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PETROLEUM PITCH-BASED CARBON FIBERS WITH MODIFIED TRANSVERSE MICROSTRUCTURE

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Introduction

Carbon fibers possess superior specific mechanical properties and have been used in industries like aviation and aerospace. Recently, carbon fiber composites have also entered industries like transportation and infrastructure where cost of the carbon fiber is very important. PAN-based carbon fibers dominate the usage, about 95% of total [1], but their cost is still a major drawback for use in cost-sensitive applications. Mesophase pitch, due to melt-spinnability, high carbon yield and low precursor cost is a potential cost-competitive precursor.

Pitch-based carbon fibers are categorised as either general performance or high-performance [1] with the high performance ones being produced from mesophase pitch. Mesophase pitch-based carbon fibers (MPCF) are more graphitic and have higher elastic modulus than PAN-based carbon fibers. The highly graphitic nature of MPCFs also makes such fibers flaw-sensitive and generally weaker than PAN-based counterparts. Therefore, control of microstructure is very important for pitch-based carbon fibers.

Mesophase pitch is discotic liquid crystalline polynuclear aromatic obtained from petroleum or coal tar bottom product. The discotic liquid crystalline behaviour of pitches also leads to challenges in the control of the fiber microstructure arising from the extreme temperature sensitivity of pitch viscosity to temperature and the brittle nature of the resultant fiber [1]. Further, shear flow typically encountered in spinnerets leads to radial flow-induced alignment of disk-like molecules. This orientation is retained in the final carbon fiber because it is not possible for this textural orientation to relax during stabilization or carbonization steps (unlike PAN-based precursors). Unfortunately,
radial alignment of carbon/graphitic layer planes leads to radial cracks forming Pac-man splits. Therefore, the primary goal of this study was to generate non-radial microstructure within carbon fibers using scalable fiber spinning routes.

Materials and Methods

Petroleum pitch with a nominal 75% mesophase content was used to spin fibers. A 1-inch diameter single screw extruder with a Zenith gear pump was used for continuous fiber spinning. A proprietary design of spinnerets was used throughout this study. Pitch fibers were stabilized in a forced-air convection oven followed by carbonization at 2100 and 2400°C in an Astro 1000 furnace (Thermal Technology LLC). Scanning electron microscopy was conducted on samples using Hitachi S4800 high resolution FESEM scope.

Results and Discussion

Fig.1 shows different types of microstructure generated using a standard circular capillary and a specially designed spinneret. With the standard circular capillary, fiber microstructure was the typical line-origin radial (like spokes of a wheel). In contrast, the specially designed capillaries led to non-radial textures with two variations of onion-skin microstructure: one with a pronounced circular core but radial outer rim, and another fine-textured circular. It was also found that by changing the die design, the relative area of outer radial rim could be controlled.

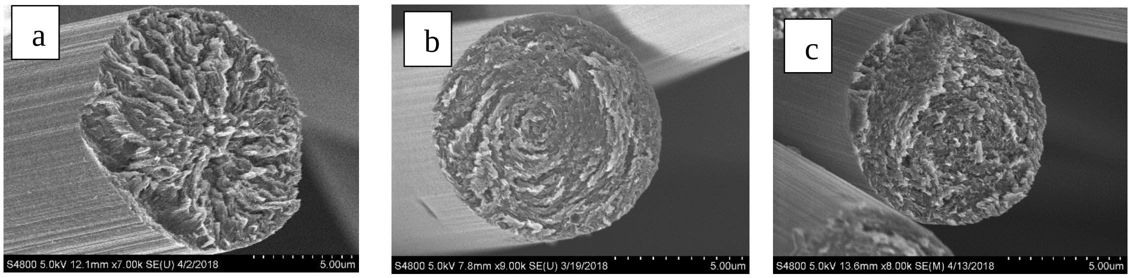

Figure 1. SEM micrographs of carbon fibers produced from petroleum-based mesophase pitch: (a) radial texture (b) onion-skin core and radial periphery, and c) fine textured circular

A representative Raman spectrum for fibers carbonized/graphitized at 2400°C is displayed in Fig. 2. Fibers displayed the typical D- and G-peaks respectively at 1314 and 1582 cm^{-1} associated with disordered and graphitic carbon. Fibers carbonized at 2400°C had an I(D)/I(G) ratio of 0.74 ± 0.04 whereas fibers treated at 2100 °C had I(D)/I(G) ratio of 0.91 ± 0.05. As expected, the smaller I(D)/I(G) ratio for fibers treated at 2400 °C is consistent with their higher graphitic content.

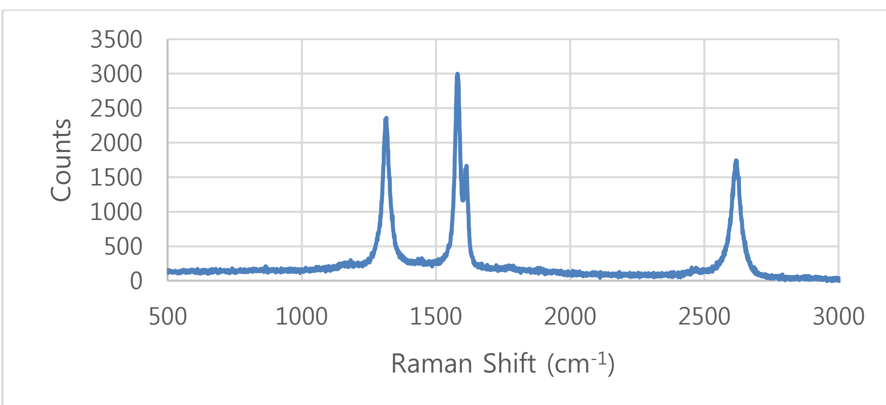

Figure 2: Raman spectra of petroleum pitch-based carbon fibers graphitized at 2400 °C

Results from wide-angle x-ray diffraction are displayed in Figure 3. For fibers displaying the two different types of microstructure, the position of the (0 0 2) peaks reveal no significant differences in the degree of crystallinity between the fibers displaying radial versus onion-skin texture. For fibers grpahitized to 2100C, both types displayed (002) peaks at 26.01^0 indicating a d_{002} spacing of 0.341 nm. As expected, a higher heat treatment temperature of 2250°C led to tighter layer packing and resulted in a smaller d_{002} of 0.340 nm and a correspondingly higher 2-theta of 26.2^0.

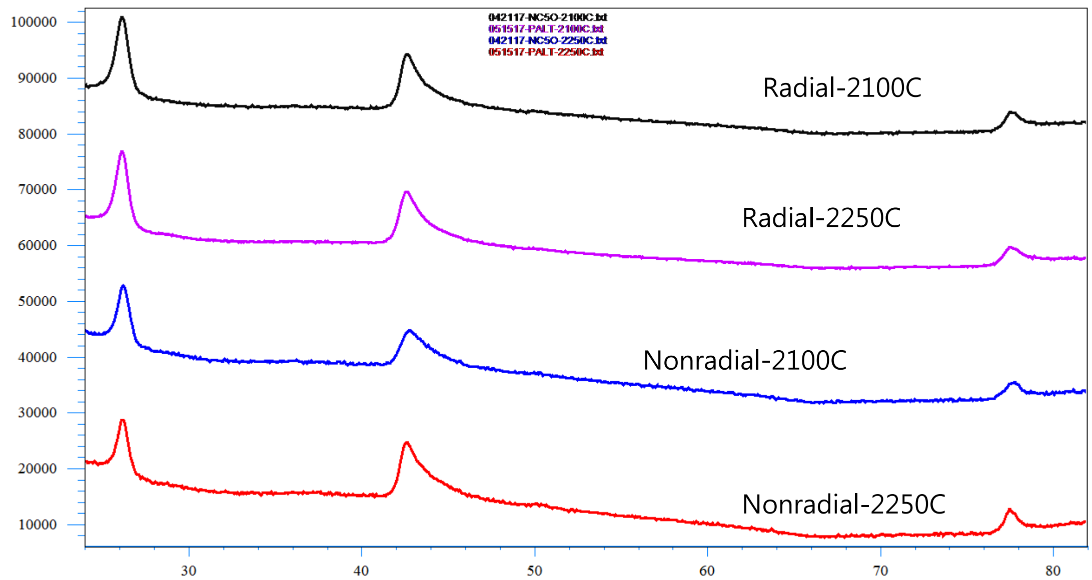

Figure 3. WAXD spectra for carbon fibers possessing radial versus non-radial (quasi onion-skin) texture in the cross-section

Conclusions

Results from the current study have established that the flow modification achieved by specially designed spinnerets led to the desired non-radial graphitic texture within resulting carbon fibers without any significant change in the extent of graphitic crystallinity. Initial results indicate that both types of carbon fibers possess a tensile modulus exceeding 350 GPa, which is significantly greater than that of carbon fibers derived from PAN-precursors. For fiber diameters of about 9-10 µm, the tensile strength was significantly higher (2.2±0.4 GPa) for non-radial texture, in contrast to that (1.6±0.3 GPa) for fibers possessing radial texture. This level of tensile strength and modulus is amongst the highest reported for carbon fibers derived from petroleum pitch with less than 100% mesophase content, which can be conveniently melt-spun at temperatures below 350°C. Ongoing studies are addressing other mechanisms for defect reduction for further enhancement of carbon fiber properties.

Acknowledgment

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