RHEOLOGY AND FIBER SPINNABILITY OF SELECT PETROLEUM AND COAL-TAR PITCHES

Young-Pyo Jeon[#], Meng Zhang[#], and Amod A. Ogale[#]
Chris Levan[*]
James Connell[+]

[#]Chemical Engineering and Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC 29634
* Carbon Fiber Solutions, Alpharetta, GA 30004
+ Advanced Thermal Technology, Upton, MA 01568

Introduction

Carbon fibers are important in a wide range of specialized applications because of their superior properties, such as high strength, stiffness, thermal stability, and thermal conductivity [1]. Carbon fibers are produced from mesophase pitch precursors, which in turn are derived from isotropic petroleum pitch and coal-tar. Such precursors can be cost-competitive if they can be melt-processed. In this research, characteristics of selected pitches, S_2-S_6, have been investigated and compared with those of a synthetic grade Mitsubishi AR-MP (labeled S_1).

S_2 and S_3 samples were coal-tar based, S_4 was petroleum based experimental pitches, and S_5 and S_6 were isotropic pitches. L_1 and L_2 were experimental petroleum based pitches prepared by Carbon Fiber Solutions, based on KOPPERS' isotropic pitch, and contained nominally 75 and 100% mesophase, respectively. The research on these selected pitches was initiated by testing material properties, namely, softening point (SP) and shear viscosity. Transient shear viscosity of experimental grades and their mixtures with AR-MP were measured. The characteristic maxima and minima observed for transient viscosity of discotic liquid crystalline AR-MP are compared with that for the experimental grades.

Experimental

The softening points of these experimental pitches were measured at a scanning rate of 2°C/min using a Mettler SP unit. The transient shear viscosity of selected pitches was measured using cone-plate fixtures in a *ARES II* rheometer. For rheological experiments, about 1g of pitch powder was compacted at 15,000 psi for 5 mins. Viscosity measurements were conducted under N_2 atmosphere. After 1 hour annealing of the melt at the test temperature [2], viscosity of experimental mesophase pitches, L_1 and L_2, was measured.

A batch, melt-spinning machine was used throughout the study for the assessment of fiber spinnability. AR-mesophase pitch (Mitsubishi Gas and Chemicals, Japan) was used for control purposes, and selected experimental pitches were used for spinnability study. The 12-hole spinneret consisted of capillaries with a diameter of 150 μm. Thicker fibers were spun at lower take-up speed, whereas thinner fibers were spun at higher take-up speeds.

For the study of oxidation kinetics of experimental pitch fibers, series of thermal analysis were conducted. Optimum stabilization condition for each carbon fiber was determined based on these thermal studies. The high temperature treatment of the stabilized fibers was conducted in *Astro1100* furnace equipped with suitable temperature controllers and vacuum pumps. Stabilized fiber samples were loaded in the furnace, and the furnace was evacuated to 0.1 Torr and then purged with helium gas; this cycle was repeated three times to ensure an inert environment. The heating rate was 20°C/min, dwell-time was one hour at the final temperature, and cool-down to ambient temperature was at a rate of 30°C/min.

Fiber diameters were measured by three techniques: (a) *Olympus BX60* optical microscope, (b) custom built laser scattering method, and (c) scanning electron microscopy (SEM *Hitachi, S4800 FESEM*). SEM was also used to characterize the microstructure and obtain the cross-sectional areas of heat treated fibers.

Next, single filament tensile comprehensive testing was conducted using *MTI Phoenix* testing equipment following standard procedures. Then, the thermal conductivity of the heat treated fibers was predicted based on the electrical resistivity data, which is obtained by using 4-probe resistivity measuring method. For thermal conductivity predictions, Lavin-Issi [3] correlation proposed for mesophase pitch–based carbon fiber was used

$$k = 440,000 / (\rho+258) - 295 \qquad (1)$$

where k [W/m·K] is thermal conductivity and ρ [μΩ·cm] is the resistivity.

Results and Discussion

Table 1 displays the softening points of experimental pitches, $S_2 \sim S_6$, and their mixture with a synthetic grade pitch S_1 (AR-MP). Two isotropic pitches, S_5 and S_6, showed lower softening point (~110°C), whereas S_2-S_4 pitches displayed higher softening point, over 330°C. As shown in Table 1, viscosity of S_4 at 380°C was over 1800 Pa·s indicating that S_4 is likely not suitable as a fiber grade.

As an indication of mesophase structure breakage, the transient viscosity curve of S_1 (AR-MP) pitch at 300°C showed a typical peak behavior, which was not observed in the viscosity of isotropic pitches, S_5 and S_6.

The softening point and viscosity reduction by adding S_1 synthetic pitch into S_3 introduced a possibility of spinning at alower temperature. However, impurities in S_3 made the mixture difficult to spin. Overall, the idea of mixing synthetic grade AR pitch with other pitch seems plausible; however, the target pitch should be purified to ensure stable spinning.

Table 1. Rheological properties of experimental pitches

	Softening point [°C]	Steady shear viscosity [Pa·s]		
		Temperature [°C]	Shear rate	
			$1s^{-1}$	$3s^{-1}$
S_1	280	300	35	34
S_2	343	380	115	150
S_3	334	380	100	140
S_1/S_3(1:1)	303	380	40	10
S_4	361	380	1800	2500
S_5	109	135	28	26
S_6	108	135	17	18
L_1	309	350	26	24
L_1S_1(4:1)	303	342	30	25
L_2	337	370	109	99
		393	69	48

Table 2. Tensile and electrical properties experimental pitch based carbon fibers HT at 2500°C

	d_{fiber} [μm]	ρ [μΩ·m]	k_{pred} [W/m·K]
L_1 (806*)	11.3 ± 0.4	5.4	254
L_2 (444)	17.3 ± 1.5	3.0	495
L_2 (828)	9.1 ± 0.9	4.6	315
S_1 (828)	11.7 ± 1.1	2.5	570

* numbers in brackets represent take-up speed in m/min.

On the other hand, pure L_1 and 20% S_1 added L_1S_1 (4:1) mixture spun well. The 20 wt% addition of S_1 pitch reduced the spinning temperature by about 10°C. Since L_1 pitch contains 75% mesophase, addition of pure mesophase pitch S_1 increased total mesophase content, and enhanced spinnability of the mixture.

To obtain carbon fiber with higher thermal conductivity, we used L_2 experimental pitch and varied spinning conditions. Fiber properties resulting from higher melt temperature and low take-up speed are listed in Table 2. Thermal conductivity of L_2 carbon fibers heat treated at 2500°C was predicted at 495 W/m·K, which is comparable to that of S_1 (within experimental error).

As displayed in Fig. 1, carbon fibers showed a very well developed radial structure as a result of flow induced orientation. We also observed split fibers (Fig. 1b), which is often found in radially-structured thick fibers.

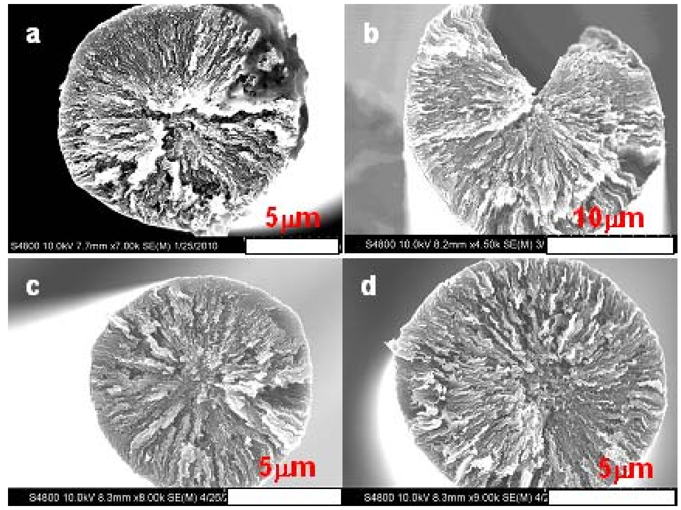

Fig. 1 SEM micrographs of carbon fibers being heat treated at 2500°C: a. L_1 (806), b. L_1S_1 (680), c. L_2 (444), and d. S_1 (443).

Conclusions

The softening temperatures, shear rheology, and fiber spinnability of selected experimental pitches was examined. Based on these results, down-selected experimental pitches and their mixture with a synthetic pitch (S_1) were melt-spun to produce carbon fibers. Spun fibers were heat treated at 2500°C, and preliminary tensile and electrical properties of carbon fibers were measured. L_2 pitch was spun at optimized conditions to obtain carbon fiber with high thermal conductivity approaching 500 W/m·K. Radial structure development was found in heat-treated carbon fibers from L_1 pitch, similar to that found for carbon fibers derived from S1 precursor.

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References

[1] E. Fitzer and L. M. Manocha: *Carbon Reinforcements and Carbon/Carbon Composites*, 1998, Springer-Verlag Publishers, Berlin
[2] Kundu S, Ogale, AA. Rheostructural studies on a synthetic mesophase pitch during transient shear flow. Carbon 2006; 44:2224-2235
[3] Lavin JG, Boyington DR, Lahijani J, Nystem B, & Issi JP. The correlation of thermal conductivity with electrical resistivity in mesophase pitch-based carbon fiber. Carbon 1993;31:1001-1002