

Stress transfer in polyacrylonitrile/carbon nanotube composite fibers



Bradley A. Newcomb^a, Han Gi Chae^a, Prabhakar V. Gulgunje^a, Kishor Gupta^a,
Yaodong Liu^a, Dmitri E. Tsentalovich^{b,c}, Matteo Pasquali^{b,c,d}, Satish Kumar^{a,*}

^aSchool of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

^bDepartment of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, USA

^cDepartment of Chemistry, Rice University, Houston, TX 77005, USA

^dRichard E. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, TX 77005, USA

ARTICLE INFO

Article history:

Received 15 January 2014

Received in revised form

24 March 2014

Accepted 6 April 2014

Available online 13 April 2014

Keywords:

Carbon nanotubes

Nanocomposite

Stress transfer

ABSTRACT

Gel spun polyacrylonitrile/carbon nanotube (PAN/CNT) composite fibers have been produced, and the stress-induced G' Raman band shifts in the CNTs have been monitored to observe stress transfer during fiber strain. Improvements in CNT quality, CNT dispersion, and post-processing fiber drawing are shown to increase the stress transfer from the matrix to the CNT. Radial breathing mode (RBM) intensity of specific CNT chiralities confirms CNT debundling during fiber processing. During PAN/CNT fiber straining, there reaches a plateau in the CNT G' downshift, signifying that the stress on the CNT is maintained despite continued straining of the PAN/CNT fiber. Correlating CNT strain with CNT modulus and volume fraction allows for the interfacial shear strength (τ_i) of the PAN-CNT interface to be determined. The as-spun and fully drawn PAN/CNT-A (99/1) nano composite fibers exhibit τ_i of 13.1 and 30.9 MPa, respectively, while an improved CNT dispersion (PAN/CNT-A (99.9/0.1)) results in τ_i equal to 44.3 MPa.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

PAN/CNT composite fibers have successfully been processed using dry-jet wet spinning [1–3], gel-spinning [4,5], and electro-spinning [6,7]. Improvements in the tensile properties of the PAN/CNT fibers as compared to the similarly processed PAN fibers provide evidence of stress transfer from the polymer matrix to the CNT [2,4]. CNTs exhibit well-defined Raman spectra as well as stress-induced Raman band shifts which have been investigated in individual single walled carbon nanotubes (SWNTs) [8,9] as well as in epoxy/CNT [10] and polymer/CNT composites [11,12]. Downshifts (lowering vibrational frequency) in CNT D (~ 1300 cm^{-1}), G (~ 1590 cm^{-1}) and G' (~ 2580 cm^{-1}) Raman band peak positions are attributed to the stretching and weakening of the carbon–carbon (C–C) bond [13]. It was shown that the G' band shift is the most sensitive to the induced strain [8], and is therefore typically monitored for stress or strain transfer in polymer/CNT composites [14].

In the current study, gel-spun PAN and PAN/CNT fibers containing up to 1 wt% few-walled carbon nanotubes (FWNTs) were

processed using techniques described elsewhere [4]. CNT quality, extent of CNT dispersion, and the effect of fiber drawing are examined by monitoring the stress induced G' Raman band shift to characterize the stress transfer in the gel-spun PAN/CNT composite fibers. These results are expected to impact the processing and properties of the PAN/CNT composite fibers and the resulting carbon fibers [5,15,16].

2. Experimental

2.1. Materials and fiber processing

CNTs were obtained from Continental Carbon Nanotechnologies, Inc. (CCNI, Lot # XOC231U) and Unidym, Inc. (Lot # XO122UA). TEM images of the two types of CNT, XOC231U (CNT-A) (Fig. 1a) and XO122UA (CNT-B) (Fig. 1b) used in this study are provided, as well as their corresponding Raman spectra (Fig. 2), which were obtained using a 785 nm laser on a Kaiser Raman Microscope System. Raman spectra show a higher G/D band ratio for CNT-A as compared to CNT-B, indicating a more perfect structure for CNT-A. Table 1 provides the summary of the material characteristics for CNT-A and CNT-B as determined by TGA (% impurity) [17], extensional rheology (aspect ratio), Raman spectroscopy (G/D band ratio), and TEM (average diameter and number of walls). Extensional viscosity was measured with a Trimaster Capillary Thinning

* Corresponding author. Tel.: +1 404 894 7550; fax: +1 404 894 8780.

E-mail addresses: satish.kumar@gatech.edu, satish.kumar@mse.gatech.edu (S. Kumar).

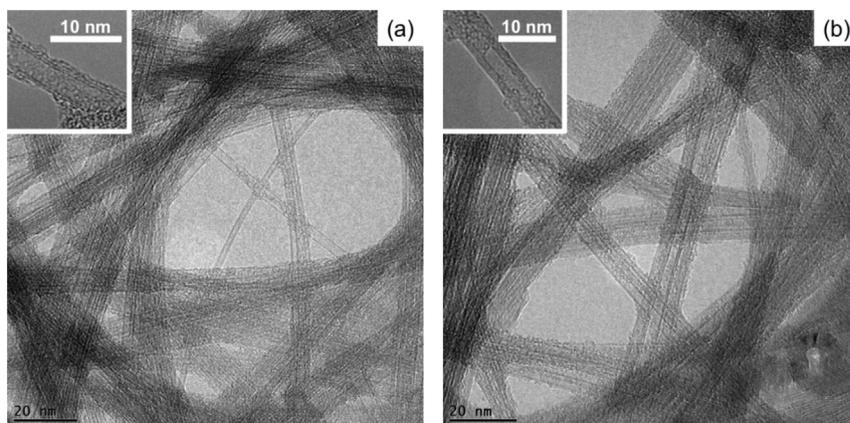


Fig. 1. TEM images of the two kinds of CNTs used in this study (a) CNT-A and (b) CNT-B. CNT-A has a smaller diameter, lower impurity content, and larger aspect ratio as compared to CNT-B.

Rheometer [18] for solutions of 0.05 wt. % CNT-A and CNT-B dissolved in chlorosulfonic acid. The theory of Shaqfeh and Fredrickson for semidilute rigid rod solutions [19] was then used to determine the CNT aspect ratios from the extensional viscosity of the CNT solutions [20]. The average CNT diameter and average number of walls were determined by analyzing TEM images of both CNT-A and CNT-B. During TEM observation, it was confirmed that both batches of CNTs are a mixture of single, double, triple, and four-walled carbon nanotubes. Approximately 10% of CNT-A and 4% of CNT-B were determined to be SWNTs. CNT density was calculated based on the average CNT diameter and the average number of walls determined by TEM. Details of the density calculations are provided elsewhere [21–23]. CNT-A and CNT-B were dispersed using 24 h bath sonication at a concentration of 2 mg/L in dimethylformamide (DMF) before placing on a transmission electron microscopy (TEM) grid (C-Flat 200 mesh, Electron Microscopy Sciences) and by drying at 40 °C for two days prior to TEM observation.

PAN and PAN/CNT solutions were prepared at a solid concentration of 10.5 g/dL using a polyacrylonitrile-co-methacrylic acid copolymer, (PAN-co-MAA) (96/4 by weight) with a viscosity

average molecular weight of 513,000 g/mol (Japan Exlan, Osaka, Japan). CNTs were dispersed in distilled DMF (Sigma Aldrich). CNT-A was used for two fiber spinning trials, where CNT concentration was 1.0 and 0.1 wt% with respect to the weight of the polymer. These samples are referred to as CNT-A and CNT-A(0.1), respectively. CNT-A was dispersed at a concentration of 7 mg/L using 24 h bath sonication (Branson 8510-MT), and CNT-A(0.1) was dispersed using a dispersion concentration of 10 mg/L using 30 min of homogenization (IKA T18) prior to 30 min of horn sonication (QSonica, Q700 Series) in an attempt to further disperse the CNTs during solution processing due to the higher sonication power of the horn sonicator. CNT-B was dispersed at a concentration of 25 mg/L using 60 min of homogenization prior to 24-h bath sonication. CNT-B concentration in the fiber was 1 wt% with respect to the weight of the fiber. It has been observed by dynamic light scattering and the preparative ultracentrifuge method that the bundle diameter of CNT-A when dispersed at a concentration of 10 mg/L using 24 h bath sonication resulted in a CNT bundle diameter of 22.9 ± 2.6 nm. CNT-B was dispersed at a concentration of 30 mg/L under 24 h of bath sonication and yielded a bundle diameter of 12.8 ± 1.4 nm [24]. These results indicate that CNT-A is more difficult to disperse than CNT-B due to its longer length, and therefore the dispersion concentrations for CNT-A and CNT-B should be different. A spinning system supplied by Hills Inc was used for all fiber spinning trials. Fibers were gel-spun using a 100-hole spinneret (diameter, $D = 200$ μm , length to diameter (L/D) ratio of 5) maintained at 85 °C with a solution flow rate of 0.5 cc/min/hole. Fibers were extruded through an air gap of 19 mm into a methanol bath maintained at -50 °C, and were collected at a spin draw ratio of 3. These fibers were subsequently kept immersed in methanol at -40 °C for two days prior to drawing. Post spinning fiber drawing was done in three stages using godet rolls maintained at room temperature (CDR), 110 °C (HDR1), and 185 °C (HDR2). Various fiber processing

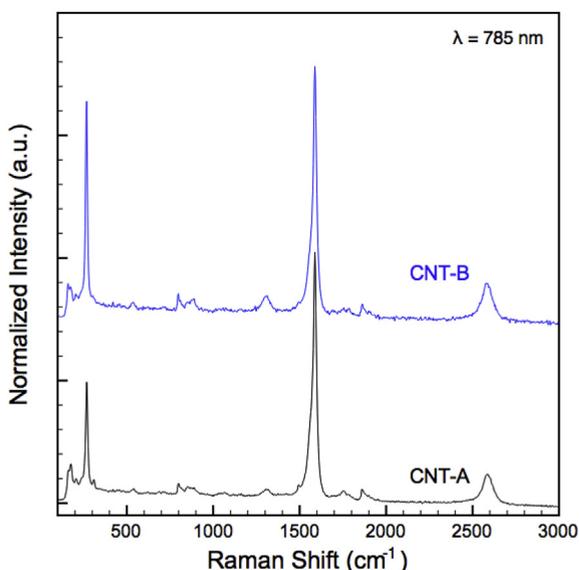


Fig. 2. Raman spectra of CNT-A and CNT-B CNTs. CNT-A has a G/D band ratio of ~ 42 and CNT-B has a G/D band ratio of ~ 17 .

Table 1

Material properties of CNT-A and CNT-B as determined by TGA, Raman spectroscopy, extensional rheology, and TEM. 30 CNTs were averaged for diameter and number of wall measurements.

	% Impurity ^a (wt %)	Raman G/D ratio	Aspect ratio (L/D) ^b	Average diameter (nm)	Average number of walls	Calculated density (g/cc)
CNT-A	1.1	42	2820 ± 200	2.7	2.6	1.66
CNT-B	3.3	17	1050 ± 50	3.0	2.6	1.60

^a % Impurity measured by TGA.

^b Aspect ratio determined from extensional viscosity measurements.

Download English Version:

<https://daneshyari.com/en/article/5181346>

Download Persian Version:

<https://daneshyari.com/article/5181346>

[Daneshyari.com](https://daneshyari.com)