Incorporation of Nano Particles of Cobalt Ferrite into Conjugated Polymer Matrix for EMI Shielding Applications

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CERTIFICATE

This is to certify that the thesis entitled "**Incorporation of Nano Particles of Cobalt Ferrite into Conjugated Polymer Matrix for EMI Shielding Applications**" submitted by Miss Namita Gandhi in the partial fulfillment of the requirement for the award of the degree of M. Tech in Materials Science and Engineering from the School of Physics and Materials Science, Thapar University, Patiala, is a record of candidate's own work carried out by her under our supervision and guidance. The matter embodied in this report has not been submitted in part or full to any other university or institute for the award of any degree.

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ABSTRACT

Intrinsic conducting polymer along with conjugated bonds has been attracting much attention as advanced materials. Especially Polyaniline is one of most attractive conducting polymer because of its high conductivity & stability in air. The research work deals with conducting ferromagnetic nanocomposite prepared by the insitu emulsion polymerization of aniline monomer with cobalt ferrite in different monomer to ferrite weight ratio at 0°C in aqueous solution of dodecyl benzene sulfonic acid(DBSA). The structures of the polymer composites were characterized by X-Ray Diffraction, Fourier Transform- Infra Red, Ultraviolet–visible (UV–Vis) absorption behaviors, thermal stability by Thermogravimetric Analysis, particle size was measured through XRD, and the microwave absorption properties in 12.4-18GHz are carried out with Network analyzer. The resulting composite possesses the conductivity of 0.2-0.4S/cm and saturation magnetization of 22emu/g respectively. These conducting polymer–ferrite nanocomposites are particularly used as electromagnetic wave absorbers and EMI shielding materials, it is very important to explain the variation of permeability and permittivity in the measured frequency ranges. The effects of the weight fraction of PANI-cobalt ferrite composite on the frequency dispersion characteristics of the complex permittivity and the electromagnetic interference shielding effectiveness of conducting polyaniline PANI- cobalt ferrite composites has been studied in the range of 12.4 to 18 GHz. It was observed that shielding effectiveness of the PANI-cobalt ferrite nanocomposites increases with the increase in the concentration of cobalt ferrite in conducting polymer composites. The shielding effectiveness of PANI-cobalt ferrite nanocomposite has been found to be 22.3 dB between 12.4-18 GHz for the nanocomposite of 1:3 volume ratio

LIST OF PUBLICATIONS

[1] " Incorporation of nano particles of Cobalt ferrite into conducting polymer matrix for EMI Shielding application " abstract accepted in Asian Polymer Association (APA) InternationalConference 20-22 december 2009**,** New Delhi.

[2]"Microwave absorption studies of Phenitidine doped with activated graphite and NiCo ferrite nanoparticles in X(8-12.4 GHz) and P(12.4-18 GHz)" band manuscript ready for communication.

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Chapter 1

Introduction

1.1 Introduction

Conducting polymers have emerged as an important class of electronic materials because of their potential applications in solid state batteries[1,2], electrochromic displays[3,4], and microelectronic devices, antistatic coating [13,14] etc. The electrical conductivities of the intrinsically conducting polymer systems now range from those typical of insulators ($<10^{-10}$ S/cm) to those typical of semiconductors such as silicon ($\sim10^{-5}$ S/cm) to greater than 10^{4} S/cm (nearly that of a good metal such as copper, 5×10^{5} S/cm) [4,15]

The various examples of conducting polymers are polyethylene, polyacetylene, polythiophene , polypyrole, together with derivative of these polymers. Among these polymers, polyaniline is one of the most studied conducting polymer due to its tunable electrical conductivity, redox and ion exchange properties, excellent environmental stability and ease of preparation.

Polymer-based nanocomposites[5-8] represent a new concept in the development of systems exhibiting functional properties resulting from the synergistic interaction between the disperse phase and the matrix.

In recent years much research attention has been paid to the conducting polymer composites with one or more magnetic materials so that polymer possesses both electrical as well as magnetic properties. For the absorption of electromagnetic radiations, ferrites are incorporated in the polymers as they possess high magnetization values which make them useful at higher frequencies

Nanocomposites of polyaniline are very significant due to their wide application ranging from medical sciences to electronic applications. [9] The composites of polyaniline with nanoparticle of different functional oxides have been studied [10]. The prospect applicability of polyaniline – nanoferrite composite in electromagnetic shielding [11,12] has allured scientific community since last decades.

1.2 Conducting Polymers

The discovery of electrical in polyacetylene [26], has been seen as new era in science and technology because it has opened the door of plastic electronics. The partial oxidation of

polyacetylene by iodine made it 10^9 times more conducting than it was originally. This discovery has been appreciated as nobel prize in the field of chemistry in 2000 [27,28,29]. The conductivity in such polymers is a result of two important factors i.e. density of charge carriers (electrons and holes) and carrier mobility. The density of charge carriers in conducting polymers is $10^{21}$to 10^{23} per cc but the mobility of charge carrier is limited only to $10^{-4}$to 10^{-5}cm2 per volt sec. Therefore higher mobility is necessary criteria for higher conductivity. The higher mobility will come with more crystalline, better oriented defect free material to be utilized in different applications. This improved aspect could be achieved by improving processability. The various polymers and there conductivities are shown in fig. 1.1

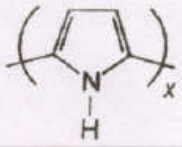
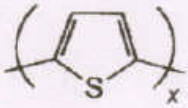
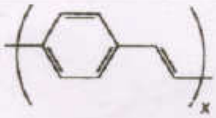
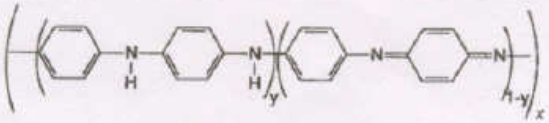
Polymer	Structure	Approximate Conductivity (Siemens/cm)
Polyacetylene	$(CH)_x$	10^5
Polypyrrole		500-7500
Polythiophene		1000
Polyphenylene vinylene		10^4
Polyphenylene		10^3
Polyaniline		10

Fig. 1.1 various conducting polymers with their structures and conductivity

1.3 Types of Conducting Polymer

The conducting polymers have been categorized in three main groups. They are as follows:

(a) Intrinsically inherently conducting polymers(ICPs)

(b) Conducting polymer composites

(c) Ionically conducting polymers

The important characteristics of them are discussed in following subsections.

1.3.1 Intrinsicaly conducting polymers (ICPs)

An organic polymer that possesses the electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical properties, processibility etc.commonly associated with a conventional polymer, is termed an "intrinsically conducting polymer" (ICP) more commonly known as "synthetic metal". In 1975, the first papers on the novel metallic polymer, poly (sulfur-nitride), (SN)x appeared in the literature. It was in 1976 that A.G.MacDiarmid, H.Shirakawa, A.J.Heeger and coworkers[27-31] discovered organic conducting polymers and their ability to dope these polymers over the full range from insulator to metal. That event heralded the dawn of a new era of conducting polymers.

The most common examples of intrinsically / inherently conducting polymers are Polyacetylene, Polyaniline, Polypyrrole, Polythiophene, Poly (p-phenylene), Poly(phenylene vinylene) etc. The unique electronic properties of the conjugated polymers are derived from the presence of π electrons, the wave functions of which are delocalized over a long portion of the polymer chain when the molecular structure of the backbone is planar. It is therefore necessary that there are no large torsion angles at the bonds, which would decrease the delocalization of the π electrons system. The essential properties of the delocalized π electrons system, which

differentiate a typical conjugated polymer from a conventional polymer with sigma bonds, are as follows:

(a) The electronic (π) band gap (Eg) is relatively small (~ 1 to 3.5 eV), with corresponding low excitation and semi-conducting behaviour;

(b) the polymer molecules can be easily oxidized or reduced, usually through charge transfer with atomic or molecular dopant species, to produce conducting polymers;

(c) Net charge mobilities in the conducting state are large enough so that high electrical conductivities are realized, and

(d) Quasi - particles, which, under certain conditions, may move relatively freely through the material.

The electrical and optical properties of these materials depend on the electronic structure and basically on the chemical nature of the repeating unit. The electronic conductivity is proportional to both the density and drift mobility of the carriers.

1.3.2 Conducting polymer composites

These are usually prepared by the addition of conducting fillers in the insulating polymer matrix. The conductive filler commonly used are metal flakes, graphite, conductive carbon black, etc. These filler are loaded in the common insulating. Polymers like PP, PVC, LDPE, etc, to get conducting polymer composites or master batches. These are the materials exclusively used as the commercial conducting polymers. These are used as "semiconducting layers in high voltage applications", EMI Shielding materials, etc. The major problem in this area is the processing problems created due to the filler loading. To get sufficient conductivity for these applications, filler loading of more than 20% is required. This higher addition of these rigid fillers will cause a drastic increment of melt viscosity, which causes serious processing problems. Moreover, these fillers also affect the properties of finished products like aesthetics, brittleness, poor finish, etc. Hence, there is need to develop process where an alternative material or blend can be prepared preferably from conducting polymers.

1.3.3 Ionically conducting polymers/charge transfer complexes

Charge transfer complexes are formed as a result of the interaction of the electron donor and acceptor molecules which are in neutral ground states. When a complex of the donor tetra-thiafulvane (TTF) and the acceptor 7, 7',8, 8'-tetracyano pquinodimethane (TCNQ) in 1: 1 mole ratio was mixed, a charge transfer complex was formed having conductivity at room temperature of the order of 500 $ohm^{-1}cm^{-1}$ which increases to 10^4 $ohm^{-1}cm^{-1}$on cooling. In this class of organic metals, the general requirement of this class of materials conductivity is that either of the two or both components in these are planar molecules with delocalized π electron system.

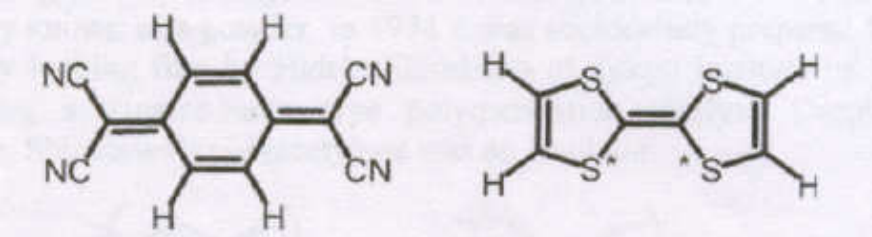


Fig 1.2 structure of TCNQ and TTF

1.4 Conduction Mechanism

A major obstacle to the rapid development of conductive polymers was the lack of understanding of how electrical current passes through them. All conductive polymers have one thing in common: they contain extended π conjugated systems. In becoming electrically conductive, a polymer has to imitate a metal, that is, its electrons need to be free to move and not bound to the atoms. The first condition for this is that the polymer consists of alternating single and double bonds, called conjugated double bonds. Polyacetylene, prepared through polymerization of the hydrocarbon acetylene, has such a structure:

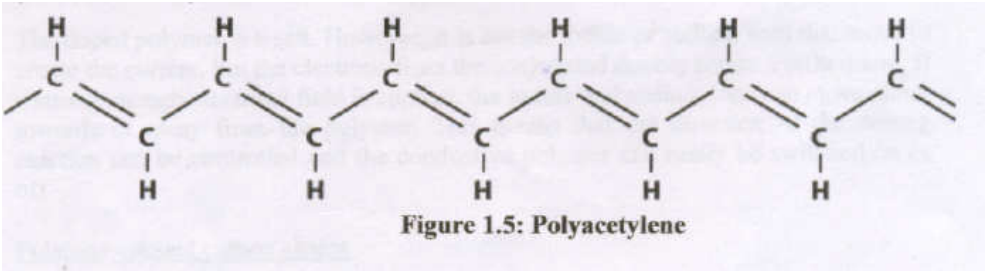


Figure 1.5: Polyacetylene

Fig 1.3 Structure of polyacetylene

However, it is not enough to have conjugated double bonds. To become electrically conductive, the plastic has to be disturbed - either by removing electrons from (oxidation), or inserting them into (reduction), the material. The process is known as doping.

1.5 Process of Doping

When we compare some common compounds with regard to conductivity, we see that the conductivities of the polymers vary considerably. Doped polyacetylene [30,31] is, e.g., comparable to good conductors such as copper and silver, whereas in its original form it is a semiconductor.

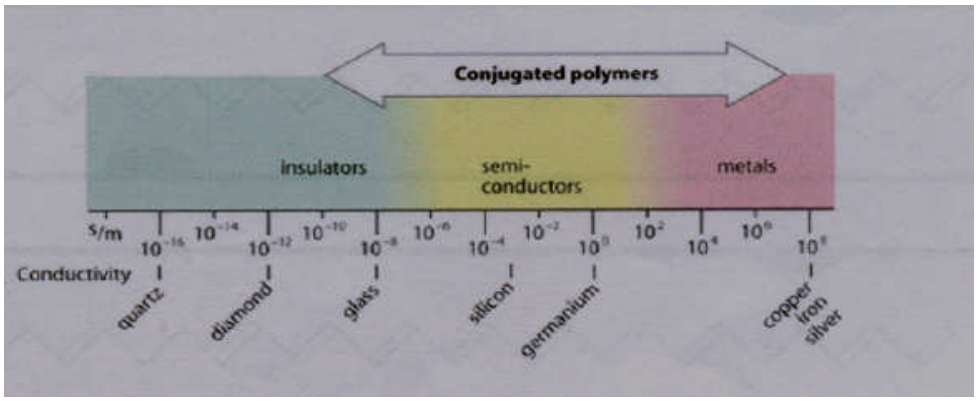


Fig 1.4 -Conductivity series

The polymer molecules, consists two bonds viz. sigma bonds and π bonds. The sigma bonds are fixed and immobile. They form the covalent bonds between the carbon atoms. The π electrons in a conjugated double bond system are also relatively localized, though not as strongly bound as the sigma electrons. Before a current can flow along the molecule one or more electrons have to be removed or inserted. If an electrical field is then applied, the electrons constituting the 1t bonds can move rapidly along the molecule chain. The conductivity of the plastic material, which consists of many polymer chains, will be limited by the fact that the electrons have to "jump" from one molecule to the next. Hence, the chains have to be well packed in ordered rows.The process of doping is of two types i.e oxidation and reduction doping.

Oxidation with halogen (p-doping): $[CH]_n + x\ h^- \longrightarrow [CH]_n^{x+} + x\ e^-$

Reduction with alkali metal (n-doping): $[CH]_n + x\ Na^+ \longrightarrow [CH]n^{x-} + x\ Na+$

1.6 Polaron Doped Conjugated Structures

As discussed earlier in oxidation type of doping, the halogen molecule attracts an electron from polyacetylene chain become h^- , the polyacetylene molecule now becomes positively charged and is termed as radical cation or soliton.

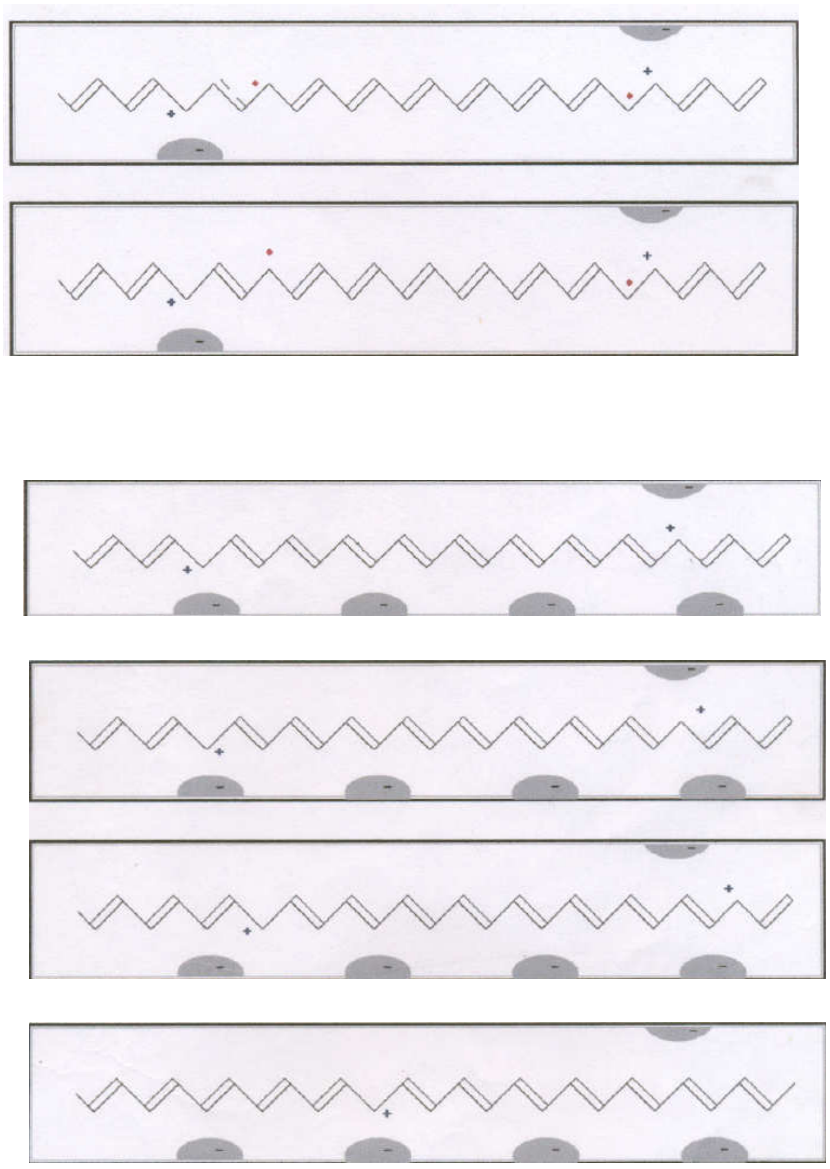
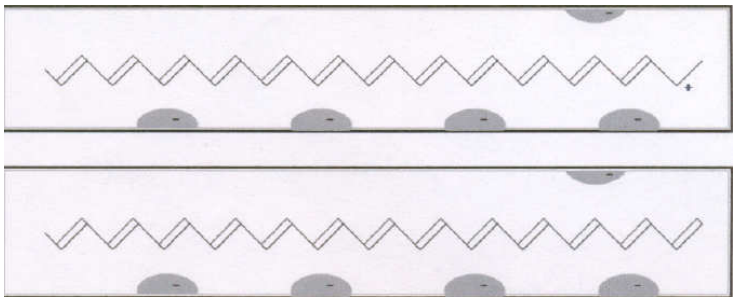


Fig 1.5 Polaron transfer mechanism

The lonely electron of the double bond, from which an electron was removed, can move easily. As a consequence, the double bond successively moves along the molecule.



In the same way the double bond moves further throughout the chain. The positive charge, on the other hand, is fixed by electrostatic attraction to the iodide ion, which does not move so readily. If the polyacetylene chain is heavily oxidized, polarons condense pair-wise into so-called solitons.The charge moves throughout the chain simultaneously moving the double bonds. These solitons are then responsible, in complicated ways, for the transport of charges along the polymer chains, as well as from chain to chain on a macroscopic scale.

1.7 Polyaniline

Polyaniline was the first conducting polymer to be prepared, when in 1862 H.Letheby of the college of London Hospital in the U.K. anodically oxidized aniline in sulfuric acid but there had been only limited interest in this polymer until the resurgence of interest in conductive polymers driven by the high conductivities found in polyacetylene when doped. Polyaniline is easily produced by oxidation of aniline.

Due to its ease of synthesis and processing, environmental stability, relatively high conductivity and cost economics, polyaniline is probably the most industrially important conducting polymer today. Polyaniline is a typical phenylene based polymer having a chemically flexible -NH- group in the polymer chain flanked by phenyl ring on either side. Polyaniline represents a class of macromolecules whose electrical conductivity can be varied from an insulator to a conductor by the redox process.

This polymer can achieve its highly conductive state either through the protonation of the imines nitrogen's or through the oxidation of amine nitrogen. For example the conducting state of PANI can be obtained in its 50% oxidized emeraldine state in aqueous acids like HCI and the resulting material is a p-type semiconductor.

1.7.1 Different Forms of Polyaniline

Polyaniline has several oxidation states as shown in figure. The most stable of those is emeraldine base (EB), having equal amounts of reduced and oxidized repeating unit.The fully oxidized form is pemigraniline and fully reduced form is leucoemeraldine. Doping emeraldine

base with acid (dopant) results to a conductive emeraldine salt (E8).The polyaniline EB is the basic building block of polyaniline products.

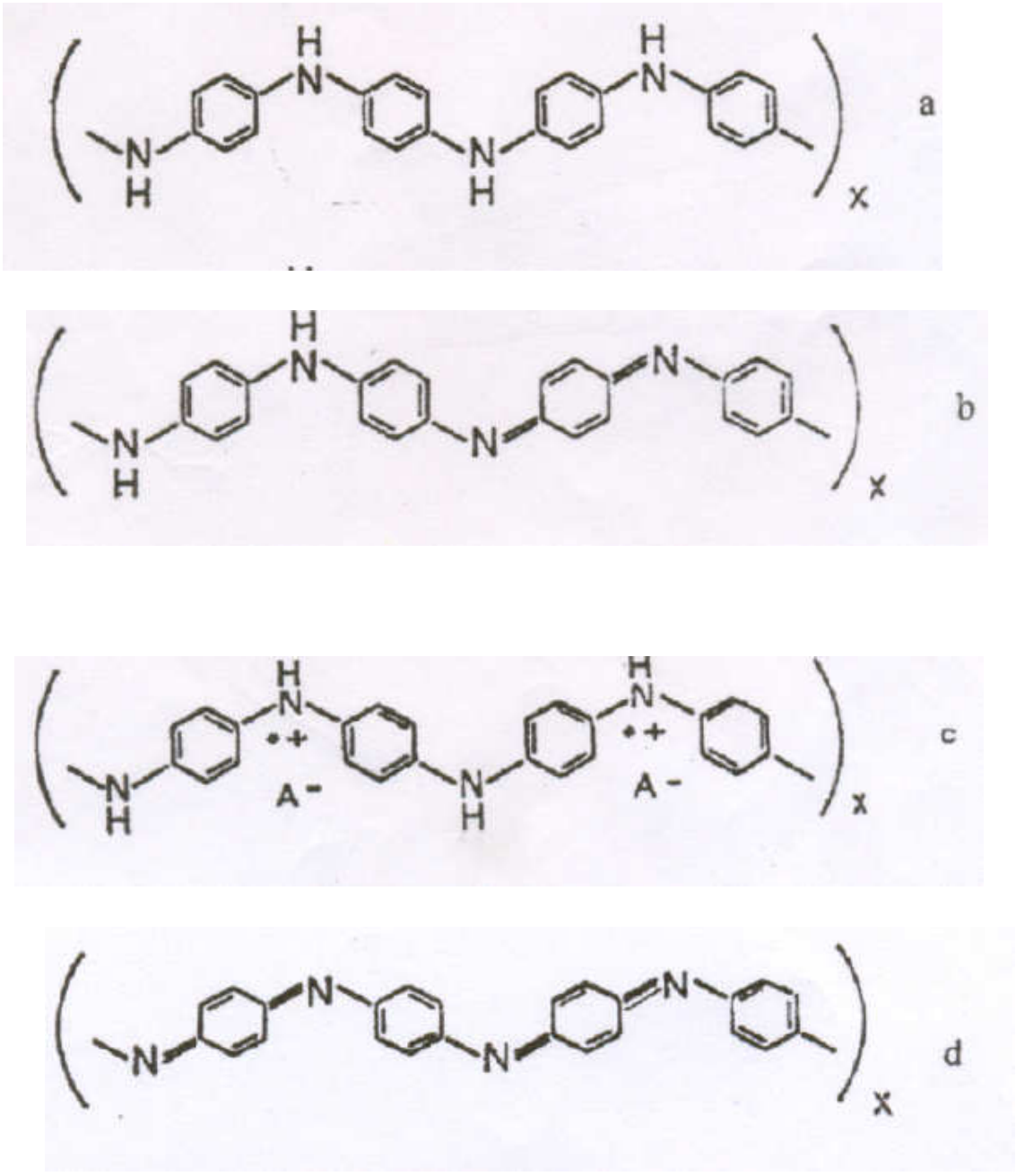


Fig. 1.6 Various forms of polyaniline (a) leucoemaralidine base (b) Emeralidine base (EB), (c) Emeralidine salt (d) pernigraniline base

Besides offering the prospect for cheap scale-up, polyaniline has very important properties that distinguish it from most of the other polymers, in that the state of conductivity is determined not just by the state of oxidation but also by the state of protonation. This extra degree of freedom accounts for the rather wider range of forms for polyaniline than for the other polymers. It exists in several oxidation states with electrical conductivity varying progressively from 10^{-11}S/cm^{-1} to more than 10 S/cm^{-1}. Different compositions of polyanilines have different colours and electrical properties. However, only one form, called the emeraldine salt, is electrically conducting. It is synthesized easily by electrochemical or chemical oxidation of aniline in aqueous acidic media, using common oxidants, such as ammonium peroxydisulfate. Mechanically flexible, dark-blue films of conductive polyaniline also have been achieved by protonic doping of emeraldine films cast from Nmethylpyrrolidinone (NMP) solutions. Protonic doping, accomplished by dipping the emeraldine films in acid or passing a gaseous acid over them, protonates the imine nitrogen atoms in the backbone of the polymer. The conductive emeraldine salt becomes the insulating emeraldine base when treated with aqueous alkali. In its emeraldine form, polyaniline differ from other conductive polymers because partial oxidation or reduction is not necessary to dope it. A highly conducting state is accomplished by simple protonation of imine nitrogen atoms in the emeraldine base backbone. Because protonic doping does not change the number of electrons in the polymers, its conductivity depends on the pH of the solution it is treated with. The first three forms show a progression in degree of oxidation:

(a) Leucoemeraldine base, in which the polymer is fully reduced.

(b) The emeraldine base in which 50% of the nitrogens are now in imine units rather than the amine groups of (a).

(c) Pernigraniline base in which all nitrogens are in imine groups and the all three forms, (a) to (c) are non-conducting with full or zero occupation of energy bands.

What gives polyaniline its particular significance is that the partially deprotonated forms of the polymer, emeraldine base, can be protonated without change in the oxidation state. This protonation results in the emeraldine salt form, in which all the nitrogens are protonated but with only 50% of them charged and carrying an associated anion (commonly a chloride for polymer formed in aqueous HCl).Although it might be expected that the degree of oxidation of the base

forms might vary smoothly from 0% imine, to 100% imine, it is now well established that the emeraldine base, which represents the mid-way point in this progression, is a welldefmed phase. The emeraldine salt is the highly-conducting form of the polymer. Conductivities for non-oriented films produced with chloride as counter-ion are not much more than I S/cm, but recent improvements to above 100 S/cm have been made by replacement of the chloride by species such as camphorsulphonic acid. Within band models for the conduction processes in the emeraldine salt, the metallic behaviour arises from the presence of a half-filled π bond and, in a polymer chain which is taken to possess a uniform structure (the polaron lattice, with no dimerisation associated with a regular arrangement of counter ions alongside the chain.

Control of the state of protonation is easily affected in the laboratory, and the chloride salt is readily taken from highly conducting state at low pH to the low conductivity state at pH above 4 or 5. However, for applications as a conducting material, it is very important that there is no long term loss of acid (here HCI), and there have been efforts made in various ways to prevent this from taking place. Attachment of the anion to the polymer chain has been achieved by treatment of the polymer with fuming sulphuric acid. This replaces one of the protons on the ring with a sulphonic acid group, and produces a material which shows a conductivity which is very much less sensitive to pH than the standard emeraldine hydrochloride. This sulphonated form of the polymer shows a lower conductivity than emeraldine hydrochloride, no higher than I S/cm, but retains its conductivity up to pH 7 or 8. An alternative strategy is to use a large, polymeric poly-anion, and it has been found that the salt formed with polyvinyl sulphonic acid, [-CH2-CH $(S0_3H)^-$] x, shows very similar properties in terms of conductivity and sensitivity to pH to the directly-sulphonated polymer.

Solution processing of polyaniline has now been achieved in a number of ways. Firstly, the emeraldine base form is soluble in N-methyl pyrrolidone, NMP. This has allowed a fair measure of control of the material, although it would be more desirable to process directly in the conducting form. Concentrated sulphuric acid is also a solvent for the emeraldine salt form, and there has been some considerable effort made to process in this way. Sulphate anions are not, however, the anions of choice to give a highly stable conducting polymer.

1.7.2 Synthesis Of Polyaniline

Polyaniline can be synthesized mainly by chemical or electrochemical oxidation of aniline under acidic conditions. The method of synthesis depends on the intended application of the polymer. For bulk production chemical method, whereas for thin films and better patterns electrochemical method is preferred.

a) Chemical Synthesis :

The conventional method of synthesis of emeraldine salt is the solution polymerization of aniline monomer in aqueous media in presence of a mineral acid like HCl. An oxidant like ammonium peroxydisulphate can be used to initiate the reaction. The ideal molar ratio of monomers acid to oxidizing agent is proved to be 0.1: 1.0: 0.1.The principle function of the oxidant is to withdraw a proton from the aniline monomer. The oxidative polymerization of aniline proceeds via following steps:

- Oxidation of monomer to radical cation.
- Dimerization of radical cations to a neutral dimer followed by the loss of proton.
- Oxidation of dimer to its diradical cation.
- Combination of dimer radical cation with another radical cation to form trimer radical cation.
- Formation of trimer, tetramer and finally polymer. The polymerization reaction is summarized as follows:

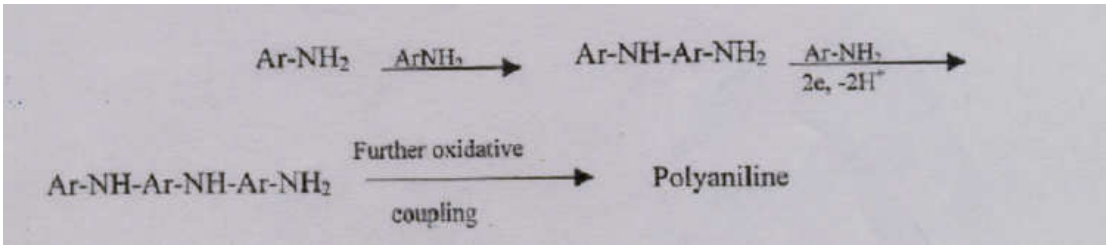
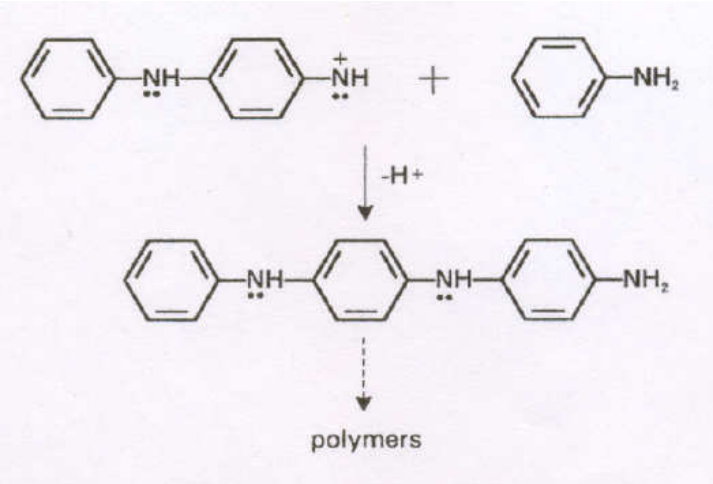


Fig 1.7 Polymerization of aniline

Polymer results from the preferential head to tail couplings of oxidized species. The proposed mechanism for polymerization of aniline is:



1.8 Mechanism of polymerization in aniline

In chemical oxidative polymerization, increase in oxidant concentration causes rapid formation of radical cations providing shorter polymer. But, in case of low oxidant concentration, the formation of radical cation is slower and polymer chain length is longer in comparison to the previous case. Therefore, lower the rate formation of radical cations, larger will be the conjugation length and hence higher will be the conductivity of the resulting polymer. Thus, increase in oxidant/monomer ratio causes increase in polymer yield while conductivity of the polymer decreases.The factors affecting the polymerization process are the pH of the solution, type of the acids used, its concentration, effective size, salvations and electro negativity of the conjugate base associated with a given acid.

b) Electrochemical synthesis

Electrochemical polymerization is a radical combination reaction and is diffusion controlled. The anodic oxidative polymerization is the preferable method to obtain a clean and better-ordered polymer as a thin film. Electrochemical synthesis is achieved by:

1. Galvanostatic method

2. Potentiostatic method-keeping potential constant 0.7- 1.1V verses SCE

3. Potential sweep method - between two potential limits -0.2 to + 1.0 verses SCE.

1.7.3 Dopants For Polyaniline

Polyaniline can be easily doped by non-redox doping method. Polyaniline holds a special position amongst conducting polymers in that its highly conductive doped form is accessible by two completely different processes - protonic acid doping and oxidative doping. Protonic acid doping of emeraldine base units results in the complete protonation of the imine nitrogen atoms to give the fully protonated emeraldine salt.There are plenty of reports available on different acid as well as ester dopants used for polyaniline. They include common mineral acids, high molecular weight long-chain organic sulfonic acids, phosphoric acids and their esters, etc. The standard route of synthesis of doped polyaniline is the one with Hydrochloric acid (HCI) as dopant ions. The other mineral acids commonly used include Sulfuric acid (H2SO4), Hydrofluoric acid (HF), Perchloric acid ($HCl0_4$) etc. The low molecular weight organic acids include Formic acid, Acetic acid, Acrylic acid etc. High molecular weight long-chain organic sulfonic acids include Camphor sulfonic acid (CSA), Methane sulfonic acid (MeSA), p-Toluene sulfonic acid (PTSA), Dodecylbenzenesulfonic acid (DBSA), Polystyrenesulfonic acid (PSSA) etc. Other than the above-mentioned acid dopants, esters of phosphoric acid as well as phthalic acid were also used as effective non redox dopant ions. Some examples of the organic sulfonic acid dopants:

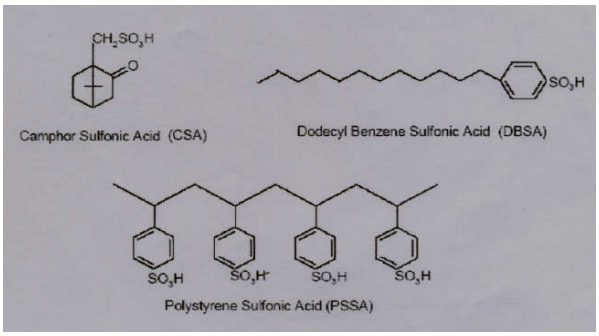


Fig. 1.9 Structures of sulphonic acids used as dopant for aniline

It was seen that the dopant ion could alter the properties of the conducting polyaniline formed. It can affect properties like conductivity, crystallinity, solubility and hence processibility. Amongst these, the organic sulfonic acids have been found to impart many interesting properties like high solubility and thermal stability to polyaniline. The sulfonic acids like DBSA, PSSA. etc. Which have long-chain alkyl groups can plasticize the polyaniline formed by increasing the interchain separation. Thereby facilitating the solvent molecules penetrating into the polyaniline lattice. Also, the alkyl chain can act as an effective solvent compatible group to improve the solubility of the polymer. These groups can also act as compatibilizers as well as plasticizers when blended with other polymers.

1.7.4 Polyaniline -NanoComposites

The conducting polymer nano composites with one or more magnetic materials so that polymer possesses both electrical as well as magnetic properties. For the absorption of electromagnetic radiations, ferrites are incorporated in the polymers as they possess high magnetization values which make them useful at higher frequencies [15-17]. Many attempts to produce the colloidal polyaniline composite containing the ferrite have been made using the different charge carriers for doping the polymer [18–24]. However, the resultant polymer composites lose its conductivity and have low magnetization value.

These conducting polymer nano composites can find applications as:

1. Antistatic materials for the dissipation of electrostatic charge.

2. For the shielding of electronic equipments from electromagnetic radiations in the radio frequency range from 10Hz to 108Hz, microwave range and W band range.

3. For the storage of IC-chips in software and electronic packaging industries.

1.8 FERRITES

Ferrites are the oldest magnetic material known to mankind is magnetite, which corresponds to the chemical formulae Fe_3O_4, or more specifically, to $Fe^{2+}Fe^{3+}O_4$. [10]When one replaces, the divalent ferrous ion by another divalent metal such as Mn, Co, Cu ,Mg,Zn or Cd, one obtains a ferrite of general composition $Me^{2+}Fe^{3+}{}_2O_4$where $Me^{2+}$is a divalent metal ion. In mixed ferrites

the Fe^{2+}ion is replaced by a mixture of ions. The dc resistivity of ferrites is 10^4 to 10^{11} times as large as that of iron, therefore can be used in high frequency application in EMI applications.

1.8.1 Structure of ferrites

The physical property of ferrites is intimately related to the structure of these solids. They belong to the large class of compounds which have the spinel structure. The oxygen ion with a radius of 1.32 Å, to good approximation, a closed packed cubic structure. The unit cell contains 32 oxygen ions 16 Fe^{3+}ions and 8 divalent metal ions. The total of 24 metal ions , ranging in radius between 0.4 and 1 Å are distributed amongst 8 tetrahedral interstices (surrounded by O^{2-} ions) and sixteen octahedral interstices (surrounded by six O^{2-}ions). The distribution of the metal ions is very important for an understanding of the magnetic property of these materials .

Therefore these ferrites are very much suitable for the application at higher frequency. Ferrites have inverse spinel structure. Spinels can be used in the 3-30 GHz band. The crystal structure of spinels is isomorphous. The crystal structure is shown in the figure below they have other structure as well i.e. garnet structure which is beyond the scope of this thesis.

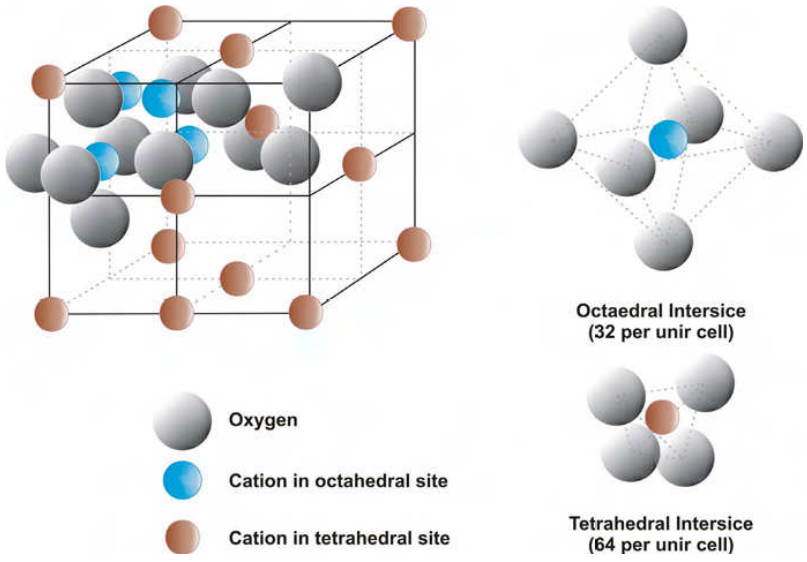


Fig 1.10 The spinel structure of ferrite

1.9 Electromagnetic Shielding

Electromagnetic shielding is the process of limiting the flow of electromagnetic fields between two locations, by separating them with a barrier made of conductive material. Typically it is applied to enclosures, separating electrical devices from the 'outside world', and to cables, separating wires from the environment the cable runs through. Electromagnetic shielding used to block radio frequency , microwave frequency, electromagnetic radiation, is also known as RF shielding.The shielding can reduce the coupling of radio waves, electromagnetic fields and electrostatic fields, though not static or low-frequency magnetic fields. (A conductive enclosure used to block electrostatic fields is also known as a Faraday cage.) The amount of reduction depends very much upon the material used, its thickness, the size of the shielded volume and the frequency of the fields of interest. The life time and efficiency of electronic devices and electrical equipments can be increased through effective electromagnetic shielding [32].Electromagnetic energy consists of a magnetic (H-field) and an electric (E-field) component perpendicular to each other and propagates at right angles to the plane containing the two components. The ratio of E to H is defined as the wave impedance (Z_w, in ohms) and depends on the type of source and the distance from the source. Large impedances characterize electric fields and small ones characterize magnetic fields. Far from the source, the ratio of E to H remains constant and equal to 377 Ω, the intrinsic impedance of free space. In EMI shielding, there are two regions, the near field shielding region and far field shielding region, need to be considered. When the distance between the radiation source and the shield is larger than $\lambda/2\pi$ (where λ is the wavelength of the source), it is in the far field shielding region. The electromagnetic plane wave theory is generally applied for EMI shielding in this region. When the distance is less than $\lambda/2\pi$, it is in the near field shielding and the theory based on the contribution of electric and magnetic dipoles is used for EMI shielding. SE in decibel (dB) is a measure of the reduction of EMI at a specific frequency achieved by a shield, such as a coating, and is defined as:

$$SE = 10 \log \frac{P_o}{P_t} = 20 \log \frac{E_o}{E_t} = 20 \log \frac{H_o}{H_t}$$

where P_o, E_o and H_o are the power, the electric and magnetic field intensities incident on the shield and P_t, Et and H_t are the counterparts transmitted through the shield . the EMI shielding effectiveness (SE) in wide frequency range depends on intrinsic properties of shielding material, dielectric constant and conductivity[32].

1.9.1 The Theory of EMI Shielding

The theory of electromagnetic interference shielding will be described in section 4.7 i.e microwave absorption techniques, which seems to be more pertinent with results and discussion. The details of EMI Shielding can also be found elsewhere [32, 34].

1.9.2 EMI Shielding Material

The various class of material can be utilized for EMI Shielding applic ations such as metals [32, 35,36]. Ceramic and ceramic composite [39], conducting polymer[35,37], polymer metal composite[38]. The present work mainly focuses on polyaniline based nanocomposite as shielding materialwhich has been described in following subsection**.**

1.9.2.1 Polymer nanocomposite as shielding material.

Conducting polymer such as doped polyaniline are promising material to replace or supplement typical metals for EMI Shielding application[35,37]. Conducting polymers have merits such as light weight, physical flexibility, and tunable shielding response and conductivity.

The carbon fiber coated with polyaniline has been reported shielding material[41,42].The polyaniline Fe_2O_3 nanocomposite has been characterized for EMI shielding application [1] and the value of SE has been found to be 11.2 dB

More recently Ohlan *et al.* [39] have studied the microwave absorption properties of conducting polymer barium ferrite nanocomposite and the value of SE has been found to be 28.9 dB. There are several other studies that utilize the polymer nanocomposite hexagonal ferrite[43] and MWCNTs

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Chapter 2

Motivation and aim of this work

2.1 Introduction

The importance of ferrite nano composite as electromagnetic shielding material has already been discussed. The applicability of such a composite is related to shielding effectiveness, conductivity, saturation magnetization, permeability, coercivety, remanence magnetization, etc. Different studies have been done in this field. But the shielding effectiveness change with frequency since magnetic permeability changes with frequency.

2.2 Motivation

Ohlan et al.[1]Conducting polymer nanocomposites of polyphenyl amine with barium ferrite nanoparticles (50–70 nm) were synthesized via emulsion polymerization. The complex permittivity, permeability, and microwave absorption properties of the composite were studied in the 12.4–18 GHz (Ku band) frequency range. The composite has shown high shielding effectiveness due to absorption (SEA) of 28.9 dB (99.9%), which strongly depends on dielectric loss, magnetic permeability, and volume fraction of barium ferrite nanoparticles. The high value of SEA suggests that these composites can be used as a promising radar absorbing materials

The most suitable route to get an optimum dispersion of the magnetic phase within the PAni matrix is of key importance to judge the effectiveness of this type of nanocomposites as EMI shielding material. Yavuz *et al* [2] synthesized polyaniline in presence of MnZn ferrite and NiMnZn ferrite, 5.9 micrometers in size. Ferrite particles in suspensions were contacted with the aniline monomer solution. Yavuz's work used FT-IR analyses to verify the presence of the absorption bands of the monomer from the ferrite surface. In turn, XRD was used to confirm the crystalline structure of bare ferrite powder and that of the ferrite in the nanocomposite..

Mathur *et al* [3] worked with the room temperature synthesis of magnetic composites of a copolymer with nanoparticles of MnZn ferrites in different sizes. Mössbauer, X-ray diffraction and infrared studies established the formation of nanoparticles of MnZn ferrite in the size range of 5 - 10 nm depending on the concentration of Zn ions, which also affected the magnetic properties of the nanocomposites.

Poddar *et al* [4], used 15 nm manganese zinc ferrites ($Mn_{0.68}Zn_{0.25}Fe_{2.07}O_3$) synthesized in inverse micelles as the disperse phase for PAni/polypirrole-based nanocomposites. Poddar's research was focused on the magnetic behavior of those compounds at different temperatures. They also investigated the dispersion of the magnetic phase in a matrix of wax. The measurement of magnetic behavior showed low coercivity for the wax nanocomposite but bigger saturation magnetization for those that are in the polymer matrix. The values of saturation magnetization are not easily comparable because they were of Fe the saturation magnetization was 11.5 emu/g. Although they claimed a suitable dispersion of the magnetic phase, no clear experimental evidence on this point was provided.

Sharma *et al* [5] verified that when iron oxides are used as dispersed phase, a critical factor is the dependence of functional properties of the composite with the sizes of the oxide particles and the polyaniline concentration. They used 10-20 nm γ -Fe_2O_3 nanoparticles for their experiments. The maximum saturation magnetization value was 53.37 emu/g for a weight concentration of 1:0.1 (γ -Fe_2O_3: PAni) at ambient temperature. The same report suggested the convenience in adding the disperse phase during the polymerization process in presence de HCl (as required for the protonation of aniline). Despite the improvement on the dispersion of the oxide phase, some agglomeration of the oxides was still observed that was more evident at larger oxide/PAni ratios

Other investigators such as Naishadham [7] also focused on the improvement of the conductivity of the polymer for EMI shielding applications. Two new materials, namely, polyacetylene and PBT doped by ion implantation with iodine, were evaluated as a function of frequency, electrical thickness, doping, polarization, and angle of incidence. The measured conductivity value was used in a multilayer model of the polymer in order to calculate reflection and transmission by the

shield for various layer parameters. Obtained results showed that the polymer performed well as EMI shield over a wide frequency band. Multiple layers were found to provide better shielding effectiveness than a single layer with thickness about the same as that of the multilayer.

Baek *et al* [7] synthesized aniline with poly-o-aminophenethyl alcohol in aqueous hydrochloric acid medium. The research addressed the achievement of better conductive properties for EMI applications. XRD, FTIR, UV, conductivity (7.1 to 5.2×10^{-5} S/cm),
lectrochemical response, and thermo-gravimetric analysis suggested the applicability of
is composite as potential conducting material. The synthesis of PAni is critical in order to ob ain the best conductivity values. Previous investigators have used different processes to achieve it.

Wojkiewicz *et al* [8] worked with PAni doped with HCl and polyvinyl chloride (PVC) and PAni doped with camphor sulfonic acid. These materials were used in combination with polyurethane (PU) to enhance the mechanical properties of the final product. DC conductivity values for PAni-PVC were between 1 and 100 Sm^{-1} whereas PAni-PU reported conductivities up to 1000 Sm^{-1} (10 S/cm). The dielectric properties were analyzed in the microwave band (50 MHz - 20 GHz) and the millimeter band (30 GHz - 110 GHz). The shielding effectiveness (SE) measurements showed attenuation up to 30 dB. At very high frequencies, the film thickness became an important parameter.

Zhang *et al* [9] also used PAni-based magnetic nanocomposites where the disperse electric conductivity of the nanocomposite was decreased by increasing the quantity of ferrite nanoparticles in the matrix. Conductivity values of the nanocomposite were aro nd 4.0×10^{-4} S/cm, with a corresponding magnetization of saturation 6 emu/g for 26. % of
Fe_3O_4. The composite containing γ -Fe_2O_3 nanoneedles reported 16 emu/g for 33 3 wt% of the disperse phase.

The effectiveness of the use of the polyaniline for EMI shielding has been studied and confirmed by several investigators. Yuping *et al* [10] investigated the inclusion of silicon rubber in the polyaniline and the interaction of the grain size with the magnetic properties at low frequencies. The aniline solution was polymerized using ammonium peroxydisulfate as the oxidant and HCl

to protonate the polymer structure. The silicone rubber (SR) was blended in the aniline solution using a mixing bowl. The cross-linking agent of liquid silicone rubber was ethyl orthosilicate, whereas dibutin dilaurate was used as the catalyst.

2.3 Aim of This Work

The soft material are extremely used as microwave absorber . The main objective is to determine the most suitable conditions for the shielding effectiveness of PAni based Magnetic nanocomposite. These materials have attracted extensive interest because of high resonance frequency, high permeability and high electrical resistivity. The nano ferrite conducting polyaniline would replace the metallic materials utilized for shielding. For making the polymer ferrite nano composite $CoFe_2O$ has been selected for polyaniline matrix.

The studies of this thesis are aimed at

(1) The synthesis of PANI –cobalt ferrite nano composite

(2) Study of dielectric and microwave absorption behavior.

(3) Studies of electrical transport mechanism.

(4) Studies of Thermal stability

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Chapter 3

Experimental details

3.1 Introduction

This chapter presents the details of experimental techniques applied for synthesis and characterization , magnetic, dielectric and transport measurement of polyaniline – cobalt ferrite (PC) nanocomposite. The nanocomposite of cobalt ferrite has been synthesized by precursor method. And for the synthesis of Polyanilne- cobalt ferrite nanocomposite emulsion polymerization method is used. The X Ray Diffraction studies has been carried out to determine the particle size and for phase identification. The incorporation of nanoparticles of ferrite in polymer matrix has been confirmed by UV-Visible and Fourier transform Infrared spectroscopy. Thermogravimetric studies established the thermal stability of composite. The vector network analyzer (Agilent E8362B) is employed for microwave absorption and EMI shielding determination. The DC electrical conductivity of the nanocomposite is measured by using Four probe technique.

3.2 Synthesis of Polyaniline – $CoFe_2O_4$ Nano Particles Composite

The preparation of the polymer nanocomposite involved the following steps:

Step 1 Synthesis of Co Ferrite nano particles:

The synthesis of co ferrite nano particles was carried out by precursor route [1]by dissolving (Qualigens, India), 1: 2: 0.3 weight ratio of cobalt nitrate (Qualigens, India), ferric nitrate and citric acid (Merck, India), respectively, in distilled water aqueous ammonium solution (Merck, India) was added to maintain the pH of the solution at 9.0. The resulting solution was heated at 900°C with continuous stirring to form a viscous gel. The gel so formed was ignited resulting in the formation of dendrite structure, which was crushed to powder and calcined in a programmable tubular furnace at 900°C for 4 h. The cobalt ferrite particles so obtained were further grinded using Retsch ‘‘PM-400’’ planetary-ball mill with tungsten balls in tungsten carbide jars.

Step 2 Synthesis of PANI - Co Ferrite Nano Composite:

- Chemical oxidative polymerization of aniline was carried out in the presence of Nano ferrite particles in aqueous medium. 0.3M DBSA(selected as dopant ion for polyaniline to provide better properties and processability) and Co ferrite particles were homogenized by using the ART-Miccra D-8 (N0-10956) homogenizer at 10500 rpm for 2–3 h.

- To this 0.1M of aniline (An) was added and supersonic stirring was continued for 1 h to form an emulsion.

- The oxidant ammonium peroxydisulfate (0.1M)(as oxidant) was added drop-by-drop keeping the temperature of the reactor at −2.0 ◦C with vigorous stirring for 5–6 h to the above emulsion in a reactor.

- The green polymer precipitate so obtained was treated with isopropyl alcohol under vigorous stirring for 2–3 h.

- The resulting precipitate was then filtered and washed thoroughly and dried at 60–65 ◦C in a vacuum oven.

- Several composition of the polymer composite having different weight ratio of monomer to ferrite Aniline:-$CoFe_2O_4$:: 2:1(PC 21), 1:1(PC 11), 1: 2(PC1 1.5), 1:3(PC 13) were also synthesized in DBSA medium to check the effect of ferrite constituents in the polymer matrix.

- Beside this, for comparison of results, polyaniline doped with DBSA in 1:3 molar ratio (PD13) without ferrite particles is also synthesized using emulsion polymerization.

3.3 Structural Characterization:

The XRD studies have been carried out for phase identification. The details of this techniques is described in following section.

3.3.1 X-Ray Diffraction (XRD)

The crystalline structures of various polymeric composites [2,4] were investigated by Wide Angle X-Ray Diffraction (WAXD), using a powder X-Ray diffractometer (Siemens D 500 model) with CuKα source and βNi filter (Figure 3.1). All the scans were recorded in the 2θ regions of 15 - 75° at a scan rate of 0.02° per second.

Fig. 3.1 XRD setup

X-ray Diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phases present in materials and to measure the structural properties (strain state, grain size, epitaxy, phase composition, preferred orientation, and defect structure) of these phases. XRD is also used to determine the thickness of thin films and multilayers, and atomic arrangements in amorphous

materials (including polymers) and at interfaces. Figure 3.2 shows the basic features of an XRD experiment set up, the diffraction angle 2 θ is the angle between the incident and diffracted X rays . Form 2θ values for reflection, 'd' values were calculated using Bragg equation and average crystallite size calculated of ferrite nanoparticles by Scherrer's equation[2,3]

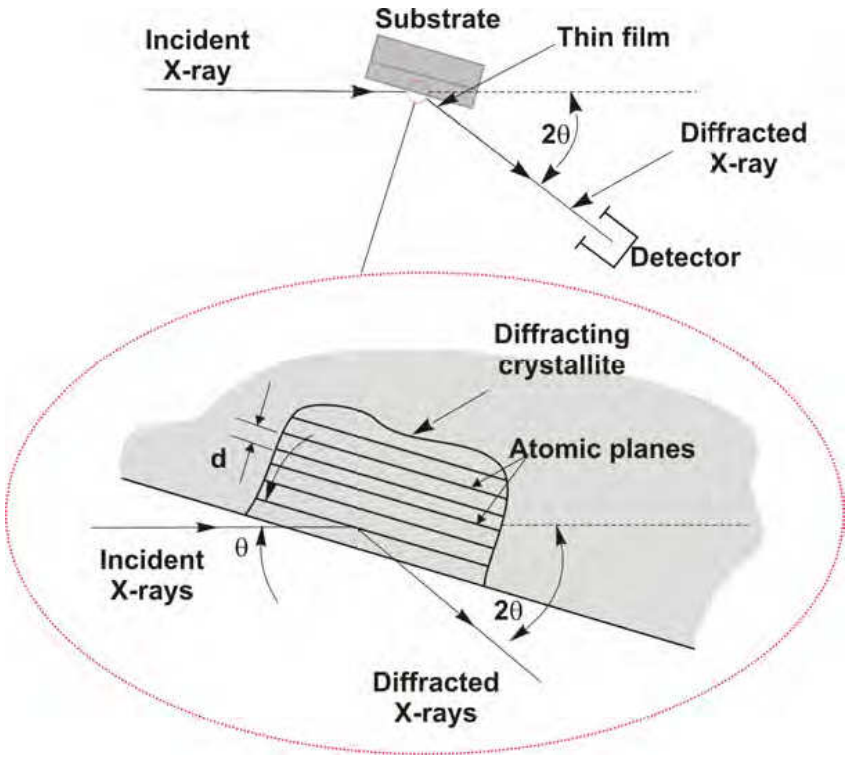


Figure 3.2 The basic features of XRD experiment set up

Considering the some important properties of crystalline materials, crystals consist of planes of atoms that are spaced a distance d apart (Figures 3.2), but can be resolved into many atomic planes, each with a different d-spacing. To distinguish between these, we introduce a coordinate system for the crystal whose unit vectors a, b, and c are the edges of the unit cell (Figure 3.3). For the familiar cubic crystal, these form an orthogonal system. Any atomic plane can now be uniquely distinguished by its Miller indices. These are the three reciprocal intercepts of the plane with the a-, b-, and c-axes and are reduced to the smallest integers having the same ratio. Thus, an (hkl) plane intercepts the crystallographic axes at a/h, b/k, and 4; examples are shown in Figure 3.3 . The d-spacing between (hkl) planes is denoted d_{hkl}, and for cubic crystals, it is where a_0 is the lattice constant of the crystal (fig. 3.1)

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

when there is constructive interference from X rays scattered by the atomic planes in a crystal, a diffraction peak is observed. The condition for constructive interference from planes with spacing d_{hkl} is given by Bragg's law

$$\lambda = 2 \cdot d_{hkl} \cdot Sin\theta_{hkl}$$

where θ_{hkl} is the angle between the atomic planes and the incident (and diffracted) X-ray beam (Figure 3.2). For diffraction to be observed, the detector must be positioned so that the diffraction angle is $2\theta_{hkl}$, and the crystal must be oriented so that the normal to the diffracting plane is coplanar with the incident and diffracted.

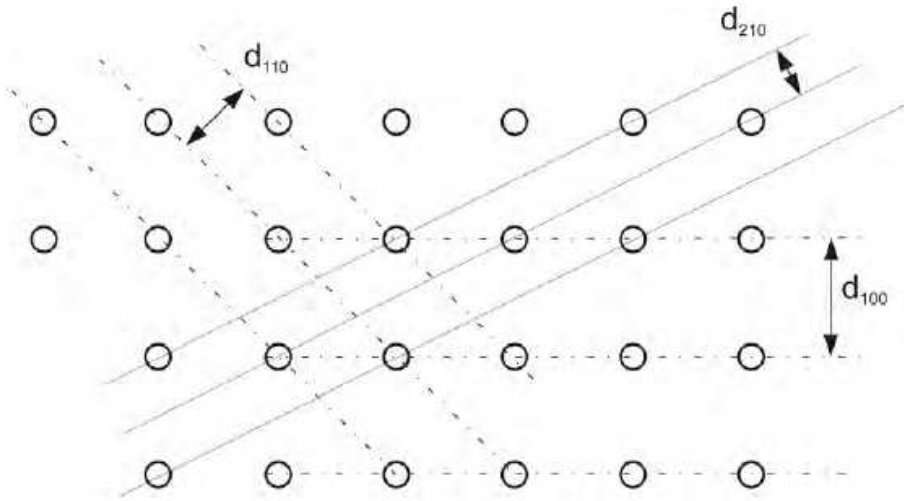


Fig 3.3 Diffraction planes in a material

3.4 Spectroscopic Characterization

The spectroscopic characterization has been carried out for determining the incorporation of Co ferrite nanoparticles in polyaniline matrix. The spectroscopic characterization includes fourier transform (FTIR) and UV- Visible (UV-Vis). The details of these techniques are given in following section:

3.4.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectroscopic studies were carried out. PAni samples with different conc. of ferrite nano particles were analyzed by using "Shimadzu FTIR 8201" spectrometer (Figure 3.4).

Chemical bonds vary widely in their sensitivity to probing by infrared techniques. For example carbon-sulfur bonds often give no infrared signal, and so cannot be detected at any concentration, while silicon-oxygen bonds can produce signals intense enough to be detected when probing submonolayer quantities, or in the order of 10^{13} bond/cc. Thus, the potential utility of infrared spectrophotometry (IR) [5.6,8]is a function of the chemical bond of interest, rather than being applicable as a generic probe.

The goal of the basic infrared experiment is to determine changes in the intensity of a beam of infrared radiation as a function of wavelength or frequency (2.5 - 50 μm or 4000 – 200 cm^{-1} respectively) after it interacts with the sample. The centerpiece of most equipment configurations is the infrared spectrophotometer. Its function is to disperse the light from a broadband infrared source and to measure its intensity at each frequency. The ratio of the intensity before and after the interaction of light with the sample is determined.

Let us define I_o to be the intensity of the light incident upon the sample and I as the intensity of the beam after it has interacted with the sample. The goal of the basic infrared experiment is to determine the intensity ratio I/I_0 as a function of the frequency of light (w).

A plot of this ratio versus the frequency is the infrared spectrum. The infrared spectrum is commonly plotted in one of three formats: as transmittance, reflectance, or absorbance. If one is measuring the fraction of light transmitted through the sample, this ratio is defined as

$$T_w = \left(\frac{I_t}{I_0} \right)_w$$

Fig. 3.4 FTIR instrument NICOLET 5700

.

where T_w, is the transmittance of the sample at frequency w, and I_t is the intensity of the transmitted light. Similarly, if one is measuring the light reflected from the surface of the sample, then the ratio is equated to R_w, or the reflectance of the spectrum, with I_t being replaced with the intensity of the reflected light I_r. The third format, absorbance, is related to transmittance by the Beer-Lambert Law:

$$A_w = -\log T_w = (\varepsilon_w)(b \cdot c)$$

where c is the concentration of chemical bonds responsible for the absorption of infrared radiation, b is the sample thickness, and. ε_w, is the frequency-dependent absorptivity, a proportionality constant that must be experimentally determined at each w by measuring the absorbance of the samples with known values of bc. As a first order approximation the Beer-

Lambert Law provides a simple foundation for quantifying FTlR spectra. For this reason, it is easier to obtain quantitative results if one collects an absorbance spectrum, as opposed to a reflectance spectrum.

3.4.2 UV-Visible Spectroscopy

UV-Visible is spectroscopy [5,6] probes the electronic transitions of molecules that absorb light in the ultraviolet and visible region of the electromagnetic spectrum and is considered a reliable and accurate analytical technique for the qualitative as well as the quantitative analysis of samples. When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption (*i.e*. intensity) at each wavelength. The resulting spectrum is presented as a graph of absorbance versus wavelength. UV-Visible spectroscopy is usually applied to molecules and inorganic ions or complexes in solution.. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law.

Fig.3.5 UV spectrometer shimadzu 1603

Various kinds of electronic excitation may occur in organic molecules by absorbing the energies available in the 200 to 1100 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called an excited state. Because the absorbance of a

sample will be proportional to the number of absorbing molecules in the spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The corrected absorption value is called "molar absorptivity", and is particularly useful when comparing the spectra of different com functions (chromospheres) The presence of chromospheres in a molecule is best documented by UV-Visible spectroscopy. A diagram of the components of a typical spectrometer is shown in the following diagram (Figure3.7). The functioning of this instrument is relatively straightforward. A beam of light from a visible and/or UV light source (colored red) is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam (colored magenta), passes through a small transparent container (curette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference (colored blue), passes through an identical curette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I_0. The intensity of the sample beam is defined as I.

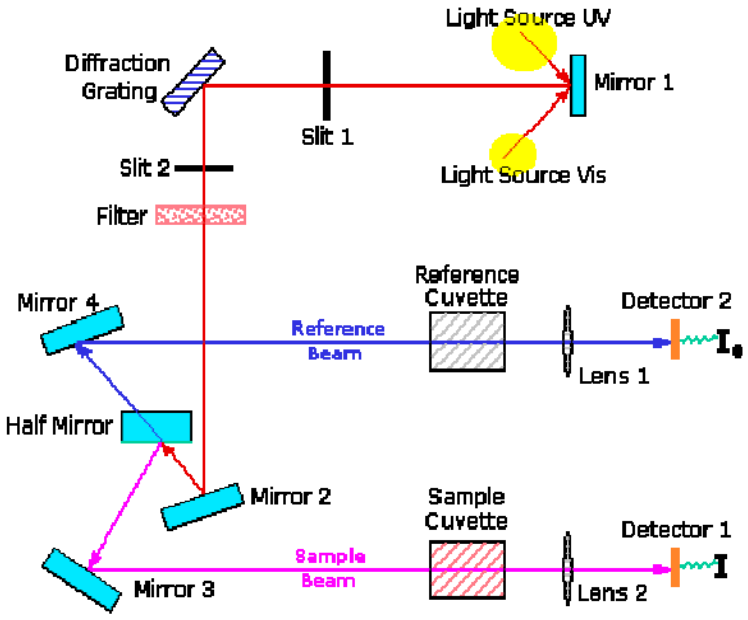


Fig 3.6 Components of a typical spectrometer

3.5 Thermal characterization

For thermal characterization thermogravimetric analysis was done which is briefly explained as follows:

3.5.1 Thermogravimetric Analysis (TGA):

TGA of PAni with Co ferrite were recorded over a temperature range of 25 ºC to 800ºC in nitrogen atmosphere using a METTLER thermal analyzer TGA/SDTA 851 (Figure i), in order to analyze the thermal behavior pattern of these blends.

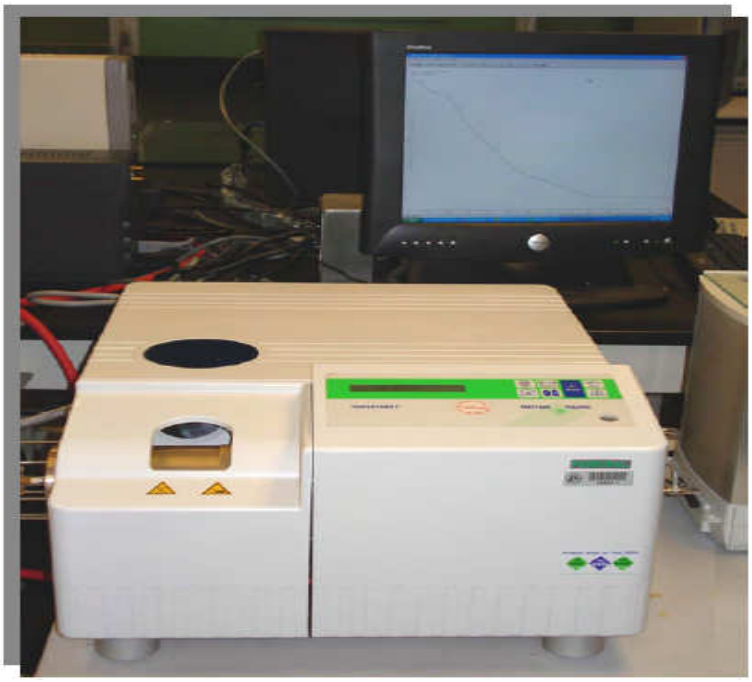


Fig 3.7 TGA METTLER 851

The basic principle in TGA is to measure the mass of a sample as a function of temperature. This, in principle, is a simple measurement but offers an important and powerful tool in solid state chemistry and materials science. The method, for example, can be used to determine water of crystallisation, follow degradation of materials, determine reaction kinetics, study oxidation and reduction, or to teach the principles of stoichiometry, formulae and analysis

3.6 Magnetic Properties Measurement:

The magnetic properties of polyaniline – cobalt ferrite nanocomposite such as retentivity, coerecivity, and saturation magnetization has been measured using vibrating sample magnetometer(VSM). The details about this instrument are given in the following subsection

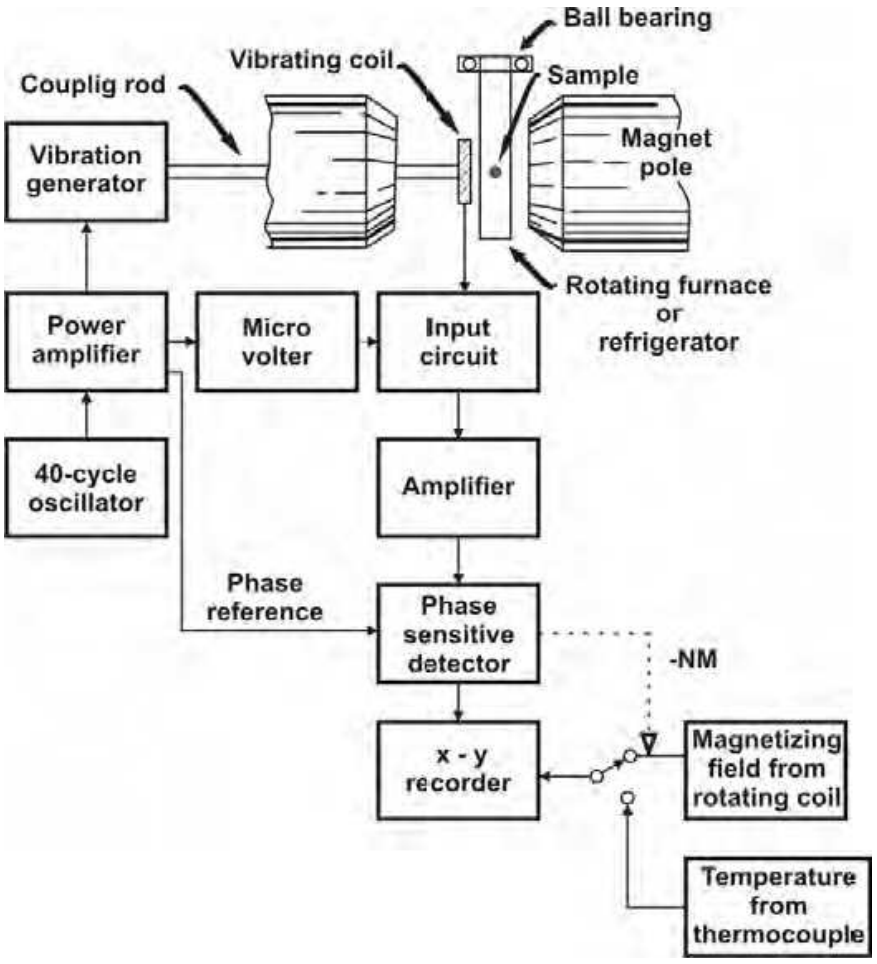
3.6.1 Vibrating Sample Magnetometer (VSM)

The magnetic characterization of various polymeric composites has been investigated by VSM technique

Fig 3.8 vibrating sample magnetometer

In order to obtain a measurement of the magnetic induction it is also possible to use various moving-coil instruments. The simplest of these is the rotating coil which rotates at a fixed angular velocity. Therefore the amplitude of the generated voltage by rotating coil is proportional to the magnetic induction and therefore the amplitude can be used to measure magnetic induction

(B) or magnetic field (H) in free space. The signal can be read directly as an AC voltage or converted to a DC voltage which is proportional to the amplitude.

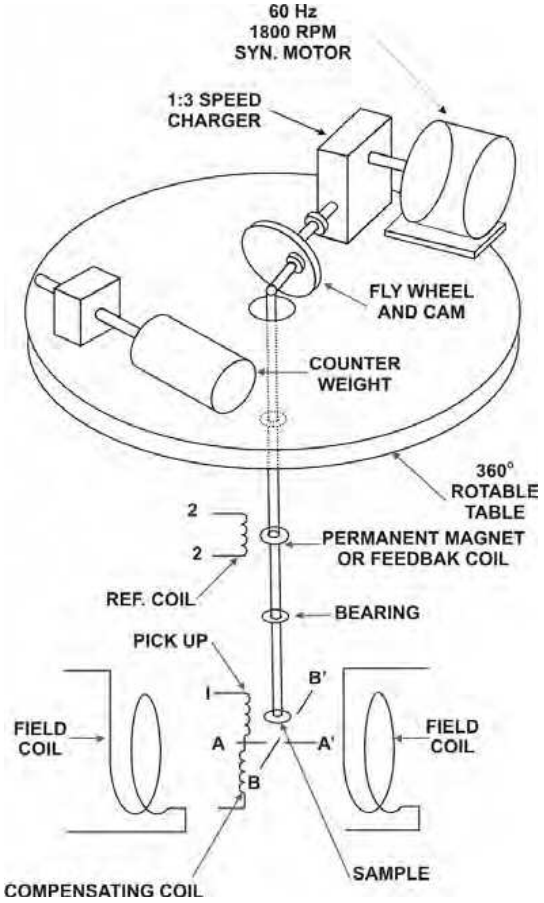


3.9 Schematic diagram of a vibrating coil magnetometer.

The vibrating-coil magnetometer is based on the same principles as the previous technique, but is used primarily as a method of determining the magnetization (M). The arrangement is shown in Figure 3.9. The coil vibrates between the sample and a region of free space and thereby acts as a gradiometer by measuring the difference in induction in the two positions.

The output of vibrating coil magnetometer is independent of H, but is dependent on M

The vibrating-sample magnetometer (VSM) is identical in principle to the vibrating-coil magnetometer except that the sample is moved instead of the coil. The VSM was first described by Foner and has now almost completely superseded the vibrating-coil device.



3.10 Schematic diagram of a vibrating sample magnetometer.

A VSM is really a gradiometer measuring the difference in magnetic induction between a region of space with and without the specimen. It therefore gives a direct measure of the magnetization. A schematic of a typical VSM is shown in Figure 3.10. The specimen in general has to be rather short to fit between poles of the electromagnet. The method is therefore in most cases not well suited to the determination of the magnetization curve or hysteresis loop because of the demagnetizing effects associated with the short specimen.

However it is well suited for the determination of the saturation magnetization (M_s).

The detected signal, being an AC signal of fixed frequency, is measured using a lock-in amplifier. A reference signal is provided for the lock-in amplifier as shown in Figure3.10 by using a permanent magnet and a reference pick-up coil. Magnetic moments as small as 5×10^{-4}A m^2 ($5\times10^{5.}$ emu) are measurable with a VSM. Its accuracy is better than 2%

3.7 Electromagnetic Shielding Measurements

Microwave measurements were carried out on Agilent E8362B Vector Network Analyzer (fig. 3.11) [9,10] in microwave range of 12.4–18.0 GHz (Ku-band) through 15.8 mm 3 7.9 mm 3 6 mm copper sample holder connected by wave-guide flanges back by perfect conductor. To avoid air gap, the above sample holder is modified with a grove of 1.5 mm on each side with a depth of 3 mm.

This instrument is use to measure S parameters (S_{11}, S_{22}, S_{12}, S_{21}), dielectric constant, dielectric losses, permeability, in microwave bands i.e. in different frequency (GHz) region like X band (8-12 GHz), P(12.4-18 GHz) band etc.

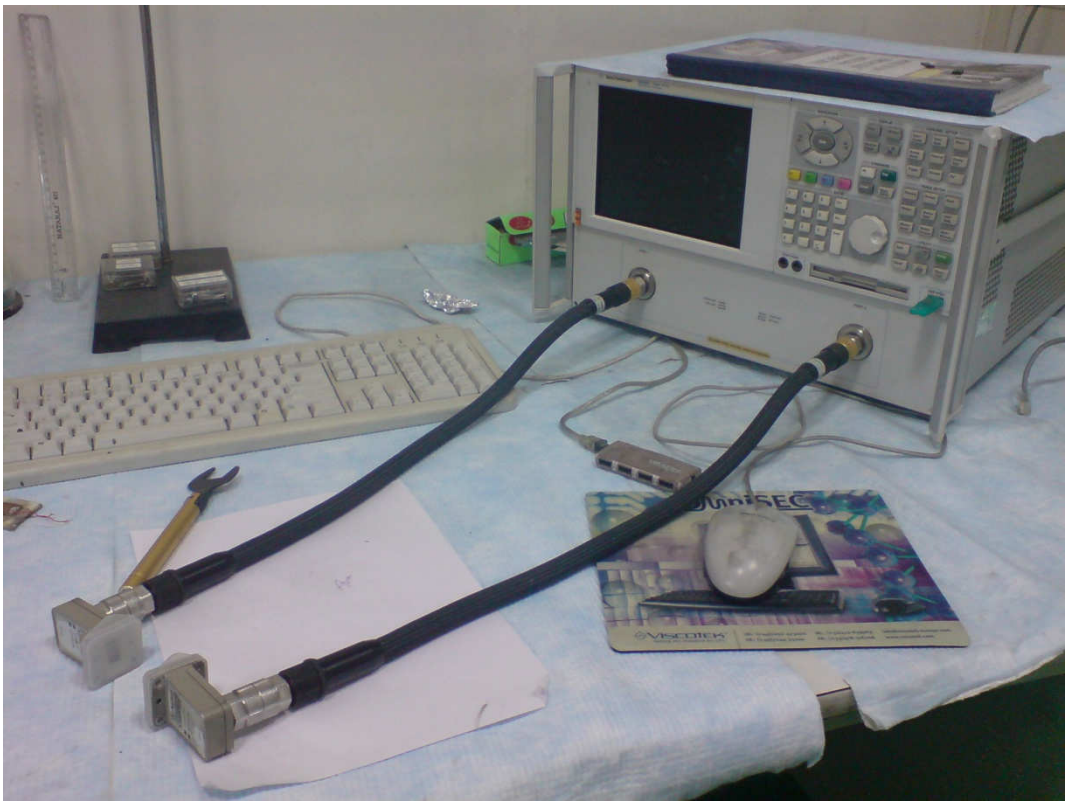


Fig 3.11 Vector Network Analyzer

3.8 Electrical transport measurements

3.8.1 Conductivity Measurements

For the measurements of conductivity with temperature of polyaniline cobalt ferrite nanocomposite Four probe technique [10,11] has been employed which is described as follows:

Four Probe method

The resistivity of the polyaniline cobalt ferrite nanocomposite is determined using four-point probe technique. With a four-probe, two of the probes are used to source current and the other two probes are used to measure voltage. Using four probes eliminates measurement errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each metal probe and the semiconductor material. Because a high impedance voltmeter draws little current, the voltage drops across the probe resistance, spreading resistance, and contact resistance are very small. Two common Kelvin techniques for determining the resistivity of a semiconductor material are the four-point collinear probe method and the van der Pauw method. The Model 4200-SCS Semiconductor Characterization System can be used for both. Because of its high input impedance ($>10^{16}\Omega$) and accurate low current sourcing, the Model 4200-SCS with pre assumptions is ideal for high resistance samples. This application note explains how to make resistivity measurements of semiconductor materials using the Model 4200-SCS.

The dc conductivity refers to the net charge which traverses (flow) the entire conducting polymer pellet Four-points-probe method is advantageous over two-points-probe method because it overcomes the problem of contact or lead resistance. This technique is used for the determination of conductivity of doped conducting polymer films or pressed pellets.

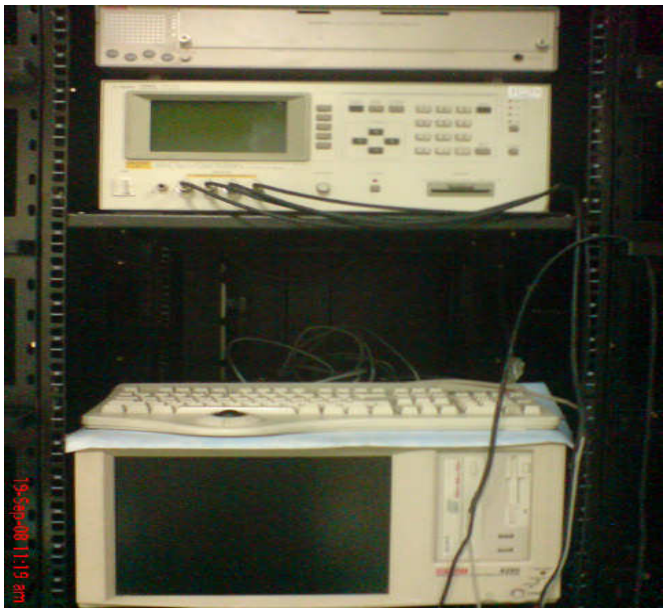


Fig . 3.12 : 4200 Keithley Semi Characterization system for conductivity measurement.

The dc conductivity (σ_{dc}) depends upon the net charge flowing in the sample. On the other hand , σ_{dc} is measured as a function of an alternating electric field. A difference in the behaviour of σ_{dc} is expected when conduction occurs by the motion of charge carriers in the extended states by hopping among localized states (such as solitons, polarons and bipolarons)[12] or by a transport between the metal particles embedded in host particles.

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Chapter 4

Results and Discussions

4.1 X Ray Diffraction

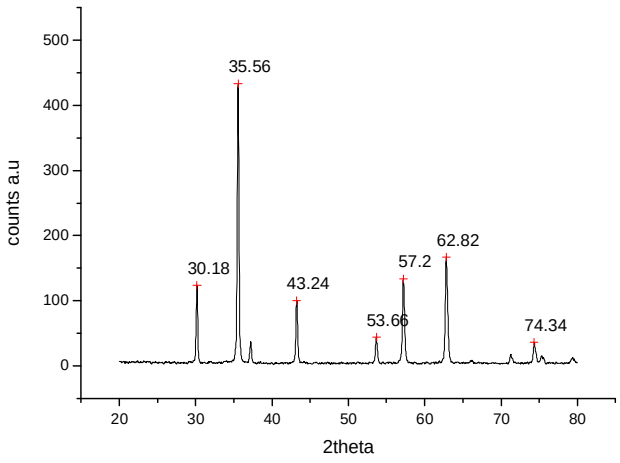
4.1.1 The Cobalt Ferrite

Figure 4.1 (a) show the XRD patterns of the cobalt ferrite . A reaction time of 4 hours was found to be suitable for complete formation of the ferrite under mild heating. As seen, all peaks correspond to ferrite structure. According to Scherrer's equation:

$$t = \frac{k\lambda}{\beta \cdot Cos\theta} \tag{4.1}$$

where λ is the X-ray wavelength, *k* is the shape factor, *t* is the average diameter of the crystals (in angstroms), θ is the Bragg angle (in degrees) and β is the line broadening measured at half-height and expressed in units of 2θ. The value of k depends on several factors, including the Miller index of the reflecting plane and the shape of the crystals. If the shape is unknown, k is often assigned a value of 0.89..

The average size of cobalt ferrite nano particles by substituting in eq. 4.1 has been found to be ~9nm



4.1 XRD pattern of cobalt ferrite

4.1.2 Pani Cobalt Ferrite Nano Composite

The XRD patterns of Figure 4.2 evidence reorganization in the structure of the polymer and the co-existence of the ferrite reflections suggesting its effective and stable incorporation in the nanocomposite structure.

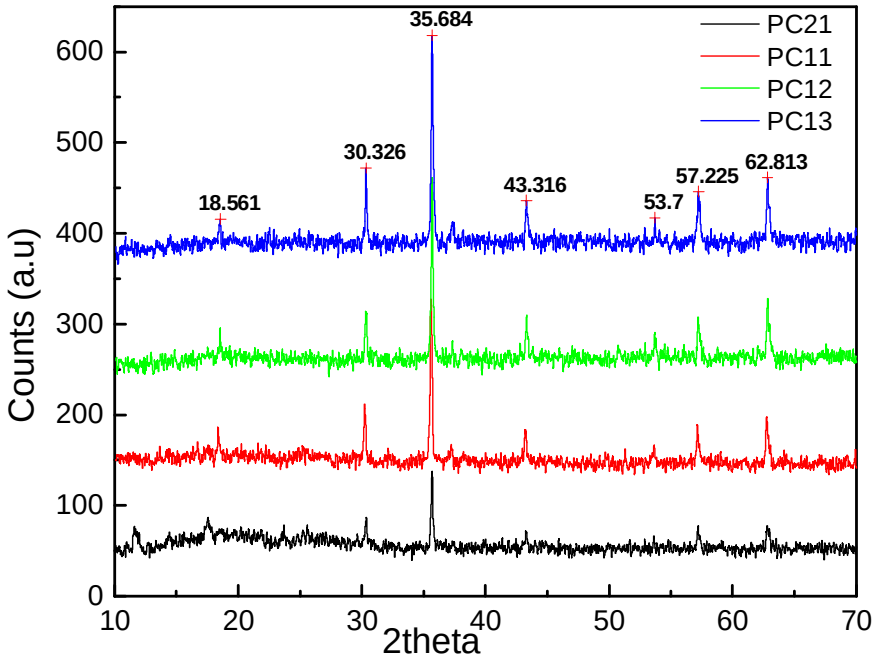


Fig: 4.2 XRD Analysis Of Pani Cobalt Ferrite having Different weight Ratios 2:1 (PC21), 1:1 (PC11), 1:2(PC12) ,1:3(PC13)

4.2 FTIR Analysis

The FTIR spectra is recorded on Nicolet 5700 in the region 4000 cm^{-1} to 400cm^{-1}. The spectra has been carried by making the pallet in KBr. The main peak of polyaniline observed are shown in the in the FTIR spectrum[1]. Each peak in the graph corresponds to a functional group present in the molecule. The increase in the number of peaks with Pani-cobalt ferrite composite [1] as compared to pristine polyaniline shows the incorporation of ferrite particles in the composite.

The FTIR spectra of polyaniline doped with Dodecyl benzene sulphonic acid (DBSA) is measured. The main characteristics bands for the polyaniline doped with DBSA are found at 1515 and 1458 cm^{-1}which are assigned for the C=C bond stretching of quinoids and benzenoid ring, respectively. Bands at 1257 and 1164cm^{-1} are due to C-N stretching and in-plane bending of the C-H bond while peak at 1024 cm^{-1} is due to $-SO_3H$ group. The peak at 1640 cm^{-1} may be due to the formation of the carbonyl group arising due to the over oxidation of the alkyl chain of the DBSA [1,2]. While the FTIR spectra of Polyaniline-Cobalt ferrite shows the prominent peak at 3423 cm^{-1} assign for the N-H stretching vibration for the aromatic amine while the band at 2924 and 2856 cm^{-1} was assign for the –CH stretching. In the polymer composite the shifting in the peaks for the main characteristics bands are observed at 1605 and 1458 cm^{-1} which are assigned for the C=C bond stretching of quinoids and benzenoidring, respectively. Bands at 1296 and 1164 $cm^{-1}$are due to C-N stretching and in-plane bending of the C- H bond while peak at 1024 cm^{-1} is due to $-SO_3H$ group. This shifting clearly indicates that the NH group of aniline ring is interacting to the Fe^{2+} ion of the ferrite[3]. The presences of the peaks at 672 cm^{-1} and 587 cm^{-1} which are the characteristic band of Fe–O band stretching clearly indicate the presence of $CoFe_2O_4$ in the polymer matrix.

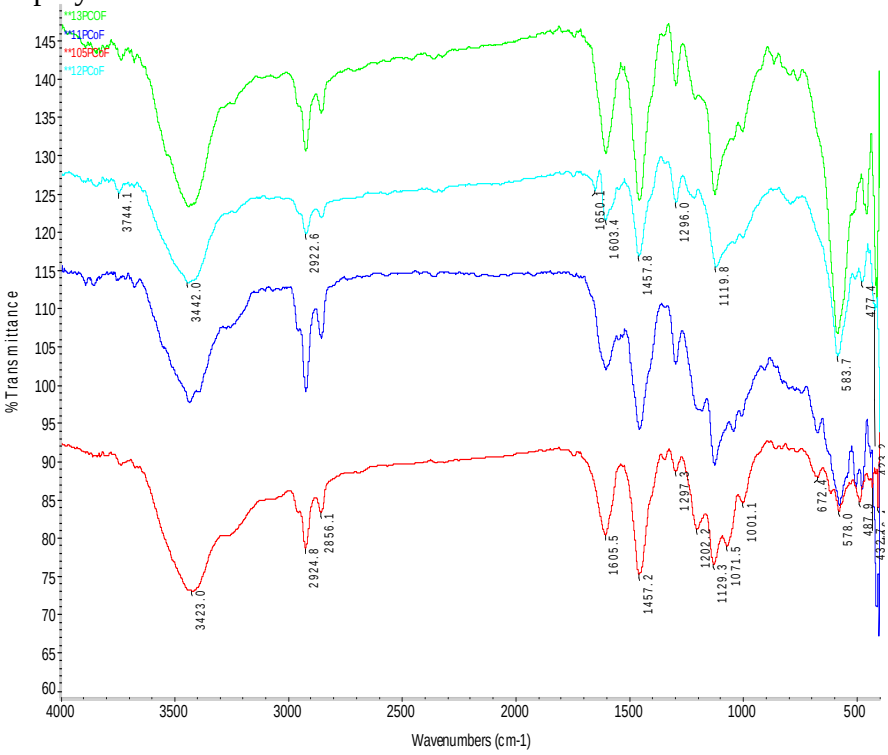


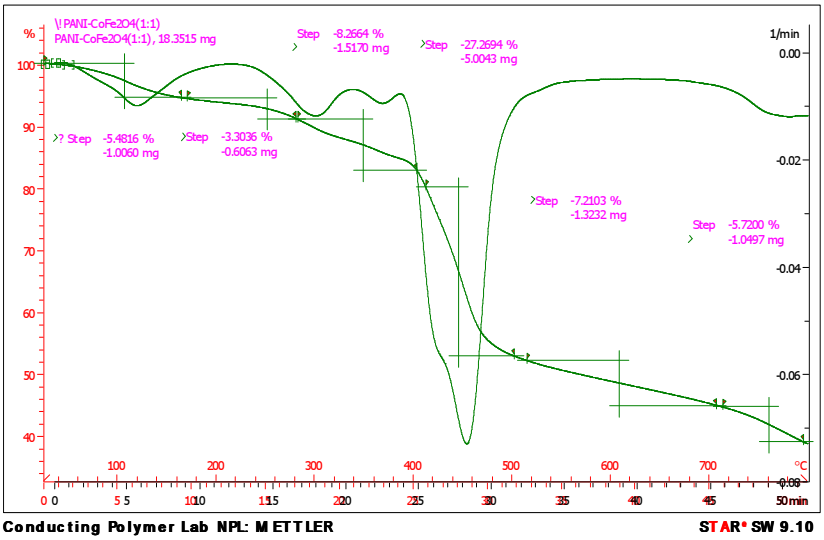
Fig . 4.3 FTIR spectra of polyaniline cobalt ferrite composite

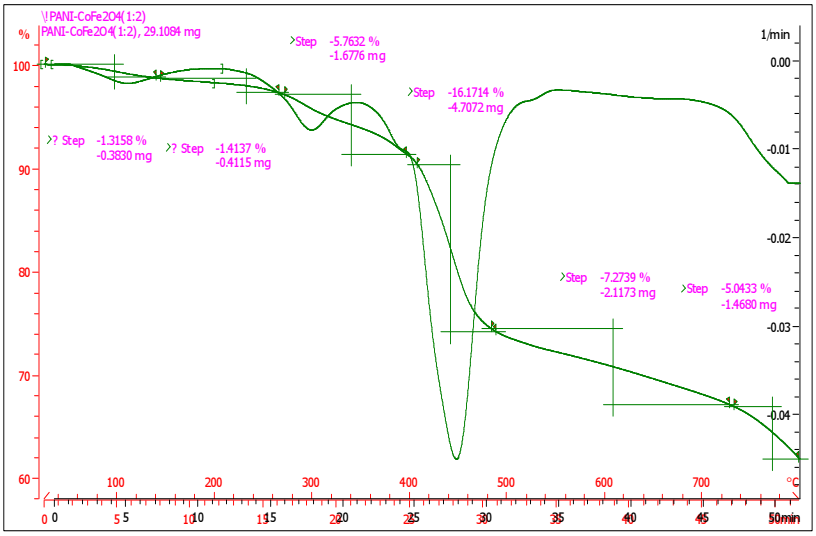
4.3 THERMAL ANALYSIS

The thermal analysis was performed to explore the effect of the loading of ferrite to the thermal stability of the polymer composite. The typical thermograms of different samples are shown in Figur 4.3(a), 4.3(b), 4.3(c) The thermograms indicate three major stages of weight loss which are attributed to different causes, first weight loss at lower temperature near 100-110^{0}C results from moisture evaporation, second weight loss at higher temperature between 220-380^{0}C arises due to the loss of degradation of dopant DBSA from the polymeric chain and third one is attributed to the structural decomposition of the polymer backbone. From the thermo gram it was observed that incorporation of ferrite particle to the polymer increases the thermal stability than the pristine polyaniline doped with DBSA. The themogram suggest that the polyaniline doped with DBSA is thermally stable up to 200^{0}C while the polyaniline cobalt ferrite is stable up to 230^{0}C.

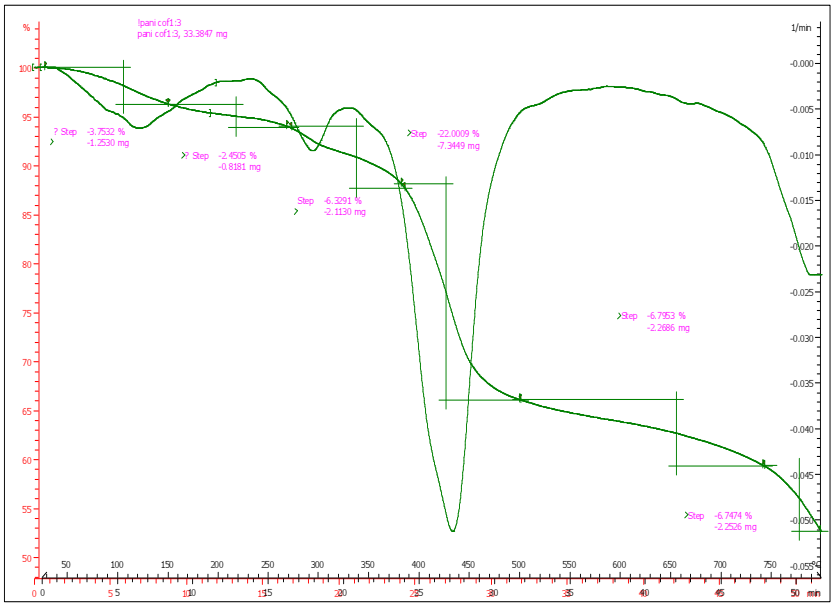
From the thermogram it was concluded that increase in the concentration of ferrite the thermal stability of the composites increases.

Fig 4.4 : The thermogram of polyaniline- ferrite nanocomposite with different weight ratio (a) 1:1 (PC11) (b). 1:2 PC(1:2), (c) 1:3 (PC13) are shown below





Conducting Polymer Lab NPL: METTLER STAR° SW 9.10



Conducting Polymer Lab NPL: METTLER STAR° SW 9.10

4.4 UV-Visible Absorption Spectra

Fig 4.5 shows the UV absorption spectra of the different samples of polyaniline and its composite with cobalt ferrite. The main peaks and calculated energy bands are shown in Table 1. Emeraldine base form of polyaniline in N-methyl pyrrolidione (NMP) shows two characteristic bands at 326 and 630 nm while the conductive form of polyaniline doped with DBSA has shown the red shift to 353 nm and 739 nm which are assigned to the π-π* transition of the benzenoid ring and polaronic transition respectively. But in case of polyaniline composite, two changes were observed. First a red shift was observed for the band from 739 to 726 nm, which is ascribed to polaronic transition. The reason behind this shifting may be the possible interaction of the $CoFe_2O_4$with polyaniline ring leading to the formation of ferromagnetic composite. Second when the $CoFe_2O_4$ content increases in different samples, absorption spectra shows the bathochromic shift for the band 353 to 349 nm.

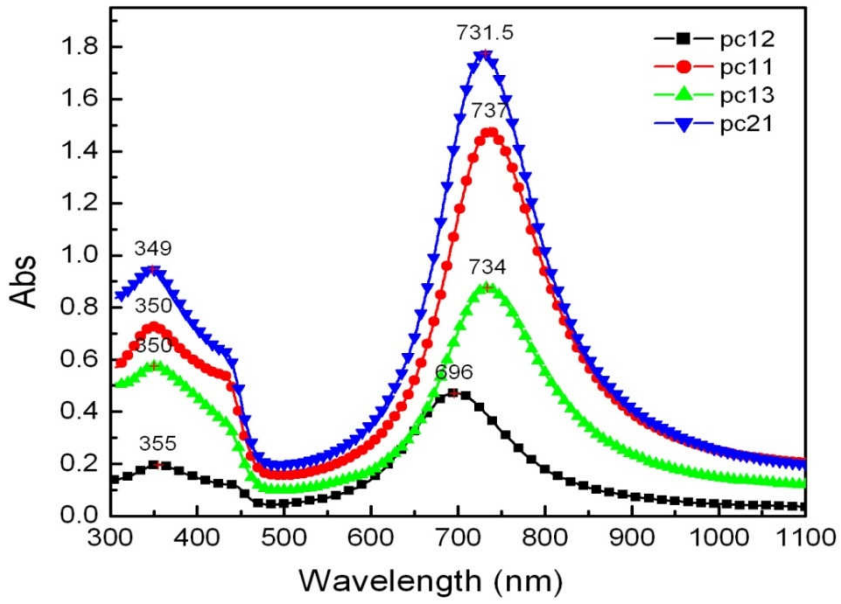


Fig 4.5 UV-Vis Spectra of PANI Cobalt Ferrite (a) 1:1 (PC11) (b). 1:2 (PC12) (c) 1:3 (PC13)

4.5 Magnetization Measurements

Magnetic characterization of the particles was done using vibrating sample magnetometer (VSM), at room temperature with maximum applied field upto 800G (see Fig. 4.6 for M–H loops). Cobalt ferrite ($CoFe_2O_4$) is a well-known hard magnetic material with high coercivity and moderate magnetization. $CoFe_2O_4$ which has a cubic spinel type structure like (AB_2O_4) with vacant B site and two distinct sub lattices (A and B in the spinal structure) which give origin to ferromagnetic ordering in the compound. From the B-H (curve shown in fig 4.6(a)) the saturation magnetization was found 49.6 emu/g with the coercivity of 295.11G. When these particles are incorporated in the polymer matrix resulting in the formation of PANI-$CoFe_2O_4$ composite, the magnetization value was found to 3.8 emu/g with the coercivity of 1045 G for the composite PC21 which increases to 22.3 emu/g (Fig 4.5(b)) and coercivity of 1172 G with increase of ferrite content in the polymer matrix. The detail of magnetic properties of the of PANI-$CoFe_2O_4$ composite are shown in the table below. The low saturation magnetization (Ms) is the result of non-magnetic coating layer of polyaniline which is considered as a magnetically dead layer over the surface of $CoFe_2O_4$ particles, thus affecting the magnitude or uniformity of magnetization due to quenching of surface moments . While the almost nearly same coercivity values, in all cases, can be explained as that both the number and the strength of the magnetic dipole in magnetic domain and the relations between adjacent magnetic domains determine the coercivity of the magnetic materials, and therefore less effect of the coating layer of polyaniline on the coercivity of the magnetic core $CoFe_2O_4$ in hybrid polyaniline $CoFe_2O_4$composites. From these results it is clear that the PANI-$CoFe_2O_4$ composite is ferromagnetic in nature and will work as a good absorber of the microwave in the GHz range.

S.No	MAGNETISATION(emu/gm)	CORECIVITY(Gauss)	RETENTIVITY(emu/gm)
COFe2O4	49.9emu/gm	800G	12 emu/gm
PANI+ COFe2O4(2:1)	3.8663emu/gm	1045G	1.8940 emu/gm
PANI+ COFe2O4(1:1)	14.5emu/gm	1100G	7.5 emu/gm
PANI+ COFe2O4(1:2)	17.03emu/gm	1173G	8.693 emu/gm
PANI+ COFe2O4(1:3)	22.347emu/gm	1172G	11.621 emu/gm

Table 1 Saturation magnetization, coerecivity, retentivity of different polyaniline- cobalt ferrite composite with different weight ratio.

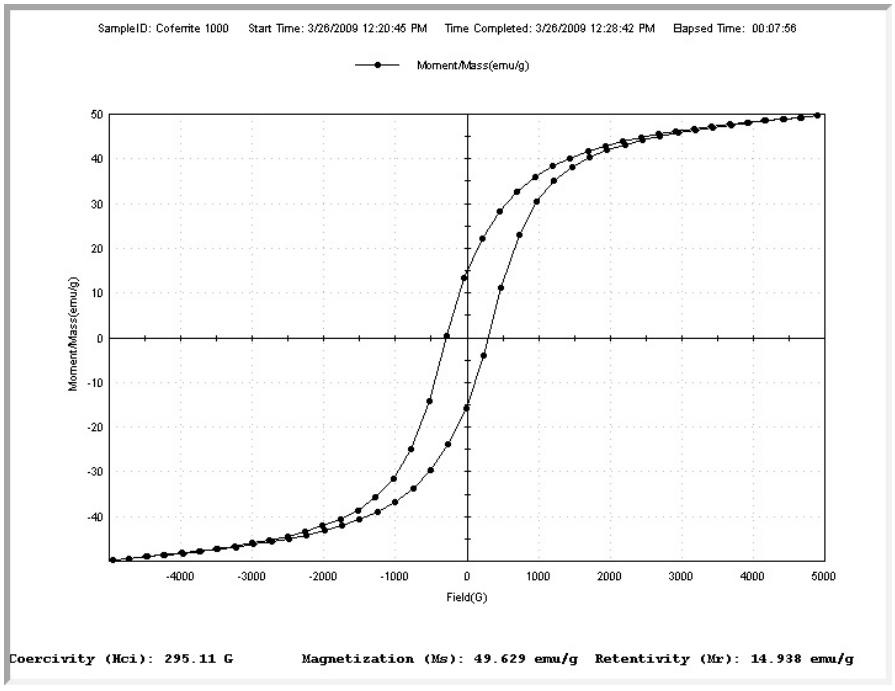


Fig. 4.6 B-H loop cobalt ferrite

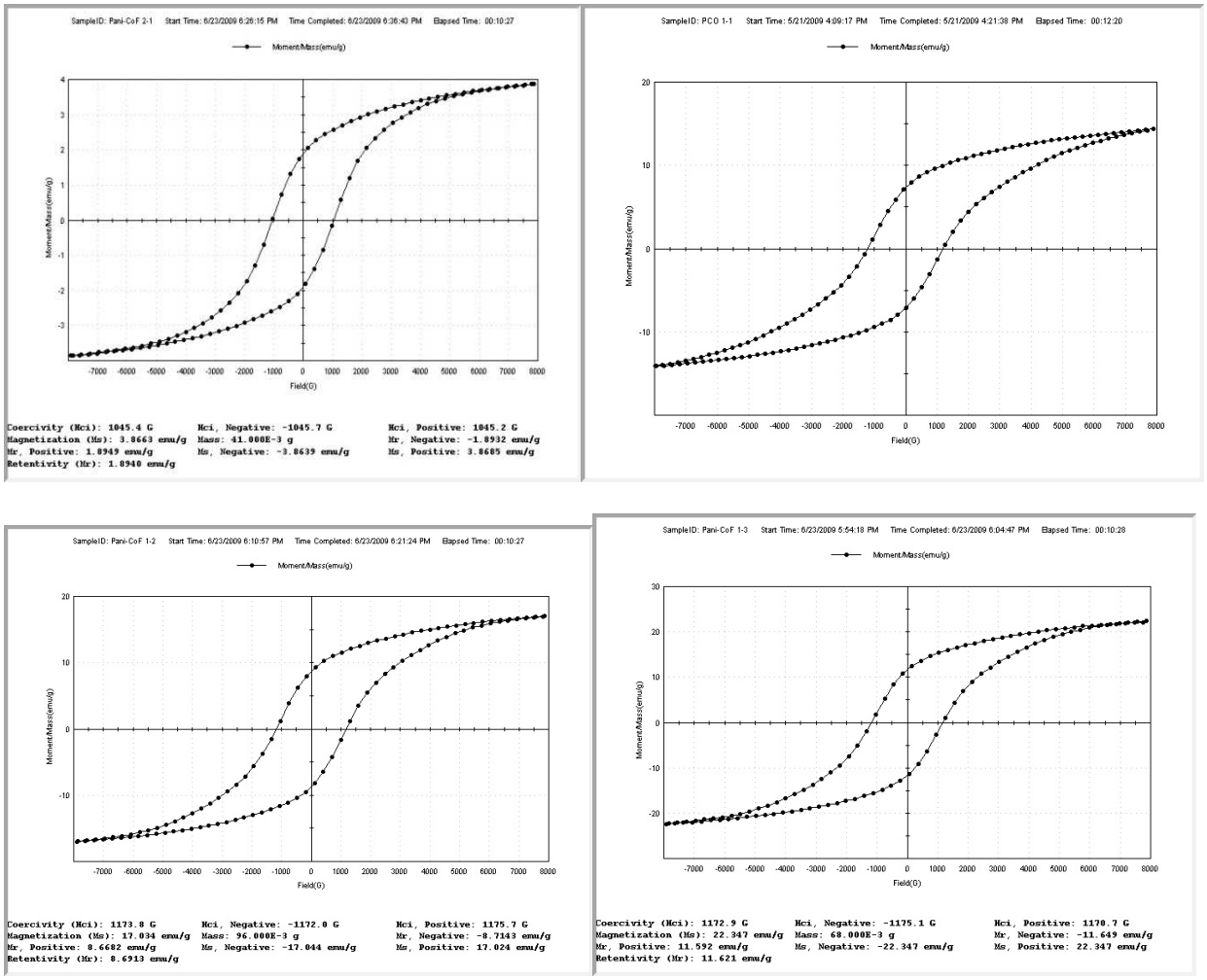


Fig. 4.7: BH loop showing saturation magnetization of Pani Cobalt ferrite nano particleswith different molar ratios PC21, PC11, PC12, PC13

4.7 Microwave Absorption Technique

The EMI shielding effectiveness (SE) of a material is defined as the ratio of transmitted power to incident power and given by

$$SE(dB) = -10\log\left(\frac{P_T}{P_O}\right) \qquad (1)$$

where P_T and P_o are the transmitted and incident electromagnetic power respectively. For a shielding material, total SE = SE_R + SE_A + SE_M, where, SE_R is due to reflection, SE_A is due to absorption and SE_M is due to multiple reflections.

In two port network, S-parameter S_{11} (S_{22}), S_{21} (S_{12}) represents the reflection and the transmission coefficients given as

$$T = \left|\frac{E_T}{E_I}\right|^2 = \left|S_{21}\right|^2 = \left|S_{12}\right|^2, \qquad (2)$$

$$R = \left|\frac{E_R}{E_I}\right|^2 = \left|S_{11}\right|^2 = \left|S_{22}\right|^2, \text{ and} \qquad (3)$$

$$\text{Absorption coefficient (A)} = 1 - R - T \qquad (4)$$

Here, it is noted that absorption coefficient is given with respect to the power of the incident EM wave. If the effect of multiple reflection [9, 10] between both interfaces of the material is negligible, the relative intensity of the effectively incident EM wave inside the materials after reflection is based on the quantity as 1-R. Therefore, the effective absorbance (A_{eff}) can be described as $A_{eff} = (1 - R - T)/(1 - R)$ with respect to the power of the effectively incident EM wave inside the shielding material. It is convenient to express the reflectance and effective

absorbance in the form of -10log (1-R) and -10log (1-A_{eff}) in decibel (dB) respectively, [33] which give SE_R and SE_A as SE_R = -10 log (1-R) and

$$SE_A = -10\log(1 - A_{eff}) = -10\log\frac{T}{1-R} \quad (5)$$

For the material the skin depth (δ) is the distance up to which the intensity the of the electromagnetic wave decrease to 1/e of its original strength. The skin depth is related with the attenuation constant (β) of the wave propagation vector $\delta = 1/\beta = \sqrt{2/\omega\mu\sigma_{ac}}$ with the approximations that σ >> ωε. As $\delta \propto \omega^{-1/2}$, therefore, at low frequencies for the electrically thin samples (d << δ) the shielding effectiveness of the sample is describe as

$$\text{SE (dB)} = 20\log\left(1 + \frac{1}{2}Z_O d\sigma\right) \quad (6)$$

where σ is the ac conductivity, Z_o is free space impedance and d is the sample thickness.

Whereas for the higher frequencies, sample thickness (electrically thick samples) is sufficiently greater than skin depth and EMI shielding effectiveness for the plane electromagnetic wave [34] is given as

$$\text{SE (dB)} = SE_R\text{ (dB)} + SE_A\text{ (dB)}, \quad (7)$$

$$SE_R(dB) \approx 10\log\left(\frac{\sigma_{AC}}{16\omega\varepsilon_o\mu_r}\right), \text{ and} \quad (8)$$

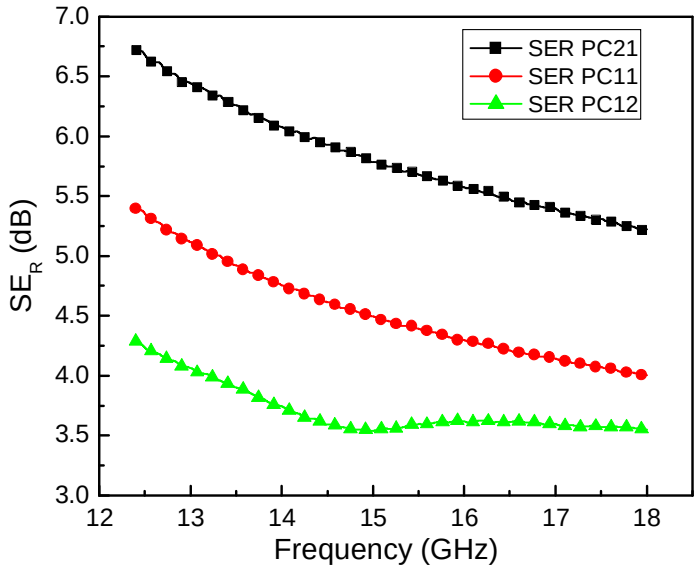
$$SE_A(dB) = 20.\frac{d}{\delta}.\log e \quad (9)$$

where σ_{AC} depends upon the dielectric properties ($\sigma_{AC} = \omega\varepsilon_0\varepsilon''$) of the material, ω is the angular frequency ($\omega=2\pi f$), ε_o is the free space permittivity and μ_r is the relative magnetic permeability of the sample. In equation (7), the first term is related to the reflection of the EM wave and contributes as the shielding effectiveness due to reflection[11,12] . The second term expresses the loss due to the absorption of the wave when it passes through the shielding material. In microwave range, the contribution of the second part becomes more as compared to the reflection term.

Figure 4.6(a) shows the variation of the SE with frequency in the 12.4-18 GHz range. It has been observed that conducting ferromagnetic composite of PC11&PC2 have shielding effectiveness (SE) mainly due to absorption. Using equation (5) the shielding effectiveness due to absorption (SE_A) was found to be 18 dB and 22dB for PC11 PC12 while the shielding effectiveness due to reflection (SE_R) was nominal and contributed very little.

The electromagnetic absorption behavior of material depends on complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$). The real (ε´) and imaginary (ε˝) part of complex permittivity vs. frequency are shown in figure 4.6(b) The real part (ε´) is mainly associated with the amount of polarization occurring in the material and the imaginary part (ε˝) is related with the dissipation of energy. In polyaniline strong polarization occurs due to the presence of polaron/bipolaron and other bound charges, which leads to high value of ε` & ε”

Figure 4.7(c) shows the variation of real part of magnetic permeability (μ´) with frequency while change in the induced magnetization with the applied field is shown in figure (4.6c)..... The PC12 nanocomposite has relative permeability value of 4.5, which decrease to 3.7



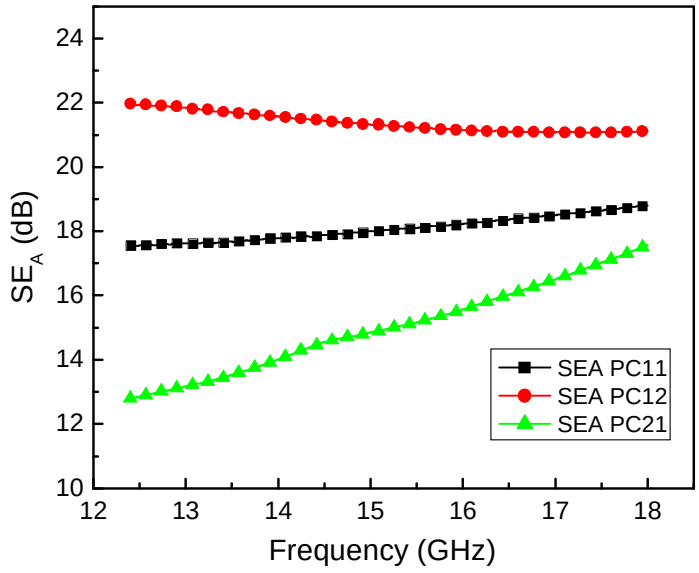


Fig : 4.8 Variation in the EMI shielding effectiveness, SE_A and SE_R of polyaniline composites having different weight ratios of cobalt ferrite:PC 11, PC21, PC12 with frequency.

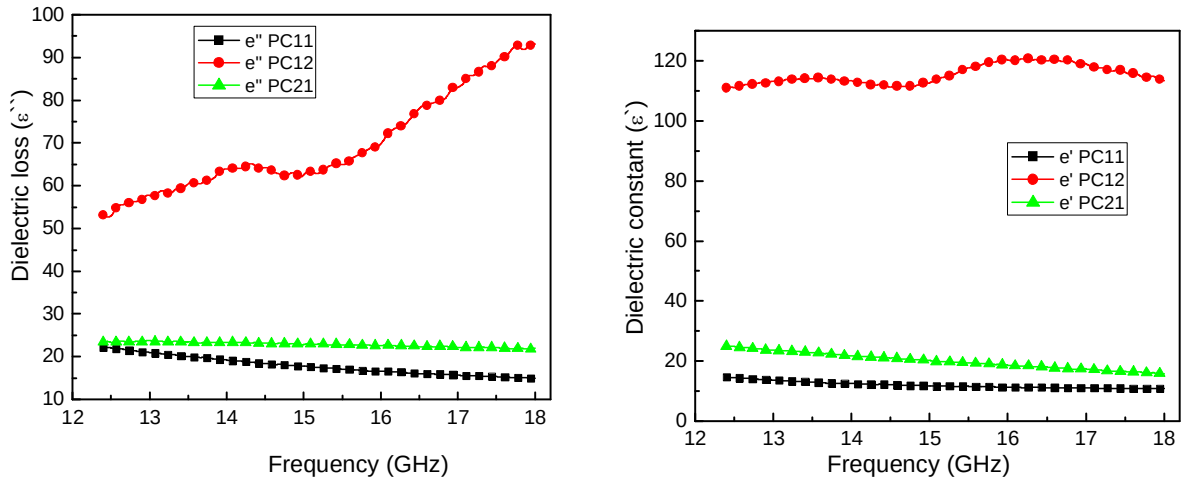
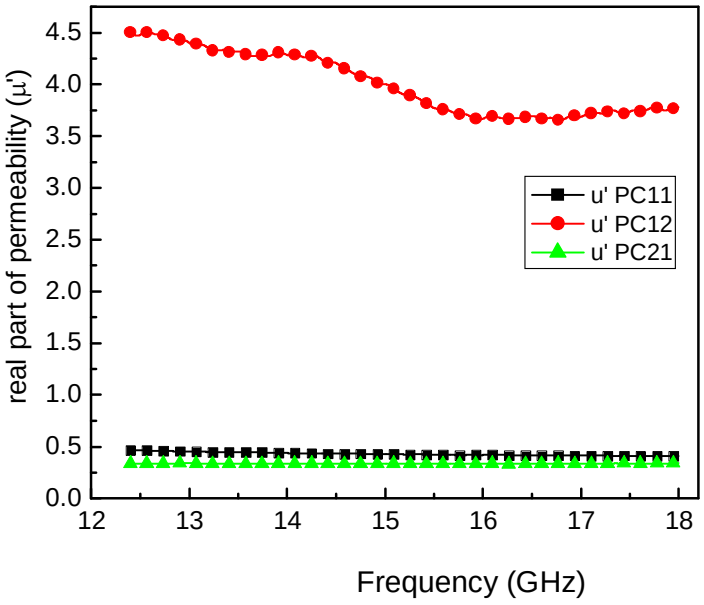


Fig. 4.9 Dielectric loss (curve a) and Dielectric constant (curve b) of pani cobalt ferrite composite (PC11), PC21, (PC12), measured in Ku band (12.4–18) GHz as a function of frequency.

The complex permittivity and permeability of the polyaniline composite (PC)with different amounts of cobalt ferrite nanoparticles were obtained from scattering parameters (*S*11 and *S*21) using Nicholson-Ross-Weir method [5,6]The real part of complex permittivity (ε') and imaginary part of complex permittivity (ε")versus frequency are shown in Fig. 4.7 (b). In all the samples, ε' is found to be decreased with an increase in frequency. First, in polyaniline strong polarization occurs due to the presence of polaron/bipolaron and other bound charges, which leads to high value of ε' and ε". With the increase in frequency, the dipoles present in the system cannot reorient themselves along with the applied electric field, as a result dielectric constant decreases. Secondly, for the magnetic nanoparticles effective anisotropy, which includes magneto crystalline anisotropy and shape anisotropy, rotation of domain may become more difficult. Furthermore, the particle size of cobalt ferrite is in the range of nanometer. The surface area, number of dangling bond atoms, and unsaturated coordination on the surface are all enhanced.

These variations lead to the interface polarization and multiple scattering, which is useful for the absorption of large number of microwaves. In polyaniline composite both the phenomenons happen together resulting in high SE_A value. The polyaniline composite PANI-Co (1:2) has

higher dielectric constant (ε'=110) and higher dielectric loss (ε"=52)and magnetic permeability (μ'=2.2), which corresponds to enhanced value of SE due to absorption.



(a)

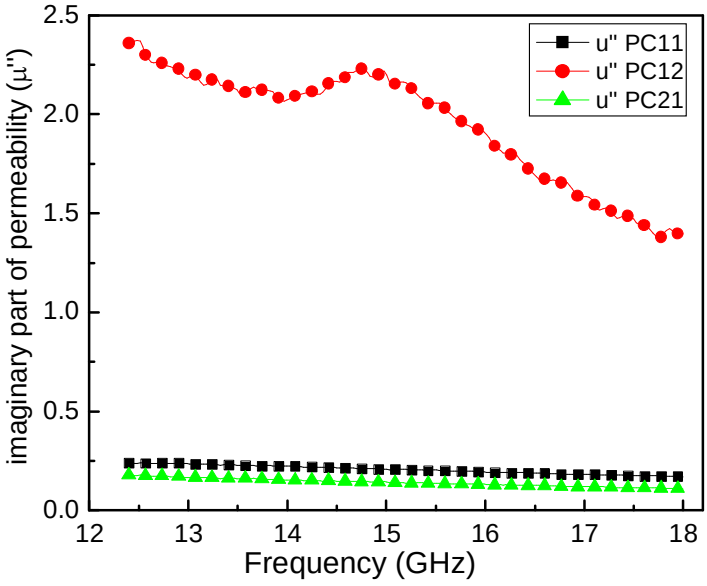


Fig.4.10: Real part of Permeability (curve a) and imaginary part of permeability (curve b) of PC11, PC21, PC12, measured in Ku band (12.4–18) GHz as a function of frequency.

4.7 CONDUCTIVITY MEASUREMENT OF PANI AND ITS COMPOSITES

The room temperature conductivity of the polyaniline composite PC11 and PC12 is found to be order of 0.2 S/cm, which shows the semiconducting behavior and found to be decreased with temperature (inset figure 4.11). In general, the dc conductivity (σdc) of conjugated polymers can be assumed to consist of three components, σ_B, σ_H and σ_T, i.e.

$$\sigma_{dc} = \sigma_B + \sigma_H + \sigma_T, \quad (1)$$

Where σ_B is conductivity due to intra-chain transport of charge carriers [8] which can be described by the band conduction mechanism and is usually observed at high temperatures. σ_H is the contribution to the total conductivity (σ_{dc}) due to inter-chain transport of charge carriers, i.e. hopping of charge carriers between the polymer chains and is observed at intermediate temperature or below room temperature. σ_T is the conductivity usually observed at low temperature and is due to thermally activated tunnelling. The macroscopic conductivity in most of the conjugated polymers is assumed to result from the hopping process except in ordered polyacetylene. In the hopping conduction process, each state can have only one charge carrier for each spin direction. In the case of strong localization, the charge carrier will hop to a nearest-neighboring state and the hopping conductivity will be proportional to Boltzmann's factor $\exp(-W/k_BT)$, where W is the difference of energy between two states and is called the hopping energy or activation energy required for a charge carrier to hop from one site to another. However, when charge carriers are not strongly localized, a charge carrier can jump to the sites for which the activation energy is small and can reside further away; then the transport occurs by VRH which follows Mott's equation

$$\sigma(T) = \sigma_O \exp\left[-\left(\frac{T_O}{T}\right)^{1/\gamma}\right] \quad (2)$$

where σ_o and T_o are constants and exponent γ is the dimensionality factor having values 2, 3, 4 for 1 dimension, 2 dimensions and 3-dimension conduction mechanism.

For 3-D conduction mechanism, the plot $\log\sigma_{dc}$ vs. $T^{-1/4}$ gives the values of Mott characteristic temperature (T_o) and σ_o (conductivity at T= ∞) as

$$T_O = 16\alpha^3 / [k_B N(E_F)] \quad (3)$$

$$\sigma_O = e^2 R^2 \nu_{ph} N(E_F) \quad (4)$$

Where $$R = [9/\{8\pi\alpha K_B T N(E_F)\}]^{1/4} \quad (5)$$

is the average hopping distance, α^{-1} is the localization length, $N(E_F)$ is the density of states at the Fermi level, and ν_{ph} is the phonon frequency (~10^{13} Hz). The average hopping energy W can be estimated by knowing the average hopping distance R and the density of states at the Fermi level $N(E_F)$ by the following relation

$W = 3/4\pi R^3 N(E_F)$. (6)

The values of various Mott's parameters T_0, $N(E_F)$, R, and W for the nanocomposite can be calculated by using the above equations(1-6). It is observed that the conductivity data fits for the 3D- VRH model [2]with γ = 4 having the linearity factor of 0.995 for PC1 and 0.995 for PC2 composite. Thus it was concluded that 3D–VRH model is suitable for explaining the conduction mechanism wherein the charge transport occurs by phonon aided hopping or by thermally stimulated jumps between the localized site. Below 70 K it was observed that conductivity data

deviate from the straight-line behavior because in low temperature region charge conduction is mainly dominated by the thermally stimulated tunneling through the localized sites. Therefore, the observed DC conductivity is contributed as the sum of hopping conduction and tunneling conduction.

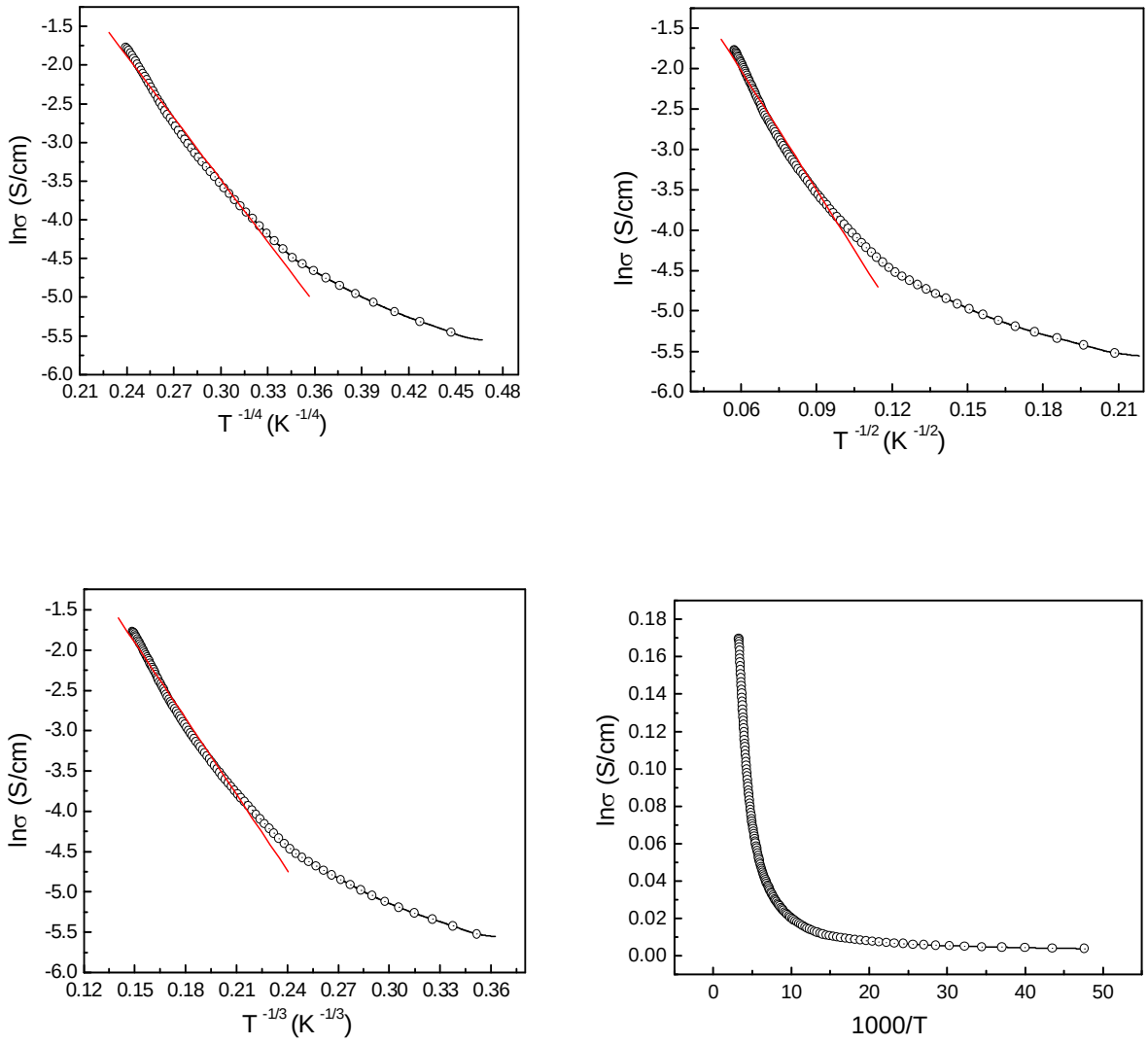


Fig4.11 Temperature dependence of conductivity of (a) PANI CoFerrite(1:1) along with temperature from 70 to 300K and

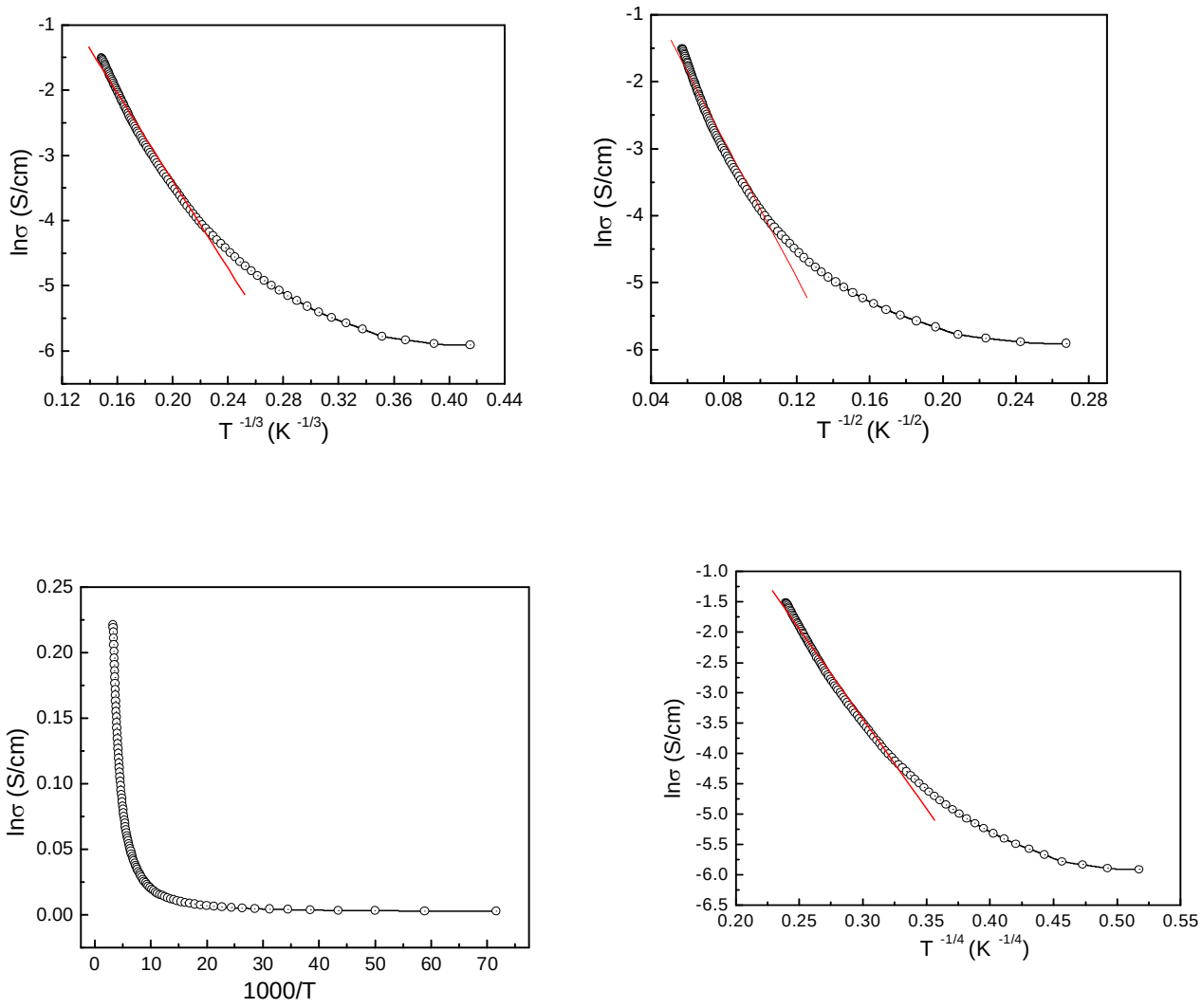


Fig 4.12 : Temperature dependence of conductivity of (a) PANI CoFerrite(1:2) along with temperature from 70 to 300K and

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Chapter 5

Conclusion and future Scope

5.1 Conclusion

The result presented in this thesis leads to following conclusion

1) The polyaniline cobalt ferrite nanocomposite were synthesis by emulsion polymerization.
2) The cobalt ferrite nanoparticle used here was synthesized by using precursor method.
3) X-ray diffraction confirmed that the average particle size of cobalt nano particle ~9 nm. The nanocomposite formation was also confirmed from X-ray diffraction.
4) FTIR studies were confirmed the characteristics peaks corresponding to polyaniline.The stretched band $–SO_3H$ suggest the nanopowder of $CoFe_2O_4$ is interacting with polyaniline. The multiple peaks in FTIR spectra at wave number below 600 cm^{-1} confirms the presence of $CoFe_2O_4$ nanopowder.
5) The UV-Visible absorption studied has shown in the shifting of the absorption maxima as compared to pristine polyaniline. This was also conformation of incorporation of Co ferrite nanoparticle in polymer matrix.
6) The saturation magnetization values were also determined for different composition. These values were stable for electromagnetic shielding application.
7) The effectiveness of electromagnetic shielding was checked by dielectric measurement in microwave region. The shielding effectiveness due to absorption and reflection was found in range (20-40 dB) and (4-6 dB) respectively.

8) The temperature dependent conductivity studies were also important for shielding application. The conductivity result revealed that the conductivity model followed by nanocomposite is VRH model.

5.2 Future Scope

The studies embedded in thesis further suggest some areas of technology and academic importance. They are as follows-

1) The investigation in the present thesis are related with microwave absorption and dc transport studies of polyaniline-CoFe composite. Similar type of properties need to be investigated for polyaniline and other soft ferrite nano composite.
2) The EMI shielding devices cover a range of frequencies in different application. Therefore polyaniline -soft ferrite nano-composite need to be investigated for effective and versatile application.

The shielding effectiveness (SE) of polyaniline - cobalt ferrite nano-composite has been found to be 22.4 dB, which is not constant with frequency. Therefore, the processability of polyaniline cobalt-ferrite nanocomposie such as multilayer, thin films etc. need to be optimized so that shielding effectiveness (SE) would become stable with frequency