Nylon - Exfoliated Graphite Nanoplatelet (xGnP) Nanocomposites with Enhanced Mechanical, Electrical and Thermal Properties

Hiroyuki Fukushima 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, 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, exfoliate graphite nanoplatelets [xGnP]. The xGnP is fabricated from natural graphite and can be used as a nanoreinforcement for polymers as an alternative to expensive carbon-based nanomaterials. The thickness of the xGnP became around 5-10nm. The diameter can be controlled from sub-micron level to few hundred um, indication the aspect ratio can be controlled. The surface area of the material reached more than $100m^2/g$. 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 fur 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. Several papers related to this topic have been published since 1990's. [1-17]

In this research, the xGnP was used as nanoreinforcements for nylon 6 and Nylon 66 composites. The xGnP could improve the modulus of nylons better than other commercially available reinforcements. Impedance measurements have shown that the aspect ratio of the xGnP affect the percolation threshold of the composites. By using xGnP with high aspect ratio, the percolation threshold reached below 5vol%. Thermal conductivity measurement revealed that it reached almost 4 W/m*K for xGnP/nylon nanocomposite. Gas permeation test showed that the barrier property was significantly improved with xGnP, almost as good as nanoclays.

KEY WORDS: Nylon, Nanocomposite, Graphite,

1. EXPERIMENTAL PROCEDURE

1.1 Materials

Nylon66 (Zytel 101 NC010, Du Pont) and Nylon 6 (Durethan B40SK Extrusion Grade, Bayer) were used as the matrices. Graphite Intercalated Compounds [GICs, Grafguard] were obtained from UCAR International Inc. PAN based chopped carbon fiber (CF, HTA-C6-N, ϕ=6.8-7.2um, l=6mm, d=1.73-1.81g/cm^3, Toho Tenax Co.Ltd.), chopped glass fiber (GF, CS3G-225S, ϕ=12-14um , l=4mm, d=2.58g/cm^3, Nitto Boseki Co. Ltd.,), VGCF (Pyrograf III, PR-19 PS grade, Length: 50~100um, Average diameter: 150nm, Specific gravity: 2.0 g.cm^3, Pyrograf Products, Inc.), nanosize carbon black (CB, KETJENBLACK EC-600 JD, Average diameter: 400~500nm, Specific gravity: 1.8 g/cm^3, Akzo Novel Polymer Chemicals LLC), and two kinds of nanoclays (Nanomer I.34.TCN, Nanocor Co. Ltd) (Cloisite 93A, Southern Clay Co.) were used as comparison.

The UCAR graphite was processed thermally. After the treatment, these graphite flakes showed significant expansion. At this point, each flakes were still attaching each other and formed worm-like structure. The expanded graphite platelets were dispersed in a solvent and pulverized by ultrasonic processor. After the process, the worm-like structure was divided into exfoliated graphite nanoplatelet. At this point, the average size of the graphite was 15um while the thickness was around 10nm. (xGnP-15) By applying a mechanical milling process, the diameter and thickness of the milled platelets became 0.86 um and 5-10 nm, respectively (xGnP-1).

1.2 Composite Fabrication

A DSM Micro 15 Compounder, (vertical, co-rotating twin-screw miniextruder, capacity 15cc) and a Daca Micro Injector were used to make composite samples. The temperature of the extruder was set to 290°C (Nylon 66) or 260ºC (Nylon 6). 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 (Nylon 66) or 260ºC (Nylon 6). 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 mechanical tests were performed at lease 30 hours after the injection process.

2. RESULTS AND DISCUSSION

2.1 Processability

Composites reinforced with up to 20 vol% of xGnP, CF, or GF 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 a considerable increase in viscosity and it was very difficult to make injection-molded samples without voids. Composites with 15 vol% carbon black could not be fabricated. Composites with more than 15 vol% of nanoclays became very brittle.

2.2 Flexural Modulus

Flexural test was performed by UTS SFM-20 machine [United Calibration Corp.] at room temperature by following ASTM D790 standard test method (3-point bending mode). The samples were made in standard bar shape and the span was set to 2 inches. The final dimension of the bar samples was 63 x 12.5 x 3.15 mm (2.5" x 1/2" x 1/8"). The test was performed at flexural rate of 0.05 inches per minute under ambient condition.

Figure 1 shows the results of the flexural modulus of the xGnP/nylon 66 systems. The nylon 6 composites showed somewhat similar results. Nanoclays showed a modulus improvement up to 10 vol% loading, but then the modulus decreased at higher loading level. This is a result of the re-aggregation of the clay nanoplatelets. The xGnP-1 and xGnP-15 showed the best improvement among these reinforcements. Both nylon 66 and nylon 6 composites with 20 vol% of xGnP produced samples with a modulus of about 12 GPa, which was more than 400% over that of the control nylons. The effect of CF on the improvement of modulus was about 65% of the xGnP. VGCF showed less than 50% of the improvement of the xGnP. The improvement of modulus by CB and GF was significantly lower than the others. These results suggest that the xGnP was well dispersed and has a high modulus compared to the other carbon materials.

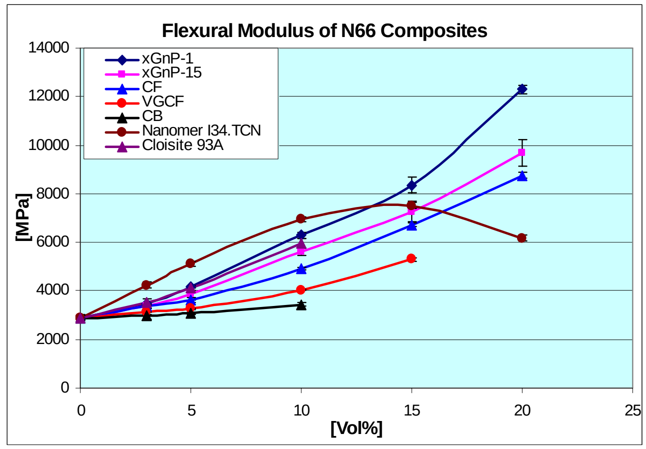

Figure 1. Flexural Modulus of Nylon 66 Composites with Various Reinforcements

2.3 Flexural Strength

Figure 2 shows the results of the flexural strength of thexGnP/nylon 66 systems. The nylon 6 systems also showed the similar results. In this case, CF, VGCF, and GF showed better improvement in the flexural strength than the xGnP, especially at higher loading levels. These results suggest that the surface condition of the xGnP has not been optimized for Nylon systems resulting in low strain debonding of the particles with their associated flaw generation. However, the xGnP samples showed improved strength at all loading levels while the nanoclays showed a significant decrease in strength above the 5 vol% loading levels suggesting these nanoclays are not appropriate reinforcements for nylons at concentrations greater than 5%.

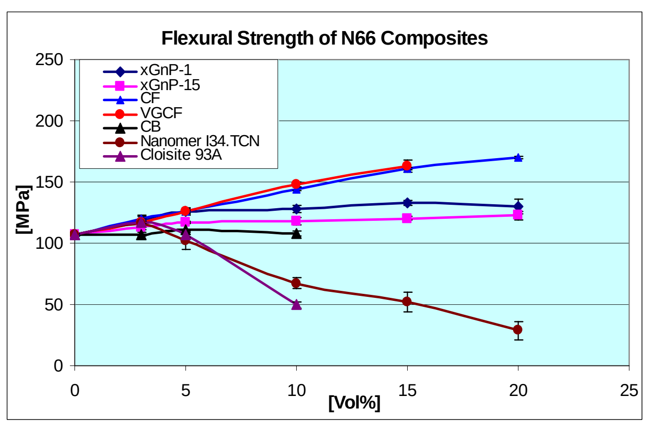

Figure 2. Flexural Strength of Nylon 66 Composites with Various Reinforcements.

2.4 Impact Strength

The notched impact strength was measured by 43-02-01 Monitor/Impact machine [Testing Machines Inc.] by following ASTM D256 standard method. The samples with dimension of 63 x 12.5 x 3.15 mm were made by injection molding and 0.25 mm notch was made by TMI notch cutter 48 hours prior to the experiment. A 5ft-lb pendulum was used for the measurement.

Figure 3 showed the results of the impact strength of the composite samples. The composites with xGnP-1 showed very little decrease in impact strength compared to the control nylon 66. The composites filled with other carbon materials showed a more significant decrease in impact strength. Especially in the case of carbon black, the impact strength decreased as much as 50% at 3 vol% loading level. Nanoclays also showed significant decrease in impact strength.

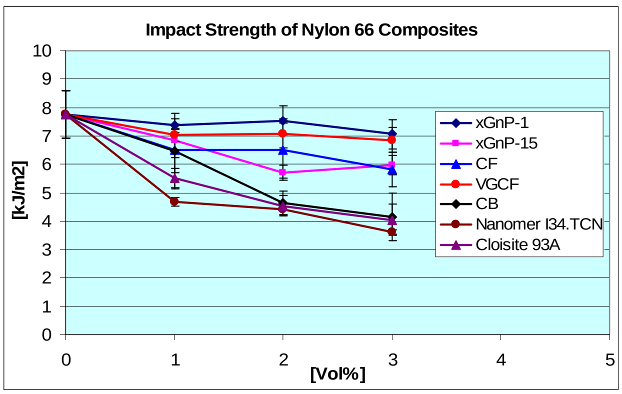

Figure 3. Impact Strength of Nylon 66 Composites with Various Reinforcements

2.5 Heat Deflection Temperature (HDT)

HDT data for each sample was measure by DMA 2980 [TA Instrument] using 3 point bending mode according to ASTM D638 standard. The size of each sample was 63 x 12.5 x 3.15 mm. The temperature range was 25ºC to 120ºC and the ramp rate was 2ºC per minute. The force applied to the sample was calculated from the sample dimension so that the load became 1.82MPa (264psi).

In the case of Nylon 66, the nanoclays improved HDT by about 15ºC. The xGnP-1 showed comparable results with improvement of about 12 ºC. Other reinforcements showed a lower effect in HDT. In the case of nylon 6, xGnP-1, CF, and nanoclays showed the best improvement of about 12ºC.

2.6 Electrical Conductivity

The electrical conductivity of composite samples was measured with Impedance Spectroscopy by applying the two-probe method at room temperature. The size of each sample was about 12.5 x 6 x 3.15 mm. The measurement was done through the 6 mm thickness. Since sample dimension and surface condition greatly affect the data, a polishing process was applied with extreme care. After polishing, an O_2 plasma was applied on the sample to etch polymers in surface region. After the process, a gold coating of about 20nm thickness was applied. During the process, sidewalls of each sample were masked so that no conductive connections between top and bottom planes occur through the gold coatings. Copper tape was attached to the top and bottom surfaces of the sample and connected to the instrument. The resistance of sample was measured in the frequency range of 0.1 to 100,000Hz. The impedance was recalculated to conductivity by incorporating the sample dimensions. The conductivity at 0.1Hz was considered as the AC conductivity since the difference should be very small.

Figure 4 shows the electrical conductivity of the composites with various reinforcement contents. Carbon black and in-situ xGnP (that is, one in which the exfoliation was thermally induced within the polymer) showed the best percolation threshold of around 2 vol%. In-situ processed xGnP has a diameter of around 300um, which is a very high aspect ratio. xGnP-15 graphite percolated around 6vol% and CF, VGCF, and xGnP-1 showed percolation threshold of around 10 to 12 vol%. Thus, by utilizing the in-situ process, large aspect ratio graphite platelets can be dispersed. As a result, the in-situ xGnP showed very low percolation threshold and high conductivity.

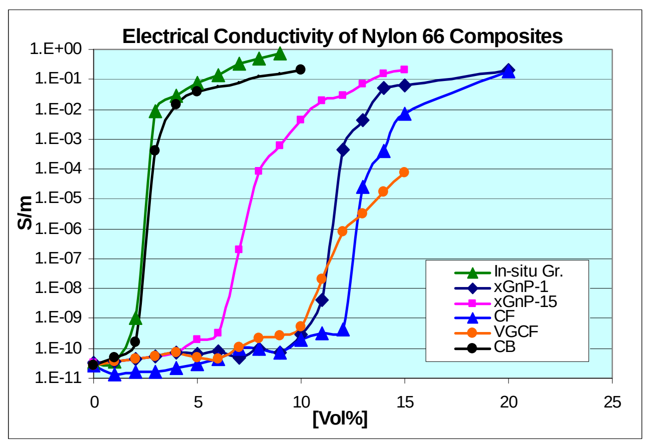

Figure 4. Electrical Conductivity of Nylon 66 Composites

2.7 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.

Figure 5 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.

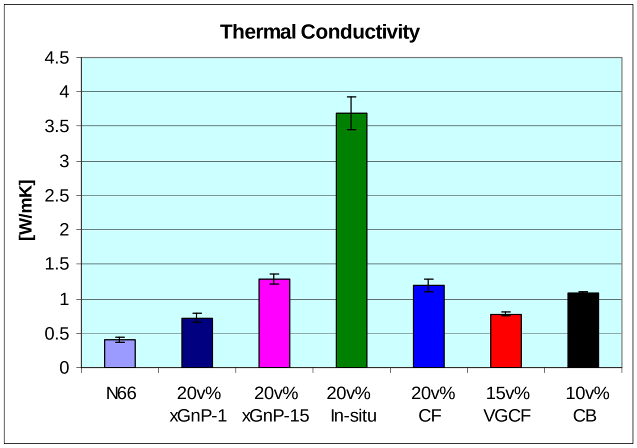

Figure 5. Thermal Conductivity of Nylon 66 Composites

2.8 Barrier property

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 100um. Five hours of conditioning was applied before the start of the measurement. **Figure 6** 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.

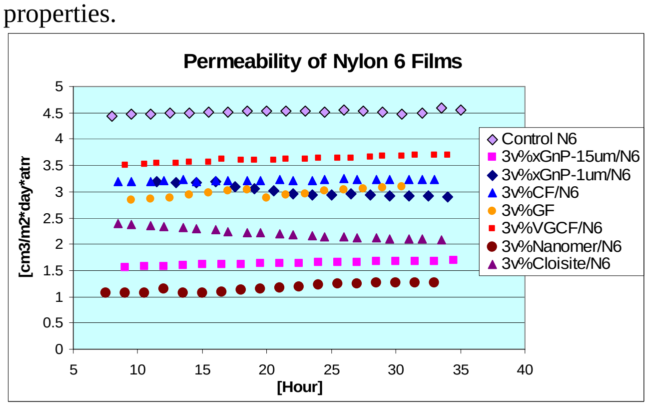

Figure 6. Oxygen Barrier Property of Nylon 6 Composite Films

3. CONCLUSION

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 nylon polymers.

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