An innovative approach to construct photodegradation curves for TiO₂ incorporated latex coatings via probing localized degradation

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ABSTRACT

The main objective of this study was to establish a new approach to construct local photodegradation curves for TiO₂ incorporated latex coatings via innovatively probing polymer photodegradation in the vicinity of nanoparticle agglomerates using laser scanning confocal microscope (LSCM) under a wet and a dry conditions. First, nanoparticle dispersion in surface/subsurface of latex coatings was investigated with LSCM. Second, 2D LSCM images were used to show how nanoparticles were gradually revealed with UV exposure. Third, 3D and ortho LSCM images were applied to illustrate how polymer surface was gradually decreased and how the polymer/nanoparticle interface regions were gradually degraded. The ortho images were also used to calculate the relative vertical height change in polymer matrix and in interface regions referred to the front of nanoparticle agglomerates. Finally, local photodegradation curves in the polymer matrix and in the interface regions were obtained under the wet and dry conditions by plotting the relative changes in height as a function of the UV exposure time. By comparison of the local photodegradation curves in different stages, at different locations and under different exposure conditions, it was found that under UV radiation, after the exposure of nanoparticles onto polymer surface, the photocatalytic effect of nanoparticles could significantly affect the photodegradation of the interface of filled coatings, which would result in severely inhomogeneous photodegradation, especially under the wet condition.

Keywords: Photodegradation; Titanium dioxide; Laser scanning confocal microscope;

Latex coating; Local photodegradation curve

1. Introduction

Polymeric coatings have been extensively used on infrastructure, automobiles and furniture for appearance, protection or decoration purposes. Nanoparticles are widely used in polymeric coatings for many applications where good mechanical performance and appearance are required [1-5]. Titanium dioxide (TiO_2) has been one of the mostly used particles due to its availability, non-toxicity and chemical stability. However, polymeric coatings are susceptible to outdoor exposure, like ultra-violet (UV) radiation, moisture and heat. Incorporation of photoactive TiO_2 would accelerate photodegradation of polymer binders under these weathering variables, and thereby would significantly shorten the durability and service life of the materials in end uses [5-9].

Many studies have been carried out to investigate the effect of TiO_2 on photodegradation of polymeric coatings in terms of particle dispersion and photoreactivity [5, 7, 8]. Wang et al. [7] reported that both particle dispersion and photoreactivity of TiO_2 exerted a significant impact on surface/subsurface morphology change of acrylic-urethane (AU) and epoxy coatings. Clerici et al. [8] reported that the dispersion of pigmentary TiO_2 in epoxy resins prominently affected morphology change and gloss loss. Our previous study [5] showed that the dispersion of nano-sized TiO_2 significantly affected the photodegradation patterns of AU coatings. Based on the previous literature [5, 7, 8], it has already been well accepted that the incorporation of photosensitive TiO_2 could prominently impact the polymer degradation, while the studies thus far have not thoroughly addressed an important

issue that how it quantitatively affects the degradation rate of polymeric coatings. Recently, Gu et al [4] found that polymer/nanoparticle interface played a critical role in photostability in nanoparticle incorporated coatings. Thus, clarification of photodegradation rates in the polymer/nanoparticle interface regions and in the nanoparticle-poor polymer matrix would be of great significance to quantitatively understand the polymer photodegradation processes of filled coatings.

To study how the polymer photodegradation rate is quantitatively affected by nanoparticles, it is very important to build up the photodegradation curves under the exposed condition. Based on the previous literature [5, 10, 11], polymer photodegradation curves could be obtained by following chemical changes as a function of the UV exposure time. Numerous studies [10-15] have reported that Fourier transform infrared spectroscopy (FTIR) in the transmission mode was employed for quantitatively characterizing photodegradation for unfilled polymer coatings. However, FTIR in the transmission mode is generally inapplicable to characterize the chemical changes of filled coatings, as the coatings are usually too opaque due to the incorporation of fillers for IR radiation to go through. Attenuated total reflectance-FTIR (ATR-FTIR) is collected by scanning sample surface in the reflection mode, and may be suitable to study the chemical changes for filled coatings in the early-stage degradation, when the sample surface still remains quite smooth [5, 7]. For the late-stage degradation, the intensity of chemical changes obtained using ATR-FTIR usually deviates largely in values due to the severely increased surface roughness, and thus cannot reliably or accurately represent the real changes. Thus, up

to now, it still remains a challenging task to construct photodegradation curves for filled coating systems over a long period of UV exposure.

As a nondestructive tool, laser scanning confocal microscope (LSCM) has always been applied by researchers at NIST to study the nanoparticle dispersion in polymer coatings and also the surface/subsurface morphology change during polymer degradation [5, 7, 8, 13, 16]. It could be imagined that for filled polymer coatings, if a nanoparticle agglomerate could be used as a reference, the relative vertical height change in nanoparticle-poor polymer matrix and in polymer/nanoparticle interface regions after UV exposure could be obtained by using LSCM to follow the localized photodegradation in the vicinity of the nanoparticle agglomerate. If this would be proved feasible, the local photodegradation curves could be obtained for the filled coatings by plotting the relative vertical height changes as a function of the UV exposure time. Thus, a new approach could be established for generating local photodegradation curves for filled coatings, which has been demanded for a long while due to the failure of chemical monitoring means.

The objective of this study was to establish a new approach to construct local photodegradation curves for nanosized TiO₂ incorporated latex coatings under UV exposure by using LSCM. One type of nanosized TiO₂ was selected to mix into a water-borne butyl-acrylic styrene latex coating to generate a desired dispersion state with large nanoparticle agglomerates. Two accelerated weathering conditions: wet (30 °C and 75 % relative humidity (RH)) and dry (30 °C and 0 % RH), were selected to study the effect of humidity on the photodegradation process and rate of the

coatings. LSCM was used to characterize the TiO_2 dispersion and monitor the surface/subsurface morphological changes after UV exposure, particularly the localized polymer degradation in the vicinity of large agglomerates in the latex coatings. Local photodegradation curves in the nanoparticle-poor polymer matrix and in the polymer/nanoparticle interface regions were constructed for both the wet and dry conditions by plotting the relative vertical height changes referred to the agglomerate front as a function of the UV exposure time.

2. Experimental section[#]

2.1. Materials and sample preparation

Commercially available VHP D nanosized TiO_2 used in this study was supplied by Altair. According to the manufacturer, the crystal form was anatase and the crystal size was approximately 35 nm in diameter, with an organic treatment on the surface. The nanoparticle was labeled as P_C in this study.

The polymeric matrix used in this study was a waterborne butyl-acrylic styrene latex (UCAR 481, Dow Chemical) coating. Nanoparticles were incorporated into the latex coatings at a particle volume concentration (PVC) of 5%. The TiO_2 incorporated latex films (named as “latex- P_C ” in this study) were prepared according to the latex E2216-C formulation, which can be found in the previous documents [17, 18]. The latex solution with nanoparticles was mechanically mixed, followed by a drawdown

[#] 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.

application on release paper, and then the wet films were dried under ambient conditions for one week prior to use. The dry films were ca. 80 μm in thickness.

2.2. UV exposure experiments

The film specimens were first mounted in a sample holder and then were exposed in an accelerated UV weathering chamber, the NIST SPHERE (Simulated Photodegradation by High Energy Radiant Exposure) [19, 20]. The UV flux was produced by a mercury arc lamp system. UV radiation below 290 nm was eliminated by mounting a cut-off filter in the optical path between the lamps and the interior of the SPHERE. Most portions of the visible light and infrared radiation emitted from the lamps were removed through installing dichroic reflectors in the lamps. UV flux of approximately 480 W/m^2 in the range of 290 nm and 400nm was used to accelerate photodegradation of the exposed specimens. High uniformity of the UV irradiance was guaranteed with the integrating sphere-based technology. In this study, a wet condition (30 °C and 75 % RH) and a dry condition (30 °C and 0 % RH) were selected to degrade the specimens with UV radiation. Specimens were removed from the chambers at sequential intervals for measurements.

2.3. Laser scanning confocal microscopy

A Zeiss LSM510 reflection laser scanning confocal microscope (LSCM) with regular lens was used to characterize the TiO_2 dispersion in the surface/subsurface of the latex coating. A detailed description about the mechanism and functions of LSCM can be found in the previous literature [16, 21]. The laser wavelength used was

543 nm and the images at a magnification of 150x were taken with a z -step of 0.2 μm . To eliminate the strong reflection from polymer surfaces and obtain images with a clear nanoparticle dispersion, an oil lens with a magnification of 100x was also employed. LSCM images presented in this study about nanoparticle dispersion were two dimensional (2D) projection images in the xy and xz planes, and a single frame depth-profile image in the xy plane. The 2D projection image in the xy plane (512 pixel $\times$ 512 pixel) was formed by summing a stack of the images in the z direction, while the 2D lateral projection image in the xz plane was projected in the y direction. The depth profile was selected from the stack of the images to display the nanoparticle dispersion 3 μm underlying the polymer surface.

LSCM was also used to characterize the surface/subsurface morphology change of the latex coatings after photodegradation. A custom-designed stage was equipped to LSCM to reproducibly image the same location on the specimens. The 2D projection images in the xy plane were used to show the surface/subsurface morphology change. The 3D LSCM images and the ortho images in the xz plane were constructed and projected from the corresponding 2D image stack, respectively. The 3D and ortho images were used to show the change of polymer surface in height relative to the nanoparticle agglomerates and the polymer photodegradation in the polymer/nanoparticle interface regions after UV exposure.

3. Results and discussion

3.1. Nanoparticle dispersion in surface/subsurface of latex coating

The TiO_2 dispersion in surface/subsurface of latex- P_C coating before UV exposure was investigated with LSCM (Figure 1). The images in Figure 1a-c were obtained with a regular lens (used in air) while that in Figure 1d was obtained with an oil lens (immersed in oil). Nanoparticles were invisible in the 2D projection image in the xy plane (Figure 1a) due to the strong light reflection from polymer surface. The depth profile in the xy plane (Figure 1b) showed some large and small nanoparticle agglomerates buried within polymer layers. The lateral image in the xz plane (Figure 1c) was then applied to illustrate the nanoparticle dispersion in the z direction. It was observed that many large nanoparticle agglomerates were formed deeper in the coating, due to that the agglomerates tended to sink within the wet films after the drawdown application. This resulted in a thick clear layer at the polymer surface. According to the previous literature [22], a clear layer was referred as a layer of pigment-poor or unpigmented medium formed at the surface of pigment incorporated coatings. In addition, the image in Figure 1d clearly showed that large nanoparticle agglomerates with small ones were dispersed in the coating. Formation of large agglomerates was desired in this particular study to more easily monitor and also to more clearly show the polymer photodegradation in the vicinity of the large agglomerates. A schematic in Figure 1e illustrates the nanoparticle distribution and the clear layer formation in the latex coating. The label Z indicates the depth that laser light can penetrate within the coating. The nanoparticle distribution is revealed by detection of the backscattered laser light. A clear layer formed on the top surface was indicated by a blue box. Note that it was specially described the formation of the clear

layer and the underlying large nanoparticle agglomerates in the latex coating, as the photodegradation rates in the underlying nanoparticle-poor polymer matrix and the polymer/nanoparticle interface regions could be different from that of the clear layer.

3.2. Nanoparticle revealing under UV exposure

For monitoring the surface/subsurface morphology changes under UV exposure, LSCM was applied as a nondestructive technique at sequential intervals. 2D projection images in Figure 2 were used to show the morphology changes at the same location of latex- P_C coating under the wet and dry conditions. For the latex- P_C coating under the wet condition without UV exposure (week 0 of Figure 2a), no features were observed except for some surface defects created during the film formation. The nanoparticle agglomerates beneath the polymer surface were invisible due to the strong light reflection from polymer surface. As P_C agglomerates were buried deep in the latex coatings, the clear layer was the first regions attacked by UV radiation. The erosion of the clear layer of the latex- P_C coating was similar as the photodegradation of the unfilled latex coatings (not shown here), without surface features being formed. After the gradual erosion of the clear layer, the front of nanoparticle agglomerates emerged onto polymer surface at around week 4 under the wet condition, and in the meantime, surface features started to appear (Figure 2a), i.e., degradation patterns reflected by the exposure of nanoparticle agglomerates and the severe polymer degradation in the surrounding interface regions. It indicated that the polymer photodegradation of the nanoparticle incorporated coatings could be seen as a process

of gradual revealing of the nanoparticles buried within the polymer matrix. After the exposure of nanoparticles onto polymer surface, polymer photodegradation had showed different characteristics between the nanoparticle/polymer interface regions and the nanoparticle-poor polymer matrix. As the photodegradation proceeded, on one hand, nanoparticle agglomerates were revealed more in number and bigger in size, and on the other, polymer degradation in the interface regions were observed more obvious and more severe (week 6 and week 8 of Figure 2a). The polymer photodegradation in the latex- P_C coating under the dry condition is shown in Figure 2b. By comparing the degradation patterns under the wet and dry conditions, it was found that the nanoparticle agglomerates were revealed in similar manners under both conditions, indicating similar degradation processes.

3.3. Polymer surface change in height during photodegradation

As discussed above, polymer surface could decrease in height relative to the nanoparticles under the UV radiation, and polymer photodegradation in the nanoparticle/polymer interface regions was more severe compared to that in the nanoparticle-poor polymer matrix. To more clearly illustrate these phenomena, probing localized polymer photodegradation in the vicinity of large nanoparticle agglomerates as a function of the UV exposure time was believed to be an innovative and feasible approach.

The 3D LSCM images and the corresponding surface height profiles of latex- P_C coatings at week 0 and week 8 under the wet condition are shown in Figure 3. The

surface height profiles represent the surface height change of the cross-section, indicated with red lines on the 3D images. At week 0 (in a_1 and b_1), the nanoparticle agglomerate was buried within the polymer, while at week 8 (in a_2 and b_2), the nanoparticle agglomerate was exposed onto polymer surface, with its front above the polymer surface and the surrounding polymer matrix severely degraded. The results confirmed that the polymer surface did decrease in height, and that the polymer/nanoparticle interface was more vulnerable to UV radiation.

To display the gradual decrease of the polymer surface height relative to the nanoparticle agglomerate and the gradual polymer degradation in the interface regions, ortho images obtained using LSCM were applied. Ortho images are composed of three 2D projection images: in the xy plane (top view), xz plane (side view) and yz plane (side view), respectively. In the present study, the ortho images in the xz plane, i.e., lateral profiles, were employed in Figure 4 of the latex- P_C coating under the wet and dry conditions. The nanoparticle agglomerate front was placed at the same height level, as indicated by a red straight line. Thus, the polymer surface height change can be revealed more markedly. For the wet condition (Figure 4a), the polymer surface was higher than the nanoparticle agglomerate front before week 4, about the same height at week 4, and then lower after. For the dry condition (Figure 4b), the polymer surface was above the nanoparticle agglomerate front before week 4, and the latter was about to emerge onto polymer surface at week 4. After week 4, the polymer surface became gradually lower and lower than the nanoparticle agglomerate front. Under both conditions, after the exposure of the nanoparticle agglomerates onto

polymer surface, a faster polymer photodegradation was observed in the interface regions relative to the polymer matrix.

3.4. Photodegradation curves constructed via probing localized polymer degradation

3.4.1. Local photodegradation curves in nanoparticle-poor polymer matrix

Based on the discussions above, the photodegradation rates in the nanoparticle-poor polymer matrix and polymer/nanoparticle interface regions would be different. To understand how nanoparticles quantitatively affects the photodegradation processes of the latex coatings, local photodegradation curves of nanoparticle-poor polymer matrix and the interface regions in the vicinity of large nanoparticle agglomerates will be built under both the wet and the dry conditions.

Local photodegradation curves in the nanoparticle-poor polymer matrix could be generated by plotting the relative height change of polymer surface that was flat (e.g., d_8 on Figure 4a for wet and d_{23} on Figure 4b for dry) versus the UV exposure time. The schematic in Figure 5a of the lateral view of a large nanoparticle agglomerate within polymer matrix was drawn to more clearly describe how to build the local photodegradation curves. The position of the nanoparticle agglomerate front was defined as 0 in z direction, with the assumption that the large nanoparticle agglomerate remained unmoved during the experiment. The vertical displacement from the flat polymer surface to the nanoparticle agglomerate front was defined as positive if the polymer surface is higher than the nanoparticle agglomerate front, and negative if otherwise. The displacement was obtained via multiplying the interval of

slices (0.2 μm in this study) and the number of slices from polymer surface to the agglomerate front in the image stack. When the polymer surface is higher than the nanoparticle agglomerate front, the laser light penetrated in polymers. The corresponding positive displacement was corrected by multiplying a coefficient of 1.5, which is an approximate reflective index of polymers. The local photodegradation curves of the nanoparticle-poor polymer matrix in the vicinity of the large nanoparticle agglomerates of latex- P_C coatings were thereby generated by plotting the displacement as a function of the UV exposure time under both the wet and the dry conditions (Figure 5b).

It is shown in Figure 5b that before week 4, the trend of the local photodegradation curves was similar under the wet and dry conditions, with no significant difference observed except for a slight faster rate under the former condition. From week 4 on, the polymer photodegradation under the wet condition became much faster relative to that under the dry condition. Some previous studies have already shown that higher humidity could accelerate photodegradation or hydrolysis [5, 10, 23-28]. In this study, for the dry condition, even after the TiO_2 agglomerate was exposed onto the polymer surface, the polymer photodegradation in the nanoparticle-poor polymer matrix was not significantly accelerated. However, for the wet condition, after the exposure of the nanoparticle agglomerate onto polymer surface, the polymer photodegradation in the nanoparticle-poor polymer matrix was dramatically accelerated. It could possibly be due to the synergistic effect between UV radiation and water, the washing way effect of water, and the photocatalytic effect

of the small nanoparticle agglomerates accumulating and/or migrating on the polymer surface under the wet condition, etc [5, 10].

3.4.2. Local photodegradation curves in polymer/nanoparticle interface region

To construct the local photodegradation curves in the polymer/nanoparticle interface regions, the same strategy was adopted as above, using the relative vertical height change of one spot in the interface region (e.g., d_8' on Figure 4a for wet and d_{23}' on Figure 4b for dry) as a function of UV exposure time. To compare the photodegradation rates of the polymer matrix and the interface region in the vicinity of big nanoparticle agglomerates under both wet and dry conditions, all the relevant local photodegradation curves were plotted in Figure 6.

For the wet condition, before the nanoparticle was exposed onto polymer surface, the photodegradation rates in clear layers were observed similar on the local photodegradation curves. It was speculated that when the nanoparticle agglomerate was still buried within the polymer matrix, the photocatalytic effect of TiO_2 on polymer degradation was inhibited due to limited exposure to UV radiation and humidity, and the polymer photodegradation was probably mainly caused by UV radiation. In comparison, after the nanoparticles emerged onto polymer surface, severe polymer photodegradation in the interface regions were observed. It was interpreted that with UV exposure, TiO_2 was immediately photoexcited, generating electrons and positive holes. The electrons and holes reacted with oxygen and water to form $\text{OH} \cdot$, which is highly reactive in initiating and accelerating polymer

photodegradation, thus resulting in severely degraded interface regions [5, 6, 29-31]. However, it was observed from the local photodegradation curves in Figure 6 that, from week 4 to week 7, the photodegradation rates were similar for the nanoparticle-poor polymer matrix and the interface region and a faster photodegradation rate was observed in the interface region only after week 7. It was believed to be due to the position in the interface regions taken as the spot to monitor the relative vertical height change. It could be imagined that, if it was chosen closer to the nanoparticles, the photodegradation curve constructed of the interface region would show a faster photodegradation rate sooner relative to that of the polymer matrix. Otherwise, if it was farther away from the nanoparticles, the photodegradation curve constructed of the interface region would almost overlap with that of the polymer matrix over a long UV exposure time before a larger degradation rate could be observed. It makes sense that the local photodegradation curves constructed in this study in the vicinity of nanoparticle agglomerates are closely dependent on the localized environments, especially for those of the interface regions. It could be interpreted that large variations of photodegradation in the interface regions (see Figure 4) would arise from many factors, such as the size of the nanoparticle agglomerate, the interfacial adhesion and the distance away from the nanoparticle agglomerate, etc. Therefore, after the exposure of the nanoparticle agglomerate onto polymer surface, the photodegradation rate in the interface region would generally be larger than that of the polymer matrix, but it could vary from spot to spot.

For the dry condition, by comparing the local photodegradation curves in the

nanoparticle-poor polymer matrix and in the interface regions, similar trends were observed as those under the wet condition. Similar as the wet condition, after the exposure of the nanoparticle agglomerate onto polymer surface, the local photodegradation curves in the polymer matrix and in the interface almost overlapped during week 4 to week 12, while after week 12, the photodegradation rate of the interface was observed relatively faster than that of the polymer matrix.

It is also meaningful to compare the local photodegradation curves of the interface regions under the wet and dry conditions. After the exposure of the nanoparticle agglomerates onto polymer surface, the photodegradation rate in the interface regions were generally faster under the wet condition. This phenomenon was not quite obvious just after the exposure of the nanoparticle agglomerates observed on the local photodegradation curves in Figure 6. The reason was that the spots taken from the interface regions for calculating the vertical height change were not very close to the nanoparticles. However, it is still not clear about the thickness of the interface layers that could be attacked by the photocatalytic effect of nanoparticles, which could be affected by the size of the nanoparticle agglomerate, the time expand of UV exposure, and the exposure conditions, etc. Anyway, after the nanoparticle agglomerates merged onto polymer surface, the photodegradation rate in the polymer/nanoparticle interface regions was generally faster under the wet condition, thus resulting in more severely degraded interface regions. Therefore, water has proved as an important factor in accelerating photocatalytic effect of TiO_2 incorporated latex coatings. Similar results have also been reported in the previous

studies [32, 33] documenting that the photocatalytic reaction in TiO_2 incorporated polymer composites mainly occurred at polymer surface layers due to lack of water in polymer matrix, thus resulting in a low photodegradation rate. A novel degradable polypropylene system was designed via addition of poly(ethylene oxide) (PEO) microcapsule containing TiO_2 [32]. PEO can absorb water from environments due to its hydrophilic characteristics, and thus more $\text{OH}^\bullet$ could be produced under UV radiation to speed up the photodegradation.

3.5. Nanoparticles in affecting photodegradation processes

With understanding of the photodegradation characteristics and rates in the clear layers and in the underlying nanoparticle-poor polymer matrix and the polymer/nanoparticle interface regions (Figures 4-6), it would help to more deeply understand the photodegradation process of the filled coatings. The photodegradation of the latex-Pc coating could be approximately seen as an erosion of the clear layer and a subsequent severely inhomogeneous process. The latter one was a combination of the erosion in nanoparticle-poor area and severe polymer photodegradation in the interface regions around the nanoparticle agglomerates once after the nanoparticle agglomerates emerged onto the polymer surface [12, 13, 26, 34].

Schematics were drawn in Figure 7 to more clearly illustrate the photodegradation processes in the vicinity of a large nanoparticle agglomerate in the nanoparticle incorporated coatings in the xz plane (lateral view) and xy plane (top view). Before UV exposure (Figure 7a), a nanoparticle agglomerate was buried within

polymer layers, which can be seen in the xz plane but not in the xy plane. After a short period of UV exposure (Figure 7b), the thickness of the clear layer was decreased, but the nanoparticle agglomerate was still buried within polymer layers and did not emerged onto polymer surface. With a longer period of UV radiation (Figure 7c), the clear layer was eroded and the front of the nanoparticle agglomerate was exposed onto polymer surface. With prolonged UV radiation (Figure 7d), the polymer surface continued to decrease, and severe polymer photodegradation occurred in the polymer/nanoparticle interface regions. Thus, the nanoparticle agglomerate was revealed bigger in size in the top view, with surrounding polymer interface regions severely degraded. With a further longer period of UV exposure (Figure 7d), the polymer surface was decreased in height even more, and the degraded interface regions was further enlarged.

Based on the results and discussions above, the photodegradation processes of the nanoparticle incorporated coatings showed very different characteristics in the underlying polymer bulks relative to that in the clear layer. It was probably due to the severely inhomogeneous polymer photodegradation arising from the different photodegradation rates in the nanoparticle-poor polymer matrix and in the polymer/nanoparticle interface regions, and the faster photodegradation rate in the interface was attributed to the photocatalytic effect of the nanoparticles. The results in this study could well explain the phenomena in the previous literature [35-38], which documented that the surface appearance showed different changes during weathering in clear and pigmented coatings. Hence, systematic studies as well as deep

understandings of the effect of nanoparticle on the photodegradation rate of filled coatings possessed great significance to quantitatively understand the photodegradation processes under different exposure conditions. Therefore, the meaning of this study lies in: it innovatively established the local photodegradation curves via probing polymer photodegradation in the vicinity of nanoparticle agglomerates and thus quantitatively showed the differences of the photodegradation processes in the clear layer and the underlying nanoparticle-poor polymer matrix and the polymer/nanoparticle interface regions in the nanoparticle incorporated coatings. This approach could be applied to many other filled coatings. This way, more weather-resistant nanoparticle incorporated coatings could be designed for applications, and occupation of the active sites of the nanoparticles via surface treatment to inhibit the photoreactivity could be a feasible way to reduce the polymer photodegradation in the interface regions.

4. Conclusions

Local photodegradation curves in the nanoparticle-poor polymer matrix and in the polymer/nanoparticle interface regions were innovatively constructed for the TiO₂ incorporated latex coatings under the wet and dry conditions by plotting the relative vertical height change referred to the front of large nanoparticle agglomerate as a function of UV exposure time. LSCM was applied as a nondestructive tool to sequentially probe the localized polymer photodegradation in the vicinity of large nanoparticle agglomerates after UV exposure. The effect of nanoparticles on the

photodegradation rates of the filled coatings under different conditions was thus quantitatively revealed through comparing the polymer photodegradation in the clear layers and the underlying nanoparticle-poor polymer matrix and the interface regions. It was found that under UV radiation, after the nanoparticles were exposed onto polymer surface, the photocatalytic effect of the nanoparticles would lead to a relatively larger photodegradation rate in the interface regions compared to the polymer matrix, which thus resulted in severely inhomogeneous photodegradation patterns. Based on the understanding of the effect of nanoparticles on the photodegradation rate of the filled coatings, the polymer/nanoparticle interface regions could be very vulnerable to UV radiation due to the photocatalytic effect of the nanoparticles. The approach in this study to construct local photodegradation curves using LSCM could be applied to quantitatively evaluate polymer photodegradation and thus to design more weather-resistant nanoparticle incorporated coatings.

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Figure 1. LSCM images of latex- P_C coating before UV exposure: (a) a 2D projection image in the xy plane, (b) a depth profile at 3 μm in the xy plane, (c) a 2D projection image in the xz plane (lateral view), (d) a 2D projection image in the xy plane obtained with oil lens, and (e) a schematic of laser penetration in the latex coating. The blue dashed line box represents the clear layer of the latex coating. Images (a), (b) and (c) were obtained with regular lens.

Figure 2. 2D projection LSCM images of the morphological change of the latex-P_C coatings after UV exposure under the (a) wet and (b) dry conditions.

Figure 3. (a_1 and a_2) 3D LSCM images and the corresponding (b_1 and b_2) surface height profiles of the latex- P_c coating at week 0 and week 8 after UV exposure under the wet condition. The surface height profiles represented the surface height change of the cross-section indicated with red lines on the 3D images.

Figure 4. Ortho LSCM images (lateral view, in the xz plane) of the latex-PC coatings after UV exposure under the (a) wet and (b) dry conditions. The nanoparticle agglomerate front was placed at the same height level as indicated by a red straight line.

Figure 5. (a) A schematic of a lateral profile and (b) the local photodegradation curves of the nanoparticle-poor polymer matrix obtained in the vicinity of large nanoparticle agglomerates in the latex- P_C coatings after UV exposure under the wet and dry conditions. The position of the nanoparticle agglomerate front was defined as 0 in z direction, and the displacement calculated by the vertical height change between the flat polymer surface and the nanoparticle agglomerate front was defined as positive if the polymer surface was higher than the nanoparticle agglomerate front, and negative otherwise.

Figure 6. Comparison of the local photodegradation curves of the nanoparticle-poor polymer matrix and the polymer/nanoparticle interface regions in the vicinity of large nanoparticle agglomerates in the latex- P_C coatings after UV exposure under the wet and dry conditions. The displacements were obtained by calculating the vertical height change between the flat polymer surface or a location in the interface regions and the nanoparticle agglomerate front.

Figure 7. Schematics of polymer photodegradation processes of nanoparticle incorporated polymeric coatings in the xz plane (lateral view) and xy plane (top view). (a) to (b) represent gradually prolonged UV exposure time.