

Effects of Temperature and Humidity on the Photodegradation of TiO₂-Filled Acrylic Urethane Films

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INTRODUCTION

Metal oxide fillers, such as titanium dioxide (TiO₂), are utilized in polymeric coatings for opacification and mechanical enhancement¹. The addition of TiO₂ in polymeric coatings can also protect against UV degradation; however, the inherent photoreactivity of TiO₂ may also promote the degradation of the polymeric matrix²⁻⁴. Previous studies in our group have examined the effects of TiO₂ photoreactivity on filled polymer photodegradation under both ambient and elevated temperature and humidity conditions⁵⁻⁶. Furthermore, outdoor weathering conditions, especially temperature and relative humidity (RH), can cause severe damage to polymeric coatings^{2,4}. The combination of filler type and outdoor weathering conditions is complex and difficult to separate.

In this study, the effects of TiO₂ photoreactivity, temperature and RH on the photodegradation of an acrylic-urethane coating are examined separately. TiO₂ photoreactivity is a function of surface treatment and particle size, as well as degree of dispersion in the polymer matrix. Changes in morphology and chemistry in TiO₂/polymer films were monitored using a suite of techniques, including laser scanning confocal microscopy (LSCM) and attenuated total reflectance -Fourier transform infrared spectroscopy (ATR-FTIR), as a function of ultraviolet (UV) exposure, temperature, and RH. Accelerated photodegradation was performed with the Simulated Photodegradation by High Energy Radiant Exposure (SPHERE) device developed at the National Institute of Standards and Technology (NIST)⁷.

EXPERIMENTAL*

Materials. TiO₂ particles were selected based on their photoreactivity, which is a function of their surface treatment: TiO₂ H (d= 100 nm, no surface treatment, high reactivity), TiO₂ M (d = 250 nm, 6 % alumina surface treatment, medium reactivity) and TiO₂ L (d = 250 nm, 12 % alumina-silica surface treatment, low reactivity). Electron paramagnetic resonance (EPR) spin trap studies were used to determine that TiO₂ H was most photoreactive followed by TiO₂ M, then TiO₂ L. A 10 % pigment volume concentration (PVC) and unfilled control samples were used. The acrylic-urethane (AU) matrix was formulated using a 65: 35 ratio of styrene-acrylic polymer in N-butyl acetate (hydroxyl number: 120, S.C. Johnson Polymer) to aliphatic polyisocyanate (Bayer). Composite films were prepared by first dispersing the filler into the resin using a Dispermat (BYK Gardner) mixer and then mixing a curing agent into the suspension. AU mixtures were degassed for 1 h and films were drawn down with a 1.016 mm bar on release paper. The films were cured at room temperature for 12 h, followed by 30 min at 130 °C. Resulting film thicknesses ranged from 70 μm to 150 μm. Circular, free-standing samples having a 19 mm diameter were cut from each film.

Measurements. Exposure: AU films were exposed to UV radiation on the SPHERE using two exposure conditions: high temperature (55 °C and 0 % RH) and high humidity (30 °C and 75 % RH). The SPHERE output wavelengths were between 300 nm and 400 nm with an

average incident irradiance of 102 W/m². Complete details regarding this instrument and its configuration are found in reference 7.

Laser Scanning Confocal Microscopy (LSCM): Reflection LSCM (Zeiss LSM510) with a 543 nm laser was used to characterize coating degradation by monitoring changes in surface morphology and roughness. LSCM images are two-dimensional (2D) intensity projections, which is effectively the sum of all the light back scattered by different planar layers of the film. The pixel intensity level represents the total amount of backscattered light. Images were taken at several magnifications (5x, 50x, and 150x) and approximately 6 micrographs were obtained for each sample, with representative images reported here. The root mean square (RMS) surface roughness was determined from a (61.4 x 61.4) μm area. Details of instrument specifications and measurement protocols are given elsewhere⁸.

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR): ATR-FTIR analysis was performed on all the films using a Nexus 670 (Thermo Nicolet) with an MCT detector and an ATR accessory with a diamond crystal (Durascope). Each specimen was sampled at three different locations and 128 spectra at 4 cm⁻¹ resolution were collected and averaged at each location. Normalization of the C=O peak (1724 cm⁻¹) and the C-H peak (2935 cm⁻¹) intensities, respectively, was accomplished using

$$I_{norm}(t, 1724) = \frac{I_{t, 1724}}{I_{t, 2935}} - \frac{I_{o, 1724}}{I_{o, 2935}} \quad (1)$$

$$I_{norm}(t, 2935) = 100 - 100 * \frac{I_{o, 2935} - I_{t, 2935}}{I_{o, 2935}} \quad (2)$$

where $I_{o, 1724(2935)}$ and $I_{t, 1724(2935)}$ are the IR absorbance values at 1724 cm⁻¹ (2935 cm⁻¹) for 0 weeks and t weeks of exposure.

RESULTS AND DISCUSSION

Before UV Exposure

To effectively investigate effects of photoreactivity of TiO₂ fillers on a polymer system, TiO₂ was dispersed into the polymer without the use of dispersing agents, which may influence the polymer degradation mechanism⁹. Uniform dispersion of fillers within a polymer film is essential in achieving the maximum benefit of UV absorbance from TiO₂¹⁰. A range of particle agglomerate sizes was observed when TiO₂ was dispersed into the AU matrix used in this study⁵. Particle agglomerate sizes for TiO₂ H dispersed in AU (H-AU) samples ranged from 200 nm to 5 μm. H-AU also had a greater number of large particle agglomerates compared to M- AU and L-AU samples.

Chemical analysis of filled films prior to UV exposure showed that fillers had no effect on the resulting surface composition of the polymer films. All ATR-FTIR spectra were characteristic of cured, unfilled AU and no spectra showed evidence of exposed filler on the surface of the polymer film.

After UV Exposure

In our previous studies^{5,6}, results of photodegradation studies carried out on the SPHERE showed that a highly photoreactive filler caused degradation at the surface of a polymer film at a greater rate than a less photoreactive filler. In this study, the effects of temperature and humidity on the photodegradation of filled AU films were examined in an attempt to separate the effect of filler photoreactivity and outdoor weathering conditions. The hypothesis is that, for high humidity conditions, an increased presence of hydroxyl groups both on the filler surface and on the polymer surface for further reaction with TiO₂ radical species would promote a faster rate of polymer degradation via hydroxyl radical generation, especially for films containing highly photoreactive fillers.

LSCM was used to follow the changes in particle cluster size, polymer matrix pits/holes, and coating surface roughness over the UV exposure period. The 2D projection images in Figure 1 and 2 show a changing degradation pattern as a function of UV exposure for H-AU and L-AU films exposed to high temperature and high humidity, respectively. M-AU was visually similar to L-AU films and is not shown here. Unique patterns from fillers and pits were observed for the various filler/ polymer combinations. For all AU films, the size and

* Certain instruments or materials are identified in this paper in order to adequately specify experimental details. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for experimental procedure.

number of pits and filler clusters increase as a function of exposure time. LSCM images reveal that H-AU films were more highly degraded regardless of temperature and humidity conditions compared to the less photoreactive fillers, L and M. However, for H-AU films high humidity conditions produced greater degradation for early exposure periods, i.e. 2 weeks. This was also observed in previous studies using the same fillers and AU matrix under both high temperature and high humidity conditions⁶. Later in the exposure (≥ 4 weeks) more pits were observed for the high temperature conditions.

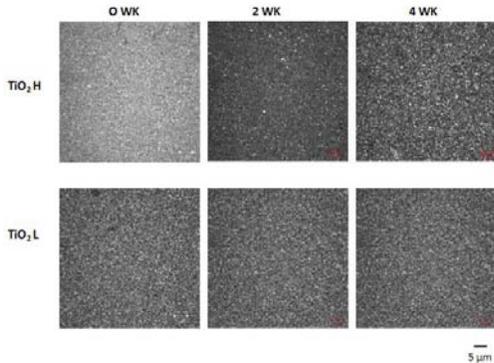


Figure 1. LSCM 2D projection images for AU films containing TiO_2 H and L as a function of UV exposure time in weeks (WK) at 55 °C and 0 % RH. All LSCM micrographs are 61 μm x 61 μm and scale bar is 5 μm .

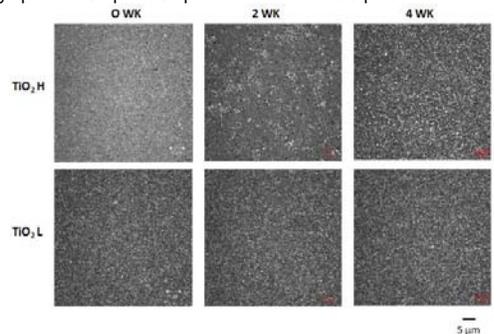


Figure 2. LSCM 2D projection images for AU films containing TiO_2 H and L as a function of UV exposure time in weeks (WK) at 30 °C and 75 % RH. All LSCM micrographs are 61 μm x 61 μm and scale bar is 5 μm .

Chemical changes in photodegraded AU films were followed with ATR-FTIR; results were observed to be consistent with the literature^{11,12}. The degree of oxidation and chain scission, respectively, was quantified by measuring the C=O stretch absorbance at 1724 cm^{-1} and C-H stretch at 2937 cm^{-1} . Figure 3 and 4 illustrate the degree of oxidation for the AU films using equation (1) for high temperature and high humidity conditions, respectively. The results show that the degree of oxidation was much greater for all AU films exposed at high temperature. For H-AU in particular, the relative change was 3 times

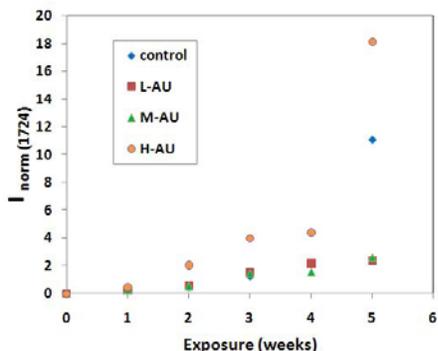


Figure 3. Normalized values for IR absorbance at 1724 cm^{-1} for control and filled AU films versus UV exposure time at 55 °C. Uncertainty in the data is $\pm 2\%$.

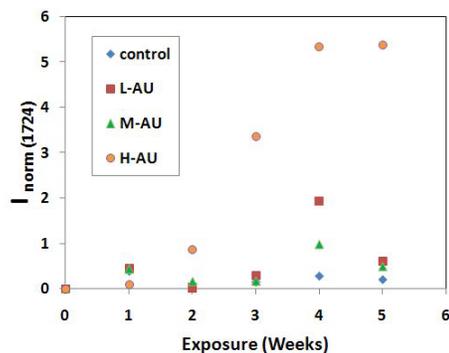


Figure 4. Normalized values for IR absorbance at 1724 cm^{-1} for control and filled AU films versus UV exposure time at 75 % RH. Uncertainty in the data is $\pm 2\%$.

greater at high temperature. Yet, a similar decrease in the 2937 cm^{-1} band (or increase in chain scission) was observed for all TiO_2 fillers at the two exposure conditions. These results show that degradation observed by monitoring chemical changes is different than that observed by monitoring morphology. That is, chemistry changes indicated greater oxidation for high temperature conditions, but morphological changes in specimens exposed at high temperature were not significantly different from those observed at high humidity, particularly at longer exposure times. Moreover, both chemistry and morphology show that the high humidity equals more photodegradation hypothesis is incorrect; i.e., for both conditions no significant differences in morphology at longer UV exposures were observed, but chemistry revealed more oxidation at high temperature.

CONCLUSIONS

Exposure of TiO_2 -filled acrylic-urethane coatings were carried out at in separate high temperature and high humidity testing to separate effects of TiO_2 photoreactivity (surface treatment and particle size) and degree of dispersion on the degradation of an AU system. LSCM was used to monitor the degradation process in filled AU films, showing that filler photoreactivity influenced the generation of pits/holes in the AU matrix. Changes in morphology were greater at earlier exposure times at high humidity, but both high humidity and temperature resulted in similar morphology (greater number of pits and protruding filler clusters) after prolonged exposure to both conditions. Chemical analysis using ATR-FTIR followed the degree of oxidation and chain scission, but trends were different from those determined from LSCM. ATR-FTIR showed greater oxidation for filled AU films exposed at high temperature. These results show that trends in degradation observed via chemistry changes can be different from those observed via morphology changes and that high humidity alone does not necessary result in greater photodegradation of filled polymer systems.

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