Article

A Route for Polymer Nanocomposites with Engineered Electrical Conductivity and Percolation Threshold

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Abstract: Polymer nanocomposites with engineered electrical properties can be made by tuning the fabrication method, processing conditions and filler's geometric and physical properties. This work focuses on investigating the effect of filler's geometry (aspect ratio and shape), intrinsic electrical conductivity, alignment and dispersion within the polymer, and polymer crystallinity, on the percolation threshold and electrical conductivity of polypropylene based nanocomposites. The conductive reinforcements used are exfoliated graphite nanoplatelets, carbon black, vapor grown carbon fibers and polyacrylonitrile carbon fibers. The composites are made using melt mixing followed by injection molding. A coating method is also employed to improve the nanofiller's dispersion within the polymer and compression molding is used to alter the nanofiller's alignment.

1. Introduction

Recently, there is an increased interest in using conductive materials such as carbon black (CB) [1], vapor-grown carbon fibers (VGCF) [2,3], carbon nanotubes [4–7], as well as graphite [8–11], as reinforcements for polymers due to their superior thermal and electrical properties. Conductive composites can be used in place of metals when properties such as weight, toughness and corrosion resistance are required. An electrically conductive material can be used for dissipation of static charge, imparting electrically conductivity for applications such as electromagnetic and radio frequency shielding as well as protection against lightning strikes in aircraft, battery components, power cables and even membrane in fuel cells.

The two important properties in electrically conductive composites are the electrical conductivity, which depends mainly on the filler volume fraction, and the percolation threshold, defined as the minimum volume content of the filler, above which the filler particles form a continuous network, as described by percolation theory [12], at which point the composite becomes electrically conductive.

In order to utilize a material as conductive filler, it is necessary to identify each one of the factors that affect the percolation threshold and conductivity of composites, study them independently, and fully understand the mechanisms and interactions or synergistic phenomena at the nanoscale. These factors are [13–15]: the conductivity of the constituents, the volume fraction and filler characteristics such as size, shape, surface area and morphology, the distribution and orientation of the filler as well as the interparticle filler spacing within the polymer matrix and the crystallinity of the matrix [16]. Many of the above factors depend on the processing method and conditions used to fabricate the composites.

Design of electrically conductive composites can start with the use of theoretical models that can predict and describe the percolation threshold and electrical conductivity as a function of all the factors mentioned above. However, as mentioned in a review study [17] none of the proposed models, which can be classified in the following main categories, is generally valid. These categories are: (i) statistical, which are using percolation theory and predict the conductivity based on the probability of particle contacts within the composite *i.e.*, models proposed by Kirkpatrick [18], Zallen and McLachlan [19], (ii) thermodynamic models that take into account the filler and polymer surface energies as well as the polymer melt viscosity *i.e.*, the model proposed by Mamunya *et al.* [20], (iii) geometric models which proposed to predict the conductivity of sintered mixtures of conducting and insulating powders and take into account the diameter of the nonsintered particles or the edge length of the sintered ones, and (iv) structure-oriented models that account for structural properties such as aspect ratio and filler orientation, which are a result of the composite processing techniques *i.e.*, model proposed by Nielsen [21]. These models have limitations because they do not consider all the key factors that affect the conductivity and/or they contain empirical parameters that cannot be measured experimentally and need to be assumed or calculated for each filler-polymer system.

The objective of this research is to experimentally determine the effects of all the factors discussed above on the electrical conductivity and percolation threshold of polymer nanocomposites in order to identify the shortcomings of the existing theoretical models and lead to nanocomposites with engineering electrical properties. In particular, the percolation threshold and the electrical conductivity of carbon reinforced PP composites are determined for: (i) different filler characteristics such as

conductivity, size, shape aspect ratio and surface area, (ii) different conditions of filler orientation/alignment *i.e.*, injection versus compression molding and, (iii) various compounding methods *i.e.*, melt-mixing, polymer solution and a coating method where polymer powder is coated with individual filler particles, (iv) different crystallization characteristics of the matrix.

2. Results and Discussion

2.1. Effect of Filler Characteristics

The electrical conductivity of carbon reinforced PP composites, made by melt mixing and injection molding, as a function of the filler content is shown in Figure 1. The percolation threshold varies with filler composition starting at less than 2 vol % for CB, 5–8 vol % for VGCF, 8–9 vol % for xGnP-1 and xGnP-15, followed by 8–10 vol % for PAN based carbon fibers. The only difference between xGnP-1 and xGnP-15 is their diameter which is ~1 micron and 15 microns respectively.

Figure 1. Electrical conductivity of carbon reinforced PP composites as a function of the filler loading.
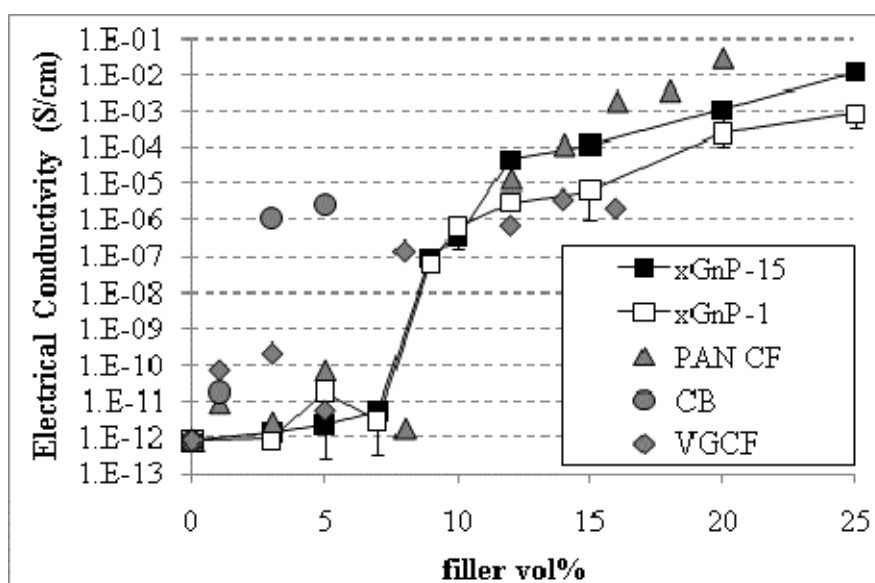

For spherical particles (e.g., CB), at constant volume fraction, the interparticle distance increases with increasing diameter such that it becomes more difficult to form a conductive pathway (13, 14). Thus, it was anticipated that CB should have a high percolation threshold. However, the CB used in this study does not consist of individual spherical particles but is a highly agglomerated ('highly structured') carbon black with a high degree of porosity having a surface area of 1400 m^2/g [22], that allows for polymer penetration. It can create a conductive network by occupying a large occluded volume at low concentrations [23] and by eliminating many of the particle-polymer interfaces as a result of its aggregated structure.

For non-spherical particles (e.g., fibers, platelets), as the aspect ratio of the conductive fillers increases the critical concentration to induce bulk conductivity in the composite decreases significantly [4]. That is, the large aspect ratio particles can still maintain point-to-point contact at low

concentrations, which allows electron conduction through the particle and tunneling between particles thus decreasing the percolation threshold. The effect of aspect ratio on lowering the percolation threshold can be seen in Figure 1 for carbon fibers *i.e.*, VGCF with an aspect ratio of ~350–650 have a percolation threshold of 5–8 vol % while the corresponding value for the shorter PAN carbon fibers (aspect ratio of ~24) is in the range of 8–10 vol %. It is noted that the lower percolation threshold of VGCF-PP composites is a result of the synergistic effect of the high aspect ratio, the highly convoluted, entangled morphology, and the lower electrical resistivity of VGCF of ~55 ohm cm compared to that of PAN (1400 ohm cm) [24] and xGnP (100 ohm cm) [24].

According to Figure 1 it seems that there is no effect of xGnP's aspect ratio on the percolation threshold since both xGnP-1 (aspect ratio ~100) and xGnP-15 (aspect ratio ~1500) percolate at 8–9 vol %. The minimal effect of aspect ratio on the percolation threshold results from the less than optimal mixing in the small extruder during melt mixing which is incapable of optimally dispersing the xGnP-15 agglomerates. In addition, a morphological study of xGnP-15/PP composites shows that a large fraction of the xGnP-15 platelets do not maintain their platelet geometry but they often have a bent, buckled and "rolled-up" morphology which reduces their aspect ratio [25]. Representative ESEM images of xGnP-15/PP microstructures illustrating the agglomerated and "roll-up" structures are shown in Figure 2a and 2b respectively.

Figure 2. ESEM images of fracture surface of 1 vol % xGnP-15/PP (a) xGnP-15 agglomerates (scale bar 50 μm) and (b) xGnP-15 "roll-up" (scale bar 5 μm).
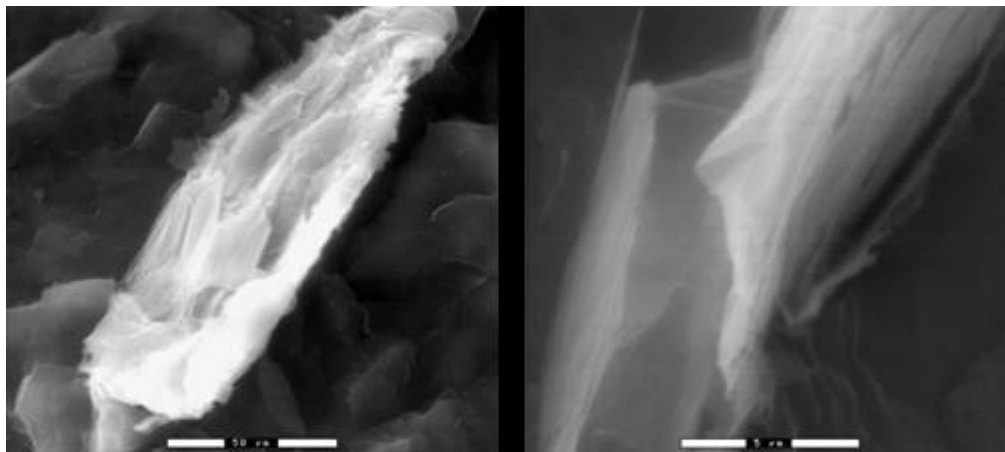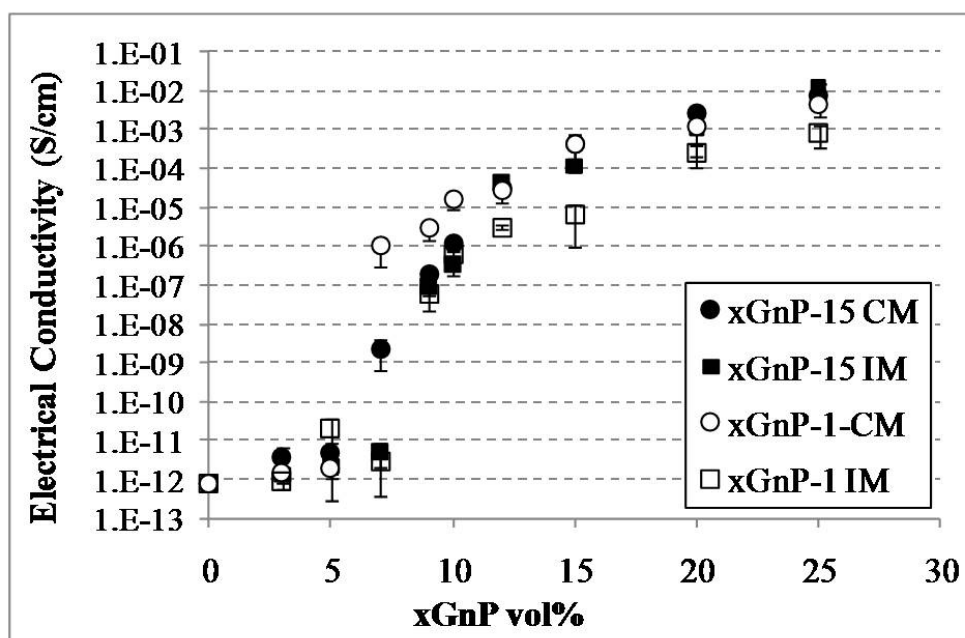

2.2. Effect of Filler Orientation

The xGnP orientation in the polymer matrix is another factor affecting the percolation threshold and electrical conductivity of the composites. In order to investigate this effect and alter the orientation conditions during 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 is shown in Figure 3. As discussed earlier the xGnP aspect ratio has little effect on the composite conductivity. The electrical conductivity of both the xGnP-15 and the xGnP-1 IM samples begin to increase at ~7 vol %, while the corresponding value for the CM samples is ~5 vol % for both types of xGnP. Injection molding introduces filler alignment along the flow direction as confirmed by ESEM morphological study [25,26]. Initially the platelets are

aligned parallel to each other along the flow direction and only at higher loading levels will they start intersecting with each other and form a conductive path as shown schematically in Figure 4. In case of compression molding the lack of preferred filler orientation facilitates the formation of the conductive network and thus lowers the percolation threshold. This claim is in agreement with previous studies where it was reported that CB-PP composites have a percolation threshold of 5 and 10 wt % when made by compression and injection molding respectively [27].

It is noted also that the xGnP-15-PP composites show a slightly higher conductivity than the xGnP-1-PP composites at higher loadings (>12 vol %). This can be attributed to the presence of fewer but larger xGnP platelets for the xGnP-15 as compared to the xGnP-1, thus reducing the number of xGnP-PP interfaces and therefore reducing the contact resistance.

Figure 3. Effect of filler orientation on the percolation threshold and conductivity of xGnP-PP nanocomposites.


Figure 4. Schematic representation of filler distribution in the polymer matrix: (a) filler orientation along the flow direction in injection-molded specimen, and (b) random filler orientation in a compression-molded specimen.
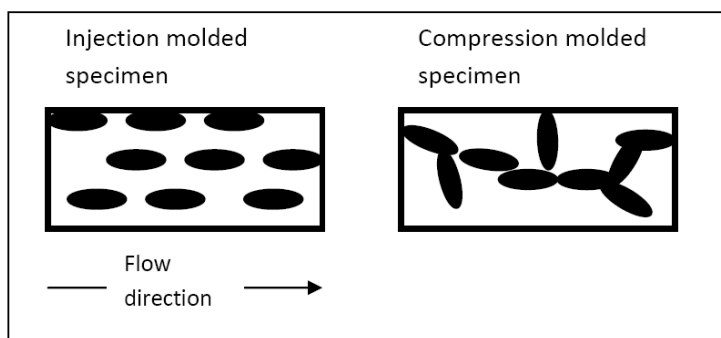
2.3. Effect of Filler Anisoptropy

When asymmetrical conductive fillers such as fibers or platelets are used, it is expected that both the percolation threshold and the conductivity of the composites will vary directionally. In all of the above cases, the conductivity was measured along the flow direction *i.e.*, along the fiber axis or parallel to the graphite plane. In order to investigate how the percolation threshold and conductivity vary due to filler anisotropy, samples were fabricated by melt mixing and injection molding using stainless steel molds of different geometry. One mold has a rectangular geometry (flexural bar) with dimensions of $3.2 \times 12.3 \times 63.5$ mm^3 and the other mold has a disk-shape geometry with a diameter of 25 mm and thickness of 1.5 mm. The gate location for the two molds and the direction along which the resistivity was measured, indicated by the arrows, are shown in Figure 5.

Figure 5. Schematic of molds used to explore the effect of xGnP anisotropy. The red arrow shows the direction of measurement (a) along the flow direction, parallel to the graphite plane and (b) normal to the flow, parallel to graphite c-axis.
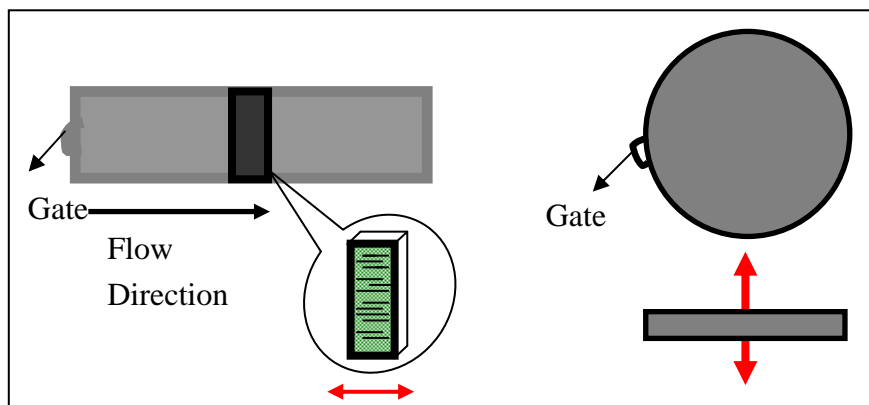

The electrical conductivity results are shown in Figure 6. The disk shape samples show higher percolation threshold (9 vol % for xGnP-1 and 10–12 vol % for xGnP-15) and lower conductivity, which is expected since in these samples the conductivity is measured through the plane, *i.e.*, along the c-axis of the graphite plane. The graphite platelets orient along the flow front, pictured with the white dotted lines in the schematic of Figure 7, created during the filling of the disk-shape mold. The orientation of xGnP along the flow front and parallel to each other in the sample's thickness direction is also confirmed by ESEM as shown in Figure 7. At low concentrations the distance between the graphite platelets is large especially in the case of xGnP-15; since due to their large size the number of platelets contained in a given xGnP volume is smaller compared to xGnP-1 which explains the higher percolation threshold of xGnP-15 in the disk samples. The distance between the platelets will be small enough to allow electron tunneling or the platelets will start touching forming a conductive network only at higher loadings. It is noted that the electrical conductivity of graphite along the plane is ~10^4 ohm^{-1}cm^{-1} whereas along the c-axis is much lower *i.e.*, ~1 ohm^{-1} cm^{-1} [24].

Figure 6. Effect of filler anisotropy on the percolation threshold and conductivity of x GnP-PP nanocomposites.
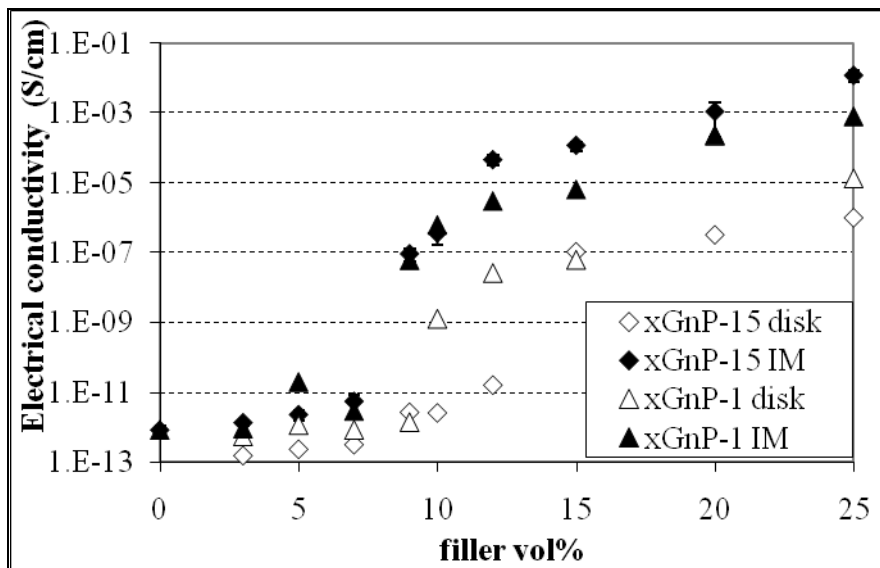
Figure 7. Orientation of xGnP in a disk shape xGnP-15/PP, (a) ESEM image (scale bar 450 μm) (b) schematic representation of the xGnP orientation along the flow front.
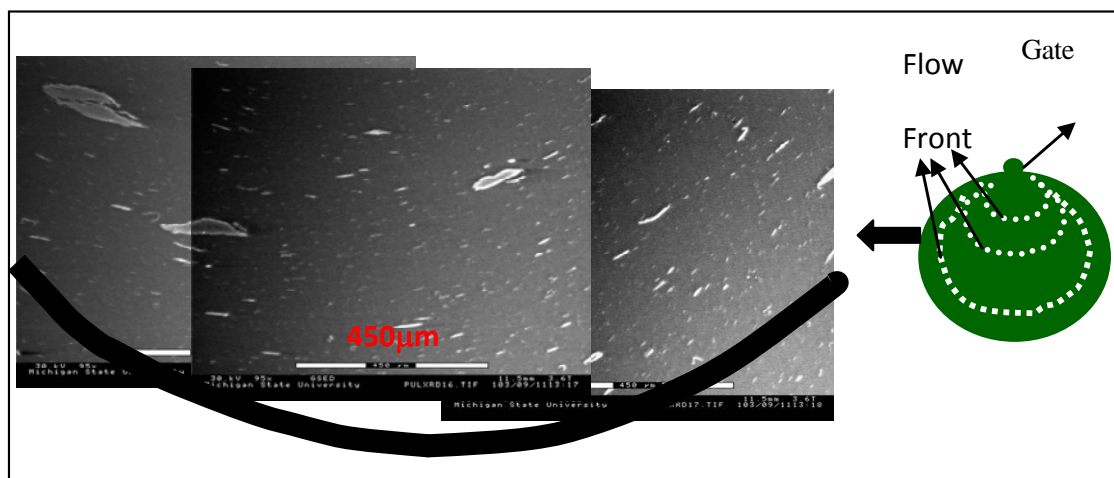

2.4. Effect of Compounding

The fabrication method and processing conditions of the composites play an important role in the percolation threshold and conductivity since they affect the orientation, dispersion and interparticle spacing within the polymer matrix and they may alter the filler's aspect ratio or enhance the interactions between filler and matrix. The effect of the three compounding methods; (i) melt mixing, (ii) polymer dissolution and (iii) coating (premixing) of the PP powder with xGnP-1, on the percolation threshold and electrical conductivity of xGnP-1-PP composites is shown in Figure 8. All the samples were compression molded using a rectangular shape mold and the electrical conductivity was measured in the direction parallel to the sample's length. As shown the conductivity of xGnP-1/PP composites made by the coating compounding method is as high as 10^{-3} S/cm at a loading of 3 vol %,

indicating that the percolation threshold is much lower. In case of composites with 5 vol % xGnP-1 the coating compounding method results in conductivity higher than the conductivity of the solution processed samples. This indicates that the coating 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 coating there are no aggregates of xGnP due to the use of sonication and the homogeneous coating of PP powder by xGnP. When the polymer melts in the mold the xGnP platelets move along on the surface of the melting particle. However during the solution process xGnP aggregates may exist and in addition, the xGnP will be completely coated with dissolved PP. When the solvent evaporates the particle coating remains intact and prevents xGnP to xGnP contact reducing the ability to form low resistance contacts, which are necessary to form a low percolation network.
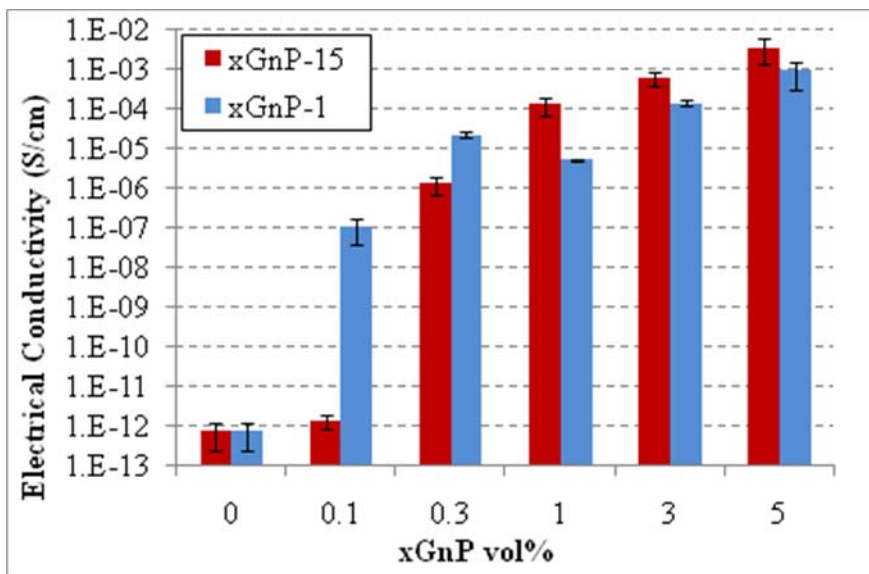
Figure 8. Effect of compounding on the percolation threshold and conductivity of xGnP-1-PP nanocomposites made by compression molding.
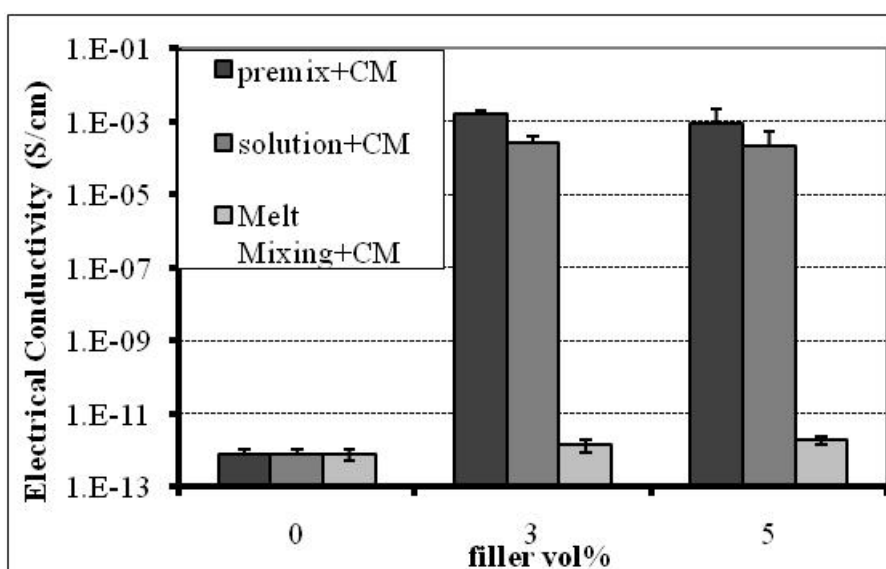

Composites with lower xGnP content were made by coating and compression molding using both 1 and 15 μm xGnP in order to determine the percolation threshold. As indicated in Figure 9 xGnP-1 has a percolation threshold of 0.1 vol % while the corresponding value for xGnP-15 is 0.3 vol % using the coating method. The larger aspect ratio particles did not have the lower percolation threshold as it was expected according to the percolation theory. This is the result of the fewer number of xGnP-15 particles ~225X compared to xGnP-1 particles at the same volume fraction. The PP powder is coated more effectively if there are more and smaller particles rather than fewer larger ones.

Figure 9. Percolation threshold and electrical conductivity of xGnP/PP nanocomposites made by coating (premixing) and compression molding.

Figure 10. Effect of compounding on the percolation threshold and conductivity of xGnP-15-PP made by injection molding.
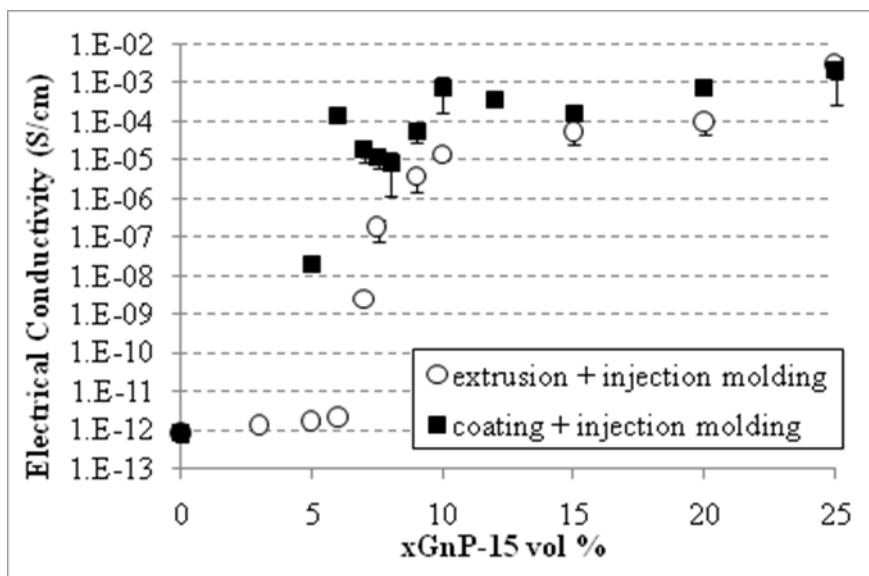
It is evident that combination of the coating and compression molding yields composites with a vastly lower percolation threshold and higher conductivity. However, it is of practical interest to explore what is the effect of coating followed by injection molding. Composites were made using (i) melt mixing and injection molding and (ii) coating, melt mixing and injection molding, since it is not practical to injection mold the coated PP powder without passing it first through the extruder. Figure 10 indicates that the coated samples followed by melt mixing and then injection molding have a percolation threshold less than 5 vol % while the melt mixed ones followed by injection molding have a percolation threshold ~7 vol %. As the xGnP content increases the difference in electrical conductivity of the composites made with the two methods decreases. The reason that the percolation

thresholds is much higher than for compression molding is that coating starts with a well dispersed system of xGnP particles which is then disturbed during the extrusion/injection molding phase.

2.5. Effect of Polymer's Crystallinity

The crystallinity of the PP matrix may also affect the conductivity of the composites. A highly crystalline matrix may force the conductive particles to the outside of the crystallites resulting in the formation of the continuous conductive path compared to a less crystalline polymer or amorphous polymer where a more homogeneous particle distribution may result [16] in higher percolation threshold. In addition to the degree of crystallinity, other crystallization characteristics of the polymer matrix such as the crystal morphology and the number and size distribution of the spherulites might also affect the electrical conductivity and percolation threshold [28].

The crystallization of the PP matrix was altered by using different cooling rates after compression molding of the specimens was completed. The coating method was used for compounding of xGnP-1 and xGnP-15 with PP. Two extreme cases were used i) fast cooling (fc) at a rate of ~20 °C/min and ii) slow cooling (sc) at a rate of ~0.3 °C/min. In both cases the slowly cooled composites had lower percolation threshold (~0.1 vol % for xGnP-1 and between 0.3 and 0.5 vol % for xGnP-15) as shown in Figure 11.

Figure 11. Effect of cooling rate (crystallization behavior of polymer matrix) on the electrical conductivity of xGnP/PP nanocomposites made by coating (premixing) and compression molding).
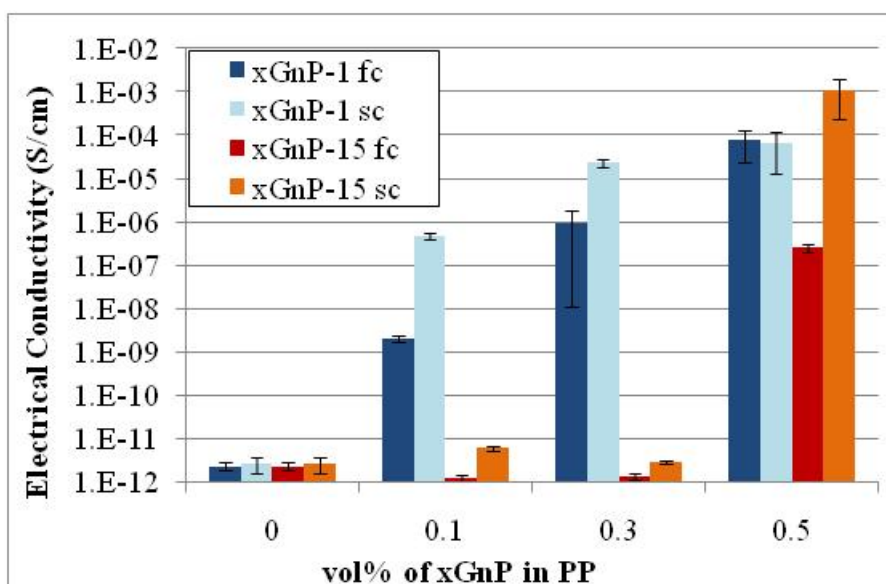
As reported in our previous study [28], xGnP is a nucleating agent for PP, the crystals grow around the platelets and that although the crystallization behavior of PP is altered upon addition of xGnP the degree of crystallinity remains constant. The number of spherulites increases and their size decreases with the number of graphite platelets available for nucleation. In case of xGnP-15 there are far fewer platelets at a given volume of graphite compared to xGnP-1 and since they act as nucleating sites, more xGnP-15 platelets are confined and isolated in the center of the spherulites and thus they are not

available to form the percolated conductive network resulting in composites with higher percolation threshold. For a given type of xGnP the percolation threshold can be lowered by using slow cooling rate during the xGnP-PP fabrication because during slow cooling the crystallization takes place at higher temperatures and the final crystal structure consists of larger but fewer spherulites. This means that fewer platelets are isolated in the spherulite center and thus more are available to form the conductive network [28].

3. Experimental Section

Powdered PP (Basell, Pro-fax 6301: melt flow index 12 g/10 min, ASTM D1238) was used as the matrix for all composite specimens prepared in this work. The carbon reinforcements used are (i) PAN based carbon fibers (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). In addition, exfoliated graphite nanoplatelets, were also used.

The graphite nanoplatelets, now available commercially as xGnP™ by XG Sciences, East Lansing MI, were prepared as follows: Sulfuric acid-based intercalated graphite (UCAR International Inc.,) is heated in a microwave oven and the entrapped intercalants vaporize as a result of the coupling of the conductive graphite to the microwave radiation. The graphite flake particles undergo significant expansion (~500 times) obtaining a worm-like or accordion-like expanded structure. This structure is broken down to individual graphite sheets by pulverization using an ultrasonic processor resulting in graphite nanoflakes that are less than 10nm thick and have a diameter of ~15 μm, 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 1 μm, xGnP-1. These two types of xGnP are used in order to investigate the effect of the reinforcement's aspect ratio on the percolation and electrical conductivity of polymer nanocomposites. The thickness of xGnP, which is the same for both xGnP-1 and xGnP-15, was determined using TEM and it was found that each platelet consists of more than 10 graphene sheets. Taking into account that the basal plane distance of graphite is 0.335nm [29] it is estimated that the average thickness of the graphite nanoflakes is ~5nm with a distribution of platelets having thicknesses in the nanometer range expected.

Three compounding methods followed by injection or compression molding were employed to fabricate the composites. These are: melt mixing, polymer solution and a coating method. A DSM Micro 15cc Compounder, (vertical, co-rotating twin-screw microextruder) and a Daca Micro Injector system were used for melt mixing and injection molding. The processing conditions used are mixing time=3 *min*, T_{barrel}=180 °C, T_{mold}=80 °C, screw speed= 245 rpm, T_{barrel}=180 °C and injection pressure of 160 psi which were the optimum based on a design of experiments study (2^3 factorial design).

In the polymer solution method [30,31], the xGnP is dispersed in xylene using sonication for 2 hrs and the PP is dissolved in refluxing xylene at 130 °C for 0.5 hrs. The graphite suspension was added drop wise to the PP solution and after refluxing for 1.5 hrs it was filtered. After cooling to about 70 °C, acetone was added to the solution and the polymer solution precipitated. The precipitate was filtered and dried in vacuum oven. The resulting composite powder was compression molded.

In the coating method [25], PP powder was coated with xGnP in a non-solvent liquid system. In particular, the xGnP is dispersed in isopropyl alcohol by sonication (18–20 W) for 1 hr at room temperature. The PP powder (spherical particles with an average diameter of ~300 μm) is added to the suspesnion and sonication is continued for 0.5 hrs. Finally, the solvent is evaporated at 80 °C resulting in complete coverage of the powder particles with the xGnP. This is the only method out of the three compounding methods used in this research to insure that the large platelet morphology of xGnP can be preserved in the final composite.

The conditions used for compression molding are 200 °C for 20 minutes with no pressure applied and followed by 20 minutes at 200 °C under pressure of ~137 MPa. During the compression molding vacuum was applied to remove any trapped air. The effect of polymer's crystallization behavior on the percolation threshold and electrical conductivity of the nanocomposites was investigated by using two different cooling rates 0.3 and 20 °C/min after compression molding. The slow cooling rate was accomplished by cooling the molded specimens on the hot press overnight whereas the fast cooling rate was accomplished by using dry ice.

The resistivity of carbon reinforced PP composites *i.e.*, xGnP-1/PP, xGnP-15/PP, CB/PP, VGCF/PP and PAN/PP, was measured along the flow direction for the injection-molded samples, using impedance spectroscopy by applying the two-probe method at room temperature. Each data point is the average of 3 to 5 measurements and error bars are employed to describe the scatter of the data. Samples with dimensions of $3.2 \times 5 \times 12.3$ mm^3 were cut from the middle portion of flexural bars, and the resistivity was measured along the width direction (5 mm). The two surfaces that were connected to the electrodes were first treated with O_2 plasma (10 *min*, 550 W) in order to remove the top surface layers which are rich in polymer and then gold coated to a thickness of 1–2 nm to ensure good contact of the sample surface with the electrodes. The resistance of samples was measured over the frequency range of 0.1 to 100,000 Hz and converted to conductivity by taking into account the sample dimensions. 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 20–30 kV.

4. Conclusions

This detailed experimental study demonstrated the complex dependence of percolation threshold and electrical conductivity of thermoplastic composites on a variety of factors, including filler characteristics (shape, aspect ratio, and morphology), and fabrication/processing conditions, which affect the filler's distribution and orientation and the filler-matrix interactions. It was also concluded that the crystallization characteristics of the polymer, which can be tuned using the proper processing conditions (cooling rate during molding), strongly affect the percolation threshold of composites. This is the first time such an effect is reported.

Composites made by melt mixing and injection molding show a higher percolation threshold because of limitations in the ability of the melt mixing equipment to disperse the xGnP and maintain their platelet type morphology. Furthermore, injection molding creates morphology with preferential alignment of the platelets along the flow direction. As a result, no improvement in electrical conductivity resulting from the effect of larger xGnP aspect ratio was detected.

It is concluded that in order to reduce the percolation threshold in PP composites and induce electrical conductivity with low filler content, the composites should be made using the coating method followed by compression molding and small cooling rates (slow cooling). If injection molding has to be used, then either multiple gates should be used to assure alignment of the filler along various directions and formation of a random network, or the design of the gate should be such to allow the flow direction to be parallel to the desired direction of conductivity.

The results obtained in this study can be the basis for developing a predictive model and/or more realistic assumptions for simulation studies on electrically conductive composites.

Acknowledgements

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