

Effects of Temperature on Surface Accumulation and Release of Silica Nanoparticles in an Epoxy Nanocoating Exposed to UV Radiation

Chun-Chieh Tien^{1,2}, Ching-Hsuan Chang¹, Bernard Haochih Liu¹, Deborah Stanley², Savelas A. Rabb², Lee L. Yu², Tinh Nguyen², and Lipiin Sung²

¹National Cheng Kung University, No.1, University Rd., Tainan 701, Taiwan (R.O.C.)

²National Institute of Standards and Technology, 100 Bureau Dr, Gaithersburg, MD 20899, USA

ABSTRACT

Polymer nanocoatings are increasingly used outdoors and in harsh environments. However, because most common polymers degraded by the weathering elements, nanoparticles in polymer nanocoatings may be released into the environments. Such nanoparticle release potentially poses an environmental health and safety risk. This study investigated the effects of temperature on the surface accumulation and release of nanosilica for an epoxy nanocoating exposed to ultraviolet (UV) radiation. Specimens of an amine-cured epoxy containing 5 mass % nanosilica were exposed to 295 nm to 400 nm UV radiation at three temperatures (40 °C, 50 °C, and 60 °C). Surface accumulation and release of nanosilica as a function of UV dose were measured by atomic force microscopy and inductively-coupled plasma optical emission spectrometry, respectively. Nanosilica accumulated rapidly on specimen surface at low UV doses but the rate of accumulation slowed down at high UV doses. Further, the amount of surface accumulation increased with increasing temperature. The mass of Si release increased with increasing temperature for high UV doses; but at low doses, the trend was different: the mass of Si release was greatest at 50 °C and smallest at 60 °C. Kinetic parameters derived from this study are essential for developing credible models to predict the long term risks of polymer nanocoatings used outdoors.

Keywords: nanosilica, epoxy, degradation, nanocoating, nanocomposite, nanoparticle release, UV radiation.

1 INTRODUCTION

Polymeric materials containing nanofillers (polymer nanocomposites) have attracted steadily growing interest due to their outstanding properties as well as their unique applications [1-5]. Among polymer nanocomposites that have a substantial commercial application in various industries are polymer nanocoatings. Because of its excellent mechanical, gas barrier, self-cleaning, and ultraviolet (UV) resistance properties, polymer nanocoatings are increasingly used outdoors such as on building structure, airplane, and automobile.

Studies in the past few years have indicated that most common polymers undergo significant degradation during

exposures to outdoor environments [6-8]. A serious consequence of the matrix degradation is that the nanofillers that were embedded in the polymer matrices could be released via the effect of rain, snow, condensed water, and wind. As such, nanofillers will eventually be released to some extent from polymer nanocoatings during their life cycle. Engineered nanofillers have been shown to be hazardous to the environment and human health [9-11]. Although the release of nanofillers from polymer nanocomposites during exposure to UV radiation has been detected [12], the role of temperature on the release has not been investigated. Because temperature is an important factor in the degradation process of polymers, this study has examined how this factor affects both the surface accumulation and release of nanosilica during UV exposures of an epoxy nanocoating. Surface accumulation and release of nanosilica as a function of UV dose were determined by atomic force microscopy (AFM) and inductively-coupled plasma optical emission spectrometry (ICP-OES), respectively.

2 EXPERIMENTAL

2.1 Materials and Preparation

For the surface accumulation study, the nanosilica was an untreated material, having an average diameter of 15 nm and purity greater than 99.5 %. To optimize the dispersion, a silane-treated nanosilica having similar diameter was used for the nanosilica release study. The epoxy matrix was a stoichiometric mixture of a diglycidyl ether of bisphenol A (DGEBA) epoxy resin and a tri-polyetheramine curing agent. There was no UV stabilizer added to the epoxy matrix. Free-standing films of the epoxy coating containing 5 mass % of nanosilica and having a thickness between 125 μm and 150 μm were prepared. To obtain well dispersed nanocoating films, nanosilica particles were first sonicated in toluene at a nanosilica:toluene ratio of 5 g:100 mL for 1.5 h using a 50 kHz tip sonicator. An appropriate amount of the epoxy resin was then added to the nanosilica suspension and sonicated for an additional 2 h. After adding the amine curing agent, the suspension was sonicated for another hour followed by stirring for 0.5 h with a mechanical stirrer. After the mixing step, the epoxy/amine/nanosilica mixture was degassed under vacuum for 30 min at room temperature and then drawn

down on a polyethylene terephthalate sheet. All films were cured at ambient conditions (24 °C and 50 % relative humidity) for 1 d, followed by post-curing for 45 min at 110 °C in an air circulating oven. The quality of all epoxy nanosilica coating (epoxy nanocoating) films was good, with no evidence of air bubbles or defects by visual inspection.

2.2 UV Exposure

Specimens of epoxy nanocoating were exposed to < 1 % relative humidity (RH) and three different temperatures, 40 °C, 50 °C and 60 °C in the National Institute of Standards and Technology (NIST) SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) UV chamber [13]. The very dry condition was used to minimize any effect of water on the photodegradation of epoxy. The NIST SPHERE UV chamber produced a highly uniform UV flux of approximately 140 W/m² in the wavelength range of 295 nm to 400 nm. To obtain sufficient masses of released particles for ICP-OES analyses, a special designed sample holder with a large exposure area (60 cm²) was used. For surface morphology characterization and surface accumulation of nanosilica, specimens having a surface area of approximately 5 cm² were exposed. Specimens were removed at specific UV doses for surface accumulation and release measurements.

2.3 Surface Morphology Characterization

Surface morphological changes of nanocoating were measured by tapping mode AFM at ambient conditions (24 °C, 50 % RH) using a Dimension Icon system (Bruker, USA) and silicon probes (TESP, Bruker). A scan size of 20 μm and a scan speed of 1 Hz were used. Height images were analyzed by the image software provided by the AFM instrument, and the function of bearing analysis was used to follow the nanosilica accumulation on the nanocoating surface with UV exposure. The results are average of at least three different locations.

2.4 Measurement of nanosilica release

A rinsing system simulating the rain was used to remove released nanoparticles on the UV-exposed surface, and the runoff waters were collected for ICP-OES analysis. The water rinsing and sample collection for nanosilica release analysis were performed using the following protocol. After exposing to a specified UV dose, specimens were removed from the UV chamber, held vertically, and rinsed with de-ionized (DI) water. To provide a reproducible rinsing procedure, a chromatographic atomizer and a pressure controller were employed to produce a constant flow rate of 16 L/min. Other rinsing parameters used included the following: distance between the atomizer nozzle and the specimen was 10 cm, rinsing period was 10 min, and water volume for each rinsing period was

approximately 25 mL. After rinsing, specimens were placed back in their respective holders in the SPHERE for further UV irradiation. ICP-OES analysis of runoff waters was carried out using a PerkinElmer Optima 5300 DV instrument (Shelton, CT), and a method of standard addition was used to quantify the mass of Si in runoff waters. Through this procedure, the mass of Si (mostly from nanosilica) release as a function of UV was quantified, and each data point is the average of four specimens.

3 RESULTS AND DISCUSSION

Figure 1 displays AFM height and phase images of unexposed and UV-exposed epoxy nanocoating surface at, as an example, 40 °C. The contrast in the height images of Figure 1a is due to the surface roughness, with little evidence of nanoscale particles being present on the surface, which is also confirmed in the featureless phase image (Figure 1a, right). As UV dose increased, the surface roughness increased and nanoparticles or clusters of nanoparticles appeared on the surface, as shown in both the height and phase images of Figure 1b. The brightness of the particles in the height image indicates that they were above the surface. The phase image also shows a strong contrast between the nanoparticles and matrix, which is typically observed for mixtures of a high modulus inorganic material and a low modulus polymeric material.

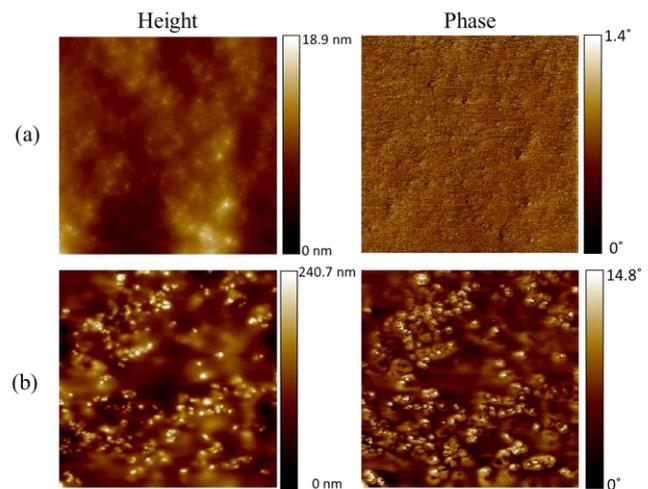


Figure 1 AFM height images (left column) and phase images (right column) of (a) unexposed and (b) nanocoating exposed for 30 MJ/m² UV dose and at 40 °C. Scan sizes are 20 μm × 20 μm. The scale bars represent the height and phase range of each graph.

Figure 2 shows the surface morphological changes of the nanocoating exposed to different UV doses in three temperatures (40 °C, 50 °C and 60 °C). All three temperatures showed similar effects. The number of particles on the surface increased with increasing UV dose, and the size of the particle clusters and the number of

connected clusters also increased with UV dose. After 400 MJ/m² dose, a layer of compact particles almost covered the entire surface for all three temperatures. Similar results were observed in NIST previous studies for a treated nanosilica in a similar epoxy system [8,12].

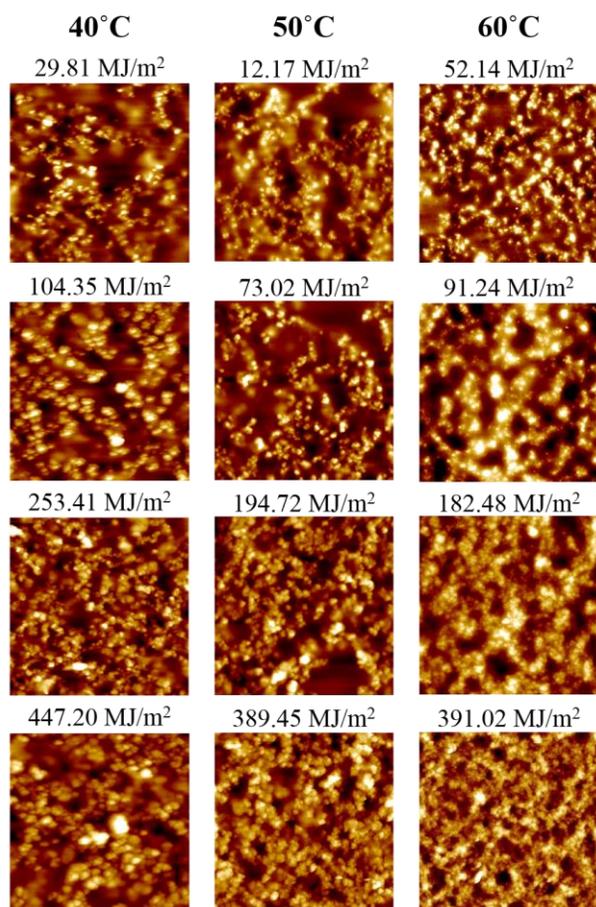


Figure 2: AFM height images of epoxy nanocoating as a function of UV doses for three different temperatures; scan size: 20 μm × 20 μm. The z-height range of the images are roughly from 0 nm to 1.5 μm.

To follow the accumulation of nanosilica on the nanocoating surface, an AFM software image (bearing) analysis was used. Figure 3 displays the surface coverage (in %) of revealed particles (assuming as nanosilica clusters) as a function of UV dose. It shows that the accumulation of nanosilica on the UV-exposed nanocoating increased rapidly between 0 MJ/m² and 300 MJ/m² dose but slowed down substantially thereafter. The shape of nanosilica coverage vs. UV dose curve is similar to the chemical changes (data not shown here) such as oxidation measured by Fourier transform infrared spectroscopy with UV dose, suggesting that the accumulation of nanosilica on the nanocoating surface with UV exposure is closely related to photodegradation of the epoxy matrix. That is, as the epoxy layer on the nanocoating surface degraded by UV

radiation, silica nanoparticles that were embedded in the matrix were increasingly exposed on the surface. Figure 3 also shows that, except for 750 MJ/m² dose or greater where there is essentially no difference in surface coverage between 50 °C and 60 °C, a higher exposure temperature has resulted in a higher amount of surface accumulation of nanosilica. For example, at an exposure dose of 400 MJ/m², the surface coverages were approximately 50 %, 56 %, and 60 % for 40 °C, 50 °C, and 60 °C, respectively.

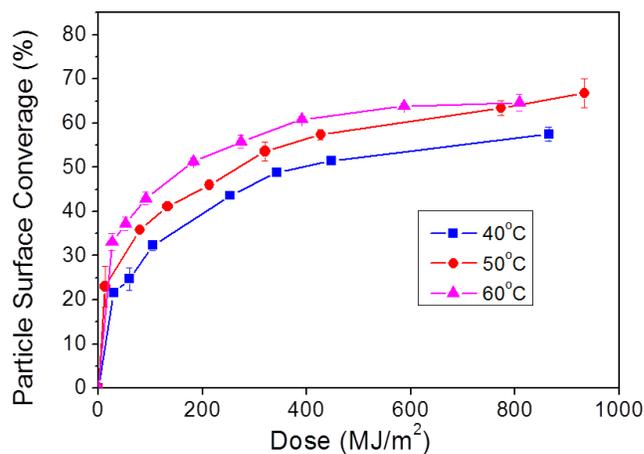


Figure 3: Nanosilica coverage on epoxy nanocoating surface as a function of UV dose. Each data point is the average of three measurements (20 μm × 20 μm scan area). The error bars represent one standard deviation.

The amounts of Si released (collected in run-off water and measured by ICP-OES) as a function of UV dose for three different temperatures are depicted in Figure 4. As indicated in the experimental section, silane-treated nanosilica was used for the nanoparticle release study, and the mass of Si from the silane layer contributes only approximately 1 % of the total Si mass from nanosilica. As seen in Figure 4, the mass of Si release increased nearly linearly with UV dose for all three temperatures up to 500 MJ/m², with both the release rate and release quantity being highest for 50 °C and lowest for 60 °C. Above this UV dose, however, the effect of temperature on the Si release was different: the mass of Si release for 60 °C increased rapidly, reaching a value of approximately 300 mg (per 60 cm² irradiated area) at 900 MJ/m². Further, above this dose, the effect of temperature on the Si mass release appeared to follow the same trend with that of the surface accumulation. That is, the higher exposure temperature, the greater the Si release mass. Figure 4 also revealed that the standard deviations between specimens for the two highest temperatures were high at high UV doses (> 700 MJ/m²). It is noted that the reproducibility of the ICP-OES measurement for Si is good, with the coefficient of variation was < 4 %. Further studies are needed to explain this high variability between specimens as well as the drastic change on the temperature effect at 600 MJ/m².

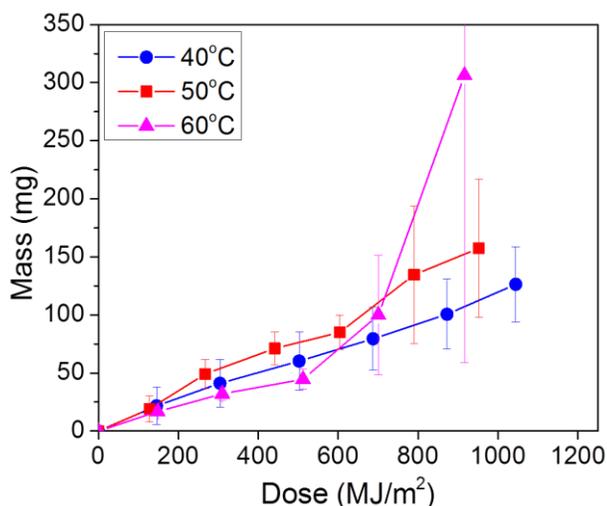


Figure 4: Mass of Si release as a function of UV dose. Each data point is the average of four measurements at specific exposure dose. The error bars represent one standard deviation.

4 CONCLUSION

Polymer matrices in nanocomposite coatings are susceptible to degradation during outdoor uses, which may release nanoparticles from the products. Such nanoparticle release potentially poses an environmental health and safety risk. The effect of temperature on surface accumulation and release of nanosilica as a function of UV exposure for an epoxy nanocoating has been investigated using AFM and ICP-OES techniques. The amount of nanosilica accumulated on the nanocoating surface was observed to increase rapidly between 0 MJ/m² and 300 MJ/m² UV doses but substantially slowed down thereafter. The nanosilica surface coverage was greater for higher exposure temperature. The trend of temperature effect on the Si release was not straightforward. Below 600 MJ/m², the rate of Si release was highest for 50 °C, but above this dose, 60 °C exposure produced the highest Si release rate. The result also revealed a high variability in the amounts of Si release between specimens, and more studies are needed to address this problem.

5 DISCLAIMER

Certain commercial products or equipment are described in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.

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