THE EFFECT OF MESOPHASE COMPOSITION ON RHEOLOGY AND FINAL FIBER PROPERTIES

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Introduction

The ability of mesophase pitch to develop a high degree of molecular orientation during flow makes it an ideal precursor for high modulus carbon fibers [1]. However, as one might expect, the lattice-dependent properties of these fibers are highly influenced by the microstructure generated during flow through the spinneret [2-3].

In this study, the rheological behavior of synthetic naphthalene-based (AR) mesophase pitch, supercritically extracted (SCF) mesophase pitch, and mixtures of the two were examined in both the steady and dynamic modes. Then round-shaped carbon fibers were spun from the same mesophase samples, and after heat treatment, their properties were compared.

Experimental

The synthetic naphthalene-based (AR) mesophase pitch used in this study was provided by Mitsubushi Gas Chemical Company. The supercritically extracted (SCF) mesophase pitch was prepared at Clemson with a pilot-scale apparatus at conditions of 320°C, 94 bar, and a solvent-to-pitch ratio of 3.5 [4]. Mesophase mixtures were prepared in a reaction kettle under inert atmosphere at temperatures between 300°C and 320°C. These mixtures were 25% wt. SCF & 75% wt. AR, 50% wt. SCF & 50% wt. AR, and 75% wt. SCF & 25% wt. AR.

The rheological behavior of each mesophase type was determined using the Rheometric Dynamic Spectrometer (RDS-II). The shear viscosity response was measured using a cone and plate, and the oscillatory (dynamic) response was measured using parallel plates. Master curves for the dynamic responses were created via a time-temperature superposition [5].

Round-shaped carbon fibers with as-spun diameters between 12 to 14 μm were produced using a bench melt spinning apparatus at different shear rates. The as-spun fibers were then stabilized and carbonized to enhance their electrical and mechanical properties.

Results and Discussion

Figure 1 shows the viscosity as a function of shear rate for each mesophase type. The viscous response of each mesophase was measured at the appropriate melt spinning temperature with the same plateau viscosity of 45 Pa s. The low shear viscosity (0.1 to 1 s^{-1}) of all the mixtures is lower than the parent mesophase pitches (AR and SCF). This could be because the mixing of the mesophase pitches may decrease the intermolecular forces and/or decrease the average domain size.

Figure 2 shows the dynamic response of AR mesophase, and Figure 3 shows the typical dynamic response of all the mixtures. Delta (δ), the phase angle between the imposed strain and resulting stress, provides insight on the elastic nature of a given material. Delta for the AR mesophase begins at a value of 50°, while for all the mixtures it begins at a value of 65° in the low frequency range. This shows that all the mixtures are less elastic than the AR mesophase in this range.

Table I shows that incorporating a small fraction (25% wt.) of AR mesophase pitch with SCF pitch increased spinning yields by a factor of seven compared to the yields of pure SCF.

Table II shows the final fiber properties of the mesophase mixtures used in this study. The electrical resistivity and tensile modulus follow a similar trend. As the percent SCF is increased, the shear rate has to be increased to achieve desired properties. The 25% SCF mixture at a shear rate of 6200 s^{-1} has the best final properties of all the fibers in this study (i.e. lowest electrical resistivity and highest modulus). Carbon fibers with these properties are preferred so that they can be used in various industrial applications, e.g, C/C composites.

Conclusions

Surprisingly, even with their different structures and domains, mesophase mixtures all display similar rheological responses. These mesophase mixtures have successfully been spun into carbon fibers with desirable final properties (high modulus and low electrical resistivity).

References

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Acknowledgements

Research sponsored by the Army Research Office and Office of Naval Research.

This work made use of ERC shared facilities supported by the National Science Foundation under award number EEC-9731680.

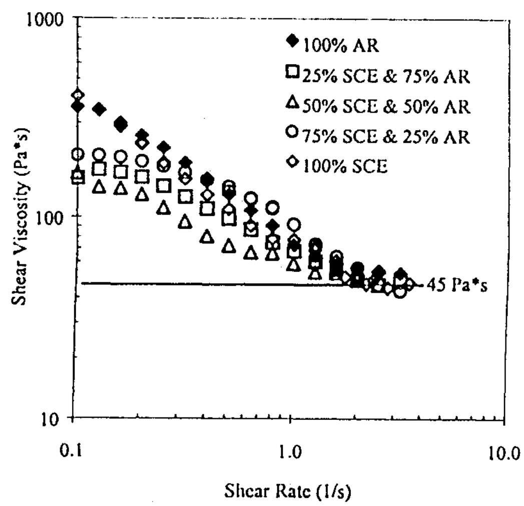

Figure 1. Shear Viscosity versus Shear Rate

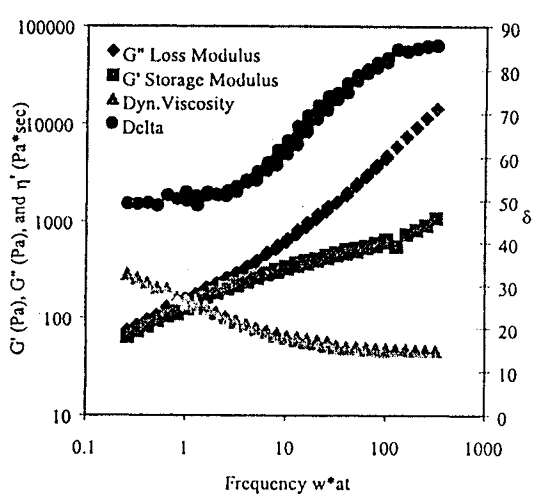

Figure 2. Master Curve for AR Mesophase

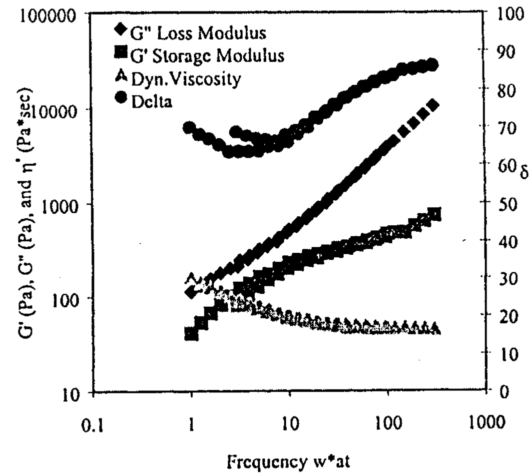

Figure 3. Typical Master Curve for Mixtures

Table I. Percent Spinning Yield

Mesophase Type	% Yield
100% AR (unmixed)	20.0
25% SCF & 75% AR (mixed)	18.3
50% SCF & 50% AR (mixed)	18.5
75% SCF & 25% AR (mixed)	17.5
100% SCF (unmixed)	2.4

Table II. Final Fiber Properties of Mesophase Mixtures

% SCF	25	50	75
T^a (°C)	319	335	341
η^b (Pa s)	36 ± 5	31 ± 5	47 ± 9
Shear Rate (s^{-1})	Electrical Resistivity[c] (μΩm)		
6200	**4.23 ± 0.07**	**4.53 ± 0.10**	4.93 ± 0.25
8300	4.63 ± 0.19	**4.53 ± 0.12**	5.16 ± 0.26
11000	4.66 ± 0.15	4.98 ± 0.21	**4.63 ± 0.12**
Shear Rate (s^{-1})	Tensile Strength[d] (GPa)		
6200	2.86 ± 0.24	2.73 ± 0.22	2.83 ± 0.37
8300	2.53 ± 0.20	2.57 ± 0.22	2.48 ± 0.23
11000	1.97 ± 0.40	2.35 ± 0.22	2.16 ± 0.25
Shear Rate (s^{-1})	Tensile Modulus[e] (GPa)		
6200	**901 ± 31**	804 ± 26	773 ± 61
8300	775 ± 38	**854 ± 30**	724 ± 44
11000	772 ± 39	784 ± 40	**791 ± 46**

a melt temperature ± 2°C c,d,e ±95% c.i.
b extrusion viscosity