GRAPHITE PLATELET/NYLON NANOCOMPOSITES

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ABSTRACT

Natural crystalline graphite based graphite intercalated compounds [GICs] were exfoliated into sub-micron graphite flakes. Graphite nanocomposites were fabricated by combining the exfoliated graphite flakes with nylon66 resin. The mechanical properties of these composites showed considerably higher modulus than those of composites made with commercially available carbon reinforcing materials (i.e., CF, VGCF, and Carbon Black). Also the electrical property was improved by adopting appropriate fabrication conditions.

INTRODUCTION

Nanocomposites has been a subject of intense composite research since 1987 when a research group in TOYOTA introduced the concept for the first time. These materials are composed of polymer matrices with reinforcements of less than 100 nm in size. Until now many polymer systems and nanoreinforcements have been investigated to achieve good properties for applications such as interior and exterior accessories for automobiles, fuel cell systems, batteries, structural components for portable electronic devices, and films for food packaging. In the nanocomposite field, the exfoliated clay nanocomposites have been investigated intensely and some of the materials are now used in commercial applications such as automobile exteriors and food packaging. [1, 2] Carbon-based nanomaterials have also been attracting much attention for the past 10 years. Single walled carbon nanotubes (SWNT), vapor grown carbon fibers (VGCF), and fullerenes (buckyballs) are considered to be the most interesting materials in the field.

Since late 1990's, research has been reported where intercalated, expanded, or exfoliated graphite nanoflakes have been added to polymer systems to fabricate a new type of nanocomposite materials. [3 - 16] Graphite is the stiffest material found in nature (Young's Modulus = 1060 MPa), having a modulus several times that of clay, and in addition it has excellent strength and electrical and thermal conductivity. Because of this, graphite nanocomposites can offer advanced properties that clay platelet nanocomposites cannot achieve. The key to utilizing graphite as a platelet nanoreinforcement is in the ability to exfoliate graphite using Graphite Intercalated Compounds [GICs]. [17]

Also graphite nanoflakes have an advantage over other carbon-based nanomaterials, which is the cost. Since the natural crystalline graphite is abundant, the cost of GICs based on this material is very reasonable. A recently completed study in our group showed the cost of producing graphite nanoplatelets is expected to be $5/lb or less. This is significantly less expensive than SWNT (>$45,000/lb) or VGCF ($40-50/lb), yet the mechanical, electrical, and thermal properties of crystalline graphite flakes are comparable to those of SWNT and VGCF. If the appropriate process conditions are applied, the graphite nanocomposites can offer materials with excellent mechanical, electrical, and thermal properties at reasonable cost, which opens up many new structural applications as well as non-structural ones where electromagnetic shielding and high thermal conductivity are requirements. Thus, these graphite nanoflakes could be an alternative material for carbon nanotubes.

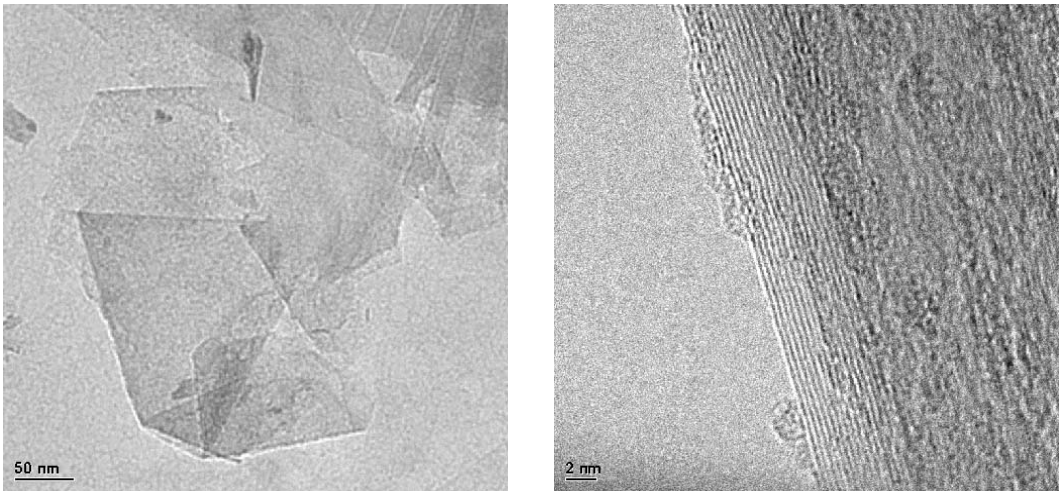
In this research, a special thermal treatment and process were applied to produce graphite nanocomposites. The composite material was fabricated by combining the exfoliated graphite flakes with nylon66. X-ray Diffraction (XRD), Scanning Electromicroscopy (SEM) and Transmission Electron Microscopy (TEM) were used to assess the degree of exfoliation of the graphite platelets and the morphology of the nanocomposites. The mechanical properties of these composites were investigated by flexural testing.

EXPERIMENTAL PROCEDURE

Materials

Nylon66 (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 um, average diameter: 7.2 um, specific gravity: 1.81 g/cm^3, Zoltek Co.), VGCF (Pyrograf III, PR-19 PS grade, Length: 50~100um, 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 UCAR 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. At this point, the average size of the graphite was 15um while the thickness was around 10nm. (15um exfoliated graphite) By applying a mechanical milling process, the diameter and thickness of the milled flakes became 0.86 um and 5-10 nm, respectively (Graphite nanoplatelet). The TEM images of nanoplatelets are shown in **Figure 1**. The average diameter of the flakes could be controlled by changing the pulverization and milling conditions and graphite flakes with large aspect ratio were also fabricated. **Table 1** summarizes the basic dimensional data of these carbon materials.



A: Scale bar = 50 nm **B**: Scale bar = 2nm

Figure 1 TEM images of graphite nanoplatelets. [**Offered by Professor Rodney S. Ruoff, Department of Mechanical Engineering, Northwestern University**]

Table1. Surface Area of Carbon Materials

Carbon Material	Length	Thickness	Aspect Ratio	Surface Area (m^2/g)
Milled Carbon Fiber	175 um	7.2 nm	24	16 ± 1*
VGCF	50-100 um	150 nm	333-666	25 ± 5**
Carbon black	20-30 nm	20-30 nm	~ 1	> 500**
Graphite nanoplatelet	0.86 um	10 nm	86	94 ± 5*
15um Exfoliated Graphite	15 um	10 nm	~1500	105± 7*

* Data were determined from BET measurement by using the region between P/P_0 of 0 to 0.2.

** Data were obtained from manufactures

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. **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 lease 30 hours after the injection process.

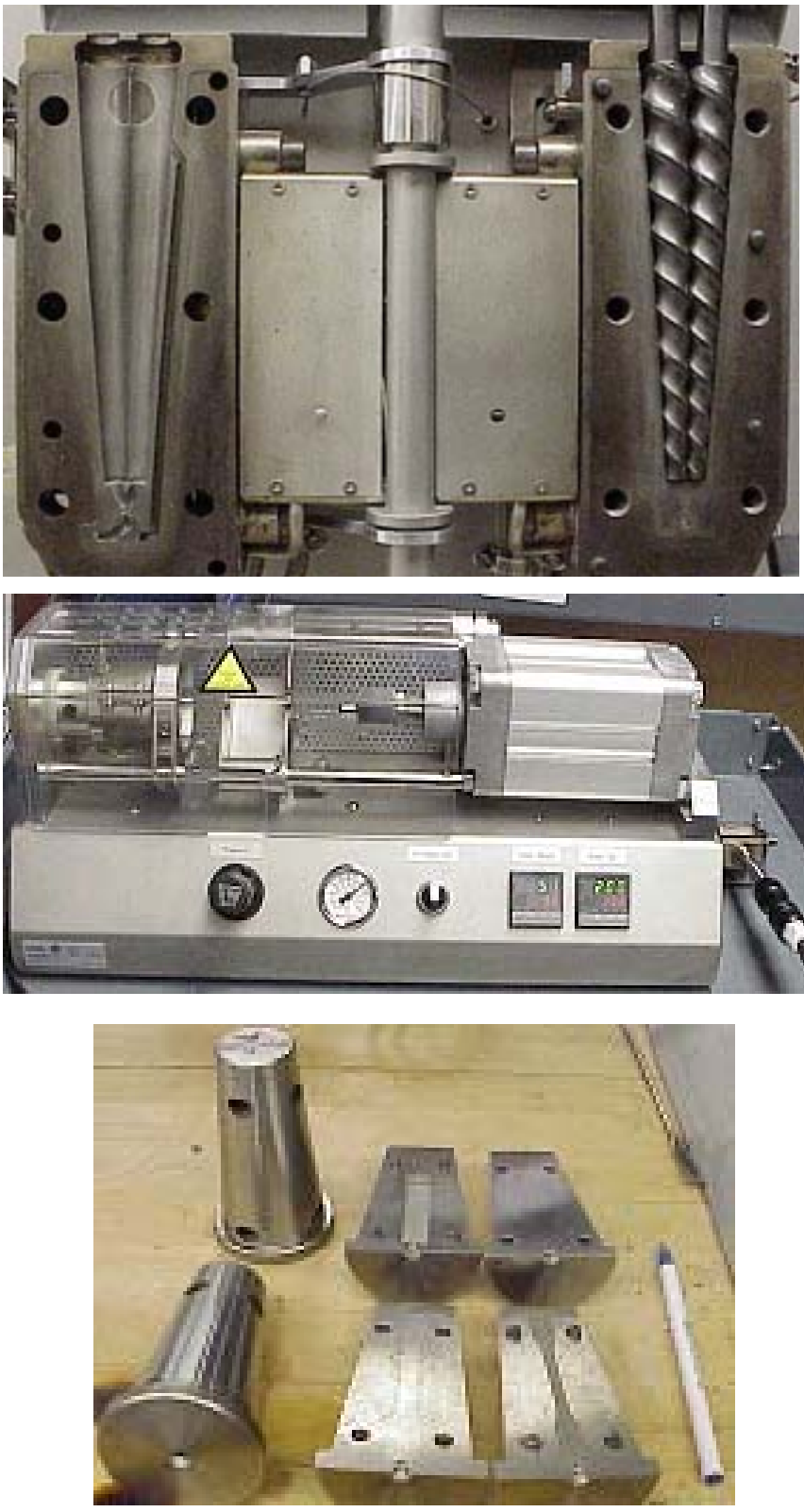


Figure 2. Mini-extruder, Micro Injector, and Molds.

RESULTS AND DISCUSSION

Processability

Composites reinforced with up to 20 vol% of exfoliated graphite 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 injection-molded samples without voids. Composite with 15 vol% carbon black could not be fabricated.

Orientation of fillers in Composite Samples

To investigate the orientation of the fillers, flex samples were fractured in the middle and the fracture surfaces were checked by ESEM. The images were taken from one edge area to the other and combined to assess the orientation condition.

Figure 3 shows the ESEM images of the fracture surface of a 15vol% in-situ exfoliated graphite/nylon composite sample. These images were chosen because the filler size was big and easy to assess the orientation of fillers. As the images show, fillers were randomly oriented in the mid portion (about 1/3 of the total thickness) while they were oriented in the outer area. Fracture surfaces of other samples were also investigated and also showed similar filler orientation condition.

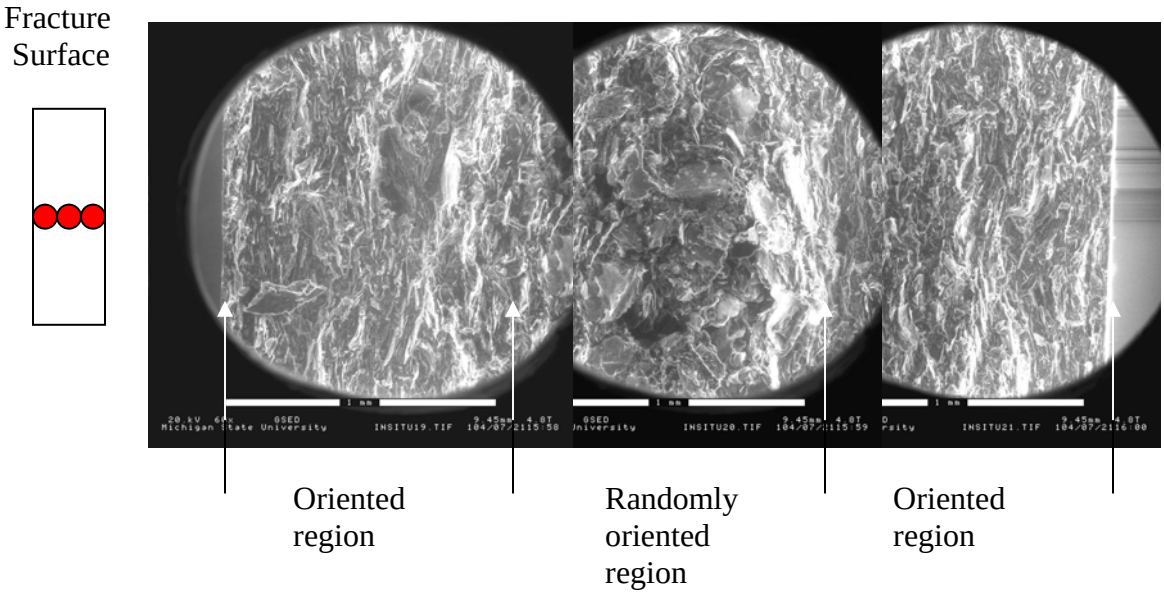


Figure 3. ESEM Images of the Fracture Surface of 15vol% In-situ exfoliated/ Nylon 66 composite

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. The test was performed at flexural rate of 0.05 inches per minute.

Figure 4 shows the results of the flexural modulus of the composite samples. The graphite nanoplatelet showed the best improvement among these carbon materials followed by 15um exfoliated graphite. The effect was considerably better than the commercially available carbon materials. The composite with 15 vol% of graphite nanoplatelet produced a modulus of about 8.4 GPa, which was almost 300% of that of the control nylon66. The effect of carbon fiber on the improvement of modulus was about 2/3 of the graphite nanoplatelet. 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 graphite nanoplatelets have a modulus similar to highly crystalline graphite.

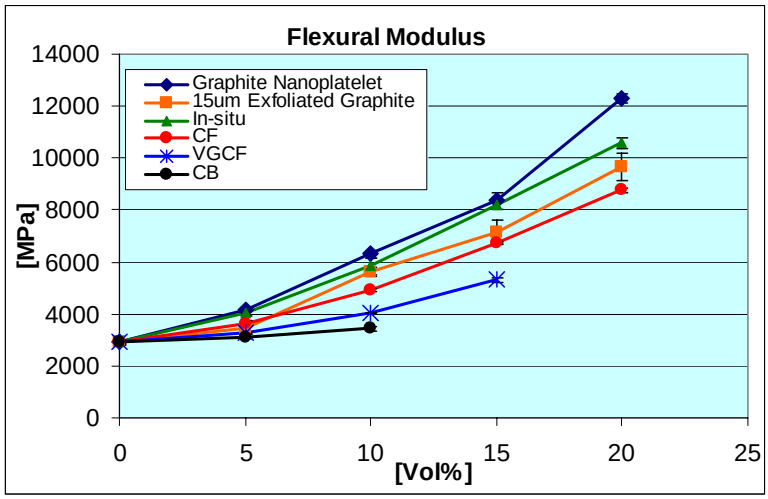


Figure 4. Flexural Modulus of Nylon66 Composites with Various Reinforcements

Flexural Strength

Figure 5 showed the results of the flexural strength of the composite samples. Up to 5 vol% loading, composites reinforced with CF, VGCF, and the graphite nanoplatelet showed almost the same improvement. But CF and VGCF showed better improvement than the graphite nanoplatelet at higher loading levels. These results suggest that the surface condition of the graphite nanoplatelet has not been optimized for Nylon66 system. Also the process conditions for better dispersion in the melt need to be optimized. Composites with in-situ exfoliated graphite showed decreased strength. This is because of the degradation of polymer chains caused by acid vapor occurred during the in-situ exfoliation process.

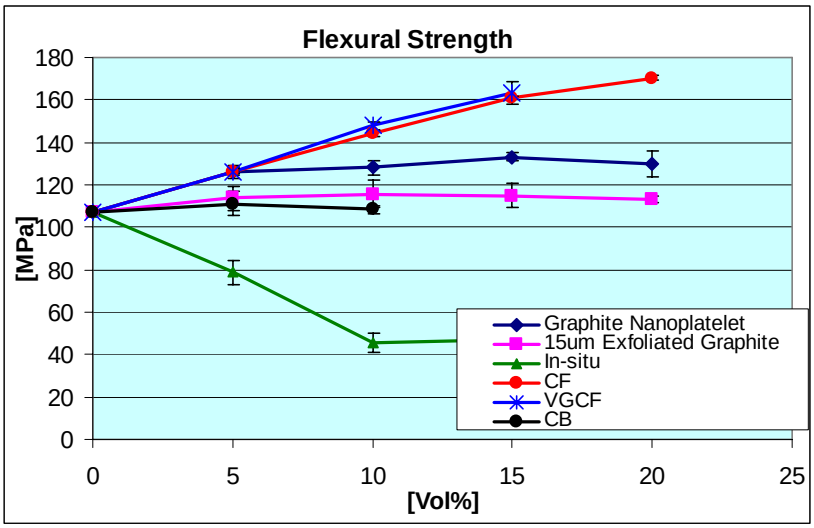


Figure 5. Flexural Strength of Nylon66 Composites with Various Reinforcements.

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 6 showed the results of the impact strength of the composite samples. The composites with graphite nanoplatelet showed very little decrease in impact strength compared to the control nylon 66. The composites filled with other carbon materials showed decreased impact strength. Especially in the case of carbon black, the property was decrease as much as 50% at 3 vol% loading level.

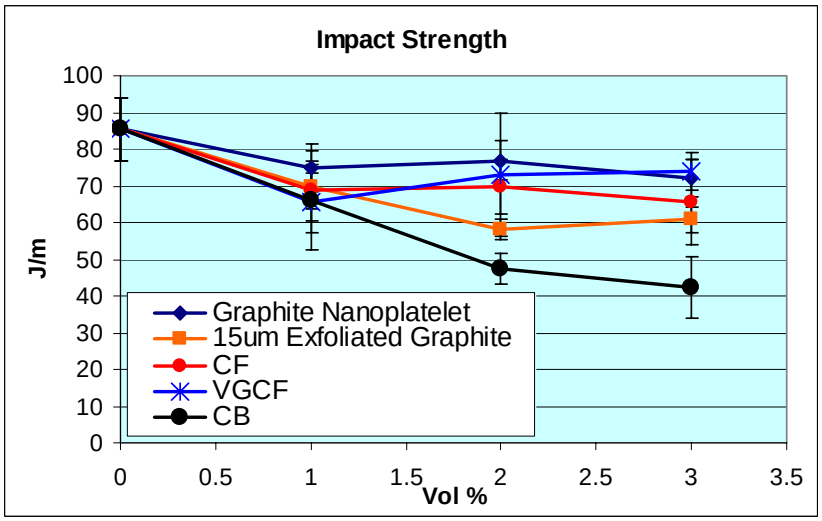


Figure 6. Impact Strength of Nylon66 Composites with Various Reinforcements

Coefficient of Thermal Expansion

The coefficient of thermal expansion (CTE) was measure by TMA 2940 (TA Instrument). The samples were cut into small pieces, approximately 10 x 5 x 5 mm, and dimension change was measured during heating process. Temperature range was -25ºC to 150 ºC and ramp rate was 2ºC per minute.

Figure 7, and 8 shows the CTE of composites with 3 vol% of reinforcements. In both cases, the graphite nanoplatelet showed the lowest CTE, suggesting the best dimension stability. 15um exfoliated graphite, CF, and VGCF showed almost the same results. Carbon black was the worst, showing almost no improvement compared to the control.

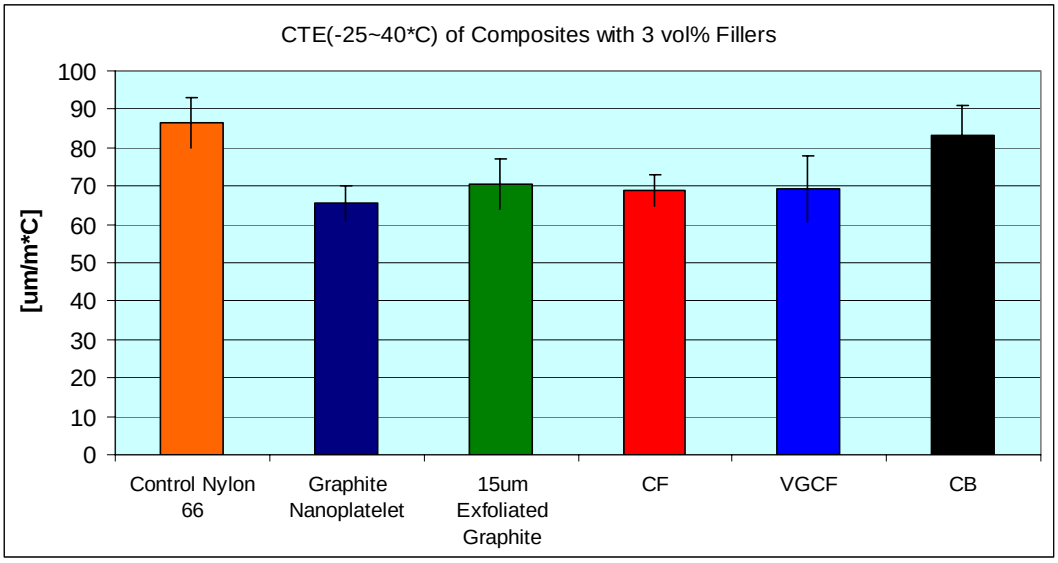


Figure 7. Coefficient of Thermal Expansion of Nylon66 Composites with Various Reinforcements (-25ºC to 40 ºC)

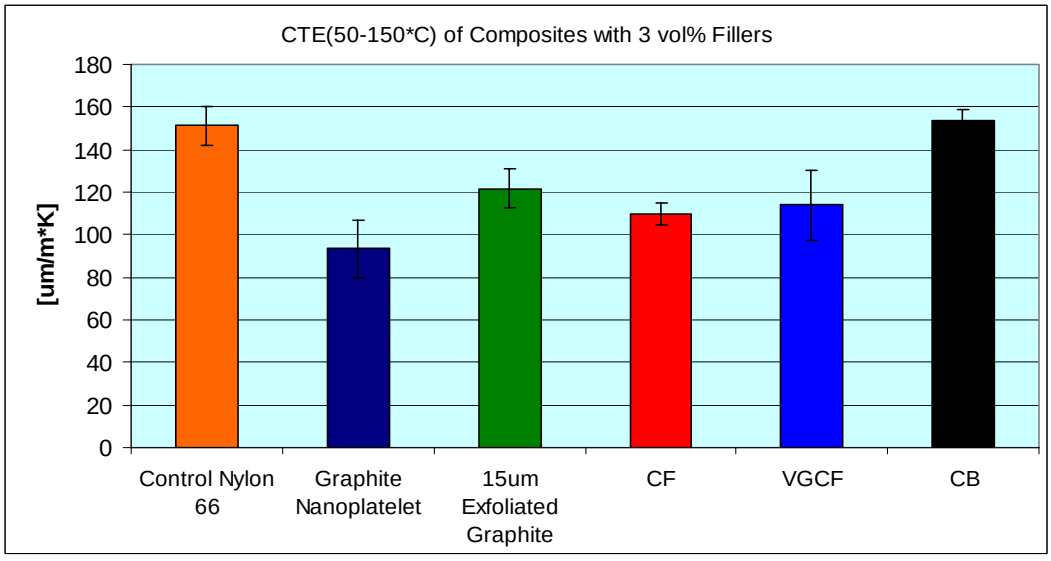


Figure 8. Coefficient of Thermal Expansion of Nylon66 Composites with Various Reinforcements (50ºC to 150ºC)

Heat Deflection Temperature (HDT)

HDT data for each sample was measure by DMA 2980 [TA Instrumrnt] 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).

Figure 9 showed the heat deflection temperature of the composite samples with 3 vol% loading level. The graphite nanoplatelet improved HDT by 12 ºC, which is the best result among the carbon materials compared.

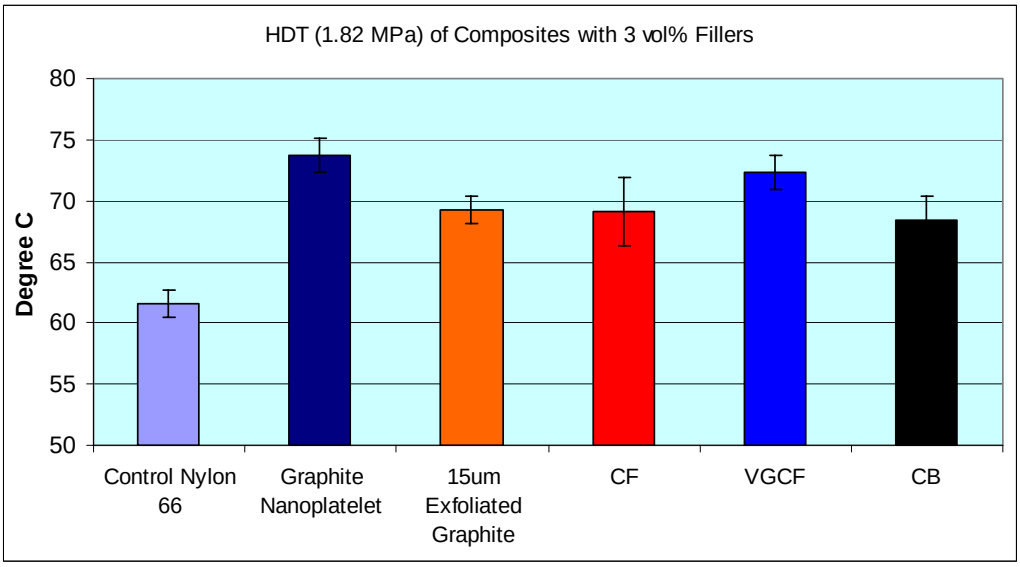


Figure 9. Heat Deflection Temperature of Nylon66 Composites (3vol%)

Electrical Property

The resistivity of injection direction of composite samples was measured in Impedance Spectroscopy by applying 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 6mm thickness. Since sample dimension and surface condition greatly affect the data, polishing process was applied with extreme care. After polishing, O_2 plasma was applied on the sample to etch polymers in surface region. After the process, 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 gold coatings. Then, 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 frequency range of 0.1 to 100,000Hz. Then the data was recalculated to conductivity by incorporating dimension factors. The conductivity at 0.1Hz was considered as the AC cunductivity since the difference should be very small.

Figure 10 shows the electrical conductivity of the composites with various reinforcement contents. Carbon black and in-situ exfoliated graphite showed the best percolation threshold of around 2 vol%. 15um ex-situ exfoliated graphite percolated around 6vol% and CF, VGCF, and graphite nanoplatelet showed percolation threshold of

around 10 to 12 vol%. Thus, by applying in-situ process, it is concluded that graphite flakes can maintain high aspect ratio and appropriate dispersion condition to form conductive paths in the composite.

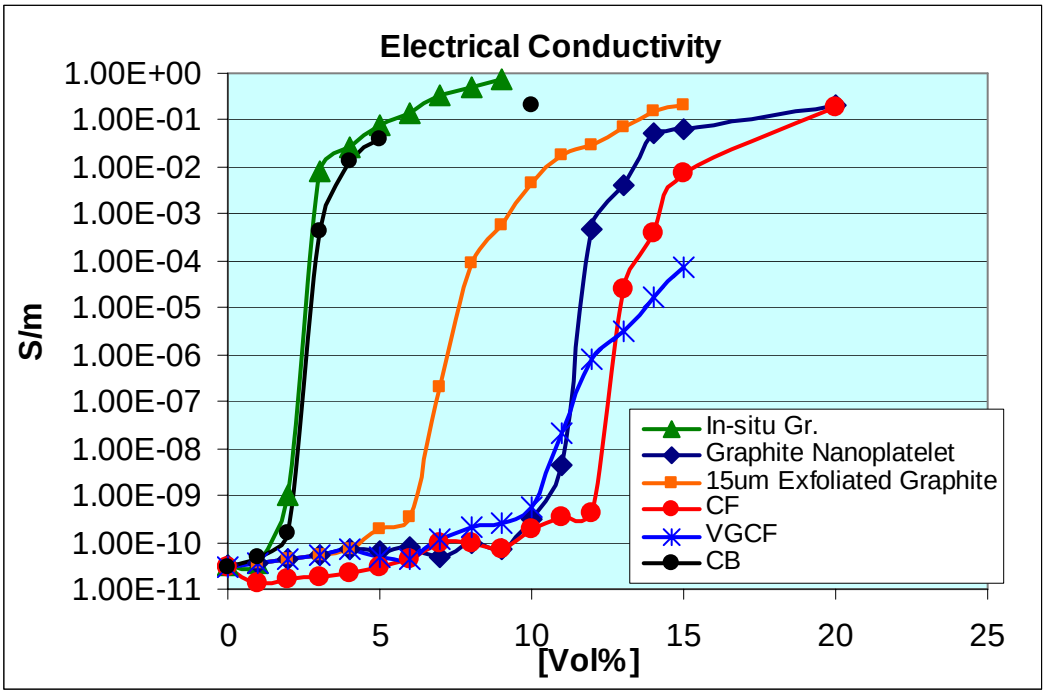


Figure 10. Conductivity of Nylon66 Composites

CONCLUSION

A new nanoplatelet graphite material was developed by exfoliation of graphite. This material showed considerably better improvement in modulus than some commercially available carbon materials at the same volume percentage. This suggests that the exfoliated graphite has properties similar to highly crystalline graphite. The flexural strength data showed the surface condition of the exfoliated graphite has not been optimized for the nylon system. This will be investigated in the future. Graphite nanoplatelet also showed good results in impact strength, coefficient of thermal expansion, and hest deflection temperature. By applying in-situ exfoliation process, the percolation threshold was greatly improved.

ACKNOWLEDGEMENTS

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