

STABILIZATION BEHAVIOR OF CARBON FIBERS MELT SPUN FROM MESOPHASE PITCH MIXTURES

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Introduction

High-performance (high modulus) carbon fibers have been melt-spun from various types of mesophase pitches over the years. The as-spun properties and stabilization reactivity of the fibers are a function not only of operating conditions (i.e., spin temperature, drawdown rate, etc.), but also the chemical composition of the precursor mesophase. Previous work has shown that fibers melt-spun from a catalytically polymerized naphthalene-based (AR) mesophase pitch stabilize faster than fibers spun from supercritically extracted (SCE), heat-soaked mesophase pitches [1]. Here we examine the effect of adding various amounts of AR mesophase pitch to SCE mesophase pitch prior to spinning on the fiber stabilization behavior and final fiber properties (tensile strength, Young's modulus, etc.).

Experimental

AR and SCE mesophase pitches were mixed in an inert atmosphere at temperatures approximately 40 – 60 °C above their softening points (approximately 300 – 320 °C). Three mixtures were studied: 25% SCE – 75% AR, 50% SCE – 50% AR, and 75% SCE – 25% AR. The mixtures were then analyzed using diffuse reflective infrared Fourier transform spectroscopy (DRIFTS), supercritical fluid chromatography, and elemental analysis to monitor chemical or compositional changes during the mixing process; none were observed. Then the mesophase mixtures and pure mesophases were melt-spun into round fibers with as-spun diameters ranging from 12 to 15 μm . The experimental apparatus and procedure used for melt spinning are described in detail elsewhere [2].

Thermogravimetric analysis (TGA) was used to determine an adequate stabilization schedule for each of the fiber sets. A temperature ramp rate of 2.5 °C/min to 250 °C was used and the soak time at 250 °C was varied until the fibers gained ~8 weight percent. These stabilization schedules were then used to stabilize bundles of actual fibers. The bundles were stabilized in an air atmosphere using a Thermolyne 9000 series forced convection oven. Then the stabilized fibers were graphitized to 2400 °C using an Astro carbon resistance

furnace. Final fiber properties, such as tensile strength, tensile modulus, electrical resistivity, and degree of mis-orientation (Z-value), were measured for each graphitized sample. Techniques used to measure final fiber properties are described in detail elsewhere [2].

After the final properties were measured to ensure that the stabilization schedules determined from TGA were adequate, DRIFTS was used to monitor the chemistry of stabilization. Samples of chopped fibers were removed throughout the stabilization process, diluted with KBr to make a solution with ~4 weight percent fibers, and finally ground into a fine powder. The spectrum was then collected for each sample using a Nicolet Avantar 360 FTIR ESP with a diffuse reflectance attachment.

Results and Discussion

Figure 1 shows the change in weight percent of the carbon fiber during the oxidation process with respect to time, which was measured during the TGA experiments. The graph shows that all of the fiber sets spun from mesophase mixtures stabilize faster than fibers spun from either of the pure mesophases. Careful examination of Figure 1 shows that the two pure mesophases have significantly different stabilization behaviors. The pure AR fibers show a quick initial weight gain, while the pure SCE mesophase fibers show a much higher weight gain in the latter stages of the stabilization process. It is believed that the AR fibers possess a relatively small number of highly reactive sites for oxygen addition, while the SCE fibers possess more, but less reactive sites.

Figure 2 shows an example of the DRIFTS spectra used to monitor the progression of chemical reactions during the stabilization process. The bands associated with the bending and stretching of various hydrocarbons (2968-2864, 1444-1377, 3045, 870-750) decrease throughout the stabilization process, while the bands associated with oxygen functional groups (1692, 1735, 1841, 3400-3450, 3550) increase in intensity. A detailed description of the functional groups and their bands is presented elsewhere [3]. The DRIFTS spectra confirmed the trends seen from the TGA experiments. Namely, fibers produced from pure AR mesophase showed a quick initial change in the relative intensities of the oxygen-containing functional groups, while the fibers

produced from pure SCE mesophase showed a much higher weight gain in the latter stages of the process.

Table 1 shows the final properties of the fibers melt-spun at a constant shear rate. The fibers produced from the mesophase mixtures exhibited higher moduli and comparable or lower electrical resistivities than fibers produced from either of the pure mesophases.

Conclusions

High-performance carbon fibers can be melt-spun from mixtures of SCE and AR mesophase pitches. The TGA experiments showed, and the DRIFTS experiments confirmed, that the AR mesophase pitch had a quicker initial weight gain, while the SCE mesophase had a greater weight gain in the latter stages of the stabilization. The fibers produced from the mesophase mixtures stabilized faster, exhibited higher moduli, and comparable or lower electrical resistivities than fibers produced from either of the pure mesophases. It is believed that the reactivity and molecular structure of the different pure mesophases account for the observed trends.

Acknowledgements

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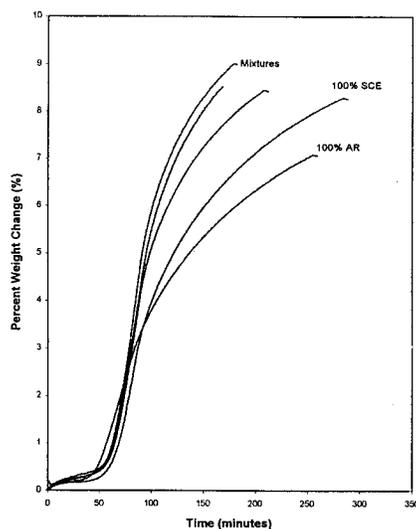


Figure 1. TGA graphs used to determine the stabilization schedules.

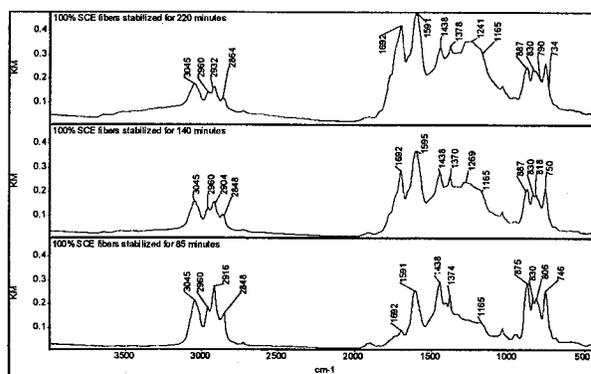


Figure 2. DRIFTS spectra for fibers melt-spun from pure SCE mesophase pitch at various times throughout the stabilization process.

Table 1. Final properties for fibers melt spun with a constant shear rate of 6200 s⁻¹.

Percent SCE Mesophase	0	25	50	75	100
Spin Temperature (°C)	300	319	335	341	355
Viscosity (Pa·s)	37	36	31	47	16
Tensile Strength (GPa)	2.83 ± 0.14	2.86 ± 0.24	2.73 ± 0.22	2.82 ± 0.36	2.46 ± 0.21
Young's Modulus (GPa)	561 ± 23	901 ± 31	804 ± 27	773 ± 61	754 ± 40
Resistivity (μΩ·m)	5.51 ± 0.19	4.23 ± 0.08	4.53 ± 0.11	4.93 ± 0.25	4.44 ± 0.23
Z-value	n/a	9.67	9.99	10.56	n/a

^a ± 95% Confidence Intervals