Analysis of the Spinnability of Mesophase Pitch

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Introduction

Recent research at Clemson University has focused on the use of AR mesophase, a naphthalene based mesophase pitch, as a precursor for high thermal conductivity carbon fibers. This pitch yields fiber with excellent thermal and mechanical properties, but its spinnability, as with most other mesophase pitches, is erratic. To date, three different batches of AR mesophase have been processed. The first batch of AR mesophase, designated pitch A, exhibited excellent spinnability; however, the next batch of mesophase, pitch B, was virtually unspinnable. Furthermore, the third batch of pitch, pitch C, spun well initially, but after about 30 minutes the fibers began to break and spinnability gradually declined. The above situation has provided an excellent opportunity to investigate the loss of spinnability.

The most obvious sign of poor stability is frequent filament breaks during wind-up. However, loss of spinnability can also be detected by visual inspection of the as-spun fiber. As spinnability decreases, the fiber's texture becomes much coarser, indicating the presence of bubbles or voids within the fibers. Analysis of these fibers by scanning electron microscopy (SEM), as seen in figure 1, supports this conclusion. Various analytical techniques, such as thermogravimetric analysis (TGA), modulating differential scanning calorimetry (MDSC), and supercritical fluid chromatography (SFC), have been applied in the effort to achieve a better understanding of the nature of AR mesophase and the reasons for loss of spinnability.

Experimental

Pitch samples from each batch (denoted pitch A, pitch B, and pitch C) of AR mesophase were subjected to analysis by MDSC and SFC. MDSC utilizes a sinusoidal heating method that allows the overall heat flow curve to be separated into its reversible and non-reversible components. All pitch samples were heated from 0°C to 250°C at a rate of 5°C/min.

A Dionex Model 602 SFC with a SB-Cyano (50% cyanopropyl and 50% polymethylsiloxane) open tubular column was utilized to detect differences in chemical composition among the pitches. The SFC utilizes carbon dioxide as the carrier fluid and is equipped with a flame ionization detector (FID). Temperature and pressure programming was used to control the chromatographic column.

As previously mentioned, carbon fibers were spun from each batch of pitch. Pitch C has yielded excellent fibers, but because it exhibited progressively decreasing spinnability with increased spinning time, green fibers spun from pitch C were collected at the beginning, middle, and end of spinning. The fibers were extruded through a 9:1 aspect ratio, flat entry, rectangular channel spinnerette with spinning conditions listed in Table I. The winder speed was varied from about 600 rpm to about 1100 rpm, depending on the spinnability of the pitch. A TGA was performed for each of the as-spun fiber samples to determine if pitch degradation had occurred during extrusion. In addition, samples of pitch C were taken about one month apart and TGA was utilized to detect any changes that may have occurred to this pitch while in storage.

The TGAs were performed with a TA Instruments Hi-Res 2950 Thermal Analyzer. All analyses were carried out in a nitrogen atmosphere with a heating rate of 5°C/min. In the first set of experiments, weight loss of the as-spun fiber samples and the pitch samples was monitored over temperatures ranging from 25°C to 800°C. In a second experiment, pitch C was brought to 300°C, approximately the spinning temperature, and held there for three hours in an attempt to simulate extrusion conditions.

Results and Discussion

The MDSC scans generated curves that differed only slightly for pitches A, B, and C. Nevertheless, small differences between pitch A and B concerning the contribution of the non-reversible component to the overall heat flow appear to exist. The effect of the non-reversible curve on the total heat flow does seem to be more pronounced for pitch B, indicating the importance of kinetic transitions in pitch B.

In contrast, obvious differences existed among the chromatograms for pitches A, B, and C. Only the methylene chloride solvent peak is observed for pitches A and C, whereas several small peaks at retention times greater than 17 minutes are discernible for pitch B. These peaks are attributed to discernible for pitch B. These peaks are attributed to low molecular weight species in pitch B that volatilize at lower temperatures. The chromatogram for pitch B (excluding the solvent peak) is presented in figure 2.

TGA was then utilized to analyze the as-spun pitch C fiber samples taken at the beginning, middle, and end of spinning. The curves for each of the samples nearly overlap, indicating that no significant degradation of the pitch takes place during extrusion. Similarly, the TGA scans for two samples of pitch C taken weeks apart are virtually identical, implying insignificant change in the pitch between spins. In addition, each of these curves show that pitch C begins losing mass at about 300°C, just above the spinning temperature.

While the recorded extrusion temperatures are nominally below 300°C, this loss of mass at could be important. The reason being that the pressure gradient with the extruder causes back mixing of the pitch. This phenomenon can greatly increase the residence time of the pitch in the extruder. Velocity profiles for pitch flow through the extruder screw channel are depicted in figure 3. These profiles demonstrate the significant back flow that exists at high pressures. To determine the effect of residence time, pitch C was subjected to a temperature of 300°C for a period of three hours. This TGA shows a 0.5% loss of mass for pitch C after only 30 minutes. At the conditions in the extruder, just 10g of pitch would produce 14ml of gas, assuming methane had evolved. This is approximately 50% of the total fiber volume.

Conclusions

SFC has proven to be a valuable tool in determining spinnability of newly received pitches, whereas MDSC did not clearly differentiate between pitch samples of varying degree of spinnability. The TGA scans of the as-spun pitch C fibers demonstrate that, although AR mesophase appears to be an excellent precursor, a build up of gases due to residence time may be causing voids to form in the fibers.

Table I.
Spinning Conditions

Feed Zone Temperature	160°C
Transition Zone Temperature	260°C
Metering Zone Temperature	300°C
Pump Temperature	292°C
Pack Temperature	281°C
Extruder Pressure	270psi
Pump Pressure	900psi
Mass Flow Rate	2.7g/min

Figure 1. SEM Photograph of Fiber with Pores

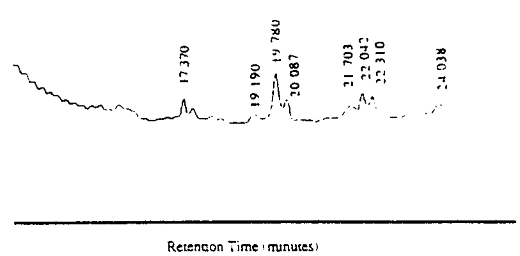

Figure 2. SFC Chromatogram for Pitch B

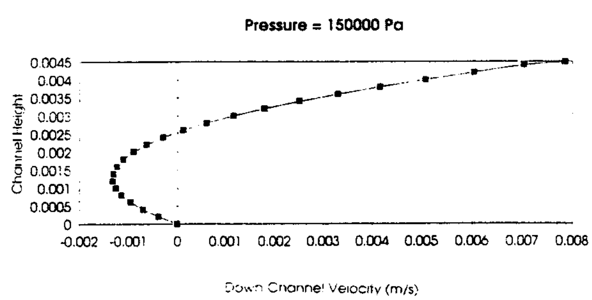

Figure 3. Velocity Profile for the Extruder