# Microscopy approaches to assess surface morphological changes of graphene oxide/waterborne polyurethane coatings exposed to UV radiation

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Graphene oxide (GO) nanofillers have been incorporated into polymeric coatings and composites to improve mechanical, barrier, and thermal properties of the system. This study aims to develop methods for investigating and assessing surface morphological changes of waterborne polyurethane (WBPU) coatings containing GO under different UV exposure conditions to understand how the GO nanofillers affect the integrity of coating surface and eventually long-term performance of the coatings. Morphological changes are important to track because they can alter a protective coatings appearance as well as barrier, scratch, and crack-resistance properties. Specimens of GO/WBPU coatings with different GO mass loadings were exposed to high intensity ultraviolet (UV) light using the NIST (National Institutes of Standards and Technology) SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) device at 55 °C and two relative humidity (RH) levels ( $\approx 0$  % and 75 %). Laser scanning confocal microscopy (LSCM), atomic force microscopy (AFM), and scanning electron microscopy (SEM) were used to characterize the surface morphological changes at different UV exposure times and conditions. The general approach was to use LSCM optical method to quickly screen the surface morphological changes of samples in multiscale, then zoom into a smaller scanning area to identify GO particles versus polymer features on UV-degraded surfaces using AFM and SEM. In addition, AFM in Peak Force QNM mode (quantitative nanomechanical property) mapping was used to measure increases in surface modulus to validate the presence of GO particles at the surface that accompanied the surface morphological changes. Overall, a combination of microscopic methods was found useful to assess the change in surface morphology of GO/WBPU coatings, and to understand the effect of GO particles on degradation behavior under different exposure conditions. This approach can be employed for other polymer coatings that incorporate graphene nanomaterials.

Key words: AFM; Coatings; Graphene oxide; Laser scanning confocal microscopy; nanofiller; waterborne polyurethane; UV

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# Introduction

Due to its excellent mechanical, electrical, and thermal properties, graphene-based materials [1-3] have been incorporated into polymeric coatings and composites to improve multifunctional properties of polymeric systems. However, unmodified graphene materials are costly, hydrophobic, chemically inert, and tend to aggregate during mixing with hydrophilic polymers [4-6]. Graphene oxide (GO) can be produced in large quantities by thermally or chemically oxidizing low cost graphite, followed by separation/exfoliation of the resulting graphite. GO becomes more compatible with a variety of polymeric matrices due to the presence of oxygen functional groups. Because of its high solubility in water and good dispersion in aqueous media, GO has also been investigated as a promising nanofiller for water-soluble polymers [7-14] for improving materials performance. For this reason, we have incorporated GO into water-borne polyurethane (WBPU) coatings for our studies. Water-borne polyurethane (WBPU) has been increasingly used in many applications, because it is environmentally friendly and has a number of properties such as good adhesion to a variety of substrates, high abrasion resistance, and good weathering resistance[15,16]. GO is an attractive nanofiller for WBPU because of its good dispersion in water, exceptional mechanical properties, low permeability, strong interactions with various functional groups in WBPU, and low cost. Recent results from our laboratory have demonstrated that GO material prepared by the Hummers method [17] was well dispersed in a one-part, water-based aliphatic polyurethane and imparted great improvement in mechanical modulus and thermal properties [18, 19].

Despite research that shows greatly enhanced short-term performance with GO nanofillers, little information is available on either the long-term performance or surface damage under environmental stresses during the service life. The advantage of adding GO nanofillers into WBPU coatings is to enhance abrasion/scratch, corrosion (as barrier to water intake) and weathering resistance. However, the coating surface is often the first target during degradation process initiated by ultraviolet (UV) radiation or mechanical stressors (via scratch and abrasion). Surface damage (abrasion, scratch, cracking) of coatings can lead to changes in optical, morphological, and mechanical properties, and can result in pathways for ingress of moisture and corrosive agents. Therefore, it is important to track and assess the integrity of the coating surface during the service life. A previous study from our laboratory revealed that the presence of GO

appeared to decrease the photo-oxidation of WBPU by UV radiation with the formation of a GO layer on the UV-irradiated GO nanocoating surfaces [19]. These results were like those for other UV-degraded nanocoatings containing other types of nanoparticles [20-24]. The main objective of the present study is to assess the detailed surface morphological changes during exposure of GO/WBPU coatings to UV radiation under dry and humid conditions, to understand how GO nanofillers affect the integrity of coatings surface and eventually the long-term performance of the coatings. Both neat WBPU and GO/WBPU coatings were exposed to a high intensity UV radiation at 55 °C and two relative humidity levels (0 % and 75 %) in a well-controlled UV environmental chamber (NIST SPHERE). The results of chemical degradation, mass loss, and spectroscopic measurements of GO particle accumulation were reported elsewhere [25]. This report focuses on the investigation and assessment of nanocoating surface morphological changes under different UV exposure conditions using a variety of complementary microscopic techniques. Furthermore, the study will show how this combination of microscopy techniques, which has been successfully used on other nanocomposites, can be applied to other graphene family nanomaterial/polymer composites. Specifically, methods to quickly screen the surface morphological changes of samples and identify GO particles versus polymer features are highlighted.

# **Experimental**

## Materials and sample preparation

Graphene oxide (GO) was prepared using the Hummers's method [17]. The exfoliated GO sheets had a thickness of 0.8 nm to 1.5 nm and lateral dimensions of 1  $\mu$ m to 2  $\mu$ m as measured by atomic force microscopy of a spin casted, diluted GO suspension on a silicon wafer. More characterization data for this GO material can be found elsewhere [19]. GO was blended into waterborne polyurethane (WBPU, one-part aliphatic WBPU, Bayhydrol 110, Covestro, Pittsburgh, PA) at two mass fractions, 0.4 % and 1.2 % (dry mass of GO relative to dry mass of WBPU material). The GO/ WBPU films had a thickness of 127  $\mu$ m ± 3  $\mu$ m and the neat WBPU films had a thickness of 97  $\mu$ m ± 3  $\mu$ m, as measured with cross-sectional scanning electron microscopy (SEM) at least five randomly chosen cross-sections from three replicates. The numbers after ± are one standard deviation from the average of five randomly chosen crosssections from three replicates measurements. Detailed sample preparation and SEM measurements are described elsewhere [25].

## UV Exposure Experiments

Coating specimens were mounted in a sample holder and exposed using an advanced accelerated ultraviolet (UV) -weathering chamber: the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) [26]. The SPHERE generates high intensity UV radiation and allows accelerated photodegradation of exposed specimens to be carried out. The SPHERE is equipped with environmental chambers in which temperature, humidity, and UV spectral irradiance can be individually controlled. In this study, exposure conditions were at 55 °C with two relative humidity (RH) levels ( $\approx 0$  % and 75 %) for time periods ranging from 15 d to 140 d, which is the equivalent to UV doses (irradiance • time) of 181 MJ/m<sup>2</sup> to 1693 MJ/m<sup>2</sup>. Although a direct comparison to outdoor weathering time cannot be made due to the presence of complex weather patterns, the equivalent exposure time to outdoors in South Florida (280 MJ/m<sup>2</sup> = 1 year) was 0.64 years to 6.05 years in terms of UV dose only. In parallel, coating specimens were also exposed to the same conditions without the UV light. Surface mechanical and morphological changes in the GO/WBPU coatings were measured at sequential intervals using laser scanning confocal microcopy (LSCM), atomic force microscopy (AFM), and scanning electron microscopy (SEM).

### Characterization of Surface Degradation and Morphological Changes

Surface morphological changes were characterized by laser scanning confocal microscopy (LSCM, Zeiss model LSM 510, Thornwood, NY, reflectance mode, 543 nm), atomic force microscopy (AFM, Bruker Dimension Icon AFM, Billerica, MA), and scanning electron microscopy (SEM, JEOL 7600f, 6.0 kV, Peabody, MA). Thickness loss was measured with cross-sectional SEM with at least three SEM images were measured per specimen and at least five cross-sectional lengths were measured per SEM image. Triplicate specimens were used for each of these microscopy measurements. At each exposure time, one specimen of each GO loading was removed sacrificially for AFM and SEM measurements. These specimens were first imaged with LSCM,

AFM followed by SEM since the addition of a conductive coating was required for SEM imaging. The surface morphological change and root-mean-square surface roughness values ( $S_q$ ) were measured using LSCM and AFM at three randomly chosen locations. The measurement uncertainties are one standard deviation calculated from at least three replicate images of different coatings area.

### Characterization of Surface Elastic Modulus

AFM in peak force quantitative nanomechanical mode (PF-QNM) was used to quantitatively map surface topography and elastic modulus of the neat WBPU and GO/WBPU nanocoating surfaces. PF-QNM atomic force microscopy (AFM) could precisely control the forces applied to the sample and limit the indentation to several nanometers in most cases, which facilitated high resolution data collection with minimal sample damage. PF-QNM measurements were performed on a Bruker Dimension Icon AFM (Billerica, MA) equipped with silicon probes (TESP, Bruker) at ambient conditions. The probe RTESPA-300 was selected in this work based on the Young's modulus range of samples. Unlike traditional tapping mode where the feedback loop keeps the cantilever vibration amplitude constant, PF-QNM controls the maximum force (peak force) on the tip. The PF-QNM technique is non-destructive to the AFM tips and samples when parameters are tuned correctly, and allows for adhesion, modulus, dissipation, and deformation to be distinguished [27, 28]. The tip radius was calibrated using the relative method [28] by scanning a standard polystyrene sample with a known elastic modulus of 2.7 GPa. An oscillation frequency of 2 kHz was used. AFM images with  $(256 \times 256)$  pixels and a size of 50  $\mu$ m  $\times$  50  $\mu$ m were measured. Modulus was obtained by fitting the retract curve using the Derjaguin-Muller-Toporov (DMT) model [29]. This model considers the adhesion force and is appropriate when the deformation of the sample is lower than the tip radius. The modulus distribution across the surface could be quantified by the bearing analysis, which generated the average modulus of each area on the surface and the corresponding proportion of the total area. All PF-QNM-AFM measurements were taken in at least three different areas of a given specimen. All reported measurement uncertainties are one standard deviation from the average of three replicates measurements

# **Results and Discussion**

#### Initial Surface Characterization

GO/WBPU coatings at 0 % mass fraction, 0.4 % mass fraction, and 1.2 % GO mass fraction were characterized using AFM and LSCM for surface morphology before UV irradiation. Figure 1 displays surface morphology of GO/WBPU coatings at 0 % mass fraction, 0.4 % mass fraction, and 1.2 % GO mass fraction at four different scan sizes as indicated in the figure caption. The scratch/wear patterns on the surface of neat WBPU control coatings (0 %) were greatly reduced with addition of 0.4 % GO and disappeared on the surface of 1.2 % GO/WBPU coatings at 5x magnification. Without the addition of GO nanofillers, the coatings surface was easily damaged through handling. This observation indicates that GO nanofillers improve the scratch resistance of GO/WBPU coatings. Note that all coatings had similarities in surface roughness: neat WBPU had a roughness of 0.35  $\mu$ m  $\pm$  0.05  $\mu$ m while 0.4 % mass fraction and 1.2 % mass fraction GO/WBPU had a similar roughness of 0.41  $\mu$ m  $\pm$  0.10  $\mu$ m and 0.44  $\mu$ m  $\pm$  0.08  $\mu$ m, respectively in 169 µm x 169 µm images (the 2<sup>nd</sup> column in Figure 1). The reported measurement uncertainties are one standard deviation from the average of at least three measurements from different locations and different samples. The similarities in the LSCM results of both the neat WBPU and GO/WBPU samples surface indicated that polymer features were predominantly responsible for the initial surface roughness in both coatings.

At higher magnification (150x, measured area 56  $\mu$ m x 56  $\mu$ m, the 3<sup>rd</sup> column in Figure 1), there are many particle-like features protruding on the surfaces. It appears that the size of the particles and clusters are larger on the surface of 1.2 % GO/WBPU coatings when compared with the neat WBPU. Note that LSCM images presented in this paper are two-dimensional X-Y intensity projection (an image formed by summing the stack of images over Z- direction). The scanning depth Z values are estimated to be around 200  $\mu$ m at 5x magnification (measured area 1700  $\mu$ m), around 20  $\mu$ m to 30  $\mu$ m at 50x magnification (measured area 169  $\mu$ m x 169  $\mu$ m), to around 7  $\mu$ m to 10  $\mu$ m at higher magnification (150x), depending on the surface roughness. The LSCM images capture surface and subsurface microstructures, while the scanning height limitation of AFM is around 6  $\mu$ m. A comparison of AFM (the 4<sup>th</sup> column) and LSCM (the 3<sup>rd</sup>)

column) images indicates that consistent particle-like and cluster-like features are present. Furthermore, SEM images indicated similarly rough polymer surface features for both the neat WBPU control and the GO/WBPU coatings (shown later) respectively.

#### Surface Morphological Changes after UV Exposure

GO/WBPU coatings were exposed to accelerated UV weathering under dry (55 °C, 0 % RH) and humid conditions (55 C, 75 % RH) for 15 d, 30 d, 60 d, and 140 d in the NIST SPHERE. Surface morphological changes were tracked with LSCM, AFM, and SEM. In this general approach, LSCM optical method was used to quickly screen the surface morphology of samples in multiscale first, then AFM and SEM were used to identify GO particles versus polymer features on the UV-degraded surfaces in a smaller scanning area.

Figure 2 displays LSCM images of degraded GO/WBPU coatings after 140 d exposure to (a) dry UV (b) humid UV conditions at three GO mass fractions (0%, 0.4%, 1.2%). The images of parallel controlled experiments under dark conditions (no UV) are also presented for comparison. For the dry UV exposure conditions, all surfaces became smoother after 140 d (compared to the LSCM images in the 2<sup>nd</sup> column of Figure 1), except for the 1.2 % mass fraction GO/WBPU coatings. It appears that some subsurface microstructures are present within the 1.2 % coatings (later confirmed by AFM images). Under dark dry conditions, the changes were minor, likely due to just thermal effects. Compared with LSCM images of the initial surfaces in the 2<sup>nd</sup> column of Figure 1, the surface morphological changes at humid UV conditions (as well as at humid dark) were different from that under dry UV conditions. All surfaces appeared smooth and no larger protruding particle-like features were observed at the surface, but some particle-like features appeared in the sub-surface. Note that thickness loss (by cross-sectional SEM) was measured around 50  $\mu$ m ± 10  $\mu$ m for neat and 1.2 % GO/WBPU coatings after 140 d exposed to humid UV conditions, while there was little thickness loss after 140 d exposure under dry UV conditions [25]. Under humid dark conditions, the sample surfaces smoothed out more than sample surfaces exposed to dry dark conditions.

As mentioned previously, LSCM is an optical measurement in which images capture the light scattering from subsurface structures (around 20  $\mu$ m to 30  $\mu$ m below the surface at 50x

magnification) and the degree of light scattering depending on the optical contrast of the composition of coatings and surface roughness. With this technique, it is challenging to identify the location and depth of microstructures. To more closely examine the surface morphological changes in GO/WBPU after the UV irradiation, SEM and AFM measurements were made. Figure 3 displays topographic AFM images of 0.4 % mass fraction GO/WBPU coatings surfaces exposed to dry UV and humid UV conditions for 0 d, 30 d, 60 d, and 140 d. The corresponding surface roughness of the AFM surface morphologic changes are also recorded in Table 1.

Under the dry UV conditions, a systematic change in surface morphology was observed with increasing UV exposure time. The same trends were observed for both 0.4 % and 1.2 % mass fraction GO/WBU coatings, and these trends are described using the 0.4 % mass fraction GO/WBPU coating. At 0 d, the surface of 0.4 % (mass fraction) GO/WBPU coatings was rough, with a mixture of polymer features and GO particles. The rough polymer features were like those observed for neat WBPU at 0 d (Figure 1). With increasing exposure time at dry UV conditions, the polymer surface features of GO/WBPU coatings decreased in roughness with more GO particles becoming visible by 30 d (Figure 3). At 60 d, the rough polymer features almost disappeared to form a smooth surface containing some GO particles (at a low concentration), indicating that some of the initial GO particles potentially released. The corresponding surface roughness changed from 396.0 nm  $\pm$  16.0 nm at 0 d, to 62.3 nm  $\pm$  7.7 nm at 60 d. The numbers after  $\pm$  are one standard deviation from the average of three replicates measurements (see Table 1) The surface of neat WBPU was also found to become smooth by 60 d, but without the presence of any particles similar in shape or size to those on the nanocoating surface. At 140 d of dry UV exposure, after more polymer had degraded, GO particles became more apparent for the GO/WBPU coating surfaces (brighter spots). These particle-like features were not present on the neat WBPU (Figure 2a LSCM image) at 140 d of UV exposure.

Under humid UV conditions, the rate of degradation appeared to be faster than the rate under dry UV conditions. At 30 d, there are larger protruded particles (assuming mostly GO-related particles) on the surface, than those that appeared on 60 d or 140 d under dry UV conditions. By 60 d, GO particles protruded further from the coatings surface and formed larger, crumpled aggregates (Figures 3). The observation of GO particle crumpling and aggregating was more noticeable in the SEM measurements. Figure 4 shows SEM images of the 0.4 % mass fraction GO/WBPU coatings

surfaces exposed to dry UV and humid UV conditions at 500x and 4500x magnification. SEM images showed the same trends in surface morphological change and GO particle accumulation observed with AFM images (Figure 3). These crumpled, aggregated GO particles were above the 0.4 % mass fraction GO/WBPU coating surface (Figure 4b) after 60 d of humid UV exposure. After 140 d of UV exposure under humid conditions, the large GO aggregates disappeared, indicating that the protruding GO particles present at 60 d likely released from the surface (Figures 4). This observation was confirmed by a large thickness loss observed for neat WBPU and 1.2 % mass fraction GO/WBPU coatings (reported elsewhere [25]) after humid UV exposure which explains the rapid changes in surface morphology and loss of GO particles on the 0.4 % by mass GO/WBPU coating surface change when thickness loss was minimal. SEM images of the neat WBPU and GO/WBPU coatings were also collected under dry dark and humid dark conditions. Under both dry and humid dark conditions, there was no visible surface GO accumulation over time and the rough polymer surface features gradually smoothed out (as shown in Figure 2).

#### Changes in Surface Modulus after UV exposure

Observation of crumpled aggregated GO-related particles above the 0.4 % mass fraction GO/WBPU coating surface were consistent with AFM (topographic) and SEM measurements (Figures 3 and 4) after 15 d humid UV exposure. To track and determine the GO formation and the composition of these aggregates, AFM in PeakForce QNM mode was carried out to measure the surface modulus of the polymer-GO crumpled aggregated features. Figure 5 displays topographic (top) and Derjaguin-Muller-Toporov (DMT) modules (bottom) of (a) 0 % and 1.2 % (mass fraction) GO/WBPU before UV exposure, and (b) the corresponding area percentage of DMT modulus distribution of 0 % and 1.2 % mass fraction GO/WBPU obtained from Figure 5a. Average modulus measurements were determined from the average of three replicate areas to qualitatively show consistency in measurements.

Before UV exposure, there was not much difference in modulus between neat WBPU and 1.2 % mass fraction GO/WBPU coatings (see Figure 5b). Average modulus of both coatings is less than 0.5 GPa, which is close to polymer modulus (0.4 GPa  $\pm$  0.1 GPa), but smaller than GO modulus

(1.1 GPa  $\pm$  0.1 GPa). All numbers present here are average and one standard deviation of five replicate areas. This result indicates that these GO-related particles on the coatings surface were likely coated with a thin layer of polymer or mixture of GO-polymer clusters. After 30 d dry UV exposure, significant changes can be observed in surface modulus map in Figure 5c, overall the surface modulus values increase across the whole areas (much brighter in the right-hand-side DMT modules images) of 1.2 % (mass fraction) GO/WBPU coatings at 30 d dry UV than the darker images of left-hand-side DMT modules images of 1.2 % (mass fraction) GO/WBPU coatings at 30 d dry UV to 30 d dry UV conditions.

Since more crumpled aggregated GO-related particles were observed above 1.2 % mass fraction GO/WBPU under humid UV conditions, a series of surface modulus measurements were carried out to characterize those coatings and neat WBPU coatings at same exposure conditions and exposure times. Figure 6 presents the percentage of area as a function of modulus for 0 % and 1.2 % mass fraction GO/WBPU coatings before and after 15 d and 30 d of humid UV exposure. Average modulus measurements were made on three duplicate areas. For neat WBPU (dashed lines), a noticeable increase in modulus was detected from 0 d to 15 d, but no significant change from 15 d to 30 d. For 1.2 % WBPU coatings (solid lines), at 0 d, as shown previously, there was not much difference in modulus between neat WBPU and 1.2 % GO/WBPU coatings (see Figure 5b). After 15 d, the shape of percentage-modulus distribution changed dramatically. It is no longer a simple gaussian/normal distribution, the percentage of high modulus component increased as in creasing UV exposure time. After 15 d (red solid line), the distribution curve peaks up around 1 GPa. After 30 d (blue solid line), the distribution curve forms a bimodal curve with two peaks around 0.8 GPa and 2.0 GPa. The shape of distribution shifts to high modules because of the presence of GO at the surface (as seen in Figures 3 and 4 with higher GO concentrations). To further quantify the distribution, a threshold was selected at 2 GPa at which no polymer modulus was present for neat WBPU exposed to UV irradiation at each UV exposure time. For 1.2 % WBPU coatings, the percentage of the modulus higher than 2 GPa is  $(22 \pm 4)$  % after 15 d, and increases to  $(34 \pm 3)$  % after 30 d. The numbers after  $\pm$  are one standard deviation from the average of three replicates measurements. This finding confirms the presence of GO particles on the surface of 1.2 % GO/WBPU coatings under 15 d and 30 d humid UV exposure.

# Summary

Effect of GO nanoparticles on surface morphology of waterborne polyurethane/GO coatings during exposure to UV radiation has been investigated using various microscopy techniques including LSCM, SEM and AFM. These imaging techniques were complementary and were used to help monitor the change in GO particle concentration at the surface and the change in polymer surface morphology during UV exposure. Morphological changes in GO/WBPU coatings provide useful information on how GO nanofiller affects degradation behavior of GO/WBPU coatings. In addition, AFM (in PeakForce QNM mode) modulus measurements can provide more confidence on the presence of GO at the surface of degraded nanocoatings.

Overall, this general approach, using LSCM optical method to quickly screen the surface morphology of samples in multiscale first, then to identify GO particles versus polymer features on the UV-degraded surfaces in a smaller scanning area using AFM and SEM, was very useful for assessing all surface integrity of coatings under various environmental stresses. Furthermore, AFM modulus measurements can be successfully used in future studies for distinguishing higher modulus carbonaceous nanoparticles (CNPs).

# **NIST disclaimer**

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.

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Table 1. Root-mean-square surface roughness values (S<sub>q</sub>, unit nm) of GO/WBPU coatings at 0 % mass fraction, 0.4 % mass fraction, and 1.2 % GO mass fraction for different exposure times at dry ( $\approx$  0 % RH) and humid (75 % RH) conditions. At least three randomly chosen locations were measured by AFM (50 µm scan size, as seen in Figure 3). Average S<sub>q</sub> values were obtained using AFM software, the numbers after ± are one standard deviation from the average of at least three measurements.

	0 d	30 d	60 d	140 d
0.4 %, dry UV	$396 \pm 16$	$155 \pm 7$	$62.3 \pm 7.7$	$42.9\pm9.9$
0.4 % humid UV	$396 \pm 16$	$946 \pm 82$	$932\pm26$	$26.9\pm6.1$
1.2 % dry UV	$441\pm88$	$118\pm7$	$112\pm39$	$84.5 \pm 26.1$
1.2 % humid UV	$441\pm88$	$500 \pm 4$	$897 \pm 58$	$142 \pm 10$
0 % dry UV	$131 \pm 28$	-	9.9 ± 3.3	9.4 ± 3.3
0 % dry UV	$131 \pm 28$	-	-	$17.6 \pm 5.3$



Figure 1. Surface images of GO/WBPU coatings at 0 % mass fraction, 0.4 % mass fraction, and 1.2 % GO mass fraction at four different scan sizes. First three columns are LSCM images at scan area of 1700  $\mu$ m x1700  $\mu$ m (5x), 169  $\mu$ m x 169  $\mu$ m (50x), and 56  $\mu$ m x 56  $\mu$ m (150x), respectively. The last column (right-hand-side) are AFM height images at 50  $\mu$ m x 50  $\mu$ m scan size.



Figure 2. (a) LSCM images of degraded GO/WBPU coatings at three mass fractions (0 %, 0.4%, 1.2 %) after 140 d exposure to (a) dry (b) humid conditions. Images for UV exposed samples are in the top row while samples exposed to dark (no UV) conditions are shown in the bottom row. The scale bars are 50  $\mu$ m.



Figure 3. Topographic AFM images of 0.4 % mass fraction GO/WBPU coatings surfaces exposed to dry UV and humid UV exposure conditions for the indicated time periods. Scale bars are 10  $\mu$ m.



Figure 4. SEM images of 0.4 % (mass fraction) GO/WBPU coatings at (a) 500x and (b) 4500x magnifications before and after UV exposure under dry and humid conditions. The scale bars in (a) and (b) are 50  $\mu$ m and 5  $\mu$ m, respectively.





Figure 5. Topographic (top) and Derjaguin-Muller-Toporov (DMT) modulus (bottom) AFM images of (a) 0 % and 1.2 % (mass fraction) GO/WBPU before exposure to UV irradiation, (b) replicate DMT modulus measurements of 0 % and 1.2 % mass fraction GO/WBPU coatings before UV exposure. Each curve represents one DMT modulus measurement at one sample. Average modulus measurements were made on average of three replicates + one standard deviation. (c) 1.2 % (mass fraction) GO/WBPU coatings at 0 d and 30 d dry UV exposure times. Note that the scale bar in the DMT images of left-hand-side bottom (c) has been adjusted for easy visual comparison.



Figure 6. Average AFM (in PeakForce QNM mode) modulus measurements of (0 % and 1.2 %) mass fraction GO/WBPU coatings before and after 15 d and 30 d of humid UV exposure. Average modulus measurements were made on three duplicate areas.