

Linking Degree of Filler Dispersion to Photodegradation Rate in a NanoTiO₂-latex Coating: An Accelerated Weathering Study

Li-Piin Sung, Yongyan Pang, and Stephanie S. Watson

Polymeric materials Group, Materials and Construction Research Division, Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899

Introduction

Poor filler dispersion is often blamed for deficiency in appearance, mechanical properties, and life cycle performance of polymeric systems. Many studies have been carried out to investigate the effect of TiO₂ on photodegradation of polymeric composites [1-5]. Clerici et al. [2] investigated the effect of pigmentary TiO₂ dispersion on the durability of epoxy coating. Dispersant was employed to prepare "well dispersed" and "poorly dispersed" specimens, and the different dispersion states were found playing a significant role in polymer degradation process. Wang et al. [3] investigated the effect of TiO₂ pigment type in terms of surface treatment and particle size, and its dispersion on the photodegradation of filled coatings. In their work, nanosize TiO₂ with high photoreactivity and microsize TiO₂ with low photoreactivity were used in polymeric coatings, and diverse dispersion states were obtained. It was found that both particle dispersion and photoreactivity had significant effect on the degradation of the polymeric coatings. Specimens with poor particle dispersion and highly photoreactive pigments exhibited the most severe degradation, while little or no degradation occurred in films with good particle dispersion and pigments with low photoreactivity. Based on these studies, particle dispersion and photoreactivity were proven to be significant factors affecting polymer degradation process. However, until now, the effect of nano-TiO₂ dispersion on photodegradation has not been thoroughly addressed.

The objective of this study is to investigate the influence of the filler dispersion of nano-TiO₂ in polymeric coatings on the morphology evolution of coatings under ultra-violet (UV) exposure. Two types of nano-TiO₂ with different surface treatments were chosen to mix into a water-borne butyl-acrylic styrene latex coating to generate different dispersion states. Two accelerated weathering conditions: wet (30 °C and 75 % relative humidity (RH)) and dry (30 °C and 0 % RH), were selected to investigate the effect of humidity on morphology development of polymeric coatings. Laser scanning confocal microscopy (LSCM) was used to characterize filler dispersion and monitor the surface morphological changes in the latex coatings during the UV exposure. Surface roughness of larger areas and localized degradation of polymer matrix around large nanoparticle clusters were investigated. It was found that morphology evolution patterns were strongly affected by nanofiller dispersion, and that severe degradation was observed around large particle clusters. Photodegradation was much faster under wet condition than under dry condition. The displacement between polymer-air surface and nanoparticle cluster front as a function of exposure time was obtained to estimate the local degradation rate at a given exposure condition.

Experimental[#]

Materials and Sample Preparation. Two commercially available nanoparticles were chosen for this study: P25 TiO₂ (Evonik Degussa Corporation) (designated as P_A) and VHP-D TiO₂ (Altair) (P_B). The reported particle diameters for P_A and P_B from the manufacturer were about 25 nm and 35 nm, respectively. There is no surface treatment for P_A, but an organic treatment was used for P_B. The polymer matrix is a water-borne butyl-acrylic styrene latex (UCAR 481 from Dow Chemical) (latex). Particle-filled coating films were prepared using a high-speed mixer and a draw-down application on release paper. Detailed sample

[#] 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 the experimental procedure.

preparation, processing, and curing conditions were reported elsewhere [6]. The particle volume concentration (PVC) was 5 % in this study. Final thickness of dry films was ca. 80 μm.

Laser Scanning Confocal Microscopy (LSCM). A Zeiss model LSM510 reflection laser scanning confocal microscope (LSCM) was used with a laser wavelength of 543 nm to characterize the surface morphology and nanoTiO₂ spatial distribution on surface and near the surface. A detailed description of LSCM can be found elsewhere [7-8]. LSCM images are effectively the sum of all the light backscattered by different planar layers of the coating, as far into the film as light is able to penetrate and scatter to collecting optics. Some of the LSCM images presented in this study are 2D projections, formed by summing the stack of images over the z direction (512 pixel x 512 pixel) of the coatings. The pixel intensity level represents the total amount of back-scattered light.

UV Exposure. Film specimens were mounted to a sample holder and exposed using an advanced indoor accelerated UV weathering chamber, the Simulated Photodegradation by High Energy Radiant Exposure (SPHERE) device at National Institute of Standards and Technology [9]. The SPHERE makes it possible to generate ultra-high UV radiation intensity and thus the accelerated photodegradation of specimens is achieved. The SPHERE is equipped with different chambers which allow for individually controlled conditions of temperature, humidity, and UV exposure. In this study, two exposure conditions were selected: a wet condition (30 °C and 75 % RH) and a dry condition (30 °C and 0 % RH). After each period of UV exposure, surface and subsurface morphological changes in the nanosize TiO₂ filled coatings were characterized at sequential intervals using LSCM.

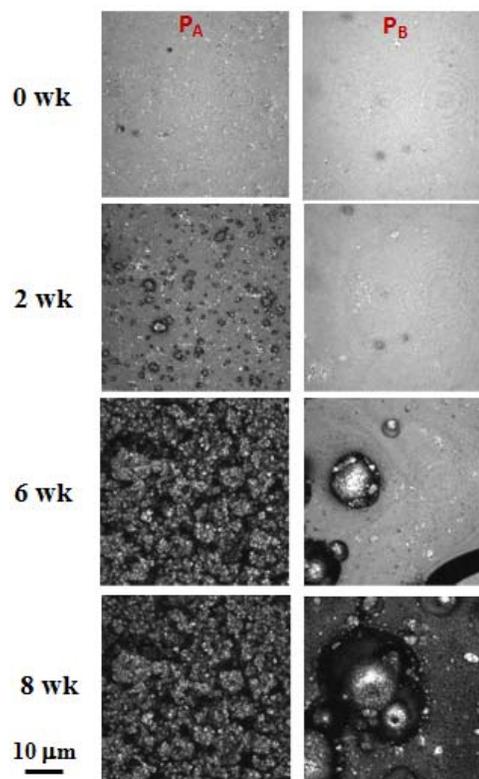


Figure 1. 2D LSCM images of topographical evolution of latex coatings with P_A and P_B during UV exposure under wet condition. The scale bar is 10 μm. Each image size is 56.1 μm x 56.1 μm.

Results and Discussion

Nanofiller dispersion characterization were described in previous reports [10-11]. In summary, in terms of particle cluster size and spatial distribution, P_A-particles were distributed uniformly near the

surface; while P_B -particles were loosely packed, showing few larger particle cluster buried inside the coatings. A thick clear layer (filler-poor) exists in the P_B -latex system, similar to the "poorly dispersed" coatings in reference 2. The heterogeneity in multi-scale microstructure and the thickness of the clear layer due to different states of filler dispersion were expected to strongly affect the durability of latex coatings, especially under UV exposure.

Figure 1 shows the topographical evolution for latex coatings containing P_A and P_B during UV exposure at wet condition at different exposure times. The measurements were carried out at the same location with a total scanned area of $56.1 \mu\text{m} \times 56.1 \mu\text{m}$. The surface morphology of latex- P_A coating did not show significant change at week 1 (not shown here), but degradation around particle clusters began from about week 2. From this point, topographical features, i.e. dark regions, began to appear around these particle clusters, and they grew larger with UV exposure. By comparison, the morphology evolution of the blank latex coating after an 8-week period of UV exposure showed no significant surface morphological change compared to the unexposed specimen. The degradation pattern of latex- P_B coating was different from that of latex- P_A . The topographical morphology of latex- P_B coating did not change significantly under UV exposure before week 4, due to the fact that the P_B clusters were buried in the latex coatings and that the erosion first happened at the clear layer. After the erosion of the clear layer, the particle clusters appeared, and the dark-region (valley-like) features grew larger around larger particle clusters.

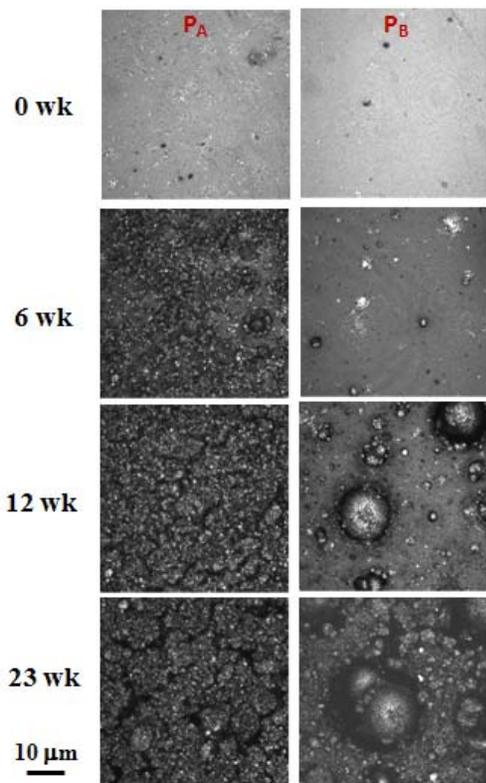


Figure 2. 2D LSCM images of topographical evolution of latex coatings containing P_A , and P_B during UV exposure under dry condition. The scale bar is $10 \mu\text{m}$. Each image size is $56.1 \mu\text{m} \times 56.1 \mu\text{m}$.

Figure 2 displays the topographical evolution for latex coatings under the dry condition. For latex- P_A coating, the evolution of topographical patterns under dry condition appeared similar to that under wet condition, but the degradation rate was much slower. The degradation of latex- P_B coating was quite non-uniform, and severe local degradation was found around large particle clusters. The development of surface and subsurface structural features was similar

as that of latex - P_B coating under wet condition, and the degradation process was much slower as well.

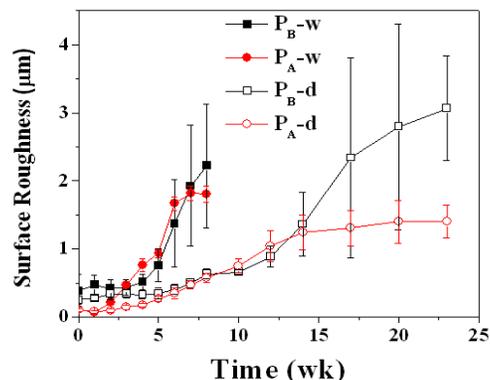


Figure 3. Surface roughness as a function of UV exposure time for latex coatings containing P_A and P_B during UV exposure under wet and dry conditions. The error bar represents the standard deviation from the average of 4 measurement areas.

In summary, it was found that the morphology changes during UV exposure under wet and dry conditions were similar for latex coatings containing the same type of nanoparticles. It was also found that morphology evolution patterns were strongly affected by nanofiller dispersion, and that severe degradation was observed around large particle clusters. To quantify the degradation rate, two approaches were taken: (1) using the averaged surface roughness values (as shown in Figure 3) calculated from many larger areas to estimate the global degradation rate, and (2) using the displacement between polymer-air surface and particle cluster front (as seen in the latex- P_B coatings) as a function of exposure time to estimate the local degradation rate. Results and detailed discussion will be presented in the meeting.

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