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Graphene oxide/waterborne polyurethane nanocoatings: effects of graphene oxide content on performance properties

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Abstract

Graphene oxide (GO) is a good nanofiller candidate for waterborne coatings because of its outstanding physical and mechanical properties, good dispersibility in water, and low cost relative to graphene. Here, we report on the performance of a one-part, waterborne polyurethane (WPU) nanocoating formulated with four different GO loadings ([0.4% to 2.0%] by mass). The degree of GO dispersion/adhesion was evaluated using scanning electron microscopy, laser scanning confocal microscopy, and Raman microscopy. Nanocoating performance was evaluated using a dynamic mechanical thermal analyzer for mechanical properties, a customized coulometric permeation apparatus for oxygen barrier properties, a combustion microcalorimeter for flammability, a hot disk analyzer for thermal conductivity, thermogravimetric analysis for thermal stability, and a moisture sorption analyzer for water uptake. The results show that GO sheets were well dispersed in, and have good adhesion to, WPU. At the higher mass loadings ([1.2% or 2%] by mass), GO increased the modulus and yield strength of WPU by 300% and 200%, respectively,

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increased the thermal conductivity by 38%, reduced the burning heat release rate (flammability) by 43%, and reduced the oxygen permeability by up to sevenfold. The presence of GO, however, increased water vapor uptake at high humidity; the moisture content of 2% mass loading GO/WPU nanocoatings at 90% RH was almost twice that of the moisture content for unfilled WPU. Overall, with the exception of water uptake at very high humidity (> 70% RH), the observed improvements in physical and mechanical properties combined with the ease of processing suggest that GO is a viable nanofiller for WPU coatings.

Keywords

Graphene oxide; Nanocoatings; Polymer nanocomposites; Performance properties; Waterborne polyurethane; Graphene oxide loading

Introduction

Graphene, which consists of a two-dimensional sheet of sp^2 -bonded carbon atoms from which graphite, carbon nanotubes, and fullerenes are derived, has emerged as a promising class of nanomaterials.^{1–4} Similar to its cylindrical carbon nanotube (CNT) form, graphene has exceptional mechanical, electrical, and thermal properties.^{2,5,6} Because of these outstanding attributes, extensive efforts have been made to incorporate graphene-based materials as nanofillers to enhance multifunctional properties of polymeric materials, as demonstrated in numerous reviews.^{1,4,7–12} However, because graphene-based materials are hydrophobic and chemically inert, their use as graphene nanofillers can result in several processing challenges, which complicates dispersion into hydrophilic polymers. Furthermore, graphene tends to aggregate during mixing in most polymer systems, has a high cost, and can only be produced on a small scale.^{3,5} In contrast, graphene oxide (GO), a modified type of graphene, can overcome some of the disadvantages of graphene nanofillers, particularly in terms of cost and dispersibility in polar polymeric matrices.^{13,14} GO is still generally high in cost relative to traditional fillers (e.g., $CaCO_3$, talc, mica, glass powder, clays, etc.) due to scale-up issues, but there is a lot of ongoing research to help eventually bring the cost down.¹⁵

Graphene oxide (GO) consists of individual graphene sheets functionalized with hydroxyl and epoxide groups on the basal plane and carboxylic acid groups at the edges.^{5,16} GO can be produced in large quantities by thermally or chemically oxidizing low-cost graphite (i.e., stacks of graphene sheets), followed by separation/exfoliation of the resulting graphite oxide (i.e., stacks of graphene oxide sheets).^{5,16} Due to the presence of oxygen atoms, GO loses most of its electrical conductivity and behaves as an electrical insulator.¹⁶ The functional groups on the GO surface not only interact strongly with hydrophilic polymers but can also provide grafting points for chemical modifications, making GO a promising material for composites prepared with a variety of polymeric matrices.^{1,5,9,16} Furthermore, due to the presence of oxygen functional groups and adsorbed water, the distance between two GO sheets (inter-layer spacing) under ambient conditions is over twice that of the distance between graphene sheets in graphite (> 0.7 nm for former vs 0.34 nm for the latter).^{17,18} Such large inter-layer spacing in GO can facilitate the intercalation of polar monomers,

oligomers, and small molecules into these locations, which results in strong adhesion, or mechanical interlocking, between the matrix and GO sheets after nanocomposite solidification.^{19–21}

To avoid costly modification steps during GO/polymer nanocomposite preparation, water-soluble or water-dispersible polymers can be used as an alternative to solvent-based polymer matrices since GO disperses best in aqueous media and polar polymers.^{21–27} Thus, this study systematically reports several enhanced performance properties of a commercial, one-part, waterborne polyurethane (WPU) nanocoating containing a highly oxidized GO. WPU coatings are increasingly used in many applications, such as interior wood coatings and automotive finishes, because they are environmentally benign and have several excellent properties such as good adhesion to a variety of substrates, high abrasion resistance, and strong weathering resistance.^{28,29} Studies of adding various nanofillers, such as CNTs, nanoclays, and nanosilica, into WPU have also shown an improvement in the corrosion resistance, hardness, flame retardancy, and antifriction properties of WPU.^{30–32} In WPU coatings, graphene oxide is very appealing as a nanofiller because of its exceptional mechanical properties, good dispersion in water, enhanced barrier properties with respect to gas transmission, strong interactions with various polar groups in WPU, and low cost with respect to graphene. A few studies of GO or functionalized graphene sheet incorporation into WPU coatings have been reported, and some performance property improvements have been observed for WPU containing GO nanofillers and indicate that GO may be worth including in polymer coating systems.^{33–36} However, a systematic study of WPU polymer improvements using a consistent type of highly oxidized GO at different mass loadings is needed to more clearly assess the benefits and limitations of GO as a waterborne polymer nanocoating filler.

In this study, GO/WPU nanocoatings with different mass loadings were compared with unfilled WPU in terms of mechanical strength, barrier properties, flammability, thermal conductivity, and thermal stability. Compared to other studies, where a lack of wide range in GO mass concentration only serves to indicate the presence or impact of GO on a particular performance property, this study comprehensively investigates a wide range of GO mass concentrations in a commercial WPU coating to determine the effect trend due to GO mass concentration and the optimal GO mass concentration for a particular property. Improved performance was achieved by optimizing the dispersion quality, the strong GO/polymer interfacial interactions, and the high aspect ratio of the GO nanofiller. While other properties have been studied for GO/WPU nanocoatings, the characterization of GO homogeneity by Raman spectroscopy and imaging, the sorption behaviors of GO nanocoatings at different relative humidity levels, and several other important performance properties were studied for the first time in combination for an easily processed, highly oxidized GO/commercial WPU system.

Experimental materials and methods

Materials and preparation of GO/WPU nanocoatings

The waterborne polyurethane (WPU) used in this study was a one-component, anionic dispersion of an aliphatic polyester urethane resin in a mixture of water (35% by mass) and

N-methyl-2-pyrrolidone (NMP) (15%, by mass) (Bayhydrol 110, Bayer MaterialScience LLC). After curing, this WPU had two glass transition temperatures (T_g), $-18.5^\circ\text{C} \pm 0.2^\circ\text{C}$ and $87.8^\circ\text{C} \pm 0.4^\circ\text{C}$ (average $\pm$ standard deviation, $N=3$), as determined by dynamic mechanical thermal analysis (DMTA, RSA III, TA Instruments). The exact chemical structure and other ingredients, such as surfactants and additives, in this coating are unknown.

As-received GO material was in powder form (i.e., unexfoliated graphite oxide) and was prepared by the University of Texas, Austin, TX, using Hummers' method.³⁷ Analysis of the as-received material with infrared spectroscopy showed that the GO material contained hydroxyl, epoxide, and carboxylic acid groups. After dilution and sonication in water, the GO (spin-casted onto a Si wafer) had a thickness of between 0.8 and 1.5 nm as measured by atomic force microscopy (AFM) (Dimension 3100, Veeco), which is approximately the thickness of a single hydrated GO layer, and a width of between a few hundred nanometers and a few micrometers, similar to the results reported previously.^{37–39} The as-received GO also contained $40\% \pm 0.2\%$ water by mass, as measured by thermogravimetric analysis (TGA, conditions described later).

WPU nanocoating films were prepared with four different mass fractions of GO nanofiller (0.4%, 0.8%, 1.2%, and 2% relative to the dry mass of the PU material) following the process illustrated in Fig. 1. It should be mentioned that, because the as-received GO material contained 40% mass fraction of water at ambient condition (24C, 50% RH), the quantity of GO added to the nanocoatings was adjusted accordingly to provide the desired mass loadings.

Specified amounts of GO (depending on mass loading) were first added to deionized (DI) water to achieve a mass concentration of approximately 6 mg GO in 1 mL DI water. After sonication at 40 kHz for 5 h to 8 h (longer time for higher GO loadings) in an ultra-sonic bath, the water-dispersed GO was placed in a beaker containing a specified amount of WPU. The GO/WPU mixture in water and NMP solvent was mixed in a high-shear mixer (Dispermat, VMA) at a rate of 126 rad s^{-1} (1200 rpm) for 1 h 30 min at room temperature and pressure, followed by degassing under vacuum for 1 h and storage at room temperature and atmosphere for 12 h. It should be mentioned that under the mixing and processing conditions in the aqueous medium used in this study, it is expected that the majority of GO sheets were individually separated, as reported in previous studies.^{39,40} After undergoing further high-shear mixing for 45 min followed by degassing under vacuum for 1 h 30 min to remove most of the trapped air, the viscous GO/WPU mixture was applied onto a poly(ethylene terephthalate) (Mylar) sheet and spread into a film using a 175- μm drawdown blade. The nanocoating films were cured for 12 h at room temperature, followed by 10 min at 120°C in an air-circulating oven. The free-standing cured films were removed from the Mylar substrate and had a thickness of $140\text{ }\mu\text{m} \pm 10\text{ }\mu\text{m}$, as measured by field-emission scanning electron microscopy (FE-SEM) of the film cross section. The FE-SEM (HITACHI S-4700) was operated at 1 keV, and the films were coated with carbon to prevent charging under the electron beam.

Characterization of GO/WPU nanocoating properties

Various performance properties of WPU nanocoatings as a function of GO loading were characterized in this study including mechanical properties, oxygen permeability, flammability, water vapor sorption, thermal conductivity, and thermal stability. The number of replicate samples or sample areas measured, and standard deviation of each measurement are provided in the figure captions throughout the “Results and discussion” section. Dispersion quality, an important characteristic related to nanocomposite performance properties, was qualitatively assessed using laser scanning confocal microscopy (LSCM) in reflectance mode and by FE-SEM on cryo-fractured cross sections that were coated to improve conductivity. LSCM was performed using a Zeiss model LSM510 with a laser wavelength of 543 nm. The images were taken at a magnification of $50\times$ with an optical slice (z-step) of 0.1 μm . Raman spectroscopy was also used to assess dispersion quality of GO in WPU coatings. Spectra were accumulated for 50 s with 1 mW laser power at 785 nm, at a magnification of $50\times$, using a Raman Senterra microscope (Bruker Scientific). A concave rubber band background correction (20 iterations of 1000 points) was applied from 450 to 3200 cm^{-1} .

Mechanical properties were obtained using a dynamic mechanical thermal analyzer (DMTA) in transient mode at a 0.5 mm s^{-1} extension rate on dog-bone specimens having a 20.0-mm gage length, a 3.3-mm width, and a thickness of $140\ \mu\text{m} \pm 10\ \mu\text{m}$ (measured with SEM, described earlier). Oxygen permeability was measured on 20 mm $\times$ 50 mm film samples. For this measurement, a custom-modified Oxtran-100 coulometric permeation apparatus was used and a difference in O_2 partial pressure on both sides of the film drove the permeation while the total pressure (1 atm) of each side was held constant (balance N_2). The analysis of O_2 relied on the reaction between O_2 and H_2 utilizing a catalysis-based sensor. Details of this measurement are described elsewhere.⁴¹ Flammability was evaluated using a combustion microcalorimeter described elsewhere.⁴² Thermal conductivity was measured using a hot disk thermal constants analyzer described elsewhere.⁴³ This measurement was taken at 24°C, using specimens having a diameter of 50 mm and a thickness of 5 to 7 mm (a mold was used to fabricate these specimens), at a power of 0.02 W applied for 20 s. Thermal stability was assessed by thermogravimetric analysis (TGA, Q500, TA Instruments) at a heating rate of 10°C min^{-1} under N_2 . Water sorption isotherm (i.e., water uptake as a function of relative humidity) was obtained using an IGAsorp moisture sorption analyzer having a mass resolution of 10^{-7} g and an accuracy of 1% for relative humidity (RH) from 0 to 90%. For each RH, a nanocoating specimen of approximately 8.5 mg was first loaded into a holder and dried in the analyzer until it reached a minimum (to 1% RH after sitting overnight at 25°C). The sorption experiment was then started until the amount of water uptake in the specimen at a particular RH reached an equilibrium, usually between 500 and 1000 min depending on the RH level. All sorption experiments from 0% RH to 90% RH were conducted at 25°C.

Results and discussion

Characterization of GO/WPU nanocoating dispersion quality

The properties of a polymer nanocomposite depend strongly on how well the nanofiller disperses in the polymer matrix.^{7,8} A good dispersion will maximize the interfacial interactions, minimize stress concentrators (e.g., agglomerates, bundles, etc.), and increase load transfer efficiency. The dispersion of GO in WPU was investigated by two different methods. The first method used LSCM imaging and Raman spectroscopy to characterize the nanocoating subsurface. The second method employed field-emission SEM on a cryo-fractured nanocoating cross section.

Figures 2a and 2b display LSCM images and Raman spectra, respectively, of unfilled WPU (control) and 1.2% mass fraction GO/WPU nanocoatings. LSCM was useful for characterization of the surface morphology, homogeneity of GO dispersion, and roughness of the GO/WPU nanocoating surface. Although the darker areas (Fig. 2a) cannot be spectroscopically identified as GO at or near the surface with this technique, the surface morphology observed is not present on the WPU controls and can be used to qualitatively assess the distribution of the filler in the subsurface of the material (top 30 μm or less). The homogeneity of the GO dispersion is visible on many areas of the subsurface, with some darker areas consistent with the lateral dimensions of the GO used (1 μm to 2 μm), some darker areas smaller than these dimensions (GO nanoparticles that are curled or crimped), and some darker areas larger than GO (large aggregates). The three-dimensional stacking of image planes in LSCM also allows for calculation of the surface roughness (root mean square, RMS) of GO/WPU nanocomposites relative to the WPU control.⁴⁴ At 1.2% GO mass fraction, the nanocoatings were slightly rougher ($\text{RMS} = 0.44 \mu\text{m} \pm 0.08 \mu\text{m}$) than the WPU controls ($\text{RMS} = 0.35 \mu\text{m} \pm 0.05 \mu\text{m}$).

In the right-hand part of Fig. 2b, Raman spectra containing the G band (1602 cm^{-1}) for the graphitic, sp^2 -hybridized network and the D band (1306 cm^{-1}) for the defective, sp^3 sites around the edges, voids, and oxygen functional groups of GO⁴⁵ were used to assess the homogeneity of GO dispersion at the sample subsurface (1 μm to 4 μm). The intensity of the D and G bands can be used to quantitatively or semiquantitatively assess dispersion quality for GO nanocoatings, depending on the conditions used. This can be done by measuring the D and/or G band intensity from spectra taken at several different areas of the sample and comparing the intensities. As shown in Fig. 2b, the intensities of each area were similar [$(2700 \pm 300) \text{ A.U.}$ for the D band at 1306 cm^{-1}], indicating a homogeneous surface. Although not the case with the GO/WPU nanocomposite samples in this study, the intensities of Raman bands can be affected by large changes in surface roughness at different sample locations (as indicated by LSCM). Thus, it is good practice to eliminate any effect of surface roughness on Raman band intensity when possible either by normalizing one band (the D or G) to the other or by normalizing the bands to a consistently present polymer band. In this case, normalization of the D or G bands to a polymer band was not possible for WPU since the Raman spectrum for this polymeric material does not have any intense bands as shown in the left-hand part of Fig. 2b. Instead, the D band was normalized to the G band intensity to compare the normalized intensities of the D bands in different areas. The

normalized D band intensities in various sample areas were found to have a standard error of approximately 13%, indicating a fairly homogenous dispersion quality among different sample areas. For reference, the D and G bands are also shown for the GO powder, prepared the same way as the GO added to the nanocoating. The intensities of these bands were similar to those of the GO in the nanocoatings.

FE-SEM images of cryo-fractured, cross-sectional areas of WPU nanocoatings containing 0.4% and 2% mass fractions of GO are displayed in Fig. 3a and 3b, respectively. These fractured specimens were prepared by immersing each 1 cm × 1 cm nanocoating film in liquid nitrogen for 30 min, followed by fracturing with forceps. Figure 3 shows a layered structure of GO (mostly indicated by the brighter edges normal to the viewer) uniformly dispersed in the matrix with little evidence of aggregated features, indicating that the sonication/high-shear mixing procedure was sufficient to homogeneously disperse GO sheets into the WPU coating, consistent with LSCM and Raman spectroscopy results. The homogenous dispersion of GO in WPU nanocoatings is consistent with other studies involving the dispersion of GO in polar media.^{37–39} These other studies have demonstrated that, under sonication, mechanical stirring, or a combination of the two, graphite oxide is readily intercalated by water and polar solvents and exfoliated into single graphene oxide sheets having thicknesses between 1.0 and 1.5 nm. Due to the presence of adsorbed water, this thickness value is higher than the value of 0.75 nm observed for graphene oxide sheets in an anhydrous graphite oxide.^{17,46} Based on the individual GO sheets observed in nanocomposite cross sections, the term graphene oxide is used instead of graphite oxide throughout the text even though the latter material was actually added to the polymer solution during processing.

The homogenous dispersion and complete exfoliation of graphite oxide to graphene oxide in water or in water-based polymers can be attributed to both the hydrophilicity of GO and its negatively charged state in water. The hydrophilicity provides a strong affinity for water by graphite oxide that enables water molecules to penetrate into the nanofiller inter-layer space and exfoliate it into single sheets. After this occurs, the electrostatic repulsion introduced by the negative charge (due to ionization of carboxylic acid and phenolic hydroxyl groups) can prevent the reaggregation of individual GO sheets.⁴⁷ Furthermore, entanglement of two-dimensional, flake-like GO nanofillers with each other is less of a concern compared to the entanglement generally observed for CNTs in polymers, even with the aid of surfactants, due to both the high aspect ratio of CNTs and the strong van der Waals interactions between them.⁴⁸

Figure 3b also shows the presence of some air gaps/voids between the sheets for the 2% mass fraction GO/WPU nanocoating (arrows in Fig. 3b, high magnification). This feature suggests that the exfoliation of GO sheets in the highest loading (2% mass fraction) specimens was not quite complete and/or there were some aggregated GO particles at high GO content. Thus, the spaces between some sheets were not filled with polyurethane molecules during mixing. Longer time and/or stronger shear mixing may be required for more complete dispersion of higher GO mass loadings in WPU.

A strong nanofiller/matrix interface is essential for effective stress transfer and good barrier properties in polymer nanocomposites.^{7,8,12} The images in Fig. 3 provide a qualitative assessment of the adhesion between GO and WPU. High-magnification images (Fig. 3, bottom row) show that (with the exception of the air gaps due to incomplete exfoliation as noted above) the polymer-coated GO sheets are protruding out of the fractured surface, with little evidence of delamination/separation between the polymer layer and the GO sheets. This observation suggests that the adhesion between GO and WPU is good, as expected due to the good wetting characteristics and polar surface functionality of GO. The good wetting of WPU is also indicated by the low contact angle of water on the same type of GO used in this study, prepared separately with the same method (Hummers' method), which was measured to be 62.8.⁴⁹ Furthermore, FTIR analysis revealed that this WPU coating contained a substantial amount of polar NH-CO groups, which can interact strongly with various polar groups on dehydrated or hydrated GO surfaces via hydrogen bonding.^{33,50}

Due to their compliant nature, stacks of GO sheets in the matrix are not straight, rigid features, but rather bent, folded, or crumpled, similar to that reported previously (Fig. 3).^{7,51} This kind of structure has been postulated to contribute to the enhancement of mechanical adhesion between graphene and polymers and to the stress transfer process within graphene/polymer nanocomposites.^{51,52}

Mechanical properties

Figures 4 and 5 display stress-strain behavior and mechanical properties, respectively, of WPU nanocoatings containing different mass concentrations of GO. The results in Fig. 4 are representative curves for each GO mass loading, and those in Fig. 5 are the average of 18 specimens from nanocoating films prepared at three different times. To provide a clearer representation of the modulus change with GO loading, Fig. 4 also includes an inset presenting the tensile strength at low strain. Above 1% mass loading GO, both the modulus and yield strength increased with the addition of GO. At 2% mass loading, the Young's modulus increased nearly 300% (from 200 MPa for WPU to 600 MPa at 2% mass loading GO), and the yield strength increased about 200% (from 13 MPa for WPU to 26 MPa at 2% mass loading GO). The substantial increases in modulus and tensile strength observed in this study is similar to those reported previously for GO/WPU,³⁴ GO/water-soluble polyethylene oxide,²⁴ and GO/latex²⁶ nanocomposites. One reason for the large increase in modulus and yield strength was due to effective stress transfer in the GO/WPU nanocoatings, which was attained by the strong molecular adhesion between the hydrophilic GO and hydrophilic WPU and possible mechanical adhesion, as discussed in the dispersion/interaction section. This is understood by examining the moduli of both the nanofiller and the matrix. The in-plane elastic modulus of GO has been measured to be between 250 and 650 GPa depending on the level of oxidation.⁷ Although these GO modulus values are only about 1/4 to 1/2 of that of a defect-free graphene, they are more than three orders of magnitude greater than the WPU material used in this study (200 MPa) and improve this WPU modulus by up to 300% (Fig. 5). The strong GO/WPU interface coupled with the large interfacial area provided by the nanofiller allows GO to be the primary load-bearing component of the polymer composite. Strong hydrogen bonding between GO and its polymer host has been cited as the major factor for large modulus and strength improvements for GO/polymer nanocomposites.

^{8,51,53} On the other hand, crumpled and aggregated GO sheets may reduce the effective modulus, because crumpled GO sheets tend to unfold rather than stretch under applied stress and aggregated sheets reduce the aspect ratio and introduce defect sites.⁵⁴ This may be the rationale for the differences in mechanical properties observed across several studies.

Another reason for the modulus gains observed may be due to the large difference in the modulus between GO and the WPU material used in this study, which has been observed for several elastomer/graphene nanocomposites.^{8,9} For such systems, the modulus enhancement is attributed to the large modulus disparity between the matrix and the filler.

Figure 5 also reveals that the elongation at break decreases with increasing GO mass loading, except for the 2% mass loading, which exhibits a slight increase over the 1.2% mass loading. This behavior is typically observed for nanofiller/polymer composites where, as the mass loading of the stiff nanofiller is increased, the thickness of the compliant polymer between the filler particles is decreased and the tendency for filler particles to agglomerate increases.⁷ The former results in segmental mobility restriction of the polymer chains, and the latter introduces mechanically weak regions, both of which will decrease strain at break. However, as seen in the stress–strain curves (Fig. 4), the GO/WPU nanocoatings still behave as a ductile material for all mass loading levels studied, suggesting that any low levels of GO aggregation in the 2% GO/WPU nanocoatings did not offset mechanical property improvement.

Oxygen permeability

Defect-free, two-dimensional graphene sheets are impermeable to all gas molecules.⁵⁵ Thus, incorporation of GO into polymers can result in excellent barrier films that have high mechanical strength and other improved properties suitable for many applications. In this study, the impact of GO loading on O₂ permeability of WPU coatings was investigated, and the results are illustrated in Fig. 6. In this diffusion-driven transport test, the permeability is expressed as the oxygen volume that passes through a unit thickness of the film, per unit area, per second, per unit pressure [$\text{cm}^3 \text{ (STP) cm}^{-1} \text{ s}^{-1} \text{ cmHg}^{-1}$].⁴¹

Oxygen permeability in WPU coatings decreased with increasing GO content from 0.4 to 1.2%. At 1.2% mass loading, the O₂ permeability was nearly sevenfold lower than that of the unfilled WPU ($5.29 \times 10^{-11} \text{ cm}^3 \text{STP/cm-s-cmHg}$ for unfilled WPU vs $0.739 \times 10^{-11} \text{ cm}^3 \text{STP/cm-s-cmHg}$ for 1.2% mass fraction GO/WPU composites), indicating that high-aspect-ratio, two-dimensional GO sheets can provide an effective barrier to oxygen transport in this polymer system. The slightly higher O₂ permeability at 2% GO mass loading as compared to 1.2% mass loading is probably due to incomplete exfoliation or increased aggregation in the 2% GO mass loading, as observed in Fig. 3.

The large oxygen barrier enhancement observed here for GO/WPU nanocomposites is consistent with those reported in the literature for permeability of O₂ in GO/water-based polymer nanocomposites,^{26,27,56} and for permeation of other gases into graphene-based/polymer nanocomposites.^{8,9,57–59} The barrier enhancement is attributed to the tortuous transport path provided by the network of graphene-based materials (including graphene, GO, graphite oxides, and reduced GO), which retards molecular diffusion through the

polymer matrix. Strong interfacial adhesion, good dispersion, and high aspect ratios that cannot be achieved with graphene and CNTs are believed to be the major factors contributing to the O₂ barrier enhancement of GO in WPU and other polar polymers.^{8,59,60} The improved oxygen barrier property of WPU obtained by adding a small amount of GO is attractive because GO-based nanocoatings can potentially be used for many applications such as protective coatings, electronic devices, and food packaging. Although O₂ permeability is also a useful criterion for corrosion mitigation in protective coatings, data on the transport of Cl⁻ in this material are required to better assess the potential of GO/WPU nanocoatings as a material for corrosion control; such information is not available and further research in this area is needed.

Water sorption of GO/WPU nanocoatings at different relative humidity levels

The effect of GO on water sorption during exposure to liquid water has been investigated for several GO/polymer nanocomposites,⁶¹ which showed that the presence of GO in different polymer systems increases the water uptake as compared to the neat polymers. The sorption of water at different RH levels for graphite oxide (i.e., stacks of unexfoliated GO) prepared by Hummers' method (the same method used in this study) was also reported, which revealed that the amount of water uptake in this material goes up sharply at high humidity (80% to 100%).^{62,63} However, no data are available on the water sorption at different RH levels for GO/WPU nanocoatings, or even for GO/polymer nanocomposites. For this reason, we have investigated the effect of GO mass loading on the equilibrium water uptake at different RH levels, i.e., water sorption isotherm, for GO/WPU nanocoatings. The results are illustrated in Fig. 7 for RH levels from approximately 0% to 90% and GO mass loadings from 0% mass loading (i.e., neat or unfilled WPU) to 2% mass loading. The sorption isotherm experiment was conducted at 25°C ± 1°C as stated in the "Experimental materials and methods" section. Each data point on the vertical axis is the mass gain at equilibrium for each RH, which is expressed as % of the dry initial mass (i.e., moisture content, Mc). Due to instrument limitations, the Mc values for RH > 90% were not obtained.

The curves for both neat WPU and GO/WPU nanocoatings (Fig. 7) have a sigmoidal shape of the type II sorption isotherms in the BET classification.⁶⁴ This type of water uptake is often identified with a multiple-layer physical sorption process, in which the first water layer interacts with the adsorption sites on the substrate surface and subsequent water molecules associate with the primary layer forming a liquid water-like structure. Figure 7 reveals that the amount of water uptake in neat WPU and all the GO/WPU nanocoatings increase almost linearly from 0 to 60% RH. The adsorption in this RH range is generally characterized by the Langmuir type and corresponds to a complete monolayer.⁶⁴ In this RH range, except for the 2% GO mass loading, there is essentially little difference in the water uptake between the neat coating and the filled ones containing 0.4%, 0.8%, and 1.2% mass fraction GO. The 2% mass fraction GO-filled nanocoating exhibited a slightly higher amount of water uptake in the 0% RH to 60% RH range than the neat WPU coating or other GO/WPU nanocoatings at lower GO mass loadings. This is likely due to an increase in the adsorption sites afforded by an increase in the GO content in the film.

The effect of GO mass loading on water sorption of WPU coatings is clearly seen above 70% RH. The upward curvature becomes more pronounced as the amount of GO added to the coating increases. Both the rate and quantity of water adsorbed between 70% RH and 90% RH increased with increasing GO mass loading. At 0.4% GO mass loading, there is a small increase in the amount of water uptake at 90% RH as compared to the neat coating. For nanocoatings containing higher GO mass loadings (0.8%, 1.2%, and 2.0%), the upward deviation from the unfilled material is more clearly observed around 70% RH and higher. At 70% RH, the effect of GO on the water uptake of WPU is still relatively small. For example, the moisture content at 70% RH for neat WPU, 1.2% mass loading GO/WPU, and 2% mass loading GO/WPU are $1.6\% \pm 0.1\%$, $2.0\% \pm 0.1\%$ and $2.5\% \pm 0.1\%$, respectively. However, at 90% RH, the effect of GO is much greater: The water uptake in the neat WPU is $3.5\% \pm 0.1\%$, while that in the 2% (mass fraction) GO-filled material is almost double ($6.9\% \pm 0.2\%$). Based on the shape of the curves in Fig. 7, more than one monolayer of water appears to have adsorbed at the GO/WPU interface at RH near 70% where the upward curvature became sharper; the thickness of this interfacial water layer increases with increasing RH. It is also worth noting that the increase in the distance between GO layers in graphite oxide has been reported by other researchers to be sharper above 75% RH, which is attributed to the adsorption of more than one monolayer of water on the graphite oxide surface.⁶⁵

A thickness increase in the GO/polymer interfacial water layer at high RH and upon immersion of the GO/WPU nanocoating in liquid water will likely cause swelling, generate internal stresses, and adversely affect the mechanical performance of GO/WPU nanocoatings. One solution is to make use of rGO or GO with a lower oxygen content to substantially reduce the water uptake and water transport rate in polymers.^{60,66,67} Esterification of the OH groups on the GO surface by α -bromoisobutryl bromide has also been shown to substantially reduce the water uptake effect of GO and may be another option.²⁶ However, GO modifications can add cost and may compromise the GO dispersion quality which, in turn, can affect the other performance properties. Thus, further studies are necessary to determine the effect of water uptake on coating performance, especially in terms of mechanical and barrier properties. This will allow for an understanding of appropriate uses and limitations of GO/WPU nanocoatings in outdoor and wet environments. Nevertheless, the isotherms shown in Fig. 7 are useful for estimating the equilibrium moisture content in GO/WPU nanocoatings at a particular RH during use.

Flammability

The flammability characteristics of GO/WPU nanocoatings were evaluated using a combustion microcalorimeter. The combustion microcalorimeter tests provide data on the combustion properties of the investigated materials, including heat release rate (HRR), peak heat release rate (PHRR), and time to ignition (TTI). In this study, PHRR was used at 370°C to discern the effects of GO mass loading on the flammability of WPU, and the results are summarized in Fig. 8. The PHRR is associated with the rate at which the material decomposes in a fire. It was determined that the presence of GO reduces the PHRR by a significant amount (Fig. 8), even at a mass loading as low as 0.4%, indicating that this carbon nanofiller is effective at reducing the flammability of WPU coatings. This

observation is consistent with previous results obtained with well-dispersed, oxidized graphene-based materials^{68,69} and CNT⁷⁰ polymer nanocomposites. However, the effect appears to become less dramatic with increasing GO mass loading, approaching a PHRR reduction of $43\% \pm 4\%$ at about 2% mass fraction GO. The results suggest that the reduction in flammability is limited by the increase in thermal conductivity that accompanies higher mass concentrations of carbon nanofiller.⁷⁰

The reduced heat release rates exhibited by many nanocomposite materials depend, in large part, on the ability of the nanofillers to form a protective layer that insulates the unburnt polymer in the interior of the burning object from thermal energy incident on its surface.⁷¹ Studies conducted by one of the co-investigators of this postulation support the hypothesis that as the polymer (in a nanocomposite) decomposes in a fire, a network structure or scaffold is left behind that consists primarily of free volume, but which is sufficiently strong to withstand thermal motion that might otherwise break it apart.⁴² This network structure can insulate some of the polymer as the matrix decomposes in a fire.

In poorly dispersed nanocomposites, this scaffold has less free volume (because the nanofillers are agglomerated) and the insulation is less effective. The extent to which it is possible to achieve and sustain good nanofiller dispersion, especially while the nanocomposite experiences high temperatures during burning, depends on the nature of the nanofiller/polymer interactions. In general, the flammability performance of nanocomposites is improved with increasing thermodynamic compatibility between the nanofiller and polymer, e.g., for WPU and GO.

Thermal conductivity and thermal stability

As indicated, graphene has exceptional thermal properties. For example, at room temperature, its thermal conductivity has been measured and was found to exceed $3000 \text{ W m}^{-1} \text{ K}^{-1}$,^{2,72} which is more than four orders of magnitude higher than that of polymer matrices. When mixed into a nanocomposite, the thermal conductivity of a graphene/polymer nanocomposite is much lower than that of pristine graphene due to interfacial thermal resistance, the degree of dispersion, and percolation of the graphene. Nevertheless, the thermal conductivity of a polymer matrix can be greatly improved by the addition of graphene. This has been shown with epoxy which increased in thermal conductivity from $0.2 \text{ W m}^{-1} \text{ K}^{-1}$ by up to $12.4 \text{ W m}^{-1} \text{ K}^{-1}$ after graphene incorporation.⁷³ To understand how this property of graphene applies with GO, we have also investigated the thermal conductivity and thermal stability of WPU coatings at different GO mass loadings, and the results are presented in Figs. 9 and 10, respectively. The thermal conductivity of WPU increases with GO mass loading, from $0.23 \text{ W m}^{-1} \text{ K}^{-1}$ for unfilled WPU to $0.33 \text{ W m}^{-1} \text{ K}^{-1}$ (a 38% increase) for nanocoatings containing 2% mass fraction GO (Fig. 9). The thermal conductivity improvement observed is attributed to the homogenous dispersion and strong interfacial adhesion between GO and WPU. This is because, unlike electrical charges that flow and can tunnel through barriers, thermal energy is transferred primarily through the interaction of adjacent particles in the form of lattice vibrations.^{72,74} Therefore, strong coupling of vibrational modes at the interfaces resulting from strong filler/matrix and filler/filler interactions causes improvement in thermal conductivity of the nanocomposites. In

contrast, poor coupling of vibrational modes at the filler/matrix and filler/filler interfaces would lead to a decrease in thermal conductivity.

The thermal conductivity improvement observed in this study is similar in magnitude to that observed by other composites as given in Table 1. The variations in thermal conductivity improvements from one polymer system to another may be a result of differences in GO/polymer compatibility, which can affect GO dispersion and GO–polymer interactions.⁷⁵

Although only low GO mass loading levels (2% mass fraction or lower) were investigated in the present study, the results demonstrate that the thermal conductivity of WPU coatings can be effectively improved with the addition of GO. Because good thermal conductivity of materials can greatly help heat management, the result suggests that adding a small amount of GO in this WPU coating would decrease curing time by heat dissipation and hence promote energy and cost savings. The thermal conductivity of GO/WPU nanocoatings may also make these materials useful in applications where good heat conduction is required, e.g., electronic devices, heat-actuated, shape-memory coating films. Furthermore, since GO nanofillers will impart a black color to the nanocoating that will lead to an increase in surface temperature upon exposure to sunlight, the GO nanofillers can help dissipate radiation-induced thermal energy in WPU and prevent damage to the nanocoating.

TGA was employed to assess the effects of GO mass loading on the thermal stability of WPU. Unlike graphene, many of the oxygen functional groups on GO are not much higher in thermal stability ($\approx 300^{\circ}\text{C}$ to 400°C) than that of WPU (322°C), while the thermal stability of the graphitic fraction of GO is much higher ($\approx 700^{\circ}\text{C}$ to 800°C) as determined by some of our control experiments. Figure 10a displays TGA thermograms and their derivative curves for WPU nanocoatings containing different mass concentrations of GO, and Fig. 10b illustrates the decomposition temperature, or the temperature at which the first, maximum mass loss rate occurs by degradation, as a function of GO mass loading. For clarity, the curve for the 1.2% GO mass loading is not shown in Fig. 10a. There are two maximum peaks (i.e., temperature at maximum degradation rate) in the derivative TGA curves for this WPU polymer, corresponding to the degradation of hard (urethane linkages) and soft segments (ester groups), respectively.⁷⁷ In this study, the decomposition temperature, also called the thermal stability, was assessed by the temperature at which the first, maximum degradation rate occurs (i.e., the 1st peak of the derivative curve). The first peak degradation temperature increased from 322°C for neat WPU to 343°C at 1.2% GO mass loading, an increase of 21°C . At mass loadings higher than 1.2%, there was no further improvement in the thermal stability. Overall, the results are similar to other studies that reported a 20°C to 30°C thermal stability increase with the addition of GO to polymers.^{22,78} The thermal stability is likely improved by the graphitic fraction of the GO that chars to protect against thermal decomposition of the polymer.⁷¹ Furthermore, some recent studies have suggested that the defect sites of oxidized graphene are able to capture free radicals (GO acts as free radical scavenger) generated by polymer degradation,^{71,79} similar to that proposed for explaining the thermal stability increase of polymers by CNT and C_{60} materials.^{80,81} Because GO is thermally unstable itself, research is needed to better understand the mechanism of thermal stability enhancement of polymeric materials by GO.

As with many of the other property enhancements, thermal stability is also likely affected by GO dispersion quality.

In addition to these performance properties, we have previously investigated the weathering resistance of 2% mass fraction GO/WPU nanocoatings subjected to UV radiation from 300 to 400 nm, which has been published elsewhere.⁵⁰ The presence of GO substantially decreased the photooxidation of the WPU matrix, with the formation of a layer of GO flakes on the nanocoating surface resulting from UV irradiation. These observations are similar to those for CNT/polymer nanocomposites exposed to UV radiation.^{82–85} The photostabilization of polymers by CNTs has been attributed to the ability of this nanocarbon structure to absorb incoming radiation energy and thus shield the underlying polymer matrix,^{82,86} while the formation of a nanofiller layer on the nanocomposite surface is due to the photodegradation and removal of the polymer matrix surface layer by UV radiation.^{83,85,86}

Conclusions

Graphene oxide has emerged as a promising nanofiller for polymer nanocoatings and is especially attractive for use as a nanofiller in waterborne coatings. In this study, the performance of a one-part commercial waterborne PU (WPU) coating containing different mass fractions of GO was investigated. The properties characterized included degree of dispersion/adhesion, mechanical, oxygen barrier, flammability, water sorption at relative humidity levels from approximately 0% to 90%, thermal conductivity, and thermal stability. It was observed that GO sheets were well-dispersed and had good adhesion with WPU, resulting in enhancements of numerous properties. At 2% mass loading, GO increased the modulus and yield strength of WPU by 300% and 200%, respectively, and decreased the burning heat release rate (flammability) by 43%; at 1.2% GO loading, the oxygen permeability was reduced sevenfold. However, GO increased the water uptake of WPU exposed to high humidity; the moisture content of WPU containing 2% mass fraction GO at 90% RH was $6.9\% \pm 0.17\%$, which is nearly twice that for neat WPU at the same RH. In summary, except for increased water uptake at high humidity, GO/WPU nanocoatings have superior mechanical, barrier, flammability and weathering resistance, and thermal properties as compared to the unfilled WPU coating. These improvements, in combination with the ease of processing GO in aqueous media, the good interfacial interactions of GO with WPU, and the low manufacturing cost of GO relative to graphene, indicate that GO is a strong nanofiller candidate for waterborne PU coatings.

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References

1. Stankovich S, Dikin DA, Dommett GH, Kohlhaas KM, Zimney EJ, Stach EA, Piner RD, Nguyen ST, Ruoff RS, “Graphene-Based Composite Materials.” *Nature*, 442 (7100) 282–286 (2006) [PubMed: 16855586]

2. Geim AK, Novoselov KS, "The Rise of Graphene." *Nat. Mater*, 6 (3) 183–191 (2007) [PubMed: 17330084]
3. Park S, Ruoff RS, "Chemical Methods for the Production of Graphenes." *Nat. Nanotechnol*, 4 (4) 217–224 (2009) [PubMed: 19350030]
4. Sadasivuni KK, Ponnammam D, Thomas S, Grohens Y, "Evolution from Graphite to Graphene Elastomer Composites." *Prog. Polym. Sci*, 39 (4) 749–780 (2014)
5. Zhu Y, Murali S, Cai W, Li X, Suk JW, Potts JR, Ruoff RS, "Graphene and Graphene Oxide: Synthesis, Properties, and Applications." *Adv. Mater.*, 22 (35) 3906–3924 (2010) [PubMed: 20706983]
6. Li D, Kaner RB, "Graphene-Based Materials." *Nat. Nanotechnol*, 3 101 (2008) [PubMed: 18654470]
7. Potts JR, Dreyer DR, Bielawski CW, Ruoff RS, "Graphene-Based Polymer Nanocomposites." *Polymer*, 52 (1) 5–25 (2011)
8. Kim H, Abdala AA, Macosko CW, "Graphene/Polymer Nanocomposites." *Macromol*, 43 (16) 6515–6530 (2010)
9. Ammar A, Al-Enizi AM, AlMaadeed MA, Karim A, "Influence of Graphene Oxide on Mechanical, Morphological, Barrier, and Electrical Properties of Polymer Membranes." *Arab. J. Chem*, 9 (2) 274–286 (2016)
10. Kuilla T, Bhadra S, Yao D, Kim NH, Bose S, Lee JH, "Recent Advances in Graphene Based Polymer Composites." *Prog. Polym. Sci*, 35 (11) 1350–1375 (2010)
11. Bhattacharya M, "Polymer Nanocomposites—a Comparison between Carbon Nanotubes, Graphene, and Clay as Nanofillers." *Materials*, 9 (4) 262 (2016)
12. Hu K, Kulkarni DD, Choi I, Tsukruk VV, "Graphene-Polymer Nanocomposites for Structural and Functional Applications." *Prog. Polym. Sci*, 39 (11) 1934–1972 (2014)
13. Mohan VB, Lau K-t, Hui D, Bhattacharyya D, "Graphene-Based Materials and Their Composites: A Review on Production, Applications and Product Limitations." *Compos. Pt. B Eng.*, 142 200–220 (2018)
14. Xu B, Yue S, Sui Z, Zhang X, Hou S, Cao G, Yang Y, "What Is the Choice for Supercapacitors: Graphene or Graphene Oxide?" *Energ. Environ. Sci*, 4 (8) 2826–2830 (2011)
15. Lin L, Peng H, Liu Z, "Synthesis Challenges for Graphene Industry." *Nat. Mater*, 18 (6) 520–524 (2019) [PubMed: 31114064]
16. Dreyer DR, Park S, Bielawski CW, Ruoff RS, "The Chemistry of Graphene Oxide." *Chem. Soc. Rev*, 39 (1) 228–240 (2010) [PubMed: 20023850]
17. Buchsteiner A, Lerf A, Pieper J, "Water Dynamics in Graphite Oxide Investigated with Neutron Scattering." *J. Phys. Chem. B*, 110 (45) 22328–22338 (2006) [PubMed: 17091972]
18. Hontoria-Lucas C, López-Peinado AJ, López-González JdD, Rojas-Cervantes ML, Martín-Aranda RM, "Study of Oxygen-Containing Groups in a Series of Graphite Oxides: Physical and Chemical Characterization." *Carbon*, 33 (11) 1585–1592 (1995)
19. Bissessur R, Scully SF, "Intercalation of Solid Polymer Electrolytes into Graphite Oxide." *Solid State Ionics*, 178 (11) 877–882 (2007)
20. Matsuo Y, Hatase K, Sugie Y, "Preparation and Characterization of Poly(Vinyl Alcohol)- and Cu(OH)2-Poly(Vinyl Alcohol)-Intercalated Graphite Oxides." *Chem. Mater*, 10 (8) 2266–2269 (1998)
21. Matsuo Y, Tahara K, Sugie Y, "Structure and Thermal Properties of Poly(Ethylene Oxide)-Intercalated Graphite Oxide." *Carbon*, 35 (1) 113–120 (1997)
22. Xu Y, Hong W, Bai H, Li C, Shi G, "Strong and Ductile Poly (Vinyl Alcohol)/Graphene Oxide Composite Films with a Layered Structure." *Carbon*, 47 (15) 3538–3543 (2009)
23. Wu J, Tang Q, Sun H, Lin J, Ao H, Huang M, Huang Y, "Conducting Film from Graphite Oxide Nanoplatelets and Poly (Acrylic Acid) by Layer-by-Layer Self-Assembly." *Langmuir*, 24 (9) 4800–4805 (2008) [PubMed: 18358052]
24. Cao Y-C, Xu C, Wu X, Wang X, Xing L, Scott K, "A Poly (Ethylene Oxide)/Graphene Oxide Electrolyte Membrane for Low Temperature Polymer Fuel Cells." *J. Power Sources*, 196 (20) 8377–8382 (2011)

25. Oh SH, Kim KR, Yun JM, Kang PH, "Graphene Oxide and Water-Soluble Polymer Composite Materials as Efficient Hole Transporting Layer for High Performance Organic Solar Cells." *Phys. Status. Solidi A*, 212 (2) 376–381 (2015)
26. Guan Y, Meyers KP, Mendon SK, Hao G, Douglas JR, Trigwell S, Nazarenko SI, Patton DL, Rawlins JW, "Ecofriendly Fabrication of Modified Graphene Oxide Latex Nanocomposites with High Oxygen Barrier Performance." *ACS Appl. Mater. Interfaces*, 8 (48) 33210–33220 (2016) [PubMed: 27934160]
27. Huang H-D, Ren P-G, Chen J, Zhang W-Q, Ji, X, Li Z-M, "High Barrier Graphene Oxide Nanosheet/Poly (Vinyl Alcohol) Nanocomposite Films." *J. Membr. Sci.*, 409 156–163 (2012)
28. Wicks ZW, Wicks DA, Rosthauser JW, "Two Package Waterborne Urethane Systems." *Prog. Org. Coat*, 44 (2) 161–183 (2002)
29. Engels HW, Pirkl HG, Albers R, Albach RW, Krause J, Hoffmann A, Casselmann H, Dormish J, "Polyurethanes: Versatile Materials and Sustainable Problem Solvers for Today's Challenges." *Angew. Chem. Int. Ed.*, 52 (36) 9422–9441 (2013)
30. Kuan H-C, Chuang W-P, Ma C-CM, Chiang C-L, Wu H-L, "Synthesis and Characterization of a Clay/Waterborne Polyurethane Nanocomposite." *J. Mater. Sci.*, 40 (1) 179–185 (2005)
31. Chen J-J, Zhu C-F, Deng H-T, Qin Z-N, Bai Y-Q, "Preparation and Characterization of the Waterborne Polyurethane Modified with Nanosilica." *J. Polym. Res.*, 16 (4) 375–380 (2009)
32. Zeng Z, Chen M, Jin H, Li W, Xue X, Zhou L, Pei Y, Zhang H, Zhang Z, "Thin and Flexible Multi-Walled Carbon Nanotube/Waterborne Polyurethane Composites with High-Performance Electromagnetic Interference Shielding." *Carbon*, 96 768–777 (2016)
33. Raghu AV, Lee YR, Jeong HM, Shin CM, "Preparation and Physical Properties of Waterborne Polyurethane/Functionalized Graphene Sheet Nanocomposites." *Macromol. Chem. Phys.*, 209 (24) 2487–2493 (2008)
34. Hu L, Jiang P, Bian G, Huang M, Haryono A, Zhang P, Bao Y, Xia J, "Effect of Octa(Aminopropyl) Polyhedral Oligomeric Silsesquioxane (OapPOSS) Functionalized Graphene Oxide on the Mechanical, Thermal, and Hydrophobic Properties of Waterborne Polyurethane Composites." *J. Appl. Polym. Sci.*, 134 (6) 44440 (2017)
35. Hsiao S-T, Ma C-CM, Liao W-H, Wang Y-S, Li S-M, Huang Y-C, Yang R-B, Liang W-F, "Lightweight and Flexible Reduced Graphene Oxide/Water-Borne Polyurethane Composites with High Electrical Conductivity and Excellent Electromagnetic Interference Shielding Performance." *ACS Appl. Mater. Interfaces*, 6 (13) 10667–10678 (2014) [PubMed: 24921939]
36. Hu J, Zhang F, "Self-Assembled Fabrication and Flame Retardant Properties of Reduced Graphene Oxide/Waterborne Polyurethane Nanocomposites." *J. Therm. Anal. Calorim.*, 118 (3) 1561–1568 (2014)
37. Hummers WS Jr., Offeman RE, "Preparation of Graphitic Oxide." *J. Amer. Chem. Soc.*, 80 (6) 1339 (1958)
38. Park S, An J, Jung I, Piner RD, An SJ, Li X, Velamakanni A, Ruoff RS, "Colloidal Suspensions of Highly Reduced Graphene Oxide in a Wide Variety of Organic Solvents." *Nano Lett.*, 9 (4) 1593–1597 (2009) [PubMed: 19265429]
39. Paredes J, Villar-Rodil S, Martínez-Alonso A, Tascon J, "Graphene Oxide Dispersions in Organic Solvents." *Langmuir*, 24 (19) 10560–10564 (2008) [PubMed: 18759411]
40. Dimiev AM, Alemany LB, Tour JM, "Graphene Oxide. Origin of Acidity, Its Instability in Water, and a New Dynamic Structural Model." *ACS Nano*, 7 (1) 576–588 (2012) [PubMed: 23215236]
41. Celina M, Gillen K, "Oxygen Permeability Measurements on Elastomers at Temperatures up to 225°C." *Macromol.*, 38 (7) 2754–2763 (2005)
42. Lyon RE, Walters RN, Stolarov SI, "A Thermal Analysis Method for Measuring Polymer Flammability." *J. ASTM Int.*, 3 (4) 1–18 (2006)
43. Bentz D, "Combination of Transient Plane Source and Slug Calorimeter Measurements to Estimate the Thermal Properties of Fire Resistive Materials." *J. Test. Eval.*, 35 (3) 1–5 (2006)
44. Faucheu J, Wood KA, Sung L-P, Martin, JW, "Relating Gloss Loss to Topographical Features of a Polyvinylidene Fluoride Coating." *J. Coat. Technol. Res.*, 3 (1) 29–39 (2006)

45. Konios D, Stylianakis MM, Stratakis E, Kymakis E, "Dispersion Behaviour of Graphene Oxide and Reduced Graphene Oxide." *J. Colloid Interface Sci*, 430 108–112 (2014) [PubMed: 24998061]
46. Lerf A, He H, Forster M, Klinowski J, "Structure of Graphite Oxide Revisited." *J. Phys. Chem. B*, 102 (23) 4477–4482 (1998)
47. Li D, Mueller MB, Gilje S, Kaner RB, Wallace GG, "Processable Aqueous Dispersions of Graphene Nanosheets." *Nat. Nanotechnol*, 3 (2) 101–105 (2008) [PubMed: 18654470]
48. Lu W, Chou T-W, "Analysis of the Entanglements in Carbon Nanotube Fibers Using a Self-Folded Nanotube Model." *J. Mech. Phys. Solids*, 59 (3) 511–524 (2011)
49. Moon IK, Lee J, Ruoff RS, Lee H, "Reduced Graphene Oxide by Chemical Graphitization." *Nat. Commun*, 1 1067 (2010)
50. Bernard C, Nguyen T, Pellegrin B, Holbrook RD, Zhao M, Chin J, "Fate of Graphene in Polymer Nanocomposite Exposed to UV Radiation." *J. Phys.: Conf. Ser*, 304 012063/1–012063/8 (2011)
51. Ramanathan T, Abdala A, Stankovich S, Dikin D, Herrera-Alonso M, Piner R, Adamson D, Schniepp H, Chen X, Ruoff R, "Functionalized Graphene Sheets for Polymer Nanocomposites." *Nat. Nanotechnol*, 3 (6) 327–331 (2008) [PubMed: 18654541]
52. Rafiee MA, Rafiee J, Wang Z, Song H, Yu Z-Z, Koratkar N, "Enhanced Mechanical Properties of Nanocomposites at Low Graphene Content." *ACS Nano*, 3 (12) 3884–3890 (2009) [PubMed: 19957928]
53. Liang J, Huang Y, Zhang L, Wang Y, Ma Y, Guo T, Chen Y, "Molecular-Level Dispersion of Graphene into Poly (Vinyl Alcohol) and Effective Reinforcement of Their Nanocomposites." *Adv. Funct. Mater*, 19 (14) 2297–2302 (2009)
54. Wakabayashi K, Pierre C, Dikin DA, Ruoff RS, Ramanathan T, Brinson LC, Torkelson JM, "Polymer-Graphite Nanocomposites: Effective Dispersion and Major Property Enhancement Via Solid-State Shear Pulverization." *Macromolecules*, 41 (6) 1905–1908 (2008)
55. Bunch JS, Verbridge SS, Alden JS, Van Der Zande AM, Parpia JM, Craighead HG, McEuen PL, "Impermeable Atomic Membranes from Graphene Sheets." *Nano Lett*, 8 (8) 2458–2462 (2008) [PubMed: 18630972]
56. Huang H-D, Ren P-G, Xu J-Z, Xu L, Zhong G-J, Hsiao BS, Li Z-M, "Improved Barrier Properties of Poly (Lactic Acid) with Randomly Dispersed Graphene Oxide Nanosheets." *J. Membr. Sci*, 464 110–118 (2014)
57. Kim H, Miura Y, Macosko CW, "Graphene/Polyurethane Nanocomposites for Improved Gas Barrier and Electrical Conductivity." *Chem. Mater*, 22 (11) 3441–3450 (2010)
58. Compton OC, Kim S, Pierre C, Torkelson JM, Nguyen ST, "Crumpled Graphene Nanosheets as Highly Effective Barrier Property Enhancers." *Adv. Mater*, 22 (42) 4759–4763 (2010) [PubMed: 20830709]
59. Cui Y, Kundalwal S, Kumar S, "Gas Barrier Performance of Graphene/Polymer Nanocomposites." *Carbon*, 98 313–333 (2016)
60. Yoo BM, Shin HJ, Yoon HW, Park HB, "Graphene and Graphene Oxide and Their Uses in Barrier Polymers." *J. Appl. Polym. Sci*, 131 (1) 39628 (2014)
61. Lee D, Yang H, Park S, Kim W, "Nafion/Graphene Oxide Composite Membranes for Low Humidifying Polymer Electrolyte Membrane Fuel Cell." *J. Membr. Sci*, 452 20–28 (2014)
62. Korobov MV, Talyzin AV, Rebrikova AT, Shilayeva EA, Avramenko NV, Gagarin AN, Ferapontov NB, "Sorption of Polar Organic Solvents and Water by Graphite Oxide: Thermodynamic Approach." *Carbon*, 102 297–303 (2016)
63. Zinadini S, Zinatizadeh AA, Rahimi M, Vatanpour V, Zangeneh H, "Preparation of a Novel Antifouling Mixed Matrix PES Membrane by Embedding Graphene Oxide Nanoplates." *J. Membr. Sci*, 453 292–301 (2014)
64. Adamson AW, Gast AP, *Physical Chemistry of Surfaces*. Interscience, New York (1967)
65. Lerf A, Buchsteiner A, Pieper J, Schöttl S, Dekany I, Szabo T, Boehm H, "Hydration Behavior and Dynamics of Water Molecules in Graphite Oxide." *J. Phys. Chem. Solids*, 67 (5) 1106–1110 (2006)

66. Etmimi HM, Mallon PE, Sanderson RD, "Polymer/Graphite Nanocomposites: Effect of Reducing the Functional Groups of Graphite Oxide on Water Barrier Properties." *Eur. Polym. J.*, 49 (11) 3460–3470 (2013)
67. Starkova O, Chandrasekaran S, Prado L, Tölle F, Mülhaupt R, Schulte K, "Hydrothermally Resistant Thermally Reduced Graphene Oxide and Multi-Wall Carbon Nanotube Based Epoxy Nanocomposites." *Polym. Degrad. Stab.*, 98 (2) 519–526 (2013)
68. Huang G, Gao J, Wang X, Liang H, Ge C, "How Can Graphene Reduce the Flammability of Polymer Nanocomposites?" *Mater. Lett.*, 66 (1) 187–189 (2012)
69. Higginbotham AL, Lomeda JR, Morgan AB, Tour JM, "Graphite Oxide Flame-Retardant Polymer Nanocomposites." *ACS Appl. Mater. Interfaces*, 1 (10) 2256–2261 (2009) [PubMed: 20355860]
70. Rahatekar SS, Zammarano M, Matko S, Koziol KK, Windle AH, Nyden M, Kashiwagi T, Gilman JW, "Effect of Carbon Nanotubes and Montmorillonite on the Flammability of Epoxy Nanocomposites." *Polym. Degrad. Stab.*, 95 (5) 870–879 (2010)
71. Guo Y, Bao C, Song L, Yuan B, Hu Y, "In Situ Polymerization of Graphene, Graphite Oxide, and Functionalized Graphite Oxide into Epoxy Resin and Comparison Study of on-the-Flame Behavior." *Ind. Eng. Chem. Res.*, 50 (13) 7772–7783 (2011)
72. Ghosh S, Calizo I, Teweldebrhan D, Pokatilov EP, Nika DL, Balandin AA, Bao W, Miao F, Lau CN, "Extremely High Thermal Conductivity of Graphene: Prospects for Thermal Management Applications in Nanoelectronic Circuits." *Appl. Phys. Lett.*, 92 (15) 151911 (2008)
73. Shtein M, Nadiv R, Buzaglo M, Kahil K, Regev O, "Thermally Conductive Graphene-Polymer Composites: Size, Percolation, and Synergy Effects." *Chem. Mater.*, 27 (6) 2100–2106 (2015)
74. Zhong H, Lukes JR, "Interfacial Thermal Resistance between Carbon Nanotubes: Molecular Dynamics Simulations and Analytical Thermal Modeling." *Phys. Rev. B*, 74 (12) 125403 (2006)
75. Wang S, Tambraparni M, Qiu J, Tipton J, Dean D, "Thermal Expansion of Graphene Composites." *Macromolecules*, 42 (14) 5251–5255 (2009)
76. Yu A, Ramesh P, Itkis ME, Bekyarova E, Haddon RC, "Graphite Nanoplatelet – Epoxy Composite Thermal Interface Materials." *J. Phys. Chem. C*, 111 (21) 7565–7569 (2007)
77. Cervantes-Uc J, Espinosa JM, Cauch-Rodriguez J, Avila-Ortega A, Vazquez-Torres H, Marcos-Fernandez A, San Román J, "TGA/FTIR Studies of Segmented Aliphatic Polyurethanes and Their Nanocomposites Prepared with Commercial Montmorillonites." *Polym. Degrad. Stab.*, 94 (10) 1666–1677 (2009)
78. Yang X, Li L, Shang S, Tao X-m, "Synthesis and Characterization of Layer-Aligned Poly (Vinyl Alcohol)/Graphene Nanocomposites." *Polymer*, 51 (15) 3431–3435 (2010)
79. Cheng S, Chen X, Hsuan YG, Li CY, "Reduced Graphene Oxide-Induced Polyethylene Crystallization in Solution and Nanocomposites." *Macromolecules*, 45 (2) 993–1000 (2011)
80. Watts P, Fearon P, Hsu W, Billingham N, Kroto H, Walton D, "Carbon Nanotubes as Polymer Antioxidants." *J. Mater. Chem.*, 13 (3) 491–495 (2003)
81. Kodjie SL, Li L, Li B, Cai W, Li CY, Keating M, "Morphology and Crystallization Behavior of HDPE/CNT Nanocomposite." *J. Macromol. Sci. B*, 45 (2) 231–245 (2006)
82. Najafi E, Shin K, "Radiation Resistant Polymer-Carbon Nanotube Nanocomposite Thin Films." *Colloids Surf. A: Physicochem. Eng. Aspects*, 257 333–337 (2005)
83. Petersen EJ, Lam T, Gorham JM, Scott KC, Long CJ, Stanley D, Sharma R, Alexander Liddle J, Pellegrin B, Nguyen T, "Methods to Assess the Impact of UV Irradiation on the Surface Chemistry and Structure of Multiwall Carbon Nanotube Epoxy Nanocomposites." *Carbon*, 69 194–205 (2014)
84. Nguyen T, Petersen EJ, Pellegrin B, Gorham JM, Lam T, Zhao M, Sung L, "Impact of UV Irradiation on Multiwall Carbon Nanotubes in Nanocomposites: Formation of Entangled Surface Layer and Mechanisms of Release Resistance." *Carbon*, 116 191–200 (2017) [PubMed: 28603293]
85. Nguyen T, Wohlleben W, Sung L, "Mechanisms of Aging and Release from Weathered Nanocomposites" In: *Safety of Nanomaterials Along Their Lifecycle: Release, Exposure, and Human Hazards*, pp. 315–334. Taylor and Francis, New York (2014)

86. Lankone RS, Wang J, Ranville JF, Fairbrother DH, “Photodegradation of Polymer-CNT Nanocomposites: Effect of CNT Loading and CNT Release Characteristics.” *Environ. Sci.: Nano*, 4 967–982 (2017). 10.1039/C6EN00669H

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Fig. 1:
Procedure and conditions used for preparation of GO/WPU nanocoatings

Fig. 2:

LSCM images (a) and Raman spectra (b) of neat WPU and a 1.2% mass fraction GO/WPU nanocoating (raw data, not normalized), revealing a uniform distribution of GO particles in the nanocomposite. The two spectra for the WPU coating were taken from two different locations of one specimen. The four spectra for the GO/WPU nanocoating were taken from four different locations of one specimen. More spectra were taken for the GO/WPU nanocoating in order to conduct peak intensity analysis of the signature D and G bands of GO, which are denoted

Fig. 3:
FE-SEM images of cryo-fractured surfaces of WPU containing 0.4% (a) and 2% (b) GO mass fractions. Arrows indicate the presence of some air gaps that formed due to incomplete exfoliation or some GO aggregation

Fig. 4:
Representative stress–strain curves, with inset of the expanded low strain region, for WPU coating containing different GO contents

Fig. 5: Mechanical properties as a function of GO mass loading for WPU coatings; (a) tensile strength, (b) Young's modulus, and (c) elongation at break. All results are the average of 18 specimens, and error bars represent one standard deviation

Fig. 6:

O₂ permeability as a function of GO mass loading in WPU coatings. Except for the 0.4% and 0.8% GO mass loading results where only one specimen was used, the results at other mass loadings are the average of two replicates. The error bars represent one standard deviation

Fig. 7: Sorption isotherms of WPU containing different GO mass loadings. Each data point is the average of three specimens, and error bars represent one standard deviation

Fig. 8: Heat release rate (HRR) vs temperature curves for WPU nanocoatings containing different GO mass loadings. Data were collected using a combustion microcalorimeter. The inset shows the peak heat release rate (PHRR) as a function of GO mass loading; the results of the inset are the average of three specimens, and the error bars represent one standard deviation

Fig. 9:
Thermal conductivity as a function of GO mass loading for WPU coatings. The results are the average of ten measurements from one specimen, and the error bars represent one standard deviation

Fig. 10:

(a) TGA and derivative TGA curves for GO/WPU nanocoatings containing different GO mass loadings, and (b) decomposition temperature as a function of GO mass loading for WPU coatings. The results of (b) are the average of three specimens, and the error bars represent one standard deviation; the error bars for 0%, 1.2%, and 2% are smaller than the figure symbol

Table 1:

A comparison of thermal conductivity enhancements between this study and other studies

Composite type	Nanomaterial mass loading (%)	Thermal conductivity increase (%)
GO/WPU (this study)	2	138
GO/epoxy	2.2	>100 ⁷⁶
GO/epoxy	5	400 ⁷⁵