RHEOSTRUCTURAL EVOLUTION OF AR-HP MESOPHASE PITCH IN SHEAR FLOW

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Introduction

The properties of pitch-based carbon fibers are known to depend on the microstructure developed during the melt-spinning process [1]. Several experimental and modeling studies have described the microstructural development during melt spinning process for different mesophase pitches [2-6]. However, the anisotropic nature of the textured, liquid crystalline precursors makes the rheological characterization process very difficult. The objective of this study is to perform a rheostructural study for a high performance grade AR mesophase pitch (AR-HP). The rheological response is related to microstructure evolution during transient, low-shear experiments (0.1, 1, and 10 s^{-1}). Before reaching steady state, the shear stress displayed local maximum and minimum values that could be attributed to textural evolution. The shear stress and textural evolution were similar at the three different shear rates. However, the steady-state texture was observed to become finer as the shear rate increased from 0.1 to 1 s^{-1}. Flow reversal experiments confirmed that the transient stress response is directly related to textural changes.

Experimental

A naphthalene-derived mesophase pitch (AR-HP grade, Mitsubishi Gas Chemical Company) prepared with HF/BF_3 catalyst was used throughout the study. The softening point of the material was approximately 270°C. The low shear rate experiments, both rate sweep and transient tests at individual shear rates, were carried out on Rheometrics ARES rheometer using a cone and plate of 25 mm diameter with a cone angle of 0.1 radian, at a temperature of 297°C. Before rheological experiments, vacuum pelletized samples were annealed for 80 minutes in nitrogen environment while keeping the cone separated from the plate to remove gas bubbles from the samples. These bubbles were likely due to the air entrapped during sample preparation, in addition to a small extent of sample volatilization (less than 0.5 wt% as measured by thermogravimetric analysis). All the rheological experiments were repeated at least three times and 95% confidence intervals are shown on the graphs.

After rheological experiments, the samples were quenched and carefully embedded in epoxy blocks for microstructural study. The polished samples were studied under an Olympus BX-60 microscope with a parallel-polarized light and a quarter wave plate. A pyrolytic graphite sample was used for color calibration to determine the orientation of a sheared sample. The regions parallel to the flow direction appeared orange-red, whereas those perpendicular to flow direction appeared light blue (cyan); the isotropic regions appeared gray.

Results and Discussion

Figure 1a displays the steady shear viscosity values at different shear rates. Regions I and II that are typical of liquid crystalline materials were observed for AR-HP. The viscosity values were about 50% lower than those measured for other grades of pitches reported in earlier studies [3,4]. The “kink” in region I viscosity curve, observed in earlier study [3], was also noticed for ARHP. The measured primary normal stress difference (N_1) values are displayed in Figure 1b; the N_1 values, however, were small and within the transducer resolution limit (~ 80 Pa).

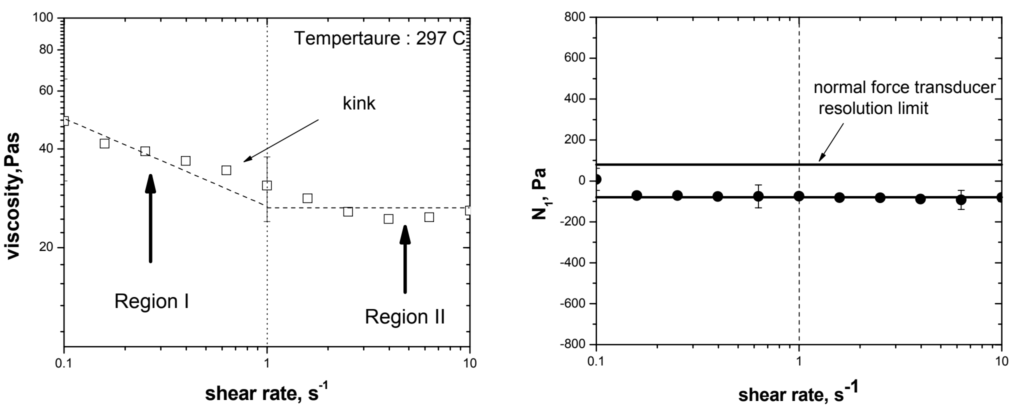

Figure 1: Viscosity and primary normal stress difference (N_1) vs. shear rate for AR-HP mesophase pitch at a temperature of 297°C

Figures 2a and 2b display on linear and semi-log scale, respectively, the transient viscosities of ARHP at two different shear rates, 1 s^{-1} and 10 s^{-1}. For both shear rates, local maxima at 1 strain unit (su) and minima at 6 su were observed. The viscosity values reached a steady state after ~100 su. For the shear rate of.1 s^{-1}, a small second overshoot was noticed before the viscosity reached steady state. The viscosity response for a calibration fluid is shown in Figure 2c; the steady value of 14 Pa.s confirms the accuracy of the viscosity measurements. No undershoot or overshoot was observed for the calibration fluid, which also confirms that the peculiar transient response observed for the mesophase is not an experimental artifact, but a likely consequence of the structure of the liquid crystalline fluid.

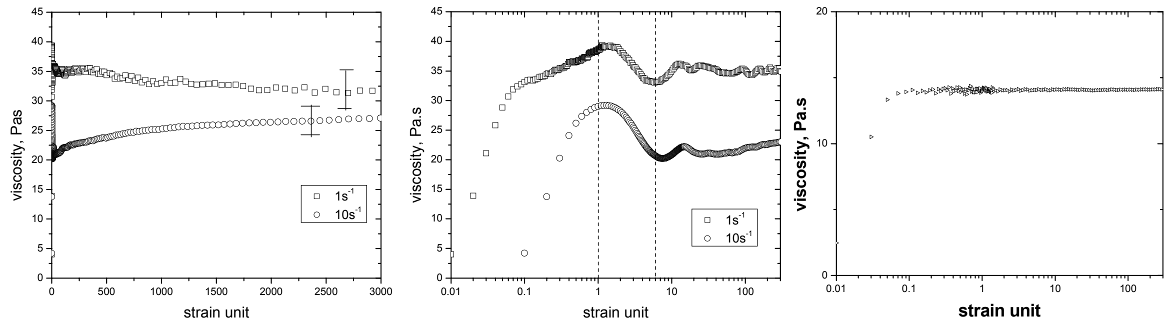

Figure2: Transient rheological responses for the shear rates of $1s^{-1}$ and $10s^{-1}$ plotted in: a) linear scale, b) semi-log scale for AR-HP and c) for calibration fluid

To investigate the origin of the stress maxima/minima, the microstructure of the quenched molten samples was characterized by polarized optical microscopy at various stages of the shearing history. The microstructure for a melt that was annealed for 80 minutes on the bottom plate of the rheometer is displayed in Figure 3a. The texture appears to be of the order of 100 μm in size and fairly random. After the cone was brought into contact with the melt and the normal stress generated due to squeezing flow was allowed to relax, a sample was again obtained. For this sample, radial pattern is evident in the microstructure of Figure 3b even though the normal stress had decayed to 0 after about 5 minutes. Thus, the textural relaxation time can be estimated to be at least of the order of few minutes, in contrast to a few seconds for flexible chain polymeric melts.

(a) (b)

Figure 3: Microstructure of a) annealed sample; (b) after 5 minutes of waiting with cone and plate together (the arrow ↑ shows the radial direction of the plate)

The evolution of the texture from the initial "radial" state described above is illustrated in Figure 4 for a shear rate of 1 s^{-1}. Initially, the stress increased with strain. The maximum value of stress reached at ~1 su, where the microstructure was still radial. Then the melt started to orient along the flow direction and the stress started to decrease. As seen in the next micrograph, the entire sample started to orient along flow direction at ~6 su, which corresponds to a minimum in shear stress. After the minimum, the stress increased with increasing strain and ultimately reached a steady state. The domains appear more oriented along the flow direction at ~20 su, and reached a steady orientation and size after ~100 su.

Figure 5 shows the initial, intermediate, and steady state microstructure for quenched melts after flow at shear rates of 0.1, 1, and 10 s^{-1}. Microstructure evolution was similar for all the shear rates, i.e., initial “radial” structure transformed to flow aligned structure. However, the texture became finer at high shear rates. At the highest shear rate of 10 s^{-1}, the texture became very fine and could not be distinguished clearly by optical microscopy.

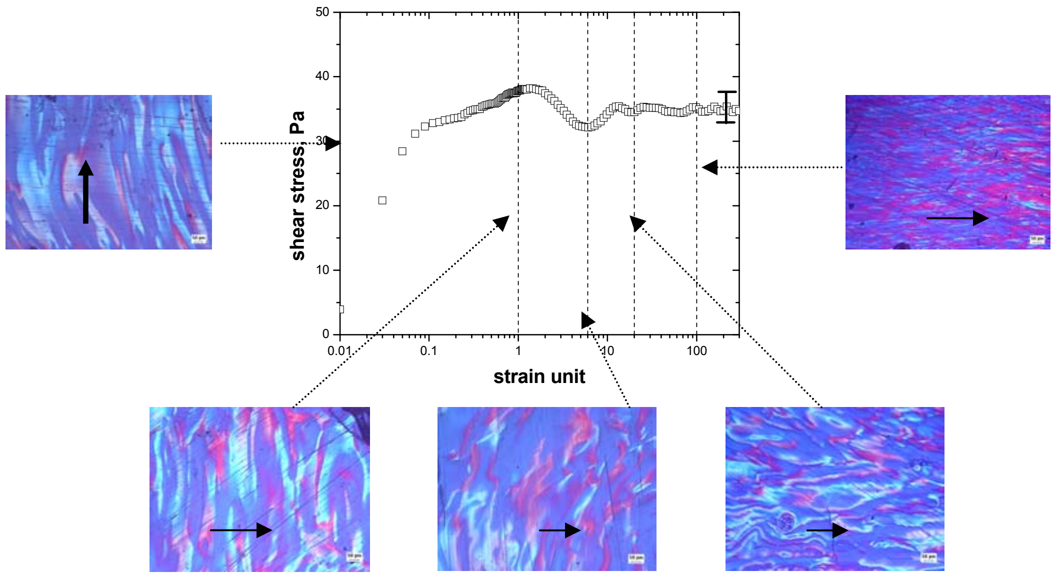

Figure 4: Rheological and microstructural data for AR-HP pitch at a shear rate of 1s^{-1} (the arrow ↑ represents the radial direction of the cone-plate fixture and the arrow → represents flow direction)

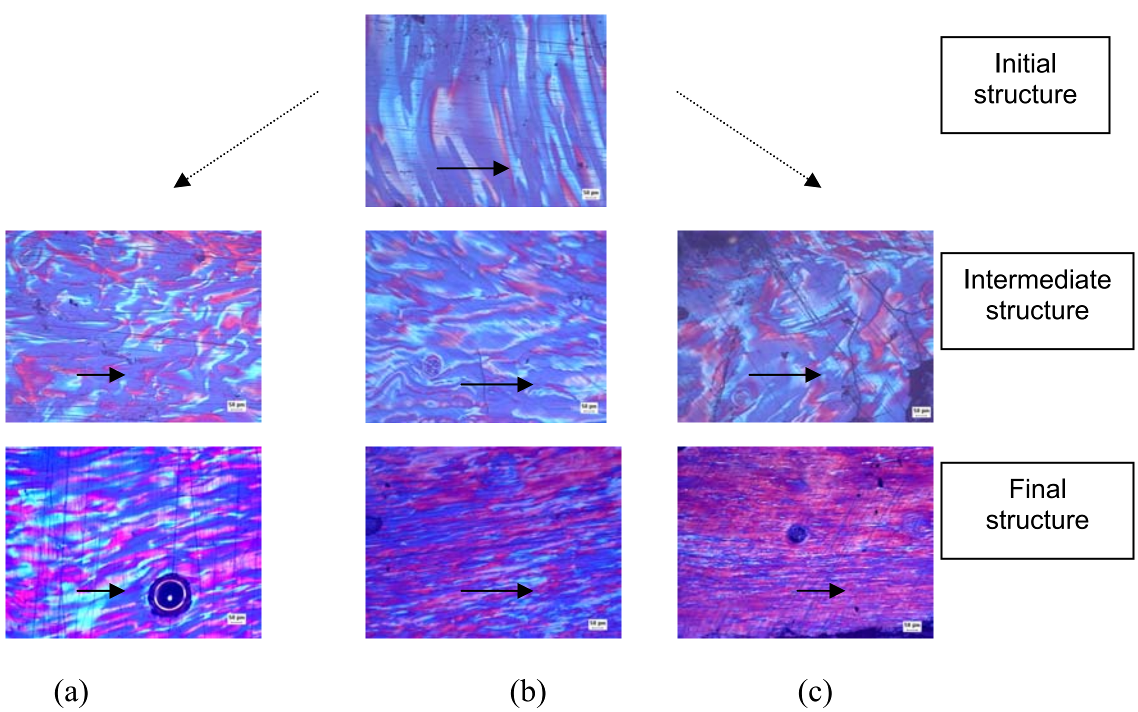

Figure 5: Evolution of microstructure for AR-HP mesophase pitch at 297C at shear rates of (a) 0.1 s^{-1}, (b) 1 s^{-1}, (c) 10 s^{-1} (the arrow → represents flow direction)

Flow reversal experiments were also performed at a shear rate of 1 s^{-1} and results are displayed in Figure 6. On a linear strain scale, Figure 6a shows that after the first steady state is achieved and the flow direction is reversed (at 3000 su), the stress rapidly approaches an identical steady state (as the first one, except in the opposite direction). To evaluate the transience associated with the flow reversal, the same data are also plotted in Figure 6b on a logarithmic strain scale. It is evident that no maxima or minima are observed during flow reversal. Furthermore, the final microstructure observed after flow reversal is similar to that obtained after the first steady state. Thus, it can be inferred that texture evolved during the initial startup of flow and reached a steady state, but did not change when the flow direction was reversed. As a result, a fairly monotonic transient response was obtained during flow reversal.

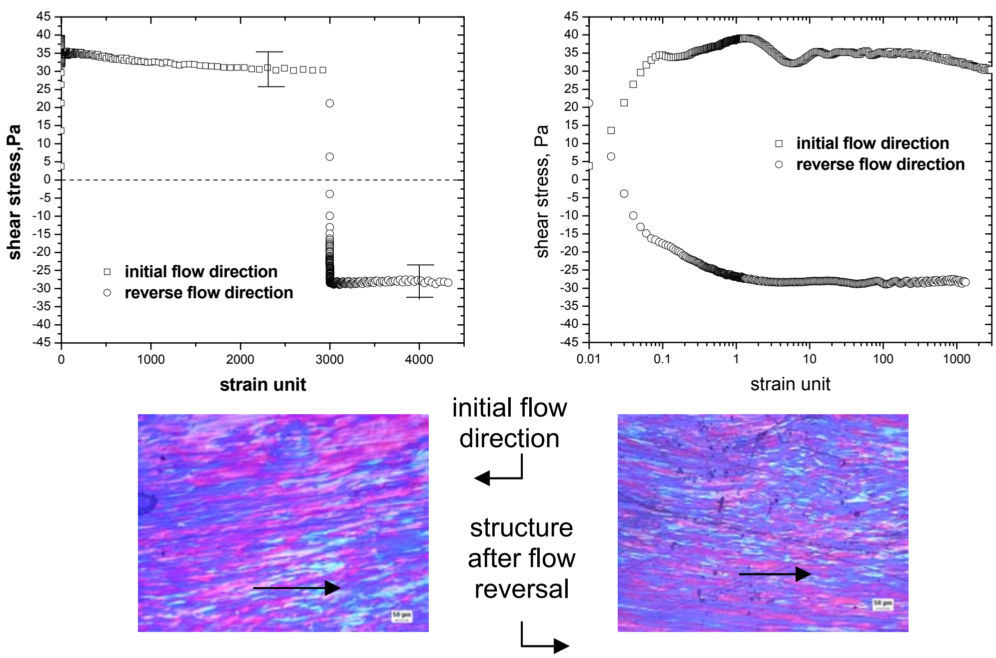

Figure 6: Typical shear stress response of AR-HP to flow reversal experiment at a shear rate of 1s^{-1}. Also illustrated is the microstructure after flow reversal experiment, compared to a steady state microstructure (the arrow → represents flow direction)

Conclusions

The rheostructural evolution of discotic AR-HP mesophase melt with increasing strain history was measured at different shear rates. The occurrence of local maxima and minima in transient viscosity could be attributed to the transformation of structure to a flow-aligned state. This steady state structure did not change when the flow direction was reversed; the local maxima and minima were also not observed during flow reversal transience.

Acknowledgements

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