

# Multi-method analysis of multiwall carbon nanotube polymer nanocomposite samples after photodegradation

E. J. Petersen,<sup>\*</sup> T. F. Lam,<sup>\*\*</sup> J. M. Gorham,<sup>\*\*\*</sup> K. Scott,<sup>\*\*\*</sup> C. J. Long,<sup>\*\*\*\*,\*\*\*\*\*</sup>  
R. Sharma,<sup>\*\*</sup> L. P. Sung,<sup>\*\*\*\*</sup> and J. A. Liddle<sup>\*\*</sup>, T. Nguyen<sup>\*\*\*\*</sup>

<sup>\*</sup> Biosystems and Biomaterials Division, Materials Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899

<sup>\*\*</sup> Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899

<sup>\*\*\*</sup> Materials Measurement Science Division, Materials Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899

<sup>\*\*\*\*</sup> Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899  
<sup>\*\*\*\*\*</sup> Maryland Nanocenter, University of Maryland, College Park, MD 20742

## ABSTRACT

Nanomaterials can be used as nanofillers to enhance the properties of polymeric materials. However, the effect of weathering on nanocomposites and the potential for nanomaterial release is not yet well understood. Multiple analytical methods are needed to address these issues. Multiwall carbon nanotube (MWCNT) epoxy nanocomposite materials at two concentrations (3.5 % and 0.72 %) were exposed to carefully controlled ultraviolet (UV) doses (equivalent of up to  $\approx 4$  years in Florida). These samples were analyzed with a suite of optimized gravimetric, spectroscopic, and microscopic techniques. The presence of MWCNTs at both loadings retarded the photodegradation of the nanocomposite samples, and multiple techniques showed the accumulation of MWCNTs on the sample surface. The analytical methods developed in this study provide important information on the life-cycle impacts of polymer nanocomposites.

**Keywords:** carbon nanotube, polymer composites, UV, degradation, analytical methods.

## 1 INTRODUCTION

One exciting potential application of nanotechnology is incorporating nanoscale fillers into polymer composites. When the fillers have one or more characteristic dimensions between 1 nm and 100 nm, they are referred to as nanofillers. While the incorporation of nanofillers may dramatically improve the properties of composite materials (e.g., increased strength, fire resistance, etc.) [1-4], it is not well understood how the presence of the nanofillers affect the degradation of the composite, and the extent to which nanoparticles may be released during use, either by physical (e.g., abrasion) or environmental (e.g., ultraviolet radiation, moisture) processes. There have recently been several studies by our group at National Institute of Standards and

Technology (NIST) [5-12] and others [13-15] to investigate these questions.

Multiwall carbon nanotube (MWCNT) is one of the main nanofillers that is being tested for application by a large number of industries. There have been a few studies that have tested nanoparticle (NP) release from MWCNT polymer nanocomposites [8,10,13-18]. However, the effect of natural environmental processes, such as degradation by sun light, on the structure of MWCNT polymer nanocomposites has not yet been thoroughly studied, partly as a result of a lack of optimized analytical methods.

Epoxy nanocomposites at two MWCNT loadings (3.5 % and 0.72 % by mass) were exposed to controlled ultraviolet (UV) doses using the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) [19]. These samples were then analyzed using multiple analytical methods. Results from the 3.5 % MWCNT nanocomposite samples using gravimetry, Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy filtered TEM (EFTEM) were described in a recent publication [12]. To provide an overview of the effects observed during photodegradation of the MWCNT polymer nanocomposites by UV irradiation, XPS results from that publication will be included here, as well as unpublished AFM results from the same samples. Preliminary, qualitative results from the 0.72 % samples will also be described.

## 2 EXPERIMENTAL

Epoxy MWCNT composites were processed from MWCNTs supplied commercially as a 1 % and 5 % mass fraction (based on the mass of the epoxy resin) pre-

dispersed in the same liquid epoxy resin (ZyveX). The epoxy polymer was a stoichiometric mixture of a diglycidyl ether of bisphenol A epoxy resin (189 equivalent mass) (Epon 828, Resolution Performance Products) and an aliphatic polyetheramine curing agent (73.3 equivalent mass) (Jeffamine T403, Huntsman Corporation). Full details of the fabrication of the epoxy-3.5 % MWCNT nanocomposite are given in Reference [12]. The nanocomposites were then exposed to a uniform UV flux of approximately  $480 \text{ W/m}^2$  in the 295 nm to 400 nm wavelength range at  $50^\circ \text{C}$  and 70 % relative humidity (RH) using the NIST SPHERE [19].

Details of methods used to characterize the photodegraded nanocomposite samples have been described fully in Reference [12]. Because AFM and XPS results are presented in this study, a brief description of these techniques is given here. AFM was performed using a Cypher AFM and a MFP-3D AFM (Asylum Research/Oxford Instruments, Santa Barbara, CA). The AFM images were taken in tapping mode (in air at room temperature and using Si cantilevers with a spring constant of  $\approx 40 \text{ N/m}$  and a resonant frequency of  $\approx 300 \text{ kHz}$ ) in order to minimize the possibility that lateral forces applied by the AFM tip would perturb the exposed nanotubes. XPS was carried out on a Kratos Axis Ultra DLD spectrophotometer (Chestnut Ridge, NY). All XPS spectra were acquired using 150 W (10 mA, 15 kV), monochromatic, Al  $K\alpha$  X-rays, and spectral analysis was conducted using CasaXPS (CasaXPS LTD, Teignmouth, UK). The XPS of control samples were analysed for both the MWCNT powder and the pure amine-epoxy, the latter of which could only be measured with the charge neutralizer due to its insulating properties. However, unless specified, all XPS data presented were taken without the charge neutralizer. Elemental and chemical compositions were not determined in this study due to either charging or inability to separate the asymmetric MWCNT peak from the epoxy components. All epoxy-MWCNT nanocomposite spectra are presented with no energy adjustment.

### 3 RESULTS AND DISCUSSION

Figure 1a shows an AFM image of the epoxy-3.5 % MWCNT composite prior to UV exposure. The nanocomposite surface starts with sub-micron roughness. With increasing exposure to UV, the surface topography of the nanocomposite evolves (as shown in Figures 1b-1c). After a  $166 \text{ MJ/m}^2$  UV dose, the surface topography has a z-height range of  $1.5 \mu\text{m}$ . The tallest features (bright features in Figure 1b) on the  $166 \text{ MJ/m}^2$  sample exhibit a nm-scale roughness that is indicative of exposed MWCNTs, while the topographically lower features (dark features in Figure 1b) are quite smooth, indicating epoxy rich regions. As the degradation continued, a trend was observed where regions with exposed MWCNTs (as shown after  $425 \text{ MJ/m}^2$  of UV exposure in Figure 1c) protrude

from the surface to a greater and greater degree in comparison to those areas that are epoxy rich and do not have exposed MWCNTs. These results are in agreement with those obtained using SEM and TEM for the 3.5 % MWCNT epoxy nanocomposite samples [12] as well as those for the 0.72 % samples (data not shown).

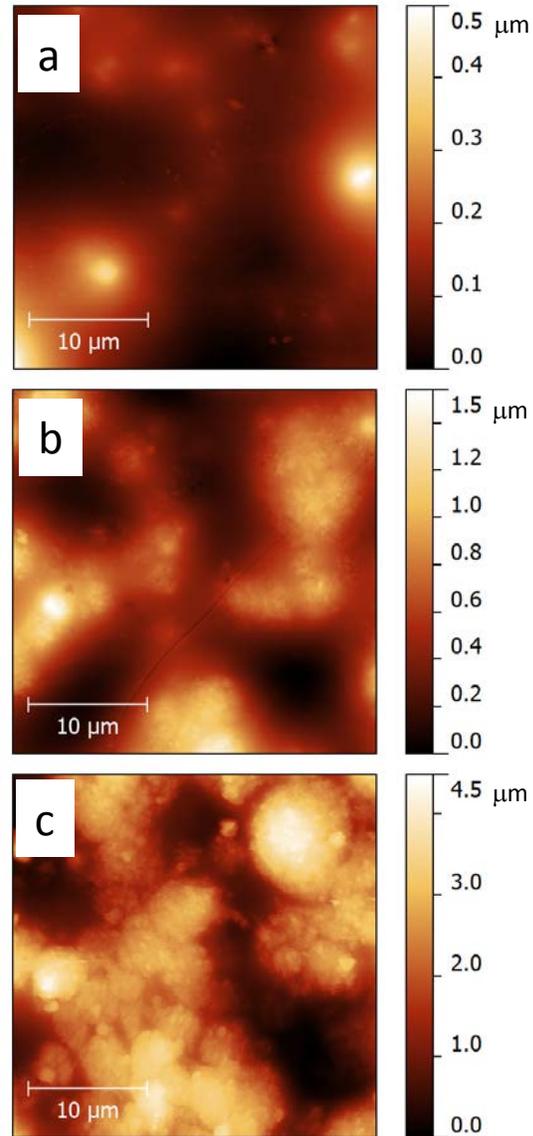
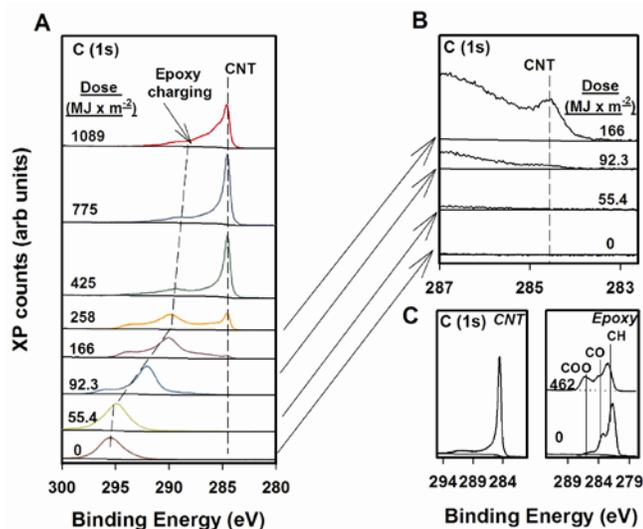


Figure 1: AFM images of the epoxy-3.5 % MWCNT composite before exposure (a), after  $166 \text{ MJ/m}^2$  (b), and after  $425 \text{ MJ/m}^2$  (c) UV exposure. The corresponding z-height scale bars (number, in  $\mu\text{m}$ ) are presented next to each AFM image.

XPS analysis of the epoxy-3.5 % MWCNT nanocomposite samples reveals MWCNT accumulation on the sample surface after UV irradiation (Figure 2). For samples with a UV dose greater than  $166 \text{ MJ/m}^2$ , a distinct MWCNT peak is observable (Figure 2 part B). Figure 2 part C shows data

from the raw MWCNT powder and the pure amine-epoxy sample. Figures 1 and 2 clearly show that, while AFM provided surface topographic information, XPS offered unequivocal identification of the presence of MWCNTs on the sample surface. Additional details of the XPS analysis, including the innovative methodological advance by measuring under different sample charging conditions are described in full details in our recent publication [12]. The 0.72 % MWCNT epoxy nanocomposite samples also showed accumulation of MWCNTs on the sample surface after a sufficient UV dose (data not shown).



**Figure 2.** XPS results of the surface transformations of epoxy-3.5 % MWCNT nanocomposite with increasing dose of UV irradiation. A) Stack plot of the C (1s) region from 0 to 1089 MJ/m<sup>2</sup>. B) Magnification of low dose studies with a focus on the CNT component of the C (1s) region. C) Control spectra of raw MWCNT powder (left) and pure amine-epoxy (right). The pure epoxy sample has a reference at (0 and 462) MJ/m<sup>2</sup> UV dose. Reprinted with permission from [12].

## CONCLUSIONS

In conclusion, the UV-exposed epoxy-MWCNT nanocomposites show the formation of a MWCNT-dense region on the sample surface with sufficient UV dose. The detailed evolution of the surface degradation by UV radiation and the resulting subsurface features as determined by various additional analytical techniques (gravimetric analysis, FTIR-ATR, EFTEM, and SEM) for the 3.5 % MWCNT samples have been recently described [12]. AFM and XPS analyses reveal distinct yet complementary information about chemical and morphological transformations at the surface of polymer-MWCNT nanocomposites during their exposure to UV radiation.

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