MESOPHASE PITCH-DERIVED CARBON NANOCOMPOSITE FIBERS CONTAINING ULTRA-DILUTE CONCENTRATIONS OF CARBON NANOTUBES

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Introduction

Carbon fibers derived from mesophase pitch exhibit a high degree of molecular orientation resulting in a relatively high tensile strength coupled with superior thermal conductivity, but the layer-plane orientation also results in poor compressive properties [1]. We report on carbon fibers derived from ultradilute concentrations (0.1 wt% to 0.3 wt%) of multi-wall and single-wall carbon nanotubes (MWNTs and SWNTs) in AR-HP mesophase pitch.

In past studies, we have shown that long aspect ratio MWNTs lead to a disruption of the in-plane radial microtexture within carbon fibers [2]. This study is an ongoing project where we are systematically investigating the role of different size and length of carbon nanotubes, including MWNTs and SWNTs. The materials used in this study consisted of mesophase pitch as the matrix material and multi-walled carbon nanotubes as the filler. The pitch was a high performance grade mesophase pitch obtained from Mitsubishi Gas Chemical Co. (New York, NY) with an experimentally-determined softening point of 286.5˚C (285°C quoted from manufacturer). The low aspect ratio nanotubes were 90%+ purity multi-walled nanotubes (1212-TY, Nanostructured and Amorphous Materials, Houston, TX). They have an outer diameter between 10 nm and 30 nm with a length averaging 1 μm. Purified SWNTs (FF922 grade, Carbon Nanotechnolgies, Inc.) were melt-mixed with mesophase pitch using a DSM minicompounder.

In previous studies, we have investigated a batch mode of mixing [2], whereas in the present study dispersion was achieved by twin-screw extrusion, a continuous route for mixing. The twin screw extruder (model MP2015, APV Chemical Machinery, Saginaw, MI) consists of a co-rotating, intermeshing 10-mm diameter screws and 4 distinct zones of temperature control. Excellent dispersion of these MWNTs in the pitch matrix was observed using a continuous, twin screw extrusion process, as displayed in Fig.1a. In contrast, SWNTs were significantly more difficult to disperse under similar processing conditions, as inferred from the SWNT agglomerate of Fig.1b.

Experimental

Fiber spinning was performed using a plunger-barrel batch extruder [Alex James and Associates, Greenville, SC] at a nominal spin-pack temperature of 305°C. The nanosuspensions were extruded through 150 μm circular holes and taken up on a rotating spool at a drawdown ratio of approximately 50. Stabilization of the as-spun pitch nanocomposites was performed at 250˚C for 24 hours. The fibers were carbonized in an inert helium atmosphere at a temperature of 2400˚C for 1 hour. Tensile testing was performed using a MTI Phoenix single-filament testing machine equipped with a 500 g load cell. Compressive strength was obtained by the "tensile-recoil test" [4]. Wide angle x-ray diffraction (WAXD) was performed on a XDS 2000, Scintag unit using Cu K_α radiation (λ=1.5406Å) over the 2θ range of 5 to 90°.

Results and Discussion

First, carbon fibers were produced as the control batch, i.e., containing no MWNTs but processed under identical conditions as those containing 0.1 and 0.3 wt% MWNTs. The tensile and compressive strength of these fibers were 2.6 GPa and 0.8 GPa, respectively. As expected, the compressive strength was only about one-third of that observed in the tensile mode, showing the imbalance of properties. With the addition of 0.1 wt% MWNTs, a decrease of tensile strength (1.8 GPa) was observed, but this was accompanied by an increase in compressive strength (0.9 GPa). For 0.3 wt$ MWNTs, the tensile strength did not decrease much (1.8 GPa), but the compressive strength showed further improvement (1.2 GPa). Thus, the ratio of tensile-to-compressive strength improved from 0.3 for 0 wt% MWNTs to 0.6 for 0.3 wt% MWNTs.

To investigate the microstructure of the resulting nanocomposite carbon fibers, WAXD study was performed. The complete 2θ scan, displayed in Figure 2, indicates the presence of strong peaks at approximately 26°, as expected from *(002)* planes [5]. Carbon fibers containing 0 wt% MWNTs showed a peak at 26.0°, whereas those containing 0.1wt% and 0.3 wt% MWNTs showed peaks at 26.2° and 25.8°, values not significantly different than 26.0°.

Much weaker peaks from *(004)* planes were observed at 54°. At intermediate angles, *(100)* peaks were observed at 42° and *(101)* peaks at 44°. The reason for a somewhat stronger (101) peak for 0.1 wt% MWNT fibers is not known at this time. Additional experiments are under progress to verify these weaker peaks for both MWNT and SWNT-modified carbon fibers. However, existing results indicate that the addition of up to 0.3 wt% MWNTs did not change the diffractograms significantly. Ultrahigh magnification TEM studies are also underway to understand the fundamental mechanisms of composition-based textural control.

References

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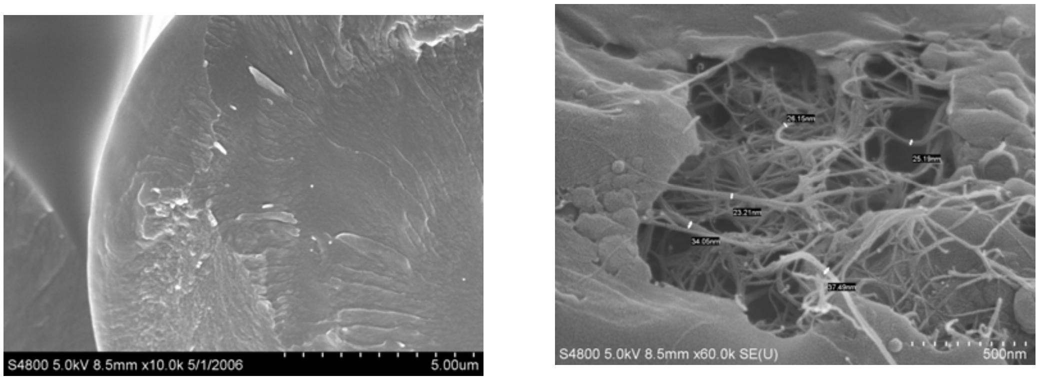


Figure 1. (a) Uniformly dispersed MWNTs in as-spun 0.3 wt% MWNT/ AR-HP mesophase pitch; (b) poor dispersion of 0.3 wt% SWNTs in AR-HP mesophase pitch.

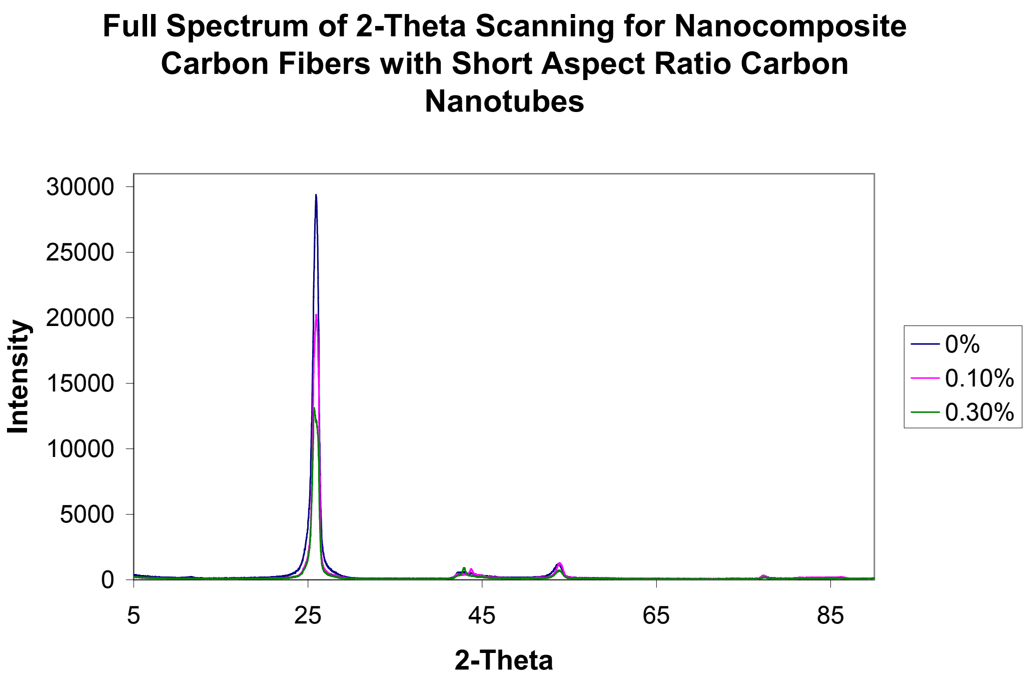
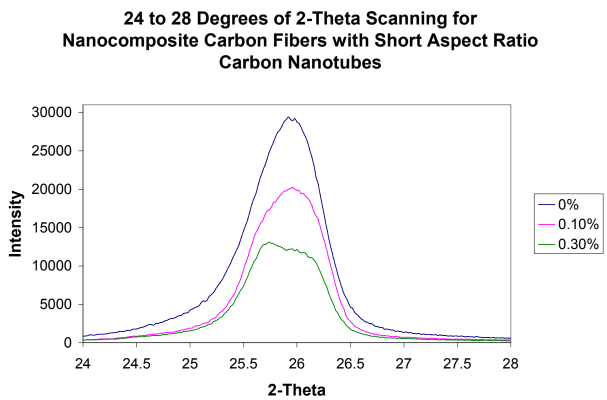
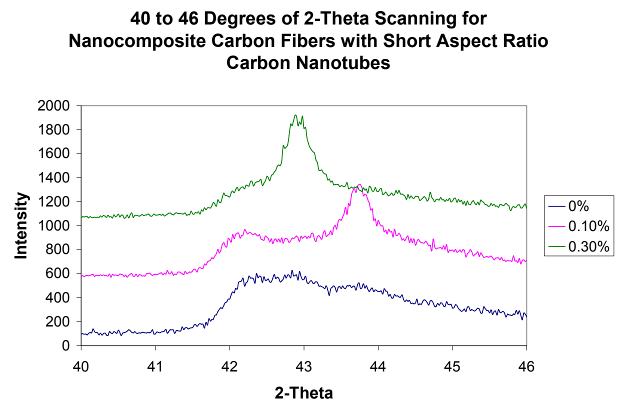


Figure 2. A complete 2θ spectrum from powder-diffraction experiment for carbon fibers derived from 0 wt%, 0.1 wt% and 0.3 wt% short aspect-ratio MWNTs and AR-HP mesophase pitch.





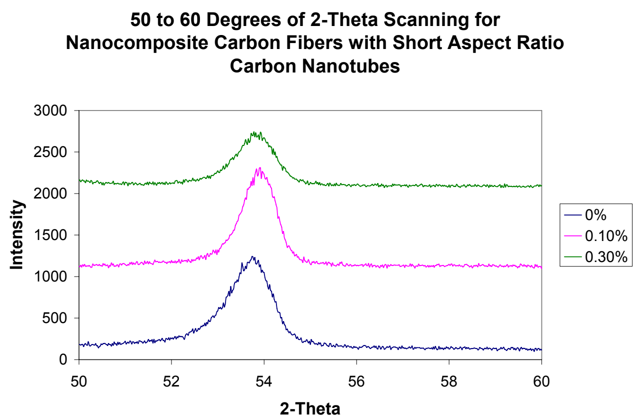


Figure 3. Magnified WAXD 2θ plots for (a) 26° peak for *(002)* planes; (b) 42° peak for *(100)* and 44.7° peak for *(101)* planes; and (c) 54° peak for *(004)* planes.