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 matrix$^{1}$. 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 polymers$^{4,7}$. 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 studies$^9$, 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.
exposure: (a) 2.5 % TiO₂ H, (b) 2.5 % TiO₂ L; x: g = 2.011, and y: g = 1.977.

Figure 4 shows changes in EPR signal intensity for trapped holes from EP films with greater TiO₂ concentration (not shown) are not as simple to determine as for EP films with lower TiO₂ content. Trends for EPR data for filled polymer systems represent 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 TiO₂ metal oxide fillers.

CONCLUSIONS

EPR spectroscopy is a useful tool for characterizing the dynamics of paramagnetic species generated in TiO₂ 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 TiO₂ during in-situ UV experiments is dominant for filled polymer films. The EPR spectra of UV-irradiated TiO₂-filled polymers display signals which are characteristic of trapped holes and electrons. The type and concentration of TiO₂ 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 TiO₂ metal oxide fillers.

REFERENCES