Rapid oxidative activation of carbon nanotube yarn and sheet by a radio frequency, atmospheric pressure, helium and oxygen plasma

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ABSTRACT

Carbon nanotube yarn and sheet were activated using radio frequency, atmospheric pressure, helium and oxygen plasmas. The nanotubes were exposed to the plasma afterglow, which contained 8.0×10^{16} cm^{-3} ground state O atoms, 8.0×10^{16} cm^{-3} metastable O_2 ($^1\Delta_g$), and 1.0×10^{16} cm^{-3} ozone. X-ray photoelectron spectroscopy and infrared spectroscopy revealed that 30 s of plasma treatment converted 25.2% of the carbon atoms on the CNT surface to oxidized species, producing 17.0% alcohols, 5.9% carbonyls, and 2.3% carboxylic acids. The electrical resistivity increased linearly with the extent of oxidation of the CNT from 4 to 9×10^{-6} Ω m. On the other hand, the tensile strength of the yarn was decreased by only 27% following plasma oxidation.

1. Introduction

The characterization of the multiwall carbon nanotubes (CNTs) by Iijima in 1991 [1] initiated a two-decades long research effort to exploit the mechanical, electrical, and thermal properties of these materials. One of the proposed uses of carbon nanotubes is to serve as a reinforcement material in composites. The ability of the nanotubes to improve composite properties depends heavily on their compatibility with the polymer matrix. Carbon nanotubes tend to agglomerate, and are difficult to disperse in organic or inorganic solvents [2]. Thus, one of the challenges in fabricating carbon nanotube reinforced composites is to uniformly distribute a high percentage of the nanotubes in the resin. In more recent years, the production of nanotube fibers, yarn and sheet, has provided a means of making large-scale structures out

of CNT reinforced composites. However, the carbon nanotube yarns and sheets exhibit tensile strengths well below their theoretical limits, i.e., in the range of 1.0–2.0 GPa, due to fiber pull out within the nanotube bundles [3]. To overcome this problem, methods are being developed to crosslink together the CNT with resins.

Currently, the standard approach to activate carbon nanotubes for chemical coupling is to immerse them in an acid solution at elevated temperature for several hours [4]. Acids commonly used to treat nanotubes include nitric acid, sulfuric acid, piranha solution, or a mixture of nitric and sulfuric acids. This treatment inserts hydroxyl (–OH) and carboxylic acid (–COOH) groups onto the nanotube surface, which enables it to form covalent bonds with polymers. The harsh reaction conditions in the acid bath convert a large fraction of the sp^2 carbon atoms into ketones and carboxylic acids

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through ring opening reactions. This can lead to structural damage of the CNT and reduces the tensile strength of yarns and sheets [5]. Alternatively, the carbon nanotubes may be activated under more mild conditions using plasma chemistry [6].

Plasma treatment of carbon nanotubes has been performed under vacuum and at atmospheric pressure. The length of nanotubes exposure to vacuum plasma can vary from 5 to 1800 s, and up to 25% of the carbon atoms are oxidized [7–11]. By comparison, atmospheric pressure plasmas are more suitable for continuous processing of CNT. Previous work on treating nanotubes includes: arc-like discharges [12,13], dielectric barrier discharges [5,14,15], and radio frequency (RF) argon and oxygen plasma [16–18]. The plasma treatment time of CNTs at atmospheric pressure ranges from 3 to 120 s. Up to 9.0 atom% oxidized carbon groups have been generated.

In this work, we report on the activation of carbon nanotube yarn and sheet using a radio frequency (RF), atmospheric pressure (AP), helium and oxygen plasma. Changes in the chemical properties of the CNT have been analyzed by water contact angle measurements (WCA), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). In addition, the mechanical and electrical properties of the nanotube yarn were measured using a microforce tensile machine and a multimeter. It was found that a maximum of 25% of the exposed carbon atoms on the CNT were oxidized by the plasma over an exposure time of 30 s, which is a significantly higher level of activation. This doubled the electrical resistivity, while decreasing the yarn tensile strength from about 550 to 404 MPa.

2. Experimental methods

2.1. Materials

Both the carbon nanotube yarn and sheet used in this work were acquired from Nanocomp Inc. The nanotubes were grown by chemical vapor deposition and were spun into a yarn or compressed into a sheet after exiting the furnace. The average diameter of a yarn ranged from 35 to 45 μm, whereas the thickness of the sheets was approximately 20 μm. Tensile strength and electrical resistivity measurements were performed using the yarn, conversely, the surface characterization by XPS, FT-IR, and SEM was performed on the sheet.

2.2. Plasma treatment

An Atomflo™ 400L2 from Surfx® Technologies LLC was used in this work. The 2-inch wide linear plasma source was powered by an RF generator with a matching network operating at 27.12 MHz. The plasma was fed with 30.0 L/min of industrial grade helium (99.995%) and 0.5 L/min of ultrahigh-purity oxygen (99.999%) at 1 atm, and it was operated with 150 W of applied power. An XYZ robot, RB300-XY from Surfx® Technologies LLC, was used to accurately and reproducibly translate the plasma source over the samples.

Prior to plasma treatment, the nanotube yarn was cut into 4.0 or 10.0 cm segments, while the sheet was cut into squares with dimensions of 1.0×1.0 or 2.0×2.0 cm^2. The samples were fixed to a stage during the experiment, and the plasma device was adjusted to a 5.0 mm vertical distance from the sample. The plasma device was then scanned over the sample at 200 or 20 mm/s depending on the desired exposure time. The exposure time under the plasma was calculated by dividing the effective plasma beam width, L, by the scan speed, and then multiplying by the number of scans. For the linear beam plasma, the effective width was $L = 2.1$ cm [19].

2.3. Surface characterization

The water contact angle (WCA) on a carbon nanotube sheet was measured using a Krüss EasyDrop goniometer. To make the measurement, a 2 μL water droplet was brought into contact with the sample surface. The shape of the water droplet was captured by a digital camera, and a software program quickly calculated the contact angle. Six measurements were made for each sample, and the average contact angle was reported.

The surface composition of carbon nanotube sheet before and after the plasma treatment was analyzed by X-ray photoelectron spectroscopy (XPS). The 1.0×1.0 cm^2 square sheets were mounted on a molybdenum sample holder and loaded onto the stage in the ultrahigh vacuum chamber. Core-level photoemission spectra of C 1s and O 1s lines were collected with a PHI 3057 spectrometer using Mg Kα X-rays source at 1253.6 eV. All XPS spectra were taken in small-area mode with a 7° acceptance angle and 23.5 eV passing energy. The detection angle with respect to the surface normal was 25°. The resolution of the source + analyzer is 1.4 eV. The collected spectra data were analyzed using XPS Peaks version 4.1. The background contribution to signal intensity was removed via method proposed by Tougaard and Jansson [20]. The surface atomic composition was calculated by integrating the area under the carbon 1s and oxygen 1s photoemission peaks and divide the results by their respective sensitivity factor, 0.30 and 0.71, respectively [21].

Fourier transform infrared spectroscopy was used to identify the functional groups that were formed on the carbon nanotube surface by plasma treatment. The FTS-50A spectrometer used in these experiments was manufactured by Bio-Rad, and it was equipped with a mercury cadmium telluride (MCT) detector. For these measurements, the CNT sheet was cut into a 2.0×2.0 cm^2 square and fixed over a 13.0 mm circular opening on a stainless steel slide. The sample thickness was reduced through layer by layer removal with Kapton® tape until the light throughput across the sample became measureable by the detector. The spectra were collected at 8 cm^{-1} resolution with signal-averaging over 2048 scans. A single beam spectrum of the pristine sheet was taken first. Subsequently, the sheet was exposed to the plasma while remaining attached to the slide. A single beam spectrum was collected after each iteration of plasma treatment. Absorbance spectra were calculated of the treated samples, using the untreated sample as the background reference.

The surface topography of the carbon nanotube sheet before and after plasma treatment was obtained using a Nova