Mechanical and EMI shielding behavior of ABS based Hybrid Composites

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MS Materials and Surface Engineering

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To my Parents,

&

To my siblings
This humble work is a sign of
my love to you!

Acknowledgement

“Truly my prayer and my service of sacrifice, my life and my death, are (all) for ALLAH, the Rabb (Only God, Cherisher and Sustainer) of the Worlds”. (Quran 6:162)

All prays and glory is due to **ALLAH**, Whose worth cannot be described even by the greatest rhetoricians of all times, Whose blessings and bounties cannot be enumerated by beckoners and enumerators of all ages, and homage due to Him cannot be adequately paid even by the most assiduous and revering attempters.

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Ammad Ali

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Abstract

The rapid development of wireless telecommunications has revolutionarily modernized the ubiquitous society, whereas it has created serious concerns on harmful effects of the electromagnetic interference (EMI) on human health and performance of commercial, military, and electronic devices, especially in the gigahertz (GHz) band range. These problems can be minimized through using EMI shielding materials, which block or shield the devices from unwanted electromagnetic waves and provide an effective solution to meet working requirements of such devices. As a shielding material, metals have been widely used to mitigate the EMI problems due to their excellent electrical conductivity and resulting effective shielding efficiency. Recently, polymer composites with conductive nanocarbons, for instance, carbon nanofibers (CNFs) , carbon nanotubes (SWCNTs and MWCNTs) and graphene, have taken a growing attention over metals due to several advantages of low cost, light weight, good resistance to corrosion, and ease of processibility.

In this research we used simple solution casting method in order to synthesize hybrid composites of ABS based on graphene and Barium Hexaferrite as fillers. These two phase and three phase hybrid systems are prepared using solution casting route and characterized using Wide angle X-rays diffraction (WAXD), Scanning electron microscope (SEM), Impedance analyzer , Ultimate tensile testing machine and Vector network analyzer (VNA) test. Barium Hexxaferrite phase is confirmed using WAXD.

Graphene is dispersed evenly in the ABS polymer matrix up to 0.5 weight% but show some densification at 1 and 5 weight% which was confirmed by SEM and WAXD. The mechanical properties were enhanced in case of ABS/GN composites up to 0.5 wt % of graphene. The EMI shielding behavior of the Hybrid composite was enhanced drastically. The dielectric constant enhanced up to 84 % in case of Hybrid composites, and dielectric loss was increased by 98%. The EMI shielding value was raised up to 30 dB which indicates 99.9 % blockage of the incident wave. Considering the simplicity and versatility of solution casting method, Hybrid composites are found to be easy to manufacture and effective as well.

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CHAPTER-1

INTRODUCTION

1.1 INTRODUCTION TO ABS

ABS is a thermoplastic co-polymer. It has a glass transition temperature at about 100°C.
It has a wide range of application zone starting from domestic to commercial ones. The reason behind wide range of application lies in its structure because it constitute of 3 different polymeric systems, which are responsible for imparting different chemical and physical properties within ABS. ABS is a non toxic and a chemical resistant polymer and it has got good impact strength and good mechanical properties. As per the concern of engineers they are replacing the traditional materials from ABS because of its wide area applications. Nowadays ABS is mainly used in the manufacturing of pipes in many piping industries as in most of the polymers has failed to provide necessary properties that are required in piping system, for them ABS is a cheap and a very innovative replacement.

ABS is a co-polymer made by polymerization of styrene, butadiene and acrylonitrile.

a. POLY ACRYLONITRILE (PAN)

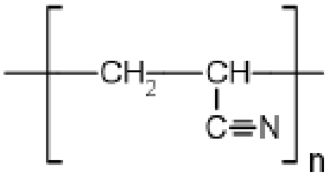


Fig-1(a) PAN Chemical formula

PAN itself is a semi crystalline polymeric resin. The monomer for PAN is Acrylonitrile which is synthetic resin and made up from polypropylene and Ammonia. As it is a tough thermo plastic it does not melt under normal conditions, it usually melts at 300°C only if the heating rate is is 50°C/min or even more.

PAN has also got variety of uses, it can be used as ultra filtration membranes, most of the fibers are also utilized in fiber or textile industry. PAN is also a chemical precursor used in the preparation of carbon fibers.

It has got good chemical resistant and mechanical properties.

b. POLY STYRENE (PS)

Polystyrene belongs to the aromatic class of polymers with styrene as a monomer. As shown in the figure 1(b) styrene takes part as an integral unit of the whole polymeric chain. It has a variety of usage but still it got poor resistance barrier properties against water and oxygen.

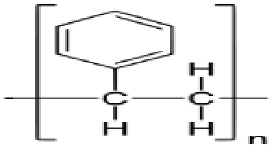


Fig-1(b) PS Chemical formula

As per isomeric forms are concerned it has got two different forms syndiotactic and atactic forms, they are semi crystalline and amorphous respectively and has a melting temperature of 270°C and 90°C respectively.

Mostly its is seen that PS is always atactic in nature and can be utilized in the manufacturing of bottles, trays etc.

c. POLY BUTADIENE (PB)

Poly butadiene lies in the category of elastomers, it is made synthetically by the polymerization of 1, 3 butadiene. It is actually a rubber which contains an amorphous and a cross linked type of a structure. Isomers of poly butadiene are formed due to its structure (cis, Trans and vinyl poly butadiene).

The manufacturing of tires and its various components involve poly butadiene. The cis type poly butadiene is used by 70% tire industry.

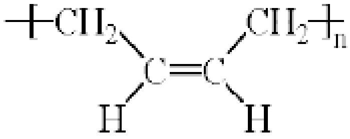


Fig-1(c) PB chemical structure

PB has got low rolling resistance and high wear resistance because of its low glass transition temperature and physically rubbery at room temperature. This made itself very useful in tire industry because of its long lasting property and lesser fuel consumptions. Some other useful properties of PB include good impact strength, toughness and resistance to abrasion. [1]

d. ACRYLONITRILE BUTADIENE STYRENE (ABS)

ABS has an amorphous structure, belongs to a family of thermoplastics having a Tg around 100^{o}C

It is considered to be superior to many other different polymers due to its high toughness, high Hardness and also good electrical insulation properties.

The main composition contains styrene with a different weight percentage of butadiene and acrylonitrile. The ABS can be made up of different grades because of changing proportions of these monomers to achieve properties like hardness, rigidity and toughness.

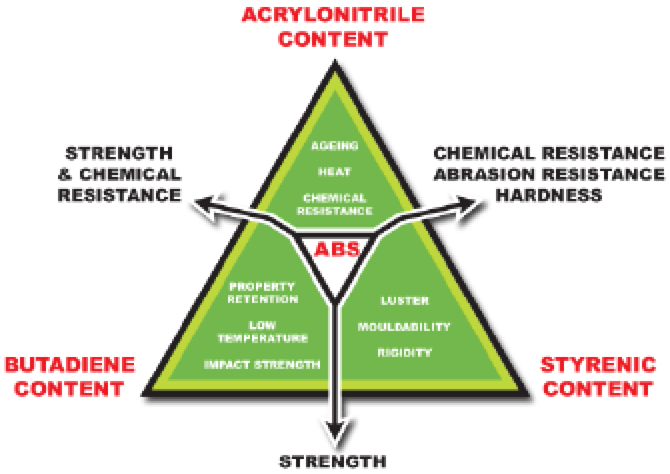


Fig-1(d) properties of ABS with respect to monomer concentration

1.2 PROPERTIES OF ABS

Some of the basic properties of ABS are given below

a. IMPACT STRENGTH

ABS has high impact strength and a very high ductility rate at lower temperatures as compared to other thermoplastics as uPVC. Now where ever high impact strength is required ABS is mainly used. [2]

For example in car bumpers and head helmets for bikers ABS is used to provide high impact strength.

The graph given below shows a comparative analysis of ABS and uPVC piping systems regarding their impact strengths vs temperature

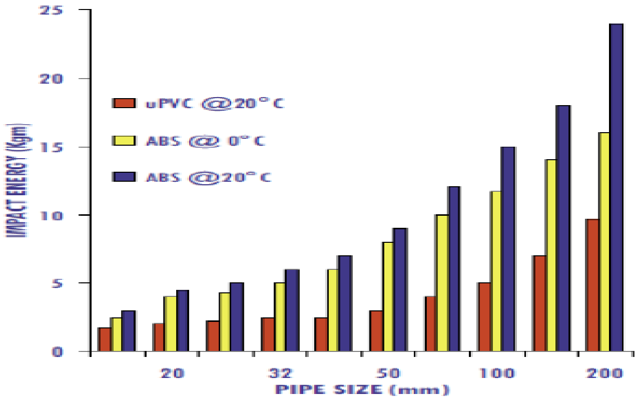


Fig-1.2(a) variation of impact strength with respect to pipe size of different polymers at 20 degree Celsius [2]

b. THERMAL EXPANSION

It is a property of all types of thermoplastics that they expand more than metals. The figure shows same kind of a behavior. The coefficient of linear thermal expansion for ABS polymer is 10.1x10^{-5}mm/^{o}C. [2]

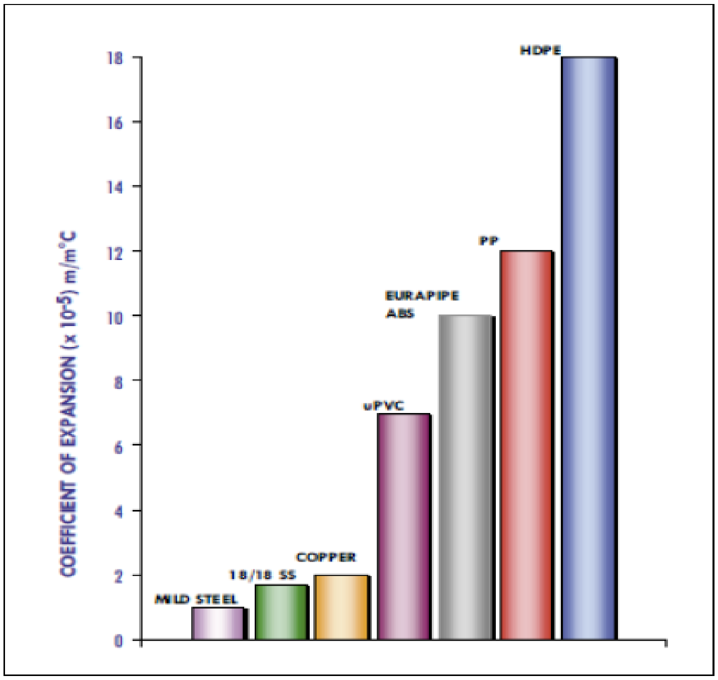


Fig-1.2(b) coefficient of thermal expansion of different polymers

c. TOXICITY AND TAINT

Some times to manufacture thermoplastics heavy metals are used as stabilizers. But when it comes to ABS, no metals stabilizers are required to manufacture ABS so it contains no metal traces which indicates whenever ABS is used there will be no chance of leaching a metal from ABS especially when we are using it in piping systems.

ABS is also known for its non taint property and as per this reason we can easily utilize them to transportation of portable water, kind of eatables like (soft drinks/ caramel/wine etc) and different kinds of similar type products [2]

d. ABRASION RESISTANCE

When it comes to abrasion resistance ABS is even consider to be more useful than steel [2]. The application area includes piping systems that are used in slurries of mining, waste water treatment and power etc. for corrosive and erosive conditions, the chemical resistance and high impact strength property of ABS makes it more workable in these kind of environments , as if we use metals there life is more less as compare to ABS.

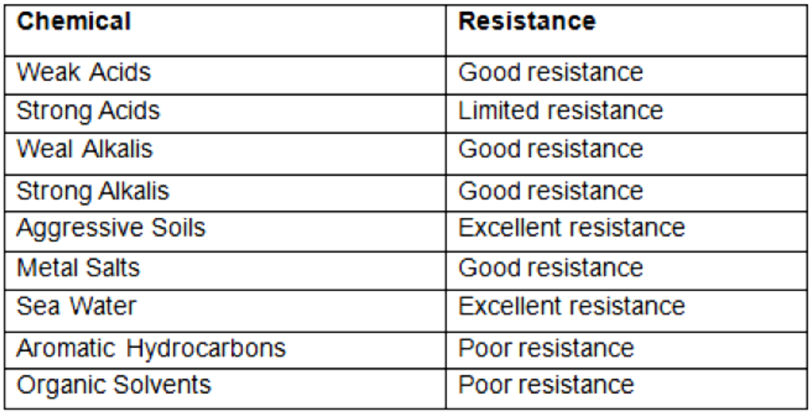
The rubber like butadiene phase is responsible for the high abrasion resistance of the ABS polymer

e. RIGIDITY AND STIFFNESS

As ABS is a rigid plastic, it has a recommended useable temperature to be present between (**-30 to 60^{o}C)** but it is reported that more reliable supports are to be used when it comes to temperature above 60^{o}C.

f. CHEMICAL RESISTANCE

The chemical resistance is an intrinsic property of ABS polymer which makes it useable in any kind of environment, some of the resistances vs chemicals are given below in the table [2]

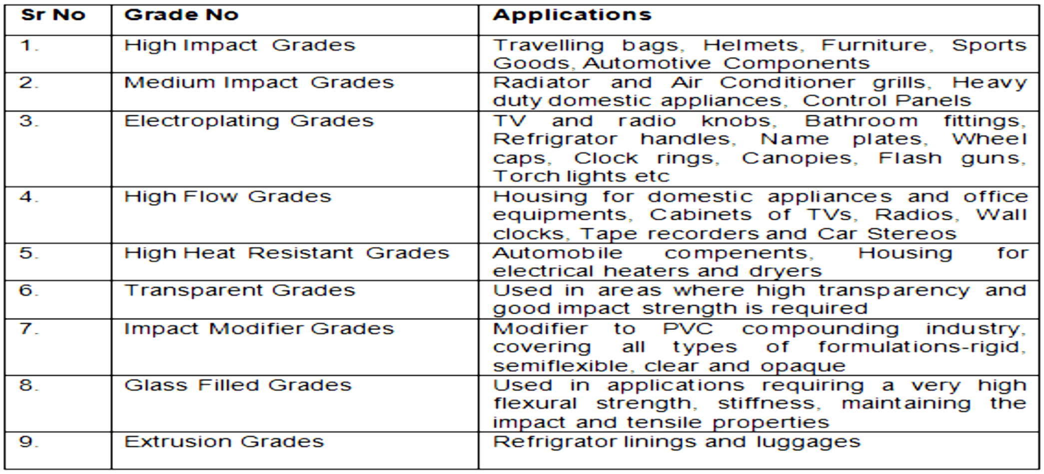


Chemical	**Resistance**
Weak Acids	Good resistance
Strong Acids	Limited resistance
Weal Alkalis	Good resistance
Strong Alkalis	Good resistance
Aggressive Soils	Excellent resistance
Metal Salts	Good resistance
Sea Water	Excellent resistance
Aromatic Hydrocarbons	Poor resistance
Organic Solvents	Poor resistance

Table 1.1 Chemical behavior of ABS polymer

1.2.1 GRADES OF ABS

ABS granules are processed into different kind of desired products using many thermoplastic processing techniques, as different grades are available internationally. Some of the basic grades are listed below in the following table



Sr No	**Grade No**	**Applications**
1.	High Impact Grades	Travelling bags, Helmets, Furniture, Sports Goods, Automotive Components
2.	Medium Impact Grades	Radiator and Air Conditioner grills, Heavy duty domestic appliances, Control Panels
3.	Electroplating Grades	TV and radio knobs, Bathroom fittings, Refrigrator handles, Name plates, Wheel caps, Clock rings, Canopies, Flash guns, Torch lights etc
4.	High Flow Grades	Housing for domestic appliances and office equipments, Cabinets of TVs, Radios, Wall clocks, Tape recorders and Car Stereos
5.	High Heat Resistant Grades	Automobile compenents, Housing for electrical heaters and dryers
6.	Transparent Grades	Used in areas where high transparency and good impact strength is required
7.	Impact Modifier Grades	Modifier to PVC compounding industry, covering all types of formulations-rigid, semiflexible, clear and opaque
8.	Glass Filled Grades	Used in applications requiring a very high flexural strength, stiffness, maintaining the impact and tensile properties
9.	Extrusion Grades	Refrigrator linings and luggages

Table 1.2 Grades of ABS with respect to applications

1.3. INTRODUCTION TO GRAPHENE

Graphene is an allotropic form of carbon that have carbon atoms have bounding to each other in a honey comb structure where each carbon atom have the same valency throughout the lattice[3]. If it comes to the complex structures the graphene is in the form of sp^2 hybridized carbon atoms having a molecular bond length of 0.142 nm. There are different layers of graphene that are stacked together on each other with an interplanar spacing of 0.335 nm forms of graphite.

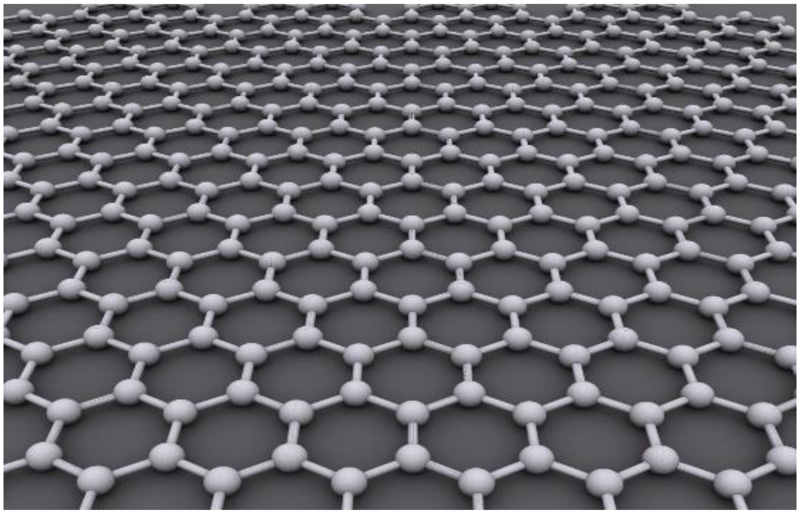


Fig-1.3(a) graphene sheet structure 2D

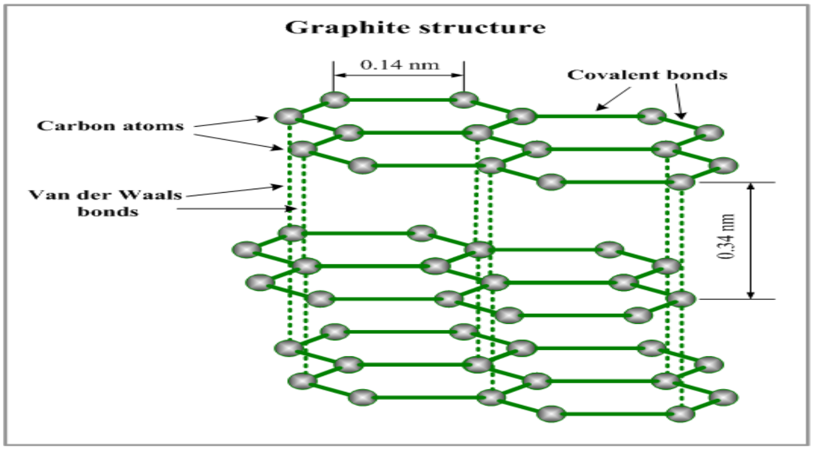


Fig-1.3(b) graphene sheet structure 3D

1.4. NOMENCLATURE OF GRAPHENE

In accordance to the research presented by Alberto Bianco et al. he has presented a set of principles related to recommend definitions related to graphene. [4]

a. GRAPHENE

It is a sheet having a thickness of one atomic thickness with sp^2 hybridized carbon atoms bounded in a hexagonal structure to form a substrate. The lateral dimension ranges from several nano meters to macro scale.

b. GRAPHENE LAYER

It is a sheet having a thickness of one atomic thickness with sp^2 hybridized carbon atoms bounded in a hexagonal structure to form a substrate. The sturucture of the graphene can be 3 D as well.

c. MULTI LAYER GRAPHENE (MLG)/ FEW LAYER GRAPHENE(FLG)

This is a 2D sheet like material and has a form of free standing fils/flakes, substrate that is bounded coating consist of a few layers (2-10 for multi layers an 2-5 for few layers) of graphene. These layers are countable and have well defined stacked layers of graphene.

d. GRAPHITE NANOPALTES/ NANO FLAKES / NANO SHEETS

These graphene also have a 2D structure with ABCA or ABA stacking. There lateral dimension ranges from less than a nano meters.

e. GRAPHENE OXIDE (GO)

Oxidation and exfoliation of graphene is incorporated by heavy oxidation of the basal plane of graphene. GO itself is a monolayer material and has a high content of oxygen within itself.

f. REDUCED GRAPHENE OXIDE (rGO)

There are several methods as in thermal, chemical, microwave, photo-chemical, microbial, photo-thermal or bacterial methods in order to reduce to GO to get rGO in which the oxygen content is reduced.

g. EXFOLIATED GRAPHITE

The exfoliation of graphite using thermal, chemical and mechanical methods in order to form thin multi layers packets retaining the 3D structure.

h. GRAPHENIZATION

“It is a process of development, growth, or precision of graphene layers during the processing of disordered carbonaceous solids’’

1.5. PROPERTIES OF GRAPHENE

a. MECHANICAL PROPERTIES

Considering the strength of its 0.142 nm long C-C bonds, graphene is found as one of the strongest material, having an ultimate tensile strength of 130 GPa compared to 400 MPa for structural steel A36, or 375 MPa for Kevlar (Aramid) . Moreover, graphene is very light as well with 0.77 mg/ sq. m (1000 times lighter than 1 sq. m of paper). [5]

Graphene has elastic properties as well. AFM tests performed in 2007, on SiO2 suspended graphene sheets of thickness 2-8 nm shown that spring constants of these sheets are 1-5 N/m and young’s Modulus of 1500 GPa. However, data is based on graphene which contains no defect, which are very costly and very difficult to fabricate, fabrication techniques are enhancing with passage of time thus reducing cost.

b. ELECTRICAL PROPERTIES

Graphene consists of zero-overlap semi-metal structure with high electrical conductivity, because of both holes and electrons behave as charge carriers. Carbon atoms present in the structure have got 6 valence electrons; 4 in the outer and 2 in the inner orbit. These 4 outer orbit electrons in an atom are for chemical bonding, but in hexagonal lattice, each C atom is connected to 3 other C atoms in the 2-D plane, as leaving 1 free electron in the 3-D for electronic valance conduction band. These highly mobile electrons are present on both sides of graphene sheets and are known as as π electrons. These overlapping π orbitals assist to improve the C-C bonds in graphene. Hence, the electronic properties of graphene are restricted by bonding and anti-bonding i.e. valance and conduction bands of π orbitals.[5]

c. THERMAL PROPERTIES OF GRAPHENE

The in plane thermal conductivity of graphene is very high that is strongly affected by interfacial interactions atomic defects and edges but as the out of plane conductivity is concerned it is relatively low.

The specific heat is endorsed by phonons and it is a bit higher than that of graphite and even diamond at room temperatures.

Composites made from graphene utilized in electronics efficiently controls the heat dissipation [5]

1.6. Structure of Barium Hexaferrite BaM

There are two blocks i.e, S and R blocks that overlap hexagonally and cubically packed layers which are responsible for the construction of the unit cell of BaM. In a mirror plane barium atom is present in the basal plane, two S blocks are stacked above and below on R block therefore around the C-axis they have a capability of 180° rotation. Therefore to continue the structure a minor R block R^* is required and the unit cell formula become SRS^*R^*.

The sign * shows 180 degree rotaion of the block through c-axis

Lattice parameter is 23.7 A^0 [6]

The figures below shows the blocks and overall BaM structure

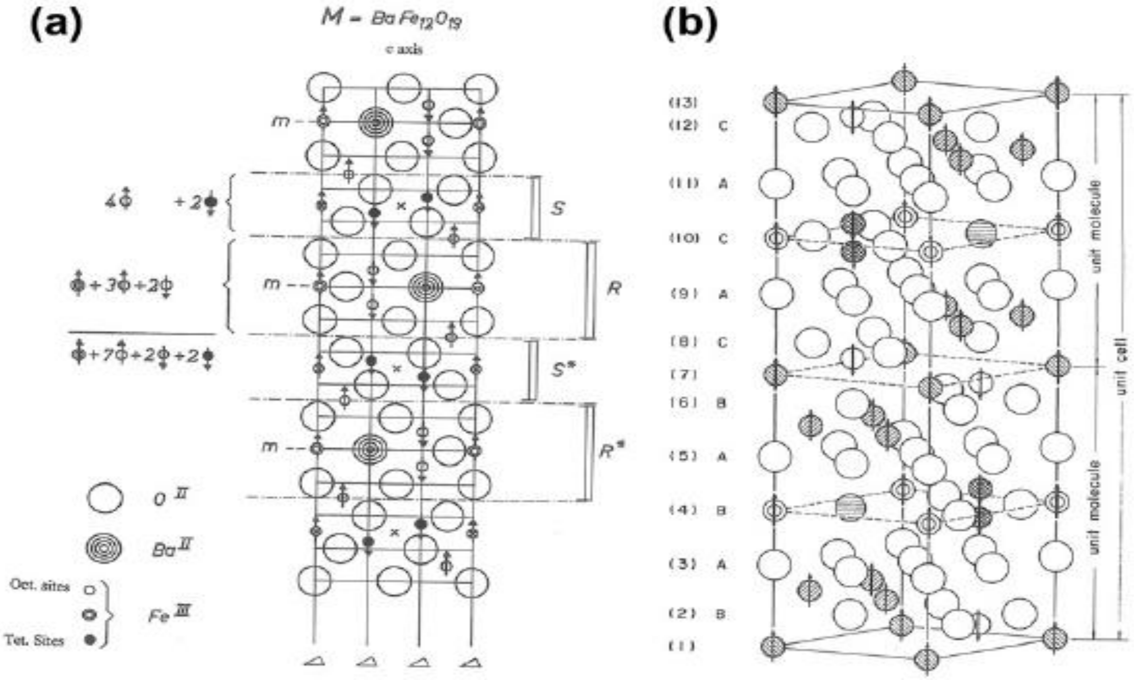


Fig-1.6(a) BaM structure 2D (b) BaM structure 3D

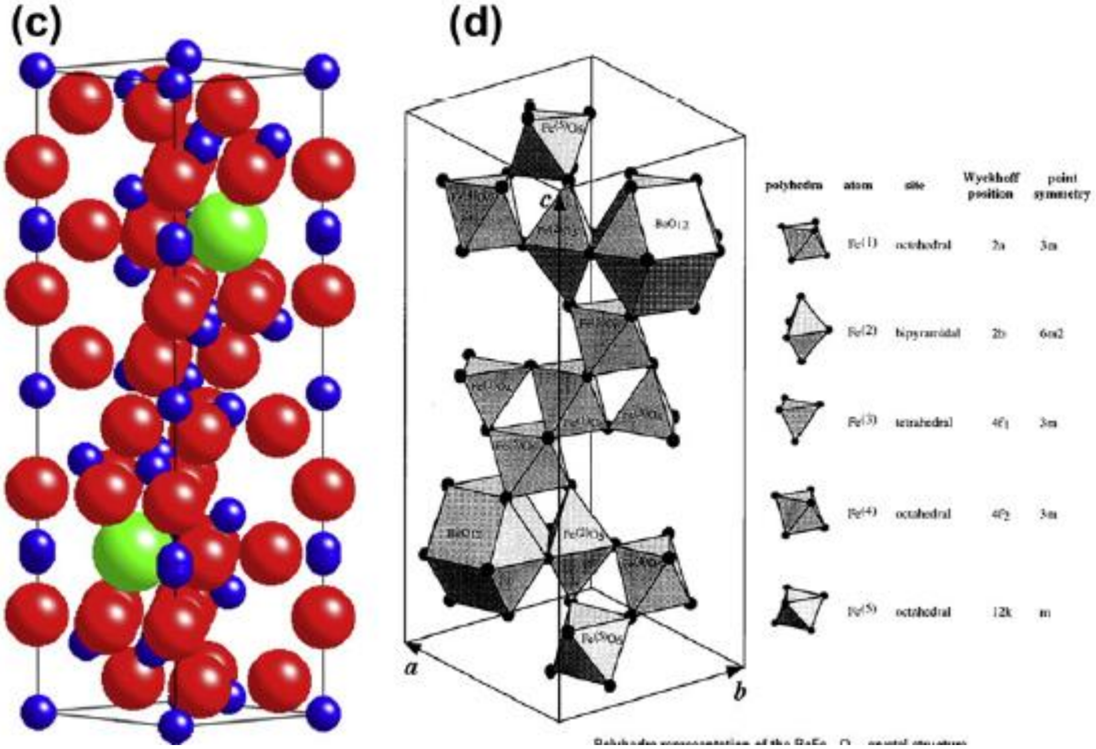


Fig-1.6(c) BaM structure 3D atomic positions (d) The polyhedra of the BaM unit cell [6]

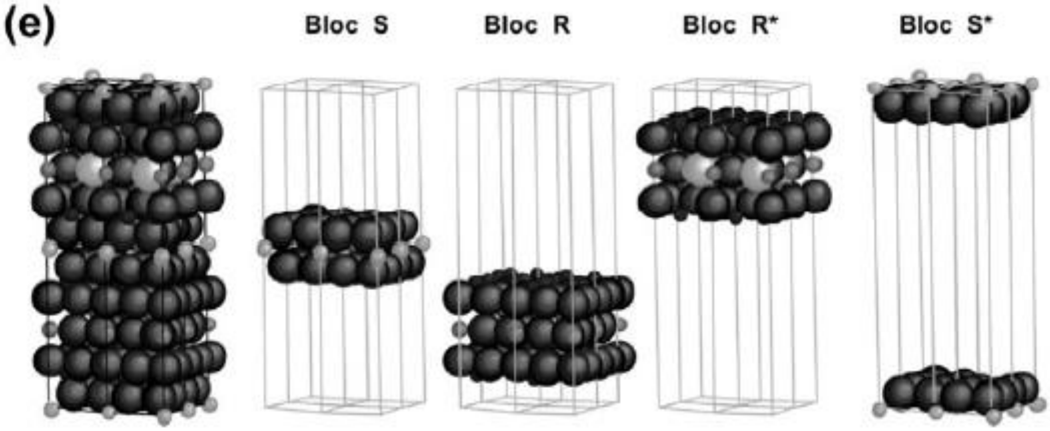


Fig-1.6(e) The RSR*S*stacking sequence

1.7. PROPERTIES OF BaM Nano Particles

- The BaM compound has been know for many years, it has the melting point of 1390^{o}C
- It possess a Hexagonal structure
- It was first studied by Philips in 1950
- It contain no cobalt and nickel but at the same time is a Hard magnetic material with a coercivity of 160-255kA/m.
- Electrically resistive with resistivity of 10^8 ohm/cm.
- Molecular mass 1112 g and density is 5.295 g/cm3 [6]

CHAPTER-2

ABS BASED NANOCOMPOSITES

2.1 NANOCOMPOSITES

Structurally Nanocomposites are considered to be multiphase materials where the reinforcement phase is in the dimension of less than 100 nanometers (nm) or simply it can be explained as a material having nano-scale repeat distances between different phases that make up the material .

The material of the matrix and reinforcements decides the mechanical, thermal, optical, electrochemical and catalytic properties of the nanocomposites. For the above mentioned properties the limiting factor is the size of the nano particles used as nanofillers and the proposed size limits are as follow [7]

- less than 5nm for catalytic activity.
- Less than 20 nm for making hard magnetic material.
- Less than 50 nm for refractive index changing
- Less than 100 nm for achieving super para-magnetism, it can also be used for strengthening or restricting matrix dislocation movement.

As the CNTs and Graphene based nanocomposites possess high strength and stiffness, both are considered to be good reinforcements for structural point of view and the composites will be having light weight and high strength".[8]

2.2 COMPOSITE FABRICATION TECHNIQUES

Considering the type of polymer used, different type of methods/routes can be used for CNT-Polymer nanocomposites. Some of the majorly used techniques can be used for this process listed below

a. SOLVENT CASTING METHOD

The simplest method used for the synthesis of CNT based nano polymer composites is solution casting method. But we have a limitation in which polymers that can dissolve themselves in a particular solvent can be used only. In this technique nanotube are dispersed in a suspension of CNTs in the polymer solution by energetic agitation (Sonication or magnetic stirring). Then the solvent is allowed to evaporate in a desired environment to cast a polymer nanocomposite film. We can find a lot of study for formation of nanocomposites using solvent casting method [9-10].

The agglomeration of nanotubes may occur during solvent evaporation, as too much time is required for the evaporation (slow process) and this may lead to inhomogeneous distribution of nanotubes in polymeric matrix. However the evaporation time can be decreased by use of hot substrate [11] or rotating substrate surface [12]. Moreover, choice of solvent can have a significant impact on dispersion of CNTs and same has been studied by Lau KT et al. for SWCNTs [13].

b. MELT MIXING METHOD

Thermoplastic polymers are mostly used of this manufacturing method. Polymeric melt is made under applied high temperatures and then shear mixing is done to homogenize the CNTs within the polymeric matrix. A variety of shapes can be produced by processes such as compression/injection molding or by using an extruder.

Andrew et al. [14] synthesized composites by using commercial polymers such as high impact PP, PS and ABS with MWCNT using melt processing method. The master batches of CNT s loaded polymer composites were made using high shear mixing at elevated temperatures. These master batches were then diluted with pristine polymer to make samples having lower mass fractions. Afterwards, compression molding process was used to form composite films.

Agglomeration of CNTs and their dispersion in polymer matrix is as issue when dealing with melt mixing process. Niu et al. [8] studied both cases i.e. solvent casting and melt mixing methods for synthesis of polyvinyldiene fluoride (PVDF)/CNT nanocomposites to study electrical properties and found films casted by solution casted method were performing good electrically as compare to those prepared by melt processing method.

c. IN-SITU POLYMERIZATION

In this process the dispersion of CNTs is achieved in between polymerization of the monomers. In this process a stronger and a well defined interface between polymeric matrix and CNTs can be achieved because as the polymer is in its growth stages it can form good interactions with the CNTs as compare to form them after polymerization [15, 16]. By the use of this technique CNTs can be crafted on polymeric chains effectively. This process can be used by any kind of polymeric matrix. However when we consider insoluble and thermally unstable polymers on this method will be used.

d. OTHER METHODS

In some of the methods the researchers avoid the factor of viscosity; they even have increased the viscosity by decreasing temperature to processes in the solid state [10]. By using pan milling the solid state mechano-chemical pulverization processes is used for this purpose[17] or twin-screw pulverization can also be used [18], MWCNTs with polymer matrices can be mixed.

Pulverization methods can be used alone or it can be followed by melt mixing. Grafting polymers on the CNTs can be achieved using this method, having good dispersion, improved interfacial adhesion [17], and enhanced tensile modulus [17, 18].

2.3 MANUFACTURING OF ABS/GRAPHENE NANOCOMPOSITES

Cheol Heo at al. [19] manufactured ABS nanocomposite films related to functionalized graphene sheets. First, Hummers method was used to prepare water soluble GO. Then sonicationwas done to disperse GO in water to get a dispersion contained mainly individual graphene sheets. Second, the exfoliated GO was reacted with an alkyl-amine to get a solution of functionalized graphene (C18 Graphene).

ABS/C-18 Graphene hybrid films were synthesized using solution casting method. In 30 ml of chloroform 2 gm of ABS was dissolved by stirring at room temperature for 24 hours. C-18 Graphene at a required wt% was ultra-sonicated in chloroform for 10 hours and then Nitrogen gas environment was used for mixing of these two solutions to get finally dispersed solution. For 24 hours at 45˚C the solution was casted in petri dishes in oven. At last films were dried in a drying oven for 24 hours at 85˚C. The thickness 80-100 µm were obtained by this method.

Bhardwaj Neha et al. [64] manufactured ABS based nanocomposites by using exfoliated graphene. First, the chemical route (Staudenmaier method) was adopted for the synthesis of graphite oxide (GO). Second, reduction of GO which was done to get exfoliated graphene sheets by using thermal exfoliation method

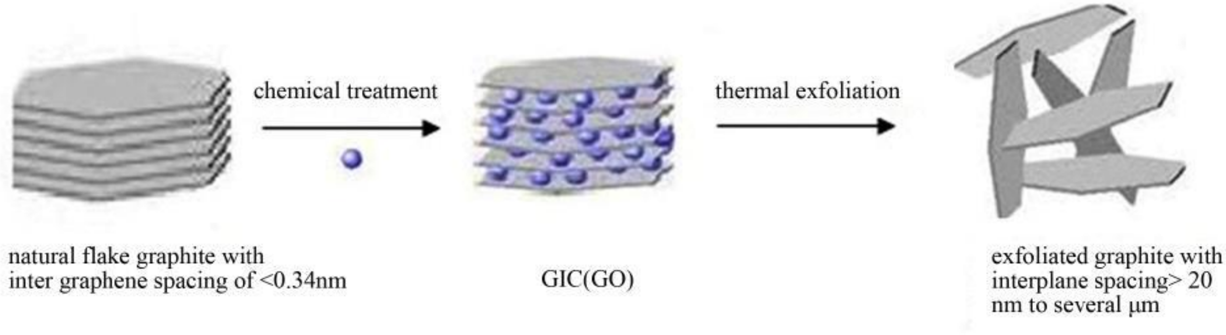


Figure-2.1. Schematic illustration of the synthesis of Exfoliated Graphite

ABS/Exfoliated Graphene composites were prepared using solution casting method. Exfoliated graphene was mixed in Tetrahydrofuran (THF) using probe sonication for about 35 min. 1 g of ABS pellets was dissolved in 10 ml of THF by stirring and then added to exfoliated graphite-THF solution. This solution was again probe sonicated for 35 min and was casted into a petri dish for 48 hours room temperature evaporation. Finally, these films were further dried in oven for 24 hours at 80°C. ABS/Exfoliated Graphene sheets of thickness 0.27 mm obtained [20]

2.4 MORPHOLOGY OF ABS/GRAPHENE NANOCOMPOSITES

Cheol Heo at al explained the morphology of the composites by the following images. [19] it can be seen by SEM images shown below in figure 2.2(a)

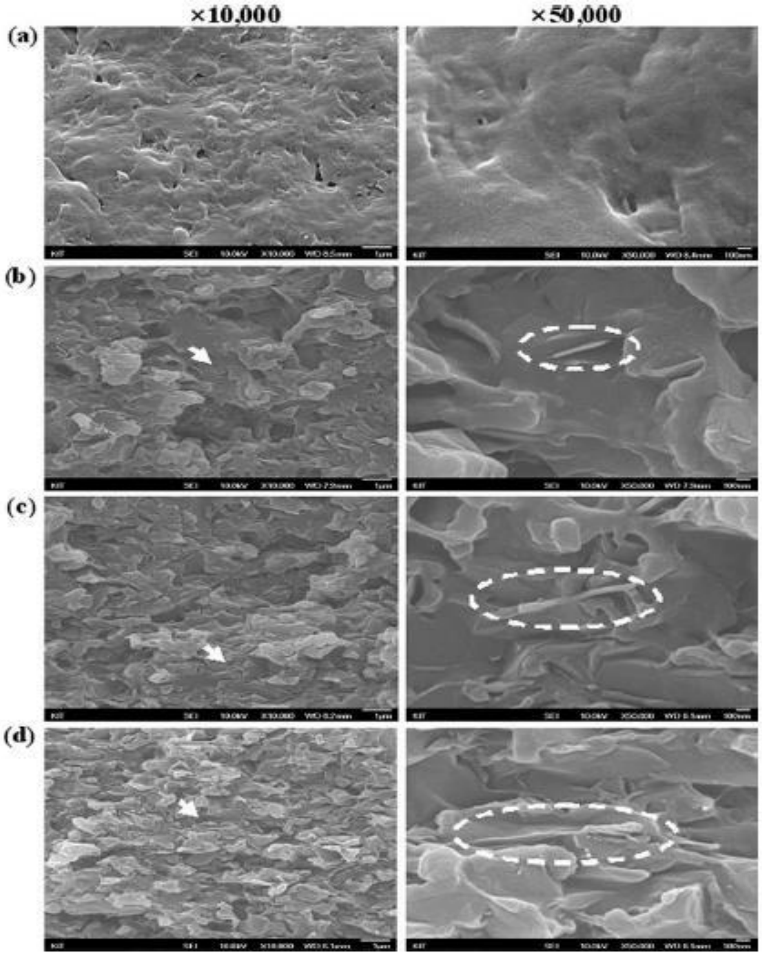


Figure 2.2(a). SEM images of ABS nanocomposites containing (a) 0 (pure ABS), (b) 1, (c) 2 and (d) 3 wt. % C18-Graphene [19]

Figure 2.4 shows fracture surfaces of the ABS composite films containing different C18-Graphene wt%. Graphene shows the platelet orientation distribution morphology. As there is a difference in the scattering densities of the graphene and the ABS polymer, graphene dispersions observed in the SEM images. Figure 2.4(a) (b–d) depicts good dispersion of the graphene in the ABS at different magnification levels. It can also be seen that graphene remains in the form of straight and rigid platelets in the composite, indicate that the graphene is very much stiff [63].

Bhardwaj Neha et al. [20] manufactured ABS based nanocomposites by the use exfoliated graphene. At first, GO was synthesized from graphite and then thermal exfoliation method was used to obtain exfoliated graphene sheets. SEM images of natural flake graphite and exfoliated graphene are shown below in figure 2.2(b)

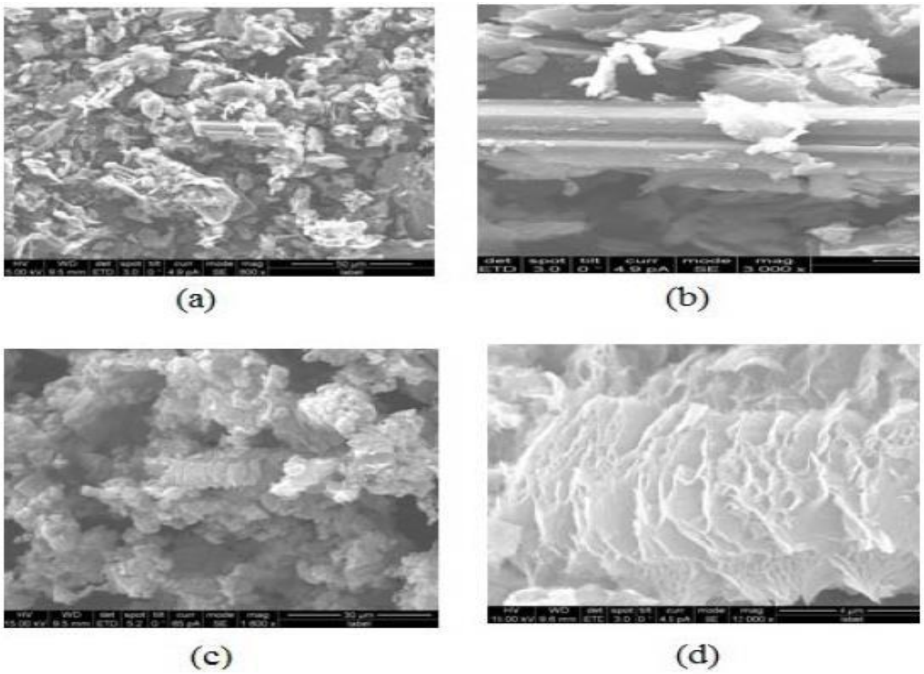

(a) (b) (c) (d)

Figure 2.2(b) . (a) SEM images of natural flake graphite at 800X, (b) Graphite agglomerates at 3000X, (c) Exfoliated graphite at 1000X and (d) Separated sheets of exfoliated graphite at 12000X [64]

SEM images of ABS nanocomposites using exfoliated graphene prepared by Bhardwaj Neha et al. [20] using solution casting method are shown below as Figure 2.2 (c).

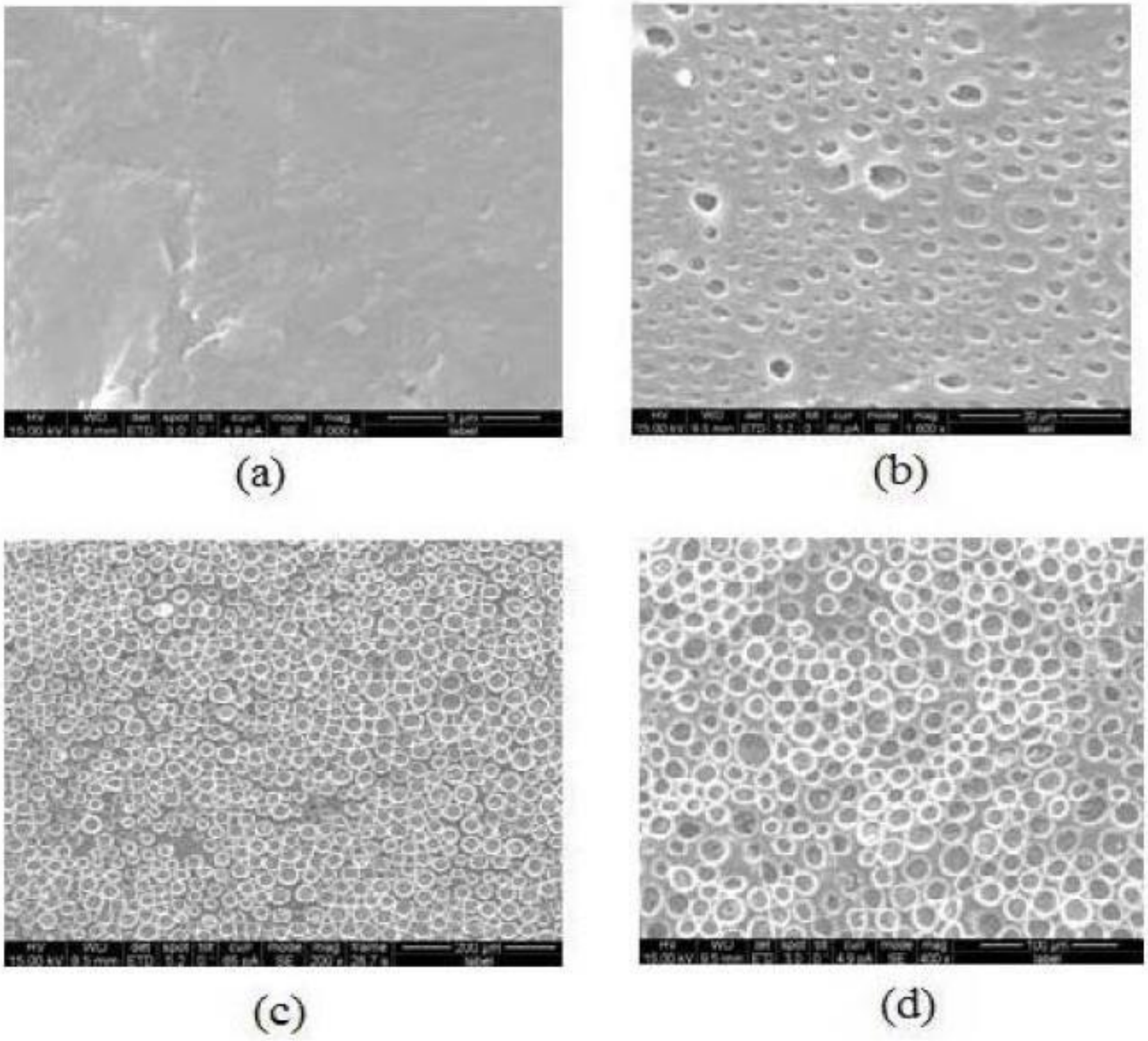


Figure 2.2(c). SEM images of ABS based nanocomposites with exfoliated graphene loading of (a) 2 wt. %, (b) 8 wt. %, (c) 12.7 wt. % and (d) 17.5 wt. % [20]

Figures 2.4 (a)-(d) show SEM micrographs of ABS composite films with varying concentration of exfoliated graphene. As revealed by the micrographs, the exfoliated graphite dispersion was found to be homogeneous within the ABS matrix

2.5 MECHANICAL PROPERTIES OF ABS/GRAPHENE NANOCOMPOSITES

Tensile mechanical properties of pure ABS and ABS/C18-Graphene nanocomposite films prepared by Cheol Heo at al. [19] are shown in Table 2.1 below.

Table 2.1 Mechanical Properties of ABS/C18-Graphene nanocomposite films

C18-Graphene in ABS (wt. %)	**Thickness (µm)**	**Max Strength (M Pa)**	**nitial Modulus (G Pa)**	**E. B. (%)**
0 (pure ABS)	132	21	1.45	2
1	102	29	1.75	3
2	93	25	1.70	2
3	99	22	1.60	2

The maximum strength of ABS-hybrid films increases with the addition of C18-graphene up to a critical graphene loading of 1 wt. % where strength of 29 M Pa (increase of 38%) was observed. However, strength decreases linearly from 29 to 22 MPa upon increase of C18-Graphene content from 1 wt. % to 3 wt. %. A similar trend was observed for initial modulus

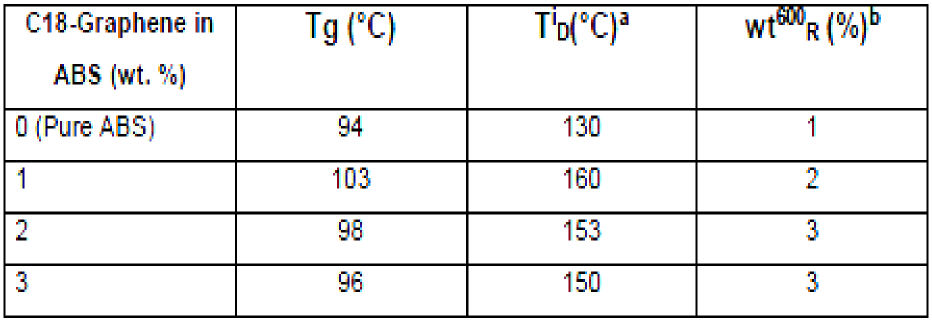
The results presented above [19] show the mechanical properties of the films containing functionalized-graphene are due to the reinforcement given by the intercalation of ABS in graphene galleries, as well as by the dispersion of graphene sheets in the polymer matrix. The improvements in the tensile mechanical properties also depend on the interactions between the ABS molecules and the layered graphene, as well as on the rigidity of the graphene sheets [21].

The elongation to break varies between 2 to 3 % upon increase of C18-Graphene content from 1 wt. % to 3 wt. % and is characteristic of materials reinforced with stiff graphene modifiers. [19]

2.6 THERMAL BEHAVIOR OF ABS/GRAPHENE NANOCOMPOSITES

Thermal behavior (glass transition temperature, Initial thermal decomposition temperature and weight percent of residue at 600°C) of ABS/C18-Graphene nanocomposite films prepared by Cheol Heo at al. [19] using solution casting method are shown in Table 2.2 below.

Table 2.2 Thermal Properties of ABS/C18-Graphene nanocomposite films



C18-Graphene in ABS (wt. %)	Tg (°C)	T^{i}_{D}(°C)^{a}	wt^{600}_{R} (%)^{b}
0 (Pure ABS)	94	130	1
1	103	160	2
2	98	153	3
3	96	150	3

a. At 2% initial weight-loss temperature

b. Weight percent of residue at 600°C

Glass transition temperature (Tg) of ABS/C18-Graphene films was found to increase from 94 to 103°C upon increase of graphene content from 0 to 1 wt. %. This increase in Tg could be due to several factors including an increase in crosslink density and the restriction of the segmental relaxation of the chain segments near the graphene sheets.

Tg of ABS hybrid films was observed to decrease from 103 to 96C upon increase of graphene loading from 1 to 3 wt. %. This decrease is possible due to agglomeration of graphene sheets [19].

The TGA results for the ABS and ABS-hybrid films are also shown in Table 2.2. A similar trend was observed in the initial thermal degradation temperature (TiD). TiD at 2% weight loss of the ABS hybrids was found to be in the range 130–160°C for C18-graphene contents of 0–3 wt. %, with a maximum increase of 30°C observed in the case of the 1 wt. % C18-graphene/ABS with respect to that of pure ABS [19].

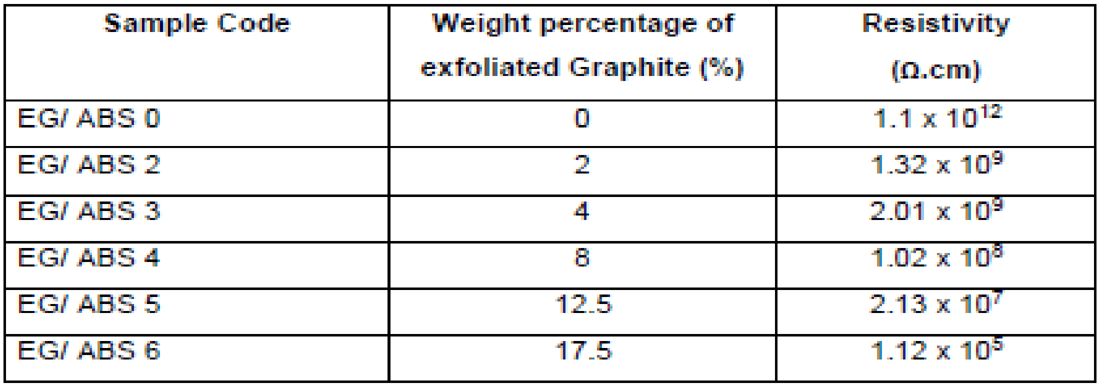
The introduction of filler components into organic polymers can improve their thermal degradation stabilities. Graphene adds thermal stability to nanocomposites because of the thermal isolation effect of the graphene sheets and the mass transport barrier they provide to the volatile products generated during thermal decomposition [19].

This kind of improvement in thermal stability has previously been observed in many hybrid systems [22].

2.7 ELECTRICAL PROPERTIES OF ABS/GRAPHENE NANOCOMPOSITES

Table 2.3 shows conducting properties (based on resistivity of hybrid films) of ABS/Exfoliated Graphene nanocomposites at varying concentrations of Exfoliated graphite sheets prepared by Bhardwaj Neha et al. [20] using solution casting method.

Table 2.3 Conducting Properties of ABS/Exfoliated-Graphite nanocomposite [20]



Sample Code	Weight percentage of exfoliated Graphite (%)	Resistivity (Ω.cm)
EG/ ABS 0	0	1.1×10^{12}
EG/ ABS 2	2	1.32×10^{9}
EG/ ABS 3	4	2.01×10^{9}
EG/ ABS 4	8	1.02×10^{8}
EG/ ABS 5	12.5	2.13×10^{7}
EG/ ABS 6	17.5	1.12×10^{5}

It can be seen from the results that, although there is gradual decrease in resistivity value upon increase of exfoliated graphite loading in ABS matrix but it remains in insulating range for lower concentrations of exfoliated graphite. However, composite with 17.5 wt. % of exfoliated graphite was found to be moderately conducting due to the formation of conducting networks within the polymeric matrix [20].

2.8 OBJECTIVES OF RESEARCH WORK

Following are the main objectives of this research work.

a. Synthesis of ABS based nanocomposites by “solution casting” method using GN and BaM as nanofillers at varying concentration of nanofillers.

b. Characterization and analysis of ABS nanocomposite films for their morphology, mechanical and electrical properties.

c. Highlighting threshold concentration level for every type of filler used in ABS matrix and to compare them together.

CHAPTER-3

EXPERIMENTAL

3.1 MATERIALS

The materials used in the synthesis portion are listed in the table below

Table 3.1 Specifications of materials used

Sr no	Material	Manufacturer /specification
1	1,2 Di-chloro Ethane (DCE)	Labscan Analytical Sciences (RCI Labscan Ltd, Thailand) (Lab Grade)
2	ABS	ABS granules with MFI of 3.07 gram/ 10 min
3	Graphene	xGnPs M25 grade/ XG SCIENCES
4	BARIUM NITRATE	SIGMA ALDRICH USA
5	IRON NITRATE	SIGMA ALDRICH USA
6	NaOH	SIGMA ALDRICH USA

3.2 SYNTHESIS OF BARIUM HEXAFERRITE

The BaM nano particles were synthesized from traditional co-precipitation method.

First the aqueous solution of barium nitrate and iron nitrate in molarity ratio of (1:12) are prepared in 100 ml of water in different beakers. Stirring is performed until homogenous solutions of both nitrates are prepared. Then both the aqueous solutions were heated up to 90^{o}C and mixed together. In another beaker 5M aqueous solution of sodium hydroxide is prepared and heated up to 90^{0}C. Now 5M solution of sodium hydroxide is added drop wise in the solution of iron nitrate and barium nitrate maintained at 90^{0}C. Now the solution is allowed to stir at this temperature for an hour and then it is allowed to stir overnight at room temperature.

After 24 hrs the stirring is stopped and the solution is allowed to get settled down, access amount of water present is removed, more distilled water is added into the system to wash the particles and check the pH after every wash. After 7 washes the pH was maintained at 7. The residual water was dried from the sample in oven over night drying at 100^{o}C.

Then the sample was crushed in mortar and pestle for 1 hour and then I was calcinated in muffle furnace at 1050^{0}C for 6 hours. After calcination the sample was again grinded in mortar and pestle of 1 hour to obtain final BaM nano particles.[23] The schematic representation is given below in figure 3.1

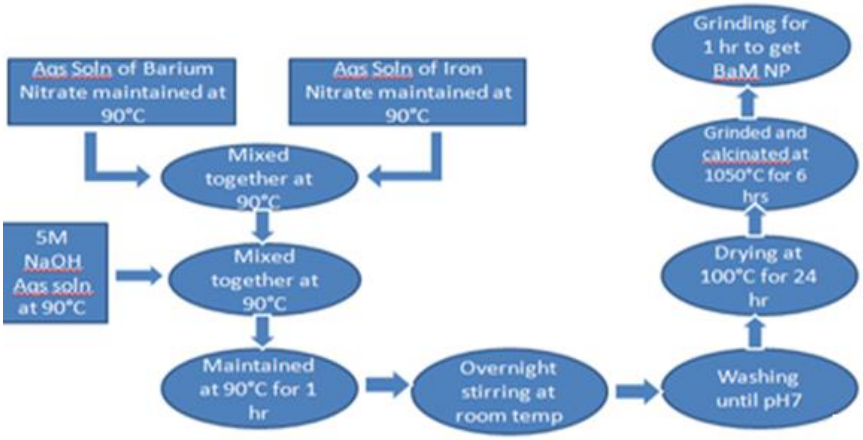


Fig-3.1 schematic synthesis Barium Hexaferrite

3.3 SYNTHESIS OF ABS/GN NANOCOMPOSITES

The ABS/GN nanocomposites were prepared from simple solution casting method.

2grams of ABS was dissolved in 10 ml DCE and left for stirring four about 4 hours. In another system GN was dispersed in 10 ml DCE and ultra sonicated for 30 min. Both solutions were mixed together and left for stirring overnight. After 24 hrs of mixing the mixture is then again ultra sonicated for one hour and then casted into a dried petri dish and placed under the hood for overnight drying. When the sample is fully dried it is casted out of the petri dish. Then the dried film is again placed into a vacuum oven at 40°C for 5 hours in order to confirm any traces of the solvent should be left over within the film. [24]

The schematic representation is as below

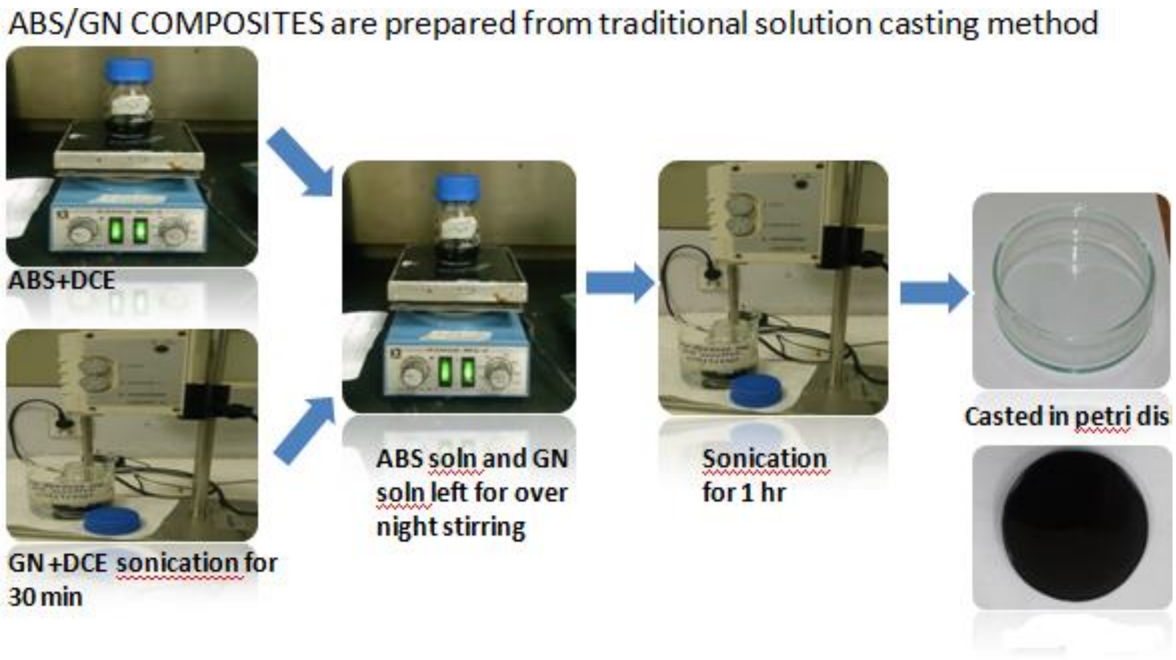


Fig 3.2 schematic Synthesis ABS/GN composites

3.4 SYHTHESIS OF ABS/GN/BaM NANO HYBRID COMPOSITES

The ABS/GN solution that was mixed over night and BaM nano particles dispersed in DCE sonicated for 1 hour were mixed together using a mechanical stirrer made up of Teflon. The reason behing using a mechanical stirrer of Teflon is that the magnetic stirrer used to attract the ferrite particles and then dispersion is not achieved so we used this alternative. Now the stirring was kept for 5 hours and then the whole mixture was again sonicated for 1 hour and casted in the petri dish. Now same method was adopted for vacuum drying as explained above to get the final Hybrid composites. [25]

The schematic is explained below

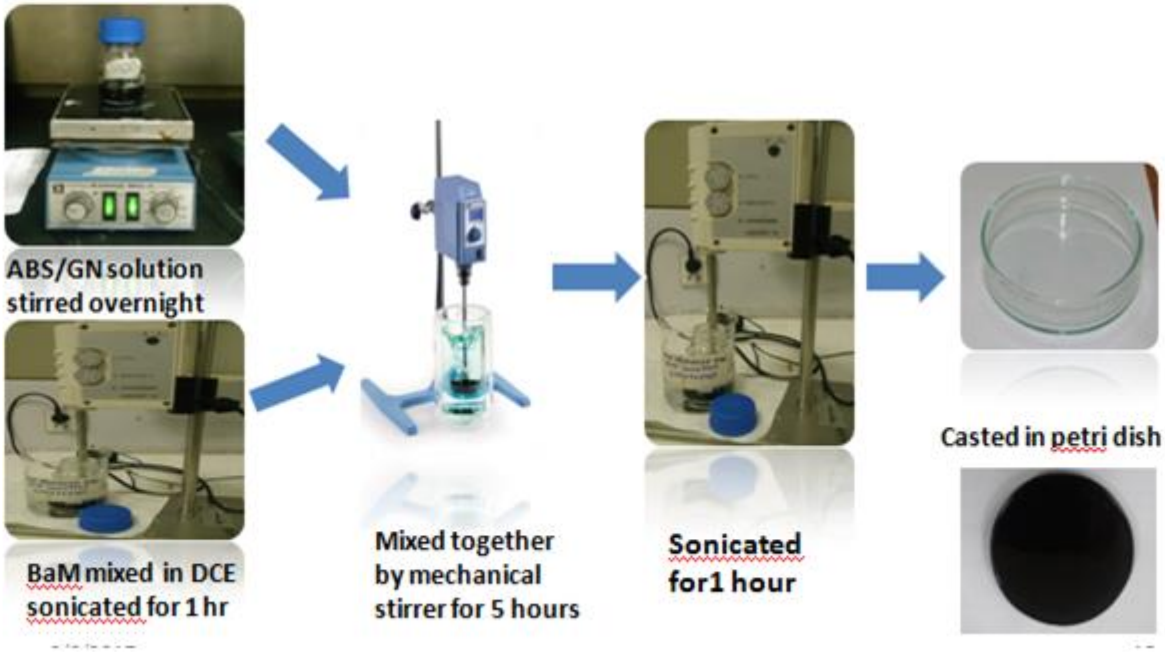
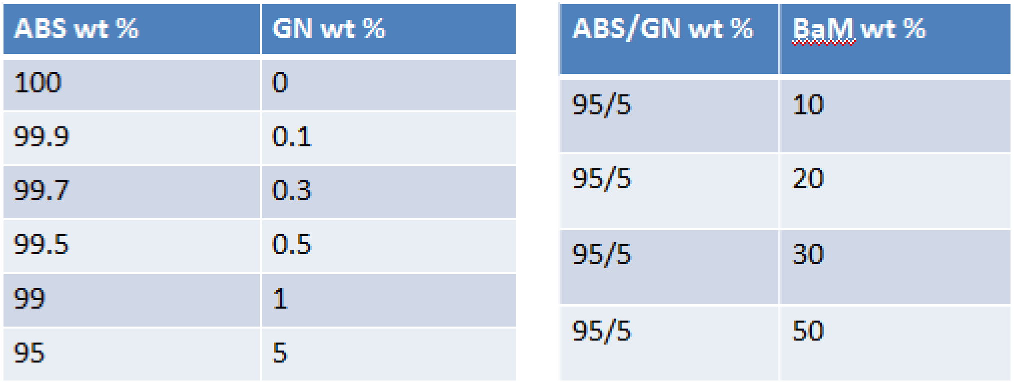


Fig 3.3 schematic Synthesis ABS/GN/BaM composites

Total samples prepared

Table 3.2 Samples prepared at different GN wt% and BaM wt%



ABS wt %	GN wt %
100	0
99.9	0.1
99.7	0.3
99.5	0.5
99	1
95	5

ABS/GN wt %	BaM wt %
95/5	10
95/5	20
95/5	30
95/5	50

CHAPTER-4

RESULTS AND DISCUSSION

4.1 WIDE ANGLE X-RAY DIFFRACTION (WAXD)

a. ABS neat polymer

The neat polymer sheet of ABS was subjected to WIDE ANGLE X-RAY DIFFRACTION (WAXD). The pattern clearly shows an amorphous plateau of ABS. It shows a hump on $2\theta=20^{o}$that shows the characteristics of amorphous ABS polymer [26]

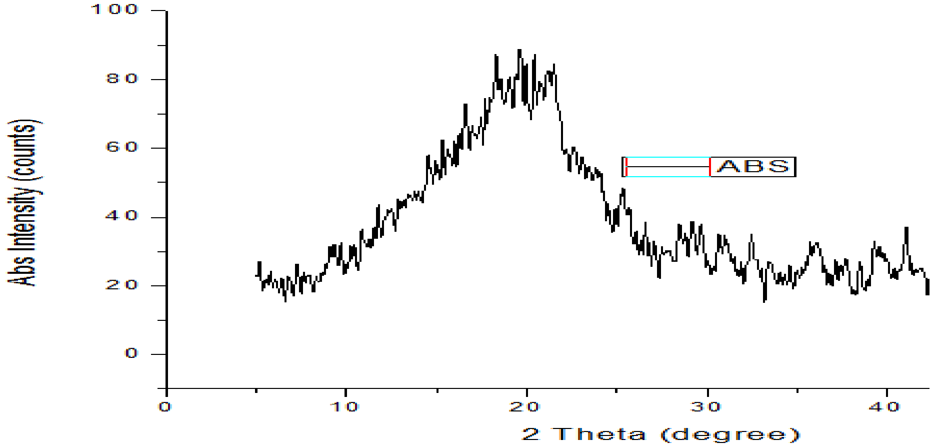


Fig 4.1(a) XRD neat ABS

b. Barium Hexaferrite (BaM)

Finely grinded BaM powder was taken under XRD analysis. The result shows a clear evidence for the successful formation of BaM particles in Hexagonal phase. The literature reported that if we increase the calcinations temperature above 1000°C the single phase $BaFe_{12}O_{19}$ is formed and the amount of unreacted $Fe_2O_3$is significantly reduced. The peak values completely matches the JCPDS ref no 39-1433.[27]

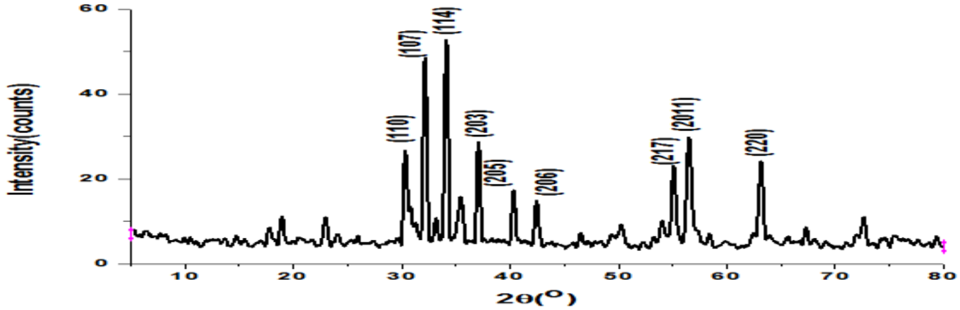


Fig 4.1(b) XRD neat BaM

c. ABS/Graphene NANOCOMPOSITES

The X-ray diffraction pattern of ABS/ graphene nanocomposites in comparison with the neat polymer is shown in the figure. The figure shows the hump of at 2θ=20° indicating the presence of ABS, at lower percentage loadings of graphene there is no peak appearance of graphite shows the proper dispersion of graphene nano-particles with the polymeric mixture but if we go on increasing the loading percentages the agglomeration within the system has occurred and stacking of graphene layers happens which results in the appearance of graphitic peak at2θ=26.4° for (002) plane which is the characteristic graphite peak.[28]

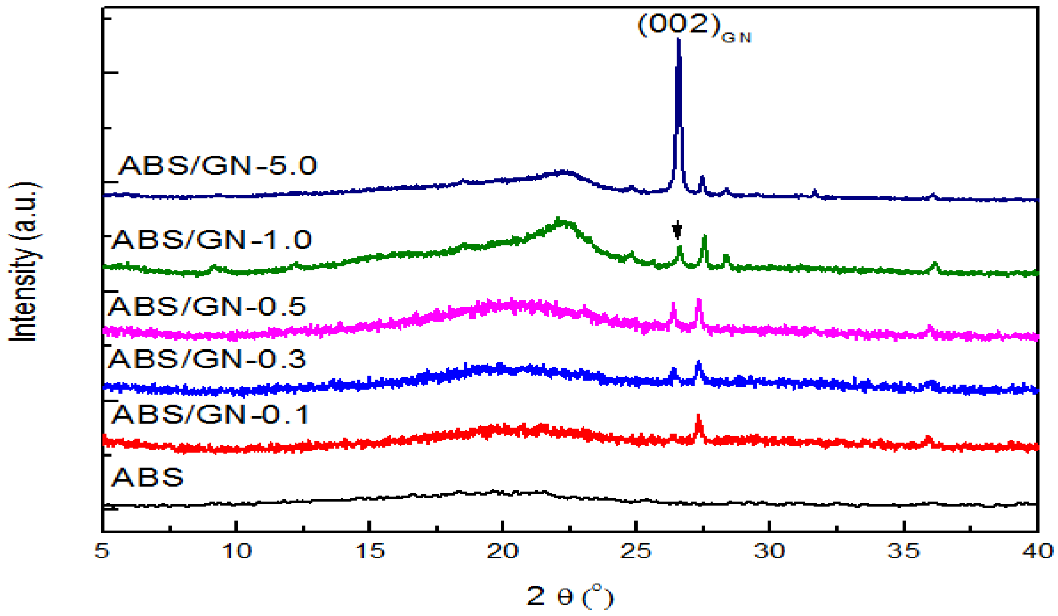


Fig 4.1 (c) XRD ABS/GN Composites

d. ABS/GRAPHENE/BaM Nano-Hybrid composites

The sample containing the 5 wt % of graphene was incorporated with different weight percentages of BaM . The X-ray diffraction pattern of Hybrid composites of ABS/GN/BaM is shown in the figure below. It can be seen that the graphite peak is present in all samples, but introduction of BaM nano particles do not affect the peaks with the increasing concentrations indicating the good dispersion of BaM nano particles within the ABS/GN composite. Somehow there are very small peak appearances at (112) and (006) in the composites, planes corresponding to BaM indicate the dispersion and presence of BaM in the matrix. There is a small peak appearance near the ABS plateau at 2θ=16.7° indicating that the polymeric chains are aligning and crystallinity is imparted in the polymeric chains.[29]

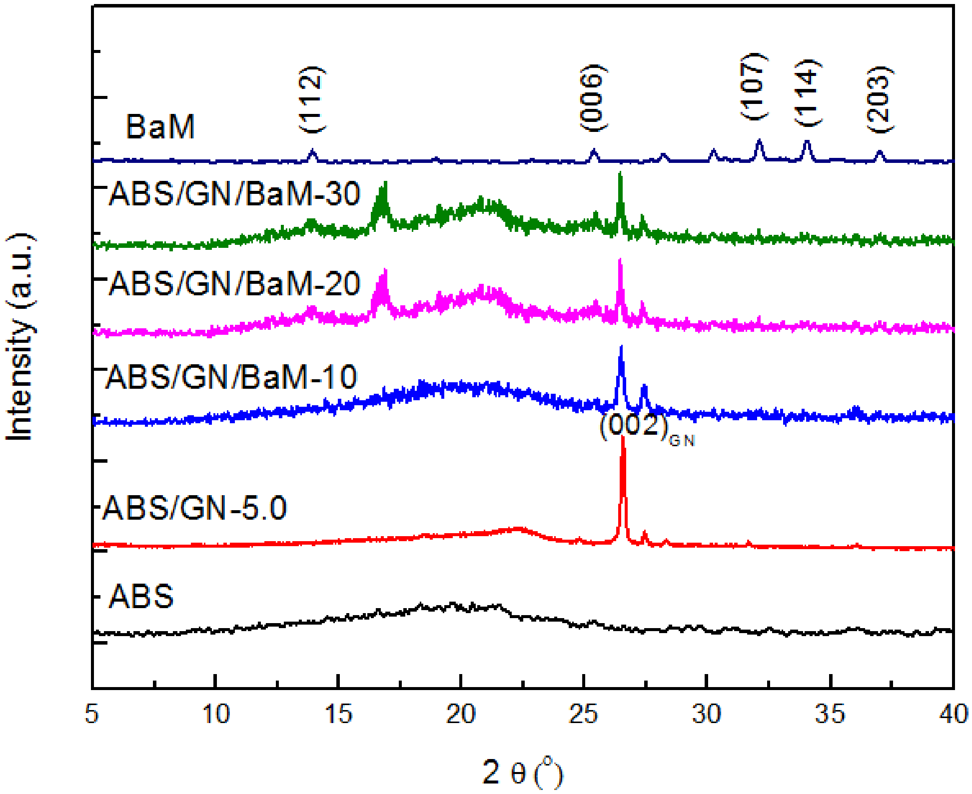


Fig 4.1 (d) XRD ABS/GN/BaM Composites

4.2 SCANNING ELECTRON MICROSCOPY (SEM)

The morphology of ABS and ABS based Hybrid composites were examined using scanning electron microscopy as mentioned below

a. ABS

The SEM image of ABS polymer shows a dispersion of poly-butadiene phase in the continuous phase of styrene acrylonitrile(SAN), which is responsible for the formation of multiphase structure of ABS polymer. This type of dispersive distribution is also reported by M.H Saleh et al.[30]

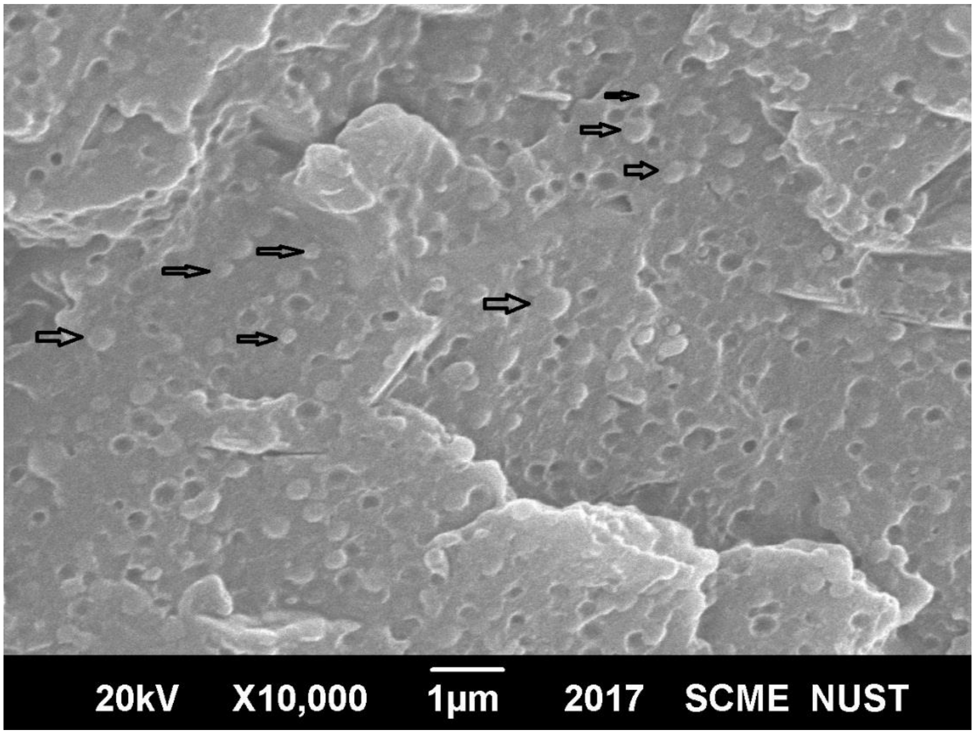


Fig 4.2 (a) SEM neat ABS

b. Barium Hexaferrite (BaM)

The SEM results of BaM nano particles were obtained in order to observe the morphology of BaM nano particles and to find whether the particles are agglomerated or dispersed efficiently.

The SEM results show the spherical particle formation of BaM nano particles and the dispersion of the particles is good as they are not agglomerated. The average particle size that can be seen is ranging between 20-40nm. The SEM images can be seen in the following figures.[31]

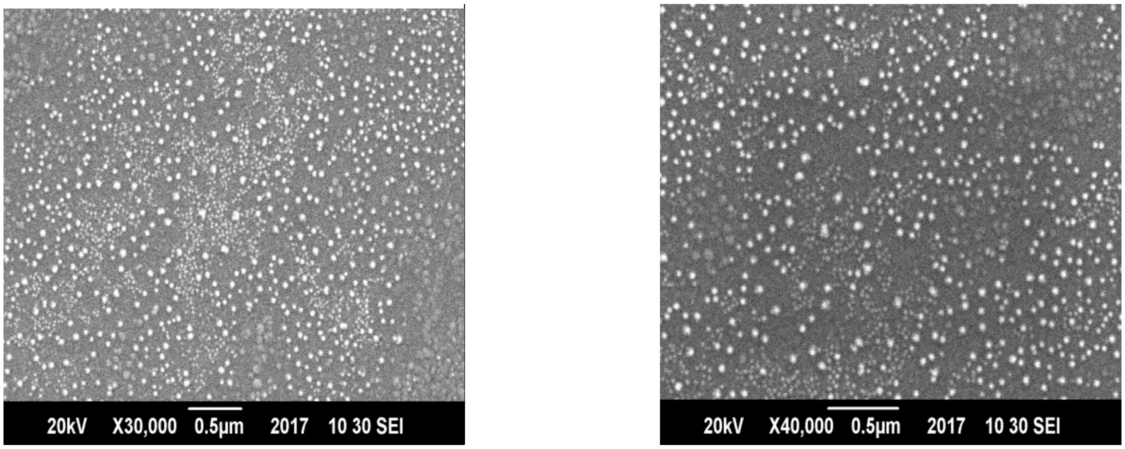


Fig 4.2 (b) SEM neat BaM

c. ABS/Graphene NANOCOMPOSITES

Different weight percentages were examined in order to observe the dispersion of the graphene layers within the polymeric matrix. As explained in the literature the graphene layers were dispersed in the SAN (styrene acrylonitrile) phase rather than the poly-butadiene phase. The second affect that was observed is that above approximately 1 weight percent of graphene in the ABS matrix, there is a formation of agglomerates of graphene in localized areas and the disruption of graphene network within the polymeric mixture. This property is further examined in Tensile and DSC results as well with respect to their effect of properties. [19]

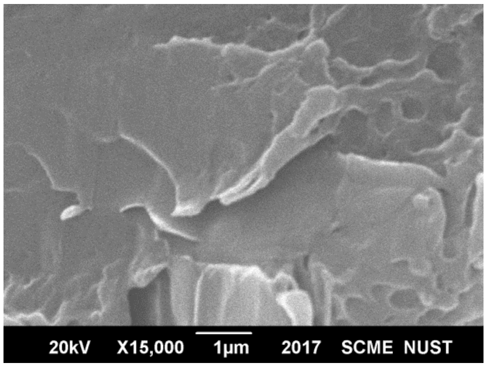


Fig 4.2(c) SEM ABS/GN(0.1)

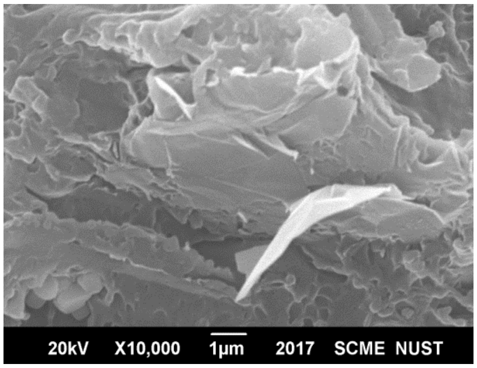


Fig 4.2(c) SEM ABS/GN(0.1)

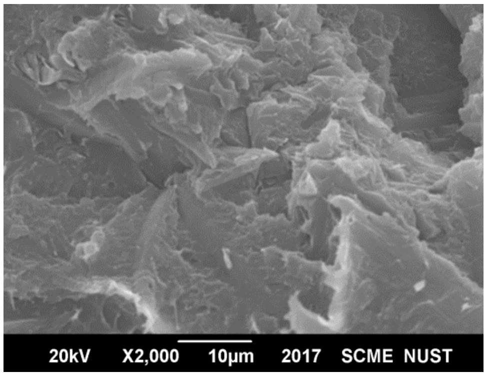


Fig 4.2(c) SEM ABS/GN(0.3)

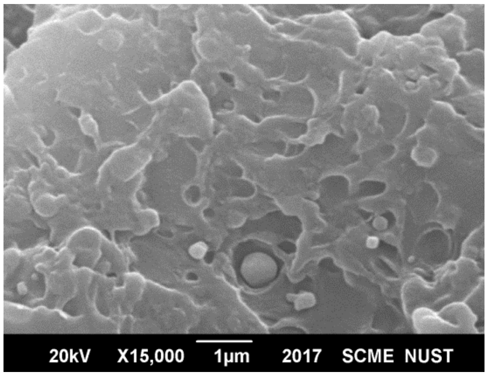


Fig 4.2(c) SEM ABS/GN(0.3)

d. ABS/GRAPHENE/BaM Nano-Hybrid composites

The ABS composite with highest weight percentage of graphene was incorporated with different weight percentage of ferrites. The SEM results at 5% graphene show that there are cracks and voids formation within the polymer, but at the same time the BaM particles were well dispersed within the system at all concentrations of BaM.

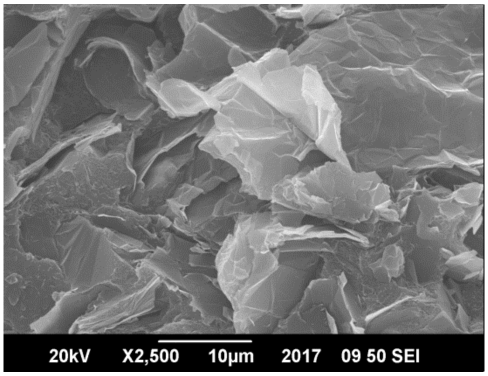


Fig 4.2(d) SME ABS/GN/BaM-10

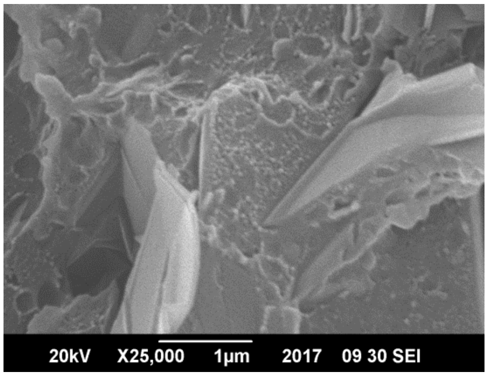


Fig 4.2(d) SME ABS/GN/BaM-10

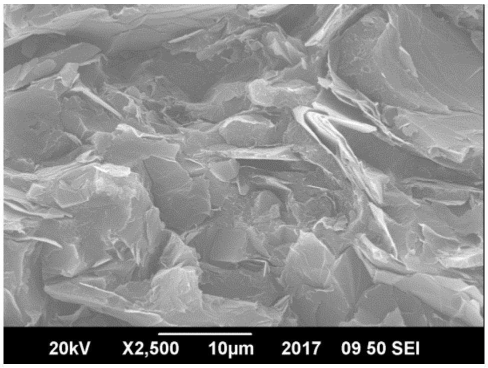


Fig 4.2(d) SME ABS/GN/BaM-20

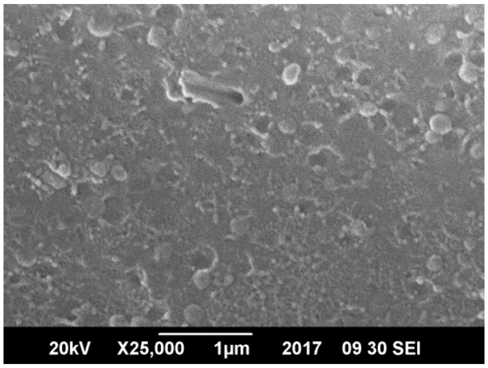


Fig 4.2(d) SME ABS/GN/BaM-20

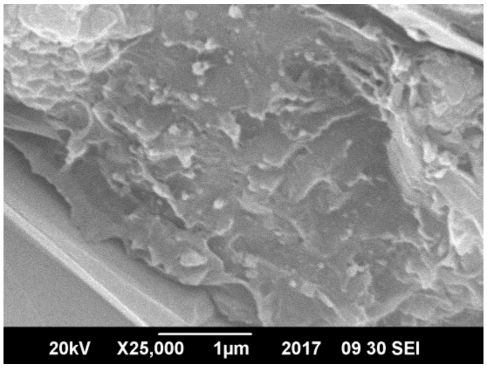


Fig 4.2(d) SME ABS/GN/BaM-50

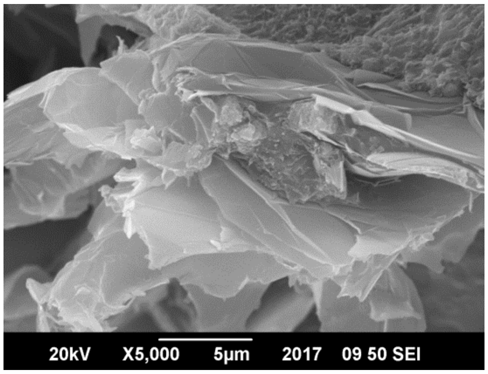


Fig 4.2(d) SME ABS/GN/BaM-50

4.3 TENSILE PROPERTIES (UTM)

a. ABS/Graphene NANOCOMPOSITES

Tensile properties of ABS/Graphene nano composites is explained in the table and the figure showing stress with respect to strain% graph given below

Table 4.1 Mechanical properties of ABS/GN composites

SAMPLES	Tensile Strength	Elastic Modulus	Elongation at Break
ABS-Filler wt %	(MPa)	(MPa)	(% age)
ABS	17.5	600	5.4
ABS-GN(0.1)	17.7	676	5.8
ABS-GN(0.3)	18.3	756.2	6.1
ABS-GN(0.5)	20.0	950	8.8
ABS-GN(1)	13.8	543	5.2
ABS-GN(5)	9.7	436	4.9

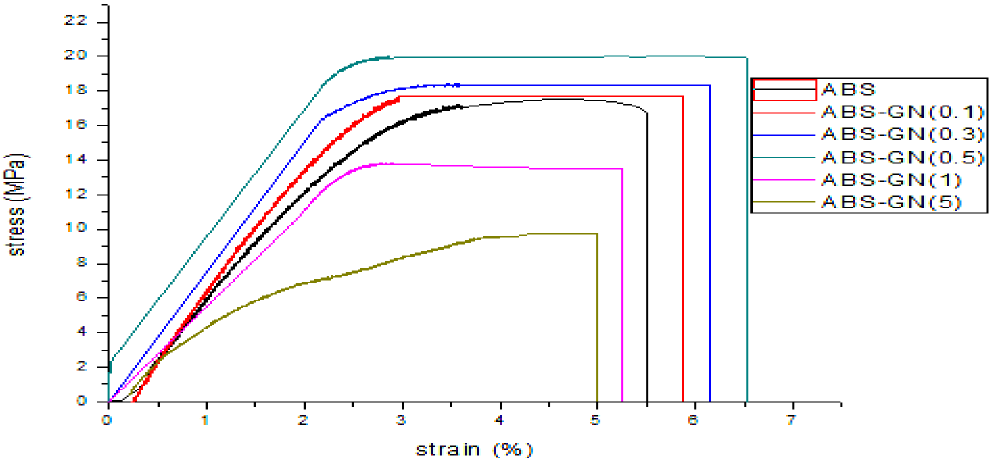


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Fig 4.3(a) S-S curve ABS/GN

The table and graph both tells us that the strength of polymer composite is increased up to 20.0 MPa at critical loading of 0.5 wt % age of graphene from 17.5 MPa i.e. is the max strength of pristine polymer ABS. Further addition of the filler in polymer causes segregation of graphene within the system and results in agglomeration and formation of voids and cracks within the system, this result for decrement of the tensile strength up to 9.7 MPa at 5 wt % of graphene loading which is even less as compare to the strength of pure ABS polymer.

A similar kind of trend is shown in the modulus values of the composites. The pure ABS polymer has a value of 600 MPa but increment in the filler loading enhances the modulus value up to 950 MPa at 0.5 wt % age of loading, but further loading enhances the agglomerate formation causing to decrease modulus up to a value of 436 MPa at 5 % age loading of graphene.

The polymer is supported by addition of graphene filler in ABS polymer up to a percentage of 8. at 0.5 wt % age of graphitic loading as compare to 5.54 percent value that is obtained by pure ABS polymer and goes on decreasing to a value of 4.99 at 5 wt % age of loading.[32]

b. ABS/GRAPHENE/BaM Nano-Hybrid composites

The ABS/GN composite at 5 wt % age of graphene loading was incorporated with different wt % ages of BaM nano particles. The tensile mechanical behavior is shown in the table and figure (S-S Curve) below

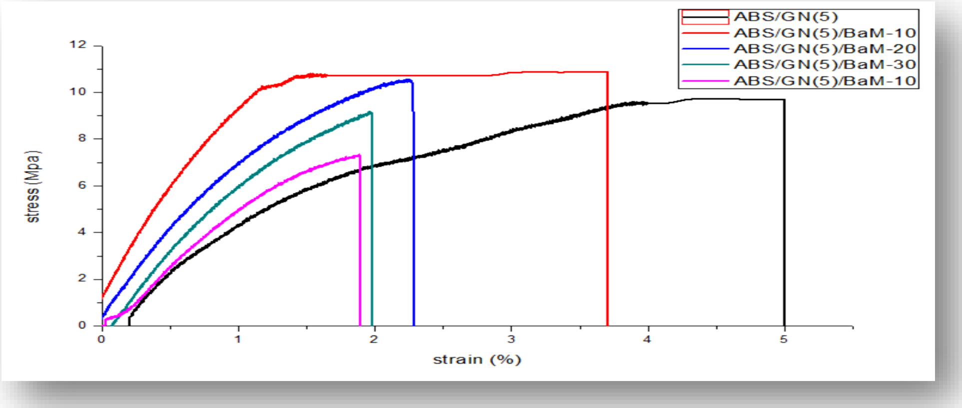

Fig 4.3(b) S-S curve ABS/GN/BaM

Table 4.2 Mechanical properties of ABS/GN/BaM nanocomposites

Samples	**Max Tensile strength**	**Modulus**	**% Elongation at break**
Units	MPa	MPa	%
ABS/GN(5)	9.7	436	4.9
ABS/GN(5)-BaM10	10.7	917	3.7
ABS/GN(5)-BaM20	10.5	643	2.2
ABS/GN(5)-BaM30	9.6	540	1.9
ABS/GN(5)-BaM50	7.3	469	1.8

The graph and table both shows that the introduction of BaM particles in ABS/GN composite indicates that the good dispersion within the polymeric matrix introducing strength and increase its crystallinity as well.

The increasing BaM concentration increases the modulus of the hybrid composite indicates that the BaM particles have dispersed good within the polymeric system and the deformation of the composite at higher loads is hindered by incorporation of BaM particles.

The decreasing values of the elongation at breakage indicate that more and more incorporation of ferrites in composite is increasing brittleness of the polymer. [33]

b. STRENGTHENING MECHANISM FOR MECHANICAL PROPERTIES

1. ABS/GN composites

The graphs for maximum tensile strength v/s concentration, modulus v/s concentration and maximum elongation at break v/s concentration are shown in the figures below

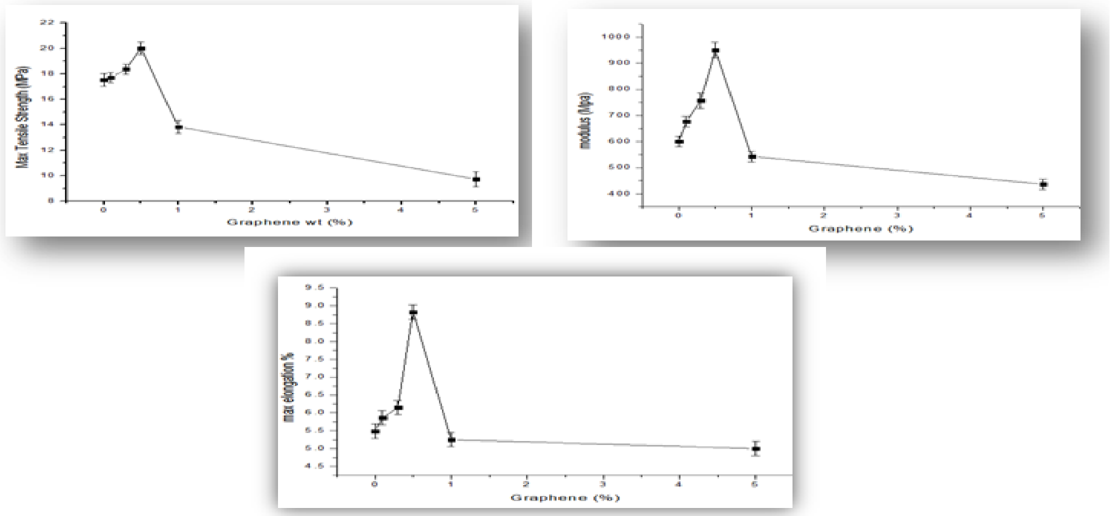

Fig 4.3(c) Max strength, Modulus and Elongation V/s GN wt%

As it is seen in all the related figures all the tensile properties like tensile strength, Modulus and percentage Elongation at break all of these properties are enhancing as compare to pristine ABS up to a weight percentage of 0.5 wt % of graphene which clearly indicates that up to this level of reinforcements the graphene was well dispersed within the system

MAX TENSILE STRENGTH ACHIEVED W.R.T PURE ABS

(17.5MPa - 20MPa) 12.5% increase

MAX MODULUS ACHIEVED W.R.T PURE ABS

(600MPa-950Mpa) 36.8% increase

MAX ELONGATION AT BREAK ACHIEVED W.R.T PURE ABS

(5.49%-8.826%) 38% increase

Enhanced mechanical properties i.e. the tensile strength ad modulus is directly related to the reinforcement affects that are imparted by the interfacial bonding of ABS with the graphene. These properties are also due to the dispersion of graphene within the ABS matrix.

As a result of good interactions constraining effects dominates due to which the mechanical properties are enhanced. Polymeric chains wrap up and adhere at the surface of the filler cause the main source of interfacial interactions between ABS and graphene. The rigidity of graphene sheets can also improve the mechanical properties of the ABS composite with graphene. As we see the results all the mechanical properties of the composites have decreased due to possible agglomeration of graphene within the ABS matrix and also due to π-π interactions.

The Elongation percentage is also increasing up to a wt % of 0.5 GN due to possible alignment of graphene nano palates with the polymeric matrix and successfully transferring from filler to the matrix.[21-34]

2. ABS/GN/BaM Nano Hybrid Composites

The graphs for maximum tensile strength v/s concentration, modulus v/s concentration and maximum elongation at break v/s concentration are shown in the figures below

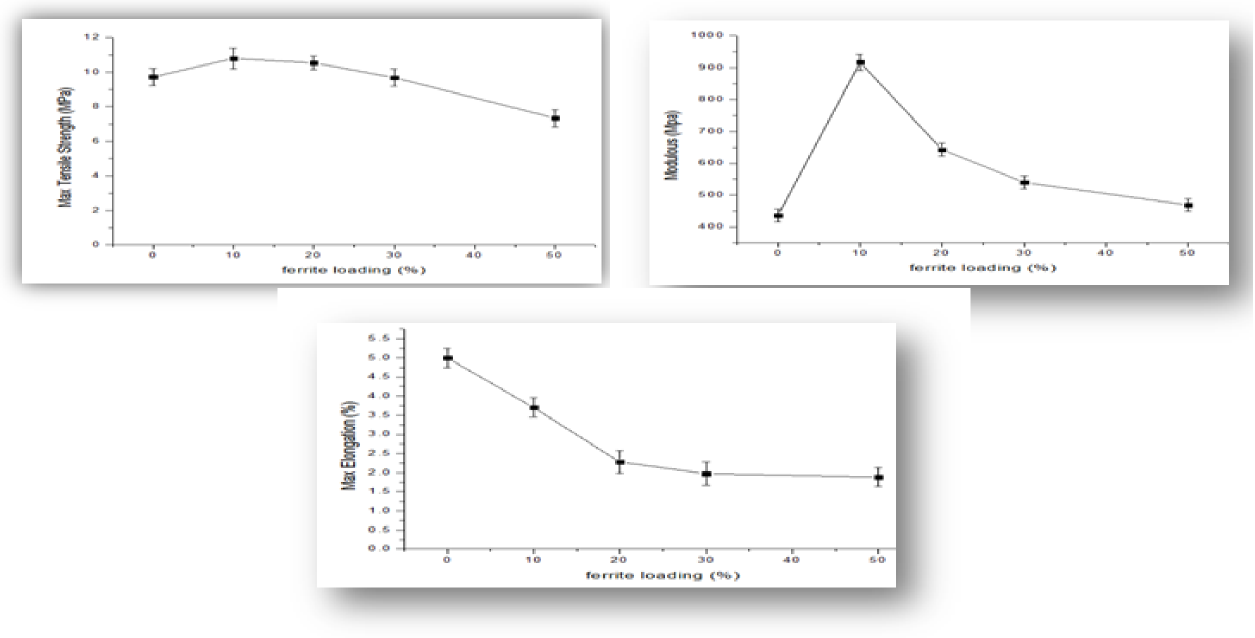

Fig 4.3(d) Max Strength, Modulus and Elongation v/s GN/BaM concentration

The tensile strength of the ABS/GN composite has increased up to a filler loading of 10 weight % of ferrites that shows that due to good dispersion of the ferrite particles within the ABS/GN matrix has resulted in to good reinforcement capabilities of ferrites within the polymeric matrix. But as filler loading is enhanced above that, the tensile strength decreases due to possible agglomeration and creation of vacant spaces between the polymer matrix.

The modulus somehow has increased overall as we go on increasing the filler content due to good dispersion of ferrite particles.

Elongation percentage has dropped with increase in the filler content is due to the brittleness of the ABS/GN/BaM composite, that is caused by increasing the weight percentages of ferrites within the ABS/GN matrix.

4.4. Differential Scanning Calorimetry (DSC)

a. ABS/GN COMPOSITES

The thermal analysis of the composites was performed under differential scanning calorimetry. The thermal analysis consists of three phase first heat, cooling and second heat. The behavior of the composite films with respect to pure polymer is illustrated in the figures below

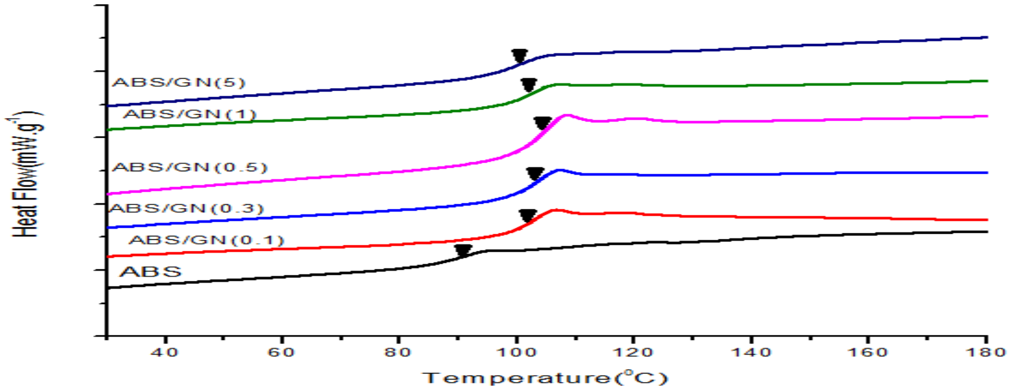

Fig 4.4(a) Heating curves ABS/GN nanocomposites

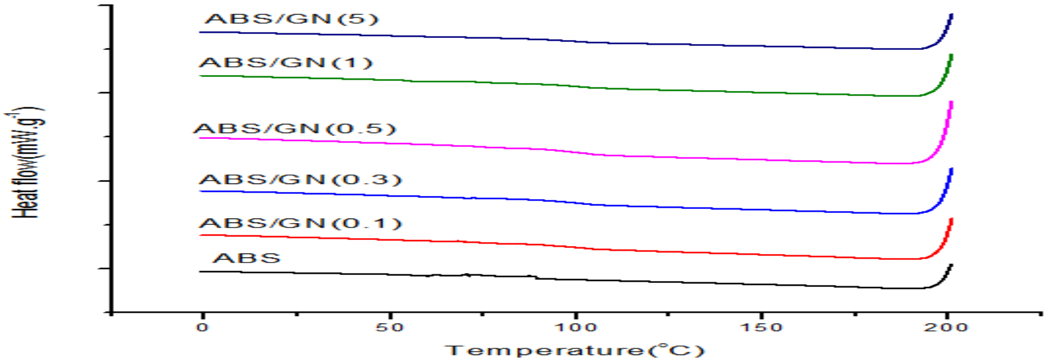

Fig 4.4(b) Cooling curves ABS/GN nanocomposites

The Heating curve shows that the Tg of pristine polymer is increased in case of composites, with increasing amount of Graphene the constraining affects applied by the graphene sheets on polymeric chain causes to restrict the chain mobility and hence increase the Tg. [35]

There is no Tm peaks present in the heating indicating full amorphous system of ABS.

As we look into the cooling curves the curves suggest that there is no exothermic peak present within the system indicates amorphousness of ABS polymer.

The question arises why there is no Tm peak present for the case of amorphous materials??

The answer lies in the statement ‘’ because it is not a phase transition. In amorphous polymers already randomness is there and the segments are moving even at room temperature. By increasing temperature you are only increasing the frequency of the chain segments so you don't see a peak.

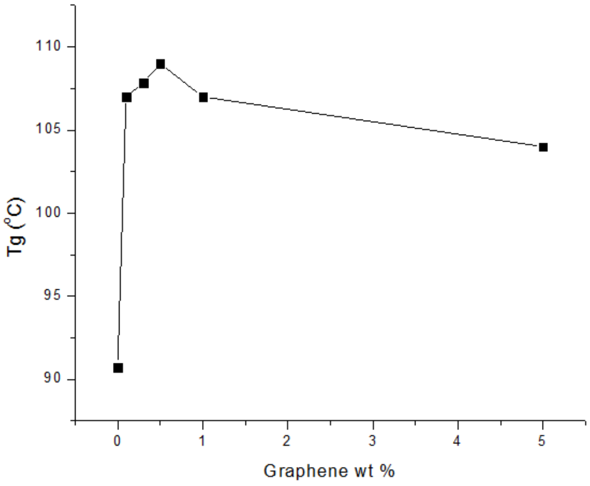

Fig 4.4(c) Tg variation with respect to GN wt%

Similar kind of a trend in variation of Tg with respect to graphene weight percent is shown in the above figures as well.

The maximum Tg value was obtained at 0.5 weight percent and after that there is a small decrement in the Tg values due to possible agglomeration and also a creation of a bit free volume to enhance chain mobility.

Maximum Tg enhancement

At 0.5 weight % of graphene

(90-109°C) 17.5% increase

b. ABS/GN/BaM Nano Hybrid composites

The thermal analysis of the composites was performed under Differential Scanning Calorimetry. The thermal analysis consists of three phase first heat, cooling and second heat. The behavior of the composite films with respect to ABS/GN (5) i.e. 5 wt % of graphene is illustrated in the figures below

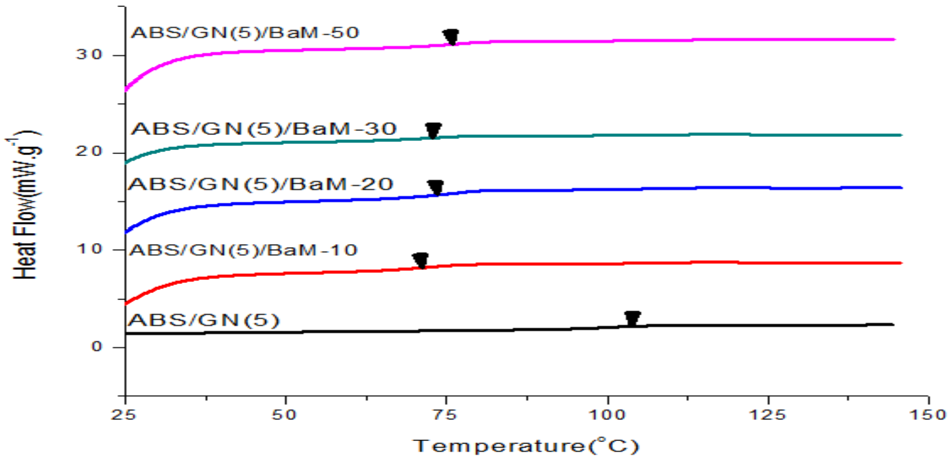

Fig 4.4(d) Heating curves of ABS/GN/BaM nanocomposites

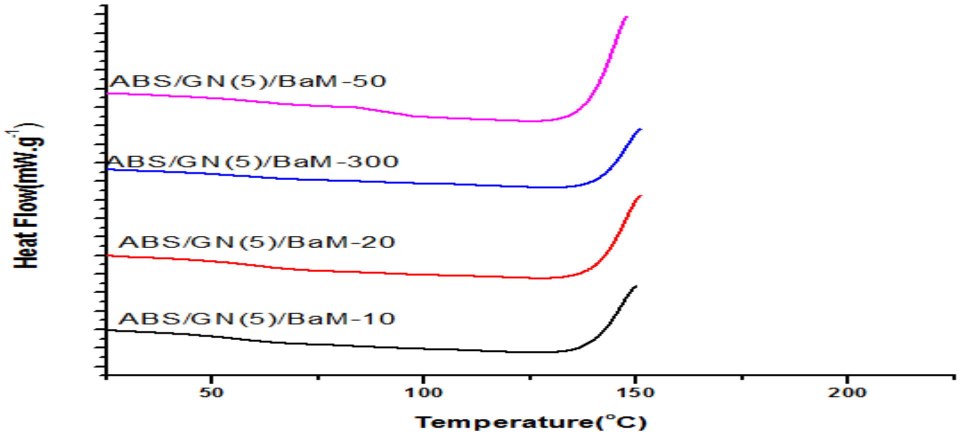

Fig 4.4(e) Cooling curves of ABS/GN/BaM nanocomposites

The introduction of BaM nano particles causes to increase free volume within the polymer matrix due to which there is a decrement of Tg shown within the Hybrid composites. It shows that the Hybrid composite has become a bit thermally unstable with the introduction of ferrites.

Maximum decrement

(104-76°C) 27% decrease

This decreasing trend can be seen through the graph of filler concentration v/s Tg in the figure given below

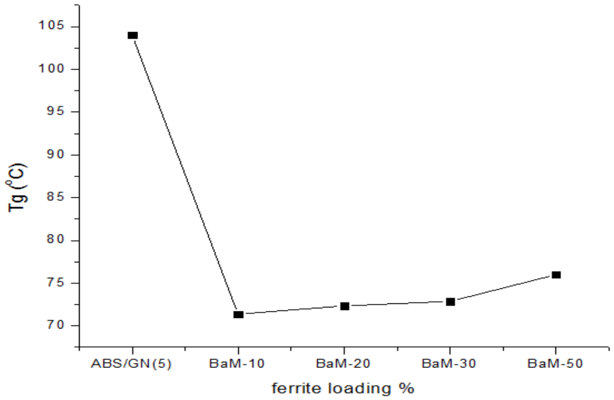

Fig 4.4(f) Tg Variation with respect to BaM concentration

4.5. DIELECTRIC PROPERTIES

It is expressed in terms of real (Ɛ') and imaginary part (Ɛ") of dielectric permittivity which is obtained from complex permittivity as follows [73]

$$\varepsilon = \varepsilon' - \varepsilon''$$

The dielectric constant is the ability of a substance to store charge, it can be expressed by relation

$$\varepsilon' = \frac{Cd}{A\varepsilon_o}$$

Dielectric properties were analyzed using ENA5071C Agilent Network Analyzer with a coaxial wire method which is consisted of toroidal-shaped specimen which has dimension of 7 mm outer diameter, 3.04 mm inner diameter, and 0.2 mm thick. The frequency ranges from 8GHz to 13GHz .This characterization was performed by Korean institute of Science and Technology.

a) Dielectric Constant

i) ABS/GN composites

The graph of Dielectric constant v/s frequency for ABS/GN composites is given below

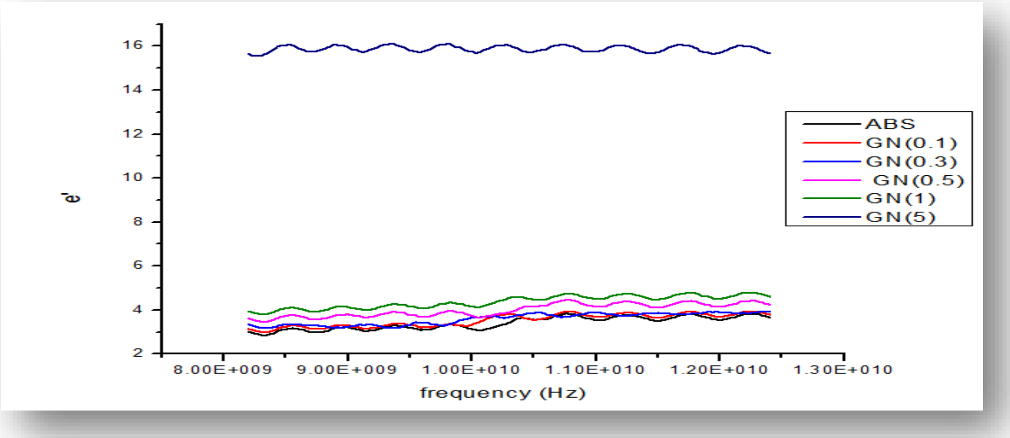

Fig 4.5(a) Dielectric constant v/s frequency for ABS/GN composites

The values for the dielectric constants indicate that the pristine ABS has the negligible values for the dielectric constant because the dipole creation within the ABS polymer is not favored. But due to graphene addition there is a slight improvement in the dielectric values due to availability of charge storing domains i.e. graphene but at the same time this increment is not up to a level until the weight percent of graphene is reached 5wt% and the dielectric constant has readily reached up to a value of 15 at 8GHz frequency.

This drastic increment of dielectric constant indicates a network of graphene has formed within the polymeric system which allows the charges to pass through it and charge storage is enhanced sharply at 5 wt% of graphene.

The values of the dielectric constant in an insulating polymer containing a conductive filler is calculated on the basis of number of microcapacitors and polarization centers.

The microcapacitors are formed when the conductive filler behaves as an electrode when it is incorporated in an insulating polymer. [37]

The movement of free charges at boundary of conductive filler and insulating polymer corresponds to interfacial polarization which can also produce dielectric relaxation which is responsible of the dielectric properties within the microwave frequency ranges .

This particular weight percent was selected for the synthesis of BaM hybrid composites with ABS/GN composite in order to enhance its charge storing capacity.

ii) ABS /GN/BaM nano Hybrid Composites

The graph of Dielectric constant v/s frequency for ABS/GN/BaM composites is given below

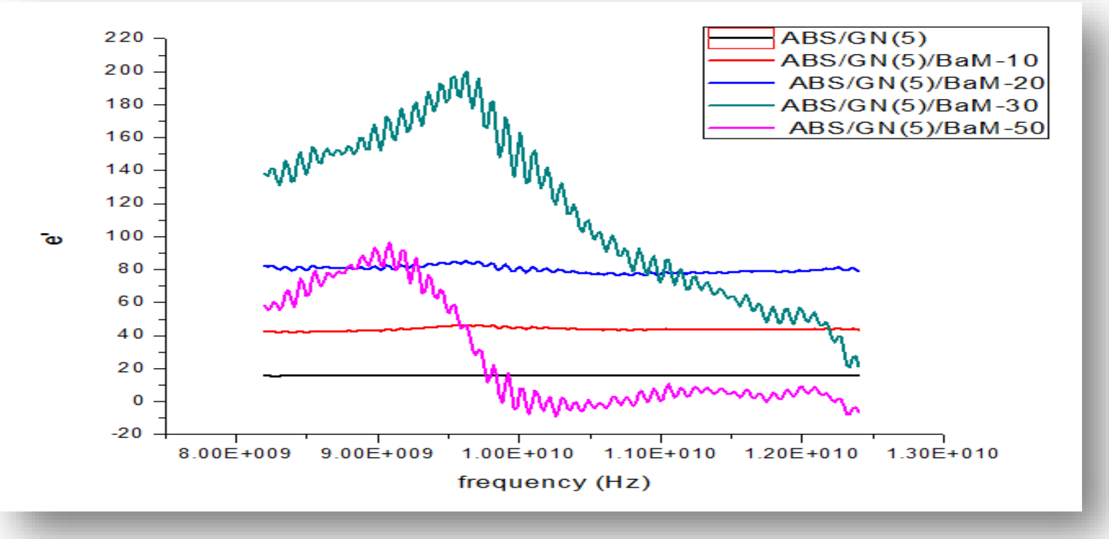

Fig 4.5(b) Dielectric constant v/s frequency for ABS/GN/BaM composites

It is clearly shown by the graph, the value of dielectric constant for ABS/GN/BaM hybrid composites have increased a lot. This increase is due to enhancement of electric polarization in the relative complex permittivity is due to polarization of the material, causes electrical and dipolar polarization when activated by an EM wave. [38]

b) DIELECTRIC LOSS

i) ABS/GN composites

The graph of Dielectric constant v/s frequency for ABS/GN composites is given below

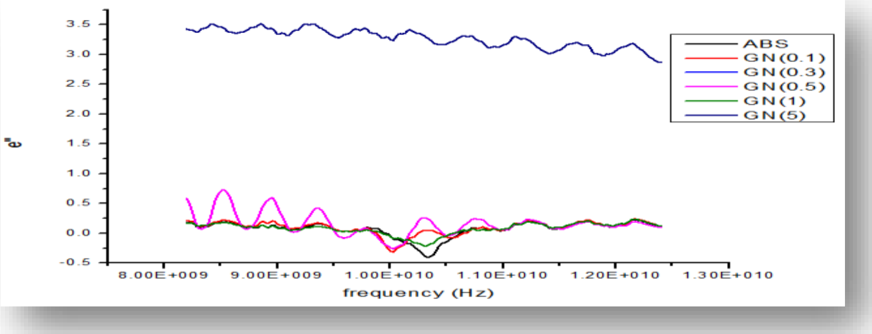

Fig 4.5(c) Dielectric loss v/s frequency for ABS/GN composites

Similar kind of trend has been shown for dielectric loss as well, the composite containing 5 wt %age of graphene has the maximum value for the dielectric loss.

ii) ABS/GN/BaM Hybrid Nano Composites

The graph of Dielectric loss v/s frequency for ABS/GN/BaM composites is given below

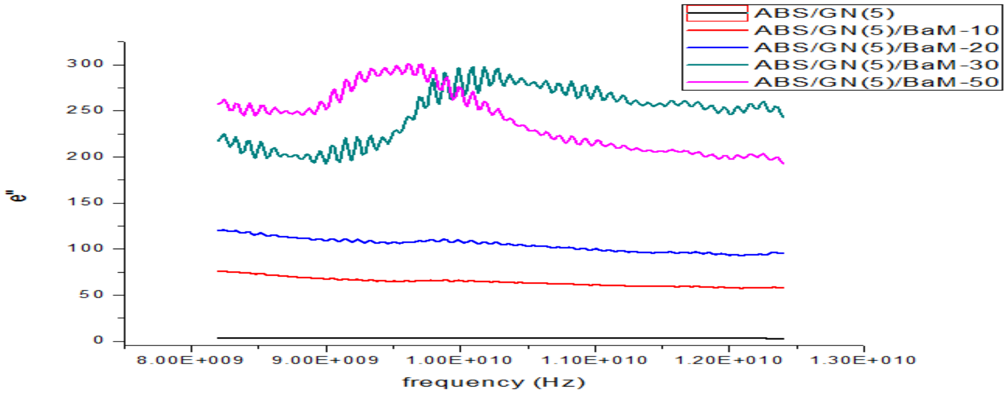

Fig 4.5(d) Dielectric loss v/s frequency for ABS/GN/BaM composites

As the values of dielectric constants were increased due to addition of ferrites, same kind of a trend is shown in the dielectric loss values as well

The values for the dielectric loss has increased for 50 wt % of BaM nano particles at lower frequencies and on the other hand as the frequency increases the dielectric loss values for 30 wt % of BaM nano particles has also increased.

These all parameters are decided by magnetic polarization as well as electrical polarization of the fillers within the polymeric system. [38].

4.6. DC CONDUCTIVITY

The DC electrical resistivity of the polymer nano composite was evaluated using four-pin probe method (MCP-TP06P PSP) with Loresta GP meter (MCP-T610 model, Mitsubishi Chemical, Japan). The composites were cut into dimensions of 10 mm diameter and 0.2mm thickness.

a. ABS/GN composite

The graph for DC conductivity with respect to graphene filler concentration is shown below

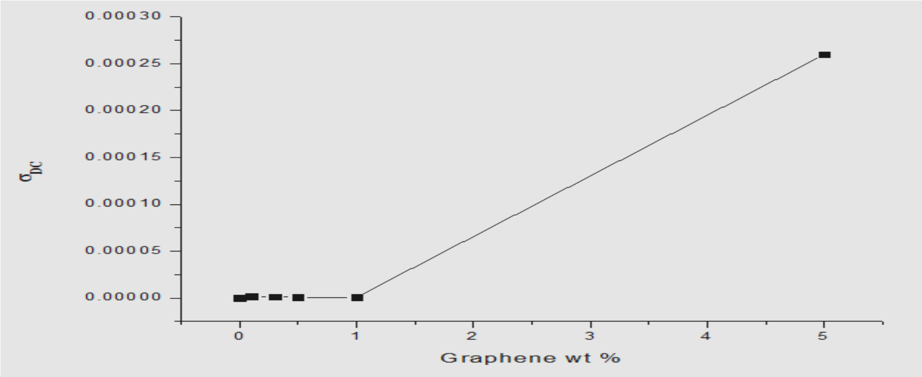

Fig 4.6(a) DC conductivity for ABS/GN composites

The graph clearly shows that increasing concentrations of graphene within the polymeric mixture do not show any kind of conducting behavior up to a loading of 1 wt % this shows up till this concentration there is no formation of a conducting network between graphene sheets within the ABS polymer, as the concentration is increased to 5 wt % the graphene the formation of a conducting network is clearly observed as the conductivity of the composite has increased drastically. [39]

This phenomenon is also known as percolation. In percolation there is a threshold value for the loading of fillers at which the conductive network is formed and conductivity as well as dielectric properties has increased and the composite has become suitable for EMI shielding.

(b) ABS/GN/BaM Nano Hybrid Composites

The DC conductivity of Hybrid nano composites with respect to the BaM nano filler concentration are illustrated below

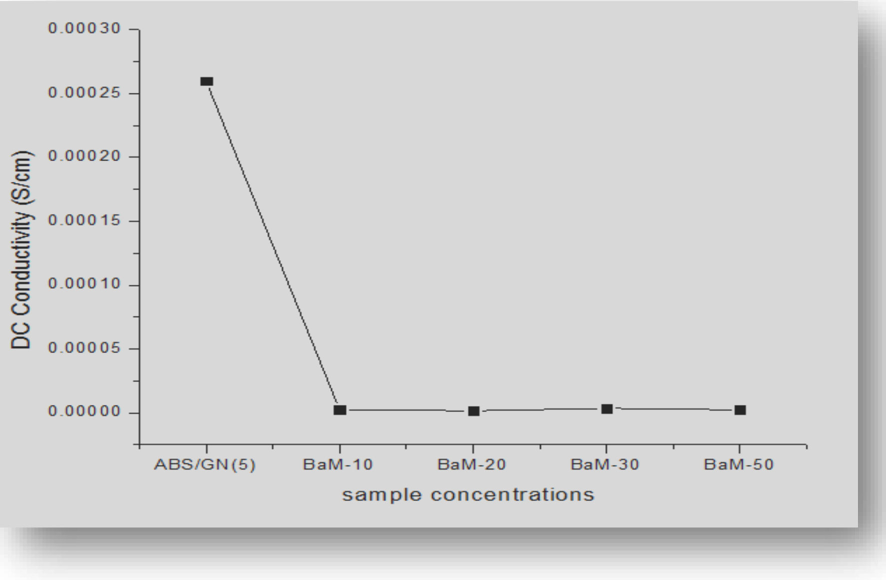

Fig 4.6(b) DC conductivity for ABS/GN/BaM composites

The BaM nano particles were incorporated with ABS/GN composite with 5 wt % of graphene as it has got the highest values for dielectric conctant as well as DC conductivity.

It can be seen that the DC conductivity of the Hybrid composites have reduced a lot as the BaM nano particles are insulative in nature as well as they have decorated themselves on the GN sheets within the polymer and also causes to disrupt the network of graphene that was formed before[40]

4.7. EMI (ELECTRO MAGNETIC INTERFERENCE) SHIELDING

EMI SHIELDING properties were analyzed using ENA5071C Agilent Network Analyzer with a coaxial wire method which is consisted of toroidal-shaped specimen which has dimension of 7 mm outer diameter, 3.04 mm inner diameter, and 0.2 mm thick. The frequency ranges from 8GHz to 13GHz

The ability of a material to attenuate Electromagnetic waves is calculated in terms of total EMI shielding effectiveness (SE_T)

The SE_T can be calculated by following Equation

$$SE_T(dB) = 10\log\left(\frac{P_I}{P_T}\right)$$

Where Pi is the power of incident EM wave and Pt is the power to transmitted wave in decibels (dB). The SE_T can also be calculated in terms of reflection loss and absorption loss

$$SE_T = SE_R + SE_A$$

Where SE_R is corresponding to impedance mismatch between air and material
SE_A is the energy dissipation of EM waves in the shield [41]

a) ABS/GN composite

The total EMI shielding effectiveness for ASB/GN composite v/s the frequency is illustrated in the graph below

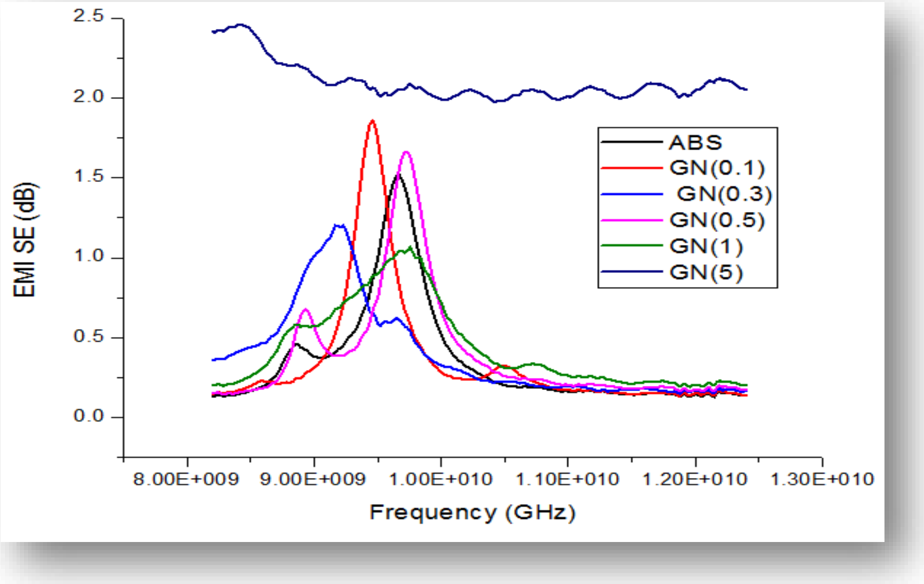

Fig 4.7(a) EMI SE (dB) v/s frequency ABS/GN nanocomposites

The graph indicates that the EMI shielding of ABS/GN composite achieved the highest value of 2.4 dB at 5 wt % of graphene loading on 8 GHz frequency which shows round about 20-25 % shielding (blockage of incident wave). The increasing value of the EMI shielding indicates a network of graphene has been formed within the ABS matrix that is attributing in the overall shielding effectiveness of the material.[41]

b) ABS/GN/BaM Nano Hybrid composites

The total EMI shielding effectiveness for ASB/GN/BaM Nano Hybrid composites v/s the frequency is illustrated in the graph below

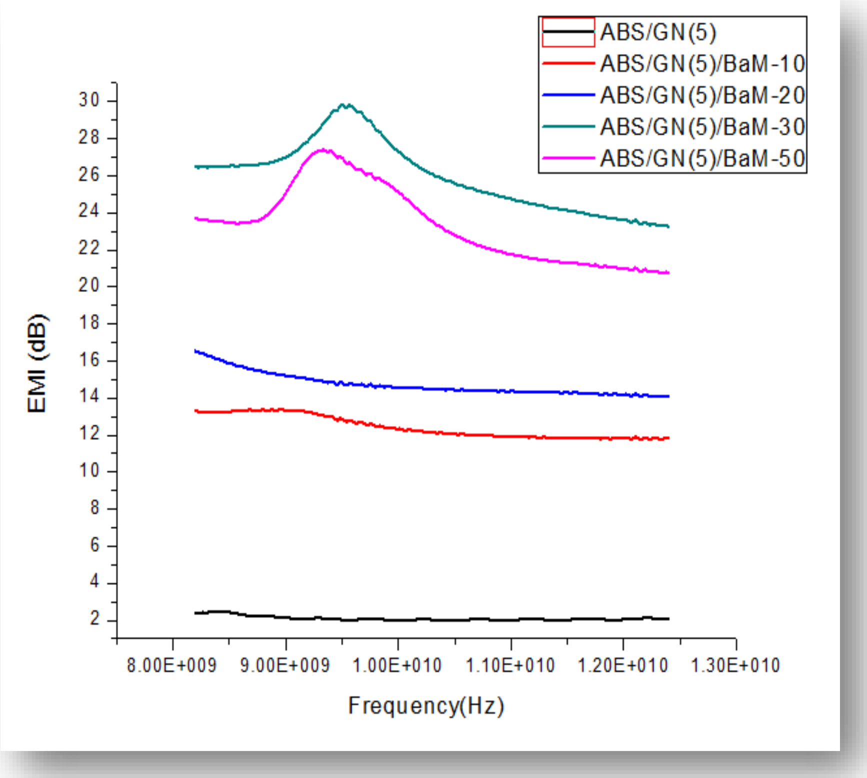

Fig 4.7(b) EMI SE (dB) v/s frequency ABS/GN/BaM nanocomposites

EMI shielding of ABS/GN/BaM nano Hybrid composites shows a very good increment in the in the EMI shielding effectives of the Hybrid composites. The value of EMI shielding at 30 wt % of BaM nano particles have reached to a value of 30 dB which is equivalent to 99.9 % blockage of the Incident radiation.[42]

This increment is associated with the polarization centers formation with the introduction of BaM nano particles and high value of magnetic permeability .

CHAPTER-5
CONCLUSIONS

ABS is a an amorphous ter-polymer structure with a morphology of two phases in which poly butadiene particles are dispersed in continuous SAN phase, confirmed by XRD and SEM results.

The BaM nano particles were successfully synthesized by co-precipitation method. The XRD have shown a clear cut hexagonal phase formation of the barium hexaferrites and clearly matched the JCPDS number as well.

The nano polymer composites as well as the hybrid nao composites were successfully prepared by solution casting method and possess a uniform thickness of 0.1 mm .

The XRD results have shown that the ABS totally shows an amorphous behavior and it showed a hump at $2\theta=20^{o}$. The introduction of graphene at lower weight percentages yields no significant peak appearance of graphene within the composite shows good dispersion of graphene within the composite. At higher weight percentages the graphitic peak increased its intensity clearly indicating aggregation or agglomeration at higher weight percentages.

The ABS/GN/BaM nano hybrid composites peaks show good dispersion of BaM nano particles within the hybrid composite. It is also noticed that the graphitic peak intensity is lowered due to introduction of BaM particles due to the decoration of BaM nano particles on the graphitic sheets.

The SEM results indicate the dispersion of poly butadiene particles in styrene acrylonitrile phase in case of pure ABS. The introduction of graphene shows the graphitic particles dispersed in SAN phase rather than going in to PB phase. The ABS/GN composites show a good dispersion of graphene at lower weight percentages and aggregation above 1 wt%. ABS/GN/BaM nano hybrid composites shows good dispersion of BaM nano particles at almost all concentrations but the inclusion results in to free space and voids.

The tensile tests performed showed a17.5 MPa strength and 600 MPa Modulus of pure ABS polymer. With the introduction of graphene the strength and modulus values increased up to 20

MPa of strength and 950 MPa Modulus at 0.5 wt % of graphene due to the good dispersion and strengthening affects generated by graphene sheets. Further increase in graphene wt% results into agglomeration and decrease in strength and modulus up to 9.7 MPa and 439 MPa respectively. The ABS/GN/BaM nano hybrid composites in comparison to 5 wt% of graphene has increased its tensile strength from 9.7 MPa to 10.7 MPa at 10 wt% of BaM nano particles and the modulus from 436 MPa to 917 MPa because of good dispersion of BaM nano particles in the ABS/GN matrix.

The thermal analysis of the composites was performed under differential scanning calorimetry. The maximum Tg value was obtained at 0.5 weight percent was 109°C and after that there is a small decrement in the Tg values due to possible agglomeration and also a creation of a bit free volume to enhance chain mobility. The introduction of BaM nano particles causes to increase free volume within the polymer matrix due to which there is a decrement of Tg shown within the Hybrid composites. (104-76°C) 27% decrease

The values for the dielectric constants indicate that the pristine ABS has the negligible values for the dielectric constant because the dipole creation within the ABS polymer is not favored. But due to graphene addition there is a slight improvement in the dielectric values due to availability of charge storing domains i.e. graphene but at the same time this increment is not up to a level until the weight percent of graphene is reached 5wt% and the dielectric constant has readily reached up to a value of 15 at 8GHz frequency, the value of dielectric constant for ABS/GN/BaM hybrid composites have increased a lot and reached up to a value of 138 at 8 GHz frequency.

The EMI shielding of ABS/GN composite achieved the highest value of 2.4 dB at 5 wt % of graphene loading on 8 GHz frequency which shows round about 20-25 % shielding (blockage of incident wave). The value of EMI shielding in case of hybrid composites at 30 wt % of BaM nano particles have reached to a value of 30 dB which is equivalent to 99.9 % blockage of the Incident radiation.

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