Effect of Carbon Nanotube Diameter, Length, and Concentration on the Electrical Conductivity of Polymer Fibers

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Introduction

Polymer based composite materials are prevalent in many applications including aircraft and automobile structures, industrial machines, structural elements for industrial structures, bullet-proof vests, and armor materials. There are some specific applications like in semiconductor industry machine elements, computer and server housing, and in hospital equipments where the materials need to possess decent electrical conductivity for electrostatic dissipation and/or electromagnetic shielding.

The carbon nanotubes are attractive conductive reinforcements. When properly incorporated and dispersed, because of their large aspect ratio, the carbon nanotube are entangled and/or bound with the polymer system. Therefore the CNTs will not wear-off with time and a reasonable conductivity can be achieved at very low percolation. The conductivity of the composite can actually be tailored within wide ranges by changing the length, concentration, orientation, and type of nanotubes.

In this paper, we report the first electrically conducting CNT/polymer composite fibers spun by conventional spinning in which the MWNT concentration has been achieved as high as 20 wt% and CNFs concentration as high as 30 wt%. We also report the electrical conductivity of fibers loaded with a variety of CNTs, including SWNT, FWNT, MWNT, and CNFs. Our results show that by properly choosing the type of CNT, length of CNTs, dispersion of CNTs, fiber spinning method, fiber draw ratio or orientation of CNTs, and type of polymer, one can get electrically conducting fibers with wide range of conductivities for different applications.

Experimental

Materials and Processing

PAN/CNT and PVA/CNT composite fibers were considered for this study. PAN/SWNT and PAN/MWNT composite fibers were spun using dry-jet wet spinning and gel spinning, and PAN/CNF composite fibers were spun using dry-jet wet spinning. PVA/SWNT and PVA/MWNT fibers were spun using gel spinning. The materials and methods of PAN/SWNT and PVA/SWNT has been described elsewhere [1-3]. The PAN/MWNT and PAN/CNF composite fibers spun using dry-jet wet spinning has also been described elsewhere [4].

Composite Fiber Characterization

The orientation of polymer and CNTs was measured using wide-angle X-ray diffraction (WAXD) on a multi-filament bundle using Rigaku Micromax-002 (operated at 45 kV, 0.66 mA, and λ = 1.5418 Å). Diffraction patterns were obtained using Rigaku R-axis IV + + detection system. The diffraction patterns were analyzed using AreaMax V. 1.00 and MDI Jade 6.1. For composites in which CNT concentration was low, the CNT orientation was determined from the peak intensity of the tangential band (ca. 1590 cm^{-1}) in the Raman spectrum (Holoprobe Research 785 Raman Microscope made by Kaiser Optical System). A LEO SEM (Model 1530; operated between 5 to 15 kV) was used for the microstructure analysis. In-plane dc electrical conductivity of the composite fiber was measured using a four-probe (four point probe head made by Signatone) opearated by Keithley 2400 Sourcemeter.

Results and Discussion

Figure 1 shows the electrical conductivity of various PAN/CNT composite fibers as a function of CNT %. As mentioned before, the conductivity of a composite fiber is a function of CNT %, state of dispersion, aspect ratio, purity, defects, type and degree of interaction with polymer, orientation of nanotubes, and tunneling distance between nanotubes.

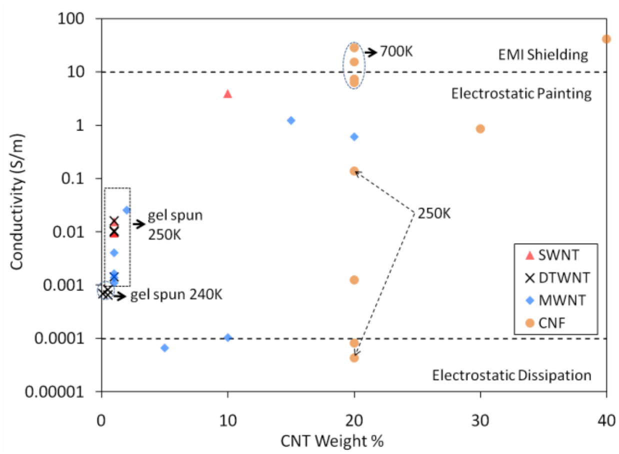

Figure 1. Electrical conductivity of PAN based composite fibers with different types of CNTs as a function of CNT concentration. The low CNT containing (≤ 2 wt.% CNT) fibers were spun using gel spinning and higher CNT containing fibers (≥ 5 wt.%) were spun using dry-jet wet spinning. PAN with four different molecular weights of 100K, 240K, 250K, and 700K was used. Fibers based on 240K, 250K and 700K PAN are marked and the rest of the unmarked fibers are based on 100K PAN. Note: PVA based composite fibers with 1% SWNT or 1% MWNT showed electrical conductivity in the range of 0.001 to 0.1 S/m (PVA /CNT data are not included in this Figure).

Fibers with different draw ratios were spun to achieve different degrees of CNT orientation in the fiber. A higher draw ratio results into a fiber with higher degree of CNT orientation. In general, the electrical conductivity increased with increase in draw ratio. The drawing affects the composite fiber morphology in three ways which may increase the fiber conductivity: (i) the effective aspect ratio of CNTs increases (a SWNT bundle has lower aspect ratio than individual SWNT and a MWNT agglomerate has lower aspect ratio than a non-agglomerated MWNT), (ii) orientation of CNTs increases in the fiber direction, and (iii) separation (tunneling distance) between CNTs decreases.

The processing of nanocomposites has a huge influence on the morphology and microstructure of the composite. For example, drawing/stretching may increase the effective aspect ratio of SWNT or MWNT (by de-bundling or de-agglomeration) and decrease the separation distance between CNTs. Furthermore, the effects of electron hopping and tunneling become more important when the separation distance decreases to tens of nanometers or less. For example, even at just 1 vol%, SWNTs of 1 nm diameter have a separation distance of just 9 nm. The separation distance can be correlated to the CNT-CNT contact resistance. A larger separation means higher tunneling resistance.

In general, the electrical conductivity increased with increase in CNT concentration. Since the fibers with different concentration of CNTs could not be drawn to the same degree, the trend of increasing conductivity was not linear.

In general, the conductivity showed this trend: SWNT>MWNT>CNF. This trend could be a result of the fact that the inherent conductivity of these fillers follows the same trend. In fact, for a particular CNT concentration, the tunneling distance also increases with increase in CNT diameter. Therefore, for a particular volume fraction of CNTs, the nanotube-nanotube separation would be maximum for CNFs and minimum for SWNTs. A lower tunneling distance would result in lower percolation threshold and higher conductivity.

References

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