GRAPHITE NANOPLATELET-POLYPROPYLENE NANOCOMPOSITES

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Abstract

Exfoliated graphite nanoplatelets (graphene sheets ~10nm thickness, ~1μm diameter), a new material developed in our lab, is used as nanoreinforcement in polypropylene. Exfoliated graphite nanoplatelet (xGnP) polypropylene (PP), nanocomposites are fabricated by (i) solution method and (ii) melt mixing and their thermo-mechanical and electrical properties are determined. Comparison of xGnP-PP nanocomposites to composites made using other carbon-based electrically conductive fillers indicates that xGnP is a multifunctional reinforcement that enhances the overall performance of polymers. Results include thermal (coefficient of thermal expansion and thermal conductivity), and mechanical properties (flexural strength, modulus of elasticity, and impact strength). In addition, the electrical conductivity and the percolation threshold of the xGnP-PP nanocomposites will be determined as a function of the xGnP's aspect ratio and the processing method used.

Introduction

Recently, researchers both in industry and in academia have focused their interest in polymeric nanocomposites, which represent a radical alternative to conventionally filled polymers or polymer blends. In contrast to conventional systems, the reinforcement in the nanocomposites has at least one dimension in the nanometer range. This characteristic enables the nanoreinforcements whether inorganic i.e., clays or organic i.e., carbon nanotubes to enhance the overall material performance by accessing new properties and utilizing unique synergistic phenomena between materials that only occur when the length-scale of morphology and the fundamental physics associated with a property coincide i.e., on the nanoscale [1,2].

The first report on fabrication clay-nanocomposites i.e., nylon 6-clay hybrid composite where individual silicate layers were homogeneously dispersed in a continuous polymer matrix was published in 1980's [3,4]. Since then the nanocomposites research has flourished and a plethora of studies that cover the design and fabrication, characterization, properties and the potential applications of the nanocomposites from both an experimental and theoretical perspective can be found in the literature [5,6].

A wide range of polymer resins have been proposed and used as matrices such as polystyrene, polyolefins, nylon, as well as, thermosets i.e., epoxies. The most common nanoreinforcement used is exfoliated clays, however, there is an increased interest in using organic materials such as carbon nanotubes as reinforcements for polymers due mainly to their superior thermal and electrical properties.

Studies on intercalated, expanded, or exfoliated graphite nanoflakes used as reinforcements in polymers have been reported since late 1990's [7-11]. Graphite is one of the stiffest material found in nature, with a modulus several times that of clay and excellent strength, 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) [12].

Research underway at a MSU [13] has shown that the nanoreinforcement concept can be successfully applied to graphite nanoplatelet reinforced polymer composites. Exfoliated graphite nanoplatelets (xGnP) is a promising material that combines the layered structure of clays and the superior thermal and electrical properties of carbon nanotubes with the additional advantages of low cost and simple preparation. Thus, the xGnP nanocomposites can be used not only for structural and packaging applications but also for electrostatic dissipation, (ESD), electromagnetic and radio frequency interference shielding (EMI, RFI), and heat dissipation.

In this research, a special thermal treatment and process were applied to produce exfoliated graphite nanoplatelets from acid intercalated GIC. The xGnP-PP nanocomposites were fabricated by compounding carried out either by melt mixing or solution method and molding, injection or compression. Transmission electron microscopy (TEM) and environmental scanning electron microscopy were used to assess the degree of exfoliation of the graphite platelets and the morphology of the nanocomposites respectively. The mechanical properties including flexural strength and modulus and impact strength; the thermal i.e., coefficient of thermal expansion and thermal conductivity and the electrical properties such as conductivity and percolation threshold were determined as a function of xGnP loading and aspect ratio.

Experimental Procedure

Materials

The polymer matrix used is polypropylene powder with the trade name Pro-fax 6301 (melt flow index 12 g/10min, ASTM D1238) which was kindly supplied by Basell. PP is used as a model to provide insight into the interaction between xGnP and other semi-crystalline polymers because it is one of the most widely used thermoplastics due to its well-balanced physical and mechanical properties, easy processibility and low cost [14]. It has a lower density, in comparison to other thermoplastics, allowing for potential weight reductions, moderate heat resistance and high resistance to solvents and other chemicals allowing for uses in very harsh environments.

The exfoliated graphite nanoflakes (xGnP) were made using GICs obtained from UCAR International Inc. The control carbon materials used for comparison with the xGnP were (i) PAN based carbon fiber (PANEX 33 MC Milled Carbon Fibers, Zoltek Co), (ii) VGCF (Pyrograf III, PR-19 PS grade, Pyrograf Products, Inc.) and (iii) nanosize High Structure carbon black (KETJENBLACK EC-600 JD, Akzo Novel Polymer Chemicals LLC). The geometrical and surface characteristics of all the reinforcements used are given in Table I.

Table I: Characteristics of the Conductive Fillers Used

Material	Length (μm)	Diameter (nm)	Aspect Ratio	Surface Area (m^2/g)	Cost ($/kg)
xGnP-1	>0.01	860	~77	100	12.5
xGnP-15	>0.01	1500	~150		~5
CF	175	7200	~24	16	11-14
VGCF	50-100	150	333-666	25	88-110
Carbon Black	0.4-0.5	400-500	1	1400	26.4

The exfoliated graphite nanoflakes are produced by heat treatment i.e., microwave, of the sulfuric acid-based intercalated graphite, which is in form of thick platelets as shown in Figure 1a. During the microwave heating, a cost and time effective exfoliation process initially proposed by Fukushima [13], the residual intercalates trapped inside the graphite galleries vaporize and significant expansion (~500 times) of the graphite flakes is observed. The result of the exfoliation process is worm-like or accordion-structure graphite as shown in Figure 1b.

The next step is to break down the worm-like structure in order to obtain individual graphite sheets. This is done by ultrasonic pulverization which reduces the graphite nanoflakes to less than 10nm thick with a diameter of ~15μm. Their diameter can be further reduced by milling with a vibratory mill, resulting thus in nanoflakes with the same thickness but with diameter less than 1μm. This way, two type of graphite nanoflakes are produced which differ in their aspect ratio. Figures 2a and 2b show the 15μm and 1μm exfoliated graphite nanoflakes respectively. The thickness of the nanoflakes was determined using TEM and it is shown in Figure 3.
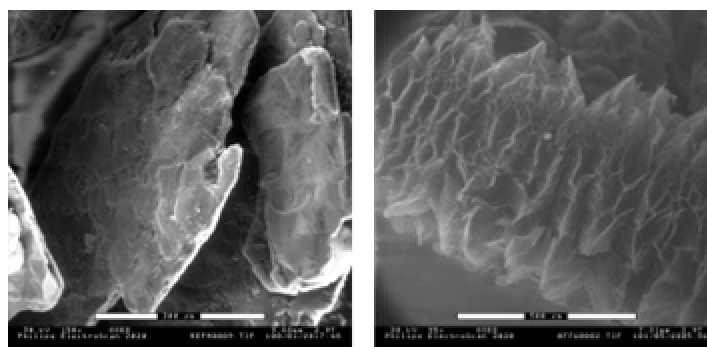

Figure 1. ESEM micrographs of a) acid intercalated graphite (scale bar 300μm),
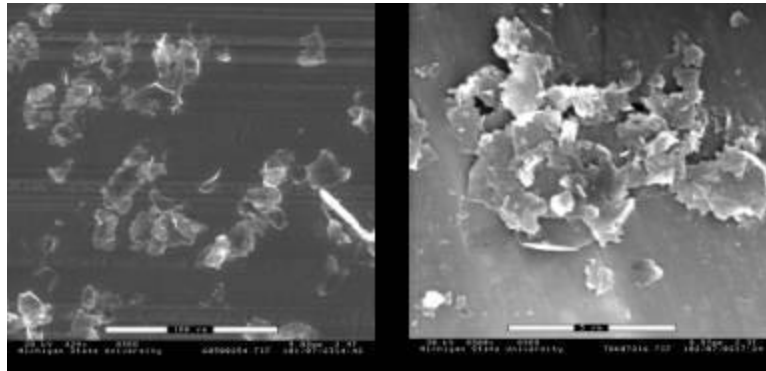and b) expanded graphite(scale bar 500μm)

Figure 2. ESEM micrographs of a) pulverized graphite nanoflakes 15μm, xGnP-15 (scale bar 100μm), and b) milled graphite nanoflakes 1μm, xGnP-1 (scale bar 5μm)
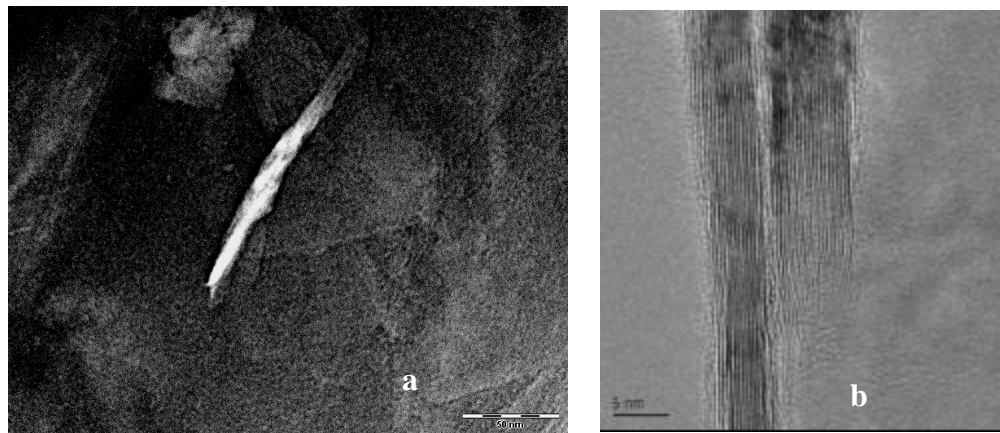

Figure 3. TEM Images of the side and top view of xGnP-1, the scale bars are 50nm (a) and 5nm (b)

As indicated in Figure 3b, which shows two adjacent nanoflakes, each nanoplatelet consists of more than 10 graphene sheets. Taking into account that the basal plane distance of graphite is 0.335nm [4] it is estimated that the average thickness of the graphite nanoflakes is ~5nm with a distribution of platelets having an expected thickness in the nanometer range.

Processing

Melt Mixing Approach

The basic fabrication method used in this project is melt mixing due to its simplicity and compatibility with existing polymer processing techniques such as extrusion, injection molding and compression molding. The nanocomposites were fabricated by melt mixing in a DSM Micro 15cc Compounder, (vertical, co-rotating twin-screw microextruder), at 180 $^{\circ}$C for 3 minutes at a screw speed of 200rpm.

The injection-molded samples were made using a Daca Micro Injector. The cylinder temperature was 180 ^{0}C and the mold temperature used was 80 ^{0}C. An injection pressure of 0.7MPa was used. The compression-molded samples were made using the composite pellets made by extrusion. The conditions used are at 200 ^{o}C for 20 minutes no pressure applied and 200 ^{o}C for 20 minutes under pressure ~50.44tonnes/cm^{2}. During compression molding vacuum was applied to remove any trapped air.

Solution Approach

The solution approach, while feasible, in case of polypropylene requires large amounts of solvents such as toluene or xylene and high temperatures that are neither practical nor safe. However, in order to understand the effect of processing method on the electrical conductivity and percolation threshold of exfoliated graphite polypropylene composites a limited number of samples were also fabricated using solution approach, a modified version of the one proposed by Shen *et al* [15]. In the solution method, the graphite nanoplatelets were dispersed in xylene using sonication for 2hrs and the PP was dissolved in refluxing xylene at 130 ^{o}C for 0.5 hrs using reflux. The graphite suspension was added drop wise to the PP solution and after refluxing for 1.5hrs the heating was stopped and a portion of xylene was extracted under vacuum. When the temperature dropped to about 70 ^{o}C the mixture was precipitated by addition of acetone, filtered, and dried under vacuum. The resulting composite powder was used for compression and injection molding.

Premixing Approach

This is a compounding method developed in MSU, which combined with compression molding was mainly used to fabricate composites for electrical conductivity measurements. 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 the sonication is continued for 0.5 hrs. Finally the solvent is removed by heating at 80°C. The main advantage of this method 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 is used for compression molding. ESEM micrographs of xGnP coated PP at a xGnP content of 0.2wt% is shown in Figure 4. In addition, due to absence of shear which as reported might break the continuous path formed by conductive fillers inside the polymer matrix it is expected that the premix method will result in composites with lower percolation threshold, defined as the minimum filler content at which a conductive path across the material is formed.
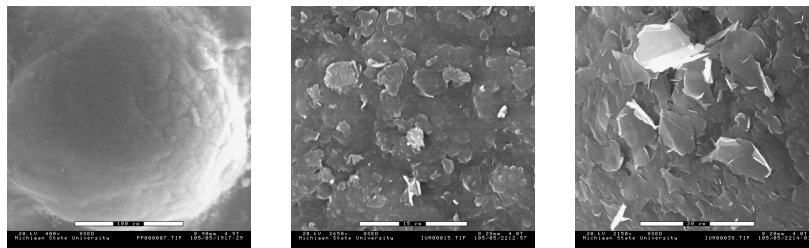

Figure 4. xGnP-coated PP, (i) neat PP particle (100um), (ii) xGnP-1 coated PP (15μm)
and (iii) xGnP-15 coated PP (20μm)

Testing Conditions

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 5.08cm. The test was performed at flexural rate of 0.127 cm per minute. Impact resistance test (Izod type) was performed following ASTM D256 standard test method.

The coefficient of thermal expansion (CTE) of xGnP-PP composites at a loading level of 3 vol% was determined by TMA 2940 (TA Instrument) for two regimes below (below T_g) and above the glass transition temperature (above T_g). 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. The thermal conductivity of xGnP-PP composites made by melt mixing and injection molding was measured using dynamic scanning calorimetry (DSC). The samples were disks (diameter of 5mm, and thickness~0.5mm).

The resistivity of composites along the injection direction was measured using 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 the thickness (6mm). Since sample dimensions 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 and finally, the sample surface was gold coated to ensure good contact with the electrodes. The resistance of samples was measured in frequency range of 0.1 to 100,000Hz and converted to conductivity by taking into account the sample dimensions.

Results and Discussion

Mechanical Properties

Flexural Strength and Modulus

The flexural strength and modulus of elasticity of both 1 and 15µm xGnP-PP nanocomposites at low loading levels (from 0 to 3 vol%) made with extrusion-injection molding is shown in Figures 5 and 6 respectively. It is noted that the strength of the neat PP increases even at very low content of xGnP-1µm. The xGnP-15µm also increases both the strength and modulus but only at higher loadings (>1vol%) and to a smaller extend than xGnP-1µm.
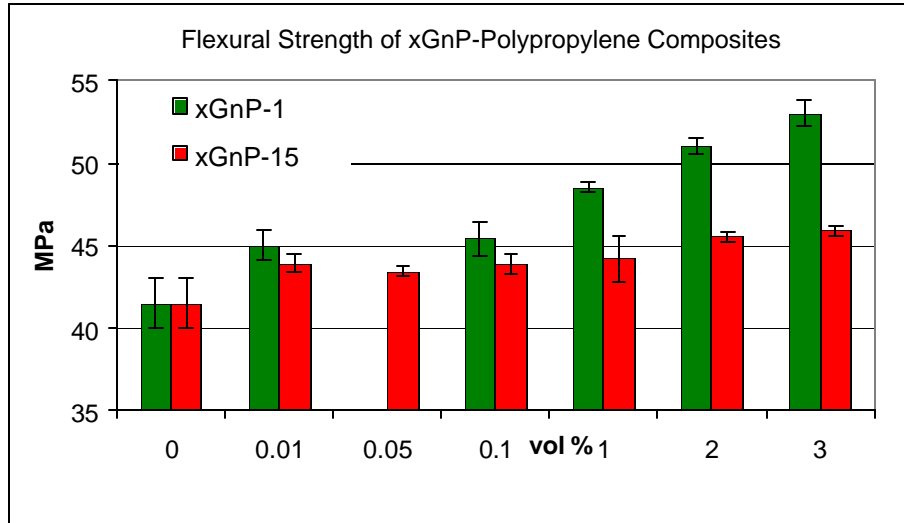
Figure 5. Flexural strength of 1 and 15μm xGnP-PP nanocomposites
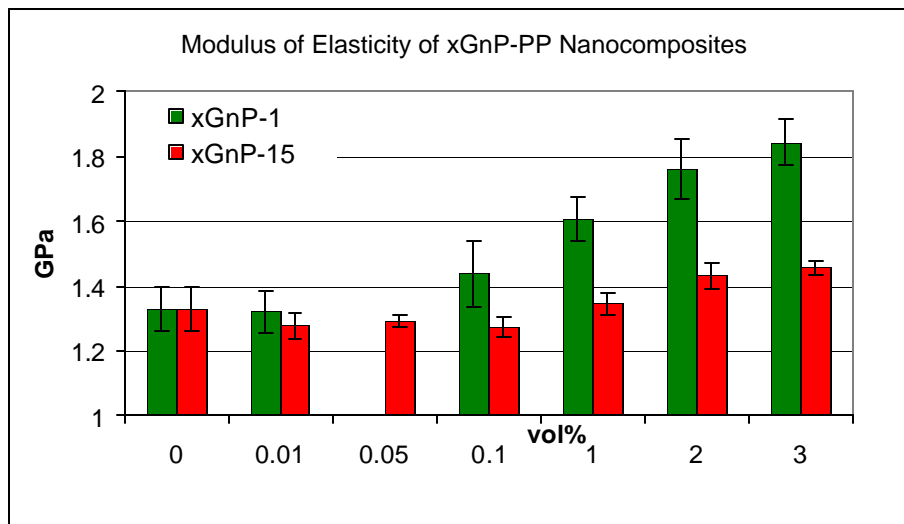

Figure 6. Modulus of Elasticity of 1 and 15μm xGnP-PP nanocomposites

Figure 7 shows the flexural strength of various polypropylene composites up to a loading level of 25 vol%. At the given processing conditions it was not possible to make samples with carbon black content higher than 5 vol%. The viscosity increased to levels where literally no material could flow out of the extruder die. Though all the reinforcements improved the strength, carbon black, due to its highly agglomerated structure and the high degree of porosity that allows for polymer penetration might enhance the adhesion to the polymer matrix resulting thus in a significant strength improvement At higher loadings both VGCF and PAN based CF show significant improvement of the strength. The nano-graphite strength curve reaches a plateau at ~10 vol% which indicates poor adhesion and insufficient dispersion of xGnP in the polymer matrix. The process conditions for better dispersion in the melt need to be optimized.
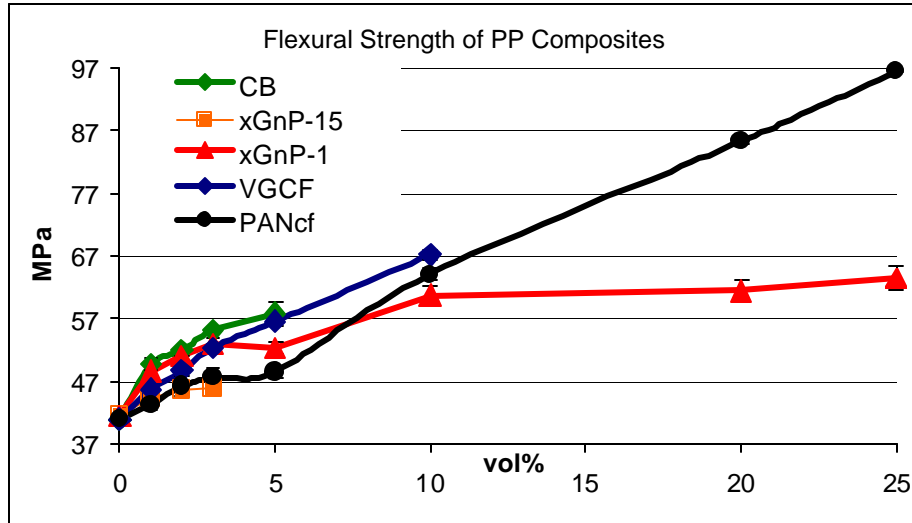
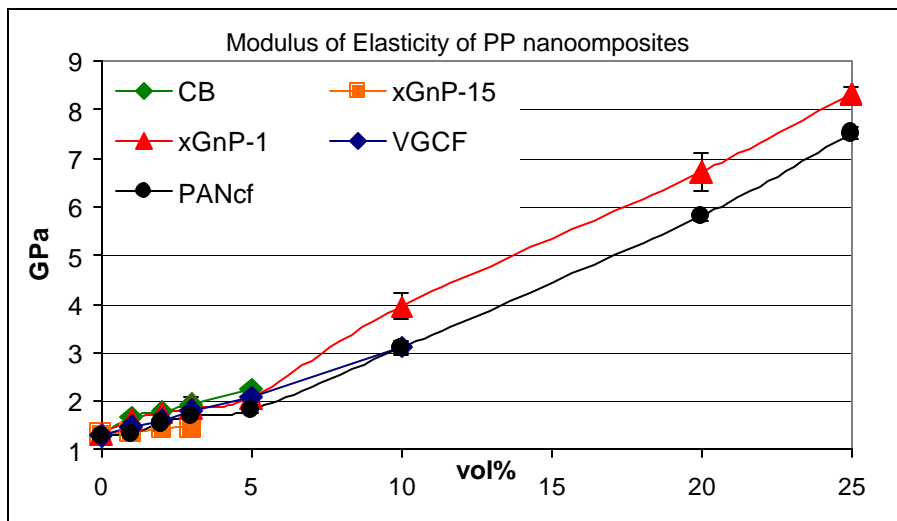Figure 7. Flexural strength of various PP composites

Figure 8. Modulus of Elasticity of various PP nanocomposites

Figure 8 shows the modulus of elasticity for various polypropylene composites. The results indicate that the best reinforcement (up to 5 vol%) is carbon black increasing the modulus ~75% followed by graphite nano-platelets (~55% improvement). Addition of more graphite nano-platelets results in further improvement of the modulus (520% at 25 vol%). PAN based CF and VGCF samples have a less significant effect on the modulus.

Impact Strength

Figure 9 shows the impact strength of various carbon reinforced polypropylene composites at loading levels of 0, 1, 2 and 3 and 10vol%. The impact strength of the composites decreases with increasing reinforcement content. Both the xGnP-1um and VGCF increase the impact strength by 60% (at 3vol%) up to 100% (at 1vol%) compared to the neat polymer.
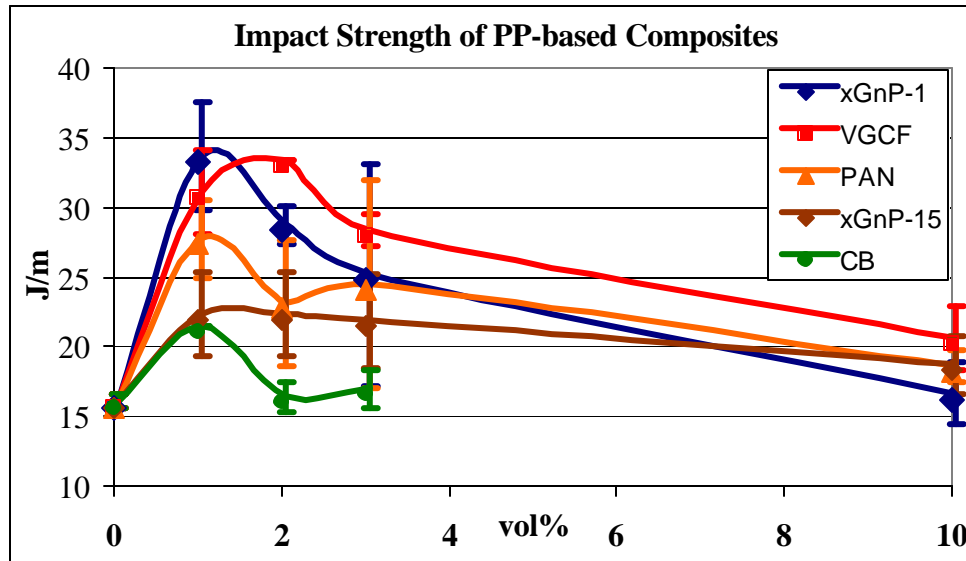

Figure 9. Impact strength of polypropylene based composites

Thermal Properties

Coefficient of Thermal Expansion

CTE was measured along two directions, the transverse, which is the direction perpendicular to the direction that the polymer melt flows into the mold, and the longitudinal, which is the direction along the flow. The results are shown in Figures 10 and 11 respectively. As shown, decrease of the CTE along the longitudinal direction was observed for all the fillers at both below and above T_g. In particular, for the regime below T_g, the xGnP had the same effect with VGCF and PAN based carbon fibers, ~25% decrease of CTE. For the above T_g regime, graphite had the same effect as carbon black and VGCF (~40% decrease) but PAN based carbon fiber had a more dramatic effect. The same trend was observed also in the measurements of CTE along the transverse direction as shown in Figure 14. The xGnP resulted in a decrease of CTE of the order of 15-20%. A similar decrease was observed also in the VGCF-PP composites.
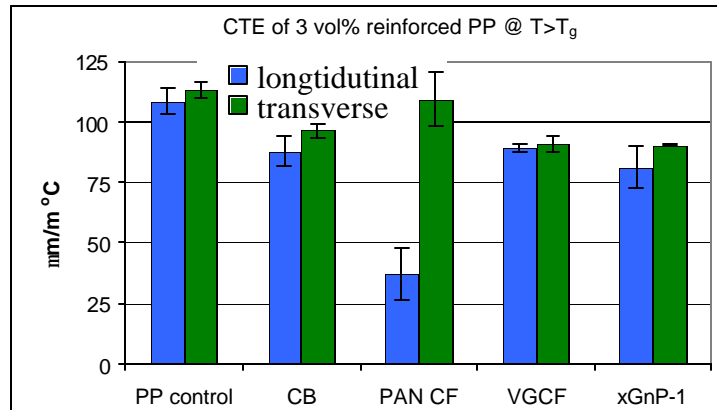
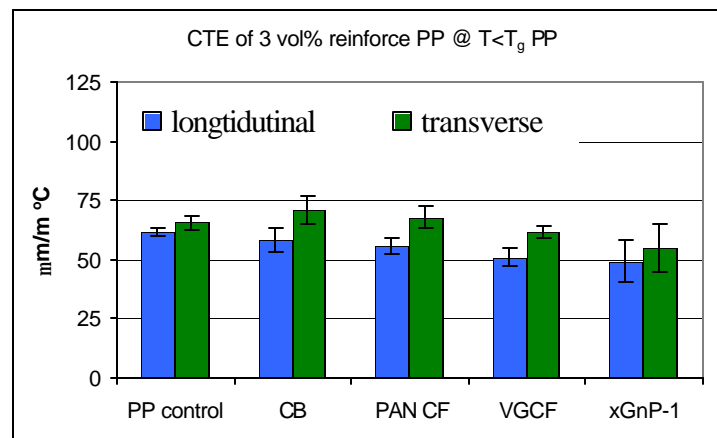Figure 10. CTE of polypropylene nanocomposites along the flow direction

Figure 11. CTE of polypropylene nanocomposites along the flow direction

Thermal Conductivity

Thermal conductivity is another important property of xGnP polymer nanocomposites that enhances their overall attractiveness. The factors affecting the thermal conductivity of composites are (i) conductivity of constituents, (ii) crystallinity of the polymer (increasing crystallinity improves conductivity), (iii) filler size, shape, concentration, dispersion, and orientation, i.e., increasing aspect ratio or mixing different fillers due to packing phenomenon conductivity can be increased and (iv) bonding between filler-matrix [16, 17]. It is reported that in the case of thermally conductive graphite-nylon 6,6 composites (i) the through plane conductivity increased significantly by increasing the amount of graphite, and (ii) the in-plane thermal conductivity is ~3 times larger than the through plane conductivity due to orientation during injection molding and the anisotropy of the fillers [18].

The results are shown in Figure 12. It is expected that xGnP-15 due to higher aspect ratio will cause larger increase in thermal conductivity since the contact resistance will be decreased. However, because of error overlapping at the xGnP loadings used no significant effect of the aspect ratio was observed at the xGnP.
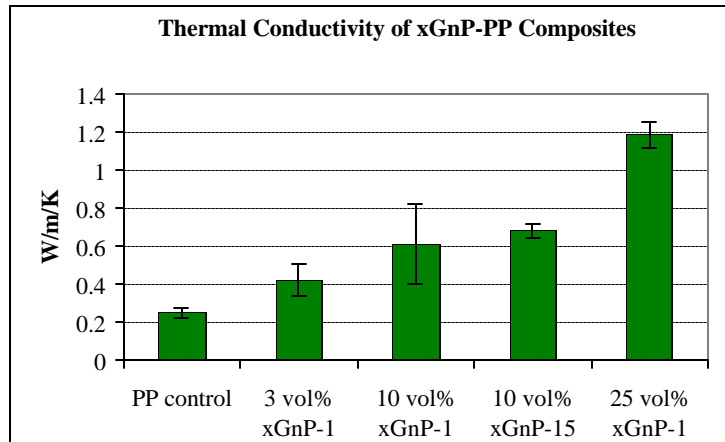
Figure 12. Thermal conductivity of xGnP-1 and xGnP-15um -PP composites

Electrical Conductivity and Percolation Threshold

The important properties in electrically conductive composites are (i) the electrical conductivity, which is reported either as bulk conductivity measured in S/cm or surface conductivity reported as S-cm; and (ii) the percolation threshold, defined as the minimum volume content of the conductive reinforcement above which the polymer composite becomes electrically conductive.

The electrical conductivity and especially the percolation threshold are the result of interactions of various factors with the most important being the volume fraction, distribution, size, shape, orientation and spacing of the filler particles within the polymer matrix. In addition, the conductivities of the constituents are also important with the conductivity of the filler defining the upper limit for the electrical conductivity of the composite. Finally, highly agglomerated (highly structured) fillers, or fillers with high degree of porosity that allow for polymer penetration and produce a conductive network by occupying a large occluded volume at low concentrations result in reduction of percolation threshold [19]. Other important factors are the crystallinity of the polymer matrix, the fabrication method and processing conditions as well as the adhesion between the filler and the polymer, which is mainly related to their surface energies.

One of the objectives of this research was to understand the effect that each one of the above-mentioned factors has on the conductivity and percolation threshold of the PP nanocomposites and explore ways to lower the percolation threshold. Results are presented in the following.

Effect of Fillers Geometry and Conductivity

The percolation threshold and the electrical conductivity for various filler contents are shown in Figure 13. Carbon black percolates at less than 2 vol%. The percolation threshold for the other reinforcements are, ~5 vol% for VGCF, 5vol% for PAN based carbon fibers, and ~8 vol% and 5 vol% for xGnP-1 and xGnP-15 respectively.
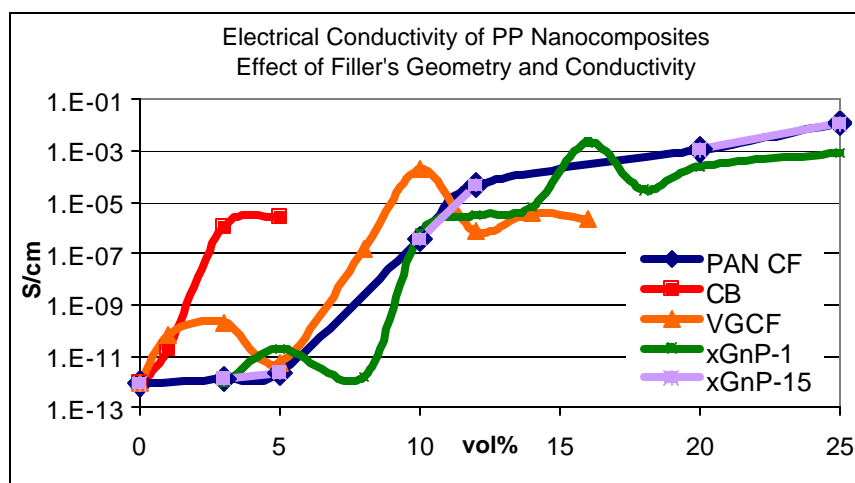
Figure 13. Electrical conductivity of PP nanocomposites-Effect of filler's geometry and conductivity

The carbon black used in this study does not consist of individual spherical particles but it is highly agglomerated (highly structured) with a high degree of porosity that allows for polymer penetration and may create a conductive network by occupying a large occluded volume at low concentrations this is why carbon black percolates at very concentrations.

For non-spherical particles, as the aspect ratio of the conductive fillers increases the critical concentration to induce bulk conductivity in the composite reduces significantly [20]. That is, the large aspect ratio particles can still maintain point-to-point contact at low concentrations and allow for electron tunneling. The effect of aspect ratio on lowering the percolation threshold is obvious in case of the carbon fibers used. VGCF with an aspect ratio of ~350-650 percolates at ~5 vol% while the shorter PAN carbon fibers (aspect ratio of ~24) percolate at ~8 vol%.

Effect Of Fillers Aspect Ratio

IN more details, the effect of aspect ratio on the conductivity and percolation threshold of xGnP-PP nanocomposites was studied using two types of xGnP. Both are platelets of the same thickness (~10nm), but they have different diameter; one is xGnP-15μm (aspect ratio ~150) and the other is xGnP-1μm (aspect ratio <100). The results are shown in Figure 14.

Both xGnP-15μm and xGnP-1μm PP nanocomposites made by injection molding (IM) percolate at ~7 vol%. This does not lead to the conclusion that both sizes of graphite have the same percolation threshold since more data points in the percolation regime are necessary. It is expected however that the xGnP-15um will percolate at lower loadings since the larger the aspect ratio the easier it is to form a continuous conductive path. It is noted also that at higher loadings (>12 vol%) the xGnP-15μm-PP composites show higher conductivity than the xGnP-1μm-PP composites. The reason might be that the conductive path in the case of the high aspect ratio graphite consists of fewer but larger platelets so it has fewer discontinuities, which means less resistance.
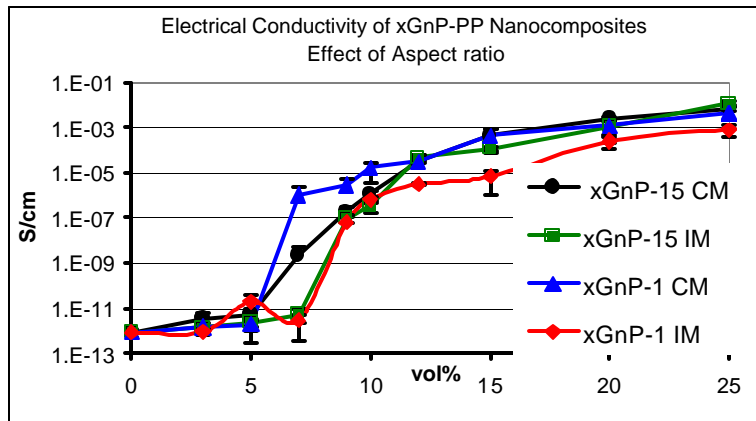
Figure 14. Electrical conductivity of xGnP-PP-Effect of aspect ratio

ESEM investigation indicated that there is not good dispersion of xGnP-15 in PP, which forms large agglomerates thus reducing its aspect ratio. In addition, "roll up" of xGnP-15 flakes, shown in Figure 15, inside the polymer matrix was also observed. So there is evidence that xGnP-15 does not maintain the aspect ratio or the platelet-type geometry once the composite is fabricated. This might be a reason why no effect of xGnP's aspect ratio on percolation threshold of the xGnP-PP nanocomposites was observed.
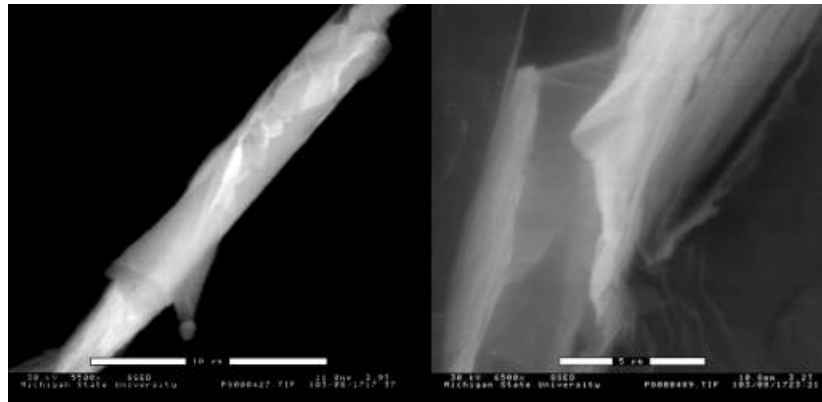

Figure 15. ESEM image "rolled" graphite nanoplatelet in 1vol% xGnP-15/PP nanocomposites

Effect of Fillers Orientation

Another important factor for the percolation threshold is the processing conditions used during the fabrication of nanocomposites. Extensive mixing i.e., twin screw extruder or long mixing using roll mill, can destroy the conductive network [19, 21, 22] and also reduce the aspect ratio of the fillers [19, 23] in both cases resulting in composites with increased percolation threshold. Besides the reduction of the aspect ratio, injection molding introduces alignment of the filler along the flow direction [23] and thus the sample percolates at higher loadings compared to a compression-molded one where the random orientation of the filler facilitates the formation of the conductive network.

The effect of reinforcement alignment introduced during processing was also studied by fabricating the samples using two different methods: (i) extrusion-injection molding (IM), that introduces alignment of the graphite flakes along the flow direction and (ii) extrusion-compression molding (CM), which results in random orientation of xGnP within the polymer matrix. The results are shown in Figure 14. For both types of graphite (xGnP-1 and xGnP-15 um) the compression molded samples (CM), show lower percolation threshold i.e., 5vol% than the injection molded (IM) ones which percolate at 7vol%. ESEM was used to study the morphology of these composites and it was observed that in the case of the injection molded samples there is orientation of the xGnP, especially of the xGnP-15um ones, along the flow direction. Thus, initially the platelets are aligned parallel to each other along the flow direction and only at high loading levels when there is not enough space available, they will start intersecting with each other and form a conductive path.

Conclusions

A new nanoreinforcement exfoliated graphite nanoplatelets was developed by microwave exfoliation of graphite-intercalated compounds. This material showed higher improvement in modulus than some commercially available carbon materials at the same loading levels, indicating that the exfoliated graphite has properties similar to highly crystalline graphite. The flexural strength data point toward the need for surface treatment of the exfoliated graphite in order to improve dispersion within the polymer matrix and improve adhesion, work which is currently in progress. It is also concluded that graphite nanoplatelets enhance the impact strength, increase the thermal conductivity and reduce the coefficient of thermal expansion of the neat polypropylene. Furthermore, it was found that the percolation threshold is higher for injection-molded samples due to the alignment of graphite platelets along the flow direction introduced during processing. Finally, no effect of graphite's aspect ratio on the percolation threshold could be detected although it was found that the larger graphite platelets (higher aspect ratio) resulted in higher values for conductivity due the conductive path they form consists of fewer but larger platelets so it has fewer discontinuities, which means less resistance.

Acknowledgements

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