

# Investigation of Silica Nanoparticles Accumulated on the Surface of Polymer Nanocomposites Exposed to UV Radiation Using ICP-OES

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## ABSTRACT

Silica nanoparticles (nanosilica) are being utilized to enhance the mechanical performance of polymeric materials used in many industries. However, cumulative effects of ultraviolet (UV) radiation will degrade the polymeric molecules, resulting in a potential for release of SiO<sub>2</sub> nanoparticles into the environment. The health and environmental effects of the released nanosilica from polymer nanocomposites are not well understood. For this study, the surface accumulation of silica nanoparticles on the epoxy nanocomposite has increased after nearly two months of exposure to controlled degradation conditions at specified humidity, temperature, and UV radiation doses. The surface accumulation of nanosilica has been attributed to photo-induced degradation of the epoxy matrix. An analytical approach using a volume fraction of 5 % HF solution over a 5 min period has been employed to selectively attack silica nanoparticles on the surface of the nanocomposite film without extracting the same nanoparticles from the interior. The mass fraction of Si in the extracted solutions is measured using inductively coupled plasma – optical emission spectroscopy (ICP-OES). The results of this study will assist in establishing an accurate and predictive model for the release of SiO<sub>2</sub> nanoparticles from polymer nanocomposites exposed to weathering environments.

**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 SiO<sub>2</sub> nanoparticles from epoxy nanocomposites exposed to accelerated weathering environments via the determination of SiO<sub>2</sub> nanoparticle surface accumulation. Epoxy films containing a 10 % mass fraction of nanosilica were investigated. Silica nanoparticles on the surface of the degraded films were chemically extracted by using a volume fraction of 5 % hydrofluoric acid (HF). The Si mass fraction in the extracts was determined with ICP-OES. To assess the physical accumulation of SiO<sub>2</sub> 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 SiO<sub>2</sub> nanoparticles from epoxy nanocomposites exposed to UV radiation.

## 2. EXPERIMENTAL\*\*

### 2.1. Preparation of Nanocomposites and Procedure for UV Exposure

Epoxy films containing a 10 % mass fraction of SiO<sub>2</sub> nanoparticles and having a thickness of approximately 125 μm were prepared according to the procedure described in Nguyen et al. [6]. The epoxy matrix was a diglycidal ether of bisphenol A resin crosslinked with a triamine curing agent. SiO<sub>2</sub> nanoparticles were a hexamethyl disilazane-treated material and had a nominal 7 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 480 W/m<sup>2</sup> 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 dimensions were mounted on a 17-window exposure cell, which was exposed in the SPHERE UV chamber at 50 °C and 75 % RH. Specimens were removed after specified accumulated UV doses (e.g., specified time intervals) for AFM and ICP-OES characterization. Dose, in kJ/m<sup>2</sup>, 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 °C, 45 % 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 nm ± 2 nm (1 standard deviation).

## 2.3. Characterization of Nanosilica Accumulation on Nanocomposite Surface Using ICP-OES

The 25 mm x 25 mm specimens (3 to 4 replicates for each exposure) were removed from the SPHERE chamber, and the irradiated sections were cut from each specimen and placed in petri dishes. Specimens (6 replicates) from the unexposed nanocomposite were used to establish the baseline contribution of accumulated nanosilica. Silica nanoparticles on the surface of these sections were extracted using a 5 % (1.13 mol/L) hydrofluoric acid (HF) for 5 min in a volume of 10 mL (all concentrations of liquid used in this paper are based on volume fraction). Loss of Si as SiF<sub>4</sub> should be negligible as the solutions were not heated. After the removal of the films, the extraction solutions were diluted to 25 mL. These solutions were further diluted by a factor of 100 and analyzed. The solutions contained 2.5 % (0.07 mol/L) tetramethylammonium hydroxide (TMAH) to neutralize the remaining HF and mitigate the Si background.

The method of standard additions was used to compensate for any effects due to concomitant elements or

solution properties on the Si determinations of the extracted solutions of the SiO<sub>2</sub> nanoparticles from the polymer nanocomposites. Each extracted solution was split into two solutions and one solution was spiked with Si. The spike stock solution was 1.7 µg/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 µg/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:

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

$$U = k u_c \quad (2)$$

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

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 1 displays AFM phase images of 10 % mass nanosilica epoxy composite surface exposed to UV radiation at various doses. The nanocomposite surface before exposure appears smooth with evidence of some silica nanoparticles (more evident at higher magnification, e.g., inset). After irradiating with an UV dose of  $1.35 \times 10^5$  kJ/m<sup>2</sup> (8 days), a substantial amount of SiO<sub>2</sub> nanoparticles is observed to accumulate on the composite surface. The concentration of nanosilica continues to increase with increasing UV dose, and after an  $8 \times 10^5$  kJ/m<sup>2</sup> dose (48 days), SiO<sub>2</sub> nanoparticles have covered the entire composite surface. This observation, together with infrared spectroscopy and X-ray photoelectron spectroscopy results (not shown), suggests that the appearance and accumulation of SiO<sub>2</sub> nanoparticles on the composite surface was due to photodegradation of the epoxy matrix. On further exposure, the surface-exposed SiO<sub>2</sub> 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].

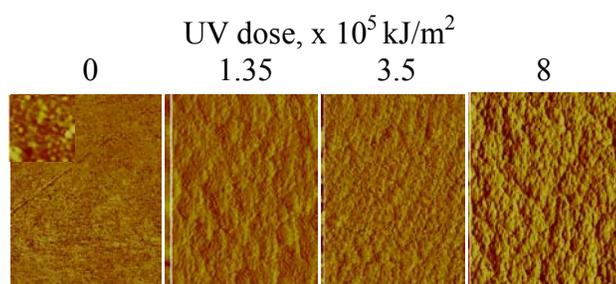


Figure 1: AFM phase images of UV irradiated nanosilica epoxy composite surface at different doses, showing the gradual accumulation of SiO<sub>2</sub> nanoparticles on the surface with exposure; the size for each image is 20 μm x 20 μm; the inset for 0 kJ/m<sup>2</sup> is 20 x magnification of the 20 μm image.

#### 3.2. Extractions of Silica Nanoparticles Using Hydrofluoric Acid

To determine the accumulation of SiO<sub>2</sub> nanoparticles on the polymer nanocomposite surface during UV exposure, a chemical extraction method was developed to selectively attack SiO<sub>2</sub> nanoparticles on the surface of the nanocomposite without extracting nanosilica from the interior. Variable concentrations of HF (1 % to 50 %) were investigated to optimize this dissolution process using the same SiO<sub>2</sub> nanoparticles (sample sizes < 10 mg), not embedded in the polymer. To generate the different concentrations of HF, H<sub>2</sub>O was added first to the nanoparticles and then concentrated HF was added to give a total of 10 mL. It was observed that concentrations of HF from 10 % to 50 % dissolved the SiO<sub>2</sub> nanoparticles in 1 min or less. The dissolutions at these concentrations are likely too rapid and could potentially attack the SiO<sub>2</sub> nanoparticles embedded in the polymer film. With 1 % HF and 5 % HF, the SiO<sub>2</sub> nanoparticles were dissolved in ≈15 min and ≈2 min, respectively. Of the two concentrations, 5 % HF was chosen as an extraction solution for this nanomaterial as the timing of dissolution was not excessively long. Extractions for the films using 5 % HF showed successful results. Differences are observed in the Si I 251 nm intensities for the films embedded with different mass fractions of nanosilica (Figure 2), before and after exposure. Successive extractions resulted in Si intensities either decreasing to signal levels of the unexposed samples or to signal levels that are consistent with extraction from the interior of the nanocomposite, showing that one extraction is sufficient.

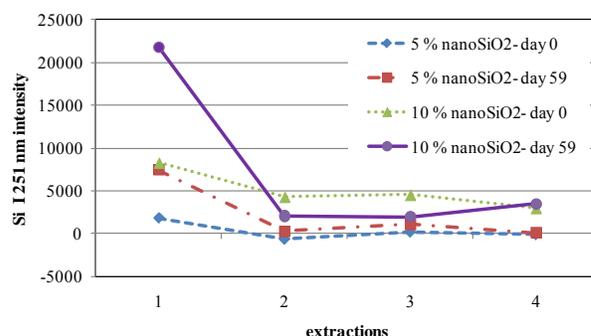


Figure 2: Observed Si I 251 nm intensity for multiple extractions of SiO<sub>2</sub> nanoparticles from the surface of the epoxy nanocomposites.

#### 3.3. Determination of Surface Accumulation of SiO<sub>2</sub> Nanoparticles during UV Exposure of Polymer Nanocomposite Using ICP-OES

The accumulation of SiO<sub>2</sub> nanoparticles on the surface of the epoxy nanocomposites is shown in Figure 3. As in previous measurements [10], nanosilica is initially observed on the nanocomposite surface before any incidence of UV exposure. An amount of 339 μg Si was observed in the previous experiment on the unexposed 10 % nanosilica film compared to 141 μg Si for this

experiment (Figure 4). One possible reason for this difference is due to variation in surface morphology of the nanocomposites fabricated at different times. This variation is difficult to avoid when filled polymer films are prepared at ambient conditions in the laboratory. Nevertheless, this variation between fabrication batches should not affect the results here, because all composite specimens used in this study were from several large sheets prepared at the same time.

During this current period of exposure (Figure 3), a gradual increase in nanosilica on the surface is shown as a function of cumulative UV dose (a course of 65 days). The first substantial increase is observed at  $1.35 \times 10^5$  kJ/m<sup>2</sup>, consistent with the AFM result. At the end of the observation period, a net accumulation of 216 μg Si (Si mass after 65 days minus Si mass before exposure) is observed on the surface of the nanocomposite, similar to the previous experiment (Figure 5) where the exposure was for 59 days. This suggests that the degradation of the epoxy nanocomposite and the surface accumulation rate of the nanosilica is fairly consistent from experiment to experiment. If the accumulation is assumed to be linear with radiation dose, the accumulation rate is estimated to be  $1.7 \times 10^{-4}$  μg Si/kJ·m<sup>2</sup>.

Multiple replicates (3 to 4 specimens) of the nanocomposite were analyzed for a given radiation dose to determine repeatability of nanosilica accumulation for the current experiment (Figure 3). The relative expanded uncertainty ranges from 6.0 % to 38 % for the different doses. The larger cases of variability could be due to losses of material during transfer and/or to inhomogeneous degradation of the epoxy. The latter reason will result in non-uniform distribution of SiO<sub>2</sub> nanoparticles on the irradiated nanocomposite surface. Amine-cured epoxy has been known to undergo inhomogeneous degradation under UV radiation.

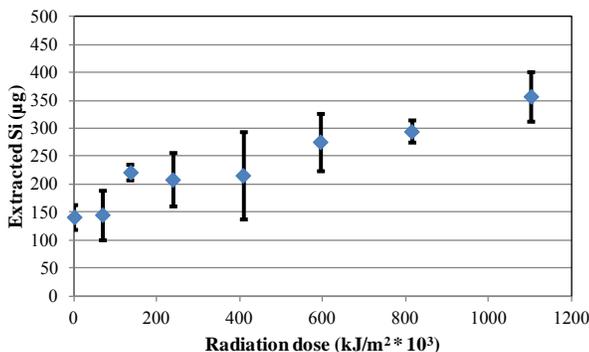


Figure 3: Average mass of Si extracted from the surfaces of 10 % nanosilica epoxy composites as a function UV dose. The error bars represent the 95 % confidence interval.

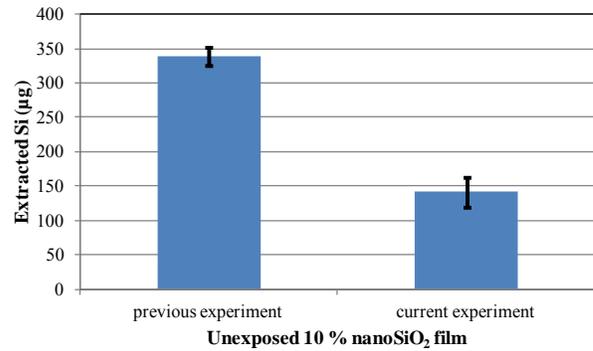


Figure 4: Comparison of Si average masses extracted from surfaces of unexposed 10 % nanosilica epoxy composites used in previous and current experiments. The error bars represent the 95 % confidence interval.

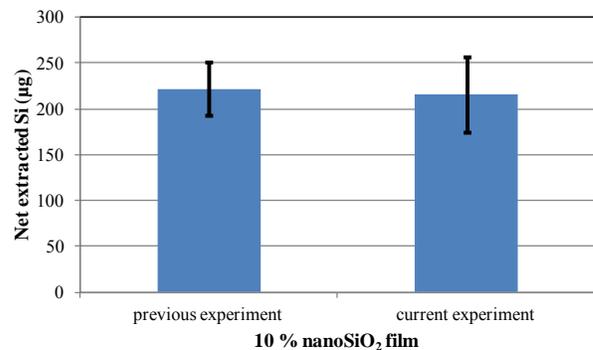


Figure 5: Comparison of net Si masses extracted from UV-irradiated surfaces of the 10 % nanosilica epoxy composites used in previous and current experiments. The error bars represent the 95 % confidence interval.

## 4. CONCLUSIONS

A technique using ICP-OES has been successfully developed to determine the surface accumulation of SiO<sub>2</sub> nanoparticles on polymer nanocomposites after exposure to weathering conditions such as UV radiation. The SiO<sub>2</sub> nanoparticles are chemically extracted from the film surface using 5 % HF for a period of 5 min, and the solutions are diluted and analyzed. Results demonstrate that over a period of 65 days exposed to UV radiation, a gradual increase in nanosilica surface accumulation is observed. Also, a substantial increase in accumulation can be seen in as few as 8 days. These ICP-OES results will aid in the assessment of the release rate of SiO<sub>2</sub> 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.

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