

Graphite Nanoplatelets to Improve Mechanical, Electrical and Thermal Properties of Polymers and Composites

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ABSTRACT

Many research efforts have been focusing on exfoliated clay systems, the same nanoreinforcement concept can be applied to another layered material, graphite. The key to utilizing graphite as a platelet nanoreinforcement is in the ability to exfoliate this material. If the appropriate surface treatment can be found for graphite, its exfoliation and dispersion in a polymer matrix will result in a composite with not only excellent mechanical properties but electrical properties as well, opening up many new structural applications as well as non-structural ones where electromagnetic shielding and high thermal conductivity are required.

In this research, a special thermal treatment was applied to the graphite flakes to produce exfoliated graphite reinforcements. Intercalated natural crystalline graphite compounds [GICs] were formed followed by exfoliation and milling to produce sub-micron graphite flakes. SEM and TEM images showed that the average size of graphite became 0.86 μm with a thickness of around 5 nm. With the proper surface treatment, the graphite nanoplatelets in polymeric matrices showed better flexural strength than composites with other carbon materials. Impedance measurements have shown that the exfoliated graphite plates percolate at below 3 vol% and the composites showed resistivity close to $10^1 \text{ ohm}\cdot\text{cm}$. The cost of this new nano-size graphite material was estimated to be around \$5/lb or less. Since exfoliated graphite has superior mechanical, electrical, thermal properties and cost effectiveness, this material has been shown to be a superior potential reinforcement for polymer nanocomposites for many applications including fuel cells, batteries and composites for electrical shielding.

1. INTRODUCTION

Recent advancement in synthesizing, controlling, and characterizing materials on an atomic scale has attracted much attention to nano-size materials. Polymer nanocomposites are a new category of composites that have been developed since late 1980's. Among these, polymer-exfoliated clay composites are most widely investigated nanocomposites that show considerable improvement in mechanical properties such as strength, modulus, and/or toughness with significantly lower reinforcement content than their conventional counterparts. The exfoliated clay nanocomposites can also provide other unique properties such as high temperature resistance and reduced permeability. Because of these advantages, clay-polymer nanocomposites are considered to be useful in applications such as interior and exterior accessories for automobiles and aircrafts, structural components for portable electronic devices, and films for food packaging. [1, 2, 3, 4, 5, 6]

The same nanoreinforcement concept can be applied to graphite platelet reinforced polymer composites, since graphite also has layered structures. Graphite flakes have been known as host materials for intercalated compounds for many years. Some of the graphite-intercalated compounds (GICs) can be expanded by rapid heating and show significant volume increase of 100 times or more. These expanded graphite flakes have been used as reinforcements for polymer composites, primarily for adding electrical conductivity to polymer systems. Many literatures explained their systems as “lightweight and conductive polymer composites” [7, 8, 9, 10, 11]. But most of the researches have shown relatively poor mechanical properties because of insufficient separation of the exfoliated graphite sheets, lack of good interaction between graphite and matrix, and the existence of many voids trapped in the composites.

Crystalline graphite has excellent mechanical properties as well as electrical and thermal conductivity. Also natural crystalline graphite is still abundant and available at low cost. If the appropriate exfoliation condition and surface treatment can be found for the graphite material, its dispersion in a polymer matrix will result in a composite with excellent mechanical properties. Also composites with good electrical and thermal properties could be achieved by appropriate design of the composite systems. These graphite nanocomposite materials could be used in many applications such as electromagnetic shielding and thermal conductors.

The graphite nanocomposite is a new research field that has many possibilities in the future. Just recently, some research groups have reported various graphite nanocomposite systems by using several fabrication techniques. These techniques include the *in-situ* polymerization with expanded graphite (In-situ polymerization technique) [12, 13, 14], the solution intercalation [15, 16], the melt blending [17], and the *in-situ* polymerization with initiator-intercalated graphite (polymerization-filling technique) [18, 19, 20, 21, 22, 23, 24, 25]. These researches reported good electrical and/or thermal resistance conductivity with low percolation threshold values. Some researches showed improved strength [13, 14], but many literatures reported decreased mechanical properties.

Since graphite nanocomposite is a new field, not many papers have been published to date and the concept of nanoflake-reinforced composite has not been fully accomplished yet and basic knowledge is still missing such as the efficient exfoliation techniques to process graphite flakes into nano-scale layers, systematic knowledge to design optimal surface condition of graphite nanoflakes for better nanocomposite systems, and the total design method to control properties of graphite nanocomposites to fit many applications. Thus, more detailed research efforts are required to understand this area, including design and evaluation of the interface and adhesion between graphite nanoplatelets and polymers. The theoretical and previous experimental results suggest the graphite nanocomposites could have realistic possibility to achieve high performance within cost limitations. Total characteristics of the fabricated composites need to be examined and assessed.

2. EXPERIMENTAL

Materials

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. By applying ultrasonic process, these

expanded graphite rods were pulverized into flakes. The average size of these flakes was around 15 μm at this point. **Figure 1** shows the SEM images of as-received, expanded, and pulverized graphite materials. The average size of the graphite flakes became less than 1 μm after applying vibratory ball milling. The BET measurements gave the surface area data of the pulverized and milled graphite as 105 m^2/g and 94 m^2/g , respectively. The thickness of these flakes was calculated as around 9 to 10 nm based on the surface area data, which is well agreed to the TEM images of milled graphite flakes in **Figure 2**. Three commercially available carbon materials were used as comparison, which were 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: 10-30 nm, Specific gravity: 1.8 g/cm^3 , Akzo Novel Polymer Chemicals LLC). The detailed characterization of the exfoliated graphite materials and other carbon materials are summarized in **Table 1**.

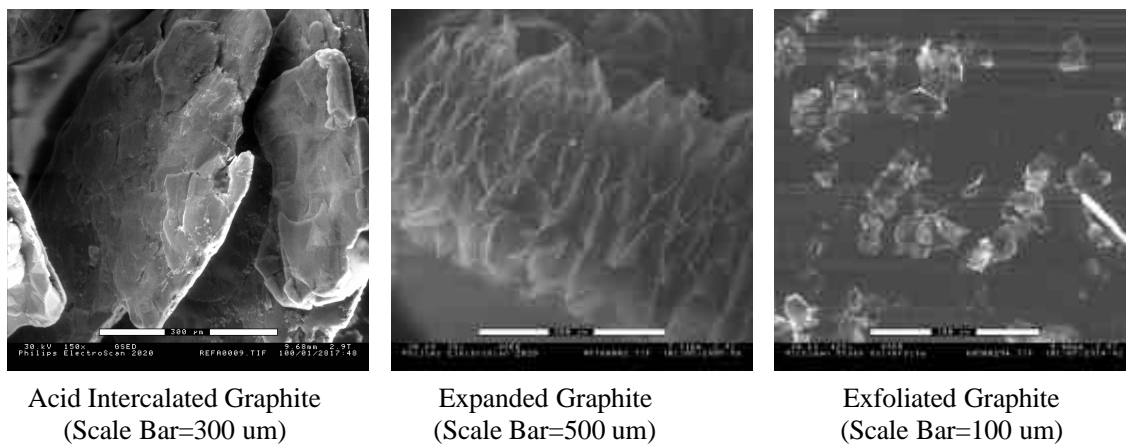


Figure 1. SEM Images of As-received, Expanded, and Exfoliated Graphite

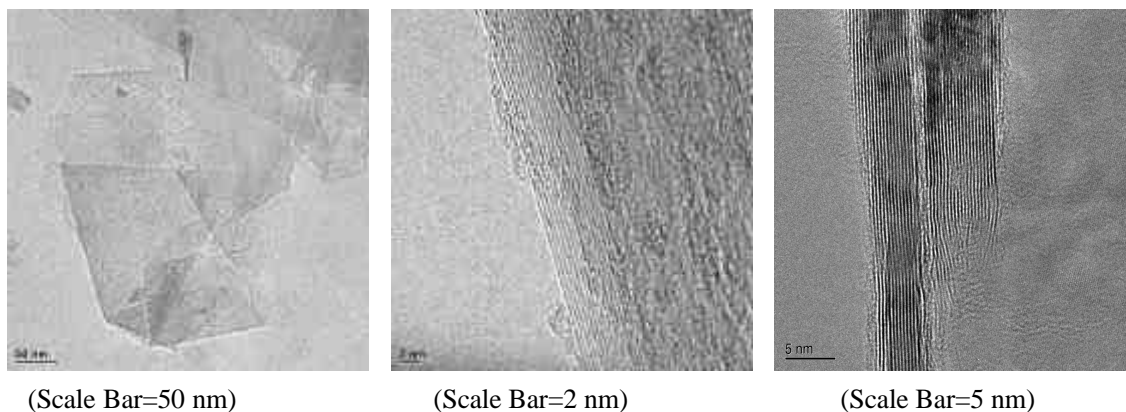


Figure 2. TEM Images of Exfoliated and Milled Graphite Flakes

First two images were offered by Professor Rodney S. Ruoff, Department of Mechanical Engineering, Northwestern University

Table 1. Specifications of Carbon/Graphite Materials

	Length/ Diameter	Diameter/ Thickness	Aspect Ratio	Density (g/cm ³)	Surface Area (m ² /g)
As-received Graphite	300 um	5.2 um	58	2.0	0.2
Expanded Graphite	15 um	9.5 nm	1579	2.0	105
Milled Graphite	0.86 um	10.9 nm	79	2.0	94
Carbon Fiber	175 um	7.2 um	24	1.81	16
VGCF	50-100 um	160 nm	312-625	2.0	25
Carbon Black	10-30 nm	10-30 nm	~ 1	1.8	1400

Composite fabrication

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. 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 was 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/cm³. The densities of other carbon materials were obtained from manufactures. The density of the epoxy matrix was measured as 1.159 g/cm³. Using these values, the volume fraction of graphite platelets in composite samples was calculated.

Surface Treatment of Graphite

Graphite nanoplatelets were treated by O₂ plasma to introduce peroxide groups, which can initiate radical polymerization. Then the sample was dispersed in 1M acrylamide/benzene solution and heated at 80°C for 5 hours to graft and polymerize acrylamide. The sample was washed with acetone and dried in a vacuum oven. [26]

3. RESULTS AND DISCUSSION

Mechanical Properties

Composites with 1, 2, and 3 vol% of carbon fiber, VGCF, carbon black, and acrylamide grafted graphite nanoplatelets were fabricated. Flexural and tensile properties of these samples were measured in accordance with the ASTM D790 and ASTM D638 standards. The results were shown in **Figure 3** and **4**, respectively. These measurements revealed that acrylamide grafted graphite nanoplatelets showed the best reinforcing effect in terms of both strength and modulus followed by carbon fiber. VGCF and carbon black didn't show improvement in strength. Thus, it is concluded that graphite nanoplatelets with an appropriate surface treatment can be a better reinforcement than commercially available carbon materials.

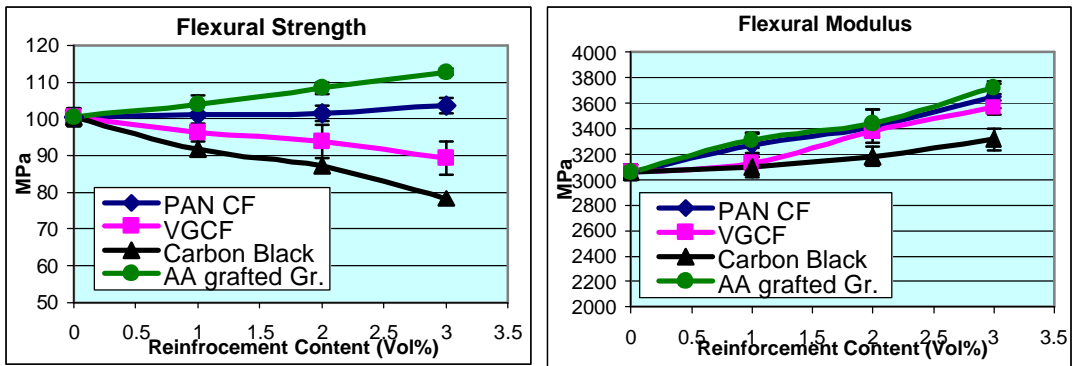


Figure 3. Flexural Properties of Composites reinforced with Various Carbon/Graphite materials

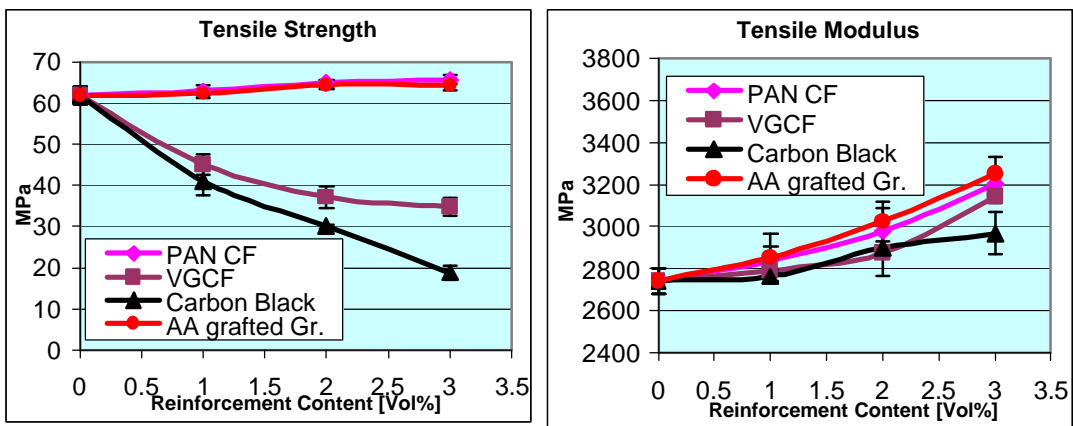


Figure 4. Tensile Properties of Composites reinforced with Various Carbon/Graphite materials

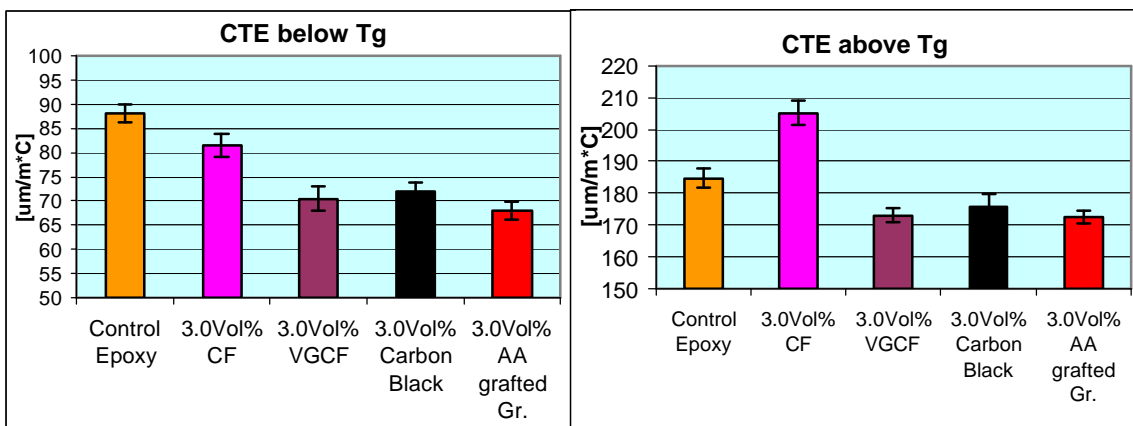


Figure 5. Coefficient of Thermal Expansion of Composites reinforced with 3 Vol% of Various Carbon/Graphite materials

Coefficient of Thermal Expansion

The coefficient of thermal expansion (CTE) was measured 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 30 to 200 °C and ramp rate was 2°C per minute. **Figure 5** shows the CTE of composites with 3 vol% of reinforcements. The acrylamide grafted nanographite showed the lowest CTE in both below and above T_g, which indicates that these nanoflakes were well dispersed and also had good interaction with epoxy matrix. Thus, it is concluded that acrylamide grafted nanographite is considered to be a good reinforcement compared to the commercially available carbon materials used in this research.

Electrical Property and percolation Analysis

The electrical resistivity of the composites with various reinforcement contents were determined. The reinforcements used were PAN based carbon fiber, VGCF, nanosize carbon black, exfoliated graphite, and milled graphite. The size of each composite sample was about 30 x 12 x 8 mm. Each sample was polished and gold coating was deposited on the surface to insure good electrical contacts. The results of resistivity measurements are summarized in **Figure 6**.

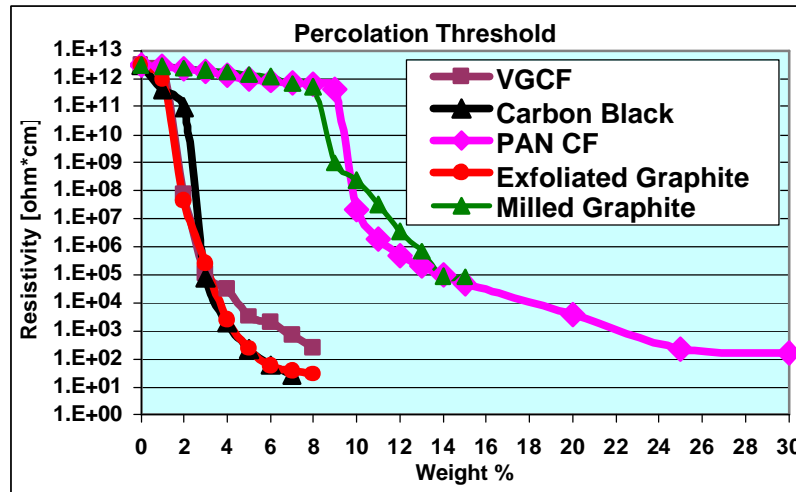


Figure 6. Resistivity of Composites reinforced with Various Carbon/Graphite materials

According to the percolation theory, the effective resistivity follows a simple power law, which can be written as;

$$\mathbf{r}_{eff} = \mathbf{r}_0 (p - p_c)^{-t} \quad \text{for } p > p_c \quad (1)$$

where ρ_{eff} is the effective resistivity of composite, ρ_0 is the resistivity of conductive phase, p is the volume fraction of conductive phase, p_c is the percolation threshold, and t is the conductivity exponent. Equation (4-1) can be rewritten as;

$$\log \left[\frac{\mathbf{r}_{eff}}{\mathbf{r}_0} \right] = -t \bullet \log [p - p_c] \quad \text{for } p > p_c \quad (4-2)$$

Thus, t can be experimentally available by least-square linear fit of $\log[\rho_{\text{eff}} / \rho_0]$ vs $\log[p-p_c]$ data. The parameters are p_c , t , and ρ_0 and this analysis is called three-parameter fit analysis. Gaines et al. showed that the change of p_c by 0.5% produced changes in t by 0.5, which could lead inaccurate data analysis [27, 28]. Therefore, they recommended to determine p_c experimentally to eliminate ambiguity of conventional three-parameter fit. In the following analysis, the preliminary percolation threshold value was first determined from experimentally obtained resistivity data. Then, least-square linear fit of $\log[\rho_{\text{eff}} / \rho_0]$ vs $\log[p-p_c]$ data was performed to obtain t by changing ρ_0 and p_c . During the fitting, the change in p_c value was limited up to 0.2% to avoid inaccurate analysis. Once t , ρ_0 and p_c were determined, these values were substituted into equation (1) and theoretical resistivity curve was made and compared to the experimental data. **Figure 7** shows the results of percolation analysis for exfoliated graphite composites.

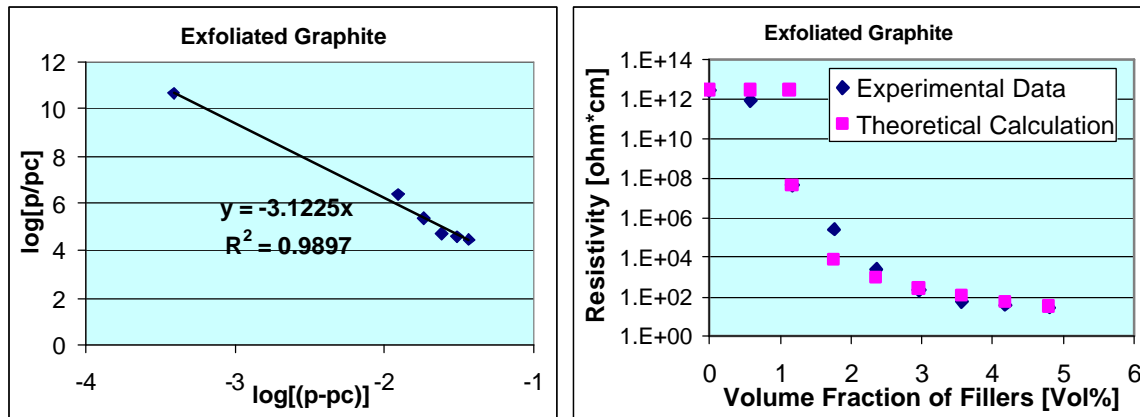


Figure 6. Percolation Analysis for of Composites reinforced with Exfoliated Graphite

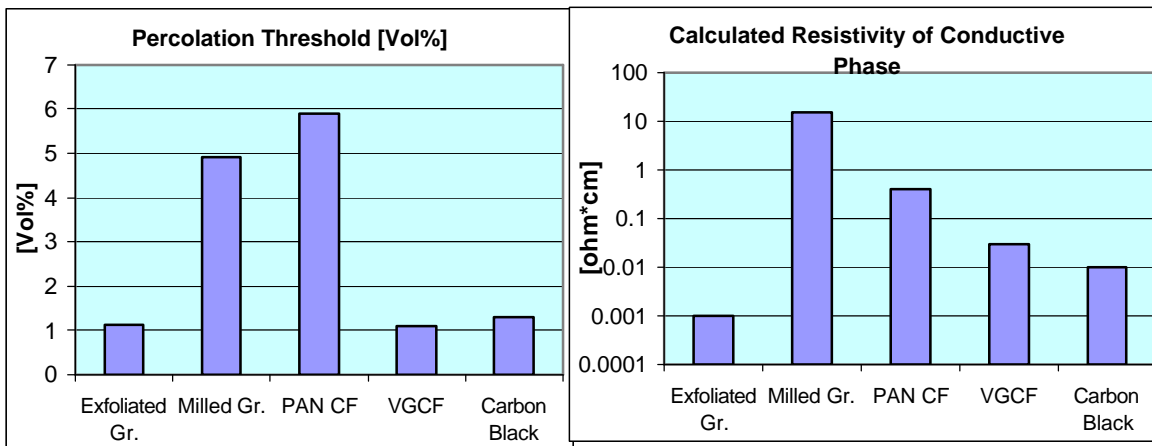


Figure 7. Results of Percolation Analysis

The same percolation analysis procedure was applied to all composite systems. **Figure 7** summarizes the results. The VGCF, carbon black and exfoliated graphite percolated at around 1 vol% (2 wt%) while conventional carbon fiber and milled graphite showed percolation threshold of about 5 to 6 Vol% (8 to 9 Wt%). The ρ_0 values showed that exfoliated graphite has the lowest resistivity. Thus, the exfoliated graphite sample showed excellent electrical property as reinforcement in polymer matrix. The critical exponent, t , for all systems were around 3, which suggests all of these samples follow the non-universal model. So it is concluded that these reinforcements were agglomerated in matrix.

4. CONCLUSIONS

A newly developed graphite nanoflakes were used as reinforcements in epoxy matrix. The acrylamide grafting was found to be very effective to enhance the interaction with epoxy matrix. The acrylamide treated graphite nanoflake reinforced composites showed better flexural and tensile properties than those reinforced with commercially available carbon materials. The electrical conductivity of composites was also investigated. The results revealed the exfoliated graphite with high aspect ratio was an excellent conductive filler, which showed comparable or better percolation threshold and conductivity than conventional fillers. From these results and predicted low cost (\$ 5/lb), this new type of graphite material has realistic possibility to replace conventional carbon materials or newly developed carbon nanotubes. The possible application fields are broad, including automobile, electrical/electronics, and aerospace.

5. ACKNOWLEDGEMENT

The authors would like to thank UCAR Co. for providing the acid intercalated graphite compounds. Also we thank Professor Thomas J. Pinnavaia, Department of Chemistry, Michigan State University for providing BET surface area data and Professor Rodney S. Ruoff, Department of Mechanical Engineering, Northwestern University for providing TEM images of the nano-size graphite flakes. Partial support for this research was provided by a grant from NASA LaRC, *Graphite Nanoreinforcements for Aerospace Nanocomposites* NAG1-01004, Thomas Gates, Program Director.

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