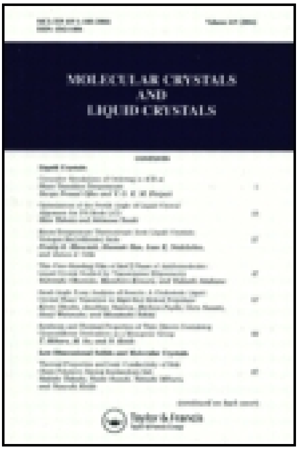

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The Relationship Between the Microstructure and Physical Properties of Injection Molded Naphthalenic-Based Liquid Crystal Copolyester

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THE RELATIONSHIP BETWEEN THE MICROSTRUCTURE AND PHYSICAL PROPERTIES OF INJECTION MOLDED NAPHTHALENIC-BASED LIQUID CRYSTAL COPOLYESTER

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Abstract Holding pressure was expected to change the free flow of the liquid crystalline melt. Because of the complex mold used and the two variables, nozzle and mold temperature, the shear and elongational flow were in the injection molding study evaluated by means of the notched Charpy and Izod impact strength. The tensile modulus, the flexural strength and modulus mainly depended on the elongational flow induced skin. On the grounds of the microstructure composed of 4 distinct layers a free flow model of the liquid crystal polymer having a yield stress is proposed.

INTRODUCTION

Synthetic liquid crystal polymers consist of a succession of rigid units. At present the general opinion of the structure of liquid crystalline melts suggests a randomly oriented domain texture. These melts exhibit flow properties of liquids, usually with a yield stress[1], but optical properties of crystalline solids.

Morphological studies of injection-molded liquid crystal polymers have shown that the elongational flow-induced layers have a higher degree of orientation than the shear-induced core (anisotropy)[2-3]. A successful fabrication of LCPs requires knowing and controlling the processing parameters. The aim of this study is to reveal the relationship between the processing conditions, morphology and the mechanical properties of injection-molded thermotropic copolyesters.

EXPERIMENTAL

The neat LCP resin used is the commercial Celanese extrusion trade (VECTRA A900), which is based on hydroxybenzoic acid and naphthalene derivative.

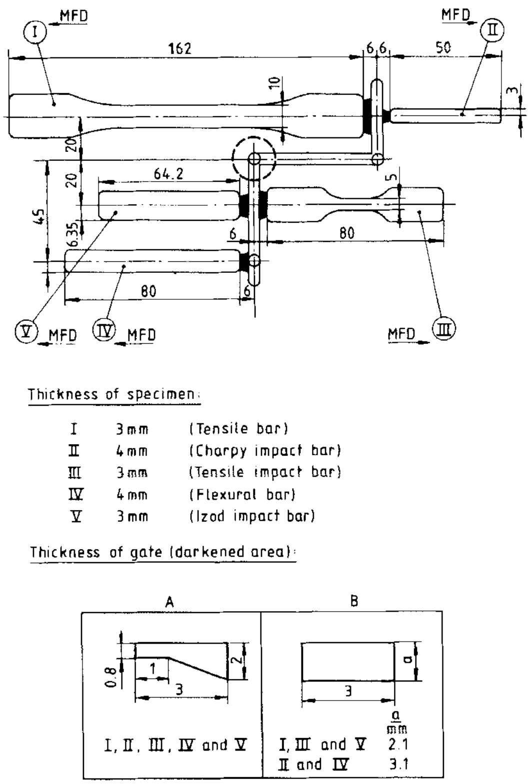

FIGURE 1 The dimensions of different specimens and gates (MFD = mold filling direction). The broken line circle indicates the sprue.

The nematic liquid crystal, isotropic and mesophase glass transition of the LC copolyester were measured with a Perkin-Elmer DSC-2C/TADS.

The dynamic mechanical study was performed using a Polymer Laboratories DMTA over a temperature range (-100...100 ^{o}C) at a heating rate of 4 ^{o}C/min and at 1 Hz, in Neste Oy.

Charpy and Izod impact bars were embedded in epoxy matrix and thereafter milled in the longitudinal direction. Optical photographs were taken with polarized light.

The LCP granules were injection molded into test samples by means of the direct digital controlled lose sloop industrial machine, ENGEL ES 240/65 ST CC80. The mold with two gates (A and B) used is shown in Fig. 1. The injection molding study was divided into two periods, the optimation and variation stage. Mechanical properties were tested in accordance with DIN and ASTM standards.

TABLE I Processing parameters for two variable stage, nozzle and mold temperatures were varied. There were also three additional holding pressure runs. Gate B was used in all of these runs.

Run	Nozzle temperature ^{o}C	Mold temperature ^{o}C	Holding Pressure MPa	Duration of holding pressure s
B1	250	65	0	0
B2	290	65	0	0
B3	250	80	0	0
B4	290	80	0	0
B5	250	65	52.0-1.5	5.0
B6	250	80	52.0-1.5	5.0
B7	290	80	52.0-1.5	10.0

Cylinder temperatures (280, 285 and 290 ^{o}C), injection rate and pressure (16.5 cm^{3}/s and 52.0 MPa) were constant.

RESULTS

Mesophase Glass Transition and Relaxation Properties

The DSC analysis revealed a nematic liquid crystal transition at 280 °C and an isotropic transition at 360 °C. When the dynamic mechanical measurement is performed at 1 Hz, the maximum of internal friction (tan α) occurs at a temperature that is closely related to the glass transition phenomenon. The mesophase glass transition of VECTRA A900 was detected by DSC and DMTA to occur at 97–98 °C. This was a surprisingly low value (Figure 2).

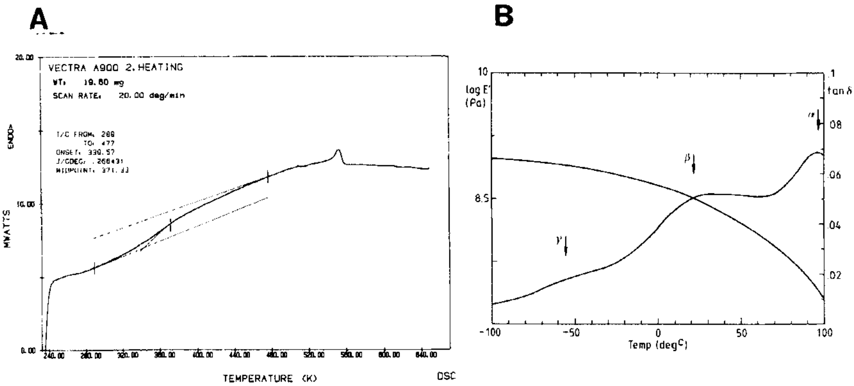

FIGURE 2 A. DSC trace of VECTRA A900
B. Dynamic mechanical properties of VECTRA A900.

Secondary relaxations were observed at about 20 °C (β-process) and at about -55 °C (γ-process).

Mechanical Properties and Morphology

Optimizing stage Because of the complex mold the processing parameters of injection molding were fine-tuned with the longest flow length assigned to the tensile bar (288 mm). Fan gate A, which is typically used in the processing of conventional folded polymers, resulted in an unstable flow, weld lines, and low mechanical properties. As the injection rate and pressure were low, 12.5 cm^3/s and 52.0 MPa (run A1), the skin layers of Charpy impact bar were forced into a zig-zag pattern in the longitudinal direction, see Figure 3. By increasing injection pressure to 135.0 MPa the rate was kept nearly constant, at 12.0 cm^3/s (run A2) the thin core in turn bended.

When the fan gate was replaced by gate B, all mechanical properties except the notched Charpy impact strength improved.

Two variable stage, the nozzle and mold temperature The holding pressure can be expected to have a disturbing effect on the microstructure of injection molded bars originated in free melt flow. Table II summarizes the research strategy adopted in the study. The mold temperature was kept below the measured LC-glass transition so the friction of the polymer should not increase shear[3].

TABLE II The effect of the nozzle and mold temperature on the mechanical properties of VECTRA A900 (A, B, C and D). Procedures E, F and G represent the addition of the holding pressure to molding. The percentile change is computed from the first-mentioned run.

A) A raise in nozzle temperature 250 °C (B1) --> 290 °C (B2), shear is increasing.
B) A raise in mold temperature 65 °C (B1) --> 80 °C (B3), shear is increasing.
C) A reduction in nozzle temperature 290 °C (B4) --> 250 °C (B3), shear is decreasing?
D) A reduction in mold temperature 80 °C (B4) --> 65 °C (B2), shear is decreasing.
E) The addition of holding pressure 0 s. (B1) --> 5 s. (B5), resulting in denser structure.
F) The addition of holding pressure 0 s. (B3) --> 5 s. (B6), resulting in denser structure.
G) The addition of holding pressure 0 s. (B4) --> 10 s. (B7), resulting in denser structure.

Procedure	A percentile change of property %					
	Notched Charpy	Noched Izod	Tensile strength	Tensile modulus	Flexural strength	Flexural modulus
A	+49.0	-21.0	+3.5	-4.0	-3.0	-21.5
B	+63.0	-33.5	-5.0	-14.0	-5.0	-21.5
C	+5.0	-24.0	-3.5	+6.0	-1.5	-12.5
D	-4.0	-9.5	+5.5	+18.5	+0.5	-12.5
E	+37.0	-28.0	-1.5	-7.5	+4.5	+9.0
F	-3.5	+2.5	-3.5	-1.0	+10.5	+41.5
G	-2.5	-5.5	+9.0	+21.0	+6.5	+8.5

As expected, run B1 represented the highest extensional flow because it had the lowest nozzle and mold temperatures. In run B4 the conditions should be reversed. Yet Figure 3. shows that the extreme microstructures were generated in runs B1 and B3, which is also reflected in the notched Charpy and Izod impact strength, see Table IV. Because the impact energy is directed to the core in the notched Charpy test and to skin layers in the notched Izod test the former should characterize shear and the latter elongational flow.

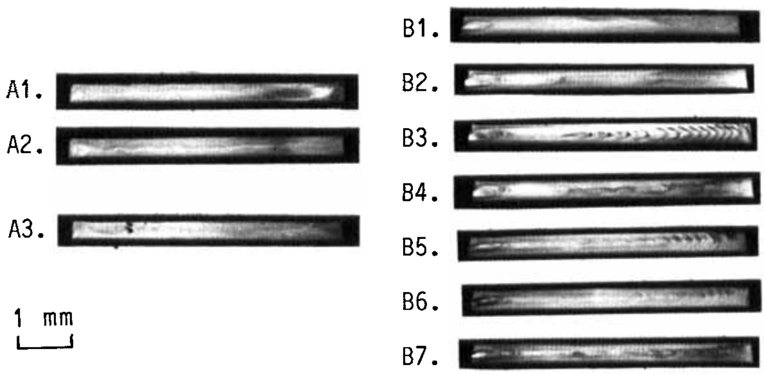

FIGURE 3 Cross-sectional view of some Charpy impact bars which were milled into half of their original size.

The microstructure of run B3 was attained by increasing the mold temperature (B1—>B3) or by decreasing the nozzle temperature (B4—>B3), which also applies to run B2 (B1—>B2<—B4). In run B1 the elevated temperature should reduce extensional flow whereas the decrease in temperature in run B4 should diminish shear. This assumption was verified by the Izod parameter in run B1. The Charpy parameter, by contrast, showed a reduction of nozzle temperature (B4—>B3) to increase shear by 5 % and a fall in mold temperature (B4—>B2) to decrease shear by 4 %. The shear thus grows in the following order B1 —> B2 —> B4 —> B3, which is also apparent in Figure 3.

DISCUSSION

The effect of the gate on the mechanical properties

The residual tensile strength was computed by the method presented in Ref. 3 (gates A and B). The results presented in Table III show that tensile strength in the former case depended on the core and in the latter case on the skin layers.

TABLE III The residual tensile strength (runs A3 and B5)

Fractional Thickness	Residual tensile strength (MPa) A3	B5
1.0	108.2	172.5
0.9	90.2	515.2
0.8	49.4	348.5
0.7	115.7	284.5
0.6	113.9	264.3
0.5	118.7	232.0

The effects of shear, extensional flow and holding pressure on the layered structure of the Izod specimen

Four basic layers can be found by inspecting cross-sections cut

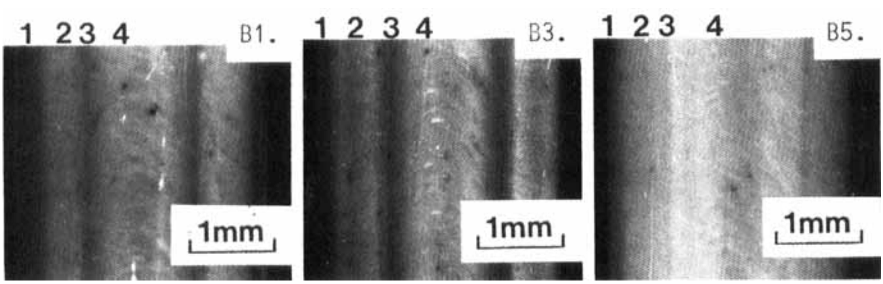

FIGURE 4 Cross-sectional view of some Izod impact bars. The tints of the 1st and 3th layer are rather similar in runs B1 and B3. The flow direction is upwards.

in the longitudinal direction from the Izod bars originating in the free melt flow (B1 and B3), see Figure 4. These can yet divide into many more parts the sum total being about 20. The addition of the holding pressure (B5) equalized the difference in the orientation of the basic layers. The percentage of the area occupied in the middle of the bar in the longitudinal direction by four layers measured in the above-mentioned runs:

	B1	B3	B5
1.	18 %	9 %	12 %
2.	32 %	35 %	36 %
3.	12 %	20 %	4 %
4.	38 %	36 %	48 %

According to Table IV the shear would be lowest in B1 and highest in B3, which accounts for the disparities in skin thickness between these runs. The raise of the mold temperature resulted in a reduced heat conduction rate which increased the thickness of the third layer, while the 2nd and the 4th layers remained almost unaltered.

Table IV A) The effect of the increase of shear on the mechanical properties (two variable study).
B) The holding pressure runs.

Property	A) Run B1	B2	B4	B3	B) Run B5	B6	B7
Notched Charpy kJm-2	35.6	53.1	55.2	58.0	48.8	55.9	53.8
Notched Izod J/m	1065.0	842.0	929.7	707.7	765.0	724.7	878.3
Tensile strenght MPa	174.8	180.8	171.6	165.8	172.5	159.7	187.1
Tensile elongation, %	10.4	13.4	12.4	10.8	12.0	11.2	14.0
Tensile modulus GPa	10.6	10.2	8.6	9.1	9.8	9.0	10.4
Flexural strenght MPa	169.1	163.9	163.0	160.4	176.6	176.8	174.3
Flexural modulus GPa	8.0	6.3	7.2	6.3	8.7	8.9	7.8

The holding pressure expanded the 2nd layer at the expense of the 1st layer and the 4th layer at the expense of the 3rd, thus the proportion (1+2)/(3+4) remained almost unchanged. Moreover, in the two variable study the thickness of the 2nd and 3th layers grew at the expense of the 1st and 4th respectively with increasing distance from gate B.

The dependence of mechanical properties on shear, extensional deformation and holding pressure

The notched Izod impact strength, the tensile modulus, the flexural strength and modulus were mainly governed by the first, elongational flow induced skin layer, which must occupy at least 20 % of the total cross-sectional area, see Table IV. The notched Charpy impact strength depended on the fourth, shear induced layer.

When the stress is greater than the modulus of the 1st layer and when the difference in orientation between the 1st and the 2nd layer is too great, for instance in a tensile test, the deformation rate becomes very high and the microstructure breaks. This explains why the maximum tensile strength is not attained in run B1. The holding pressure equalizes the molecular orientation in the 2nd, 3th and 4th layer, which in some cases increases e.g. the tensile strength (B4—>B7).

CONCLUSIONS

In the complex mold used it should be possible to characterize the shear and elongational flow with the aid of the notched Charpy and Izod impact strength respectively. The holding pressure was expected to disturb the free LCP melt flow. On the basis of the microstructure of the Izod specimens (B1-B4) injection molded without holding pressure a flow model of the LCPs is proposed which would account for the generation of the 4 layers, see Fig. 5.

The mold filling process of a LCP is controlled by the rotational shear, heat conduction, viscous heat generation, a time parameter, mass temperature, the thickness and length of a cavity,

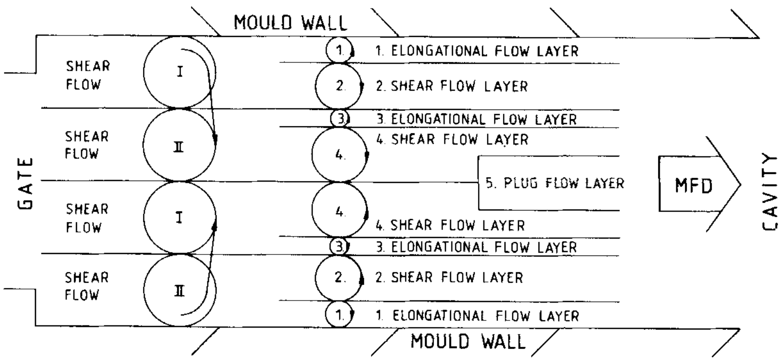

FIGURE 5 A free flow model of a LC melt for the mold cavity filling process resulting in a microstructure composed of 4 layers. The situation corresponds to run B1.

the shape of the gate and the mold wall temperature. These all have an effect on the velocity gradient. The motion of a liquid crystalline melt decelerates as the melt approaches the cavity through the gate, and the melt regains the domain structure. Because of the low mold wall temperature the heat conduction reduces the rotational velocity of domain I in relation to domain II. The mold wall tears a small part, tumbled in the reverse direction, from domain I, whose propagation velocity slows down. Since the domains II and 2 with free shafts have a tendency to rotate in the reverse direction, domain II also divides into two sections due to the heat conduction and the velocity profile. The reverse rotary motion caused by mold walls meet in the middle of the cavity, producing a 5th plug flow layer.

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