ELASTIC BEHAVIOR OF MESOPHASE PITCH

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INTRODUCTION

Mesophase pitch exhibits elastic behavior, and this peculiarity has a direct impact on fiber formation [1,2]. Elasticity influences the stability of flow into and through the spinnerette capillary. It is responsible for any elastic recovery which might occur as the mesophase emerges from the capillary. Elasticity even affects the fiber drawdown. Obviously, if the development of structure during mesophase fiber spinning is to be accurately modeled, the elasticity of this material must be first quantified.

Recently, McHugh [2] compared the viscoelastic nature of various fiber precursors at their appropriate spinning temperature by dynamic mechanical analysis (DMA) using a Rheometrics RDS II Dynamic Spectrometer. The results showed that synthetic, naphthalene-based mesophase (AR-mesophase, produced by Mitsubishi Gas Chemical Co.) was more elastic than heat soaked mesophase pitch (see Figure 1). However, no attempt was made to quantify the elasticity of either mesophase.

In the early 1980s, Onogi et al. [3] studied the relationship between shear viscosity and rate of shear for liquid crystalline polymers (LCPs). As described schematically in Figure 2, they found that LCPs are shear thinning at low shear rates (region I), the viscosity levels off at intermediate shear rates (region II), and finally, shear thinning behavior reappears at higher shear rates (region III). This peculiarity was attributed to a "polydomain" structure (a domain being defined as a region of relatively uniform molecular alignment) which exists in stationary LCPs. Initially, as the shear rate increases, the domains are stretched, and the size scale of the structure decreases (region I and II). This behavior is similar to observations of flow-induced microstructures in mesophase pitch made by White et al. [4]. If the shear rate is further increased (region III), the polydomain structure transforms to a monodomain continuum.

McHugh assumed a monodomain structure and successfully modeled the fully developed flow of mesophase pitch through capillaries at high apparent shear rates. However, if the flow in the capillary entrance is to be modeled, the influence of the polydomain structure must be considered. Several studies [5,6,7] have shown that polydomain flow depends on the elasticity of the fluid and the elasticity, in turn, can be estimated by the fluid's flow behavior at low rates of shear.

EXPERIMENTAL

Steady shear viscosity measurements were performed at constant temperature on a synthetic, naphthalene-based mesophase pitch (AR-mesophase, provided by Mitsubishi Gas Chemical Co.) using a Rheometrics RDS II Dynamic Spectrometer. A cone and plate geometry was utilized and the spectrometer was operated at steady rotation. The plate diameter was 25 mm and the cone angle was 0.1 radians. Prior to testing, a small cylindrical sample (approximately 500 mm^3) of mesophase pitch was formed by vacuum pelletization. The sample was placed in the Rheometrics' convection oven, between the cone and the plate. The oven was continuously purged with nitrogen to prevent sample oxidation at high temperatures. During each experiment the oven temperature was controlled to $\pm$ 0.2°C. Also, in order to eliminate transient phenomena, the mesophase was sheared between the cone and the plate for one minute at a fixed rate of shear before each viscosity measurement.

Flow curves were obtained at 305, 310 and 315°C. Finally, fragments of samples were analyzed under polarized light in order to observe the domain structure of the mesophase pitch before and after the experiments.

RESULTS AND DISCUSSION

The naphthalene-based mesophase pitch exhibited shear thinning behavior in the low shear rate region ($\gamma<1$ s^{-1}) at all three temperatures (see Figure 3). However, at higher shear rates the viscosity appeared to become constant (additional experiments in the 0.01-0.1 s^{-1} and 1-10 s^{-1} regions are currently being performed to verify these trends). Polarized light observations of fragments of mesophase pitch not subjected to shear showed that the size scale of the domains was about 20 mm. In contrast, after the experiments the size scale had decreased significantly to about 3 mm. Therefore, the flow curves shown in Figure 3 represent region I and the onset of region II, as defined for the LCPs.

Furthermore, Figure 3 shows that in region I the flow curve has a slope of approximately -1/2

for all three temperatures. This slope is consistent with the model developed by Marrucci [7] for LCPs. In region I, he predicts the following linear relationship between $\log(\eta)$ and $\log(\gamma)$:

$$\log(\eta) = -\frac{1}{2}\log(\gamma) + \frac{1}{2}\log\left(\frac{2\,K\,\eta_0}{a_i^2}\right)$$

where K is an average elastic constant, η_0 is the region II plateau viscosity, and a_i is the size scale of the domains in the quiescent state. This line intersects the horizontal line $\log(\eta) = \log(\eta_0)$ at a critical shear rate γ_c such that;

$$\gamma_c = \frac{2\,k}{a_i^2\,\eta_0}$$

Applying this result to the flow curves of Figure 1 provides an estimate for the average elastic constant of polydomain AR-mesophase pitch at 305 and 310°C. These estimated values, presented in Table 1, are three orders of magnitude higher than those reported for other discotic nematic liquid crystals [8,9]. This high elasticity for polydomain flow is consistent with the long-range flow disturbances on domain structure [10].

CONCLUSIONS

A model developed for LCPs was applied to analyze the low shear rate behavior of AR-mesophase. Based on this approach, the polydomain elasticity of this material at its spinning temperature was estimated to be approximately 1.6×10^{-8} N.

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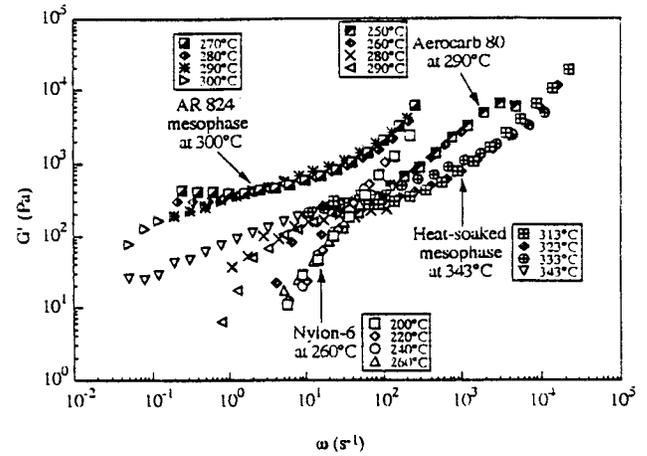10. Nazem F. F., U.S. Patent n° 4,480,977 (1984)

Figure 1: Storage modulus master curves for various pitches and nylon-6 (curves shifted to each material's spinning temperature)
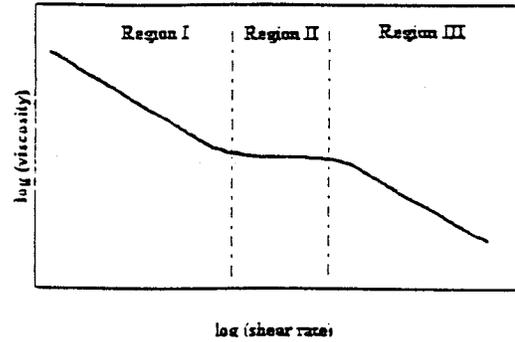

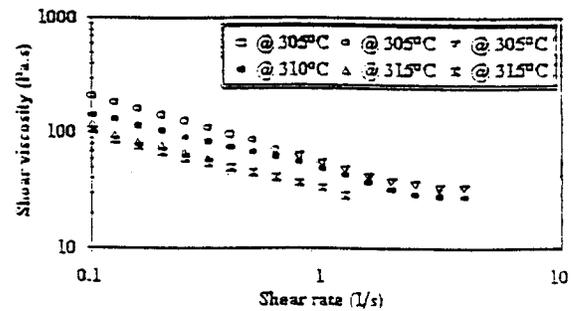Figure 2: Typical flow curve of polymeric liquid crystals

Figure 3: Flow curves for AR-mesophase as a function of temperature

Table 1: Elastic constants for various discotic nematic liquid crystals

Liquid Crystal	Elastic Constant
AR-mesophase pitch	$K = 1.8 \times 10^{-8}$ N @ 305°C
	$K = 1.5 \times 10^{-8}$ N @ 310°C
triphenylene derivative (H7OBT)	$K = 10^{-11}$ N (splay)
truxene derivative ($C_{12}HATX$)	$K = 3 \times 10^{-12}$ N (splay)
	$K = 6 \times 10^{-12}$ N (bend)