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Low-temperature graphitic formation promoted by confined interphase structures in polyacrylonitrile/carbon nanotube materials

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ABSTRACT

In this work polyacrylonitrile (PAN)/single wall carbon nanotube (SWNT) composites with 50 wt% SWNT loading were studied. A previously studied solvent-based phase separation process was used to enhance PAN-SWNT crystallization conditions and interphase formation within the composites. Two types of SWNT species were used here to produce two composites materials with well-ordered PAN-SWNT interphase structures. All precursor composite films were stabilized and subsequently carbonized at temperatures ranging from 900 to 1500 °C under various carbonization times. Wide-angle X-ray diffraction and electron microscopy were used to analyze the structural change in these precursors during carbonization. It was found that ordered graphitic structures were formed using specific temperature/time conditions as early as 900 °C. This low-temperature graphitic structure can be tracked directly to the PAN interphase structure within the precursors. This paper discusses the linkage between precursor PAN-SWNT interphase formation and subsequent low-temperature graphitic formation.

1. Introduction

Polyacrylonitrile (PAN) is widely used as a precursor for carbon fiber production [1–7]. Typically, a three-step heat treatment process is performed in order to convert PAN precursors to carbon fibers. These steps are: (i) thermal stabilization, (ii) carbonization, and (iii) optional graphitization. During stabilization between a temperature range of 200–300 °C, a ladder structure will be formed due to cyclization of PAN molecules [8,9]. Carbonization processes increase the carbon content through formation of a near-amorphous microcrystal structure [10]. Carbonization is usually performed within a temperature range from 1000 to 1700 °C [5,6]. Optional graphitization will further enhance the ordering of the carbon structure by formation of graphite and this process occurs at temperatures greater than 2000 °C and up to 3000 °C [5,6]. By increasing the heat treatment temperatures and applying tension to the fibers during pyrolysis, ordering of the carbon structure increases [11–13]. Semi-crystalline carbon is referred to turbostratic, while highly ordered carbon is graphitic. The inter-layer distance between turbostratic carbon planes varies and is on average > 0.34 nm [14,15], while the distance between perfect graphite planes is 0.3345 nm [15,16]. Conversion to this graphitic structural form in the material improves the mechanical properties of carbon fibers.

New research on carbon fiber development and processing have been of interest toward decreasing the gap between commercial and theoretical tensile strength properties for the materials [17,18]. An increase in tensile strength properties is expected to occur in the presence of oriented graphitic regions which can be increased throughout the fibers, while minimizing defective carbonaceous regions. To this end many studies have focused on the use of filler particles such as carbon black [19,20], graphene [21,22], and carbon nanotubes (CNTs) [23–27] to modified the PAN matrix in order to improve precursor properties and subsequent carbon fiber performance. In addition, the use of these carbonaceous materials may also enhance the conductive properties of these materials broadening their applications [19–33]. There have been several recent studies focused on understanding the role of controlling the precursor polymer structure toward producing a specific variation of carbonaceous structure upon pyrolysis by addition of CNTs to the PAN matrix [18,34–37]. CNTs have been shown to induce ordered interphase [38,39] which can promote the ordering of the PAN ladder structure after stabilization [18,35]. This interphase structure leads to PAN conversion to graphitic structures at ~1100 °C

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[18,35,37,40,41]. However, while it has been shown that graphitic structure can form at 1100 °C at the interphase, studies focused on understanding the mechanism behind this conversion process and subsequent structure are still needed. In this paper, PAN/CNT composites (with 50 wt% CNT total loading) were prepared to purposely isolate interphase regions in the composite. Several studies have looked at much lower CNT loading in the composite [18,35,37,40,41]. However, the direct linkage between filler content and PAN conversion during carbonization heat treatment has been difficult to observe. The choice of 50 wt% CNT loading in this work is based on the previously studied method of preparing PAN/CNT films by phase separation [42]. This technique allows for the development of regions in the composite with high interphase content [42]. At 50 wt% CNT the level of interfacial content is sufficient to directly study carbonization behavior. In addition, the bulk PAN and CNT interaction can also be distinguished from the interphase. This work is performed to confirm the value of introducing ordered PAN interphase regions to the precursor to control graphitic forms in the final carbon material. This work also shows the role of polymer confinement effects in early carbonaceous and graphitic formation.

2. Materials and method

2.1. Materials

The PAN used in this work is a poly(acrylonitrile-co-methacrylic acid) random copolymer with methacrylic acid content of 4 wt% (M_w ~513,000 g/mol), obtained from Exlan Co. Japan. Two types of CNT materials were used, (i) PT (purified single wall carbon nanotubes (SWNT), ~94.5%, Continental Carbon Nanotechnologies, Inc.) and (ii) SW (SWNT, ~90%, SouthWest Nano Technologies, Inc. batch SG76).

2.2. Solution processing and film fabrication

2.2.1. Dispersion preparation

The materials used in this study are PAN/CNT composite films. For hybrid polymer/CNT buckypaper (hPBP) fabrication, PAN powders were first dissolved in 90 °C DMF (obtained from Sigma Aldrich) at a concentration of 250 mg/L. CNTs of equal amount were then dispersed in the polymer solution for 24 h via a bath sonicator (Fisher FS30, frequency 43 kHz, power 150 W). For control buckypaper (BP) fabrication, CNTs were dispersed in DMF using similar sonication conditions.

2.2.2. BP and hPBP films preparation

After sonication, the PAN/CNT dispersion was subjected to a solution-based shear crystallization process by stirring the dispersion at 90 °C. Simultaneously vacuum distillation was applied to remove half the volume of solvent at a controlled time and temperature. Subsequently, this overall system was cooled down to room temperature (~25 °C). A non-solvent for PAN (i.e., water [42]) was added into dispersion at various solvent:non-solvent (S:NS) ratios. The two ratios chosen in this work were 7:1 and 1:2, respectively. This S:NS treatment during solution processing of the PAN/CNT films help to isolate regions, where PAN has enhanced interfacial interaction with the CNT. The isolation of this interphase region is important for studying subsequent carbonization process effects. The final PAN/CNT dispersions were then filtered through a nylon membrane (0.45 μm pore size obtained from Millipore) to form the PAN/CNT hPBP. The films made using PT-SWNT with S:NS ratios of 7:1 and 1:2, respectively, were named PT-1 and PT-2, accordingly. The films made with SW-SWNT were named SW-1 and SW-2, respectively at similar S:NS ratios of 7:1 and 1:2. A free-standing hPBP was removed from the filter paper after drying in a vacuum oven and further characterized to understand the effect of processing on the structure of the hybrid films. Control CNT BPs were also fabricated using a similar filtration process for comparison.

2.2.3. Heat-treatment processes

A Lindberg/Blue M™ Mini-Mite™ tube furnace equipped with a quartz tube (diameter 1 inch, obtained from Quartz Scientific Inc.) was used for heat-treatment to conduct both stabilization and carbonization procedures. Two flow meters were used to control the inlet and outlet gas flow through the furnace. The entire system was sealed and the outlet gas flow was directly released into a venting system. The film samples were held in compression using a customized sample holder throughout both heat treatment processes. For stabilization (in air), the temperature was (i) ramped up at 1 °C/min from room temperature (~25 °C) to 250 °C or 300 °C; (ii) maintained isothermally for 10 h; and (iii) gradually decreased to room temperature. For carbonization (in argon), the temperature was (i) ramped up at 5 °C/min from room temperature to 900, 1000 or 1100 °C; (ii) maintained isothermal for 20 or 40 min at 900 °C, 5 or 20 min at 1000 °C, and 5 min at 1100 °C; and (iii) gradually decreased to room temperature (~25 °C). In both processes, the required air or argon gas flow was maintained constant at 3000 ccm until the chamber was cooled down to room temperature (~25 °C). To confirm the existence of structural features the early onset graphite (i.e., formed between 900 and 1100 °C), the pyrolysed composite films were further heat-treated at up to 2100 °C for 40 min in vacuum using high temperature furnace (Red Devil vacuum furnace WEBB 124). Fig. 1 summarizes the time-temperature profile for the stabilization, carbonization, and graphitization procedures.

2.2.4. Sample characterization

Morphology characterization was performed using a Zeiss Supra 25 field emission scanning electron microscope (SEM) (operating voltage 5 kV). All film samples were fractured and mounted to a 90° pin stub with the fractured end facing up for SEM observation. Precursor (non-carbonized) samples were coated with a thin gold/palladium layer (15–20 nm) for image purposes using a Gatan high-resolution ion beam coater. Wide-angle X-ray diffraction (WAXD) was performed on a Rigaku RAPID II equipped with a curved detector X-ray diffraction (XRD) system with a 3 kW sealed tube X-ray source (operating voltage 40 kV and current 30 mA). XRD curve fitting and analysis was performed using software PDXL 2 (version 2.0.3.0) and 2DP (version 1.0.3.4). Raman spectroscopy was conducted on a Jobin Yvon LabRam HR800 (laser wavelength 532 nm). Differential scanning calorimetry (DSC) analysis was conducted by heating samples from 40 to 400 °C at a heating rate of 1 °C/min. DSC curves were examined using the TA Instrument Universal Analysis software.

3. Results and discussion

3.1. Precursor films

A non-solvent (water) is added during filtration to process the hPBPs in order to isolate PAN-CNT interactions. PT-1 and SW-1 hPBPs are fabricated using a 7:1, S:NS ratio, while PT-2 and SW-2 materials utilize a 1:2, S:NS ratio. Based on previous computational and experimental studies, it was found that as the non-solvent increases, PAN-CNT isolated interactive regions also increase and these changes are observed in the composite morphology. The presence of the water leads to higher interaction between the PAN and CNT leading to a ‘trapping’ of the CNT by the