The microstructure of injection-moulded thermotropic copolyester: 1. Optical and scanning electron microscope studies

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The microstructure of a naphthalene-based liquid-crystalline (LC) copolyester originating from injection moulding was systematically examined by varying the processing parameters. Optical and scanning electron microscopy revealed a layered structure of four strata in half cross-sections of standard Izod impact bars. The processing parameters had the most pronounced influence on the third layer, which seems to have a slow solidification rate. The formation of the third layer and simultaneous band pattern development occurred at the measured LC glass transition point of about 100°C. The thermotropic copolyester demonstrated a significant elastic response and shear sensitivity according to rheological measurements. The fractured specimens showed an overall sheet-like microstructure. Thermodynamic behaviour, especially the LC glass transition, appears to be an important factor in microstructure formation of the thermotropic copolyester used.

(Keywords: liquid-crystalline polymer; thermotropic; injection moulding; optical microscopy; scanning electron microscopy; mechanical properties; microstructure development)

INTRODUCTION

The injection moulding of thermotropic liquid-crystalline polymers offers one way to attain high Young's modulus in the longitudinal direction in relatively thick profiles[1]. Other methods can be found, for example, in composites technology. The moduli of polymers are related to the morphology of the solid state, which in turn depends on the processing conditions. Thermotropic main-chain liquid-crystalline polymers (LCPs) consisting of rigid rod-like molecules have a domain texture in the quiescent melt state[2–4]. The degree of order of anisotropic liquid-crystal melts is characterized by an average molecular orientation about the nematic axis and a preferred direction of this axis, i.e. the director[2–4]. In polydomain nematic melts the director is not uniform throughout space, for its direction varies from one domain to the next[3,4]. Light scattering and optical microscopy have revealed that the dimensions of homogeneous orientation in both monomeric and polymeric liquid crystals exceed 10^2 to 10^4 nm[5,6]. This value could be taken as the radius of a quiescent domain of a nematic medium.

Thermoplastic polymer processing methods involve flow mechanisms that generate microstructures of solids[7,8]. In the case of isotropic polymers, there have been a number of studies concerned with rheological behaviour and the resulting orientation and morphology, and at the moment it seems that these are understood quite well[9]. For the flow of liquid-crystalline polymers the situation appears more complicated[3,4,9,10] but yet at the same time much easier. Compared to flexible-chain polymers, new phenomena have been observed: a band texture during/after flow and negative normal stresses. In addition, thermotropic polymeric liquid crystals have a similar anisotropy and structure as low-molecular-weight liquid crystals.

Rheological measurements, especially capillary rheometry, have displayed some similarities with flexible-chain polymers[9]. On the other hand, morphological observations on the microstructures of thermotropes should show some evidence of flow behaviour of the nematic melt because stress relaxation is much quicker than orientation due to long relaxation times[2,11].

Earlier liquid-crystalline polymer research has mainly concentrated on synthesis and chemical structure. Nowadays the number of studies on the relationship between processing parameters, morphology and physical properties of liquid-crystalline polymers is increasing rapidly because of the good end-use properties. Former morphological studies of injection-moulded LCPs[12–16] have revealed the typical layer structure of a longitudinal skin and a transversely oriented core. Normally the former is thought to originate in elongational flow and the latter in plug flow[12,16]. In the literature, the layered structure formation is usually interpreted by models that have been developed for isotropic polymers[12,17]. The general opinion is that only elongational flows effectively align LCPs[18,19]. However, recent research has shown that shear flow during cooling can also orientate polymeric liquid crystals[20]. Current theoretical studies on the rheology of LCPs[3,5] have noticed the polydomain nature of liquid-crystalline polymer melts. If the yield behaviour[21] is attributed to domain structure, then the interface between domains will play an important role. The flow behaviour of polymeric liquid crystals is also analysed by applying the Leslie–Ericksen continuum theory of the mechanics of monomeric liquid crystals and the Doi molecular theory of rigid rod-like polymers[3–5,10].

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Previous studies on the structure of LCPs[13,14] originating from injection moulding have mainly considered microstructure under limited processing conditions. This experimental study systematically surveys the effect of holding pressure, mould and nozzle temperature on the morphology of injection-moulded liquid-crystalline polymer. The holding pressure was thought to change the microstructure that developed during the filling stage due to extra material flow into the cavity. The effect of thermal history on the morphology of LCPs was examined with the aid of a reduced nozzle temperature, which should supercool[22] the nematic melt before mould filling. The variation in mould temperature was expected to reveal some details in the layer structure formation of polymeric liquid crystals. The morphology of the processed specimens was examined by fractographic methods, optical and scanning electron microscopy. On the grounds of these observations, some qualitative conclusions were made on the flow behaviour of a thermotropic naphthalene-based LC copolyester.

EXPERIMENTAL

Material

The LCP used was the commercial Hoechst–Celanese extrusion-grade product Vectra® A900, consisting of *p*-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid. The published melting point is 280°C and the viscosity is 600 P at 300°C (1000 s^{-1}). D.s.c. measurements[23] revealed a nematic liquid-crystal transition at 280°C and an isotropic transition at 360°C. The mesophase glass transition occurred at 97–8°C, which was previously detected by d.s.c. and d.m.t.a.[23].

Injection moulding

The neat LCP resin was injection-moulded into specimens by means of a direct digitally controlled loose-loop industrial machine, Engel ES 240/65 ST CC80. The mould contained five cavities and has been shown elsewhere[23]. The oil temperature of the machine was kept at 40°C in all runs. *Table 1* shows the processing parameters. The mould was water-cooled at 10°C, and otherwise oil-heated. Mould temperature was measured on the cavity surfaces.

Table 1 Processing parameters in the injection-moulding study of thermotropic copolyester; machine settings

Constants	
Cylinder temperatures	280, 285, 290°C (zones 1, 2, 3)
Injection rate	16.5 cm^3 s^{-1}
Injection pressure	52.0 MPa
Variables	
Nozzle temperature	250 or 290°C (zone 4)
Mould temperature	10, 45, 65, 80, 95 or 115°C
Holding pressure	on/off on = 52–1.5 MPa (10 steps) 5 s (duration) off = 0
Used symbols	
○ = 250°C (nozzle temperature), holding pressure off	
● = 250°C (nozzle temperature), holding pressure on	
□ = 290°C (nozzle temperature), holding pressure off	

Rheological measurements

The apparent viscosity of the thermotropic copolyester as a function of shear rate was measured with a Rheograph capillary rheometer (2001 TA 1006) at three different temperatures, 282, 290 and 300°C. Small-amplitude oscillatory shear was studied using a Rheometrics System 4 (Dynamic Head). Samples were placed in a plate–plate geometry.

Mechanical testing

The mechanical properties were tested in accordance with DIN and ASTM standards. The tensile modulus was measured on an Instron testing machine with an extensometer. The cross-head speed was set at 10 mm min^{-1} and gauge length at 25 mm. The initial flexural modulus was calculated from stress–strain curves. A bar 64.2 mm long, 12.7 mm wide and 3.17 mm thick was used in the ASTM D256 Method A impact resistance test. Specimens were notched in a group of 10 pieces on a milling machine in conformity with the standard.

Microstructure examinations

In order to study microstructures, Izod impact bars were embedded in epoxy matrix and thereafter milled to half of their original size in the longitudinal direction. Cut surfaces were carefully polished before taking optical micrographs from the middle of the specimen length by reflected light microscopy. The cross-sectional area of the layered structure of Izod bars was calculated from these photographs in enlarged size. The value obtained is an average of three measurements. Fracture surfaces of Izod impact bars were examined in an ISI-40 scanning electron microscope in order to support optical microscopy.

RESULTS

Rheological properties

The capillary rheometer revealed that the viscosity of the LC copolyester used was highly temperature- and shear-dependent (*Figure 1*). The viscosity was about half an order of magnitude higher at 282°C than at 300°C over the whole measured shear-rate range. Owing to the shear dependence, the viscosity also decreased nearly half an order of magnitude over the measured shear-rate range at every test temperature.

Previously[25] it has been shown from plate-and-plate rheometry that the LCP used had a yield stress that would result in plug flow in shear[11]. When the dynamic viscosity was determined as a function of temperature at constant frequency (1 Hz), the values of the storage modulus (G') and loss modulus (G'') decreased abruptly in the temperature range 300 to 320°C (*Figure 2*). The elasticity of the polymer decreased with increasing temperature and the curves of G' and G'' cross over beyond 320°C. So there seem to be structural changes in the nematic melt which are apparently related to the melting of *p*-hydroxybenzoic acid segments[22].

Mechanical properties

The notched Izod impact strength, tensile and flexural moduli are all orientation-sensitive properties. The tensile modulus was measured in the flow direction. It seems that holding pressure reduced the tensile modulus in the case of the run at a lower nozzle temperature of 250°C

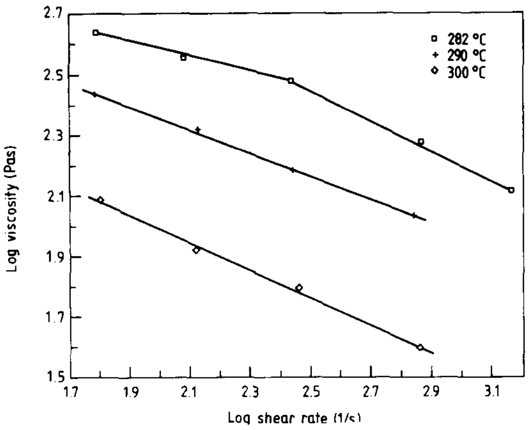

Figure 1 Apparent viscosity vs. shear rate for Vectra A900 samples at different measurement temperatures

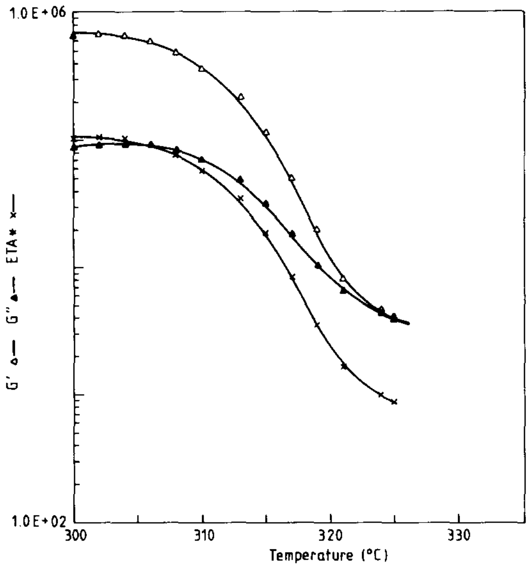

Figure 2 Storage modulus (G') and loss modulus (G'') with complex viscosity (η^*) vs. temperature for Vectra A900, measured at $\omega = 1\,s^{-1}$ in autostrain mode. The gap was 3.6 mm

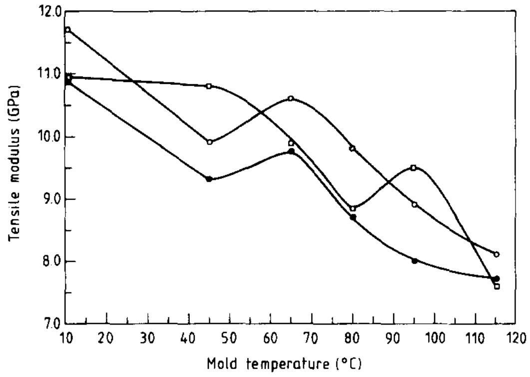

Figure 3 The dependence of the tensile modulus of Vectra A900 on the holding pressure, nozzle and mould temperatures in injection moulding (the symbols are depicted in *Table 1*)

at all mould temperatures (*Figure 3*). However, the use of holding pressure was beneficial for flexural modulus, as *Figure 4* demonstrates. The mutual order of the three runs remained the same over the measured mould temperature range; the lowest was always the higher nozzle temperature run of 290°C without holding pressure. Deviation between the runs reached a maximum at 80°C. The tensile and flexural moduli decreased with increasing mould temperature, as could be expected. Holding pressure seems to have the reverse effect on these moduli over the whole measured mould temperature range.

The Izod impact strength is measured perpendicular to the flow direction. Generally it decreases sharply with increasing melt temperature. The best values in all runs were achieved with the highest mould temperature. In addition, there existed a regularity in the order of the different runs at the same mould temperature, with the exception of 95°C (*Figure 5*). All the curves went through a minimum at 65 and 95°C in the case of the lower nozzle temperatures without and with holding pressure, and at 65°C in the case of the higher nozzle temperature without holding pressure. All the measured specimens partially broke in the test.

Optical observations

The main reason for the study is to show the effect of injection-moulding parameters on microstructure development of a thermotropic copolyester. The mould and melt temperatures along with holding pressure are the key factors, and their influence can easily be examined owing to the long relaxation times of liquid-crystalline polymers. Injection-moulded Izod bars show a typical layer formation in the thickness direction of a skin–core structure. By proceeding from the skin to the centre of a cross-section of a specimen, the following four strata could generally be detected: a dark skin layer, a light layer under it, a dark interior layer and a bright core layer (*Figure 6*). This agrees to some extent with

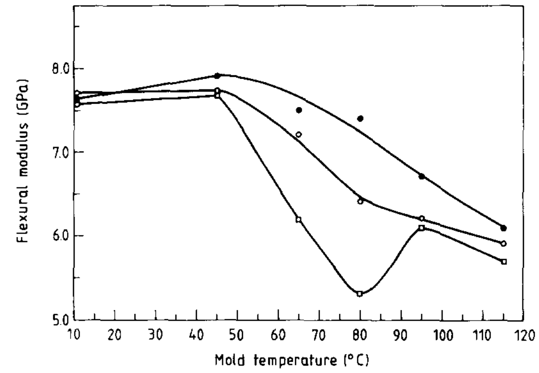

Figure 4 The depencence of the flexural modulus of Vectra A900 on the holding pressure, nozzle and mould temperatures in injection moulding (the symbols are depicted in *Table 1*)

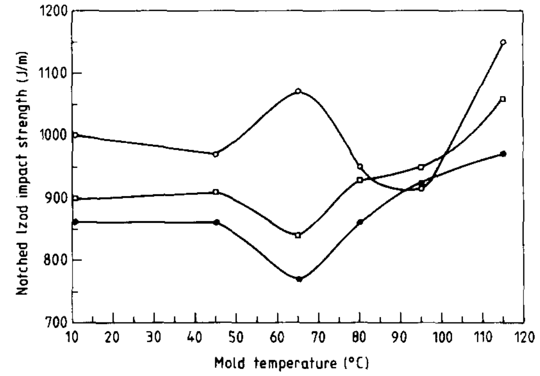

Figure 5 The dependence of the Izod impact strength of Vectra A900 on the holding pressure, nozzle and mould temperatures in injection moulding (the symbols are depicted in *Table 1*)

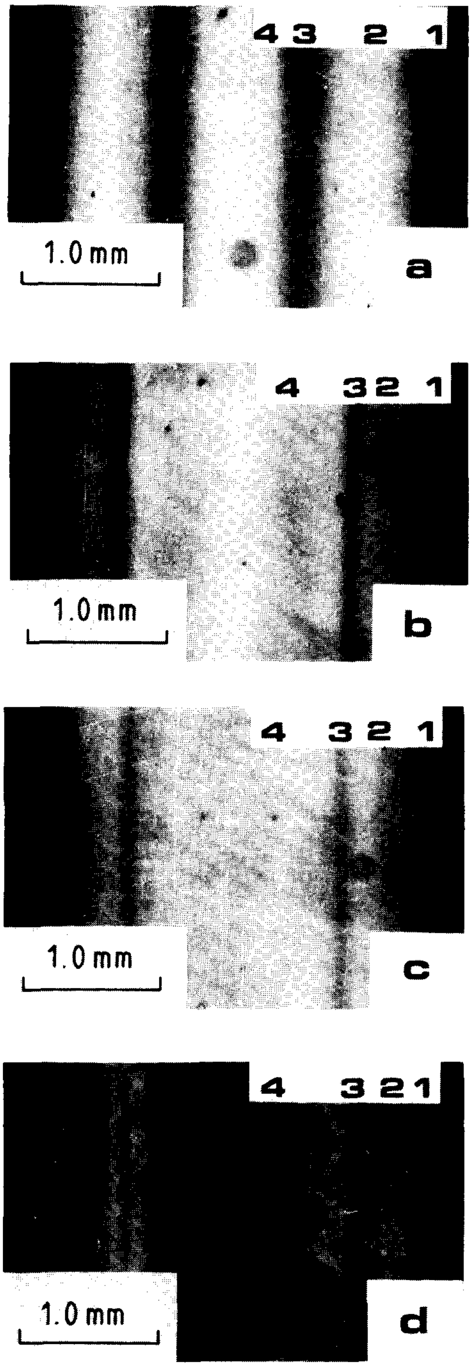

Figure 6 Reflected light micrographs of polished cross-sections of Izod bars injection-moulded: (a) without and (b) with holding pressure at a mould and nozzle temperature 10 and 250°C; (c) without holding pressure at 115 and 290°C; and (d) with holding pressure at 80 and 250°C. The flow direction is upwards

published results[12]. Actually, the first layer may be divided into two parts, a light edge and a dark stratum under it. Sometimes it was also possible to observe a change in the tint of the core layer. The layer structure also remained nearly constant along the Izod bars. Recently it has been noticed that dark layers are more oriented than light ones[24].

Figure 6 shows optical cross-sectional micrographs of the Izod bars injection-moulded with varying processing parameters. *Figures 6a, 6b* and *6d* indicate the lower nozzle temperature run of 250°C without and with holding pressure, and *Figure 6c* the higher nozzle temperature run of 290°C without holding pressure. Some distinct features could be seen. First, the rise from 10 to 115°C in the mould temperature and the addition of holding pressure at 10°C had a similar effect on the third layer, reducing it (*Figures 6a, 6b* and *6c*). Secondly, an arc-like band pattern developed in the core area in the mould temperature interval from 45 to 95°C in the case of lower nozzle temperature. In holding pressure runs this phenomenon is very clear over 65°C and weakens below it (*Figure 6d*). The banded structure formation perpendicular to the longitudinal direction disappeared when the nozzle temperature was raised by 40°C. Overall, the holding pressure altered the microstructure of the bars very strongly even at low mould temperatures.

The thickness of the first layer decreased slightly with increasing mould temperature (*Figure 7a*). The thickness of the second layer in the runs without holding pressure remained nearly the same over the whole mould temperature range. The holding pressure reduced this stratum at low mould temperatures but expanded it at the highest mould temperature used (*Figure 7b*). The effect of holding pressure was more pronounced in the interior third and fourth strata. Without holding pressure a decrease in the mould temperature expanded the third layer at the expense of the fourth, but the addition of holding pressure reduced the third layer over the whole measured mould temperature range. The biggest change was observed at low mould temperatures (*Figures 7c* and *7d*). Moreover, there is a local maximum in both lower nozzle temperature runs at 80°C.

SEM analysis

The SEM micrographs seem to support reflected light microscopy. At low mould temperatures the number of layers is the same as in optical micrographs. There are four distinct layers in the cross-section of a fractured Izod bar, three of them being clearly visible (*Figures 8a* and *8b*). Bearing in mind the symmetry of a specimen, these strata can be divided into a bulb-shaped core, two arc-like middle and two outer longitudinally oriented layers. The outermost skin does not appear in *Figure 8*, because it locates in the opposite fracture region. The calculated cross-sectional areas occupied by these layers of a sample injection-moulded without holding pressure at mould and nozzle temperatures of 10 and 250°C coincide with the corresponding points in *Figure 7*. The computed values are about 35% (the second layer), 27% (the third layer) and 23% (the fourth layer). The measuring position is shown by arrows in *Figure 8a*. There are two distinct layers in a half cross-section at high mould temperatures. The fracture surface of the core was more fibrillar without holding pressure than with it at a mould temperature of 95°C (*Figures 8c* and *8d*).

The middle stratum, i.e. the third, which is inclined towards the core, disappeared when the mould temperature was above 80°C. The third layer consisted of stratified sheet-like lamellae, which are at an angle to the flow direction, and at elevated mould temperatures its fracture surface gradually transforms into a wave-like texture, as shown at higher magnification in *Figure 9*. The holding pressure seems to densify this layer, which is evident from the smoother texture (*Figures 9a* and *9b*). In the fracture region the plane surface of the core turned to fibrillar at mould temperatures above 65°C, which was opposite to the effect of holding pressure. This was most

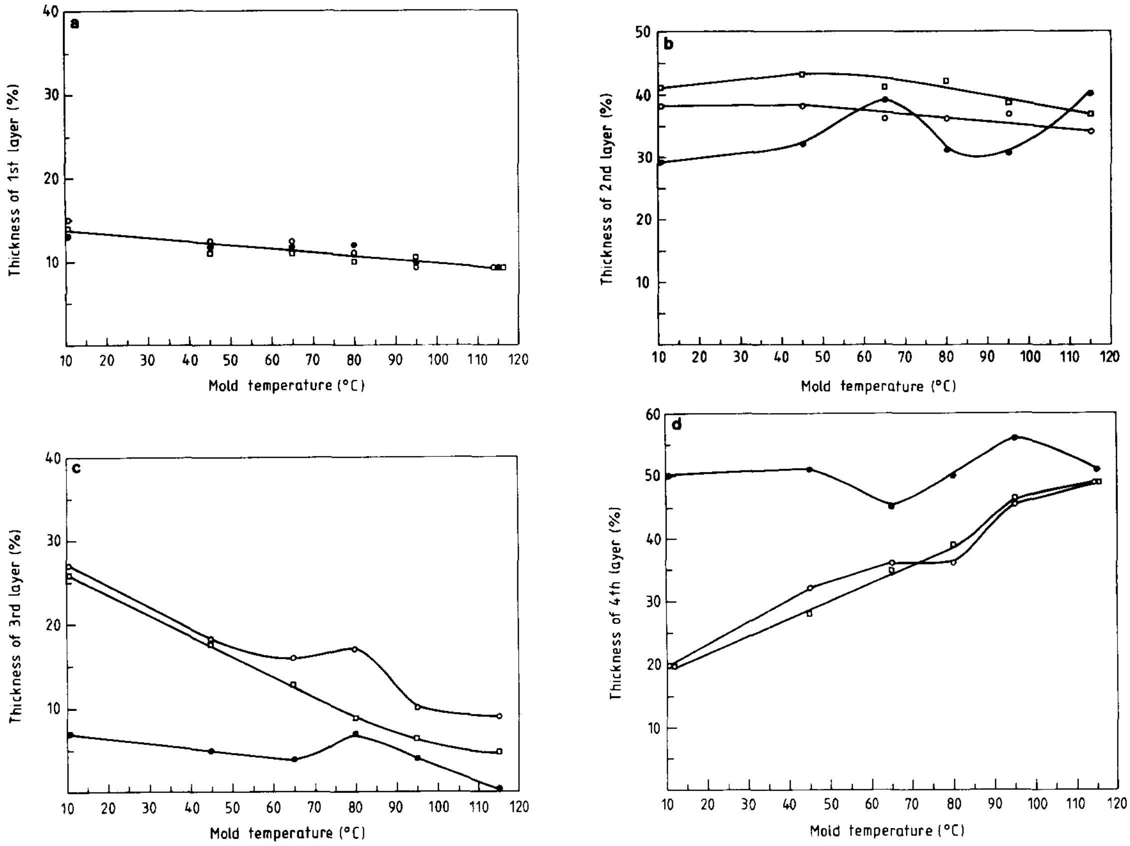

Figure 7 A change in the thickness of the four layers shown in reflected light micrographs vs. mould temperature: (a) the first layer; (b) the second layer; (c) the third layer; and (d) the fourth layer

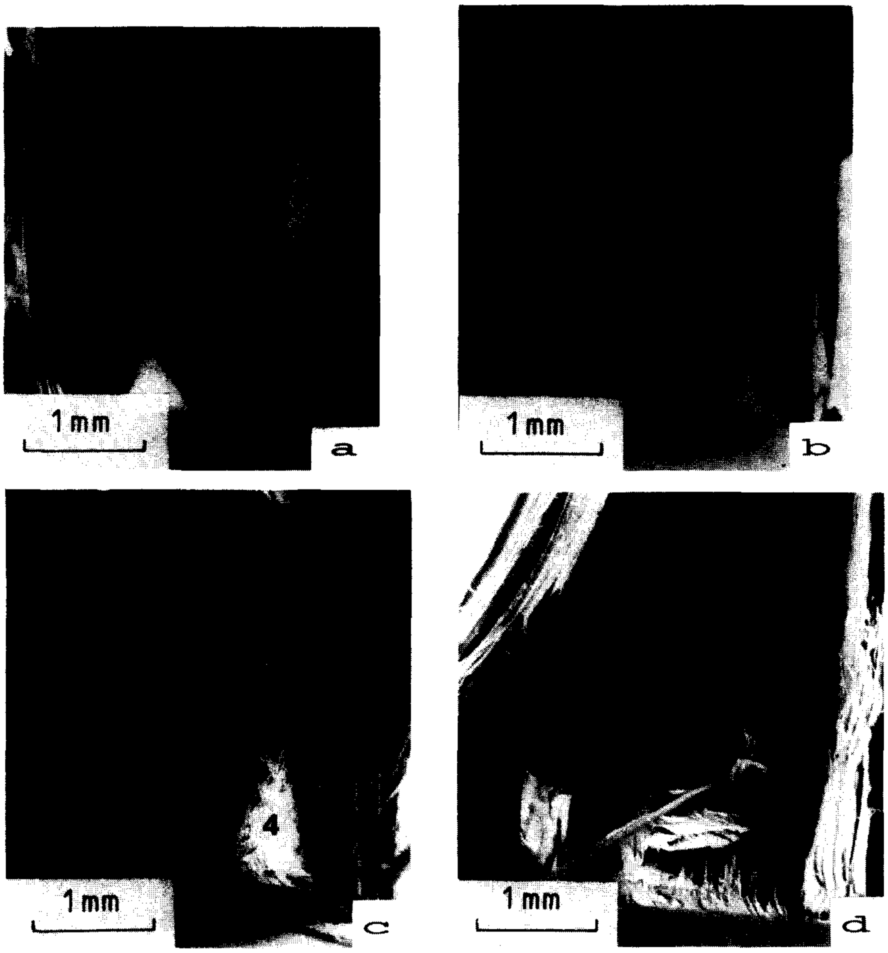

Figure 8 Scanning electron micrographs of a fractured surface of notched Izod impact bars injection-moulded: (a) without and (b) with holding pressure at a mould and nozzle temperature 10 and 250°C; (c) without and (d) with holding pressure at 95 and 250°C. The flow direction is upwards

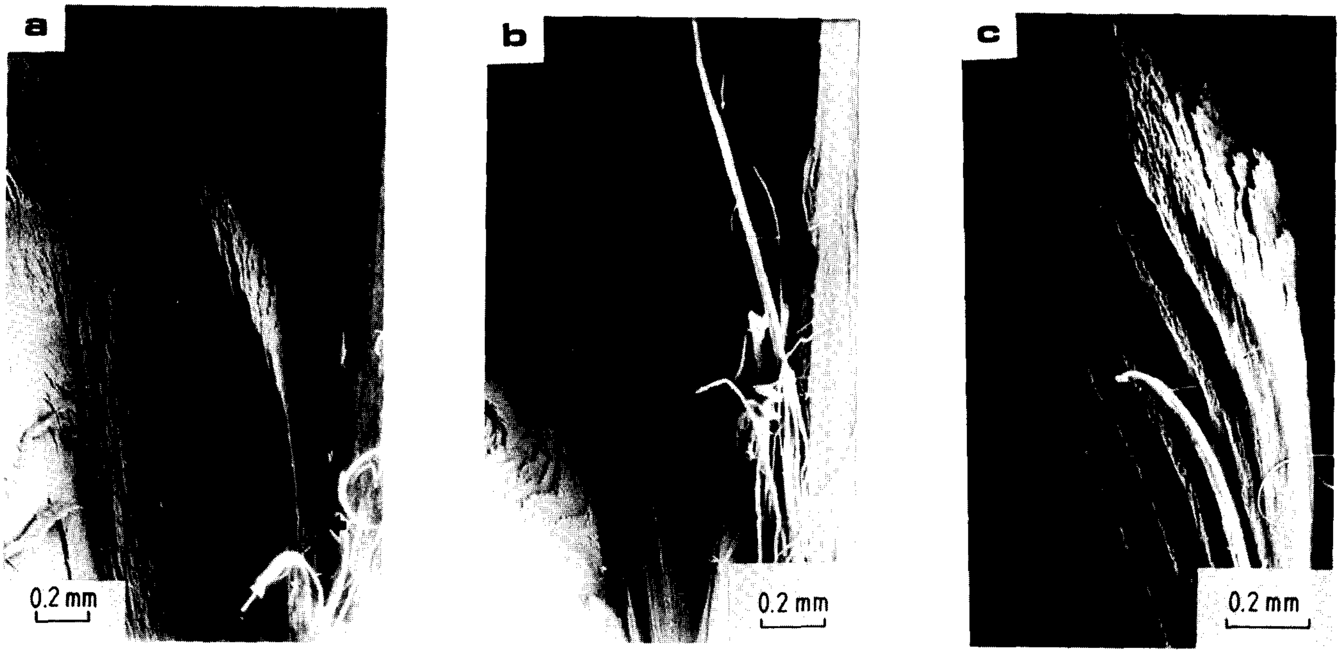

Figure 9 Higher-magnification scanning electron micrographs of the third layer of fractured Izod bars injection-moulded: (a) without and (b) with holding pressure at a mould and nozzle temperature 10 and 250°C; (c) without holding pressure at 45 and 250°C. The flow direction is upwards

pronounced near the measured LC glass transition temperature. The overall structure of the first, second and third layers is sheet-like, a texture dominantly formed in shear flow[20].

In the case of specimens injection-moulded at mould temperatures below 80°C, the third and fourth layers primarily fractured in the impact test, as shown in *Figures 8a* and *8b*. Above this point, breakage occurred in the core (the fourth layer). The holding pressure tends to enlarge the boundary zone between the second and third layers. The diameter of the boundary region expanded from 60 to 180 μm, which is shown by two arrows in *Figures 9a* and *9b*. The binding force between the second and third layers should be lowest at this zone. This is also reflected in the value of the notched impact strength: the holding pressure regularly decreased it, as can be seen in *Figure 5*. As the observed region resulted from specimen failure, it might be an artefact.

DISCUSSION

Morphology of Izod bars

Generally the cross-sections of the Izod impact bars can be divided roughly into two parts, one containing the first and second and the other the third and fourth layers. At the lowest mould temperatures without holding pressure, this proportion has a value of about 1:1. The percentile area occupied by the two inner layers was expanded by about 5–10% due to holding pressure and rise in mould temperature, which could be related to a lower solidification rate of the nematic melt.

When each layer was inspected individually, it could be noticed that a decrease in mould temperature expanded the third layer noticeably at the expense of the fourth. The thicknesses of the outer layers remained nearly constant. A reduced nozzle temperature increased the thickness of the third layer most near the LC glass transition. As is generally known, at this point the internal friction of a polymer reaches a maximum, which seems to have a considerable effect on cavity filling of the polymeric liquid crystal used. The author has obtained some evidence that, on exposure to strong elongational flows, this LCP could be supercooled into an LC glass[25]. Recently it has also been shown that the same kind of liquid-crystalline polymer exhibited an increase in die swell and elasticity in the supercooled nematic state[22]. A plate-and-plate rheometer revealed a noticeable rise in the storage modulus (G') in the temperature range 300 to 320°C, so the elasticity of the naphthalene-based LC copolyester used increases (*Figure 2*). The solidification rate of the third layer is low because it deformed very easily under holding pressure even at the lowest mould temperature. A supercooling effect with enhanced polymer elasticity at low temperatures might be the main reason for the formation of this layer.

The SEM micrographs elucidate the origin of the third layer. As could be seen from the fracture surfaces of the Izod specimens, distinct flow lines existed, which should be related to the velocity profile (*Figure 8*). This texture is flat at a mould temperature of 115°C and becomes more parabolic due to the drag effect of the cold mould walls. It is possible to measure the angle of the third layer with the flow direction from the higher-magnification micrographs (*Figure 9*). The values obtained are about 20° at 45°C and about 15° at 10°C. The holding pressure seems to have no effect on this angle (*Figure 9b*). The basis for the formation of the third layer should be the LC glass transition point. The SEM micrographs show that between the longitudinally oriented skin and the transverse core there exists the third layer whose angle of inclination to the flow direction varies from 15 to 20°, depending on the mould temperature. The LC glass transition point could create defects in the flowing nematic melt, which in part might increase the internal elastic energy deformations as for elastic bend distortions[9]. This might be the case on making deductions from the angle measurements. Thus at low mould temperatures, the cavity walls show a tendency to align the third layer with the shear direction, i.e. to minimize distortions. Moreover, the third as well as the second and first layers are sheet-like, a structure that should mainly be due to shear flow[20].

In the optical micrographs, it can be seen that there exist band patterns perpendicular to the machine direction in the core layer. Their development occurred simultaneously with the formation of the third layer, so the starting point for band patterns is the LC glass transition. The band patterns should be related to the supercooling of the nematic melt because they are not visible in the higher nozzle temperature runs. The holding pressure seems to enhance them. The mechanism of band pattern development has been interpreted in the case of thermotropic copolyester extrudates[26]. Here their development should imply an increase in shear stress between the third and second layers, which weakens the binding force between molecules of these layers. This is also reflected in the notched impact strength (*Figure 5*). In addition, SEM micrographs revealed that between the second and third layers there exists some kind of boundary zone. In this region, molecules should be stretched because fibrils are formed. This zone could thus be a defect core[3], which might represent an area of discontinuity in molecular orientation and higher viscosity, i.e. a region of isotropy[3].

Mechanism of polymeric liquid-crystal flow

In the injection moulding of the LCP, the development of molecular orientation depends greatly on the geometric and dimensional factors of the mould gate and cavity. The material flow involved in cavity filling is pressure-driven. Because of their elastic constants and viscosity coefficients[3,5], which are mainly unknown, the flow behaviour of LCPs is very complex. The nematic melt could be homogeneous or polydomain[3–5]. In the former case a rough estimate of the flow behaviour of the LCP used has been made using the rheology measurements, optical and scanning electron results, according to the concepts reviewed by Marucci[3]. The high shear rates present in injection moulding probably turn a nematic melt into a homogeneous state. The polymer used shows a great shear sensitivity, and thus during cooling the shear should be capable of orientating the nematic melt in the supercooled state[20,22]. This is evident from the overall sheet-like microstructure of fractured specimens. It is believed that in the supercooled state the nematic melt has a tendency to align at a fixed angle with regard to the flow (xy plane, i.e. the thickness direction in Cartesian coordinates; x is the shear direction), in agreement with the SEM results.

The angle between the director and the shear direction in the shear plane (xz plane) results from competition between Frank elastic constants and polymer elasticities[3]. There is also a clearly visible diagonally banded texture on the surface of tensile bars. The angle between this diagonal and the shear direction was measured in the xz plane. The average values are 15° at 10°C and 30° at 115°C. According to this, the polymer elasticity seems to increase with decreasing mould temperature.

If liquid-crystalline polymers bear similarities with low-molecular-weight crystals[4], in a non-isothermal case the mould wall should fix the director along the shear. The director should orient more perpendicularly to the shear owing to the decrease in viscosity towards the core. Capillary rheometer measurements indicated that the apparent shear viscosity reduced with a rise in melt temperature. The LC glass transition was supposed to be the driving force for the formation of the third layer, which should by nature be a kind of transition or boundary zone[3,14]. Thus it will increase the viscosity locally while at the same time generating defects in a flowing nematic substance[3] which should be pronounced in the supercooled melt. This results in increased elasticity in a flowing LCP melt[10] and further to the formation of a new distortion-minimizing layer (the third layer).

Another explanation for the formation of a layered structure could be found in the effect of decelerating flow during mould filling[9,23]. The melt again approaches a polydomain structure while the shear rate is decreasing. Each particular domain may rotate, resulting in the observed stratified layer structure. One sheet-like lamella should represent a region of coherent rotation of several domains. Between two lamellae the direction of rotation may be either reversed or the same. To some extent plate-and-plate rheometer measurements seem to support the tumbling nature of the LCPs in a shear field[11,25].

By comparing a topographical scan[24] across samples composed of *p*-hydroxybenzoic acid, hydroquinone and isophthalic acid in molar fractions of 36/32/32 and 27/36.5/36.5 with the SEM micrographs, some similarities could be noticed (e.g. *Figures 8a* and *8d*). Thus the change of about 100°C in mould temperature should have the same kind of effect on the macroscopic molecular orientation as chain linearity[24]. The molecular orientation of the solid probably correlates with the shear distribution profile of the LC melt, which should have four maxima in the thickness direction at low mould temperatures or high chain linearity, and two maxima at high mould temperatures or low chain linearity. In the former case, multilayer shear flows could be generated which are fully developed conditioned Poiseuille flows[27].

CONCLUSIONS

A systematic experimental study was performed in order to reveal the effect of injection moulding parameters on the microstructures of a naphthalene-based LC copolyester. The cross-section of an Izod bar usually comprised four symmetric layers. One of these layers, the third, depended very strongly on temperature and pressure. A reduction in the mould temperature expanded it at the expense of the inner core layer, but the condition was reversed in the case of pressure. The solidification rate was relatively slow in the third layer, which means that the molecules have more time to relax. This was apparent from the SEM micrographs, which were taken from the fracture region of notched Izod specimens.

The LC glass transition seems to play a very distinct role in the formation of the third layer. At this transition the band patterns obviously also begin to develop perpendicular to the shear direction. The band patterns existing only in the reduced nozzle temperature runs would suggest a supercooling effect with low mould temperatures, which should increase the internal elasticity of a polymeric liquid crystal. This is also evident from small-amplitude oscillatory measurements. At the LC glass transition point, defects could be generated in the nematic melt. Then the third layer would form to compensate these elastic distortions. In the fluid dynamics of liquid-crystalline polymers the competition between flow and thermal motion is usually neglected[10], but the thermodynamic behaviour of polydomain structures might be important in microstructure development. The possible structural changes of the thermotropic copolyester used should occur in domains because conformational changes could only happen above T_g (ref. 28).

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