

Studying Long-term Performance of a Nano-ZnO filled Waterborne Polyurethane Coating using Spectroscopies and Microscopies

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Abstract: Although inorganic UV absorbers such as zinc oxide (ZnO) and cerium oxide (CeO₂) exhibit numerous advantages compared to organic UV absorbers, the mechanisms of how these nanoparticles affect the long-term performance of polymeric coatings are less than clear. Researchers have different views on this issue. In this study, the effect of ZnO nanoparticles on the performance of a waterborne polyurethane coating exposed to UV radiation was assessed and the photodegradation mechanism involved with ZnO nanoparticles was investigated. Specimens of nano-filled polyurethane thin films were prepared by spin casting a mixture of waterborne polyurethane with different loadings of waterborne ZnO dispersion onto calcium fluoride substrates. Exposure was carried out on the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) at both dry (0% RH) and humid (75% RH) conditions at 45 °C. The chemical degradation was examined by FTIR and UV-visible spectroscopies. Changes in surface morphology were characterized by confocal microscopy, atomic force microscopy (AFM), electric force microscopy (EFM) and scanning electron microscopy combined with energy dispersive X-ray spectroscopy microanalysis (SEM/EDX). The results clearly showed that the photo-catalytic effect of ZnO nanoparticles was dominant in the photodegradation of the studied nano-filled polyurethane system. This effect was greatly influenced by the loadings of the nanoparticles and the relative humidity of the exposure environment. The origin of the photo-catalytic effect of ZnO nanoparticles was further investigated by electron paramagnetic resonance (EPR) spectroscopy.

Introduction:

Recent development in nano-particle technology prompts the use of inorganic UV absorbers such as zinc oxide (ZnO) and cerium oxide (CeO₂) for UV protection due to their unique UV absorbing abilities and versatile functionalities. However, the mechanisms of how these nanoparticles affect the long-term performance of polymeric materials are less than clear. In fact, the contributions of these metal oxide nanoparticles to UV protection of the polymeric matrix are complicated as a result of their photoreactivity. For ZnO nanoparticles, both photo-catalytic and UV protection effects have been reported.^{1,2} In this paper, we investigated the effect of ZnO nanoparticles on the performance of a waterborne polyurethane coating under UV exposure. Nano-filled polyurethane thin films were prepared with different

loadings of ZnO nanoparticles. The exposure was conducted on the NIST SPHERE at different relative humidities at 45 °C. Chemical changes of the films were examined by Fourier Transform Infrared Spectroscopy (FTIR) and UV-visible spectroscopy. Changes in surface morphology were characterized by confocal microscopy, AFM, electric force microscopy (EFM) and SEM combined with energy dispersive X-ray spectroscopy microanalysis (SEM/EDX). Further, the photoreactivity of ZnO nanoparticles is studied by electron paramagnetic resonance (EPR) spectroscopy to understand the origin of the photocatalytic effect of ZnO nanoparticles on the photodegradation of the polymers.

Experimental[‡]:

Materials and Specimen Preparation

A waterborne dispersion of ZnO nanoparticles (NANOBYK-3820, BYK) and a waterborne dispersion of polyurethane (PU, Bayhydrol 110, Bayer Material Science) were selected for this study. The average diameter of the ZnO nanoparticles was 20 nm (provided by manufacturer). ZnO nanoparticle/PU films (hereafter referred to as ZnO/PU) were prepared by mixing the PU dispersion with different loadings of ZnO dispersion using a mechanical stirrer (Dispermat, VMA). Thin films having a thickness of approximately 6 μm were prepared by spin coating onto calcium fluoride (CaF₂) substrates at 209 rad/s (2000 rpm) for 30 s. All films were dried overnight under ambient conditions, followed by an oven post-cure at 150 °C for 10 min.

High UV Radiant Laboratory Exposure

The UV exposure of ZnO/PU films was conducted on the NIST SPHERE, a 2 m-diameter integrating sphere-based weathering chamber at 45 °C, 0 % RH and 45 °C, 75 % RH. The details about the exposure in the SPHERE can be found elsewhere³. The exposed specimens were removed every 3-4 days for characterization. To study the photolytic effect of nanoparticles, specimens were also exposed at the same temperature and RH conditions in the absence of UV radiation.

Fourier Transform Infrared Spectroscopy (FTIR) and UV-visible Spectroscopy

Chemical degradation of the ZnO/PU films coated on CaF₂ was measured by a FTIR spectrometer (Nicolet Nexus 670x) equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. The UV-visible absorption spectra of the specimens were recorded between 190 nm and 820 nm at a resolution of 2 nm, using an HP 8452a UV-visible spectrometer. The details of the FTIR and UV-visible spectroscopic measurements can be found elsewhere³.

Atomic Force Microscopy (AFM) and Electric Force Microscopy (EFM)

A Dimension 3100 AFM (Veeco Metrology) was used to image the morphology and the microstructure of the nano-ZnO filled PU before and after UV exposure. The AFM was operated in the tapping mode using commercial silicon probes (TESP 70, Veeco Metrology). Successive AFM measurements were performed at essentially the same locations on the specimen to facilitate the study of morphological changes occurring in the films as a function

[‡] Instruments and materials are identified in this paper to describe the experiments. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST).

of UV exposure. EFM was conducted on the same AFM using a conducting Pt coated EFM probe (Olympus AC240-TM) with two pass scanning techniques.

Results:

Chemical degradation of ZnO/PU films during UV exposure was characterized by transmission FTIR. Figure 1 displays the intensity change of representative FTIR bands as a function of exposure time for ZnO/PU films with different ZnO loadings. The decreases in the intensities of the bands at 1732 cm^{-1} and 1528 cm^{-1} are corresponding to the losses of C=O stretching of the ester group, amide II band (mostly due to NH bending) and C-O-C stretching, respectively, indicating that the chain scission and mass loss have taken place in the PU molecules during UV exposure. An increase in the intensity of the band at 1756 cm^{-1} is attributed to the formation of acetylurethane linkage (O=C-NH-C=O) due to the oxidation of urethane groups. The rates of both chain scission and acetylurethane formation increase with increasing ZnO nanoparticle loadings. The FTIR data (not shown) from specimens exposed to the same conditions without UV light shows that the effect of the nanoparticles on the degradation is very small. These results clearly indicate the photo-catalytic effect of ZnO nanoparticles on the PU degradation. This photo-catalytic effect is observed for both dry ($45\text{ }^{\circ}\text{C}$, $0\text{ }\% \text{RH}$) and wet ($45\text{ }^{\circ}\text{C}$, $75\text{ }\% \text{RH}$) conditions during UV exposure. Additionally, as shown in Figure 1d, such a photo-catalytic effect appears to be significantly enhanced by high RH at $5\text{ }\%$ ZnO loading.

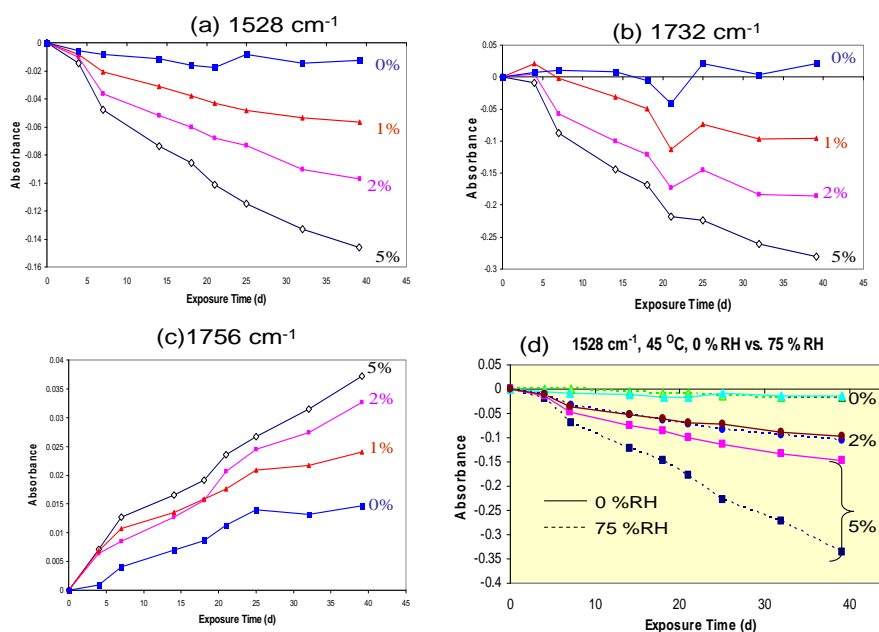


Figure 1. Plots of FTIR intensity changes at (a) 1528 cm^{-1} , (b) 1732 cm^{-1} , and (c) 1756 cm^{-1} as a function of exposure time to SPHERE at $45\text{ }^{\circ}\text{C}$, $0\text{ }\% \text{RH}$ for ZnO/PU films containing $0\text{ }\%$, $1\text{ }\%$, $2\text{ }\%$, and $5\text{ }\%$ ZnO by mass; (d) a comparison of FTIR intensity loss at 1528 cm^{-1} as a function of exposure time for ZnO/PU films containing $0\text{ }\%$, $2\text{ }\%$ and $5\text{ }\%$ ZnO exposed to SPHERE at $45\text{ }^{\circ}\text{C}$, $0\text{ }\% \text{RH}$ and $45\text{ }^{\circ}\text{C}$, $75\text{ }\% \text{RH}$. Each data point in this figure is the average of four specimens. The standard deviation is less than $\pm 5\text{ }\%$ of the average value.

The morphological changes of ZnO/PU films exposed to SPHERE at $45\text{ }^{\circ}\text{C}$, $75\text{ }\% \text{RH}$ for 2 months are displayed in Figure 2. All specimens exhibit a smooth surface before UV exposure (Figure 2a). After UV exposure, however, substantially different topographic features are observed for ZnO/PU films with different ZnO loadings. A surface degradation pattern with circular pits is observed for pure PU. For an exposed $2\text{ }\%$ ZnO/PU film, a

number of protruding clusters with heights approaching 300 nm are observed. A further EFM study (not shown) on the clusters indicates that they are mostly composed of ZnO nanoparticles with some aggregates. For 5 % ZnO/PU film, a very rough surface is observed after UV exposure. The RMS roughness of this surface is approximately 208 nm (based on 50 $\mu\text{m} \times 50 \mu\text{m}$ scan size), which is much higher than that of the 2 % ZnO/PU films (12.4 nm) and the pure PU films (7.4 nm) exposed to the same condition. The SEM-EDX and FTIR data (not shown) indicate that this degraded surface is dominated by the ZnO aggregates after severe degradation of PU. These morphological changes are consistent with the chemical degradation.

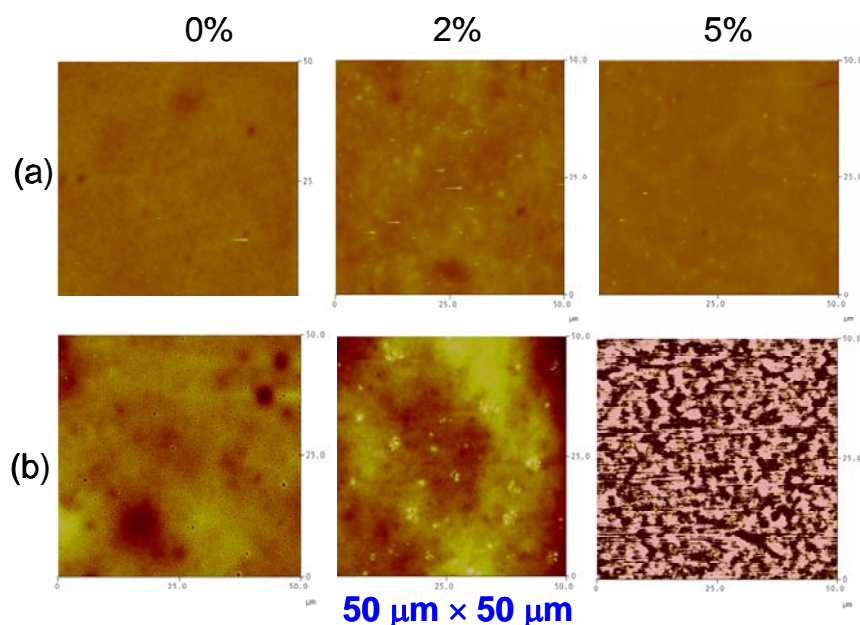


Figure 2. AFM height images of ZnO/PU films containing 0 %, 2 % and 5 % ZnO nanoparticles by mass (a) before and (b) after exposure to SPHERE at 45 °C, 75 % RH for 2 months. The measurement was performed at approximately the same location for the same specimen. Scan size is 50 $\mu\text{m} \times 50 \mu\text{m}$ and the height scale is 100 nm.

Conclusions:

The effect of ZnO nanoparticles on the performance of a waterborne polyurethane coating under UV exposure has been investigated. Both chemical degradation and morphological changes indicated that the ZnO nanoparticles behaved as photo-catalysts, accelerating the photodegradation of the PU. The photo-catalytic effect of ZnO nanoparticles was enhanced at a higher nanoparticle loading and an elevated RH of the exposure environment. Based on the results of this study, one should be cautious when predicting long-term performance of a polymer containing a nanosize inorganic UV absorber.

References:

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