

Exfoliated Graphite Nanoplatelets (xGnP): A Carbon Nanotube Alternative

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ABSTRACT

Since the late 1990's, research has been underway in our group at MSU 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 a multifunctional nanoreinforcement for polymers as an alternative to expensive carbon-based nanomaterials. Research on the mechanical, thermal and electrical properties of xGnP thermoset and thermoplastic polymer composites (epoxy and nylon), including modulus, strength, coefficient of thermal expansion, as well as electrical and thermal properties has been completed. The resulting composite can have three times the modulus of nanoclay platelet reinforced composites. With the proper surface treatment of the nanographite, no reduction in composite tensile strength was detected. Impedance measurements have shown that these platelets percolate at below 3 volume percent and exhibit a ~10 order of magnitude reduction in impedance at these concentrations.

Keywords: exfoliated graphite, nanoparticles, nanocomposites, nanoplatelets

1 INTRODUCTION

While most nanocomposite researches have focused on exfoliated clay platelets, the same nanoreinforcement concept can be applied to another layered material, graphite, to produce nanoplatelets and nanocomposites. Graphite is the stiffest material found in nature (Young's Modulus = 1060 MPa), having a modulus several times that of clay, but also with excellent strength and electrical and thermal conductivity. The key to utilizing graphite as a platelet nanoreinforcement is in the ability to exfoliate Graphite Intercalated Compounds [GICs] [1]. Since the cost of GICs based on natural crystalline graphite is quite cheap, around \$1.5-1.6/lb, the cost of graphite nanoplatelets is expected to be \$5/lb or less. This is significantly less expensive than carbon nanotubes (~\$100/g) or VGCF (\$40-50/lb), yet the properties of crystalline graphite flakes are comparable to those of NT and VGCF. If the appropriate surface treatment can be found for graphite nanoflakes, its exfoliation and dispersion in a polymer matrix will result in a composite with not only excellent mechanical properties but electrical and

thermal properties as well, opening up many new structural applications as well as non-structural ones where electromagnetic shielding and high thermal conductivity are requirements.

In this research [2], a special thermal treatment was applied to the graphite flakes to produce exfoliated graphite nanoplatelets (xGnP) for use as a multifunctional polymer additive and reinforcement. The composite material was fabricated by combining the exfoliated graphite flakes with various polymers. X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) were used to assess the degree of exfoliation of the xGnP. The mechanical properties of these composites were investigated by flexural testing. The glass transition temperature (T_g) of composite samples was determined by Differential Mechanical Thermal Analysis (DMTA). The coefficient of thermal expansion was examined by Thermal Mechanical Analysis (TMA). The electrical conductivity was investigated by impedance measurements using the 2-probe method.

2 EXPERIMENTAL

2.1 Materials

Epoxy was used as the matrix material. Diglycidyl ether of bisphenol A (Epon 828) was purchased from the Shell Chemical Co. Jeffamine T403 from Huntsman Petrochemical was used as the curing agent for this matrix system. Nylon 66 (Zytel 101 NC010, Du Pont) was used as the matrix. Graphite Intercalated Compounds [GICs] were obtained from UCAR International Inc. PAN based carbon fiber (PANEX 33 MC Milled Carbon Fibers, average length: 175 μm , average diameter: 7.2 μm , specific gravity: 1.81 g/cm^3 , Zoltek Co.), VGCF (Pyrograf III, PR-19 PS grade, Length: 50-100 μm , Average diameter: 150nm, Specific gravity: 2.0 g/cm^3 , Pyrograf Products, Inc.), and nanosize carbon black (KETJENBLACK EC-600 JD, Average diameter: 400-500nm, Specific gravity: 1.8 g/cm^3 , Akzo Novel Polymer Chemicals LLC) were used as comparison.

The intercalated graphite was processed thermally. After the treatment, these graphite flakes showed significant expansion due to the vaporization of intercalated acid in the graphite galleries. The expanded graphite flakes were pulverized by use of an ultrasonic processor and mechanical

milling. The average diameter and thickness of the flakes pulverized only by an ultrasonic processor were determined as 13 μm and 10-20 nm, respectively. Those of the flakes after milling were determined as 0.86 μm and 5-10 nm, respectively (xGnP-1 and xGnP-15). Table 1 summarizes the surface area of these carbon materials.

Carbon Material	Surface Area (m^2/g)
Milled Carbon Fiber	16 ± 1
VGCF	25 ± 5
Carbon black	> 500
xGnP-Graphite Nanoplatelet	107 ± 7

2.2 Composite Fabrication

Epoxy. The calculated amount of reinforcements were added to DGEBA and mixed with the aid of an ultrasonic homogenizer for 5 minutes. Then stoichiometric amount of Jeffamine T403 were added and mixed at room temperature. The ratio of DGEBA/Jeffamine is 100/45 by weight. The system was outgassed to reduce the voids and cured at 85°C for 2 hours, followed by post curing at 150°C for 2 hours. The density of graphite flakes was assumed as 2.0 g/cm^3 . The densities of other carbon materials were obtained from manufacturers. The density of the epoxy matrix was measured as 1.159 g/cm^3 . Using these values, the volume fraction of xGnP in composite samples was calculated.

Nylon 66. A DSM Micro 15 Compounder, (vertical, co-rotating twin-screw miniextruder, capacity 15cc) and a Daga Micro Injector were used to make composite samples. Figure 2 shows the images of these machines. The temperature of the extruder was set to 290°C . At first, polymer matrix and reinforcements were mixed in the mini-extruder for 5 minutes at a screw speed of 200 rpm. Then the mixed system was transferred to the molding cylinder. The temperature of the injection-molding cylinder was set to 290°C . Then the material was injected into a mold with the injection pressure of 100 psi. The mold temperature was set to 90°C . The sample was removed from the mold immediately after the injection process and cooled down under the room temperature. The flexural test was performed at least 30 hours after the injection process.

Composites reinforced with up to 15 vol% of xGnP or carbon fiber did not show any difficulty in the injection molding process. Composite with 15 vol% VGCF exhibited an increased viscosity, but the composition was still moldable. Composite with 10 vol% carbon black showed considerable increase in viscosity and it was very difficult to make an injection molded sample. Composite with 15 vol% carbon black could not be fabricated.

Surface Treatments of xGnP. The xGnP were treated with various surface treatments that can introduce carboxyl and/or amine groups. The treatments include nitric acid oxidation, O_2 plasma treatment, UV/Ozone treatment, amine grafting [3], and acrylamide grafting [4].

3 RESULTS AND DISCUSSION

3.1 Mechanical Properties (Epoxy Matrix)

Composites reinforced with PAN based carbon fibers, VGCFs, and nanosize carbon blacks were fabricated. The flexural properties of these composites were measured and compared with those of composites with acrylamide-grafted nanographite. The results are shown in Figure 1. Here acrylamide-grafted xGnP showed the best results in terms of both strength and modulus enhancement. This implies that the acrylamide grafting treatment is a very effective surface treatment for graphite nanoplatelets.

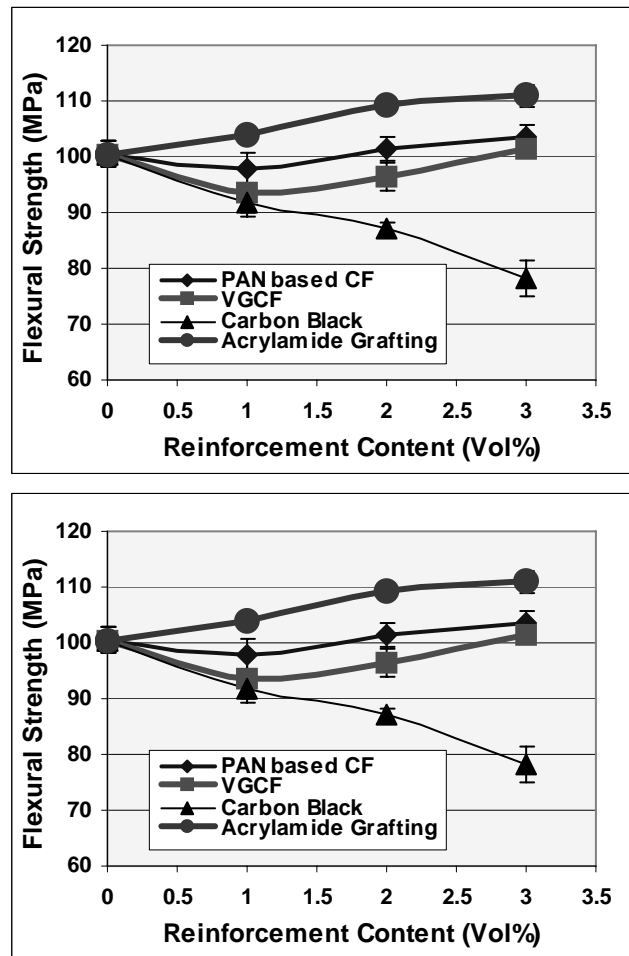


Fig 1. Flexural Strength and Modulus of xGnP and other Carbon Reinforcements in Epoxy.

3.2 Mechanical Properties (Nylon Matrix)

Flexural Modulus. Figure 2 shows the results of the flexural modulus of the composite samples. The exfoliated graphite showed the best improvement among these carbon materials and the effect was considerably better than the commercially available carbon materials. The composite with 15 vol% of exfoliated graphite produced a modulus of

about 8.4 GPa, which was almost 300% of that of the control nylon66. Carbon fiber was the next best, but the improvement effect was about 2/3 of the exfoliated

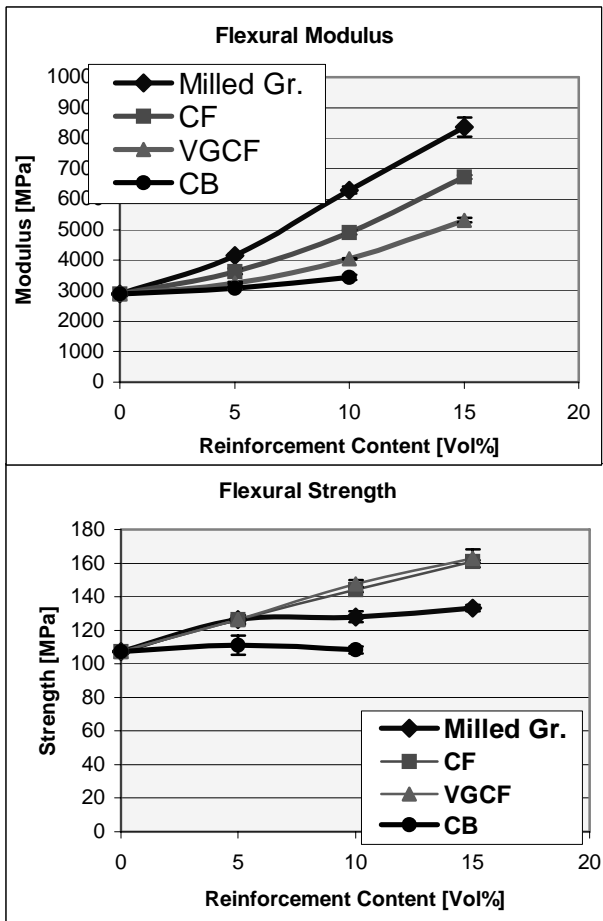


Fig 2. Flexural Modulus of Nylon66 Composites with Various Reinforcements

graphite. VGCF showed less than half of the improvement than that of the exfoliated graphite did. The improvement of modulus by carbon black was significantly lower than the others. These results suggest that the exfoliated graphite has much higher modulus than other carbon materials, indicating that after exfoliation the nanographite platelets have a modulus similar to highly crystalline graphite.

3.3 Electrical Properties

The electrical resistivity of the composites with various reinforcement contents was determined. The reinforcements used were PAN based carbon fiber, VGCF, nanosize carbon black, graphite nanoplatelet (exfoliated and sonicated, but not milled), and graphite nanoplatelet. The size of each composite sample was about 30 x 12 x 8 mm. Each sample was polished and gold was deposited on the surface to insure good electrical contacts. The results are summarized in Figure 3. The VGCF, carbon black and graphite nanoplatelet percolated at less than 5 wt% (3 vol

%) while conventional carbon fiber and graphite nanoplatelet showed percolation threshold of about 10wt% (7 vol %). Among the former three reinforcements, graphite microplatelets and carbon blacks produced composites with the lowest resistivity, which reached around $10^{-1.5}$ ohm*cm. Thus, the exfoliated graphite sample also showed excellent electrical property as reinforcement in polymer matrix.

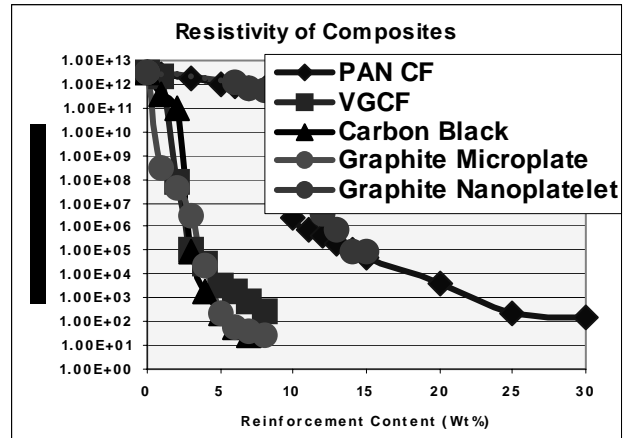


Fig 3. Resistivity of composites with different reinforcement content.

3.4 Thermal Conductivity

A laser flash lamp method was used to measure thermal conductivity of composite samples. Disc shape samples with a diameter of 25mm (1") and a thickness of 1.5mm (1/16") were used for the measurement. A laser flash lamp fires a pulse at the sample's lower surface while the temperature of the reverse surface is measured by detectors. Specific heat is measured by comparing the temperature rise of the sample to the temperature rise of a reference sample of known specific heat. The thermal conductivity was calculated by applying the density of the materials.

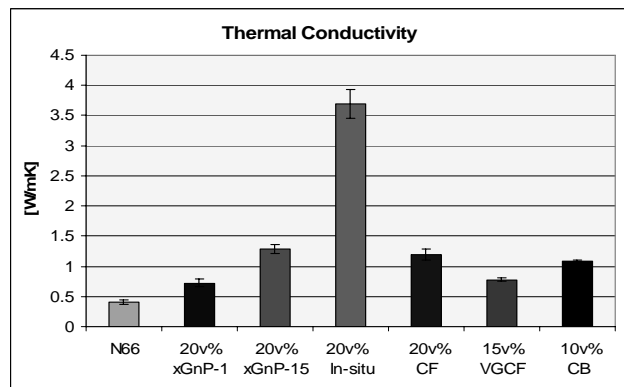


Fig 4. Thermal Conductivity of composites with different reinforcement content.

Figure 4 shows the thermal conductivity of the nylon 66 composites. The in-situ processed xGnP produced a

nanocomposite with a thermal conductivity of 3.7 W/mK. The thermal conductivity of the other samples was less than 1.5 W/mK. These results suggest that composites reinforced with disc shape reinforcements and a high aspect ratio could achieve very high thermal conductivity.

3.5 Barrier Properties

Oxygen permeability was measured with a MOCON OX-TRON permeability cell. 100% oxygen gas was used and measurement was performed at room temperature. The thickness of film samples was around 100µm. Five hours of conditioning was applied before the start of the measurement. Figure 5 shows the results. Nanomer I.34.TCN nanoclay showed the best barrier properties, that it the lowest permeability. xGnP-15 showed the second best results and the value was better than that of Cloisite 93A. These results suggest that xGnP with high aspect ratio can improve barrier properties as much as nanoclays do. Other reinforcements were less effective at improving the barrier properties.

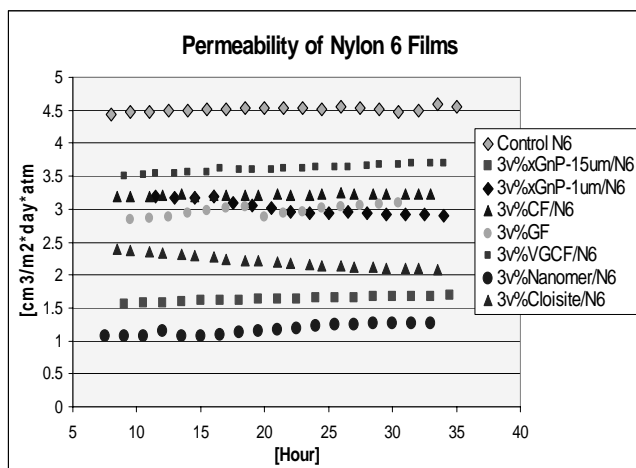


Fig 5. Oxygen Barrier Property of Nylon 6 Composite Films

4 CONCLUSIONS

A new graphite nanoplatelet material (xGnP) was produced by exfoliation of intercalated graphite. This material produced significantly better improvements in modulus than commercially available reinforcements at the same volume percentage, and especially at high loading levels. This suggests that the exfoliated graphite has properties similar to highly crystalline graphite. A new graphite nanoplatelet material was produced by exfoliation of intercalated graphite. This material produced better improvement in modulus than commercially available reinforcements at the same volume percentage, and especially at high loading levels. This suggests that the exfoliated graphite has properties similar to highly

crystalline graphite. Even though the lower flexural strength data for xGnP indicated that the surface condition of the exfoliated graphite has not been optimized for the nylon system, the xGnP did significantly improve the strength compared to control nylons. xGnP also showed good results in impact strength and heat deflection temperature. By applying in-situ exfoliation process, the percolation threshold was greatly improved and both electrical and thermal conductivity were improved significantly. Because of its platelet morphology and high aspect ratio, xGnP increased the barrier properties almost as well as nanoclays. In summary, xGnP has the potential to improve the mechanical, electrical, thermal and barrier properties of thermoset and thermoplastic polymers.

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