suggest that the LCP is trying to minimise its interfacial contact area with the PES.

However when sections microtomed perpendicular to the flow direction are thermally cycled there is no decrease in cross sectional area of the

birefringent regions, due to the contact area already being minimised in these sections ie. thickness ~ diameter.

Discussion

The results show that considerable advantages may be obtained by blending small amounts of LCP with conventional thermoplastics, provided they have mutually compatible processing temperatures.

Firstly the reduction in viscosity will reduce the energy requirements to achieve a given throughput of the extruded blend. However this can clearly only be considered an advantage if the end product has desirable properties. The observed morphology - oriented cylinders of LCP towards the outside of the pellet, changing to more spherical inclusions at the centre where there is less extensional flow - suggests that careful control of the processing conditions will be required to optimise mechanical properties. Furthermore, since the pellets themselves are subsequently likely to be melt processed (eg. in injection moulding) due consideration of these flow fields will also need to be made.

Compatibility between a rigid rod molecule, such as the LCP and the flexible PES is not to be expected, as shown for ternary systems by Flory[4] and Bianchi et al.[5,6]. It is perhaps not surprising then, that when constraints are removed (as in the thin films) minimisation of the contact area between the two phases takes place. Clearly in the bulk such shape changes will no longer take

place, but it suggests that the interface will be mechanically weak. This view is substantiated by the observation that in ultrathin sections the LCP phase usually decoheres leaving voids. This effect may therefore limit the mechanical reinforcement obtainable by this route. Finally it is not yet clear whether the high surface energy plays a part in the dramatic viscosity reduction for low LCP additions; no mechanism for this reduction has been established to date.

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