

Effect of Processing on the Mechanical and Electrical Properties of Exfoliated Nano-Graphite Reinforced Polypropylene

Kyriaki Kalaitzidou, Hiroyuki Fukushima and Lawrence T. Drzal

Department of Chemical Engineering and Materials Science
Composite Materials and Structure Center, Michigan State University
East Lansing MI, 48824-1226, USA

ABSTRACT

The potential use of a new material, exfoliated graphite nano-platelets as a practical alternative to organoclays and carbon nanotubes is explored as a reinforcement in a thermoplastic matrix. Polypropylene based nanocomposites are fabricated at various loading levels of exfoliated graphite (1 up to 25 vol%) using (i) injection molding and (ii) compression molding under vacuum conditions. Microscopy (TEM and ESEM) is being used to determine the average size of the flakes and their distribution in the matrix. The mechanical properties (flexural and impact strength, and modulus of elasticity), and electrical properties (percolation threshold and electrical conductivity) of the graphite-reinforced polypropylene composites are determined and compared to composites made with clays and various carbon-based electrically conductive reinforcing materials, i.e., nanoscopic high-structure carbon black (CB), vapor growth carbon fiber (VGCF) and PAN based carbon fibers. In addition, the effect of the processing method i.e., injection vs compression molding on the mechanical properties of the graphite reinforced composites is investigated.

1. INTRODUCTION

Polymer nanocomposites comprise a new class of materials where inorganic (i.e, clay) or organic (i.e., nanotubes) nanoscale reinforcements are finely dispersed within a matrix. Even at very low loadings nanocomposites exhibit remarkably improved properties as compared to pure polymers or conventionally filled polymers. For instance, clays are expected to be effective at a loading under 5% by weight introducing only a minor increase in materials cost. Clay-nanocomposites are primary candidates for a variety of applications especially in the automotive industry because they provide significant improvement in modulus, thermal and dimensional stability, surface hardness and barrier properties [1]. However, clay nanocomposites lack electrical and thermal conductivity that limits their potential applications. On the other hand, if conductive nano-size fillers are used instead, i.e., carbon black or graphite, then nanocomposites can be used not only as structural materials but also in other applications such as electrostatic dissipation (ED), shielding from electromagnetic and radio frequency interference (EMI, RI), and heat dissipation [2].

Graphite is an abundant natural mineral and one of the stiffest materials found in nature (Young's Modulus ~1060Gpa) with excellent electrical and thermal conductivity. Research underway at MSU on polymer matrices reinforced with a new filler, exfoliated graphite (~10nm thickness, ~1um diameter) has shown that nanoreinforcement concentrations of up to 5 wt% are easy to achieve with low viscosity thermoset materials and alignment of the platelets producing the best mechanical, thermal and electrical properties [3, 4].

Exfoliated graphite nano-platelets have the potential to be a practical alternative to carbon nanotubes which due to their unusual mechanical [5] and electronic properties [6] are ideal candidate reinforcements for all the above applications but the low purity grades (single wall carbon nanotubes contain impurities up to 30%) that are now available and their high cost (~100\$/g) [7], limit their use significantly at this time. Finally, the lower cost of crystalline graphite (\$3.5/kg and less than \$12.5/kg for the graphite nanoplatelets), compared to other

conductive fillers i.e., VGCF, (\$88-110/kg), carbon fibers (~\$11-14/kg), and carbon black (~\$26.4/kg) makes graphite an exciting new choice for commercial applications that require both physical-mechanical property improvements and electrical conductivity of the final product.

Currently the most commonly used methods for fabrication of polymer nanocomposites [8] are: (i) Direct mixing, usually used when the matrix is a low viscosity thermosetting resin such as an epoxy, (ii) in situ polymerization, where the nanoreinforcement is added to a solution containing the polymer monomer, in both methods the nanoparticles initially stay dispersed due to mixing and finally are locked into the polymer matrix by either curing or polymerization; (iii) solution method where a solvent is used to dissolve a thermoplastic polymer, the reinforcement is added to the solution and finally, the polymer resolidifies as the solvent evaporates and (iv) melt processing where the nano-particles are mechanically dispersed into a polymer melt using a mixer or a compounder. The fabrication method used in this work is melt mixing due to its simplicity and compatibility with existing polymer processing techniques such as extrusion, injection molding and compression molding. Besides, using the solution approach in case of polypropylene would require large amounts of solvents such as toluene or xylene and high temperatures that are neither practical nor safe.

The goal of this research is two-fold: (i) To optimize the possible processing method for fabrication of polypropylene reinforced with exfoliated graphite nano-platelets, that will not only have superior thermo-mechanical properties but will also be electrically conductive with a low percolation threshold and (ii) to compare the graphite-reinforced polypropylene with composites made with clays and various carbon-based electrically conductive reinforcing materials, i.e., nanoscopic high-structure carbon black, VGCF and PAN based carbon fiber.

2. EXPERIMENTAL

2.1 Materials

The polypropylene with the trade name Pro-fax 6301 (melt flow index 12 g/10min, ASTM D1238) is kindly supplied by Basell. Graphite Intercalated Compounds (GICs) are obtained from UCAR International Inc. The control carbon materials used are (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 Nobel Polymer Chemicals LLC). Finally, the nano-clay I.9OP (Nanocor Inc.) used is montmorillonite, a layered alumino-silicate. The geometric characteristics, the density, and the cost of these materials are presented in Table 1.

Table 1. Geometric and surface characteristics of the various reinforcements

Material	Length/thickness (μm)	Diameter (nm)	Aspect Ratio	Surface Area (m^2/g)	Density (g/cm^3)	Cost (\$/kg)
1 μm EGF	0.01	860	~86	94	2	12.5
15 μm EGF	0.01	15000	1500	94	2	~5
CF	175	7200	~24	16	1.81	11-14
VGCF	50-100	150	333-666	25	2	88-110
CB	0.4-0.5	400-500	1	1400	1.8	26.4
Clay	0.001	1000	1000		2.85	3-5

2.2 Preparation of Exfoliated Graphite

The intercalated graphite was exfoliated using a special thermal treatment, a rapid heating process as proposed in [4]. During the exfoliation a significant volume expansion of the graphite flakes on the order of 500% is observed due to the vaporization of the intercalated acids in the graphite galleries. The expanded graphite flakes (EGF) were pulverized using an ultrasonic processor and milled using a vibratory mill. The resulting graphite nanoplatelets, shown in Fig. 1, have an average thickness of ~10nm and a diameter of ~1 μ m. The effect of the nanographite aspect ratio on the properties of the final composite was explored using two different type of graphite nanoplatelets: The 15 μ m EGF, which have a diameter of ~15 μ m and the 1 μ m EGF with a diameter of ~1 μ m.

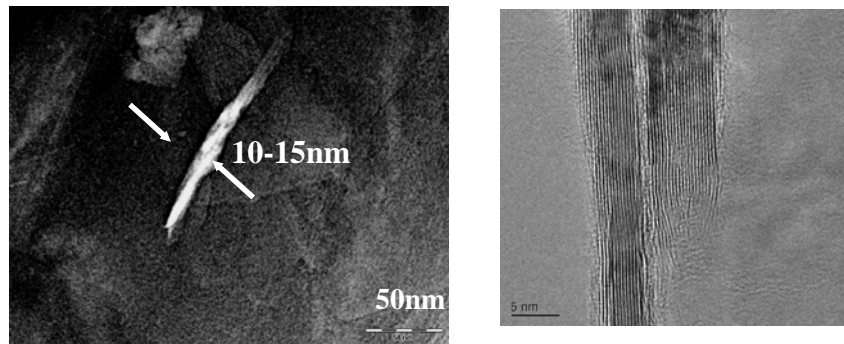


Fig. 1. TEM Images of the new nano-graphite material, the scale bars are 50nm (left) and 5nm(right)

2.3 Fabrication of Composites

The nanocomposites were fabricated by melt-mixing in a DSM Micro 15 Compounder, (vertical, co-rotating twin-screw microextruder) shown in Fig.2a. The processing conditions used are a barrel temperature of 180 $^{\circ}$ C, mixing time 3 minutes and screw speed 200 rpm. The composite material was molded into flexural bars using a Daka Micro Injector, shown in Fig. 2b, where the cylinder temperature was 180 $^{\circ}$ C and the mold temperature was 50 $^{\circ}$ C. An injection pressure of 690 KPa was used. These were the optimum processing conditions, determined based on a 2^3 factorial design, that maximized the flexural properties of the 3 vol% 1 μ mEGF-polypropylene nanocomposites.

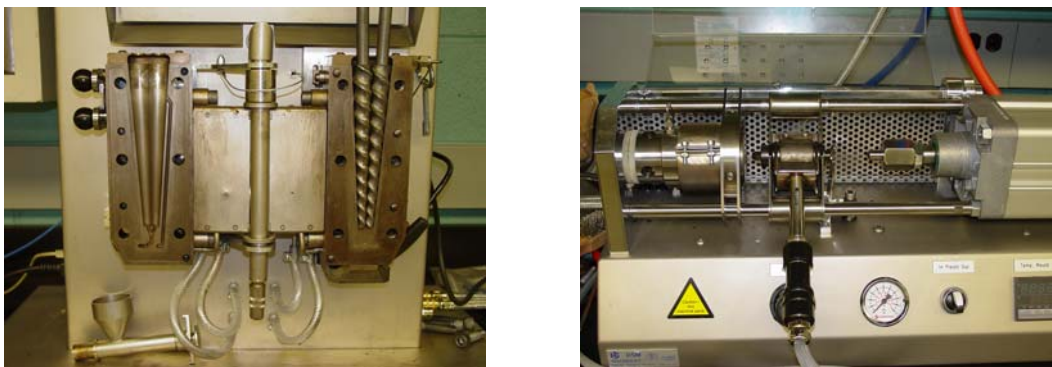


Fig. 2. a) DSM Microextruder, b) DSM injection molding unit

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties: Flexural Strength and Flexural Modulus

Flexural testing was performed using a UTS machine [United Calibration Corp.] at room temperature following ASTM D790 standard test method. The test was performed at a strain rate of 0.05 in/minute. Fig. 3 shows the flexural strength for the various polypropylene composite systems at loading levels of 0, 1, 2, 3, 5, 10, 20 and 25-vol%. (At the given processing conditions it was not possible to make samples with carbon black content higher than 5vol% and with clay content higher than 10vol%. The viscosity increased to levels where literally no material could flow out of the extruder die.)

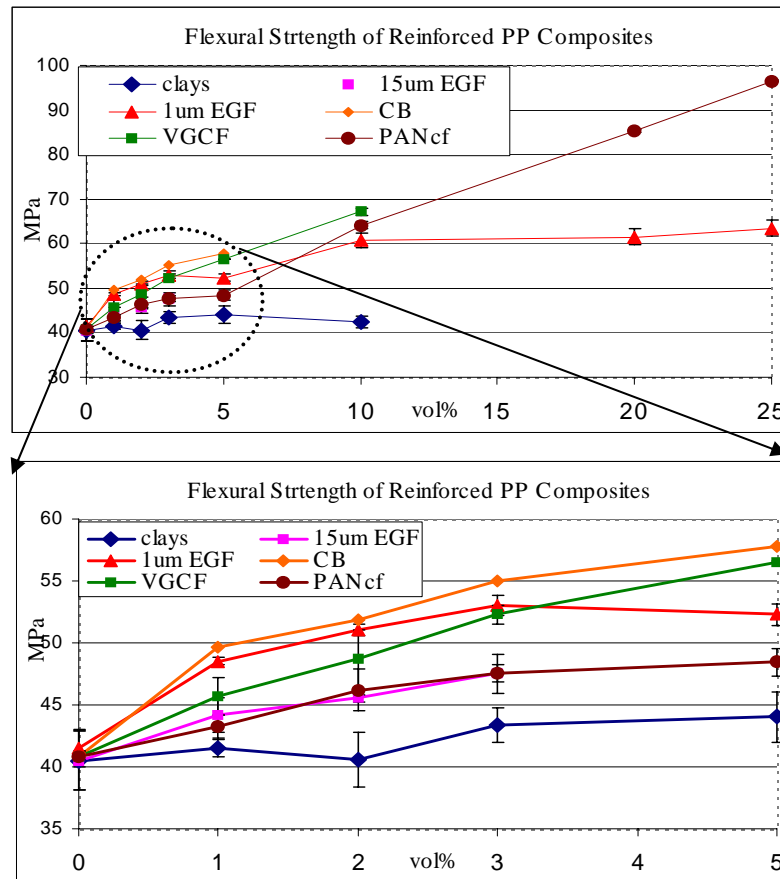


Fig. 3. Flexural strength of reinforced PP composites a) 0 to 25vol% and b) magnification of the area 0-5vol%

All the reinforcements used in this study improve the strength as shown in Fig. 3 but the carbon black had a more profound effect up to a loading of 5 vol% resulting in ~40% increase of the flexural strength compare to that of the neat polypropylene. VGCF composites (up to 5 vol%) show also similar improvement. At higher loadings both VGCF and PAN based CF show significant improvement of the strength. In particular, addition of 25 vol% of PAN based CF results in a strength increase of 135% while addition of the same amount of exfoliated graphite nano-platelets (1μmEGF) improves the strength only by 55%. Furthermore, it is noted that the nano-graphite strength curve reaches a plateau at ~10 vol% which indicates inadequate dispersion of the graphite nano-platelets in the polymer matrix. The same phenomenon is observed in the case of the nano-clays where the strength levels off at ~5 vol%

The key point in utilizing the superior properties of both graphite particles (1 μ m and 15 μ m EGF) in addition to sufficient exfoliation, which will result in separation into single or few layers of graphene sheets is an appropriate surface treatment, which will improve the adhesion to the polymer matrix, prevent agglomeration of the graphite nano-flakes resulting thus in a well dispersed system and in strengthening of the composite material. The montmorillonite clays are not compatible with most polymers due to their hydrophilic nature, and must be chemically modified to render their surface more hydrophobic. The most popular surface treatments are organic ammonium cations, which can be exchanged for the inorganic cations existing on the silicate surface [9]. The treated clay is then incorporated into the resin matrix either during polymerization or by melt compounding.

Fig. 4 shows the modulus of elasticity for the various polypropylene composites at loading levels of 0, 1, 2, 3, 5, 10, 20 and 25 vol%. As mentioned earlier, there are no samples with carbon black content larger than 5 vol %, and no samples with clays and VGCF with 20 and 25 vol%. 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). However, increasing the graphite nanoplatelet content results in further improvement of the modulus (520% at 25 vol%). PAN based CF and VGCF samples have a smaller effect on the modulus.

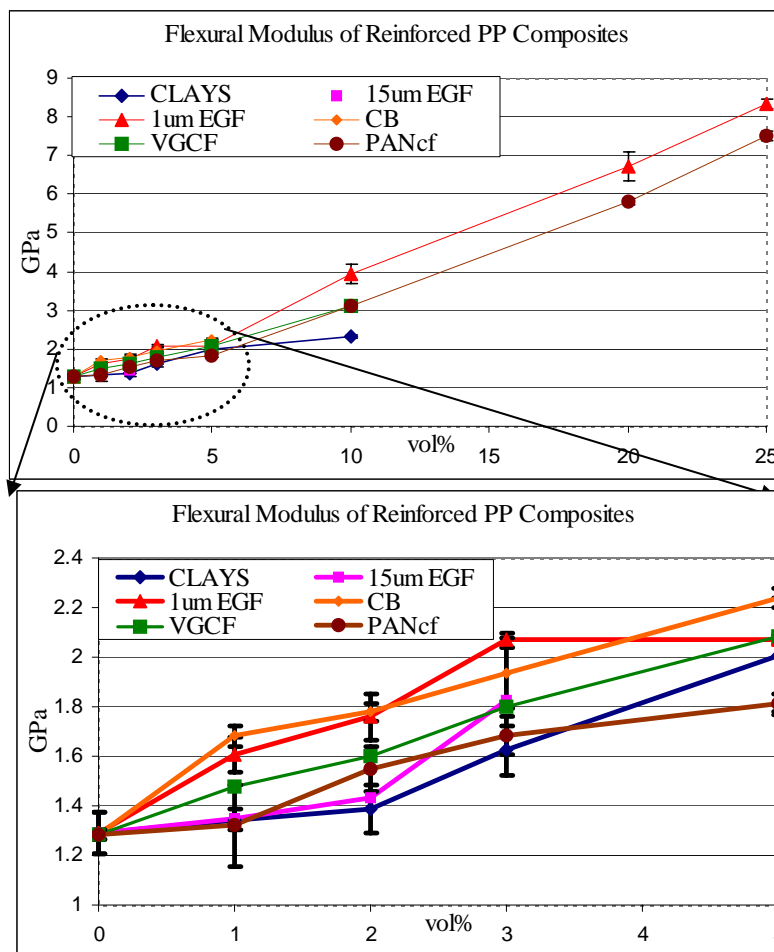


Fig.4. Flexural modulus of reinforced PP composites a) 0 to 25vol% and b) magnification of the area 0-5vol%

3.2 Mechanical Properties: Impact Strength

Impact resistance test (Izod type) was performed following ASTM D256 standard test method. Fig. 5 shows the impact strength for the various polypropylene composite systems at loading levels of 0, 1, 2 and 3vol%. The graphite used in these samples is 1 μ m EGF. As shown in Fig.5 the impact strength of the composites decreases with increasing reinforcement content. In more details, the carbon black reinforced polypropylene up to 3vol% has the same impact strength as the neat polypropylene. Both the 1 μ mEGF and VGCF increase the impact strength by 60% (at 3vol%) up to 100% (at 1vol%) compared to the neat polymer.

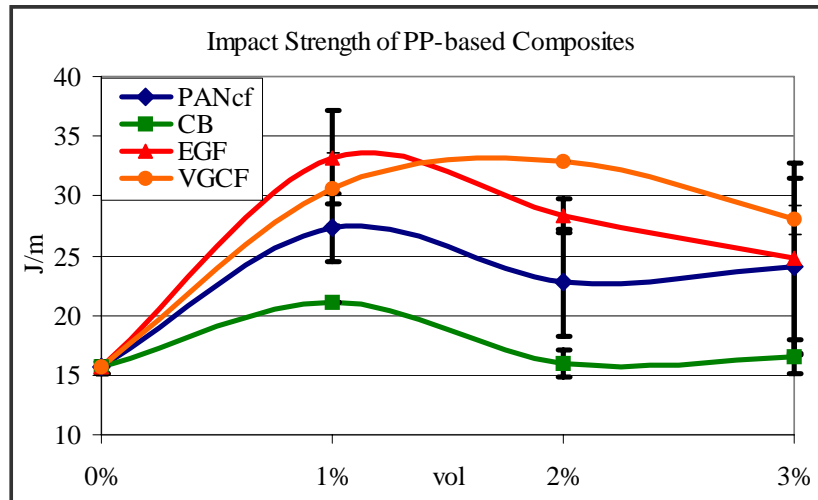


Fig. 5. Impact strength of polypropylene based composites

3.3 Flexural Properties: Compression versus Injection Molding

In order to explore the effect of the processing method i.e., injection versus compression molding, and the effect of processing conditions i.e., temperature of the mold (in injection molding) or cooling rate (in compression molding) on the mechanical properties of the nanocomposites, graphite-polypropylene and carbon fiber reinforced polypropylene samples were made using both methods and compared in terms of flexural strength and modulus.

In the case of the 15 μ m EGF-PP composites, the injection-molded samples were made using the DSM twin-screw extruder and the accompanying injection molding unit at the conditions described above. The compression molded samples were made in three steps: (i) the 15 μ m graphite was pre-mixed with the polypropylene in the DSM twin screw extruder for 3 minutes at 180 °C with a screw speed at 200rpm (ii) the material was pelletized under liquid N₂ and (iii) the composite pellets were compression molded (at 200 °C for 10 minutes no pressure applied and 200 °C for 10 minutes under pressure ~50.44tones/cm²). As shown in Fig.6 and 7 the injection-molded samples have a slightly higher flexural strength (~10%) and modulus (~35%) compared to compression molded samples and their difference increases with increasing graphite content. Since in both cases graphite and polypropylene are pre-mixed in the twin-screw extruder under the same conditions, the observed difference in the flexural properties is attributed to the alignment of the graphite flakes during the injection molding and to the presence of voids remaining after compression molding.

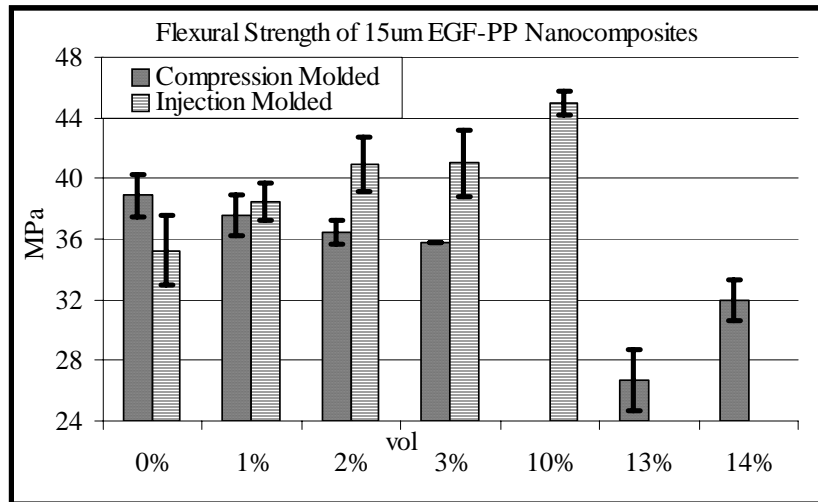


Fig. 6. Flexural strength of compression molded and injection molded polypropylene based composites

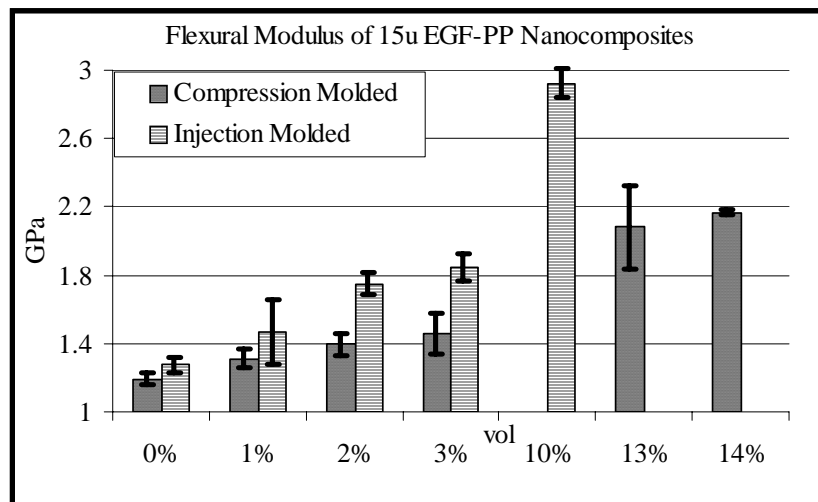


Fig. 7. Flexural strength of compression molded and injection molded polypropylene based composites

In the case of carbon fiber reinforced polypropylene composites the effect of both the processing method and the processing conditions on the flexural properties was studied by making samples using (i) injection molding at two different mold temperatures ($T_{\text{mold}}=40^{\circ}\text{C}$ and $T_{\text{mold}}=80^{\circ}\text{C}$) and (ii) compression molding at two different cooling rates (slow, $\sim 0.5^{\circ}\text{C}/\text{min}$ and fast $\sim 40^{\circ}\text{C}/\text{min}$ cooling rate). Samples were made using VGCF and PAN carbon fibers at 3 and 10vol% for each of the four conditions. The flexural strength and modulus of the fiber-reinforced polypropylene composites are given in Fig. 8a and 8b respectively. As expected the injection-molded samples show higher strength and modulus due to alignment of the fibers. Another major reason for the poor properties of the compression-molded samples is the presence of voids after compression. Voidformation can be avoided by performing the compression under vacuum so any trapped air is removed from the mold cavity and by keeping the sample at the mold temperature $T\sim 200^{\circ}\text{C}$ for longer times so that the material has sufficient time to melt and flow filling the mold completely. Although the compression molding process can be optimized, it may be difficult to produce composites with values of strength and modulus comparable to the injection molded ones.

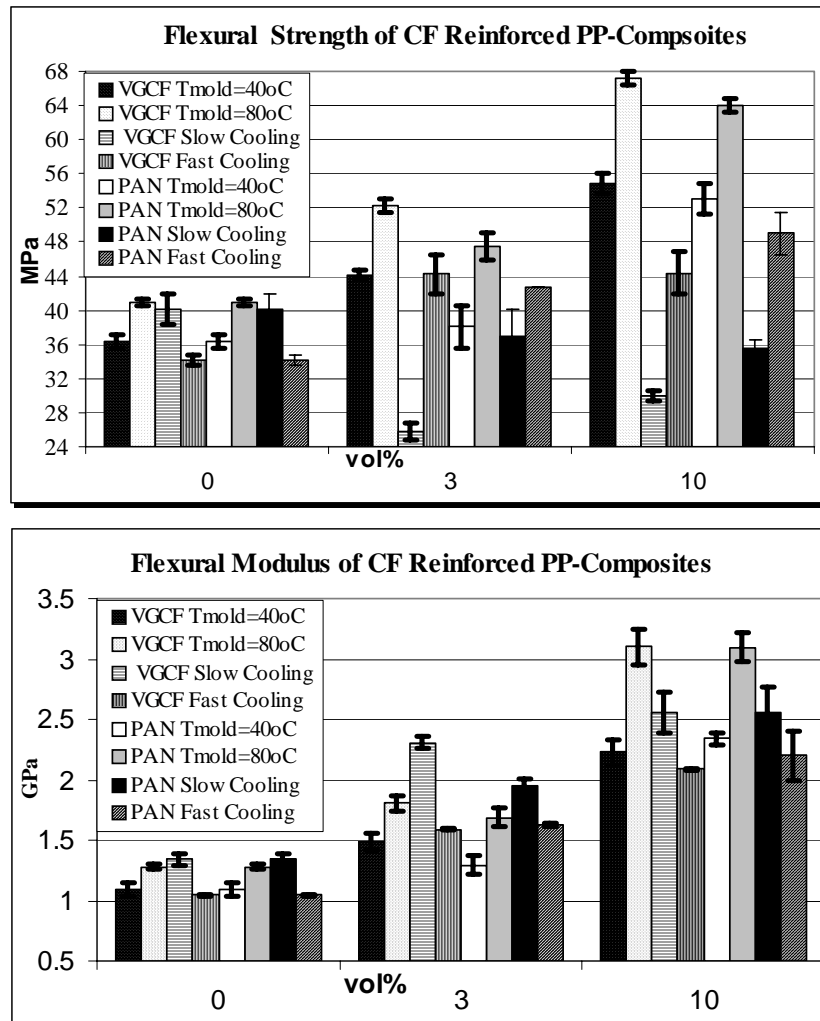


Fig. 8. Fiber reinforced polypropylene composites a) flexural strength and b) flexural modulus

The observed difference in the flexural strength and modulus of the pure polypropylene (0vol% in Fig.8a and 8b respectively) is probably due to the different degree of crystallinity or/and the different spherulite size. In the case of injection molded samples the lower the mold temperature is, the less time the material has before it solidifies so it is more amorphous and has lower strength and modulus. The same is true for the compression-molded samples that were cooled at fast rate. The difference between the neat polypropylene strength of the injection molded/high mold temperature and compression molded/slow-cooling rate samples is not statistically significant since there is overlapping of the error bars. The optimum processing condition for both VGCF-PP and PANcf-PP composites is injection molding with $T_{mold}=80^{\circ}\text{C}$.

3.4 Electrical Properties: Percolation Threshold and Electrical Conductivity

The electrical conductivity of the injection molded polypropylene based composites was measured along the flow direction using a three-probe method. Samples with dimensions of $5 \times 3 \times 12 \text{ mm}^3$ were cut from the middle of flexural bars, treated with O_2 plasma (10min, 550W) and gold coated to ensure good contact of the sample surface with the electrodes. The percolation threshold is defined as the minimum volume percent of the conductive reinforcement above

which the polymer composite becomes electrically conductive. The results are summarized in Fig. 9. The carbon black percolates at less than 2 vol%. The percolation threshold for the other reinforcements are, ~8 vol% for VGCF, 10 vol% for PAN based carbon fibers, and ~12 vol% for the 1 μ m exfoliated graphite nanoflakes. The same reinforcements were used with a thermoset matrix [3,4] and it was found that CB, VGCF and 15 μ mEGF percolate at less than ~3 vol%. It is noted that the carbon black used here is a special grade (KJ 600) that has a percolation threshold six times smaller than the regular carbon black fillers.

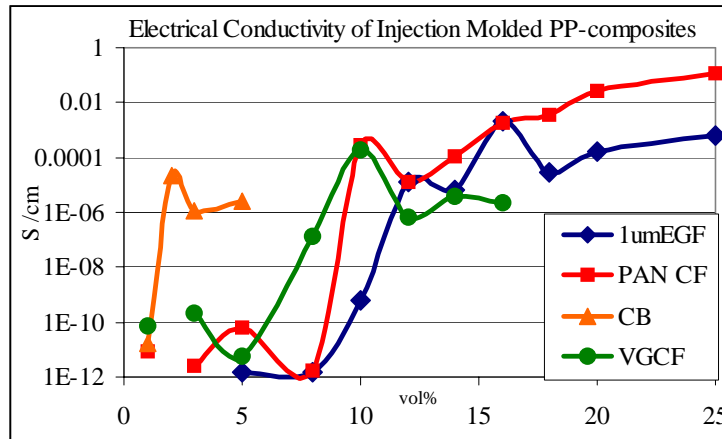


Fig. 9. Electrical conductivity and percolation threshold for polypropylene based composites

The difference in percolation threshold between the thermoset and the thermoplastic based composites might be explained by taking into consideration that the percolation threshold is the result of interactions of various parameters with the most important being the volume fraction, distribution, size, shape, orientation and spacing of the filler particles within the polymer matrix, as well as, the fabrication method of the composite. It has been shown [2], that the aspect ratio of the fillers is reduced after the composite is made due to the presence of high shear rates during the extrusion. Furthermore, it was observed [10] that there is orientation of the reinforcements along the flow direction. The particles are oriented during injection molding. The reduction of aspect ratio and the orientation of the reinforcement particles during the fabrication of thermoplastic composites explain partially the high percolation threshold observed in the thermoplastic systems.

4. CONCLUSIONS

The experimental values for the properties of the polypropylene nanocomposites determined during this study are much lower than the theoretical expected ones based on the reinforcing ability of the materials used. This indicates that a surface treatment of the reinforcements i.e., modification of the graphite's surface to become more compatible with the non-polar polypropylene matrix is required to achieve load transfer across the reinforcement-matrix interface a necessary condition for improving the mechanical properties of the composites. Furthermore, the effective utilization of nano-reinforcements in multifunctional composite applications depends strongly on the ability to disperse them homogeneously throughout the polymer matrix without destroying their integrity, i.e., reduction of the reinforcement's aspect ratio due to high shear rates in the twin-screw extruder.

It was found that the injection-molded samples have a higher percolation threshold and show a higher degree of improvement of mechanical properties compared to the compression molded ones. Both the lack of electrical conductivity at low loading levels and the superior mechanical performance of injection molded samples are contributed to the orientation of the reinforcements along the flow direction introduced during the injection molding, a hypothesis confirmed by ESEM study.

Flexural tests also show that nanocomposite materials made with the nanographite platelets have higher strength and modulus than composites made with nanoclays and commercially available carbon reinforcing materials. The superior mechanical properties of exfoliated graphite nanoplatelets combined with the low cost of crystalline graphite makes the graphite nano-flakes an attractive choice for commercial applications that require both mechanical strengthening and electrical conductivity of the final product.

ACKNOWLEDGEMENTS

Partial support for this research was provided by a grant from NASA LaRC, "Graphite Nanoreinforcements for Aerospace Nanocomposites" NAG1-01004, Thomas Gates, Program Director. The authors also thank Basel Chemical Company for providing the polypropylene resin, and UCAR Co. for providing the acid intercalated graphite compounds.

References

1. Giannelis, E.P., "Polymer Layered Silicate Nanocomposites", *Adv. Mater.* **8**/1, (1996), 29-35.
2. Clingerman, M.L., Weber, E.H., King J.A. and Schulz, K.H., "Development of an Additive Equation for Predicting the Electrical Conductivity of Carbon- Filled Composites", *Journal of Applied Polymer Science*, **88**, (2003), 2280-2299.
3. Fukushima H. and Drzal, L.T., "Graphite Nanoplatelets as Reinforcements for Polymers: Structural and Electrical Properties", Proceedings of The American Society for Composites, Seventeenth Technical Conference, (2002), 160-164.
4. Fukushima, H., "Graphite Reinforcements in Polymer Nanocomposites", PhD Dissertation, Michigan State University (2003).
5. Treacy, M.M.J., Ebbesen, T.W. and Gibson, J.M., "Exceptionally high Young's modulus observed for individual carbon nanotubes", *Nature* **381**, (1996), 678-680.
6. Saito, R., Fujita, M., Dresselhaus, G. and Dresselhaus, M.S., " Electronic structure of chiral graphene tubules", *Appl. Phys. Lett.* **60**/18 (1992), 2204-2206.
7. <http://www.fuentek.com/technologies/carbon-nanotubes.htm>
8. Tang, W., Santare, M. and Advani, S., "Melt processing and mechanical property characterization of multi-walled carbon nanotube/high density polyethylene (MWNT/HDPE) composite films" *Carbon* **41** (2003) 2779-2785.
9. <http://www.plasticstechnology.com/articles/199906fa4.html>
10. Kalaitzidou, K., Fukushima, H., and Drzal, L.T. "Graphite Nanoplatelets as Nano-Reinforcements for Polymers: Comparison between a Thermoset and a Thermoplastic Matrix", Proceedings of The 14th International Conference for Composite Materials, Technical Conference, San Diego CA, (2003).