INVESTIGATION OF FLOW AND MICROSTRUCTURE IN RHEOMETRIC AND PROCESSING FLOW CONDITIONS FOR LIQUID CRYSTALLINE PITCH

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Introduction

The microstructure development within mesophase pitch based carbon materials depends on the flow history that the pitch is subjected to. Therefore, a fundamental understanding of the flow and its influence on the microstructure is required to obtain carbon materials with desired properties. Despite several studies, the flow-microstructural behavior of mesophase pitch is not completely understood and therefore, the goal of this study was to investigate flow-microstructural behavior of a recently available, naphthalene-based mesophase pitch (AR-High Performance grade, Mitsubishi Gas Chemical). The softening point of the AR-HP grade of mesophase pitch is 285°C, approximately 10°C lower than that reported for previous grades of mesophase pitches. The lower softening point was likely caused by different molecular constituents as compared to those present in previous grades. Such differences in molecular constituents can result in different flow behavior and processability of the precursor. In this research the flow and microstructural behavior of AR-HP mesophase pitch was investigated in rheometric and processing flow conditions. In addition, simulation studies were performed in simple shear flow to establish a frame work for modeling the flow behavior of this complex material in different flow situations.

Results and discussion

The rheological experiments were conducted after developing an experimental protocol [Kundu and Ogale, 2006] on a well-calibrated TA Instruments ARES rheometer using a cone-plate fixture of 25 mm diameter with a cone angle of 0.1 rad. A majority of the tests were conducted at 297°C; limited tests were also performed at 290 and 305°C. These temperatures were selected for rheological experiments due to good melt-processability of AR-HP mesophase in this range [Cho et al., 2003]. Steady shear viscosities, as measured by conventional rate-sweep experiments, are displayed in **Figure 1** starting from a low shear rate of 0.1 s^{-1} and extending to 10 s^{-1}. Shear-thinning (Region I) and Newtonian plateau (Region II) responses were observed for the AR-HP mesophase pitch, which are similar to those reported in prior studies on other mesophase pitches [Mochida et al., 2000; Dumont et al., 2003; Cato et al., 2005] and TLCPs [Guo et al., 2005]. However, the plateau viscosity of 15 Pa.s for AR-HP at 305°C was approximately 2-3 times lower than that reported for ARA24R [Cato et al., 2005]. The viscosity in Region I was found to decrease with shear rate, however, the power-law exponent of -0.2 observed for AR-HP grade was found to be smaller in magnitude than -0.5 reported in the literature for ARA24R and other mesophase pitches [Cato et al., 2005 and references therein].

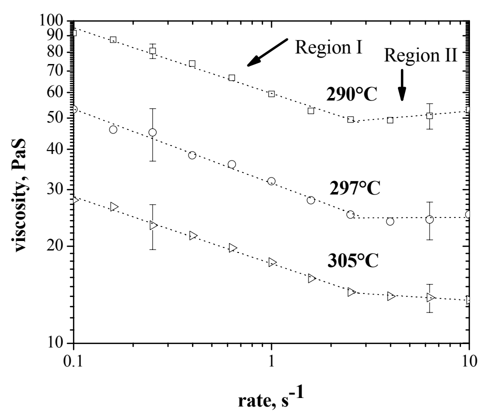

Figure 1: Steady shear viscosity of mesophase pitch from rate-sweep experiments for increasing shear rates. Dotted lines represent linear least-squares fit.

The theoretical basis for the -0.5 slope has been provided by the scaling arguments of Marrucci that equate elastic stresses to viscous stresses [Larson, 1999]. However, for this scaling argument, it was assumed that the number of disclinations remains unchanged and the domains deform under shear flow without any coalescence or break-up. These simplifying assumptions need not hold in real systems, and as a result the predicted slope need not be exactly -0.5. Also, slopes shallower than -0.5 are not uncommon for liquid crystalline polymers [Walker et al., 1995], with some displaying little initial shear-thinning [Kim and Han, 1993] (i.e., a power-law exponent of ≈0).

The evolution of the transient shear stress response to a steady state was measured, and is reported as a function of strain (product of shear strain-rate and test time). **Figure 2** shows the results for a shear rate of 1 s^{-1} at 297°C. After the initial transience, the shear stress approached a steady-state value, and remained fairly constant at 35±2 Pa over 3000 strain units

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(*su*). To investigate the transient response that got masked in **Figure 2a** due to a compressed strain-scale, the same stress results are plotted up to a strain of 100 units on a logarithmic strain scale (**Figure 2b**). A local stress maximum was observed at a strain value ranging from 1.1 to 1.7 *su,* and a local minimum was observed in the range 5-8 *su*; these strain values are approximated as ~1 *su* and ~6 *su*. During transient tests, local maxima and minima were observed in transient shear stress for various shear rates and temperatures tested [Kundu and Ogale, 2006].

After rheological experiments, the samples were collected by developing an experimental protocol for preservation of the sample for microstructural analysis. Microstructural observations obtained for three orthogonal sections such as r-ϕ or vorticity-flow plane, r-θ or vorticity-gradient plane, and θ−ϕ or gradient-flow plane (inset of **Figure 3**). The microstructure evolution for the shear rate of $1s^{-1}$ is displayed in **Figure 3**. It was observed that the local maximum in shear-stress was due to yielding of initial microstructure. The microstructure became flow-oriented with further shearing and structure size decreased with increasing shear rates [Kundu and Ogale, 2006]. Also, during flow reversal experiments following steady flow at $1s^{-1}$, where the microstructure was already evolved, absence of maximum/minimum confirms that the nonmonotonic behavior during flow startup was directly related to the initial microstructure of the discotic AR-HP mesophase pitch [Kundu and Ogale, 2006].

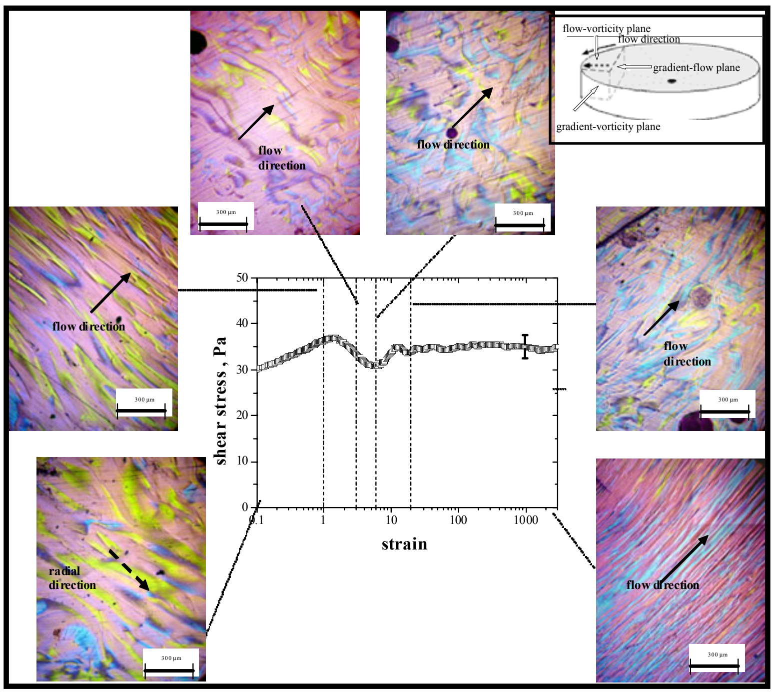

Figure 3: Rheo-structural evolution of mesophase pitch at 297°C and a shear rate of $1s^{-1}$.

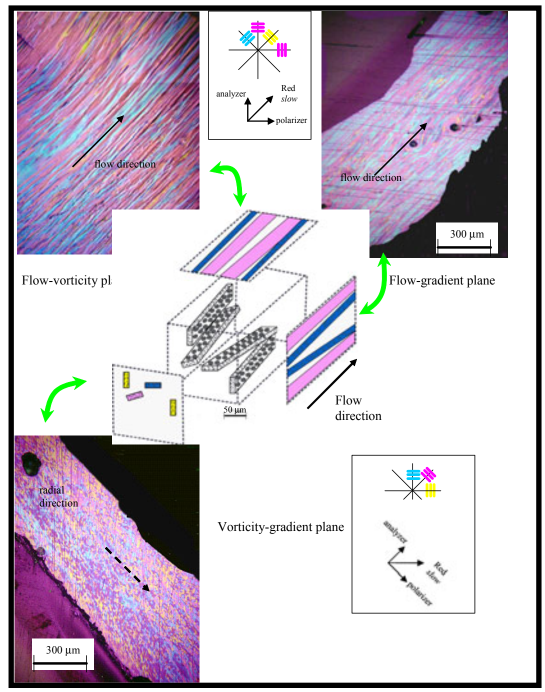

Figure 4: Microstructure for three orthogonal sections for a steady-sheared sample at $1s^{-1}$ together with possible schematic of 3-d structures is shown. A few isochromatic regions are shown schematically. Position of polarizer-analyzer is also shown.

Based on the microstructural evidence, a possible three-dimensional schematic for the steady-sheared (at 1 s^{-1}) mesophase sample is constructed and is shown in **Figure 4**. The actual micrographs and the projected microstructure for three orthogonal sections are also shown. The flow direction is identified in the schematic and the rectangular boxes representing the isochromatic regions observed in the optical micrographs. These boxes indicate the average orientation of collection of molecules in a particular direction. The average director orientation of these molecules is along the normal to the largest rectangular face. For the typical configuration of polarizer -analyzer and first order red plate that was used in this study, sections of the ioschoromatic regions where the layer-plane orientation was edge-on in vorticity-flow plane and gradient-flow plane will appear blue. It was surmised that the director orientation of steady-sheared sample was in the vorticity or gradient direction or at some angle in between. Therefore, similar microstructure was observed in vorticity-flow plane and gradient-flow plane. The cross-sectional view of these structures, as viewed in vorticity-gradient plane, would be rounded, finer, and oriented in all directions, leading to blue, yellow, and magenta colors (note the polarizer-analyzer direction for vorticity-gradient plane).

The flow-microstructural study was extended to the processing flow conditions and in this case AR-HP mesophase pitch was extruded through custom-made dies using a single-screw extruder. Due to changing dimensions of these dies, the mesophase pitch was subjected to varying shear rates. In these dies, the wall-shear rate was low (~$10s^{-1}$) in the counterbore, but quite high (~1000 s^{-1}) in the capillary. Microstructural observations, as displayed in **Figure 5a**, suggest that in the capillary region of these dies, the orientation of the layer-plane was approximately radial near the wall. Away from the wall, the deviation of orientation of the layer-planes from the radial direction was significant and some layer-planes were oriented tangentially. In the core, the microstructure was coarse and no preferred orientation of mesophase layer-planes was observed. A schematic showing the layer-plane orientation for a typical cross-section is displayed in **Figure 5b** for the microstructure shown in the second quadrant. The lines in this schematic represent the edge-on layer-planes. Also, as observed from the microstructure in the longitudinal mid-plane, both in the counterbore and in the capillary, the layer-planes nominally remained in the flow plane [Kundu, 2006].

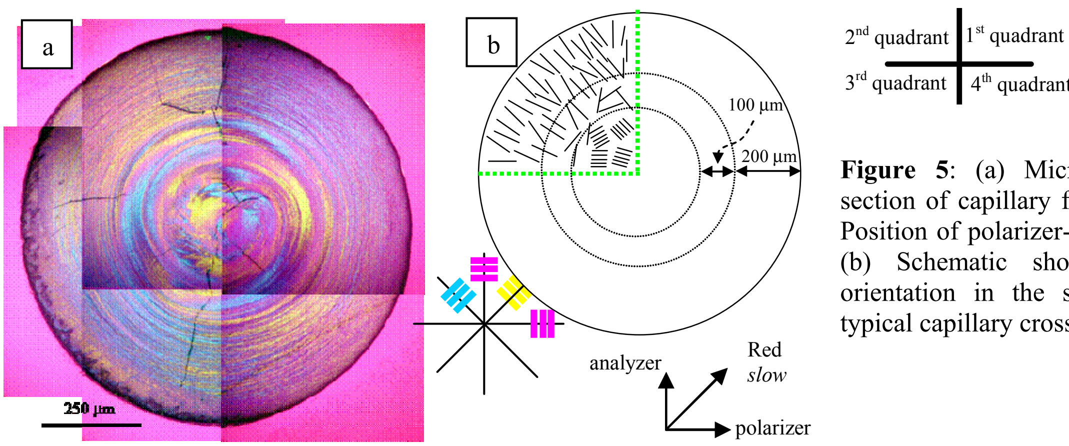

Figure 5: (a) Micrograph of the cross-section of capillary for a die with L/D =20. Position of polarizer-analyzer is also shown. (b) Schematic showing the layer-plane orientation in the second quadrant for a typical capillary cross-section.

Simulation studies were performed using constitutive equations for discotic liquid-crystalline materials [Grecov and Rey, 2003] in simple shear flow [Kundu, 2006; Oehsen et al., 2007], for different initial conditions, corresponding with the experimental studies. As shown in **Figure 6b**, initially the discs were oriented in such a way that directors were oriented in the flow-direction (the coordinate system and the director for a typical disc are defined in **Figure 6a**). At steady state, simulation results indicate that the bulk of the discs were found to be oriented at a flow-alignment angle, which is consistent with the theoretical predictions [Grecov and Rey, 2003]. At the boundaries, the orientation was pre-determined by the strong anchoring, but the orientation gradually changed to a flow-aligned state. Although the simulation studies could not capture the complex flow-aligned structure observed experimentally, similarities in results were observed. This study establishes a frame work for future simulation of the flow dynamics of complex mesophase pitch system in multiscale-mulidimensional problems.

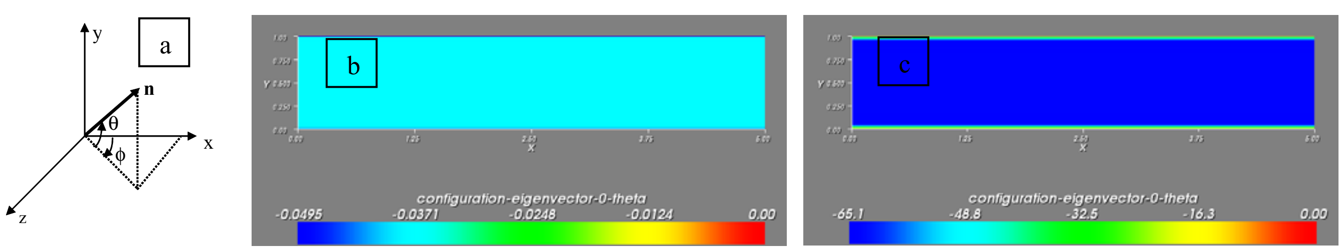

Figure 6: (a) Cartesian coordinate system used in this study, where x is the flow direction, y is the velocity-gradient direction, and z is the vorticity direction. **n** represents the director orientation. θ and ϕ are the tilt and twist angles, respectively, (b) Contour plot of tilt angle, θ over the entire computational domain initially (after 5 iterations), (c) Contour plot of tilt angle, θ, over the entire computational domain at steady state (after 52550 iterations).

Concluding remarks

This research captures the flow, microstructure and their interrelationship in different flow situations. The evolution of microstructure was uniquely studied in three orthogonal planes. The systematic understanding of flow and its effect on microstructure will help the scientists to predict/model the complex flow behavior and microstructural evolution of this material, which in turn will help to design carbon materials in more efficient ways.

Acknowledgements

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