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Full Length Article

Quasi-static and dynamic interfacial evaluations of plasma functionalized carbon nanotube fiber

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ABSTRACT

Carbon nanotube (CNT) fibers composed of well-oriented and twisted CNT bundles are desirable as a strong and lightweight reinforcement for the high-performance composites. Herein, CNT fibers were functionalized by atmospheric pressure helium/oxygen plasma to build up the sufficient fiber/matrix interfacial bonding. The micro-bond test (quasi-static test) and electrical resistance measurement under cyclic loading (dynamic test) were carried out to evaluate the interfacial properties between CNT fiber and epoxy resin. The results illustrated 84.6% improvement in the interfacial shear strength (IFSS) of the functionalized CNT fiber and epoxy from 17.37 MPa to 32.08 MPa, since the generated oxygenic groups and roughed morphology on CNT fiber surface. Moreover, the linear and repeatable gauge factors (between 1.1 and 1.4) of the functionalized CNT fiber embedded in epoxy under dynamic cyclic loading demonstrated their good interfacial bonding as well. In addition, the tensile strength of the functionalized CNT fiber showed 49.5% increment. Our study for the first time reveals the interface interaction in a fiber-matrix system to provide the direct evidence for the interfacial enhancement of the plasma functionalized CNT fiber. The interface-enhanced CNT fiber can be generally applied in composites with much improved mechanical and electrical performance.

1. Introduction

CNTs exhibited outstanding electrical, mechanical, and structural properties, and proved to be an extremely promising candidate for various applications in material science [1]. The creation of assembly made out of CNTs enable macroscopic nanotube devices and structures to be constructed [2]. For instance, CNT fibers and sheets possess excellent performance for super-capacitors, actuators, lightweight electromagnetic shields and etc. [3].

CNT fibers are among the materials with high-strength, lightweight, and high thermal and electrical conductivities [4,5]. Strength, stiffness, and light in weight are critical properties required for materials used in the construction of space shuttles, airplanes, and space composite structures [6]. Thus, CNT fibers have the potential as reinforcement for composite materials such as, current commercial high performance fibers [7,8]. Despite their great potentials, CNT fibers have shown some severe restrictions regarding the inert property of the graphitic network for the CNT material [9]. Therefore, for polymer composite applications, CNT functionalization is required to promote interfacial bonding and transfer of fiber-to-matrix properties [10]. Whereas, chemical oxidation [11,12], acid treatment [13] and plasma treatment [14] are the most common methods. Among them, the plasma treatment is the most feasible method due to its advantages such as, inducing the fixation of different chemical groups on the surface, shorter treatment time and nonpolluting [15].

In recent decades, plasma treatment was adopted as an effective method to modify the surface of various fibers, such as: carbon fiber [16], aramid fiber [17], polyester fiber [18], glass fiber [19] and some natural fibers [20,21]. Besides, Park et al. [22] reported the increment of mechanical properties of CNT fibers treated by atmospheric-pressure plasma. Hicks et al. [10] systemically investigated the surface composition and mechanical and electrical properties of the plasma activated CNT yarn and sheet. However, very few researchers reported about the fiber-matrix interactions of the plasma functionalized CNT fiber. Though, Jiang et al. [23–25] narrated the improved interfacial properties of the plasma-treated CNT film in comparison with the mechanical properties of the untreated CNT composites, nevertheless, there was no evidence of the plasma modification on the CNT assembly.

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In this study, the atmospheric pressure radio frequency (RF) plasma with various treatment time durations (i.e., 1 s, 2 s, 3 s and 4 s) was adopted to modify the CNT fibers. The interfacial shear strength (IFSS) between the CNT fiber and epoxy was calculated by the micro-bond test. Furthermore, by measuring electrical resistance of CNT fibers embedded in epoxy resin under dynamic loading, the adhesion of fiber-matrix was also characterized. Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) were used to observe the morphologies of the CNT fiber. In addition, X-ray photo-electron spectroscopy (XPS), Raman spectroscopy and static contact test were conducted to characterize surface functionalization and micro-structures.

2. Materials and methodology

2.1. Materials

The few walled (FW) CNT fibers synthesized and spun by floating catalyst chemical vapor deposition (FCCVD) method, where ethanol as a carbon source and ferrocene as a catalyst precursor were injected into a furnace reactor at high temperature (> 1000 °C), a stocking-like CNT aerogel was synthesized and drawn out continuously to form the CNT fiber [26], which were mainly double- and triple-walled with diameters of 6–10 nm. The CNT fiber with average diameter of 13 μm was supplied by Suzhou Institute of Nano-Tech and Nano-Bionics (SINANO), Chinese Academy of Science. The epoxy (EPOLAM 2008) and curing agent (EPOLAM 2008-F) were purchase from AXSON Technologies Shanghai Co. Ltd., China.

2.2. Plasma treatment

The CNT fibers were treated by an atmospheric-pressure RF plasma jet Atomflo™$_{400}$ (Surfx technologies, US) as shown in Fig. 1. A 13.56 MHz power supply for the discharge was connected to the electrode via matching network to discharge plasma with 150 W power. A flow rate of 30 L/min of nitrogen gas was released for the plasma discharge, with 0.3 L/min of oxygen to optimize the generation of the functional groups. The plasma treatment time varied by adjusting the plasma scanning velocity and was calculated by dividing the dimensions of the jet with the moving speed. All the CNT fibers samples were placed 4 mm apart from the jet.

2.3. Characterizations

The chemical composition of the CNT fiber was analyzed by XPS (Thermo ESCALAB 250). The XPS experiment were carried out in an ultra-high system equipped with an electron analyzer. A constant analyzer pass energy and the Mg Kα (1253.6 eV) line were used in all XPS measurements. The inelastic scattering background of $C1_S$ and $O1_S$ electron core-level spectra was subtracted using Shirley's method. Static water contact angle was measured via Video-Based Optical Contact Angle Mater (Dataphysics, OCA15EC). To make the measurement, a micro-droplet was brought into contact with the fiber. The shape of the droplet was captured by a digital camera, and a software program quickly calculated the contact angle. The morphologies and micro-structure of the fiber were observed using FESEM (JEOL JEM-2100). The CNT fibers were placed on mica substrates and sputtered with gold before imaging. The carbon-based nanostructure of the CNT fibers was detected by Raman spectroscopy analysis (Via-Reflex) in air at room temperature. The excitation laser wave-length was 633 nm with a data acquisition time of 10 s. TEM (JEOLJEM-2100) was employed to observe the structure of individual CNTs in the fiber.

2.4. Interface shearing strength

The IFSS of CNT fiber and epoxy resin was calculated by the micro-bond test [27]. Compare with the typical interfacial testing method, like pull-out test, micro-indentation test, fragmentation test, micro-bond test is a micro-mechanical pull-out technique which is quasi-static tensile test that applies a measured force on a solid matrix droplet [8]. The droplets with a diameter of around 100 μm and an embedded fiber length of about 120 μm were selected for the micro-droplet test. The IFSS can be derived by the following equation according to the shear-lag model [28].

$$\tau_i = \frac{nP_{max}\coth(nL/r)}{2A} \quad (1)$$

where P_{max} is the maximum force recorded during the micro-droplet debonding process, A is the cross-sectional area of the fiber, L is the embedded length, r is the fiber radius, and n is defined as,

$$n = \frac{E_m}{E_f(1+v_m)\ln(R/r)} \quad (2)$$

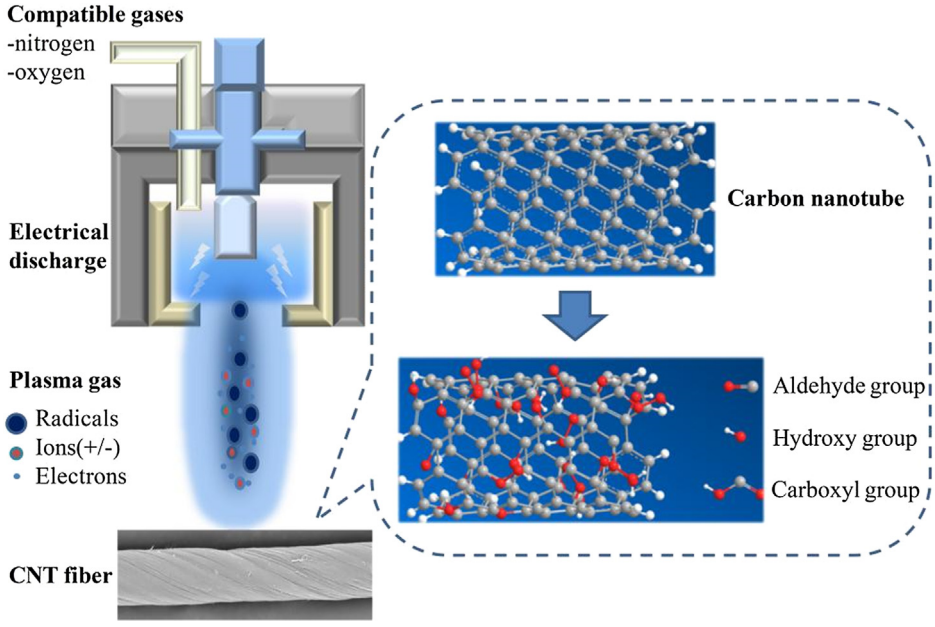

Fig. 1. Schematic showing the atmospheric pressure plasma treatment on the CNT fiber.