

DEGRADATION AND NANOFILLER RELEASE OF POLYMER NANOCOMPOSITES EXPOSED TO ULTRAVIOLET RADIATION

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Abstract

Nanofillers are increasingly used to enhance multifunctional properties of polymers. However, recent research suggests that nanomaterials could pose a negative impact on the environmental health and safety. Since polymers are susceptible to photodegradation by solar ultraviolet (UV) radiation, nanofillers that are embedded in a polymer nanocomposite will be released eventually. Such release of nanofillers may have an adverse effect on the environment and present a roadblock to more widespread acceptance of these innovative materials. This study investigated the degradation and potential nanofiller release of amine-cured epoxy nanocomposites containing multi-walled carbon nanotube (MWCNTs) and nanosilica fillers exposed to UV radiation from 295 nm to 400 nm at 50 °C and 75 % RH. During the exposure period, measurements of chemical degradation, mass loss, and surface morphological changes were carried out on the samples. Amine-cured epoxy underwent rapid photodegradation, resulting in substantial mass loss and increase in MWCNTs and nanosilica concentrations at the composite surface. The rates of mass loss and chemical degradation were lower for the MWCNT-filled epoxy than those of the unfilled or nanosilica-filled materials, suggesting that MWCNTs may have enhanced the photostability of amine-cured epoxy. Further, while silica nanoparticles almost uniformly covered the composite surface after prolonged exposure, MWCNTs formed an aggregated network at the degraded surface. Research is in progress to provide direct evidence of any nanofiller release to the environment during the exposure.

1 INTRODUCTION

Polymer nanocomposites refer to a multicomponent system in which the major constituent is a polymer or polymer blend and the minor constituent is a filler that has at least one dimension below 100 nm (i.e., nanofiller). The numerous reports of large property enhancements with small additions (1-5 mass %) of nanofillers have fueled intensive industrial and academic research in the past decade (1-4). Polymer nanocomposites are being used in many large-volume industries including construction, automotive, and aerospace. Research on these high-performance, advanced materials has focused primarily on processing and short-term performance. In addition, to address the potential risks of nanofillers, current studies on the effects of these materials on human health and the environment concentrate on exposures during the manufacturing process. For polymer nanocomposites, whatever the application, both the long-term performance of the products themselves and the fate of nanofillers in the matrix play a key role in acceptance and use of these products. This is because the matrix in a polymer nanocomposite is susceptible to degradation during service and post-service. This could lead to exposed nanofillers at the composite surface, and likely release of nanofillers into the environment via rain, condensed water, and wind. Since nanofillers could pose potential risks to human health and environment (5-7), the release of these very small materials during service and post-service would present a roadblock to their innovation and commercialization.

The release of nanofillers from polymer nanocomposites exposed to end-use environments is tied closely to degradation of the polymeric matrix, which is an inherently complex phenomenon influenced by environmental factors, processing, and material properties. Nanofillers also possess unique properties that likely affect the rate and degradation mechanism of the polymer matrix, and hence, the release rate of the nanofiller. Yet, little information is available on the degradation of polymer nanocomposites, the state of the embedded nanofillers during exposure, or how they are released during their service and post-service. As a result, the long-term performance of polymer nanocomposites and the potentially harmful effects of the nanofillers incorporated in polymers on the environment and health safety have not been determined. Previous work in our laboratory has shown that, although both unmodified and isocyanate (NCO)-functionalized multi-walled carbon nanotubes (MWCNTs) substantially reduce the photodegradation rate of polyurethane (PU), NCO-functionalized CNTs are less effective in photo-stabilizing this polymer (8). Additionally,

although several studies have reported a reduction of photodegradation in polymers containing zinc oxide nanoparticles (9,10), our research has shown that nano-zinc oxide actually accelerates the photodegradation of water-borne PU (11).

The main objective of this study was to investigate the effects of nanofillers on the degradation rates and mechanism of amine-cured epoxy exposed to UV radiation, and to determine how degradation of the epoxy matrix affects the behavior of nanofiller release. The results of this study should provide valuable information for assessing the potential risk of nanofillers in epoxy matrix during service in an outdoor environment.

2. EXPERIMENTALS*

2.1 Materials and Nanocomposite Preparation

The matrix studied was an amine-cured epoxy commonly used in coatings and fiber-reinforced polymer composites, and the nanofillers were multi-walled carbon nanotubes (MWCNTs) and silica nanoparticles (nanosilica). The epoxy was prepared as a stoichiometric mixture of a diglycidyl ether of bisphenol A (DGEBA) epoxy resin (EPON 828, Resolution Performance Products) having an equivalent mass of 189 (grams of resin containing one gram equivalent of epoxide) and a polyoxypropylenetriamine curing agent (Jeffamine T403, Hunsman Corporation). The epoxy polymer was used without additional additives. Figure 1 presents the chemical formula of this amine-cured epoxy, showing, in addition to the cross-linked structure, the residual epoxide group which also plays an important role in the photodegradation of epoxy resins. MWCNTs and silica nanoparticles were obtained from commercial sources. MWCNT was a 1 % mass fraction pre-dispersed product in Epon 828 epoxy resin (Zyvex). The silica nanoparticles (Aerosil R974, Evonik Degussa Corp) were surface modified, had an average diameter of 7 nm, and a purity of > 99.8%. Reagent grade toluene (purity > 99.5 %) was used for composite processing.

** Certain commercial product or equipment is described in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.*

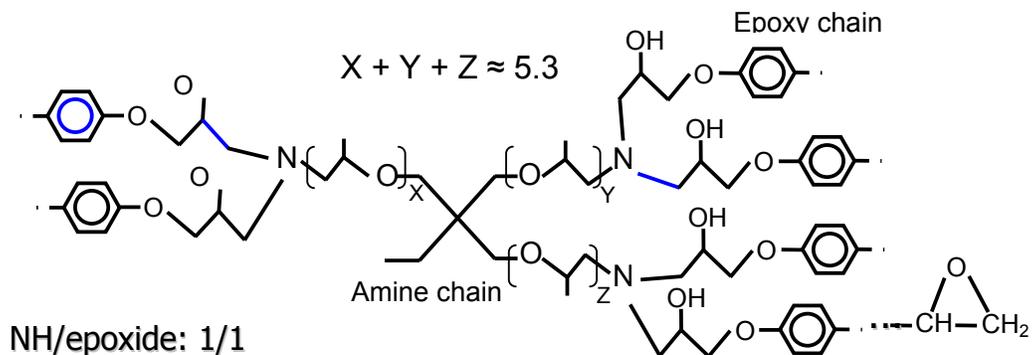


Figure 1. Postulated chemical structure of the amine-cured bisphenol A epoxy.

Free-standing films of 1) unfilled, 2) 0.72 % MWCNT-filled, and 3) 5 % nanosilica-filled amine-cured epoxy were fabricated. The filler 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.) Figure 2 shows the process used for preparations of unfilled, MWCNT- and nanosilica-filled epoxy composite samples. Unfilled epoxy and MWCNT/epoxy composite films were prepared by 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, silica 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/nanofiller mixtures were degassed for 1 h at room temperature and then drawn down using a bar film applicator on a polyethylene terephthalate sheet (Mylar). Unfilled and nanocomposite films 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. All films had a dry film thickness between 200 μm and 250 μm .

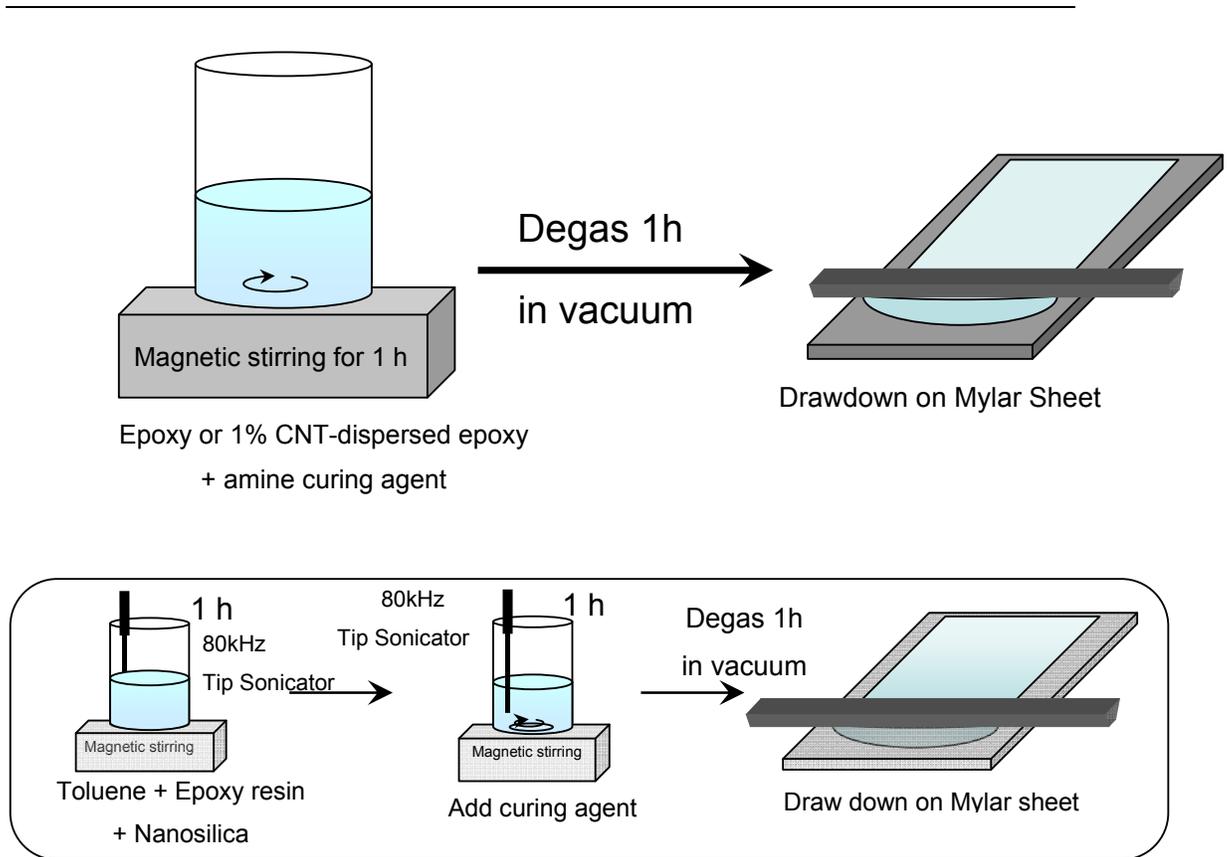


Figure 2. Process used for preparation of unfilled and nano-filled amine-cured epoxy composite films.

2.2 UV Exposure Conditions

The degradation of unfilled films and nano-filled epoxy composites was studied using a 2 m integrating sphere-based weathering chamber, referred to as SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) (12). This SPHERE UV chamber utilizes a mercury arc lamp system that produces a collimated and highly uniform UV flux of approximately 480 W/m^2 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 $50 \text{ }^\circ\text{C}$ and 75 % RH. Specimens were removed at specified time intervals for characterization.

2.3 Characterization of UV-exposed Samples

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: $(M_t - M_o)/M_o \times 100$ where M_t is the specimen mass at time t , M_o is the specimen mass before exposure. Surface morphology was characterized by field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) in the tapping mode. Both topography (height) and phase AFM images were obtained. AFM phase imaging is sensitive to material properties and can reveal clear nanoscale features. Chemical changes were followed by FTIR spectroscopy in the attenuated total reflection mode (FTIR-ATR) using a ZnSe prism. Spectra were recorded at a resolution of 4 cm^{-1} employing dry air as a purge gas and a spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. All FTIR results were the average of at least four specimens.

3 RESULTS

3.1 Mass Loss

Figure 3 displays the mass loss of unfilled, MWCNT-filled, and nanosilica-filled epoxy samples as 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-filled composite and greatest for nanosilica-filled material. After 43 days of exposure, the maximum mass losses in unfilled, 0.72 % MWCNT-, and 5 % nanosilica-filled epoxy films were $2.36 \% \pm 0.27 \%$, $1.27 \% \pm 0.30 \%$, and $3.96 \% \pm 0.96 \%$, respectively.

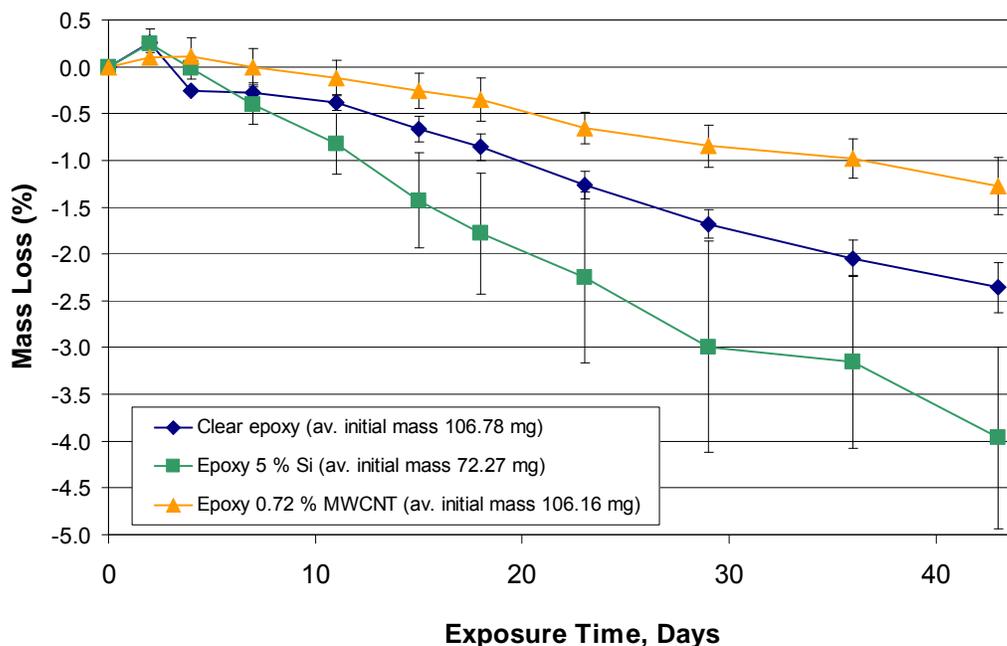


Figure 3. Mass loss Vs. exposure time for unfilled, MWCNT- and nanosilica-filled amine-cured epoxy composite samples exposed to UV/50 °C/75 % RH. Results presented are the average of 4 specimens, and the error bars represent one standard deviation.

3.2 Degradation of Epoxy/MWCNT and Epoxy/Nanosilica Composites

Figures 4a and 4b display difference FTIR-ATR spectra collected at different exposure times for 0.72 % MWCNT-filled and 5 % nanosilica-filled epoxy composites, respectively, exposed to UV/50 °C/75 %RH condition. These spectra were obtained by subtracting spectrum of the unexposed sample from spectra of the samples exposed at different times. To account for variations due to sampling, all spectra were normalized by the least-changed band at 1380 cm^{-1} (CH_3 bending, gem-dimethyl) before the subtraction. Bands below and above the zero absorbance line in a difference spectrum represent a loss and gain (e.g., oxidation), respectively, of a functional group in the sample. This type of FTIR spectra can provide useful data for elucidating the degradation mechanism of polymers exposed to weathering environments. Except for the 1000 cm^{-1} - 1150 cm^{-1} region, which covers the absorption of both the Si-O-Si and C-O bonds, little difference is observed in the difference spectra of the MWCNT and

nanosilica composites or the unfilled epoxy film (not shown). These results suggested that the degradation mechanism for unfilled epoxy, MWCNT- and nanosilica-filled amine-cured epoxy composites is similar.

Figure 4 shows 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 (13-15) have appeared. These changes were 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 (14,15). 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 nanosilica-filled epoxy 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 (16).

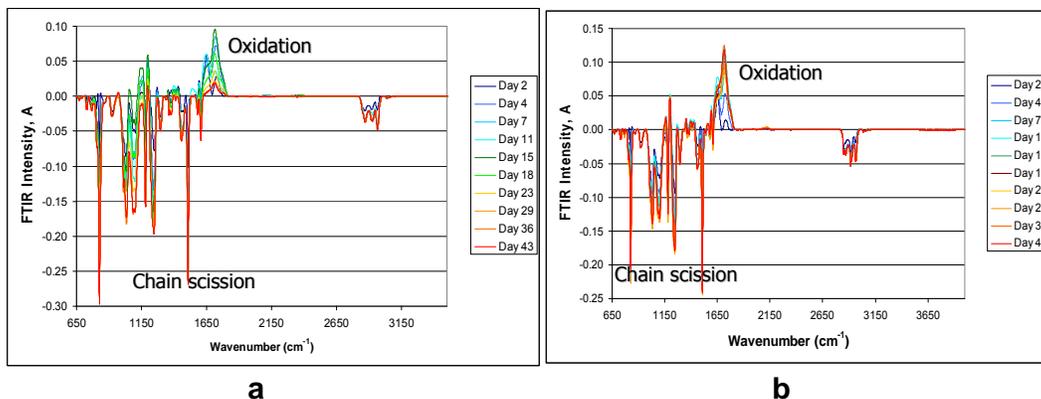


Figure 4. Difference FTIR-ATR spectra taken at different times for: a) 5% nanosilica-filled, and b) 0.72 % MWCNT-filled amine-cured epoxy composites exposed to UV/50 °C/75 % RH. All spectra were normalized by the 1380 cm^{-1} band before subtraction.

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 films and nano-filled epoxy composites exposed to UV radiation. The results are depicted in Figure 5. The intensity changes have been normalized to both the initial absorbance and that of the 1380 cm^{-1} band to minimize sampling variations by the ATR probe.

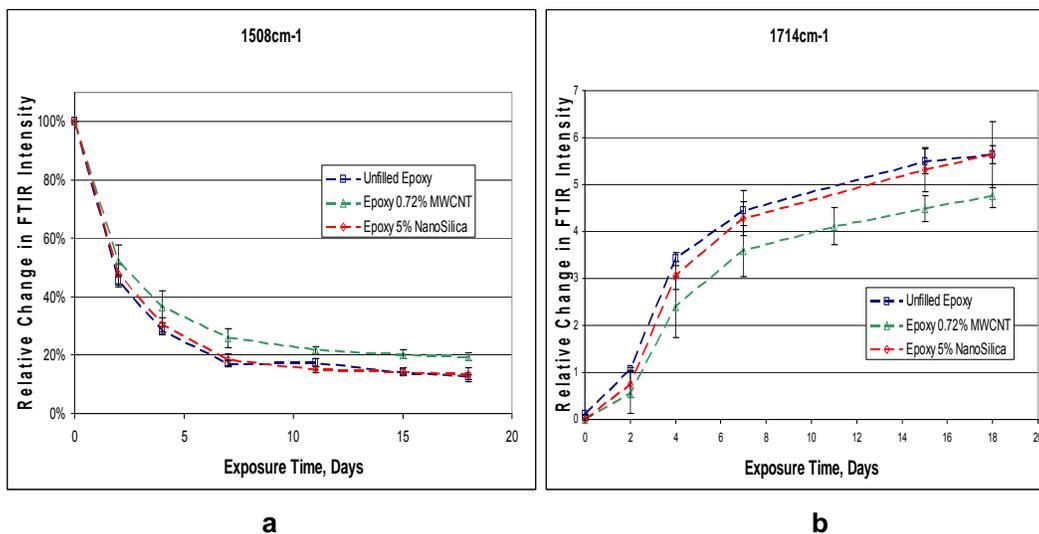


Figure 5. a) Chain scission and b) oxidation vs. time for unfilled, 0.72 % MWCNT-filled, and 5 % nanosilica-filled amine-cured epoxy samples exposed to UV/50 °C/75 % RH. Each data point is the average of four specimens and error bars represent one standard deviation,

Figure 5 indicates that both unfilled and nano-filled amine-cured epoxy films underwent rapid chemical degradation when exposed to this UV/RH/T condition. The degradation rates of all three materials reached a plateau in less than 10 days of exposure. It should be noted that the probing depth in the epoxy polymer of the FTIR-ATR technique using a ZnSe probe in the 800 cm^{-1} - 3000 cm^{-1} range is between $0.5\text{ }\mu\text{m}$ and $2.5\text{ }\mu\text{m}$ from the surface. Therefore, the chemical changes observed here originated from the epoxy polymer layer at or near the composite surface. Figure 5 also showed that both the rates of oxidation and chain scission of MWCNT-filled epoxy composite were lower than those of the unfilled or nanosilica-filled materials. This observation is consistent with our previous results for polyurethane/MWCNT composites (8) and is similar to that reported in the literature for PMMA/CNT composites subjected to high-energy radiation (17). 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 (17). Although not shown here, the intensity of the band at 1080 cm^{-1} , due to Si-O-Si and C-O, of the nanosilica-filled composites decreased at first then started to rise sharply after two days, suggesting that the concentration of silica nanoparticles on the composite surface has substantially increased, consistent with SEM and AFM data to be shown later.

3. 4. Surface Morphology

Figure 6 presents FE-SEM and AFM images of the 0.72 % MWCNT-filled epoxy composite exposed to UV/50 °C/75 % RH environment for different times. The composite surface appeared smooth with no evidence of nanofillers before UV exposure. However, CNTs became visible on the surface after 11 days, and their concentration on the surface continued to increase with exposure time (SEM images). After 43 days, the CNTs have formed a dense network on the composite surface. From these microscopic results and FTIR data shown in Figure 5, it is reasonable to suggest that the increased MWCNT concentration at the composite surface with exposure time resulted from matrix photodegradation. As the epoxy matrix degraded and was removed, MWCNTs were increasingly exposed on the surface. 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 and are thus are not likely to be released to the environment to any great extent until a critical concentration of CNTs on the surface is reached. Work is being conducted to answer these questions.

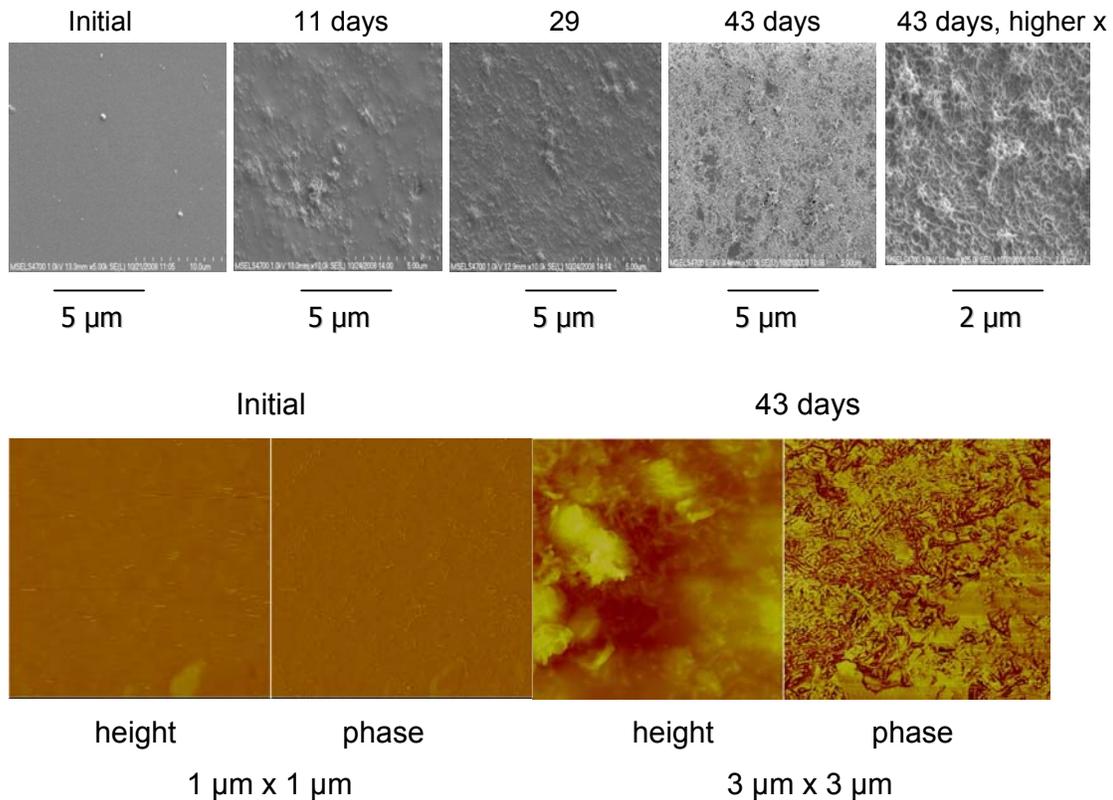


Figure 6. FE SEM (top row) and AFM (bottom row) images taken at different times for the 0.72 % MWCNT-filled amine-cured epoxy composite exposed to UV/50 °C/75 % RH, showing the aggregated network of MWCNTs at the composite surface after UV exposure. For each AFM pair, height image is on the left and phase image is on the right.

Figure 7 displays FE-SEM and AFM images taken at different times for the 5 % nanosilica-filled epoxy composite exposed to UV/50 °C/75 % RH. The surface before exposure appeared smooth with evidence of some silica nanoparticles on it (AFM images). After four days of exposure, silica nanoparticles were clearly seen on the composite surface. The concentration of nanosilica continued to increase with exposure time, and after 43 days, silica nanoparticles have covered the entire composite surface. As with the MWCNT/epoxy composites, these results suggest that the increase of nanosilica concentration at the composite surface is due to the photodegradation of epoxy. Under the action of rain and condensed water, the exposed silica nanoparticles are likely to be released into the environment. Research is being conducted to verify this postulation.

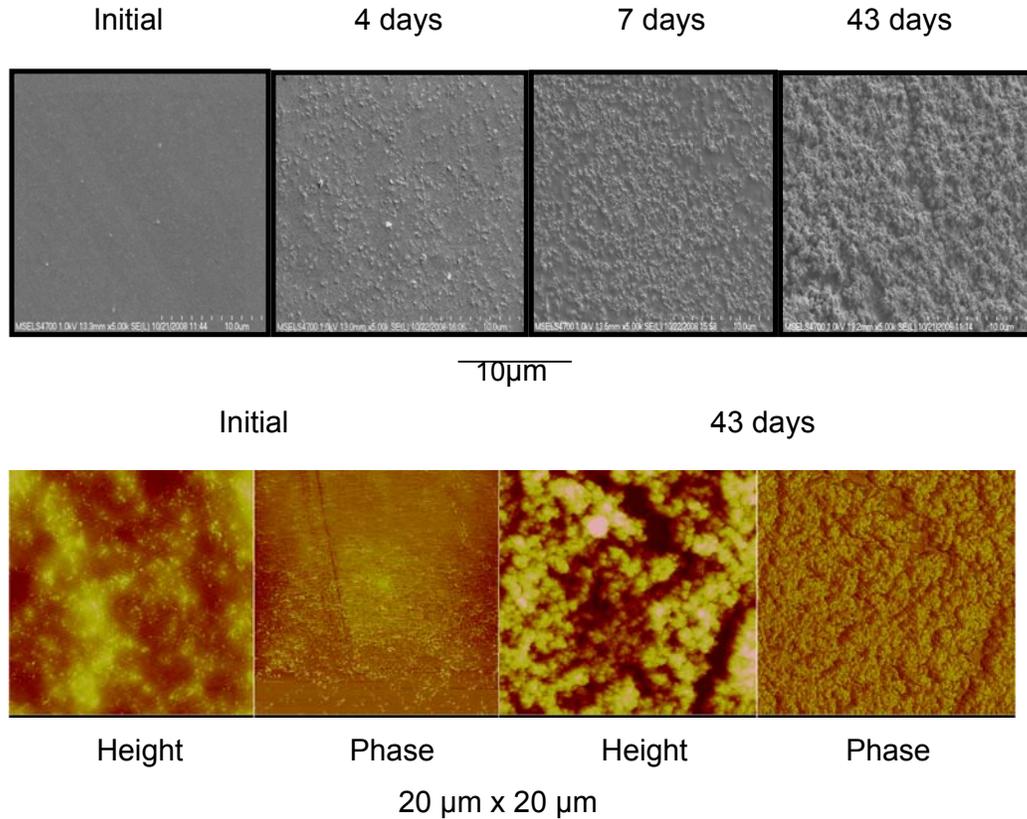


Figure 7: FE-SEM (top row) and AFM (bottom row) images of 5 % nanosilica–filled epoxy composite exposed to UV/75 %RH/50 °C for different times. For each AFM pair, height image is on the left and phase image is on the right.

3 CONCLUSIONS

The degradation and surface morphology of unfilled, 0.72 % MWCNT- and 5 % nanosilica–filled amine cured epoxy composite films exposed to UV/50 °C/75% RH condition have been investigated by various techniques. This study also examined how degradation of the polymer matrix affects the behavior of nanofillers at the composite surface. The results showed that amine-cured epoxy underwent rapid photodegradation, which resulted in a substantial mass loss and an increase of MWCNT and nanosilica concentration at the composite surface. Further, the rates of mass loss and chemical degradation of the MWCNT-filled epoxy were less than those of the unfilled or nanosilica-filled materials, suggesting that MWCNT enhances the UV resistance of amine-cured epoxy. Work is in progress to provide direct evidence of nanofiller release to the environment during exposures.

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