Development of surface chemical approaches for detection and characterization of multi-walled carbon nanotubes dispersed in a polymer composite

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ABSTRACT

Multi-walled carbon nanotubes (MWCNT) and other carbon nanofillers are used in different applications to enhance the materials and electrical properties of consumer products such as polymer composites. As a result, concern has arisen regarding the potential for nanoparticle release from the surface of nanocomposites. To address this concern, a methodology was developed to (A) detect *and* (B) characterize dispersion properties of MWCNT at the polymer composite's surface by imaging X-ray photoelectron spectroscopy (XPS)[1]. The presentation will demonstrate how 1 %, 4 %, and 5 % (by mass) MWCNT-epoxy composites were characterized using XPS by taking advantage of the disparate electrical conductivity of the starting materials. Specifically, by employing differential charging, conductive regions could be identified by XPS imaging. Orthogonal techniques will be included in the talk to verify the identity of the MWCNT-rich regions, as has been previously discussed[1].

In this paper, the potential for semi-quantitative characterization of MWCNT composites using imaging XPS is explored. A set of parallel images were acquired under charge neutralization of a 4 % MWCNT composite as described in the previous paragraph. Both in-house analysis and commercially available XPS software were employed to qualitatively identify regions of low and high surface conductivity. By extracting spectra from regions of low and high electrical conductivity, a set of line shapes could be developed to perform semi-quantitative analysis of any point across the entirety of the image and provide information regarding the percentage of carbon atoms from the two different materials in the composite.

Keywords: Carbon Nanotubes, X-ray photoelectron spectroscopy, nanoEHS, composites, characterization

1. INTRODUCTION

Detection and quantification of multi-walled carbon nanotubes (MWCNT)-polymer composites by X-ray photoelectron spectroscopy (XPS) is complicated by separating carbon photoelectrons generated from the filler and the matrix material. These carbon photoelectrons are of comparable energies making them challenging to separate by XPS[2]. However, recent studies have demonstrated that for some composites, the photoelectrons associated with the polymer can separate by differential charging from the MWCNT photoelectrons making qualitative to semi-quantitative characterization by XPS possible[3-4]. Differential charging occurs in materials with two or more components of different conductivity, such as low conductivity of the epoxy versus the high conductivity of the MWCNTs[1, 5-6]. When exposed to an X-ray flux, the photoelectrons emitted leave unfilled vacancies in the non-conductive portion of the composite and that surface becomes positively charged (see Figure 1), causing a decrease in subsequent photoelectrons' kinetic energy (e^-_{KE}). Furthermore, if X-ray flux is non-uniform the charging will also be non-uniform, making it impossible to quantify the sample.

Recently, we exploited differential charging to determine the dispersion properties of three different concentrations of MWCNT:epoxy composites by probing the surface with parallel, or hyperspectral, XPS imaging[1]. It was determined that a large component of the conductive region was aggregates of MWCNTs, yet it was also true that there was some evidence for conductivity, or MWCNTs, in the non-conductive charging regions. However, quantification in this system was not possible due to the excessive and inconsistent charging.

In the current study, we discuss using charge neutralization using low energy electrons (LEE) as a means for making imaging XPS more quantifiable. By exposing the differentially charging surface to a uniform flood source of LEE (Fig 1), the non-conductive surface experiences a negative bias resulting in an increase in e^-_{KE} which

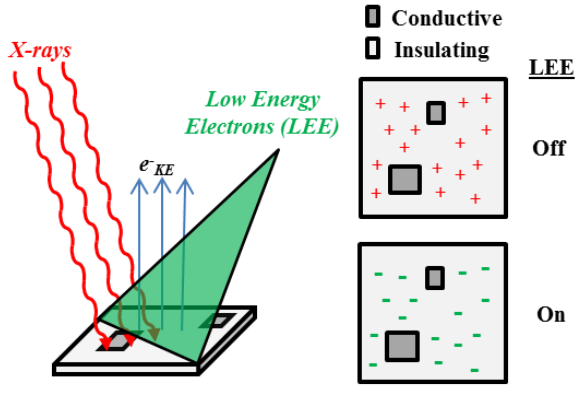


Figure 1: Schematic of X-ray exposure on a surface of varied conductivity with and without LEE to illustrate the impact on differential charging. On insulating regions (light), photoelectrons emitted from a surface will be energetically skewed by a local positive or negative bias depending if the LEEs are off or on, respectively. Photoelectrons from conductive surfaces (dark) will be unaffected.

effectively overcompensates for the charging. Additionally, both commercial software and in-house coding were employed to generate masks to cross compare and validate analysis approaches.

2. MATERIALS AND METHODS[1]

2.1 Sample preparation

A complete description of how the samples were generated and prepared for analysis can be found in the literature[1]. Briefly, composites in this paper were created from 4 % (by mass) MWCNT from Arkema (King of Prussia, PA) and a 2-part epoxy of diglycidal ether of bisphenol A from Sigma Aldrich and Jeffamine d2000 from Huntsman (Pensacola, FL). The surface of the prepared composite was further modified after curing by removing the surface layer, which is known to be epoxy-rich compared with the bulk of the sample. For the sample discussed in this paper, mechanical milling was employed using a Sherline Model 2000 mill (Vista, CA).

2.2 X-ray photoelectron spectroscopy

XPS imaging was performed on the 4 % MWCNT composites using an Axis Ultra DLD from Kratos Analytical (Chestnut Ridge, NY) using non-monochromatic Mg Kα X-rays operating at 405 W (27 mA; 15 kV). The composite was exposed to a LEE flood source that is included as a charge neutralizer in the Axis Ultra. Each image was generated from photoelectrons collected along the surface normal at pass energy 40 eV using FOV3/high resolution imaging settings, representative of a 185 µm x 185 µm region. Images were acquired every 0.2 eV for 3000 s/image from 293.2 eV to 277 eV. Processed images were compared and contrasted with others taken in the absence of the charge neutralizer.

2.3 Data analysis

The un-neutralized images were first processed and analyzed using an in-house Mathematica procedure (Wolfram, Boston, MA) which was previously described[1]. Analysis of the neutralized images was carried out using the in-house Mathematica-based procedure *and* the image processing capabilities found in CasaXPS (Teignmouth, UK) to identify regions of high and low conductivity. With respect to the CasaXPS, further processing was performed to generate line shapes representative of the non-conductive and conductive C(1s) region for epoxy and for MWCNTs, respectively. These line shapes were ultimately used to provide semi-quantitative assessment of the distribution of epoxy and MWCNTs at the surface.

[1] Certain trade names and company products are mentioned in the text or identified in illustrations in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

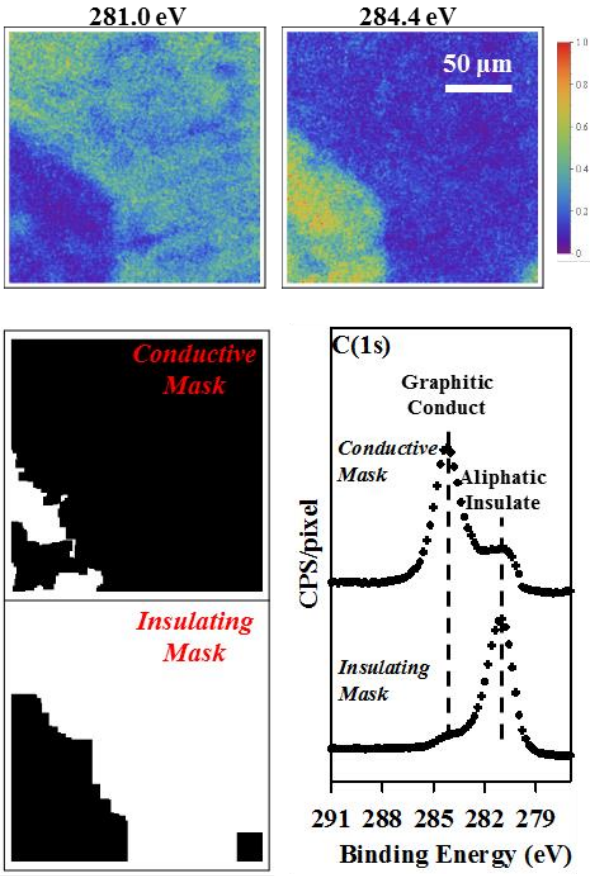


Figure 2: Summed XPS images taken of 4% MWCNT composites neutralized with LEE reflect non-conductive/insulating and conductive ROIs around 281.0 eV and 284.4 eV, respectively. Image masks (Left) were created to identify the ROIs representative of MWCNTs-rich and epoxy-rich regions. The masks were applied to the neutralized image series to demonstrate the spectral differences in the two ROIs.

3. RESULTS AND DISCUSSION

3.1 Qualitative characterization of MWCNT composites

Preliminary image analysis of the neutralized XPS images for the 4 % MWCNT composites was carried out in a manner consistent with unneutralized XPS images for the same sample reported in the literature [1]. To that end, summed images were generated by combining images from five different energies to enhance image clarity for conductive and insulating carbon near 284.4 eV and 281.0 eV, respectively. Indeed, the summed images in Figure 2 (top) demonstrate that differential charging still persists even in the presence of LEEs. However, the insulating regions effectively decreased in binding energy as a result of a localized negative bias caused by the LEEs. In order to extract spectra, image masks were created by processing the top 60 % of pixels in the summed image around 284.4 eV creating a conductive region of interest (ROI). An insulating ROI was generated by taking the negative of the

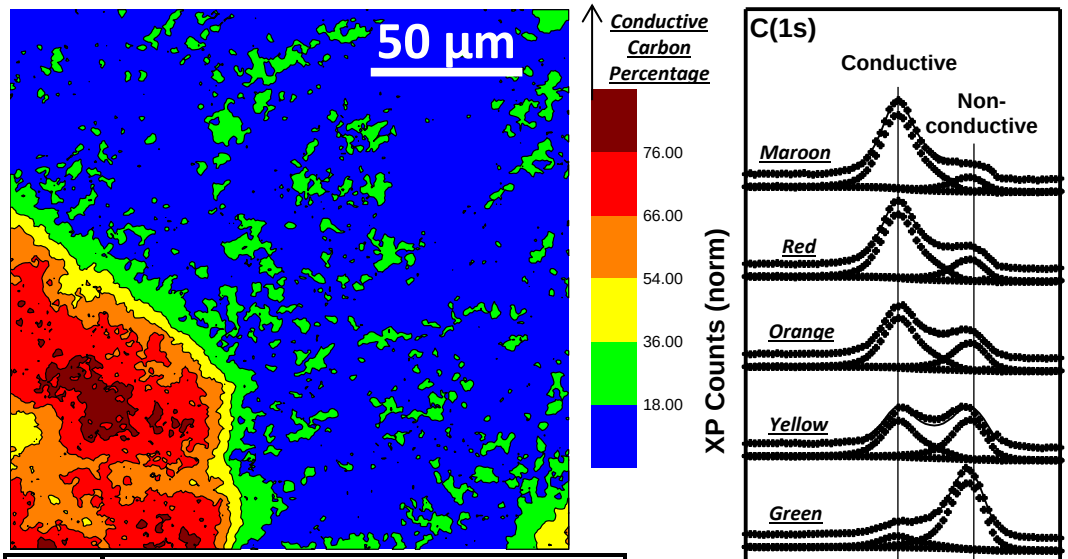
conductive ROI less an interfacial border in efforts to eliminate overlap (Figure 2, bottom left).

In efforts to extract XP spectra to qualitatively compare the different ROIs for the 4 % MWCNT composites, the conductive and insulating masks were applied to each image to average the counts per second per pixel (CPS/pixel) for a given energy. The reconstructed spectra are presented in Figure 2 (bottom right) where the conductive mask has a peak maximum at 284.2 eV and the insulating mask has peak maximum at 280.8 eV, representative of the MWCNT's graphitic carbon and the epoxy's aliphatic carbon, respectively. In both cases the conductive and insulating spectra also have minor contributions from epoxy and MWCNTs, respectively, suggesting that these regions are not purely composed of one type of carbon.

The findings in Figure 2 are consistent with previous work done on the 4 % MWCNT composites, with a few exceptions [1]. First, application of the LEE source resulted in a negative bias and a negative shift in binding energy for the epoxy signature which is over adjusted from its traditional position of ≈ 284.5 eV [2]. Secondly, the epoxy-rich peak in the current study yielded a smaller full width half maximum (FWHM) compared to the previous work, which supports the idea that all non-conductive photoelectrons are 'overcorrected' consistently. Third, in the previous work the conductive mask appeared to be purely composed of MWCNTs. The shoulder in the conductive spectra of Figure 2 suggests that this is either incorrect or that the sample had changed since the previous data was acquired. Lastly, the binding energy for the conductive, MWCNT-rich carbon in this study is shifted to lower binding energy as compared with 285.0 eV from the 4 % MWCNT not exposed to LEE. One possible reason for this is the low amount of charging epoxy closely associated with the MWCNTs which, by way of adding photoelectron intensity to the conductive spectra, could appear as a positive or negative shift in binding energy. A second reason for this could be that photoelectrons emitted from the conductive surface may be weakly impacted by the bias, due to the proximity of non-conductive regions.

3.2 Semi-quantitative image analysis

While it is possible to further characterize the spectra in Figure 2 to obtain semi-quantitative information using synthetic peak models with an arbitrary combination of Gaussian and Lorentzian tailoring, we decided to generate spectral line shapes from the experimental data following



	Carbon percentages by region			
	% Conductive (CNT)		% Non-conductive (Epoxy)	
Region	Average	St Dev	Average	St Dev
Blue	4.5	0.1	95.5	0.1
Green	15.7	0.1	84.3	0.1
Yellow	50.1	0.1	49.9	0.1
Orange	66.6	0.1	33.5	0.1
Red	76.5	0.1	23.5	0.1
Maroon	85.0	0.2	15.0	0.2

Figure 3: Image processing of LEE neutralized XPS images of 4 % MWCNT composites using commercially available XPS software. An image mask (upper left) was created and applied to generate six C(1s) spectra from different ROI's. The spectra (right) were fitted with data generated lineshapes, representative of MWCNT and epoxy contributions, and a Shirley background fit which are presented as offset below the raw data and a composite fit. Semiquantitive estimates are provided of the MWCNT-rich regions and the epoxy-rich regions.

procedures recently explained in the literature and online[7-8]. In order to perform the semi-quantitative analysis, the raw image series was processed in CasaXPS. After filtering data outliers and creating abstracts factors, 65536 C(1s) spectra were extracted from the 82 images representative of each individual pixel in the 256 x 256 image (data not shown). While these spectra were artificially enhanced, they were representative of the raw data and could be fit with a Shirley background. These 65536 C(1s) spectra were then separated, arbitrarily, into two regions separated from each other at 282.7 eV. The integrated photoelectron intensity at binding energies less than 282.7 eV was assigned to the epoxy-rich contributions while the integrated photoelectron intensity greater than 282.7 eV was associated with the MWCNT-rich contributions.

Atomic concentration images were generated from these integrated intensities for the epoxy and the MWCNT fractions of the C (1s) spectrum, the latter of which is presented in the upper left of Figure 3. This image is consistent with the image presented in Figure 2 which has the conductive, MWCNT-rich region in the lower left of the image. The image in Figure 3 has been further separated into ROIs by increasing MWCNT area, as calculated from the integrated photoelectron intensity and separated at the percentages indicated along the legend.

The image was then used as a mask and reapplied to the raw, unprocessed images to extract six, average spectra representative of the different ROIs (Figure 3, right). All six spectra had components of the conductive MWCNTs and the insulating composite. Suitable line shapes to represent MWCNTs and epoxy-rich regions were obtained by generating difference spectra from the blue and red ROIs. Examples of how to perform this task can be found elsewhere[8].

Ultimately, the spectra were fit with these line shapes. The fits were constrained to the same FWHM and peak to peak separation as was true for the original components. These components were used to fit the spectra and a Monte Carlo simulation was performed to assess the goodness of the fit. The atomic percentages of carbon atoms and a standard deviation (based on Monte Carlo simulations) of the MWCNT-type carbon and epoxy-type carbon are provided in tabular format in Figure 3 (bottom).

The results from this method of XPS imaging and spectral analysis reveal that even the most MWCNT-rich ROIs were not free of an epoxy component, and the same held true for the epoxy-rich ROIs. With respect to the quality, the cumulative fit tracked reasonably well with the raw data in regions with a high concentration of either epoxy or MWCNTs. In interfacial regions, fitting with the extracted lineshapes did not completely account for the entire C (1s) envelop (*e.g.* Yellow ROI). Future work will investigate means of more completely accounting for the photoelectron intensity in these interfacial spectra.

CONCLUSION

Methods for the qualitative characterization of dispersion properties and semi-quantitative characterization of chemical contributions of MWCNT:epoxy composites have been demonstrated. Differential charging continues to be an effective means for separating overlapping photoelectron signatures. The introduction of charge neutralization with LEE led to a semi-quantitative approach, revealing that the composite is likely composed of more than two conductivities. Different software packages revealed comparable results increasing confidence in the validity of both analysis approaches.

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