Chapter 4

NATURAL RUBBER/NANO Fe₃O₄ COMPOSITES

Part A
Synthesis and characterization of Fe₃O₄ nanoparticles

Part B
Preparation and characterization of Natural rubber/nano Fe₃O₄ composites

Part A

Synthesis and characterization of Fe₃O₄ nanoparticles

4A.1 Introduction

Nanoparticles, with at least one of the dimensions less than 100 nanometers, exhibit properties which are largely different from the bulk materials. The difference may be expressed as a manifold improvement in the existing properties or the appearance of a completely new property. These special characteristics of nanoparticles arise due to the presence of a large fraction of atoms on the surface of the particles. As a result, the particles possess high surface energy and reduced imperfections compared to bulk materials [1]. This reflects in the optical, magnetic, electrical and other properties of the particles. These improved properties make nanoparticles interesting in electronics, medicine, energy, food, space and many other fields [2]. Magnetic nanoparticles too owe their superior
properties to the size and surface effects [3]. Their unique properties include super paramagnetism, high coercivity, low Curie temperature, high magnetic susceptibility etc. They find applications in a broad spectrum of disciplines like magnetic fluids, water treatment, information storage, catalysis and medicine [4-5].

There has been great interest in the synthesis and applications of iron oxide based magnetic nanoparticles and their composites due to the tuneable physical and chemical properties they acquire in their nano form. Among the iron oxide nanoparticles Fe$_3$O$_4$ has attracted particular attention on account of its unique structure and interesting properties. In Fe$_3$O$_4$, oxide anions are arranged in a cubic close packed lattice with tetrahedral and octahedral interstices occupied by Fe$^{2+}$ and Fe$^{3+}$ ions forming an inverse cubic spinel structure. The super paramagnetic Fe$_3$O$_4$ nanoparticles present 'near zero' values for coercivity and remanence [6].

Unique properties of Fe$_3$O$_4$ nanoparticles make them attractive for an extensive range of applications. The main areas of application include recording materials, magnetic separation of suspended particles, ferrofluids, catalysts, chemical sensors, electrophotographic developers, magnetic resonance imaging, drug delivery, detoxification of biological fluids, hyperthermia, cell separation etc. [7-10]. Size and properties of the nanoparticles can be controlled by using different synthetic pathways and reaction conditions such as, reactant type and concentration [11]. The size effect is particularly important in magnetic particles since sufficiently small particles act as single domains with one giant magnetic moment as a geometric resultant of all the individual magnetic moments of the atoms in it. Many applications require the mean particle sizes of magnetic Fe$_3$O$_4$ to be within the single domain range (<128 nm) to maintain uniform physical properties and distribution [12].
There are different methods for the preparation of nano Fe\(_3\)O\(_4\) such as co-precipitation, thermal decomposition, hydrothermal synthesis, microemulsion, sonochemical synthesis, electrochemical synthesis, laser pyrolysis techniques, bacterial synthesis etc. [13-15] of which the most popular one is co-precipitation due to its simplicity, low cost and possibility to scale up. In this method aqueous solutions of ferrous and ferric salts are mixed together followed by precipitation with a strong alkali. The size and shape of the prepared nanoparticles can be controlled by the type of salts used, ferric to ferrous ratio, reaction temperature, pH of the reaction media, stirring rate, speed of addition of alkali solution etc. [16].

Mascolo et al. used room temperature co-precipitation to prepare magnetite nanoparticles using different bases and varying pH [17]. Kulkarni et al. prepared magnetite (Fe\(_3\)O\(_4\)) nanoparticles by co-precipitation method at 50 °C [18]. Dependence of particle size and magnetic properties on temperature in rapid mixed co-precipitation was investigated by Fang et al. [19]. Jing et al. used a modified co-precipitation method to prepare magnetite (Fe\(_3\)O\(_4\)) nanoparticles with a size range of 8–20 nm [20].

In this part of the chapter preparation of Fe\(_3\)O\(_4\) nanoparticles through co-precipitation from a ferrous/ferric mixture in strong alkaline medium and its characterization by VSM, SEM, TEM, XRD and TGA is discussed.

4A.2 Experimental

4A.2.1 Materials

Ferrous sulphate (FeSO\(_4\)), ferric chloride (FeCl\(_3\)) and ammonia solution (NH\(_4\)OH).

4A.2.2 Synthesis of nano Fe\(_3\)O\(_4\)

FeCl\(_3\) and FeSO\(_4\) dissolved in water were mixed in a beaker, keeping the molar ratio of Fe\(^{3+}\) and Fe\(^{2+}\) in the mixture at 2:1. The mixed solution
was stirred well and an excess amount of NH₄OH solution added. The solution turned to black brown as Fe₃O₄ precipitate was formed *in situ*. The principal reaction is

\[
\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}
\]

The obtained precipitate was settled by placing a magnet at the bottom of the beaker, washed several times with distilled water and dried in an air oven.

**4A.2.3 Characterization**

Morphology studies, magnetic parameters (VSM), X-Ray diffraction and thermogravimetry analysis were used to characterize NR/Fe₃O₄ composites.

**4A.3 Results and discussion**

**4A.3.1 Morphology**

SEM images of prepared nano Fe₃O₄ at different magnifications are shown in Figs. 4.1 (a & b). Figs. 4.2 (a & b) show the TEM image of the nanoparticles.

![SEM images of Fe₃O₄ nanoparticles](image_url)
SEM and TEM images show that the particles have a spherical geometry. From TEM images it is observed that size of the particles is in the range 10-20 nm, though some of these particles are in an agglomerated state.

### 4A.3.2 X-Ray diffraction studies

The powder XRD pattern of the Fe₃O₄ nanoparticles is shown in Fig. 4.3.
The characteristic XRD pattern of $\text{Fe}_3\text{O}_4$ is obtained, establishing the formation of crystalline $\text{Fe}_3\text{O}_4$ in the synthesis. The cubic lattice parameter is calculated as 8.370 Å, which is comparable to the bulk value of 8.394 Å. The broad peaks in the XRD pattern indicate the nanocrystalline nature of the particles. The average crystallite size is calculated to be 12 nm using the Scherrer formula,

$$D = \frac{0.9\lambda}{\beta\cos\theta},$$

where $D$ is the crystallite size, $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum after correcting for instrumental contribution and $\theta$ is the Bragg angle.

### 4A.3.3 Magnetic properties

The room temperature magnetization of the $\text{Fe}_3\text{O}_4$ nanoparticles, measured as a function of magnetic field is shown in Fig 4.4. Magnetization continuously increases at high magnetic fields because of the very small size of the particles, with a magnetization of 41.2 emu/g at 15 kOe.

![Fig. 4.4: Room temperature magnetization curve of the Fe$_3$O$_4$ nanoparticles](image-url)
This value is almost half of that expected for bulk Fe\(_3\)O\(_4\) (~95 emu/g) and the reduction in the magnetization is due to the smaller size of the particles. For magnetic nanoparticles, the magnetization is considerably reduced on decreasing the particle size due to the ‘magnetically dead’ layer on the surface of the particles in which the magnetic moments are randomly oriented and therefore do not contribute much to the magnetization. The surface contribution increases as the surface area to volume ratio increases with reduction in the particle size. The saturation magnetization of the nanoparticles is related to the bulk value through the equation

\[ Ms(n) = Ms(b) \left( 1 - \frac{6t}{d} \right) \]

where \( Ms(d) \) and \( Ms(b) \) are the saturation magnetizations of nanoparticles of diameter ‘\( d \)’ and the bulk, respectively, \( d \) is the diameter of a spherical particle and ‘\( t \)’ is the thickness of the magnetically dead layer on the surface of the particles.

**4A.3.4 Thermogravimetric analysis**

Figs. 4.5 and 4.6 show the thermal degradation pattern of the Fe\(_3\)O\(_4\). As there should not be any degradation of the ferric oxide in the temperature range of the test the weight loss should be due to physically adsorbed water or chemically attached hydroxyl groups on the surface of the ferric oxide nanoparticles. The weight loss proceeding beyond 200 °C involves not only water and hydroxyl groups but other absorbed species like alkaline counter ions (here NH\(^{4+}\) coming from the ammonium hydroxide solution used for co-precipitation). A similar behavior was observed by Franger et al. [22]
4A.4 Conclusions

Nanoparticles of Fe$_3$O$_4$ were synthesized by co-precipitation method. The nanoparticles were characterized by SEM, TEM, XRD, VSM and TGA. The particles were found to be of uniform particle size in the range (10-20) nm with crystalline structure. Saturation magnetization of the particles was found to be 41.2 emu/g at 15 kOe. Thermogravimetric analysis reveals the presence of hydroxyl groups and alkaline counter ions on the surface of the nanoparticles.
Part B

Preparation and characterization of Natural rubber/nano Fe\textsubscript{3}O\textsubscript{4} composites

4B.1 Introduction

The major drawbacks of ceramic materials are their rigidity and difficulty to mold into complex shapes. Ferrites are traditionally used in the ceramic form for different applications. Rubber-ferrites, i.e. rubber filled with magnetic materials can be used to overcome these drawbacks. Apart from the main advantages of flexibility and easy mouldability, they also possess low weight and cost, resistance to corrosion and capability of high production rates [23]. These composites can be used in various applications such as microwave absorbers and flexible magnets [24-26]. Metals and metal oxides are commonly used as ferrite materials for incorporation into elastomeric matrices to obtain composites with improved magnetic properties. Choi et al. investigated the effect of Fe\textsubscript{3}O\textsubscript{4} content on NBR. They found that Fe\textsubscript{3}O\textsubscript{4} improves the tensile strength and modulus of NBR [27]. The incorporation of barium ferrite in NR gives a composite with improved mechanical, magnetic and electrical properties [28]. Incorporation of metals as magnetic materials will increase the weight of the resulting composites due to the high density of metal. When coarse metal oxides are used, large quantities are necessary for uniform magnetization in the composites. Large amounts of fillers in the rubber matrix may impair their mechanical properties. One possible way to overcome this problem is the use of nanometer-sized magnetic oxides in the composites which impart uniform magnetic properties even at moderate loading. This is achieved by the reduced mean distance between particles dispersed in the composites. Lower the particle size, shorter will be the inter particle distance [29].
Nanocomposites with elastomeric matrices and magnetic nanoparticles have attracted much attention due to their potential novel applications in different fields. Jamal et al. [30] prepared nickel nanocomposites of natural and chloroprene rubbers and found that elastic modulus of composites had improved by the addition of nickel particles. Kong et al. [31] used thermoplastic natural rubber as the matrix for commercially available Fe$_3$O$_4$ nanoparticles through a melt blending process. They observed a shift in the maximum attenuation to a lower frequency and increased absorption with increase of filler content. Makled et al. prepared barium ferrite–natural rubber composites with low weight and high flexibility [32]. Varga et al. prepared poly (dimethyl siloxane)/carbonyl iron composites with controlled filler orientation and found that the anisotropic composites exhibit a larger increase in modulus on application of magnetic field, compared to composites with random particle dispersions. These composites with tuneable elastic properties can be used in elastomer bearings and vibration absorbers [33].

In this part of the work, Fe$_3$O$_4$ nanoparticles synthesized by the coprecipitation method are incorporated into natural rubber on a mixing mill. The composites prepared by subsequent compression moulding in a hydraulic press were characterized for morphology, cure characteristics, mechanical, thermal, magnetic, conductive, dielectric and microwave properties.

**4B.2 Experimental**

**4B.2.1 Materials**

Natural rubber (ISNR-5), zinc oxide, stearic acid, TQ (1,2-dihydro-2,2,4-trimethylquinoline), ZDBC (zinc dibutyldithiocarbamate) and sulphur. Fe$_3$O$_4$ nanoparticles were prepared by the process discussed in section 4A.2.2 of this chapter.
4B.2.2 Preparation of NR/nano Fe$_3$O$_4$ composites

Table 4.1: Formulation of the mixes

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>100</td>
</tr>
<tr>
<td>Nano Fe$_3$O$_4$</td>
<td>0, 15, 30, 45 and 60</td>
</tr>
<tr>
<td>ZnO</td>
<td>4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>TQ</td>
<td>1</td>
</tr>
<tr>
<td>ZDBC</td>
<td>1.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2</td>
</tr>
</tbody>
</table>

A series of NR/nano Fe$_3$O$_4$ composites were prepared, with varying amounts of the filler as per the processing method described in section 2.2 of Chapter 2.

4B.2.3 Characterization

Cure characteristics, mechanical properties, thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), morphology studies, vibrating sample magnetometer (VSM), dielectric properties, microwave properties and shielding measurements were used to characterize NR/nano Fe$_3$O$_4$ composites.

4B.3 Results and discussion

4B.3.1 Cure characteristics

Differential torque is the difference between maximum and minimum torque experienced in Rubber Process Analyzer during the curing process at 90 °C. Fig. 4.7 shows the variation of differential torque with Fe$_3$O$_4$ loading. Differential torque increases with Fe$_3$O$_4$ loading. This shows that the matrix is being increasingly restrained with increase in the amount of Fe$_3$O$_4$. 
Fig. 4.7: Variation of differential torque with Fe$_3$O$_4$ loading

Fig. 4.8: Variation of cure time with Fe$_3$O$_4$ loading
The variation of cure time and scorch time, with Fe$_3$O$_4$ loading, is shown in Figs. 4.8 and 4.9 respectively. Both cure time and scorch time decreases with Fe$_3$O$_4$ loading. This is because of the basic nature of nano Fe$_3$O$_4$ due to the adsorbed NH$_4^+$ ions on the surface as evidenced from thermogravimetric analysis of the nanoparticles. Alkaline filler generally accelerates the curing rate in sulphur vulcanization [34].

4B.3.2 Mechanical properties

The effect of the nano Fe$_3$O$_4$ on the tensile strength of the composites is shown in Fig. 4.10. Tensile strength increases with Fe$_3$O$_4$ content upto 45 phr loading. On further loading of Fe$_3$O$_4$, tensile strength decreases. As evident from the SEM images, the prepared nano Fe$_3$O$_4$ is partly in an aggregated state. By the high shearing forces developed during the mixing of the composites these aggregates are broken down and get distributed throughout the matrix as a uniform dispersion. This can be clearly observed from the SEM pictures of the fracture surface of the composites (Figs. 4.18(a,b,c,d)). The increased surface area of the nano Fe$_3$O$_4$ facilitates...
better matrix-filler interaction. This, naturally, will increase the reinforcement of the matrix and result in increased tensile strength of the composites. Beyond a loading of 45 phr, dispersion of filler in the rubber matrix becomes difficult causing agglomeration of the nanoparticles. At large strains the filler-filler interaction in these agglomerates may not be sufficient to hold them together and cracks will initiate. These cracks will act as points of stress concentration. At higher strains the composite break at these points giving lower tensile strength values without realizing the full potential of the reinforcement imparted by nano Fe$_3$O$_4$.

Variation of tear strength of composites with Fe$_3$O$_4$ content is shown in Fig. 4.11. Tear strength decreases with Fe$_3$O$_4$ content. The spherical shaped nano Fe$_3$O$_4$ particles may not be able to resist crack propagation effectively, unlike one dimensional particles such as nanofibers or nanorods.

![Fig. 4.10: Variation of tensile strength with Fe$_3$O$_4$ loading](image-url)
Natural rubber/nano Fe$_3$O$_4$ composites

The variation of modulus with Fe$_3$O$_4$ content is shown in Fig. 4.12. The modulus goes on increasing with Fe$_3$O$_4$ content in contrast to the case of tensile strength where the property decreases beyond a particular loading. The modulus is measured at low strains. The stress developed at these strains may not be sufficient to cause stress concentration at agglomerates formed at higher nano Fe$_3$O$_4$ loadings. So the effect of agglomeration of filler is not observed in modulus values.

**Fig. 4.11: Variation of tear strength with Fe$_3$O$_4$ loading**

**Fig. 4.12: Variation of tensile modulus with Fe$_3$O$_4$ loading**
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Fig 4.13: Variation of elongation at break with Fe$_3$O$_4$ loading

Variation of elongation at break of the composites with Fe$_3$O$_4$ content is shown in Fig 4.13. A decrease in elongation at break is noted with Fe$_3$O$_4$ content. This is due to the increased reinforcement of the matrix which restricts the elongation caused by the uncoiling of molecular chains. Dilution effect due to the Fe$_3$O$_4$ content on the matrix also plays a part.

4B.3.3 Thermogravimetric analysis

The thermal degradation patterns of the NR/Fe$_3$O$_4$ composites are shown in Figs. 4.14 and 4.15. NR/Fe$_3$O$_4$ composites are represented as NR P F x where 'x' denotes the Fe$_3$O$_4$ content. Thermal degradation of the ferric oxide composites almost follows the similar pattern as that of the gum compound (without any filler) as shown in Fig. 4.14. There is no substantial change in the point of initiation of thermal degradation among the composites except for the one with 45phr filler content. This shows that the incorporation of the ferric oxide does not affect the thermal stability of the composites. The 45 phr composite shows a weight loss as early as 200 °C while all the other composites starts degradation at about 350 °C only. This exceptional behavior may be due the optimum filler dispersion in the composite as
Natural rubber/nano Fe$_3$O$_4$ composites
evidenced by the optimum level of mechanical strength at that filler loading. The fine dispersion without agglomeration makes the surface hydroxyl groups and adsorbed water on the nanoparticles more accessible to the heat treatment and subsequent removal of the same, from the composites. This is reflected in the weight loss from 200 °C to 350 °C in the composite.

![Graph of TG curves of NR/Fe$_3$O$_4$ composites](image1)

**Fig. 4.14: TG curves of NR/Fe$_3$O$_4$ Composites**

![Graph of DTG Curves of NR/Fe$_3$O$_4$ composites](image2)

**Fig. 4.15: DTG Curves of NR/Fe$_3$O$_4$ composites**
Fig. 4.15 shows the derivative thermograms of the composites. It can be seen that the maximum rate of degradation of the composites decreases with filler content. This may be due to the reinforcing nature of \( \text{Fe}_3\text{O}_4 \) which improves thermal stability of the composites. In the case of composites with 45 phr filler content the decrease in degradation rate is same as that of 60 phr composites. This again is in agreement with the effective filler dispersion and improved reinforcement in the 45 phr composites.

4B.3.4 Dynamic mechanical analysis

The dynamic mechanical properties of the ferric oxide composites as a function of frequency of the oscillation are shown in Figs. 4.16 and 4.17. The frequency dependence of the storage modulus of the composites is shown in Fig. 4.16.

![Graph showing variation of storage modulus with frequency of NR/Fe\(_3\)O\(_4\) composites](image_url)

**Fig. 4.16: Variation of storage modulus with frequency of NR/Fe\(_3\)O\(_4\) composites**

With increase in filler content storage modulus of the composites increases showing an increase in stiffness of the composites. But the trend is not followed in the case of 45 phr composites. Storage modulus of the
45 phr composites is more than that of the 60 phr composites. This may be due to optimum dispersion of fillers in this case as shown by the tensile properties. For all composites, beyond 21 Hz, the increase in storage modulus is more pronounced. In dynamic mechanical test increase in frequency is equivalent to a decrease in temperature. So the increase in storage modulus beyond 21 Hz can be equated to the transition region in the case of temperature sweep test of the composites, where the material becomes glassy. A corresponding trend is observed in the loss modulus graph of the composites shown in Fig 4.17.

![Graph showing variation of loss modulus with frequency for NR/Fe$_3$O$_4$ composites.](image)

**Fig. 4.17: Variation of loss modulus with frequency of NR/Fe$_3$O$_4$ composites**

### 4B.3.5 Morphology studies

Figs. 4.18(a, b, c & d) show cross sections of the natural rubber/Fe$_3$O$_4$ composites with 15, 30, 45 and 60 phr filler content respectively. Fe$_3$O$_4$ particles can be seen distributed throughout the matrix in a more or less homogeneous manner in 15, 30 and 45 phr composites. In 60 phr composites, agglomerates of Fe$_3$O$_4$ nanoparticles can be seen throughout the matrix.
suggesting the optimum amount of filler for proper dispersion to be 45 phr. Better dispersion at this filler content is further confirmed by the improved the mechanical and dynamic mechanical properties of the composites.

![SEM images of NR/Fe\textsubscript{3}O\textsubscript{4} composites with different filler contents](image)

**Fig. 4.18:** SEM of cross sections of the NR/Fe\textsubscript{3}O\textsubscript{4} composites with different filler content a: 15 phr, b: 30 phr, c: 45 phr, d: 60 phr

### 4B.3.6 Magnetic properties

The magnetization curves of the natural rubber composites are shown in Fig. 4.19. As the Fe\textsubscript{3}O\textsubscript{4} content increases in the composites, the saturation magnetization increases almost linearly, as shown in the inset of the figure. This shows that the iron oxide nanoparticles are uniformly distributed in the rubber matrix which is very crucial for applications.
Fig. 4.19: Magnetization curves of the NR/Fe₃O₄ composites

Magnetic hysteresis is not observed for the composites and thus very low energy is lost by the composites during magnetization and demagnetization. The reduced magnetic hysteresis is likely to be due to the decreased inter-particle interactions arising from the uniform distribution and increased inter-particle distance of nano Fe₃O₄ in the matrix. Matrix-particle interface also plays a part in the determination of saturation magnetization [35]. This shows the effectiveness of the composites as flexible ferromagnetic materials.

4B.3.7 Dielectric properties  

(i) Effect of frequency on dielectric properties of NR/Fe₃O₄ composites

Dielectric properties of NR/Fe₃O₄ composites were evaluated at room temperature. Variation of dielectric constant (real part of permittivity) with frequency of the composites is shown in Fig. 4.20. Dielectric permittivity decreases with increase in frequency for gum and Fe₃O₄ composites. For all frequencies, Fe₃O₄ composites show higher dielectric permittivity than the
gum sample. Among the composites, dielectric permittivity increases with increase in Fe$_3$O$_4$ content. In composites, Fe$_3$O$_4$ particles are embedded in an insulating matrix resulting in space charges to accumulate at the interfaces on the application of an electric field. The resulting Maxwell-Wagner-Sillars polarization [36-37] accounts for the dielectric constant of the composites. As the frequency is increased, the polarization of interfacial charges and dipoles would not be able to keep up with the alternating electromagnetic field and therefore dielectric permittivity decreases.

Fig 4.21 shows variation of dielectric loss with frequency at different filler loadings. Dielectric loss shows a slight increase at low frequencies followed by a decrease at higher frequencies. The polarization of the dipoles in the composites lags behind the electric field by relaxation time and this phase difference appears as dielectric loss which increases with frequency in the low frequency range.

![Graph](image)

**Fig. 4.20:** Variation of dielectric constant with frequency of NR/Fe$_3$O$_4$ composites
Fig. 4.21: Variation of dielectric loss with frequency of NR/Fe$_3$O$_4$ composites

But at high frequencies, that is, when the period of oscillation is much smaller than the relaxation time, the polarization would not be able to keep up with the alternating electric field which reduces the dielectric loss [38].

Fig. 4.22: Variation of AC conductivity with frequency of NR/Fe$_3$O$_4$ composites
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Variation of AC conductivity with frequency of composites with different filler loadings is shown in Fig. 4.22. All composites behave similarly in the frequency range with initial increase in conductivity, attainment of a maximum and decrease at higher frequencies. The increase in AC conductivity with frequency is due to the increase in hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ ions in Fe$_3$O$_4$ [39]. With increase in frequency, hopping increases and reaches a maximum value. Beyond a certain frequency, the electron hopping lags behind the alternating field resulting in decrease of conductivity.

(ii) **Effect of nano Fe$_3$O$_4$ loading on dielectric properties of NR/Fe$_3$O$_4$ composites:**

The loading dependence of dielectric constant with respect to some selected frequencies is shown in Fig. 4.23. With increase in Fe$_3$O$_4$ content, the dielectric constant increases almost linearly. Interfaces and dipoles in the composite increase with filler content causing a corresponding increase in interfacial and dipolar polarization. This, in turn, improves the dielectric constant. At higher frequencies, the dielectric constant reduces. Variation of dielectric loss with filler content shows the same behaviour as that of dielectric constant, with respect to Fe$_3$O$_4$ content (Fig. 4.24). Dielectric loss is a result of dielectric relaxation of dipoles in the composite which increases with Fe$_3$O$_4$ content. At all frequencies dielectric loss increases with increase in Fe$_3$O$_4$ content. Reduction in dielectric loss at high frequencies is attributed to the decrease in polarization.
Fig. 4.23: Variation of dielectric constant with Fe$_3$O$_4$ loading of NR/Fe$_3$O$_4$ composites

Fig. 4.24: Variation of dielectric loss with Fe$_3$O$_4$ loading of NR/Fe$_3$O$_4$ composites
Fig. 4.25: Variation of AC conductivity with Fe$_3$O$_4$ loading of NR/Fe$_3$O$_4$ composites

AC conductivity of the composites with respect to filler content is shown in Fig. 4.25. An increase in conductivity with Fe$_3$O$_4$ content is observed at all frequencies. AC conductivity in Fe$_3$O$_4$ composites is the result of hopping between Fe$^{2+}$ and Fe$^{3+}$ ions. When the number of Fe$_3$O$_4$ particles increases, hopping conduction naturally increases.

4B.3.8 Microwave Properties

Variation of real part of permeability ($\mu'$) of NR/Fe$_3$O$_4$ composites in X and S bands with Fe$_3$O$_4$ content is shown in Figs. 4.26.a and 4.26.b respectively. $\mu'$ increases with Fe$_3$O$_4$ content and the increase is more pronounced beyond 30 phr loading. As the permeability of the composites originates from the dispersed Fe$_3$O$_4$ nanoparticles, increase in the amount of the magnetic filler improves the permeability of the composite.
Natural rubber/nano Fe₃O₄ composites

Fig. 4.26.a: Variation of real part of permeability with Fe₃O₄ loading of NR/Fe₃O₄ composites in X band

Fig. 4.26.b: Variation of real part of permeability with Fe₃O₄ loading of NR/Fe₃O₄ composites in S band
In both bands increase in frequency is associated with a decrease in $\mu'$, which is more visible towards lower frequencies and higher Fe$_3$O$_4$ content. The drop in $\mu'$ can be attributed to the skin effect and eddy current losses which is present even in nanometer sized particles [40]. Imaginary part of permeability ($\mu''$) also shows similar behaviour as that of $\mu'$, with the increment being more pronounced beyond 30 phr of Fe$_3$O$_4$ content (Figs. 4.27.a and 4.27.b). Rotational magnetization is responsible for the magnetic losses at high frequencies which increases with the magnetic filler content. With increase in frequency $\mu''$ decreases as the magnetic moments may not be able to keep up with the alternating field. Tan $\delta$, or ratio of imaginary and real parts of permeability, which represents the energy dissipated, also follows the same trend as that of $\mu''$ (Figs 4.28.a and 4.28.b) showing increase with Fe$_3$O$_4$ content and decrease with frequency.

Fig. 4.27.a: Variation of imaginary part of permeability with Fe$_3$O$_4$ loading of NR/Fe$_3$O$_4$ composites in X band
Fig. 4.27.b: Variation of imaginary part of permeability with Fe$_3$O$_4$ loading of NR/Fe$_3$O$_4$ composites in S band

Fig. 4.28.a: Variation of tan δ with Fe$_3$O$_4$ loading of NR/Fe$_3$O$_4$ composites in X band
4B.3.9 Electromagnetic interference (EMI) shielding

Figs. 4.29 and 4.30 show the variation of EMI shielding effectiveness of NR/Fe\textsubscript{3}O\textsubscript{4} composites in S and X bands. Compared to the gum, composites with Fe\textsubscript{3}O\textsubscript{4} show a higher shielding efficiency. It is well known that the microwave absorption characteristics of an EMI shield is highly dependent on its dielectric loss and magnetic permeability. Fe\textsubscript{3}O\textsubscript{4}, due to its ability to improve the microwave conductivity and polarization of the composites, increases the dielectric loss (imaginary part of permittivity) in the composites [41]. This increases lossy nature of the composites and enhances the attenuation, thereby improving the shielding efficiency [42]. Apart from this, the addition of Fe\textsubscript{3}O\textsubscript{4} nanoparticles improves the magnetic permeability of the composites. The shielding due to absorption is given by

\[ S_{EA} = 20 \cdot \frac{d}{\delta} \cdot (\log e) \text{ and} \]

\[ \delta = \sqrt{2/\omega \mu \sigma} \]
where \( d \) is the sample thickness, \( \delta \) is the skin depth, \( \omega \), the angular frequency, \( \mu \), the magnetic permeability and \( \sigma \), the microwave conductivity [43]. From these relations, it is clear that the increase in magnetic permeability decreases the skin depth thereby increasing the shielding efficiency due to absorption.

Fig. 4.29: EMI shielding efficiency of NR/Fe\(_{3}\)O\(_{4}\) composites in S band

Fig. 4.30: EMI shielding efficiency of NR/Fe\(_{3}\)O\(_{4}\) composites in X band
On another note, single domain magnetic nanoparticles (particles that are small enough to have all the magnetic spins aligned in same direction) have been shown to cause large effective anisotropy with high hysteresis loss [44]. The prepared nanoparticles have their size in 10-20 nm range. This falls well below single domain size of Fe₃O₄ nanoparticles, which is about 128 nm [12]. The low particle size increases the surface area of the Fe₃O₄ particles thereby enhancing unsaturated coordination and the number of ions adsorbed on the surface. This will lead to increased interfacial polarization and multiple scattering which helps to increase the absorption of electromagnetic radiations [45].

4B.4 Application NR/Fe₃O₄ elastomer composites

NR/Fe₃O₄ composites as damping materials

Those materials whose properties can be altered by parameters such as stress, temperature, pH, moisture, electric or magnetic fields are called smart materials [46]. An elastomer with magnetic nanoparticles dispersed in the matrix can be counted in this group on account of the tuneability of modulus by the application of an external magnetic field. The extend of tuneability will depend on nature of both elastomer matrix and the magnetic materials including the size, dispersion, loading percentage and orientation of magnetic particles in the elastomer matrix. The important advantage of elastomeric composites as magnetorheological materials is their ability to stretch reversibly to high elongations of the order of 600-700 %. Moreover, they overcome the common problems of magnetorheological fluids and gels like settling and difficulty in handling.

If the direction of orientation of the particles in the matrix can be controlled, more effective tuning of mechanical properties is possible. In the case of a matrix with a dispersed magnetic phase, control of anisotropy is of
Natural rubber/nano Fe$_3$O$_4$ composites

paramount importance if the elastic properties are to be tuned suitably by the application of a magnetic field. Many of the common rubber processing operations like milling, calendaring and extrusion are able to align the molecular chains in the polymer in a preferential direction during processing. The filler particles dispersed in the matrix tend to follow the directional orientation of molecular chains thereby producing a considerable amount of anisotropy in the compounded stock which remains as such in the final cured product. This processing induced anisotropy can be utilized beneficially in the modulus tuning of the elastomer composites with magnetic fillers.

To demonstrate the effect of process induced anisotropy in the rubber composites, NR/Fe$_3$O$_4$ sheets were prepared in which Fe$_3$O$_4$ nanoparticles were oriented in the processing direction of the two-roll mill. Strips were cut from the sheets keeping the longitudinal axis both parallel and perpendicular to the mill direction. The strips were subjected to dynamic mechanical analysis in the presence of a magnetic field to showcase the effect of magnetic filler orientation direction in modulus tuning. A locally made setup was used to place permanent magnets on both sides of the clamp in the dynamic mechanical analyzer. The set up had provision to adjust the distance between the magnets and the sample fitted in the clamp, thereby altering the strength of the magnetic field. According to the distance, the experienced magnetic field is denoted as low and high. Dynamic mechanical analysis in frequency sweep mode was carried out on composites in low field, high field and without field which were denoted as WLF, WHF and WOF respectively. The results are shown in Figs. 4.32 and 4.34. Fig. 4.32 shows the variation of storage modulus with frequency when the magnetic field is parallel to the direction of orientation of Fe$_3$O$_4$ nanoparticles, that is, when samples cut in transverse direction to the filler orientation were used for the experiment. (A schematic diagram of the set up is shown in Fig. 4.31) Here it can be seen
that, at all frequencies, storage modulus of the samples placed in a magnetic field is higher than that of the samples tested without magnetic field. When the strength of the field is increased a corresponding increase in storage modulus is observed. The results show the influence of filler orientation on the tuning of modulus. The magnetic field acting on a direction parallel to the magnetic filler orientation would exert a pinning effect on the composite which increases the stress required to maintain the sinusoidal strain giving higher values for storage modulus.

Fig. 4.31: Schematic diagram showing transverse samples in magnetic field

Fig. 4.32: Variation of storage modulus with frequency when magnetic field was applied in the direction of orientation of Fe₃O₄ particles
When the experiment is repeated with longitudinal samples, where the direction of orientation of fillers is parallel to the length of the sample (Fig. 4.33 shows the schematic diagram), a reverse trend is observed. Longitudinal samples when tested without magnetic field show higher storage modulus than transverse samples. This is attributed to the arrangement of nanoparticles in the composite in a direction parallel to the application of force during the measurement. But, interestingly, when the samples were tested in magnetic field storage modulus shows lower values than when tested without field (Fig. 4.34). When the strength of magnetic field increased the storage modulus values further decreased. When the application of magnetic field is in a direction perpendicular to filler orientation in the composites, a distortion in the filler arrangement results, causing a decrease in storage modulus. The distortion increases with magnetic field further decreasing the storage modulus.

Thus the tuning of elastic modulus can be effected by applying magnetic field of different strengths together with preferential orientation of magnetic filler particles in the elastomeric composites. This modulus tuning could be employed in magneto elastomers for real-time damping applications.

![Schematic diagram showing longitudinal samples in magnetic field](image)

**Fig. 4.33: Schematic diagram showing longitudinal samples in magnetic field**
4B.5 Conclusions

Iron oxide nanoparticles were incorporated into natural rubber by mill mixing. Cure time and scorch time of the composites decrease with nano Fe$_3$O$_4$ loading. Scanning electron micrographs revealed a homogeneous distribution of Fe$_3$O$_4$ in the composites except at high loading. The mechanical properties of NR improved upon adding Fe$_3$O$_4$ nanoparticles. Dynamic mechanical analysis shows that storage modulus of the 45 phr composites is greater than that of the 60 phr composites which is due to better dispersion of fillers in the rubber matrix. However, the thermal stability of the composites decreased upon loading Fe$_3$O$_4$ nanoparticles, especially when well dispersed. Magnetic properties of the composites were improved with increased filler content. Dielectric measurements show an increase in dielectric constant, dielectric loss and AC conductivity of the composites with filler content. In microwave frequencies real and imaginary part of permeability as well as loss tangent improves upon Fe$_3$O$_4$ addition. Emi shielding effectiveness increases with filler content.

Fig 4.34: Variation of storage modulus with frequency when magnetic field was applied in the direction perpendicular to the orientation of Fe$_3$O$_4$ particles.
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content especially in X band. The tuneability of storage modulus by the application of magnetic field on NR/Fe\textsubscript{3}O\textsubscript{4} composites with preferential orientation of nanoparticles is demonstrated which can be employed for damping applications.

References


