Degradation and Nanoparticle Release of Epoxy/Nanosilica Composites Exposed to UV Radiation

B. Pellegrin, T. Nguyen, L. Mermet, A. Shapiro, X. Gu, and J. Chin

National Institute of Standards and Technology, Gaithersburg, MD

ABSTRACT

This study investigates changes of surface nanosilica concentration, rate and amount of nanosilica loss, and degradation of epoxy/nanosilica composites during exposure to UV radiation. The polymer matrix was a stoichiometric mixture of a diglycidyl ether of bisphenol A epoxy and an aliphatic tri-amine. Epoxy nanocomposite free films containing 5 % and 10 % silica nanoparticles in the 200 μm to 250 μm thickness range were fabricated. Thin films on CaF_2 substrate were also prepared and investigated. Nanocomposite specimens were exposed to 75 % RH, 50 ^{o}C, and 290 nm - 400 nm UV radiation in a NIST-developed UV chamber. Exposed samples were removed to measure photodegradation, mass loss, and surface morphology using Fourier transform infrared spectroscopy (FTIR), gravimetry, field emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM) techniques. The amount and rate of nanosilica release were estimated by thermogravimetry (TGA), which can separate nanosilica from epoxy matrix. Amine-cured epoxy/nanosilica composites exposed to UV radiation were observed to undergo rapid photodegradation, resulting in a substantial mass loss of both the polymer and nanosilica. An increase of nanosilica concentration was observed on the composite surface.

1 INTRODUCTION

Thermosetting epoxies have many useful properties for structural engineering applications, such as excellent adhesion, high modulus and failure strength, and good elevated temperatures performance. However, the structure of such thermosetting polymers also causes them to be relatively brittle, with poor resistance to crack initiation and growth. This brittleness is one major drawback that prevents broader applications of epoxies. To overcome this limitation, it has been widely claimed for several decades that mixing or hybridization of epoxy polymer with fillers, such as rubbery particles, greatly increases their toughness without significantly impairing the other properties [1]. More recently, new technologies consisting of adding nano-reinforcements such as nanoplatelets, nanoparticles, and carbon nanotubes have emerged [2,3,4]. Those nano-reinforcements, as opposed to traditional reinforcements, have been shown to improve the mechanical and thermal properties at much lower filler loading levels [5,6,7]. Nevertheless, polymers are prone to undergo photodegradation in UV condition, which could liberate nanoparticles from the polymer nanocomposites during their life cycle. The release of nanoparticles may have a negative effect on the environment, and presents a roadblock to their potential uses in many industries, such as construction and automotive [8]. While the benefits of nanotechnology are widely published, discussion of the potential effects of their widespread use in consumer and industrial products is just beginning. This paper reports on changes of nanosilica concentration at the surface, mass loss and degradation of epoxy/nanosilica composites during their exposures to UV radiation.

2 EXPERIMENTAL[**]

2.1 Materials

The silica nanoparticles or nanosilica used in this study were surface modified, had an average diameter of 7 nm and a purity of > 99.8%, and were obtained from a commercial source (Aerosil R974, Evonik Degussa Corp). The polymer matrix was a stoichiometric mixture of a diglycidyl ether of bisphenol A epoxy resin (EPON 828, Resolution Performance Products), having an equivalent mass of 189 (grams of resin containing one gram equivalent of epoxide) and an aliphatic tri-polyetheramine curing agent (Jeffamine T-403, Hunsman). Reagent grade toluene (purity > 99.5 %) was used for composite processing.

2.2 Epoxy Nanocomposites Preparation

Free-standing films of unfilled and nominal 5 % and 10 %-filled nanosilica amine-cured epoxy composites were fabricated. The loading percentages were based on mass fraction of the solid amine-cured epoxy. Figure 1 illustrates the process used for their preparation. Silica nanoparticles were first sonicated in a large amount of toluene for 30 minutes. After adding epoxy resin, the nanosilica suspension was stirred and sonicated for an additional 1 h using an 80 kHz tip sonicator. The amine component then was added to the suspension and stirred for another hour. After degassing for 1 h at room temperature, the mixture was drawn down on a polyethylene terephthalate sheet (Mylar). All coated films were cured under ambient conditions (24 °C and 45 % relative humidity) for three days, followed by post-curing for 4 h at 110 °C in an air circulating oven. Free films having a dry thickness between 200 μm and 250 μm were obtained. In addition to the nanocomposite free films, thin coatings of unfilled and nanosilica-filled epoxy on CaF_2

substrates were also prepared by spin coating for use in transmission FTIR measurements. Spin-coated samples were cured under ambient conditions for three days, followed by post-curing for 30 min at 110 °C in an air circulating oven. The average thickness of the spin-coated films was approximately 6 µm, as measured by laser scanning confocal microscopy on equivalent films coated on silicon wafers.

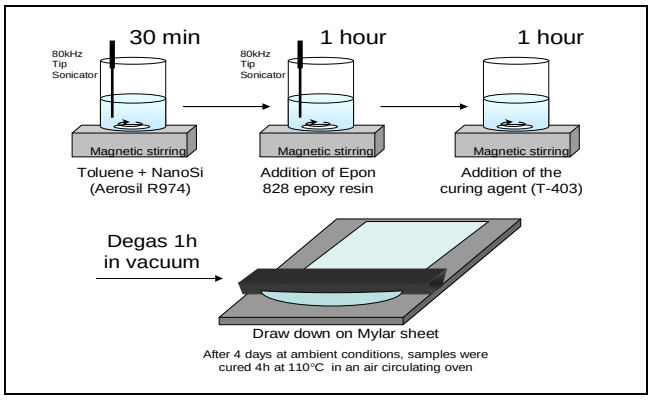

Figure 1: Process used for preparation of amine-cured epoxy/nanosilica composites.

2.3 Characterization of UV-exposed Samples

The UV degradation of the unfilled epoxy and its nanocomposites was investigated using a 2 m integrating sphere-based weathering device, referred to as SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) [9]. This device utilizes a mercury arc lamp system that produces a collimated and highly uniform UV flux of approximately 480 W/m^2 in the 290 nm to 400 nm range. Relative humidity (RH) and temperature can also be controlled in this device. In this study, 20 mm diameter free film and spin-coated samples were exposed in the SPHERE UV chamber at 50 °C and 75 % relative humidity (RH), and were removed at specified time intervals for measurements of photodegradation, surface morphologies, and mass losses. Photodegradation was measured by Fourier transform infrared spectroscopy in the attenuated total reflection (FTIR-ATR) and transmission (t-FTIR) modes. FTIR spectra were recorded at a resolution of 4 cm^{-1} using dry air as a purge gas and a spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. All FTIR results were the average of at least three samples. Surface morphology was characterized by field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). Mass losses of nanocomposites and nanosilica were determined by an analytical balance and thermogravimetry analysis (TGA), respectively. TGA measurements were conducted from 25 ^{o}C to 1000 °C at a heating rate of 5 °C/min. In order to prevent silica nanoparticle loss during TGA measurement, nitrogen was used from 25 ^{o}C to 550 ^{o}C and air was then introduced between 550 °C and 1000 ^{o}C.

3 RESULTS AND DISCUSSION

3.1 Degradation of Epoxy/Nanosilica Composites Exposed to UV Radiation

Effects of UV exposure on spin-coated unfilled epoxy and epoxy/5 % nanosilica samples were monitored by t-FTIR. Figure 2 displays the results obtained for epoxy/5 % nanosilica samples. Under UV exposure, unfilled epoxy and epoxy/nanosilica composite samples show similar spectral changes, suggesting that nanosilica-filled epoxy follows the same degradation mechanism as that of the unfilled epoxy. For examples, the existing bands at 1245 cm^{-1}, 1296 cm^{-1}, and 1508 cm^{-1}, assigned to aryl-O, H_2C-O, and benzene ring, respectively, decrease as a function of time for both materials. Also, both unfilled and filled films show the formation of two new bands near 1714 cm^{-1} and 1667 cm^{-1}, assigned to the C=O and C=C bands, respectively. The latter assignment is consistent with previous reports on the formation of unsaturated compounds after UV or thermal treatment of amine-cured epoxies [10,11]. Because they correspond to the chemical groups present in the main chain of the epoxy resin, the decrease of the 1245 cm^{-1} and 1508 cm^{-1} bands intensity signifies a chain scission process.

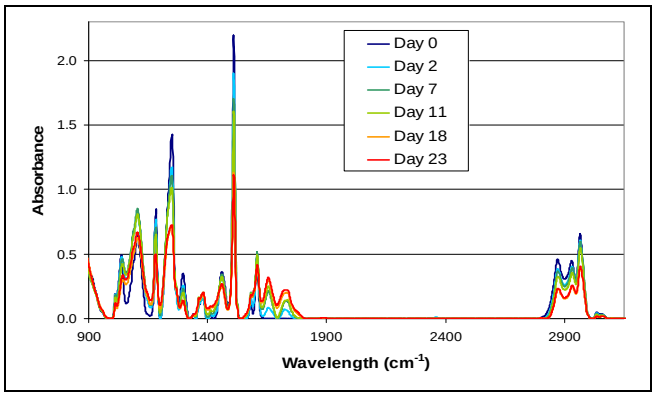

Figure 2: t-FTIR spectra for several exposure times of epoxy/5 % nanosilica composites.

FTIR-ATR intensity changes of unfilled (clear) epoxy and epoxy/5 % nanosilica composite free films are shown in Figure 3. Because intensity of the FTIR-ATR spectra depends on contact area between the sample and the prism, which may vary due to UV exposure, the intensity change must be normalized to a band that is not affected by the exposure. Based on evidence from t-FTIR measurement, the 1380 cm^{-1} band (CH_3, gem-dimethyl) appears to be invariant during the first 20 days of exposure. Therefore, the intensity of this band has been used for normalizing the FTIR-ATR spectra. Note also that, for the ZnSe prism used in this study, the probing depth of the ATR technique in the sample is between 0.5 µm and 2.5 µm. Thus, the degradation observed in Figure 3 originates from the film layer close to the surface. Figure 3a shows a rapid decrease

NSTI-Nanotech 2009, www.nsti.org, ISBN 978-1-4398-1782-7 Vol. 1, 2009

of the 1245 cm^{-1} band intensity, corresponding to chain scission, during the first five days of exposure. The intensity loss of the unfilled films after 5 day exposure appears to be greater than that for the nanosilica-filled film. Further, the rates of oxidation (Figure 3b) are different for unfilled and nanosilica-filled films, with the latter systems show a greater rate at early (<5 days) and late exposure times. Figure 3c illustrates the evolution of the 1080 cm^{-1} band, attributed to Si-O-Si group of the silica nanoparticles. The intensity of this band for the 5 % and 10 % composites starts to increase after two days, rises sharply and reaches a maximum at approximately 7 days, suggesting that the concentration of nanosilica on the surface increases, goes through a maximum, and then decreases.

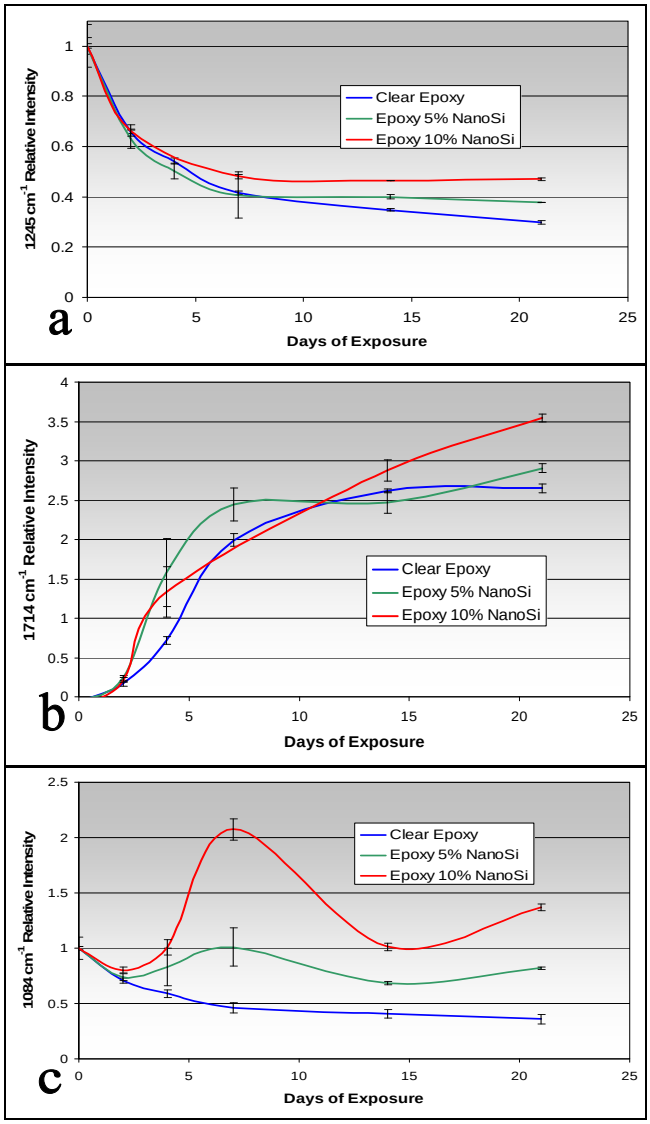

Figure 3: FTIR-ATR intensity changes of the bands at 1245 cm^{-1} (a), 1714 cm^{-1} (b), and 1080 cm^{-1} (c) with exposure time for unfilled, 5 % and 10 % nanosilica-filled epoxy films. Symbols are data points and lines are best-fitted curves. Error bars represent one standard deviation.

3.2 Surface Morphology of Epoxy/Nanosilica Composites Exposed to UV Radiation

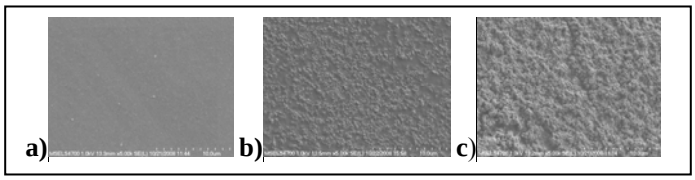

Figure 4: FE-SEM images (1.0 kV x 5.00 k magnification) of epoxy/5 % nanosilica composite before (a) and after UV exposure: seven days (b), and 43 days (c).

Figure 4 shows FE-SEM images of the epoxy/5 % nanosilica composite surface for different times of exposure. The FE-SEM image before exposure (Figure 4a) appears smooth and nearly featureless, with almost no evidence of silica nanoparticles. The absence of nanosilica and the smooth appearance suggest that a thin layer of epoxy material covers the nanocomposite surface. The presence of such a layer potentially influences the rate of polymer degradation and nanosilica release. After seven days of UV exposure, the degradation of the surface epoxy layer has exposed the silica nanoparticles at the composite surface (Figure 4b). After 43 days of exposure, silica nanoparticles have covered almost the entire composite surface (Figure 4c). Topographic (left) and phase (right) AFM images (Figure 5) taken at the epoxy/5 % nanosilica composite surface before and after 43 day exposure show similar results. Combining these microscopic data with the FTIR-ATR measurements (showing intensity increase of the characteristic silica band), we can conclude that the increase of nanosilica concentration at the composite surface with exposure time is due to the photodegradation of epoxy.

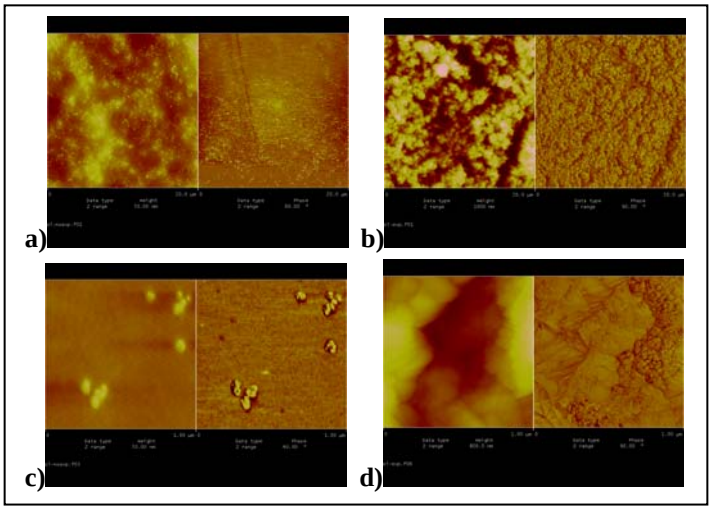

Figure 5: AFM images of epoxy/ 5% nanosilica composite before and after exposure to the UV environment: (a) before, and (b) after 43 days (scan size a & b: 20 μm); (c) before, and (d) after 43 days (scan size c & d: 1 μm).

3.3 Mass Loss of Epoxy/Nanosilica Composites Exposed to UV Radiation

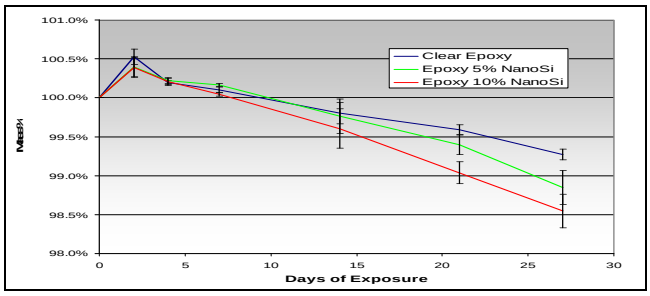

Figure 6: Mass losses of unfilled epoxy and epoxy/nanosilica composites as a function of exposure time in UV/50 °C/75 % RH. Error bars indicate one standard deviation.

Figure 6 displays the total mass loss as a function of exposure time. After 27 days of exposure, the maximum mass losses in unfilled epoxy and epoxy/10 % nanosilica composite are 0.7 % and 1.4 %, respectively, and the rate of mass loss is greater for nanosilica-filled than unfilled films. TGA was used to determine the percentage of nanosilica in the composites at different exposure times, and the results are depicted in Figure 7. In this figure, the difference in the TGA residual masses between the nanocomposite and the unfilled samples represent the total amount of nanosilica in the composites. Further, the coefficients of variation of all the data points were < 0.1 % (average of three samples), indicating that the reproducibility of the TGA technique is high. These results demonstrate that TGA is an effective technique to determine precisely the amount of nanosilica in a polymer composite. However, Figure 7 shows little change in nanosilica concentration in the composites with UV exposure. This result is not consistent with the SEM, AFM, and FTIR data, which clearly show increased nanosilica concentration at the composite surface with exposure. One explanation is the TGA technique, which measures bulk property, may not have enough sensitivity to detect minute mass changes of nanoparticles at the surface of thick composite samples. Additional experiments are being conducted using thinner films and with longer exposure times to verify this postulation.

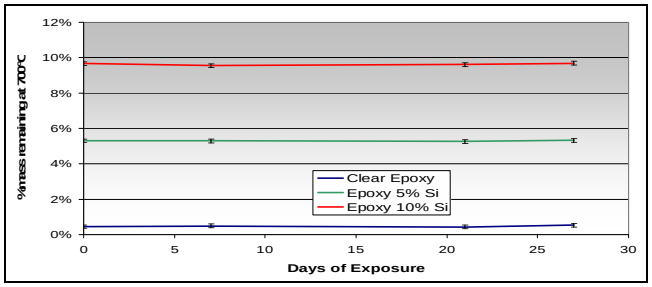

Figure 7: Percentage of mass remaining at 700 °C during TGA measurement as a function of exposure time for unfilled epoxy and epoxy/nanosilica composites.

4 CONCLUSION

Photodegradation, surface morphology, total mass loss, and nanoparticle loss of amine-cured epoxy/nanosilica composites exposed to UV/50 °C/75% RH condition have been investigated by spectroscopic, microscopic, and gravimetric techniques. Under UV exposure, the epoxy matrix undergoes rapid photodegradation, which results in a substantial mass loss and gradual build-up of nanosilica concentration at the composite surface with time. This result should be valuable for knowing the status of nanoparticles during the lifetime of epoxy nanocomposites.

** *Certain commercial product or equipment is 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.*

References

[1] A.J. Kinloch, S.J. Shaw, D.A. Tod, D.L. Hunston, *Polymer* 24:1341-1363, 1983.
[2] S. Kanga, S. I. Honga, C. R. Choeb, M. Parkb, S. Rimb, J. Kim, *Polymer* 42: 879, 2001.
[3] L. Mascia, L. Prezzi, B. Haworth, *J. Mater. Sci* 41: 1145, 2006.
[4] Z. Yaping, Z. Aibo, C. Qinghua, Z. Jiaoxia, N. Rongchang, *Mater. Sci. and Eng.* A 435–436: 145, 2006.
[5] M. Alexandre, P. Dubois, *Mater. Sci. and Eng.* 28: 1, 2000.
[6] B.R.K. Blackman, A.J. Kinloch, J. Sohn Lee, A.C. Taylor, R. Agarwal, G. Schueneman, S. Sprenger, *J. Mater. Sci.* 42:7049, 2007.
[7] Y. Breton, G. Desarmot, J.P. Salvetat, S. Delpeux, C. Sinturel, F. Beguin, S. Bonnamy, *Carbon* 42: 1027, 2004.
[8] A. Nel, T. Xia, L. Madler, N. Li, *Science* 311,622, 2006.
[9] J. Chin, E. Byrd, N. Embree, J. Garver, B. Dickens, T. Fin, J.W. Martin, *Review Scientific Instruments* 75: 4951, 2004.
[10] N. Grassie, M.I. Guy, N.H. Tennent, *Polym Deg Stab* 13: 249, 1985.
[11] M.A Keenan, D.A. Smith, *J. Appl. Polym. Sci.* 11: 1009, 1967.