Multifunctional Nanocomposites made of Polypropylene Reinforced with Exfoliated Graphite Nanoplatelets (xGnP)

K. Kalaitzidou*, H. Fukushima** and L. T. Drzal***

Department of Chemical Engineering and Materials Science, and
Center for Composite Materials and Structures, Michigan State University, MI, USA,
* kalaitzi@egr.msu.edu,** fukushi3@egr.msu.edu, *** drzal@egr.msu.edu

ABSTRACT

This research investigates the interactions between exfoliated graphite nanoplatelets (graphene sheets ~10nm thickness, ~1um diameter), a new nano-material developed by Drzal's group, with polyolefin based thermoplastics. It provides an understanding about how the processing method/conditions used affect the properties of xGnP/PP nanocomposites i.e., mechanical, thermal, barrier properties; electrical conductivity and percolation threshold and therefore can lead to materials with desired properties. A significant development is a new compounding method, which is more effective than the solution method widely used, in terms of lowering the percolation threshold of thermoplastic nanocomposites, and maintaining the platelet morphology of xGnP. The feasibility of using xGnP-PP nanocomposites was investigated by evaluating the properties of this system and comparing the xGnP-PP with composites made with commercial available reinforcements.

Keywords: multifunctional nanocomposites, exfoliated graphite, percolation

1 INTRODUCTION

In recent years researchers both in industry and in academia have focused their interest on polymeric nanocomposites, which represent a radical alternative to conventional filled polymers or polymer blends. The small size of nanoreinforcements whether inorganic i.e., clays or organic i.e., carbon nanotubes, is responsible for enhancing the overall material performance by synergistically producing unique material properties resulting from phenomena that occur only when the morphology and the physics coincide at the nanoscale [1,2].

Besides layered silicate nanoclays and carbon nanotubes, exfoliated graphite nanoplatelets (xGnP) are also among the leading nano-scale fillers in research and development and commercial projects [3]. Research in the Drzal group [4,5] has shown that they can be a cost effective alternative to carbon nanotubes and provide excellent competitive functional properties. They combine the layered structure and low price of clays and the superior electrical and thermal properties of nanotubes. There is a wide variation of the properties of the xGnP-polymer nanocomposites depending on the origin, form, morphology and aspect ratio of graphite used, on the graphite-polymer interactions as well as on the fabrication method used.

The objectives of this research are to (i) explore the possible fabrication methods and understand the effect of the processing conditions on the various properties of the nanocomposites, (ii) investigate how addition of xGnP alters the physical properties of the polymer matrix, (iii) determine the mechanical, thermal, barrier and electrical properties of xGnP nanocomposites, and (iv) provide systematic knowledge about the interactions between xGnP and polymer chains by understanding how the nanocomposites properties are related to xGnP's microstructure; state of dispersion, aspect ratio and orientation of the nanoplatelets within the polymer matrix.

2 EXPERIMENTAL

2.1 Materials

The polymer used in this research is polypropylene powder with the trade name Pro-fax 6301 (melt flow index 12 g/10min, ASTM D1238) which was kindly supplied by Basell [6].

xGnP is produced [4] by rapid heating and the entrapped intercalants vaporize. The graphite flake particles undergo significant expansion (~500 times). The result of this exfoliation process is a worm-like or accordion-like expanded structure which by sonication can be separated into individual graphite sheets that are less than 10nm thick and have a diameter of ~15μm (xGnP-15). Their diameter can be further reduced by milling using a vibratory mill, resulting thus in nanoflakes with the same thickness but with diameter less than 1μm (xGnP-1).

PAN based carbon fibers (PANEX 33 MC, Zoltek Co), VGCF (Pyrograf III, PR-19 PS, Pyrograf Inc.), carbon black (KETJENBLACK EC-600 JD, Akzo Novel LLC) and montmorillonite clays (Nanomer I.30P from Nanocor) were also used as reinforcements in PP for comparison with the xGnP.

2.2 Fabrication Methods

Melt mixing followed by injection molding was the main processing method used to fabricate the nanocomposites. A DSM Micro 15cc Compounder, (vertical, co-rotating twin-screw microextruder), operating at 180 ^{o}C for 3 minutes at a screw speed of 200rpm was employed for melt mixing and the injection molding was carried out by a Daca Micro Injector ($T_{cylinder}$ =180^{0}C, T_{mold}=80 ^{0}Cand 160 psi injection pressure).

Polymer solution intercalation, using the conditions proposed by Shen *et al* [6], was also employed for compounding of xGnP with PP. The solution approach, while feasible, in the case of PP requires large amounts of solvent i.e., xylene and high temperatures that are neither practical nor safe.

Premixing of graphite and polypropylene in presence of isopropyl alcohol, a new compounding method developed in our lab, is proposed as an alternative to the commonly used solution method. The xGnP is dispersed in isopropyl alcohol (IPA) by sonication for 1 hour at room temperature. The PP powder is added to the solution and sonication is continued for 0.5 hrs. The isopropyl alcohol can be recycled by using filtration and reused. This method is simple, environmental friendly and more cost and time effective compared to the solution approach. Its main advantage is that sonication breaks down the xGnP agglomerates and the thick xGnP-IPA solution covers the PP particles very efficiently resulting in a homogeneous xGnP coated PP powder that can be used for further processing.

2.3 Characterization Techniques

Flexural tests were performed with a UTS SFM-20 machine [United Calibration Corp.] at room temperature by following the ASTM D790 standard test method Do not put page numbers on page. Impact resistance tests (Izod type) were performed following the ASTM D256 standard test method. The morphology of the nanocomposites was investigated by Environmental Scanning Electron Microscopy (Electroscan 2020). The samples were gold coated to avoid charging and the voltage used was 20-30kV

The CTE of PP composites was determined by TMA 2940 (TA Instrument). The through plane thermal conductivity of xGnP-PP composites was measured using DSC. The O_2 permeability of PP composite films at a reinforcement loading of 3vol% was measured based on ASTM method D3985 using Ox-Tran (Modern Controls Inc., Minneapolis, MN).

The electrical conductivity of carbon reinforced PP composites was measured using impedance spectroscopy by applying the two-probe method at room temperature. The two surfaces that were connected to the electrodes were first treated with O_2 plasma (10min, 550W) and then gold coated to ensure good contact of the sample surface with the electrodes.

3 RESULTS AND DISCUSSION

The flexural strength, modulus and the impact strength of up to 20vol% reinforced pp composites are shown in figures 1, 2 and 3 respectively. xGnP-1 is the best reinforcement in terms of flexural modulus and impact strength throughout the composition range used whereas in case of flexural strength, xGnP-1 is the best at low loadings i.e., up to 10vol%. At higher contents of xGnP-1 the flex strength reaches a plateau value indicating week adhesion along the xGnP-pp interface. The clays used are modified with octadecylamine and are specifically designed for pp matrix but require the presence of a coupling agent i.e., maleic anhydride-co-polypropylene [7]. However, in the absence of the coupling agent there is weak adhesion of the modified clays with the non-polar pp matrix, poor dispersion and agglomeration of the clay particles that as shown in figures 1-3 leads to poor mechanical properties.

The highest impact properties are obtained with xGnP-1

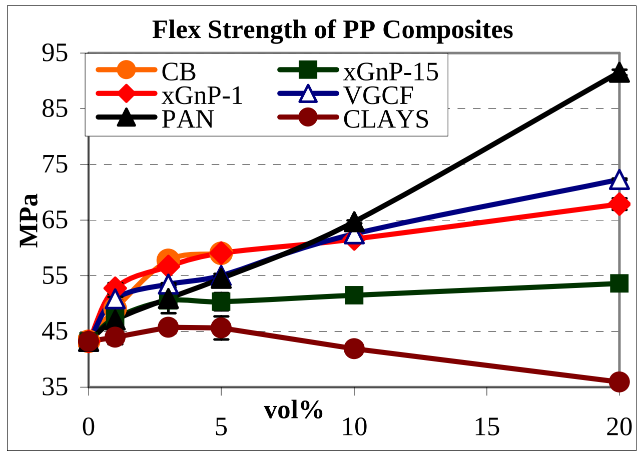

Figure 1: Flexural strength of PP composites

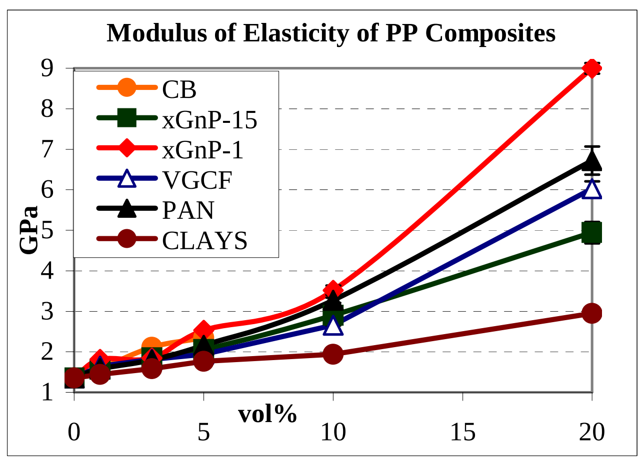

Figure 2: Flexural modulus of PP composites

at an optimum concentration of 3vol% where the impact strength of PP is increased by a factor of two. Carbon black has a negative effect i.e., at 5vol% the impact strength of neat PP is reduced by 50%.

The coefficient of thermal expansion and the O_2 barrier of xGnP-PP composites are shown in Figures 4 and 5 respectively. Due to its platelet structure xGnP reduces the CTE in two dimensions rather than in one as in the case of fibers, Figure 4, and can decrease significantly the permeability of small molecules i.e., O_2 as shown Figure 5.

The thermal conductivity of xGnP-PP composites measured normal to the graphite plane as a function of xGnP's aspect ratio and concentration is shown in Figure 6. Even at low loadings xGnP increases the conductivity of neat PP and due to graphite's anisotropy the conductivity along the graphite plane is reported to be at least three times larger [8]. It is expected that the larger platelets i.e., xgnP-15 will enhance more the conductivity of PP due to the decreased thermal resistance along the interface however, no effect of xGnP's aspect ratio was determined mainly because xGnP-15 is not homogeneously dispersed, forms

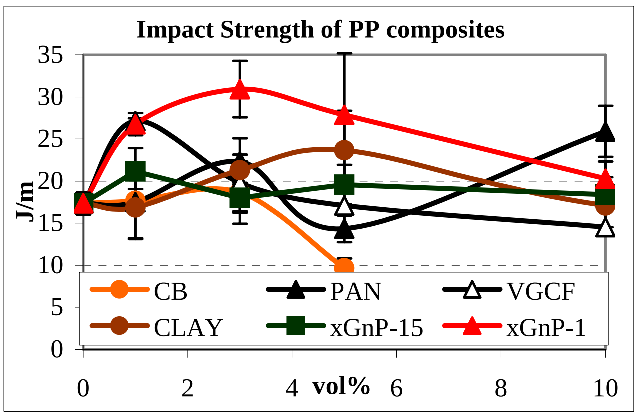

Figure 3: Impact strength of PP composites

large agglomerates and does not maintain its platelet structure once the composite is made as shown in Figures 7a and 7b respectively.

The percolation threshold and electrical conductivity of polymer composites is influenced by various factors; the most important are the characteristics of the filler, the filler-matrix interactions and the fabrication method used to make the composites that affects the dispersion and orientation of the filler within the polymer matrix.

The effect of orientation on the percolation threshold of xGnP/PP composites was investigated by altering the xGnP orientation through processing. xGnP-PP composites were fabricated by (i) melt mixing and injection molding (IM) and (ii) by melt mixing and compression molding (CM). The reinforcements used were xGnP-1 and xGnP-15. The electrical conductivity data are shown in Figure 8. As discussed earlier the xGnP aspect ratio has no effect on the composites conductivity. The electrical conductivity of both the xGnP-15 and the xGnP-1 IM samples begins to increase at ~7 vol%, while the corresponding value for the CM samples is ~5 vol% for both types of xGnP. The reason is that injection molding introduces filler alignment along the

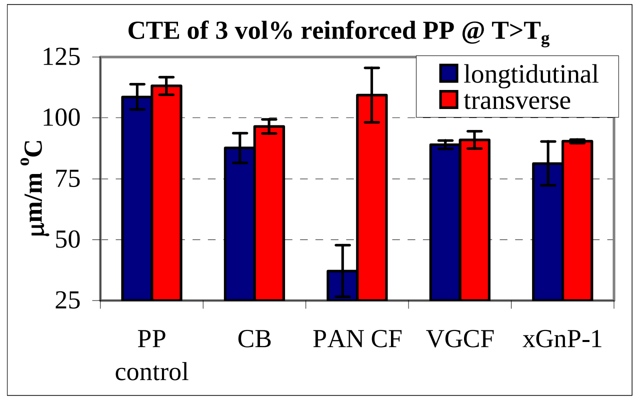

Figure 4: CTE of carbon reinforced PP composites

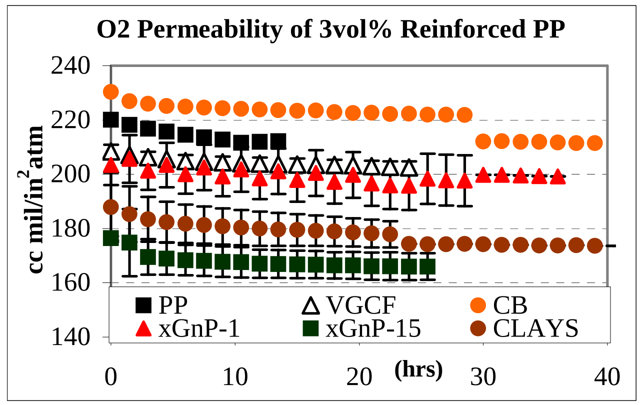

Figure 5: O2 permeability of 3vol% PP composites

flow direction. Initially the platelets are aligned parallel to

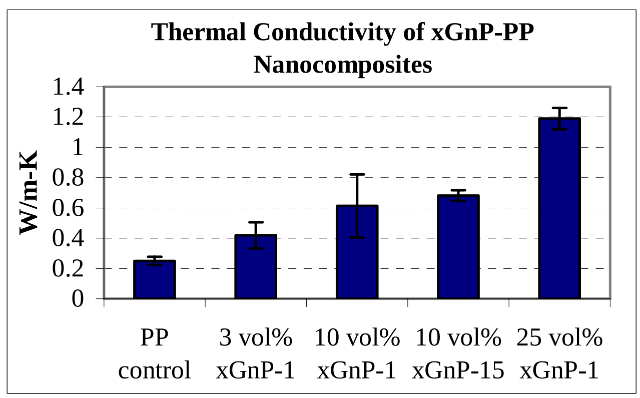

Figure 6: Thermal conductivity of xGnP/PP composites

each other along the flow direction and only at higher loading levels will they start intersecting with each other and form a conductive path. Therefore, the injection molded specimens have a higher percolation threshold compared to the compression-molded ones where the random orientation of the filler facilitates the formation of the conductive network.

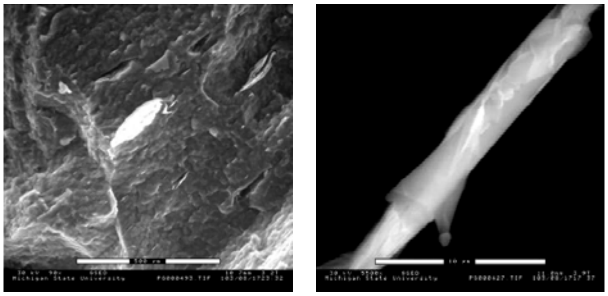

Figure 7: ESEM of 1vol% xGnP-15/PP a) agglomeration (scale bar 450µm) and b) "roll up" scale bar 5µm

In addition to altering the xGnP orientation the fabrication method and processing conditions used affect the dispersion and interparticle spacing within the polymer matrix. The effect of the three compounding methods; (i) melt mixing, (ii) polymer dissolution and (iii) premixing by coating the PP powder with xGnP-1, on the percolation threshold and electrical conductivity of xGnP-1-PP nanocomposites is shown in Figure 9. All the samples were compression molded. As shown the conductivity of xGnP-1/PP nanocomposites made by the premix compounding method is as high as 10^{-4} S/cm at a loading of 3vol%, indicating that the percolation threshold is much lower. For

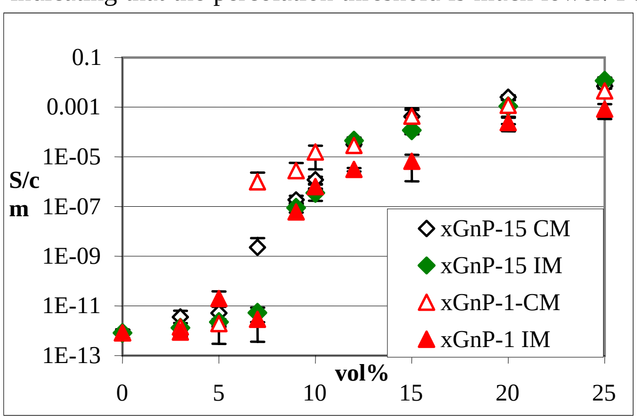

Figure 8: Effect of filler orientation on the percolation threshold of xGnP-PP nanocomposites

the two xGnP-1 loadings used i.e., 3 and 5vol% the proposed compounding method results in conductivity higher than the conductivity of the solution processed samples indicating that the premixing method is at least as efficient in facilitating the formation of conductive network as the commonly used solution method.

The reason is that in case of premixing there are no agglomerates of xGnP due to the use of sonication and the PP powder is homogeneously coated by xGnP. When the polymer melts in the mold the xGnP platelets move along with the melt but they always remain out of polymer chain entanglements. However, during the solution process xGnP agglomerates may exist and in addition, based on the fact that the composite powder obtained after the polymer precipitates has a non homogeneous gray color, it is possible that some xGnP may be trapped inside chain

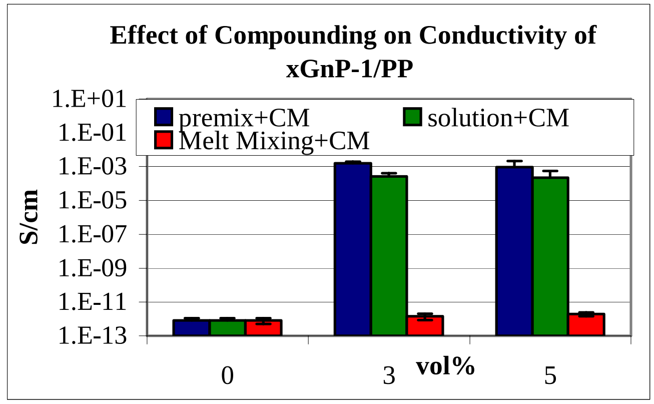

Figure 9: Effect of compounding on the percolation threshold of xGnP-PP nanocomposites

entanglements and therefore these xGnP is not available to form the conductive network.

4 CONCLUSIONS

In conclusion, this research provides systematic knowledge about the interactions between xGnP and polymer chains by understanding how the nanocomposite properties are related to xGnP's microstructure; state of dispersion, aspect ratio and orientation of the nanoplatelets within the PP polymer matrix. Therefore, xGnP-PP composite materials can be engineered to have a desired combination of mechanical, electrical and barrier properties.

REFERENCES

[1] Vaia, "Polymer Nanocomposites Open a New Dimension for Plastics and Composites", The AMPTIAC Newsletter, vol 6 no 1, 17-24, 2003

[2] R. Krishnamoorti, and R. A. Vaia, "Polymer Nanocomposites Synthesis, Characterization and Modeling", American Chemical Society, Symposium Series 804, Washington, DC, 2001

[3] L. M Sherman, "Chasing Nanocomposites", Plastics Technology, Online Article can be found in http://www.plasticstechnology.com/articles/200411fa2.html

[4] H. Fukushima, "Graphite Nanoreinforcements in Polymer Nanocomposites", PhD Thesis, Michigan State University, 2003

[5] K. Kalaitzidou, "Exfoliated Graphite Nanoplatelets as Reinforcements for Multifunctional Polypropylene Nanocomposites", PhD Thesis, Michigan State University, 2006

[6] http://www.basell.com/portal/site/basell/

[7] J-W. Shen, X-M. Chen and W-Y. Huang, "Structure and Electrical Properties of Grafted Polypropylene /Graphite Nanocomposites Prepared by Solution Intercalation", *Journal of Applied Polymer Science*, 88 1864, 2003

[8] J. King, K. Tucker, B. Vogt, E. Weber and C. Quan, Electrically and Thermally Conductive Nylon 6,6", *Polymer Composites* **20**, 5, 643 (1999).