Chapter 3

Synthesis and Characterisation of Nickel Ferrite and Gamma Ferric oxide Nanoparticles

Preparation of phase pure materials is a prerequisite for any study in material science. The purity of the synthesised compound can be established only by a systematic and thorough characterisation using various analytical techniques at different intermediate stages. For the synthesis of rubber ferrite composites, preparation of phase pure precursors assumes importance. The history of precursor samples, the nature of heat treatment and the method of preparation are all vital inputs for a proper correlation and correct interpretation of data after an exhaustive study. This chapter emphasises the importance of synthesising pristine compounds and their characterisation for incorporation into matrices like ethylene propylene diene and neoprene rubber.

Since the focal theme of this particular investigation is on the influence of nano ferrite fillers in polymer composites like RFCs, emphasis is laid in preparing ultrafine ferrites. Nano nickel ferrite and maghemite (γ-Fe₂O₃) are chosen as fillers for synthesising RFCs because they find applications in a horde of devices ranging from transformer cores, to high density recording [1], magnetocaloric refrigeration [2], contrast enhancement in magnetic resonance imaging [3], magneto-optical devices and ferrofluid technology [4]. Normally, they are employed in the form of ceramic components. It is known from literature that different methods of preparation are in vogue for the synthesis of ferrites in the nano regime. Methods such as co-precipitation [5] micelle/reverse micelle [6,7], hydrothermal [8,9], high energy ball milling [10] and sol-gel [11-13] method are employed for the synthesis of ferrite nanoparticles.

A. Kale et al. utilised the technique of reverse micelle for the synthesis of nickel ferrite nanoparticles and were found to exhibit superparamagnetism [14]. Well crystallised ultrafine particles of zinc ferrite were prepared by Shu-Hong Yu et al.
using a low temperature hydrothermal method [15,16]. Nickel ferrite nanoparticles were synthesised by Yoshiaki Kinemuchi by pulsed wire discharge of iron and nickel in an oxygen rich environment [17]. However, the final product was contaminated with traces of nickel oxide impurities. Zhang et al. prepared nanorods of nickel ferrite by employing polyethylene glycol [18].

A low temperature technique, namely sol-gel method is adopted here for the preparation of spinel ferrites. It is also important that the crystal structure of the prepared compounds is evaluated and the particle size and particle size distribution are estimated properly. Powder X-ray diffraction is an effective tool for the precise determination of the crystal structure and evaluation of lattice parameters. This technique can also be employed for the particle size evaluation. However, particle size determination using the phenomenon of line broadening and employing Debye-Sherrer equation is not without uncertainties. Hence, alternate and complimentary techniques like Transmission electron microscopy are to be adopted. The employment of electron microscopy reveals information about shape and size of the particles. Electron microscopy aided by SAED/EDS will also reveal compositional details of the compounds. The structural details of the inorganic fillers for impregnation also assume significance. A wealth of information on bonding and existence of functional groups can be obtained by carrying out Fourier transform infrared spectroscopy on these samples. Spectral studies can be considered as the first step in fingerprinting the samples.

Thermal studies on precursor samples are useful in determining the exact decomposition temperature. Thermogravimetry reveals information on the temperature at which thermal decomposition or degradation of different groups occurs and the corresponding weight losses. These are crucial parameters for preparing the fillers in bulk.

The synthesis and characterisation of nanosized nickel ferrite and gamma ferric oxide is explained in this chapter.

3.1 Synthesis of nickel ferrite and gamma ferric oxide

Nickel ferrite and gamma ferric oxide nanoparticles were prepared by sol-gel technique. In this method, nitrate precursors were employed and ethylene glycol was
used as solvent. Chemical and structural changes that take place during combustion of gel precursors can be followed by infrared spectroscopy supported by thermogravimetric analysis.

The gel obtained during the preparation of nickel ferrite was subjected to thermogravimetric analysis. The thermogram is shown in figure 3.1. It can be seen that the weight loss occurring at around 200°C corresponds to the complete escape of ethylene glycol. The onset of decomposition is at around 260°C and the completion of this process is noticeable at around 370°C. Thermogravimetric studies provide information about phase formation. The dried gel samples were then heat treated corresponding to the decomposition temperature for further studies.

![Thermogram of the dried gel obtained in the preparation of NiFe₂O₄](image)

*Figure 3.1 Thermogram of the dried gel obtained in the preparation of NiFe₂O₄*

Chemical and structural changes that take place during combustion can be ascertained by recording the IR spectrum. The FTIR spectra of the dried gel of nickel ferrite precursor was recorded and a typical spectrum is shown in figure 3.2a.
Figure 3.2a FTIR spectrum of dried gel precursor for nickel ferrite synthesis

Characteristic bands at 3218 cm\(^{-1}\), 2882 cm\(^{-1}\) and 1565 cm\(^{-1}\) corresponding to -OH, -CH\(_2\) and (NO\(_3\)) functional groups are observed in the spectrum. The band at 1059 cm\(^{-1}\) is attributable to C-O deformations. The presence of the band at 1565 cm\(^{-1}\) indicates that metal ions and the nitrate ions are trapped in the gel structure, which on further ignition, converts to nickel ferrite.

The spectrum corresponding to the ignited sample is also shown in figure 3.2b. It can be seen that except the band at 540 cm\(^{-1}\) all bands which are present in the spectrum corresponding to the dried gel sample vanishes. The disappearance of characteristic bands corresponding to -CH\(_2\) and NO\(_3\)\(^{-}\) ions in the IR spectrum indicates that these groups play an active role in the reaction process during combustion leading to the formation of nickel ferrite. The combustion can be considered as thermally induced redox reaction of the gel wherein ethylene glycol acts as a reducing agent. The nitrate ion acts as an oxidant. Nitrate ion provides an in situ oxidising environment for the decomposition of the organic component [19,20].
Compounds having spinel structure should possess four IR bands $\gamma_1$, $\gamma_2$, $\gamma_3$ and $\gamma_4$ at 550 cm$^{-1}$, 630 cm$^{-1}$, 268 cm$^{-1}$ and 178 cm$^{-1}$ respectively. In the spinel lattice, every oxygen anion is bonded to three octahedral cations and one tetrahedral cation. These two give rise to two modes of vibration; $\gamma_1$ (550 cm$^{-1}$) and $\gamma_2$ (630 cm$^{-1}$). Two other modes $\gamma_3$ and $\gamma_4$ are related to displacement of cations in the lattice and these bands are reported to be at 268 cm$^{-1}$ and 178 cm$^{-1}$. The IR absorption band obtained at 540 cm$^{-1}$ (figure 3.2b) may be assigned to the stretching vibrations of octahedral groups.

The IR spectrum of the dried gel precursor for gamma ferric oxide synthesis is shown in figure 3.3a. The identical nature of IR spectrum of the dried gel obtained in both the cases suggests a similar mechanism for the preparation of gamma ferric oxide particles.
Figure 3.3a FTIR spectrum of dried gel precursor for gamma ferric oxide synthesis.

Figure 3.3b FTIR spectra of ignited gel (gamma ferric oxide)
FTIR spectrum of the ignited gel (gamma ferric oxide) is shown in figure 3.3b. The bands observed in the IR spectrum of gamma ferric oxide at 630 cm\(^{-1}\) (\(\gamma_2\)) and 536 cm\(^{-1}\) (\(\gamma_1\)) are assigned to the stretching vibrations of tetrahedral and octahedral groups respectively.

### 3.2 Structural studies of nickel ferrite

Nickel ferrite prepared by the method of sol-gel was then subjected to X-ray powder diffraction studies using Rigaku Dmax-C and employing Cu K\(\alpha\) radiations (\(\lambda = 1.5418\text{Å}\)). The diffractogram is depicted in figure 3.4.

![X-ray powder diffractogram for NiFe\(_2\)O\(_4\) prepared by sol-gel method](image)

*Figure 3.4 X-ray powder diffractogram for NiFe\(_2\)O\(_4\) prepared by sol-gel method*

The d values and the corresponding relative intensities are then compared with a standard spectrum of nickel ferrite (JCPDS No. 74-2081). Lattice parameter is then evaluated assuming cubic symmetry and found to be 8.329 Å. The powder diffractogram is characteristic of an inverse spinel and prominent planes are identified. This is shown in figure 3.4. Average particle size estimated using Debye-Sherrer formula is 19 nm.

Transmission electron micrograph of NiFe\(_2\)O\(_4\) was recorded on a Joel JEM 2200 FS electron microscope using an accelerating voltage of 200 kV. The micrograph and the electron diffraction diagram are shown in figures 3.5 and 3.6.
The histogram representing the particle size distribution is given in figure 3.7. Transmission electron micrograph reveals that the nickel ferrite samples are pure and polycrystalline in nature and have wide particle size distribution in the range 15-26 nm. The average particle size obtained from the histogram is about 19 nm. These results match well with the results obtained from X-ray diffraction studies.
Figure 3.7 Histogram of particle size distribution of $\text{NiFe}_2\text{O}_4$

Mapping picture of the nickel ferrite is shown in figure 3.8. The identical nature of the mapping diagram of iron, nickel and oxygen shows the phase formation of nickel ferrite particles and also shows the homogeneous nature of the prepared sample.

Stoichiometric formation of nickel ferrite can be evidenced from the mapping picture which is further supported by data collected from experiments using inductively coupled plasma analysis. The iron/nickel ratio obtained from ICP analysis is 1.78. From this, the actual stoichiometry of the nickel ferrite can be written as $\text{Ni}_{1.0894}\text{Fe}_{1.9106}\text{O}_4$. 
The surface area of the polycrystalline nickel ferrite is measured by Brunauer-Emmet-Teller method. The surface area thus determined is found to be 53 m$^2$/g. The theoretical X-ray density of nickel ferrite was calculated using the lattice parameters evaluated from X-ray diffraction. Particle size was also estimated using the relation 

$$S = \frac{6000}{D\rho}$$

where $D$ is the diameter of the particle and $\rho$ is the theoretical density. $D$ is found to be about 20 nm. This is in good agreement with the results obtained from X-ray diffraction results.

Porosity of the sample was calculated using the equation $(\rho_a - \rho_s)/\rho_a$ where $\rho_s$ is the theoretical density and $\rho_a$ is the actual density of the sample. Porosity of the sample is 39%.

3.3 Structural studies of gamma ferric oxide

Structural parameters of gamma ferric oxide are evaluated using the data from X-ray diffraction and electron diffraction. A typical X-ray diffractogram for gamma ferric oxide is shown in figure 3.9. All the planes are identified and the crystal planes are indexed. On comparison with standard spectrum of $\gamma$-Fe$_2$O$_3$, peaks corresponding to $\alpha$-Fe$_2$O$_3$ are found. The formation $\alpha$-Fe$_2$O$_3$ is probably because of the high temperature during the reaction.

![Figure 3.9 X-ray diffraction diagram of gamma ferric oxide](image)
The average particle size calculated using Debye–Sherrer formula is about 24 nm. The XRD pattern matches well with the JCPDS data (No. 391346) [21]. The lattice parameter is found to be 8.361 Å. The interatomic spacing and their relative intensities were also estimated.

Transmission electron micrographs of gamma ferric oxide are recorded and representative micrographs are shown in figures 3.10a and 3.10b. It is evident from micrographs that the particles are spherical in shape and in the range of 8-28 nm in size.

![TEM images of gamma ferric oxide](image1)

*Figure 3.10 TEM image of γ-Fe₂O₃ (a) at 50 nm scale (b) at 10 nm scale*

The average particle size estimated from these micrographs is found to be 20 nm. This is in good agreement with that of results obtained from X-ray diffraction.

![Selected area electron diffraction](image2)

*Figure 3.11 Selected area electron diffraction of γ-Fe₂O₃*
The electron diffraction pattern of $\gamma$-Fe$_2$O$_3$ is shown in figure 3.11. Bright spots observed in the diffraction pattern confirm the formation of polycrystalline gamma ferric oxide.

High resolution transmission electron micrograph of $\gamma$-Fe$_2$O$_3$ is shown in figure 3.12. Prominent crystalline planes are clearly observed in the diagram.

Surface area of the powdered sample was determined by BET nitrogen adsorption method. Surface area of the sample is found to be 36 m$^2$/g. Porosity of the sample is calculated as explained in section 3.2 and is found to be 21%.

3.4 Conclusion

Phase pure nano nickel ferrite was prepared by using the sol-gel method. The particle size was evaluated by different complimentary techniques and was found to be 19 nm. The results obtained using different techniques were in good conformity. Gamma ferric oxide was also prepared using the sol-gel technique. However, traces of $\alpha$-Fe$_2$O$_3$ were found along with $\gamma$-Fe$_2$O$_3$. Thermal and infrared spectroscopic studies carried out on gel precursors for nickel ferrite and gamma ferric oxide, confirm the belief that metal ions do not have any active role leading to the formation of their corresponding gels. Particle size evaluated using X-ray diffraction and Transmission electron microscopy indicate that $\gamma$-Fe$_2$O$_3$ particles are in the nano regime and lie in the range 24 nm. Consistency in particle size and structural parameters were obtained.
for various batches prepared in identical condition. Samples prepared in various batches were further homogenised using high energy ball milling and used for making rubber ferrite composites.

References