

Relationship Between Processing, Microstructure, and Mechanical Properties of Injection Molded Thermotropic LCP

Y. L. Wang,¹ C. Y. Yue,¹ K. C. Tam,¹ X. Hu²

¹*School of Mechanical & Production Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798*

²*School of Materials Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798*

Received 10 May 2002; accepted 1 August 2002

ABSTRACT: A commercial thermotropic liquid crystalline polymer (LCP), Vectra A950, was injection molded into rectangular sheets of thickness ranging from 1 to 4 mm. By changing the thickness of the mold, the shear rate experienced by the TLCP melt in the mold could be varied. The 1-mm test sample was highly anisotropic while that with larger thickness (4 mm) was less anisotropic. X-ray diffraction profile at various depths for each of the test sample corresponded to the degree in the fiber orientation present in the test samples. The anisotropy can be described macro-

scopically by measuring the tensile strength and modulus in the longitudinal and transverse direction. The ratio between the longitudinal and transverse property decreases proportionally to the thickness of the test sample. This reduction corresponded to the reduction in the shear field as the thickness of the mold was increased. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1713–1718, 2003

Key words: liquid crystalline polymers (LCP); orientation

INTRODUCTION

Thermotropic liquid crystalline polymers (TCLPs) are a relatively new class of materials, which have received considerable scientific attention. Commercial applications of these polymers have mostly been based on their high performances, dimensional stability, and ease of processing. The unique feature of thermotropic LCPs is that the molecules behave as rigid rods, this rigidity being conferred by the aromatic units and ester linkages. Orientation of rods in flowing melt leads to easy processability, but when the melt solidifies, in a mold or extruded sheet, the resulting orientation remained. Generally, the mechanical properties of polymers are strongly influenced by the molecular order and orientation. This is particularly true for liquid crystalline polymer, which gives rise to mechanical anisotropy in the component.

Copolyester of 73 mol %HBA and 27 mol %HNA is marketed by Hoechst Celanese under the trade name of Vectra A. Investigations on this material have focused on the mechanical properties of orientated fibers,^{1–3} thermodynamic,^{4–6} and thermal^{7,8} properties.

The morphology of Vectra A has been extensively studied by various authors.^{9–14} The investigation on the chain orientation in injection-molded tensile bars of Vectra A has shown that the chains are preferentially oriented parallel to the extrusion direction.^{15–17} Nevertheless, the orientation varied strongly at different locations within the sample, i.e., close to the surface, the orientation is comparatively large, while it becomes much lower in the center of the sample. Detailed studies on the orientation in LCPs have shown that the skin layer (typically 1 mm thick in a 3 mm-thick molding) consists of a number of much thinner layers, each with a distinct orientation.¹⁷

As a simplification of this layered structure, the injection moldings can be considered to be microcomposites made up of layers in which the direction of reinforcement changes from layer to layer. The observed mechanical modulus of the overall molding will reflect the integrated effect of the sum of the individual layer. The important factors governing the modulus would be expected to be the thickness of the component layers and the direction and degree of orientation of the polymer chains within the layers. These factors will depend partly on the injection-molding conditions and partly on the intrinsic response of the polymer chains to the flow conditions.¹⁸ A number of previous studies on these behaviors have

Correspondence to: C. Y. Yue (mcyue@ntu.edu.sg).
Contract grant sponsor: Ministry of Education.

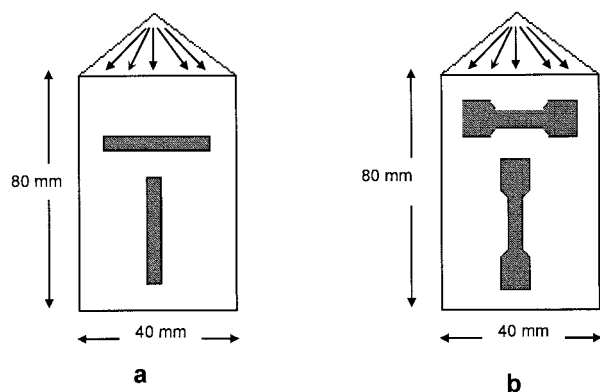


Figure 1 Schematic representation of injection-molded plaque and rectangular sample cut from it for X-ray diffraction measurement.

focused on the effects of processing conditions^{19–21} and chain linearity.¹⁷

In this study, rectangular plaques with different thickness were injection molded. It is believed that with the variance of the thickness of the mold, the shear stress experienced by the TLCP melt during mold filling changes with processing conditions. An attempt to make a qualitative correlation between shear rate, orientation, and the resultant mechanical properties are explored. XRD studies were carried out to evaluate the fiber orientation at various processing conditions.

EXPERIMENTAL

The thermotropic LCP used is a random copolyester of 73% 4-hydroxybenzoic acid (PHB) and 27% 2-hydroxy-4-naphthoic acid (HNA). It was prepared by melt condensation polymerization of acetyl derivatives of the above monomers in a batch process as licensed to Hoechst Celanese Co., which bears the commercial name of Vectra A950. It forms a nematic mesophase at temperature above 280°C.

Rectangular plaque moldings (80 × 40 mm) were injection molded using the Manumold Injection Molding Machine. The processing temperatures were 270, 260, and 250°C from hopper to mold orifice. Plaques with a thickness of 1, 2, 3, and 4 mm were injection molded. The “coat-hanger” plaque produced a straight flow front across the entire width of the mold insert.

Rectangular samples of approximately 20 × 15 mm were cut from the center of the injection-molded plaques, as shown in Figure 1(a). A Phillips APD 1700 Automated Powder Diffractometer was used for the X-ray analysis. A CuK α X-ray tube with a long fine focus was used with a power setting of 40 kV and 30 mA. The divergence slit and the scatter slit were both

fixed at 1°, with the receiving slit having an opening of 0.1 mm. The step scan used was at 0.02° per step, with 1 s allowed for each step, yielding 50 s per degree of 2θ . All scans were done from 10 to 30° 2θ . This range is sufficient to cover all the major crystalline peaks for LCP. The diffraction intensity (I) was recorded as a function of 2θ . The maximum of diffraction intensity (I_{\max}) was taken as an index of LCP orientation. The profile of I_{\max} within this plaque was investigated by polishing the sample in incremental steps. The local variation of I_{\max} was resolved into steps of 100 μm .

To measure the mechanical anisotropy of LCP, minidumbbell-shaped bars were cut from the injection-molded plaque at both the longitudinal and transverse directions, as shown in Figure 1(b). The Instron Mechanical Tester (4204) was used to measure the tensile strength and tensile modulus of these dumbbell-shaped bars. Specimen gauge lengths of 20 mm and a crosshead speed of 1 mm/min were used. The ratio of tensile properties between the longitudinal and transverse directions was used as an index of anisotropy.

RESULTS AND DISCUSSION

Injection moldings are known to exhibit a layered structure as a consequence of the complex combinations of converging and diverging stress during the process of mold filling. If the layers within the thickness of the molding contain materials that can orient (such as long polymer chains in LCP), then the properties in one layer are likely to be different from those in the next layer. A complex anisotropy is likely to develop in the plane of the molding and through the thickness of the molding.

To determine the local variations of the orientation, the samples were carefully polished using fine sandpaper to reveal every layer from skin to core. Each time nearly 100- μm thickness was polished away. X-ray diffraction can measure the crystalline structure of a surface; hence, we can utilize this method to explore the molecular orientation of LCP at different depths starting from the skin to the core. Figure 1(a) schematically represents rectangular sample cut from the injection-molded plaque for X-ray diffraction measurement. The XRD intensity as a function of the scattering angle 2θ of skin and core layers for LCP samples with different thicknesses is shown in Figure 2. It is apparent from the height of the peaks in Figure 2 that the chains are highly oriented in the skin layer, while the degree of orientation is much lower in the core layer. The XRD intensities demonstrate that the orientation at skin layer for samples with different thicknesses follows the trend: 1 mm > 2 mm > 3 mm > 4

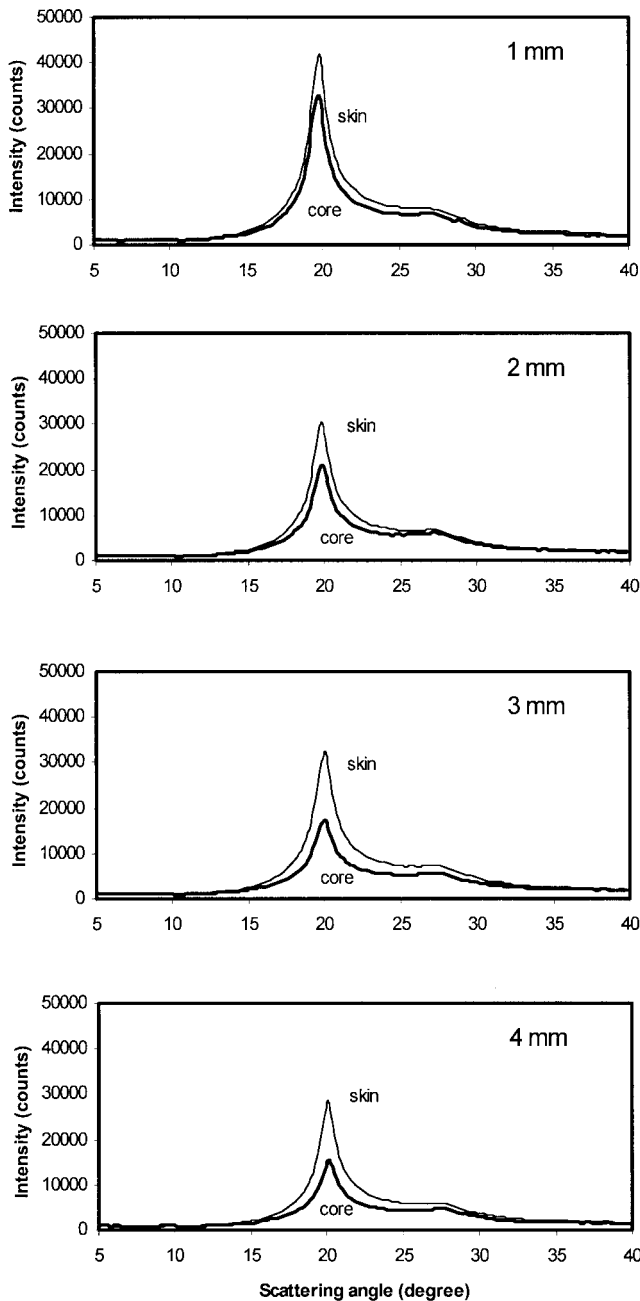


Figure 2 Experimental profiles of X-ray diffraction for skin and core layers of LCP with different thicknesses.

mm. However, at the core layer, the difference is small.

As the maximum intensity (I_{max}) could be used to represent the orientation of LCP, the variation of I_{max} at every layer from skin to core would provide orientation topography in injection-molded samples. The I_{max} distribution at different depths from skin to core for samples with different thickness is shown in Figure 3. It is obvious that all samples show a reduction in fiber orientation from the skin to the core.

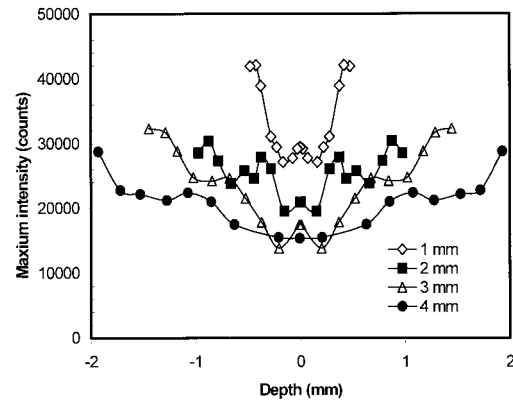


Figure 3 X-ray diffraction intensity across the depth of LCP with different thicknesses.

The 1 mm-thick sample gave the most dramatic changes in the topographic profile of the intensity. However, the orientation falls gradually from the skin to core for the 4 mm-thick sample. There is no distinctive layer across the depth. Blundell et al.¹⁷ used a wide-angle XRD to measure the absorption intensity across the depth for injection-molded tensile bars. They classified nine distinctive layers across the depth according to the absorption intensity. The samples in this study were cut from the center of injection-molded plaques, where shear stress changes continuously across the depth. The shear stress and thermal distribution across the depth would account for the observed orientation changes. As the shear stress changes continuously across the depth, the orientation of LCP chains also changes continuously.

The average intensity across the thickness, \bar{I} was determined from the expression:

$$\bar{I} = \frac{\int_{-x/2}^{x/2} I(x)dx}{x} \tag{1}$$

The shear rates during the mold-filling process may account for the difference in orientation for these four samples. The nominal shear rate $\dot{\gamma}$ in the plaque during mold filling was in the range of 100 to 2000 s^{-1} , as calculated from the injection-mold output Q , according to the expression below:

TABLE I
Shear Rate and Intensity for LCP Plaques with Different Thickness

Thickness of plaque (mm)	1	2	3	4
$\dot{\gamma}(s^{-1})$	2230	558	248	139
I (counts)	3153	2489	2200	1940

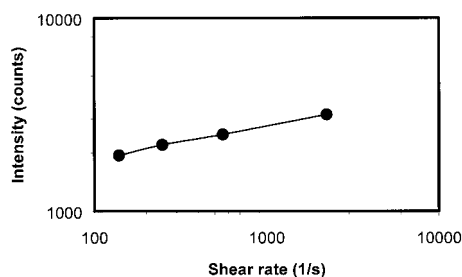


Figure 4 Logarithm diagram of average intensity (I) vs. shear rate ($\dot{\gamma}$) for LCP injection molding.

$$\dot{\gamma} = \frac{6Q}{WH^2} \quad (2)$$

where H is the thickness of the mold, W is the width of the mold, and Q is the volume output (calculated from the mass output and the material density). Q is $14.9 \text{ cm}^3/\text{s}$ for the setting used in the injection molding. Table I lists the shear rates and I for LCP samples.

The intensity is proportional to the shear rate experienced in the mold, as shown in Figure 4 for the plot of intensity (I) vs. shear rate ($\dot{\gamma}$). The higher the shear rates, the higher the probability for LCP molecular chain to orient along the flow direction. In injection molding, shear stress is the sole external force. In fiber spinning, elongation force is the primary force experienced by the melt as it is spun from the orifice. The higher the draw ratio, the higher will be the orientation of the LCP fiber. Hence, in both injection molding and fiber spinning, the orientation of the LCP fiber is dependent on the magnitude and direction of the external applied force.

As the microstructure of the LCP determines the mechanical properties, the highly oriented LCP molecular chains in injection-molded plaques will yield highly anisotropic products. Different degrees of orientation will bring about different degrees of mechanical anisotropy. Hence, by measuring the mechanical

TABLE III
Mechanical Anisotropy for Plague of LCP

Sample	AR	LM + TM
1 mm	4.94	11.76
2 mm	2.32	6.24
3 mm	2.20	6.27
4 mm	1.96	5.42

anisotropy, the structure–property correlation can be obtained.

Following the procedure adopted by Morin and Quentin²² to quantify the anisotropic character of the molding samples, an anisotropic ratio (AR), defined as the ratio between the longitudinal tensile modulus (LM) and transverse tensile modulus (TM) of the material, was adopted. At the same time the sum of LM and TM (LM + TM) was used as a measurement of the changes in the actual properties of the material. Mini-dumbbell tensile bars as shown in Figure 1(b) were cut from injection-molded plaques at both longitudinal and transverse directions. Tensile strength and modulus were measured, and the results are listed in Table II. Table III lists AR and (LM + TM) of samples with different thickness.

Plaque with 1-mm thickness possesses a remarkably high degree of mechanical anisotropy, the AR is as high as 5. This is in contrast to conventional thermoplastics, for which significant anisotropy is only observed in short fiber-filled grades, and the anisotropy ratios do not generally exceed 2. With the increasing mold thickness, the properties at the longitudinal direction are reduced, accompanying the increased properties at the transverse direction. Thus, mechanical anisotropy is inversely proportional to the mold thickness. The overall orientation of LCP in the 1-mm plaque is the highest, which accounts for the high anisotropy.

Figure 5 shows the tensile strength and modulus vs. thickness for injection-molded LCP. With the increase in the mold thickness, the gap between the tensile

TABLE II
Tensile Properties at Both Longitudinal and Transverse Directions for LCP

Thickness	Direction	Tensile strength (MPa)	Tensile modulus (GPa)	Strain at maximum load (%)
1 mm	longitudinal	231.8 ± 13.8	9.78 ± 0.82	5.6 ± 0.8
	transverse	40.6 ± 2.0	1.98 ± 0.16	4.9 ± 1.0
2 mm	longitudinal	151.8 ± 15.8	4.36 ± 0.55	7.5 ± 0.7
	transverse	47.8 ± 6.6	1.88 ± 0.12	8.3 ± 2.9
3 mm	longitudinal	130.6 ± 14.2	4.31 ± 0.87	7.1 ± 0.8
	transverse	52.0 ± 4.1	1.96 ± 0.07	9.6 ± 2.6
4 mm	longitudinal	122.0 ± 11.9	3.59 ± 0.56	7.0 ± 1.3
	transverse	55.0 ± 2.1	1.83 ± 0.11	9.6 ± 1.5

strength and modulus in the longitudinal and transverse directions decreases. As can be deduced from this result, the processing conditions have a significant effect on the structure and the resultant mechanical properties. Figure 6 shows tensile strength and modulus vs. shear rate experienced during mold filling. Higher shear rates increase the mechanical properties in the flow direction, but reduces the properties in the transverse direction. In practice, it is then possible to tailor the processing conditions to produce products with the desired properties. Besides shear deformation, other processing conditions, such as processing temperature, mold temperature, and injection pressure, can also affect the structure and mechanical properties. For the present study, these parameters were kept constant so that a simplified correlation between processing, structure, and properties of LCP can be developed.

It is evident that the fibers are more orientated at the skin than at the core regions. This is correlated to the higher shear rates encountered near the wall than at the center of the mold. As the mold thickness is decreased, larger shear rates and also shear gradients are encountered, which produce more orientated samples that yielded better mechanical properties.

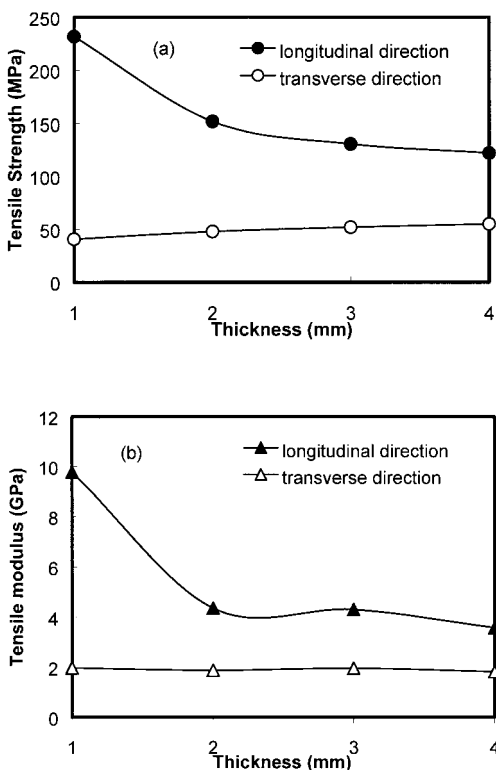


Figure 5 (a) Tensile strength, and (b) modulus vs. thickness for injection-molded LCP.

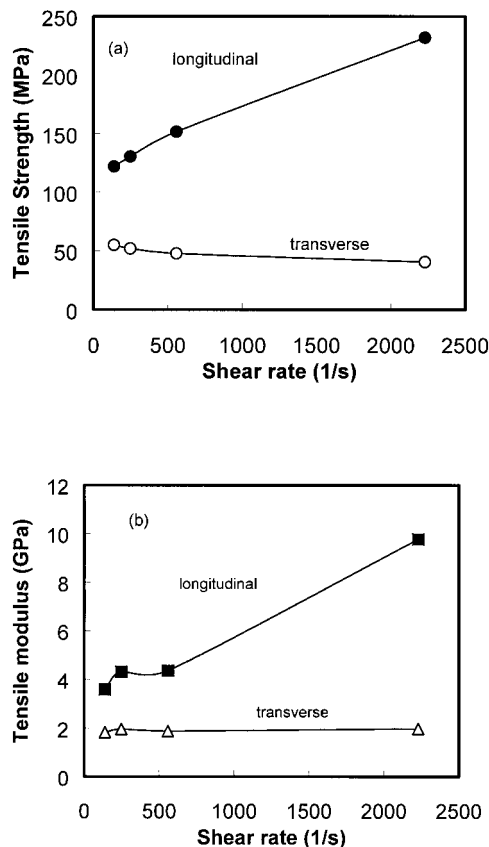


Figure 6 Tensile strength and modulus vs. shear rate for injection-molded LCP.

CONCLUSIONS

The orientation of LCP depends greatly on the shear stresses present during mold filling. The higher the shear stresses the higher the orientation of LCP in the flow direction. High orientation of LCP causes high mechanical anisotropy. The higher shear stress in this study was obtained in molds with smaller thicknesses. A graphic representation of the dependence of the tensile strength and modulus on the nominal shear rate has been established.

References

1. Troughton, M. J.; Unwin, A. P.; Davies, G. R.; Ward, I. M. *Polymer* 1988, 29, 1389.
2. Troughton, M. J.; Davies, G. R.; Ward, I. M. *Polymer* 1989, 30, 58.
3. Yoon, H. N. *Colloid Polym Sci* 1990, 268, 230.
4. Butzbach, G. D.; Wendorff, J. H.; Zimmermann, H. J. *Polymer* 1986, 27, 1337.
5. Lin, Y. G.; Winter, H. H. *Macromolecules* 1988, 21, 2439.
6. Cheng, S. Z. D. *Macromolecules* 1988, 21, 2475.
7. Green, D. I.; Orchard, G. A.; Davies, G. R.; Ward, I. M. *J Polym Sci Polym Phys Ed* 1990, 28, 2225.
8. Crispin, A. J.; Greig, D. *Polym Commun* 1986, 27, 264.
9. Windle, A. H.; Viney, C.; Golombok, R.; Donald, A. M.; Mitchell, G. R. *Faraday Discuss Chem Soc* 1985, 79, 55.

10. Hanna, S.; Windle, A. H. *Polymer* 1988, 29, 207.
11. Biswas, J.; Blackwell, J. *Macromolecules* 1988, 21, 3146.
12. Biswas, J. *Polym Sci* 1992, B30, 1375.
13. Guiterrez, G. A.; Chivers, R. A.; Blackwell, J.; Stamatoff, J. B.; Yoon, H. *Polymer* 1983, 24, 937.
14. Blackwell, J.; Biswas, A. In *Developments in Orientated Polymers*; Ward, I. M., Ed.; Elsevier: New York, 1987, 2nd ed.
15. Plummer, C. J. G.; Zulle, B.; Dermarmels, A.; Kausch, H. H. *Appl Polym Sci* 1993, 48, 751.
16. Zulle, B.; Dermarmels, A.; Plummer, C. J. G.; Kausch, H. H. *Polymer* 1993, 34, 3628.
17. Blundell, D. J.; Chivers, R. A.; Curson, A. D.; Love, J. C.; McDonald, W. A. *Polymer* 1988, 29, 1459.
18. Ide, Y.; Ophir, Z. *Polym Eng Sci* 1983, 23, 261.
19. Sawyer, L. C.; Jaffe, M. *Mater Sci* 1986, 21, 1897.
20. Weng, T.; Hiltner, A.; Baer, E. J. *Mater Sci* 1986, 21, 744.
21. Thapar, H.; Bevis, M. *Mater Sci* 1983, 2, 733.
22. Morin, A.; Quentin, J. P. U.S. Pat. No.: 4994518 (1991).