Effect of matrix type on the mechanical and magnetic properties of ferrite based natural and nitrile rubber nanocomposites

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Abstract. Copper doped nickel ferrite particles were prepared using co-precipitation method. The prepared particles were analysed using FTIR, XRD and SEM to confirm the formation of spinel ferrite structures, particle size and distribution. These ferrite nanoparticles are then embedded in natural and nitrile rubber at different loadings to compare the effect of matrix type on the mechanical and magnetic properties of composite samples. Nitrile rubber (NBR) composites show excellent magnetic properties than natural rubber (NR) composites. Saturation magnetisation, magnetic coercivity and magnetic retentivity values of NBR composites are superior to NR composites. In contrast mechanical properties are found to be inferior for NBR composites.

1. Introduction
Nickel ferrite is a class of soft magnetic materials because of its appealing and significant characteristics and has numerous technical perspectives. They have distinctive ferromagnetic properties, low conductivity and hence less eddy current losses, superior electrochemical steadiness, catalytic performance, large quantity in nature, etc. Studies on magnetic properties based on introducing ferrite into elastomers are significant from fundamental as well as application viewpoint [1, 2]. This class of materials are perfect models to probe phenomenon that could produce impact on the physico mechanical properties of composite structures. Magnetic property of spinel structured ferrites depends on a several aspects such as particle aspect, way of preparation, thermal methods and the microstructure [3-4]. Nickel ferrite is a representative of a wide range of combinations named spinels. Nickel ferrite (NiFe$_2$O$_4$) is having an inverse spinel structure and is likely to display fascinating magnetic stuffs in the nano system whose insertion into systems like natural rubber will definitely impart magnetism to the elastomer matrix.
The unusual magnetic behaviour of NiFe$_2$O$_4$ nanoparticles [5-6] are recognized to be suitable for high energy applications. The most important property associated with the ferrite nanoparticles is the realistic reduction in saturation magnetization (Ms) with respect to the bulk complement [7-8]. This lessening in Ms is concurrent with different particulars like surface effects [9], spin canting [10] and dead layer formation [11].

Introduction of magnetic fillers into elastomers lead to the development of flexible magnets. The flexibility along with unique magnetic properties enable these materials to be used in many high performance applications. Elastomer composites are capable of sensing vibrations and oscillations of various wavelengths. Hence they find application in dc-motors, radars, memory devices, radars and other technical fields [12-14]

The scope includes a novel method for preparing nickel ferrite with copper as dopant ion using co-precipitation method. The prepared ferrite particles are then embedded in natural rubber as well as nitrile rubber at different loadings to develop rubber nanocomposites. The prepared samples were characterized for structural determination and used for magnetic and mechanical studies.

2. Experimental

2.1 Preparation of nickel ferrite/doped nickel ferrite
Doped nickel ferrite powders were synthesised using co-precipitation method. The method is described elsewhere [15]. The resultant compounds were characterised using FTIR and XRD to confirm the modification and particle size.

2.2 Composite sample preparation:

| Sample            | Ni(NO$_3$)$_3$ | Cu(NO$_3$)$_3$ | Fe(NO$_3$)$_3$ $9\text{H}_2\text{O}$ |
|-------------------|---------------|----------------|-------------------------------------|
| NiFe$_2$O$_4$     | 5g            | 0g             | 8.3g                                |
| Ni$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$ | 4.01g         | 0.8g           | 8.3g                                |

2.3 Preparation of rubber nanocomposites
Rubber, filler and compounding ingredients are taken in the ratio as given in the following tables 2 and 3 and are mixed uniformly in a two roll mill compounded for 15 minutes by cautiously monitoring the temperature and nip gap. The samples were milled sufficiently to ensure the uniform dispersion of the fillers in the matrix at a mill opening of 1.25 mm. The fillers were added at the end of the mixing process. When the mixing is complete, the mix was allowed to pass through a close nip gap and eventually sheeted at a specific nip gap. The composites were left for a day in a desiccator before vulcanization.

| Ingredients in phr | Gum NR | NF5/NR | NF15/NR | NF25/NR | DNF5/NR | DNF15/NR |
|--------------------|--------|--------|---------|---------|---------|---------|
| NR                 | 100    | 100    | 100     | 100     | 100     | 100     |
| Nickel ferrite     | 0      | 5      | 15      | 25      | 0       | 0       |
| Doped nickel ferrite | 0      | 0      | 0       | 0       | 5       | 15      |
| Stearic acid       | 1      | 1      | 1       | 1       | 1       | 1       |
| Zinc oxide         | 5      | 5      | 5       | 5       | 5       | 5       |
| TDQ                | 1      | 1      | 1       | 1       | 1       | 1       |
| CBS                | 1      | 1      | 1       | 1       | 1       | 1       |
| Sulphur            | 2.5    | 2.5    | 2.5     | 2.5     | 2.5     | 2.5     |
Table 3 Formulation of Nitrile rubber composites

| Ingredients in phr | Gum NBR | NF5/NBR | NF15/NBR | NF25/NBR | DNF5/NBR | DNF15/NBR |
|-------------------|---------|---------|----------|----------|----------|----------|
| NR                | 100     | 100     | 100      | 100      | 100      | 100      |
| Nickel ferrite    | 0       | 5       | 15       | 25       | 0        | 0        |
| Doped nickel ferrite | 0  | 0       | 0        | 0        | 5        | 15       |
| Stearic acid     | 1       | 1       | 1        | 1        | 1        | 1        |
| Zinc oxide       | 5       | 5       | 5        | 5        | 5        | 5        |
| TDQ               | 1       | 1       | 1        | 1        | 1        | 1        |
| CBS               | 1       | 1       | 1        | 1        | 1        | 1        |
| Sulphur           | 2.5     | 2.5     | 2.5      | 2.5      | 2.5      | 2.5      |

3. Results and discussion

3.1 Fourier Transform Infra-Red (FTIR) spectroscopy
The FTIR spectrum in figure 1 shows two major absorption bands $v_1$ and $v_2$ as which is general quality of all spinel compounds [16]. In copper nickel ferrite ($\text{Cu}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$), IR absorption bands are obtained in the scope of 600–400 cm$^{-1}$. The absorption band $v_1$ is related to the stretching vibration form of $\text{Fe}^{3+}$–$\text{O}_2^-$ in tetrahedral A-site, and $v_2$ is related to metal–oxygen vibrations in octahedral sites. The disparity in the band location is normal due to the variation in the $\text{Fe}^{3+}$–$\text{O}_2^-$ for the octahedral and tetrahedral complexes. The occupation of $\text{Cu}^{2+}$ ions in octahedral and tetrahedral sites is responsible for the broadening of the bands. Shoulders are found at lower frequency bands $v_2$ which may be attributed to the Jahn–Teller effect.

Figure 1. FTIR of $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$
3.2 X-Ray Diffraction

The XRD patterns of prepared nickel ferrite nano particles are given in figures 2 and 3. It confirms the growth of single phase spinel structure for all the samples. The development of spinel cubic structure was established by the subsistence of (311), (400), (422), (511) and (440) crystal planes in the XRD patterns, which is in agreement with the JCPDS powder diffraction file. The most intense reflection arise from (311) which confirms the spinel plane [17]. The particle size was calculated for all the samples related high intensity (311) plane using Scherer formula.

| Sample           | Average particle size |
|------------------|-----------------------|
| Ni$_0.8$Cu$_0.2$Fe$_2$O$_4$ | 22 nm                 |
| NiFe$_2$O$_4$     | 21 nm                 |

**Figure 2.** XRD of NiFe$_2$O$_4$
3.3 Scanning Electron Microscopy
The FE-SEM images of the copper doped nickel ferrite nanocrystals have been shown in figure 4. The average grain size of the Ni$_{0.8}$Cu$_{0.2}$Fe$_2$O$_4$ and NiFe$_2$O$_4$ nanocrystals are 31, and 30nm, respectively. Note that the typical grain size of the samples produced from SEM images is bigger than nanocrystals size as determined using the XRD calculations, which shows that each particle is obtained by aggregation of a numerous nanocrystals. The samples are sphere-shaped and consistent, and solidity of grains is due to the magnetic pull.
3.4 Magnetic Studies

The magnetic properties were measured using Vibrating Sample Magnetometer (VSM) of model EG and G PAR. Factors like magnetic remanence, saturation magnetisation and coercivity were obtained at room temperature using the corresponding hysteresis loops.

**Table 5 Magnetic parameters of prepared samples**

| Sample     | Saturation Magnetization (Ms) (emu/g) | Magnetic coercivity (Hc) | Magnetic Retentivity (Mr) |
|------------|--------------------------------------|--------------------------|---------------------------|
| Gum NBR    | 0.0941                               | 72.05                    | 0.2261                    |
| NF25/NBR   | 0.2793                               | 184.03                   | 4.56                      |
| DNF15/NBR  | 0.1555                               | 173.81                   | 3.17                      |
| NF25/NR    | 0.1867                               | 183.44                   | 3.39                      |
| DNF15/NR   | 0.1229                               | 172.01                   | 2.46                      |
| NF15/NR    | 0.1418                               | 155                      | 2.69                      |

From the table 5, it is very clear that magnetic properties are superior for doped samples. Also the properties get enhanced when taken in nitrile rubber matrix on comparison with natural rubber matrix. This is attributed to the inherent magnetic property of nitrile rubber. The results prove that there is a slight interaction between the filler particles and matrix in the domain region. The coercivity values are almost similar for nanoparticles and composites.

**Table 6 Mechanical properties of Naturel rubber nanocomposites**

| Sample     | Tensile strength (MPa) | Elongation at break (100%) | Modulus at 100% (MPa) | Hardness (Shore A) |
|------------|------------------------|----------------------------|-----------------------|-------------------|
| Gum NR     | 11.10                  | 1598.36                    | 0.81                  | 35.8              |
| DNF5/NR    | 9.17                   | 1512.92                    | 0.75                  | 40.2              |
| DNF15/NR   | 7.11                   | 1431.01                    | 0.68                  | 40.8              |
| NF5/NR     | 12.12                  | 1673.50                    | 0.88                  | 41.0              |
| NF15/NR    | 14.27                  | 1880.12                    | 0.85                  | 40.9              |
| NF25/NR    | 11.12                  | 1480.53                    | 0.83                  | 41.2              |

3.5 Mechanical studies

Tensile strength and related properties were studied according to ASTM method D 412-98 on INstron 4411 (England) Universal Testing Machine (UTM) at a cross head sped of 500 mm/min.
Table 7 Mechanical properties of Nitrile rubber nanocomposites

| Sample        | Tensile strength (MPa) | Elongation at break (100%) | Modulus at 100% (MPa) | Hardness (Shore A) |
|---------------|------------------------|----------------------------|-----------------------|--------------------|
| Gum NBR       | 3.84                   | 1391.73                    | 0.88                  | 31.1               |
| DNF5/NBR      | 2.25                   | 1033.13                    | 1.00                  | 32.3               |
| DNF15/NBR     | 2.77                   | 1099.22                    | 1.18                  | 32.5               |
| NF5/NBR       | 2.82                   | 1009.22                    | 1.10                  | 31.8               |
| NF15/NBR      | 3.21                   | 1341.64                    | 0.81                  | 32.0               |
| NF25/NBR      | 3.82                   | 1451.30                    | 0.85                  | 32.8               |

The mechanical properties of nickel ferrite based NR and NBR composites are compared with gum in tables 6 and 7. The values of tensile strength, elongation at break and modulus shows that presence filler decreases mechanical properties but this decrease is not steady. The decrease may be attributed to the tendency of fillers to resist the orientation to form crystallites. The variation of hardness with filler loading shows an opposite trend.

The tensile strength decrease with the increase in the amount of ferrites. One reason for this is the inferior interfacial bonding among the filler and the matrix. Due to the reduction in the effective cross section of the matrix in the composites there is a rise in internal stress, for every point of external loading when compared with the bare rubber matrix. Plastic distortion in a micro level happens about the filler particles, which enable destruction of the material at lesser external load, when related to the unfilled material. Due to the differential thermal expansion coefficient, thermally initiated internal stresses may also take place about the filler particles. This donates to a rise in the de-wetting stress. Another reason for diminishing property is the dilution effect, which may be attributed to the decreasing volume fraction of rubber in the composite.

4. Conclusion

Doped nickel ferrite particles were well prepared using the co-precipitation method. FTIR, XRD and SEM techniques confirmed the formation of spinel ferrite particles and their particle size to be in the nano regime. Magnetic studies proved that doping synergistically support the magnetic behaviour of prepared composites. Nitrile rubber composites were found to be superior to natural rubber composites which may be ascribed to the slight conducting nature of nitrile rubber matrix. Mechanical properties showed an opposite trend as it decreases with filler loading except the hardness.

5. References

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