Conductive Nanocomposite fabrication by Graphene enriched Polypropylene Master Batch

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Abstract - **The nanocomposites are the most attentive topic of the study currently in the material science world which is likely to bring the industrial revolution. Graphene reinforced polypropylene nanocomposite was fabricated in the balanced formulation of filler & carrier additives through melt mixing process at the trend of industrial practices. The concept of molecular arrangement was hypothesized and executed out practically. The master batch was prepared as the primary preparatory work using Twin Screw Extruder and the finished product was obtained by using the same master batch through injection molding. The percolation threshold was considered to be 5% wt. Graphene in finished product which has been proved as the innovative product line. A series of destructive and non-destructive tests and characterization techniques were conducted, analyzed and presented. First time the entire range of properties has been explored including electrical, thermal, gas barrier & mechanical properties. The resulted product has proven to be used at the industrial scale immediately and has opened the new directions in making use of other class of polymers innovatively.**

Key words - **Nanocomposite, Electrical conductivity, Graphene, Polypropylene, Industrial applications, Nanotechnology**

I. Introduction

Nanomaterials own the Quantum confinement which consequences the exceptional outstanding properties and lead to the enormous range of revolutionary applications. In this regard, the discovery of graphene and graphene-based polymer nanocomposites is playing a vital role in modern science and technology [1]. Graphene is a single layer carbon sheet with a hexagonal packed lattice structure which has shown many unique properties such as the quantum Hall effect (QHE), high carrier mobility at room temperature,[2], large theoretical specific surface area $(2630 m^2/g)$[3], good optical transparency(>97.7%)[4], high Young's modulus (>1 TPa)[5] and excellent conductivity (3000–5000 Wm"1K"1)[6].

Furthermore the excellent electrical, mechanical and thermal properties of graphene resulted into nanocomposites which are electrically conductive with improved heat resistance and stiffness [7–9].The polymeric nanocomposites are multicomponent materials composed of organic or inorganic fillers and polymers, where at least one dimension of the dispersed particles is in the nanometer range [10].[There is a wide variety of possible graphene applications, including the creation of new materials and the production of innovative electronic devices [11]. Polypropylene, a thermoplastic polymer, when reinforced with micro- and nanofillers, shows high stiffness and strength, and it is commonly used in the automotive and aerospace industries [12].There are some reports of the preparation of isotacticpolypropylene (iPP) nanocomposites with graphite or graphite oxide by molten state blending [13–15], solid state shear pulverization[16] and solution processes [17] which are adding values to this work.

The balanced properties of the finished product are not absolute in all previous work in the domain and thereby the interest of this work initiated. In this study the main objective is to achieve the conductive polymer nanocomposite alongside the enhancement of other basic properties of common thermoplastic, Polypropylene [PP]. As presented in the fig number 1, the conductive range allows respective applications. A composite can be used as shielding for electromagnetic or radio-frequency interference if the surface electrical conductivity is higher than 10^{-6} S/cm. The superior properties of graphene compared to polymers are also reflected in polymer/graphene nanocomposites. Polymer/graphene nanocomposites show superior mechanical, thermal, gas barrier, electrical and flame retardant properties compared to the neat polymer [18-21].

Figure 1: Applications of materials on the basis of conductivity range

It was also reported that the improvement in mechanical and electrical properties of graphene based polymer nanocomposites are much better in comparison to that of clay or other carbon filler-based polymer nanocomposites in the above cited references.

Summarizing the application of an electrically conductive material as 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. High EMI shielding performance gives CPCs the potential to be used widely in laptops, cell phones, aircraft electronics, and medical device housings.

It is desirable to minimise the conductive-filler percolation-threshold as much as possible and should be simple in the compounding & fabrication procedures from techno-commercial viewpoints,

Figure 2 enlists the core benefits of such innovative nanocomposites which are readily acceptable in the industry.

Figure 2: The core benefits of the nanocomposites

As per the percolation theory [22], the two important properties in electrically conductive composites are volume fraction of the conductive filler, and the percolation threshold, defined as the minimum volume content of the filler, above which the filler particles form a continuous network, at which point the composite becomes electrically conductive.

These factors are [23–25] named as 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 inter-particle filler spacing within the polymer matrix and the crystallinity of the matrix [26].These factors can be controlled by the addition of other carrier additives of the suitable geometry. And Silicon dioxide has been used as carrier herein this study.

Many of the above factors depend on the processing method, parameters and conditions used to fabricate the composites.

The preparation method depends on the polarity, molecular weight, hydrophobicity, reactive groups etc. present in the polymer, graphene and solvent [27].In general, there are three ways for incorporating the polymer at the core of the host-layered materials namely, in-situ intercalative polymerization, solution intercalation and melt intercalation. We opted for melt mixing procedures using twin screw extruder & injection molding considering to avoiding the additional chemical incorporation required and time consuming process. In this method, graphene or modified graphene is mixed with the polymer matrix in molten state. A

thermoplastic polymer is mixed mechanically with graphene or modified graphene at elevated temperatures using conventional methods like extrusion and injection molding [28].

Conductive polymer composites (CPCs) have been studied intensively due to their many advantages, such as good process ability, corrosion resistance, and comparatively low weight and cost.

In order to meet the prerequisite factors for nanocomposite fabrication a concept of using a mix of two nanomaterials and molecular arrangement have been adopted as shown in the fig. 3.

II. Materials and Methods

A unique concept of molecular arrangement of the dispersed phase in dispersed media was hypothesized which leads this work innovative. The illustrative image of the concept is presented in fig. 3.The previous works in this direction as cited in the references are inspiring to us and also enabled to take this work forward. We assumed 5% wt graphene presence in the final product as the effective concentration or percolation threshold value. These final products were prepared from the master batch of 10% wt. Graphene in polypropylene.

The graphene as filler into host matrix cause the effect if the anisotropy of the filer, the orientation of the dispersed phase and the Griffith mechanism are well maintained. Earlier work cited as references herein are achieving significant properties but loses some property while achieving other properties. Also being understood the percolation threshold as 5% wt of graphene into the host we minimized to take various concentrations as trial.
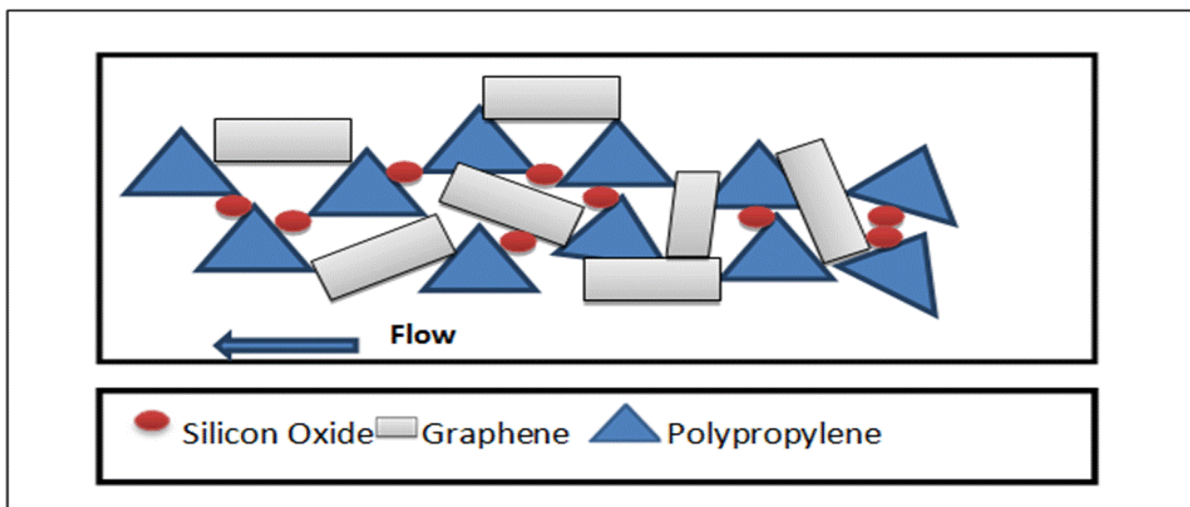

Figure 3: Illustration of the molecular arrangement in nanocomposite-Targeted

One of the most common techniques for the dispersion of fillers in a polymer is the master batch approach. This technique consists in a first step where a mixture, the master batch, with a high amount of nano-filler is produced, followed by dilution of the master batch in the polymer matrix by melt mixing. This approach has proved effective in improving the dispersion of nano-fillers such as CNTs or GNPs [29,30].This is due to the high shear stresses applied to primarily agglomerates, as a consequence of the high viscosity of large-loadings mixtures involved in master batch production. Other benefits of using a master batch include the limitation of health and safety risks and handling difficulties as is a dust-free approach in comparison with the bulk nano-filler dispersion approach.

Homopolymer Polypropylene H1100MA [REPOL[TM]] with a melt flow rate of 5g·(10min)-[1] (ASTM D1238) purchased from Reliance Polymer, India was used as host matrix in the form of almost spherical particles ranging 200-500 μm average size. As conductive filler, Graphene (Ugray [TM] of United Nanotech Innovations P.Ltd, India) manufactured by modified Hummer`s Method was used. Purity of the Graphene, as received, was 99%. Scanning electron microscopy (SEM) examination revealed that the Graphene were having high aspect [~1000] ratio exfoliated with large surface area. The average lateral dimensions were ranged from 10 - 20 micron while their thickness was 3nm.The various characterizations techniques were adopted to check the as receive graphene nanomaterial and discussed herein the literature in the separate section. Fumed Silica as >99.9% of Silicon dioxide [AEROSIL 200 obtained from EVONIK INDUSTRIES] was used as one of the important additives or carrier to achieve the targeted concept and continuous molecular arrangement. Fumed silica is recommended for rheology and thixotropy control of liquid systems, binders of polymers as per technical data sheet of Aersoil-200 product.

The basic information about the core components used is presented in table1&2.

Table 1: Basic properties of the core additives

MATERIAL	POLYPROPYLENE	GRAPHENE	Silica[Fumed]
DENSITY	0.92g/cc	0.93g/cc	0.50g/cc
TEHRMAL STABILITY	175 -210 ^{0}C	>750 ^{0}C	>1750 ^{0}C
Size	400-500micron	10micron of 3nm thickness	80-100nm
Form	Spherical solid	Light flakes powder	Powder
Colour	Greyish	White	White

Table 2: Formulation for master batch production 10% Graphene-PP

Sl.#	Constituents	Quantity
1	Homo-polymer Polypropylene	8.9kg
2	Graphene[Ugray]	1kg
3.	Fumed Silica	100gm
4	Silicon oil	50ml
5	Tween 80	10ml

The accurately weighed polymer was dried in a vacuum oven at 120 ^{0}c for 2 hour to make it moisture free. Silicon oil and Tween 80 were used as the lubricant and processing additives for extrusion. The exfoliated graphene as received was mixed into PP polymer in a closed jar with other additives as mentioned in the formulation table 2.

The blending was performed manually in a closed plastic closed jar by vigorous shaking for half an hour. The entire blended materials were appeared to be dark greyish and ensure proper mixing visually at this stage. The blended polymers were processed in a Twin screw extruder of lab set up [L/D ratio 15]. The actual processing parameters are presented in fig. 4.
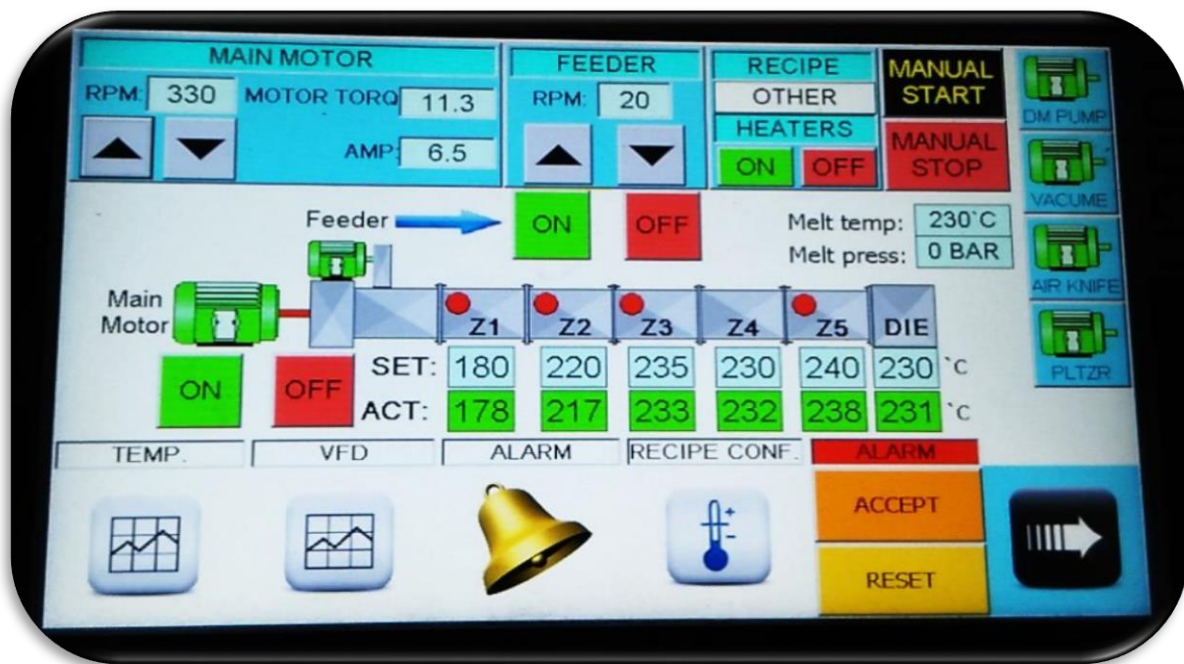

Figure 4: The master batch compounding using Twin Screw Extruder and its parameter.

The compounding temperature maintained was 180 ^{0}C to 240 ^{0}C with the die temperature 230^{0}C.

The running set up of this experiment is presented in the fig. 5 where the master batch in the form of dark pellets is collected in a bucket.

Figure 5: The running Twin Screw Extruder lab set up for master batch production

The master batch formed at this stage contains 10%wt of Graphene in suitable other additives environment and called as Master Batch of nanocomposite herein.

The master batch formed was in the form of pellet and is presented in figure number 6 having 2-3 mm length with0.5mm diameter in the form of solid dark pellet.

Figure 6: The master batch of GNP

In order to make the final product the master batch was diluted by 5%wt Graphene in final product. The injection molding was used for product specimen fabrication and the general processing parameters were kept as-Injection Pressure: 90 MPa,Melt Temperature 185°C,Mold Temperature 60°C and Drying 2 hrs @ 79 °C.

The finished products as specimen were fabricated by injection molding which are represented in figure number 9.

The product specimen sizes were 9 inches in lateral dimension with 3 mm of thickness.

Neat PP samples of same dimension were also fabricated at the same parameter without graphene.

These samples were further processed as per the standard of the different tests required.
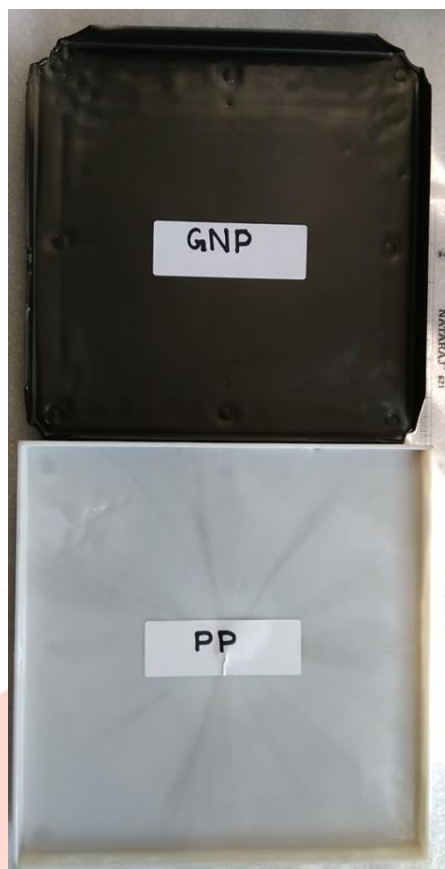
Figure 9: The finished product [GNP]-a nanocomposite & PP-Neat polypropylene

III. Measurements

Scanning electron microscopy (SEM) was done on gold sputtered surfaces of samples cryofractured perpendicularly to the surface of the plates using LEO VP 435 microscope (Zeiss, Germany).SEM analysis of the graphene and nanocomposite were conducted and presented.

Transmission electron microscopy (TEM) of the Graphene was performed using an STEM [Scanning transmission electron microscopy] of LEO 912 (Leo, Germany) microscopes at 30 KV voltages. TEM analysis of as received Graphene was conducted.

Fourier transform infrared [FTIR] –Raman measurements were performed using an RFS- 1000/s (Bruker, Germany). Laser light of 1064 nm from a Nd- YAG laser was used for excitation. A power density of about 0.5 mW/cm^2 was used to avoid blackbody radiation arising from the dark greyish graphene. X-ray diffraction (XRD) measurements were obtained on a diffractometer Rigaku DMAX 2200 equipped with a Cu tube and a secondary monochromator . The goniometer was a Siemens D500, and the detector was a scintillator (NaI and Tl). The samples were analysed in powder form at room temperature. Graphene and nanocomposite were analyzed to ensure the graphene and coupling bond formation with polymer.

Calorimetric analyses were carried out in a TA Instruments Q20 calorimeter at a heating rate of 10 ^{0}C/min^{-1} from 25 to 220 ^{0}C to obtain a DSC [Differential Scanning Calorimetry] curves.

The GNP specimens were having dimension as, length 70 mm, width 20 mm, and thickness 1 mm. The electrical conductivity of the composite was measured through the vertical thickness of the composite sheets by the standard, four-point-probe method. A DC precision power source (Keithley, Model 6280) and nano-voltmeter (Keithley, Model 2182A) were used for volume resistivity measurements. An electrical current of 1 mA was maintained in all measurements. Values of the volume electrical conductivity, σ, were obtained by simply inverting the corresponding values of the resistivity as follows:

$$\sigma = \rho^{-1}$$

5 bar-specimens of each composite material were tested and 5 repeated measurements of the volume resistivity were done for each of them by the four-point-probe method at different locations on each specimen. The results were used to calculate an average value and then converted to average conductivity [31].

Tensile test was performed on dog bone size cut from the molded plates with a gauge 10 mm long. A universal testing machine Zwick Rowell (2.5 kN) was used and the speed of 5 mm/min was applied. Seven samples were measured for each composition.

Gas barrier test & flame retardant tests were also performed as per the standard and description herein. The air permeability test conducted as per the Method ASTM D 73 using equipment Textest FX 3300, Lab air at the 125 Pa of Test Pressure.

IV.RESULT AND DISCUSSION
A.   Morphology and structural analysis of Graphene

FESEM images of as received Graphene nanosheet were taken to see the dimension of the nanomaterials.
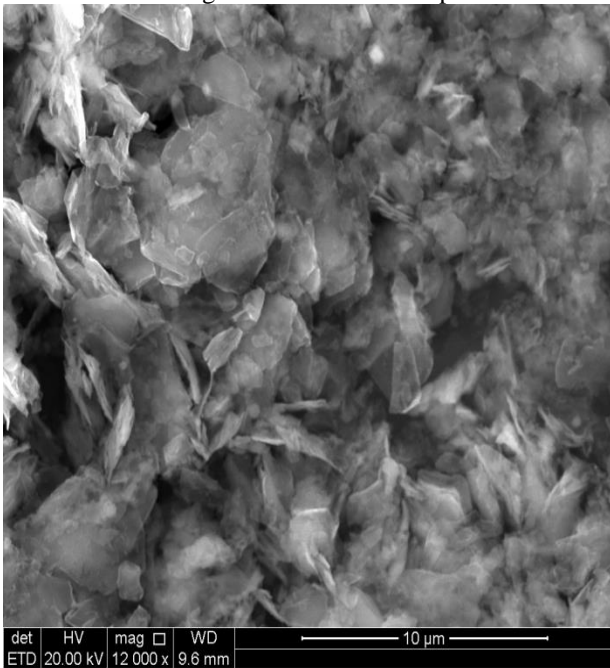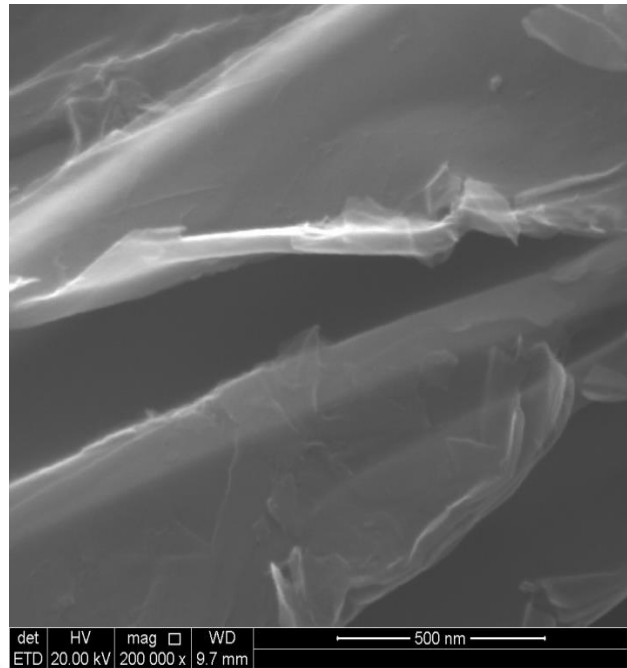

Figure:10a

Figure:10b

Figure 10a&10b: SEM images of Graphene used

The graphene sheet found to be having the lateral dimension 5-10 micron in and 3nm in the thickness. The sheets are highly exfoliated and enlarge surface area which is ideal property for such applications.

TEM Microscopy of the graphene conducted to see the number of layers and degree of exfoliation. The graphene found to be very thin [2-3 layered] sheet and enlarge surface area. The images are presented in the figure number 11.
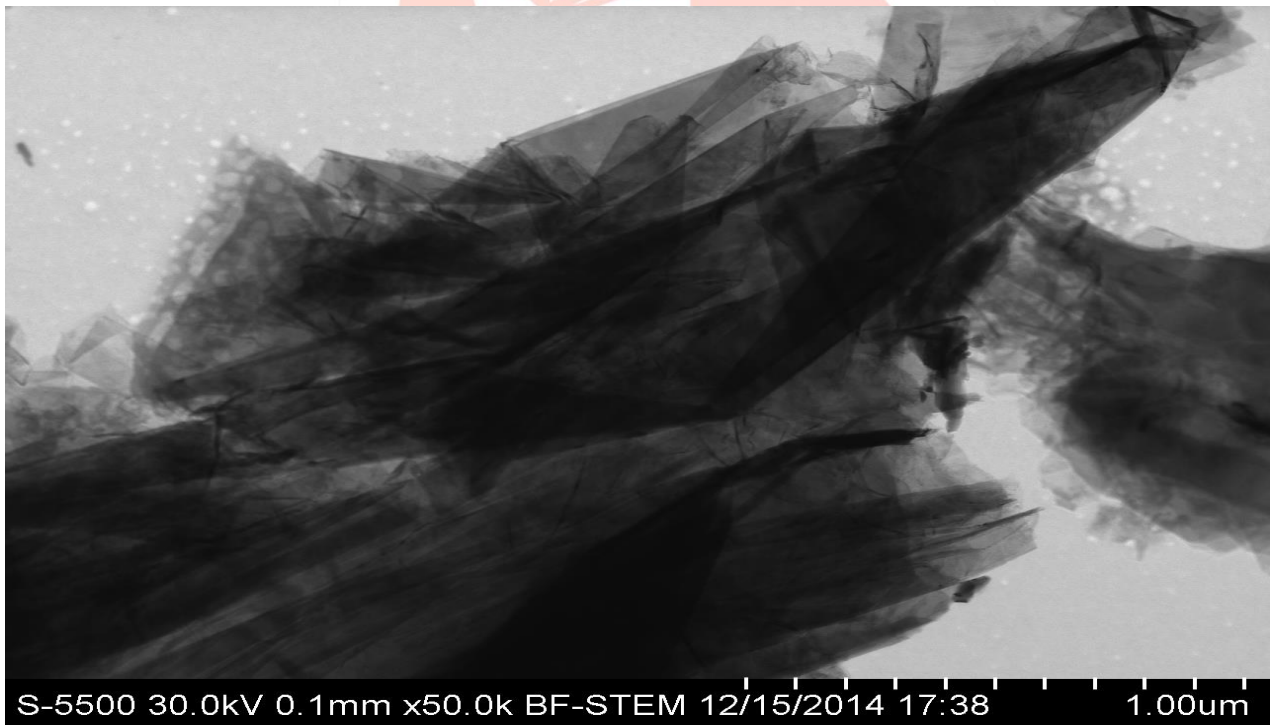

Figure 11: TEM image of Graphene showing high surface area exfoliated thin sheet

Raman spectra shown in fig12 revealed the graphene nanosheet with having 2D/G ratio>0.6.The
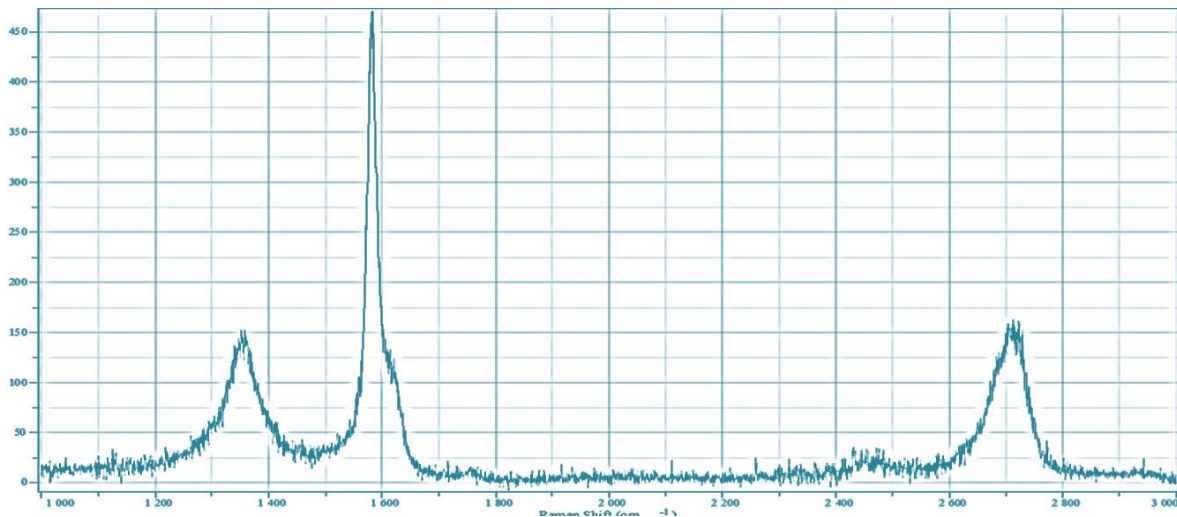
Figure 12:Raman spectra of Graphene

The Raman signature of the graphene found to be aligned to the references spectra with the due defects surfaces as D-peak[1352cm^{-1}]whereas the G peak appeared at 1581 cm^{-1}.The presence of dominant high 2D peak at around 2702cm^{-1} confirms the graphene with very thin layer with .

X-ray diffraction (XRD) pattern of Graphene is presented here in the fig 13 a.2Theta angle values are appeared at around 26.5 which is the confirmatory peak for graphene.
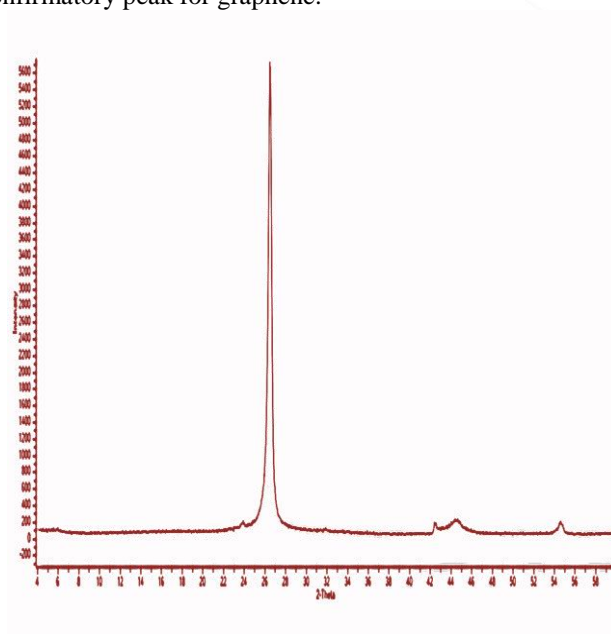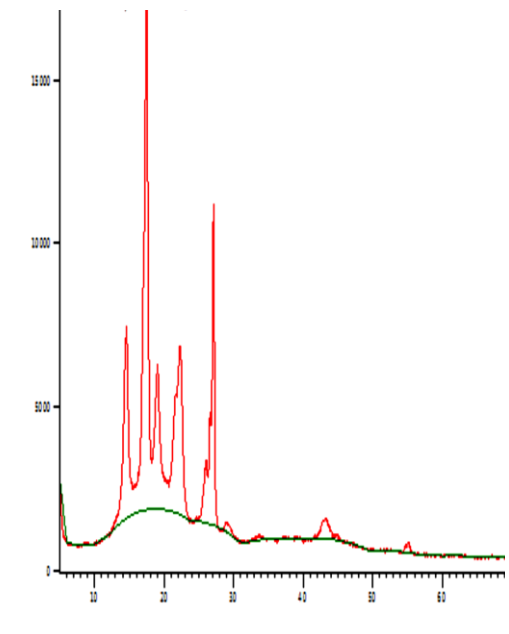
XRD pattern of Graphene   XRD Pattern of Graphene nanocomposite

Figure13 a &13 b:XRD pattern of the graphene and nanocomposite

B. Morphology and nanocomposite :

The FESEM analysis was conducted to see the distribution of Graphene in polymeric matrix. The fractured portion of the nanocomposite was examined .The image presented in figure 14 clearly revealed the uniform distribution of graphene in the polymer matrix as per the conceptual diagram shown in fig3.
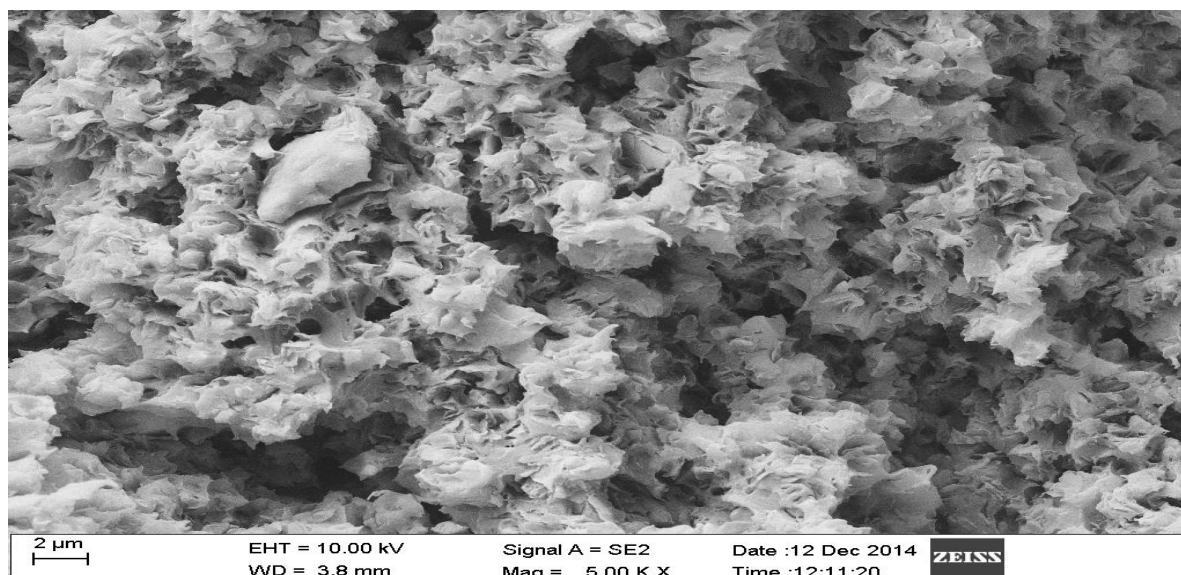
Figure 14:The FESEM of fractured Nanocomposite

The graphene with its balanced formulation of additives are uniformly distributed in the polymer matrix. Further, the coupling and bound formation between Graphene and polymer is confirmed by FTIR analysis. FTIR –ATR spectra shown in fig 15 confirmed the presence of the nanocomposite formation. The peaks at $2949cm^{-1}$, $2916\ cm^{-1}$,$2666\ cm^{-1}$,$1451\ cm^{-1}$,$972\ cm^{-1}$ represent the reference peaks for polypropylene whereas the peaks at $1600\ cm^{-1}$ and $2837\ cm^{-1}$ represented the carbon peaks for graphene in a nanocomposite structures and thereby confirmed the formation of nanocomposites.
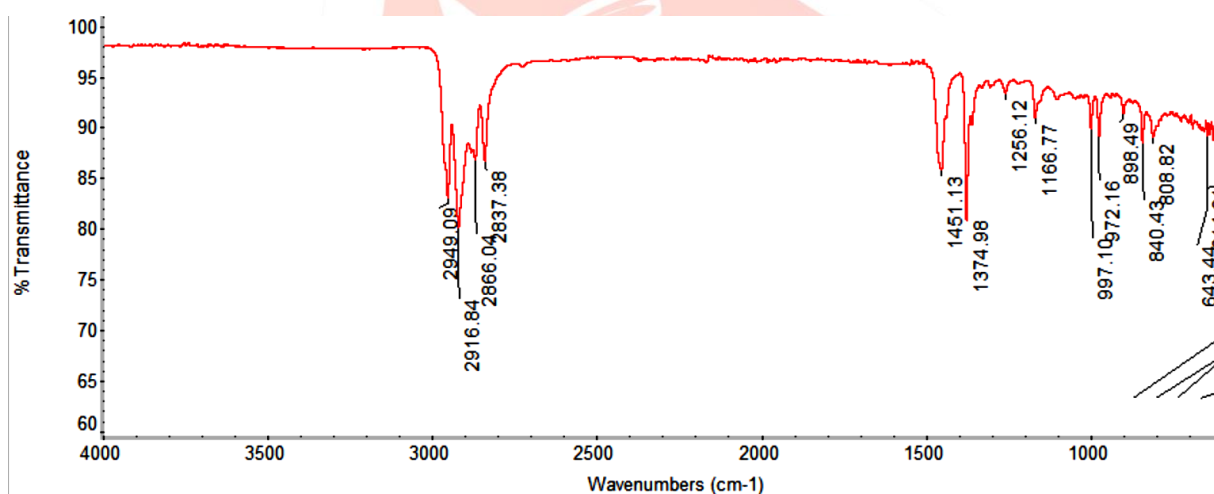

Figure 15: FTIR-ATR spectra of nanocomposite

The presence of peaks in the above XRD pattern in fig 12b, the peak appeared at 2theta of 12,16&21 which are respective peaks for PP polymer whereas in the same figure presence of 2 theta at 26.5 indicates the presence of graphene. Thus, fig12b is confirmatory evidence in regard to the nanocomposite formation.

Fig. 13a &13b show the X-ray diffraction pattern of the graphene nanosheets and the nanocomposites. The graphene image 13a diffractogram has a strong peak at 2 Theta 26.5 degrees that is characteristic of the spacing between graphene units in the 002 plane.

In the XRD pattern of In figure number13b] GNP, the characteristic peaks peak appears at 12,16,21,22 of 2Theta values. This indicates complete exfoliation and a good dispersion of the graphene nanosheets in the nanocomposites with low GNS contents.

C. PROPERTIES TESTING

The Electrical Conductivity Test results the 5%wt graphene having GNP has been improved in the volume conductivity in comparison to the insulated neat PP. This range of the conductivity has many applications in the industrial product ranging from EMI shielding to electronic devises. The   conductivity of the nanocomposite was found to be 10^{-6} Siemen/cm .This value of conductivity changes this finished material as the conductive from insulative PP polymer .The extent and effort to make such concept seems to be workable. The values are represented in below table number 3.

Table 3: Electrical conductivity

Neat PP	Nanocomposite
10^{-14}	10^{-6}
Siemen/cm	Siemen/cm

The conductivity is enhanced in case of nanocomposite which is obvious effect of the only conductive filler, Graphene. The excellent volume conductivity indicates the potential of graphene as conductive filler.

Flammability test as per the UL94 standard cosnducted.Specifically the UL94 standard,popularized by underwriter Laboratiries[UL] as an element to obtain a UL listing for end devices,classifies plastics by how different thickness burn in various orientations.We conducted vertical falmabilit test as per the UL94 standard of a thickness 2.5mm sample cut rectangular.Results are prensted in table number 4

Table 4:The falme resistivity test

Specimen	Burn length in 60 minute
Neat	40mm
Nanocomposite	23mm

The GNP found to be fire retardant grade materials and seeks application for air craft construction materials .The burn length is 23 mm in case of GNP which is excellent FR properties. The char length and dripping gave the idea of being FR materials. This can be assumed that the surface energy of the polymer is increased due to reinforcement by graphene. Also there is discontinuation of fire caused due to obstacle cause by graphene molecules in the molecular structure.

1.The air permeability test conducted as per the Method ASTM D 73 using equipment Textest FX 3300,Lab air at the Test Pressure: 125 Pa Test Areas: $38cm^2$ Sample 0.1mm thick

The tests were repeatedly conducted and presented as below in table number 5.

Table 5:air permeability test

Specimen	AIR PERMEABILITY Cm3/cm2/sec	% improvement efficiency
Neat	0.0524	-
Nanocomposite	0.0429	18

There was an improvement of 18% of the air permeability barrier which is suggestive to make use of this material for making the container or coating to protect from the gases or prevent from oxidation. This also suits well for EMI shielding where the corrosion resistant packaging is required.

Another thermal properties tests conducted were DSC and theor graphs are presneted in figure 15a& 15b.
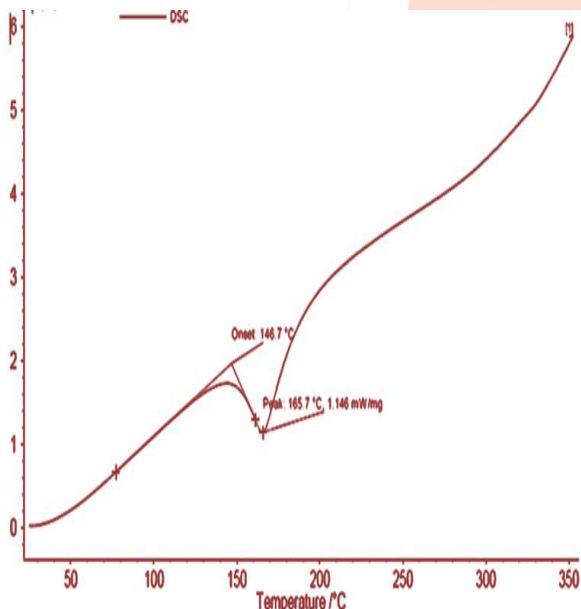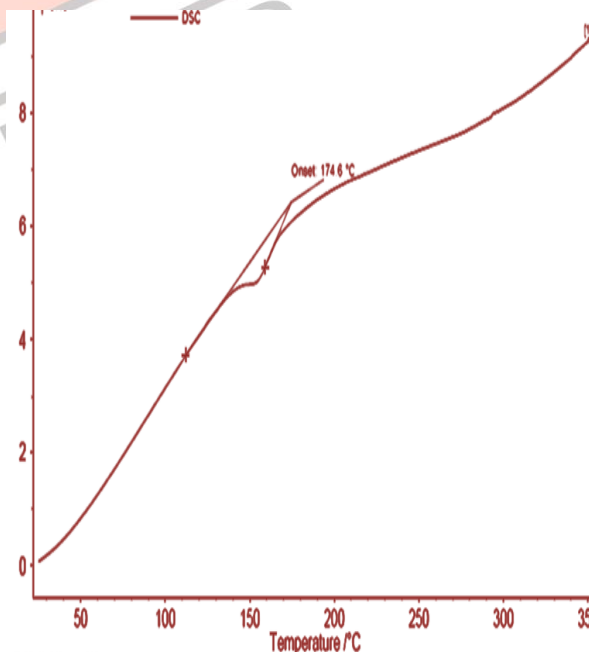

Figure 15a:DSC curve Neat PP   Figure 15b: DSC Curve PP nanocomposite

Figure 15: Show the thermal properties of PP and its nanocomposites .DSC curves obtained in Nitrogen gas at 10degreec/minute heating rate.

An enhancement of approximately 27.9 ^{0}C in onset temperature and about 8.9 ^{0}C in peak temperatures is observed using only 5wt % Graphene. These features are strong indications that graphene can function as a flame retardant, significantly improving the thermal stability of isotactic polypropylene. The works explained in references [32&33] are aligned to this result.

In-fact, our processing measures have significantly higher values than the reports in these references. Probably it causes because of the minute quantity of other additives as silicon which proves to be complementary to fill the void if any and helps in ceasing the burning trend.

The Mechanical test data represented data[table 6] herein clearly indicate the increase in the tensile strength of nanocomposite by 34 % and Young modulus by 39%.The shore hardness test is increased by 19%.

Table6: Mechanical properties

Mechanical property	Neat	Nanocomposite
Tensile Strength	23 MPa	31MPa
Young Modulus	630.51MPa	752.2 Mpa
Shore Hardness	62.60	75.02

The tensile strength increased to 31 MPa from 23 MPa showing more than 37 % improvement. There was also improvement in Young Modulus by about 19.30% which is very significant improvement. The materials are become harder reading a shore hardness values 75.02 from 62.60. These mechanical performance tests are suggestive the effect of graphene caused in the polymer which are reinforced significantly.

The graphene has reinforced the base polymer and seek immediate applications wherever tougher polypropylene materials are required. The defined parameters of the filler in polymer for effective result [26] have been successfully achieved in this experiment resulting into the innovative products.

Thus, the ready master batch can be used as per the user`s own threshold values to achieve the tailored properties of the finished product. Earlier work in this direction lacks the maintenance of complementary inherent properties while advancement in other properties was conducted. The respective standard samples were prepared and tested for electrical conductivity, flame resistivity, gas barrier and mechanical properties. The work presented herein contains the novel concept of molecular arrangement of the constituents in a complex environment of the nanocomposite. The real demonstration of the processing equipment, images are presented .The Graphene based nanocomposite considering 5% wt graphene in final product is considered as the percolation threshold. The conductive nanocomposite with enhanced properties was obtained. The immediate applications allow using this material as EMI shielding materials which have exceptional mechanical and thermal properties.

V.CONCLUSION
The exfoliated graphene found to be of ideal grade having very thin active layers with large surface area as evidenced by STEM image. The conceptual design for molecular arrangements was successfully implemented as shown in fig 14. The nanocomposite developed with 5% graphene content in final product is optimized. The nanocomposite has shown multi-directional property enhancement. The non-conductive PP polymer turned to conductive nanocomposite with significant improvement in the mechanical properties, thermal properties and gas barrier properties. Such material with overall improvement seeks immediate applications as structural materials in the industries.

Graphene based nanocomposite developed successfully. The ready master batch can be used for easy processibility in the industrial practices.

VI.ACKNOWLEDGMENT

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