

Exfoliated Graphite Nanoplatelet (xGnP) /Polypropylene Nanocomposites

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Abstract

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 new filler, exfoliated graphite (~10nm thickness) has shown that nanoreinforcement concentrations of up to 10 vol% in thermosets and 25 vol% in thermoplastics are easy to achieve and appropriate processing can result in composites with the best mechanical, thermal and electrical properties. Research is to explore the fabrication method and processing conditions via factorial design of experiments, and how they influence the properties of exfoliated graphite nanoplatelet (xGnP)/PP nanocomposites. A significant development is a new compounding method, i.e., premixing of xGnP and PP powder in isopropyl alcohol using sonication to disperse the xGnP by coating individual PP powder particles prior to compression molding. This premixing method is more effective than the widely used melt compounding method, in terms of lowering the percolation threshold of thermoplastic nanocomposites (NC) and enhancing the probability that the large platelet morphology of xGnP can be preserved in the final composite. The flexural strength and modulus of pellet-type PP/xGnP-1 NC was higher than that of powder- or flake-type PP/xGnP-1 NC. In the electrical conductivity study, the percolation threshold of the flake and the pellet type PP is only 0.6 wt% of xGnP-1. This lower percolation threshold is due to network formation of xGnP on the surface of PP. The results of this study provide a fundamental understanding of how the processing and resulting distribution of xGnP within the final composite can affect the physical and mechanical properties of xGnP/PP nanocomposites.

1. INTRODUCTION

Graphite flakes have been known as host materials for intercalated compounds. By applying rapid heating some of the graphite-intercalated compounds (GIC) expanded and a significant increase in volume takes place. Many literature citations identify the expanded graphite flakes with polymer systems for 'lightweight and conductive polymer composites' [1-3]. EG consists of a large number of delaminated graphite sheets [4, 5]. Epoxy composites containing 1–2 wt% of EG were fabricated by sonication, shear, and a combination of sonication and shear mixing methods [6]. Shioyama [7] reported the improved exfoliation at weight fractions of graphite below 1 wt% through polymerization with vaporized monomers such as styrene and isoprene.

PP is one of the most widely used polymers. It is an attractive material because of its combination of mechanical properties, ease of processing and low cost. This research explores modification of PP through the addition of xGnP with ~10nm thickness and ~1um diameter which is a new multifunctional material developed at MSU [16] and is a promising additive capable of producing new and desirable multifunctional properties in PP. The main fabrication method used to produce PP/xGnP nanocomposites is melt mixing-injection molding [17].

Generally, the preparation of nanocomposites by melt blending is performed either with a batch mixer [8-10] or an extruder [11, 12]. Gopakumar et al. reported that PP/EG nanocomposites (NC) using a thermo-kinetic mixing (Gelimat) method [13]. In a Gelimat, blades on a high speed shaft accelerate the particles and impart to them high kinetic energy, which is converted to thermal energy when they hit the chamber wall [14]. Page et al. studied PP/EG by melt mixing using maleated PP (PP-g-MA) as compatibilizing agents. Melt mixing was achieved using a Gelimat, a high-speed thermo-kinetic mixer. The PP-g-MA helped the dispersion of the graphite on a nano-scale and improved flexural properties and more significantly the impact strength of the material [15].

The focus of this research is to investigate the xGnP reinforced thermoplastics PP nanocomposites. The approach is to fabricate xGnP / PP NC with different raw PP, xGnP and mixing processing and to determine their effects on the properties and the nanostructures in xGnP /PP NC. The flexural and tensile properties, impact strength, electrical conductivity and percolation threshold of the xGnP /PP NC are discussed. Various fabrication methods were explored to prevent the agglomeration of the xGnP and understand the effect of the processing conditions including injection and compression molding on the various properties of the nanocomposites.

2. EXPERIMENTAL METHODS AND CHARACTERIZATIONS

2.1 Materials

Polypropylene (PP): SunAllomer PP-PM 900A (pellet type), Basell -Pro-Fax 6301 (flake type i.e., a small pellet) and Equistar-FP 809-00 (micro powder type), respectively. Graphite: GrafGuard 160-50A- the UCAR GrafTech, Inc.

2.2 Preparation of the xGnP

xGnP was prepared via the usual Michigan State University (MSU) exfoliation method and further downsized by pulverization process to produce xGnP [16] in sizes of 1 μm and 15 μm for compounding into the PP nanocomposites. The former is designated as xGnP-1 and the latter as xGnP-15. xGnP from different sources is produced by a processing method consisting of rapidly heating the intercalated graphite causing the entrapped intercalants to vaporize causing the graphite flake particles to undergo significant expansion. This exfoliation process results in a worm-like or accordion-like expanded structure. Their size of the exfoliated graphite nanoplatelets can be further reduced by ultrasonication, resulting in nanoplatelets with thicknesses of less than 10nm and with diameters less than 15 μm . In this way, many types of graphite nanoplatelets having differing lateral dimensions are produced.

2.3 Melt compounding of injection molding

The basic fabrication method used in this research is melt mixing through a twin-screw extruder followed by injection molding. The PP pellet and xGnP powder were mixed mechanically for about 1 min and then were melt-compounded at 190 $^{\circ}\text{C}$ for 3-5 minute at 200 rpm with a DSM micro-compounding molding equipment (DSM Micro 15 cc compounder, DSM research, Netherlands, twin screw mini extruder with injection molder). The mini extruder is equipped with a screw having a length of 150mm, L/D 18, net capacity 15 cm^3 . After extrusion, the melted hybrid samples were transferred through a preheated cylinder to the mini injection molder (pre-set to the desired temperature) to obtain the sample specimens for various measurements and analysis. The processing conditions used such as the temperature of the

barrel, the screw speed, the processing time and the temperature of the mold were optimized using factorial design of experiments.

2.4 Pre-coated compounding

An alternative processing method is premixing of graphite and polypropylene in a dispersant such as isopropyl alcohol as a new compounding method developed in our lab. The xGnP is dispersed in isopropyl alcohol (IPA) by sonication at room temperature. The PP particle is added to the suspension and sonication is continued for 30 minutes. Finally, the solvent is evaporated at 80°C resulting in complete coverage of the powder particles with the xGnP. Alternatively, the isopropyl alcohol can be recycled by using filtration and reused. Thus, this new premixing method can be environmental friendly and more cost and time effective compared to the solution approach. The main advantage of this method is that sonication breaks down the xGnP agglomerates and the xGnP-IPA solution covers the PP particles very efficiently resulting in a homogeneous xGnP™ coated PP particles that are used for compression molding.

2.5 Compression molding

The compression-molded samples were made using Carver Laboratory Press (model 2518-single or 2731- double, made by Fred S. Carver Inc. Menomonee Falls, Wisconsin, USA). The composite pellets or powder was obtained by the melt mixing or premixing method. The conditions used are at 200 °C for 20 minutes with no pressure applied and 200 °C for 20 minutes under pressure ~1,054 kg_f/cm² (=15,000 lb_f/in²). During the compression molding vacuum was applied to remove any trapped air.

2.6 Characterization of nanocomposite

Tensile properties and flexural properties of injection mold specimens were measured with a United Testing System SFM-20 according to ASTM D638 and ASTM D790 respectively. System control and data analysis were performed using Datum software. Notched Izod impact strength was measured with a Testing Machines Inc. 43-02-01 Monitor/Impact machine according to ASTM D256 with a 1 ft-lb pendulum. XRD studies of the samples were carried out using a Rigaku 200B X-ray diffractometer (45 kV, 100 mA) equipped with CuK α radiation ($\lambda= 0.1516$ nm) and a curved graphite crystal monochromator at a scanning rate of 0.5~2 °/min.

Electrical conductivity was measured using Gamry Instruments by electrochemical alternating current (AC) impedance. Samples with dimensions of 5x3x12 mm³ were cut from the middle portion of flexural bars, and the resistivity was measured along the thickness direction (5mm). In this way, the conductivity could be measured in longitudinal direction along the flow of melt during injection molding. The two surfaces that were connected to the electrodes were first treated with O₂ plasma (10 min, 550W) in order to remove the top surface layers which are rich in polymer after cutting. And then gold coated to a thickness of 1-2nm to ensure good contact of the sample surface with the electrodes. The resistance of samples was measured in the frequency range of 0.1 to 100,000Hz. The resistance was taken at 1 Hz frequency at room temperature in the resistance-frequency curve. Finally electrical conductivity (ρ , S/cm) was calculated by following equation (1):

$$\rho = \frac{1}{R'} = \frac{1}{R \times \frac{A}{t}} \quad \text{----- (1)}$$

Where ρ is conductivity, R' is the resistivity, R is the resistance, A is surface area, t is distance.

3. RESULTS AND DISCUSSION

The pre-coated xGnP-1/PP nanocomposites are fabricated as described in 2.4 part. The composite with pre-coated pellets fabricated by injection molding shows alignment of the xGnP-1 along the flow direction, but the composite prepared by compression molding shows a more random morphology. The electrical conductivity of the nanocomposites is measured along the flow direction using a two-probe method. The electrical conductivity and mechanical properties of xGnP/PP NC prepared by the melt mixing-injection molding (IM) or compression molding (CM) were compared.

Figure 1 shows the effect of various PP particle sizes in the premixing (pre-coated) xGnP-1/PP step on the electrical conductivity after compression molding.

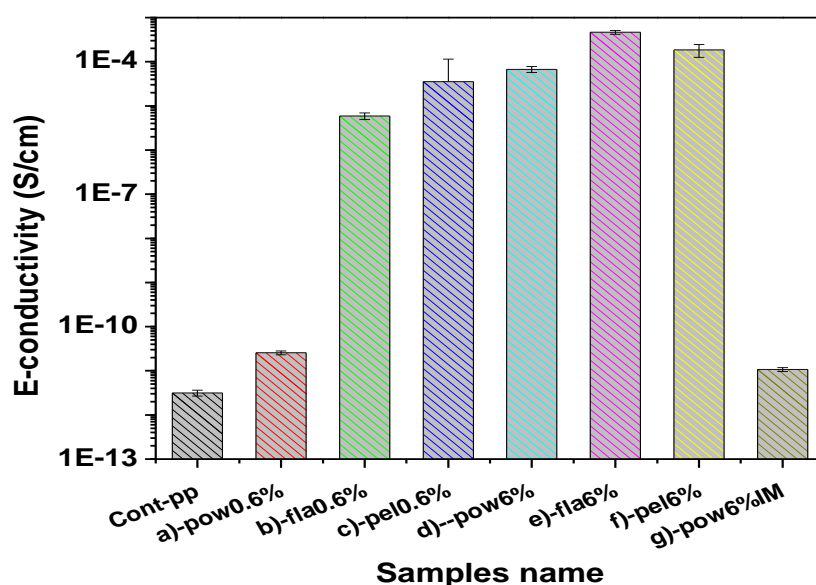


Figure 1. Electro conductivity on the effect of PP particle size in the premixing and compression molded the PP/ xGnP-1 NC : a) ~f) compression molded : a) micro fine powder PP/ 0.6 wt% xGnP-1 , b) flake PP/ 0.6wt% xGnP-1 , c) pellet PP / xGnP-1 0.6wt% , d) micro fine powder PP/ 6 wt% xGnP-1 e) flake PP/ 6wt% xGnP-1, f) pellet PP / xGnP-1 6wt% xGnP, g) extrusion-injection molded the pellet PP / xGnP-1 6wt%.

The pellet PP/xGnP-1 with 6 wt% of xGnP-1(Figure 1 f)) contains an excess of the xGnP as a separated phase, meanwhile the others show good dispersion with no obvious agglomeration of excess xGnP. This means that a smaller amount of the xGnP is needed as the particle size of the raw PP increases. Figure 1 shows the effect of PP particle size on electrical conductivity of premixed and then compression-molded PP/ xGnP-1 NC. It is found that in the flake and the pellet type PP case, only 0.6 wt% of xGnP-1 was required to make the PP NC electrically conductive due to network formation of xGnP on the surface of the PP particles. However, PP NC produced by extruding and injection molding process showed much lower conductivity even at 6 wt% xGnP-1 as seen in Figure 1g.

Figure 2 shows the effect of PP particle size on the flexural strength and modulus of the premixing and compression molded PP/ xGnP-1 NC. In case of 6wt% loaded xGnP-1/ powder

PP NC, the flexural modulus was best among investigated NC, but the flexural strength was almost similar regardless of different PP particle size. This may be due to homogeneity or dispersion of xGnP in PP matrix.

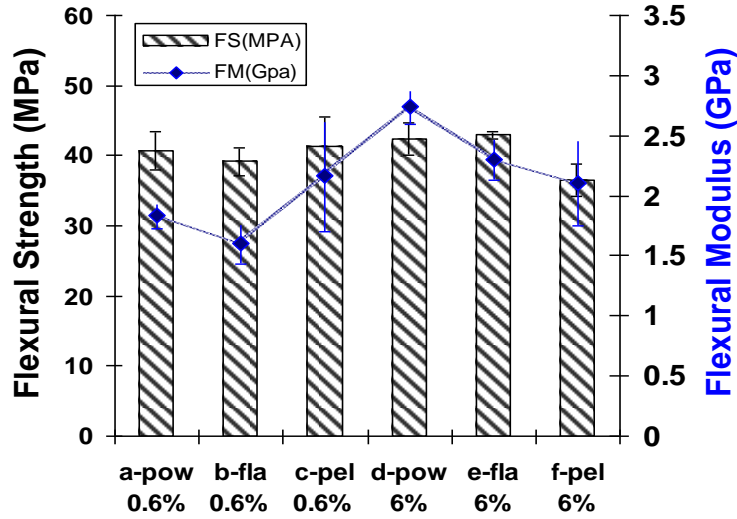


Figure 2. Flexural strength and modulus on the effect of PP particle size in the premixing and compression molded the PP/ xGnP-1 NC : a) ~f) compression molded : a) micro fine powder PP/ 0.6 wt% xGnP-1 , b) flake PP/ 0.6wt% xGnP-1 , c) pellet PP / xGnP-1 0.6wt% , d) micro fine powder PP/ 6 wt% xGnP-1 e) flake PP/ 6wt% xGnP-1, f) pellet PP / xGnP-1 6wt% xGnP-1.

The flexural strength and modulus of xGnP/PP NC made by IM and CM are shown in Figure 3. Also, the effect of the NC processing method on the notched impact strength and electrical conductivity are shown in Figure 4. In case of the PP/xGnP-IM, the pellet type PP showed best mechanical properties. But, in case of the PP/xGnP-CM, the powder or flake type PP is better for dispersion of xGnP and mechanical properties than pellet PP. Considering electrical conductivity and mechanical properties, for the PP/xGnP-IM, the pellet type PP is better than powder type, but in PP/xGnP-CM case, powder or flake type is better than pellet PP.

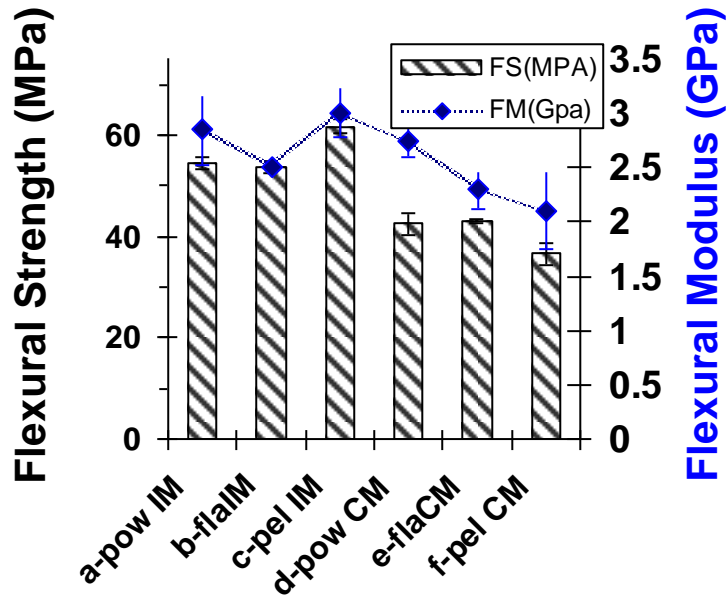


Figure 3. Flexural strength & electrical conductivity on the effect of comparison between extruded - injection molded (IM) or compression molded (CM) with different PP particle size: all samples are xGnP-1um 6 wt% fixed and premixed-coated: a) micro fine powder PP/ xGnP, IM; b) flake PP/xGnP, IM; c) pellet PP / xGnP, IM ; d) micro fine powder PP/ xGnP, CM; e) flake PP/ xGnP,CM; f) pellet PP / xGnP, CM.

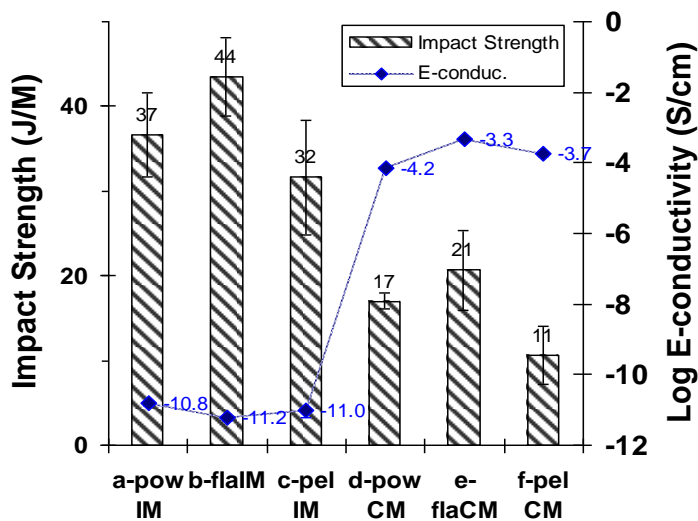


Figure 4. Impact strength & electro conductivity on comparison between extruded - IM or CM with different PP particle size: all samples are xGnP™ -1um 6wt% fixed and premixed-coated : a) micro fine powder PP/ xGnP, IM; b) flake PP/xGnP, IM; c) pellet PP / xGnP, IM ; d) micro fine powder PP/ xGnP, CM; e) flake PP/ xGnP,CM; f) pellet PP / xGnP, CM.

Figure 5 shows the electrical conductivity result of these NC. The percolation content of the flake and the pellet type PP is only 0.6 wt% of xGnP-1. This low percolation threshold is due to network formation of xGnP on the surface of PP particles, meanwhile, in case of the extrusion and injection molding, the percolation threshold increases to more than 15 wt%. This is a result of the orientation of the xGnP along the flow direction introduced during the injection molding, which was confirmed by an ESEM study [18].

The percolation threshold of xGnP-1/PP and xGnP-15/PP composites made by using xGnP-coated PP and followed by compression molding is 0.2wt% and 0.6wt%, respectively as shown in Figure 5. To the best of our knowledge, this is the lowest percolation threshold reported for thermoplastic composites. The results contradict the expected outcome i.e., the larger the aspect ratio the lower the percolation threshold.

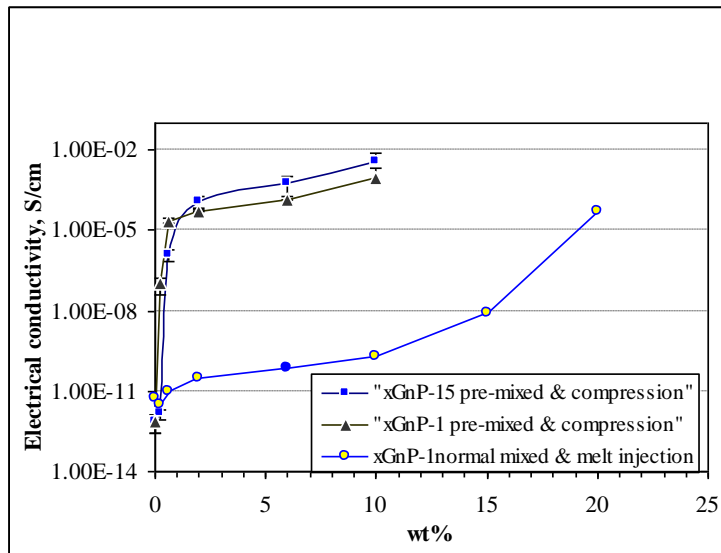


Figure 5: The percolation threshold of electrical conductivity of xGnP/ flake PP NC with different mixing and compounding methods.

This can be explained by considering the larger number of particles present in the same volume of xGnP-1 in comparison to xGnP-15. The probability of the xGnP coating the PP powder more effectively during premixing is higher for the smaller platelets. Another factor to consider is the geometry i.e., size and shape, and the aspect ratio of the conductive filler. Comparing the xGnP-1 and the xGnP-15, both are platelets of the same thickness (~10nm), which means same geometry, but they have different diameter. xGnP-15 is 15um (aspect ratio ~150) and xGnP-1 is less than 1um (aspect ratio <100). The electrical conductivity of both xGnP-15 and xGnP-1 appears to undergo an additional increase at ~7 vol% (~14 wt%) [19]. It is expected that the 15um graphite will percolate at lower loadings since the larger the aspect ratio the easier the formation of conductive path. It is noted also that the xGnP-15 composites show higher conductivity than the xGnP-1 ones at high loadings of >12 vol% (~24 wt%). The reason might be that the conductive path for the high aspect ratio graphite consists of fewer but larger platelets, resulting in fewer discontinuities which mean less contact resistance [19].

Another important factor for the conductivity of the composites is the processing method used for composite fabrication. The processing method affects the orientation, dispersion and spacing of the conductive filler within the polymer matrix. The processing method in the presence of high shear rates during the extrusion can even result in reduction of the platelet aspect ratio [20]. Furthermore, different fabrication techniques can significantly decrease the

percolation threshold i.e., *in situ* polymerization [21] yields composites with a threshold of ~1vol%, while melt mixing [22] method results in composites with threshold ~6-9vol%. In this study only melt mixing method is used in an effort to study not only the effect of filler orientation in the polymer matrix IM vs. CM but also the effect of mixing methods i.e., premixing-coating or simple physical mixing.

In Figure 5, the conductivity of 6 wt% xGnP-1/PP nanocomposites made by the coating method, reached at about 10^{-3} S/cm which is higher than the conductivity of samples made by the melt injection mold method. The reason is that in coating method there are no agglomerates of xGnP due to the use of sonication and the PP flake is homogeneously covered by xGnP. When the polymer melts in the mold the xGnP platelets can maintain their network since the degree of disruption due to mixing is minimal and do not undergo restacking.

XRD investigation was performed to support the restacking phenomena of xGnP. Figure 6 shows the XRD curve of various graphites which were different heat treatments. Figure 6a) shows intercalated peak of mixed acid at $2\theta = 25.4^\circ$ and an original graphite peak appear at $2\theta = 26.5^\circ$ while the exfoliated graphite (xGnP) samples (Figure 6b~6d) show a peak at only $2\theta = 26.5^\circ$. After drying the xGnP™, the position of $2\theta = 26.3^\circ$ peak was shifted a small amount toward a larger angle and the peak height increased. This indicates that heating (80°C) induces some restacking of the xGnP™ platelets during drying. The average stacked layer was calculated as ~30 layers by XRD-Scherrer equation $t = ky/(\beta \cos\theta)$: t = appearance crystal size β - broadening factor (FWHM radian, $\beta = 0.465$, $t = 21$ nm).

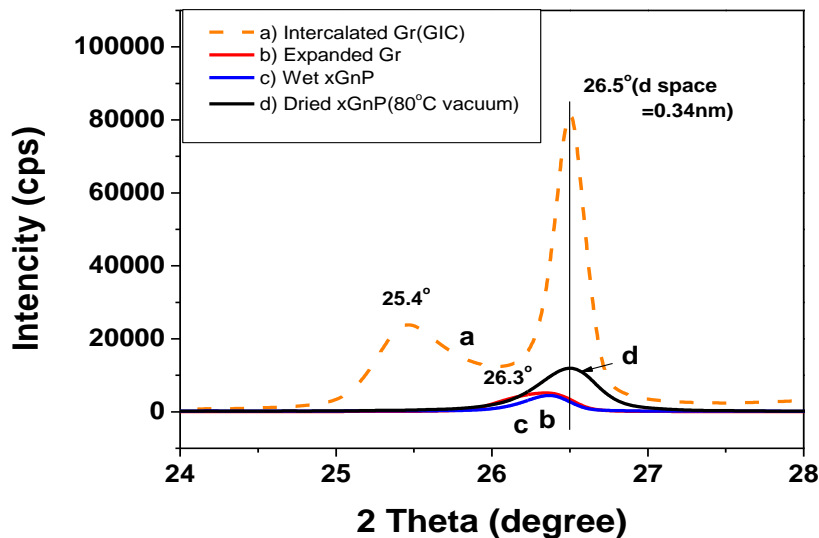


Figure 6. XRD curve of a various Graphite with heat treatment.

4. CONCLUSIONS

It was demonstrated that the addition of exfoliated graphite nanoplatelets added to an appropriate PP matrix could achieve high mechanical properties. The flexural strength and modulus of pellet-type PP/ xGnP-1 NC was higher than that of power- or flake-type PP/xGnP-1 NC. Electrical conductivity was enhanced by almost nine orders of magnitude. The percolation threshold of the flake and the pellet type xGnP-1/PP NC is only 0.6 wt%. This lower percolation

threshold is due to network formation of xGnP on the surface of the PP. Meanwhile, in case of the melt mixing-injection molding, the percolation threshold increases to more than 15 wt%. The flexural strength of both xGnP-1 and xGnP-15 reinforced PP composites increases at low concentrations of xGnP but reaches a plateau value at higher loadings. In particular, with premixing there was an improvement of the flexural strength of ~8% at 5 and 10 vol% and increase of the modulus up to 60% at 10 vol% compared to the samples made just by melt mixing. This result is interpreted as indicating the need for a better mixing/dispersion process and/or surface treatment of xGnP in order to improve dispersion within the polymer matrix and improve adhesion. It is noted that the processing conditions for the DSM microextruder injection molding system used were optimized for 3vol% of xGnP-1. Higher loadings might require higher barrel or mold temperatures or longer mixing time. The enhancement of the flexural properties is attributed to the fact that sonication breaks the graphite agglomerates and results in a homogeneous graphite-coated PP powder which is used as the feedstock in the extruder.

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