

# Exfoliated Graphite Nanoplatelets [2] Surface Treatment

Per A. Askeland, Hiroyuki Fukushima, Inhwan Do, Kyriaki Kalaitzidou and Lawrence T. Drzal  
Composite Materials and Structures Center, Michigan State University,  
East Lansing MI, 48824-1226  
Tel: 517-353-7759  
Fax: 517-432-1634

E-mail: [fukushi3@egr.msu.edu](mailto:fukushi3@egr.msu.edu), [doinhwan@egr.msu.edu](mailto:doinhwan@egr.msu.edu), [kalaitzi@egr.msu.edu](mailto:kalaitzi@egr.msu.edu),  
[askelano@egr.msu.edu](mailto:askelano@egr.msu.edu), [drzal@egr.msu.edu](mailto:drzal@egr.msu.edu)

## Abstract

Since the late 1990's, research has been underway in our group at Michigan State University to investigate the fabrication of new nano-size carbon material, exfoliated graphite nanoplatelets [xGnP]. The xGnP is fabricated from natural graphite and can be used as nanoreinforcements for polymers as an alternative to expensive carbon-based nanomaterials. Extensive work in our lab has produced a xGnP around 5-10 nm with a surface area larger than 100 m<sup>2</sup>/g. The diameter (and hence the aspect ratio) can be controlled from sub-micron level to few hundred micrometers. Since graphite is the stiffest material found in nature (Young's Modulus = 1060 MPa), having a modulus several times that of clay, accompanied with excellent strength, electrical and thermal conductivity, the xGnP should have similar properties to carbon-based nanomaterials, including carbon nanotubes, nanofibers, and fullerenes, yet the estimated cost is far less than these materials. The cost of the graphite nanoplatelets was estimated to be \$5/lb or less, which makes the material highly cost effective.

One of the biggest problems found in nanocomposite research area is the dispersion of the nano-fillers in polymer matrix systems. Since many carbon-based materials have very stable chemical and physical structure, it is often very difficult to introduce appropriate functional groups onto their surfaces to improve the dispersion in a polymer matrix, leading to poor composite properties.

In this research, many surface treatments have been applied and a variety of functional groups have been introduced onto the surface of xGnP. XPS investigation revealed the amount and type of the functional groups can be controlled, indicating the surface condition of the xGnP can be optimized to many polymer systems.

## 1. Experiment

### 1.1. Graphite Samples

The graphite nanoflakes were fabricated from graphite-intercalated compounds [GICs] offered by UCAR

Carbon Co. The grade of the graphite was GrafGuard™ 160-50A, which contains about 20 wt% of acid mixtures (sulfuric and nitric acid) intercalated into the galleries of graphite layers. Upon rapid heating, these acid contents were vaporized and forced graphite layers apart, forming worm-like rods. Following ultrasonic treatment, these expanded graphite rods were pulverized into flakes with an average size of around 15 μm (xGnP-15). The average size of the graphite flakes became less than 1 μm after applying vibratory ball milling (xGnP-1). The BET measurements gave the surface area data of the pulverized and milled graphite as 105 m<sup>2</sup>/g and 94 m<sup>2</sup>/g, respectively. The thickness of these flakes was calculated as around 9 to 10 nm based on the surface area data, which is in agreement with TEM images of the milled graphite flakes.

### 1.2. Surface Treatments

According to the XPS data of exfoliated graphite samples, these materials have very few functional groups on their surface, implying poor interaction with polymer matrices. To improve the surface condition of exfoliated graphite samples, various surface treatments were applied and the surface condition was investigated by XPS. The treatments used were liquid oxidation by nitric acid [1], nitric and sulfuric acid, and nitric acid, sulfuric acid, and ozone; plasma treatment under oxygen, heating under ozone atmosphere, UV treatment under ozone atmosphere, and grafting amine grafting [2]; and acrylamide polymerization [3].

### 1.3. X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectra were obtained from a Physical Electronics PHI 5400 ESCA system. A non-monochromatic Mg source (with a K<sub>α1,2</sub> wavelength at 1253.6 eV) was used with a take-off angle of 45 degrees. Data was collected by a multi-channel detector with an Omni VI lens assembly. The instrument was operated with a pass energy of 93.90 eV for survey scans and 29.35 eV for regional scans. All peaks were referenced to adventitious carbon at 284.6 eV. Semi quantitative atomic concentrations were calculated using pre-determined

sensitivity factors. XPS samples were prepared by applying the graphite directly to double side copper tape on a stainless steel stub. A non-linear least square curve fitting routine was used to interpret the carbon, nitrogen, and oxygen peaks into functional groups, which exist on graphite samples. [4 -7]

## 2. Results and Discussion

### 2.1. Surface Chemistry of Graphite Samples

Surface chemistry of exfoliated graphite samples was investigated with XPS. Five to seven data points were collected and the average values were calculated. Based on these data, the ratio of oxygen/carbon (O/C) and nitrogen/carbon (N/C) was calculated. These data revealed that the diameter affects the functionality of graphite flakes while thickness does not. Calculations show that the edge area of flake materials increases significantly when the diameter becomes small, while it is affected very little by thickness of the flakes, which supports these XPS results. Thus, it is concluded that the graphite flakes with smaller diameter could have more functional groups than those with larger diameters. Also the results revealed that these materials have no nitrogen or sulfur. Curve fitting analysis of XPS data showed that the graphite flakes with smaller diameters have more hydroxyl and ether groups than those with larger diameters do, but the amount of carboxyl group was almost the same for all of these graphite flakes.

### 2.2. The Effect of Various Surface Treatments

#### ▪ O<sub>2</sub> Plasma Treatment

XPS data showed that the O/C ratio increased in all cases, suggesting functional groups were introduced. Functional group analysis revealed that the O<sub>2</sub> plasma treatment could introduce mainly hydroxyl and carbonyl groups. The hydroxyl groups could improve surface condition and enhance adhesion to some polymers.

#### • Nitric Acid Treatment

XPS data showed the O/C ratio was not increased as much as it was in the case of the O<sub>2</sub> Plasma treatment. Also functional group analysis showed little increase in functionality. Thus, it is concluded that the nitric acid treatment was not as effective as O<sub>2</sub> plasma treatment.

#### • Nitric Acid/Sulfuric Acid Treatment

However, when xGnP is treated with a combination of nitric and sulfuric acid, a significant increase in the O/C ratio is observed. Most of this uptake comes in the form of hydroxyl groups.

#### • Acid/Oxidizer Treatment

When ozone is added to the nitric and sulfuric acid mixture, not only is a large increase in oxygen observed on the xGnP surface, but a significant increase in the carboxyl as well as hydroxyl functionalities are observed.

#### • Ozone/Heat Treatment

XPS data revealed that the O/C ratio was not increased after the treatment, suggesting this treatment is not effective for these graphite materials. Functionality analysis supported this conclusion. It is considered that this treatment is effective for amorphous regions of graphite samples, but not for highly crystalline graphite structures.

#### • UV/Ozone Treatment

XPS data revealed that the O/C ratio was not increased after the treatment, suggesting this treatment was not effective for these graphite materials. Functionality analysis showed this process could introduce carboxyl groups, but not significantly. It is considered that this treatment is also effective for amorphous regions of graphite samples, but not for exfoliated graphite samples, which have highly crystalline structures.

#### • Amine Grafting Treatment

XPS data revealed the O/C ratio was not increased after the treatment, but nitrogens was introduced and N/C ratio increased significantly, suggesting many functional groups that include nitrogen were attached to the surface of the sample. Functionality analysis revealed that the primary and secondary amines were the main functional groups introduced on the graphite surface. Also amide groups were added. TGA measurement showed about 1.56 wt% of organic content was introduced after the treatment.

#### • Acrylamide Grafting Treatment

XPS data revealed that both the O/C ratio and N/C ratios were increased significantly, suggesting many functional groups that include oxygen, nitrogen, or both were introduced. In fact, acrylamide grafting treatment showed the biggest increase in both oxygen and nitrogen contents. The functionality analysis revealed that amide groups were the main functional groups introduced. Also primary and secondary amines were added. These functional groups can form covalent bonds with some polymers, including epoxies, and improve adhesion between the matrix and reinforcements. TGA analysis showed about 34 wt% of organic content was introduced after the treatment.

## 3. Conclusions

Various surface treatments were applied to the exfoliated graphite samples. Among these, O<sub>2</sub> plasma, nitric acid and sulfuric acid, nitric/sulfuric acid and ozone, amine grafting, and acrylamide grafting treatments showed increased O/C and/or N/C ratio. Nitric acid, ozone/heat, and UV/ozone treatments did not increase these atomic contents and were considered to be less effective methods to treat these samples. Since these samples are highly pure crystalline graphite, it is difficult to improve functionality

by some surface treatments used for conventional carbon fibers.

Curve fitting analysis was completed on the XPS data of the exfoliated graphite samples before and after various surface treatments. It revealed that the nitric and sulfuric acid treatment introduced hydroxyl groups, O<sub>2</sub> plasma treatment introduced hydroxyl and carbonyl groups, but not ether or carboxyl groups while the nitric/sulfuric/ozone treatment introduces hydroxyl and carboxyl groups. Amine grafting treatment introduced primary amine, secondary amine, amide bond, and oxidized amine groups. Acrylamide grafting introduced a large number of functional groups, especially amide, primary/secondary amines, and carboxyl groups. Among these functional groups shown, hydroxyl, carboxyl, primary/secondary amines, and amide groups have ability to react with epoxy molecules and make covalent bonds, which gives good interaction between graphite flakes and epoxy matrix.

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