

A Study of Nanosilica Release From “Weathered” Polymer Nanocomposites at Different Temperatures Using ICP-OES

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ABSTRACT

The impact of nanoparticles on the environment and, more importantly, the human population has been of great interest for the past few years. Release of these nanoparticles from different materials from wear or climate exposure has been explored to aid in the assessment of risk to the ecosystem. In our studies, the release and surface accumulation of silica nanoparticles on polymer nanocomposites due to weathering under controlled conditions (i.e., humidity, temperature, and UV radiation) has been investigated. Inductively coupled plasma-optical emission spectrometry (ICP-OES) is one of the techniques utilized to ascertain the release of nanosilica. Previous results have shown the surface accumulation of nanosilica to increase gradually over a period of 10 weeks. Significant accumulations could be observed after a week of exposure. Current experiments studied the release of nanosilica as a function of temperature up to 16 weeks. The surface of the nanocomposites was rinsed with H₂O to emulate a rain event at the end of each exposure period (2 weeks). The release of nanosilica during each period of exposure was not significantly different due to large variability among the replicates. However, most of the release amounts were between 10 µg Si and 40 µg Si for each exposure. Net total release ranged from 114 µg Si to 308 µg Si for the various temperatures. Temperature did not appear to be a major factor, with the exception of 60 °C at weeks 8 and 10, in the release of nanosilica. These results will contribute to establishing an accurate and predictive model for the release of silica nanoparticles from UV-irradiated polymer nanocomposites.

keywords: nanocomposites, release, ICP-OES, silica, nanoparticles, UV radiation, surface accumulation.

1. INTRODUCTION

Nanocomposites have generated widespread interest in areas such as construction, transportation, optics and

electronics [1,2]. These materials are typically polymers containing nanomaterials such as nanoparticles and nanotubes. The nanomaterials contribute to the increased resistance to scratching, UV radiation and corrosion of the polymer nanocomposites. As the polymer degrades or mechanically weakens, the nanomaterials used to fill the polymer matrix could be released to the environment. The release of these nanomaterials is a concern as its impact on human health and the ecosystem is not fully known [3-5]. However, current research is lacking in the accurate assessment of the release of nanomaterials upon degradation of the nanocomposites. The National Institute of Standards and Technology (NIST) has developed a technique using inductively coupled plasma-optical emission spectrometry (ICP-OES) to aid in assessing the release of SiO₂ nanoparticles from epoxy nanocomposites exposed to accelerated weathering environments via the determination of SiO₂ nanoparticles after rinsing the nanocomposite surface. Epoxy films containing a 5 % mass fraction of nanosilica were investigated. Silica nanoparticles on the surface of the degraded films were rinsed to simulate a rain event. The Si mass fraction in the collected rinses was determined with ICP-OES. To assess the physical accumulation of SiO₂ nanoparticles on the nanocomposite surface as a function of UV irradiation, atomic force microscopy (AFM) was also performed. Results will lead to an accurate methodology for determining the release rates of SiO₂ nanoparticles from epoxy nanocomposites exposed to UV radiation.

2. EXPERIMENTAL**

2.1. Preparation of Nanocomposites and Procedure for UV Exposure

Epoxy films containing a 5 % mass fraction of SiO₂ nanoparticles and having a thickness of between 125 µm and 150 µm were prepared according to the procedure described in Nguyen et al. [6]. The epoxy matrix was a diglycidyl ether of bisphenol A resin crosslinked with a triamine curing agent. The SiO₂ nanoparticles were untreated and had a nominal 15 nm diameter. The dispersion of nanosilica in the epoxy matrix was qualitatively good, as determined by atomic force

microscopy (AFM) after irradiating the nanocomposite with UV to remove the epoxy surface layer. The photodegradation of this epoxy polymer and its nanocomposites has been presented elsewhere [6]. Nanocomposite films were exposed in the NIST Simulated Photodegradation *via* High Energy Radiant Exposure (SPHERE) UV chamber, a 2 m integrating sphere-based environmental system [7]. The SPHERE utilizes a mercury arc lamp system that produces a collimated and highly uniform UV flux of approximately 140 W/m^2 in the 295 nm to 400 nm range. This chamber can also precisely control the relative humidity (RH) and temperature. For ICP-OES measurement of released silica nanoparticles, a specially designed sample holder (divided into four sections each with an exposure area of 16 cm^2) was used. For surface morphology characterization and surface accumulation of nanosilica, specimens having a surface area of approximately 5 cm^2 were exposed. Specimens were removed at specific UV doses for release and surface accumulation measurements. Dose, in kJ/m^2 , is defined here as the total accumulated energy resulting from repeated UV radiation exposures at a particular time period per unit irradiated surface.

2.2. Surface Morphology of Epoxy/Nanosilica Composite Exposed to UV

Surface morphology of the epoxy nanocomposite as a function of UV exposure was characterized by AFM. The measurement was carried out at ambient conditions ($24 \text{ }^\circ\text{C}$, 50 % relative humidity) using a Nanoscope Dimension 3100 system (Bruker AXS, Madison, WI) and 9 nm radius Si tips having a spring constant of 42 N/m. AFM samples were prepared by mounting unexposed and UV-irradiated nanocomposite films to a glass slide using double-sided tape. Both topographic and phase images were obtained simultaneously using a free-oscillation amplitude of $62 \text{ nm} \pm 2 \text{ nm}$ (1 standard deviation).

2.3. Characterization of Nanosilica Release from the Nanocomposite Surface Using ICP-OES

The specimens (4 replicates for each exposure and temperature) were removed from the SPHERE chamber and rinsed with DI water using a special apparatus (Figure 1) to simulate a rain event. The water was collected and stored in polyethylene bottles. After the sample collection was completed, 1 ml of tetramethylammonium hydroxide (TMAH) was added to each solution. All solutions were loosely capped, heated for 30 min at $60 \text{ }^\circ\text{C}$ to $70 \text{ }^\circ\text{C}$, and then diluted to 20 g with H_2O . Some solutions were further diluted by a factor up to 50. All solutions were analyzed and contained $\leq 2 \%$ TMAH to mitigate the Si background.

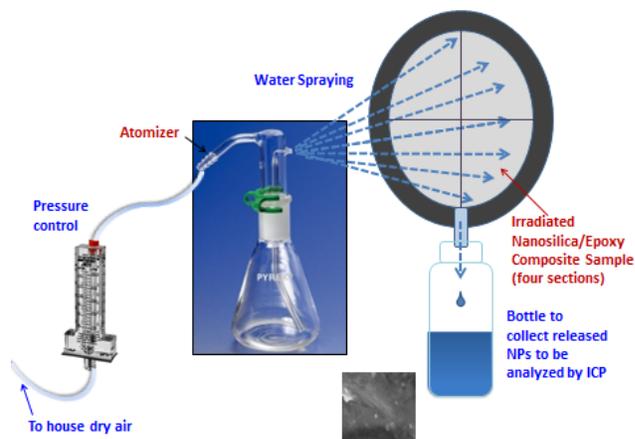


Figure 1: Schematic illustrating the collection of nanosilica released from an irradiated nanocomposite film after a simulated rain event.

The method of standard additions was used to quantitate the mass of Si released from the exposed nanocomposites into the rinse solutions. Each rinse solution was split into two solutions and one solution was spiked with Si. The spike stock solution was between $6 \mu\text{g/g}$ Si and $9 \mu\text{g/g}$ Si. A 0.5 g spike was taken from each Si spike stock solution and added to a 5 g sample solution. The Si spike stock solutions were prepared from the SRM 3150 Silicon Standard Solution (Lot# 071204). P was used as an internal standard at $1 \mu\text{g/g}$.

A PerkinElmer Optima 5300 DV ICP-OES instrument (Shelton, CT) was used for the analyses. The Si mass fractions in the solution samples were measured according to the parameters in Table 1. Each measurement comprised five replicates, and each solution was measured at two different times.

Table 1: Operating conditions for ICP-OES

Power (kW)	1.5
Plasma gas (L/min)	15
Auxiliary gas (L/min)	0.5
Nebulizer gas (L/min)	0.6
Nebulizer	MiraMist
Spray chamber	Cyclone
Viewing	Axial
Sample uptake (mL/min)	0.7
Analyte wavelength (nm)	Si I 251.611
Reference wavelength (nm)	P I 213.617
On-chip integration time (s)	0.256
Total read time (s)	8.192

All uncertainties shown for the data consist of expanded uncertainties expressed at the 95 % level of confidence and are calculated according to the principles of the *ISO Guide to the Expression of Uncertainty in Measurement* (GUM) [8]. Expanded uncertainties were determined for ICP-OES silicon measurements by using the following equations:

$$u_c = \sqrt{u_1^2 + u_2^2 + u_3^2 + \dots} \quad (1)$$

$$U = ku_c \quad (2)$$

$$U_{rel} = \frac{U}{w_{Si}} * 100 \quad (3)$$

where u_i represents the individual component of uncertainty, u_c is the combined uncertainty, k is the expansion factor based on the Student's t for the chosen level of confidence, U is the expanded uncertainty, U_{rel} is the relative expanded uncertainty, and w_{Si} is the observed mass fraction of Si. Propagated components of uncertainty include observed measurement repeatability, observed variability in the determination of ICP-OES sensitivity, and uncertainties in the known values for the calibration standards.

3. RESULTS AND DISCUSSION

3.1. Morphology of UV-Irradiated Nanocomposite Surface

Figure 2 displays AFM height and phase images of 5 % mass nanosilica epoxy composite surface before and after exposure to UV radiation at, as an example, 40 °C. The nanocomposite surface before exposure appears smooth with possible evidence of some silica nanoparticles. After irradiating with an UV dose of 30 MJ/m², a substantial amount of SiO₂ nanoparticles is observed to accumulate on the composite surface. The concentration of nanosilica continues to increase with increasing UV dose for multiple temperatures (data not shown). These observations imply that the appearance and accumulation of SiO₂ nanoparticles on the composite surface was due to photodegradation of the epoxy matrix. On further exposure, the surface-exposed SiO₂ nanoparticles would likely be released from the nanocomposite, as reported elsewhere for the same epoxy containing 5 % mass fraction of nanosilica exposed to the same UV condition [9].

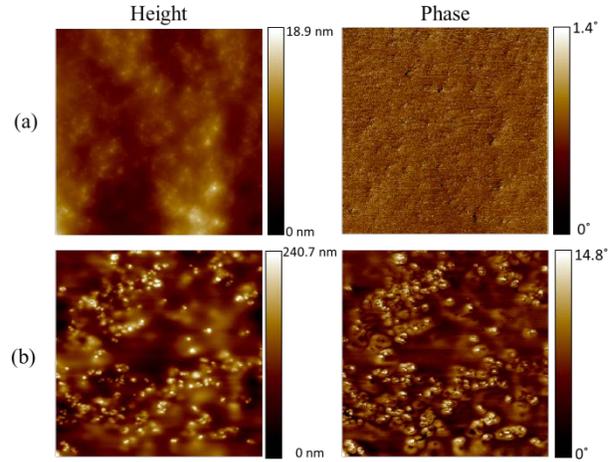


Figure 2: AFM height images (left column) and phase images (right column) of (a) unexposed and (b) nanocoating exposed for 30 MJ/m² UV dose and at 40 °C. Scan sizes are 20 μm × 20 μm. The scale bars represent the height and phase range of each graph.

3.2. Determination of Release of SiO₂ Nanoparticles during UV Exposure of Polymer Nanocomposite Using ICP-OES

Previously, HF extractions were used to remove the nanosilica present on the surface of the nanocomposites after UV exposure for subsequent ICP-OES analysis [9,10]. Figure 3 shows the gradual increase in nanosilica on the surface as the UV exposure increased over time (65 days). For the current set of experiments, the exposed nanocomposites were rinsed with DI H₂O to simulate a rain event. The observed Si could be less in these experiments as the displacement of surface accumulated nanosilica would be less harsh for each nanocomposite sample; however more representative of release after UV exposure. Figure 4 illustrates the SiO₂ nanoparticle release for four different temperatures (30 °C, 40 °C, 50 °C and 60 °C) as a function of UV dose. A gradual increase in nanosilica is observed for all temperatures initially, and then an abrupt rise is shown for 60 °C and 40 °C at 916 MJ/m² and 1216 MJ/m², respectively. However, these points are not significantly different from the lower exposures at the same temperature due to the high variability among the replicate samples. This could be due to an inconsistency in the spraying method, losses of material during transfer and/or to inhomogeneous degradation of the epoxy. The latter reason will result in non-uniform distribution of SiO₂ nanoparticles on the irradiated nanocomposite surface. Amine-cured epoxy has been known to undergo inhomogeneous degradation under UV radiation. In comparison to Figure 3, less nanosilica is detected in the DI H₂O rinse than that in the HF extract. However, once the 141 μg Si found in the non-exposed sample is subtracted from the rest of the HF extracted

samples as a normalization of the “harshness” of an HF extraction, the result of Figure 3 is comparable to that of Figure 4 (50 °C), taking into account that the 10 % nanosilica composite for Figure 3 contained twice as much Si as the 5 % counterpart for Figure 4.

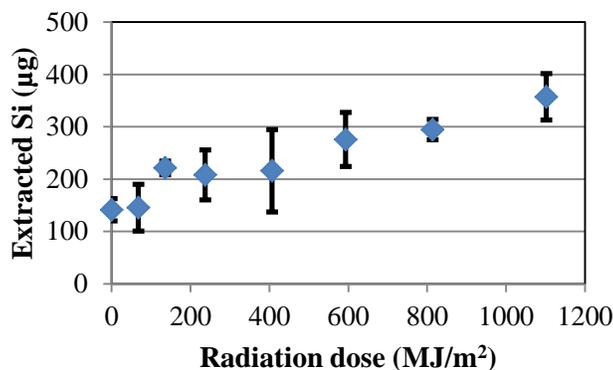


Figure 3: Average mass of Si extracted from the surfaces of 10 % nanosilica epoxy composites as a function of UV dose. The error bars represent the 95 % confidence interval.

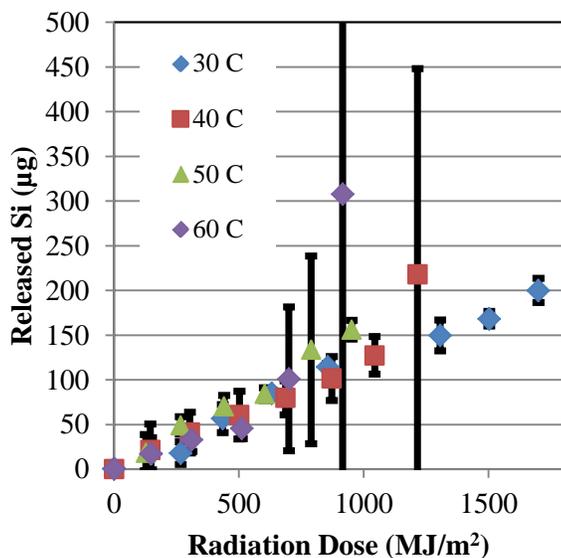


Figure 4: Average mass of Si released from the surfaces of 5 % nanosilica epoxy composites as a function of UV dose at various temperatures. The error bars represent the 95 % confidence interval.

4. CONCLUSIONS

The release of SiO₂ nanoparticles from the surface of polymer nanocomposites after exposure to weathering conditions such as UV radiation at four different temperatures was conducted using ICP-OES. The SiO₂

nanoparticles were rinsed from the nanocomposite surface with DI H₂O to simulate a rain event. The collected solutions were diluted and analyzed to determine the release of nanosilica. Results demonstrated that over a period up to 16 weeks exposed to UV radiation, a gradual increase in nanosilica release is observed. These measurements were corroborated by AFM. Also, a substantial increase in the release was observed for 40 °C and 60 °C near the end of the exposure time series. Issues related to high variability will need to be further investigated to improve overall precision. These ICP-OES results will aid in the assessment of the release rate of SiO₂ nanoparticles during the life cycle of polymer nanocomposites.

**Identification of commercial products in this paper was done in order to specify the experimental procedure. In no case, does this imply endorsement or recommendation by the National Institute of Standards and Technology.

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. Barnard, Nanoscale 1, 89, (2009).
4. H. Hildebrand, D. Kuhnel, A. Potthoff, K. Mackenzie, A. Springer and K. Schirmer, Environ. Pollut. 158, 65, (2010).
5. V. K. Sharma, J. Environ. Sci. Health, Part A 44, 1485, (2009).
6. T. Nguyen, B. Pellegrin, L. Mermet, X. Gu, A. Shapiro, and J. Chin, in Natural and Artificial Aging of Polymers, T. Reitcher, Ed., GUS Publisher, Pfnztl, Germany, 2009, pp 149-161.
7. J. Chin, E. Byrd, N. Embree, J. Garver, B. Dickens, T. Fin, and J. W. Martin, Review Scientific Instruments 75, 4951, (2004).
8. JCGM 100:2008; *Guide to the Expression of Uncertainty in Measurement*; (ISO GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology: BIPM, Sèvres Cedex, France (2008); available at http://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf.
9. T. Nguyen, B. Pellegrin, C. Bernard, S. Rabb, P. Stutzman, J. M. Gorham, X. Gu, L. L. Yu, and J. W. Chin, J. Nanoscience and Nanotechnology, 12, 6202, (2012).
10. S. A. Rabb, L. L. Yu, C. Bernard and T. Nguyen, Proc, Nanotech 2010, Anaheim, CA.