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Effects of functional group of carbon nanotubes on mechanical properties of carbon fibers

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ABSTRACT

The effects of surface functionalization of carbon nanotubes (CNTs) on the mechanical properties of carbon fibers (CFs) have been investigated. The surface functionalization of CNTs was carried out with a diazonium reagent. Compared to pure PAN, only the fluoro phenyl functionalized CNTs (F-Ph-CNT) incorporated PAN composites showed a significant increase up to 22 °C of T_g and displayed the second peak due to the interfacial interaction between F-Ph-CNT and PAN. Among the samples, 0.5wt% of F-Ph-CNT reinforced CFs exhibited a 46% increase in tensile strength (4.1 GPa) and a 37% increase in modulus (302 GPa), respectively compared to that of pure CFs.

1. Introduction

Carbon fibers (CFs) are widely used in the manufacture of CF reinforced composites (CFRP) with enhanced mechanical and thermal properties. CF is produced by the thermal decomposition of various organic fiber precursors, such as polyacrylonitrile (PAN), pitch and rayon. PAN is used as a carbon fiber precursor for making high performance CFs due to its high tensile strength and modulus [1]. The fibers impart excellent specific strength and stiffness combined with light weight. The high strength-to-weight, combined with superior stiffness, has made PAN based CFs the materials choice for high performance composite structures in aerospace, defense and other industries [1,2]. Thus, the synthesis, structural characterization, and cyclization study of this polymer have received a great deal of attention in recent years. The stabilization process has a very important influence on the final properties of CFs [3,4]. The stabilization process is found to play an important role in converting PAN fiber to an infusible stable ladder polymer structure that converts $C\equiv N$ to $C=N$ [5]. Hence, the mechanical properties of PAN are strongly dependent upon the degree of stabilization during the stabilization process.

The surface functionalization of CNTs had a strong influence on the cyclization mechanism of PAN composites [5–7]. In addition, CNTs can be homogeneously dispersed in PAN, resulting in composites with improved mechanical properties [2]. Hence, significant developments are now being reported in processing wholly CNTs reinforced CFs. CNTs have been expected to produce materials with improved tensile strength and modulus [8,9]. Therefore, significant research efforts have been made on the development of CNTs reinforced CFs due to their excellent mechanical properties [10,11]. Furthermore, CNTs can be used as functional materials for a wide range of applications [12–14] due to superior mechanical, electrical [12] and thermal properties [13]. PAN/CNTs composite fibers containing 10 wt% of SWNTs exhibited a 50% increase in tensile strength, 100% increase in modulus, and a reduction in thermal shrinkage, compared to the

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pure PAN fibers [15,16]. All of these findings suggest that CNTs reinforced CFs have a significant potential for producing high performance composites.

Our previous work suggested that the fluorophenyl group functionalized CNTs (F-Ph-CNT) can act as a more effective exothermal initiator for nitrile cyclization in homo PAN compared to the acid groups functionalized CNTs [5]. Based on this result, herein we report the effect of surface modification of CNTs on the mechanical properties of CNT/PAN composites and resulting CFs.

2. Material and methods

2.1. Materials

Multi-wall carbon nanotubes (CNTs) were obtained from Nanocyl, Belgium. Sodium nitrite was purchased from Tokyo Chemical Industries Ltd, Japan. Sulfuric acid and nitric acid (60%) were purchased from PFP Matunoen Chemicals Ltd, Japan. *N, N′*-Dimethylformamide (DMF) was obtained from Samchun Chemical, Korea. Ethanol was purchased from Wako Pure Chemicals Industries Ltd, Japan. Dimethyl sulfoxide (DMSO) was obtained from Sigma–Aldrich, USA. In addition, 4-fluoroaniline and 4-amino benzoic acid were purchased from TCI, Japan. Commercial poly(AN-*co*-IA) was purchased from Bluestar Co., Ltd, China. And commercial homo PAN was obtained from Sigma–Aldrich (Mw: ~100,000 g/mol).

2.2. Preparation of functionalized CNTs (COOH-CNT, COOH-Ph-CNT and F-Ph-CNT)

The 0.5 g of CNTs were immersed in a 1:3 mixture of concentrated HNO_3 and H_2SO_4 and sonicated at room temperature for 1 h. The oxidation process was carried out at 80 °C for 3 h. The oxidized CNTs (COOH-CNT) were washed with excess deionized (DI) water. 0.3 g of COOH-CNT was immersed in a 100 mL of H_2SO_4 solution at room temperature and sonicated for 30 min. After that, 1.8 g of 4-amino benzoic acid/4-fluoroaline and 0.69 g of sodium nitrite were quickly added via syringe. The suspension mixture was stirred at 60 °C for 1 h. After cooling to room temperature, the suspension was diluted with DMF solution, washed with DMF and finally washed with ethanol. The product was dried at 60 °C for 24 h in a vacuum oven. Fig. 1 shows the scheme of surface functionalization of CNTs.

2.3. Preparation of functionalized CNTs incorporated PAN composite films (CNT/PAN)

The 1 mg of CNTs were immersed in a 1 mL of DMF and sonicated for 1 h. The 0.1 g of PAN was separately dissolved in 1 mL of DMF at 50 °C, and the PAN/DMF solution was added to the CNT/PAN dispersion and homogenized while stirring for 3 h. The mixture was casted on the polyimide film by a doctor blade. The casting CNT/PAN films were dried at 60 °C under a vacuum oven to remove the residual solvent. For the stabilization, CNT/PAN composite films were heated from room temperature to 290 °C in air at 5 °C/min and held at 290 °C for 30 min. The stabilized CNT/PAN films were cooled down to room temperature.

2.4. Preparation of CNTs incorporated poly(AN-co-IA) dope

The certain amount of F-Ph-CNT was immersed in 79 g of DMSO solution, undergoing sonication at room temperature for 10 h. After that 21 g of poly(AN-*co*-IA) and F-Ph-CNT/DMSO solution were charged stainless steel vessel and mixed at 50 °C for 12 h using polymer dissolving machine (DLS-6000, Daelim Starlet co., Ltd, Korea). Finally, F-Ph-CNT/Poly(AN-*co*-IA) mixture was evaporated at 50 °C for 12 h in an oven.

2.5. Preparation of CNTs reinforced carbon fiber by wet spinning method

A spinneret with 150 holes was mounted for wet spinning at 50 °C. A wet spinning line had four baths: one coagulation bath, two washing baths and one drawing bath. The coagulation bath contained a DMSO/DI-water (distillated water) (=5:5) mixture at 50 °C, and the two washing baths were filled with distillated boiling water. The drawing bath was stretched 4 to 5 times in boiling DI-water. After spinning, fibers were dried using an in-line heater for 5 min at 110 °C. The F-Ph-CNT incorporated poly(AN-*co*-IA) fibers were thermally stabilized in a convection oven. A constant tension was applied to fiber tows to maintain the molecular orientation during stabilization. The precursor fibers were stabilized at 240 °C for 1 h under air atmosphere in a convection oven. After stabilization, the fibers were carbonized from room temperature to 1200 °C in a nitrogen gas at a heating rate 5 °C/min, and fibers were cooled down to below 100 °C without hold.

2.6. Characterization

The surface functional groups were characterized by Fourier transform infrared spectroscopy (FT-IR) (IS 10, Sinco, Japan) and X-ray photoelectron microscopy (XPS, AXIS-NOVA, Kratos Inc, USA). Al Kα (1485.6 eV) was used as the X-ray source at 14.9 keV of anode voltage, and 4.6 A and 20 mA were used as the filament current and mission current, respectively. The dynamic mechanical properties of CNT/PAN composite films were determined using the Seiko Exstar 6000 machine (Sinco instrument, Japan) in the rectangular tension mode. The strain rate was 0.01% and the viscoelastic properties were measured in the temperature range of −50 °C to 350 °C. Dynamic mechanical tests were conducted at a frequency of 10 Hz at a heating rate of 5 °C/min. The mechanical properties of composite films and CFs were determined using a universal testing machine (UTM, 5567A, Instron. USA). The 20 samples were prepared with 25 mm of length, and the rate of crosshead was set at 2 mm/min. The mechanical properties of fibers were averaged. Fiber diameters were measured by an optical microscope (Olympus BX51, Japan).

The cross-section of CFs was imaged by a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi Co., Japan) and CNT dispersion in CFs was investigated by a transmission electron microscope (FE-TEM, TecnaiG2 F20, FEI, USA).

3. Result and discussions

3.1. Characterization of functionalized CNTs

The surface functional groups of CNTs were investigated by FT-IR and XPS. The FT-IR spectra of COOH-CNT and COOH-Ph-CNT suggested that carboxylic groups are present on the CNTs (Fig. 2). The peaks at 1640 cm^{-1} and 1560 cm^{-1} were assigned to the ester groups C=O and -C-O-C-stretching, respectively. A broad peak at around 3410 cm^{-1} can be assigned to the –OH stretching vibration of the surface hydroxyl groups on the acid functionalized CNTs (COOH-CNT and COOH-Ph-CNT) [17,18]. The characteristic peak of the C–F band on the surface of F-Ph-CNT is shown in Fig. 2. The appeared C–F stretch bands consist of three bands at around a spectra of 1160 and 1215 cm^{-1}. Peaks at 1160 and 1215 cm^{-1} are assigned to the semi-ionic C–F bands and a characteristic of the covalent C–F bonds, respectively [19,20].