polymer communications

Transient isothermal elongational flow of thermotropic liquid crystalline polymers

D. E. Turek* and G. P. Simon
Department of Materials Engineering, Monash University, Clayton, VIC 3168, Australia

F. Smejkal and M. Grosso
CEAST SpA, Via Asinari di Bernezzo 70, Torino 10146, Italy

and L. Incarnato and D. Acierno
Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno, Fisciano (SA), 84084, Italy
(Received 25 May 1992)

The shear and transient isothermal extensional flow properties of a semicrystalline and an amorphous thermotropic liquid crystalline polymer are investigated. Independent estimates of the relationship between extensional viscosity and strain rate are derived from the measurement of (i) pressure loss in converging flow and (ii) filament tension in isothermal fibre spinning. The former material, a copolyester of hydroxybenzoic acid and naphthoic acid, flows readily in extension and shear. Results for the amorphous material suggest the need for a more detailed investigation of important elongational flow properties.

(Keywords: thermotropic liquid crystalline polymers; extensional flow; elongational flow; rheology; semicrystalline; amorphous)

Introduction

The study of the unique rheological properties of thermotropic liquid crystalline polymers (TLCPs) in the mesophasic state is an area of great current interest. Previous publications have dealt mainly with the steady, transient and oscillatory shear flow properties. The study of extensional (or elongational) flow properties of TLCPs has been limited by the difficulties associated with measurement and the appropriateness of employing existing analysis methods. The extensional properties of a lyotropic liquid crystalline polymer have been studied by Metzner and Prilutski[1]. La Mantia and Valenza[2] have characterized the drawability of a TLCP in non-isothermal elongational flow. Recently Wilson and Baird[3] reported measuring the transient extensional viscosity growth function of a TLCP. The knowledge of extensional flow behaviour of TLCPs is important to the understanding of property development in the many processes that involve stretching flows.

The development of a high degree of macromolecular orientation is attributed to the presence of an extensional flow regime in processing. The application of extensional strain in the non-isothermal spinline, following die extrusion, produces increased macromolecular anisotropy resulting in increased tensile properties[4]. The extensional flow field present in the converging section of the die has also been associated with flow-induced orientation[5]. This orientation is preserved in the solidified material, due to the long orientation relaxation times inherent in these rigid-rod polymers[6]. In addition to fibre spinning and extrusion, extensional flow fields predominate in injection moulding in the spreading flow front, and in flow through contractions. In the case of blends involving a TLCP, the presence of extensional flow is associated with the creation of dispersed matrix-reinforcing TLCP fibrils. Theoretical predictions of the development of blend–fibril morphology depend, amongst other factors, on shear viscosity ratio[7]. As these fibrils are produced in an extensional flow field, a knowledge of extensional properties is expected to be an important parameter, given that the extensional viscosity ratio cannot always be related directly to the zero shear viscosity (Trouton ratio).

In this study, estimates of transient isothermal extensional-flow properties of a commercial semicrystalline and an amorphous TLCP are investigated. Two independent estimates of extensional viscosity have been determined based on the measurement of (i) pressure loss in converging flow, and (ii) stretching force in isothermal fibre-spinning experiments. Given the gross assumptions made about the flow behaviour of these novel materials, the value of additional corroborating experiments cannot be understated. The physical, thermal, shear flow and tensile properties of these two materials have been compared previously[8].

Analysis

From the measurement of the pressure drop in flow through a contraction, reasonable estimates of the extensional viscosity of conventional thermoplastic materials can be determined. In this study, Cogswell's[9] method has been employed. Laun and Schuch[10], using several measurement techniques for polyolefins, have confirmed that this method can provide a reasonable quantitative estimate of extensional viscosity. Tremblay[11], using the methods of Cogswell[9] and Binding[12], found that predictions of entrance flow convergence angles agree well with experimental data for polyolefins. Kwag and Vlachopoulos[13] recently validated Cogswell's technique using finite element analysis and the experimental

* To whom correspondence should be addressed

0032-3861/93/010204-03

data of Laun and Schuch[10]. The application of Cogswell's analysis to anisotropic TLCPs cannot be assumed due to the large, and poorly understood, entry-pressure-loss values characteristic of these materials.

Using the analysis of Cogswell[9], the average elongational viscosity $\eta_{\text{ext-avg}}$, can be determined using the relation:

$$\eta_{\text{ext-avg}} = \tfrac{9}{32}(n+1)^2 \frac{\Delta P_{\text{ent}}^2}{\dot{\gamma}^2 \eta} \quad (1)$$

where ΔP_{ent} is the entrance pressure drop, $\dot{\gamma}$ is the apparent wall shear rate, η is the shear viscosity and n is the power law index. For the purposes of this study, the exit pressure drop is neglected, and the value of ΔP_{ent} is assigned the value of the pressure drop through an orifice length die. The average extensional strain rate $\dot{\varepsilon}_{\text{avg}}$ is calculated from:

$$\dot{\varepsilon}_{\text{avg}} = \frac{4}{3(n+1)} \eta \frac{\dot{\gamma}^2}{\Delta P_{\text{ent}}} \quad (2)$$

Estimates of extensional properties can be determined from melt spinning experiments. Calculations vary in complexity, and measurements can be made under isothermal or non-isothermal conditions. In the fibre spinline, a uniaxial extensional flow field predominates. Petrie[14] has reviewed experimental techniques and results for several thermoplastics analysed. The use of an isothermal chamber eliminates the influence of the dominating temperature effect that occurs in non-isothermal spinning. As a first estimate, extensional viscosity can be calculated using the measurement of take-up force only. A filament diameter and hence extensional strain rate profile can be assumed, eliminating the need for measurement of the filament diameter or velocity profile. Following the analysis of Laun and Schuch[10], the log of the molten filament diameter is assumed to decrease linearly with distance from the die. This assumption is supported by non-isothermal spinning data[15] of a TLCP, which shows a logarithmic change in filament diameter with spinline distance. The extensional strain rate $\dot{\varepsilon}_{\text{end}}$ and extensional (tensile) stress $\sigma_{\text{ext-end}}$ at the end of the spinline are determined by:

$$\dot{\varepsilon}_{\text{end}} = \frac{2\pi v r_w}{h} \ln\left[\frac{8\pi v r_w}{\dot{\gamma} r_d}\right] \quad (3)$$

$$\sigma_{\text{ext-end}} = \frac{8 v r_w F}{r_d^3 \dot{\gamma}} \quad (4)$$

Strain rate and stress are determined using take-up wheel rotation speed v, take-up wheel radius r_w, die radius r_d, isothermal chamber length h, apparent wall shear rate $\dot{\gamma}$ and measured filament tension F. A transient elongational viscosity $\eta_{\text{ext-end}} = \sigma_{\text{ext-end}}/\dot{\varepsilon}_{\text{end}}$, can be calculated from these two parameters. This method may not produce quantitatively correct values; however, good correspondence with more precise techniques has been obtained for polyolefins[10].

Experimental

The two TLCPs employed are semicrystalline Hoechst-Celanese VECTRA® A950 and amorphous DuPont HX-2000®. Polymers were dried overnight under vacuum at 120°C. Barrel temperatures of 300 and 310°C were employed for VECTRA and HX-2000, respectively. The amorphous material is believed to exist in a mobile nematic mesophase state[8] at 310°C.

Converging flow measurements were undertaken using an Instron 3211 capillary rheometer at Monash University. The entrance pressure loss was equated to the pressure drop associated with flow through a zero-length die. This was determined from extrapolation of the pressure drop measured using dies with length/diameter ratios of 0.5, 2.5 and 5.0 (0.78 mm diameter), at varied wall shear rates from 55 to 550 s^{-1} (VECTRA) and 15 to 150 s^{-1} (HX-2000). These dies have a 45° half-angle conical converging section. No significant difference in extrusion pressure was observed when a flat-entry die (90°) was used.

Melt-spinning measurements were made at the Università di Salerno using a commercial Ceast Rheovis 2100 with thermostatic environmental chamber and tensile module. The experimental arrangement is depicted in *Figure 1*. Specimens were extruded at barrel temperatures of 300°C (VECTRA) and 310°C (HX-2000), into the isothermal chamber maintained at 300°C. A capillary die of diameter 1 mm (length/diameter = 20) and a wall shear rate of 120 s^{-1} was employed. Filament tension was mesured at varied extensional strain rates corresponding to varied take-up wheel speeds. For VECTRA, take-up pulley speeds of 56–250 rev min^{-1} (pulley diameter 80 mm) resulted in filament tension measurements ranging from 0.002 to 0.005 N. For HX-2000, take-up pulley speed varied from 20 to 44 rev min^{-1}, and filament tensions ranging from 0.145 to 0.184 N were observed. Filament draw-down is assumed to occur completely within the 100 mm long temperature chamber.

Results and discussion

The steady shear viscosity and extrapolated pressure loss values for both polymers are plotted against apparent shear rate in *Figure 2*. At the slightly higher temperature of 310°C, HX-2000 is substantially more viscous than VECTRA at 300°C. The characteristic strong shear thinning behaviour of TLCPs in the nematic state is apparent. The shear viscosity–shear rate relationship can be described by a power law relationship. Values of power law index n of 0.47 and 0.49 for VECTRA and HX-2000, respectively, are calculated from a plot of shear stress against apparent shear rate. Significant levels of entrance pressure loss are observed, which is characteristic for this class of materials.

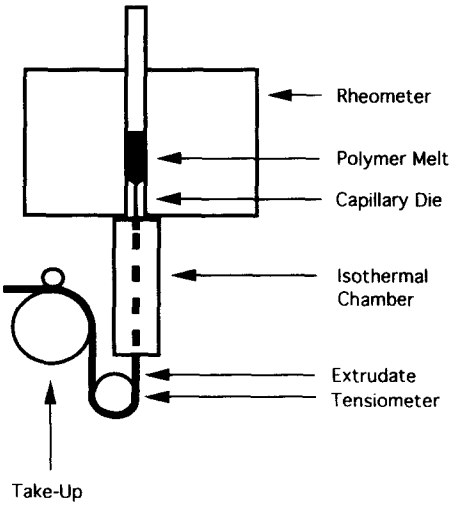

Figure 1 Isothermal melt-spinning apparatus for measuring extensional flow properties

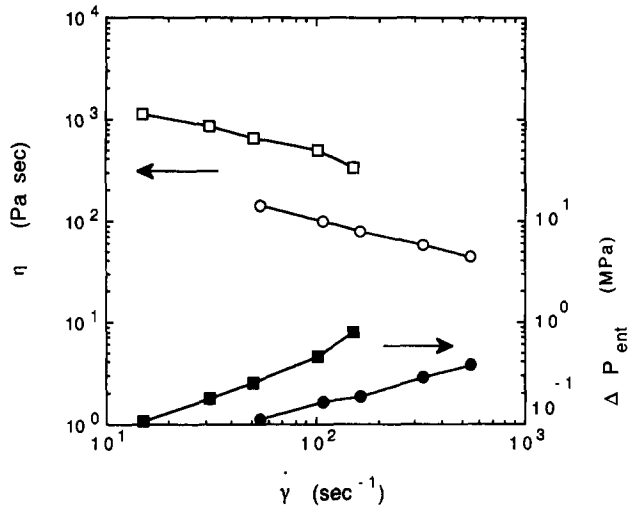

Figure 2 Shear viscosity of VECTRA at 300°C (○) and HX-2000 at 310°C (□), and entry pressure loss of VECTRA at 300°C (●) and HX-2000 at 310°C (■) *versus* apparent wall shear rate

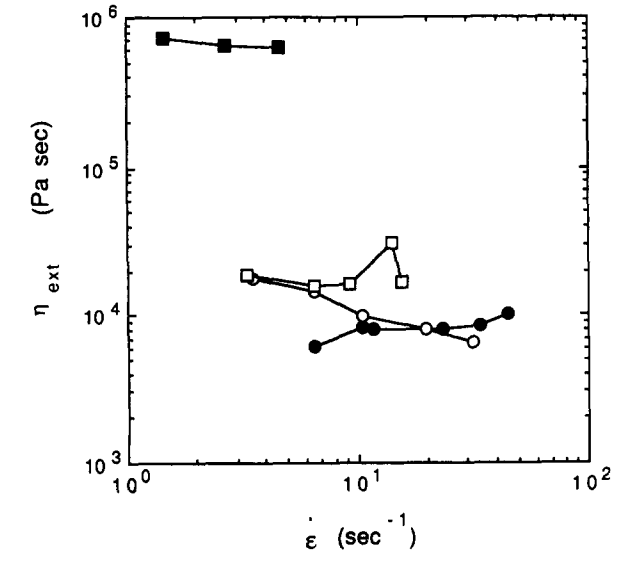

Figure 3 Estimates of extensional viscosity *versus* extensional strain rate measured using (i) converging flow analysis for VECTRA at 300°C (○) and HX-2000 at 310°C (□), and (ii) isothermal melt spinning for VECTRA at 300°C (●) and HX-2000 at 300°C (■)

Estimates of transient elongational viscosity *versus* extensional strain rate, calculated using converging flow analysis and isothermal spinning, are depicted in *Figure 3*. The former represents average values based on the stretching flow history in convergence (prior to the spinline). The latter is derived from the prediction of the maximum strain rate at the end of the isothermal chamber and the tensile stress in the spinline.

The data of *Figure 3* indicate agreement between the two methods for VECTRA, and disagreement for HX-2000. The extensional viscosity values predicted for VECTRA are less than the values reported for other thermoplastics (e.g. HDPE, LDPE and PS[10,16]). This demonstrates that this TLCP flows readily in both shear and extension, as indicated by the respective viscosities. The observed small tension required to strain the material in the spinline further reflects this result. The agreement between the differing methods suggests that the simplifying assumptions made here are appropriate.

The results for HX-2000 differ depending on the method employed. The extensional viscosity of this more shear viscous material is only slightly higher than VECTRA based on converging flow analysis. From the observed large spinline pulling force, the predicted extensional viscosity of HX-2000 in isothermal spinning is at least an order of magnitude higher. Due to maximum temperature limitations, the isothermal chamber was maintained at 10°C below the extrusion temperature. The amorphous nature of this material results in a high degree of sensitivity of rheological properties to temperature. Given that the application of converging flow analysis to TLCPs has not been established previously, it is not possible to explain this discrepancy further.

The favourable results for VECTRA suggest that the application of converging flow and spinline analysis techniques to elucidate extensional properties for certain TLCPs may be possible. However, the results with HX-2000 confirm that further experimentation is necessary. A reduction in the number of assumptions employed will improve the accuracy of these methods. This includes the monitoring of the filament draw-down profile within the isothermal chamber. The use of a constant stretching rate extensional rheometer, possibly requiring modification for operation at higher temperatures, is also appropriate.

Acknowledgements

The financial support of a Canadian Natural Science and Engineering Research Council 1967 Award is acknowledged (D.E.T.).

References

1 Metzner, A. B. and Prilutski, G. M. *J. Rheol.* 1986, **30**, 661
2 La Mantia, F. P. and Valenza, A. *Polym. Eng. Sci.* 1989, **29**(10), 625
3 Wilson, T. S. and Baird, D. G. Abstracts of the 63rd annual meeting of the Society of Rheology, Rochester, New York, 1991, p. 34.
4 Ide, Y. and Ophir, Z. *Polym. Eng. Sci.* 1983, **23**(5), 261
5 Turek, D. E. and Simon, G. P. *Polymer* in press
6 Baird, D. G. in 'Polymeric Liquid Crystals' (Ed. A. Blumstein), Plenum Press, New York, 1985, p. 119
7 Taylor, G. I. *Proc. R. Soc. London* 1934, **A146**, 501
8 Turek, D. E. and Simon, G. P. *Polym. Int.* 1992, **27**, 165
9 Cogswell, F. N. *Polym. Eng. Sci.* 1972, **12**, 64
10 Laun, H. M. and Schuch, H. *J. Rheol.* 1989, **33**, 119
11 Tremblay, B. *J. Non. Newt. Fluid Mech.* 1989, **33**, 137
12 Binding, D. M. *J. Non. Newt. Fluid Mech.* 1988, **27**, 173
13 Kwag, C. and Vlachopoulos, J. *Polym. Eng. Sci.* 1991, **31**(14), 1015
14 Petrie, C. J. S. 'Elongational Flows', Pitman, London, 1979
15 Sarlin, J. and Törmälä, P. *J. Appl. Polym. Sci.* 1990, **40**, 453
16 La Mantia, F. P., Acierno, D. and Curto, D. *Rheol. Acta* 1982, **21**, 452