MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF NANO MODIFIED MESOPHASE PITCH-BASED CARBON FIBERS

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Introduction

Liquid crystalline mesophase pitches produce highly graphitic carbon fibers that possess thermal conductivities up to 1000 W/m*K [1-3]. Unfortunately, this highly crystalline structure is extremely flaw-sensitive, making it prone to microbuckling of the super-aligned graphene layers. As a result, these fibers are quite brittle, and are characterized by a very low strain-to-failure and poor compressive strength. Due to their poor mechanical properties, such carbon fibers suffer from poor handleability and cannot be used directly in woven or braided forms, which impeding their use in thermal management applications.

In prior studies, we have proposed the addition of multi-wall carbon nanotubes to mesophase pitch in an attempt to modify the properties of the resulting carbon fibers [4,5]. These studies primarily used long aspect ratio nanotubes and led to an improvement of the ratio of the compressive to tensile strength [6]. The goal of our current work is to control nanotexture of pitch precursors by the introduction of different types of nanoparticles, thereby modifying the structure of the resulting fibers. Here we present some preliminary results on the characterization of microstructure and electrical properties for fibers modified with short aspect ratio multiwalled carbon nanotubes (SAR MWCNTs), carbon black (CB) or boron nitride (BN) nanoparticles.

Experimental

All fibers were produced using ARHP grade mesophase pitch from Mitsubishi Gas Chemical with a measured softening point of 286^{o}C. Nanoparticles used for this study include: SAR MWCNTs, CB or BN nanoparticles.

Dispersion of nanoparticles was performed via melting mixing using a twin-screw extruder (Model #MP2015) made by APV Chemical Machinery. All dispersion studies were done in a nitrogen atmosphere at 305±1^{o}C). The compounded mixtures were melt-spun into fibers using a plunger-and-barrel batch unit (Alex James and Associates, Greenville, SC), which operated at a constant volumetric flow rate. All spinning was performed under a nitrogen atmosphere to minimize pitch oxidation. A 12-hole spinnerette with 150 µm diameter holes was used throughout. The spinning temperature was 305±2 ^{o}C. The take-up roller speed was 440±10 m/min. A volumetric flow rate of 2 to 3 cc/min was used for thicker A-series fibers, while a volumetric flow rate of 1.5 cc/min was used for thinner B-series fibers.

As-spun fibers were thermo-oxidatively stabilized by spreading them on a screen rack in an air convection oven, preheated to 205^{o}C, for 24 or 48 hours depending on the sample size. All fibers were found to have an average weight gain ranging from 8 to 10%, consistent with prior studies that showed that an 8% weight gain corresponds to sufficiently stabilized fiber. After stabilization, the fibers were then graphitized in an Astro 1100 furnace, under a helium atmosphere, at a maximum temperature of 2600^{o}C, for 1 hour holding time.

The microstructure of both oxidized and graphitized fibers were observed using an Olympus BX60 optical microscope with cross polarizing filter and a full wave-plate retarder. The average diameter and percentage of carbon fibers which exhibit "pac-man" types splitting was determined from these optical micrographs of fiber cross sections. No fewer than 100 fibers were counted to obtain these statistics. In order to view the carbon fiber microstructure in great detail, a field-emission scanning electron microscope (Hitachi S-4800) was employed.

Single filament samples were tested for electrical resistivity (ρ) using a four-point probe technique, with a 10 mm gauge length, in conjunction with a Keithley 580 micro-ohmmeter. Fiber diameter measurements for electrical resistivity were performed using laser diffraction. Electron microscopy was used to check fibers for splitting. Corrected cross section areas were also calculated by correcting the measured area by the average angle of splitting.

Results & Discussion

Optical micrographs of typical 0 wt%, 0.1 and 0.3 wt% SAR MWCNT carbon fibers from series A and B are presented in Fig. 1. Due to a larger draw down ratio during fiber spinning, series B fibers have smaller diameter (0 wt%: 11.6±0.4 µm, 0.1 wt%: 10.6±0.4 µm) than those in series A (0 wt%: 17.4±0.3 µm, 0.3 wt%: 17.2±0.5 µm). For the 0 wt% fibers, the larger A-series fibers are found to split about 83% of the time, while the smaller B series fibers only split about 17% of the time. The A-series fibers, modified with 0.3 wt%, and the B-series, fiber modified with 0.1 wt% SAR MWCNTs, split only 5% and <1% of the time. By comparing cross polarized micrographs, it can be observed that the addition of SAR MWCNTs also corresponds with a blurring of the radial microstructure (Fig 1a&c) present in the 0 wt% fibers (Fig. 1b&d.)

SEM micrographs of experimental carbon fibers are presented in Fig. 2. Fig. 2a gives a detailed view of the radial orientation of graphite planes around the fiber axis for a split 0 wt% A-series carbon fiber. In contrast, the A type carbon fiber containing 0.3 wt% SAR MWCNTs (Fig. 2b) exhibits a modified Pan Am structure. The smaller 0 wt% B series fibers (Fig. 2c) possess a radial texture, while 0.1 wt% SAR (Fig. 2d) MWCNTs modified fibers exhibit some disruption of the radial structure. Further, unlike fibers modified with SAR

MWCNTs, those containing 0.3wt% CB or BN (Fig. 4e&f), show no extreme change in the typical radial structure, but also exhibit no radial splitting.

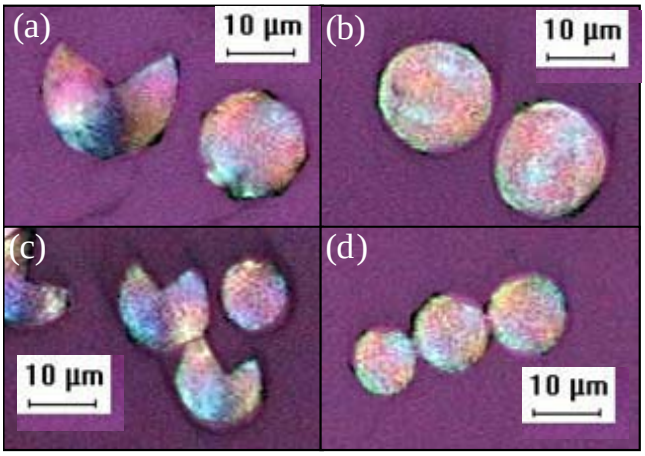

Fig. 1 Optical micrographs of (a) A-series 0 wt% (b) A-series 0.3 wt% SAR MWCNT, (c) B-series 0 wt% (d) 0.1 wt% SAR MWCNT.

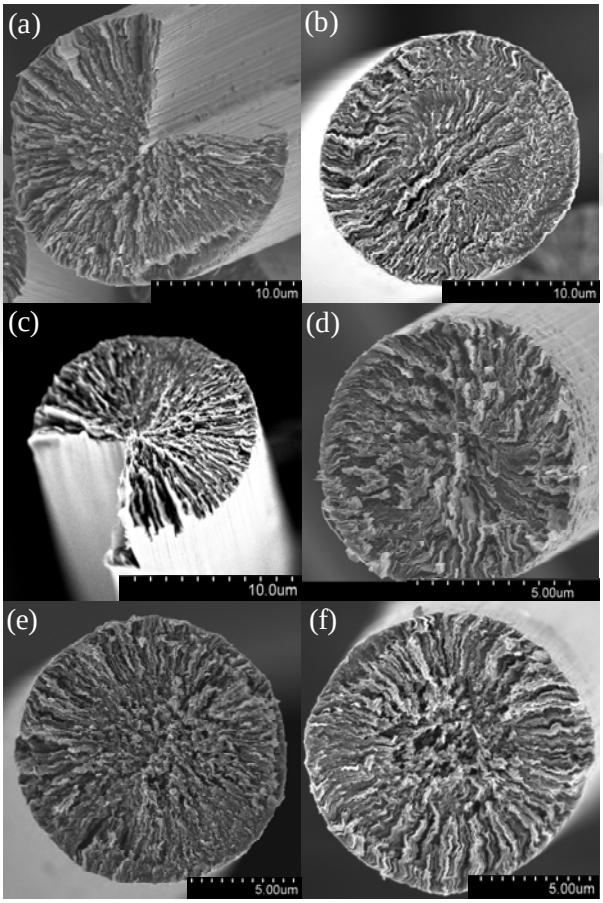

Fig. 2 SEM images of (a) 0wt% and (b) 0.3 wt% SAR MWCNT A-series carbon fibers, and (c) 0wt% (d) 0.1 wt% SAR MWCNT (e) 0.3 wt% BN and (f) 0.3 wt% CB B-series carbon fibers.

Electrical resistivity measurements for 0 wt% (3.2±0.2 µΩ·m) and 0.3 wt% SAR MWCNT (3.3±0.2 µΩ·m) A-series fibers show no statistically significant difference. However, when the measured value for 0 wt% is corrected for a reduced cross sectional area due to splitting, the electrical resistivity (2.4±0.1 µΩ·m) was found to be less than that of the 0.3 wt% fibers.

Conclusions

From the data presented in this paper, it is apparent that radial splitting of mesophase pitch based carbon fibers is an issue over a range of diameters, though less so for smaller diameter fibers. The addition of 0.1 to 0.3 wt% of SAR MWCNT to the pitch precursor has proven sufficient to disrupt the structure of the resulting fibers, thus preventing splitting. Carbon fibers containing 0.3 wt% carbon black or boron nitride showed very little disruption in the radial texture of the fiber, similar to 0 wt% fibers, but also prevent splitting, similar to those modified with SAR MWCNTs. Electrical resistivity measurements of larger diameter (A-series) fibers showed that the addition of 0.3 wt% of SAR MWCNT did increase fiber resistivity to some degree. This is expected since transport properties are known to be closely linked with microstructure. Future work will focus on characterizing crystalline structure and orientation via wide angle x-ray diffraction, and further quantification of electrical, thermal and mechanical properties.

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