

## EXTRUSION, SPINNING AND INJECTION MOULDING OF BLENDS OF POLY(ETHYLENE TEREPHTHALATE) WITH LIQUID CRYSTALLINE POLYMERS

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**Abstract**—Blends of poly(ethylene terephthalate) (PET) and two different types of liquid crystalline polymers (LCP) have been prepared with different processing operations and characterized. The processability of PET improves in all processing operations by adding small amounts of LCP. Both melt and solid properties of the blends seem mainly to depend on the ratio between the viscosity of the matrix and that of the LCP. Indeed, fibrillation of the LCP particles, and then the improvement of the mechanical properties, is possible only when the viscosity of the LCP is lower than that of the flexible matrix, also in elongational flow. The adhesion between matrix and LCP particles depends on the structure of the LCP. The presence of flexible spacers in the chain of the LCP improves the adhesion with the thermoplastic matrix.

### INTRODUCTION

Poly(ethylene terephthalate) (PET) has been used as matrix in several blends with liquid crystal polymers (LCP) [1-5]. White *et al.* [1] studied blends of PET with a liquid crystal copolyester synthesized from PET and hydroxybenzoic acid (PET/60PHB). The viscosity of PET is dramatically reduced by adding small amounts of LCP. The mechanical properties, modulus and tensile strength of PET improve on increasing the LCP content.

Ko and Wilkes [2] investigated the effect of extrusion variables on the properties of blends of PET with HBA/HNA copolyester. The elastic modulus in the flow direction is considerably improved by adding 30% of LCP and increasing the screw speed.

Amano and Nakagawa [3] studied spinning and drawing of blends of PET and PET/50PHB. With increasing LCP content, the drawing temperature and the maximum draw ratio necessary to achieve the maximum modulus decrease. The sonic modulus increases with LCP concentration.

Shin and Cheng [4] used a semirigid liquid crystal in blends with PET. They attributed the good mechanical properties, and in particular the high values of the elongation at break, to the good adhesion between the flexible matrix and the semirigid LCP. This improved adhesion arises from the flexible spacers used in this LCP sample.

Baird and coworkers [5] studied blends of PET with a mixture of PET/60PHB and PET/80PHB. Fibrillation of the LCP phase in extruded rods is achieved only if extensional flow is present. The authors suggested that the rheology during cooling of the pure components is an important factor in obtaining fibrillation of the LCP phase.

A new class of semirigid liquid crystal copolyester has been described in previous papers [6-9]. Although their mechanical properties can be slightly lower than

those of wholly aromatic liquid crystal polymers, semirigid LCPs can remarkably improve the processability and, when oriented, the mechanical properties of thermoplastic matrixes [10-12]. In particular, it has been demonstrated [12] that blends of polycarbonate with a sample of LCP of this class, show better adhesion between the two phases than that between the same matrix and a rigid copolyesteramide.

In this work, processing and mechanical properties of PET/semirigid LCP blends are compared with those of PET/rigid LCP blends, considering in particular the processing aid action and the resulting morphology in different processing operations.

### EXPERIMENTAL PROCEDURES

PET was kindly supplied by Enichem Polimeri (Italy); its intrinsic viscosity, measured in tetrachloethane/phenol at  $T = 25^\circ$ , was  $\eta = 0.62$  dl/g. The semirigid LC copolyester was synthesized by Eniricerche (Italy) from sebacoic acid, (S), 4-4-hydroxybiphenyl (B) and hydroxybenzoic acid (H). The sample used in this work will be referred as SBH 1-1-2, the figures indicating the relative contents of the three units. Synthesis, characterization, rheology and mechanical properties of this material have already been presented [6-9]. The wholly aromatic copolyester is commercially known as Vectra A-900 (VA) (Hoechst-Celanese, U.S.A.). This liquid crystal polymer was synthesized from 73% hydroxybenzoic acid and 27% 2-hydroxy-6-naphthoic acid moieties.

All the materials were carefully dried at  $110^\circ$  under vacuum for at least 12 hr, and then blended using a laboratory single screw extruder ( $D = 19$  mm,  $L/D = 25$ ) Brabender equipped with a die assembly for ribbon. This die presents a long conical inlet followed by a short rectangular channel. The extrudate was drawn and the average draw ratio (DR) of the extruded ribbons was about four.

The thermal profile used for PET/SBH system was 230, 250, 270,  $270^\circ$  and for PET/VA system was 240, 260, 280,  $280^\circ$ . In both cases the rotational speed was 100 rpm. During extrusion the torque was continuously recorded and

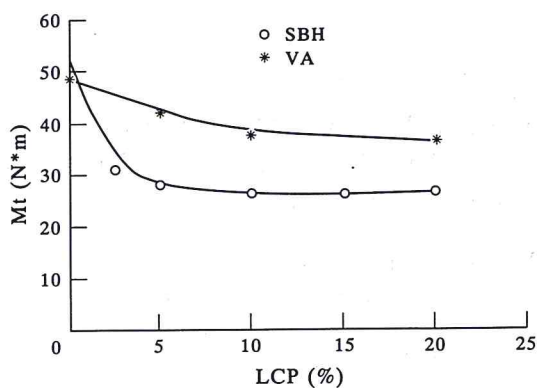


Fig. 1. Torque vs LCP content.

flowrate determined by direct weighing. The contents of LCP in the blends were 2.5, 5, 10, 15, 20%/wt.

Rheological measurements were carried out using a capillary viscometer Rheoscope 1000 (CEAST, Italy), at 270°. The capillary was 1 mm diam and length-to-diam ratio of 40. In order to evaluate the temperature dependence of the viscosity, measurements were also carried out at various temperatures. The pure polymers were heated at the extrusion temperature, then cooled to the desired temperature and after allowing sufficient time to reach thermal equilibrium, the measurements were made. For these tests, the shear rate was 24 sec<sup>-1</sup>.

The melt spinning tests were carried out using a capillary viscometer, Rheoscope 1000 (CEAST, Italy), equipped with the drawing module and with a conical capillary with 1 mm in diameter and with length-to-diam. ratio  $L/D = 0$ . The extrusion temperature was 270°. The extruded monofilament, passed through a pulley system, was then drawn by two counter-rotating rolls; the velocity of the roll was varied in order to obtain different draw ratios (DR). The spinning draw ratio was determined by measuring the decrease in diameter of the fibres.

Mechanical properties of fibres and strips cut from the extruded ribbons in the flow direction were evaluated using an Instron mod. 1122 at an elongational rate of 2 min<sup>-1</sup>. All the reported results are averages of at least eight measurements.

Samples for Izod tests were obtained by injection moulding using a Negri & Bossi reciprocating screw injection moulding machine model NB 25 with clamping force of 25 tons and maximum shot size of 50 cm<sup>3</sup>. The operating conditions were: temperature profile in extruder 263–275–275°, mould temperature 25°, holding time 3 sec. Impact tests were carried out with Fractoscope (CEAST, Italy), in the Izod mode.

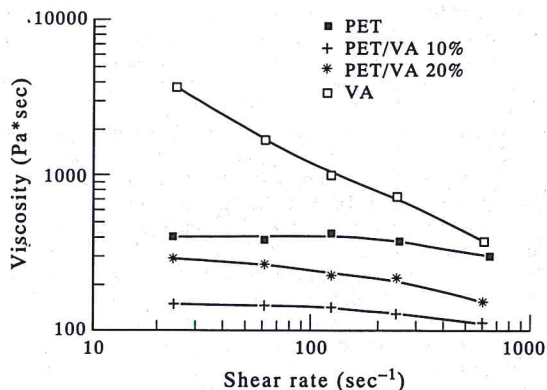


Fig. 2. Flow curves of PET/VA blends

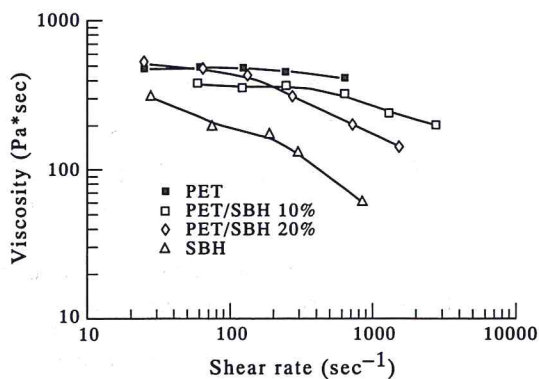


Fig. 3. Flow curves of PET/SBH blends.

SEM micrographs were obtained using a Philips Scanning Electron Microscope (model 501). The samples fractured in liquid nitrogen were coated with gold to make them electrically conducting.

## RESULTS AND DISCUSSION

### Extrusion

**Processability.** Torque and output flowrate can be considered as measures of polymer processability: low torque and high output flowrate values indicate good processability. Figure 1 shows the torque values of the two system as a function of the LCP content. The values of the torque decrease for both system but the reduction due to the presence of the semirigid LCP is remarkably larger. For the latter system, the torque decreases and, at low LCP concentration, the torque-composition curve flattens and is almost unchanged in the 5–20% LCP composition range.

As for the output flowrate, only a small decrease with respect to the pure PET was observed. It has been observed for other LCP containing blends [12–16] that the decrease of the torque was accompanied by a significant reduction of the output flowrate. This behaviour cannot be explained only in terms of a decrease of viscosity, but it is necessary also to consider a decrease of the friction factor in the zone of transport of solids of the extruder due to a migration of the solid LCP particles towards the polymer-metal interfaces. This layer leads to a reduction of the friction between polymer and barrel decreasing the solid output. In the case of these

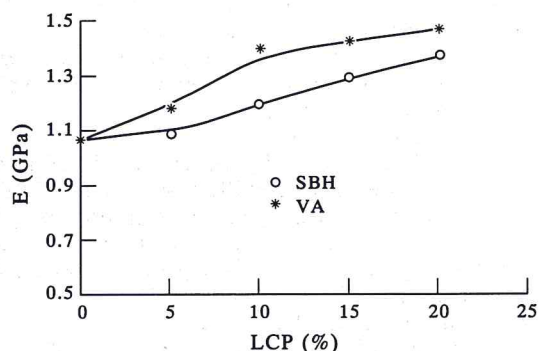


Fig. 4. Elastic modulus of extruded ribbons vs LCP content.



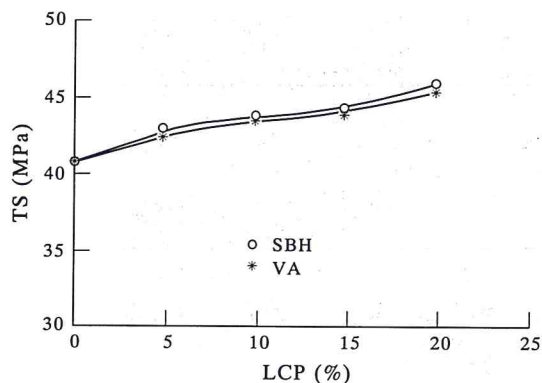


Fig. 5. Tensile strength of extruded ribbons vs LCP content.

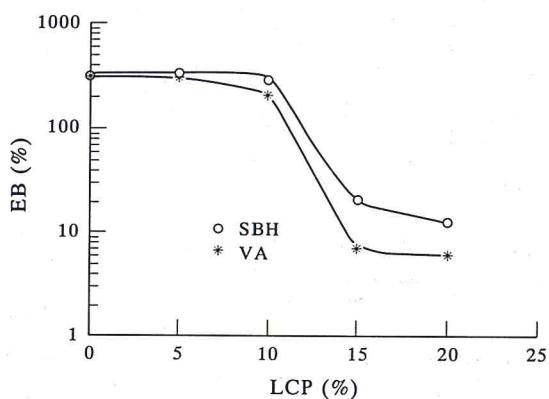


Fig. 6. Elongation at break of extruded ribbons vs LCP content.

blends, a very slight increase of the flowrate is, on the contrary, observed.

The flowrate in the extruder depends on both drag flow and on pressure back flow. Only this latter

depends on the viscosity and increases on decreasing the viscosity of the material. This means that, on lowering the viscosity, the flowrate decreases. The flowrate in the die increases, on the contrary, on decreasing the viscosity. If the temperature in the pumping zone and in the die are equal, changes of viscosity in these two zones can depend only on the shear rate. In the extrusion of these blends, a rough evaluation of the shear rates in the extruder and in the die indicates that the two values are very similar ( $130\text{--}150\text{ sec}^{-1}$ ). As is well known [17], the same decrease of viscosity in both zones does not change the flowrate. Therefore, in this case, the more important factor causing decreasing of the torque is the reduction of viscosity. However, some reduction of the flowrate suggests that a reduction of the friction in the zone of transport of solids should be taken into account.

The flow curves of the blends with 10 and 20% of LCP together with the parent polymers are reported in Figs 2 and 3. The flow curve of the Vectra sample shows only a non-Newtonian region, whereas the flow curve of the SBH sample shows also the Newtonian plateau. The viscosity curve of PET is almost Newtonian but becomes more non-Newtonian on increasing the LCP concentration.

The semirigid LCP sample shows a viscosity lower than that of the PET and the flow curves of the blends are intermediate. On the contrary, the viscosity of VA is higher and the flow curves of the blends are below those of the pure polymers. A minimum is shown by the flow curve of the blend with 10% VA.

The reduction of the viscosity of the thermoplastic matrix by adding small amounts of LCPs is already well established and various mechanisms have been proposed [18–20]. In a recent paper [21], it has been proposed that the viscosity of the blends falls between those of the two polymer parents when the viscosity of the matrix is higher than that of the LCP; on the contrary, the flow curves of the blends are below

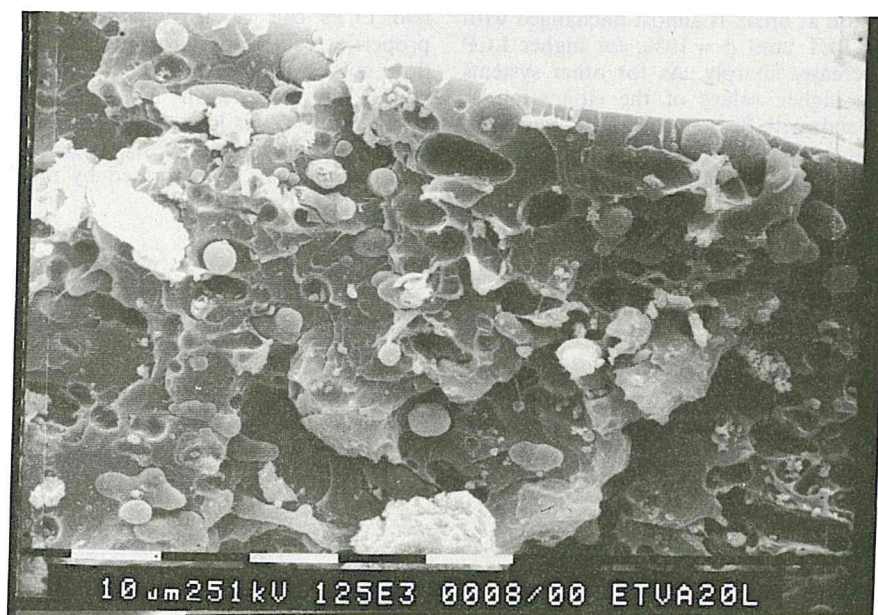


Fig. 7. SEM micrograph of extruded ribbon of PET/VA 20%.



Fig. 8. SEM micrograph of extruded ribbon of PET/SBH 20%.

those of the pure polymer. The results of this work confirm this hypothesis.

**Mechanical properties.** Elastic modulus, tensile strength and elongation at break of ribbons are reported in Figs 4–6 respectively, as a function of the LCP content. The elastic modulus of the blends is slightly affected by the presence of LCP; it is similar to the modulus of the pure polymer up to a LCP content of 10% and increases for larger LCP contents. The values of modulus obtained for the blends with VA are slightly better. This effect is probably due to the better mechanical properties of the rigid LCP sample. The values of the tensile strength are also slightly influenced by the content and the nature of LCP. An increase is however observed on increasing the LCP content of both LCPs.

The elongation at break is almost unchanged with respect to the PET until  $\phi = 10\%$ ; for higher LCP content, it decreases sharply. As for other systems [4, 10–12], the higher values of the elongation at break of the blends with the semirigid LCP, especially for LCP contents  $> 10\%$ , suggest some adhesion between the two phases. As already proposed [4, 12],

this improved compatibility can be caused by the flexible segments of the LCP sample.

The SEM micrographs of the extruded samples with 20% LCP are shown in Figs 7 and 8. The SBH particles show good adhesion with the PET matrix and are mostly elongated in the drawing direction. Fibrils with high aspect ratio are also observed. The micrograph of the blend with VA shows, on the contrary, a complete lack of adhesion and all the particles are spherical in form. Considering that both elastic modulus and tensile strength of the rigid VA sample are higher than those of the semirigid one, the blends of the two system show very similar mechanical properties because of the better fibrillation and adhesion of the SBH sample.

The different shapes shown by the particles of the two LCPs can be attributed to their rheological properties with respect to those of the matrix. The flow curves of the three components (see Figs 2 and 3), show that, at the extrusion temperature, the viscosity of PET is lower than that of the Vectra A, while is larger than that of SBH. Therefore, this latter LCP sample can be deformed by the PET matrix,

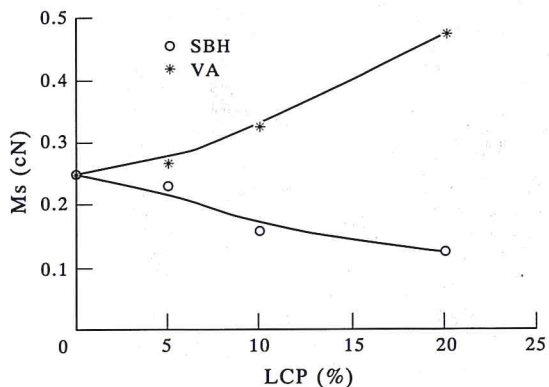


Fig. 9. Melt strength vs LCP content.

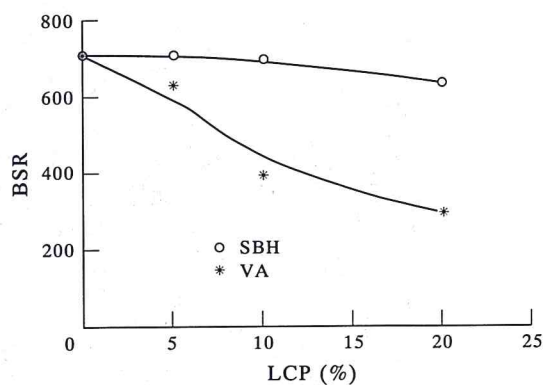


Fig. 10. Breaking stretching ratio vs LCP content.



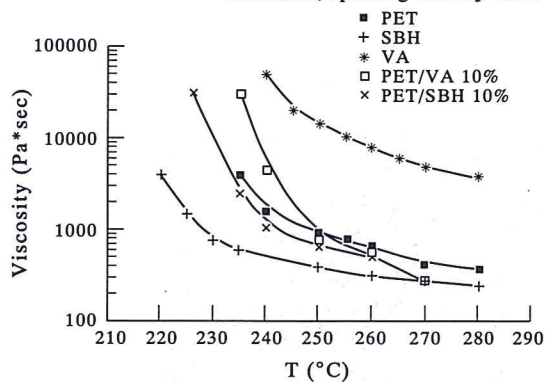


Fig. 11. Viscosity-temperature curves.

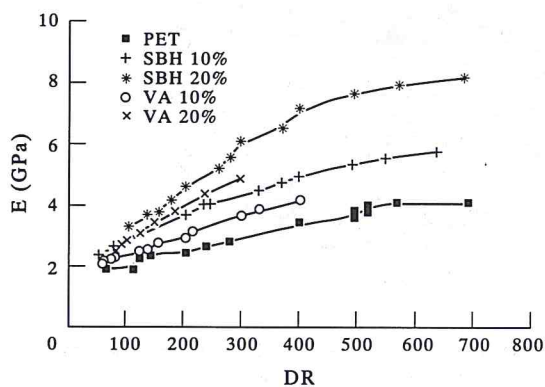


Fig. 12. Elastic modulus vs draw ratio.

while this is not possible for the high viscosity Vectra A sample.

#### Spinning

**Processability.** The remarkable decrease of the viscosity of PET and the incompatibility between PET and LCPs can cause a dramatic reduction of the

spinnability of the blends with respect to the pure matrix.

Melt strength (MS) and breaking stretching ratio (BSR) can be used as parameters of the spinnability. Indeed, high BSR values mean high draw ratios and high MS values are required to sustain the drawing force. MS and BSR are reported in Figs 9 and 10 as a function of the LCP content. BSR is almost uninfluenced by adding SBH, while it is reduced by VA. The reduced BSR can be attributed to the biphasic structure of these blends and to the poor adhesion between the two phases. The slight influence of SBH on the BSR can be considered as further confirmation of the good adhesion with PET due to the presence of the flexible spacers.

MS decreases, as expected, for the blends with SBH, whereas it increases with VA. This latter result is unexpected on the basis of the lower viscosity of the PET/VA blends. This behaviour has to be attributed [22] to the temperature dependence of viscosity of the different polymers. In Fig. 11, the viscosities of the pure components and of the blends with 10% of LCP are reported as functions of the temperature. These data have been obtained by cooling the polymers down from the extrusion temperature, taking into account that the viscosity of the LCP is greatly dependent on the thermal history [8]. The viscosity curve of PET/VA blend is, at high temperature, lower than that of PET, but becomes higher at 250°; the curve of the PET/SBH blend is lower over all the whole temperature range. This behaviour can explain the increase of the MS values for the PET/VA system and the decrease for the PET/SBH blends.

**Mechanical properties.** Elastic modulus of the fibres of the pure PET and of the blends with 10 and 20% LCP are reported in Fig. 12 as a function of the draw ratio. As discussed above, the spinnability of PET/VA decreases and the blend with 20% VA is very difficult to spin. For all the samples, the elastic modulus rises with increasing DR. This effect seems,

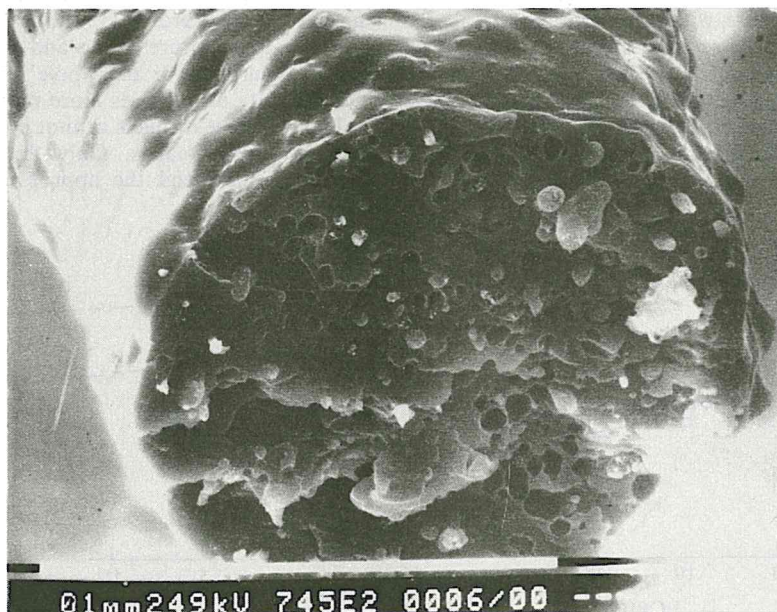


Fig. 13. SEM micrograph of fibre of PET/VA 20%.

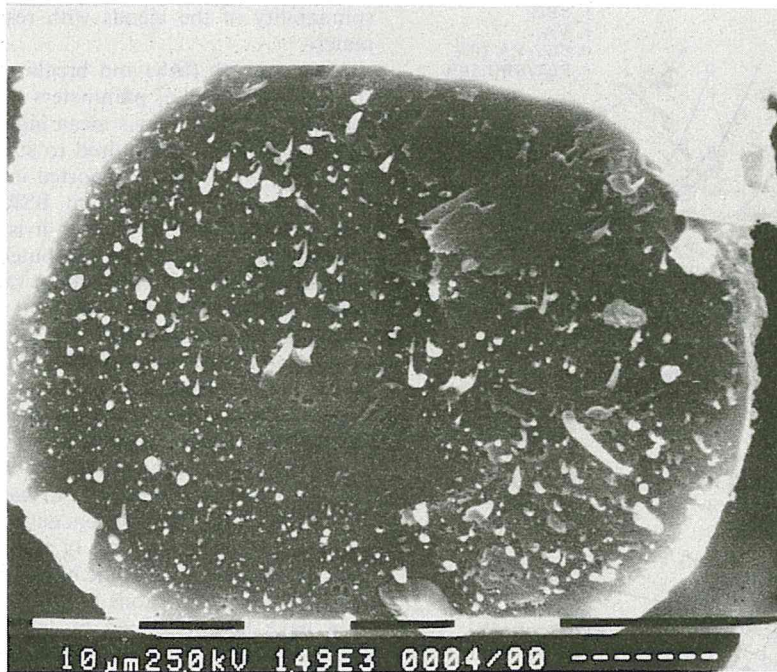


Fig. 14. SEM micrograph of fiber of PET/SBH 20%.

however, larger the higher is the LCP content. The E-DR curves of the two systems show similar trends but, due to the better spinnability, the blends with SBH reach higher draw ratios and higher values of the elastic modulus. In particular, for the blend containing 20% SBH, the elastic modulus doubles with respect to pure PET. For the blend with 10% of SBH, the elastic modulus increases by about 50% with respect to the pure matrix.

The SEM micrographs of fibres with 20% SBH and VA are reported in Figs 13 and 14 respectively. Fibrils of the dispersed phase, concentrated in particular in a zone between the centre and the skin, are observed in the fibre with SBH. Moreover, all the particles of the dispersed phase seem to adhere well to the PET matrix. On the contrary, the Vectra particles are in spherical form and many voids suggest slight adhesion between the two phases.

As already pointed out, in shear flow the high viscosity VA particles cannot be deformed by the

PET matrix; in elongational flow, on the contrary, fibrils can be obtained even if the viscosity of the matrix is lower [23]. It has been demonstrated [24, 25] that in spinning operations, carried out in non-isothermal conditions, the temperature dependence of the viscosity can play an important role in determining morphology and properties of these blends. In particular, the viscosity-temperature curve of the dispersed phase should not exceed that of the matrix [24, 25].

At the extrusion temperature of 280° VA shows a viscosity higher than that of PET matrix which, in turn, is higher than that of SBH, see Fig. 11. Decreasing the temperature, PET and SBH shows similar viscosity-temperature curves and the viscosity of the matrix is larger over the whole temperature range. The viscosity of VA rises more rapidly and becomes so large that the droplets cannot be deformed during cooling by the matrix. Only the SBH, therefore, shows in this blend the appropriate viscosity and

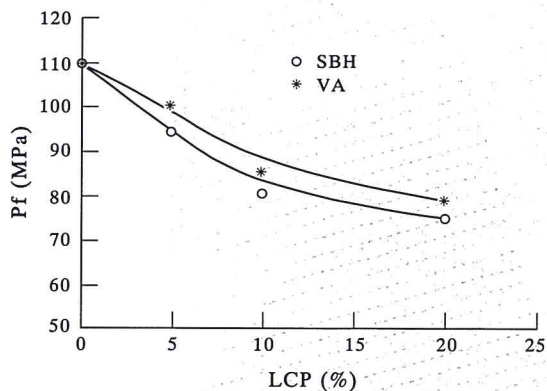


Fig. 15. Filling pressure vs LCP content.

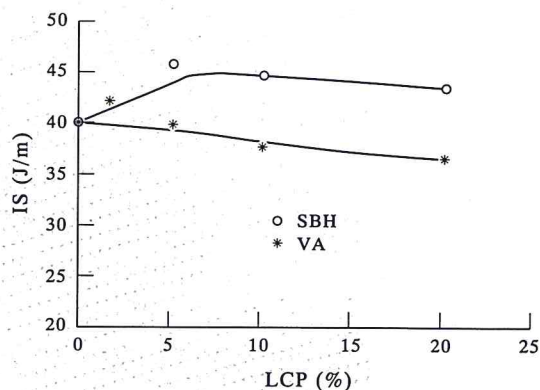


Fig. 16. Impact strength vs LCP content.



solidification behaviour which allows the formation of fibrils.

#### Injection moulding

*Processability and mechanical properties.* The reduction of the viscosity due to small amounts of LCP can be very favourable in injection moulding because low viscosities give rise to low pressure and short moulding cycles. The data reported in Fig. 15 indicate that the filling pressure noticeably decreases also for blends with small amounts of LCP. The two samples of LCP show similar behaviour reflecting the decrease of viscosity discussed above. It is interesting to notice that, as for other LCP based blends [11, 12, 14–16], whereas the pure extrusion grade PET is injection moulded with great difficulty, the blends are easily mouldable.

The impact strengths of the moulded bars are reported in Fig. 16. The impact strength of PET does not change significantly on adding VA; a small maximum is observed for the blends with SBH for a concentration of about 10%. Once again, this behaviour can depend on adhesion between SBH and PET.

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