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Mechanical and electrical properties of thermochemically cross-linked polymer carbon nanotube fibers

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ABSTRACT

We report an effective post-treatment method to improve the mechanical and electrical properties of carbon nanotube fibers (CNTF) by using an aryl radical coupling reaction of polymers. The modified CNTF were analyzed using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). The results demonstrated that chemical cross-links formed by Poly(*p*-iodostyrene) (PIS) inside the CNTF affected the mechanical and electrical properties. Compared with pristine CNTF, the cross-linked CNTF using PIS exhibited about 160%, 200% and 53% increased tensile strength (1.4 N/tex), elastic modulus (103 N/tex) and electrical conductivity (1480 S/cm), respectively. This post-treatment method using polymer impregnation followed by thermochemical reaction may provide a general strategy for enhancing both mechanical and electrical properties of directly spun CNTFs.

1. Introduction

Many efforts have been made to spin continuous CNT fibers (CNTFs) to fully exploit the excellent mechanical properties (Tensile strength: ~150 GPa and Young's modulus: ~1 TPa) and electrical conductivity (~10^4 S/cm) of individual carbon nanotubes (CNTs) for specific structural applications [1–3]. Since CNTF, a macroscale structure consisting of longitudinally aligned CNTs, first reported in 2000 [4], CNTFs have been considered to be important materials to develop new applications which CNT powders could not provide. However, the mechanical properties of CNTFs fabricated by various methods are orders of magnitude lower than those of the corresponding individual CNTs because of the weak interfacial interactions between CNTFs. Despite significant research efforts that have been made to improve these CNTF properties [5–8], however, fabrication of strong CNTFs remains a great challenge.

One of the techniques for fabricating high-performance CNTFs, polymer impregnation, has been considered to improve the mechanical properties of CNTFs by increasing load transferring between individual CNTs in the CNTFs compared with that of pristine CNTFs [9–14]. The improvement of mechanical properties is attributed to the strong polymer-CNT interface interaction. However, polymer impregnation also has a detrimental effect on the electrical conductivity of the CNTFs due to the insulating properties of polymers. Improving both the electrical conductivity and mechanical properties of CNTFs is an important issue for developing high-performance CNTFs.

In this study, we developed a simple and effective post-treatment method for improving the mechanical and electrical properties of CNTFs by using aryl radical coupling reactions of Poly(*p*-iodostyrene) (PIS) as shown in Fig. 1. Uniformly polymer impregnated CNTFs were prepared using a simple dipping method of polymer solution. The process consists of dipping the fibers in diluted PIS solution and heating them at 350 °C for cross-linking of individual CNT bundle in the CNTFs. PIS is covalently bonded directly to the CNT side walls via an aryl radical coupling reaction during the thermal treatment. The mechanical properties of polymer-CNT fibers can be improved because the cross-linked

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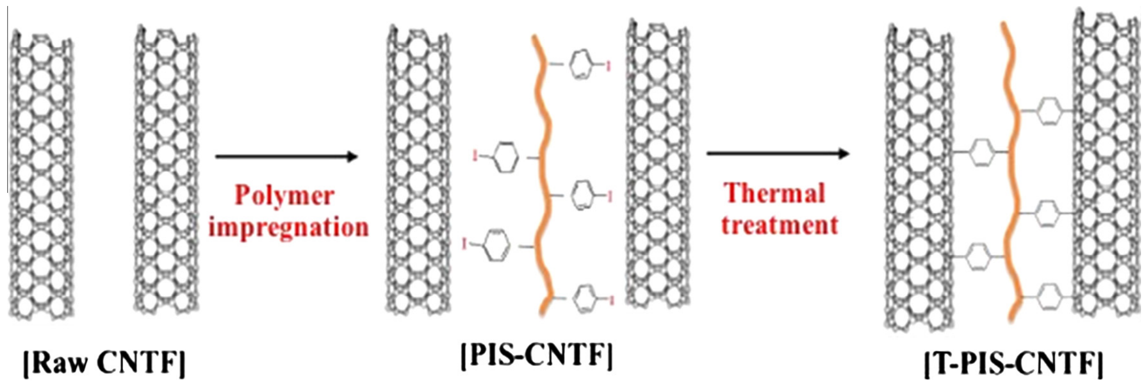

Fig. 1. Schematic depict for synthesis of PIS-cross linked CNTF by aryl radical coupling reaction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

bond between polymers and the CNT bundles in the CNTFs can enhance interfacial interaction between them. In addition, the iodine groups released from PIS during the thermal process can act as an effective doping agent for the CNTFs, resulting in improving their electrical conductivity. The mechanical properties and electrical conductivity of CNTFs were investigated by optimizing thermal treatment condition of PIS-CNTF.

2. Experimental

2.1. Materials

Poly(*p*-iodo styrene) (PIS) was obtained from Scientific Polymer Products, Inc. The molecular weight of PIS was 400,000 g/mol. N, N′-Dimethylformamide (DMF) was obtained from Samchun Chemical, Korea. Ethanol was purchased from Wako Pure Chemical Industries Ltd., Japan. Acetone (99.7%) was used as a carbon source (Samchun Chemical, Korea). Ferrocene (>98%) was used as a catalyst precursor, thiophene (>99%) as an activating agent, and polysorbate-20 as surfactants, all of which were purchased from Sigma Aldrich.

2.2. Synthesis of carbon nanotube fibers (CNTF)

CNTFs were synthesized using a direct spinning method based on floating catalyst chemical vapor deposition. The precursor solution used for CNT synthesis was a mixture of acetone (98.0 wt%), ferrocene (0.2 wt%), thiophene (0.8 wt%), and polysorbate-20 (1.0 wt%). Acetone was used as the carbon source, dispersed with ferrocene as a catalyst and thiophene as a promoter. The polysorbate was used for improving the spinnability of CNTF during the spinning process. The prepared solution was injected at a rate of 10 mL/h with a hydrogen gas flow rate of 1000 sccm into a vertical reactor heated at 1200 °C. The assembly became much denser while passing through a water bath, and the dense assembly was wound up easily as fibers. The synthesized CNTFs were wound up in the rate of 9 m/min at the bottom of the reactor. Details of the procedure have been reported elsewhere [15].

2.3. Preparation of Polymer Cross-linked Carbon Nanotube Fiber (PIS-CNTF)

PIS impregnated CNTFs (PIS-CNTF) were obtained using dipping method of diluted polymer solution. PIS (0.25 g) was added to the DMF solution (50 g) and the mixture was stirred at room temperature until the PIS was dissolved completely. The CNTFs were dipped perpendicularly into the PIS solution, immersed at 60 °C for 24 h, washed with deionized water, and dried at 60 °C for 24 h in a vacuum oven. The cross-linked CNTFs were obtained by aryl cross-linking reaction of PIS-CNTF by thermal treatment. We determined the optimum temperature and heating time for the thermal treatment, and the results are shown in Fig. S2 and Table S1. Based on the optimization experiment, the PIS impregnated CNTF (PIS-CNTF) was thermally treated at 350 °C in the air atmosphere. The PIS-CNTF was heated to 350 °C at a rate 5 °C/min and annealed. The annealing time was increased from 1 to 6 h to investigate the effect of annealing time on the mechanical properties of PIS-CNTF. The thermally treated PIS-CNTF were designated as T-PIS-CNTF.

2.4. Characterizations

The chemical bonds of PIS impregnated and cross-linked CNTFs and thermal treated PIS-CNTF were investigated using XPS (AXIS-NOVA, Kratos, USA). Thermogravimetric analysis (TGA, Q50, TA instrument, USA) was used to determine content of PIS-CNTF. The intensity ratio between the D-band and G-bands was investigated using Raman spectroscopy (LabRAM HR, Horiba, Japan) at room temperature using a 514 nm excitation laser. Tensile strength and linear density of PIS impregnated CNTFs and cross-linked CNTFs were tested using the FAVIMAT single fiber tester (FAVIMAT-AIROBOT2, Textechno, Germany). CNTFs were tested with a 10 mm gauge length and a cross head speed of 2 mm/min. Tensile strength, modulus, elongation and tex were an average value of 15 repeated measurements. The electrical conductivity was measured 5 times using the 4-point probe method with a 2 cm distance between the electrodes (FPPRS8, Dasol Eng., Korea). The calculation is based in the assumption that CNTF are in a cylindrical shape. The diameter of each cable plugged into the formula was an average based on the measurement of 30 times different locations along the fiber long axis direction using an optical microscope (Olympus BX51). The average diameter of the neat CNTF is 19 μm. After the PIS infiltration, the average diameter of the CNTF was slightly increased from 19 to 20 μm. The iodine distribution of T-PIS-CNTF was imaged by FE-TEM (G2 F20, FEI Tecnai, Netherlands) and transmission electron microscopy (Titan TEM, Titan G2 60-300, FEI, USA) analysis with element mapping to confirm the presence of iodine atoms in T-PIS-CNTF. TEM sample was prepared by drop casting method of diluted CNTF solution on the carbon coated copper grids.