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Space survivability of carbon nanotube yarn material in low Earth orbit

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ABSTRACT

Unshielded carbon nanotube (CNT) yarns were exposed in Low Earth Orbit (LEO) for 2.14 years on the exterior of the International Space Station (ISS) as part of a Materials International Space Station Experiment (MISSE-8), Payload and Optical Reflector Materials Experiment III. This work is the first to expose any commercial, continuous CNT material in a high-fluence atomic oxygen (AO) natural space environment with sample recovery. Although some chemical changes and surface roughening were observed in both the ram- and wake-exposed samples, none of the CNT yarn samples were catastrophically damaged. Yarn erosion was greater in the ram direction. Scanning electron microscopy (SEM) images showed a porous morphology that was mostly confined to the outer 1% of the yarn. This was consistent with the high degree of disorder observed in the Raman spectra. SEM micrographs also revealed that under the outer amorphous layer of oxidized carbon were pristine carbon nanotubes that were not attacked by the AO. The mechanical (tensile) data showed fairly good strength retention of the yarns exposed in the wake direction, while ram exposure resulted in a 25% strength decrease. Electrical resistivity measurements revealed that both the wake and ram samples were slightly more resistive than the control samples.

1. Introduction

Macroscopic fibers composed of tightly packed, aligned, interlocked multiwalled carbon nanotubes (CNTs) have shown great promise for future lightweight, electrically conductive wires [1–3]. These carbon nanotube materials have recently been successfully developed to replace traditional metal conductors and offer many new opportunities for wires and cables for both power and data/signal transmission cables [4–10]. Due to their low density and high specific conductivity (conductivity/weight), there is a huge potential for mass savings for future satellite applications by employing CNT-based wires. For some common wire formats, replacing both copper braid and center conductor with CNT tape and wire, respectively, reduces cable mass per unit length by 40–50% [11].

In order for CNTs to serve as a direct replacement for metal conductors in future spacecraft cables, the effects of space environment on the mechanical and physical properties need to be evaluated. Specifically, the atomic oxygen (AO) response in terms of bulk optical, electrical, and mechanical properties has not been measured for any CNT material in any orbit. The Materials International Space Station Experiment (MISSE-8) Payload is a test bed for materials attached to the outside of the International Space Station or ISS, and was utilized to evaluate the effects of space on carbon nanotube yarn materials. During the approximate 2.14 years of exposure in low Earth orbit (LEO) outside the ISS (as part Optical Reflector Materials Experiment or ORMAT III), the CNT yarns were exposed to vacuum, intense vacuum ultraviolet (UV) radiation from the sun, ionizing particle radiation (protons/electrons), thermal cycling (typically from −175 °C to +160 °C), and atomic oxygen (AO), all of which facilitate many chemical reactions in organic materials. In addition to 30-MeV protons, AO is the other predominant species found in LEO, and along with vacuum UV, is the primary cause of degradation in LEO [12]. AO is formed by the photo-dissociation of molecular oxygen (O_2) by short-wavelength energetic UV radiation. For most materials on the ISS, the effects of AO and UV can overshadow any effects of charged-particle radiation [13,14]. Spacecraft orbiting the Earth in LEO ram collide into atomic oxygen atoms producing relative impact energies greater than 5 eV. This highly reactive oxygen is energetic enough to break most chemical bonds in polymeric materials susceptible to oxygen

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attack [15]. The consequence of this hostile environment is that any surface susceptible to AO attack must be protected. In fact, current spacecraft that utilize graphite-epoxy and other carbonaceous composites for optical benches and other structural elements are coated with thin films (0.2–0.5 μm) that are already highly oxidized (i.e., SiO_2, TiO_2, Al_2O_3) to prevent mass loss and surface roughening.

To our knowledge, no work has been performed on actual space radiation-damage effects on commercial carbon nanotube materials. Although there have been many ground-based tests [16–20] and theoretical simulations [21,22] that evaluated the influence of radiation on CNT materials, this work is the first to expose CNT materials in a space environment with sample recovery. In this paper, we report on the surface analysis of CNT-based yarns as determined by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) along with mechanical and electrical measurements after 2.14 years of LEO exposure in space.

2. Experimental

2.1. Materials

Commercial carbon nanotube yarn material was purchased from Nanocomp Technologies, Inc. The nanotubes were synthesized using alcohol and iron catalyst materials in a chemical vapor deposition (CVD) method that formed nanotubes (up to 1 mm in length). This process was coupled with a post-processing manufacturing method to create the many strands (or plies) that were collected to form the yarn. The CNTs used in this work consisted of a 10 ply/1 Tex (lot number Y2511-2SA) yarn, which had an approximate 310 μm diameter. Each respective CNT yarn sample was laced through 4 holes (to expose 4 strands) in a 1-in.-dia aluminum puck, and subsequently packed inside a ruggedized Passive Experiment Container (PEC) at the Naval Research Laboratory (NRL). A control sample was stored under nitrogen at the NRL for the duration of the MISSE-8 mission. All test specimens were weighed before flight to allow an accurate determination of mass loss as a result of space exposure. All CNT test specimens were thermally baked before flight at 400 °C for 20 min in air to prevent any cross contamination of samples or outgassing during flight. Therefore, the measured mass loss can be attributed principally to atomic oxygen attack and not vacuum outgassing. The PEC was opened for long-term exposure in low Earth orbit (LEO) after arrival at the ISS. In this experiment, we flew duplicate samples (ram- and wake-facing): one puck was exposed in the ram direction (as shown in Fig. 1) and another puck was exposed to the wake direction of the ISS. The orientation in the ram direction has the greatest fluence of AO, while the wake direction (opposite face of ram) is used for studying UV effects with typically an order of magnitude less AO (compared with the ram direction) [23].

The CNT yarn samples were exposed as part of the Optical Reflector Materials Experiment (ORMatE-III). The pucks received 2.14 years of space exposure: deployed May 20, 2011 and retrieved/bagged July 9, 2013. The samples were returned to Earth on the Space X Dragon 9 capsule and de-integrated at the Naval Research Laboratory NRL.

2.2. X-ray photoelectron spectroscopy (XPS)

Surface chemical compositions were investigated using a PHI VesaProbe II Scanning XPS Microprobe (Physical Electronics, Minnesota). A narrow X-ray beam (200 mm) scanned across the surface resulted in the ejection of photoelectrons from the surface, which were collected and analyzed with a hemispherical energy analyzer. A photoelectron spectrum consists of the number of photoelectrons collected at specific electron binding energies. The measured photoelectron binding energy represents the energy to remove electrons from atoms on the surface and is used for elemental and chemical identification. Using the relative photoelectron count at each binding energy and tabulated photoelectron yields, the composition of the surface was calculated in atomic percent. For typical elemental compositional analysis, the quantitation error is roughly ±1%, thus the detection limit is about 1% for short acquisition times. For high-resolution scans, the detection limit is in the parts per thousand range. Analyzer pass energies of 187.85 and 46.95 eV were used for wide scans and high-resolution spectra, respectively. The depth sensitivity into the CNT surface is about 3–4 nm. The XPS analysis chamber is pumped by an ion pump and maintains a base pressure of 1×10^{-10} Torr.

2.3. Raman spectroscopy

Analysis was performed on a Renishaw *in Via* Raman microscope using a 514-nm laser excitation. The slit width was 0.1 mm, allowing for a resolution of 2–4 cm across the measured spectrum. The Raman shift was scanned from 50 to 3200 cm^{-1} to capture the D peak (1350 cm^{-1}), G peak (1580 cm^{-1}), G′ peak (2670 cm^{-1}), and possibly image the radial breathing mode peaks (near 180 cm^{-1}). Four locations on each yarn were sampled and averaged. The Raman intensity of the D peak, known to represent the disorder within the CNT structure, was observed to change as a result of the atomic oxygen exposure.

2.4. Field emission scanning electron microscopy

Field emission scanning electron microscopy (FE-SEM) was performed on a JEOL JSM-7600F equipped with an Oxford Instruments electron backscatter detector for energy dispersive spectroscopy (EDS) analysis. The best images were collected using secondary-electron imaging (SEI) and 2-kV accelerating voltage. EDS analysis identified iron particles embedded in the CNT material. The working distance was nominally 4.5–5 mm, and the current was on the order of 20–30 pA for the images collected.

2.5. Mechanical testing

CNT yarn samples were pulled on a tabletop Instron (model # 5966) Universal Testing System with a 10-kN load cell. The crosshead displacement rate was constant at 0.05 in./min with a gauge length of 15.4 mm. Yarn samples were physically clamped and glued in the metal fixture to prevent slippage. All samples broke in the middle of the gauge area. To determine sample “strain,” only percent displacement was plotted due to the difficulty in marking the sample for noncontact video extensometer measurements. Each yarn diameter was measured using SEM, but this value was difficult to determine accurately since it consisted of many twisted strands that left some gaps on the micro scale. In addition, the irradiated samples had an outer coating of amorphous carbon. The diameter of the control sample was approximately 310 μm (±4 μm) in diameter. Due to erosion, the irradiated yarns were smaller, on the order of 304 μm (±2 μm). The stress values were normalized to the cross-sectional area using the above diameter values measured in the gauge length.

2.6. Electrical resistivity

Four-point-probe measurements were conducted on three aluminum sample pucks that contained 4 strands of CNT yarn (ram, wake, and control) on each puck. A Keithley Model 6524 m was used to measure the resistance using a current of 500 μA. A custom, four-point-probe measurement device was made with an electrode