Synthesis & characterization of doped nickel ferrite filled natural rubber nano composites

Hema S¹, Sreedha Sambhudevan*¹, Mahitha P M¹, Rashid Sultan K¹, Malavika Raj¹,
Anjana A¹, Parvathy S U¹, Mahalekshmi M S¹ and Balakrishnan Shankar²

¹Department of Chemistry, Amrita School of Arts and Sciences, Amrita Vishwa Vidyapeetham, Amritapuri, Kerala, India, 690525, India.
²Department of Mechanical Engineering, Amrita Vishwa Vidyapeetham, Amritapuri, Kerala, 690525, India.

E-mail: sreedha@am.amrita.edu

Abstract : Synthesis of rubber nanocomposite containing differently doped ferrites were fabricated using Co-precipitation method. The nano particles characterization was carried out by SEM, FTIR and XRD to confirm that the ferrites were synthesized in nanometer dimensions. The rubber mixes were incorporated with metallic nano fillers and the obtained nanocomposites were analysed for mechanical studies such as hardness, specific gravity, tear and tensile strength. The copper doped samples shows excellent mechanical properties over other dopants and hence paving the way for decisive technical applications.

Keywords: Ferrites; Doped Ferrites; Rubber Nanocomposites; Tensile-Tear Analysis; Hardness.

1. INTRODUCTION

Polymer-inorganic nanocomposites such as Ferrites-Rubber composites have considerable interest due to its increased attention on various scientific and technological fields [1] They are commonly bolstered by doping with various metallic salts to lighten some of the limitation of filler-polymer systems and hence to increase their applications. In the past years various inorganic fillers were used as additives to several rubber matrix to improve their mechanical strength, thermal and chemical stability and the term ‘hybrid’ or ‘molecular composite’ was used instead of ‘nanocomposites’ [2]. However, the traditional fillers are in micro-size and did not possess the superior properties of nanoparticles.

The advantage of Natural Rubber over the other matrices is its flexibility, light weight and low production cost. Since the processing is effortless it can be moulded in to thin sheets by various techniques. Theses rubber matrix systems are intrinsically non-magnetic in nature but the impregnation of magnetic type fillers in polymer matrix imparts magnetic natures [3] and markedly improves the physical properties as well.

Among different magnetic materials that possess broad applications in technology, ferrites gain much attention and cannot be replaced by any other magnetic material because they are less expensive, stable and widely used in high-frequency applications. In the field of electronics ferrites found have revolutionary applications in storage systems, microwave devices and electromagnetic interference suppression [4] Ferrite nanoparticles have decisive role in different fields of science and technology
due to its highly geared applications at lower size in 10-30nm range. Basically, ferrites are ceramic compound with high flux density and dark grey appearance. They are the oxides of ferric ions with hard, brittle and ferromagnetic behaviour. [5]

In the present study ferrite doped with Magnesium, Copper, Zinc and Nickel were synthesized. The synthesized samples were characterized by SEM, XRD and FTIR. The rubber mixes were vulcanized for corresponding cure time and the obtained nanocomposites were analysed for different mechanical studies.

2. EXPERIMENTAL

2.1 Preparation of Nano sized Nickel ferrites/Doped Nickel ferrites.
Nanofillers of Nickel ferrites and corresponding doped ferrites were synthesized via Co-precipitation method. About 0.6g of polyvinyl pyrolidone (PVP) was dissolved in 100ml distilled water and stoichiometric amount of amount of nitrates was added in to solution. NaOH solution was added until the pH reaches 12. The resulting mixture was stirred for 2 hours at 80°C. Excess PVP was removed by washing with water and ethanol. The nano powder was dried in muffle furnace for 24 hours at 100°C. The dark brown powder was calcinated at 600°C for 3 hours and crushed[6].

2.2 Preparation of rubber nanocomposites.
Rubber, ferrite filler and compound blending ingredients were taken according to the given below table 1 and the samples were mixed in two roll mill and blended for about 20 minutes. In the first stage of mixing the natural rubber was preblended with functional additives such as curing agents and accelerators followed by the addition of nickel ferrite nanoparticles. About 45°C was maintained at a standard for rotor speed. When the mixing is completed, it was allowed to go through a close nip gap and sheeted at a specific nip gap[7].

| Ingredients in phr | Gum | NF/NR | NCF/NR | NMF/NR | NZF/NR |
|-------------------|-----|-------|--------|--------|--------|
| NR                | 100 | 100   | 100    | 100    | 100    |
| NiFe₂O₄           | 0   | 5     | 0      | 0      | 0      |
| Ni₀.₈Cu₀.₂Fe₂O₄   | 0   | 0     | 5      | 0      | 0      |
| Ni₀.₈Mg₀.₂Fe₂O₄   | 0   | 0     | 0      | 5      | 0      |
| Ni₀.₈Zn₀.₂Fe₂O₄   | 0   | 0     | 0      | 0      | 5      |
| Stearic acid      | 1   | 1     | 1      | 1      | 1      |
| Zinc oxide        | 5   | 5     | 5      | 5      | 5      |
| TDQ               | 1   | 1     | 1      | 1      | 1      |
| CBS               | 1   | 1     | 1      | 1      | 1      |
| Sulphur           | 2.5 | 2.5   | 2.5    | 2.5    | 2.5    |

3. RESULTS AND DISCUSSIONS

3.1. Scanning Electron Micrograph (SEM)
The Field Emission Scanning Electron Micrograph (FE-SEM) of synthesized Nickel ferrite nanoparticles have been shown in the below figure 1. The average crystalline size was of 31 and 30nm. The particles are spherical and uniform, and cohesion of grains is due to the magnetic attraction possessed by ferrite particles.
3.2. Fourier Transform Infra-red (FTIR) Spectroscopy.
The FTIR spectra of Nickel Ferrite is shown in figure 2. For nickel ferrites FTIR spectra shows two prominent peaks in the range 600-400 cm\(^{-1}\). Among these one band corresponding to metal oxygen stretching vibrations in the tetrahedral site and the other one corresponds to octahedral site metal-oxygen vibrations[8]. The presence of dopants in these sites is the reason for broadening of these bands.

3.3. X-Ray Diffraction Studies.
Figure 3. which gives the XRD profile of nickel ferrites establishes the formation of spinel structure with single phase. The spinel structure was confirmed by the presence of (311), (400), (422), (511) and (440) planes in the XRD patterns. The intense peak at (311) again proves the formation of spinel plane. Using Scherrer formula, considering FWHM corresponding to (311) plane, the particle size was found to be 21 nm[9].
3.4. Mechanical Studies.

Effect of Tensile strength, tear resistance, elongation at break, modulus and hardness of nickel ferrite and doped nickel ferrites is shown in the table 2. These mechanical properties are consistent with the result obtained from XRD and SEM data. The tensile strength is greater for Copper doped Nickel ferrite while the least is shown by Magnesium doped Nickel ferrite.

Table 2. Mechanical properties on natural rubber nanocomposites.

| Sample   | Tensile strength (MPa) | Elongation at break (100%) | Modulus at 100% (MPa) | Tear Strength (N/mm) |
|----------|------------------------|----------------------------|-----------------------|----------------------|
| Gum      | 3.13                   | 471.10                     | 0.48                  | 2.54                 |
| NF/NR    | 1.02                   | 320.52                     | 0.41                  | 2.47                 |
| NCF/NR   | 2.65                   | 308.49                     | 0.58                  | 2.54                 |
| NMF/NR   | 0.89                   | 310.03                     | 0.35                  | 2.58                 |
| NZF/NR   | 2.44                   | 295.12                     | 0.42                  | 2.50                 |

Since mechanical properties was found to be superior for copper doped samples further studies were concentrated on this particular sample. Doping was efficient with copper and zinc when compared to magnesium and this is highly evident in the above studies. This efficiency in doping also leads to proper distribution of filler in the rubber matrix thereby supporting the matrix to show high mechanical properties.

3.5. Hardness and specific gravity measurements.

Hardness and specific gravity of all the composites are depicted in the below table 3. As comparing all the doped ferrites, it is clear that copper and zinc doped specimens shows desirable hardness and this supports the increased value of specific gravity. However, higher specific gravity value is not acceptable as it increases the product weight[10].
Table 3. Hardness and specific gravity of nanocomposites.

| Sample  | Hardness (Shore A) | Relative Density |
|---------|--------------------|-----------------|
| Gum     | 18                 | 0.9845          |
| NF/NR   | 12                 | 0.937           |
| NCF/NR  | 20                 | 0.962           |
| NMF/NR  | 10                 | 0.999           |
| NZF/NR  | 16                 | 0.997           |

4. CONCLUSION

Nickel ferrite and doped Nickel ferrites blended composite were compounded. Dispersion of metallic filler over the natural rubber matrix critically enhances the mechanical properties of composites. The prepared nano fillers were characterized via SEM, FTIR and XRD and confirms the formation of spinel structure. It was found that all the mechanical properties are excellent for copper doped samples and these samples can be efficiently used for shielding purposes.

ACKNOWLEDGEMENT

We would like to acknowledge everyone who helped us to complete our work successfully. We specially thank our University Amrita Vishwa Vidyapeetham for rendering us all the facilities and guidance to reach our goals. We extend our heartfelt gratitude to faculties in Common Facility Service Centre, Kottayam for helping us in nurturing our thoughts and providing us a great opportunity to work on our area of interest to a new path.

REFERENCES

[1]. Bersweiler, M., Bender, P., Vivas, L. G., Albino, M., Petrecca, M., Mühlbauer, S., & Michels, A. (2019). Size-dependent spatial magnetization profile of Manganese-Zinc ferrite nanoparticles. arXiv preprint arXiv:1908.00343.

[2]. Wen, Y., Yin, Q., Jia, H., Yin, B., Zhang, X., Liu, P., & Xu, Z. (2017). Tailoring rubber-filler interfacial interaction and multifunctional rubber nanocomposites by usage of graphene oxide with different oxidation degrees. Composites Part B: Engineering, 124, 250-259.

[3]. Bellucci, F. S., de Almeida, F. C. L., Nobre, M. A. L., Rodríguez-Pérez, M. A., Paschoalini, A. T., & Job, A. E. (2016). Magnetic properties of vulcanized natural rubber nanocomposites as a function of the concentration, size and shape of the magnetic fillers. Composites Part B: Engineering, 85, 196-206.

[4]. Ramesan, M. T., Anjitha, T., Parvathi, K., Anilkumar, T., & Mathew, G. (2018). Nano zinc ferrite filler incorporated polyindole/poly (vinyl alcohol) blend: Preparation, characterization, and investigation of electrical properties. Advances in Polymer Technology, 37(8), 3639-3649.

[5]. Peng, C. H., Wang, H. W., Kan, S. W., Shen, M. Z., Wei, Y. M., & Chen, S. Y. (2004). Microwave absorbing materials using Ag–NiZn ferrite core–shell nanopowders as fillers. Journal of magnetism and magnetic materials, 284, 113-119.

[6]. Maaz, K., Karim, S., Mumtaz, A., Hasanain, S. K., Liu, J., & Duan, J. L. (2009). Synthesis and magnetic characterization of nickel ferrite nanoparticles prepared by co-precipitation route. Journal of Magnetism and Magnetic Materials, 321(12), 1838-1842.

[7]. Zhang, L., Wang, Y., Wang, Y., Sui, Y., & Yu, D. (2000). Morphology and mechanical properties of clay/styrene- butadiene rubber nanocomposites. Journal of Applied Polymer Science, 78(11), 1873-1878.

[8]. Naseri, M. G., Saion, E. B., Ahangar, H. A., Hashim, M., & Shaari, A. H. (2011). Simple preparation and characterization of nickel ferrite nanocrystals by a thermal treatment method. Powder Technology, 212(1), 80-88.
[9]. Nejati, K., & Zabihi, R. (2012). Preparation and magnetic properties of nano size nickel ferrite particles using hydrothermal method. *Chemistry Central Journal, 6*(1), 23.

[10]. Kumar, S., Chattopadhyay, S., Padmanabhan, R., Sreejesh, A., Nair, S., Unnikrishnan, G., & Nando, G. B. (2015). Tailoring permeation characteristics of bromobutyl rubber with polyepichlorohydrin and graphene nanoplatelets. *Materials Research Express, 2*(10), 105007.