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Extensional viscosity of a thermotropic liquid crystalline polymer measured by thread disintegration method

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Abstract

We investigated a simple method for measuring the extensional viscosity of thermotropic liquid crystalline polymer: disintegration of liquid crystalline polymer threads in a quiescent polymer matrix. The method is based on the dynamic interfacial tension between the two components, and covers strain-rate and strain ranges that are very low. Results obtained by the method show extensional rate thinning behavior and strain-hardening behavior. The trends are in agreement with previous measurements using other methods such as fiber spinning. We recommend the thread disintegration method for measuring extensional viscosity at small extensional rates and small strains.

Keywords: Extensional viscosity; Thread disintegration method; Thermotropic liquid crystalline polymer (TLCP)

1. Introduction

The structure and orientation of thermotropic liquid crystalline polymers (TLCPs) can significantly affect the mechanical performance of TLCP. Processing flows play a central role in defining the orientation on the macroscopic level. Extensional flows have been shown to be much more effective than shear flow in producing a high degree of molecular orientation. In view of the importance of extensional flow in processing of LCPs, the extensional rheological properties of LCPs, such as extensional viscosity, are crucial to understand the microstructural variation in extensional flow.

While the shear rheology of liquid crystalline polymer (LCPs) has been studied extensively, little attention was paid to their extensional behavior. Extensional viscosity of LCPs is important in processing of polymers, such as extrusion, blow molding, and fiber spinning. However, it is much more difficult to measure the extensional viscosity than the shear viscosity. Several techniques have been used to measure the extensional viscosity of LCP melts, including fiber spinning [1,2], rotary clamp method [3,5], lubricated squeezing technique [4], and the Rheometrics Melt Extensional rheometer (RME) [6,7] and entry flow [8]. Metzner and Prilutski [1] reported extensional viscosity data for lyotropic solutions of hydroxypropylcellulose (HPC) in acetic acid obtained by gravity-spinning. They found that the extensional viscosity was independent of rate over a range of 0.02–10 s^{-1} and that the Trouton ratio at low rates was about 9. Wagner et al. [2] measured the extensional viscosity using a Rheotens fiber-spinning instrument on a commercial TLCP (Vectra B950), and noted behavior similar to polyethylene. Chen et al. [3] measured the transient extensional viscosity of HPC melt at 180 °C using a single rotary clamp device, and showed extension rate-thinning behavior of extensional viscosity. Done [4] measured the equibiaxial extensional flow properties of

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three thermotropic copolyesters: 60 mol% para-hydroxybenzoic acid (HBA) and 40 mol% poly(ethylenetherphthalate) (PET), 80 mol% HBA and 20 mol% PET, and a copolymer of 73 mol% HBA and 23 mol% 2-hydroxy-6-naphthoic acid (HNA) (Celanese Vectra A900). Measurements were made by the lubricated squeezing technique. The transient biaxial extensional viscosity was found to be higher than $6\eta_s$ (η_s is shear viscosity), while the transient biaxial extensional viscosity for Newtonian or linear viscoelastic fluids is equal to $6\eta_s$ (η_s is shear viscosity). Furthermore, it decreases with increasing extension rate and increases with increasing strain. Wilson and Baird [5] measured the transient extensional viscosity of HPC and Vectra A900 on a rotary clamp extensional rheometer. They found that the extensional viscosity of liquid crystalline polymers in the nematic state exhibits stronger strain-hardening than in the isotropic state. Kernick and Wagner [6] measured the transient extensional viscosity and molecular orientation of a TLCP under simple uniaxial extensional flow. Significant strain hardening was observed for Hencky strains greater than one, with both the molecular order and transient extensional viscosity becoming independent of strain rate, and there was weak strain hardening at strains below one. X-ray scattering measurements confirmed that a high orientation order parameter was produced by the extensional flow. Gotsis and Odriozola [7] measured the transient extensional viscosity of the nematic melt of thermotropic liquid crystalline (LCP) Vectra A950 in a Rheometrics Melt Extensional rheometer (RME). They found rate-thinning behavior.

Another widely used and much simpler method to estimate extensional viscosity is by measuring the pressure drop in entry flow, usually in a capillary rheometer. There is a strong acceleration/stretching of the fluid at the entrance of the capillary along its axis, which contributes to an extra pressure drop. Gotsis and Odriozola [8] applied Binding's method to calculate the extensional viscosity of TLCP (Vectra A950).

As extensional flow is difficult to obtain, the instruments for measuring extensional viscosity are so expensive that they are not applied widely. However, the key to overcome the problem is to obtain extensional flow and choose a simple method to detect it. During the current experiments, we obtained extensional flow by a simple method: thread disintegration, which is based on the disintegration of TLCP threads in a quiescent polymer matrix. The integration of a viscoelastic jet in air to measure the extensional viscosity was suggested by Schummer and Tebel [9].

2. Theory of the estimation of extensional viscosity by thread disintegration [10]

The thread disintegration method was originally used to measure the interfacial tension between two Newtonian fluids, and regular sinusoidal disturbances are required to make use of Tomotika's theory. However, perfect sinusoidal disturbances are difficult to obtain for viscoelastic fluid even under carefully controlled conditions. The most commonly observed configuration is two bulbs connected with a long thin thread. The bulbs grow with time and the diameter of the connecting thread decreases. The flow inside the connecting thread is regarded as an extensional flow, driven by the interfacial tension between the thread and the matrix. The extensional viscosity then can be estimated from the disintegration process [10]. The extensional viscosity can be obtained from the relation:

$$\eta_\varepsilon = \frac{\tau_{zz} - \tau_{rr}}{\dot{\varepsilon}} \quad (1)$$

η_ε is the extensional viscosity, τ_{zz} and τ_{rr} are the stress components in the axial and radial direction, $\dot{\varepsilon}$ is

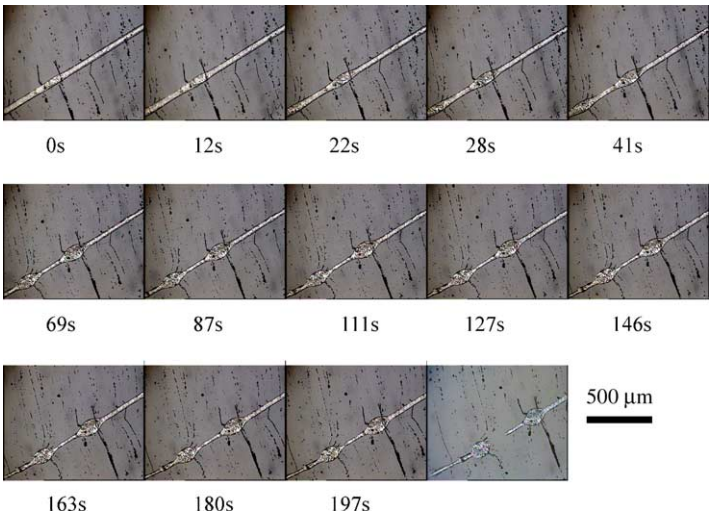

Fig. 1. Disintegration of LC-5000 thread in a quiescent matrix of PC3103 at 295 °C.

the extensional rate. Usually a long dumbbell-like shape is observed during the disintegration of a TLCP fiber; an example is shown in Fig. 1. The dumbbell shape is idealized as a perfect cylinder with radius R_f connecting the spherical bulbs with radius R_b. $\dot{R}_f$ is the time derivative of the radius R_f. The extensional rate ($\dot{\varepsilon}$) is generally not constant, but can be measured easily as:

$$\dot{\varepsilon} = -2\dot{R}_f/R_f \tag{2}$$

The stress difference ($\tau_{zz}-\tau_{rr}$) can be estimated from the difference in the interfacial pressure jumps between the bulb and the fiber. The interfacial pressure jump is given by the Young–Laplace equation and a force balance leads to:

$$\tau_{zz} - \tau_{rr} = \frac{\sigma}{R_f} - \frac{2\sigma}{R_b} \tag{3}$$

and hence

$$\eta_\varepsilon = \frac{\sigma/R_f - 2\sigma/R_b}{-2\dot{R}_f/R_f} \tag{4}$$

where σ is the interfacial tension.

The interfacial tension is an important parameter in determining the extensional viscosity in the above method. The interfacial tension between two Newtonian fluid remains constant during thread disintegration as confirmed by Mo et al. [11]. However, this is usually not the case for the interfacial tension between LCPs and flexible polymers. Our previous investigations [12,13] have shown that the interfacial tension changes with the deformation of the polydomains of TLCP, and an expression was suggested to correlate them between LC5000 and polycarbonate (PC) in Eq. (5) with $\sigma_{min}=0.078$ mN/m, $\sigma_e=3.69$ mN/m, $k=0.95955$ and $\beta=0.30369$:

$$\frac{\sigma - \sigma_{min}}{\sigma_e - \sigma_{min}} = k\, e^{-\frac{b/a-1}{\beta}} \tag{5}$$

where b/a is the aspect ratio of the polydomains of TLCP. The method of obtaining b/a is discussed in Section 3.3.

3. Experiment

3.1. Materials

The thermotropic liquid crystalline polymer used here is LC-5000 (Unichika, Japan). The as-received pellets have a nominal melting point of 275 °C. The matrix used is polycarbonate (PC3103, Bayer). LC-5000 and PC3103 were dried at 120 °C under vacuum for at least 24 h before use. The zero-shear viscosity of PC 3103 was obtained as $\eta_0=610$ Pa s by fitting dynamic viscosity results to the Ellis model. The zero-shear viscosity of LC5000 was obtained as $\eta_0=115.1$ Pa s from a creep test.

3.2. Extensional viscosity measurement by the disintegration of threads

A long, thin fiber is needed for the measurement of extensional viscosity by the thread disintegration method. Such fibers were obtained by extruding LC-5000 melt from a capillary rheometer at 295 °C, and drawing the extrudate from the die by a take-up device at a drawing speed of 400 m/min. TLCP long fibers that were cut from the same extrudate were used in the following experiments. The matrix films were compression-molded to a thickness of 0.6 mm. The long thread was placed between two films of PC at room temperature.

Observations were carried out on an optical microscope (Leica) with a camera and a hot stage at magnification of 100×. The prepared specimen was put on the hot stage of the optical microscope and heated at 20 °C/min to 240 °C. The sample was maintained at this temperature for 5 min to allow the matrix polymer, PC, to relax completely. Subsequently, the specimen was heated further at 40 °C/min to the desired temperature of 295 °C. The changes of the long fiber were imaged and recorded. In most of our experiments, the evolution of a long fiber was similar to that shown in Fig. 1. The images were analyzed using Scion image analysis software.

3.3. Characterization of the polydomain structure inside LC-5000 fiber

Light scattering (LS) methods are good choices for determination of the deformation of the texture of a TLCP [14,15]. However, it is difficult to apply LS methods here to detect the deformation of polydomains inside a TLCP drop. Instead, polarized optical microscopy (POM) was used. The aspect ratio of deformed polydomains was obtained from the power spectrum of two-dimensional discrete Fourier transformation (DFT) of the image inside a TLCP drop. Although the aspect ratio determined from the power spectrum is a weaker function than that from LS [15], it still can be used to correlate the apparent interfacial tension and the deformation of texture. We first obtained a picture of the internal structure of LC-5000 fiber by magnifying a small area from the POM of LC-5000 thread in a quiescent matrix of PC3103 at 295 °C, then used DFT to compute its power spectrum and extract the aspect ratio of polydomain (b/a). This ratio is used in Eq. (5) to determine the dynamic interfacial tension.

4. Results

Fig. 1 is a typical disintegration process of LC-5000 thread in a quiescent matrix of PC3103. Disturbances, which may initially be sinusoidal, grow in time to produce a dumbbell. The bulbs are not uniformly spaced, and tend

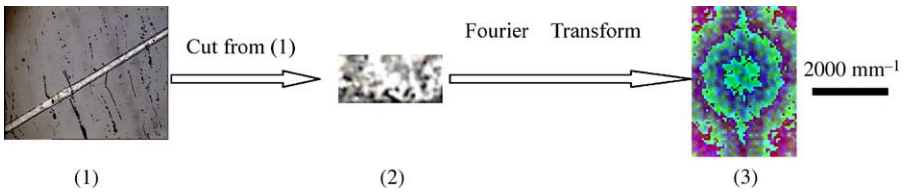

Fig. 2. The POM of LC-5000 and its power spectrum. (1) POM of LC-5000 thread in a quiescent matrix of PC3103 at 295 °C; (2) picture of internal structure of LC-5000 thread by magnifying a small area of (1); (3) power spectrum of (2).

to shift along the thread in either direction. The bulbs grow with time and the diameter of the connecting thread decreases. The flow inside the connecting thread is regarded as an extensional flow. Interfacial tension σ is an important factor in Eq. (4) for determining the extensional viscosity. Moreover, σ is not a constant during the thread disintegration due to the deformation of polydomains in the TLCP. Eq. (5) is used to correlate the interfacial tension and the deformation of polydomains of TLCP, the latter to be determined by the method described in Section 3.3.

Fig. 2 is a typical power spectrum of polydomain of LC-5000 by the DFT method. The dynamic interfacial tension σ calculated from Eq. (5) is plotted in Fig. 3 during the period of disintegration of the LC-5000 thread shown in Fig. 1. It can be seen that σ is not a constant, but decreases with time. This is consistent with prior measurements using the drop retraction method [12].

Using the radii of the bulb and the thread as well as the interfacial tension during the disintegration process, we can use Eq. (4) to calculate the extensional viscosity of LC-5000. In this process, both the strain rate and the strain are changing in time (see Fig. 4). Fig. 5 shows the extensional viscosity versus extensional rate for different fibers. The extensional viscosity decreases with increase of extensional rate. The discrepancies among different experiments are due to the different amount of accumulated strain in different fibers with different lengths. Fig. 6 shows the extensional rate against accumulated strain during the disintegration of thread, which shows that the extensional rate decreases with accumulating strain. As the thread becomes thinner, the extensional rate decreases while the accumulated strain increases. The extensional viscosity increases as well. Therefore, it is meaningless to compare the results when the accumulated strain and extensional rate are simultaneously changing. In order to elaborate the result, we decouple the two factors affecting the extensional viscosity. First, fixing the extensional rate, discussions are made on the dependency of extensional viscosity and accumulated strain (see Fig. 7). Second, we discuss the relationship between extensional viscosity and extensional rate under constant accumulated strain (see Fig. 8). We plotted extensional viscosity versus accumulated strain under different extensional rate by taking individual points out of Fig. 5 into Fig. 7, and the results show that strain hardening of the extensional viscosity appears, which is consistent with previous reports [5–7]. The only way to compare the extensional viscosity at different extensional rates by taking individual points out of Fig. 5 is to consider the values of extensional viscosity at the same accumulated strain [7,8], which is shown in Fig. 8. It can be seen that extensional rate thinning behavior appears under each strain. The extensional viscosity is larger for larger strain, which also manifest the strain-hardening behavior.

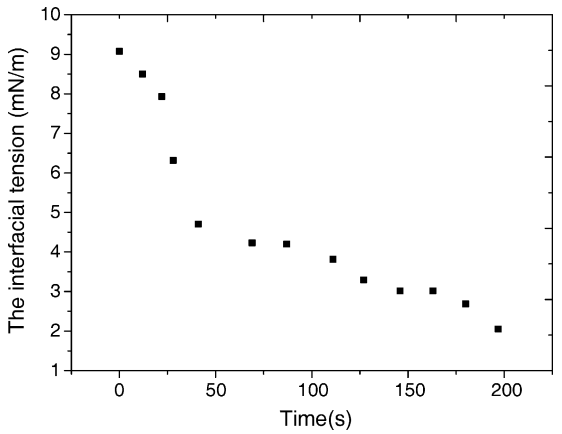

Fig. 3. Apparent interfacial tension calculated versus time of Fig. 1.

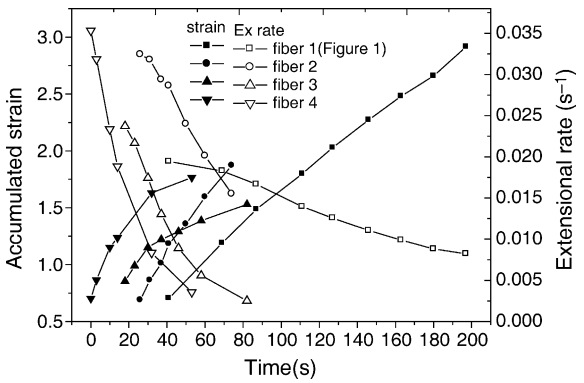

Fig. 4. Accumulate strain of LC-5000 and extensional rate during the disintegration of fiber versus time.

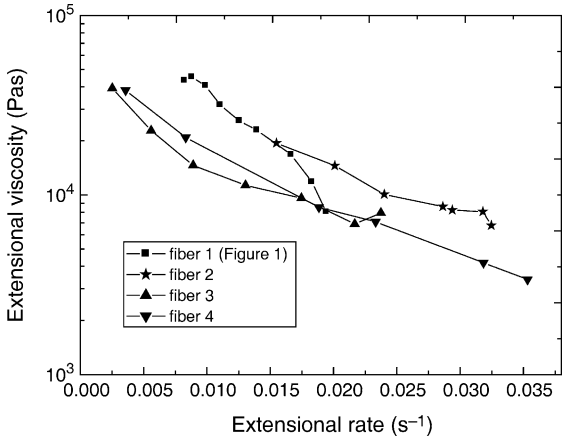

Fig. 5. Extensional viscosity of LC-5000 versus extensional rate.

As compared to the method of entry flow and RME (extensional rate is above 0.01 s^{-1} for other TLCP measured) [6,7], the range of extensional rate by the method of thread disintegration is much lower. The thread disintegration method is simple and easy to implement, and is particularly suitable for estimation of extensional viscosity under small rates and small strains.

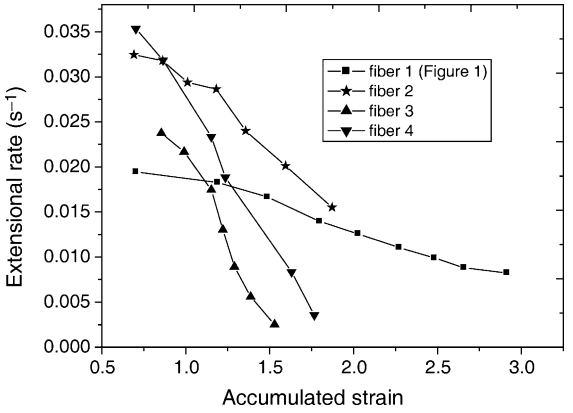

Fig. 6. Extensional rate versus accumulate strain of LC-5000.

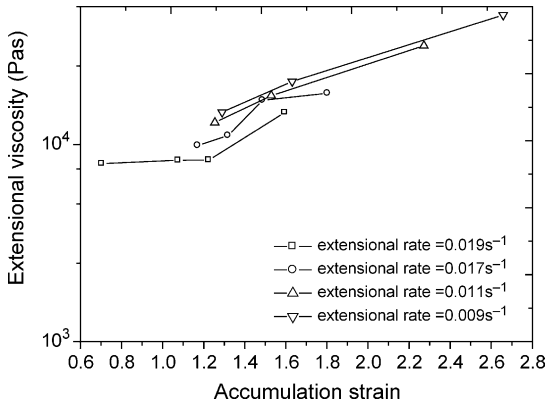

Fig. 7. Extensional viscosity versus accumulated strain under different constant extensional rate.

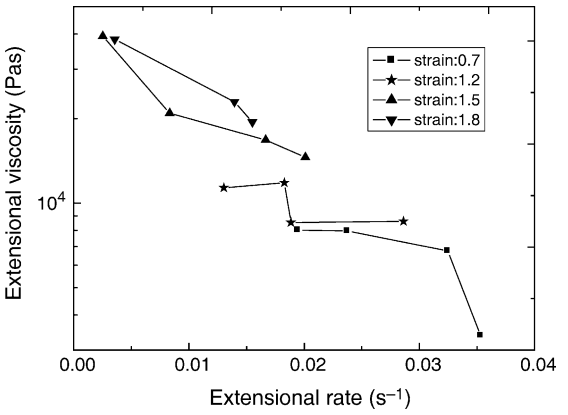

Fig. 8. Extensional viscosity at different accumulated strain versus extensional rate.

5. Conclusions

Measurement of extensional viscosity is a very difficult task. In this paper, we applied the simple method of thread disintegration, which involves recording the thinning and breakup of a polymer thread in a quiescent matrix, to measure the extensional viscosity of a thermotropic liquid crystalline polymer. The method of thread disintegration makes use of the dynamic apparent interfacial tension between the TLCP and the flexible chain matrix. The results show extensional rate thinning and extensional strain hardening behaviors. The unique advantage of the method of thread disintegration is its ability to access strains and strain rates much below those other methods.

Acknowledgements

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