

Developing a fundamental understanding of polymer nanocomposite photodegradation and CNT release characteristics

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ABSTRACT

Polymer nanocomposites (PNCs), composed of carbon nanotubes (CNTs) incorporated into a given polymer matrix, are utilized in consumer products for their resulting desirable material properties. However, the role of initial CNT loading/concentration in regulating both photodegradation of the PNC and CNT release remains not well understood. To this end, we accelerated the photodegradation of PNCs composed of single wall-CNTs (SWCNTs) and polycaprolactone with four different initial SWCNT loadings, 0%, 0.25%, 1.5%, and 5.0% (w/w). Spectroscopic characterization of the PNCs was emphasized and revealed that the addition of CNTs does not alter the mechanism of photodegradation, but rather restricts the photolysis depth to shallower regions beneath the surface. Single particle inductively coupled mass spectrometry (sp-ICP-MS) was used to characterize the released material, and found that initial CNT loading influences the magnitude and form of released material.

Keywords: polymer nanocomposite, photodegradation, sample characterization, CNT release, single particle ICP-MS

1 INTRODUCTION

Carbon nanotube polymer nanocomposites (CNT-PNCs) are particularly attractive for use in a variety of commercial products[1] and applications such as in the wingtip fairings of Lockheed Martin's F-35 Joint Strike Fighter[2] due to their improved material properties over the native polymer. However, as efforts to develop innovative applications for CNT-PNCs expand a concern that remains, due in part to CNTs' potential hazard posed to organisms[3], is the potential release of CNTs from the surrounding polymer matrix into the environment. Weathering of CNT-PNCs, specifically photodegradation of the polymer matrix, is a known pathway of CNT release[4, 5]. However, while many studies have examined the release of CNTs from CNT-PNCs[6], detailed information is still lacking on the effect CNT loading (% w/w) has on the mechanism and extent of polymer photodegradation, as well as how the quantity, kinetics, and form of release CNTs evolve as a

function of both initial CNT loading (% w/w) and the extent of irradiation.

To address these knowledge gaps, we photodegraded single wall CNTs (SWCNT) polycaprolactone (PCL) PNC samples that were composed of a span of initial CNT loadings (0%, 0.25%, 1.5%, 5.0%) under accelerated photodegradation conditions (UVC light). Sample characterization with scanning electron microscopy (SEM), attenuated total internal reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS) was carried out before and after UV exposure in order to examine the changing surface morphology, chemical structure, and chemical composition, respectively, as a result of photodegradation. These characterization techniques, along with mass loss measurements, were used to determine the means by which CNTs inhibited photodegradation as well as assess the extent to which initial CNT loading impacts the photodegradation process of PNCs.

To identify CNT release characteristics as a function of initial CNT concentration and the extent of photodegradation, the release supernatant of the irradiated samples was analyzed with single particle inductively coupled mass spectrometry (sp-ICP-MS). With sp-ICP-MS, we simultaneously quantified the concentration and characterized the form (individual CNTs vs. aggregates of CNTs embedded in polymer fragments) of released CNTs. This was accomplished through the measurement of residual metal nanoparticles from CNT synthesis which are intimately bound to the CNTs, as proxies for CNT detection[7, 8]. Greater detail on the work and findings described below are provided in a recent submission for publication[9].

2 EXPERIMENTAL

PNC samples, prepared via sonochemical solution blending, were irradiated for varying periods of time in a RPR-100 Rayonet photochemical reactor with 254 nm light (fluence = 1.62×10^{17} photons/second). Samples were bound to a

glass slide with Teflon tape, placed in a 15 mL quartz test tube filled with 12 mL of HPLC grade water, and sealed prior to irradiation. Following specified periods of irradiation, from 0 up to 125 days, the release supernatant of each sample was collected for sp-ICP-MS analysis. Single particle ICP-MS analysis was performed to determine the SWCNT content of the release supernatants using 89Y pulses as surrogates for SWCNT detection, as detailed in Reed et al[8]. All sp-ICP-MS analyses were performed in triplicate using a NexION 300Q ICP-MS (Perkin Elmer, Waltham, MA).

PNC samples were characterized before and after irradiation with scanning electron microscopy (SEM), attenuated total internal reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS). SEM was performed with a JEOL 6700F, FESEM; all samples were sputter coated with platinum for 300 seconds prior to imaging. ATR-FTIR was performed with a Nicolet iS5 FT-IR Spectrometer, equipped with a diamond window. We note the manufacturer reports a sampling depth of approximately two microns for a diamond window. XPS was performed with a PHI 5600 with Mg K α X-ray (1253.6 eV) radiation. Quantitative analysis of the carbon (C(1s)) and oxygen (O(1s)) regions was completed using a pass energy of 58.7 eV, 10 sweeps, and a step size of 0.125 eV. XPS data analysis was performed with CasaXPS. Survey scans were also collected to ensure samples were free of contamination. Mass loss measurements of all samples were also completed.

3 Results and Discussion

As shown in Figure 1, mass loss measurements of photolyzed SWCNT-PCL samples found that all PNC samples experienced a period of rapid mass loss during the first 20 days of exposure irrespective of initial CNT loading. After the first 20 days, the rate of mass loss was greatly abated and resulted in only a slight increase in the magnitude of PNC mass loss for the remaining duration of exposure. PCL is known to photodegrade through a Norrish Type II pathway[10], and XPS characterization of the samples confirmed that during the first 20 days of exposure, the concentration of ester groups at the surface of the samples was rapidly depleted. The loss of available ester groups following 20 days of exposure is what led to the subsequent plateau in mass loss. It is also observed in Figure 1 that while all PNC samples did experience an initial period of mass loss, the overall magnitude of mass loss is greatly reduced with increasing initial CNT concentration, with the final mass loss of the 5.0% CNT sample being just 7.4%, compared to 35.3% for the CNT-free polymer.

The clear reduction in mass loss with increasing initial CNT loading is understood through ATR-FTIR characterization

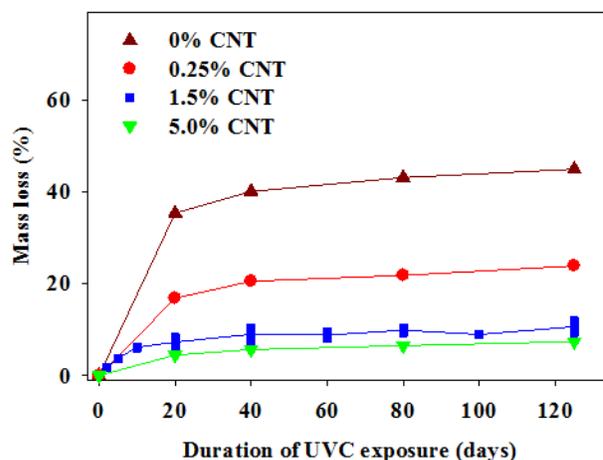


Figure 1: Mass loss measurements SWCNT-PCL samples following regimented periods of irradiation.

of the exposed PNCs. As seen in Figure 2, unexposed PCL features a prominent absorption band at 1720cm⁻¹, resulting from the presence of PCL's repeating ester functional group[11]. Following 125 days of UVC exposure, we observe that this feature is greatly diminished in intensity in the CNT-free PCL sample. However, we also find that increasing initial CNT loading leads to a systematic increase in the intensity of this feature. This indicates that the addition of CNTs to PCL reduces the depth of photolysis, thereby reducing the extent of photodegradation and mass loss, with the 5.0% CNT sample resulting in the shallowest photolysis depth of all PNC samples.

Because spectroscopic characterization (XPS and ATR-FTIR) following irradiation only measured the diminishment of spectral features corresponding to PCL's ester group and did not find the emergence of new features, we deduce that that the Norrish Type II photodegradation pathway is not altered by the addition of CNTs. Rather, as

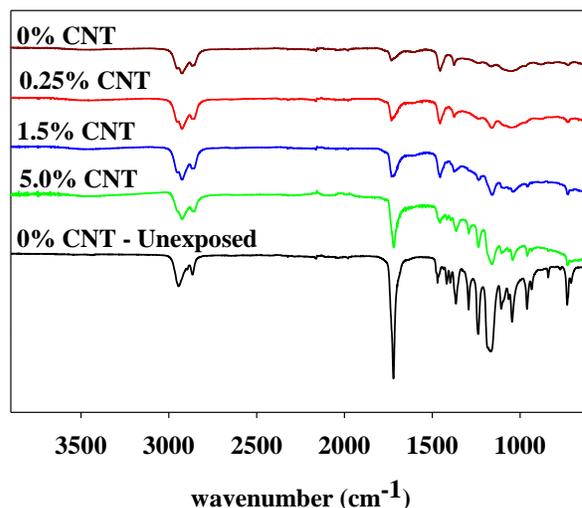


Figure 2: ATR-FTIR of SWCNT-PCL samples following 125 days of UVC exposure.

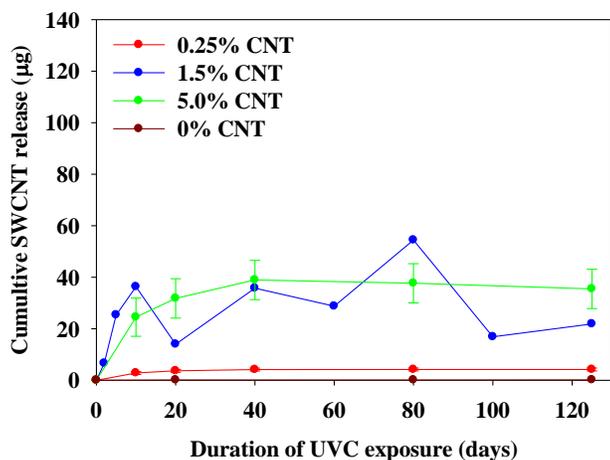


Figure 3: SWCNT release as measured by sp-ICP-MS

highlighted by ATR-FTIR, the addition of CNTs simply reduces the depth of photodegradation and this in turn reduces the extent of PNC mass loss (Figure 1). We also note that SEM imaging (not shown) of the nanocomposites did not find CNTs at the surface of any PNC sample prior to exposure. Following 20 days of exposure, for the 5.0% CNT sample, a dense CNT mat was found to have formed and persisted through 125 days of exposure. However, no such CNT mat or any evidence of individual CNTs accumulated at the surface was found for the 0.25% CNT and 1.5% CNT samples following any period of exposure.

The water that filled the sample quartz test tubes, also referred to as aqueous release supernatant, was collected and replenished following incremental periods of UVC exposure. The release supernatant was then analyzed with sp-ICP-MS to both measure the mass of CNTs released and characterize the released form (individual CNTs vs. aggregates of CNTs embedded in polymer fragments). This was accomplished through the exploitation of residual yttrium nanoparticle catalysts bound to the CNTs, whose consistent concentration associated with the CNTs allowed for the release mass of the CNTs to be measured, and through analysis of ^{89}Y pulse distribution, identified their released form[7, 8].

The masses of SWCNTs released during photodegradation are shown in Figure 3. As most clearly seen for the 5.0% CNT sample, the rate of SWCNT release tracks similarly to the rate of PNC mass loss (Figure 1). This behavior indicates that CNT release will occur to its greatest extent as its surrounding polymer matrix is being actively degraded, but as the rate of photodegradation slows, so too does the rate of CNT release. It is also clear that the overall mass of CNTs released will increase with initial CNT concentration. However, we have determined the mass of SWCNTs released from the PNCs is less than would be expected should they release along with the photodegraded polymer at their initial concentration. This indicates that CNTs are preferentially retained within the remaining PNC as it photodegrades. Additionally, we note that the CNT

mat that formed on the surface of the 5.0% CNT sample is a stable structure due to the measurement of minimal CNT release after it had formed.

The raw sp-ICP-MS data measured from a 1ppb suspension of both well dispersed SWCNTs and the release supernatants of the 5.0% CNT sample collected from

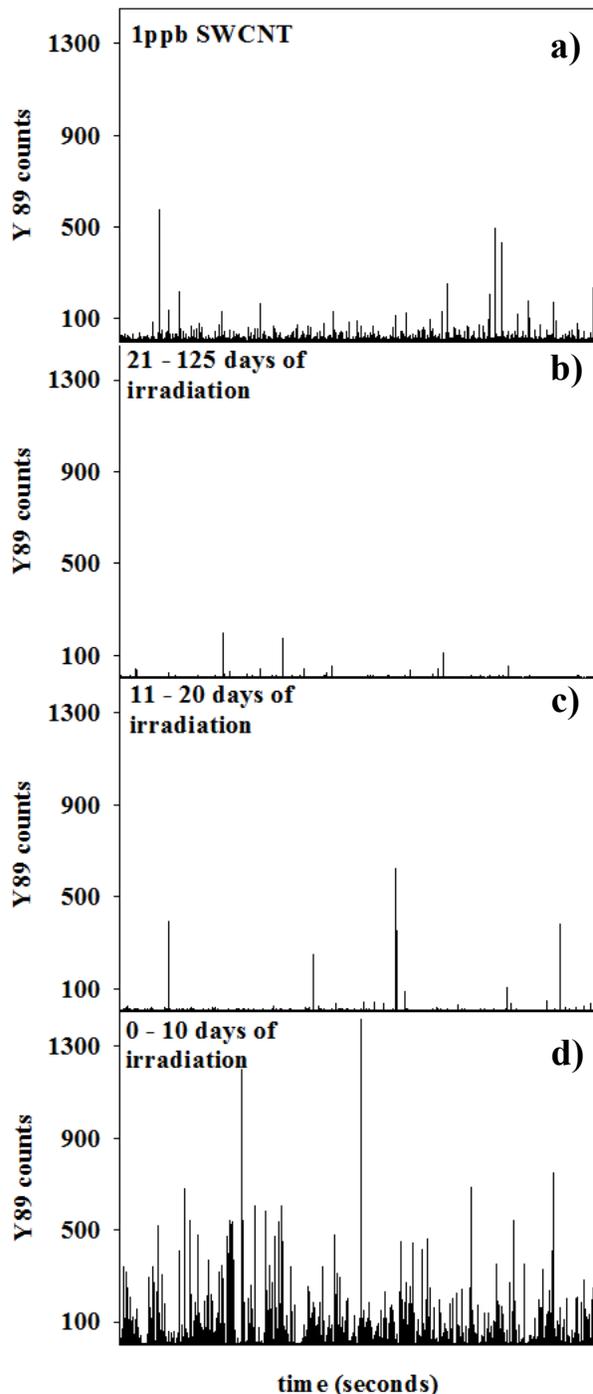


Figure 4: Raw sp-ICP-MS data collected from a 1ppb suspension of well dispersed SWCNTs and from the 5.0% CNT release supernatants following three distinct periods of exposure (labeled above).

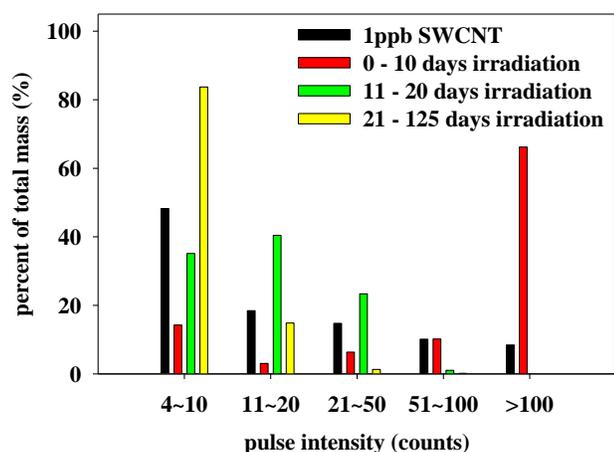


Figure 5: Pulse intensity binning of a 1ppb SWCNT suspension and of the 5.0% CNT release samples.

periods of irradiation corresponding to 0-10 days, 11-20 days, and 21-125 days are shown in Figure 4. TEM imaging (not shown) found that the average size of Y nanoparticles associated with the CNTs is on the order of 10 – 20 nm; previous studies have found a Y nanoparticle of this size results in a ^{89}Y pulse intensity of 2-4 ^{89}Y counts, per dwell time[7]. The greater than four ^{89}Y count pulses we observed from analysis of a SWCNT suspension (Figure 4a) are a direct result of many Y nanoparticles entering the plasma in a single dwell time simultaneously because they are bound to a CNT.

Analysis of a suspension of individual SWCNTs (Figure 4a) resulted in ^{89}Y pulses on the order of 10's up to several hundred counts in intensity. This “pulse intensity profile” provided a bench mark for determining if release samples contained individually released CNTs (a similar distribution of pulse intensities) or released aggregates of CNTs (much higher pulse intensities). Comparing Figures 4a and 4d makes it clear from the contrasting pulse intensities that during the first 10 days of UVC exposure, the 5.0% CNT sample released large aggregates of CNTs that were likely contained in photolyzed polymer fragments. During the next ten days of photodegradation (Figure 4c), the pulse intensities decreased, reflecting that large aggregates were no longer the predominate form of released CNT. During the final period of exposure (Figure 4b), we observe that the pulse intensities are qualitatively similar to that of a SWCNT suspension, and this reflects that single CNTs are released. A more quantitative assessment of the release behavior from the 5.0% CNT sample is accomplished through pulse intensity binning, as shown in Figure 5. With this approach, it is clear that the dominant form of released CNTs evolved as photodegradation proceeds; with CNTs first released as aggregates, and then as single CNTs. This analysis also informs us that the CNT mat observed after 20 days of exposure is not only stable following its formation, but any CNTs that are released were in fact just individual CNTs.

4 Conclusions

The accelerated photodegradation of SWCNT-PCL samples found that the inclusion of CNTs systematically decreased the depth of photolysis and thereby inhibited photodegradation. We also found that CNTs release most rapidly, and as aggregates, during the initial period of photodegradation. However, as photodegradation slows so too does the rate of CNT release, and only a small amount of individual CNTs will be further released.

Acknowledgements

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