Environmental Consequences of Nanotechnologies

Weathering of Nanomaterials to Study Potential for Release

Scientific Operating Procedure SOP-R-1

Kevin Torres-Cancel, Robert D. Moser, and Aimee R. Poda

February 2016

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Final report
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Abstract

The practice presented in this scientific operating procedure (SOP) is intended to measure weathering effects on the retention of nanomaterial properties. To obtain the information necessary for a point of comparison, the nanomaterials were characterized both before and after they were subjected to the weathering test. The weathering cycle was selected based upon the required conditions and in conformance with the selected standards that regulate the operation of the xenon-arc weathering apparatus, materials, and sample handling. The results were swelling or shrinkage percentage, mass loss or gain, and a rating on the severity of the weathering. The test also quantified the variance and the uncertainty of the results.
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Preface

This scientific standard operating procedure (SOP), SOP-R-1, is a weathering test for nanomaterials and describes how to perform a weathering test to rate the damage in nanocomposites and other technologies where nanomaterials have been incorporated. The SOP allows the user flexibility when determining which weathering cycle to apply to the nanomaterial but always references the proper way to make changes according to existing standards. The procedures described in this SOP by the main author, Kevin Torres-Cancel, Concrete and Materials Branch, Geotechnical and Structures Laboratory, Engineer Research and Development Center (ERDC) are linked to the procedures developed under the framework for testing the release of nanoparticles (Tier II) developed by Dr. Aimee R. Poda, Environmental Chemistry Branch, Environmental Laboratory (EL). The procedures are also linked to the ERDC NanoGrid (Tier IV) developed by Alan Kennedy, Environmental Risk Assessment Branch, EL; the NanoGrid user is guided to make informed decisions based on the hazards of the released nanoparticles from nanomaterials.

This study is part of the Environmental and Quality/Installations (EQ/I) Research and Development Program focus area directed by Dr. Steven Larson. This focus area is under the direct supervision of John Ballard, Assistant Technical Director, ERDC-EL, and under the general supervision of Dr. Elizabeth Ferguson, Technical Director for Military Munitions in the Environment, ERDC-EL. At the time this report was prepared, Dr. Jack Davis was Deputy Director, ERDC-EL; Dr. Beth Fleming was Director, ERDC-EL.

COL Bryan S. Green was Commander of ERDC and Dr. Jeffery P. Holland was Director of ERDC.
1 Introduction

The Scientific Operating Procedure (SOP) described herein to assess the properties of nanotechnologies was developed under Task 2: Optimized Scientific Methods of the ERDC/EL Environmental Consequences of Nanotechnologies research program. The primary goal of this task was to develop robust SOPs for investigating the environmental health and safety- (EHS) related properties of nanotechnologies, including nanomaterials and products incorporating nanomaterials. One of the areas of concern is the weathering of nanomaterials and the uncertainty surrounding the fate and risks that they pose once their degradation occurs. Consequently, this SOP was developed as a guide to conducting a weathering test for nanomaterials, in a laboratory setup. This practice takes into consideration relevant weathering parameters such as temperature, humidity, and ultraviolet irradiance as well as the exposure to simulated environmental conditions and how to incorporate them to customize the cycles according to the test requirements. The data acquired is to be used as a tool to determine the change in the physical properties of nanomaterials once exposed to weathering. Such an analysis will determine how the quantitative and qualitative variables change and contribute to the severity of the weathering. The analysis will also serve as the basis on which to draw conclusions about the potential risks that such materials will pose under certain environmental conditions. The practice described herein is intended to test solid materials — mainly composites — containing simple nanomaterials dispersed in a matrix or those that form scaffolds and other complex structures.
2 Background

There is a need to address the risks that nanomaterials pose to the environment and their physiological effects. We can assess these risks and effects through the development of tests that take into account the fate of the nano-components present in the materials. One way to do this is to develop a protocol that evaluates the weathering: measuring the physical appearance of the material, the mass loss and amount of particulate released, and mechanical behavior, if required. In order to develop a weathering procedure for a nanomaterial, it is important to 1) classify the material according to its composition, nano-assembly and type; 2) specify the weathering type, process, and cycles that said sample is to undergo under 3) a certain irradiance range, moisture and heat environment; and 4) qualitatively and quantitatively assess the rate of the weathering severity (ASTM G151-13, ASTM G156-09).

Standardized procedures and laboratory experiments have produced results indicating that weathering is detected through nano-particulate debris development, chalking, color change, cracking (Wohlleben et al. 2011), changes in tensile strength (ASTM D750-12), and failure due to oxidation (ASTM F2657-07, ASTM F2023-13, White et al. 1994) (Figure. 1).

Figure 1. Samples exposed to weathering outdoors and then tensile tested to failure: (a) end face of a polystyrene bar; (b) fracture surface of the specimen; (c) upper yield stress and extension at break vs. exposure for polypropylene extension bars weathered outdoors (ASTM C1257-15).

The results from accelerated weathering of materials versus natural weathering are difficult to correlate due to the natural variation of environmental factors when the test is done outdoors as compared to the simplifications made when setting the parameters for laboratory tests (ASTM G113-14, ASTM G1519-10). For this reason, laboratories have to choose between simulating the environment conditions at a geographical
location based on the season of the year, relying — when required — on specialized equipment to control the ultraviolet (UV) radiation level, or follow standardized laboratory testing conditions (ASTM D4364, ASTM G90, ASTM D5105, ASTM D3815, ASTM D7356). When the decision is to simulate the weathering of a material in a laboratory, it is necessary to specify the testing instrument (ISO 4892-2:2013, ASTM D1435-13, ASTM D4798), level of UV exposure, water quality, and sample conditioning based on the type of material to be tested (ASTM E0782, ASTM D5744-13e1, ASTM C1257-15, Johnson et al. 1996, Stark et al. 2003). These testing parameters play a key role in the reproducibility of the weathering results, especially when a quantitative variable product of the photodegradation, such as weathering rating, gloss retention, durability, weight loss, and film thickness (ASTM G0169, Yang et al. 2002) is to be measured (Wohlleben et al. 2013). The specimen internal structure also influences the weathering results. For this reason, when testing nanomaterials, a more reliable characterization method is needed to assess variations in microstructure due to weathering that can be reproducible among laboratories.

Although there are well-established methods to measure weathering for different types of materials, there is not a standardized method to test the weathering of nanomaterials. In the established methods, the intention is to measure weathering when the sample is exposed to sunlight. Sometimes the purpose is to expose the specimens at higher UV levels in order to accelerate the test. When this data is compared to outdoor exposures, it is difficult to correlate, since the materials have been exposed to environmental factors not found in the laboratory. This is the driver to develop a more standardized test for nanomaterials where the material type, irradiation level, exposure times or cycles, moisture, and temperature can be defined for a series of expected scenarios. Also, methods of comparison through the use of standards and unexposed samples should be considered to qualitatively and quantitatively measure the weathering effect on the different types of nanomaterials.

As part of the post-weathering characterization, the weathered material will undergo optical microscopy or scanning electron microscopy (SEM) as required by the analysis to measure and rate the severity of the weathering to the surface of the material such as swelling, color change, cracking, and microstructure change. The material will be weighed to measure losses in mass due to nanodebris and nanoparticulate release and bulk material loss.
Other methods to measure the effects of weathering, such as oxidation, changes in the nanoparticle and matrix interactions, mechanical properties, and other physical properties of interest will be suggested, but will not be explored in detail, since that is beyond the scope of this SOP.
3 Scope

This SOP applies to the weathering of composite materials and products containing nanomaterials through the exposure of nanomaterials to weathering conditions such as UV irradiance, moisture, temperature, and chemical exposure. This practice will serve as a guide for performing a weathering test in a laboratory setup to characterize the severity of the weathering on the material, including nanoparticulate release and other physical properties of the material through the acquisition of qualitative and quantitative data. The weathering exposure apparatus employs a xenon-arc light source.

![Figure 2. Weathering test flowchart.](image-url)
4 Terminology

Related Documents

- ASTM G151
- ASTM G155
- ISO 4892
- ASTM G113
- ASTM G156
- ASTM 169
- ASTM D6551
- ASTM G169
- ASTM D5870

Definitions

Nanomaterial, n material having particles or constituents of nanoscale dimensions, or one that is produced by nanotechnology

Xenon Arc apparatus, n machine based on the use of a special fluorescent bulb that emits a very controlled spectrum of light within the UV spectrum of interest

Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>SOP</td>
<td>standard operating procedure</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
</tbody>
</table>
5 Materials and Apparatus

Materials

- Optical microscope: to characterize the samples
- Scanning electron microscope: to characterize the samples
- Xenon arc light apparatus: for weathering tests
- Water (distilled): for weathering tests
- Nanocomposites materials (s): for weathering tests

Apparatus

Xenon arc light apparatus – The apparatus required to perform the tests must conform to the specifications in ASTM G155 and G151 in order to simulate nanomaterials weathering within the acceptable limits to those found when it is exposed to sunlight and moisture. This equipment must be able to run weathering cycles at different conditions of moisture, temperature, and irradiance intensity in a controlled manner to assure reliability and reproducibility of results. It should have a spray system for water, an acidic or alkaline solution. The system must be calibrated according to the manufacturer’s instructions.
6 Procedure

This procedure describes the weathering test of nanomaterials using a xenon-arc light apparatus; how to execute the test; sample characterization; and report requirements. Six specimens of a nanomaterial are weighed; their thicknesses are measured and later exposed to a weathering cycle based on the desired exposure conditions as specified in ASTM G155. After the exposure, the specimens are weighed again, the debris are collected for characterization, the thickness is measured to determine swelling, and the surface of the material is examined through SEM to rate the severity of the weathering.

Specimen Preparation

The sample preparation requires enough material to make the analysis in triplicate. It is required to have six specimens out of the received sample. Three specimens serve as the control and the other three are subjected to the determined weathering cycle. The controls should be stored under dry conditions, preferably in a dessicator under vacuum.

Specimen Preparation for the Weathering Tests

The sample must be inspected visually making sure the top and bottom surfaces are uniform and homogeneous to obtain reliable results (e.g., voids, cracks, clusters of particles in a specific area, etc.). Unless otherwise required or mutually agreed upon, the specimens are required to be 45 mm by 45 mm.

Note 1: Humidity can severely affect the overall nanomaterial properties, so it is important to maintain the control samples in a dry environment. If a significant difference in color is noted, the specimens should not be used for this test. The specimens’ dimensions must be recorded in order to rate the severity of the weathering based on the top surface of the specimen that will be exposed to the light. It is recommendable to measure the dimensions with a ruler or digital caliper. The specimen preparation takes into consideration a composite-free standing film, but it can vary depending on the as received sample shape (e.g., a small cylinder or cube). In such a case,
refer to the corresponding ISO 4892 or ASTM G 151 to adapt the specimen preparation as required.

**Reagents and Materials Preparation**

Water  It must comply with the water quality specifications in ASTM G155.

Acid Rain Solution  It must comply with the specifications and preparation practices described in ASTM D7356.

**Analysis**

**Specimen Characterization Previous to Weathering**

Three specimens will be subjected to optical microscopy to measure their thickness. Weigh the specimens and record the weight. Measure the thickness twice on the four sides of the specimen and take the average. Prepare the specimens for scanning electron microscopy (SEM) and scan the surface to take images of the microstructure. Focus the middle of the sample (at 22.5 mm from the edge) and take an image. Move 2 mm up and 2 mm to the left and take an image. Move 4 mm down and 4 mm to the right and take another image. Save the images for comparison with the weathered samples.

Note 2: The sample preparation for SEM is different for each material. For coatings or film scanning refer to the SOP-P-2 on the preparation of nanomaterial specimens for SEM, scanning transmission electron microscopy (STEM), and transmission electron microscopy (TEM) imaging.

**Test Procedure**

The specimens must be subjected to the cycles and exposures in a xenon-arc apparatus as described in G 155, D7356, or D4459, according to the test requirements. The conditions can be modified to simulate the desired weathering conditions. The minimum time of exposure shall be that necessary to produce a defined change in a material property of interest. If the testing conditions agreed upon between the parties are different than particular specification, select the radiant exposure conditions that will produce a significant difference in the property of interest.
Note 3: The properties of interest could be color change, cracking, or swelling. If another property is to be studied, refer to the corresponding procedure to assess that property, and compile the relevant information, such as the weathering conditions, and include that information in the final report. Remember that variation in results must be expected with changes in test conditions.
7 Reporting

Analysis of Results

Post-Weathering Characterization

Take the specimen out of the xenon-arc weathering apparatus and weigh it. Measure the specimen thickness twice on the four sides of the specimen and take the average. Calculate the mass loss or gain and the thickness increase or shrinkage. If there is a residue, weigh it and store it for further analysis. Prepare the samples for SEM and follow the procedure described in section 6.2.1. Compare the images visually and rate the damage from 0 (no degradation) to 1 (severe degradation). Perform an ANOVA through the use of statistical software or a property retention calculation as required and report the values according to ASTM G169 and D5870.

Note 4: The selected magnification must be the same for all the specimens and should be high enough to the sample so that the severity of the weathering can be observed and rated. The degradation scale is based on the percentage of the area shown in the image that has degraded. Signs of degradation are cracks, dark or white spots, and lines.

Key Results Provided

The test report shall include the following information:

- That the tests were made as directed in this SOP
- Laboratory name
- Model and years in service of the Xenon-Arc light apparatus
- Daily record of black panel temperature (BPT), chamber temperature and irradiance in W/m² (or radiant exposure in J/m²)
- A full description of the specimens and their origin
- Specimen preparation procedure, if different from the one presented here
- Irradiance in W/m² nm or radiant exposure in J/m²
- The exposure times and cycles (if more than one)
- All the data acquired and specified in this procedure
Quality Assurance/Quality Control Considerations

The repeatability will be quantified through the analysis of the data acquired and comparisons will be done with existing standards as needed or required. The operation should conform to ASTM 155 and 151.

Bias—the procedure in this test method has no bias, because the value of that property can only be defined in terms of a test method.
References


# Weathering of Nanomaterials to Study Potential for Release

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Nanotechnologies
Properties of nanotechnologies
Weathering of nanomaterials
Weathering test for nanomaterials

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