

Fate of nanoparticles during life cycle of polymer nanocomposites

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Abstract. Nanoparticles are increasingly used in consumer and structural polymeric products to enhance a variety of properties. Under the influences of environmental factors (e.g., ultraviolet, moisture, temperature) and mechanical actions (e.g., scratching, vibrations, abrasion), nanoparticles might release from the products and thus potentially have negative effects on the environments, health and safety. The fate of nanoparticles in polymer nanocomposites during their exposure to UV environment has been investigated. Epoxy polymer containing multi-walled carbon nanotubes (MWCNTs) and silica nanoparticles were studied. Specially-designed cells containing nanocomposite specimens were irradiated with UV between 295 nm and 400 nm in a well-controlled UV chamber. Chemical degradation, mass loss and surface morphology of the epoxy nanocomposites, and release of nanoparticles were measured. Epoxy containing MWCNTs exposed to UV radiation degraded at a much slower rate than the unfilled epoxy or the epoxy/nanosilica composite. Photodegradation of the matrix resulted in substantial accumulation of nanoparticles on the composite surfaces. Silica nanoparticles were found to release into the environment, but MWCNTs formed a dense network on the composite surface, with no evidence of release even after prolonged exposure. Conceptual models for silica nanoparticle release and MWCNT retention on the surface during UV exposure of nanocomposites are presented.

1. Introduction

The outstanding properties of nanoparticles (one of the dimensions is <100 nm) have fueled intensive research in the last decade to incorporating them in polymers (i.e., polymer nanocomposites) [1-3]. These advanced composite materials are increasingly used in many large-volume industries including consumer products, buildings, and automobiles. However, research has shown that nanoparticles pose potential risks to human health, safety and environment (EHS) [4-6]. Current research on the effects of nanoparticles on EHS mostly focuses on exposures during the manufacturing process. For polymer nanocomposites, whatever the application, the long-term performance of the composite product itself, the fate of the nanoparticles in the polymer matrix, and the hazard of the released nanoparticles play a key role in the acceptance and commercialization of these advanced products. This is because the polymer matrix in a nanocomposite tends to undergo degradation during service and post-service (e.g.,

landfills, incineration). The serious consequence of the matrix degradation is that nanoparticles will be exposed on the composite surface and could be released to the environments via the effects of mechanical vibration, rain, condensed water, and wind. The release of these small size materials during the life cycle of polymer nanocomposites would present a roadblock to innovation and commercialization of polymer nanocomposites.

The potential release of nanoparticles from a polymer nanocomposite exposed in an environment is tied closely to the degradation of the polymer matrix, which is inherently a complex process controlled by environmental conditions, processing variables, and materials properties. Nanoparticles also possess unique physical properties and create a large polymer/particle interfacial volume fraction in the nanocomposites, both of which would likely affect the rate and degradation mechanism of the matrix, and the release potential of nanoparticles during environmental exposures. Yet, little data is available on the degradation of polymer nanocomposites, the state of the imbedded nanoparticles during environmental exposures, or how they will be released during their life cycles. The lack of this type of information hinders our ability to understand the release mechanisms, to predict the long term release, and develop strategies to mitigate this potentially serious problem. For that reason, the potentially harmful effects of nanoparticles incorporated in polymers on the environment and health cannot be determined. To provide data needed to address this issue, the National Institute of Standards and Technology has initiated a study to critically assess the release of nanoparticles during life cycles of polymer nanocomposites. The study consists of four components: 1) Development of metrologies to measure the degradation of polymer nanocomposites, release rates, and chemical composition of released particles during life cycles of polymer nanocomposites, 2) generating microscopic and molecular experimental data to understand the mechanism of nanoparticle release, 3) development of experimentally-verified models, which takes into account materials, processing and environmental factors as inputs, to predict the nanoparticle release and, 4) development of standardized methods to measure the nanoparticle release rate and properties of the released nanoparticles.

The main objective of this study is to investigate the fates of silica nanoparticles and carbon nanotubes (CNTs) (both are termed nanoparticles in this study) imbedded in an epoxy matrix during its exposure to ultraviolet (UV) radiation. The degradation of epoxy polymer and the fate of nanoparticles in nanocomposites were characterized by a number of microscopic and spectroscopic techniques, including field-emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Analyses were also performed on particles released from the samples during exposures. The results showed that, under UV radiation having wavelengths similar to those of the sunlight, amine-cured epoxy in the nanocomposites underwent rapid photodegradation, resulting in mass loss, exposing large concentration of nanoparticles on the composite surface, and releasing silica nanoparticles into the environment. For CNT composites, the matrix degradation produced a dense network of CNTs on the surface, which reduced the degradation of the epoxy layer underneath and essentially prevented their release. The results of this study should provide useful information to assess the potential risk of nanoparticles in epoxy matrix during its service in an UV environment.

2. Experimental Procedures

2.1. Materials and nanocomposite preparation

The polymer matrix was an amine-cured epoxy commonly used in fiber-reinforced polymer composites, coatings and adhesives, and the nanoparticles were multi-walled carbon nanotubes (MWCNTs) and silica (SiO_2) nanoparticles (nanosilica). The epoxy was prepared as a stoichiometric mixture of a diglycidyl ether of bisphenol A (DGEBA) epoxy resin having an equivalent mass of 189 (grams of resin containing one gram equivalent of epoxide) and a polyoxypropylenetriamine curing agent. The epoxy polymer was used without additives. MWCNTs and silica nanoparticles were obtained from commercial sources. MWCNT was a 1 % mass fraction pre-dispersed product in the

same epoxy resin. The silica nanoparticles were surface modified to provide good dispersion in polymers, had an individual average diameter of 7 nm, and a purity of > 99.8%. Reagent grade toluene (purity > 99.5 %) was used for composite processing. Figure 1 presents the chemical structure of this amine-cured epoxy, which will help to better understand its degradation behaviour. The presence of the electron rich N atoms and residual epoxide groups in the cured, crosslinked structure plays a major role in the photodegradation of epoxy materials.

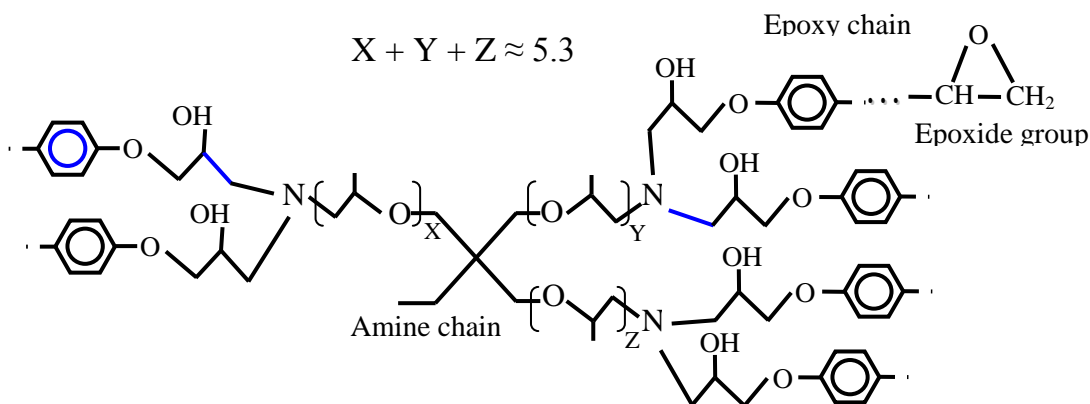


Figure 1. Chemical structure of the crosslinked amine-cured bisphenol A epoxy.

Free-standing films of 1) unfilled epoxy, 2) epoxy/0.72 % MWCNT composite, and 3) epoxy/5 % nanosilica composite were fabricated. The nanoparticle loadings were based on mass fraction of the solid amine-cured epoxy. (Note that the 1% mass fraction MWCNT in the neat epoxy resin is reduced to 0.72 % mass fraction in the amine-cured epoxy.) Unfilled epoxy and MWCNT/epoxy composite films were prepared by simply adding amine curing agent to epoxy resin or to MWCNT-containing epoxy resin, respectively, and then stirring for 1 h with a magnetic stirrer. For epoxy/nanosilica composites, SiO₂ nanoparticles were first stirred and sonicated in a large amount of toluene for 30 min. After adding epoxy resin, the nanosilica suspension was stirred and sonicated for an additional 1 h using an 80 kHz tip sonicator. The amine component was then added to the suspension and stirred for another 1 h. After the mixing step, all epoxy/amine/nanoparticles mixtures were degassed for 1 h at room temperature and then drawn down using a bar applicator on a polyethylene terephthalate sheet (PET) to produce free films having a thickness of approximately 150 μm . In addition, specimens of approximately 6 μm thick film on CaF₂ substrates prepared by spin casting were also made for chemical degradation study by transmission FTIR spectroscopy. All coated samples were cured at ambient conditions (24 °C and 45 % relative humidity) for three days, followed by post-curing at 110 °C for 4 h in an air circulating oven.

2.2. Exposure to UV radiation

The degradation of unfilled epoxy and epoxy nanocomposites was studied using a 2 m integrating sphere-based weathering chamber, referred to as SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) (7). This SPHERE UV chamber utilizes a mercury arc lamp system that produces a collimated and highly uniform UV flux of approximately 480 W/m² in the 295 nm to 400 nm range. It can also precisely control the relative humidity (RH) and temperature. In this study, 25 mm x 25 mm specimens were exposed in the SPHERE UV chamber at 50 °C and 75 % RH. Specimens were removed at specified time intervals for characterization. For assessing the release of nanoparticles during UV radiation exposure, a special sample holder displayed in Figure 2, which collects particles released from the samples during UV exposure, was employed. It consists of a sample chamber and a container located at the bottom of the holder to collect released particles. White

poly(tetrafluoroethylene) film or highly polished silicon plates was placed on the collector surface. All samples were mounted normal to the horizontal direction.

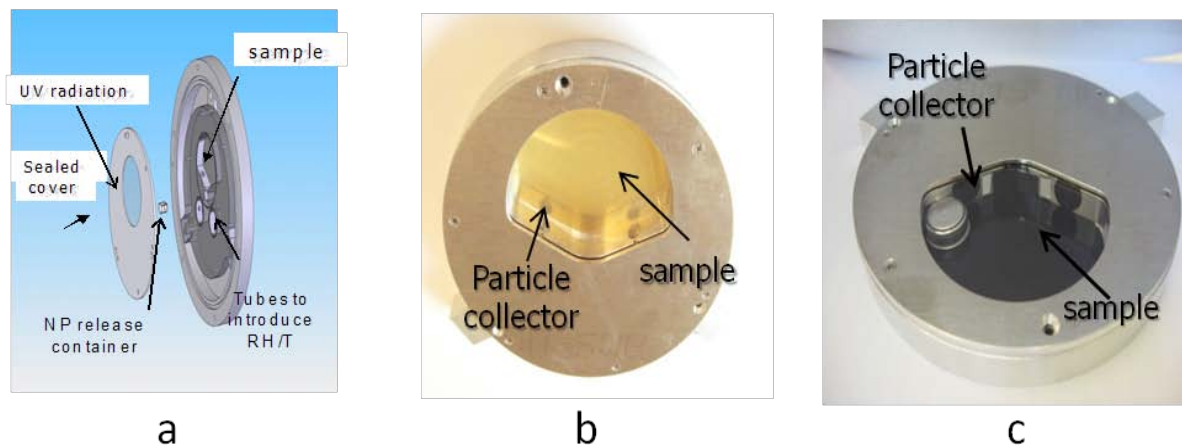


Figure 2. Sample holder to collect released particles: a) a schematic, b & c) photographs with exposed nanosilica (b) and MWCNT (c) epoxy nanocomposites.

2.3 Characterization of UV-exposed nanocomposite and fate of nanoparticles

Mass loss, surface morphology, and chemical degradation of UV-exposed specimens were characterized as a function of exposure time. Mass loss was measured using an analytical balance having a resolution of 10^{-5} g, and is expressed as: $(M_t - M_0)/M_0 \times 100$ where M_t is the specimen mass at time t , M_0 is the specimen mass before exposure. Surface morphology was characterized by field emission scanning electron microscopy (FE-SEM). The released particles were verified by FE-SEM imaging and Energy Dispersive X-ray Spectroscopy (EDS). Chemical degradation was measured with transmission FTIR (t-FTIR) and X-ray photoelectron spectroscopy (XPS). FTIR spectra were recorded at a resolution of 4 cm^{-1} using dry air as a purge gas and a spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. All spectra were the average of 128 scans. The peak height was used to represent the infrared intensity, which is expressed in absorbance, A . All FTIR results were the average of four specimens. XPS analyses were carried out using a Mg K α X-ray source (1253.6 eV) at a 45° angle between the sample surface normal and the lens/hemispherical analyzer. Spectra were acquired at a pass energy 44.75 eV and a step size of 0.125 eV/step. All XPS spectra were fit using 100 % Gaussian peaks, a Shirley baseline, and adjusted with the appropriate sensitivity factors.

3. Results and discussion

3.1. Mass loss

Figure 3 displays the mass loss of unfilled epoxy and epoxy nanocomposites a function of exposure time in the UV/50 °C/75 % RH environment. Except for a small increase at early exposure times, the mass loss in all materials was nearly linear with exposure time. The early increase was likely due to the moisture uptake, which was greater than the material loss induced by the degradation in the early stage. These samples were exposed to 75 % RH, and thus the amount of sorbed water in the sample was substantial. The rate of mass loss was lowest for MWCNT composite and greatest for nanosilica composite. After 43 days of exposure, the maximum mass losses in unfilled epoxy, epoxy/MWCNT

composite and epoxy/nanosilica composite were $2.4 \% \pm 0.27 \%$, $1.3 \% \pm 0.30 \%$, and $4.0 \% \pm 0.95 \%$, respectively.

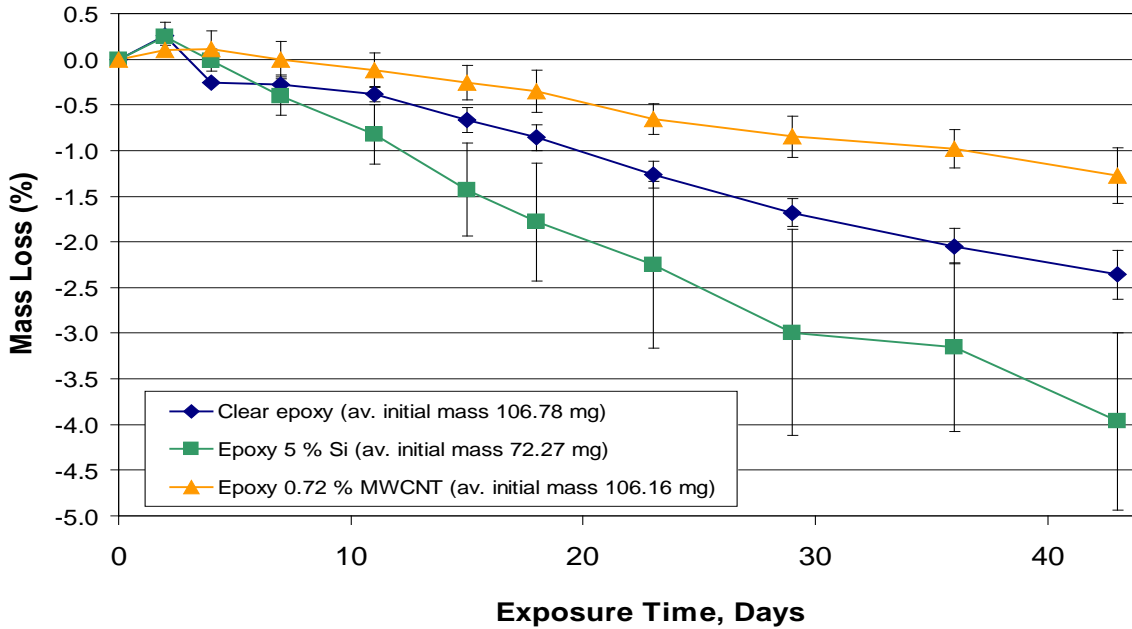


Figure 3. Mass loss Vs. exposure time for unfilled, epoxy/0.72 % MWCNT composite, and epoxy/5 % nanosilica composite samples exposed to UV/50 °C/75 % RH. Results are the average of 6 specimens, and the error bars represent one standard deviation.

3.2. Photodegradation of the polymer matrix

Chemical degradation of the matrix was followed by FTIR in the transmission mode, which can provide quantitative data on changes of functional groups of the epoxy polymer. t-FTIR spectra recorded at different exposure times showed that the intensities of numerous bands of the epoxy structure substantially decreased, including the bands at 1508 cm^{-1} due to benzene ring, 1296 cm^{-1} due to aliphatic ether, and new bands in the $1620\text{--}1740 \text{ cm}^{-1}$ region due to the formation of various carbonyl groups (C=O), such as aldehydes, ketones, and amides have appeared. These changes are attributed to photo-oxidation of amine-cured epoxy by UV in the 295 nm to 400 nm wavelength, leading to extensive chain scission of the main chains of the epoxy. Ketone formation is derived from the secondary hydroxyl groups, while amide is generated from the abstraction of a methylene hydrogen adjacent to the crosslink [8-10]. The carbonyl groups formed can absorb radiation at long wavelengths and accelerate the degradation. UV-visible spectra (not shown) showed a progressive increase of the absorbance intensity in the region above 300 nm, indicating that the degraded epoxy films did absorb UV light at longer wavelengths. Both the unfilled and epoxy/nanosilica composite films also exhibited visible yellowing after the UV exposure, suggesting that a substantial amount of conjugated structures had formed in this amine-cured epoxy. Our previous extensive study has demonstrated clearly that UV is the main weathering factor that causes severe degradation of amine-cured epoxies, with temperature and RH playing a minor role [11].

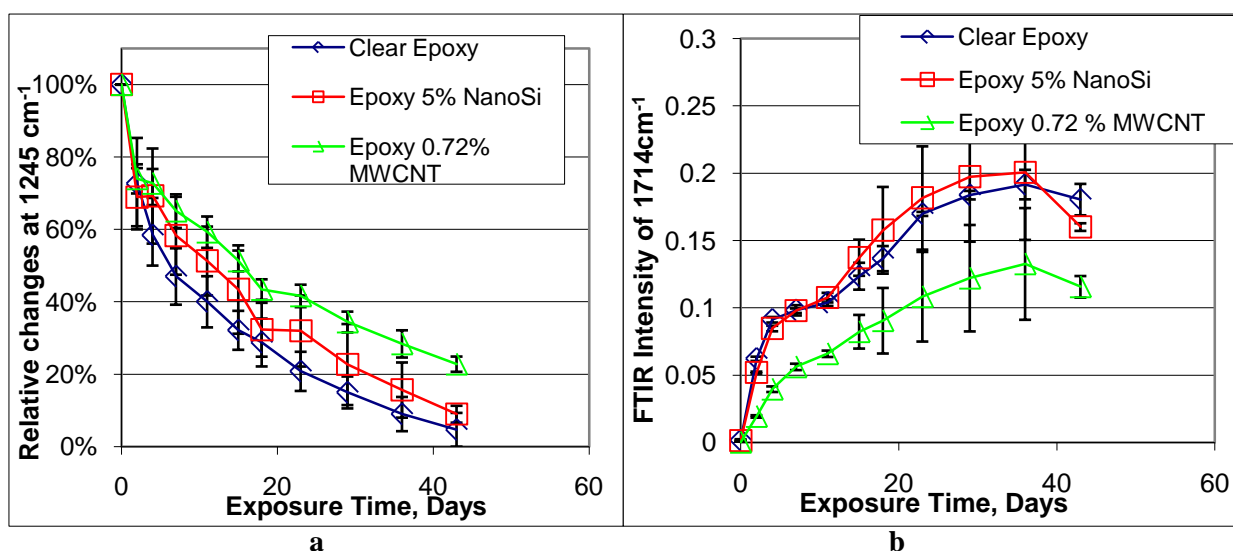


Figure 4. a) Chain scission, and b) oxidation vs. time for unfilled, epoxy/0.72 % MWCNT composite, and epoxy/5 % nanosilica composite samples exposed to UV/50 °C/75 % RH. Each data point is the average of four specimens and error bars represent one standard deviation.

The bands at 1508 cm⁻¹ and 1714 cm⁻¹, representing chain scission and oxidation, respectively, were used to follow various degradation processes of unfilled epoxy and epoxy nanocomposites exposed to UV radiation. The results are depicted in Figure 4. Both the rates of oxidation and chain scission of the epoxy/MWCNT composite were lower than those of the unfilled epoxy or epoxy/nanosilica material. This observation is consistent with our previous results for polyurethane/MWCNT composites [12] and is similar to that reported in the literature for PMMA/CNT composites subjected to high-energy radiation [13]. The higher UV resistance of polymer/CNT composites has been attributed to the CNT's ability to disperse and filter radiation energy as well as the strong interaction between free radicals (generated during irradiation) and CNTs [13]. Although not shown here, the intensity of the band at 1060 cm⁻¹, due to Si-O-Si, of the nanosilica composites decreased at first then started to rise after two days, suggesting that the concentration of SiO₂ nanoparticles on the composite surface has substantially increased, consistent with SEM data to be shown later.

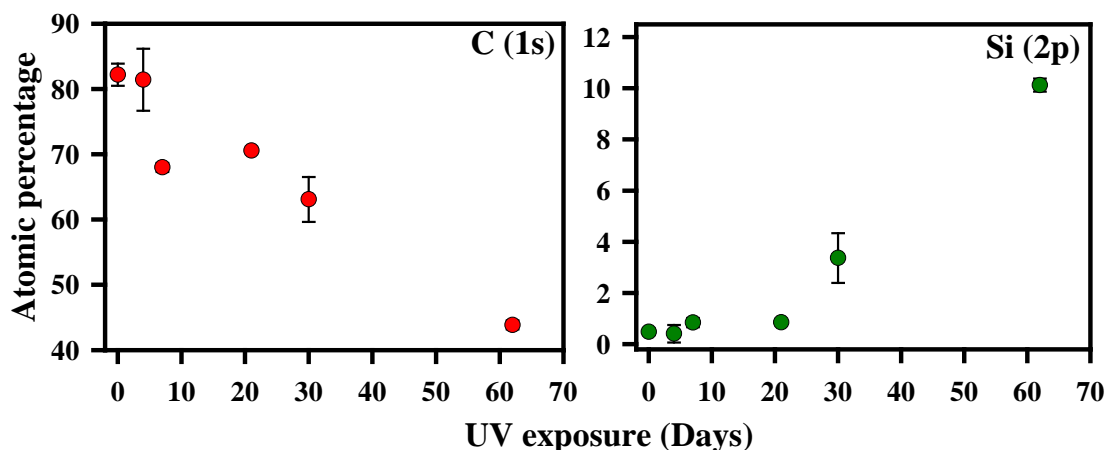


Figure 5. XPS-based C and Si concentrations on the epoxy/nanosilica composite surface Vs. time exposed to UV/50 °C/75 % RH. Except for the 21 d where only one specimen was used, other data consisted of two or more specimens

The degradation of the epoxy and an increase of the SiO₂ material near the nanocomposite surface is supported by XPS data displayed in Figure 5. The surface concentration of C decreased from 82.2 % \pm 1.7 % to 43.8 % \pm 0.7 %, while that of Si increased from 0.5 % \pm 0.1 % to 10.1 % \pm 0.3 % after 62 d exposure. The increase of SiO₂ on the composite surface following UV irradiation has also been confirmed and quantified by inductively-coupled plasma–optical emission spectroscopy (ICP-AES) analysis [14].

3.3. Fates of nanoparticles during UV exposure of polymer nanocomposites

Surface morphological changes of epoxy/5 % nanosilica composite exposed to UV condition are displayed in Figure 6; these are FE-SEM mages taken at different times. The initial surface appeared smooth with evidence of some SiO₂ nanoparticles on it. After four days of exposure, numerous SiO₂ nanoparticles can be clearly seen on the composite surface. The concentration of nanosilica continued to increase with exposure time, and after 43 days, SiO₂ nanoparticles have covered the entire composite surface.

Microscopic and spectroscopic data shown in Figures 4,5 and 6 strongly suggested that the increase of nanosilica concentration at the composite surface with UV exposure was a result of the epoxy matrix degradation. However, these results do not answer the question: did SiO₂ nanoparticles release from the nanocomposite during its exposure to UV radiation? Analysis of particles collected at the bottom of the sample holder (i.e., Figure 2b) would address this question. Figure 7 shows SEM images and EDS spectra of the particle collector surface before and after the sample was exposed to UV radiation. Before the exposure, the collector surface showed no evidence of particles (Figure 7a). After 43 d exposure, many particles were observed on the collector surface (Figure 7b), and numerous spherical nanoparticles can be seen with higher magnification (Figure 7c).

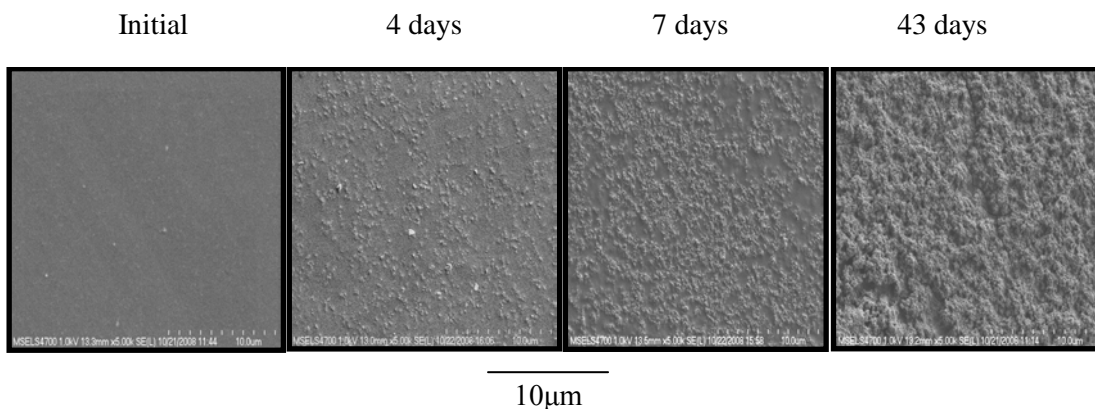


Figure 6: FE-SEM images of epoxy/5 % nanosilica composite exposed to UV/75 %RH/50 °C for different times.

EDS spectrum of the collector surface before the sample was exposed to UV radiation showed only F and C elements (Figure 7d), as expected for a poly(tetrafluoroethylene) film. However, EDS spectrum of the collector surface after the sample was irradiated by UV for 43 days revealed the presence of Si element (Figure 7e). The concentration of O also increased after the UV exposure. The increase of both Si and O elements supports the suggestion that the spherical nanoparticles on the collector surface observed in Figure 7c were likely the SiO₂ compound. The results of Figure 7 have provided direct evidence that SiO₂ nanoparticles or their aggregated form were released from the epoxy nanocomposites to the surroundings during their exposure to 295 nm-400 nm UV radiation. However, this preliminary result does not establish whether these SiO₂ nanoparticles are pristine or covered with polymer molecules. Such information is important for assessing the potential risks of released nanoparticles, because nanomaterials that are covered with an inert polymer layer are likely to

present less an EHS concern than the pristine nanomaterials do. Work is in progress to address this question.

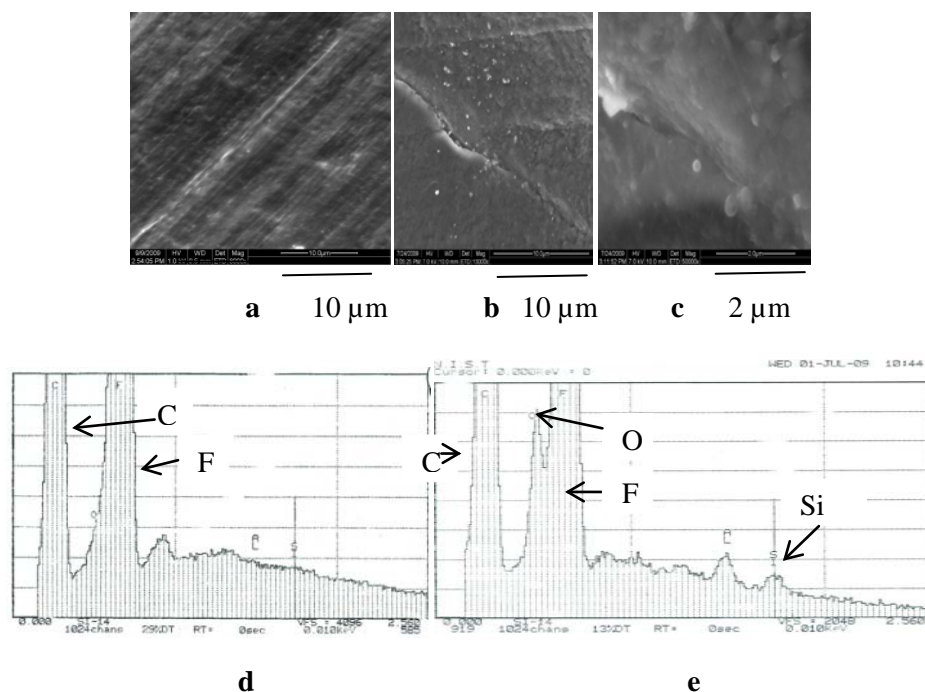


Figure 7. SEM images of particle collector surface: (a) before, and (b) after the epoxy/nanosilica composite sample was exposed to UV radiation for 43d, (c) higher magnification of b, showing numerous spherical nanoparticles; EDS spectra of the collector surface: before (d), and after the sample was exposed for 43 d (e), showing the presence of Si element.

Based on microscopic and spectroscopic evidence, the release of SiO_2 nanoparticles from the epoxy nanocomposites during UV irradiation condition used in this study probably followed the sequence shown in Figure 8. First, the epoxy polymer layer on the surface underwent photodegradation and was removed. This resulted in gradual increase of the number of SiO_2 nanoparticles on the composite surface with exposure time. At a critical thickness/concentration, particles containing SiO_2 fell off the vertical surface (release) likely by gravitation force. For nanocomposites exposed to outdoor, environmental elements such as rain, condensed water, wind, mechanical vibration, and stresses resulting from materials dimensional changes likely affect the release rate of nanoparticles. Because, in the absence of UV stabilizers, most common polymers are susceptible to degradation during exposures to the UV environment, this conceptual model for the release of SiO_2 nanoparticles should be applicable to other polymers and to other low aspect ratio, spherical nanoparticles used in nanocomposites.

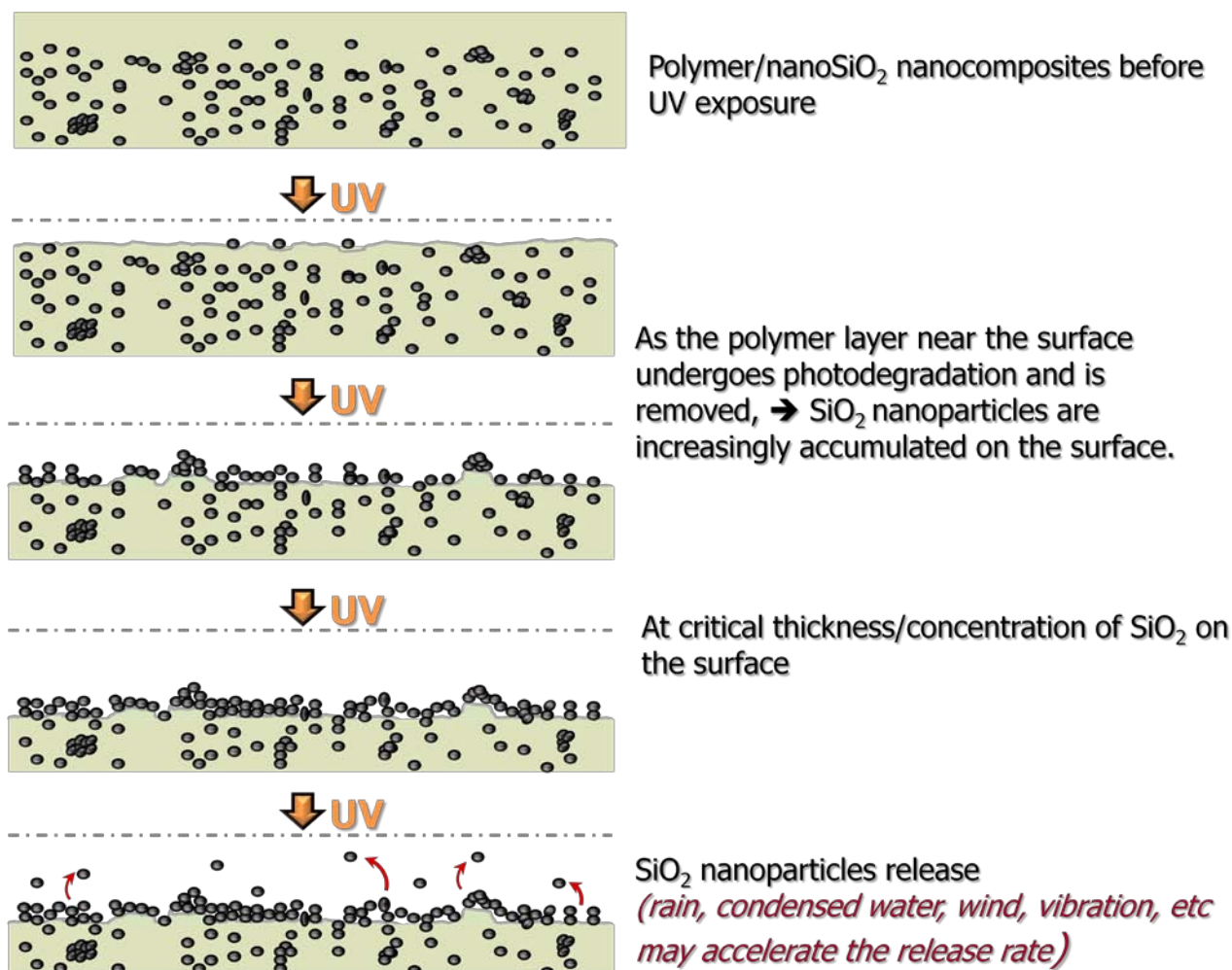


Figure 8. Conceptual model for the release of SiO₂ nanoparticles from epoxy/nanosilica composites exposed to UV radiation

Surface morphology of epoxy/MWCNT composites exposed to UV radiation are shown in Figure 9; these are FE-SEM images taken at different exposure times. The initial composite surface appeared smooth with no evidence of CNTs. However, MWCNTs became visible on the surface after 11 days, and their concentration on the surface continued to increase with exposure time. After 43 days, the MWCNTs have formed a dense layer on the composite surface, which is clearly shown in the high magnification image. From these microscopic results and FTIR data shown in Figure 4, it is reasonable to suggest that the increased CNT concentration at the composite surface with exposure time was a result of the matrix photodegradation, similar to that for nanosilica nanocomposites. As the epoxy matrix degraded and was removed, MWCNTs were increasingly exposed on the surface.

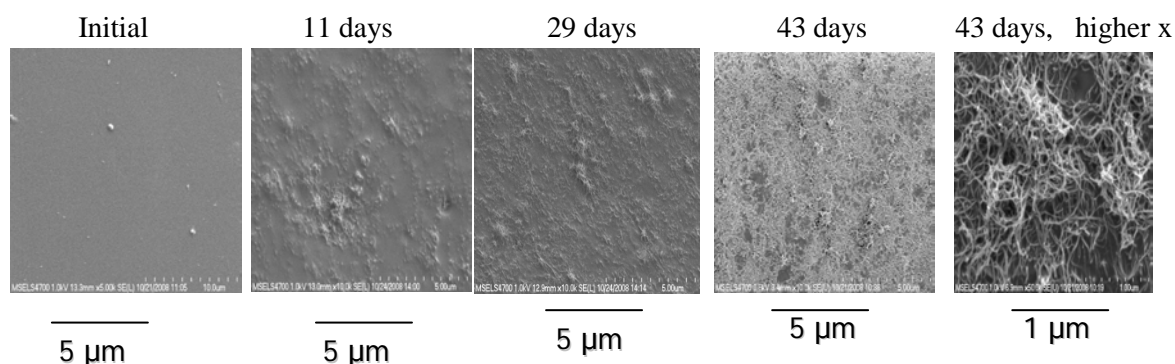


Figure 9. FE SEM images taken at different times for the epoxy/0.72 % MWCNT composite exposed to UV/50 °C/75 % RH, showing the aggregated network of MWCNTs on the composite surface after UV exposure.

One key question: does the amount of MWCNTs at the surface observed at each exposure time represent its concentration at that particular depth in the epoxy matrix before exposure, or is it an amassing of CNTs from different depths as the degradation of the matrix progressed? In the first case, as soon as MWCNTs were exposed at the surface, they would be removed from it. Thus, the rate of CNT release into the environment should be similar to that of the polymer degradation. If the second case is true, then MWCNTs would form an aggregated network as they become exposed on the composite surface. These MWCNTs were highly entangled, with some of them were still strongly imbedded in the matrix, and are thus are not likely to be released to the environment to any great extent during normal exposure conditions. To better answer this question, the collector surface of the holder in which a large epoxy/MWCNT composite sample was exposed for nine months under the same conditions as for the nanosilica composites was carefully analyzed by SEM. The result showed no evidence of CNTs on the collector surface, suggesting that essentially little or no release of MWCNTs during exposure to UV. Based on these data, the fate of MWCNTs in polymer/MWCNT composites is schematically illustrated in Figure 10. Except the last step, the sequence is similar to that of the nanosilica composite. That is, photodegradation of the matrix has resulted in accumulation of large concentration of MWCNTs on the surface, which aggregated and formed a dense structure. Such dense network structure of CNTs decreased the photodegradation of the epoxy polymer layer underneath and minimized their release to the environment. This model should be applicable for polymer nanocomposites containing high aspect ratio, fiber-like nanoparticles.

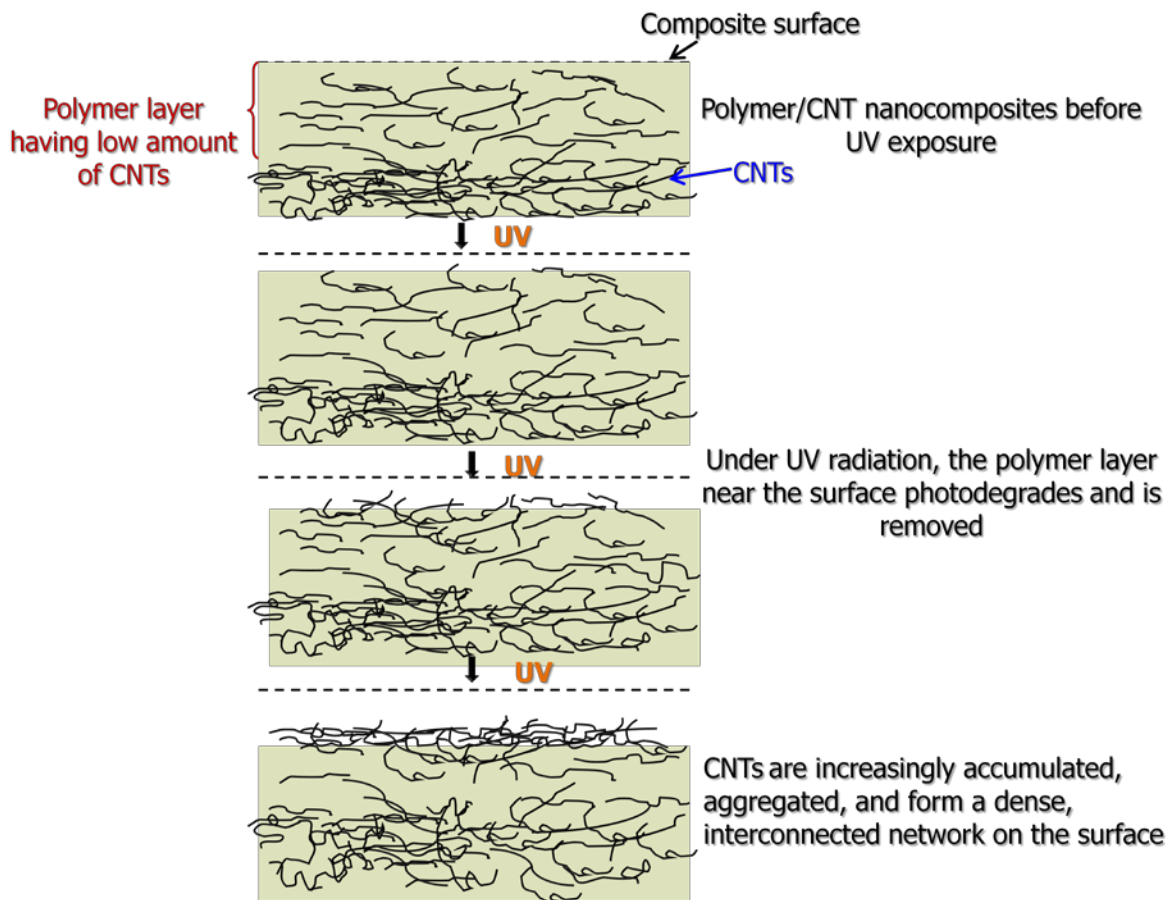


Figure 10. Conceptual model for the formation of dense MWCNT network on the epoxy nanocomposite surface during exposure to UV radiation.

4. Conclusions

The fates of nanoparticles in amine-cured epoxy containing MWCNTs and nanosilica exposed to 295-400 nm UV radiation at 50 °C and 75 % RH have been investigated. Based on experimental results, the following conclusions can be made:

- Polymer chains in amine-cured epoxy nanocomposite underwent photodegradation during exposure to 295 nm to 400 nm UV radiation, resulting in a substantial mass loss and marked increase of nanoparticle concentration on nanocomposite surfaces.
- The rates of mass loss and chemical degradation of MWCNT/epoxy composite were lower than those of the unfilled epoxy or epoxy/nanosilica composite, suggesting that MWCNTs decrease the photodegradation of the amine-cured epoxy.
- MWCNTs formed a dense, aggregated network on the nanocomposite surface, with no evidence of their release even after prolonged exposure to UV radiation; the CNT network formed on the composite was responsible for essentially eliminating the release of CNTs to the environment during exposure to UV radiation.
- Microscopic and spectroscopic analyses showed conclusively that SiO₂ nanoparticles were released to the environments after short exposure to UV radiation.
- Conceptual models for the release of nanosilica and retention of CNTs during exposure to UV have been proposed, which should be applicable to other polymers and other types of nanoparticles.

The results of this study provide valuable information to assess the potential risk of nanoparticles release from epoxy nanocomposites during service. Work is under way to predict the nanoparticle release rates and chemical compositions of the released nanoparticles.

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