

# BARRIER PROPERTIES OF GRAPHENE-BASED POLYMER NANOCOMPOSITES

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## Abstract

Exfoliated graphite nanoplatelets (herein called graphene) are nanometer-thin platelets that are being extensively researched for their high stiffness, thermal conductivity, mass transfer barrier properties, and electrical conductivity towards developing a wide range of applications such as polymer nanocomposites (PNCs). These graphene-based PNCs (GPNCs) are expected to have better properties as compared to PNCs made using carbon nanotubes or nano-layered silicates.

Graphene platelets are generally hydrophilic in nature hence difficult to disperse in polymers. In the work described here, surface treatment of graphene using 3-aminopropyltrimethoxysilane (APTMS), as shown by energy dispersive x-ray spectroscopy (EDS), results in more hydrophobic graphene which shows better dispersion. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images illustrate the effect of surface treatment on the dispersion of graphene into polyvinyl acetate (PVAc). Barrier properties of treated and untreated graphene in PVAc were measured by sorption tests of GPNCs in water at various filler concentrations and different platelet diameters which show that the graphene platelets form an excellent barrier against diffusion.

## Introduction

Graphene is being studied extensively for its phenomenal structural, mechanical, electrical, thermal, and barrier properties. An atomically thick, two-dimensional layer of carbon atoms, graphene has recently sparked much scientific interest, with thousands of publications and several reviews dedicated to it (Mukhopadhyay & Gupta 2011; Potts et al. 2011; Kim, Abdala, et al. 2010). Among other applications, graphene shows great promise as an effective mass transfer barrier, with one sheet able to block gas permeation of atoms as small as helium (Bunch et al. 2008). These barrier properties are able to be transferred to graphene-based polymer nanocomposites (GPNCs); dramatic decreases in gas permeation can be achieved at very low filler levels (1-3 wt%) for a multitude of different polymer matrices (Kim, Miura, et al. 2010; Kim & Macosko 2009; Kim & Macosko 2008). Also, specialized applications requiring opaque packaging materials may utilize the ability of GPNCs to block high-energy light (Owen et al. 2010).

Similar to those of nanoclay or nanosilicate composites, graphene's barrier

properties are a result of the tortuous path diffusing molecules must endure (Paul & Robeson 2008; Rana et al. 2005; Statler & Gupta 2008); however, GPNCs show much greater barrier properties than other fillers at similar loading levels (Potts et al. 2011). While the gas barrier properties of GPNCs have already been investigated in some detail, liquid mass transfer barrier properties have not. However, the morphological characterizations and theoretical models developed for nanoclay and nanosilicate composites (Paul & Robeson 2008; Rana et al. 2005) should be applicable to GPNCs as well. In this work, the dispersion of exfoliated graphite nanoplatelets (graphene) into polyvinyl acetate (PVAc) is discussed, and results of sorption tests of GPNCs are presented to show that graphene does form a barrier to liquid water diffusion.

## Materials and Methods

### *Materials*

Two batches of graphite nanoplatelets (xGnP<sup>®</sup>) were purchased from XG Sciences, Inc., having platelet diameters of 5  $\mu\text{m}$  and 25  $\mu\text{m}$ , respectively. Reported platelet thickness from XG Sciences, Inc., were 7 nm, meaning platelets still contained multiple layers of graphene.

### *Preparation of Polymer Nanocomposites*

The effect of surface treatment on mass transfer barrier properties was investigated by comparing samples with surface treatment, treated samples, to those without, untreated samples. Surface treatment was performed by ultrasonically treating as-received platelets in dimethylformamide (DMF) at a frequency of 50% for 20 sec, adding an equal mass of APTMS to the mixture, and ultrasonically treating again for 20 sec at 50%. The mixture was stirred overnight, filtered, washed with acetone, and dried in an oven at 75°C. Treated and untreated material were, then, ultrasonically treated in isopropyl alcohol (IPA) at 50% with 5 sec pulses, separated by 15 sec breaks, for a total ultrasonication time of 30 min to separate platelets. IPA was then evaporated from the mixture using a hot water bath at 80°C, and the material was dried in an oven at 75°C.

Desired concentrations of graphene and PVAc were mixed using an internal mixer, using 60 g batches at 110°C for 5 min with a blade rotation rate of 125 rpm. Mixed material was then compression molded in a 30-ton press using a 15 cm x 15 cm square mold of 0.5 mm thickness at 116°C and 15 ton for 4 min. Molded material was cut into 2.5 cm x 2.5 cm square samples.

### *Measurement of Barrier Properties of Graphene*

Sorption tests were performed to measure the barrier properties of graphene to water diffusion. Dry sample mass and thickness were measured to the nearest  $\mu\text{g}$  and  $\mu\text{m}$ , respectively. Samples were placed on wire-mesh stands in deionized water to

allow them to sit vertically for even diffusion into both sides of the samples. The samples were weighed on the same electronic balance periodically by removing from water, drying the surface with KimWipes®, and taking the sample weight 10 sec after placing on balance. Independent variables for sorption tests were the use of surface treatment, filler concentration (0.1, 0.2, 0.5, 1.0, and 1.5 wt%), and platelet diameter (5 and 25  $\mu\text{m}$ ). Sample jars were stored at room temperature (about 23°C).

## Results and Discussion

### *Characterization of Graphene Platelets*

Shown in Figure 1 are scanning electron microscopic (SEM) images of the as-received graphite platelets, 5  $\mu\text{m}$  platelet diameter. In Figure 1-a, the accordion-like structure of the platelets can be seen. This results from the method of production of xGnP® by volatilizing intercalated compounds within the layers of graphite. With increasing magnification, the flaky, layered structure of xGnP® can be seen to the limits of SEM imaging, shown in Figure 1-b, as well as at greater magnifications, as shown by the transmission electron microscopic (TEM) image of a GPNC in Figure 2.

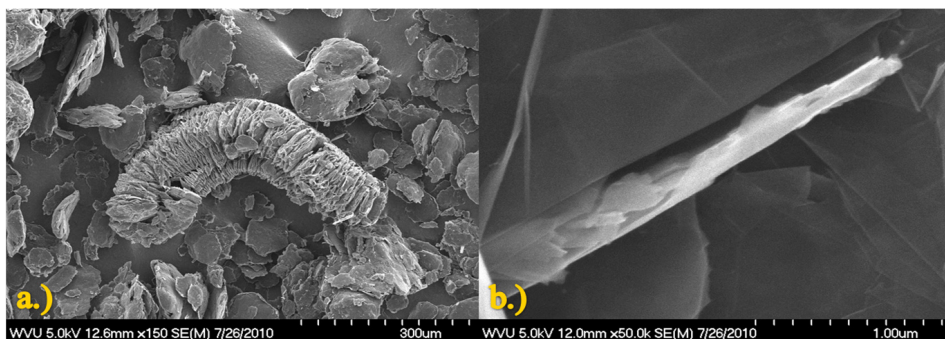
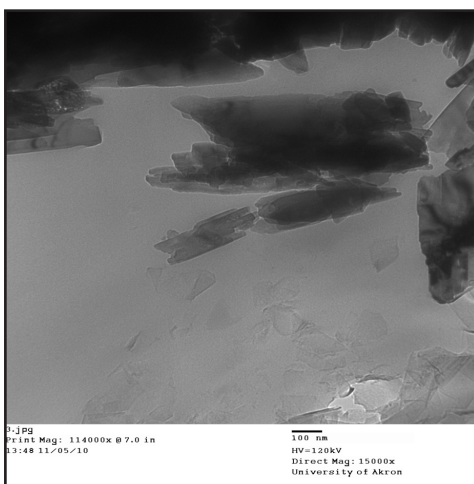


Figure 1, SEM of As-Received 5  $\mu\text{m}$ -Diameter Graphite Platelets

a) Accordion-like structure of xGnP®; b) Layered, flaky nature of xGnP®.

Figure 2, TEM of 1.5% 5  $\mu\text{m}$ -Diameter Graphene/PVAc, 100 nm.

The energy dispersive x-ray spectrometric (EDS) results comparing treated and untreated 5  $\mu\text{m}$ -diameter graphene are shown in Figure 3. Results of the treated sample, the dotted line, show a replacement of oxygen surface atoms with silicon atoms, compared to those of the untreated sample, the solid line.



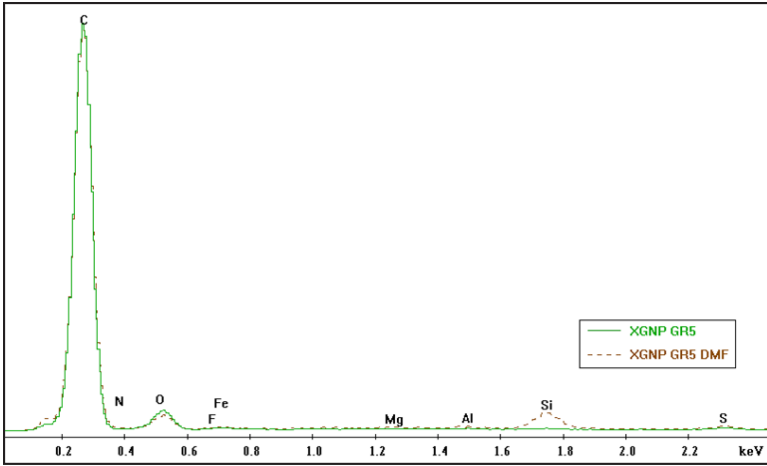


Figure 3, EDS Results Comparing Surface Treatment Techniques

### Measurement of Dispersion in Polymer Nanocomposites

The effects of filler concentration, surface treatment, and platelet diameter on the dispersion of graphene into the polyvinyl acetate matrix are shown in Figure 4. Samples were fractured under liquid N<sub>2</sub> and coated with an electrically conductive material, and SEM images were taken of the fracture surface. Graphene platelets appear as white horizontal lines, perpendicular to the direction of diffusion, and all other markings result from fracturing the polymer. This morphology, in which the platelets align parallel to one another, results from compression molding. SEM images of unmolded samples were acquired and showed unaligned platelets.

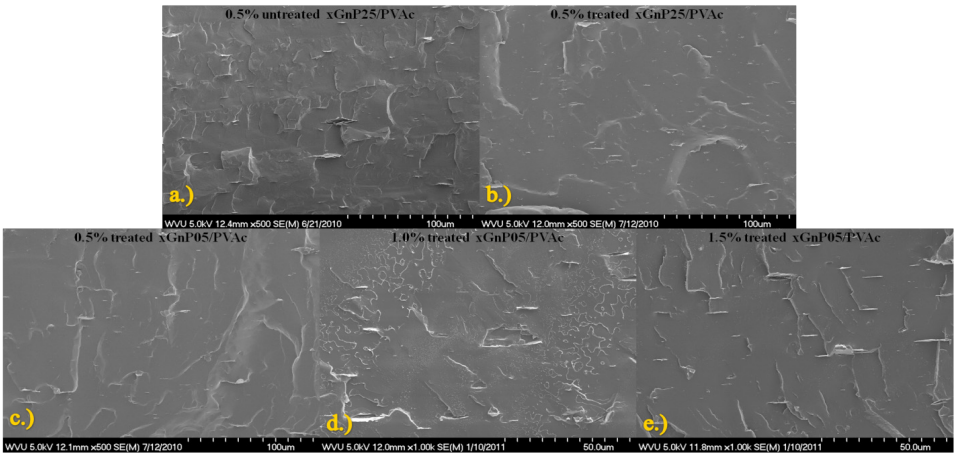


Figure 4, SEM of Dispersion of Graphene into Polymer

a) 0.5% untreated 25  $\mu\text{m}$ -diameter graphene/PVAc, 100  $\mu\text{m}$ ; b) 0.5% treated 25  $\mu\text{m}$ -diameter graphene/PVAc, 100  $\mu\text{m}$ ; c) 0.5% treated 5  $\mu\text{m}$ -diameter graphene/PVAc, 100  $\mu\text{m}$ ; d) 1.0% treated 5  $\mu\text{m}$ -diameter graphene/PVAc, 50  $\mu\text{m}$ ; e) 1.5% treated 5  $\mu\text{m}$ -diameter graphene/PVAc, 50  $\mu\text{m}$

The amount of platelets visible increases with increasing concentration of filler, Figure 4-c,d,e. Furthermore, fewer platelets can be seen in the treated sample, Figure 4-b, than in the untreated sample, Figure 4-a, because particles are smaller; therefore, dispersion is better. Average particle sizes for the 25 μm-diameter sample, Figure 4-b, are larger than those for the 5 μm-diameter sample, Figure 4-c. Though particles do appear larger for the 25 μm-diameter samples than for 5 μm-diameter samples, platelets do not appear to actually be 25 μm or 5 μm in diameter.

Measurement of Diffusion Coefficients

Figure 5 shows the normalized mass gain for a typical sorption test; the average ratio of mass uptake,  $M_t$ , to equilibrium mass uptake,  $M_{\infty}$ , of four samples each is plotted versus the square root of time over average initial sample thickness for all concentrations of treated 25 μm-diameter graphene/PVAc. Tests were not started at the same time, and the unfilled PVAc is the only test to reach equilibrium at the time this article was written. Therefore, for all other tests, an estimated  $M_{\infty}$  was used. Due to the slightly hydrophilic nature of the graphene platelets, the mass uptake and time to reach equilibrium are proportional to filler concentration. From individual sample plots as in Figure 5, the diffusion coefficient was calculated from the slope of the initial linear section as per Equation 1, where  $D$  is the diffusion coefficient (Koros & Zimmerman 2003):

$$(1) \text{ slope} = \frac{4}{\sqrt{\rho}} (D)^{\frac{1}{2}}$$

The calculated diffusion coefficients of all sorption tests are shown in Table 1. All presented values are intermediate results because sorption tests are still ongoing at the time this article was written. In general, diffusivity is inversely proportional to filler concentration and surface treatment, and though 5 μm-diameter platelets yielded slightly lower diffusion coefficients, platelet diameter had little effect on diffusivity.

Figure 5, Normalized Mass Gain for Sorption Test of Treated 25 μm-Diameter Graphene/PVAc

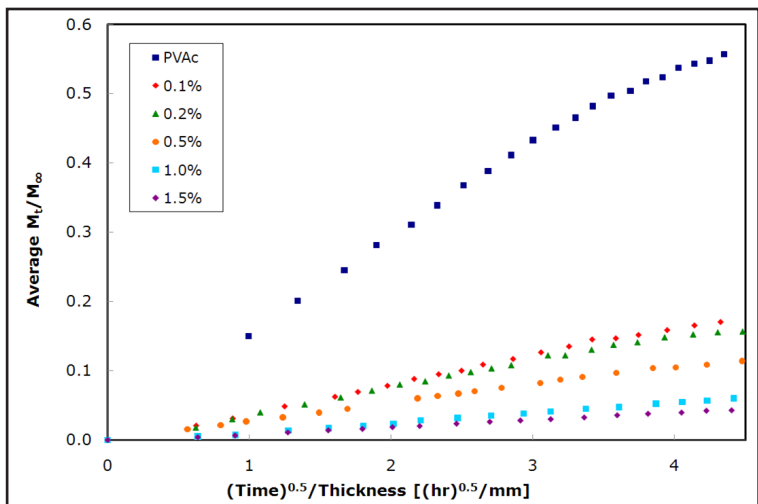


Table 1, Calculated Diffusion Coefficients

Treated Sample	Diff. Coeff. (cm <sup>2</sup> /min)	S.D. (cm <sup>2</sup> /min)
Pure PVAc	7.05E-07	4.6E-08
0.1% t. xGnP25/PVAc	5.47E-08	4.7E-09
0.2% t. xGnP25/PVAc	4.77E-08	3.1E-09
0.5% t. xGnP25/PVAc	5.23E-08	5.4E-08
1.0% t. xGnP25/PVAc	5.76E-09	4.1E-10
1.5% t. xGnP25/PVAc	3.15E-09	2.0E-10
0.1% t. xGnP05/PVAc	4.30E-08	1.6E-08
0.2% t. xGnP05/PVAc	2.35E-08	1.0E-09
0.5% t. xGnP05/PVAc	2.18E-08	1.2E-08
1.0% t. xGnP05/PVAc	6.27E-09	5.4E-10
1.5% t. xGnP05/PVAc	3.21E-09	4.0E-11
0.1% un. xGnP25/PVAc	1.08E-07	2.5E-08
0.2% un. xGnP25/PVAc	6.51E-08	4.5E-08
0.5% un. xGnP25/PVAc	4.20E-08	2.3E-08
0.1% un. xGnP05/PVAc	1.47E-07	1.5E-08
0.2% un. xGnP05/PVAc	6.32E-08	3.6E-08
0.5% un. xGnP05/PVAc	3.51E-08	1.1E-08

## Conclusions

Among its potential structural and electrical applications, graphene is applicable as a mass transfer barrier for packaging applications. In the work presented here, graphite nanoplatelets were separated and dispersed into polymer, and the effects of filler concentration, surface treatment, and platelet diameter on the diffusion of water into the resulting GPNCs were investigated.

Graphene serves as an excellent barrier to water diffusion, dramatically lowering the calculated diffusion coefficient with very small filler concentrations. Surface treatment improves its barrier properties further, while platelet diameter has little effect. Future work includes further tests at various temperatures, including temperatures above the glass transition temperature of PVAc. The effects of surface treatment on graphene platelets will be confirmed using Fourier transform infrared spectroscopy (FTIR), and additional TEM images of GPNCs will be acquired. Also, additional tests on mechanical, thermogravimetric, rheological, and other properties will be performed.

**Bibliography**

- Bunch, J.S., Verbridge, S.S., Alden, J.S., et al. 2008. "Impermeable atomic membranes from graphene sheets." *Nano Lett.* 8. 8. 2458-2462. doi: 10.1021/nl801457b
- Kim, H., Abdala, A.A., Macosko, C.W. 2010. "Graphene/polymer nanocomposites." *Macromol.* 43. 6515-6530. doi: 10.1021/ma100572e
- Kim, H. & Macosko, C.W. 2008. "Morphology and properties of polyester/exfoliated graphite nanocomposites." *Macromol.* 41. 3317-3327. doi: 10.1021/ma702385h
- . 2009. "Processing-property relationships of polycarbonate/graphene composites." *Polymer.* 50. 3797-3809. doi: 10.1016/j.polymer.2009.05.038
- Kim, H., Miura, Y., Macosko, C.W. 2010. "Graphene/polyurethane nanocomposites for improved gas barrier and electrical conductivity." *Chem. Mater.* 22. 3441-3450. doi: 10.1021/cm100477v
- Koros, W.J. & Zimmerman, C.M. 2003. "Transport and Barrier Properties." *Comprehensive Desk Reference of Polymer Characterization and Analysis.* Ed. Brady, R.F. New York: Oxford University Press. 680-699.
- Mukhopadhyay, P. & Gupta R.K. 2011. "Trends and frontiers in graphene-based polymer nanocomposites." *Plast. Engr.* Jan., 2011. 32-42.
- Owen, C.C., Kim, S., Pierre, C., et al. 2010. "Crumpled graphene nanosheets as highly effective barrier property enhancers." *Adv. Mater.* 22. 4759-4763. doi: 10.1002/adma.201000960
- Paul, D.R. & Robeson, L.M. 2008. "Polymer nanotechnology: nanocomposites." *Polymer.* 49. 3187-3204. doi: 10.1016/j.polymer.2008.04.017
- Potts, J.R., Dreyer, D.R., Bielawski, C.W., et al. 2011. *Polymer.* 52. 5-25. doi: 10.1016/j.polymer.2010.11.042
- Rana, H.T., Gupta, R.K., GangaRao, H.V.S., et al. 2005. "Measurement of moisture diffusivity through layered-silicate nanocomposites." *Mat., Interfaces, and Electrochem. Phen.* 51. 12. 3249-3256. doi: 10.1002/aic.10605
- Statler, D.L. & Gupta, R.K. 2008. "Relating nanoclay dimensions and arrangement to barrier properties of polymer nanocomposites." *Proc. Soc. Plast. Eng. ANTEC*, May 4-7, 2008. Milwaukee, WI. 163-167.