Three component hybrid nano-composites of PS/PANI/GNP for radar absorption material

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Muhammad Umar Farooq

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It is certified that the contents and the format of the thesis entitled "**Three component hybrid nano composites of PS/PANI/GNP for Radar Absorption Material**" submitted by **Mr. Muhammad Umar Farooq** has been found satisfactory for the requirement of the **Master of Science** degree in **Materials and Surface Engineering.**

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Date: ___ - ___ - 2015

Dedication

I would like to dedicate this dissertation to our respective families without whose support and dedication to our higher education, furthermore the love patience and support they have shown us throughout the course of our degree.

Abstract

Polystyrene is an amorphous polymer, insulated in nature, having good mechanical properties while Polyaniline is a conductive polymer. Blending of such polymers could give new possibilities of wide range of dielectric, thermal and mechanical properties within a single system.

In this study, firstly polymer blends of Polystyrene and polyaniline were prepared by using solution blending method. Amount of Polyaniline was varied from 1wt% to 40wt%. Mechanical, dielectric and thermal properties were investigated using extensometer, impedance analyzer and TGA. It was found that tensile strength and young's modulus of the PS/PANI blends were increased by 40% and about 200% respectively whereas elongation at break decreases for the blends as compared to the pure PS. Dielectric constant and dielectric loss at 100Hz increased upto the order of $10^7$and 10^{10} respectively. Increase of about 100°C was observed in the degradation temperature for the PS/PANI blends.

Graphene Nano Platelets (GNP) seems to be very useful material due to its mechanical, dielectric and ablative properties. This material can be used to prepare the polymer nano-composites to enhance significantly the properties of the system. GNPs were coated with insulated PANI and dispersed at various concentrations ranging from 0.1 wt% to 1.0 wt% in the PS/PANI polymer blends using solution casting method. It was found that tensile strength and the modulus increased by 16% and 20% respectively as compared to the PS/PANI blend having 5wt% of PANI (95/5) which was used as a matrix. Dielectric constant slightly increased for the composites as compared to the blend matrix. Hybrid composites were found to give maximum microwave absorption at about 19 GHz which can be used for absorption purposes in that region.

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CHAPTER-1

INTRODUCTION

1.1 Polymers

A polymer is a large molecule or a macromolecule, which is composed of many repeating subunits. They have many features, both natural and synthetic polymers play significant role in daily life. Polymers may be plastics, as polystyrene, and biopolymers like DNA, proteins etc, the basis of the biological structure. Polymers, both natural and synthetic, are prepared by polymerization of the small molecules, called monomers. The large molecular mass produced unique physical properties, viscoelasticity, hardness and also tends to include glasses and semi-crystalline structures. Polymers started by the big labs in the world highlight the need and know about new forms of rubber, plastics, adhesives, heating film, and coatings. Generally the polymer science is the interdisciplinary science, a combination of chemistry, materials, chemical engineering, and other fields. Chemical Polymers are long-chain molecules with very high value of molecular weight of hundreds of thousands. So, the word "macromolecule" is often used to refer to polymers. In the literature earlier polymers were referred as resins before chemical structure of the long chains was understood. The first used polymers were the natural products, like cotton, starch, protein and wool. In Beginning of the 20th century synthetic polymers started to be prepared. The first polymer of interest, bakelite and nylon, has demonstrated the huge potential of the new materials. The scientists found out that they do not understand many relationships between chemical structures and physical properties that crystallize. The size, shape and arrangement of the crystallites depends on how the polymer has been crystallized. Such effects like annealing are very important because they have a strong effect on the end state of molecular organization. Other polymeric materials are amorphous, usually because their chains are very irregular and doesnot allow regular packing. The onset of the chain molecular motion is the glass transition and the polymer softening point of the glassy stage to the rubbery stage. Mechanical properties include such fundamental aspects as stress, modulus, and elongation at the break point. These can be related to fundamental molecular structure and the history of the polymer [1].

1.1.1 Polystyrene

Polystyrene is the thermoplastic polymer having aromatic structure and it can be synthesized and is polymerized from styrene monomer. At room temperature it has solid or glassy state but it starts flowing if heated above 100°C which is the glass transition temperature. If cooled again it can become rigid once again.

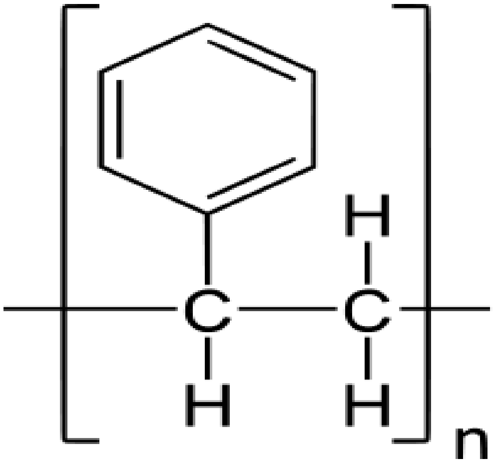


Figure 1.1 Structure of Polystyrene

Chemical formula of PS is $(C_8H_8)_n$, it is a hydrocarbon having long chains in which alternating carbon centers are attached to the phenyl group.

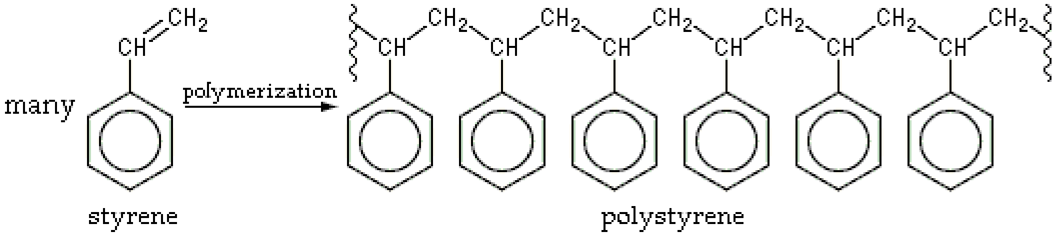


Figure 1.2 polymerization of styrene monomer to form polystyrene

Polystyrene can be semi crystalline or amorphous depending upon the configuration (the way atoms are arranged). It can be syndiotactic or atactic, in syndiotatic phenyl groups are positioned at the alternating sides in the hydrocarbon backbone. Which gives crystallinity in the PS having T_m of 270°C.The other arrangement can be a-tactic where phenyl groups are positioned randomly on both sides of the hydrocarbon backbone. This gives the amorphous structure having T_g of about 90°C. Some properties of polystyrene are mentioned in the table 1.

Table 1 Mechanical and physical properties of PS

Polymer	Tg	Thermal conductivity W/(m•K)	Density g/cm³	Tensile strength MPa	Young's Modulus MPa	Specific heat kJ/(kg•K)	Water absorption ASTM
PS	90 °C	0.033	1.05 at 25°C	40-60	3000-3600	1.3	0.03-0.1

PS is transparent naturally, but can also be colored with colorants. It find applications in protective packaging (packing peanuts and DVD and CD cases), containers, bottles, trays,lids, and disposable cutlery [2].

1.1.2 Polyaniline (PANI)

Polyaniline (PANI) is semi crystalline conducting polymer and is semi-flexible. PANI was discovered about 150 years ago, but got the intense attention of the people from the early 1980s that is because of the very high electrical conductivity. In all the conducting polymers and organic semiconductors, PANI shows good processing properties. Due to the rich chemistry which it has, polyaniline is one of the most focused conducting polymers in past 50 years [3].

Glass transition temperature T_g of PANI emeraldine salt was observed to be 130°C. The emeraldine salt has green colour and can be deprotonated to form emeraldine base by reacting with ammonium hydroxide, as shown in Fig 1.3.

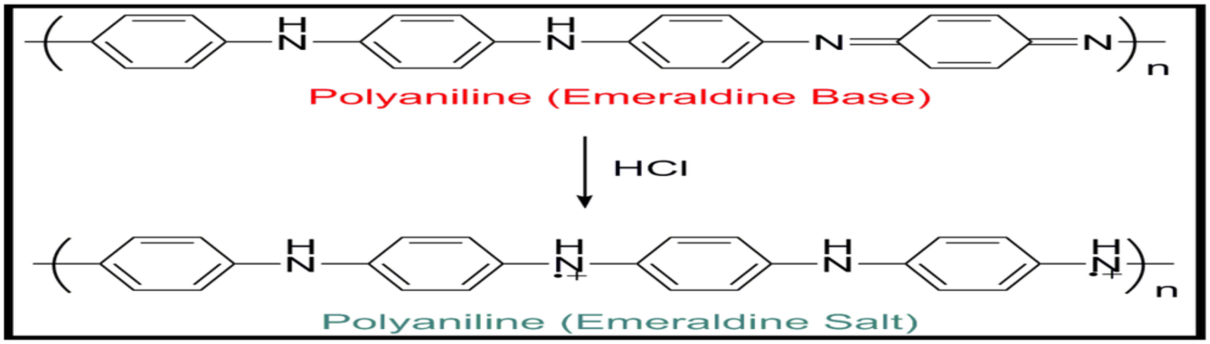


Figure 1.3 Polyaniline salt and base

PANI is, a conductive polymer, has bad mechanical properties, as low tensile strength, compressive strength and flexural strength that makes POLYANILINE a non ideal material to be used for practical applications [4].

1.2 Polymer Blending

In the mid-20th century the commercial emergence of new monomers, for preparing new polymers was endless. It was found that the development of new methods for the modifying the existing polymers would economically be feasible.

The first method developed for the modification was the polymerization, in other words the common polymerization of more than one species of the polymer.

The new modification process that is simple mechanical mixing of two polymers called as blending creates a new class of polymers called polymer blend.

In broad sense, any finely distributed combination of two or more polymers. In narrow sense it can be that there should not be any chemical bonding amongst the various polymers in the blend.

Combination of two or more polymer chains of constitutionally or configurationally different features, which are not having bonding with each other.

Blends of two polymers can be miscible or immiscible (mixture of two polymers remains phase separated). This is normally due to the positive heat of mixing and very little entropy of mixing. Some pairs like Polystyrene and polybutadiene, PS and PMMA etc are immiscible polymers.

These are the commercial polymers and their blending still gives good results for example the blend of PS and Polybutadiene has increased impact strength by adding of particular percent polybutadiene in the PS. On the other hand some polymer pairs like PS and poly vinyl ether, polyethylene oxide and poly acrylic acid are miscible blends. Polystyrene is also miscible with poly(2,6-dimethylphenylene) ,PPO. Commercial composition uses HIPS blended with PPO which increases the toughness of the system.

Glass transition temperature in case of polymer blends is an important parameter, miscible polymer blends which are single phased show the one glass transition point, whereas the immiscible polymer blends show more than one glass transition points and each polymer in blend retains its original glass transition temperature, Fig 1.4 [5].

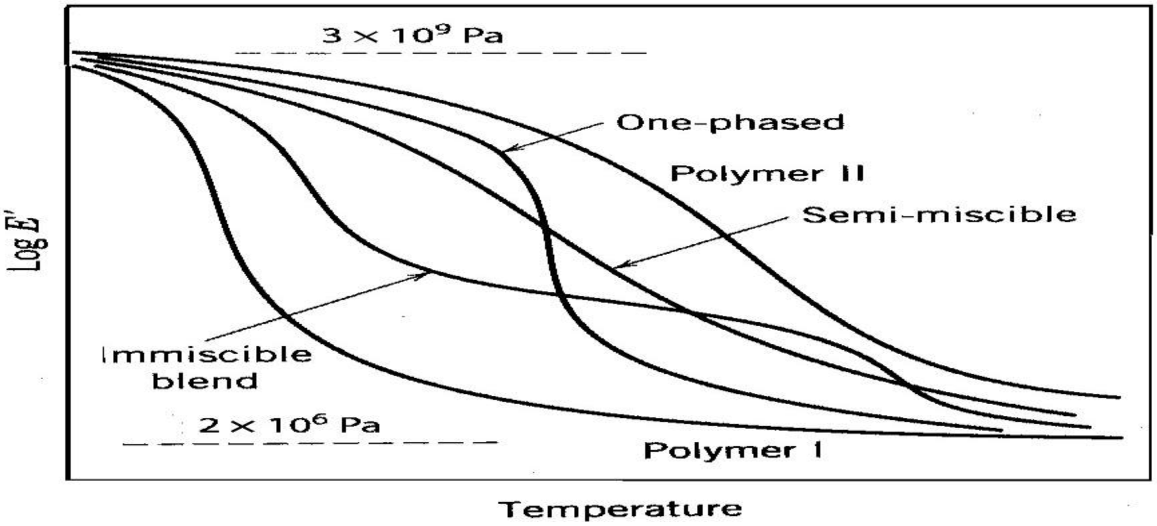


Figure 1.4 Different glass transition behavior of polymer blends. The two polymers if immiscible, showing two distinct glass transitions; miscible, with one glass transition or semimiscible, usually with one broad glass transition [5].

Polymers like polystyrene can also be blended with conducting polymers like polyaniline, so that some conducting behavior might be imparted into the polystyrene. Similarly other polymers can also be blended with polyaniline or some other conducting polymers to achieve optimum mechanical and dielectric properties.

There are many methods to prepare polymer blends like solution processing method, in-situ polymerization, melt blending etc. Blends prepared by these methods might be showing different behaviors because of differences in the preparation methods. Some suitable solvent is required for solution processing and in-situ polymerization in which polymers are soluble.

In case of melt blending no solution is required, polymers are heated above glass transition temperature then cooled to achieve some shape.

Fig 1.5 shows the difference between in-situ polymerization and solution blending technique for polystyrene and polyaniline blend, both of these techniques require some solvent, the difference is in the stage at which two different solutions are mixed together.

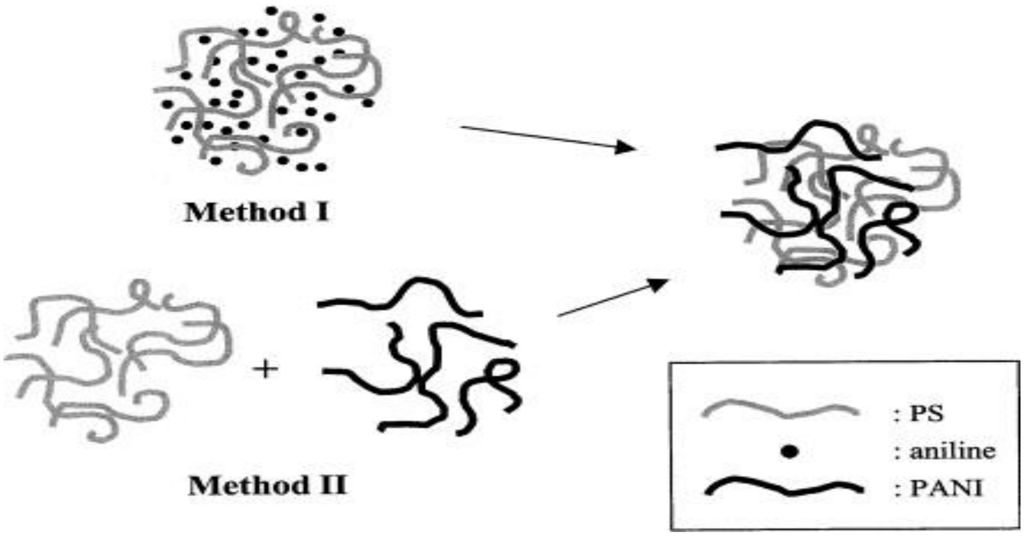


Figure 1.5 In-situ polymerization Method 1 , Solution processing method Method 2 [6]

Four basic ways of combining two and more than two polymers are known (a) Polymer blend, consists a mixture or the mutual solution of two or more than two polymers, but do not have chemical bonding in between, Fig 1.6. (b) The graft copolymer, constitutes a backbone of one polymer having covalently bonded side chains of another polymer. (c) A block copolymer, Fig 1.7 constitutes a combination of two polymers end on end by the covalent bonding clustered in separate groups. (d) A semi-interpenetrating network of polymer comprises the entangled linking of two polymers, one of them is cross-linked, which are not bonded with each other [7].

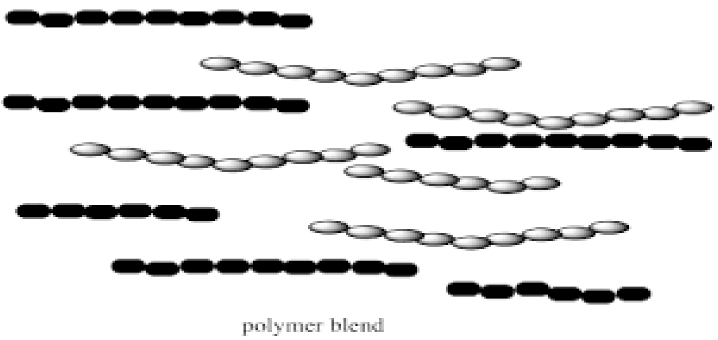


Figure 1.6 Representation of Polymer blends

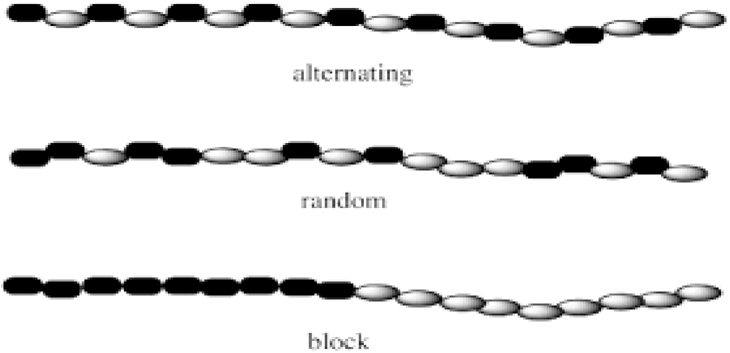


Figure 1.7 Representation of Co-Polymers

1.3 Nano Fillers

Fillers are used as a raw materials in the production of different kind of materials and have the production of about 50 million tons each year [8]. They were used mainly for reducing the cost of the expensive binding material initially and to improve the physical characteristics of the resulting composite. Filler's purpose is changing now a days, firstly their prime function was to lower the production costs that is now changing towards the improvement of properties of materials such as tensile or compression strength, workability, and flame retardancy. Nano fillers are the fillers which have at least one critical dimension less than 100nm. They can be in form of small spherical particles, rod shaped objects or flakes, fig 1.8.

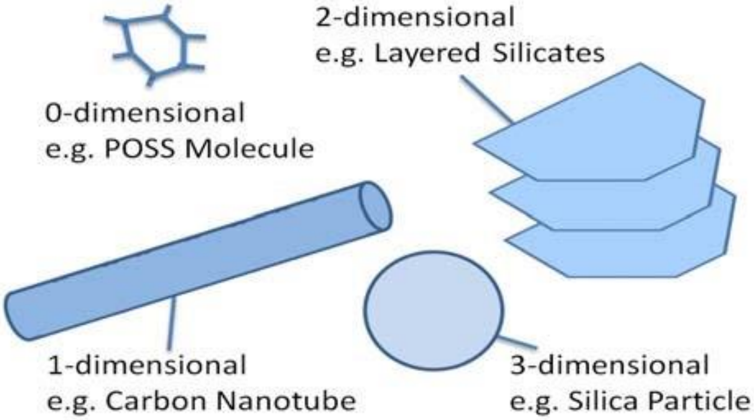


Figure 1.8 Filler geometries

Many nano fillers like POSS (Polyhedral oligomeric silsesquioxane), nano-clays , carbon nano tubes , silica particles , graphene , graphene nano platelets and carbon black are being used in polymer nano composites having their specific geometries as mentioned above in fig 1.8.

POSS (Polyhedral oligomeric silsesquioxane) molecules are a new approach to new nanocomposite. The benifit of a molecular approach is in a real dispersion in the nanometer range. POSS molecules is used as a reinforcing filler in plastic material to increase the mechanical strength. They have also been used as abrasion resistance in paints and coating as flame retardants in polymers.

Fumed silica is usually a form of silicon dioxide in non-crystalline state. Particle sizes ranges from 5-30 nm which are transferred into larger agglomerates keeping the large specific surface area of 10 to 600 m^2/g.4, fumed silica can be generally referred to as anti -klonter agent and also a thickening agent with thixotropic property [9].

Nano-clays are nanoparticles having plate like structure and are natural phyllosilicates, clays can be of various types, such as bentonites and hectorites. Bentonite is majorly montmorillonite, common nano-clay used in material applications. Montmorillonites, the stacked nanoscopic alumino silicate plates each about 1 nm high and 1 urn in diameter and are used as a filler in plastics. Montmorillonites which are organically modified, so called organo clays, are commonly used to improve the flame retardancy in polymers, particularly for cables [10].

Carbon nanotubes (CNTs) have been extensively studied because of its good mechanical and electrical properties. An important application of multi-walled carbon nanotubes (MWNT) can be that they are used as functional fillers in plastic composites and coatings [11]. They are also used as reinforcing filler in concrete and used to avoid crack propagation [12].

Graphite is also used as a filler in paints and coatings for electrical conduction, wherein the anti-static properties is obtained. Its two dimensional shape is graphene, that may be thought of as a single layer or sheet of graphite. Graphene can be used as a filler in conductive and reinforcement applications.

Graphene Nano platelets are nanoparticles, comprised of short stacks of platelet-shaped graphene sheets. GNPs are 6-8nm thick, containing 5-8 stacked layers of graphene. High barrier properties and enhanced mechanical properties (stiffness, strength, and surface hardness) can be achieved with the graphene nano-platelets due to their distinct size and morphology. The nano-platelets are also excellent electrical and thermal conductors due to their pure graphitic composition. They also improve the thermal stability. GNPs can be used to enhance the properties of polymeric materials including thermoplastics, thermo setting plastics and elastomers.

Intercalating graphite with the mixture of nitric acid and sulfuric acid GIC (compounds of the graphite molecules or the atoms, alkali metals or the mineral acids, which is between the carbon layers) which is exfoliated that is generated by heating or treatment with microwaves, that produced expanded graphene, EG keeps a layered structure but layer distance increases compared to graphite, consisting of thin plates (30-80nm) thick which have lose stacking. EG itself is a nano filler, but its properties are limited by the relatively low specific surface. To further increase the surface area of EG it can be exfoliated further by a variety of techniques to produce GNPs. GNP’s thickness depends on the production method, sonication can make GNPs having a thickness of about 10 nm and lateral dimensions of about 15um. There are many other methods to yield monolayer and multilayer graphene and each method can produce graphene of certain specifications. Another way, sonication of graphite flakes in water to give single- or multi-layer graphene, which is highly defect-free, but this method requires a lot of surfactants which have a negative impact on electrical conductivity [13].

Fig 1.9 shows the atomic structure of graphite and graphene, it can be seen that graphene is a single layer whereas graphite contains many graphene layers. Table 2 shows the thickness of different graphene derivatives.

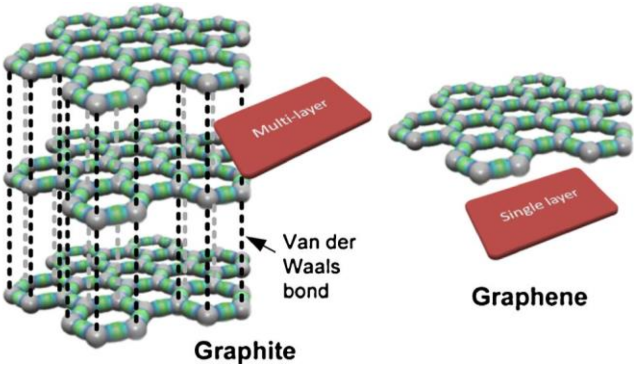


Figure 1.9 Atomic structure of graphite and graphene [14]

Table 2 Typical thickness of graphene derivatives [14]

Graphene derivatives	Thickness
Graphite	0.4-60 um
Expanded graphite	100-400nm
Graphite nanoplateles	5-100nm
Graphene nano platelets	0.34-5nm

Fig 1.10a shows that as the average thickness of graphene platelets increases, the total number of platelets and the surface area of the platelets decreases. So at low thickness values higher interaction is expected.

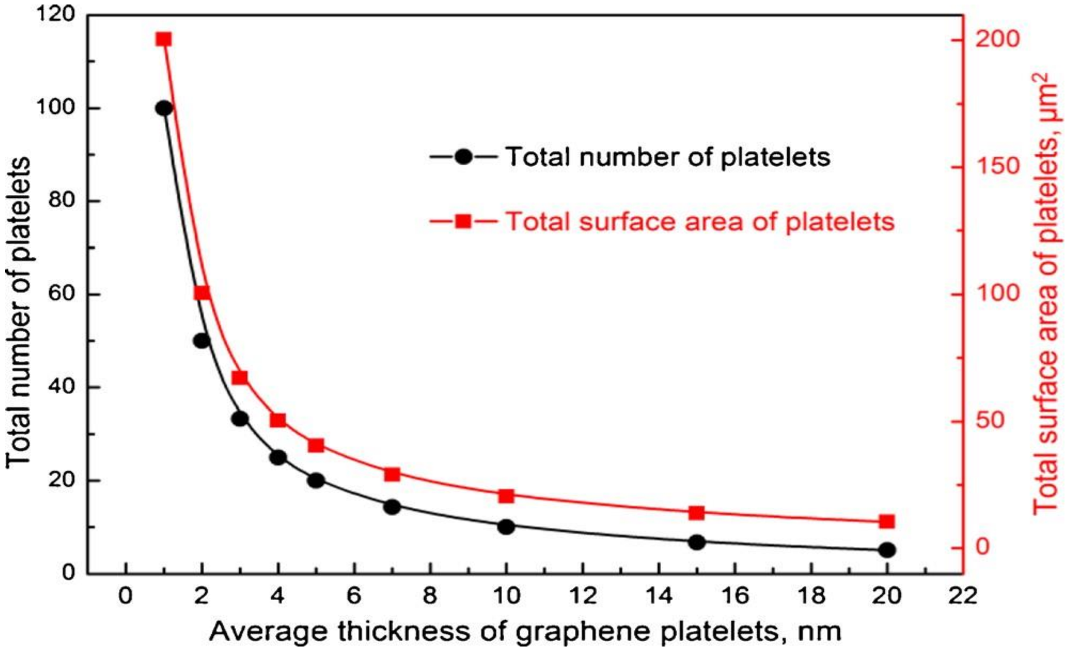


Figure 1.10a The number of graphene platelets and their total surface area at 1 vol% GnPs [14]

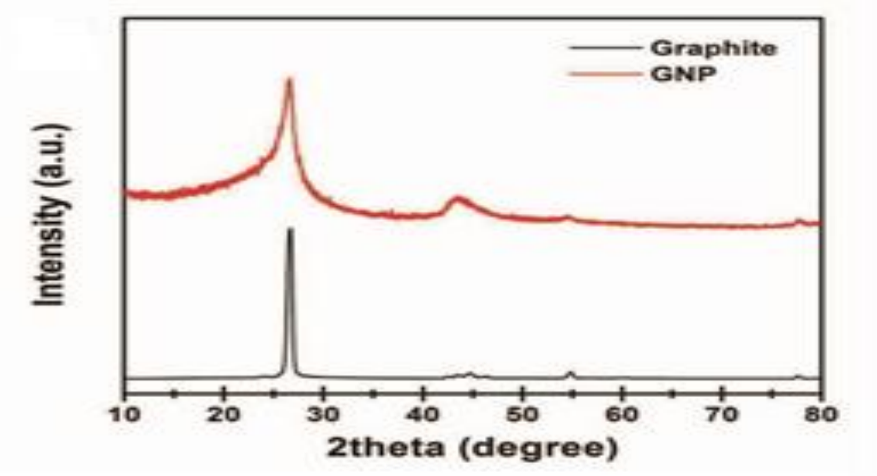


Figure 1.10b Xrd patterns for Graphite(lower one) and GNP(above one) [15]

In figure 1.10b we can see the difference between graphite and GNP as they show difference in the patterns. At 2theta 26.2 degree graphitic peak is observed in the lower pattern which is for graphite in the above pattern in fig 1.10b that graphitic peak is broadened due to decreased graphitic particle size in GNP. GNP consists of few stacked graphene layers. Diameter of GNP is few hundred nanometers.

1.4 Polymer nano composites

In Polymer nano composites polymer, copolymer or a polymer blend is used as a matrix having nano particles or nano fillers dispersed in the polymeric matrix. Nano fillers can be in different shapes as platelets, fibers or spheroids as discussed in the previous section. At least one dimension of these fillers should be below 100nm. As we move from micro to nano particles, both physical and chemical properties are changed. Two important properties are the surface area to volume ratio and the particle size. As the surface area-to-volume ratio increases, due to the reason that particles become smaller, it leads to increase the dominance of the role of atoms that are at the surface of particle over those in the interior of the particle. This effects the properties of these particles when they react with other particles. Because of the higher surface area in the nano-particles, there is an enhanced interaction with the other materials in a system, this factor increases the strength, heat resistance etc [16].

Reducing filler size in nanocomposites increases interfacial area per volume and lower surface area and surface to surface inter-particle distance. Nanocomposites have better performance as compared to the traditional composites. This factor gives the better prospects of the polymer nano-composites in the field of industrial applications.

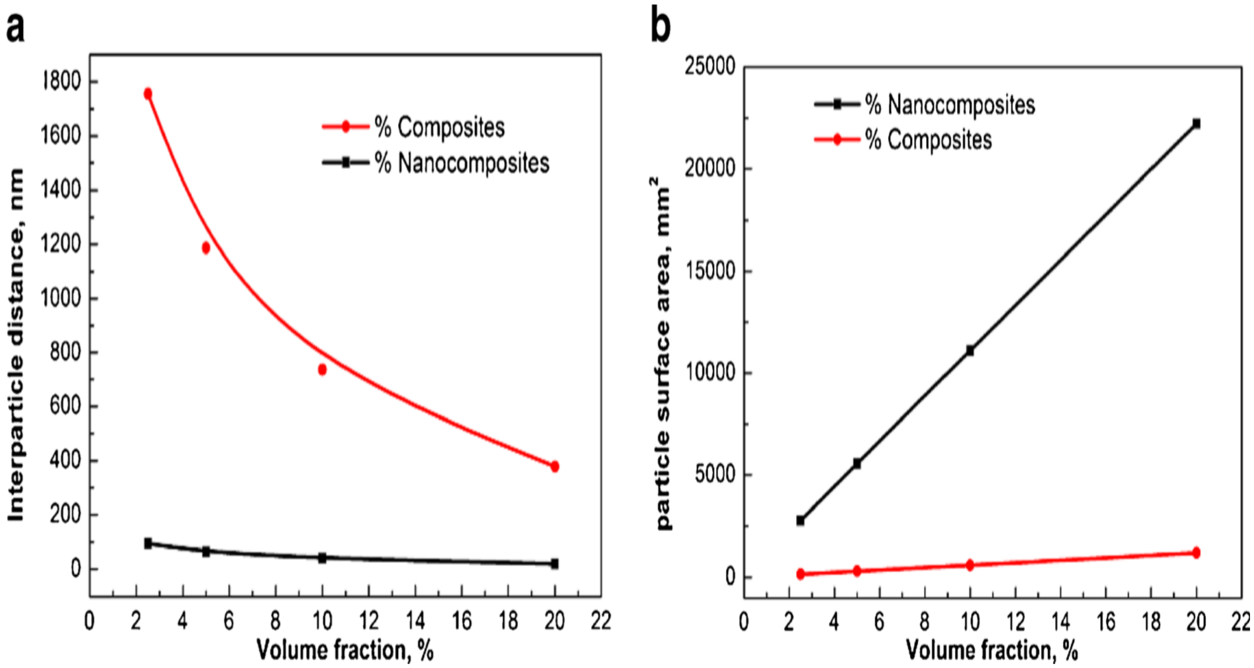


Figure 1.11 **a)** surface to surface interparticle distance vs volume fraction percent**, b)** total particle surface area with respect to volume fraction[14]

Fig 1.11a shows that for nano composites by increasing the volume fraction the surface to surface inter particle distance reduces as compared to conventional composites which means that for same volume fraction, nano particles have much more interaction than micron sized particles. Therefore the nano particles are able to interact with one another in a more effective way to restrain the molecular deformation of the matrix.

Fig 1.11b shows that the total surface area in nanoparticles is increasing significantly with the volume fraction as compared to the conventional composites this is because the nanoparticles have very high surface to volume ratio which enhances the interfacial region even at low percentages of nano filler, that leads to higher interaction with matrix.

Polymer nano composites are the well-known amongst all the nano materials, they are broadly studied for a large number of applications as flame retarding panels , high barrier films for packaging applications , anti-scratch coatings for protection of surface and high performance composites for the aerospace and automotive industry.

Unlike the materials like metals and ceramic, polymers production costs are lower and they have high specific strength, and less energy is required for the production and recycling. In the automotive industry, polymer flexibility and weight savings offered reduction in fuel consumption and a reduction of the exhaust gas as compared to the metal parts. Despite the advantages, the most important drawbacks of the polymers include a low mechanical properties and thermal stability and the lack of functionality. For example Automotive parts, should not deform when exposed to sunlight and heat from the engine, aircraft components must be able to resist lightning and pads of brakes should be bearing the heat of friction. These require the development of polymer based composites. The combination of two materials or more than two materials has the potential to enhance the properties as compared to the neat polymer.

1.5 Radar Absorption Mechanism

There is a need for certain objects, which are invisible, or at less visible for radar for military applications or for communication systems. Such products range from submarine periscope to stealth aircrafts, warships to wind turbines. Materials technology can meet these needs, providing materials, in which the microwave energy absorption happens and named as radar absorbing materials (RAM), or structures prepared for the same purpose, called Radar absorbing structures (RAS). Some solutions are, to go for plastics and other composite materials.

Energy of radar can be attenuated in two ways, one is by being absorbed in some material which converts it into some other form of energy, as heat, or due to destructive interference.
In the first case, response to the magnetic or electric fields of the wave with the material properties and the energy is used. In the second case, incident waves quench anti-phase reflection, the required 180 ° phase shift is obtained by reflecting surfaces which are separated a nominal quarter wavelength apart. Some RAM and RAS use both principles at the same time.
Useful elements include materials which have conducting nature and are able to reflect radar radiations, dielectric materials which are highly invisible to the radar, and the magnetic materials which absorb electromagnetic energy. RAM can be produced by the loading of dielectric materials with conductive, magnetic and reflective elements. As number of plastics are dielectric materials, they are used for these solutions [17].

1.5.1 Dielectric absorbers

In case of dielectric materials negative and positive charges of the atoms are in the similar position due to atomic and by the molecular forces, and also are not freely moveable. but, when electric field is applied, a dielectric material include the development of a number of electrical dipoles which arrange themselves, towards the direction of the given electric field. Inverse effect on the electric field tends to store of electrical energy that can be converted to heat by Joule’s effect. And this process happens in the dielectric absorbing materials.

The probable routes of an EM wave on a surface is shown in the figure 1.12, in which the incident wave is absorbed, reflected directly or reflected back (internal reflection) or transmitted. Whenever an electromagnetic radiation strikes a surface having RAM cover, the incident wave is absorbed not quite right. The microwave weakening may occur more complex by a RAM and various damping mechanisms can take place.

In the first case, the attenuation of wave is by magnetic or dielectric particles which have physical process, as ohmic losses and spin inversions. In the second case, the attenuation is carried back because of the scattering of the wave in different directions, with the right geometric shapes, wherein the signal detected, is reduced at the receptor. In this situation, a part of the incident wave creates secondary waves which move parallel to the surface, and when these radiations face materials having different impedance, internally reflected waves are produced, and thus improves the attenuation due to the material.

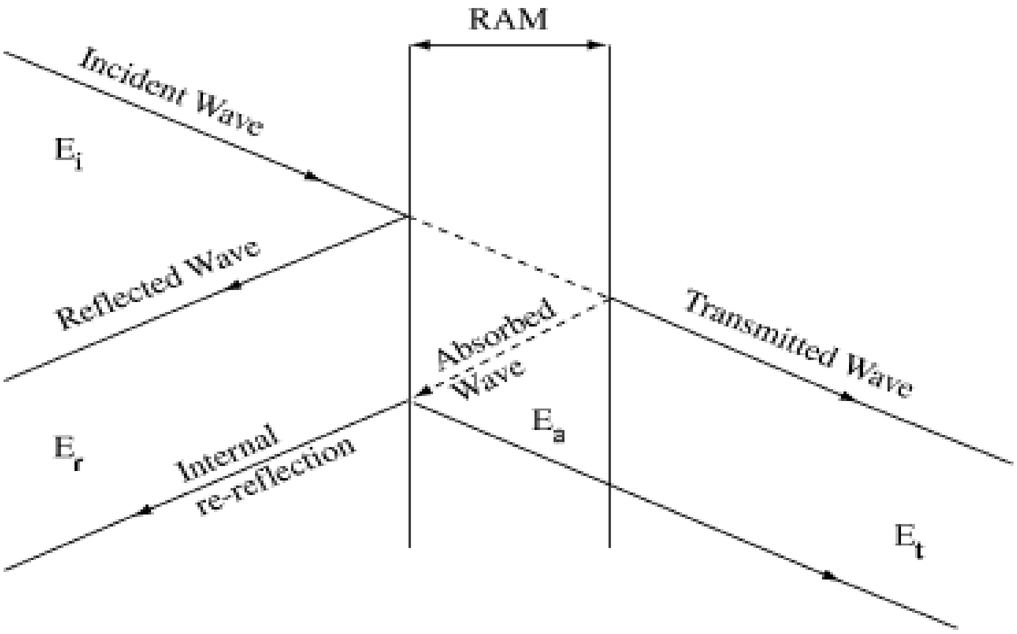


Figure 1.12 Possible paths of incident electromagnetic wave in a material

Equation 1 is showing the constituents of the distribution of theincident energy in a material, and E_i, , E_t, E_a and E_r are the incident, transmitted, absorbed and reflected energies, respectively.

$$\boldsymbol{Ei = Et + Ea + Er} \qquad \boldsymbol{Equation 1}$$

The attenuation can be represented according to Equation 2, E_i and E_r are the incident and reflected energies, respectively. Attenuation is expressed in dB (decibel).

$$\mathbf{Attenuation\ (dB) = 10.\log} \boldsymbol{Er/Ei} \qquad \boldsymbol{Equation\ 2}$$

Generally, absorbers can be made by using some polymeric matrices, stiff or might be flexible as epoxy, bismaleimide, phenolic, polyurethane, silicone resins and polyimide etc.

The dielectric material is developed by a suitable combination of absorption centers or (fillers) in a polymer matrix, adjusting the dielectric properties of the application, and the frequency domain. The right setting of the constituents during the processing, makes the material change the behavior of the transmitting or the reflecting material to Absorber.

In case of dielectric materials, the most important properties that make them the microwave absorbers are the dielectric constant and secondly the loss factor of energy. The microwave absorber can have change in the dielectric properties by the change of the thickness. This is usually achieved with the dispersion of the fillers, which modifies the electrical properties of the material. At higher frequencies and the higher values for the dielectric constant, more reflection occurs with respect to an untreated surface of the dielectric material.

Considering both air and the material used are having dielectric constant value equal to one, no reflection is noticed. The dielectric constant of nonmetallic materials shows high values. Figure 1.13a shows the front surface of a dielectric absorber material, which have surface impedance is closer to the air. In this situation, reflections of the surface are reduced to a minimum. This suits the incident wave traveling in the material in which the energy is attenuated or absorbed, which is the reason of the rise in the loss factor of the material. The impedance effect is the exponential function with respect to the thickness of the material. Figure 1.13b shows that impedance deceases exponentially according to the proximity of the metal support system. In this situation it is crucial to notice that the existence of the various layers in the material can directly be related to the amount of absorbent center or (filler) in each. Due to these corresponding arrangement of the layers, the material behavior may change to absorbing of an electromagnetic radiation from reflector behavior [18].

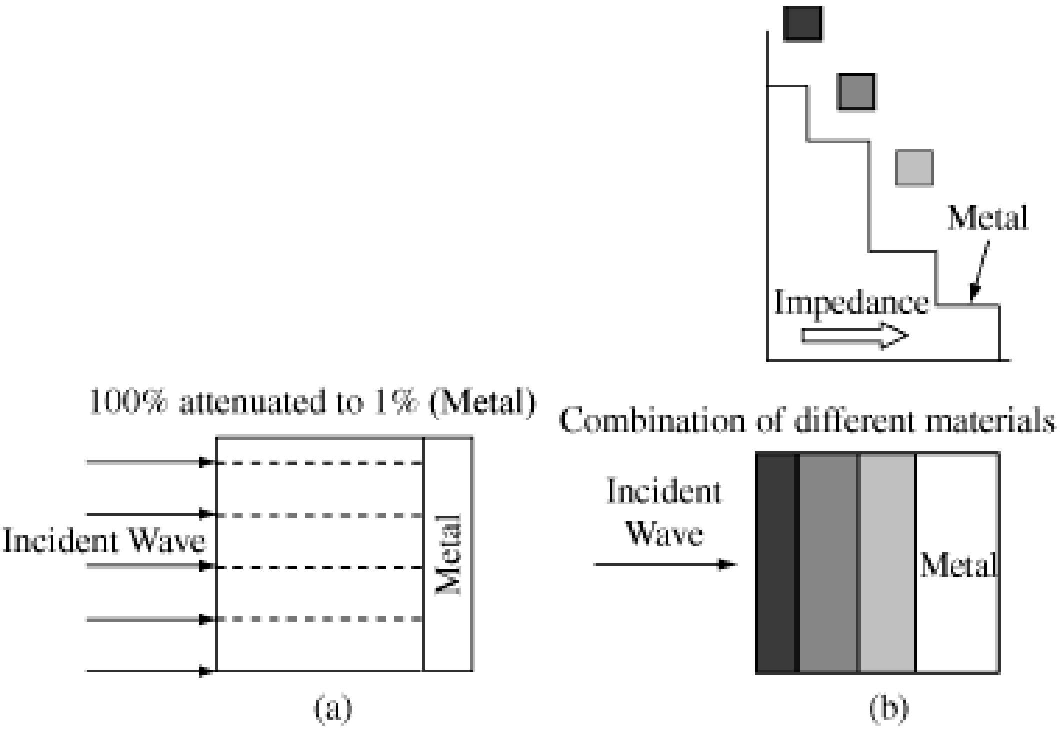


Figure 1.13 RAM showing the influence of a) thickness and b) multilayers on the wave attenuation

1.6 Research Problem

We need to develop a material having good absorption properties and dielectric properties, and at the same time these materials should have mechanical and thermal stability to withstand the conditions where these will be used. So to have good mechanical, thermal and dielectric properties within a single system we will have to develop such a system which will have all these qualities with some compromise. So that all the requirements might be fulfilled by a single system.

1.7 Aims and objectives

PS is an insulative material and PANI is a conducting material, firstly PS and PANI polymer blends are prepared at various concentrations and characterized using mechanical and dielectric techniques. Then the blend showing optimum mechanical and dielectric properties will further be embedded with PANI coated GNPs. The main focus will be to achieve material with high dielectric constant value having high dielectric loss factor and radio waves absorbing characteristics. So that they might be used for the radar absorption applications.

1.8 Scope of study

Development of nano composites for improving the stealth properties of aircrafts, energy storage in super capacitors and EMI Shielding.

Stealth coating is crucial for national security and super capacitors have their important role in miniaturization of the electronics with improved electrical properties. These materials are easily fabricated, tailored and are also economical. Such materials find vast application in aviation industry, digital electronics and telecommunication.

CHAPTER-2

EXPERIMENTAL WORK

2.1 Synthesis of Polyaniline

Oxidative polymerization

Take 20 ml distilled aniline, add 20 ml o pure conc HCl in it. Stirring is done so that aniline hydrochloride is formed. Now this aniline hydrochloride is added in the 1M solution Ammonium peroxide sulphate.

Both solutions were mixed at the room temperature by stirring for 2-3 hours. Resulting solution was initially transparent, it turned to bluish and finally greenish. Now remove from the stirrer and allow the polyaniline to settle down. As it settles down remove the excess water and other impurities which are in excess like HCl.

Now again some water was added in the beaker, stir for some time and again allow polyamine to settle down. Again remove the impurities. Repeat this process 3-4 times unless the water becomes clear. This is called as a washing process.

Now overnight drying was done to get the polyaniline in the powder form.[19]

2.2 PANI coated GNP preparation

GNP was bought from “Asbury Carbons USA” and its properties were discussed in the previous chapter. The filler to be used for the manufacturing was not the GNP directly but we coated the GNP with polyaniline. The coating of dedoped polyaniline on the GNP that was indicated by ipGNP.

Method of preparation is discussed below.

Take 20 ml distilled aniline, 0.1g GNP was added in it then stirring was done for about two hours, add 20 ml pure conc HCl in it at room temperature. 1M solution Ammonium peroxide sulphate in water was prepared and 50ml solution was added in the above recipe. Both solutions were mixed at the room temperature by stirring for 2-3 hours [20].

The other form that is the coating of dedoped PANI on the GNP has the same steps, but after adding the APS solution ,200 ml of 2M NH_4OH solution was added to neutralize the doping effect of HCl. which made the polyaniline insulated

Then washing was done three or four times which removes the excess HCl and the impurities, then overnight drying was done to get the coated GNP having insulated coating of polyaniline in the powder form.

2.3 PS and PANI Blend Preparation

Polystyrene and Polyaniline were Blended using the solution processing method. Ortho-xylene was used as a solvent. Firstly 0.06g/ml of solvent, solutions were prepared for both PS and PANI.

Different percentages of two polymers were to be prepared for the formation of blends. These percentages are shown in table 2.1

It was found that if we increase the ratio of PANI in blend above 40%, the blend sheet formed could not be made because this ratio of PANI was high enough to make the system brittle. So we just focused up to the ratio 40 which was the highest amount of PANI in blend with PS that could form a sheet.

For preparing the blend 0.06g/mol solutions for both PS and PANI were prepared separately. For PANI solution in ortho-xylene, firstly stirring was done then sonication was also done for about an hour. For PS solution stirring was done for 1.5 hours.

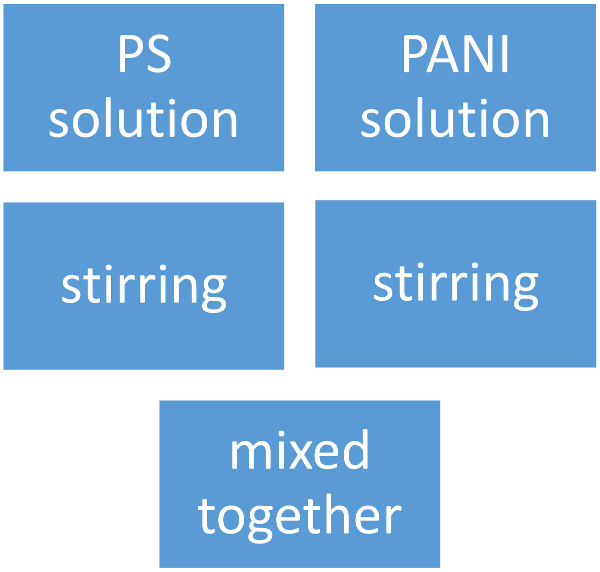


Figure 2.1 Schematic of solution processing

After the solutions were prepared, they were mixed in such a way that total volume was 12ml ,and the adjustments of the ratios of the PS solution and PANI solution were done for each type of blend which are shown in table 3. Process flow sheet diagram is shown in fig 2.1.

For that purpose small bottles were used which could contain total 12 ml mixture of both the solutions Fig 2.2.

Now these bottles were placed in the ultra sonicator of 400 MHz for the sonication. Sonication was done for about 2.5 hours. Then the bottles were taken out and the blends of different types were poured into the petri dishes which were used as a mold. Then the molds were placed in an open environment to get dried. After about 24-36 hours the blends were solidified and taken as the sheets [21].

Table 3 Percentage in which blends were formed

PS	PANI
99	1
95	5
90	10
80	20
70	30
60	40

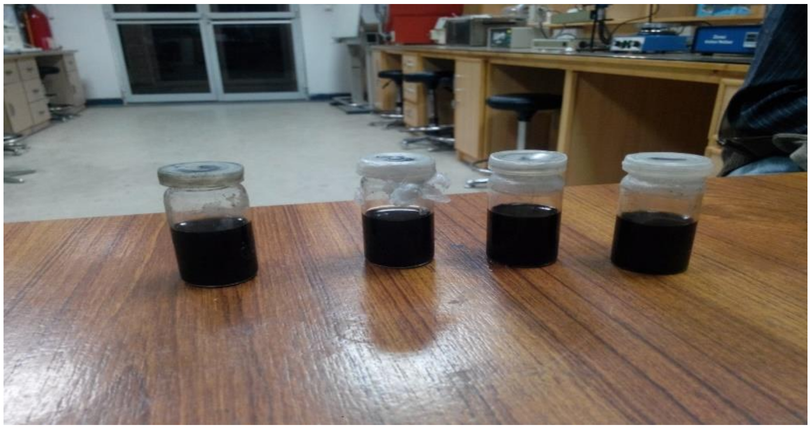


Figure 2.2 Bottles containing liquid blend before molding

All these samples were prepared with above mentioned method ,then the characterization was done to study the mechanical, thermal ,dielectric and absorption properties on the basis of which best composition was to be selected to be used as the matrix for the composites.

2.4 PS/PANI/ipGNP Composites Preparation

Solutions of PS, PANI and GNP were prepared separately in the orthoxylene. Concentration kept for each solution was 0.06g/ml.

hour, and for PANI solution in ortho-xylene after stirring, sonication was also done for about For PS solution stirring was done for an 1.5 hours.

Then these solutions were mixed together at varying proportions of GNP 0.1% to 1% , the overall volume of 12 ml was taken, PS to PANI ratio was kept constant at 95/5 which was the best ratio based upon mechanical and dielectric results which will be discussed in the next chapter.

Then the mixture was poured into the molds which were petri dishes in this case. Air drying was done for 2-3 days, then the samples were removed from the molds and vacuum dried for about 12 hours at 70 ^{o}C [22].

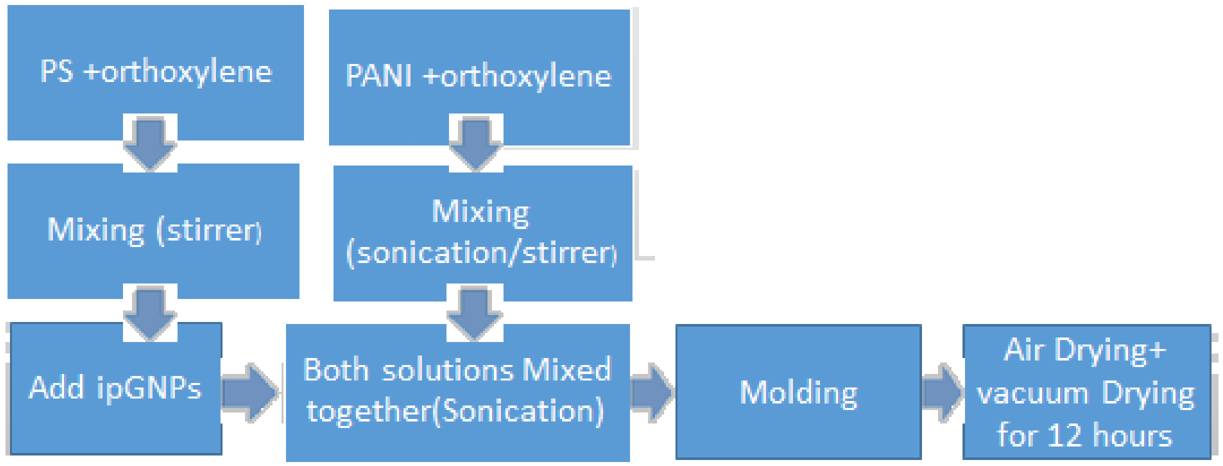


Figure 2.3 preparation method for the composites

These composites were prepared using ipGNP having coating of dedoped PANI. Composites prepared by these fillers were named as ipPNCs (Composites having ipGNP as a filler). Sampling details are mentioned in the table 4.

Table 4 compositions for the prepared composites

Composites	PS%	PANI %	iGNP %
iPNC1	95	5	0.1
iPNC2	95	5	0.5
iPNC3	95	5	1

All these samples were prepared and the mechanical, thermal, dielectric and absorption properties were studied which will be discussed in the next chapter

2.5 Specimen Testing and Characterization

Samples were characterized by the following techniques

a. X-RAY DIFFRACTION (XRD)

XRD patterns were measured at room temperature using a Theta-Theta instrument by STOE-Germany with a Cu Kα Radiations (λ = 0.15418 nm). The scanning rate was 2˚/min over the range 2Θ = 5˚ - 40˚

b. SCANNING ELECTRON MICROSCOPY (SEM)

The morphologies of Hybrid composite films were investigated using a JOEL JSM-6490A Analytical Scanning Electron Microscope. A cryogenic crack was created in the films using liquid Nitrogen i.e. the samples were frozen in liquid nitrogen where they became fragile and were broken to generate the fresh surface.

c. TENSILE MECHANICAL PROPERTIES

The tensile properties of samples were determined using Trapezium-X Universal Testing Machine (AG-20KNXD Plus) manufactured by Shimadzu Corporation at a crosshead speed of 2 mm per minute (ASTM D882). All the samples were tested at room temperature and at least 5 individual determinations were used to obtain an average value. Samples for testing were having length of 40mm and width of 10mm and the guage length of 20mm was taken.

d. DIELECTRIC PROPERTIES

Dielectric properties of specimens were determined using Precision Impedance Analyzer (Wayne Kerr 6500B) at room temperature. The capacitance C and dissipation D were measured through impedance analyzer in the frequency range of 1 Hz to 5 MHz. Circular samples having 13mm diameter were used for the dielectric testing.

e . RADAR ABSORPTION

EMI-shielding test was performed with the help of E8362B PNA Network Analyzer at room temp and in the frequency range from 8 to 20 GHz.

f . THERMAL GRAVIMETRIC ANALYSIS (TGA) :

TGA analysis was done with the help of YRIS Diamond TG-DTA High Temp Vacuum in the range from 0°C to 1000° C at 10° C per min.

CHAPTER-3

RESULTS AND DISCUSSIONS

Different techniques were used to characterize the samples as discussed in the previous chapter. These include tensile testing, TGA, impedance analyzer and absorption.

Different results obtained from these techniques will be discussed in detail in this chapter.

Results of blends will be discussed first of all on the basis of which the optimum blend system was chosen. Then using that particular system as a matrix, this was further embedded into the ipGNPs at the varying ratios , then the characterization of composites was conducted. Results for composites will be discussed in the 2nd part of the chapter.

3.1 PS/PANI Blend Results

Blends for PS/APNI were prepared in different amounts of PANI starting from 1wt% to 40 wt% .characterization was done and Mechanical , thermal , Dielectric and absorption properties are studied that are discussed below.

3.1.1 Scanning Electron Microscopy (SEM)

SEM images of PS/PANI blends and pure PS are shown in fig 3.1(a-f). PS is an amorphous polymer and has a featureless pattern fig 3.1a, we can observe that when PANI is added into the PS matrix some features are appeared PANI phase appears as the circular phase(brighter phase in dark matrix) Fig 3.1b , and by increasing the amount of PANI upto 5wt% we observe that the concentration of circular phase increases which appears as a separate phase forming a heterogeneous network fig 3.1c , at about 10% and 20wt% of PANI proper network of PANI is seen 3.1d and 3.1e respectively , and after 20 wt% of PANI this network is complete and PANI Phase seems to be interconnected fig 3.1f which is having 30wt% of PANI, further addition further densifies this network.

We can see that in fig 3.1b when PANI is in 1wt% PANI phase starts appearing and this appears as a separate phase which shows that it is forming a heterogeneous blend. Similarly other blends are also showing heterogeneous structure , which is in accordance with the literature as shown in fig 3.2 which is also a heterogeneous PS/PANI blend [23].

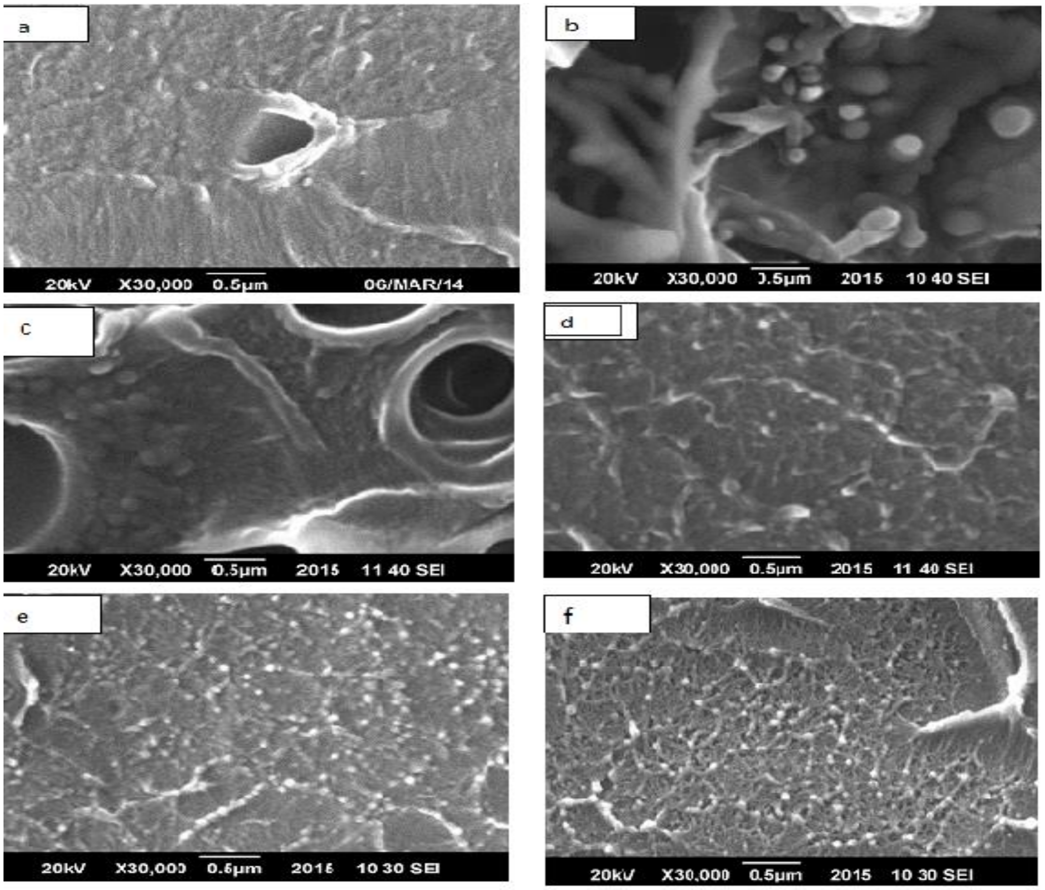


Figure 3.1 a) pure PS , b) PS/PANI blend containing 1wt% PANI , c) PS/PANI blend containing 5wt% PANI , d) PS/PANI blend containing 10wt% PANI , e) PS/PANI blend containing 20wt% PANI , f) PS/PANI blend containing 30wt% PANI

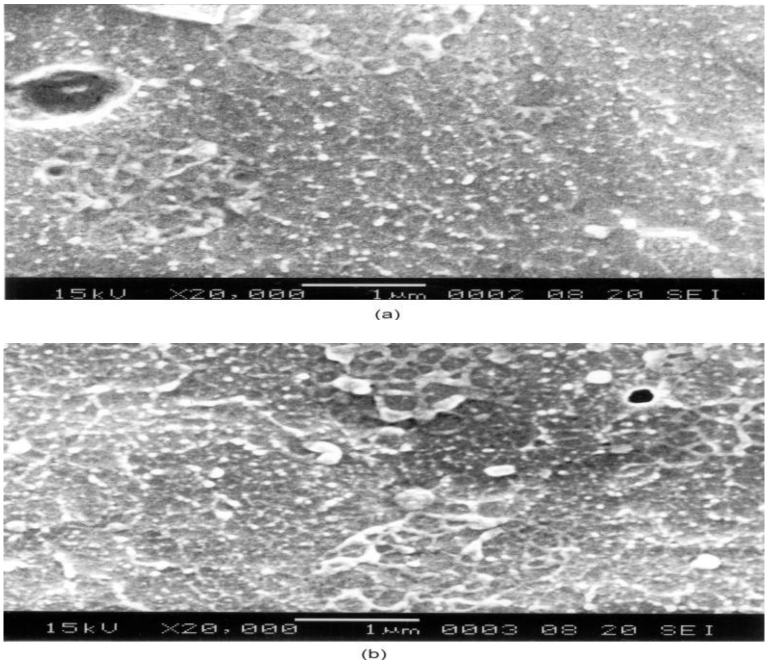


Figure 3.2 a Cross section SEM micrographs of PANI-DBSA=PS blend films containing (a) 2.5wt% and (b) 7.5wt% of PANI-DBSA [23]

3.1.2 X-Ray Diffraction (XRD) Results

XRD plots of PS, PANI and their blends is shown in figure 3.2b. The PS shows broad peak at value of 2ø = 19^{o}, which is the characteristic peak of amorphous structure in PS. In case of PANI broad scattering peak at about 2ø = 19^{o} shows the amorphous behavior of PANI. Sharp peaks at 2ø =20.7^{o} (020) and 2theta=23.59^{o}, which is the bragg's reflection of (020) plane indicating the ordered packing of the benzoid and quinoid rings, responsible for semi-crystallinity in PANI.

Now for PS/PANI polymer blends both peaks at 2ø = 19^{o} and 2ø = 23.59^{o} shows the presence of amorphous structure of PS alongwith the ordered packing of PANI. Although the peak intensity of PANI phase is reduced implying relatively less order when embedded into the PS phase. XRD plot confirmed the presence of the immiscibility of PANI in PS which is consistent with SEM results.

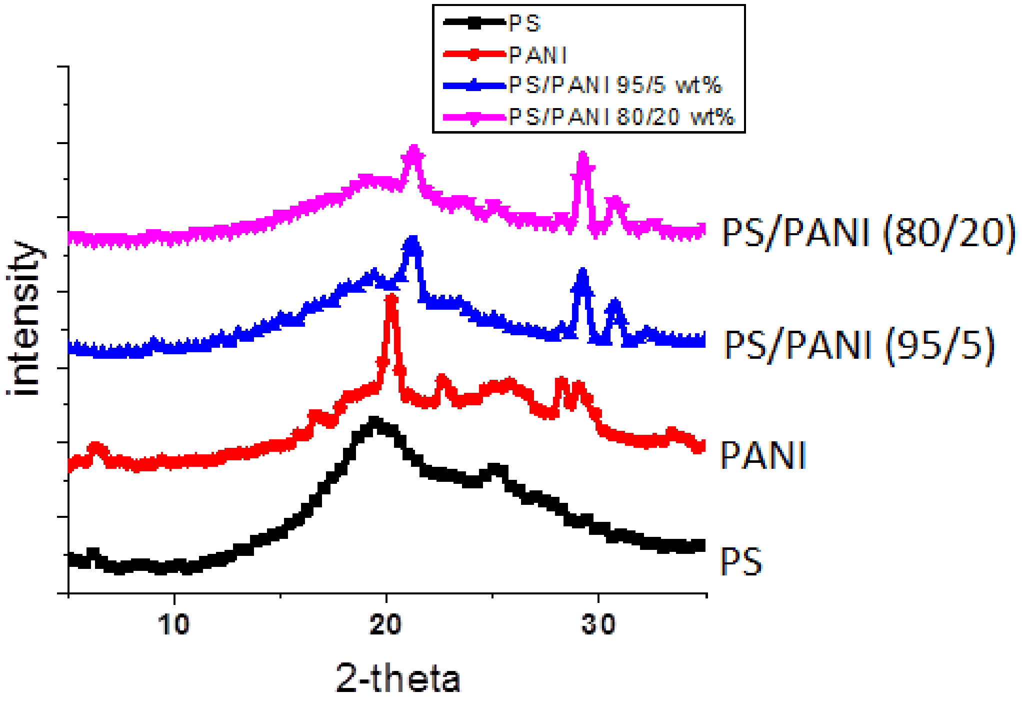


Figure 3.2b XRD Results of PS, PANI and their blends

3.1.3 Tensile testing of PS/PANI blends

Tensile testing of blends was done in which samples were cut having the dimensions of 10mm wide x40 mm long, guage length was 20mm, thickness varied from 0.1mm to 0.15mm. Fig 3.3a shows stress-strain curve for PS/PANI blends. From this curve we can get information like tensile strength, Young’s Modulus and elongation at break.

Fig 3.3b shows the tensile strength of the blends with respect to the wt% of PANI. Any clear trend was not observed in the behavior of tensile strength but About 40% increase in tensile strength was observed from 9.5MPa for PS to 13 MPa for the blend having 5wt% of PANI. The increase observed in the blends upto 5 wt% of PANI was due to reinforcement effect of PANI and constraining of the matrix by the PANI phase.

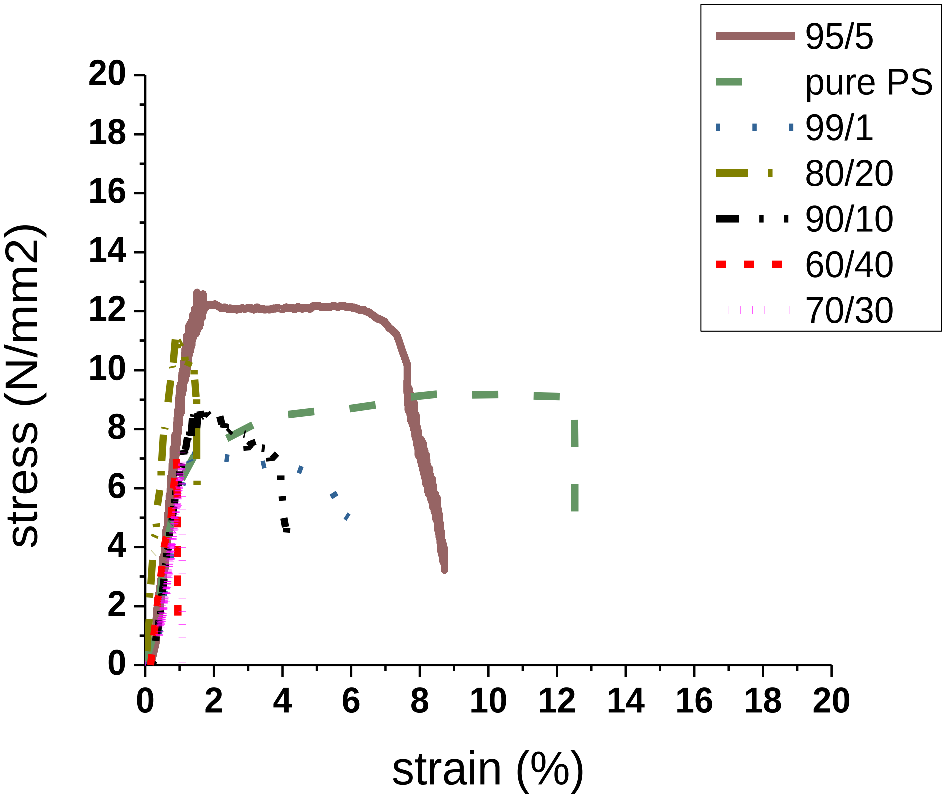


Figure 3.3a Stress strain curve of PS/PANI blends

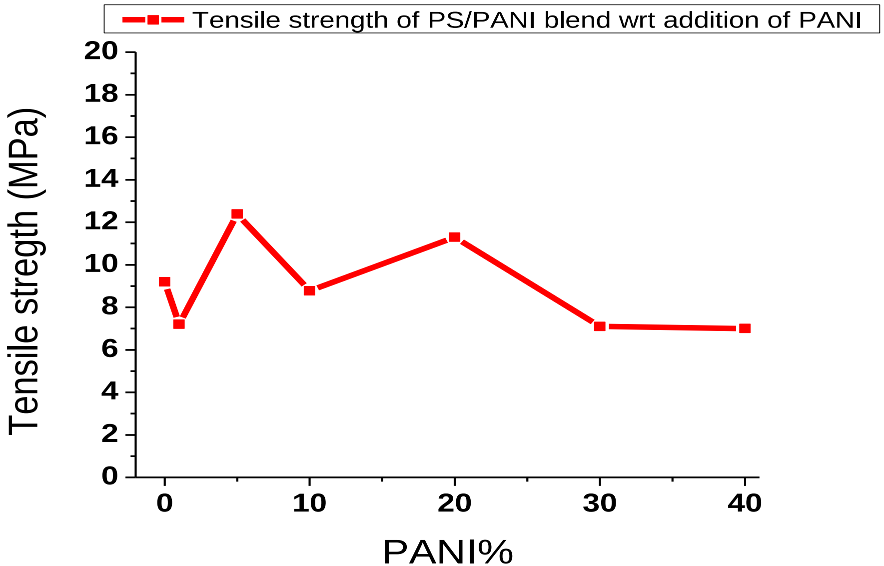


Fig 3.3b Tensile strength of PS/PANI blends with respect to PANI%

Fig 3.3c shows the effect of PANI wt% on the young's modulus of PS/PANI blends. From the figure we can observe that there is about 200% increase in the modulus starting from 450 for pure PS to 1300 MPa for PS/PANI blend having 20wt% of PANI.

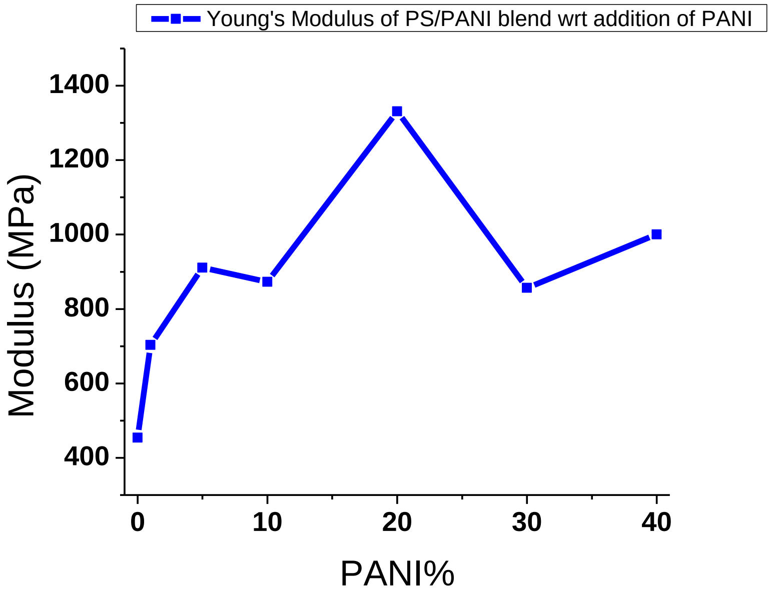


Figure 3.3c Young's Modulus of PS/PANI blends with respect to PANI%

For higher percentages dispersion become very difficult so agglomerates might be formed which reduce the modulus of the system. Increase in modulus can also be related to the constrained PS matrix whose movement is restricted by the PANI phase.

Fig 3.3d shows the effect of PANI wt% on the strain% of blends about 90% decrease in strain% was observed starting from 13% for pure PS to 1% for the blend having 40% PANI as the PANI Phase constrains the matrix [24].

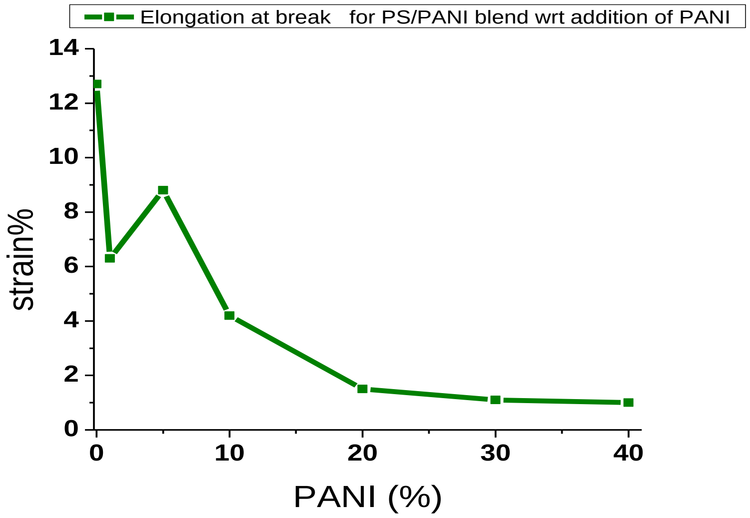


Figure 3.3d Strain% of PS/PANI blends with respect to PANI%

3.1.4 Dielectric Testing

Dielectric properties like dielectric constant, dielectric loss, tangent loss and AC Conductivity were studied for the PS/PANI blends. Results are discussed below.

Dielectric constant was measured by following relation.

$$\varepsilon' = Cd/A\varepsilon_o \qquad \textbf{Equation 3.1}$$

Fig 3.4a shows that at low frequencies ε′ increases by increasing PANI concentration upto the 20% of PANI , after which dielectric constant decreases. At higher frequencies it becomes difficult for the poles to change the orientation with applied field and they do not get time to reorient themselves, so ε′ decreases for all the samples.

Dielectric constant values with varying amounts of PANI wt% is shown in fig 3.4b. Increase from the order of 10^o for pure PS to 10^7 for 20% PANI blend is observed in dielectric constant values. At low frequencies ε′ increases by increasing PANI due to polarization in insulator-conductor interfaces. Near percolation threshold sharp increase in ε′ is due to the isolation of conducting phase. Percolation threshold is a point where a sharp increase in some property is observed, ε' is having the highest value at this point so near the percolation threshold blends can become capacitors and can be used in the charge storing devices. After percolation ε' decreases due to the the formation of conducting network.

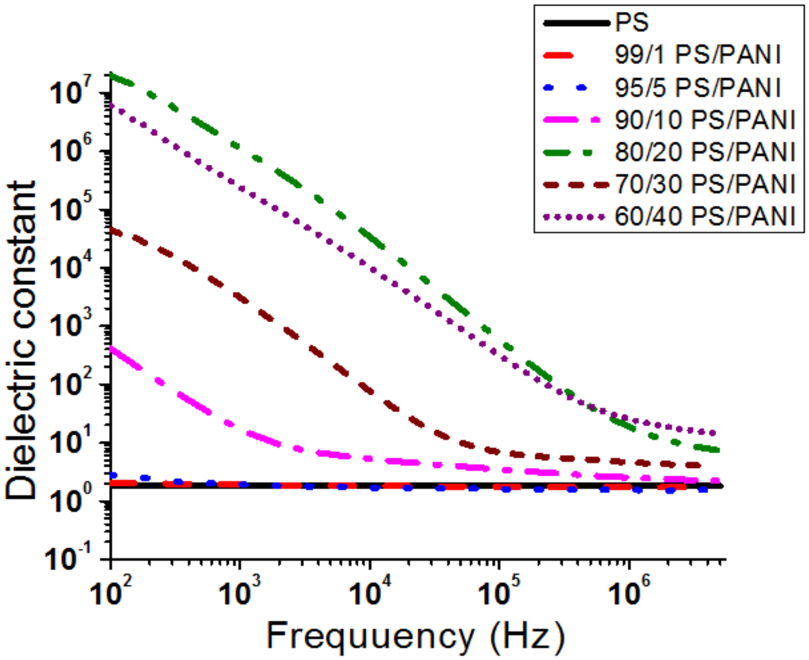


Figure 3.4a Dielectric constant of PS/PANI blends with respect to Frequency

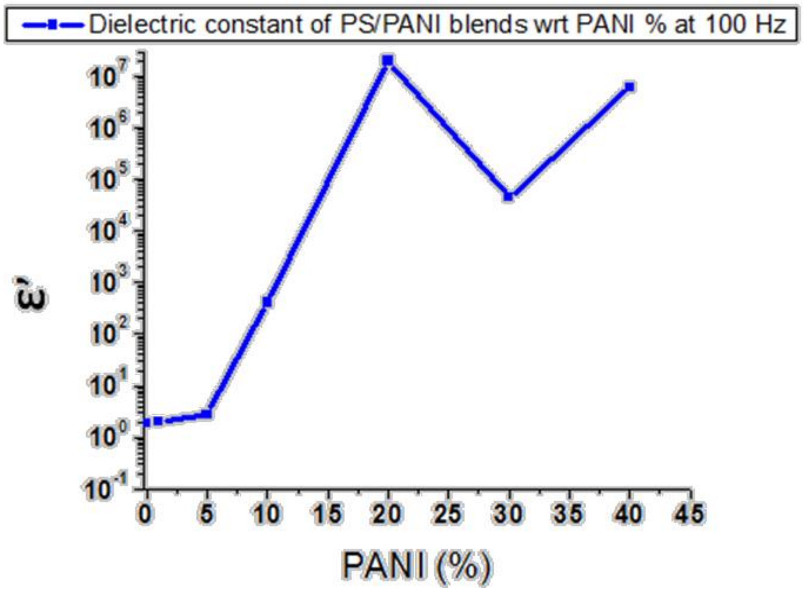


Figure 3.4b Dielectric constant of PS/PANI blends with respect to PANI%

Dielectric loss was calculated by the following equation using D-Factor.

$$\varepsilon'' = \varepsilon' \tan\delta \qquad \text{Equation 3.2}$$

Fig 3.5a shows the dielectric loss of PS/PANI blends with frequency. Due to resistance to the orientation of the dipoles some energy losses occur. At low frequency ε’’ generally increases due to these energy losses. At high Frequencies ε’’ decreases for all the samples and values come closer. Blends up to 5% of PANI are not much dependent on frequency.

Fig 3.5b shows the effect of PANI wt% on the dielectric loss of the PS/PANI blend systems.

Increase from the order of 10^{-2} for pure PS to 10^{10} for 20% PANI blend in the value of dielectric loss can be observed due to polarization of the interfaces Fig 3.5b. For PANI > 20wt% is above the percolation, energy losses decrease due to conducting network so dielectric loss decreases.

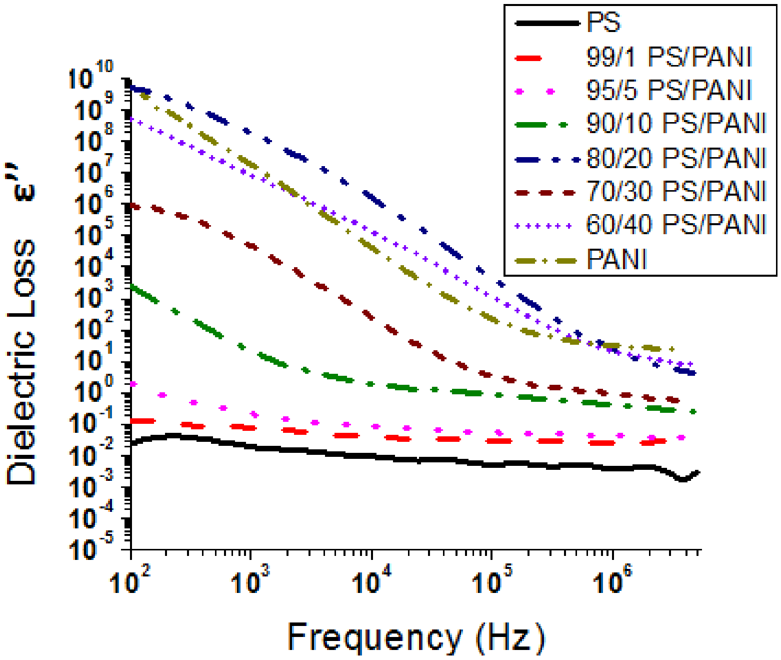


Figure 3.5a Dielectric loss of PS/PANI blends with respect to Frequency

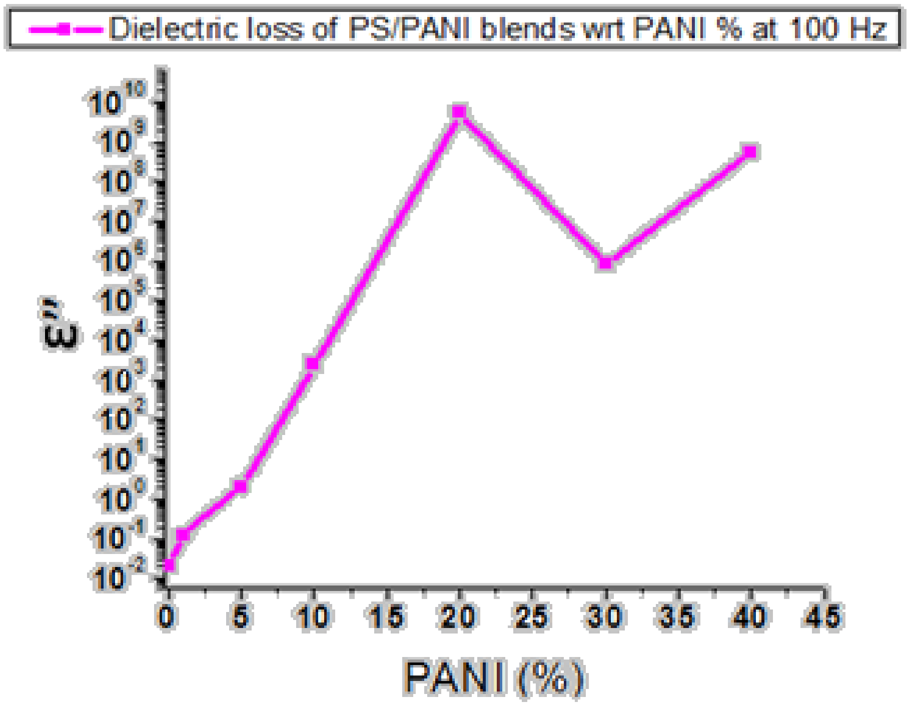


Figure 3.5b Dielectric loss of PS/PANI blends with respect to PANI%

Fig 3.6a shows the tangent loss of PS/PANI blends with respect to frequency.tangent loss can be calculated by the following equation.

Tanδ=ε''/ ε' **Equation 3.3**

When polarization is out of phase with field some energy is dissipated as heat because there is resistance to orientation. At low frequency tangent loss or D-Factor generally increases by adding PANI. Tangent loss for all the samples decreased with increase in the frequency.

Fig 3.6b shows that there is an increase from the order of 10^{-2} for pure PS to 10^{2} for 20% PANI blend in the values of tangent loss. From Resistance to polarization increases up to (20% of PANI) which increases tangent loss. For PANI>20wt% tangent loss decreases because of the conductive network which results in reduced energy losses.

AC Conductivity of PS/PANI blends is measured by the equation given below

$$\sigma_{AC}=\omega\varepsilon_o\varepsilon' \tan\delta \qquad \textbf{Equation 3.4}$$

In the above equation **ω** is the frequency , ε_o is the permittivity of the free space ε' is dielectric constant , tanδ is tangent loss.

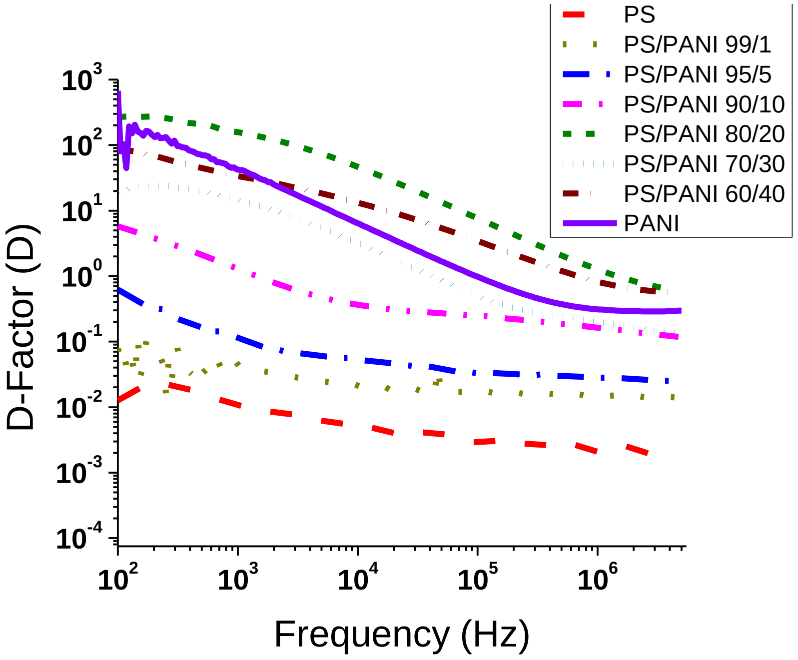


Figure 3.6a Tangent loss of PS/PANI blends with respect to Frequency

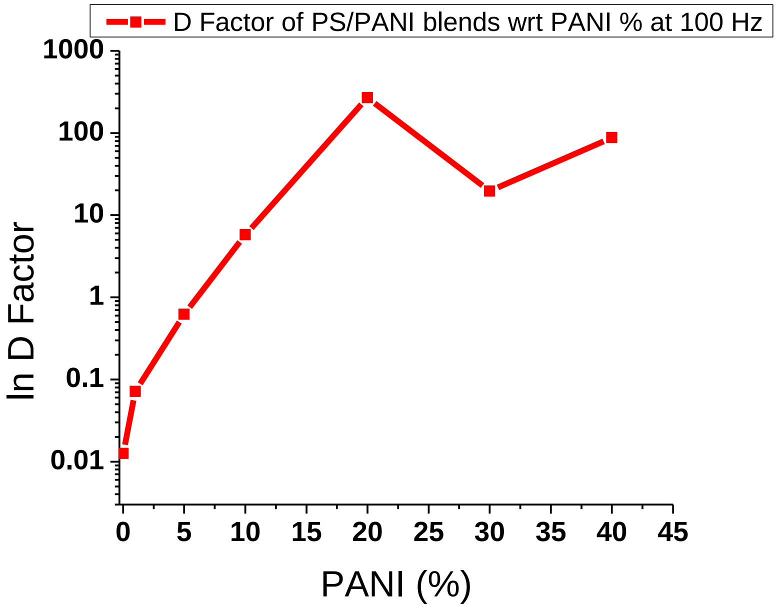


Figure 3.6b Tangent loss of PS/PANI blends with respect to PANI%

Fig 3.7a shows the AC conductivity of the PS/PANI blends with respect to frequency. AT low frequency AC Conductivity increases by adding PANI. At high frequency AC Conductivity increases due to the hopping of the electrons.

Increase from the order of 10^{-8} for pure PS to 10^{2} for 20% PANI blend is observed at 100Hz for PS/PANI blends. Conductivity increases by adding PANI , as charge is accommodated at interfaces due to polarization ,After percolation it decreases Fig 3.7b [25].

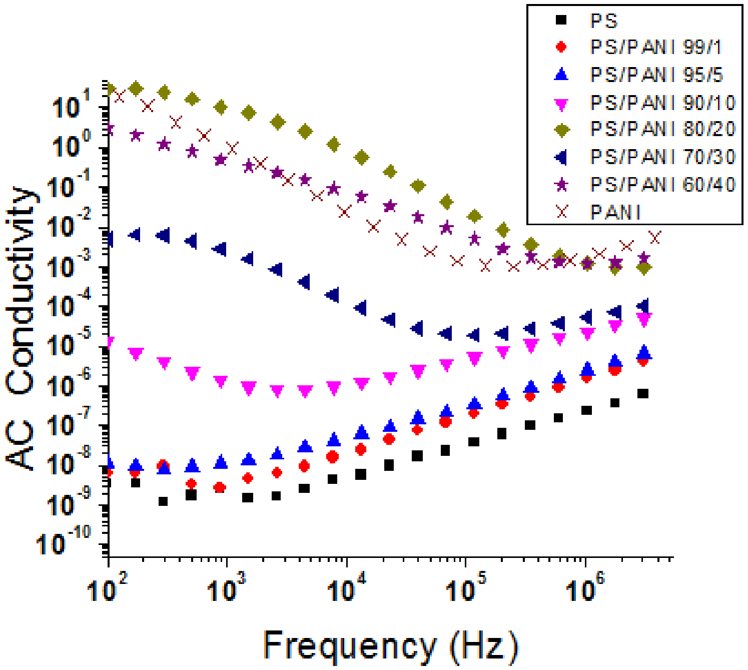


Figure 3.7a AC Conductivity of PS/PANI blends with respect to frequency

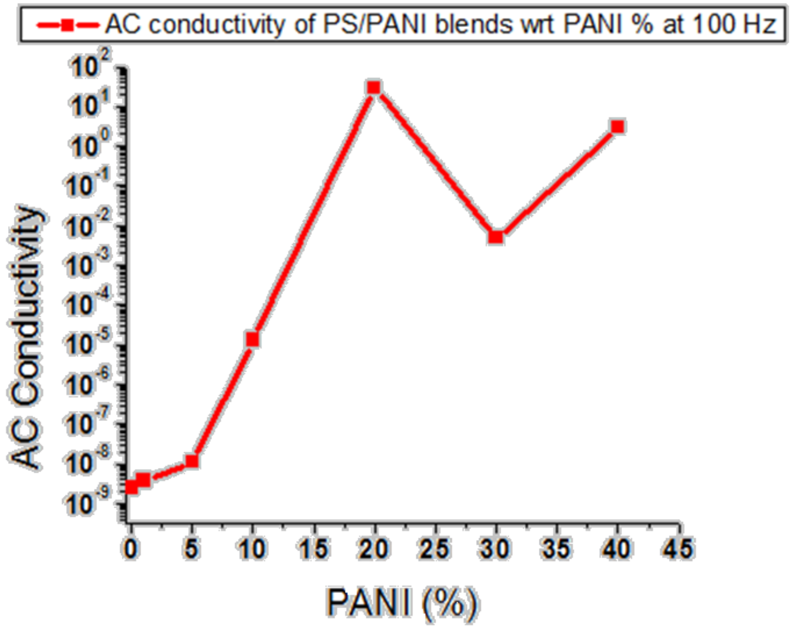


Figure 3.7b AC Conductivity of PS/PANI blends with respect to PANI%

3.1.5 TGA of PS/PANI blends

TGA was done to check the thermal stability of the PS/PANI blends. Fig 3.8 shows the TGA plot for the PS/PANI blends.

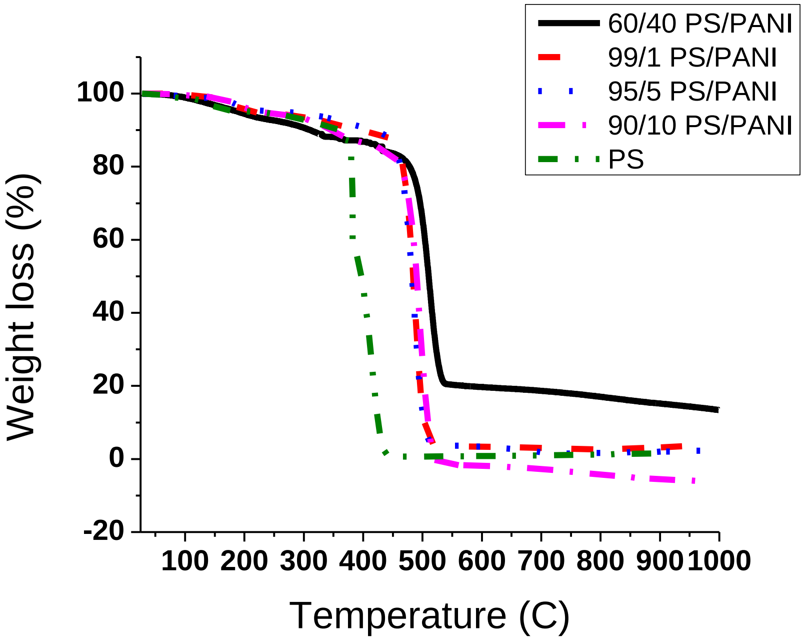


Figure 3.8 TGA of PS/PANI blends

PS shows the decline in the weight loss% vs Temp plot at about 400°C, which is the onset of decomposition temperature. As the PANI amount increases, the thermal stability of the blends increases. Addition of PANI creates additional secondary forces between the two phases and additional energy is required to overcome those forces. PANI phase acts as a barrier to the volatilization of matrix and segmental motion of PS matrix is restricted. Degradation temperature increased from about 400°C for pure PS to 500°C for the blend having 40% of PANI which shows that the thermal stability of PS/PANI blends increases by increasing the amount of PANI content in the blend [26].

3.2 Characterization of PS/PANI/ipGNP Composites

On the basis characterization of PS/PANI blends the polymer blend having 5% PANI was selected for the matrix to be used in the composites preparation where coated PANI was to be used as the filler.

Tensile testing, SEM analysis, TGA, Dielectric testing and absorption tests were performed for the Composites. Results are shown in the articles to come

3.2.1 SEM

Fig 3.9a shows the SEM image of PS/PANI(95/5) blend ,we can observe the dispersed PANI phase. Fig 3.9b shows the image of PS/PANI(95/5)/ipGNP 1% composite it can be seen that brighter phase is the ipGNP filler which is dispersed in the blend matrix.

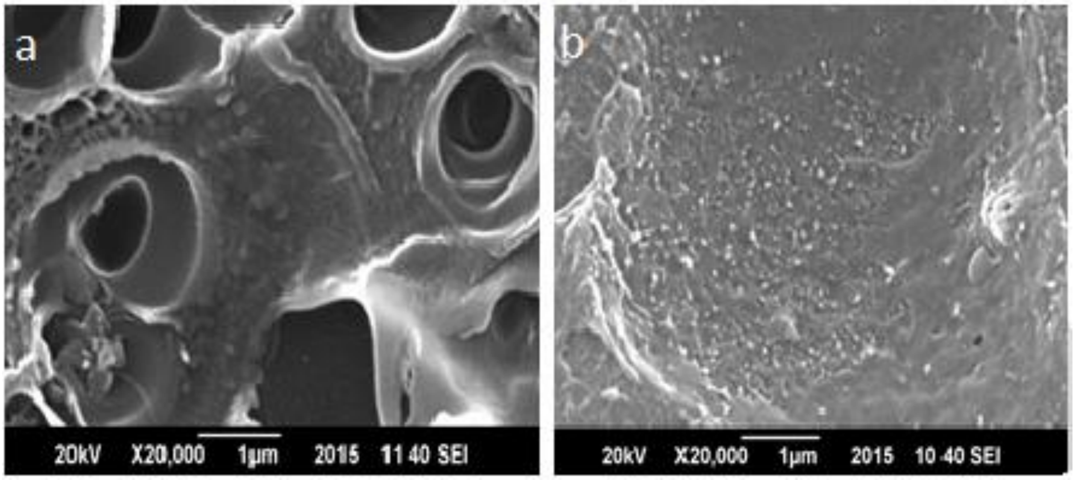


Figure 3.9 SEM images a) PS/PANI(95/5) blend, b) PS/PANI(95/5)/ipgnp 1wt% composite

3.2.2 XRD Results

Fig 3.9a shows the XRD plots for GNP and the coated GNP (ipGNP). GNP shows the typical graphitic peak at 2ø =27^o. When GNPs were coated by de-doped PANI ipGNPs were produced whose pattern is also shown in the same fig, it is observed that graphitic peak is disappeared which shows the good interaction PANI with GNPs, and another peak at 2ø =20.7^o is observed which can be thought of as the PANI peak.

XRD plots of PS/PANI blend (95/5) and its composites are shown in figure 3.9b. The PS shows broad peak at 2ø = 19^o, which is the characteristic peak of amorphous structure in PS. In case of PANI broad scattering peak at about 2ø = 19^o shows the amorphous behavior of PANI. Sharp peaks at 2ø =20.7 ^{o} (020) and 2theta=23.59^o, which is the bragg's reflection of (020) plane indicating the ordered packing of the benzoid and quinoid rings, responsible for semi-crystallinity in PANI.

In case of the PS/PANI/ipGNP composites same peaks are observed as for blends, peak at about 2ø = 27^o which is a graphitic peak is not observed in composites having ipGNPs because ipGNPS have coating of PANI which has interacted with GNPs and depressed the graphitic peak [27,28].

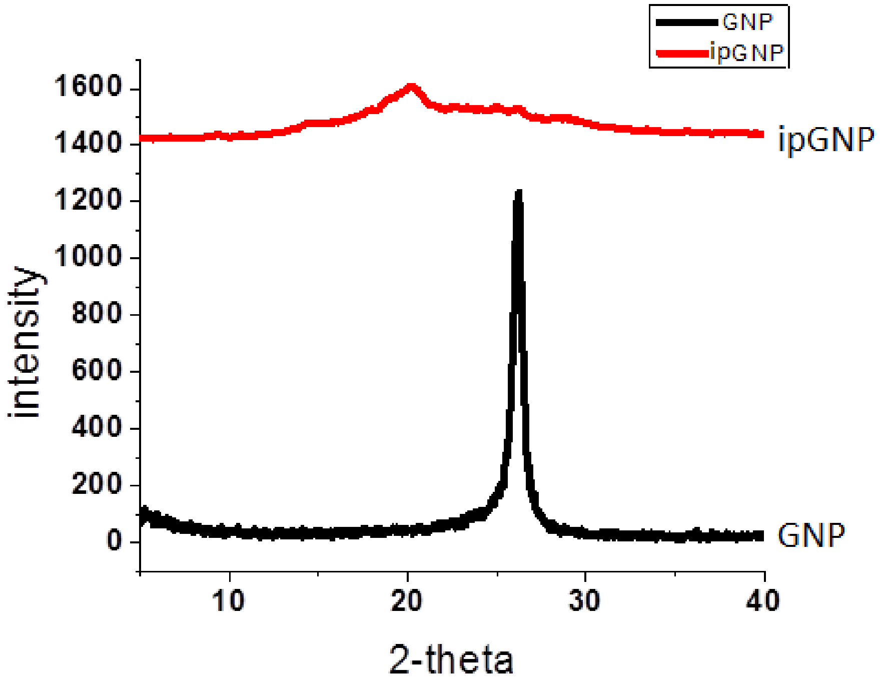


Figure 3.9a XRD pattern of GNP and PANI coated GNP (ipGNP)

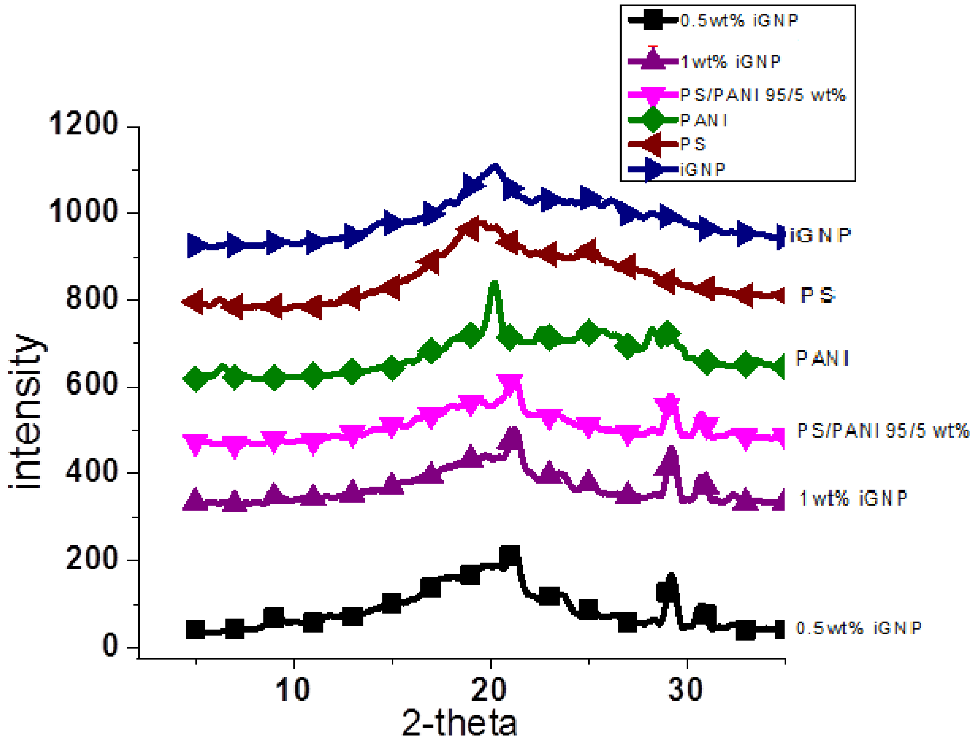


Figure 3.9b XRD Patterns of PS/PANI blend and composites

3.2.3 Tensile Testing

Fig 3.10a shows the stress strain curve of PS/PANI(95/5)/ipGNP composite. Tensile strength, young's Modulus and strain% can be determined from this graph. Fig 3.10b shows the tensile strength of PS/PANI(95/5)/ipGNP composites with the wt% of ipGNP. No clear trend was observed but there was a slight increase in tensile strength for 0.5 wt% of ip(GNP) due to interfacial interaction between ipGnP and the blend matrix which causes the tensile strength to improve. For ipGNP > 0.5 wt% its not easy to disperse the filler well so strength reduces. About 50% increase in Tensile strength from 9 to 14 MPa for the composite having 0.5% ipGNP.

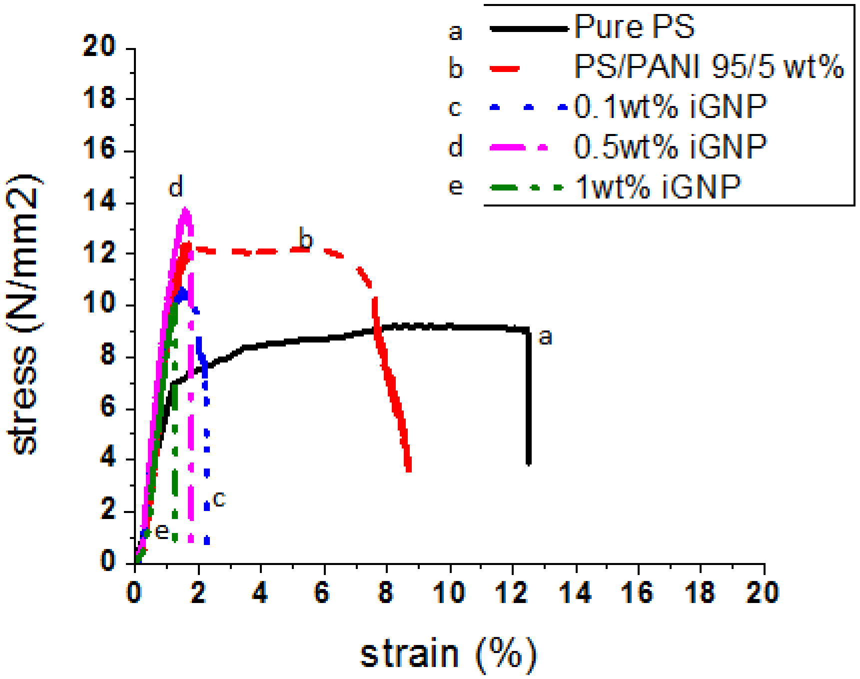


Figure 3.10a STRESS STRAIN curve of of PS/PANI/ipGNP

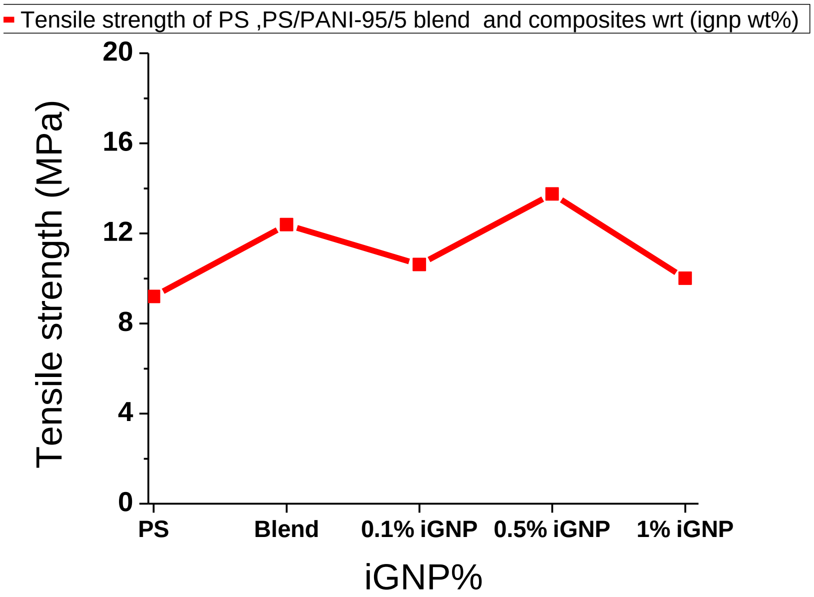


Figure 3.10b T.S of PS/PANI/ipGNP composites with respect to ipGNP%

Fig 3.10c shows the Young’s Modulus of the composites with respect to the increase in ipGNP wt%. About 150% increase in Modulus is observed from 450 for pure PS to 1100MPa for the composite having 0.5wt% of filler. And this increase in modulus is due to the constraining of the blend matrix by ipGNP filler.

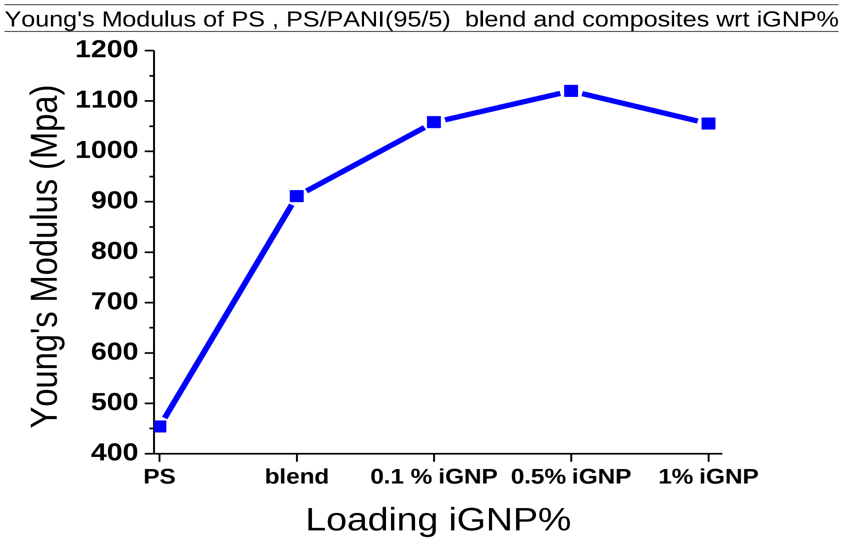


Figure 3.10c Y.M of of PS/PANI/ipGNP composites with respect to ipGNP%

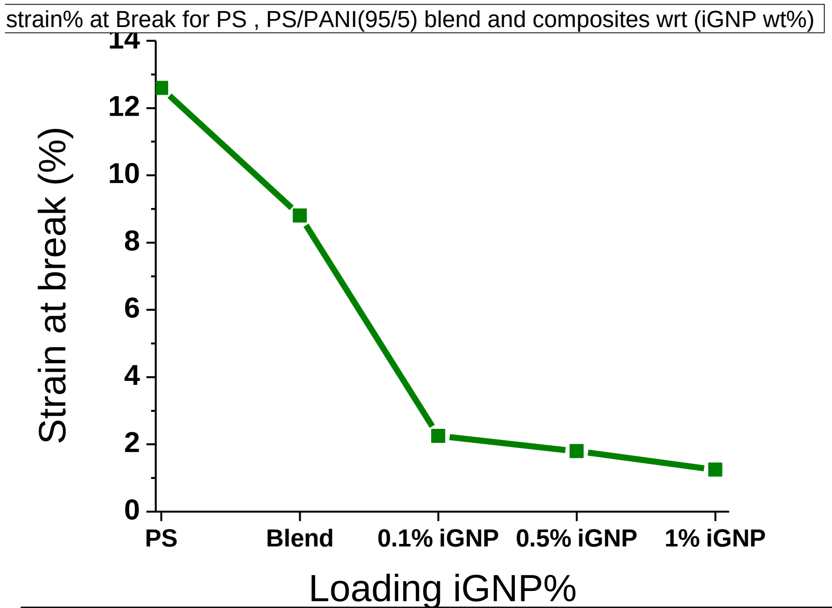


Figure 3.10d Strain at break of PS/PANI/ipGNP composites with respect to ipGNP%

Fig 3.10d shows the strain% at break with respect to the filler wt%. About 90% decrease in Strain% from 13 to 1 % can be observed and this decrease is because of the constraining of the matrix phase which restricts the movement of a matrix [29].

3.2.4 Dielectric properties of PS/PANI/ipGNP composites

Fig 3.11 shows the dielectric constant of PS/PANI(95/5)/ipGNP.

At low frequencies ε′ increases by increasing amount of ipGNPs due to polarization in insulator-conductor interfaces. At higher frequencies it becomes difficult for the poles to change the orientation with applied field so ε′ decreases slightly. Dielectric constant of composites is not much dependent on frequency.

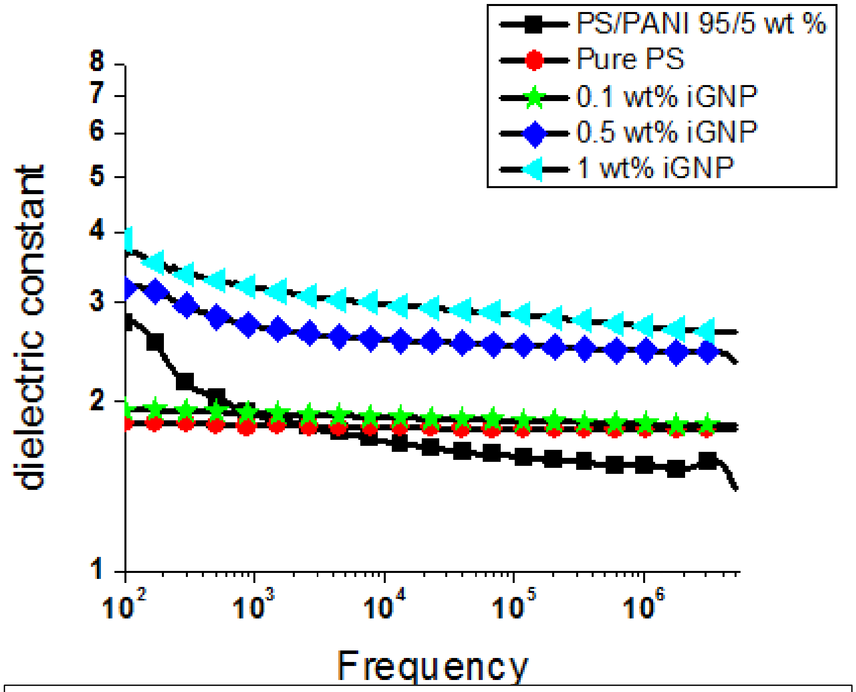


Figure 3.11 Dielectric constant of of PS/PANI/ipGNP

Fig 3.12 shows the dielectric loss of the composites. Due to resistance to the orientation of the dipoles some energy losses occur. Dielectric loss for the composites slightly decreases when compared with blends at lower frequencies because of the decrease in the leakage current due to the addition of the insulated filler. ε′′ shows very little dependence on frequency for blend and composites.

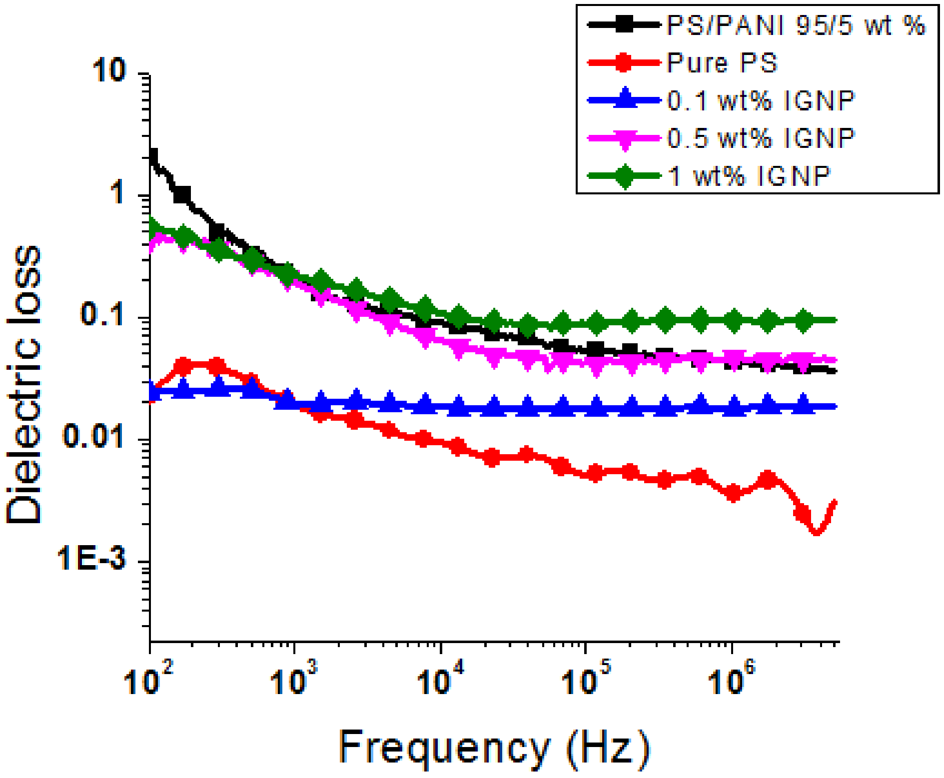


Figure 3.12 Dielecric loss of PS/PANI/ipGNP composites

Fig 3.13 shows the tangent loss of the PS/PANI/ipGNP composites. When polarization is out of phase with field some energy is dissipated as heat because there is resistance to orientation of the domains. Tangent loss or D-Factor for the composites is lower as compared to blends at lower frequencies due to the reduction in leakage current because of insulated filler. At higher frequencies tangent loss values of blend and composites are almost overlapping. Tangent loss decreases a bit for all the samples with increasing frequency and shows some dependence on the frequency

Fig 3.14 shows the AC Conductivity of the composites we can observe that at lower frequencies AC Conductivity for composites is lower than that of blends as GNP having nonconductive coating of PANI (Ignp) is used as a filler At higher frequencies AC conductivity increases for both the blend and the composites because of the hopping effect.

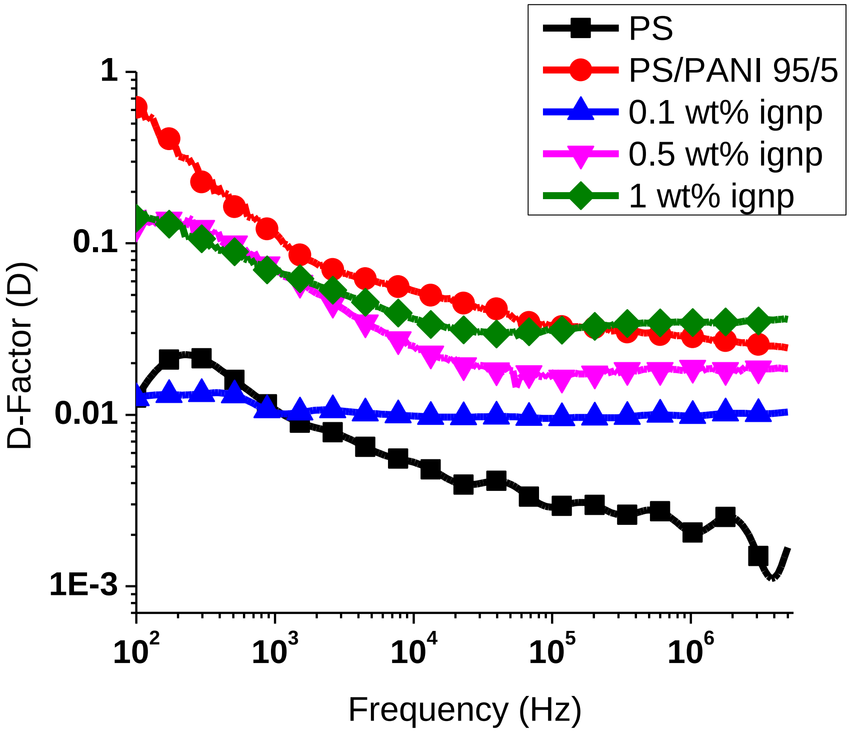


Figure 3.13 Tangent loss of of PS/PANI/ipGNP

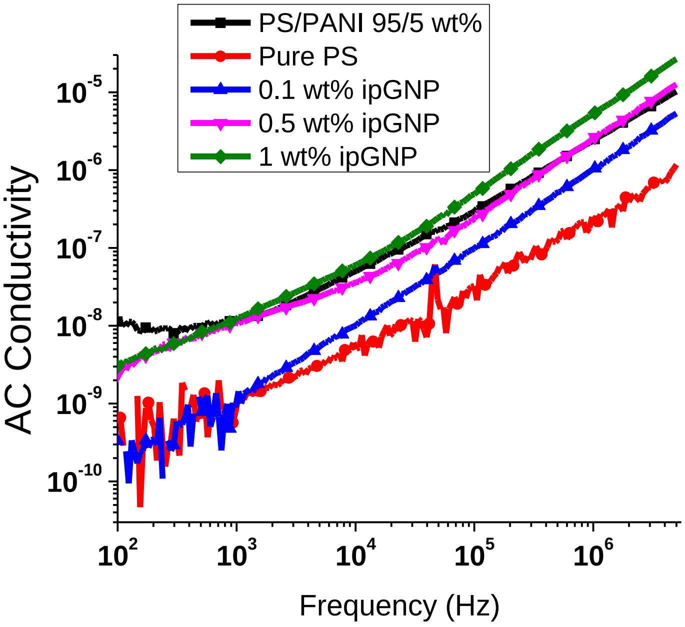


Figure 3.14 AC conductivity of of PS/PANI/ipGNP composites

3.2.5 TGA of PS/PANI(95/5)ipGNP Composites

Thermal stability of PS/PANI(95/5) blend is higher than pure PS because of increased secondary bonding in the blend because of 2nd phase , **about 100°C increase in the degradation temperature** for the blend as compared to pure PS.Thermal stability for PS/PANI/iGNP composites at 1% of filler loading almost remains the same as the PS/PANI (95/5) blend.

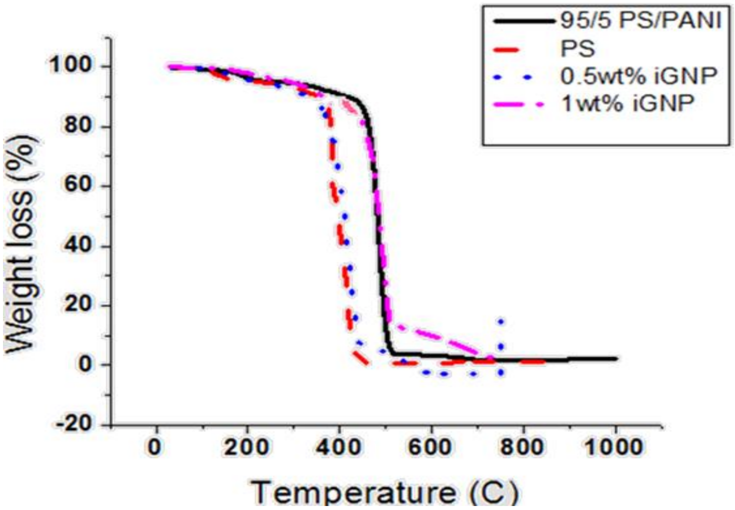


Figure 3.15 TGA of PS/PANI/ipGNP composites

3.2.6 Absorption Testing

Absorption behavior from 8GHz to 20GHz was tested on the samples having thickness ranging from 0.1-0.2mm.PANI based composites usually show narrow absorber behavior [30]. Higher absorption values at particular frequency can be attributed to Impedance matching and high dielectric loss. Figure from reference fig 3.16 shows the reflection loss of -35dB at about 9GHz when flake shaped PANI is used as a 2nd phase in the epoxy having thickness of 1mm [31].

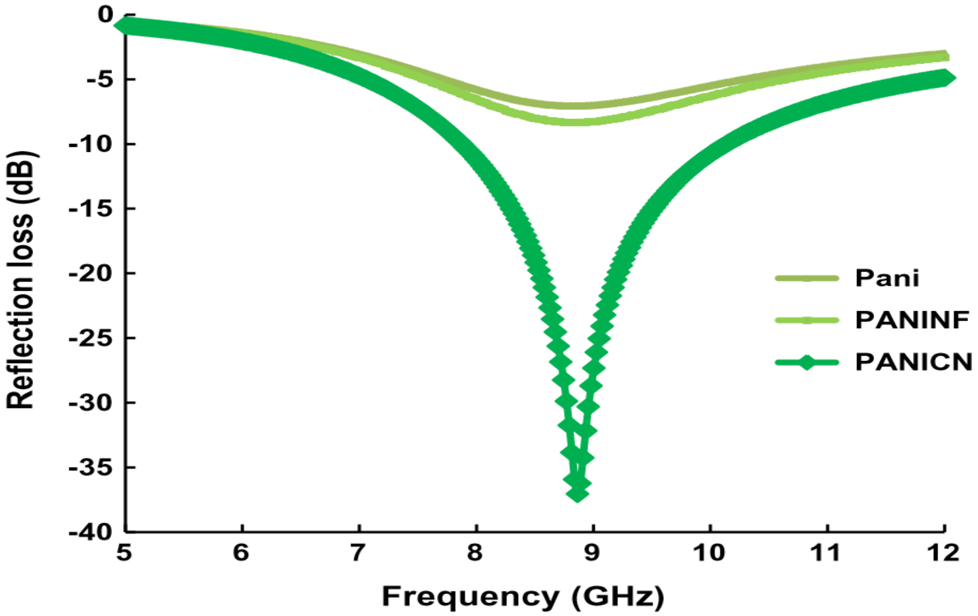


Figure 3.16 Reflection loss of 15% of PANI (Globular), PANINF (Fibrillar PANI) and PANICN (flake like PANI) in epoxy matrix [31].

Fig 3.17a shows the reflection loss of blend and composites from 8-20 GHz. Samples do not show considerable reflection upto 12 GHz. For higher frequencies from 12-16 GHz, Reflection loss of about -3.75dB at 12.2 GHz for composite having 1wt% of ipGNP is observed and reflection loss of -6dB for PS/PANI blend(95/5) at about 12.2 GHz is observed fig 3.17b.

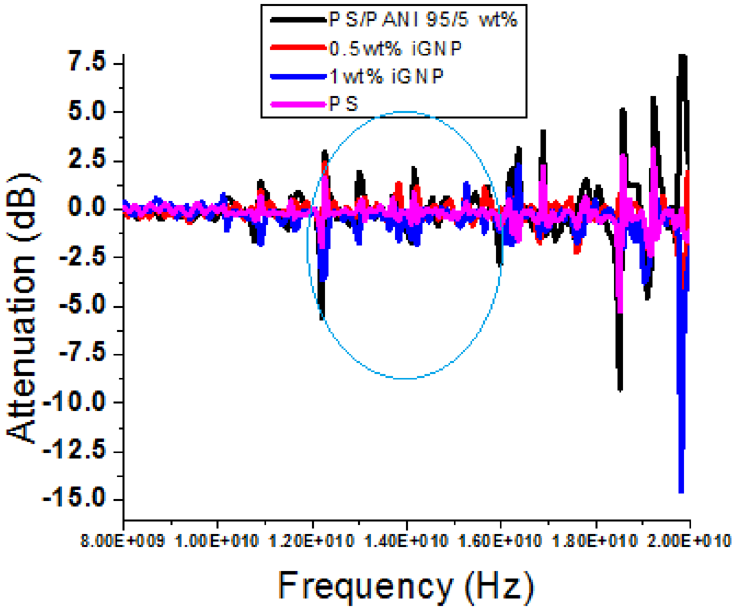


Figure 3.17a Reflection loss of PS/PANI(95/5)/ipGNP

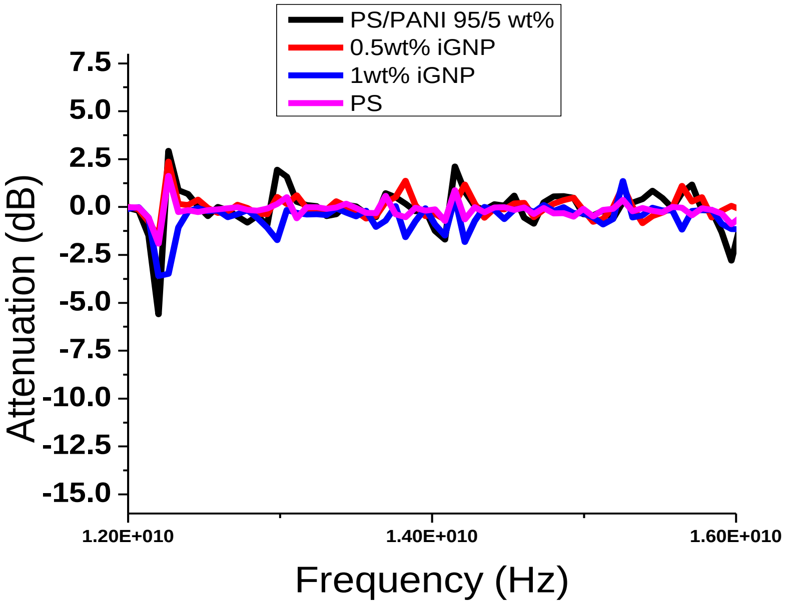


Figure 3.17b Reflection loss of PS/PANI(95/5)/ipGNP composites

Fig 3.18b shows the reflection loss at the frequencies ranging from 16-20GHz for the blend and the composites mentioned in the diagram. Reflection loss of about -10dB for PS/PANI(95/5) blend at about 18.5 GHz, -6dB for 0.5% ipGNP at about 18.5 GHz , -15dB at about 20GHz for 1wt% of ipGNP which is separately shown in the fig 3.18c , which is the highest value achieved for the reflection loss. As discussed earlier the absorption at some narrow region of frequency is the usual behavior of PANI based composites and the this is due to the impedance matching and the dielectrc loss of the material.

If we compare our results with fig 3.16 we can see that reflection loss shown by the epoxy based composites having PANI as a 2nd phase was having the highest value of reflection loss of -35Db at 9GHz and these samples were having the thickness of about 1mm , whereas our samples have thickness ranging from 0.1-0.2mm. so this shows that reflection loss also depends upon the thickness,higher the thickness higher will be the reflection loss.

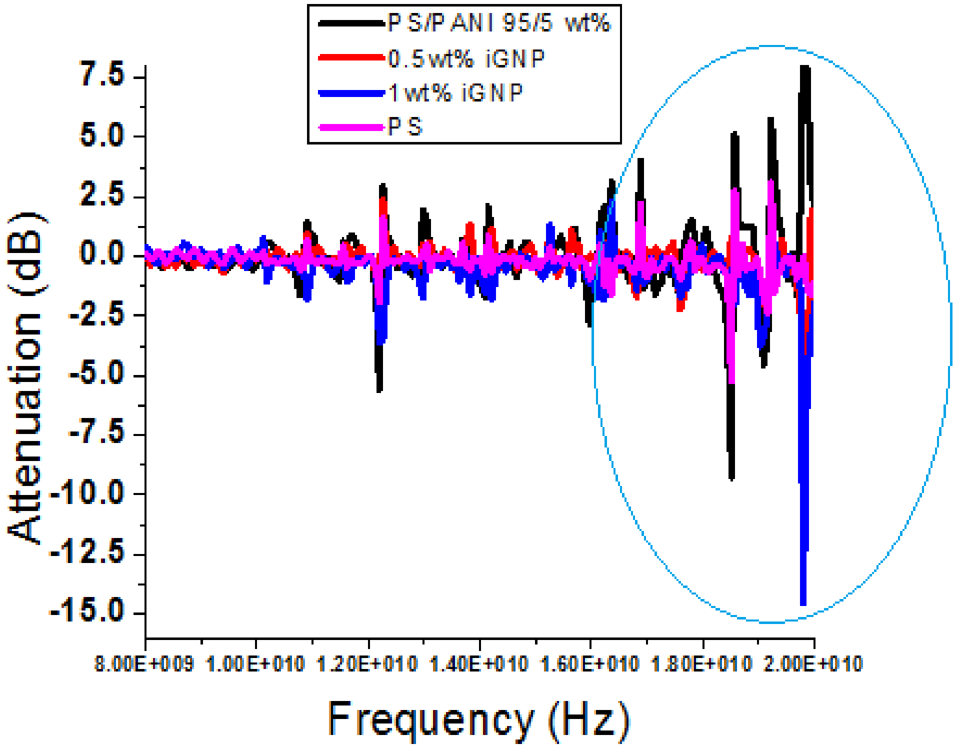


Figure 3.18a Relection loss of PS/PANI(95/5)/ipGNP composites

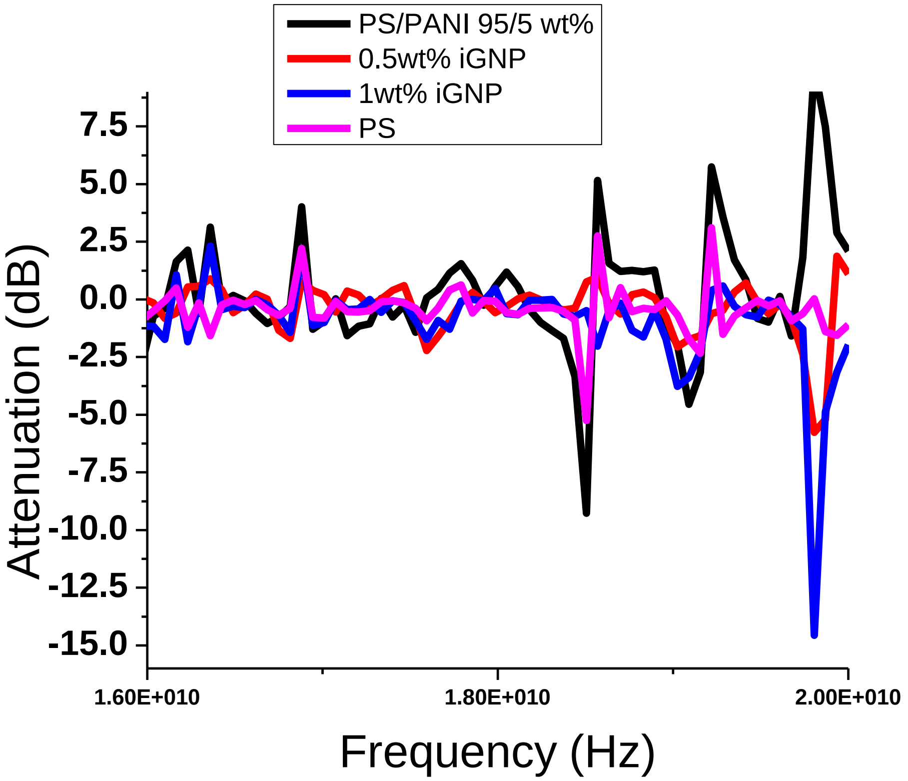
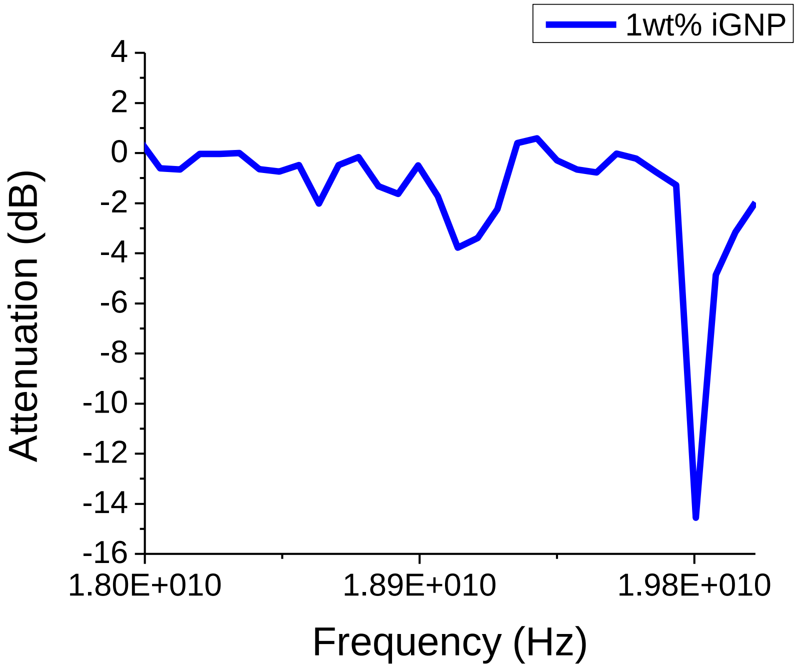


Figure 3.18b Reflection loss of PS/PANI(95/5)/ipGNP composites 16-20GHz



1 **Figure 3.18c** Reflection loss of PS/PANI(95/5)/ipGNP 1% composites 16-20GHz

CHAPTER-4

CONCLUSIONS

Morphological study by SEM revealed that the PS was having a featureless structure and by adding PANI in it the PS/PANI blends show the heterogeneous structure in which separate circular phase is visible which is a PANI phase and a network structure is formed by increasing the concentration of PANI. In case of PS/PANI/ipGNP composites the dispersion of ipGNPs was observed which is evident from mechanical properties. XRD results are in accordance with the SEM results, XRD patterns for blends show the characteristic peaks of both the PS and PANI, which also proves that the blends were immiscible.

About 40% increase in tensile strength for PS/PANI blend is observed. About 200 % increase in Modulus from 450 for pure PS to 1300 MPa for PS/PANI blend having 20% PANI was observed.

About 90% decrease in strain% from 13% for pure PS to 1% for PS/PANI blend having 20% PANI. Degradation temperature Increased from 400^{o}C for the pure PS to 500^{O}C for PS/PANI blend having 40% PANI. Dielectric constant at 100Hz Increased from the order of 10^{o} for pure PS to 10^{7} for 20% PANI blend. At higher frequencies **ε′** decreases for all samples and values of **ε′** for all samples come closer. Dielectric loss at 100Hz Increased from the order of 10^{-2} for pure PS to 10^{10} for 20% PANI blend.

At higher frequencies **ε′′** decreases for all samples and values of **ε′′** for all samples come closer

Tangent loss at 100Hz Increased from the order of 10^{-2} for pure PS to 10^{2} for 20% PANI blend

At higher frequencies tangent loss decreases for all samples. AC Conductivity at 100Hz Increased from the order of 10^{-8} for pure PS to 10^{2} for 20% PANI blend. At higher frequencies AC Conductivity increases for all samples.

Attenuation of about -10dB for PS/PANI (95/5) blend at about 18.5 GHz as compared to -5dB for PS at the same frequency is observed.

So on the basis of mechanical and dielectric properties blend having 5wt% of PANI (PS/PANI (95/5)), seemed to be the optimum ratio that was then further embedded with ipGNPs (PANI coated GNPs) to make the composites

About 16% increase in Tensile strength from 13 MPa for (PS/PANI (95/5)), to 14 MPa for PS/PANI(95/5)/ipGNP 0.5% composite was observed. About 20% increase in Modulus 1100 MPa for PS/PANI(95/5)/ipGNP 0.5% composite was noticed as compared to matrix blend. It was also noticed that about 90% decrease in Strain% upto 1 % for PS/PANI(95/5)/ipGNP 1% composite was there as compared to blend matrix.

Degradation temperature of the PS/PANI(95/5)/ipGNP 1% composite was about 500ºC which is same as the matrix PS/PANI (95/5) blend. So Blend matrix and the composite mentioned above are having almost same thermal stability.

Dielectric constant at 100Hz lightly increased from 2 for pure PS to 4 for PS/PANI (95/5)/ipGNP 1% composite. Dielectric loss at 100Hz slightly decreased for the composites as compared to the PS/PANI blend (95/5). Tangent loss at 100Hz slightly decreased for the composites as compared to the PS/PANI blend (95/5). AC Conductivity at 100Hz slightly decreased for the composites as compared to the PS/PANI blend (95/5).

Attenuation of about 15dB at about 19.8GHz for 1wt% of ipGNP, as compared to -2dB for pure PS at the same frequency was observed. So the composite having 1wt% of ipGNP seems to be useful for radar absorption at 19-20GHz.

FUTURE WORK

PS/PANI(95/5) blend was used as a matrix for blend which had 5% of PANI, in future we are interested to use PS/PANI(90/10) blend having 10% of PANI , as a matrix for the composites and some good results are expected.

As the used filler was ipGNP that was GNP having the non-conductive coating of PANI, in future we can use the GNP having conductive coating of PANI.

Thin composite films were prepared during this work having thickness in the range of 0.15 mm ,in future by increasing the thickness of the films even better absorption properties can be achieved.

References

[1] Introduction to physical polymer science ,L.H. Sperling Lehigh , University Bethlehem, Pennsylvania (2006), pages 688-695

[2] https://en.wikipedia.org/?title=Polystyrene (visited Feb 2015)

[3] https://en.wikipedia.org/?title=Polyaniline (visited Feb 2015)

[4] H.K. Choudhary, D.S Kelkar. Investigation of structure and electrical conductivity in doped polyaniline, Polymer International, 1997, Volume 42, pages 380-384.

[5] V. Thirtha, R Lehman and T Nosker. Effects of glass transition in immiscible polymer blends; Advanced Materials via Immiscible Polymer Processing(AMIPP), 2005, pages 2380-2384.

[6] W.J. Bae,W.H Jo. Preparation of polystyreneand polyaniline blends by in-situ polymerization technique and their morphology and electrical property, Synthetic Metals, 2003, Volume 132, issue 3, pages 239-244.

[7] Introduction to Polymer Blends and Alloys, A. Franck, TA Instruments Germany

[8] Market Report “Fillers” (Marktstudie Füllstoffe (UC-805)), Ceresana Research,(2007).

[9] http://www.freepatentsonline.com/20040253164.pdf (visited july 2015)

[10] http://belgianpolymergroup.be/Flame/Beyer.pdf (Visited july 2015)

[11] J.M. Makar and J.J. Beaudoin. Proceedings of 1st International Symposium on Nanotechnology in Construction, June 23-25, 2003, Paisley, Scotland

[12] Raki, L. et al. Materials 2010, volume 3, pages 918-942.

[13] J.R Potts , D.R Dreyer , C.W Bielawski , R.S Ruoff. Graphene based polymer nanocomposites, Polymer , 2010, volume 52 ,issue 1 , pages 5-25

[14] I.Zaman, B.Manshoor, A.Khalid, S.Araby. From clay to graphene for polymer nanocomposites, Journal of Polymer Research, 2014, volume 21, issue 5, pages 1-11

[15] Z Wang, J Luo, and G–L Zhaoa , Dielectric and microwave attenuation properties of graphene nanoplatelet epoxy based composites, AIP Advances, 2014, volume 4, issue 1, doi: 10.1063/1.4863687

[16] https://en.wikipedia.org/wiki/Polymer_nanocomposite (visited july 2015)

[17] http://www.materialstoday.com/composite-applications/features/going-stealthy-with-composites/ , Nov 2010 , (visited August 2015)

[18] L.C Folgueras; E.LNohara , R Faez; M.C Rezende. Dielectric microwave absorbing material processed by impregnation of carbon fiber fabric with polyaniline, Materials Research, March 2007, volume 10, issue 1, pages 95-99.

[19] CH. Srinivas , D. Srinivasu , B. Kavitha , N. Narsimlu , K.S Kumar. Synthesis and Characterization of Nano Sized Conducting Polyaniline, IOSR Journal of Applied Physics, 2012. Volume **1, issue** 5, pages 12-15.

[20] J Stejskal. Polyaniline, preparation of conducting polymer, IUPAC Technical Report, 2002 ; volume 74, issue 5, pages 857-867

[21] V.Thirtha, R. Lehman, and T. Nosker. Morphological effects on glass transition behavior in selected immiscible blends of amorphous and semicrystalline polymers, Polymer, 2006, volume **47, issue**15, pages 5392-5401, doi:10.1016/j.polymer.2006.05.014

[22] M Zanetti, S Lomakina, G Camino. Polymer layered silicate nanocomposites, Macromolecular materials and Engieering, 2000, volume 279, pages 1-9

[23] W.Pan , S Yang , G Li & J Jiang. Relationship Between Electrical Conductivity And Phase Morphology Of Polyaniline/polyacrylonitrile and Polyaniline/polystyrene Blends, International Journal of Polymeric Materials and Polymeric Biomaterial, 2006 ; volume 54, issue 1, pages 21-35.

[24] L.F Malmonge , S.d.C Langiano; J.M.M Cordeiro; L.H.C Mattos; J.A Malmonge. Thermal and mechanical properties of PVDF/PANI blends, Materials Research, 2010, vol.13, issue 4, link: http://dx.doi.org/10.1590/S1516-14392010000400007.

[25] V.Panwar, J-O.Park,S.HPark, S.Kumar, R.M. Mehra. Electrical, Dielectric, and Electromagnetic Shielding Properties of Polypropylene-Graphite Composites, Journal of Applied Polymer Science, 2010, volume 115, issue 3, pages 1306-1314.

[26] D.Galpaya, M.Wang, M.Liu, N.Motta, E.Waclawik, C.Yan. Recent Advances in Fabrication and Characterization of Graphene-Polymer Nanocomposites, Graphene, 2012, volume 1, pages 30-49.

[27] R. Morichea,, S.G. Prolongoa, M. Sáncheza, A.J Suáreza, M.J. Sayaguésb, A. Ureña. Morphological changes on graphene nanoplatelets induced during dispersion into the epoxy resin by different methods, Composite PART B Engineering, 2015,volume 72, pages 199-205.

[28] J. D. Sudha & S. Sivakala. Conducting polystyrene/polyaniline blend through template-assisted emulsion polymerization, Colloid and Polymer science, 2009, volume 287, issue 11, pages 1347-1354.

[29] J.R Potts , Daniel R. Dreyer , Christopher W. Bielawski , Rodney S. Ruoff . Graphene-based polymer nanocomposites, Polymer, 2010, Volume 52, pages 5-25.

[30] H John , RM Thomas, J Jacob , KT Mathew , R Joseph. Conducting polyaniline composites as microwave absorbers, Polymer Composites, 2007, Volume 28, pages 588–92.

[31] M Oyharçaba , S Lacomme ,V Vigneras. Influence of the morphology of polyaniline on the microwave absorption properties of epoxy polyaniline composites, Composite Science and Technology, 2012, volume 74, pages 107-112.