

Structure and Electrical Properties of Polypropylene-Graphite-Carbon black/ Nanotubes Hybrid Conducting Composites

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ABSTRACT

In the attempt to make low cost conducting polymer composite materials for fuel cell / battery applications, polypropylene (PP) with graphite (Gr) and other carbon black/ nanotubes hybrid materials were investigated. The development of crystalline structure in polypropylene (PP) graphite composite was studied with respect to composition and processing conditions. The DSC and XRD data confirmed the preferential nucleation and beta crystalline phase formation for the binary PP-Gr composites. There was dramatic increase in the electrical conductivity by addition of small amount of third component (CNT <5%) to the binary PP-Gr composite even at low graphite loading of 10%. Impedance spectroscopy analysis showed that the interfacial capacitance, with the addition of 2.75 wt% CB in PP-7 wt% graphite, increases to 52 pF from 31 pF for PP-7 wt% graphite proving the occupation of CB particles in the interspaces of graphite particles. The results of electrical conductivity were correlated with the nucleation and crystallization of the beta phase of PP by graphite flakes leading to interfacial resistive layer in binary composites while suppression of these effects in the ternary composites.

Keywords: conducting composites, polypropylene, graphite, carbon nanotubes, hybrid materials

1 INTRODUCTION

Conducting polymer composites are being focused for various applications such as fuel cells[1-3], EMI shielding devices[4], anti corrosion coatings[5-6] static charge and heat dissipation etc. due to their special properties, molding ability and reduction in weight of the finished products. Each application demands certain level of electrical conductivity which is attained by proper selection of fillers, polymer matrices or processing routes. Amongst these, conducting graphite filled composites are of special interest for fuel cell bipolar plates, antistatic heat dissipating and self lubricated bearings. It is well known that in the conducting polymer composites made from fillers (metallic or carbon based), the conductivity increases only beyond certain concentration of the filler which is the percolation threshold. The percolation threshold of binary composites depends on filler particle shape, particle size distribution,

aspect ratio etc. For ease in mixing and melt processing, the percolation threshold of the composites should be as low as possible. This is obtained for certain nano fillers such as carbon nanotubes (CNT)[7-9], carbon nano fibers (CNF)[10] or graphene[11]. However, for large scale application and lower cost, graphite is preferred as the conducting filler. In order to reduce the percolation threshold, one can use the second filler to make hybrid composite. Radhakrishnan et al.[12] have shown that addition of 5 wt% fine carbon black (CB) in polyether sulfone (PES)-graphite composites enhances the conductivity of the melt processed sheet significantly. The same principal was applied for polypropylene(PP)-graphite system in order to use commodity plastic so as to reduce the cost. However, the results were not that promising. One of the reasons was thought to be the crystalline nature of PP as compared to PES. Also, the interface between the graphite-PP could be different due to trans-crystalline zone. In order to investigate this further, the PP-graphite-carbon black as well as carbon nanotube (CNT) hybrid composites were studied for structure development and associated electrical properties by impedance analysis.

2 EXPERIMENTAL

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2.1 Materials

Isotactic polypropylene (SM85N, supplied by RIL, India) has been used for making these composites. Natural graphite, with particle size below 200 mesh and conducting carbon black powder were procured from Carbon Enterprises, Pune, India. Carbon nanotubes (SWCNT and MWCNT) samples were supplied by Sigma Aldrich. SWCNT was with 0.7-1.2 nm diameter while MWCNT had 5-10 nm outer diameter.

2.2 Preparation of composite samples

The polypropylene was made into fine powder by dissolving PP granules in hot xylene at 140 °C and then cooling to room temperature so that gel is formed to which excess acetone is added with rigorous stirring to yield PP powder. The powder was dried in vacuum oven for 24 hr before use. Powder mixed binary composites are prepared by mixing in pestle mortar an appropriate amount of PP powder and graphite keeping the total sample weight to 3 gm. The hybrid composites were made by mixing PP powder, graphite, CB for twenty minutes. In the case of MWCNT, these were mixed with PP powder in methanol with sonication followed by vigorous stirring on magnetic stirrer. The solvent was evaporated and dried off under vacuum. Disks of diameter 1 cm are made by applying 3 ton pressure for 3 min at room temperature. Melt crystallized samples were made by heating the powder mixed samples in between polished plates heated to 180 °C and immediately quenched in water. The surface of the sheet is slightly polished with emery paper so as to remove the skin layer before taking measurements of conductivity.

2.3 Characterization of Structure

The disc samples with and without sectioning were used for structural characterization. The X-ray diffraction (XRD) of composite sheet was done using Xpert pro model of X-ray diffractometer from Panalytical. Differential Scan Calorimetry (DSC) analysis has been carried out with Q-10 model from TA instruments. The heating/cooling rate was maintained at 10 °C/min in nitrogen atmosphere. The sectioned samples were examined for morphology by SEM with Joel microscope after depositing thin metallic coating for enhancing contrast and eliminating static.

2.4 Measurement of Electrical Properties

The DC resistance of different composite samples prepared as above was measured by Keithley Electrometer (Model: 6514) by placing them between platinum foils and applying a constant load (8 Kg/cm²) to reduce contact resistance. AC measurements (Impedance and Dielectric studies) are carried out in a specially constructed cell with gold plated electrodes of area 1 cm² as contact electrodes using Alpha A- high performance frequency analyzer, Novocontrol, Germany. The frequency scan range is 0.01 Hz-10 MHz. Impedance plots are fit with ZVIEW software.

3 RESULTS & DISCUSSION

Since CB particles have limited graphitization, structure development in melt crystallized PP-graphite composites has been studied. PP exists in monoclinic α form at room temperature which is the most stable form. It also exists in hexagonal β form and triclinic γ form under certain processing condition and with the addition of nucleating

agents[13]. The major reflection of α -PP is (110) approximately around 14°, For β PP, reflection at 16.2° will be the most prominent one. Figure 1 indicates XRD in binary (magenta) and ternary (blue green) PP-graphite-CNT hybrid composites indicating lower beta phase content in the hybrid composite. The reflection corresponding to (040) of PP is higher than that of (110). For pure PP (blue), the intensity of (110) reflection is the maximum. With decreasing amount of PP, the intensity of (110) decreases when compared to that of pure PP.

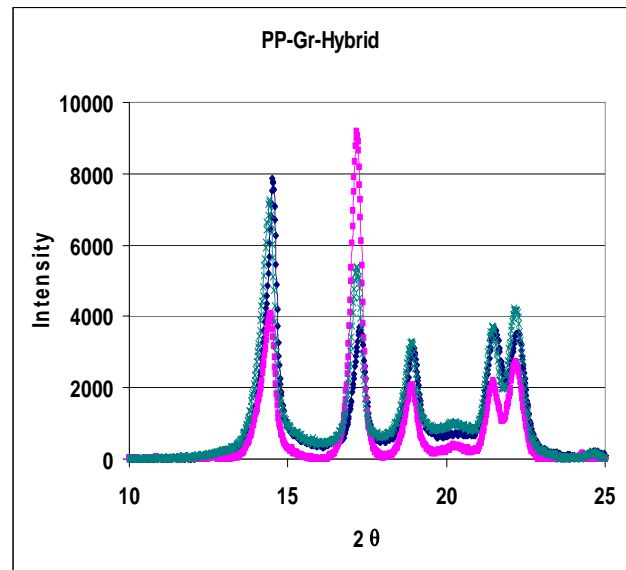


Fig.1 XRD scans for pure PP (blue), PP-Gr (magenta) and PP-Gr-CNT (blue green) samples

It is evident that in presence of the third additive such as CNT, the α -phase becomes more prominent while β form is dominant in binary PP-Gr composites. According to lattice mismatch theory [14], the mismatch factor δ is defined as

$$\delta = \frac{|p l_s - q l_g|}{l_s} \times 100 \quad (1)$$

where l is the lattice parameter along any axis; p and q are integers. The subscripts s and g represent substrate and growing media. The lattice parameters of graphite and monoclinic α phase and hexagonal β phase PP are given below.

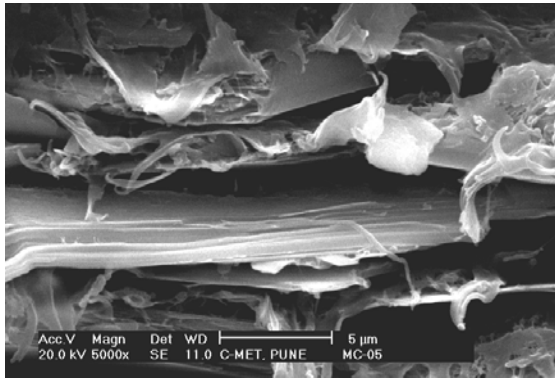
Graphite : $a=b=2.46 \text{ \AA}$, $c=6.7 \text{ \AA}$

PP α phase : $a=6.65 \text{ \AA}$, $b=20.9 \text{ \AA}$, $c=6.5 \text{ \AA}$

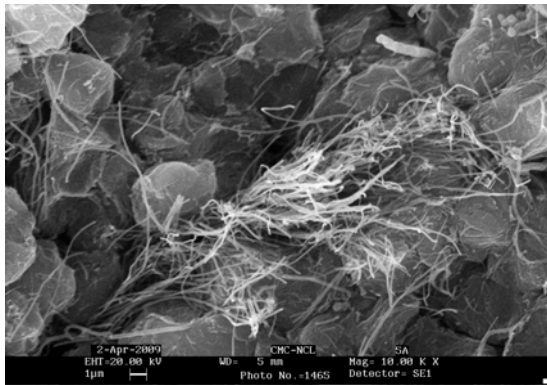
PP β phase : $a=b=19 \text{ \AA}$, $c=6.5 \text{ \AA}$

It is evident that the δ values of PP β phase c axis and Gr c axis as well as PP β phase a, b with $8x(a, b)$ of Gr are $< 3\%$ the limit of existence of nucleation and or epitaxy. Thus graphite flakes nucleate the β phase of PP. On the other hand, in presence of the third component these nucleating effects are considerably reduced as seen from the XRD. This is because the nano particles are dispersed in the matrix much more effectively and capture the polymer

molecules not allowing to interact with / wet the graphite surface. These suggestions are well corroborated with the findings from the SEM of the fractured surface of the PP-graphite composite. Fig.2 depicts the SEM of PP-Graphite composites and PP-nano carbon fibers.



(A)



(B)

Fig.2 SEM of PP-Gr composite(A) and PP-Gr-CNF composite (B)

It is evident from the SEM that the PP penetrates in the interparticle / flake spaces and forms a layered structure in the PP-Gr binary composites (see Fig.2A) . On the other hand the nano fibers do not allow such layered morphology to be formed in the ternary composites (Fig.2B).

The DSC studies on the PP-Gr composites also corroborated the above findings. Fig.3 gives the DSC scans for pure PP (blue) and PP with graphite (magenta) showing the lower melting curve corresponding to beta phase of PP. Thus, it is clear from these structural characterization studies that PP-Gr binary composites contain predominantly beta phase PP nucleated by the graphite flakes forming layered structure. On the other hand the PP-Gr-CNT composites contain mostly the alpha phase with the nano-fibers or nanotubes entangled inside the polymer matrix and there is no specific morphological feature. It may be also noted that the nucleation efficiency

of nanoparticles in PP is very much higher than the macroparticles as reported by Saujanya and Radhakrishnan [15] . In such cases, mostly the alpha phase is formed.

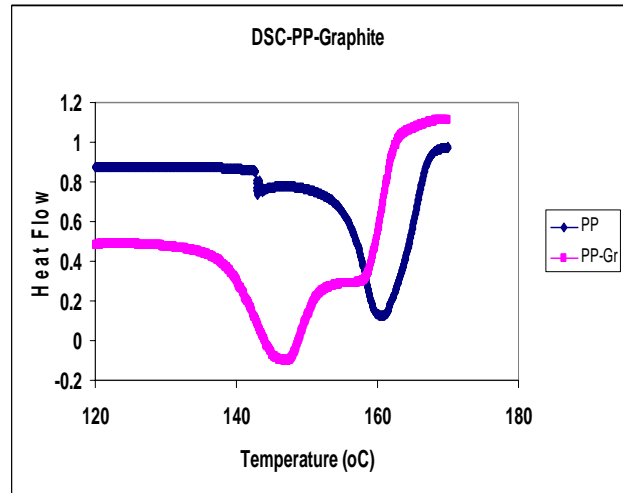


Fig.3 DSC scans for pure PP (blue) and PP-Gr composite

The electrical DC conductivity measured for various compositions of binary and ternary PP-Gr CNT composites has been consolidated in Fig. 4. This figure shows the overall results obtained in the ternary composites as compared to the binary PP-Gr composites. These curves are reminiscent of the percolation behaviour in conducting composites. There is a dramatic change in the percolation threshold, the critical concentration above which conductivity rises by several orders of magnitude, in the ternary composites.

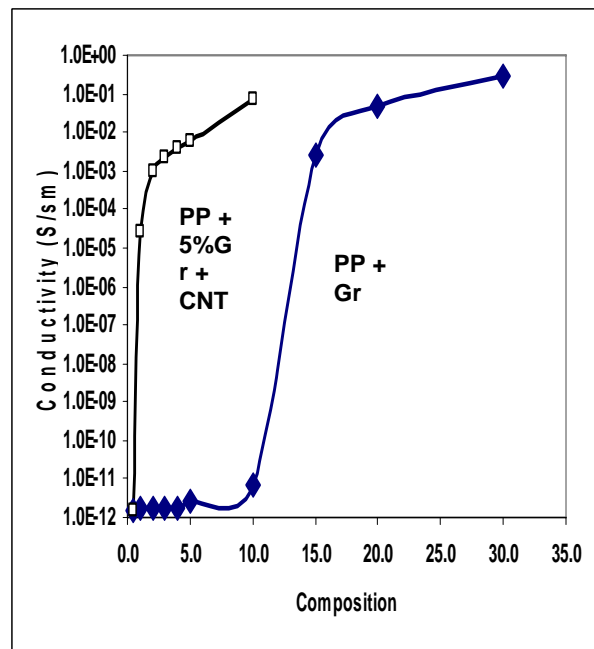


Fig.4 Compositional dependence of conductivity in PP-Gr binary and PP-Gr-CNT ternary hybrid composites

The percolation behaviour of the conducting polymer composite is described typically by the equation [16]

$$\sigma = \sigma_0 (\Phi - \Phi_c)^m \quad (2)$$

where σ is conductivity, Φ is the volume fraction of the filler, Φ_c is the critical concentration (threshold) and m the exponent related to fractal dimensions and /or type of distribution of the filler particles in the polymer matrix. The above data was analyzed as per the curve fitting procedure using the equation (2). The values obtained from such analysis for different binary as well as ternary composites are indicated in Table-1.

Table-1 Percolation equation parameters

Sample	Composition	Φ_c	m
Binary	PP + Graphite (Before Crystallization)	3.6 E-01	1.92
Binary	PP + Graphite (After Crystallization)	6.5 E-01	2.4
Ternary	PP + 10% Gr + MWCNT	1.18E-03	1.6
Ternary	PP +7 % Gr + 2.2 wt % CB	2.2 E-01	1.37
Ternary	PP + 10% Gr + CNF	1.3E-03	1.4

The value of Φ_c is seen to be dependent on the type of third conducting additive in the ternary composites. Its aspect ratio may be playing an important role in bringing about the network formation across the graphite layers. It is interesting to note that further crystallization process in the case of PP-Gr binary composite leads to more resistance in the sample. It thus appears that in the case of PP-Gr the formation of β phase PP between the graphite particles leads to more insulation while the random α phase facilitates higher contact formation and lower electrical resistance.

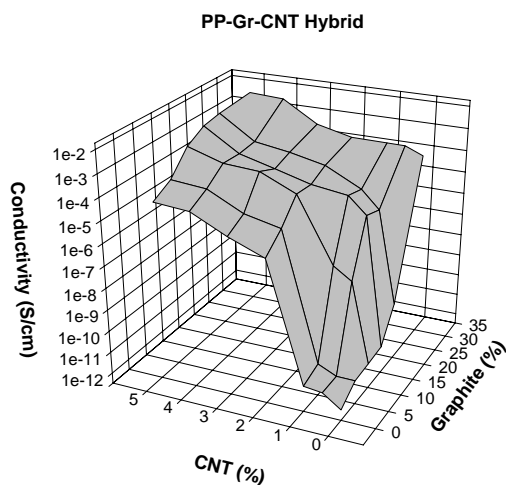


Fig.5 Conductivity over complete range of compositions for the ternary hybrid PP-Gr-CNT composites

The Fig.5 depicts the variation of conductivity over the whole range of samples studies as three dimensional plot for the ternary system. It is evident that there is tremendous advantage obtained by the addition of the third component is as much as the saturation value of conductivity is increased and that too with low filler loading.

4 SUMMARY & CONCLUSIONS

PP-Graphite- Carbon black nanotube ternary composites exhibit high conductivity at low filler content. The conductivity follows the percolation model with every low threshold. The graphite particles nucleate the β phase PP which leads to high resistance layer at inter-particulate gaps. However, the addition of third component suppresses the β phase formation and gives higher conductivity.

5 ACKNOWLEDGEMENTS

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