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Protocol for Collecting and Quantifying Release from Weathered Epoxy-Nanosilica Coatings:

Using a Simulated Rain Method and Inductively Coupled Plasma-Optical Emission Spectrometry

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Version 1.0

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Foreword

This NIST Special Publication (SP) is one of several NIST publications that has focused on the directives of the National Nanotechnology Initiative (NNI) Environmental, Health, and Safety Research Strategy updated in 2011 [1]. NIST was identified as the lead federal agency in the core research area of the Strategy. This research area includes development of measurement tools for the characterization and measurements of engineered nanomaterials during the life cycle of nanotechnology-enabled products.

Polymer coatings containing nanofillers (such as alumina, titania, silica, zinc oxide, etc.) are increasingly, or potentially will be, used in construction, aerospace, automobile, electronics, and many other coating-related industries. These nanocoatings are often exposed to severe mechanical and environmental stresses during a polymer nanocoating's life cycle. As time passes and the polymer degrades, the nanofillers migrate to the surface of the nanocoating and can be released into the environment. This SP emphasizes the assessment and measurement of nanosilica release from weathered epoxy nanocoatings. This protocol can be applied to other nanocoatings or nanocomposite systems. Updates to this protocol may be released in the future. Visit https://www.nist.gov/mml/nano-measurement-protocols for revisions of this protocol or for new protocols in the series. Users are encouraged to reference the protocol in their publications.

Keywords

nanocoatings; nanocomposites; nanoparticle release; polymers; weathering.

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1. Introduction

Metal oxide nanoparticles (e.g., alumina, titania, zinc oxide) and nonmetal oxides (e.g., silica) have been increasingly incorporated into polymer coatings used to protect, enhance, or decorate wood, plastic and metal products in construction, aerospace, automobile, electronics, and other coating-related industries [2,3]. These nanomaterial additives can enhance the mechanical, thermal, and electrical properties of a polymer coating [4-6]. Polymer nanocoatings are often used in outdoor applications, which makes them susceptible to degradation by weathering from factors such as temperature, relative humidity, and ultraviolet (UV) light [7]. A serious consequence of the host matrix degradation is that the embedded nanomaterials could be released to the environment via the effects of rain, condensed water, wind, and mechanical vibrations [8,9]. The release of nanomaterials is a concern as their impact on human health and the ecosystem is not fully understood [10-14]. However, current research is lacking in the accurate assessment of the release of nanomaterials upon degradation of the nanocoatings. For a better understanding of environmental impacts of nanocoatings and exposure risk assessment, it is important to develop methods for quantifying the release of nanoparticles from nanocoatings.

2. Principles and Scope

This protocol focuses on the assessment and measurement of nanosilica released from an epoxy nanocoating after degradation via exposure to accelerated weathering conditions. Nanomaterial accumulation at the nanocoating surface is a common observation from the polymer nanocoating degradation processes [15-19]. The primary objective of this SP is to provide a specific protocol for collecting and quantifying the amount of nanomaterial that is released after a combination of accelerated weathering and simulated rain spray. This protocol contains the procedures to conduct “simulated rain” weathering experiments for the study and measurement of nanomaterial release caused by this weathering process using inductively coupled plasma-optical emission spectrometry (ICP-OES).

3. Terminology

3.1. Nanofiller – a filler with at least one dimension smaller than 100 nm.

3.2. Polymer nanocoating/nanocomposite – polymer coating/composite containing fillers that have at least one dimension smaller than 100 nm.

3.3. Accelerated laboratory weathering device – instruments that employ controlled laboratory (artificial) weathering environments to accelerate degradation of chemical, physical, and mechanical properties of a material.

3.4. SPHERE - abbreviation of Simulated Photodegradation *via* High Energy Radiant Exposure; it is a NIST-patented accelerated laboratory weathering device based on integrating sphere technology.

3.5. Weathering - exposure of materials to environmental factors such as ultraviolet (UV) light, temperature, and/or relative humidity (RH) to assess changes to the appearance and functional properties of a material.

3.6. Nanoparticle Release - detachment of fragments from a polymer nanocoating in the form of free nanofillers, nanofiller clusters, or nanofillers embedded in the polymer fragments. In all cases, a nanofiller is present in some form.

3.7. Release - detachment of fragments from a polymer nanocoating in any form, including polymer fragments that do not contain nanofillers. Dimensions of released fragments can range from a few nanometers (nm) to several micrometers (µm) in size.

4. Reagents and Materials

4.1. Silane-treated nanosilica

4.2. Epoxy resin

4.3. Amine-curing agent (hardener)

4.4. Deionized (DI) water

4.5. Tetramethylammonium hydroxide (TMAH)

4.6. Compressed air

4.7. Autosampler vials

4.8. Polyethylene bottles

5. Equipment and Instrumentation

5.1. Inductively coupled plasma-optical emission spectrometry (ICP-OES)

5.2. NIST-developed rain simulation apparatus (sample holder, clamp, tubing, pressure gauge, flask, atomizer—see Fig. 1 and Sec. 6.3 for details)

Fig. 1. (a) An example of the sample holder comprised of four cells used for exposure. (b) The system used to create the simulated rain for rinsing and collecting runoff water from weathered samples.

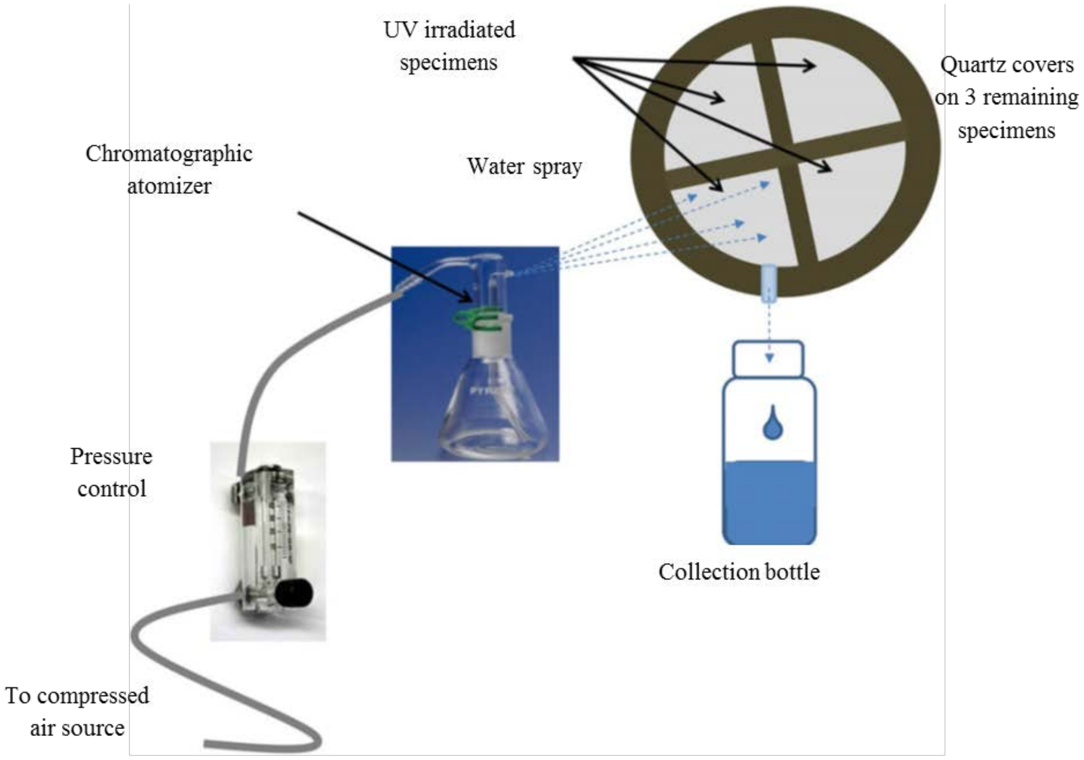

Fig. 2. A schematic of the system used for rinsing and collecting runoff water from samples exposed to UV radiation.

6. Initiation and collection of SiO_2 nanoparticle release after degradation of epoxy nanocoatings via accelerated weathering

6.1 Sample setup

Select/design a sample holder (Fig. 1a) for the exposure apparatus (e.g., SPHERE) with multiple cells (e.g., four). Insert samples and blanks (neat polymers) in different holders. *Nanocoating samples approximately 20 cm^2 in area with a ¼ circle shape have been used. The large sample size was used to increase the surface area of exposed nanocoatings and thereby maximize any material release that may occur. This arrangement allowed multiple replicates to be exposed under the same conditions.*

Secure samples (e.g., metal spring spacer) in each cell and contain (e.g., rubber seals and quartz glass covers) any nanomaterial release. Create drain for the cell to collect rinse in bottle after spray (Fig. 2). *Removable drain port was attached to holder and plugged when not in use.*

6.2 Experimental conditions

Determine UV exposure time and weathering conditions (temperature and humidity) for nanocomposites in exposure apparatus. *The SPHERE* [20] *was previously used to accomplish the degradation of the thin film nanocoatings. A detailed description of the SPHERE and its operation are beyond the scope of this protocol but can be found in NIST SP1200-15. Briefly, the SPHERE is an accelerated weathering system capable of simultaneously exposing 32 chambers to an intense, uniform ultraviolet (UV) light source. Temperature can be controlled in the range of 30 °C to 85 °C and relative humidity (RH) can be controlled in the range 0 % to 80 %. For release experiments, a sealed chamber was used so that any released material could be contained for measurement. RH was stable at approximately 80 % for each two-week interval. Each chamber has a shutter that will stop exposure to the UV light source. Exposure time was tracked and irradiance measured, which allowed the calculation of the exposure dosage to be completed.*

6.3 Nanomaterial collection

Open each cell of the holder. *Only one cell at a time should be opened to minimize cross-contamination.* Orient the cell at 45° to reduce loss of material due to splatter (Fig. 1b). *Make sure the drain port is easily accessible for collection in a bottle.* Pour 5 mL of DI water, having a minimum resistivity of 18 MΩ cm, on the samples to capture any loose particles that may become airborne.

Next generate a simulated rain spray by attaching a chromatographic atomizer or nebulizer to an Erlenmeyer flask containing 18 MΩ cm (minimum resistivity) DI water. *In the study that serves as the example for this protocol* [17], *the atomizer was operated at an air flow of 16 L/min and a pressure of 83 kPa, but select parameters appropriate for the case at hand.*

Rinse any interior spacers/clamps inside cell above sample for collection. Then rinse sample with the spray for five minutes from approximately 10 cm away, while consistently rastering the spray across the surface. Spray the back side of the sample for one minute and remove the sample from the cell. Then spray the inside of the cell for one minute. All runoff is collected for analysis. Place the sample back into the cell for further UV weathering. Repeat the process for each of the other samples in the holder. To establish the analyte baseline prior to the experimental weathering conditions, the cells of the holder will be rinsed and collected before exposure. *As mentioned above, this protocol can be applied to any combination of polymer/nanomaterial filler system as long as the nanomaterial contains an analyte detectable by ICP-OES.*

7. Measurement of collected runoff water from simulated rain spray by ICP-OES

7.1. Sample preparation

After runoff collection, add 1 mL of concentrated TMAH (25 % mass fraction aqueous solution, electronics grade, 99.9999 % metal basis) to each solution to aid in dissolution of the SiO_2 nanoparticles and reduction of signal fluctuations. *Note: TMAH is highly corrosive and can result in serious injury or death if not handled appropriately. Please consult material safety data sheet before use and wear appropriate PPE (e.g., lab coat, gloves, and safety glasses). Best practice is to (1) perform all work in a chemical fume hood, (2) double glove (highly recommended outer glove Stansolv A-10), and (3) transfer concentrated TMAH from large container to small container for ease of use.* Cap loosely all solutions, heat for 30 min between 60 °C to 70 °C, and then dilute gravimetrically to 20 g with H_2O. Dilute solutions further as needed for analysis based on instrument sensitivity. *All solutions are analyzed and contain ≤ 2 % TMAH to mitigate the Si background.*

7.2. Standard preparation

Any suitable calibration method can be used to determine the mass of Si released from the nanocoatings. The method of standard additions had been previously employed [16]. For this method, split each rinse solution into two solutions and spike one solution with Si. *Previous Si spike stock solutions were prepared from SRM 3150 Silicon (Si) Standard Solution. The spike stock solution is typically between 6 µg/g Si and 9 µg/g Si.* Take a 0.5 g aliquot from the Si spike stock solution and add to a 5 g sample solution. Phosphorus was used as an internal standard at 1 µg/g.

7.3. ICP-OES measurement

Consult instrument manual in determining optimal experimental conditions for ICP-OES analysis. A PerkinElmer Optima 5300 DV ICP-OES instrument (Shelton, CT) was used previously. The Si mass fractions in the solution samples were measured according to the operation conditions listed in Table 1. Each sample measurement was comprised of five replicates, and each solution was measured at two different times in a single day.

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)	0.512
Total read time (s)	8.192

8. Quantifying the amount of nanosilica release from the weathered epoxy-nanosilica coatings

To demonstrate results calculations, an example of nanosilica release from four specimens (each at approximately 20 cm^2) using the simulated rain method under the same weathering conditions is shown in Table 2. The specimens were exposed multiple times and rinsed after every exposure. The collected solutions were diluted and analyzed for Si. All these values are presumed to be mainly from the silica nanoparticles. The runoff water of the unexposed specimen (0 day) contained a small quantity of Si. For most of the specimens, exposure generated nanosilica release that was greater than that from the unexposed specimen. The released Si mass of specimen S1 is observed to be much smaller than the other three specimens. This could be due to poor dispersion, loss of material during transfer and/or to inhomogeneous degradation of the epoxy. The latter reason will result in non-uniform distribution of SiO_2 nanoparticles on the irradiated nanocoating surface. Amine-cured epoxy has been known to undergo inhomogeneous degradation under UV radiation.

Table 2. Mass of Si release, in µg, measured at each specified UV dose for four nanocoating specimens (S1, S2, S3, S4) sprayed with water. The exposure conditions were 40 °C/0 % RH. The uncertainties represent one standard deviation of a total of 10 measurements (five replicates per measurement, and two measurements on each solution).

UV dose (MJ/m^2)	S1	S2	S3	S4
0.00	0.446 ± 0.032	0.271 ± 0.026	0.3134 ± 0.0036	0.183 ± 0.023
145.39	0.472 ± 0.047	42.50 ± 0.96	13.98 ± 0.42	29.91 ± 0.22
303.99	< 0.13	31.88 ± 0.40	28.21 ± 0.24	18.617 ± 0.031
502.25	2.541 ± 0.068	33.687 ± 0.011	34.24 ± 0.85	7.754 ± 0.001
687.27	5.262 ± 0.046	24.5 ± 1.1	14.79 ± 0.15	33.06 ± 0.15
872.33	11.65 ± 0.35	16.040 ± 0.082	44.56 ± 0.71	14.10 ± 0.62
1044.15	16.19 ± 0.26	35.45 ± 0.78	38.82 ± 0.48	12.81 ± 0.19

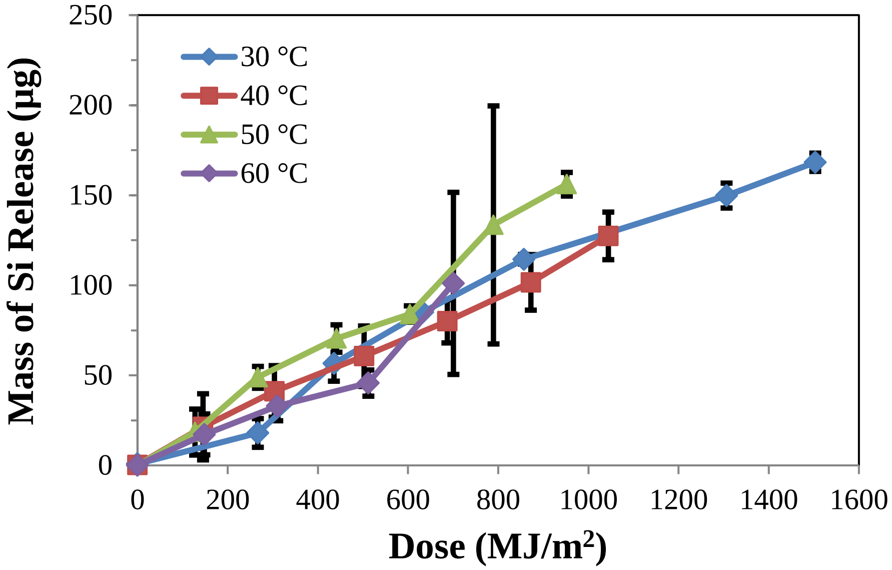

Fig. 3. Accumulated mass of Si release from epoxy/nanosilica coating as a function of UV dose for four temperatures. Each data point is the average of 8 runoff water samples collected from four 20 cm^2 nanocoating specimens. Error bars represent one standard deviation.

The kinetics of the nanoparticle release can also be determined. The accumulated amounts of Si released per 20 cm^2 irradiated area as a function of UV dose for four different temperatures are depicted in Fig. 3. Each data point is the average of 8 runoff water samples collected from four 20 cm^2 nanocoating specimens. Note that for ease of dispersion, silane-treated nanosilica was used for the nanoparticle release study. The mass of Si from the silane layer contributes only a small fraction to the total Si mass of nanosilica (approximately 1 %). As shown in Fig. 3, the mass of Si release increased nearly linearly with UV dose for all temperatures, with the quantity of Si release at 50 ºC slightly higher than that of other temperatures. After exposure for a UV dose of 1000 MJ/m^2 at 50 ºC, an average of 160 µg of Si (equivalent to 363 µg of SiO_2) was released from the 20 cm^2 nanocoating specimen. Unlike the chemical degradation or nanosilica surface coverage data [21], the result of Figure 3 does not show an orderly temperature effect on the amount of Si release. The reason for this is unclear. It should be pointed out that there were several important differences between the specimens used for nanosilica release and other measurements. First, the surface of the specimens was rinsed with water after each specified time interval. Therefore, unlike specimens used for atomic force microscopy or chemical degradation measurements, where nanosilica continually accumulated on the surface, the specimen surface for the nanorelease study at the beginning of each exposure period was mostly free of particles. Second, the specimen for nanorelease measurement was exposed to UV radiation in a tightly sealed holder. Therefore, the specimens were exposed to approximately 80 % RH or higher, not near 0 % as for other measurements. These reasons may negate the effect of temperature on the amounts of nanosilica release, as observed in Fig. 3. Data on temperature effect on nanoparticle release rate is crucial for developing a kinetic model to estimate the release of nanoparticles during the life cycle of nanocoatings; so, more research in this area is needed. Further studies are also needed to explain the high variability of nanosilica release between specimens, particularly at high UV doses (> 700 MJ/m^2).

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