Chapter 9

Magnetic Properties of NiFe₂O₄ and γ-Fe₂O₃ Based Rubber Ferrite Composites

Investigation on magnetic nanocomposites prepared by incorporating ferrites into elastomers are important not only from the fundamental point of view but also from the application perspective [1,2]. These composites are ideal templates to probe phenomenon such as particle-particle interaction in the matrix, particle-matrix interaction and their influence on the magnetic and microstructural properties.

Magnetic properties of spinel ferrites depend on a number of factors such as particle size, preparative conditions, heat treatment and the microstructure [3-8]. Both nickel ferrite and gamma ferric oxide are representatives of a large class of compounds called spinels. Nickel ferrite is an inverse spinel compound while γ-Fe₂O₃ is known to exhibit a vacancy ordered spinel with vacancies situated exclusively on the octahedral sites. Nickel ferrite and gamma ferric oxide is expected to exhibit interesting magnetic properties in the nano regime. The incorporation of these nano fillers into matrices like EPDM/CR will impart magnetic properties to the elastomer matrix.

Nickel ferrite nanoparticles exhibit anomalous magnetic behaviour [9-11] and they are found suitable for high frequency applications. The most important feature associated with the ferrite nanoparticles is the observed reduction in saturation magnetisation (Mₛ) compared to the bulk counter part [12-14]. The decrease in (Mₛ) with the decrease in particle size is associated with different reasons such as surface effects [15], spin canting [16] and dead layer formation [9,17-20].

Several studies were reported on the close relationship between structure and magnetic properties of different spinel ferrites [21-24]. The ferrimagnetism of spinel ferrites largely depends on the distribution of the metal ions in octahedral and tetrahedral lattice sites. As reported by Verma et al., the magnetic properties of nickel-
zinc ferrite system, like saturation magnetisation, coercivity (H_c) and magnetic remanence (M_r) are highly depend on the concentration of zinc ion in the tetrahedral site. The curie temperature of the system is also found to depend on the concentration and distribution of the cations between the octahedral and tetrahedral sites [25-27].

Tailoring of magnetic and mechanical properties of RFCs is also very vital as far as applications are concerned. Simple mixture equation can be formulated to foretell the magnetic properties of the RFCs. Evaluation of magnetic properties along with the modeling of these properties with known equations are significant.

Carbon black is added along with nickel ferrite/ gamma ferric oxide to enhance the microwave absorbing properties. The addition of carbon black in RFCs helps to tune the microwave properties by suitably modifying the dielectric property. So evaluation of magnetic properties of RFCs containing an optimum amount of magnetic filler together with the required amount of carbon black is also important. This is also taken up in this investigation.

Magnetic measurements of the NiFe_2O_4, γ-Fe_2O_3 and rubber ferrite composites containing these ferrites were carried out at room temperature using Vibrating sample magnetometer (VSM model EG&G PAR 4500) and the hysteresis loop parameters namely saturation magnetisation, remanent magnetisation and coercivity were determined.

### 9.1 Magnetic measurements of nickel ferrite and gamma ferric oxide

The hysteresis curve for nickel ferrite particles measured at room temperature is shown in figure 9.1. Parameters like saturation magnetisation and coercivity were determined from the hysteresis loop and are tabulated in table 9.1. The saturation magnetisation of the pristine nickel ferrite filler is found to be 39 emu/g which is less than the reported M_s value of the bulk sample (~55 emu/g) [28,29]. The coercivity of the prepared sample is ~100 Oe which is also less than the reported coercivity of bulk sample (130 Oe). The deviation in magnetic properties arises due to a number of factors. The structure of the particles could be changed by the presence of lattice defects or by a change in the distribution of the constituent ions between the tetrahedral sites and octahedral sites. In the present study, M_s of the samples is lower
than that of the bulk value, which rules out the absence of mixed spinel structure. In
the inverse spinel structure, the net magnetisation comes from the Ni\textsuperscript{2+} moments in the
B sites as the Fe\textsuperscript{3+} moments from the A and B sites cancel each other. In the mixed
spinel structure some Ni\textsuperscript{2+} ions occupy the tetrahedral site, and in that case the net magnetisation will be higher than that of inverse spinel structure [30,31].

![Hysteresis loop for NiFe\textsubscript{2}O\textsubscript{4}](image)

**Figure 9.1 Hysteresis loop for NiFe\textsubscript{2}O\textsubscript{4}**

The anomalous decrease in \( M_s \) for the prepared nickel ferrite than the bulk may be due to fine size effect and surface effects. Saturation magnetisation of particles decreases with particle size due to surface spin disorder. In fine particle systems since the surface to volume ratio is large, the ratio of number of surface spins to the total number of spins increases. This may lead to misalignment of surface spins resulting in surface anisotropy and deviation from the bulk properties. Another source of surface spin disorder for the fine particle nickel ferrite is due to broken exchange bonds that destabilise magnetic order giving rise to spin-frustration [32-34].

As the particle size decreases, coercivity increases, reaches a maximum value and then decreases after reaching a specific particle size [25,35,36]. As the particle size decreases, number of domains and domain walls decreases. The magnetisation/demagnetisation caused by domain wall movement requires less energy than that required by domain rotation. The number domain walls decreases with
decrease in grain size and the contribution of wall movement to magnetisation /demagnetisation is lower than that of domain rotation. Thus samples having lower grain size are expected to have high coercivity. In this particular study, the average particle size of the prepared nickel ferrite sample is higher than the critical diameter below which the coercivity shows a decreasing tendency with the decrease in particle size. Thus the coercivity of the prepared nickel ferrite was found to less than that of its bulk counterpart.

Similar results are also observed for gamma ferric oxide particles. Figure 9.2 represents the hysteresis loop for the γ-Fe₂O₃. The saturation magnetisation of the prepared γ-Fe₂O₃ is found to be about 52 emu/g and the coercivity is 123 Oe, whereas the corresponding values for the bulk sample is 75 emu/g and 300 Oe respectively. The magnetic characteristics of gamma ferric oxide particles are given in table 9.1. The decrease in Ms observed for γ-Fe₂O₃ is due to the fine size effect. Formation of non-magnetic alpha phase is also observed as revealed by X-ray diffraction, which also results in a reduction in magnetic properties.

The presence of superparamagnetic iron oxide could be another reason for the reduced magnetisation of γ-Fe₂O₃. The occurrence of superparamagnetic iron oxide along with ferrimagnetic iron oxide in the compound can considerably reduce the net coercive force of the compound. Magnetisation alone can't reveal the presence of
superparamagnetic components in a compound and techniques like Mossbauer spectroscopy is necessary to identify the presence of superparamagnetic components.

Table 9.1 Magnetic characteristics of NiFe₂O₄ and γ-Fe₂O₃

<table>
<thead>
<tr>
<th>Sample</th>
<th>Saturation Magnetisation Mₛ (emu/g)</th>
<th>Coercivity H_c (Oe)</th>
<th>Magnetic Remanence M_r (emu/g)</th>
<th>M_r/Mₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe₂O₄</td>
<td>39</td>
<td>101</td>
<td>5.3</td>
<td>0.13</td>
</tr>
<tr>
<td>γ-Fe₂O₃</td>
<td>52</td>
<td>123</td>
<td>8.1</td>
<td>0.16</td>
</tr>
</tbody>
</table>

9.2 Magnetic measurements of NiFe₂O₄ based RFCs

Rubber ferrite composites containing different loadings of NiFe₂O₄ and γ-Fe₂O₃ were prepared using EPDM and CR and the VSM analysis of these samples was carried out as in the case of ferrites.

9.2.1 Magnetic properties of EPDM based RFCs with nickel ferrite filler

Figure 9.3 represents the hysteresis loops for EPDM based RFCs containing 20, 40, 60, 80, 100 and 120 phr of NiFe₂O₄. From the hysteresis loop, the hysteresis loop parameters like Mₛ, H_c and M_r were evaluated and tabulated in table 9.2.
Saturation magnetisation and magnetic remanence of the EPDM based RFCs, increases with increase in ferrite content. Coercivity of the composite does not alter with variation in ferrite loading.

<table>
<thead>
<tr>
<th>NiFe$_2$O$_4$ Loading (phr)</th>
<th>Saturation Magnetisation, $M_s$ (emu/g)</th>
<th>Coercivity, $H_c$ (Oe)</th>
<th>Magnetic Remanence, $M_r$ (emu/g)</th>
<th>$M_r/M_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>7</td>
<td>126</td>
<td>1.3</td>
<td>0.20</td>
</tr>
<tr>
<td>40</td>
<td>11</td>
<td>126</td>
<td>2.0</td>
<td>0.18</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>126</td>
<td>2.9</td>
<td>0.20</td>
</tr>
<tr>
<td>80</td>
<td>17</td>
<td>126</td>
<td>3.1</td>
<td>0.18</td>
</tr>
<tr>
<td>100</td>
<td>19</td>
<td>126</td>
<td>3.6</td>
<td>0.19</td>
</tr>
<tr>
<td>120</td>
<td>22</td>
<td>126</td>
<td>4.3</td>
<td>0.20</td>
</tr>
</tbody>
</table>

The coercivity of the RFCs is higher than that of the nickel ferrite filler. Coercivity of the ceramic samples mainly depends on sintering conditions and particle size. The average particle size of the ferrite within the matrix may be different from that of the powder sample due to some degree of agglomeration. Another reason for the variation in coercivity between the ceramic and composites may be due to the interaction of the filler with the matrix. Since coercivity is a mass independent phenomena, change in coercivity of RFCs with ferrite loading is not observed.

Since saturation magnetisation of RFCs is a filler specific phenomenon, the $M_s$ value of RFCs can be tailored with the proper selection of the type and amount of the magnetic filler within the matrix. If the $M_s$ value of the ferrite is known, a simple mixture equation of the general form (equation 9.1) involving the weight fractions of the filler can be employed to calculate the $M_s$ of the composites.

$$M_{RFC} = W_1M_1 + W_2M_2$$

Where $M_{RFC}$ is the saturation magnetisation of the composite, $W_1$ and $W_2$ are the weight fractions of the filler and polymer, $M_1$ and $M_2$ are the saturation magnetisation of the filler and the polymer respectively. Since the matrix used for the preparation of RFCs is non magnetic, equation 9.1 can be reduced to the following form [37,38].
Figure 9.4 shows the variation in magnetisation values of NiFe$_2$O$_4$ filled EPDM composites with loading of the ferrite. The corresponding calculated values of $M_s$ are also plotted.

\[ M_{RFC} = W_1M_1 \]

From figure 9.4, it is clear that the calculated values are in good agreement with the experimental values especially at lower loadings. The slight variation, observed at higher loadings may be due to the deviation from the ideal dispersion of the filler within the matrix. Agglomeration of the filler particles occurs at higher loadings as evidenced from the physicomechanical studies of the RFCs.

### 9.2.2 Magnetic properties of neoprene based RFCs containing NiFe$_2$O$_4$ filler

VSM analysis of neoprene based RFCs containing different loadings of NiFe$_2$O$_4$ ranging from 40 to 120 phr were done at room temperature. Figure 9.5 represents the hysteresis loops for the neoprene based RFCs containing different amounts of NiFe$_2$O$_4$. 

---

**Figure 9.4 Experimental and calculated values of saturation magnetisation of NiFe$_2$O$_4$ filled EPDM composites**

From figure 9.4, it is clear that the calculated values are in good agreement with the experimental values especially at lower loadings. The slight variation, observed at higher loadings may be due to the deviation from the ideal dispersion of the filler within the matrix. Agglomeration of the filler particles occurs at higher loadings as evidenced from the physicomechanical studies of the RFCs.

### 9.2.2 Magnetic properties of neoprene based RFCs containing NiFe$_2$O$_4$ filler

VSM analysis of neoprene based RFCs containing different loadings of NiFe$_2$O$_4$ ranging from 40 to 120 phr were done at room temperature. Figure 9.5 represents the hysteresis loops for the neoprene based RFCs containing different amounts of NiFe$_2$O$_4$. 

---

245
The magnetic parameters calculated from the hysteresis loops of the composites are given in Table 9.3. From Table 9.3, it is observed that the $M_s$ and $M_r$ of the composites increase with increase in ferrite content. Coercivity of the neoprene based RFCs remain constant as in the case of EPDM based RFCs.

Table 9.3 Magnetic characteristics of NiFe₂O₄ filled neoprene composites

<table>
<thead>
<tr>
<th>NiFe₂O₄ Loading (phr)</th>
<th>Saturation Magnetisation, $M_s$ (emu/g)</th>
<th>Coercivity, $H_c$ (Oe)</th>
<th>Magnetic Remanence, $M_r$ (emu/g)</th>
<th>$M_r/M_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>10</td>
<td>115</td>
<td>2.1</td>
<td>0.21</td>
</tr>
<tr>
<td>60</td>
<td>14</td>
<td>115</td>
<td>2.8</td>
<td>0.20</td>
</tr>
<tr>
<td>80</td>
<td>17</td>
<td>115</td>
<td>3.5</td>
<td>0.21</td>
</tr>
<tr>
<td>100</td>
<td>19</td>
<td>115</td>
<td>3.7</td>
<td>0.19</td>
</tr>
<tr>
<td>120</td>
<td>21</td>
<td>115</td>
<td>3.8</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Coercivity of neoprene based RFCs is different from that of the NiFe₂O₄ filled EPDM based RFCs. The difference in $H_c$ between the ferrite and the RFCs gives indications of possible interaction between the ferrite and the rubber matrix. Small difference in coercivity is observed between EPDM and CR based RFCs, which may
be due to the difference in interaction of nickel ferrite filler with these matrices. However, the difference is insignificant, which indicates that there is only physical interaction between the ferrite and the matrices.

![Graph showing experimental and calculated values of saturation magnetisation of NiFe$_2$O$_4$ filled neoprene composites](image)

*Figure 9.6 Experimental and calculated values of saturation magnetisation of NiFe$_2$O$_4$ filled neoprene composites*

Saturation magnetisation value of the NiFe$_2$O$_4$ filled neoprene based RFCs are calculated using equation 9.1 and plotted along with the experimental values in figure 9.6. At lower filler contents, the calculated and experimental values agree well, but at higher loadings, deviations are observed.

A comparison of $M_s$ of EPDM and neoprene based RFCs containing same amount of nickel ferrite is given in figure 9.7. For the same loading of nickel ferrite the $M_s$ of EPDM and neoprene based RFCs were almost same and this is expected since saturation magnetisation depends only on the weight fraction of the ferrite in the matrix.
9.2.3 Effect of carbon black on the magnetic properties of RFCs containing \( \text{NiFe}_2\text{O}_4 \)

Figure 9.8 shows the hysteresis loops of EPDM based RFCs containing different loadings of carbon black and 100 phr \( \text{NiFe}_2\text{O}_4 \). Magnetic properties of composites containing different loadings of carbon black were evaluated from the corresponding hysteresis loops.

Figure 9.8 Hysteresis loops for EPDM based RFCs containing 100 phr \( \text{NiFe}_2\text{O}_4 \) and different loadings of carbon black.
The different magnetic parameters like $M_s$, $H_c$ and $M_r$ of the carbon black filled RFCs are given in table 9.4. From table 9.4, it is clear that the magnetic properties like $M_s$ and $M_r$ were found to decrease with increase in carbon black loading. Since carbon black is non magnetic, as the carbon black content increases the weight fraction of magnetic filler in the matrix decreases. The carbon black containing RFCs are still sufficiently magnetic, and are useful for application as flexible magnetic composites with improved mechanical properties. Moreover, additional loading of carbon black is expected to modify the microwave absorption property of these composites.

**Table 9.4 Magnetic properties of carbon black filled RFCs**

<table>
<thead>
<tr>
<th>Carbon black Loading (phr)</th>
<th>Saturation Magnetisation, $M_s$ (emu/g)</th>
<th>Coercivity, $H_c$ (Oe)</th>
<th>Magnetic Remanence, $M_r$ (emu/g)</th>
<th>$M_r/M_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19</td>
<td>115</td>
<td>3.7</td>
<td>0.19</td>
</tr>
<tr>
<td>20</td>
<td>18</td>
<td>123</td>
<td>3.6</td>
<td>0.20</td>
</tr>
<tr>
<td>40</td>
<td>16</td>
<td>123</td>
<td>3.3</td>
<td>0.21</td>
</tr>
<tr>
<td>60</td>
<td>15</td>
<td>123</td>
<td>3.1</td>
<td>0.21</td>
</tr>
<tr>
<td>80</td>
<td>14</td>
<td>123</td>
<td>2.7</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Figure 9.9 Experimental and calculated values of saturation magnetisation of carbon black containing RFCs
Figure 9.9 shows the comparison of the observed and calculated saturation magnetisation value of RFCs containing carbon black. Experimental $M_s$ value found to be slightly greater than the calculated value. As the ferrite content increases, agglomeration of the filler particles occurs and the effective particle size increases. Thus the calculated value of the saturation magnetisation deviates from the experimental values.

9.3 Magnetic properties of $\gamma$-Fe$_2$O$_3$ filled RFCs

Precharacterised gamma ferric oxide was incorporated into EPDM and CR matrix to prepare the corresponding RFCs.

9.3.1 Magnetic properties of $\gamma$-Fe$_2$O$_3$ filled EPDM based RFCs

Hysteresis loops for EPDM based RFCs with various loading of $\gamma$-Fe$_2$O$_3$ are represented in figure 9.10.

![Figure 9.10 Hysteresis loops of $\gamma$-Fe$_2$O$_3$ filled EPDM composites](image)

Figure 9.11 shows the variation of $M_s$ and $M_r$ with loading. Saturation magnetisation and magnetic remanence of EPDM based RFCs increases with increase in ferrite content. The increase in $M_s$ and $M_r$ is proportional to the increase in loading of the magnetic filler in the composites.
Figure 9.11 Loading dependence of $M_s$ and $M_r$ of $\gamma$-Fe$_2$O$_3$ filled EPDM composites

Figure 9.12 shows the variation of coercivity with the change in loading of $\gamma$-Fe$_2$O$_3$. Significant change in coercivity with the increase in the filler content is not observed. But slightly higher values are obtained for the RFCs compared to gamma ferric oxide.

Figure 9.12 Variation of coercivity of EPDM composites with loading of $\gamma$-Fe$_2$O$_3$
9.3.2 Magnetic properties of $\gamma$-Fe$_2$O$_3$ filled Neoprene based RFCs

Neoprene based RFCs containing different loadings $\gamma$-Fe$_2$O$_3$ were prepared and magnetic measurements were done using Vibrating sample magnetometer. The hysteresis loops for neoprene based RFCs containing different loadings of $\gamma$-Fe$_2$O$_3$ are shown in figure 9.13.

![Hysteresis loops of $\gamma$-Fe$_2$O$_3$ filled neoprene composites](image)

The magnetic characteristics calculated from the hysteresis loops are given in table 9.5. The saturation magnetisation and magnetic remanence increased with increase in ferrite loading. The increase in $M_s$ is proportional to the increase in ferrite content. The difference in $H_c$ between the filler and the RFCs are less significant.

<table>
<thead>
<tr>
<th>$\gamma$-Fe$_2$O$_3$ Loading (phr)</th>
<th>Saturation Magnetisation, $M_s$ (emu/g)</th>
<th>Coercivity, $H_c$ (Oe)</th>
<th>Magnetic Remanence, $M_r$ (emu/g)</th>
<th>$M_r/M_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>14</td>
<td>125</td>
<td>2.9</td>
<td>0.21</td>
</tr>
<tr>
<td>60</td>
<td>18</td>
<td>125</td>
<td>3.0</td>
<td>0.16</td>
</tr>
<tr>
<td>80</td>
<td>22</td>
<td>124</td>
<td>4.2</td>
<td>0.18</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>123</td>
<td>5.1</td>
<td>0.21</td>
</tr>
<tr>
<td>120</td>
<td>29</td>
<td>122</td>
<td>6.0</td>
<td>0.21</td>
</tr>
</tbody>
</table>
The calculated and experimental $M_s$ values are plotted in figure 9.14. The observed $M_s$ agrees well with the calculated values at lower loadings and a slight deviation is observed at higher loadings, which may be due to filler agglomeration.

9.4 Conclusion

Rubber ferrite composites were prepared using nickel ferrite and gamma ferric oxide as the filler and EPDM and neoprene as the host matrix. Magnetic parameters of the ferrites as well as that of the RFCs were measured using vibrating sample magnetometer. The saturation magnetisation of the prepared ferrites in the nanoregime was found to be less than that of the corresponding bulk samples. Coercivity of the nano ferrites was also found to be less than the bulk counter cousins. Saturation magnetisation and magnetic remanence of the prepared RFCs were found to be proportional to the loading of the ferrites. A simple mixture equation based on $M_s$ and the weight fraction of filler was employed to calculate the $M_s$ of the RFCs. The calculated magnetisation was found to be in agreement with the observed values especially at lower filler concentrations. The coercivity values of different set of RFCs were found to be independent of filler loading, but deviations were observed from that of the pure ferrites. The insignificant change in coercivity as well as linear dependence of $M_s$ and $M_r$ of RFCs, can be used to tailor the magnetic properties of the RFCs.
Effect of carbon black on the magnetic properties of EPDM based RFCs were studied. Magnetic properties of RFCs were found to decrease with increase in carbon black content. Coercivity values were found to be unaffected by the change in carbon black loading. Since carbon black modifies the microwave absorption properties of the RFCs, materials with desired microwave and magnetic properties can be prepared by adjusting the amount of carbon black and the ferrite.

References
24. Shannon A. Morrison, Christopher L. Cahill, Everett E. Carpenter, Scott Calvin, Raja
6392.
13.
28. V. Sepelak, M. Menzel, I. Bergmann, M. Wiebcke, F. Kruemelch and K. D. Becker, J.
31. A.E. Berkowitz, R. H. Kodama, Salah A. Makhoul, F. T. Parker, F. E. Spada, E. J.
33. Mathew George, Swapna S. Nair, Asha Mary John, P.A. Joy, M.R. Anantharaman, J.
34. Hongxia Wang, Faling Zhang, Wei Zhang, Xianjie Wang, Zhe Lu, Zhegian Qian, Yu