Fate of graphene in polymer nanocomposite exposed to UV radiation

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Abstract. Graphene is increasingly incorporated in polymers to enhance their mechanical, thermal and electrical properties. However, organic polymers are prone to degrade when exposed to UV radiation. Therefore, graphene in polymer nanocomposites could eventually be released into the environment during their life cycle, which might have a negative impact on the environment and thus presents a roadblock to their use. This study investigates the degradation of a graphene/polyurethane composite and characterizes the graphene concentration at the nanocomposite surfaces during exposure to UV radiation. The polyurethane was a one-component, water-borne polyurethane and graphene material was graphene oxide (GO) sheets. GO/WBPU composites having a thickness between 105 μm and 150 μm were exposed to 75% RH, 50°C, and UV radiation between 290 nm and 400 nm in a NIST-developed UV chamber. Chemical degradation, mass loss, and surface morphology were measured at specified exposure time using FTIR, gravimetry, SEM, AFM and LCSM techniques. Results showed that, when exposed to UV radiation having wavelengths similar to those of the sunlight, the polyurethane matrix underwent photodegradation, subsequent mass loss and accumulation of a large amount of graphene on the composite surface.

1. Introduction
The exceptional properties (e.g., mechanical, barrier, thermal) of polymer nanocomposites [1,2] make them excellent materials to be used in a wide variety of applications. Graphene – one atom thick, sheets of sp²-bonded carbon – has emerged as a new class of nanomaterial. Interest in graphene is exploding because of its unique physical properties and its potential application to nanoelectronic systems. Our previous study showed that graphene greatly enhances the mechanical, oxygen barrier, and fire resistance properties of polyurethane polymer [3].Whatever the application, long-term performance of the nanocomposite itself and the fate of the nanoparticles in the polymer matrix have an important role in the use of these products. However, the polymer matrix is susceptible to degradation during outdoor exposure, which potentially leads to nanoparticle release into the environment. Since nanoparticles have shown potential risks to human health and environment [4,5], their release during the life cycle of polymer nanocomposites could restrain commercialization of polymer nanocomposites. Currently, little information is available about the fate of graphene nanoparticles or their potential health and environment risks during the graphene/polymer composite life cycle. Such information is sorely needed for assessing the potential risks of this new class of nanomaterial. This study investigates the fate of graphene in a graphene/water-borne polyurethane nanocomposite during its exposure to ultraviolet (UV) radiation.
2. Experimental Procedures

2.1. Materials and Nanocomposite Preparation

The polyurethane was a one-component, water-borne polyurethane (WBPU), an anionic dispersion of an aliphatic polyester urethane resin in water (50%, by mass) and in n-methyl-2-pyrrolidone (NMP) (15%, by mass) (Bayhydrol 110, Bayer MaterialScience LLC). The chemical structure and other components, such as surfactants and additives, in this material are not known. The graphene material, graphene oxide (GO), used in this study was prepared at the University of Texas, Austin, using a process described elsewhere [6]. Graphene sheets (i.e., graphene oxide sheets) produced by this process have a thickness of approximately 2 nm and a width of approximately 2 µm. They contain a variety of oxygen groups, such as hydroxyl, epoxide, and carboxylic acids, on the basal planes and at the sheet edges, which can form strong hydrogen and covalent bonds with a variety of polymer matrices. This material disperses easily in water-based polymers.

PU nanocomposites containing mass fractions of 0% (i.e., unfilled) and 2% of GO were prepared following the process illustrated in Figure 1 (because 60% of the mass of the as-received GO sample was water, the amounts added to the composites were adjusted accordingly to provide the desired loadings). The amount of GO was progressively added to a water-containing flask to provide a concentration of approximately 6 mg GO in 1 ml water. After sonication (at 40 kHz) for 8 h in an ultra-sonic bath, the water-dispersed GO was placed in a beaker containing an appropriate amount of water-borne PU. The PU/GO mixture in water and NMP was mixed in a high shear mixer at 126 rad/s (1200 rpm) for 1 h 30 min followed by degassing in vacuum for 1 h and storing at room temperature for 12 h. It is expected that the GO was mostly exfoliated into graphene oxide sheets at this stage. After undergoing further high-shear mixing for 45 min followed by degassing for 1 h 30 min, the viscous GO/WBPU mixture was applied onto a polyethylene terephthalate (Mylar) sheet, followed by film spreading using a drawdown blade. All samples were cured for 12 h at room temperature, followed by 10 min at 150°C in an air-circulating oven. The dry film thickness was between 105 µm and 150 µm. In addition, specimens of unfilled and GO-filled coated films on CaF$_2$ substrate having a thickness of approximately 6 µm were also prepared for chemical degradation study.

![Figure 1](image.png)

**Figure 1.** Steps and conditions used to prepare GO/WBPU composite.
2.2. Ultraviolet (UV) Exposure Conditions.

The UV radiation source was a 2 m integrating sphere-based environmental chamber, referred to as SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) [7]. This SPHERE UV chamber utilizes a mercury arc lamp system that produces a collimated and highly uniform UV flux of approximately 480 W/m² in the 295 nm to 400 nm range. Within the specimen chambers, the relative humidity (RH) and temperature can be precisely controlled. Free standing films were cut into 25 mm square specimens, and mounted on a 17-window exposure cell, normal to the horizontal direction. All samples were exposed to UV radiation at 50°C and 75% RH up to 137 days. Specimens were removed at specified time intervals for characterization.

2.3. Characterization of UV exposed samples.

Chemical degradation, surface morphology and mass loss of UV-exposed nanocomposites were characterized before and as a function of exposure time. Chemical degradation of the GO/WBPU films was studied by Fourier transform infrared spectroscopy in both the transmission mode (t-FTIR) and attenuated total reflection (ATR) mode (FTIR-ATR) using thin coated CaF₂ and thick free standing film samples, respectively. ZnSe prism was used for the ATR measurement. The FTIR spectrometer (Nicolet Nexus 670x) was equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. FTIR spectra were recorded at a resolution of 4 cm⁻¹. Surface morphology was characterized and imaged via field emission scanning electron microscopy (FE-SEM), contact scanning mode atomic force microscopy (AFM) and laser scanning confocal microscopy (LSCM). AFM was a Dimension 3100 (Veeco Metrology), operated in the tapping mode using commercial silicon probes. Mass loss was measured with an analytical balance.

3. Results and Discussion

3.1. Chemical Degradation

Chemical degradation of GO/WBPU films during UV exposure was characterized by t-FTIR and FTIR-ATR. FTIR spectra taken at different exposure times showed that the intensity of major bands at 1250, 1530 and 1730 cm⁻¹, assigned to amide III, N-H bending (amide II), and ester C=O, respectively, decreased with increasing exposure time. In addition, intensity in the 1765 to 1790 cm⁻¹ region has increased, implying that oxidation has occurred. These results indicate that the PU has undergone photodegradation, resulting in chain scission and formation of oxidative products.

![Figure 2](image)

**Figure 2.** Plots of t-FTIR intensity changes at (a) 1530 cm⁻¹ and (b) 1772 cm⁻¹ as a function of exposure time to SPHERE at 50 °C, 75 % RH for unfilled and 2% GO-filled WBPU films. Each data point was the average of four specimens, and error bars represent one standard deviation.
Figure 2a depicts t-FTIR intensity changes of the 1530 cm\(^{-1}\) band, representing chain scission in the polymer, as a function of exposure time for 2% GO/WBPU and unfilled WBPU films. For both unfilled and GO filled film, UV exposure caused a gradual loss of this group. Figure 2b displays t-FTIR intensity changes of the 1772 cm\(^{-1}\) band, attributed to acetylurethane linkage (O=C-NH-C≡O) [8]. The rate of acetylurethane formation was higher for unfilled WBPU than GO/WBPU composites, suggesting that photo-oxidation of this polymer was suppressed by the presence of GO.

The t-FTIR data did not show significant difference on the chain scission rate (i.e., loss of NH band at 1530 cm\(^{-1}\)) between unfilled and GO-filled WBPU films. However the FTIR-ATR results reveal that intensity of this band was sharply reduced after 35 days for 2% GO/WBPU samples, with the loss being much less for the unfilled WBPU after 60 days of exposure (Figure 3a). It should be noted that chemical changes detected by the ATR method originated from the composite layer near the surface, between 0.5 \(\mu\)m and 2.5 \(\mu\)m into the polymer. The 25% difference in FTIR-ATR intensity between unfilled and GO filled films is probably due to the graphene particles stacking on the surface, which reduced the penetration depth of the evanescent wave into the polymer material and consequently spectral intensity (Figure 3b).

![Figure 3. (a) Plots of FTIR-ATR intensities changes at 1530 cm\(^{-1}\) in function of time for unfilled and 2% GO-filled WBPU films exposed to UV/50 \(^\circ\)C/75 % RH. (b) FTIR-ATR spectra for 2% GO/WBPU composite at different exposure time. Each data point was the average of four specimens, and error bars represent one standard deviation.](image)

3.2. Surface Morphology and topography of UV-exposed waterborne polyurethane Nanocomposites

Figures 4 and 5 display AFM images of unfilled and 2% GO-filled polyurethane films, respectively, exposed to UV radiation at 50\(^\circ\)C and 75% RH for different times. Both unfilled and GO-filled samples exhibited a smooth surface before UV exposure. However, different topographic features are observed between unfilled and 2% GO/WBPU films after UV exposure. Exposed unfilled WBPU film showed a surface degradation pattern with circular pits (Figure 4).
Figure 4. AFM height images of unfilled WBPU films (a) before and (b) after exposure to SPHERE at 50 °C, 75 % RH for 60 days. Scan size is 50 μm × 50 μm.

For 2% GO/WBPU films exposed to the same UV condition, a visible surface morphological change is clearly observed (Figure 5). After only 15 days exposure, some GO nanoparticles started to appear and they covered most of the surface after 60 days. At this time, several graphene layers on the composite surface can be distinguished. Further, the height contrast also increased with UV exposure, from 397 nm initially to 2 μm after 137 days irradiated with UV. Particularly between 42 and 137 days, both the size and the shape of graphene particles have changed appreciably. They become larger and more protruding at longer UV exposure time. Such changes were probably due to the combined gradual removal of the polymer layer and stacking of the graphene sheets on the surface.

Figure 5. AFM height images of WBPU films containing 2 % mass fraction of GO nanoparticles, exposed (a) 0, (b) 15, (c) 42, (d) 60 and (e) 137 days to SPHERE at 50°C, 75% RH. Scan size is 50 μm × 50 μm.
Roughness of the graphene composite surface also changed markedly with exposure time under UV radiation, as shown in Figure 6. Root mean square (RMS) value, which represents the average height of the scanned surface area, was taken directly from the instrument software. The RMS values were all measured from 50 μm square images. The roughness value for the surface after 137 days exposure was close to 375 nm, which is 40 times greater than before exposure, indicating that UV radiation has caused a substantial damage to the surface. The rate of increase was different between the first 60 days and the last 77 days of exposure. The roughness increased nearly three times faster in the first 60 days exposure than thereafter. The more rapid roughness increase at the early stage may be explained due to the degradation of the polymer layer on the surface, which allowed more graphene particles to appear at the surface and thus made the roughness increase more rapidly. In the later stage, although the polymer continued to degrade but the graphene stacking process became more dominant, and therefore the roughness was increased at a slower rate.

![Roughness value obtained for 2% GO/WBPU samples during SPHERE exposure at 50°C, 75% RH. Roughness was measured from 50 μm square images.](image)

Changes in surface morphology of the GO/WBPU composite resulting from UV irradiation can also be observed by SEM imaging as shown in Figure 7. Before exposure, the surface contained a limited amount of nanoparticles. The density of nanoparticles on the surface increased with exposure time. After 60 days exposure, almost the entire surface appeared to be covered with particles (Figure 7b). After 137 days exposure, graphene particles are clearly seen agglomerating. This result is consistent with the increase in size and height of particles observed with AFM imaging.
Figure 7. FE-SEM images of 2% GO/WBPU composite exposed to UV radiation for various times: (a) before exposure; (b) 60 days; (c) 60 days at higher magnification and (d) 137 days.

Figure 8 shows LSCM images of GO/WBPU composite surface at different magnifications before and after 60 days exposure. Images in Figure 8 show a smooth surface before exposure and a black surface was completely covered with graphene after 60 days. At higher magnification, we can clearly see uniform graphene dispersion on the composite surface.

Figure 8. LSCM images of 2% GO-filled WBPU films before and after 60 days. First row are micrographs of 2 x 2 mm (x5) and second row are micrographs of 56 x 56 μm. (x150).
The results of Figures 5, 7 and 8 showed that a substantial amount of graphene nanoparticles has accumulated on the GO/WBPU composite surface as a result of exposure to UV radiation. However, further research is needed to ascertain whether any of these graphene has released to the environment during exposure.

3.3. Mass Loss
Figure 9 displays the mass loss of unfilled and 2% GO-filled WBPU versus exposure time exposed to UV/50°C/75% RH environment. The rate of mass loss of the 2% GO/WBPU composite appeared to be lower than that of the unfilled film at early exposure stage (<25 days), but both had similar mass loss thereafter. After 42 days exposure, the maximum mass losses of unfilled and 2% GO/WBPU nanocomposite films were 1.53% ± 0.22% and 1.50% ± 0.19%, respectively. The reason for the difference in mass loss between GO-filled and unfilled WBPU during the early exposure stage is unknown at this time.

Figure 9. Mass loss vs. time for unfilled and 2% GO-filled WBPU films exposed to UV/50°C/75% RH.

4. Conclusion
The fate of GO nanoparticles in waterborne polyurethane/GO nanocomposites during exposure to UV radiation has been investigated. Analyses of chemical composition and morphology of the UV-exposed composite surfaces showed that the polyurethane matrix underwent photodegradation, resulting in accumulation of a large concentration of GO particles on the composite surface. The results of this study should provide useful information to assess the potential risk of GO in polyurethane nanocomposites during outdoor exposure.

* Certain commercial product or equipment is described in this paper in order to specify adequately 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.

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