Relationship between Chemical Degradation and Thickness Loss of an Aminecured Epoxy Coating Exposed to Different UV Conditions

Aziz Rezig, Tinh Nguyen, David Martin, Lipiin Sung, Xiaohong Gu, Joan Jasmin, and Jonathan W. Martin

National Institute of Standards and Technology, Gaithersburg, MD 20899

Abstract

The relationship between chemical degradation and thickness loss of an unpigmeted, non UVstabilized, crosslinked amine-cured epoxy coating exposed to three UV conditions has been investigated. Samples were exposed outdoors and to two accelerated laboratory UV conditions. Chemical degradation and thickness loss were measured by transmission Fourier transform infrared spectroscopy and by laser scanning confocal microscopy (LSCM). Surface roughness and morphological changes were measured by atomic force microscopy (AFM) and LSCM. Substantial chemical degradation, thickness loss, and morphological changes have occurred in the films after exposure to the three UV environments. However, the rates of chain scission and mass loss were always greater than that of the thickness loss. Further, photodegradation of an amine-cured epoxy was not a uniform thickness reduction process; instead, nanoscale localized depressions initiated at certain sites on the surface, which then enlarged and deepened with exposure. The results of this study should help to develop better conceptual and mathematical models for predicting the service life of crosslinked amine-cured epoxy coatings.

Introduction

Amine-cured epoxies are used extensively for exterior coatings and polymer-fiber composites. However, epoxy-based materials are known to undergo degradation when exposed to UV radiation (1). In the presence of oxygen, amine-cured epoxies undergo photo-oxidation, which results in chain scission with formation of various oxidation products (1-3). Photochemical degradation of the epoxy polymer leads to physical changes of the coating films, such as thickness decrease, gloss loss, and cracking. Fourier transform infrared spectroscopy (FTIR) is the most common technique to measure chemical degradation of polymeric coatings, and the information obtained is commonly used to predict long-term performance. Based on results from additive-free and UV-stabilized acrylic-melamine coatings, Gerlock and coworkers (4) have indicated that the plot of IR intensity loss of the CH band with time exposed to an UV environment is linear beyond 80 %. In another investigation, Scroll and Skaja (5) reported an approximately linear relationship between chemical changes and thickness loss for an unpigmented polyester polyurethane coating. These studies asserted that a measurement of the remaining thickness of a weathered film can provide an estimate the erosion rate of polymeric coatings. This assertion is only valid, however, if degradation is attributable to a uniform decrease of film thickness from the surface (an ablation process). However, typical unexposed clear coatings are very smooth (mean root square roughness <10 nm) and highly glossy. Thus, if the degradation is the result of a uniform ablation process, then the coating surfaces should remain smooth and should retain their glossiness. Such is not the case: UV-stabilized and non-UV stabilized clear polymeric films are known to suffer a substantial loss of gloss after exposure to UV radiation (6,7).

The notion that photodegradation is a uniform ablation process is also inconsistent with recent morphological evidence obtained by nanoscale measurement techniques. For example, atomic force microscopy (AFM) results of acrylic-melamine and acrylic-urethane coatings exposed to narrow band pass filter and full spectral UV radiation have shown that the exposed surfaces degrade non-homogeneously through the formation of pits, which deepen and enlarge with time (8-11). Further, mass loss (for materials where mass losses were measured), for the most part, were greater than one would expect relative to an independent measure of thickness loss, indicating that mass loss is attributable to some other process other than thickness loss (11). The main objective of this study was to assess the relationship between the chemical degradation

and the thickness loss for crosslinked amine-cured epoxy coatings exposed to outdoor and accelerated laboratory UV conditions. The results obtained of this study should help to better predict the service lives of amine-cured epoxy coatings.

Experimental Procedures**

Materials and Specimen Preparation

An unpigmented, non-UV stabilized model crosslinked amine-cured epoxy was used. The coating was a stoichiometric mixture of a pure diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent of 172 (grams of resin containing one gram equivalent of epoxide) (Der 332 from DOW Chemicals) and 1,3-bis(aminomethyl)-cyclohexane (1,3 BAC) (Alrich) as the aliphatic amine curing agent. Hereafter, 1,3 BAC-DGEBA system is designated as the aminecured epoxy coating. Samples of spin coating applied to 100 mm diameter Si wafers were prepared for both chemical and physical degradation studies. Si substrate was chosen because it is suitable for quantitative study of coating chemical degradation by transmission FTIR spectroscopy and for nondestructive measurement of film thickness changes with exposure time by laser scanning confocal microscopy (LSCM) in the reflection mode. Epoxy resin and amine curing agent in appropriate solvents were mixed at the required ratio, degassed, flooded onto the substrates, and spun at 2000 rpm for 30 s. The spin coating operation was carried out in an essentially CO₂-free, dry air glove box to minimize the reactions of CO₂ and moisture with amine curing agent. Coated samples were cured at room temperature for 24 h, followed by heating at 130 °C for 2 h in an air-circulated oven. The glass transition temperature, Tg, of the cured film was 123 °C \pm 2°C (by dynamic mechanical analysis). (The number after the \pm sign indicates one standard deviation.) The average thickness of the coated films was 7.2 μ m \pm 0.8 µm, as measured by LSCM. After curing, the 100 mm diameter coated Si plates were cut into 25 x 25 mm samples using a diamond saw typically employed in the semiconductor industry. These samples were used for exposures.

The main chemical structures of the individual components and in the cured film are illustrated in Figure 1. It should be noted that, due to steric hindrance and restricted transport at the late curing stages, unreacted epoxide and amino groups, and monosubstituted nitrogen chains were also probably present in the cured structures. The unreacted and partially-reacted molecules would have an influence on the degradation behavior of an amine-cured epoxy materials.

UV Exposure Conditions

Samples were exposed to outdoor and two accelerated laboratory UV conditions that differed only in the relative humidity levels, 9% (dry) and 75 % (humid). The experimental setup for the accelerated laboratory exposures is schematically shown in Figure 2. The UV radiation source consisted of a 1000 W xenon arc lamp producing radiation having wavelengths from approximately 275 nm to 800 nm. The light source was equipped with an optical system that removed most of the infrared and visible radiation and a photo-feedback controller to regulate light intensity. Therefore, the temperature of the irradiated sample was slightly above ambient temperature (24 °C). It should be emphasized that the UV light source used in the accelerated experiments contained radiation having wavelengths below 300 nm, which are absent in the terrestrial sunlight. Samples for the laboratory exposures were placed in the 12-window exposure cells containing an inlet and an outlet that allowed fresh air having a desired temperature and relative humidity (RH) to continuously enter the cell chamber, and let the outgoing air vent to the outside of the cell chamber. Each exposure cell was equipped with a thermocouple and a RH sensor. The RH flowing to the sample was supplied by a humidity generator, which is based on mixture of dry air and moisture-saturated air. The relative humidities could be independently controlled and maintained to within approximately ± 3 % of their preset values from 0 % to 90 %. The temperature within each exposure cell was controlled to within ± 1 °C in the 30 °C - 60 °C range by the use of temperature feedback control devices, heating coils, and thermocouples. All samples for the laboratory experiments were exposed to 50 °C. Complete details on the UV light source, instrumentation, exposure cells, and controlled systems have been described previously (12), and information on the RH generator was given in Ref. (13).

For outdoor exposure, which was in Gaithersburg, Maryland, samples were placed in an outdoor environmental chamber (Figure 3) at 5 degrees from the horizontal plane and facing South. The bottom of the chamber was made of black anodized aluminum, the top was covered with "borofloat" glass, and all sides were enclosed with a vortex material that allowed water vapor, but prevented dust from, entering the chamber. UV-visible spectral results showed that the

borofloat glass did not alter the solar spectrum before or after more than one-year outdoor exposure. All outdoor exposures started in April. The temperature and RH in the chamber were recorded continuously. The temperature inside the chamber was found to be as much as 20 degrees higher than the surrounding ambient temperature, and the RH in the chamber often reached 100%.

Degradation Measurements

<u>Chemical Degradation</u>

Coating chemical degradation as a function of exposure time was followed by Fourier transform infrared spectroscopy in the transmission mode (FTIR-T) using an auto-sampling accessory described previously (14). At each specified time interval, the sample-contained exposure cells were removed from the chamber and fitted into a demountable 150 mm diameter ring of the auto-sampler. The ring can be rotated and translated to cover the entire sampling area. Spring-loaded Delrin clips ensure that the samples were precisely located and correctly registered. This automated sampling device allowed rapid recording of the FTIR-T spectra of the coating at all 12 windows of the exposure cell before or after each exposure time. Since the exposure cell was mounted precisely on the auto-sampler, errors due to variation of sampling at different exposure times were essentially eliminated. The auto-sampler accessory was placed in a FTIR spectrometer compartment equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. Spectra were recorded at a resolution of 4 cm⁻¹ using a speciallywritten program and dry air as the purge gas. All spectra were the average of 128 scans. In all cases, the residence time of samples in the FTIR spectrometer compartment was < 15 minutes. The peak height was used to represent IR intensity, which is expressed in absorbance, A. All FTIR results were the average of four specimens.

Thickness Changes

Coating film thicknesses before and after exposures for different times were measured nondestructively using a Zeiss model LSM510 laser scanning confocal microscope (LSCM) in the reflection mode. LSCM was also employed to characterize surface morphology and roughness of exposed samples. LSCM utilizes coherent light and collects light exclusively from a single plane (a pinhole sits conjugated to the focal plane) and rejects light out of the focal plane. The wavelength, numerical aperture (N.A.) of the objective, and the size of the pinhole dictate the resolution in the thickness or axial direction. By moving the focal plane, single images (optical slices) can be combined to build up a three dimensional stack of images that can be digitally processed. LSCM images reported were in 2D intensity projection and representative of a series of overlapping optical slices (a stack of z-scan images) with each z-step of 100 nm. The laser wavelength used was 543 nm.

The procedure for measuring thickness of a polymer film on a Si substrate using LSCM is illustrated in Figure 4. As light is shined onto a polymer-coated Si substrate, ray 1 is reflected from the air/polymer interface, and ray 2 is reflected from the polymer/Si interface. For normal incident and assuming no substantial light absorption in the polymer film, the reflected intensity of ray 1 and ray 2 can be expressed by (15):

$$I_{Ray1} = I_O \left(\frac{n_p - n_o}{n_p + n_o}\right)^2; I_{Ray2} = I_O \left(\frac{4n_p \times n_o}{(n_p + n_o)^2}\right)^2 \left(\frac{n_p - n_{si}}{n_p + n_{si}}\right)^2$$

Where I_o is the incident intensity, and n_o , n_p , n_i are the refractive indices of the air, the polymer coating, and the Si substrate, respectively. The film thickness d_p is equal to $n_p \times d_o$, where d_o is the distance between the two interfaces, which is measured by LSCM. An n_p value of 1.5, which is typical for polymers, was used for both initial and degraded epoxy samples. Thickness measurements were performed at five different fixed positions on each of the four samples using a specially-designed holder attached to the stage of the confocal microscope. Each position was approximately 2 mm apart. Further, thickness measurements were performed only at locations that were free of pits and holes. All thickness results were the average of at least 20 measurements.

Roughness and Surface Morphological Changes

Both LSCM and atomic force microscopy (AFM) were employed to provide data on roughness and surface morphological changes due to exposure. These two techniques can provide complementary topographic features ranging from a few nanometers to hundreds of micrometers. Surface morphology measurement with a LSCM is described above. For AFM imaging, samples were periodically removed from the exposure cells and analyzed using a Dimension 3100 Scanning Probe Microscope (Digital Instruments) operated in tapping mode and commercial Si microcantilever probes. Because a low force is applied and the duration of tipsample contact is short, tapping mode operation causes minimum damage to the sample while maintaining a high spatial resolution. AFM images were obtained using a resonance frequency of approximately 300 kHz for the probe oscillation and a free-oscillation amplitude of 62 nm \pm 2 nm. The set-point ratio (the ratio of set point amplitude to the free amplitude) ranged from 0.60 to 0.80. Mean root square (rms) roughness values obtained by both LSCM and AFM were the average of four measurements.

Results and Discussion

Microstructure of Amine-cured Epoxy Coatings

Information on the surface and bulk microstructures of a polymeric coating can provide crucial information for understanding how a polymeric material degrades during environmental exposure. Topographic and phase AFM images taken from the surface (air) and the bulk (fractured) of the amine-cured epoxy employed in this study are displayed in Figures 5a and 5b, respectively. The surface images were taken on the same sample used for chemical degradation analyses, and the bulk images were from a cryo-fractured 3 mm thick section of the same epoxy mixture molded in a polypropylene beaker. It should be noted that, in addition to the curing schedule used for chemical degradation analysis samples, (i.e., 2h at 130 °C), the 3 mm thick sections were subjected to an additional 2 h post-curing at 130 °C. This section was well cured after the post-curing, as determined by attenuated total reflection (ATR) FTIR. The cryo-fractured surfaces were prepared by notching a 12 mm x 12 mm x 3mm section with a band saw, immersing the notched section in liquid nitrogen for one hour, and fracturing it with a screwdriver. In Figure 5 and other AFM figures that followed, topographic images are on the left and phase images are on the right. The bright and dark areas in the topographic images correspond to the peaks and valleys, respectively.

Both topographic and phase AFM images show that the air surface is smooth and has, although not so clear, a pattern consisting of bright and dark domains. Examination of phase images taken from a variety of amine-cured epoxies reveals that the air surface of these epoxies is generally featureless or appears as an unclear pattern (16,17). The smooth and ill-defined microstructure of the air surface has been explained as due to the presence of a very thin layer of

a lower surface-free energy material. This explanation is consistent with extensive experimental data obtained by AFM and various surface analytical techniques showing that the outer surface of a multicomponent polymer system is generally enriched with a lower surface-free-energy component to minimize polymer-air interfacial energy (18,19). A thin layer of such material would mask the microstructure underneath, and the air surface should appear smooth and featureless. It should be noted that, because AFM operates in the near field (i.e., very close to the surface), it detects only the top layer of rigidly-bound atoms and, thus, does not provide image the layer beneath the outermost surface.

The phase image of the bulk (Figure 5b, right) clearly shows that the amine-cured epoxies have a two-phase microstructure consisting of a matrix that appears bright and interstitial regions dispersed throughout the matrix that appear dark. This heterogeneous feature of the bulk is similar to that observed by Vanlandingham (20) for the surface of DGEBA cured with bis(paraaminocyclohexyl) methane (an aliphatic amine) and is also similar to that of the microtomed and interface samples of other amine-cured epoxies (16,17), polyester film surface (21), and acrylicmelamine coating interface (22). Although the exact contrast mechanism in phase imaging is not fully understood, the bright domains in the phase image have been interpreted as due to a mechanically harder area and the dark surrounding region as due to more compliant material (23,24). From these assignments, it is reasonably to conclude that the bulk microstructure of an amine-cured epoxy is heterogeneous, consisting of softer regions (dark) dispersed in a harder matrix (bright). The harder, nodular domain in the matrix has been attributed to the high crosslinked material and the soft interstitial regions to the less crosslinked, low molecular mass material (20,25,26). Such heterogeneous structures are formed in crosslinked materials because, as the high molecular mass segments polymerize and terminate to form a network, some unreacted and partially polymerized molecules are unable to merge into the homogeneous structure and are left at the periphery of the network units (27).

Degradation During Exposure to UV Conditions

Chemical Changes

Figures 6a, 6b, and 6b display FTIR-T spectra of amine-cured epoxy coatings applied to a Si substrate before and after exposures to three UV conditions for several different times. One

interesting feature of these spectra was the presence of interference fringes arising from the constructive and destructive interference of the multiply reflected components with the first transmitted components, or equivalently, with the front surface reflected component. Another feature was both the spacing and intensity of the interference fringes varied with exposure time (level of degradation in the samples). Croll and Skaja (5) have utilized these fringe spacing changes to measure film thickness loss due to exposures. As observed for other coatings (11), this type of fringe, which is more prominent when the Si substrate is used, tends to obviate the weak bands and contribute to errors in their intensity measurements. In this study, the bands used for the chemical degradation analyses are stronger absorption bands, and thus the errors due to the interference fringe was small.

The bands of interest in an amine-cured epoxy material before exposure are those at 1510 cm⁻¹, due to benzene ring stretching, at 1245 cm⁻¹ due to aryl-ether stretching, at 1085 cm⁻¹, due to aliphatic-ether stretching, and near 3400 cm⁻¹, due to hydrogen-bonded OH stretching. In addition to the intensity decreases of the existing bands, these spectra show the formation of new chemical species in the 1620 cm⁻¹ to 1800 cm⁻¹ region as a result of exposures. Figure 6 also shows that exposure to laboratory UV/75 % RH and outdoor conditions caused a shift of the 3400 cm⁻¹ peak to lower frequency. The decrease of the existing bands and the formation of new bands in a polymeric film resulting from exposures is better seen in the difference spectra shown in Figure 7. These spectra were obtained by subtracting the spectrum of the unexposed sample from that of the exposed one after adjusting for any baseline shift. It should be noted that the auto-sampling device used in this study allowed the spectra to be recorded at approximately the same location on each sample. This operation minimizes errors due to sampling and subsequent spectral subtraction. In a difference spectrum, the bands below and above the zero base line indicate material depletion and formation, respectively. In addition to the decreases of numerous bands, Figure 7 shows two new prominent bands at 1730 cm⁻¹, due to C=O stretching of a ketone, and 1660 cm⁻¹, assigned to amide C=O stretching. The formation of these oxidation products is in good agreement with a photo-oxidative mechanism proposed by Bellinger and Verdu (2,3) for epoxy cured with aliphatic amines. Ketone formation is derived from the secondary hydroxyl groups, and amide is generated from the abstraction of a hydrogen of the methylene groups adjacent to the crosslink. Radicals and oxygen are required for both reactions.

Figure 7 also shows the appearance of a band peaking near 3300 cm⁻¹, assigned to the NH stretching, which is consistent with the amide formation.

In this study, the bands at 2925 cm⁻¹ (due to CH₂ stretching), 1510 cm⁻¹, 1245 cm⁻¹, 1730 cm⁻¹ and 1660 cm⁻¹ were used to follow various degradation processes of an amine-cured epoxy exposed to different UV environments; these results are depicted in Figure 8. Each data point in this figure was the average of four specimens, and the standard deviations are shown by the error bars, which show a good reproducibility of the chemical degradation data. A decrease of the 2925 cm⁻¹ band intensity represents a mass loss of the cured material, while a decrease of both the 1510 cm⁻¹ and 1245 cm⁻¹ bands signify a chain scission process because these bands represent the chemical groups present in the main chains of the epoxy resin. Figure 8 clearly shows that unstabilized amine-cured epoxies underwent rapid chemical degradation under UV conditions. For example, both the benzene ring and the aryl-ether groups lost more than 50 %, 40 %, and 45% of their amounts after exposures for 55 days in UV/75% RH, UV/9%, and outdoor conditions, respectively. Similar relative changes have been observed for the aliphatic CH groups (2925 cm⁻¹) under the same UV/RH and outdoor conditions for the same duration. On the other hand, the formation of amide appeared to reach a maximum after approximately 40 days of exposure despite the fact that other depletion processes still continued thereafter. Such behavior suggests that the concentration of oxidation amide products in the film at any particular exposure time was likely a result of both the formation and depletion of this species.

Thickness Changes

To verify that thickness values obtained by the LSCM technique were accurate, LSCM thickness measurements of unexposed samples were compared with those measured by the scanning electron microscopy (SEM) technique using cross sections of the same samples. For these measurements, three individual 25 mm x 25 mm samples cut from the 100 mm diameter coated Si plates were used. Figure 9 shows representative SEM images at two different magnifications of the coated cross sections. Although these saw-cut cross sections were flat and can be used for thickness measurement using an SEM, obviously extreme care must be taken in obtaining the thickness values from these cross sections. From SEM images, the average thickness value of these epoxy samples taken from 18 different measurements (six different locations for each of three specimens) was 5.8 μ m \pm 0.5 μ m. The corresponding average LSCM

thickness of the same samples was $6.4 \pm 0.7 \,\mu\text{m}$. The difference between the two techniques is within the experimental measurement errors. Thickness values of other films measured by LSCM were found to agree well with those obtained by ellipsometry (11).

One aspect of film thickness measurement by LSCM that deserves comments is the values obtained for degraded samples. As indicated in the experimental section, thickness measurements were performed on locations that were devoid of pits and holes. For the early exposure stages where surface physical changes were still negligible, the average value measured represented the actual remaining thickness of the film. However, at later degradation stages where substantial pitting has occurred, the measured thickness values were probably somewhat higher than the actual remaining thickness of the entire film. However, the difference between the actual and the measured values in all cases should be small because the total areas occupied by the pits and surface depressions were still small and the pits were mostly shallow.

Changes in thickness as a function of time exposed to three UV conditions are shown in Figure 10. Each data point given in this figure was the average of at least 20 measurements, as indicated in the experimental section. The error bars given represent one standard deviation. Little change in thickness was detected in the first 10 days of exposure to UV/humid or UV/dry condition. However, thickness started to decrease nearly monotonously between 10 and 100 days. After more than four-month exposure, the film lost nearly 37 % and 28 % of its initial thickness after exposures to UV/75%RH/50°C and UV/9%RH/50°C environments, respectively. For outdoor exposure, little change in thickness was observed for the first 25 days. Thereafter, the thickness decrease was almost linear with exposure time, reaching a thickness values for samples exposed to UV/9% RH are larger than those exposed to UV/75%RH or outdoor, indicating a greater surface topographical fluctuation in samples exposed to the dry UV environment. This is consistent with the roughness change data shown later (see Figure 13).

Morphological and Roughness Changes

Morphological changes due to exposure to three conditions can be seen in the representative AFM and LSCM images displayed in Figures 11and 12. Figures 11a, 11b, and 11c are 2D (upper row) and 3D (bottom row) AFM topographic images taking at some specific exposure times of samples exposed to UV/75%RH/50°C, UV/9%RH/50°C, and outdoor

conditions, respectively. For film exposed to the UV/75%RH condition, a surface degradation pattern was clearly observed, and the RMS roughness (from AFM 20 µm scan) of this sample has increased from approximately 7 nm \pm 1 nm for fresh material to 30 nm \pm 2 nm after 38 days of exposure. LSCM results (not shown) also showed that this UV/humidity exposure condition also caused cracking in the sample after 20 days exposure. For samples exposed to UV/9%RH condition, except the dark-color dots and strings, which were the dewetting pattern and present on the film surface before exposure, morphological changes were less visible than those of the other exposure conditions (Figure 11b). The roughness of these samples increased from approximately 7 nm \pm 1 nm for the unexposed samples to 18 nm \pm 3 nm after 45 d exposure. Outdoor-exposure samples showed a definitive localized degradation pattern (Figure 11c), which became more severe with deep pitting as the degradation progressed (10). The origin of these degradation features, which have been often observed in outdoor exposure samples for this amine-cured epoxy regardless of the exposure time, is unknown at this time. Experiments are being conducted to identify the role of condense water, the low molecular mass, polar, nodular structures observed in Figure 5, and the unreacted amine on this degradation behavior. It should be noted that RH data recorded indicated that water often condensed in the outdoor chamber during the course of exposure.

Larger surface physical changes resulting exposures are presented in Figure 12, which shows typical 450 μ m x 450 μ m scan LSCM images and their corresponding surface line profiles for three exposure conditions. Initially, the surface appeared to be smooth and featureless. As the exposure time increased, surface roughness increased and the appearance of shallow pits was observed.

Change in RMS roughness with time of exposure to three UV conditions are given in Figure 13. These roughness values were obtained from LSCM 450 µm x 450 µm scans, and each data point was the average of four measurements. As exposure time increased, the surface roughness of samples exposed to UV/75%RH exhibited several different stages: a relatively rapid rise for the first 30 days of exposure, almost unchanged between 30 and 90 days, then a sharp increase again between 80 and 120 days, and appeared constant thereafter. For samples exposed to the UV/9% RH condition, although an increase trend was clearly observed, the roughness values fluctuated so widely during the exposure that no particular pattern was

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recognized. For outdoor samples, the RMS roughness varied little in the first 30 days of exposure, but increased quite rapidly thereafter, reaching a value of 450 nm after 75 days.

The changes in surface topography, the pit formation, and the increase in surface roughness of the degraded films observed in Figures 11 to 13 clearly indicated that the degradation of this crosslinked, non-UV stabilized amine-cured coating was not a homogeneous process. This localized degradation did contribute to the overall mass loss of the films.

Relation between Thickness Loss and Chemical Changes

The relationship between the thickness loss and the FTIR intensity decreases for three different functional groups in an amine-cured epoxy coatings exposed to three UV conditions are illustrated in Figure 14. Both the thickness and IR intensity decrease were expressed as relative changes with respect to the initial values. The normalization for the initial values eliminated any errors due to variations between individual samples. The standard deviations of the data are given in the graphs of Figures 8 and 10. In Figure 14, if the film thickness loss with exposure were directly proportional to the chemical degradation, the relationship should be a straight line with a slope of 1.

For the laboratory UV exposures (which contained UV radiation below 300 nm), the three chemical degradation processes, namely chain scission (aryl-o bond at 1245 cm₋₁), mass loss (CH₂ groups at 2925 cm⁻¹), and aromatic ring loss (1510 cm⁻¹ band), followed each other quite closely. However, for the outdoor exposure, the extent of the aromatic ring loss was smaller than those of the chain scission and mass loss processes. It is clear from Figure 14 that for all three exposure conditions, the chemical degradation was more rapid than the loss in film thickness. Further, although the two parameters (thickness and chemical degradation) appeared to follow a near linear relation after an initial period, the rate of thickness change was still lower than that of the chemical degradation, with a slope of approximately 0.75. If the early stage degradation data were included for the entire degradation period, the rate of thickness change was only approximately 60 % of the rate of chemical degradation.

One question that needs to be addressed is how coatings surface topography changes during exposures would affect the measured FTIR intensity. As presented above, as the film degraded pits of various sizes developed and grew, and surface roughness increased. This surface topographic changes will scatter IR radiation during the FTIR measurement. If the topographic changes were severe, such scattering might reduce the amount of IR radiation reaching the FTIR detector. This means that the transmission ratio between the detected intensity I and the incident intensity I_o (I/I_o = T, the transmittance) should decrease due to IR radiation scattering. Since absorption is an inverse function of transmission (absorption = log (100/T), a decrease of T will result an increase of FTIR absorption of the films. Therefore, if surface topography were a factor in the FTIR intensity changes during exposure, the intensity loss/time results shown in Figure 8 represented a lower estimate, and the actual difference between the thickness loss and chemical degradation should be greater than those shown in Figure 14.

Extensive microscopic and spectroscopic results presented above for an unpigmented, unstabilized, crosslinked amine-cured epoxy coating exposed to three different UV conditions clearly showed that the rate of thickness loss was lower than that of the chemical degradation. Further, photodegradation of an amine-cured coating was not a uniform thickness reduction (ablation) but was an inhomogeneous erosion process, with formation of localized nanometer-micrometer depressions and pits. Similar difference between chemical degradation and thickness loss has been observed for unpigmented, unstabilized crosslinked acrylic-melamine and acrylic-urethane coatings (11). Therefore, using the remaining thickness data to estimate the erosion rate of polymeric coatings would likely result in an underestimate of the long-term performance of these materials.

Summary and Conclusions

Several recent studies indicated that thickness decrease of weathered unpigmented coatings films is directly proportional to their mass loss and that the residual film thickness can be used to estimate the erosion rate of polymeric coatings. This assertion is inconsistent with recent AFM results of several polymeric coating exposed to UV. This study aimed to assess the relationship between chemical degradation and thickness loss of crosslinked amine-cured epoxy coatings exposed to UV light. Surface morphological changes during photodegradation were also measured to determine the degradation mode of these coatings. Samples of an unpigmented, crosslinked, non-UV stablilized amine-cured epoxy applied to a Si substrate were exposed to outdoor and to a xenon arc light source (~275 nm to 800 nm wavelength) at 9% and 75 %RH at 50 °C condition. Chemical degradation, thickness loss, and surface physical degradation as a

function of exposure time were measured by FTIR spectroscopy, laser scanning confocal microscopy, and atomic force microcopy. The results showed that the rates of chain scission and mass loss were always greater that those of the thickness loss. Further, microscopic evidence clearly showed that degradation was not a uniform ablation thickness reduction but was a localized, inhomogeneous process, with pits formed and grew at some locations. Data on the rates of chemical degradation and thickness loss and on the surface topographic changes provided by this study should help to develop better conceptual and mathematical models for predicting the service life of amine-cured epoxy coatings. For example, because the photodegradation of this crosslinked epoxy and other coatings (10,11) is a localized, inhomogeneous process, the use of residual thickness to estimate the erosion rate is not a sound approach for predicting the service life of coatings exposed to UV radiation.

**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.

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Figure Captions

- Figure 1. Chemical structures of the components and the cured epoxy coating used in this study.
- Figure 2. A schematic of the experimental setup used for laboratory UV exposures.
- Figure 3. The chamber used for outdoor exposure, showing the exposure cells, the radiometer, and the wires connecting to the temperature and relative humidity sensors.
- Figure 4. An illustration of the principle used for determination of film thickness with laser scanning confocal microscopy.
- Figure 5. 1 µm x 1 µm AFM topographic (left) and phase (right) images of the surface (a) and the bulk (b) of the amine-cured epoxy coating used in this study.
- Figure 6. FTIR spectra taken at several times of samples exposed to three UV environments: (a) Laboratory UV/75%RH/50°C, b) Laboratory UV/9%RH/50°C, and c) Outdoor in Gaithersburg, MD.
- Figure 7. FTIR difference spectra for different times of samples exposed to three UV environments: (a) Laboratory UV/75%RH/50°C, b) Laboratory UV/9%RH/50°C, and c) Outdoor in Gaithersburg, MD.
- Figure 8. FTIR intensity changes of several FTIR bands as a function of exposure to: a) Laboratory UV/75%RH/50°C, b) Laboratory UV/9%RH/50°C, and c) Outdoor in Gaithersburg, MD. Error bars represent one standard deviation.
- Figure 9. SEM images of unexposed coated-Si cross sections at two different magnifications.
- Figure 10. Thickness changes as a function of time exposed to: a) Laboratory UV/75%RH/50 °C, b) Laboratory UV/9%RH/50 °C, and c) Outdoor in Gaithersburg, MD. Each data point was the average of 20 measurements, and the error bars represent one standard deviation.
- Figure 11. 2-D (upper) and 3-D (lower) AFM images of samples exposed to: a) Laboratory UV/75%RH/50 °C for 38d, b) Laboratory UV/9%RH/50 °C for 45d, and c) Outdoor in Gaithersburg, MD, for 40d. Root mean square roughness values are given.
- Figure 12. Laser scanning confocal microscopy images and their corresponding surface line profiles of samples exposed to: a) Laboratory UV/75%RH/50°C for 77d, b) Laboratory UV/9%RH/50°C for 64d, and c) Outdoor in Gaithersburg, MD, for 74d.
- Figure 13. Root mean square roughness obtained by LSCM as a function of time exposed to: a) Laboratory UV/75%RH/50°C, b) Laboratory UV/9%RH/50°C, and c) Outdoor in

Gaithersburg, MD. Each data point was the average of four measurements, and the error bars represent one standard deviation.

Figure 14. Relation between three chemical degradation processes and thickness loss resulting from exposures to: a) Laboratory UV/75% RH/50°C, b) Laboratory UV/9% RH/50°C, and c) Outdoor in Gaithersburg, MD. The standard variations of these data are given in Figures 8 and 10.



Curing agent: 1,3-bis(aminomethyl)cyclohexane (1,3-BAC)





Outdoor Exposure Chamber

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Figure 6







6













a







b

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