Functional polymer–polymer/carbon nanotube bi-component fibers

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ABSTRACT

Bi-component fibers typically combine multiple functions that arise from at least two distinct components. As a result, these fibers can incorporate carbon nanotubes, which impart specific and controllable mechanical, electrical, and thermal transport properties to the fibers. Using gel spinning, sheath-core polyacrylonitrile–polyacrylonitrile/carbon nanotube bi-component fibers with a diameter of less than 20 μm and carbon nanotube concentrations of up to 10 wt% were produced. In these fibers, the carbon nanotubes were well dispersed and aligned along the fiber axis. The fibers exhibited a tensile strength as high as 700 MPa, and a tensile modulus as high as 20 GPa, as well as enhanced electrical and thermal conductivities when compared to the fibers without carbon nanotubes.

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1. Introduction

Bi-component fiber spinning has been an important technology in the field of fibers over the past 70 years [1–3]. From the original purpose of mimicking natural wool fiber with a side-by-side structure, which produces a self-crimping effect in 1940s [2,3], through the first commercialization of bi-component fibers in the 1960s [1,2,4], various shapes and polymer combinations have been used for this purpose. Some of the common bi-component fiber cross-section geometries (see Fig. 1) are sheath-core, sides-by-side, layer-by-layer, islands-in-the-sea, and segmented pie. Other more complex geometries can also be produced [1,3,5–8]. In addition, triple- or multi-component fiber geometries have also been made [9,10]. Bi-component fibers can be modified by introducing other materials such as coatings and mixing specific fillers or chemical compounds in one or both components [11–14]. These materials, including pigments, fragrances, metal particles, and clays, can introduce extra functionalities or enhance properties. Among the various fillers, carbon nanotubes (CNTs) [15] have high tensile properties [16–22], as well as high electrical- and thermal- conductivity [23–26] along the axial direction (Table 1). Extensive research in polymer/CNT nano-composites has been conducted using a variety of polymers, including poly (propylene) (PP) [27–30], poly (ethylene terephthalate) (PET) [31–33], poly (ethylene) (PE) [34–36], polyacrylonitrile (PAN) [37–41], poly (vinyl alcohol) (PVA) [42–45], poly (methyl methacrylate) (PMMA) [46,47], poly (ethylene oxide) (PEO) [48,49], poly (ether ketone) (PEK) [50], and PBO (Zylon™) [51]. However, few studies have been conducted on bi-component fibers utilizing carbon nanotubes [52–57]. For example, PAN sheath – SWNT core [57], PMMA sheath – SWNT core [56,57], PEO/MWNT sheath – PEO core [54], and cellulose sheath – CNT core [53] fibers have been reported by electrospinning, while polyamide sheath – PE/CNT core fibers have been processed by melt spinning [55]. Gel spinning can provide high polymer chain alignment and good mechanical properties, and as previously reported, successful gel spinning of PAN/CNT composite fibers has been achieved [38,39]. In the current research, PAN sheath and PAN/CNT core as well as PAN/CNT sheath and PAN core bi-component fibers were processed by gel spinning. These fibers exhibit good mechanical properties, as well as significantly enhanced electrical and thermal conductivities when compared to the fibers without CNTs. These new fibers can be used as functional wearable textiles that can transmit electrical signal [58,59] or can be used for thermal management [60].

2. Experimental procedure

PAN (homopolymer, molecular weight: 2.5×10^5 g/mol) was obtained from Japan Exlan Co. and dried in an oven at 100 °C for two days. Multi-wall carbon nanotubes (MWNT), with an average

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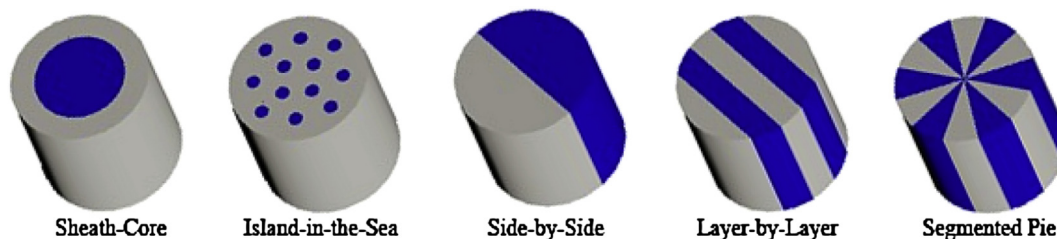 E-mail addresses: Satish.Kumar@mse.gatech.edu, satish.kumar@gatech.edu (S. Kumar).

Fig. 1. Typical bi-component fiber cross-sections.

diameter of 21.0 ± 3.1 nm were obtained from Cheap Tubes Inc. MWNT powder was dispersed in dimethylacetamide (DMAc from Sigma−Aldrich Co.) at a concentration of 0.5 g/300 ml via homogenization (T18, IKA Works Inc.) followed by bath sonication (Bransonic, 3510-MT) for 24 h. PAN powder was separately dissolved in DMAc at a concentration of 14 g/100 ml at 90 °C and MWNT/DMAc dispersion was added to this PAN solution. The excess solvent was evaporated using a vacuum distillation process. The addition of MWNT dispersion and solvent removal processes were repeated to obtain the desired MWNT concentration (10 wt%) with respect to the weight of the polymer. The final concentrations utilized in the investigation of the PAN/CNT solutions are listed in Table 2.

PAN/CNT composite fibers were spun using bi-component fiber spinning unit manufactured by Hills, Inc (Melbourne FL). This is a two piston driven unit containing two reservoirs for the sheath and the core components. This unit can be used for solution spinning or melt spinning and the temperatures and flow rates of the two solutions or melts can be controlled independently. As mentioned earlier, PAN/CNT solution was used either for the sheath or for the core component. When the PAN/CNT solution was used as the core component, the control PAN solution was used as the sheath component, and vice-versa. Both solutions were maintained at 70 °C in the reservoir and subsequently co-extruded through a single-hole spinneret with a diameter of 200 μm maintained at 100 °C. The extrudate was passed through a 25 mm air gap and then through a methanol gelation bath maintained at −50 °C. The sheath/core radii ratio was controlled by changing the flow rates of the two components. The as-spun fiber was then stored to enhance gelation in a methanol bath at −50 °C overnight, and was subsequently drawn at room temperature followed by drawing at 165 °C in a glycerol bath.

Fiber cross-sections were observed using an optical microscope and scanning electron microscope (SEM, Zeiss Ultral60). For sample preparation, the fiber bundle was embedded in epoxy resin and then microtomed (RM2255, Leica) in 10−15 μm thick sections. Fiber tensile properties were measured at a gauge length of 25.4 mm and at a cross-head speed of 0.127 mm/s, using RSA III solids analyzer (Rheometric Scientific Co.). Wide angle X-ray diffraction (WAXD) using CuK$_\alpha$ (λ = 0.1542 nm) manufactured by Rigaku Micromax-002 (operating voltage and current 45 KV and 0.65 mA) was conducted on a fiber bundle. Diffraction patterns were recorded by a detection system (Rigaku R-axis IV++) and analyzed by AreaMax (version 1.00), and MDI Jade (version 9.0). From the WAXD data, PAN crystallinity, PAN crystal size, and the Herman's orientation factors of the polymer and of carbon nanotubes were calculated following previously described methods [37,38]. Electrical conductivity along the fiber axis was measured using the 4-point probe method (Signatone probe and Keithley 2400 Sourcemeter) and thermal conductivity was measured by steady-state DC thermal bridge method (DCTBM) [61].

3. Results and discussion

The various fiber processing parameters utilized in the current investigation are listed in Table 2. The ratio of the effective outer fiber radius to that of the core radius was determined by the concentrations of the two solutions and their flow rate. This ratio was comparable to the actual ratio observed in the fiber cross-section. In the current gel-spinning process, the maxima draw ratio for the bi-component fibers of approximately 20 with PAN/CNT composite as the core and approximately 11 with the PAN/CNT composite as the sheath was achieved. This is when CNT content in the composite layer was approximately 10 wt% with respect to the weight of the polymer, while the outer diameter to the core diameter ratio varied between 1.5 and 3.8. In the previous single component investigation at 5 wt% CNT a draw ratio of approximately 10 was achieved [38], while at CNT contents higher than ∼10 wt%, the draw ratio was below 5 [40]. Thus, in the current investigation at a given MWNT concentration, PAN/MWNT − PAN bi-component fibers exhibited significantly higher draw ratios than the corresponding single component PAN/MWNT fibers. This higher draw ratio in the current bi-component fiber is attributed to the component that does not contain carbon nanotubes. This is consistent with the previous reports on layered bi-component polypropylene tapes containing fillers such as CNTs [62,63]. With high draw ratios, improved mechanical properties can be obtained in the bi-component system.

Optical micrographs of the bi-component fibers (Fig. 2) exhibited a kidney-bean cross-sectional shape for the cold drawn PAN sheath and PAN/CNT core fibers (samples A1 and A4) and somewhat irregular cross-sections for the PAN/CNT sheath and PAN core fibers (sample A7). This is related to variations in coagulation rate of different fibers. The coagulation rate depends on solution concentration, and the temperatures of the extrudate and that of the methanol coagulation/gelation bath. In the current investigation, extrudate and coagulation bath temperatures were the same in all trials. However, the solid content of the control PAN solution that formed the sheath in samples A1 and A4 (14 g/dL) was higher than that of the PAN/CNT solution that formed sheath in sample A7 (<11.6 g/dL). This difference in solution concentration is attributed to the differences in the cross-sectional shape in the two cases in the current investigation and is consistent with previous literature reports [64,65]. However, it was also noted that solvent and non-

Table 1
Properties of carbon nanotubes.

	Properties	References
Modulus	0.2 TPa ∼ 1 TPa[a]	[15−19]
Tensile Strength	10 GPa ∼ 150 GPa[a]	[18−22]
Electrical Conductivity	$10^2 - 10^7$ S/m	[23]
Thermal Conductivity	2000−6000 Wm^{-1} K^{-1}	[24−26]

[a] Modulus and strength values depend on the CNT diameter and on the presence of defects.