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Research Paper

The impacts of moisture and ultraviolet light on the degradation of graphene oxide/polymer nanocomposites

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ABSTRACT

The extent to which hydrophilic GO nanofillers regulate polymer degradation during exposure to a combination of ultraviolet (UV) radiation and moisture is presently unknown. Accordingly, this study systematically evaluated the effect of GO on polymer degradability under both humid UV and dry UV conditions. Both GO accumulation at the polymer nanocomposite (PNC) surface and GO release following degradation were also investigated. Different mass loadings of GO were incorporated into waterborne polyurethane (WBPU), a commonly used exterior coating, and the resulting GO/WBPU nanocomposites were exposed to precisely controlled accelerated weathering conditions using the NIST Simulated Photodegradation via High Energy Radiant Exposure (SPHERE) device. Thickness loss and infrared spectroscopy measurements indicated GO slightly improved the durability of WBPU under dry UV conditions but not under humid UV conditions. Raman spectroscopy, scanning electron microscopy, and atomic force microscopy modulus measurements indicated that GO accumulation occurred at and near the PNC surface under both conditions but to a more rapid extent under humid UV conditions. Minimal GO release occurred under dry UV conditions as measured with Raman spectroscopy of aqueous run-off from a simulated rain spray applied to degraded PNCs. In contrast, PNC surface transformations under humid UV conditions suggested that GO release occurred.

persibility in polar matrices.

when mixed with polar or hydrophilic polymeric materials. Furthermore, the production of unmodified graphene is often conducted on a

small scale and at a high cost (Park and Ruoff, 2009; Zhu et al., 2010).

In contrast, graphene oxide (GO), an oxidized form of graphene, can

overcome some of the disadvantages of unmodified graphene nano-

fillers, particularly with respect to reduced cost and increased dis-

contain hydroxyl and epoxide groups on the basal plane and carboxylic

acid groups at the edges (Stankovich et al., 2006; Dreyer et al., 2010,

2014). As a result, GO is highly dispersible and stable in aqueous media.

GO can be produced in large quantities by thermally or chemically

oxidizing low-cost graphite, followed by exfoliation of the resulting

graphite oxide (i.e., stacks of graphene oxide sheets). Due to the pre-

sence of oxygen functional groups and physically adsorbed water, the

distance between two GO sheets (inter-layer spacing) at ambient con-

ditions is around twice the distance between graphene sheets in gra-

phite (> 0.7 nm vs. 0.34 nm, respectively) (Buchsteiner et al., 2006;

Hontoria-Lucas et al., 1995). Such large inter-layer spacing in GO can

Graphene oxide (GO) consists of individual graphene sheets that

1. Introduction

Intensive research throughout the past decade has demonstrated that nanomaterial fillers, such as carbon nanotubes (CNTs), nanoclays, and inorganic oxide nanoparticles, often greatly improve the performance of polymers in a wide variety of applications (McNally and Pötschke, 2011; Pavlidou and Papaspyrides, 2008; Zou et al., 2008). Graphene, which consists of a two-dimensional lattice of sp²-bonded carbon atoms, has emerged as a promising class of nanofiller (Geim and Novoselov, 2007; Park and Ruoff, 2009; Zhu et al., 2010; Li and Kaner, 2008). Similar to its cylindrical CNT form, graphene has exceptional mechanical, electrical, and thermal properties (Geim and Novoselov, 2007; Zhu et al., 2010). Because of these attributes, extensive efforts have been made towards incorporating graphene-based materials into polymer matrices to enhance various properties, as outlined in numerous reviews (Stankovich et al., 2006; Potts et al., 2011; Hu et al., 2014; Bhattacharya, 2016; Chatterjee and Chu, 2016; Chee et al., 2015). Unmodified graphene materials, however, suffer several drawbacks as nanofillers because they are difficult to exfoliate, especially

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facilitate the intercalation of polymers into these locations leading to strong mechanical interlocking between the matrix and the GO sheets (Bissessur and Scully, 2007; Matsuo et al., 1997, 1998). Furthermore, the functional groups on the GO surface can form strong hydrogen bonds with hydrophilic polymer matrices leading to strong interfacial attraction. For these reasons, GO has been investigated as a nanofiller for water-soluble polymers (Xu et al., 2009; Oh et al., 2015; Guan et al., 2016; Huang et al., 2012) and other commercially-important polymers such as poly(methyl methacrylate) (PMMA), polyurethanes, and epoxies (Chatterjee and Chu, 2016; Yoo et al., 2014; Ma et al., 2014; Thakur and Karak, 2014; Pokharel and Choi, 2015; Guo et al., 2011; Luo et al., 2016).

Waterborne polyurethane (WBPU) is an important class of coatings and is increasingly used in many applications because it is environmentally benign, inexpensive, and has a number of useful properties such as good adhesion to a variety of substrates, high abrasion resistance, and good weathering resistance (Wicks et al., 2002; Engels et al., 2013). The addition of nanofillers, such as nanoclays, inorganic nanoparticles, and CNTs, into WBPU has been previously attempted to improve hardness, corrosion resistance, and flame retardancy of this matrix (Kuan et al., 2005; Chen et al., 2009; Zeng et al., 2016). Owing to the ease of GO dispersion in water, incorporation of GO or functionalized graphene sheets into WBPU has also been reported (Raghu et al., 2008; Hu et al., 2017; Hsiao et al., 2014; Hu and Zhang, 2014). Results from our laboratory have demonstrated that GO material prepared by the Hummers' method (Hummers Jr and Offeman, 1958) disperses homogeneously in a one-part, water-based aliphatic polyurethane and imparts large improvements to various properties (Bernard et al., 2011, 2020). For example, at a low, 2% by mass GO loading, the mechanical properties of WBPU were improved significantly with an increase in modulus and yield strength of 300% and 200%, respectively. The thermal conductivity, or heat dissipation ability, was increased by 38%, and the flammability, measured by the burning heat release rate, was decreased by 43%. Furthermore, the oxygen permeability of WBPU was decreased 7-fold with an addition of 1.2% mass GO in the matrix, indicating that GO can lower oxygen transmission to an underlying substrate (e.g., steel) and thereby reduce substrate corrosion (Bernard et al., 2011, 2020).

For polymer nanocomposites to be accepted and used widely in outdoor applications, both the long-term performance (i.e., weatherability) and the fate of nanoparticles in the polymer matrix during the products' life cycle must be established. The former property (i.e., longterm performance) is needed for assessment of product service life, while the latter property (i.e., fate of nanoparticles) is essential for assessing human health and environmental risks. Experimental data from nanocomposite degradation studies has established that when a polymer nanocomposite is exposed to ultraviolet (UV) radiation, the polymer matrix is often removed by photodegradation, leaving a layer of nanoparticles on the degraded nanocomposite surface that can either stabilize against or enhance polymer photodegradation (Nguyen et al., 2014; Petersen et al., 2011; Duncan, 2015; Harper et al., 2015; Froggett et al., 2014; Kingston et al., 2014; Schlagenhauf et al., 2014; Wohlleben and Neubauer, 2016; Koivisto et al., 2017; Nowack et al., 2016; Kumar et al., 2009). In previous studies, pristine (i.e., not oxidized) CNTs and graphene were shown to increase the photo-stabilization of polymeric materials under UV radiation (which is the most detrimental element among the weathering factors) due to their radiation filtering effects (Nguyen et al., 2011; Petersen et al., 2014; Dintcheva et al., 2015; Nguyen et al., 2017; Lankone et al., 2017; Gorham et al., 2012; Wohlleben et al., 2014; Long et al., 2016; Neubauer et al., 2017; Shehzad et al., 2019).

Despite research that shows greatly enhanced performance of polymers containing GO nanofillers, little information is available on either the long-term performance or the fate of GO in polymer nanocomposites during UV weathering (Goodwin Jr et al., 2018). Several studies have used nanocomposites, containing GO and photocatalytic nanoparticles such as ZnO and TiO₂ to degrade methylene blue or other model pollutants, oftentimes under visible light and with or without polymer matrix (Rokhsat and Akhavan, 2016; Zhang et al., 2015; Moon et al., 2013). But these studies have not focused on the systematic change in surface morphology of a polymer-based nanocomposite with UV weathering conditions. Our previous study revealed that the presence of GO appeared to decrease the photo-oxidation of WBPU with the formation of a GO layer on the UV-irradiated nanocomposite surface (Bernard et al., 2011). Another study observed decreased degradation of polypropylene with increasing mass loadings of GO (de Oliveira et al., 2019). However, these studies on GO/polymer nanocomposite photodegradation did not address the effects of GO mass loading and the important accelerated weathering variables such as exposure time and humidity. Humidity is especially important since GO is hydrophilic and polymer degradation rates may be affected by moisture (ISO 4982-2, 2013).

The release of GO during polymer nanocomposite degradation has also not been investigated. For spherical nanoparticles, such as nanosilica, spontaneous release (release without applied external forces) of nanoparticles during weathering has been observed (Jacobs et al., 2016; Sung et al., 2015; Nguyen et al., 2012) while fiber-like CNTs have not been observed to release as free particles during weathering or UV irradiation, unless the nanocomposite material was immersed in water during UV exposure or a strong shear force was applied to the weathered nanocomposite surface (Lankone et al., 2017; Hirth et al., 2013; Wohlleben et al., 2017; Schlagenhauf et al., 2015). Nanoclays, with stiff, hydrophilic, platelet-like structures similar to GO but with differing chemistries, have been investigated for release under mechanical (Froggett et al., 2014; Koivisto et al., 2015) and UV weathering stresses (Han et al., 2018) and have been shown to release during UV exposure. Release of platelet-shaped graphene and kaolin from polymer nanocomposites has also been investigated under both dry and wet rain cycle exposures (using ISO 4982) (ISO 4982-2, 2013; Zepp et al., 2020). Graphene was found to release less with polymer fragments under wet conditions, while kaolin released slightly more with polymer fragments under wet conditions. In both cases, the polymer matrix type was critical (Zepp et al., 2020). Considering the great differences in chemistry (e.g., oxygen functional groups and their distribution), affinity to the polymer matrix, interaction with UV light, and structure of GO, GO release behavior during UV exposure is likely different from graphene, clay-based platelets, and fiber-like nanoparticles.

The main objective of the present study is to assess the detailed surface transformations and potential nanoparticle release during exposure of GO/WBPU nanocomposites to UV radiation under dry and humid conditions, both of which must be known to develop a more complete understanding of GO/polymer nanocomposite implications in the environment. Accordingly, both neat WBPU and GO/WBPU nanocomposites at two GO loadings found to have improved performance properties in our previous study (Bernard et al., 2020) were exposed to high intensity UV radiation at 55 °C and two relative humidity levels (0% and 75%) in a well-controlled UV weathering device called the National Institute of Standards and Technology Simulated Photodegradation via High Energy Radiant Exposure (NIST SPHERE). Nanocomposite surface transformations were characterized by a variety of spectroscopic and microscopic techniques. The release potential of GO nanoparticles was evaluated using a simulated rain spray of the nanocomposite samples after UV exposure under dry conditions. The release of GO nanoparticles was assessed by Raman spectroscopy of the aqueous run-off and scanning electron microscopy (SEM) measurements of the dried run-off residue.

2. Materials and methods

2.1. Materials and nanocomposite preparation

GO was prepared using the Hummers' method (Hummers Jr and

Offeman, 1958). The exfoliated GO sheets had a thickness of 0.8 nm to 1.5 nm and lateral dimensions of 1 µm to 2 µm 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 (Bernard et al., 2011). 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) (Bernard et al., 2011). The GO/WBPU nanocomposite films had an average (and one standard deviation of n = 15 measurements from three cross-sectional SEM images of three separate specimens) thickness of 127 um \pm 3 um and the neat WBPU films had an average thickness and standard deviation (n = 15) of 97 µm \pm 3 µm, as measured with cross-sectional scanning electron microscopy (SEM) described in the Supplementary information (SI) and a later section. Further information on GO/WBPU nanocomposite preparation is provided in the SI. Characterization of the asprepared nanocomposites are provided in later sections as the characterization techniques used for the nanocomposites before and after degradation were the same.

2.2. UV irradiation experimental setup and conditions

In a precisely controlled weathering device, the NIST SPHERE (Chin et al., 2004), GO/WBPU nanocomposite specimens were exposed to UV light at an irradiance of $\approx 140 \text{ W/m}^2$ across wavelengths ranging from 295 nm to 400 nm. The NIST SPHERE has the ability to precisely control temperature and relative humidity (RH) during exposure and is designed to uniformly expose specimens to high intensity UV light, thus accelerating the degradation with respect to outdoor exposures. Specimens were exposed to UV radiation at 55 $^{\circ}$ C \pm 1 $^{\circ}$ C (average and one standard deviation) and two RH levels ($\approx 0\%$ and 75% $\pm 2\%$) (average and one standard deviation) for time periods ranging from 15 d to 140 d, which is the equivalent to UV doses (irradiance · time) of 181 MJ/m² to 1693 MJ/m². Although a direct comparison to outdoor weathering time cannot be made due to the presence of complex weather patterns, the equivalent exposure times to outdoors in South Florida (280 $MJ/m^2 = 1$ year) spanned from 0.64 years to 6.05 years in terms of average UV dose. To account for the effects of UV radiation only, specimens were also exposed to the same temperature and RH conditions but in the absence of UV light. This experiment was carried out in a dark chamber not attached to the SPHERE. The use of extreme conditions (i.e., elevated temperature and high humidity) served to provide the worst-case scenarios for weathering of GO/WBPU nanocomposites. Hereafter, the exposure conditions are listed by the condition name in Table 1.

2.3. Transformation of GO/WBPU nanocomposites exposed to UV radiation $% \mathcal{A} = \mathcal{A} = \mathcal{A} + \mathcal{A}$

2.3.1. Specimen arrangements

For GO/WBPU nanocomposite transformation studies, films were cut into 2.5 cm \times 2.5 cm squares, placed into a sample holder containing 17 specimen positions, and secured with a 17-window cover to expose a 1.9 cm-diameter circular area of each specimen (Fig. 1a). Four sample holders, each of which contained 17 specimens, were assembled

Table 1

The conditions under which neat WBPU and GO/WBPU nanocomposites were exposed.

Condition name	% UV	Temperature (°C)	% Relative humidity (RH)		
Dry UV Humid UV Dry dark Humid dark	100 100 0	55 55 55 55	0 75 0 75		

with neat WBPU (*i.e.*, 0% mass fraction GO), 0.4% mass fraction GO/ WBPU nanocomposites, and 1.2% mass fraction GO/WBPU nanocomposites. For each sample holder, replicate specimens (at a given GO mass loading) were randomly distributed among the 17 positions. Hereafter, 0% mass fraction GO/WBPU nanocomposites, 0.4% mass fraction GO/WBPU nanocomposites, and 1.2% mass fraction GO/WBPU nanocomposites are designated as 0%, 0.4%, and 1.2% GO/WBPU nanocomposites.

2.3.2. Characterization of nanocomposite degradation

Degradation of GO/WBPU nanocomposites by UV irradiation was characterized by material loss, which consisted of mass loss and thickness loss, and surface transformations, which included chemical degradation, GO particle accumulation at or near the nanocomposite surface, and surface morphological changes.

2.3.2.1. Material loss. Mass loss was measured gravimetrically (Mettler Toledo AB265-S, Columbus, OH). Triplicate specimens for each of the three GO mass loadings (0%, 0.4%, and 1.2%) were removed from their sample holder after each exposure time interval of 15 d, 30 d, 60 d, and 140 d, weighed and characterized after equilibration to ambient room conditions for at least 2 d (\approx 40% R.H., 20 °C), and then placed back into the sample holder for further exposures. Thickness loss was determined with cross-sectional SEM (SEM, JEOL 7600f, 6.0 kV, Peabody, MA) with the specimen held at a 60° angle. Thickness measurements were made post-imaging and were corrected to a 90° angle by the sine function. For cross-sectional SEM, at least three images were obtained per specimen and at least five cross-sectional lengths were measured per SEM image. The same exact specimens were not imaged before and after UV degradation since conductive coatings had to be applied for SEM imaging (i.e., destructive testing), but the specimens were cut from the same uniform thickness nanocomposite sheet in the same manner prior to imaging or UV-weathering. Three unexposed 1.2% nanocomposite specimens were cut from separate parts of the sheet and cross-sections were imaged and compared to show specimen-to-specimen consistency (see SI).

2.3.2.2. Surface transformations. Chemical degradation was monitored using Fourier transform infrared spectroscopy in attenuated total reflection mode (ATR-FTIR, 4 cm⁻¹ resolution, 128 scans/specimen, Nicolet iS50 with diamond type IIa crystal, ThermoFisher Scientific, Waltham, MA). FTIR spectra were linearly baseline corrected with the same baseline points used for all spectra. All FTIR spectra were normalized to the 1450 $\rm cm^{-1}$ peak, assigned to the –(CH₂)- rocking band in neat WBPU, which was found to change minimally following UV irradiation (Rabek, 2012). GO particle accumulation at or near the nanocomposite surface from UV exposure was measured with Raman spectroscopy (Bruker Senterra XL Raman Microscope, Billerica, MA, 785 nm, 1 mW, 5 s accumulation) using the intensity changes of the defective (D, 1306 cm^{-1}) and graphitic (G, 1602 cm^{-1}) bands, which served as unique indicators of GO concentration in the sub-surface (top 1 μ m to 4 μ m) of the GO/polymer nanocomposites. Raman spectra were baseline corrected using a concave rubberband method, and Raman spectra were not normalized due to the lack of visible reference bands in the spectra. However, changes in surface roughness were measured by laser scanning confocal microscopy (LSCM Zeiss model LSM 510, Thornwood, NY, reflectance mode, 543 nm) to assess whether changes in Raman signal might be affected by surface roughness variations in addition to GO concentration changes (Wang et al., 2014). Other surface morphological changes were characterized by atomic force microscopy (AFM, Bruker Dimension Icon AFM, Billerica, MA) and SEM imaging. 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 nanocomposite surfaces as a function of UV exposure. After AFM measurements, a conductive coating was applied to the specimens, and SEM imaging (described



Fig. 1. Images of a) specimen wheel holder and b) (0%, 0.4%, and 1.2%) GO/WBPU nanocomposites, in ascending order of GO mass loading from top to bottom, before and after 140 d dry UV exposure.

earlier) was performed. Further details about the measurement techniques used can be found in the SI.

For ATR-FTIR spectroscopy, Raman spectroscopy, and LSCM measurements (non-destructive techniques), the number of specimens and sampling procedures after UV exposure were the same as those used for mass loss measurements. Further, since Raman spectroscopy had a small spot size (2 μ m), four areas of each specimen were also measured to obtain results that were representative of the entire specimen. At each exposure time, one specimen of each GO loading was removed sacrificially for AFM and SEM measurements. These specimens were first imaged with AFM followed by SEM since the addition of a conductive coating was required for SEM imaging (details provided in the SI).

2.4. GO release studies

2.4.1. Specimen arrangements

For GO release studies, GO/WBPU nanocomposite films were cut into a quadrant shape using a template, with a surface area of approximately 20 cm². These larger specimens were utilized to maximize the surface area available for UV exposure, which can increase the potential concentration of GO release and thus aid the GO release measurement accuracy. Specimens were mounted in a separate, specially-designed sample holder with front covers containing quartz windows to permit UV light transmission while containing any materials released during exposure (Fig. S1). The sample holder contained four separate cells, each of which could be opened and closed independently (Jacobs et al., 2016). Neat WBPU and 1.2% GO/WBPU nanocomposite specimens were exposed in this sample holder under dry UV and dry dark conditions. Humid conditions were not possible to maintain in this setup because humid air could not be flowed through this type of sample holder cell. Further details can be found in the SI.

2.4.2. Simulated rain spray to collect released materials

After 60 d of dry UV exposure, sample holders were removed from the SPHERE and GO release from the GO/WBPU nanocomposites was evaluated. To assess GO release, rain was simulated after UV degradation using a deionized (DI) water spray system. The spray nozzle was consistently maintained at \approx 5 cm from the specimen surface, a distance that allowed the spray to cover the majority of the nanocomposite surface with continuous rastering across the surface. DI water was sprayed for 5 min with a liquid flow rate of approximately 1 mL/min. Run-off from the water spray was collected in a 20 mL poly(ethylene) bottle through a specially designed port at the bottom of each sample holder cell (Jacobs et al., 2016). Aqueous run-off contained in the collection bottles was analyzed for GO release as described in the following sections. Further details are provided in the SI.

2.4.3. Detection and quantification of GO release after UV irradiation

2.4.3.1. Raman spectroscopy. To determine the mass concentration of GO released from UV-exposed nanocomposites, Raman spectroscopy of released GO in DI water was measured using the intensities of the signature D band for GO. The D band was used since a water deformation band (1638 cm^{-1}) interfered with the G band (Salzmann et al., 2007). Raman spectroscopy calibration curves of GO at different mass concentrations were established and the interference of released WBPU was evaluated by measuring its Raman response. For this purpose, a Kaiser Holospec F1.8 Raman spectrometer (Ann Arbor, MI), equipped with a thermoelectrically cooled CCD detector (Apogee, Inc., Logan, UT) and a 488 nm Argon laser (Lexel, Inc., Fremont, CA) was used with 50 s accumulation and 180 mW laser power. Further information can be found in the SI.

2.4.3.2. Scanning electron microscopy. A 2 μ L aliquot of well-mixed runoff from the simulated rain spray was dried down on a 200-mesh copper grid (PELCO No. 160, Lot #030315, 0180-CB, Ted Pella, Redding, CA) that was taped to an SEM stub. The water was dried off overnight under ambient conditions. The dried run-off was then imaged with SEM by carefully searching each section of the grid for run-off materials. A conductive coating was not applied.

3. Results and discussion

3.1. Initial nanocomposite characterization

GO/WBPU nanocomposites containing 0%, 0.4%, and 1.2% GO were characterized with Raman spectroscopy for GO dispersion quality and with SEM and AFM for surface morphology. Raman spectroscopy was used to measure the Raman D and G band intensities at different sample areas, indicative of the degree of GO concentration homogeneity/inhomogeneity across the sample. The 1.2% GO/WBPU nanocomposite was found to be reasonably homogeneous with respect to GO

dispersion, with a dispersion quality in the top (1 to 4) μ m that varied by 11% based on the measured D band intensities at 1306 cm⁻¹. In our previous study, the dispersion quality within the nanocomposites was also assessed with cross-sectional SEM images and was found to be uniform (Bernard et al., 2020). The initial surface morphological features of neat WBPU and GO/WBPU nanocomposites are described later in the surface morphological changes section.

3.2. Transformations of the nanocomposites by UV irradiation

3.2.1. Physical appearance

GO/WBPU nanocomposites 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. After 140 d of UV exposure, the 1.2% GO/WBPU nanocomposite was more brittle to handle, but did not show noticeable discoloration, while the 0.4% GO/WBPU nanocomposite became slightly darker in color (Fig. 1b). The neat WBPU changed from an opaque white to translucent white color by 30 d, suggesting changes to the polymer microstructure occurred. Neat WBPU eventually yellowed by 140 d, the point at which UV exposure was stopped. Since WBPU is an aliphatic polyurethane, the yellowing observed was likely a result of monoquinone imide formation (Rabek, 2012). The discoloration of the 0.4% GO/WBPU nanocomposite was likely also from yellowing while the dark color of the 1.2% GO/WBPU nanocomposite may have obscured any color change that occurred.

3.2.2. Mass loss and thickness loss

Mass loss data indicated that GO nanofillers decreased polymer photodegradation to a small extent at each time point, most likely due to UV shielding of the polymer by the GO particles (Fig. S8). The GO/ WBPU nanocomposites exposed to dry UV conditions for 140 d did not visibly thin or lose > 2.5% mass. Under humid UV conditions, mass loss measurements of nanocomposites could not be obtained due to adherence of the nanocomposite to the sample holder's stainless steel substrate in the presence of moisture. However, visible thinning of the nanocomposites was observed under humid UV conditions (Fig. S8). Since material loss from dry UV exposure could not be compared to material loss from humid UV exposure using mass loss measurements, thickness changes of the neat WBPU and 1.2% GO/WBPU nanocomposite were measured under both dry UV and humid UV conditions after 140 d. Under dry UV conditions, the neat WBPU and the 1.2% GO/ WBPU nanocomposite lost almost no thickness ($\approx 0 \ \mu m$). In stark contrast, exposure to humid UV conditions led the 1.2% GO/WBPU nanocomposite to lose 45 μ m \pm 3 μ m of its thickness (Fig. 2, Table 2). Similarly, the neat polymer lost a thickness of 50 μ m \pm 10 μ m under humid UV conditions (Table 2, Fig. S5). Thus, humid UV conditions led to more extensive material loss during degradation than under dry UV conditions, resulting in large thickness changes. The increased removal of polymeric material in the presence of moisture is likely due to the reaction of polyurethane photoproducts with water, which allows them to form smaller molecules and eventually gas that leads to material loss. This contrasts somewhat with other studies such as Wohlleben et al. (2017) and Zepp et al. (2020), which combined UV exposure cycles with cyclic water sprays in the dark using ISO 4982 (ISO 4982-2, 2013). Cycles of rain spray led to the formation of photoproducts that were washed away and collected, which likely provided less opportunity for photoproducts to convert to gas as they would under highly humid conditions in the absence of cyclic water spray. Nevertheless, both the cyclic spray and the high humidity exposure without intermittent spray are both environmentally relevant and important weathering exposure scenarios to investigate. The specific photoproducts formed in this study were identified with FTIR as discussed in the next section.

Dark control experiments, which were performed in the absence of UV light, were also used to assess thickness changes (Fig. S7 and Table 2). Thickness measurements for the controls exposed to dry dark

and humid dark conditions were generally within experimental error and indicated that the large thickness losses observed under humid UV exposure resulted from specimen exposure to a combination of UV light and moisture.

3.2.3. Chemical transformations of the nanocomposite's polymer matrix

ATR-FTIR spectroscopy was used to assess the chemical transformation of the polymer matrix in the sub-surface, or the top few micrometers of the nanocomposites. ATR-FTIR spectroscopy was more useful for assessing polymer transformations than GO transformations because the small mass fraction of GO (< 1.2%) did not absorb significantly in the ATR-FTIR spectrum. To compare the same amount of material in all spectra, spectra were normalized to the –(CH₂)- rocking band at 1450 cm⁻¹ for the neat WBPU, 0 d exposure sample (Rabek, 2012). This normalization band was chosen since it did not change significantly during photodegradation.

Under dry UV conditions, an initial decrease in the 1727 cm^{-1} band intensity was accompanied by a gain in the carboxylic acid band intensity at 1710 cm^{-1} , indicating the accumulation of carboxylic acid photoproducts (Figs. 3 and S16–17) (Wilhelm and Gardette, 1997). The decreasing 1727 cm^{-1} band consisted of the carbonyl stretch for both esters and urethanes and its loss can be attributed to conversion of urethanes to carboxylic acids and hydrolysis of the ester groups (esters stretches are located in this region) (Colthup, 2012). The urethane component's presence at this band was confirmed with an *in situ* curing study of isocyanates in our laboratory (Fig. S21). The increasing formation of acetylurethanes at 1780 cm^{-1} also occurred at 60 d and 140 d under dry UV conditions, indicating photoproduct accumulation (Figs. 3 and S17). Further discussion of FTIR band assignments can be found in the SI.

In contrast, humid UV conditions led to an apparent reduced extent of carboxylic acid formation over longer UV exposures (i.e., 60 d to 140 d). The carboxylic acid band (1710 cm⁻¹) intensity remained constant with only marginal increases during continued humid UV exposure and little difference from the humid dark controls (line plot in Fig. 3). Although this result seems to indicate that degradation did not occur under humid UV conditions, in combination with the thickness loss measurements (presented in Table 2 and Fig. 2), FTIR results indicate that continued humid UV degradation occurred by steady-state photoproduct formation and removal as gas (Figs. 3 and S17). Specifically, the 1.2% GO/WBPU nanocomposites lost over 44 μ m \pm 3 μ m of material (Fig. 2) from humid UV degradation, indicating that the photoproducts present in the ATR-FTIR spectrum were formed and removed over time in the presence of moisture (Fig. 3). Under dry UV conditions, the build-up of photoproducts observed by ATR-FTIR was also consistent with the minimal nanocomposite thickness loss observed using cross-sectional SEM (Fig. 2).

FTIR line plots of carboxylic acid growth (1710 cm⁻¹ band, 15 d to 140 d) from polymer degradation indicated that there was less overall polymer degradation when GO nanofillers were present (Fig. 3 [righthand column]). After 140 d of dry UV exposure, the polymer matrices of the 0.4% and 1.2% GO/WBPU nanocomposites were approximately 35% less degraded (compare 1710 cm⁻¹ band intensity increases in dry UV line plot) than the neat WBPU. Under humid UV conditions, FTIR data indicated that the 0.4% and 1.2% GO/WBPU nanocomposites were only $\approx 10\%$ less degraded (compare 1710 cm⁻¹ band intensity increases in humid UV line plot) than the neat WBPU at 140 d. The $\approx 10\%$ decrease in degradation for GO/WBPU nanocomposites was not statistically significant and indicated a negligible improvement in polymer durability by GO nanofillers under humid UV conditions. Considering the steady-state removal of polymer matrix from both neat WBPU and 1.2% GO/WBPU nanocomposites under humid UV conditions as measured with thickness loss, the use of FTIR to compare the degree of WBPU and 1.2% GO/WBPU nanocomposite degradation under humid UV conditions was unreliable. Nevertheless, the similar thickness losses observed for neat WBPU and the 1.2% GO/WBPU nanocomposite



Fig. 2. Thickness of the 1.2% GO/WBPU nanocomposites before and after 140 d UV exposure under dry (left) and humid (right) conditions.

indicated that GO did not have a protective effect on polymer photodegradation under humid UV conditions. Therefore, FTIR results indicated that GO only had a protective effect on the polymer photodegradation process under dry UV conditions and that FTIR should only be used to assess differences in degradation when polymer photoproducts are not readily removed during degradation, as was the case under dry UV conditions in this study (Figs. 2 and S5).

Control samples exposed to dry dark and humid dark conditions were also analyzed with ATR-FTIR (Fig. S18). The ATR-FTIR spectra from both dark control conditions indicated that ester hydrolysis occurred initially as shown by the decrease in the 1727 cm^{-1} band (Fig. S19) but further changes to the carbonyl region thereafter were not apparent (Fig. 3). A loss of the C-O-C (1173 cm^{-1}) band intensity in the fingerprint region confirmed that ester cleavage occurred rather than a simple change in hydrogen-bonding conditions (Fig. S18). Dark controls showed that changes in the UV-exposed samples required UV radiation (Figs. S18–S19), as further elaborated upon in the SI.

3.2.4. Surface morphological changes

Changes to surface morphology during UV irradiation were evaluated microscopically using SEM and AFM imaging. Both techniques were also used to monitor the changes in GO particle concentration at the nanocomposite surface during UV exposure.

Before UV exposure, both the GO/WBPU nanocomposites and the neat WBPU control had similar topographic features in the SEM images (compare Figs. 4 and 5, respectively), indicating that both surfaces were primarily composed of polymer features. LSCM imaging was used to make a direct comparison of the Root Mean Square (RMS) surface roughness values of neat WBPU and GO/WBPU nanocomposites. Neat WBPU was glossy (< 1 μ m surface roughness) with an average roughness value (and one standard deviation) of 0.35 μ m \pm 0.05 μ m while 1.2% GO/WBPU had a similar roughness value of 0.44 μ m \pm 0.08 μ m in 169 μ m by 169 μ m images. The similarities in the LSCM roughness results for both the neat WBPU and GO/WBPU sample surfaces were consistent with the similar polymer features observed in the SEM images.

In Figs. 4 and S3, SEM images of the 1.2% GO/WBPU nanocomposite surfaces exposed to dry UV and humid UV conditions are presented at a high and low magnification. A systematic change in surface morphology was observed with increasing UV irradiation. At 0 d, the nanocomposite surface consisted of a mixture of polymer features and polymer-coated GO particles. The raised polymer features were similar to those observed for neat WBPU at 0 d (Figs. 5 and S4). With increasing exposure time to dry UV conditions, the raised polymer features of the 1.2% GO/WBPU nanocomposite surface were gradually removed and more GO particles became visible by 15 d and 30 d (Figs. 4 and S3). At 60 d, the raised polymer surface features almost completely disappeared to form a smooth surface containing some GO particles, albeit at a low concentration, suggesting that any initial GO particles present at the surface may have released. The surface of neat WBPU also smoothed by 60 d, but no particles were present that were similar in shape or size to those on the nanocomposite surface (Fig. S4). At 140 d of dry UV exposure, after more polymer had degraded, GO particles became more apparent at the 1.2% GO/WBPU nanocomposite surface (Figs. 2 and S3-S4). For neat WBPU, particle-like features were not present at the surface after 140 d of UV exposure (Figs. 5 and S4).

In contrast to dry UV conditions, humid UV conditions led to rapid and almost complete removal of the raised polymer surface features by

Table 2

Average thicknesses and thickness losses of (0% and 1.2%) GO/WBPU nanocomposites before and after different exposure conditions. At least five randomly chosen cross-sections per SEM image were measured with ImageJ (NIH, Bethesda, MD) software with at least three replicate SEM images taken of different nanocomposite areas.

Sample and conditions	Average thickness before (µm)	Std. Dev. (µm)	Average thickness after 140 d (μm)	Std. Dev. (µm)	Average thickness loss (µm)	Std. Dev. (µm)
0% GO/WBPU Humid UV	97	3	47	10	50	10
1.2% GO/WBPU Humid UV	127	3	83	2	45	3
0% GO/WBPU Dry UV	97	3	103	5	≈0	
1.2% GO/WBPU Dry UV	127	3	127	8	≈0	
1.2% GO/WBPU Humid Dark	127	3	115	8	13	8
1.2% GO/WBPU Dry Dark	127	3	123	4	5	5



Fig. 3. The carbonyl region (ATR-FTIR) of (0% and 1.2%) GO/WBPU nanocomposites exposed to UV light under dry and humid conditions (left and middle columns). The changes in the intensity of the 1710 cm⁻¹ band (ATR-FTIR) with UV exposure time for (0% and 1.2%) GO/WBPU nanocomposites under dry and humid conditions are shown in the right column. Each spectrum and line plot is consistently baseline-corrected (linear correction, same baseline points) and represents the average of triplicate specimens (and standard deviation in the line plot). IR bands of interest are denoted by dashed lines and labels.

15 d for 1.2% GO/WBPU nanocomposites. GO particle protrusions from the nanocomposite surface were also apparent to a much greater degree at 15 d under humid UV conditions compared to at 140 d under dry UV conditions (Figs. 4 and S3). Specifically, if 140 d dry UV and 15 d humid UV exposure (6 years *versus* 0.6 years in terms of UV dose, respectively) are considered similar in terms of the GO concentrations exposed at the nanocomposite surfaces, then the rate of GO exposure at the nanocomposite surface occurred approximately 10 x faster under humid UV conditions. Furthermore, when comparing 15 d humid UV exposure to 140 d dry UV exposure, GO particles were found to protrude further above the nanocomposite surface from the humid UV exposure.

After 15 d and 30 d of humid UV exposure, the presence of GO particles was most apparent (Figs. 4 and S3). By 60 d, GO particles protruded even further from the nanocomposite surface and formed larger, crumpled aggregates (Figs. 4 and S3). The GO aggregates likely formed by interconnection of GO particles at and below the nanocomposite surface as polymer matrix was removed during photodegradation. GO particles that did not interconnect with other GO particles during photodegradation might have released from the nanocomposites earlier. The GO crumpling observed may have been facilitated by the presence and removal of free and confined water under high humidity conditions, since cycles of moisture exposure were previously shown to affect the structure of GO through the interaction of water molecules with hydrophilic functional groups of GO (Jiang et al., 2015; Zhu et al., 2012; Wang et al., 2012). Furthermore, photo-reduction of GO, which is discussed later, may have also contributed to the crumpling and aggregation observed (Hou et al., 2015). By 140 d of humid UV exposure, the large GO aggregates were no longer present, suggesting that the protruding GO particles present at 60 d released from the nanocomposite surfaces (Figs. 4 and S3). The large thickness loss observed for 1.2% GO/WBPU nanocomposites after humid UV exposure (Fig. 2) explains the rapid changes in surface morphology and loss of GO particles from the 1.2% GO/WBPU nanocomposite surface (Figs. 4 and S3). Furthermore, the presence of moist air likely encouraged the release of hydrophilic GO from the nanocomposite surface. In contrast, dry UV conditions did not lead to accumulation of large quantities of GO, subsequent GO aggregate formation, and almost complete GO loss from the nanocomposite surface (Figs. 4 and S3). Instead, a little GO loss (not $> 16 \mu g$ of GO based on total mass loss of nanocomposite assuming 1.2% GO content in removed material) may have occurred from the top surface by 60 d while some underlying GO exposure occurred at the nanocomposite surface by 140 d. The slower nanocomposite surface changes were a result of the minimal thickness loss (Fig. 2). Thus, this study uniquely shows the loss of GO from a nanocomposite surface under wet conditions as the polymer matrix degrades away by a combination of UV light and humidity. More broadly, the results of this study indicate that GO would likely release from a nanocomposite under conditions that enabled polymer matrix removal and provided water or humidity for interaction with the loosely anchored, surface-bound hydrophilic GO particles.

The independent effects of temperature and humidity in the absence of UV light were assessed using SEM images of the 0% and 1.2% GO/ WBPU nanocomposites exposed to 140 d of dry dark and humid dark conditions. Under both dry dark and humid dark conditions, there was no apparent GO accumulation at the nanocomposite surface over time and the initial raised polymer surface features gradually flattened out upon heating and led to a decreased nanocomposite surface roughness (Fig. S6 for [0% and 1.2%] GO, respectively).

In comparison to SEM images, topographic AFM images showed the same trends in surface morphological changes and GO particle surface accumulation at the UV-degraded nanocomposite surface (Fig. S9). AFM peak force-quantitative nanomechanical property mapping (PF-QNM) was used to further validate the presence of GO particles at the surface of nanocomposites using the higher modulus of degraded polymer surrounding GO relative to the lower modulus of the neat WBPU polymer control (Fig. 6). Although the modulus of GO deposited onto the WBPU polymer matrix was initially found to be slightly higher



Fig. 4. SEM images of 1.2% GO/WBPU nanocomposite surfaces exposed to dry UV and humid UV conditions at a) high and b) low magnification for the indicated time periods.

than neat WBPU alone (Fig. S10, further information in the SI), UV degradation led to higher modulus polymer surrounding softer GO in the degraded nanocomposite (Fig. 6b). In contrast, neat WBPU did not stiffen as quickly as the WBPU matrix in the nanocomposite during weathering for up to 30 d, especially above a cut-off of 2 GPa (Fig. 6a).

For this reason, the amount of stiffened polymer above 2 GPa was quantified in the AFM modulus images of the 1.2% GO/WBPU nanocomposites to determine the fraction of the nanocomposite surface affected by GO. More broadly, this is one of the few techniques available in which carbonaceous nanomaterial surface concentrations during



Fig. 5. SEM images of neat WBPU (0% GO/WBPU) surfaces exposed to dry UV and humid UV conditions at a) high and b) low magnification for the indicated time periods.



Fig. 6. AFM modulus images and average AFM (in PF-QNM mode) modulus measurements of a) neat WBPU and b) 1.2% GO/WBPU before and after 15 d and 30 d of humid UV exposure. Average modulus measurements were made on duplicate or more areas of a specimen.

nanocomposite degradation can be indirectly examined in a semiquantitative manner.

Before UV exposure, there were minimal differences in modulus values between neat WBPU and 1.2% GO/WBPU nanocomposites, suggesting that GO near the nanocomposite surface was likely coated with a thin layer of polymer (Fig. 6). In Fig. 6a, the stiffness of neat WBPU increased with increasing UV exposure time under humid conditions likely due to re-orientation of the polymeric structure as well as embrittlement by cross-linking of WBPU chains (Boubakri et al., 2010), with no significant change observed between 15 d and 30 d. For the 1.2% GO/WBPU nanocomposites, parts of the surface increased in stiffness more dramatically than for neat WBPU as a function of humid UV exposure time (Fig. 6). Specifically, the modulus plot for the 1.2% GO/WBPU nanocomposites showed (Fig. 6b) a higher modulus tail at 15 d and a peak at 30 d of humid UV exposure. Since these modulus components were not present in the neat WBPU modulus plots (Fig. 6a), the stiffer areas could be attributed to the presence of increasing concentrations of GO at or near the nanocomposite surfaces. Compared to the SEM images (Fig. 4), the stiffer areas in the AFM modulus images of humid UV degraded 1.2% GO/WBPU nanocomposites generally corresponded to areas between the protruded particles and to a small extent, at the tips of the protruded GO particles. The higher stiffness at the flat areas of the surface may have been a result of both GO particles close to the surface and enhanced polymer chain re-orientation and crosslinking promoted by the presence of nearby GO particles. The actual GO particles and clusters did not appear to significantly increase in stiffness under humid UV conditions (Fig. 6b), likely due to their protruded structure at the surface that allowed them to move freely or be compressed by the AFM tip. Thus, this technique was only semi-quantitative as it indirectly indicated the level of GO present based on the surrounding polymer it impacted, thus allowing for a relative comparison of GO content at different degradation time points. The information provided by this measurement was useful considering the neat WBPU did not show similarly high levels of stiffness at the surface for the same level of UV exposure, for up to 30 d of UV exposure (Fig. 6a). By 60 d of UV exposure, the modulus of neat WBPU increased to high moduli that confounded identification of GO.

The number of stiffer areas (above 2 GPa) at the nanocomposite surface increased with humid UV exposure time from 0 d to 30 d, in line with the increased number of GO particles observed at the nanocomposite surface with SEM under the same conditions (Fig. 4). When calculated above a threshold of 2 GPa, the point at which no polymer modulus was present for neat WBPU exposed to UV radiation for the same time, the fraction of material affected by GO particles at the surface increased to (22 \pm 4) % at 15 d while at 30 d, the fraction of material affected by GO at the surface increased to (34 \pm 3) %. AFM modulus measurements for dry UV conditions showed that the fraction of material affected by GO particles at the surface (above 2 GPa) was 0% at 15 d while at 30 d, the fraction of material affected by GO at the surface increased to a range of (0 to 2) % in replicate images (Fig. S11). This was likely due to the low GO concentration observed at the dry UVdegraded nanocomposite surface with SEM imaging (Fig. 4) after 30 d of dry UV exposure.

Thus, AFM modulus measurements can be successfully used in future studies for semi-quantitatively measuring the level of carbonaceous nanoparticles (CNPs) present based on their effect on surrounding polymer material, or by their intrinsic high modulus values, which may be the case with pristine graphene. However, it should be noted that this technique cannot be applied when the neat polymer control, UVexposed for the same amount of time as the nanocomposite, has a modulus value that becomes similar to or higher than the modulus of areas in the nanocomposite.

3.2.5. Sub-surface transformations

To semi-quantitatively assess the change in GO content in the subsurface (top 1 μ m to 4 μ m as provided by the instrument manufacturer) during UV exposure of the GO/WBPU nanocomposites, Raman spectroscopy was utilized (Figs. 7 and S12). At all dry UV exposure time points, there was no statistically significant increase in GO content in the sub-surface (top 1 μ m to 4 μ m). Although SEM images indicated that the number of GO particles on the nanocomposite surface had increased by 140 d of dry UV exposure (Figs. 4 and S3), the nanocomposite had not significantly lost thickness (Fig. 2). This resulted in GO particles appearing at the surface in the SEM images but did not significantly



Fig. 7. The defective (D, 1306 cm⁻¹) and graphitic (G, 1602 cm⁻¹) Raman band intensities that indicate the concentration of GO near the sub-surface (top 1 μ m to 4 μ m) of (0%, 0.4%, and 1.2%) GO/WBPU nanocomposites before and after 140 d of UV exposure under dry and humid conditions. Line plots in the righthand column show the D band (1306 cm⁻¹) intensity changes as a function of UV exposure time under dry and humid conditions. Each spectrum and data point in the line plot represent the average (and standard deviation) of three replicate specimens, with measurements of four areas per replicate specimen.

impact the GO concentration (from D and G band intensities) measured by Raman spectroscopy in the thicker sub-surface layer (top 1 μ m to 4 µm) of the nanocomposites. In contrast, a statistically significant increase in GO content was detected by Raman spectroscopy for GO/ WBPU nanocomposites exposed for 60 d to humid UV conditions, consistent with the large build-up of GO particles on the surface observed with SEM (Figs. 4 and S3). The accumulation of GO in the subsurface (top 1 µm to 4 µm) was also consistent with the rapid decrease in polymer surface features, loss of nanocomposite thickness, and rapid appearance of GO particles over time under humid UV conditions (Figs. 4 and S3). By 140 d humid UV exposure, Raman spectroscopy results showed that GO had substantially accumulated in the sub-surface during UV exposure over the duration of the experiment. However, GO particle accumulation at the nanocomposite surface was minimal with SEM after 140 d humid UV exposure (Figs. 4 and S3), indicating that most of the accumulated GO was within the top 1 μ m to 4 μ m of the surface rather than exposed at the very top surface. Samples of 1.2% GO/WBPU nanocomposites exposed to dry dark and humid dark conditions did not show D and G band intensity changes in their Raman spectra (Fig. S13). It should be noted that the D and G band intensities were not affected strongly by surface roughness changes as further described in the SI.

3.2.6. Transformations of GO particles

UV-induced transformations of the GO nanoparticles, on and near the nanocomposite surface, were also assessed using the intensity ratio of the Raman D and G bands (I_D/I_G). Under both dry UV and humid UV conditions, a similar decrease in the I_D/I_G with exposure time was observed, indicating some UV-induced chemical reduction of GO or the loss of oxygen functional groups on the GO particles in the nanocomposite sub-surface (Figs. S14 and S15). Note, the neat WBPU had minimal D (and G band) signal (Fig. S13) so its I_D/I_G is not shown in the plots for clarity. GO chemical reduction was not found to occur under dry dark conditions and occurred to only a small extent under humid dark conditions (Figs. S14 and S15). Therefore, GO particles in the subsurface of the nanocomposites transformed by chemical reduction during UV irradiation.

This behavior is consistent with previous studies of UV-induced chemical reduction of GO in aqueous systems, and importantly, prior to this study, this phenomenon was not previously observed for GO nanofillers dispersed in a polymer matrix (Hou et al., 2015; Chowdhury et al., 2015). Of note, it was not possible to determine the specific decrease in GO surface oxygen content with X-ray photoelectron spectroscopy because the carbon and oxygen from the polymer matrix interfered. Overall, chemical reduction of GO may have slightly increased the GO hydrophobicity and contributed to the aggregated GO structures formed at 60 d humid UV exposure, but did not prevent release of these GO particles in the presence of moisture. Photodecomposition of GO may have also led to mineralization and a decrease in particle size, but a decrease in particle size was not apparent from Raman spectroscopy results. Specifically, there was no increase in the I_D/I_G from the increased number of GO edges created from fragmented particles that act as defect sites (relative to less graphitic regions in smaller particles). Thus, a particle size decrease was either less significant than GO reduction at the nanocomposite surface or smaller GO particles were released and thus were not detected by Raman spectroscopy. Particle size decreases were observed as described later in the Nanomaterial release Section 3.3.

3.2.7. Impact of GO nanofiller mass concentration on nanocomposite degradation

To assess the effect of GO mass loading on the degradation of GO/ WBPU nanocomposites, GO/WBPU nanocomposites at a lower mass loading (0.4% mass fraction) were also UV-exposed under both dry and humid conditions. This GO loading was chosen since it is on the lower end of GO concentrations that have been found to improve the properties of WBPU (Bernard et al., 2020). With SEM imaging, similar degradation trends were observed for 0.4% GO/WBPU nanocomposites (Fig. 8) compared with trends for 1.2% GO/WBPU nanocomposites (Figs. 4 and S3). Under dry UV conditions, the raised polymer features smoothed out for 0.4% GO/WBPU by 60 d and 140 d. Consistent with the 1.2% GO/WBPU nanocomposites, there were also a limited number



Fig. 8. SEM images of 0.4% GO/WBPU nanocomposite surfaces exposed to dry UV and humid UV conditions for the indicated time periods.

of GO particles apparent just at or below the surface after 60 d dry UV exposure. Under humid UV conditions, the raised polymer features also smoothed out and GO surface accumulation occurred by 15 d. At 15 d of humid UV exposure, more GO protrusion was apparent at the 0.4% GO/WBPU nanocomposite surface than after exposure to 140 d of dry UV conditions. At 60 d of humid UV exposure, the GO particles aggregated and protruded from the 0.4% GO/WBPU nanocomposite surface. This phenomenon was similar to the GO surface aggregation observed with the 1.2% GO/WBPU nanocomposites. Then by 140 d, the GO particles appear to have released from the nanocomposite surface, with very few GO particles remaining. Raman spectroscopy showed the same general trends of GO accumulation in the nanocomposite subsurface (1 μ m to 4 μ m) but with lower overall GO mass concentrations: under dry UV conditions there was no statistically significant increase in the sub-surface GO content while the sub-surface GO content steadily increased under humid UV conditions (green Raman plots in Figs. 7, S12-S13). ATR-FTIR also showed a build-up of polymer photoproducts under dry UV conditions and steady-state formation/removal of polymer photoproducts under humid UV conditions, similar to the results obtained for the 1.2% GO/WBPU nanocomposites (Figs. 3 and S16-S17). ATR-FTIR results also indicated that small differences in GO mass loading (0.4% versus 1.2%) did not have a large effect on inhibition of polymer photodegradation. Altogether, the results indicated that GO at a concentration three times lower than 1.2% had a similar effect on WBPU photodegradation under dry UV and humid UV conditions. Therefore, similar photodegradation trends can be expected with a lower concentration of nanofiller in the same polymer system. This is important information from a design perspective since it is known that this lower mass loading of GO will have the same durability as the 1.2% GO/WBPU nanocomposite while still imparting beneficial properties to WBPU and providing a lower cost nanocomposite (Bernard et al., 2020). In general, to fully understand a nanocomposite systems' durability, it is most practical to study the trends in GO/polymer nanocomposite durability at the low and high ends of the GO concentration range in which beneficial properties are imparted on a given polymer system.

3.3. Nanomaterial release

Release of GO from nanocomposites was assessed using a simulated rain spray technique after 60 d of dry UV exposure. Each nanocomposite was sprayed lightly with DI water to collect ≈ 5 mL of runoff for analysis. This technique was used to induce release of loose nanoparticles *via* a low mechanical force spray, impart water onto the nanocomposite surface to interact with hydrophilic GO particles, and enable collection of any GO particles that had spontaneously released during UV exposure and were already present in the enclosed sample holder. This spray technique approach has been used with different types of nanoparticles in our previous study (Jacobs et al., 2016). GO release studies using cyclic UV exposure/rain spray or immersion with sonication (or shaking) at the end of UV exposure are likely more aggressive and accelerate release behavior compared to rain spray at the end of UV exposure but the latter scenario may be most realistic. A comparison of the difference in released nanoparticle concentrations between these scenarios may be useful in future studies. Validation of nanoparticle release may also be useful with more outdoor studies in weathering fields such as in Florida (humid UV) and Arizona (dry UV). Weathering comparison studies may be more practical with nanoparticles that can be detected with greater selectivity and at a much lower concentration than is currently possible with GO. Unlike the measurement of carbon nanotubes released from polymer nanocomposites into water, which have been successfully quantified using embedded metal catalyst impurities detectable by sensitive techniques such as single particle inductively coupled-mass spectrometry, graphene and GO do not have impurities and cannot be detected at partsper-billion concentrations (Wang et al., 2016; Reed et al., 2013). However, the graphenic structure of released GO can be detected at higher concentrations (ppm) using Raman spectroscopy.

Therefore, Raman spectroscopy was used to measure the GO mass concentration in the aqueous runoff. The intensity of the D band (1354 cm⁻¹) was used for quantification since a water deformation band (1638 cm⁻¹) interferes with the G band (1612 cm⁻¹) in aqueous suspensions (Fig. S2a) (Salzmann et al., 2007). Using a calibration curve of aqueous GO suspensions, the GO mass concentration was measured from (1 to 30) ppm (Fig. S2b, c). From the standard deviation of the linear fit of the calibration curve, the limit of detection for the technique was determined to be 5 ppm and the limit of quantitation was determined to be 10 ppm. Since polymer fragments, polymer fragments containing nanomaterials, and free nanomaterials were previously shown to release from nanocomposites by other researchers, one of the biggest advantages of using Raman spectroscopy was that neat polymer fragments under a few microns in diameter would not generate interfering signal in the D band location of the spectrum (Fig. S2a, b) (Harper et al., 2015).

After 60 d of dry UV exposure, GO was not detected in the run-off using Raman spectroscopy (Fig. 9a). This indicates that GO did not release from the degraded GO/WBPU nanocomposite at a concentration > 1.25 μ g GO/cm² nanocomposite (0.48 μ g GO/cm² nanocomposite/year) or 5 ppm GO in rain spray, the technique detection limit, after 60 d of dry UV exposure. This was fairly close to the theoretical maximum release of 3.75 μ g GO/cm² nanocomposite (1.44 μ g GO/cm² nanocomposite/year) or 15 ppm of GO in rain spray calculated based on the mass loss data from dry UV exposure and the small additional mass loss (< 1% by mass) from simulated rain spray. The process of GO



Fig. 9. After 60 d of dry UV exposure, run-off from simulated rain was measured in aqueous form using (a) Raman spectroscopy and (b) run-off was dried on a copper grid and imaged in several areas with SEM. The sample holder for GO release studies and Raman spectroscopy controls and calibration curves can be found in the SI.

release likely did not necessarily reach the full theoretical maximum due to some GO loss during the spray process, some conversion of GO to CO or CO_2 , and some inhomogeneity that may have been present in the top surface polymer skin layer of the nanocomposite. The low amount of GO release observed (i.e., below 1.25 µg GO/cm² nanocomposite) was also consistent with SEM images of nanocomposites exposed to dry UV conditions from 0 d to 60 d since there were likely only small losses of the GO particles from the nanocomposite surfaces during the initial stages of degradation. However, the lack of GO particles in SEM images of the nanocomposite surface (Fig. 4) after 60 d of dry UV exposure suggests that a concentration of GO particles lower than 5 ppm could have released as the nanocomposite surface degraded. To determine if any GO released at a concentration below 1.25 µg GO/cm² nanocomposite or 5 ppm GO in the run-off, a fraction of the well-mixed runoff was dried on a copper grid and imaged grid-by-grid with SEM. In several grid areas, the presence of particles consistent with the size (1 µm to 2 µm laterally) and shape of GO, as well as some smaller sheetlike pieces were observed (Fig. 9b). Although an exact particle size distribution could not be ascertained due to particle aggregation and curling, in the grid areas imaged with SEM (Fig. 9b), approximately 42% of the total particles counted (152 total particles) were 10 nm to 100 nm wide, 38% were 100 nm to 1 μm wide, and 20% were 1 μm to 10 μm wide. With the assumption that particles in the 10 nm to 100 nm range were 1/100 the mass of the initial GO particles and particles in the 100 nm to 1 µm range were 1/10 the mass of the initial GO particles, the mass distribution of particles was roughly 2% [10 nm to 100 nm], 15% [100 nm to 1 µm], and 83% [1 µm to 10 µm] for released GO particles. This suggests that a little > 80% of the GO particle mass remained mostly intact at the original particle size while a little under 20% of the remaining GO particle mass visibly fragmented into smaller particles during 60 d of dry UV exposure. These results indicate that GO released but the amount of GO was low in concentration (below 1.25 µg GO/cm^2 nanocomposite or 5 ppm GO in rain spray).

Although the decrease in GO at the nanocomposite surfaces from 60 d to 140 d under humid UV conditions was much more dramatic in the SEM images than changes to the nanocomposite after 60 d dry UV exposure, GO release studies under humid UV conditions could not be performed with the specially-designed sample holder since it is not able to simultaneously contain released GO while maintaining humidity in

each of the cells. Nevertheless, based on the collective results, it is evident that GO was released (*e.g.*, fell off the surface or blew off the surface from circulated air) during UV irradiation under humid conditions, especially from 60 d to 140 d, due to the polymer degrading around it and the favorable interaction of GO with moisture in the air. Evidence includes the continuous removal of the polymer matrix, as indicated by the steady-state FTIR results and the large thickness loss observed with cross-sectional SEM; the increased protrusion of GO from the nanocomposite surface with increasing humid UV exposure time from 15 d to 60 d; and the lack of GO present at the surface after 140 d humid UV exposure despite the presence of substantial GO concentrations at the surface for earlier humid UV exposure time points.

Although detection of released GO was found to be challenging due to the lack of impurities or tracers within the carbonaceous structure (as is the case with CNTs) and the challenge of collecting released nanomaterial under humid UV conditions, this study was able to uniquely detect GO release from a degraded polymer nanocomposite by a combination of Raman spectroscopy and SEM imaging of dried run-off. Future work on improving the sensitivity of Raman spectroscopy, developing new techniques that can detect graphenic material at ppb levels, and designing specialized sample holders for humid UV exposure will enable quantification of the material released from degraded GO/ polymer nanocomposites both at the low concentrations that are released under dry UV conditions and the higher concentrations that are released under humid UV conditions. Accordingly, as GO release measurements in run-off become more quantitative, the level of GO release can still be monitored from the perspective of changes to the nanocomposite surface. As was demonstrated in this study, the low concentrations of GO detected in the aqueous run-off after 60 of dry UV exposure corresponded to the low GO content observed at the degraded nanocomposite surface at time points between 0 d and 60 d of dry UV exposure.

3.4. Potential implications of GO use in coatings

Owing to its hydrophilicity, GO will likely be used in many hydrophilic coatings that are affected by a combination of UV light and moisture. Based on the findings of this study, hydrophilic coatings containing GO will not have an enhanced lifetime relative to their corresponding neat coating during UV exposure in humid environments. However, over the course of six years of UV exposure in dry environments, GO/polymer coatings can degrade less (*e.g.*, 30% reduction in mass loss for WBPU) and potentially last longer than the same coatings without GO. The results of this study also show that GO particle accumulation at a WBPU nanocomposite surface will occur outdoors, especially under humid UV conditions, which may lead to release of GO from continued product wear, unintended dermal interaction with GO at a product surface, or interaction of GO with organisms in the environment upon disposal. Safe design of GO/polymer nanocomposites to decrease dermal contact, interaction of GO with organisms, and uptake of GO by organisms may be warranted as various studies, summarized in our previous review article, have suggested that GO may pose environmental and human health risks (Goodwin Jr et al., 2018).

In terms of GO release, the results of this study suggest that GO can have a high probability of release from polymers that are easily degraded by a combination of UV radiation and moisture by while GO release will occur to a lesser extent under dry UV conditions. GO release from nanocomposites, with the highest concentration of GO release resulting from humid UV exposure of some GO/polymer nanocomposites, could lead to the transport of hydrophilic GO in aquatic environments, the interaction of GO with organisms, and the uptake of GO by organisms in the environment. For a different type of polymer matrix that is more hydrophobic and less affected by moisture, it is currently unclear if GO exposure, accumulation, and release would be as prominent during UV degradation. Overall, since GO is relatively inexpensive and improves the properties of many hydrophilic polymers, the responsible use of GO in polymer nanocomposites should involve testing the general UV degradation mechanism and GO release potential of specific polymer systems at the low and high range of GO concentrations that are useful, in the presence and absence of moisture. This is particularly important for hydrophilic GO, which is more likely to interact with water and release in the presence of moist air after humid UV exposure or after a rain event following nanocomposite degradation under both dry UV or humid UV conditions. The release observed with GO is likely not generalizable to release of graphene from graphene/polymer nanocomposites since these hydrophobic nanoparticles are less likely to be removed by water. In fact, a study on graphene release form polymer nanocomposites by Zepp et al. (2020) showed that hydrophobic graphene released more with polymer fragments when exposed to dry UV conditions compared to UV and rain cycle exposure (i.e., wet conditions). The same study also demonstrated the importance of the polymer matrix type with respect to degree of nanoparticle release (Zepp et al., 2020). Further degradation and particle release studies involving other polymer systems with different photodegradation chemistries and types of graphene family nanomaterials will be useful.

4. Conclusions

Incorporation of GO into WBPU led to several observable effects on the resultant nanocomposite photodegradation behavior. Under dry UV conditions, the presence of GO nanofillers led to an increase in the durability of the nanocomposite relative to neat WBPU. In contrast, under humid UV conditions the presence of GO nanofillers did not improve the durability of the nanocomposite relative to neat WBPU. Under both dry UV and humid UV conditions, GO accumulated at the nanocomposite surface, but it took approximately an order of magnitude longer for GO particles to accumulate to a similar level under dry UV conditions (6 years *versus* 0.6 years in terms of UV dose). The slower GO particle surface accumulation under dry UV conditions was attributed to the build-up of polymer photoproducts that limited GO particle exposure at the nanocomposite surface. GO nanofillers were found to chemically reduce, indicating that the particles could transform at and near the nanocomposite surface during UV-induced degradation. Under humid UV conditions, polymer photoproducts were removed during UV irradiation which led to a large thickness loss of the nanocomposites and the rapid exposure and accumulation of GO at and near the surface. At the later time points of humid UV exposure, GO particle protrusion from the nanocomposite surface followed by the loss of surface-bound GO suggested the release of most GO particles from the nanocomposite surface. In contrast, GO release was directly observed under dry UV conditions but at concentrations below 0.48 µg GO/cm² nanocomposite/year (5 ppm in rain spray), likely a result of the small thickness loss of nanocomposite material over 140 d exposure. Similar photodegradation trends were found for both low and high GO mass loadings that impart beneficial properties on WBPU, indicating that both GO mass loadings similarly affected WBPU durability. Broadly, the results of this study suggest that there should be careful design of products used outdoors when they contain GO in polymer matrices that are sensitive to a combination of UV and moisture.

CRediT authorship contribution statement

David G. Goodwin: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - original draft, Writing - review & editing, Supervision. Trinny Lai: Investigation, Formal analysis. Yadong Lyu: Investigation, Formal analysis. Chen Yuan Lu: Investigation, Formal analysis. Alejandro Campos: Investigation, Formal analysis. Vytas Reipa: Conceptualization, Methodology, Investigation, Writing - review & editing. Tinh Nguyen: Conceptualization, Writing - review & editing, Supervision. Lipiin Sung: Conceptualization, Resources, Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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NIST disclaimer

Certain commercial products or equipment are described in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.

Appendix A. Supplementary data

More data and information that support the results presented in this study are provided: The sample holder used for GO release studies (Fig. S1); Raman spectroscopy controls for GO release experiments including spectra and calibration curves of varying GO mass concentrations in DI water with and without added polymer (Fig. S2); SEM images of 1.2% GO/WBPU nanocomposites at all UV-exposure time points (Fig. S3), additional SEM images of neat WBPU before and after UV degradation (Fig. S4); cross-sectional SEM images of neat WBPU for 0 d and 140 d UV exposure (Fig. S5); surface morphological and cross-sectional SEM images of dark controls for neat WBPU and 1.2% GO/WBPU nanocomposites (Figs. S6-S7); mass loss measurements of neat WBPU and GO/WBPU nanocomposites after dry UV exposure and pictures of neat WBPU and GO/WBPU nanocomposites stuck to the stainless steel substrates after humid UV exposure (Fig. S8); AFM topographic images (Fig. S9), PF-QNM-AFM modulus measurements of GO particles dropcasted on top of WBPU and discussion of the results (Fig. S10); PF-QNM-AFM measurements of neat WBPU and 1.2% by mass GO/WBPU nanocomposites exposed to dry UV conditions (Fig. S11); Raman spectra in the D and G band region of all UV-exposed specimens at different time points (Fig. S12); line plots of the D band intensity changes with UV and dark exposure (Fig. S13); the intensity ratio of the D and G bands under dry UV and dry dark conditions (Fig. S14) as well as under humid UV and humid dark conditions (Fig. S15); full FTIR spectra for all specimens at all UV-exposure time points (Fig. S16), the carbonyl region of these spectra (Fig. S17); full FTIR spectra for all specimens at all dark exposure time points (Fig. S18), the carbonyl region of the dark control spectra (Fig. S19); the photodegradation mechanisms of polyurethanes (Fig. S20); and evidence that the urethane component is present at the same wavenumber as the ester band in the ATR-FTIR spectrum using an in situ curing study of isocyanates to form urethanes (Fig. S21). Supplementary data to this article can be found online at https://doi.org/10.1016/j.impact.2020.100249.

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