ELECTRICAL AND BARRIER PROPERTIES OF EXFOLIATED GRAPHITE NANOPLATELET (xGnP) REINFORCED NANOCOMPOSITES

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Abstract

A new type of nanocarbon material called exfoliated graphite nanoplatelets (xGnP) has been developed and used as reinforcements in nylon 66, nylon 6, and polypropylene polymer composite systems. Because of the unique combination of morphology and properties, the xGnP can improve many properties of composite systems, which include improved electrical conductivity, barrier property as well as mechanical properties. In this paper, the electrical and barrier properties of xGnP nanocomposites will be presented and the factors which affect the properties will be discussed.

1 Introduction

Clays are the first nanoreinforcements used in polymeric matrices that have been studied since the late 1980's [1-3]. Many reports indicated that nanoclay based nanocomposites can achieve improved mechanical properties as well as barrier properties in polymer systems. Some drawbacks with clay materials are the lack of advanced properties such as electrical and thermal conductivities. Also an intensive milling and drying process is required for clays to be used as nanoreinforcements in polymer systems, which limits the cost of the material. Many carbon nanomaterials have been developed and used as reinforcements since the early 1990's. [4-6]. These materials have tube, fiber or spherical shapes. Although these materials showed good mechanical and conductive properties in polymer systems, they materials did not show improvements of barrier properties due to their morphology. Most of these materials are very expensive for most applications. Based on the fact that graphite has the same platelet morphology as clay, yet it has superior mechanical, electrical and thermal properties that are almost comparable to those of much more expensive carbon nanomaterials, a new nanomaterial called exfoliated graphite nanoplatelet (xGnP™) has been developed at Michigan State University. xGnP has platelet morphology with the surface area of more than 100 m^2/g and the thickness of 10 nm or thinner. The diameter of the xGnP can be controlled by adjusting the milling conditions. Since xGnP is based on very affordable and still abundant natural graphite, the cost of xGnP is expected to be substantially lower than other carbon nanomaterials. In this research, xGnP samples were used as reinforcements in nylon 6, nylon 66, and polypropylene systems and the electrical and barrier properties were measured. As a result, these xGnP based nanocomposites showed very good barrier properties while adding conductivity, which can not be achieved with clay nanocomposites.

2 Experiments

Material

Nylon66 (Zytel 101 NC010, Du Pont), Nylon 6 (Durethan B40SK Extrusion Grade, Bayer), and polypropylene (Basel ProFax 6301) were used as the matrices. Acid intercalated natural graphite was used as the starting material for xGnP. The acid intercalated graphite was processed thermally and the expanded graphite flakes were pulverized by use of an ultrasonic processor and mechanical milling. The BET measurements showed xGnP samples have surface area of more than $100m^2/g$ and their thickness became 10 nm or thinner. The average diameter of the flakes could be controlled by changing the pulverization and milling conditions.

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.), high-structure carbon black (CB, KETJENBLACK EC-600 JD, Average diameter: 20-40nm, Specific gravity: 1.8 g/cm^3, Akzo Novel Polymer Chemicals LLC), and nanoclays (1.Nanomer I.34.TCN for nylon 66, Nanocor Co. Ltd. 2. Cloisite 93A for nylons, Southern Clay Products, Inc., 3. Nanomer I30.P for PP, Nanocor Co. Ltd.) were used for comparison.

Composite Fabrication

Before injection molding, the polymers and reinforcements were dried in a vacuum oven. Also nitrogen gas was applied to the system throughout the molding process. A DSM Micro 15 Compounder, (vertical, co-rotating twin-screw miniextruder, capacity 15cc) and a Daca Micro Injector were used to make composite samples. Film samples were made by compression molding for barrier property measurements.

Measurements

Resistivity Measurement

The resistivity of composite samples was measured in Impedance Spectroscopy by applying the two-probe method at room temperature. The size of each sample was about 30 x 12.5 x 8.0 mm. 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 on the surface region. After the process, gold coating with about 20nm thickness was applied. During the process, sidewalls of each sample were masked so that no conductive connections between the top and bottom planes occurred 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 resistivity by incorporating dimension factors. The resistivity at 0.1Hz was considered as the AC resistivity since the difference should be very small.

Barrier Property Measurement

The O_2 permeability of composite films was measured by using Ox-Tran. The composite films were made by compression molding and the reinforcement loading was set to 3vol%. The thickness of the films was 100um. 100% oxygen gas was used and the measurement was performed at room temperature.

3. Results and Discussion

Electrical Conductivity

The resistivity of composite samples was measured with Impedance Spectroscopy by applying two-probe method at room temperature. **Figure 1** shows the electrical conductivity of the xGnP Nylon 66 composites with various reinforcement contents. Carbon black and in-situ xGnP showed the best percolation threshold at around 2 vol%. 15um ex-situ xGnP percolated around 6 vol%, VGCF, and 1 um xGnP showed percolation threshold of around 10 vol%, and chopped carbon fiber showed that at around 12 vol%. The carbon black used in this study is a high-structure carbon black which is highly agglomerated and is able to form a conductive path easily. Also it has a high degree of porosity having a surface area of 1400 m^2/g [7], which allows polymer chains to penetrate in. Thus, this type of carbon blacks can create a conductive network by occupying a large occluded volume at very low concentrations [8] by eliminating many of the particle-polymer interfaces through its aggregated structure.

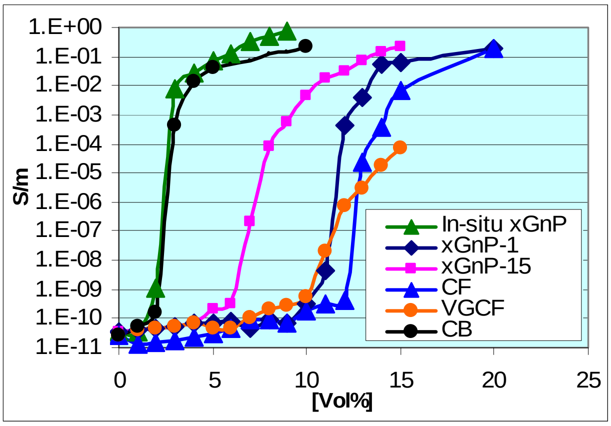

Fig 1. Electrical Conductivity of Various Nylon 66 Composites

The in-situ xGnP sample was made by adding un-exfoliated graphite into polymer matrix and processed it at high enough temperature so that the exfoliation was occurred during the compounding process. In this way the xGnP retained very high aspect ratio, almost 300,000. In general, as the aspect ratio of the conductive fillers increases the percolation threshold of the composite decreases [9]. This is because the fillers with large aspect ratio can maintain point-to-point contact at low concentrations which provide a conductive path. **Figure 2** summarizes the electrical conductivity data of xGnP/nylon 66 composites with different aspect ratio. These data shows that the xGnP with higher aspect ratio percolates at lower loading levels, which agrees the theory. Thus, it is concluded that xGnP with a high aspect ratio can percolate at low loading levels and add enough conductivity for many applications which requires electrostatic dissipation, electrostatic painting, or electromagnetic shielding.

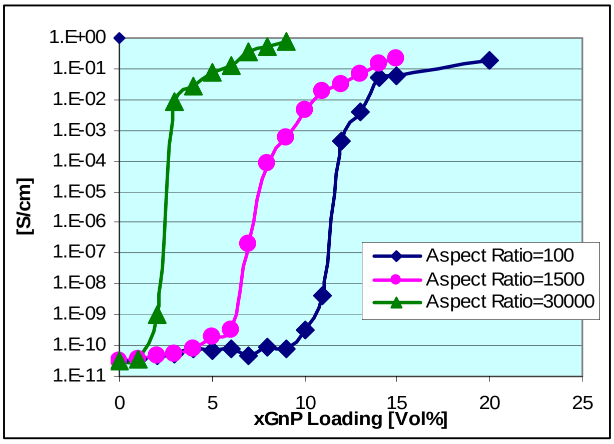

Fig 2. Electrical Conductivity of xGnP/Nylon 66 with Different Aspect Ratio

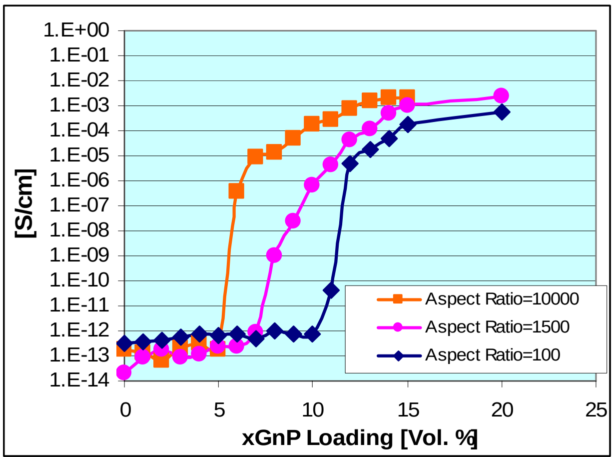

Fig 3. Electrical Conductivity of xGnP/Nylon 6 with Different Aspect Ratio

Figure 3 shows the electrical conductivity of xGnP/nylon 6 composites. In this case, xGnP-100 (Aspect ratio=10,000), xGnP-15 (Aspect ratio=1,500), and xGnP-1 (Aspect ratio=100) were used. xGnP-1 and xGnP-15 showed the percolation threshold of around 7 vol% and 10 vol% respectively. These values are almost the same percolation threshold as xGnP showed in nylon 66 composites. The xGnP-100 showed percolation threshold of around 5 vol%. These data also shows the same effect of higher aspect ratio on the lower percolation threshold.

Figure 4 shows the electrical conductivity of carbon reinforced PP composites made with various fillers. The percolation threshold varies with filler composition starting at around 2 vol% for high structure carbon black, 6 vol% for xGnP-15, 8 vol% for VGCF, 9 vol% for xGnP-1, and 10 vol% for PAN based carbon fibers.

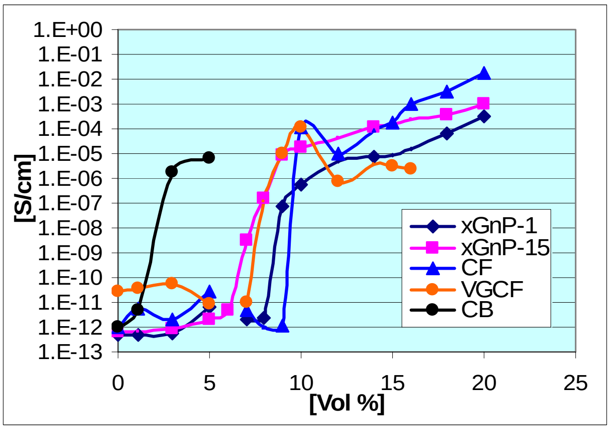

Fig 4. Electrical Conductivity of xGnP/PP Composites

In this case, morphology observation by ESEM revealed that the xGnP particles were not well dispersed in PP matrix. To improve the dispersion of xGnP in PP matrix, a new process was employed. This method was named the premixing method, in which xGnP and polypropylene powder were mixed in isopropanol, then the solvent was evaporated so that the PP powder was coated by xGnP. In this method, at first the xGnP was dispersed in isopropanol by sonication for 1 hour at room temperature. The PP powder was then added to the solution and the system was sonicated for 0.5 hrs. Finally, the solvent was evaporated at 80°C resulting in complete coverage of the powder particles with the xGnP. The isopropyl alcohol

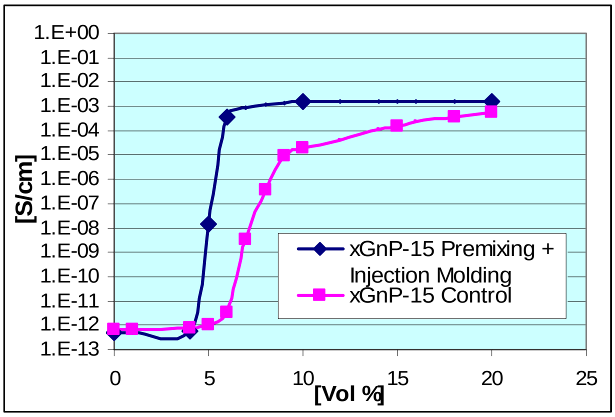

Fig 5. The Effect of Premixing Process on Percolation Threshold (Injection Molding)

can be recycled by using filtration and reused, so this new method can be environmental friendly and more cost effective. The main advantage of this method is that sonication breaks down the xGnP agglomerates so that the xGnP can cover the PP powders efficiently, resulting in a homogeneous xGnP coated PP powder that can be used for further processing.

Figure 5 shows the electrical conductivity of xGnP-15/PP composites made by premixing followed by injection molding. It also shows the data of xGnP-15/PP composites made by regular injection molding process. As the data show, the percolation threshold was improved by about 2 vol% by applying premixing process prior to the injection molding.

Figure 6 shows the electrical conductivity of xGnP-15/PP composites made by premixing followed by compression molding. In this case, the

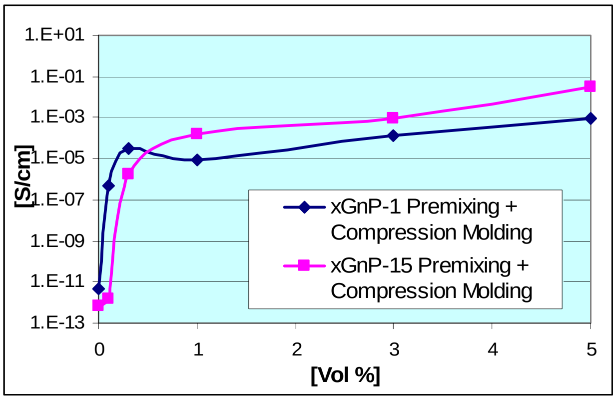

Fig 6. The Effect of Premixing Process on Percolation Threshold (Compression Molding)

coated xGnP directly forms conductive paths, resulting in an extremely low percolation threshold. In the case of xGnP-1/PP composite, the percolation threshold became around 0.1 vol% while xGnP-15/PP system percolated around 0.3 vol%.

Barrier Property

The barrier property of composite can be improved by adding impenetrable platelets with high aspect ratio into the system so that the diffusing path length (tortuosity) is increased [10]. Factors that affect the barrier properties are the aspect ratio, dispersion and orientation of the platelets, the platelet/polymer interface and the crystallinity of the polymer matrix. These factors can be controlled by changing the processing conditions. Since xGnP has a platelet morphology with a high aspect ratio, it was considered an appropriate filler to improve the barrier property.

Figure 7 shows the oxygen permeability data of nylon 6 composite films with 3 vol% reinforcements. In the case of xGnP-15um and nanomer I.34TCN nanoclay, the barrier property was reduced to around 1/3 of that of control nylon 6 sample. This is due to the very high aspect ratio of the nanoclays (~2000) and xGnP-15um (~1500). Fiber-shape fillers did not improve the barrier property as much as platelet-shape fillers.

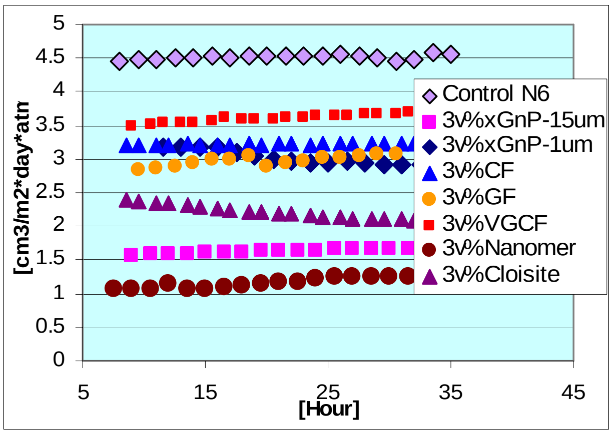

Fig 7. Oxygen Permeability of xGnP/Nylon 6 Composites

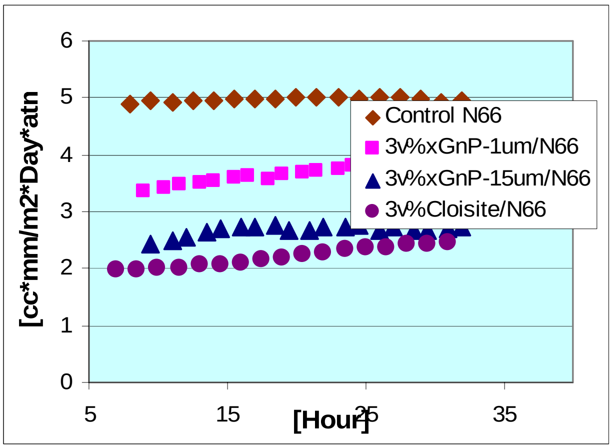

Fig 8. Oxygen Permeability of xGnP/Nylon 66 Composites

Figure 8 and **Figure 9** shows the oxygen permeability data of nylon 66 and polypropylene composite films respectively. The loading level was fixed at 3 vol%. In either case, xGnP-15um and nanoclay (Cloisite 93A in nylon 66 and nanomer I.30P in PP) showed significant improvement in the barrier properties. In the case of nylon 66, the permeability of these composites became almost ½ of that of control, while it improved about 30% in PP. These data prove that xGnP can improve the barrier property of composite systems as much as nanoclays do.

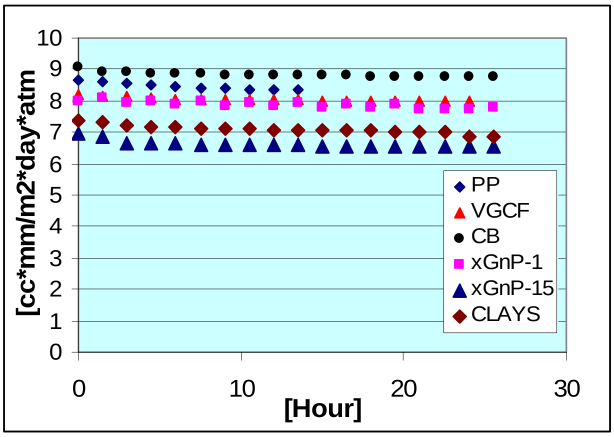

Fig 9. Oxygen Permeability of xGnP/PP Composites

4 Conclusion

xGnP™ (exfoliated graphite nanoplatelet) is a newly developed nanomaterial at Michigan State University which showed good electrical and barrier properties in many composite systems. These results proved that this new material can be used in many applications as a replacement for nanoclays or other carbon nanomaterials.

5 References

[1] Okada, A., Kawasumi, M., Kurauchi, T., and Kamigaito, O. "Synthesis and Characterization of a Nylon 6-Clay hybrid." Polymer preprint, ***194***, 10 (1987).

[2] Giannelis, E. P., "Polymer-Layered Silicate Nanocomposites: Synthesis, Properties, and Applications." Appl. Organometalic Chem., ***12***, 675 (1998).

[3] Pinnavaia, T. J. and Beal, G. W., "Polymer Clay Nanocomposites." John Wiley & Sons, Chichester, England (2000).

[4] Coleman, J. N., Khan, U., Blau, W. J., and Gun'ko, U. K., "Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites" Carbon, ***44***, 1624 (2006).

[5] Moniruzzaman M and Winey, K. I., "Polymer Nanocomposites Containing Carbon Nanotubes", Macromolecules, ***39***, 5194 (2006).

[6] Breuer, O., and Sundararaj, U., "Big Returns From Small Fibers: A Review of Polymer/Carbon Nanotube Composites", Polym. Compos., ***25***, 6, 630 (2004).

[7] J. King, K. Tucker, J. Meyers, E. Weber, M. Clingerman and K. Ambrosius, "Factorial Design Approach to Electrically and Thermally Conductive Nylon 6,6", *Polymer Composites* **22**, 1, 142 (2001)

[8] P. Banerjee and B.M. Mandal, "Conducting polyaniline Nanoparticle Blends with Extremely Low Percolation Thresholds", *Macromolecules* **28**, 3940, (1995)

[9] P. Calvert, "Nanotube Composites: A recipe for Strength", *Nature* 399, 210 (1999)

[10] L.E. Nielsen, "Models for the permeability of filled polymer system", *J. Macromol Sci Chem* **A1**, 929-942 (1967)