

Direct Evidence of Nanoparticle Release from Epoxy Nanocomposites Exposed to UV Radiation

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ABSTRACT

This study assessed the fate of SiO₂ nanoparticles (nanoSiO₂) in epoxy/nanoSiO₂ composites exposed to ultraviolet (UV) radiation. The matrix was a stoichiometric mixture of a diglycidyl ether of bisphenol A epoxy and an aliphatic tri-amine. Films of unfilled and 5 mass % SiO₂-filled amine-cured epoxy were exposed to 75 % relative humidity (RH), 50 °C, and (295-400) nm UV radiation. Photodegradation, mass loss, surface morphology of the exposed composites, and composition of the released particles were characterized. Amine-cured epoxy/nanoSiO₂ composites underwent rapid photodegradation, resulting in substantial mass loss, accumulation of SiO₂ nanoparticles on the composite surface, and release of SiO₂ nanoparticles. The results of this study will provide useful information to assess the potential risk of nanoSiO₂ in epoxy nanocomposites during outdoor use.

Keywords: epoxy, life cycle, nanocomposites, nanoparticles, release, UV.

1 INTRODUCTION

Polymer nanocomposites are being used or potentially will be used in large volumes in a wide variety of applications (1,2). Whatever the application, both the long-term performance of the nanocomposite itself and the fate of the nanoparticles in the polymer matrix play a key role in the acceptance and commercialization of these advanced products. This is because the matrix in a polymer nanocomposite undergoes degradation during service and post-service, potentially releasing nanoparticles into the environment via the effects of mechanical vibration/abrasion, rain, condensed water, and wind. Since nanoparticles have shown potential risks to human health and environment (3,4), their release during the life cycle of polymer nanocomposites could present a roadblock to innovation and commercialization of polymer nanocomposites. However, little data is available on the environmentally-induced degradation of polymer nanocomposites, the state of the embedded nanoparticles during exposure, or how they may be released during service. The lack of this type of information hinders our ability to understand the release mechanisms, predict the long-term release behavior, and develop strategies to mitigate this potentially serious problem. This study investigated the fate of SiO₂ nanoparticles embedded in an

epoxy matrix exposed to ultraviolet (UV) radiation. Results showed that, when exposed to UV radiation having wavelengths similar to those of the sunlight, the epoxy matrix underwent photodegradation and subsequent mass loss, accumulation of a large amount of SiO₂ nanoparticles on the composite surface, and release of SiO₂ nanoparticles into the environment.

2. EXPERIMENTAL PROCEDURES

2.1 Materials and Nanocomposite Preparation

The matrix was a model amine-cured epoxy commonly used for protective coatings and fiber-reinforced polymer composites. It was a stoichiometric mixture of a diglycidyl ether of bisphenol A epoxy having an equivalent mass of 189 (grams of resin containing one gram equivalent of epoxide) and a tri-polyetheramine curing agent. After curing, this amine-cured epoxy forms a crosslinked network structure. The SiO₂ nanoparticles (nanoSiO₂) had an average diameter of 7 nm and were surface-treated with a silane material, whose composition and coverage on the nanoSiO₂ surface were not known. Reagent grade toluene was used for composite processing.

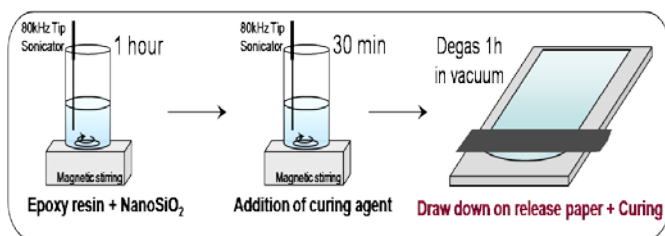


Figure 1. Process used to prepare the amine-cured epoxy/nanoSiO₂ composites.

Free-standing epoxy films containing 5 % mass fraction of SiO₂ nanoparticles having a dry thickness between 125 μm and 175 μm were prepared according to the steps shown in Figure 1. SiO₂ nanoparticles were first dispersed in a large amount of toluene using a tip sonicator. After adding epoxy resin, the nanoSiO₂ suspension was sonicated under constant stirring for an additional 1 h. Curing agent was added to the suspension, and the mixture was sonicated for 30 minutes. NanoSiO₂/amine/epoxy mixture was degassed for 1 h in vacuum at room temperature, followed by drawing down on a polyethylene terephthalate sheet. Films were cured at ambient conditions

(24 °C and 45 % relative humidity) for three days, followed by post-curing for 4 h at 110 °C in an air circulating oven. Unfilled epoxy films were also prepared for comparison.

2.2 UV Exposure Conditions

The UV radiation source was a 2 m integrating sphere-based environmental chamber, referred to as SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) (5). 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. This chamber can also precisely control the relative humidity (RH) and temperature. Specimens having 25 mm x 25 mm were mounted on a 17-window exposure cell, which was exposed in the UV chamber at 50 °C and 75 % RH. For nanoparticle release, a special sample holder (Figure 2) was employed. This holder collects particles expelled from the sample during UV exposure. It consists of a sample chamber, tubes to supply desired RH and temperature, and a container to collect released particles. A cover containing a quartz window that allows UV to irradiate the sample is used to seal the holder. In this study, a poly(tetrafluoroethylene) film was placed on the collector surface. All samples were mounted normal to the horizontal direction.

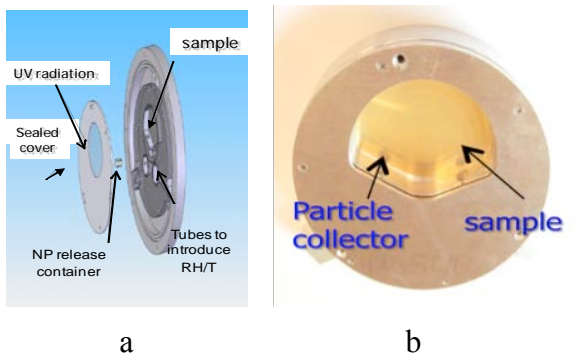


Figure 2. Sample holder to collect released particles: a) a schematic, b) a photograph with an exposed sample.

2.3. Characterization of UV-exposed Composite and Released Particles

Mass loss, surface morphology, and chemical degradation of UV-exposed composites were characterized before and after exposure. Mass loss was measured with an analytical balance, surface morphology via field emission scanning electron microscopy (FE-SEM), and chemical changes by FTIR in attenuated total reflection (ATR) mode (FTIR-ATR) and X-ray photoelectron spectroscopy (XPS). FTIR spectra were recorded at a resolution of 4 cm⁻¹ using a spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. A ZnSe prism was used for the ATR measurement. XPS analysis was

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 .125 eV/step. All XP spectra were fit using 100 % Gaussian peaks, a Shirley baseline, and adjusted with the appropriate sensitivity factors. The released particles were characterized by FE-SEM and Energy Dispersive X-ray Spectroscopy (EDS).

3. RESULTS

3.1 Mass Loss

Figure 3 displays the mass loss of unfilled and 5 % nanoSiO₂-filled epoxy samples as a function of exposure time in the UV/50 °C/75 % RH environment. Except for a small mass increase at early exposure times, which was likely due to the moisture uptake, the mass loss in both materials was nearly linear with exposure time. The rate of mass loss of the epoxy/nanoSiO₂ composite was slightly greater than that of the unfilled material. After 58 d exposure, the maximum mass losses of unfilled and nanocomposite films were 1.1 % \pm 0.05 % and 2.1 % \pm 0.28%, respectively.

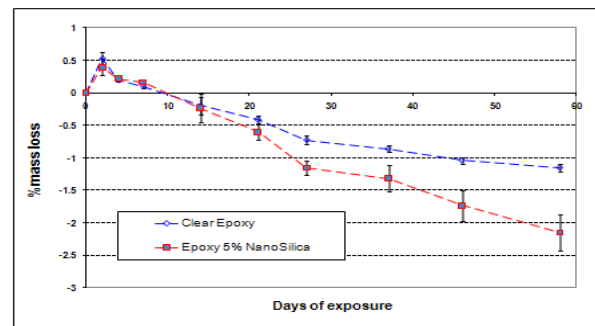


Figure 3. Mass loss vs. time for unfilled and 5 % nanoSiO₂-filled epoxy films exposed to UV/50 °C/75 % RH.

3.2 Surface Morphological Changes

Figure 4 shows FE-SEM images of epoxy/5 % nanoSiO₂ composite surface for different exposure times.

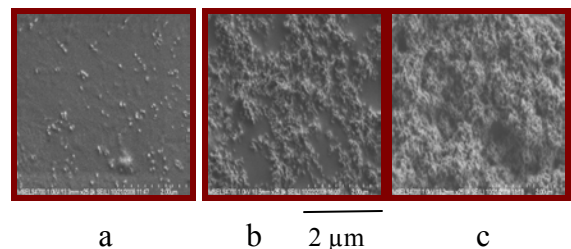


Figure 4. FE-SEM images of epoxy/5 % nanoSiO₂ composite exposed to UV radiation for various times: a) before exposure; b) 7 d; and c) 43 d.

Before exposure, the surface contained a small amount of nanoparticles. The density of nanoparticles on the composite surface increased with exposure time. After 43 d exposure, almost the entire surface appeared to be covered with nanoparticles (Figure 4c).

3.3 Surface Composition Changes

Chemical changes in the matrix surface following exposure to UV radiation can be readily observed in the FTIR-ATR difference spectra (spectra of exposed specimen minus spectrum of unexposed specimen) displayed in Figure 5a. Various epoxy absorbance bands, e.g., 1508 cm^{-1} (benzene ring vibration), decreased in intensity, and new bands in the 1650 cm^{-1} - 1750 cm^{-1} region (C=O) appeared. These changes were due to photo-oxidation by UV radiation, leading to chain scission in the epoxy and generation of various volatile products (6,7). UV radiation has been identified as the main weathering factor causing severe degradation in this particular epoxy, with temperature and RH playing minor roles (8).

Figure 5b shows FTIR-ATR intensity changes in the 1508 cm^{-1} and 1714 cm^{-1} bands, attributed to chain scission and oxidation, respectively, as a function of exposure time. Note that the intensity changes have been normalized to both the initial absorbance and that of the least-changed band (1360 cm^{-1} , due to CH_3) to minimize the effects of

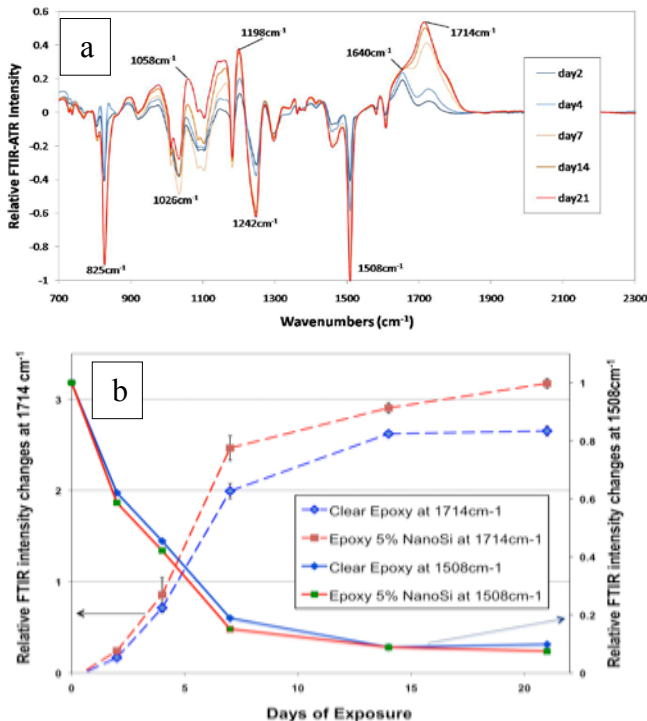


Figure 5. a) Difference FTIR-ATR spectra for different exposures times, and b) chain scission and oxidation of epoxy/nanoSiO₂ composite exposed to UV radiation. Each data point in Figure 5b was the average of four specimens, and the error bar represents one standard deviation.

thickness differences between samples and contact variations by the ATR probe on the sample. Both unfilled and nanoSiO₂-filled epoxy films underwent rapid photodegradation during UV exposure, and the presence of the SiO₂ nanoparticles appeared to have only a small effect on the oxidation rate of this epoxy. It should be noted that the depth of analysis in the epoxy polymer or the FTIR-ATR technique in the 800 cm^{-1} - 3000 cm^{-1} range and using a ZnSe prism is between $0.5\text{ }\mu\text{m}$ and $2.5\text{ }\mu\text{m}$ from the surface. Therefore, the chemical changes observed originate from the polymer layer at or near the composite surface. Figure 5a also shows that the intensity of the 1058 cm^{-1} band, assigned to Si-O-Si bond, also increased with exposure, suggesting that the concentration of SiO₂ nanoparticles near the surface increased with UV exposure.

The degradation of the epoxy polymer and an increase of the SiO₂ material near the composite surface was consistent with XPS data from the Si (2p) ($101\text{-}102.5\text{ eV}$) and C (1s) ($\sim 284.5\text{ eV}$) regions whose percent surface concentrations are reported in Figure 6. The surface concentration of carbon decreased from $82.2\% \pm 1.7\%$ to $43.8\% \pm 0.7\%$, while that of silicon increased from $0.5\% \pm 0.1\%$ to $10.1\% \pm 0.3\%$ after 62 d exposure. The O (1s) region (one major component of the composite) also increased in surface concentration with exposure (not shown), probably from both the polymer oxidation and the exposed SiO₂. The substantial increase of SiO₂ material on the composite surface following UV irradiation has been confirmed by inductively-coupled plasma-optical emission spectroscopy (ICP-AES) analysis (9).

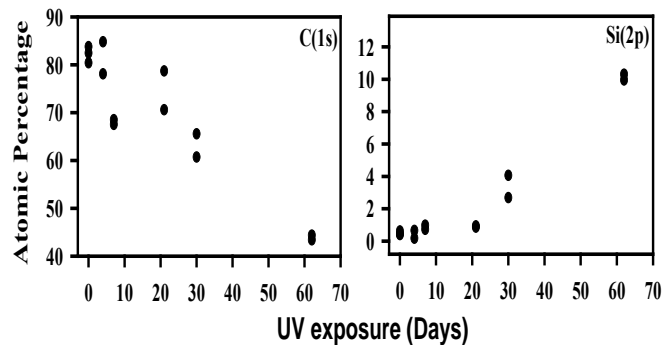


Figure 6. XPS based C and Si concentrations on the composite surface as a function of time exposed to UV radiation. Except for the 21 d where only one specimen was used, data at other exposure times consisted of two or more specimens.

Microscopic and spectroscopic data shown in Figures 4,5 and 6 strongly indicated that the increase of nanoSiO₂ concentration at the composite surface with UV exposure was a result of the epoxy matrix degradation. However, these results do not answer the question: were SiO₂ nanoparticles released from the nanocomposite during

exposure to UV radiation? Analysis of particles collected at the bottom of the sample holder (i.e., Figure 2b) 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 at higher magnification (Figure 7c).

EDS spectrum obtained from the collector surface before the sample was exposed to UV radiation showed only F and C (Figure 7d), as expected for a poly(tetrafluoroethylene) film. However, EDS analysis of the collector surface after the sample was irradiated by UV for 43 days revealed the presence of Si (Figure 7e). The concentration of O also increased after the UV exposure. The increase in O concentration supports the suggestion that the spherical nanoparticles on the collector surface observed in Figure 7c were likely due to SiO₂. The results of Figure 7 provide direct evidence that SiO₂ nanoparticles or their aggregates were released from the epoxy nanocomposites to the surroundings during exposure to UV radiation. However, these preliminary results do not reveal whether these SiO₂ nanoparticles are pristine or covered with polymer molecules. Work is in progress to address this question.

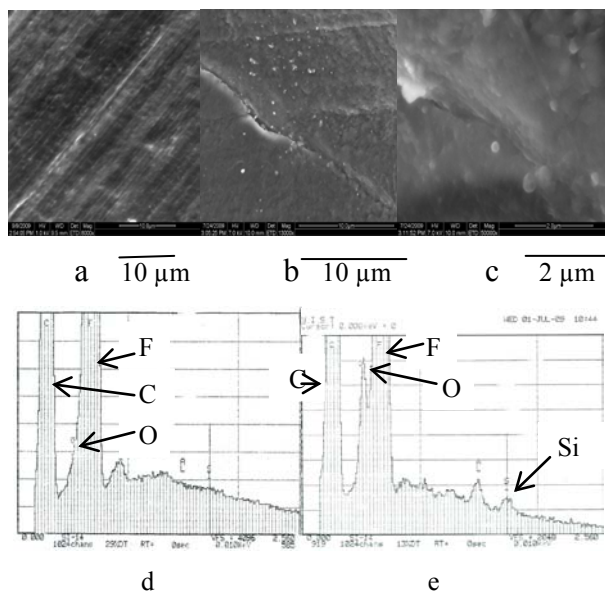


Figure 7. SEM images of particle collector surface: (a) before, and (b) after the sample was exposed to UV radiation for 43 d, (c) higher magnification of b, showing numerous spherical nanoparticles; EDS spectrum of the collector surface: before (d) and after the sample was exposed for 43 d (e), showing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

Based on microscopic and spectroscopic evidence, the release of SiO₂ nanoparticles from the epoxy nanocomposites during UV irradiation condition used in

this study probably followed the following sequence: Epoxy polymer on the surface was first removed through the photodegradation process, resulting in accumulation of a large concentration of SiO₂ nanoparticles on the composite surface. At a critical thickness/concentration, particles containing SiO₂ fell off the vertical surface likely by gravitation force. For nanocomposites exposed outdoors, environmental elements such as rain, condensed water, wind, mechanical vibration/abrasion, and stresses resulting from dimensional changes likely affect the release rate of nanoparticles.

CONCLUSIONS

The fate of SiO₂ nanoparticles in epoxy nanocomposites during exposure to UV radiation has been investigated. Analyses of chemical composition and morphology of the UV-exposed composite surfaces and released particles showed that the epoxy matrix underwent rapid photodegradation, resulting in accumulation of a large concentration of SiO₂ nanoparticles on the composite surface, some of which were then released into the surroundings. The results of this study will provide useful information to assess the potential risk of nanoSiO₂ in epoxy nanocomposites during outdoor exposure.

REFERENCES

1. F. Hussain, M. Hojjati, M. Okamoto, R. E. Gorga, J. Composite Materials 40, 1511, (2006).
2. P. M. Ajayan and J. M. Tour, Nature 447, 1066 (2007).
3. A. Poland, R. Duffin, I. Kinloch, A. Maynard, W. A. H. Wallace, A. Seaton, V. Stone, S. Brown, W. MacNee, and K. Donaldson, Nature Nanotechnology 3, 423 (2008).
4. Helland, P. Wick, A. Koehler, K. Schmid, and C. Som, Environmental Health Perspectives 115, 1125 (2007).
5. J. Chin, E. Byrd, N. Embree, J. Garver, B. Dickens, T. Fin, and J. W. Martin, Review Scientific Instruments 75, 4951 (2004).
6. J.F. Rabek, "Polymer Photodegradation: Mechanism and Experimental Methods", Chapman & Hall, NY., 1995, pp 185-216.
7. Bellinger, V. and Verdu, Oxidative Skeleton Breaking in Epoxy-Amine Networks, J. Appl. Polym. Sci. 30, 363 (1985).
8. X. Gu, et al., in "Service Life Prediction of Polymeric Materials, Global Perspectives", Eds. J. W. Martin, R. A. Ryntz, J. Chin, R. A. Dickie, Springer, NY., 2009, p. 1.
9. S. Rabb, L. Yu, C. Bernard, and T. Nguyen, in this proceedings.