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Electrical conductivity and Joule heating of polyacrylonitrile/carbon nanotube composite fibers

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ABSTRACT

Carbon nanotube (CNT) can exhibit electrical conductivity and introduce electric current into polymer. Using dry-jet-wet spin technology, polyacrylonitrile (PAN)/CNT composite fibers with 15 wt% and 20 wt% of CNT content were fabricated. The electrical conductivity of PAN/CNT fibers was enhanced by the annealing process at different temperatures and changed with time. These fibers could also respond to stretching, and the electrical conductivity decreased by 50% when the elongation reached 3%. In addition, electrical current can induce Joule heating effect and thermally transform PAN/CNT composite fibers. With the application of various electrical currents up to 7 mA at a fixed length, conductivity was enhanced from around 25 S/m to higher than 800 S/m, and composite fibers were stabilized in air. The temperature of composite fibers can increase from room temperature to several hundreds of degree Celsius measured by an infra-red (IR) microscope. Joule heating effect can also be estimated according to one-dimensional steady-state heat transfer equation, which reveals the temperature can be high enough to stabilize or carbonize fibers. As a result, this research provides a new idea of heating fabrics for thermal regulation, and a new approach for stabilizing and carbonizing PAN-based carbon fibers.

1. Introduction

Carbon nanotubes (CNTs) [1,2] can exhibit high strength and high electrical conductivity, and therefore CNTs can not only enhance mechanical properties but also introduce electrical conductivity into polymers. With the polymer properties of flexibility, low-density, and ease-of-use, the electrically conductive polymer/CNT materials can be utilized for wearable electronics or sensors [3–6]. For example, polymer/CNT composite can respond to the surrounding temperature or external force. In addition, when we apply electrical current through the conductive materials, electrical current induces Joule heating effect (self-heating). CNTs have shown significant self-heating effect due to the applied electric current [7–19], and the temperature can be enhanced high enough to burn out conductive CNTs and leave semi-conductive CNTs for computer application [20]. This active heating effect also appears in polymer/CNT composites, as reported for composite films with polyethylene [21], silicone elastomer [22], epoxy [23], and m-aramid [24].

Previously, polyacrylonitrile (PAN) and carbon nanotube composite fibers have been reported with well-dispersed and aligned CNTs along the fiber axis [25–28]. CNTs not only improved mechanical properties but also introduced electrical conductivity to composite fibers. Since the electrons are transferred through the CNT network, both the concentration and orientation [29–32] of CNTs in the composite fibers determined the structure of CNT network and therefore influenced the electrical conductivity. However, the structure of composite fibers can also be affected by other factors such as the surrounding temperature or external force on the fibers. The electrical conductivity of fibers can be changed when the fibers are placed in different temperature or stretched. This research covers the discussion on the influence of temperature and stretching process on the electrical conductivity of PAN/CNT composite fibers. In addition, since Joule heating effect also occurs when electrical current is applied on the PAN/CNT composite fibers, the self-heating behavior is also investigated in this research. The change of fibril structure and physical properties such as electrical conductivity owing to the Joule heating effect are also discussed in this report.

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2. Experimental procedure

Polyacrylonitrile (PAN, molecular weight: 10^5 g/mol) with 6.7% methyl acrylate as a copolymer was obtained from Japan Exlan Co. and dried under vacuum at 80 °C before being used. Carbon nanotubes (multi-wall carbon nanotubes) were obtained from Iljin Nanotech Co. (Korea) and used as received. The PAN powder was dissolved in dimethylformamide (DMF, Sigma–Aldrich Co.) using an impeller at 90 °C, and the CNT powder was dispersed in DMF using a bath sonicator (Branson, 3510-MT). CNT/DMF dispersion was subsequently mixed with the PAN solution for fiber spinning, and the PAN/CNT composite fibers were fabricated using a dry-jet wet spinning unit (Bradford University Research, UK) with a spinneret of 250 μm diameter and two coagulation (DMF/water) baths. The fibers were subsequently drawn in boiling water and dried in an oven at 50 °C for 7 days [26]. The draw ratios and diameters of the PAN/CNT composite fibers were listed in Table 1.

PAN/CNT composite fibers at a fixed length were annealed in an oven at 65, 135, 165, and 180 °C for two hours before the electrical conductivity was measured. Fibers were fixed using a silver paste (Electron Microscopy Sciences), and electrical conductivity along the fiber axis was measured using the four-point probe method (Signatone probe and Keithley 2400 Sourcemeter) [33]. The response of electrical conductivity to the annealing process at 180 °C was observed by connecting the fiber to a source meter unit (Keithley 2400 Sourcemeter) using silver paste and copper wires in a temperature-controlled oven (Rheometric Scientific Co.). In addition, fibers annealed at 180 °C for two hours were used to investigate the response of electrical conductivity to tensile strain. The electrical conductivity was measured at room temperature using the same setup used for the annealing effect, and the fibers were stretched simultaneously using RSA III solids analyzer (Rheometric Scientific Co.) at a cross-head speed of 0.0127 mm/s with a fiber gauge length of 25.4 mm.

Joule heating effect was induced by applying electrical current using the same source meter unit (Keithley 2400 Sourcemeter). The fiber structure was measured by real-time wide angle X-ray equipment during Joule heating process. Wide angle X-ray diffraction (WAXD) using CuK_α ($\lambda = 0.1542$ nm) was conducted with an X-ray generator (Rigaku Micromax-002) with 45 KV operating voltage and 0.65 mA current. 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 [25,27]. Before and after Joule heating process, infra-red spectra (IR) of fibers were collected using an infrared microscope (Spectrum One, PerkinElmer) with a resolution of 1 cm^{-1} and 256 scans, and analyzed with IR software (Spectrum, version 5.3, PerkinElmer). The temperature of the composite fibers during the self-heating process was also observed by the InfraScope II infra-red temperature measurement microscope system (Quantum Focus Instruments Co.).

Table 1
Listing of compositions, draw ratios, diameters, and linear density for the fibers investigated in this study [26].

Sample	MWNT content [wt%]	Draw ratio	Diameter [μm]	Linear density[a] [tex]
A	15	4	60	3.6
B	20	2.5	44	2.0

[a] Tex equals the weight in grams of 1000 m length of fiber.

Table 2
Electrical conductivities of PAN/CNT composite fibers with various annealing temperatures.

Sample	MWNT content [wt%]	Conductivity[a] [S/m]				
		Original	65 °C	135 °C	165 °C	180 °C
A	15	2.21×10^{-5}	7.37×10^{-5}	6.89×10^{-3}	1.68	4.83
B	20	3.14×10^{-5}	8.31×10^{-5}	3.61×10^{-2}	7.82	27.63

[a] The composite fibers were annealed at various temperature under fixed length for two hours before the measurement of electrical conductivity.

3. Results and discussion

3.1. Effect of annealing process

The conductivity of PAN/CNT composite fibers with 15 and 20 wt % CNT content was measured by the four-point probe method and the results are listed in Table 2. For composite fibers before the annealing process, the conductivity was around 10^{-5} S/m. Although CNT electrical conductivity is in the range of $10^5 - 10^6$ S/m and the CNT content was up to 20 wt% in these fibers, the considerable Schottky barrier [34,35] between adjacent tubes may severely reduce conductivity, and the appropriate CNT orientation [29–32,36,37] was required for effective CNT network. Electrical conductivity was significantly improved by using the annealing process [28,38–44], and after annealing at 180 °C for two hours, the conductivity was as high as 4.83 S/m and 27.63 S/m for fibers with 15 and 20 wt% CNT content, respectively. According to the data in Table 2, electrical conductivity increased with increase in annealing temperature.

The response of conductivity to the annealing process was observed using a power source meter and a temperature-controlled oven. Composite fibers with 20 wt% CNT content were controlled at 180 °C and 10 μA current was applied. The voltage and the calculated electrical conductivity with annealing time are shown in Figs. 1 and 2. The response of voltage in the beginning was fast. After only one minute, the applied voltage was reduced to 40% and the electrical conductivity increased to approximate 2 S/m. After two hours of annealing time, the voltage decreased by 95% and the conductivity approached 25 S/m.

In order to investigate the structure change due to annealing, composite fibers before and after being annealed for two hours at 180 °C were also observed using X-ray diffraction. Fig. 3 reveals that the WAXD diffraction patterns were changed after annealing process, and the corresponding structural parameters are summarized

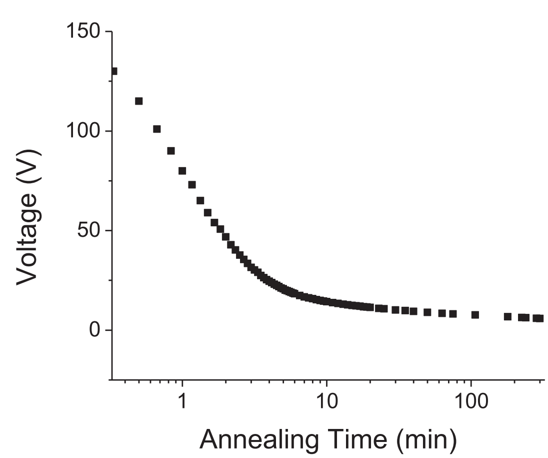

Fig. 1. Voltage of PAN/CNT composite fibers with 20 wt% CNT content during annealing process at 180 °C with 10 μA applied current at a constant length of 25.4 mm.