

Measuring Photocatalytic Response of Metal Oxide Fillers in Polymeric Films using Electron Paramagnetic Resonance Spectroscopy

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INTRODUCTION

Metal oxide fillers, such as titanium dioxide (TiO_2) are commonly used in building and construction applications. In most cases, these components are added to increase the opacity and/or improve the mechanics of a coating or plastic. The addition of TiO_2 in polymeric coatings can provide protection against UV degradation; however, the inherent photoreactivity of TiO_2 could also promote the degradation of the polymeric matrix¹. Because of complicated degradation mechanisms in polymers formulated with and without metal oxide fillers, most degradation/weathering research focuses on the fundamental understanding of changes in mechanical properties, surface morphology, and chemistry using microscopy and spectroscopy^{2,3}.

In this study, instead of utilizing conventional weathering sequences, a novel approach involving electron paramagnetic resonance (EPR) spectroscopy is used to study photodegradation in filled polymer systems. EPR is a powerful tool for identifying and monitoring changes in the concentration of free radicals, and is also capable of observing primary photochemical reactions commonly observed in the photodegradation of polymers⁴⁻⁷. The effects of TiO_2 type (i.e. surface treatment) and concentration on the degradation of two polymer systems, a degradable epoxy amine and a stable acrylic urethane, is examined. EPR spectra from filled polymer films with different loadings of TiO_2 and diverse photoreactivity are analyzed and compared to the degradation behavior of these polymer systems exposed on the Simulated Photodegradation by High Energy Radiant Exposure (SPHERE) at the National Institute of Standards and Technology (NIST)⁸.

EXPERIMENTAL*

Materials. TiO_2 particles were selected based on their reactivity, which is a function of their surface treatment: TiO_2 H ($d = 20$ nm, no surface treatment, high reactivity) and TiO_2 L ($d = 250$ nm, 12 % alumina-silica surface treatment, low reactivity). Two pigment volume concentrations (PVC), 2.5 % and 10 % were used and unfilled control samples were also prepared. The epoxy (EP) matrix was formulated using a 2.4:1 ratio of an epoxy resin based on bisphenol A diglycidyl ether (epoxide equivalent mass: 185-192, Resolution Performance Products) to polyetheramine curing agent (Huntsman). Composite films were prepared by first dispersing the pigment into the resin using a Dispermat (BYK Gardner) mixer and then mixing a curing agent into the suspension. EP mixtures were degassed for 2 h and films were drawn down with a 1.016 mm bar on release paper. EP films were cured at room temperature for 48 h, followed by 2 h at 130 °C. 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). AU mixtures were degassed for 1 h and films were prepared as above. AU films were cured at room temperature for 12 h, followed by 30 min at 130 °C. Circular free-film samples having a 19 mm diameter were cut

from each film. Resulting film thicknesses ranged from 70 μm to 150 μm .

Measurements. EPR measurements were carried out on a BRUKER BioSpin ElexSys500 spectrometer, using a square cavity (TE011 mode) operating under fixed parameter settings: microwave frequency ≈ 9.38 GHz, field modulation = 100 kHz, and microwave power = 10 mW. Each specimen was placed in a fused quartz EPR tube in the EPR cavity. A 500 W Xe Arc lamp was used as the UV source for in-situ irradiation experiments. All spectra were obtained at 77 K by sweeping the static magnetic field and recording the first derivative of the absorption spectrum. Unexposed films and empty EPR tubes were tested, respectively, for reference spectra. A weak pitch standard sample was measured under identical instrumental conditions periodically to correlate the position of EPR signals and double integrals of EPR spectra were analyzed to determine the intensity of peaks.

RESULTS AND DISCUSSION

EPR measurements were performed to detect and identify paramagnetic species or radicals present in TiO_2 -filled polymer films. Background EPR testing was conducted to confirm that signals originated from the samples rather than impurities or other artifacts. No significant EPR signals were observed from an empty EPR tube (Figure 1). With in-situ UV irradiation, a small, stable EPR signal is observed. However, it is relatively small compared to that observed in the unfilled polymers as shown in Figure 1b. The EPR signal is greater for the EP matrix, which is characteristic of UV degradable EP, but both polymers show similar constant signal when the UV irradiation ceases.

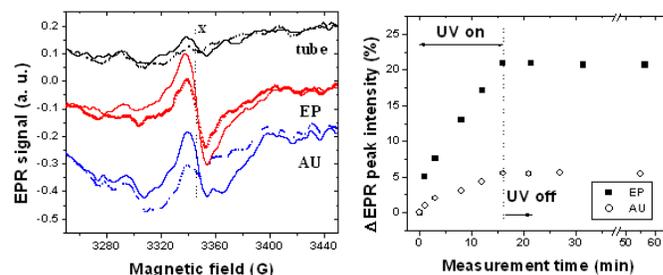


Figure 1. EPR results for controls: EPR tube and unexposed unfilled polymer films: (a) EPR spectra for controls before (dashed) and after UV exposure (solid), (b) changes in EPR intensity ($x = g = 2.003$) for control polymers with UV exposure; estimated uncertainty is 2 %.

TiO_2 particles with different reactivities, as determined by previous EPR spin trap studies⁹, were incorporated into the polymers. In addition to EPR analysis of unfilled polymer films, solid state EPR spectra of TiO_2 particles were also carried out to determine the radical contribution from each component of the filled polymer film. Figure 2 shows representative EPR spectra (taken at 77 K) for the TiO_2 particles before and after UV exposure. Prior to UV irradiation (dashed curves) each TiO_2 specimen shows weak EPR signals which are attributed to intrinsic paramagnetic species from the different crystal phases within TiO_2 . Quantities of trapped holes ($g = 2.003$) and electrons ($g < 2.0$)¹⁰⁻¹² vary greatly for the two fillers and would be expected to subsequently influence reactions with the surrounding matrix. Figure 3 shows the EPR spectra for filled EP films exposed to UV. The signal is dominated by photo-induced holes and electrons. For EP/ TiO_2 H, the EPR signal shape varies greatly with filler concentration and more trapped electrons appear to be generated in the 2.5 % film. This could be the result of non-uniform dispersion of filler in the film. For 10 % TiO_2 H, the EPR signal shape appears similar to that of the EP/ TiO_2 L films. In contrast, EPR signal shape remains the same for EP/ TiO_2 L and the intensity generally increases with increasing TiO_2 concentration.

* 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.

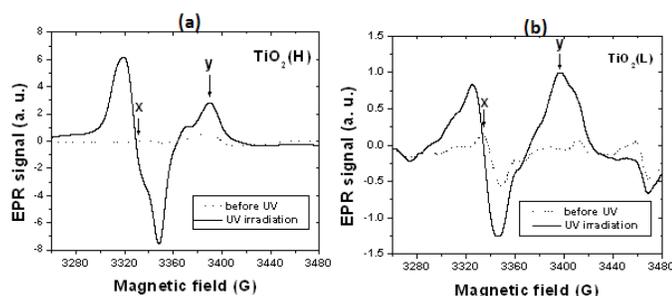


Figure 2. EPR spectra for (a) TiO_2 H and (b) TiO_2 L; dashed = before UV, solid = after UV exposure, x: $g = 2.011$, y: $g = 1.977$.

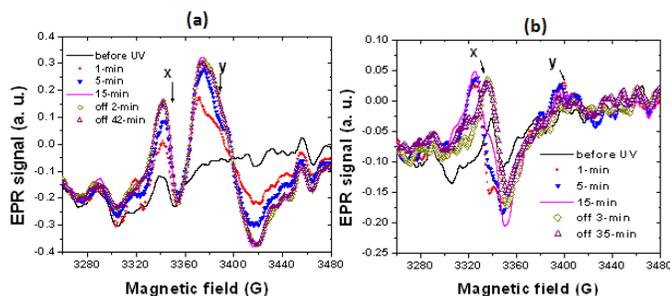


Figure 3. Time-dependent EPR spectra for filled EP films with UV exposure: (a) 2.5 % TiO_2 H, (b) 2.5 % TiO_2 L, x: $g = 2.011$, and y: $g = 1.977$.

Figure 4 shows changes in EPR signal intensity for trapped holes ($g = 2.003$) in filled EP films with lower TiO_2 concentration as a function of UV irradiation time. For more reactive TiO_2 H, the EPR signal increases markedly with UV irradiation time and plateaus at the highest level after UV irradiation ceases. Conversely, less reactive TiO_2 L shows a much lower rise in intensity with UV irradiation time, which falls to near zero after UV irradiation ceases. Similar trends were observed for trapped electrons ($g = 1.971$) in these EP films with lower TiO_2 content. Figure 4 shows that for EP/ TiO_2 H films more radicals are present during and after UV exposure, which could cause degradation to the surrounding polymer, while EP/ TiO_2 L has a much lower radical concentration, resulting in less degradation. Thus, from examination of the EPR signals for trapped holes, EP/ TiO_2 H would be expected to be more susceptible to UV degradation than the EP/ TiO_2 L film. Laser scanning confocal microscopy (LSCM) and Fourier Transform Infrared (FTIR) spectroscopic analysis of UV degraded filled EP films validate the hypothesis that EP/ TiO_2 H undergoes greater chemical degradation than EP/ TiO_2 L. Trends for EPR data from EP films with greater TiO_2 concentration (not shown) are not as simple to determine as for EP films with lower TiO_2 content. Normalization of the EPR data and consideration of both trapped hole and electron concentrations are necessary to predict the degradation of EP/ TiO_2 H films.

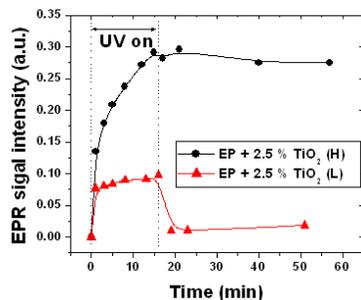


Figure 4. Changes in EPR intensity ($g = 2.011$) as function of UV exposure for EP samples with 2.5 % TiO_2 H and TiO_2 L. Estimated uncertainty is 2 %.

EPR data for filled AU films (not shown) reflect the durability of this polymer: increases in the intensity of EPR signal with UV exposure are about half of that observed for filled EP films. Variations in hole concentration trends are also observed as TiO_2 content increases, particularly for TiO_2 H. These results suggest that trapped hole analysis alone is not sufficient to predict the durability of filled polymers, and that the properties of the polymer matrix also need to be taken into account. Consequently, the lifetime or stability of photo-induced trapped holes or electrons generated in filled polymer films exposed to UV can be correlated to the recombination rate of the photo-induced carriers, which in turn impacts the UV durability of the filled polymer.

CONCLUSIONS

EPR spectroscopy is a useful tool for characterizing the dynamics of paramagnetic species generated in TiO_2 filled EP and AU polymer films during UV irradiation. EPR spectra of the unfilled polymer controls showed that radicals are produced from the polymer matrix itself, but the EPR signal from TiO_2 during in-situ UV experiments is dominant for filled polymer films. The EPR spectra of UV-irradiated TiO_2 -filled polymers display signals which are characteristic of trapped holes and electrons. The type and concentration of TiO_2 particles as well as the surrounding polymer matrix influence the structure and quantity of these trapped holes and electrons, which are monitored by peak position or g factor in EPR spectra. Stability of photo-induced EPR spectra for filled polymer systems represents recombination rates of photo-induced charges and correlates to durability. A more degradable filled polymer displays more intense trapped hole signals implying that the holes are more efficiently trapped. These trapped charges are one key factor in photocatalytic reactions of TiO_2 metal oxide fillers.

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