Chapter 1

Introduction

Polymers and polymer based composites are playing a crucial role in the day to day life of human beings. With the advent of nanotechnology aided by the capacity to modify the electrical, mechanical and magnetic properties of polymers, polymer composites are increasingly playing a lead role in everyday life. Hence research on these materials is pursued world wide by chemists, physicists and engineers alike. One such realm where abundant amount of efforts are invested is in the area of new products based on natural and synthetic rubber. This is because of the scope for devicing new materials based on rubber and its potential to synthesise materials for various applications such as flexible magnets, microwave absorbers and magnetorheological materials. Rubber ferrite composites (RFCs) belong to this class of materials derived by the incorporation of ferrite fillers in elastomer matrices. Elastomers, which are otherwise nonmagnetic, are made into magnetic when ferrites are incorporated into it. These magnetic fillers modify the mechanical, dielectric and other physical properties of the elastomer. Significant changes in magnetic and dielectric properties are observed for ferrites when the particle size is brought down to nano metric dimensions. When ferrite nanoparticles are incorporated into rubber, tremendous improvement in physicomechanical properties of the elastomer is realised.

Magnetism and magnetic materials have profound influence on human life. Magnetic materials are employed in the development of most modern electronic devices like computer chip memories, random access memory (RAM), electromagnetic interference (EMI) shields, high density storage media, television set, cell phone, refrigerator and washing machine. So, nanoscale magnetism and magnetic materials are going to play a very dominant role in developing the technology of the 21st century.
On the other side, polymers and polymer composites have established an inevitable position in the area of material research. The presence of both natural and synthetic rubber composites in different facets of human life such as transportation, communication, development of space vehicles and satellites, as well as in other daily use materials, chairs, automobile spare parts, pipes and toys, increase the importance of these materials in material world. The useful properties of polymers and magnetic materials pave the way for their combination to produce new composite materials with improved characteristics.

The central theme of this thesis is the study on rubber ferrite composites with special reference to the effect of nano ferrites on the physicomechanical properties and on the dielectric, magnetic and microwave properties of RFCs. Therefore, a general introduction is provided in the ensuing sections about elastomers, magnetic fillers and magnetism, ferrites and rubber ferrite composites. Magnetic and dielectric properties of ferrites are mainly dependent on their crystal structure. Structure of ferrites resembles the crystal structure of MgAl₂O₄ and hence these types of ferrites are called spinel ferrites. An overview of spinel structure is also given in the forthcoming sections. Since the ferrite used for the preparation of RFCs in the present study is of nano dimension, a short note is also given about the general methods of synthesis of nano ferrites. Finally, the motivation and objectives of the present study are listed.

1.1 Elastomers

Different types of elastomers such as natural/synthetic and polar/non polar are used for the preparation of rubber ferrite composites.

1.1.1 Natural rubber

Chemically, it is cis poly-isoprene characterised with low hysteresis, high resilience and low water absorption. High tensile strength, tear strength, resilience and high elongation at break are the major attractive features of natural rubber over synthetic rubbers. Poor resistance to sunlight, oxygen and ozone are the drawbacks of natural rubber compared to some synthetic rubbers. Compared to synthetic rubbers, it is inexpensive. Synthetic rubbers have their own characteristic properties, which make them special purpose rubbers and are used for the preparation of RFCs.
1.1.2 Ethylene propylene diene rubber

Ethylene propylene diene rubber (EPDM) is one of the most widely used synthetic elastomers, having both special and general-purpose applications. It is a copolymer of ethylene and propylene with a few percent of a third monomer namely a diene. The termonomer can introduce unsaturation to the otherwise saturated polymer. The commonly employed comonomers for introducing unsaturation are,

![Dicyclopentadiene (DCPD)](image)

![Ethylidene norbornene (ENB)](image)

1,4 Hexadiene

The structure of EPDM with ENB as the third monomer is given in figure 1.1. Ethylene propylene diene terpolymer vulcanisate has been used extensively in high frequency power cables, automotive radiator hose and white side walls of tyres because of the exceptional capability to accept high loading of fillers and their
excellent ozone, heat and weathering resistance [1-4]. EPDM vulcanisates exhibit excellent electrical and mechanical properties when properly formulated [5].

![Figure 1.1 Structure of EPDM with ENB as the third monomer](image)

**Figure 1.1 Structure of EPDM with ENB as the third monomer**

EPDM has found wide acceptance in wire and cable applications. Unsaturation in the side chain renders it ozone resistant. It is also resistant to heat, cold and moisture.

EPDM rubber can be vulcanised using either sulphur or peroxide as the crosslinking agent. Peroxide cure gives better heat and ageing properties and low compression set and better electrical properties. A number of factors such as the ethylene/propylene ratio, nature and amount of the termonomer used, molecular weight distribution, peroxide used and the type of fillers, influence the efficiency of peroxide curing of EPDM [6,7]. The crosslink provided by peroxide vulcanisation is a carbon–carbon bond which is similar in strength to every other bond in the polymer back bone. Thus peroxide cured EPDM vulcanisate exhibits better compression set resistance and resistance to heat and chemical attack compared to sulphur cured vulcanisate. Moisture uptake and staining are less for the finished product prepared by peroxide curing [8]. In the present study, EPDM based RFCs are prepared by peroxide vulcanisation.

1.1.3 Chloroprene rubber

Polychloroprene (CR), commercially known as neoprene is one of the widely used synthetic rubbers with excellent heat, chemical and medium oil resistance [9]. Chloroprene monomer is used for the preparation of neoprene and structure of neoprene is given in figure 1.2. There are three general purpose neoprene rubber, G, W, and T types. Within each type, a number of grades of polymers are available with
v exposition of varying mooney viscosity, rate of crystallisation and other features. W type CR has excellent raw polymer stability and better heat resistance. Their broad molecular weight distribution imparts better processability [10]. CR has good flame resistance, weather and ozone resistance. Because of its crystallising nature, neoprene gum vulcanisate has inherent high tensile strength, elongation at break and wear resistance.

![Figure 1.2 Structure of chloroprene rubber](image)

Chloroprene rubbers are generally vulcanised by the action of metal oxides [11-13]. The primary crosslinking agent is zinc oxide, which is used along with magnesium oxide. Lead oxide is also used where high water resistance is required.

1.2 Magnetic fillers

Magnetism has fascinated humans for thousands of years. Nano scale magnetic materials are increasingly used in diverse fields of applications. Synthesis of magnetic materials with nano metric dimension helps in designing newer materials with novel chemical, magnetic and electrical properties. Different types of magnetic materials such as ferrites can be used for the preparation of magnetic composites. Since the central theme of this thesis is magnetic nanocomposites based on ferrites and rubbers, an introduction to different types of magnetism is provided below. Magnetic materials are classified into different types based on their response to an external magnetic field.

1.2.1 Magnetism

Magnetism is a result of moving charges. From an atomic view of matter, there are two electronic motions: orbital and spin motion of electrons. These two electronic motions are the source of macroscopic magnetic phenomena exhibited by materials. Magnetic moment per unit volume or magnetisation M of a substance and the magnetic flux density is related by the equation
Chapter 1

\[ B = \mu_0 (M + H) \]  \hspace{1cm} 1.1

where \( H \) is the applied field and \( \mu_0 \) is the magnetic permeability of free space. The ratio

\[ \frac{B}{H} = \mu \]  \hspace{1cm} 1.2

is called absolute permeability and

\[ \frac{M}{H} = \chi \]  \hspace{1cm} 1.3

is called absolute susceptibility. \( \mu \) and \( \chi \) are related by the expression

\[ \mu = \mu_0 (1 + \chi) \]  \hspace{1cm} 1.4

The magnetic susceptibility \( \chi \) is a useful property for characterising magnetic materials.

Magnetism exhibited by different materials can be classified into five, depending upon the value of \( \chi \) and the response of the materials towards an external field [14-19].

1.2.1.1 Diamagnetism

Diamagnetism occurs when the induced magnetic field opposes the external applied magnetic field. In diamagnetic materials, the constituent atoms or molecules have their electrons paired up in so as to cancel the magnetic dipole moments. In a diamagnetic material, the presence of an external magnetic field induces a change in the magnitude of inner atomic currents. An applied external magnetic field accelerates or decelerates the orbiting electrons, such that their magnetic moment is in the opposite direction from the external field. The response of the orbiting valence electrons counteracts the external field and thus shields the inner electrons from an external magnetic field. For a diamagnetic material, \( H = -4\pi M \), where \( H \) is the external magnetic field applied and \( M \) is the magnetisation of the material in the presence of the external field \( H \).

The atomic/magnetic behaviour of diamagnetic materials is as shown in figure 1.3.
1.2.1.2 Paramagnetism

Paramagnetic substances are characterised by their intrinsic permanent magnetic moments. Atoms or ions with one or more unpaired electrons exhibit paramagnetism. An external magnetic field tries to turn the unfavourably oriented spin moments in the direction of the external field. This results in an overall magnetic moment that adds to the external magnetic field. The atomic/magnetic behaviour of paramagnetic materials is represented in figure 1.4. Paramagnetic susceptibility is independent of the applied field and is temperature dependent. Curie’s law governs the temperature dependence of paramagnetic material. The magnetic susceptibility $\chi$ is related to the temperature in degree absolute by the equation $\chi = \frac{C}{T}$. $\chi$ is small and positive for paramagnetic substances. In materials obeying Curie’s law, magnetic moments are localised at the atomic or ionic sites. There is no interaction between neighbouring magnetic moments.

Paramagnetism is usually exhibited by transition or rare earth metal compounds that possess unpaired electrons and it is known as spin paramagnetism. In most of the solids, spin paramagnetism is observed. In crystals, the electron orbits are essentially coupled to the lattice, which prevents the orbital magnetic moments from turning into the field direction. Under such circumstances the orbital moments are said to be quenched. Exceptions to this are the rare earth elements and their derivatives with unpaired electrons in the deep lying ‘4f orbitals’. As the outer electrons from the crystalline field of neighbouring ions shield these electrons, the orbital magnetic
moments of the f electrons may turn into the external field direction and contribute to electron-orbit paramagnetism. The fraction of the total magnetic moment due to the orbital motion to that of the spin motion is defined as the g-factor, which is given by the expression

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

where $J$ is the total angular momentum, $S$ is the total spin angular momentum and $L$ is the total orbital angular momentum.

**Figure 1.4 Atomic/magnetic behaviour of paramagnetic materials**

1.2.1.3 Ferromagnetism

A ferromagnetic substance has a net magnetic moment even in the absence of an external magnetic field. Like paramagnetism, ferromagnetism involves the magnetic dipoles associated with the spins of the unpaired electrons. The interaction between nearby dipoles differentiates ferromagnetism from paramagnetism. If the many individual magnetic dipoles produced in a material are appreciable, there can be long range interactions. This leads to large scale areas of magnetism called domains. In ferromagnetic materials, the dipoles within a domain are all aligned and the domains tend to align with an applied field. The atomic/magnetic behaviour of ferromagnetic materials is represented in figure 1.5.
A characteristic feature of a ferromagnetic substance is the magnetic hysteresis. The energy expended in reorienting the domains from the magnetised state back to the demagnetised state manifests into a lag in response to an applied magnetic field, known as hysteresis. Another important property of ferromagnets is the Curie temperature. For ferromagnetic materials, susceptibility $\chi$ is large and positive and varies with the absolute temperature. They obey the Curie-Weiss law, $\chi = C/(T-\theta)$, where $C$ and $\theta$ are Curie Weiss constants. Above Curie temperature, ferromagnets become paramagnets, since there is sufficient thermal energy to destroy the interaction between atoms that create domain. Iron, cobalt and nickel are examples of ferromagnetic materials. Gadollinium (Gd) which belongs to the rare earth family also exhibit ferromagnetism. The curie temperature of Gd is 295 K. Chromium oxide is another example of a ferromagnet.

1.2.1.4 Antiferromagnetism

In an antiferromagnet, exchange coupling exists between neighbouring moments that causes the moments to align in an antiparallel fashion. This anti parallel alignment causes the system to have a small positive susceptibility, because an applied magnetic field tends to align the spins and this induced alignment is larger than the diamagnetism of the electron orbital. Figure 1.6 shows the atomic/magnetic behaviour of antiferromagnetic materials. Similar to ferromagnets, the exchange energy can be defeated at high temperatures and then the system becomes paramagnetic. The temperature above which a ferromagnetic substance becomes paramagnetic is known
as Neel temperature \( T_N \). For temperatures greater than \( T_N \), the susceptibility of a ferromagnetic substance follows a paramagnetic Curie-Weiss law with a negative \( \theta \), \( \chi = \frac{C}{(T+\theta)} \). Most antiferromagnetics are found among ionic compounds such as metallic oxides, sulfides and chlorides. Oxides of manganese and chromium are some other examples of antiferromagnetic substances.

\[ \text{Figure 1.6 Atomic/magnetic behaviour of antiferromagnetic materials} \]

1.2.1.5 Ferrimagnetism

Ferrimagnetism is observed in compounds which exhibit complex crystal structures. Within these materials, the exchange interactions lead to parallel alignment of atoms in some of the crystal sites and anti-parallel alignment in the other sites. The material breaks down into magnetic domains, just like in a ferromagnetic material. The magnetic behaviour is very similar, although ferrimagnetic materials usually have lower saturation magnetisation. Ferrimagnets are similar to antiferromagnets in which the opposing dipoles are not equal, so they do not cancel out. Therefore, these materials exhibit a spontaneous magnetic moment and display hysteresis below Curie temperature. Ferrimagnets are generally ceramic materials and they are good insulators, making them very useful in preventing energy losses due to eddy currents in transformers. Ferrites are typical examples of ferrimagnets and naturally occurring magnetite and maghemite are examples of ferrimagnetic materials. The atomic/magnetic behaviour of ferrimagnetic materials is depicted in figure 1.7.
1.2.2 Nano scale magnetism

Nanomaterials exhibit altogether different electrical, magnetic, optical, electrochemical, catalytic, structural and mechanical properties with respect to their coarser sized cousins. Nano magnetic materials display unusual properties like superparamagnetism, single domain behaviour and spin glass phenomenon. Nano scale magnetism is fascinating because of their tremendous potential in finding technological applications. The unusual behaviour exhibited by nanoparticles is mainly due to two major reasons, finite size effects [20] and surface effects [21,22]. For magnetic particles, the latter is more significant since the ratio of surface atoms to bulk atoms is sufficiently high.

Nano magnetic particles are characterised by enhanced magnetic moments [23], exchanged coupled dynamics [24], quantisation of spin waves [25,26] and giant magnetoresistance [27]. These new properties can lead to potential applications in permanent magnets, data storage devices [28], new magnetic refrigeration systems [29], enhancing agents for magnetic resonance imaging, catalysis and targeted drug delivery systems.

Nano magnetic materials also exhibit interesting magneto-optical properties such as large Faraday rotation and Kerr rotation and they are potential materials for many magneto-optical applications.

Key features such as single domain particles and superparamagnetism dominate the magnetism of small ferromagnetic particles. For single domain particles,
magnetisation reversal takes place through spin rotation where as in other cases, it occurs due to the spin wall movement. Greater energy is required for spin rotation resulting in higher coercivity for single domain system [30].

1.2.3 General methods employed for the synthesis of nanomaterials

The primary step in any investigation in material science is the preparation and characterisation of materials. Any suitable method can be adopted for the preparation of micron sized particles. However, the preparation of nanoparticles requires some special methods that may be unique with respect to a particular material. There are mainly two approaches for the synthesis of nanomaterials viz. bottom up and top down approach.

In the bottom up approach, nanostructures are created, atom by atom or by assembly of components consisting of a few thousand atoms or molecules. Processes such as self organisation, self assembly or templating can be used to build a multitude of nano architectures. Examples for bottom up approach are vapour phase processing like physical and chemical vapour deposition, inert gas condensation and sputtering. Chemical synthesis like sol-gel method, precipitation method and electrochemical synthesis are based on bottom up principle.

Top down approach involves the use of conventional bulk starting materials that include solid state processing like mechanical attrition, severe plastic deformation, crystallisation of amorphous precursors and liquid-phase processing. High energy ball milling (HEBM) is employed for attrition which can impart high momentum to the milled powder through the high speed of rotation and revolution of the vials which helps in obtaining high efficiency in low milling times.

Between the two methods, bottom up process is more advantageous. Surface imperfections and strain will be less in bottom up process as it involves the formation of nano structured materials via atom by atom growth. Careful control of the preparative conditions in bottom up process ensures systematic tuning of the grain size and other characteristics of the nanoparticles. Nanomaterials produced by these methods mostly require further processing, sintering or thermal spraying to produce useful structural materials.
Several physical aerosol methods have been reported for the synthesis of nano size particles of ceramic materials. These include gas condensation techniques [31,32], spray pyrolysis [33-35] and thermochemical decomposition of metal-organic precursors in flame reactors [36,37]. On the other hand, most widely used liquid phase chemical method is sol-gel method [38,39]. Other wet chemical methods, including microemulsion [40,41] and co-precipitation have also been widely used [42].

1.2.3.1 Vapour condensation method

In this method, a super saturated vapour of the metal is condensed under inert convection of gas inside a chamber. A high pressure of inert gas is usually needed to achieve super saturation. Frequent collision with the gas atom decreases the diffusion rate of atoms from the vapour source region and cools the atoms. The powder is oxidised by allowing oxygen into the chamber. This post oxidation must be carried out slowly. Due to the highly exothermic reaction, particles heat up for short times to temperature as high as 1000°C resulting in their agglomeration into large particles by rapid diffusion processes. A subsequent annealing process at higher temperature is often required to complete the oxidation.

Advantages of this method over other techniques are versatility, ease of performance and analysis and production of high-purity products. This method is also employed to produce films and coatings. The disadvantages are high production cost and low yield. Heating techniques have other disadvantages like the possibility of reaction between the metal vapors and the heat source materials. This method can not be used to prepare a wide variety of materials as the operating temperatures are limited by the choice of the source material.

1.2.3.2 Spray pyrolysis

In this method, precipitation from a concentrated solution of cations can be performed by solvent evaporation. The starting precursor for this method is sol or suspension of appropriate salts. From this, aerosol droplets are prepared by nebulisation or atomisation of the starting sol at high pressure. The solvent is rapidly evaporated by an upward stream of hot gas. The microporous particles thus produced are compacted and calcined to produce the ceramic powders.
Advantages of this method include the formation of high purity and homogeneous products with nano metric dimensions. Since each particle/droplet undergo the same reaction conditions, no subsequent milling is necessary. Major disadvantages of this process are the requirement of large amount of solvents and difficulty in scaling up of the process. Use of nonaqueous solvents increases the cost of production, so this process is limited to the aqueous systems.

1.2.3.3 Thermochemical/flame decomposition of metal organic precursors

This is an effective method for the preparation of ceramic nanoparticles. This process is also referred to as chemical vapor condensation (CVC). The starting materials are liquid chemical precursors which are vapourised and then oxidised in a combustion process using a fuel oxidant mixture. The process involves the rapid thermal decomposition of a precursor carrier gas stream at reduced pressures with simultaneous decomposition of the condensed product particles on substrates. Organometallic based synthesis, carried out at high temperatures, facilitates the removal of crystalline defect and results in high quality magnetic nanoparticles.

1.2.3.4 Reverse microemulsion method

This is one of the promising methods for the preparation of nano crystalline materials. In this method, micelles are formed by adding surfactants, dissolved in organic solvents to the aqueous solution of reactive precursors. Nanoparticle synthesis inside the micelles can be achieved by hydrolysis of reactive precursors or by precipitation reactions of metal salts. Solvent removal and subsequent calcination lead to the final product. The final properties of the product such as particle size, particle size distribution, agglomeration and final phase formation of the ceramics are affected by several parameters such as the concentration of the reactive precursor in the micelle and mass percentage of the aqueous phase in microemulsion. Microemulsion techniques are often carried out at low temperatures but with the disadvantage that the particles are less crystalline and more polydispersed.

1.2.3.5 Sol-gel method

Sol-gel method is widely used for the preparation of a large number of inorganic and inorganic/organic composite materials. The process involves the
preparation of a sol and typically used for the preparation of metal oxide via the hydrolysis of reactive metal precursors. The sol of the metal salt is prepared by mixing concentrated solutions containing the cations of interest, with an organic solvent (usually alcohol) as the dispersion medium. The solution is then destabilised by adding water. The presence of water modifies the pH of the sol and reduces the repulsion between particles. This results in a large increase in the viscosity of the system, leading to the formation of a gel.

Addition of water to alcoholic solution of alkoxide results in the formation of corresponding hydroxide. Condensation of hydroxide molecules by elimination of water leads to the formation of a network of metal hydroxide. When all hydroxide species are linked in one network structure, gelation is achieved and a dense porous gel is obtained. The gel is a polymer of three dimensional skeleton surrounding interconnected pores. Removal of the solvents and appropriate drying of the gel results in an ultrafine powder of the metal hydroxide. Further heat treatment of the hydroxide leads to the corresponding ultrafine powder of the metal oxide.

Solvent removal from the gel is achieved by two ways. Drying is achieved by evaporation under normal conditions and the gel network shrinks as a result of capillary pressure and the hydroxide obtained is known as xerogel. Aerogels are obtained when drying is being done using a high pressure autoclave at temperatures higher than the critical temperature of solvents. Aerogel powders have higher porosities and larger surface areas than analogous xerogel powders [19].

1.2.4 Application of magnetic materials

It is well known that magnetism and magnetic materials have unprecedented role in data storage and magnetic recording. A novel substitute for the conventional magnetic materials in these fields is magnetic nano wires. For long term storage, magnetic materials should have a reasonably high coercivity, because external magnetic fields should not alter the magnetisation. At the same time it should not be too large if the medium is to be reusable. Ferromagnetic nano wires encapsulated within carbon nano tubes provide an ideal system for recording. Small size anisotropy and the single isolated domain nature of the encapsulated iron crystals provide higher coercivity. Due to the graphite protecting cover, the magnetic properties of entrapped
nano wires do not degrade with time [43,44]. Magnetic nanocomposites should also find applications in the fabrication of fine particle magnets, for use in magnetic inks and as toners in xerography.

Magnetoeleastic materials are another class of technologically important magnetic materials. These materials give the possibility of converting very small mechanical stress into electrical voltage. Magnetic devices for detecting parked vehicles are developed based on the principle of magnetoeleastic resonance. Coding devices are developed based on magnetoeleastic resonators which rely on the variation of the Youngs modulus with the bias field [45]. Frequency dependence of permeability of the nanocrystalline ribbons have been made use in devices such as current-compensated chokes, saturable reactors and inverter transformers for integrated services digital network (ISDN) telecommunications [46].

Magnetorheological elastomers composed of ferromagnetic particles dispersed in a non-ferromagnetic elastomer matrix susceptible to elastic deformations constitute a very interesting group of magnetic materials [47]. Magnetorheological elastomers are used for the production of controlled vibration dampers [48].

Superparamagnetism is a unique feature of magnetic nanoparticles and is crucially related to many modern technologies like ferrofluid technology [49], magnetocaloric refrigeration [50] magnetic resonance imaging (MRI) [51] and magnetically guided drug delivery. Ferrofluids are stable suspensions of nano magnetic particles in a suitable base fluid like oil or water. They are of great research interest because of their numerous physical, engineering and medical applications. These smart fluids show many interesting magneto-optical properties. Some of the engineering applications of these rheological fluids are in making rotary seals, pressure sensors and loud speakers. Ferrofluids can serve as contaminant exclusion seals, vacuum seals and dampers in stopper motors. With improvement in performance and production cost, nano ferrofluids may find applications as cooling fluids, nano scale bearings and in magnetically controlled heat conductivity [52]. They are also widely used in bio medical fields especially in cancer therapy [53].

Tumor specific nanocomposites are developed and the technique is named as magnetic hyperthermia. Magnetic nanoparticles are specifically attached to the cancer
cells and under the application of an ac electric field, the particles become selectively heated, damaging (hyperthermia) or destroying (thermoablation) the attached tumor cell. This method has immediate effect without any side effects. Magnetic nanoparticles can also be used for controlled drug delivery at a predetermined site within the body [54-56].

Ferromagnetic semiconductors are obtained by doping magnetic impurities in host semiconductors. They are key materials for spin electronics (spintronics) in which the correlation between the charge and spin of electron is used to bring about spin dependant electronic functionality such as giant magneto resistance (GMR) and spin field effect.

Magnetic particles coated with protective and functional materials such as silica can easily be prepared by sol-gel method or liquid phase coating process [57]. Magnetic particles embedded in polymer matrices have been synthesised for the fabrication of conductive, superparamagnetic plastic films [58-63]. Deposition of conductive polymer chains and magnetic nanoparticles in a layer by layer fashion may lead to new properties such as GMR and novel organic based nano structured GMR materials. Other than serving as a lossless transformer, the nano magnets can act as miniature switches or sensors. Polymer based nanocomposites can be used as a dielectric layer in electronic packing applications.

A new class of flexible magnetic composites can be prepared by incorporating ferrite materials into elastomer medium which are named as rubber ferrite composites. Rubber ferrite composites find applications in many devices because of their easy mouldability and microwave absorbing properties [64,65].

1.3 Ferrites

Ferrites are mixed metal oxides with Iron (111) oxides as their main component. Based on their crystal structures, ferrites are classified into three types namely spinels, garnets and magnetoplumbites. They are shown in table 1.1.

Simplest among the ferrites are the spinel ferrites. The structure of ferrites resembles that of the mineral spinel MgAl$_2$O$_4$. Spinel ferrites can again be categorised into two namely normal and inverse spinels. The unit cell of a spinel structure consists


Table 1.1 Different types of ferrites

<table>
<thead>
<tr>
<th>Type</th>
<th>General formula</th>
<th>Structure</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel</td>
<td>$M^{II}\text{Fe}_2\text{O}_4$</td>
<td>Cubic</td>
<td>$M^{II} = \text{Cd, Co, Mg, Mg,}$</td>
</tr>
<tr>
<td>Garnet</td>
<td>$\text{Ln}^{II}_3\text{Fe}<em>2\text{O}</em>{12}$</td>
<td>Cubic</td>
<td>$\text{Ln}^{II} = \text{Y, Sm, Eu,}$</td>
</tr>
<tr>
<td>Magnetoplumbite</td>
<td>$M^{III}\text{Fe}<em>{12}\text{O}</em>{19}$</td>
<td>Hexagonal</td>
<td>$\text{BaFe}<em>{12}\text{O}</em>{19}$</td>
</tr>
</tbody>
</table>

of eight formula units ($8\times\text{MFe}_2\text{O}_4$). The 32 oxygen ions form a face centered cubic lattice in which two kinds of interstitial sites are present, namely tetrahedral sites (A sites) and octahedral sites (B sites) (figure 1.8).

![Figure 1.8 Crystal structure of a cubic ferrite](image)

The interesting and useful electrical and magnetic properties of the spinel ferrites are governed by the distribution of the iron and the divalent metal ions among the tetrahedral and octahedral sites of the spinel lattice. Generally a spinel ferrite can be represented by the formula $M_5^{2+}\text{Fe}^{3+}_{1-\delta}[M_{1-\delta}^{2+}\text{Fe}^{3+}_{1+\delta}]\text{O}_4$ [66]. Ions within the square bracket represent octahedral sites and ions outside the bracket represent tetrahedral sites. The limiting case where $\delta = 1$ is called normal spinel and $\delta = 0$ is called inverse spinel.
Site preference of the cations between the octahedral site and tetrahedral site are explained using crystal field theory by Dunitz and Orgel [67] and also by McClure [68] where as Blasse [69] has used a simplified molecular orbital approach. According to the crystal field theory, the five degenerate 3d orbitals in an octahedral field are split into a lower triplet ($t_{2g}$) and higher doublet ($e_{2g}$). These two levels are separated by an energy difference of 10 Dq. This splitting of orbitals is reversed when the cations occupy a tetrahedral site. In this case, $e_{2g}$ orbitals become lower and $t_{2g}$ orbitals become higher energy levels. Thus, the crystal field stabilisation energy of a cation will be different in both tetrahedral and octahedral coordination. This determines the cation distribution in ferrites [70].

In the case of NiFe$_2$O$_4$, Ni$^{2+}$ ion with d$^8$ configuration contains two unpaired electrons irrespective of the A or B site. But crystal field stabilisation energy is more in B site, hence preferably occupies octahedral site, thus forming an inverse spinel structure. In addition to simple binary spinels, a number of mixed ferrites are also possible by partial substitution of cations, either in A or B site. As the properties of mixed ferrites are highly dependant on the composition, ferrites with predetermined material characteristics can be designed by properly adjusting the composition. A large number of mixed ferrites are studied and reported, among this the extensively studied one is Ni-Zn ferrite.

In addition to the above mentioned forms, some ferrites exhibit distorted spinel structures. Examples are magnetite (Fe$_3$O$_4$) and maghemite ($\gamma$-Fe$_2$O$_3$). $\gamma$-Fe$_2$O$_3$ has a cation deficient spinel structure with a fraction of octahedral sites occupied by vacancies at all temperatures.

1.3.1 Magnetic properties of ferrites

Ferrites are important ferrimagnetic materials. In ferrites, the metallic ions occupy two crystallographic sites; octahedral sites and tetrahedral sites. Three kinds of magnetic interactions are possible between the metallic ions, through the intermediate O$^{2-}$ ions, by super exchange mechanisms namely A-A, B-B and A-B interactions. These interaction energies are negative and induce an anti parallel orientation (as proposed by Neel in 1948). In ferrites, A-B interaction predominates. Thus spins of A
site and B site ions in ferrite are oppositely magnetised with a resultant magnetic moment equal to the difference between those of A and B site ions.

Ferrites such as MnFe$_2$O$_4$, NiFe$_2$O$_4$, FeFe$_2$O$_3$ and CoFe$_2$O$_4$ have high curie temperatures and have reasonable saturation magnetisations in agreement with Neels theory. In these ferrites, Fe$^{3+}$ ions are found in equal numbers on A and B sites. Hence, saturation magnetic moment should correspond to that of the metallic ion. In NiFe$_2$O$_4$, the net magnetisation is 2 $\mu_B$ magneton as shown below, consistent with Neel’s two sublattice theory.

\[
\begin{array}{c|c|c|c|}
A site & B site & \\
8Fe^{3+} & 8Fe^{2+} & 8Ni^{2+} \\
\uparrow\uparrow\uparrow\uparrow\uparrow & \downarrow\downarrow\downarrow\downarrow & \\
\end{array}
\]

Thus the magnetic properties of ferrites can be tuned by distributing different cations in A and B sites and is highly significant for mixed ferrites.

### 1.3.2 Electrical properties of ferrites

Ferrites are considered as magnetic semiconductors and the conductivity can be attributed to the presence of Fe$^{2+}$ and M$^{3+}$ ions. The presence of Fe$^{2+}$ results in n-type behaviour and presence of M$^{3+}$ results in p-type behaviour. Conduction process is due to the hopping of extra electrons (from Fe$^{2+}$) or the positive hole (M$^{3+}$) through the crystal lattice.

Temperature dependence of the electrical conductivity is given by the relationship $\sigma = \sigma_0 e^{-E_a/kT}$ where $E_a$ is the activation energy for conduction, which is the energy required for hopping of the electron or hole and $\sigma_0$ is a constant. k is the Boltzmann constant and T is the temperature in Kelvin. Conduction mechanism in ferrites is entirely different from that of the conventional semi conductors where in charge carriers occupy states in wide energy band. The charge carriers in ferrites are localised at the magnetic atoms. Temperature dependence of electrical conductivity of ferrites is mainly due to the variation in mobility of the charge carriers where as the concentration of charge carrier is almost temperature independent.
Dielectric properties of ferrites depend on several factors including the method of preparation, chemical composition and grain structure and size. Dielectric properties of solids can be explained based on phenomenon like polarisation. In polycrystalline ferrites, three principle mechanisms of polarisation exist within a frequency spectrum extending from zero frequency to frequencies corresponding to ultra violet radiations. The electronic contribution arises from the displacement of electron shell relative to the nucleus. Ionic polarisation comes from the displacement of charged ion with respect to other ions and dipolar polarisation due to the orientation of electric dipole in an external field. In addition to this, in heterogeneous materials interfacial polarisation occurs due to the accumulation of charges at structural interfaces. Frequency dependence on the polarisability due to several contributions is represented in figure 1.9.

1.3.3 Different methods for the preparation of ferrites

A number of chemical methods such as micro emulsion or reverse micelle method, co-precipitation method, sol-gel method and synthesis from different organic precursors are reported for the preparation of nano ferrites.

1.3.3.1 Ceramic method

This is one of the earliest and most popular methods used for the synthesis of ferrite materials. The particle size of the materials prepared by this method is often found to be of micrometric dimension. Required precursors are mixed in appropriate
molar ratio and sintered at very high temperature which results in the formation of crystalline materials [71-74].

The disadvantage of ceramic method is that it is highly difficult to control the stoichiometric composition and final structure. Since this technique requires prolonged heating at very high temperatures, some of the constituents may evaporate thereby resulting in alteration of the desired stoichiometry [75].

1.3.3.2 Co-precipitation method

In cold co-precipitation method, the precursors are taken in the appropriate molar ratio in an aqueous medium at an appropriate pH and temperature. The precipitate is then heated at high temperatures to obtain crystalline ferrite materials [76].

Nano crystalline ferrite materials can successfully be prepared from different organic precursors. Citrate and oxalate precursors are used for the synthesis of ferrite nanoparticle. This solution method allows the atomic scale mixing of the constituent cations and allows the formation of ferrite particles at low temperatures [77,78]. C. Caizer and M. Stefanescu had reported the preparation of Ni-Zn ferrite powder from the glyoxylate precursor. It is practically a low temperature method. The reaction efficiency is nearly 100% and high purity products are formed [79].

1.3.3.3 Sol-gel technique

This is one of the easiest routes for the synthesis of nanomaterials [80-82]. In this method, reactants, preferably, metal nitrates or acetates are completely dissolved in a suitable organic solvent and the solution is allowed to react at low temperature until a gel is formed. The gel is then heated at high temperature to obtain the desired final product. The detailed mechanism and sol-gel chemistry is provided in section 1.2.3.5.

1.3.3.4 High energy ball milling

In this method, mechanical energy is utilised for the synthesis of nanoparticles from micro particles. Here, due to the very high rotation and revolution, the energy
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imparted to the material is very high. The properties of nano phase materials synthesised by this method are dependant on ball milling conditions [83].

1.3.4 Applications of ferrites

Polycrystalline ferrites are good dielectric materials with low conductivity and have a wide field of technological applications. Ferrites are used extensively in many electronic devices, because of their high permeability in the radio frequency region, high electrical resistivity, mechanical hardness and chemical stability [84,85].

Hexagonal ferrites based on barium ferrite are efficient replacements for the metallic magnets in recording media and in microwave devices [86]. High stability in air, non metallic electrical properties, corrosion resistance and sharp switching fields make hexagonal ferrites superior to metallic magnets [87]. Among the different types of hexaferrites, M-type barium hexaferrite has been intensively studied as a material for permanent magnet, high density magnetic recording media and microwave devices [88,89]. Anisotropic hexaferrites are highly used in loud speakers and in dc motors. Stepping motors based on ferrite materials are needed in floppy-disc drivers, printers and other computer peripherals.

Ferrites are also used in antennas to transform an electromagnetic signal transmitted through the air into an electric signal. The application of ferrites at microwave frequencies (1-300 GHz) is based on electromagnetic wave propagation phenomena. Ferrite isolators are typically employed to isolate source from load in microwave systems. Circulators and phase shifters based on ferrites are typically used in microwave antenna systems. As microwave absorbers, ferrites can be used to suppress electromagnetic interference [90-92].

Ferrite nanoparticles possess superior magnetic properties when compared to their bulk counter parts. In ferrite nanoparticles, a strong decrease in saturation magnetisation and an enhancement in coercivity in comparison to the bulk material have been reported [93]. Property enhancement of ferrite nanoparticles makes them suitable for applications in electronics, bioprocessing, magnetic resonance imaging and ferrofluids [94].
Mixed ferrites based on Ni-Zn and Mn-Zn are the most widely used materials for different applications. These types of ferrites are used in magnetic cores of read-write heads for high-speed digital recording. Zn-Mn ferrites are important electronic ceramic materials because of their high magnetisation polarisations and electrical resistivity. These are the main constituents of transformer cores, inductors, converters and yokes [95]. High resistivity and low eddy current loss of Ni-Zn ferrite makes them adaptable for high frequency applications [96]. Mg-Zn ferrites are used as materials for coil cores like deflection coils for picture tubes in TV and computer memories [97].

1.4 Rubber ferrite nanocomposites

Development of magnetic nanocomposites leads to new composite materials such as plastic magnets or magneto polymers [45,98]. Incorporation of magnetic fillers into a polymer matrix produces plastic magnets. Rubber ferrite composites are magnetic polymer composites, prepared by the incorporation of ferrites into rubber [99,100]. They have wide range of technological applications. These flexible magnetic materials have excellent performance characteristics and often on par with ceramic magnetic materials. The unique advantages of RFCs are their easy processability and mouldability into convoluted structures. This makes them superior in many respects over conventional ceramic magnets. The degradation of the polymeric matrix limits the application potential of these materials at temperature above 200°C. However, polymer magnets are increasingly used as special purpose composites.

Addition of magnetic fillers to a polymer host medium affects its processability and mechanical properties; where as the magnetic properties of the fillers are also affected by encapsulating them with polymeric medium. Magneto polymers with tailored properties are made with suitable selection of magnetic fillers and host medium [101]. The concentration and orientation of the magnetic particles and degree of interaction of the filler with the matrix are important factors of concern in tailor making materials. In selecting the matrix, the mechanical, viscoelastic and chemical properties of the matrix must be taken into consideration. The compatibility of the matrix with magnetic particles is a significant factor. Advantages of plastic magnets over their metallic and ceramic counterparts include light weight and low
cost, resistance to corrosion, ease of machining and preparation and capability of high production rates [102,103].

Polymer composites are important commercial materials, which find application in vibration damping, electrical insulations, thermal insulations and high performance composites for use in aircraft. Rubber ferrite composites are one such special purpose composite in which the flexibility and mechanical properties of an elastomer and magnetic properties of ferrite filler have been effectively utilised.

The impregnation of magnetic fillers in the matrix imparts magnetic properties and appreciably modifies the physical properties of the matrix. Proper selection of the elastomer as well as the ferrite is important for achieving the desired properties. The polymer must have appropriate physical properties and reasonable stability. Factors like percolation limits, nature of the matrix namely saturation/unsaturation/polarity all influence the final properties of the composites. Both natural and synthetic rubbers can be used as the host matrix for RFCs.

Magnetic properties of the RFCs like saturation magnetisation, coercivity and remanant magnetisation can easily be controlled by proper selection of the magnetic filler. Both hard and soft ferrites are used as filler. Soft ferrites like nickel-zinc ferrite and manganese zinc ferrite are incorporated in the polymer matrices (both natural and synthetic) to produce RFCs [104-106]. Rubber ferrite composites based on natural/synthetic rubbers and hard ferrites like strontium ferrite and barium ferrite are also reported [107-109].

One of the important factors that determines the processability and properties of RFCs is the particle size of the filler. When the size of the filler is in the nano regime, greater enhancement of mechanical properties can be anticipated. Smaller the particle size, larger the surface area and greater is the polymer-filler interface interaction. Thus, ferrite particles can act as a semi reinforcing filler, though the main intention of incorporation of these fillers is to modify the magnetic and dielectric properties of the elastomer.

Addition of fillers to rubber has a strong impact on its static and dynamic behaviour. Surface interactions between a reinforcing filler and rubber molecules involve a range of bond energies from relatively weak Vander-Waal interaction to
very strong chemical interaction. Physical adsorption of polymers on filler surface occurs to varying degree depending on the filler surface and nature of the polymer segments \[110,111\]. Chemical interaction is possible when specific functional groups like -OH, -COOH, -NH$_2$ etc. are available on the filler surface. Since, such functional groups are absent in ferrites; the reinforcement may be due to some physical interactions \[112\].

Nanocomposite magnets, with both particle and matrix systems being magnet have received much attention, because they may have high remanence, associated with exchange coupling at interfaces separating hard and soft magnetic phases and large energy product, \((BH)_{\text{max}}\) relative to conventional magnetic materials \[113,114\]. The resistance of RFCs to mutual demagnetisation is as good as that of sintered isotropic ferrite. RFCs have enormous application potential in electrical and electronic industries where flexibility is a desired factor. Microwave absorbing characteristics of ferrites make these magnetic composites applicable in microwave and radar applications \[115,116\].

Carbon black, the unique and most widely used reinforcing filler, can improve the mechanical properties of RFCs. Incorporation of carbon black along with ferrite filler can modify mechanical, dielectric and microwave properties of elastomers \[117-121\].

1.5 Motivation for the present study

Incorporation of ultrafine ferrite fillers like nickel ferrite and gamma ferric oxide in matrices like EPDM and CR results in rubber ferrite nanocomposites. It is important that the incorporation of these fillers in definite loadings in the host matrix is according to a specific recipe. Hence specific recipes are to be formulated for preparing ferrite polymer nanocomposites. The processability of these polymer composites is to be determined by evaluating the cure characteristics. Incorporation of fillers along with other compounding ingredients in the polymer matrix should normally result in a homogeneous composite without agglomeration and segregation. Morphology study using Scanning electron microscopy (SEM) is an ideal tool for assessing the homogeneity of these composites.
Ferrites are commercially important materials due to their unique properties like appropriate magnetic characteristics, high resistivity and low eddy current lossess. They are important microwave absorbing materials and are also employed as isolators, circulators and phase shifters, where they are in the form of ceramic materials. The inherent draw back of ceramic materials is their lack of flexibility and mouldability into complex shapes. This can overcome by incorporating these materials into flexible medium like rubber.

In the present study, nickel ferrite and gamma ferric oxide are used as the magnetic fillers for the preparation of the composites. Nickel ferrite is an important member of the family of ferrites. It is an ideal template for the preparation of a number of mixed ferrites such as nickel zinc ferrites. Gamma ferric oxide is a commercially important magnetic material extensively used in audio/video recording. It is rather difficult to synthesise pure $\gamma$-Fe$_2$O$_3$ without traces of alpha ferric oxide. Precise preparative conditions are to be maintained for the synthesis of pure $\gamma$-Fe$_2$O$_3$. The synthetic route adopted for the preparation, generally influences properties of ferrites. In the present study, sol-gel method is employed for the preparation of the ferrite nanoparticles. Sol-gel method is adopted as this is one of the simplest and economic methods for the preparation of nano scale materials. This is a low temperature method and ensures the formation of pure and crystalline particles.

Before incorporation, fillers are characterised so that comparison and correlation of various physical properties after the preparation becomes less difficult. Since the fillers possess high surface area, they contribute a larger interphase and reinforce the elastomer. They also modify the electrical and magnetic properties of the composites. So investigations on the mechanical, magnetic and electrical properties of these composites assume significance. These investigations are necessary to delve into the fundamental aspects involving fine particle fillers and their interaction with the matrix.

Mechanical properties of the elastomer are a major concern in the designing of composite materials for specific applications. The extensibility of the elastomer should be high so that higher amount of magnetic fillers can be incorporated without any processing difficulty. Outdoor application of composite materials demands
appreciable ageing characteristics. The composite materials must be resistant to heat, weather, oils and chemicals, oxygen and ozone attack and a number of other factors. Compared to natural rubber, synthetic rubbers proved to have excellent resistance to all these factors. Thus, the choice of synthetic rubbers like EPDM and CR for the preparation of RFCs in the present study is mandatory.

It is also necessary that composites should have appropriate magnetisation and the required coercivity. So the loading percentage of the magnetic filler was varied to have optimal properties. Carbon black was incorporated in to the composite having optimum magnetic and electric properties. This was carried out to study the microwave absorption property of these RFCs so that the band width of absorption can be tuned. This is attempted from an application point of view. A systematic investigation in to the various fundamental aspects involving the modification of physical properties viz. mechanical, magnetic and electrical is undertaken. For the preparation of nano fillers new techniques or the modification of the existing ones are attempted. Specific recipes are formulated depending upon the nature of the host matrix. Finally attempts are made to correlate the various results and model them using simple existing models. The objectives of the present work are shown in a nutshell.

Objectives of the present work:

- Synthesis of nanosized nickel ferrite and gamma ferric oxide by sol-gel method.
- Structural characterisation of sol-gel synthesised nano ferrites using X-ray diffractometry and Transmission electron microscopy.
- Preparation of rubber ferrite composites by incorporating precharacterised nano ferrites at different loading into ethylene propylene diene rubber and neoprene rubber.
- Evaluation of cure characteristics of the RFCs and determination of kinetics of the cure reaction.
- Evaluation of mechanical properties of the RFCs.
Introduction

- Morphological studies of the RFCs using Scanning electron microscopy and Electron spin resonance spectroscopy (ESR).
- Evaluation of dielectric properties of ferrites and the RFCs in 0.1-8 mega hertz frequencies (MHz) and at different temperatures.
- Microwave absorption studies of the RFCs in X and S band frequencies.
- Determination of magnetic properties of ferrite nanoparticles and RFCs.
- Study on the effect of carbon black on processing, mechanical, dielectric, magnetic and microwave properties of the RFCs.
- Correlation of results.

References

Chapter 1

Introduction

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