A VISCOELASTIC CONSTITUTIVE EQUATION FOR MESOPHASE PITCH

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Introduction

Mesophase pitch is an important precursor for the production of high modulus and high thermal conductivity carbon fibers. The final properties of these fibers are greatly influenced by the molecular orientation induced during fiber spinning. In order to understand and control the molecular orientation of the spun fiber, the flow characteristics of mesophase pitch must first be understood.

Molten mesophase pitch is a non-Newtonian, viscoelastic fluid. In order to model the flow behavior, a viscoelastic constitutive equation must be chosen that adequately models the stresses within the fluid. Recently, viscoelastic constitutive equations developed for polymers have been used to model the response of mesophase pitch [1]. The upper-convected Maxwell model has been used to model the flow of mesophase pitch through capillaries and found to give good qualitative agreement [2].

Experimental

The material used in this study was a synthetic, naphthalene-based mesophase, produced by Mitsubishi Gas Chemical Company. This mesophase was manufactured to minimize the volatile content noted in previous AR mesophase. The sample preparation for rheological characterization involved grinding the mesophase into a fine powder and then compressing the powder into a small cylindrical pellet.

Both steady shear and oscillatory experiments were performed using a Rheometrics RDS-II controlled strain rheometer. A 25mm cone and plate (cone angle of 0.1 radians) geometry was used for the steady shear experiments, whereas a 25mm parallel plate geometry was used for the oscillatory experiments. Experiments were performed at five different temperatures that span the typical range of fiber spinning, 305°C to 325°C. During the steady shear experiments, both the torque and normal force were measured. This allowed the calculation of both the viscosity, η, and the first normal stress difference, N_1. Prior to running an oscillatory experiment at a given temperature, the linear viscoelastic region (LVER) was determined by a strain sweep. Then, based on the sample's response to the imposed strain, the storage modulus, G', the loss modulus, G", and the dynamic viscosity, η', was calculated.

Results and Discussion

The steady shear viscosity response shown in Figure 1 exhibits a shear-thinning region followed by a plateau or Newtonian viscosity. This response is typical for liquid crystals of low molecular weight [3]. The shear-thinning region of each viscosity curve can be explained using Marrucci's model of polydomain flow [4]. Marrucci's model predicts the slope of the shear-thinning region to be -1/2. In Figure 2 we see that the slope of the shear thinning region is nearly -1/2. Other researchers working with AR mesophase pitch have reported a similar result [5].

As mentioned before, the upper-convected Maxwell model was used in previous work to qualitatively model the flow of AR mesophase. As seen in Figure 3, the model does not fit the experimental data well. A reason for this is that the model uses only two parameters, λ and η, to describe the dynamic data. It is possible to use a multiple relaxation time model (1) to improve the fit to the data.

$$\tau = \sum_{k=1}^{n} \tau_k \tag{1}$$

$$\tau_k + \lambda \hat{\tau}_k = 2\eta_k D \tag{2}$$

where τ_k is the k^{th} upper-convected Maxwell model (2) with parameters λ_k and η_k. Other viscoelastic constitutive equations (White-Metzner, Phan-Thien Tanner, Giesekus-Leonov) will also be tested as possible expressions for the stress tensor. These results and the experimental oscillatory data will be also be presented.

Conclusions

This study indicated that the steady shear rheology of this AR mesophase pitch follows a typical response for a low molecular weight liquid crystal. In fact the shear-thinning region follows Marrucci's model for polydomain flow. The upper-convected Maxwell model does not adequately predict the oscillatory response of the mesophase.

References

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Acknowledgments

The authors would like to thank the Office of Naval Research (Contract #N00014-95-1-1345) for its support of this project. Thanks are also due to Mitsubishi Gas Chemical Company for providing the AR mesophase pitch. This work made use of ERC shared facilities supported by the National Science Foundation under award number EEC-9731680.

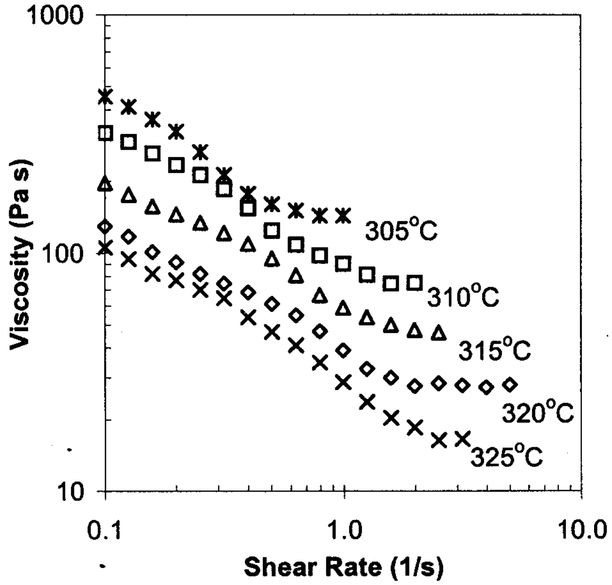

Figure 1. Steady shear viscosity vs. temperature for an AR mesophase pitch.

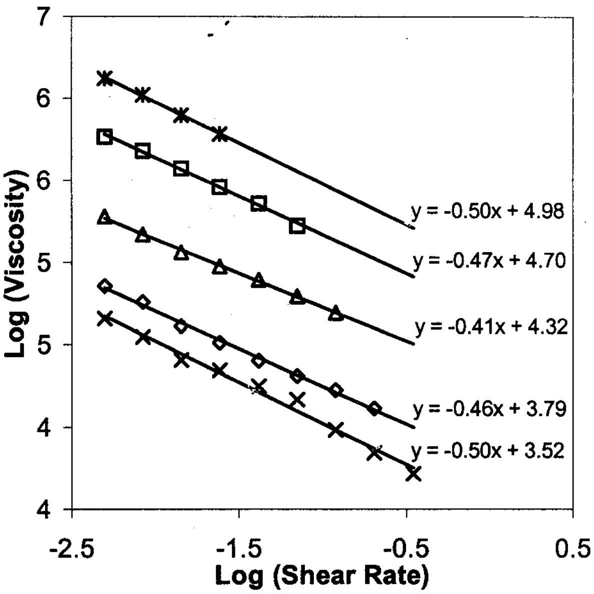

Figure 2. Slope calculation for shear-thinning region of steady shear curve.

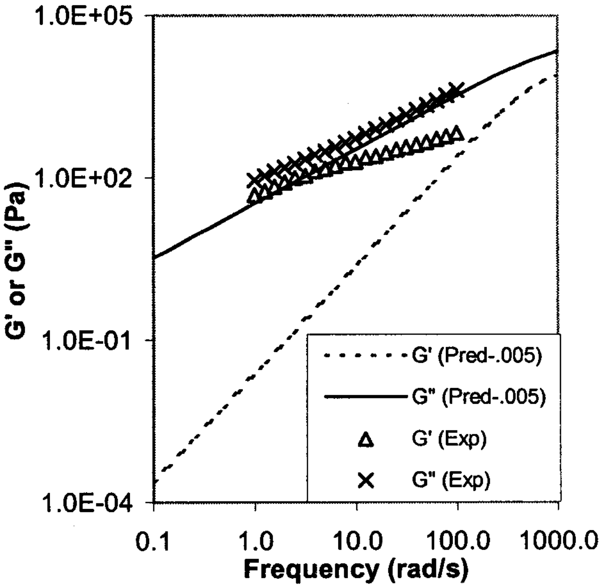

Figure 3. Upper-convected Maxwell model predictions for the storage and loss modulus vs experimental data.