Dielectric properties of low-density polyethylene based nickel ferrite and copper ferrite

Kriti Vaid
Amity School of Engineering and Technology, Rajasthan

Umesh Kumar Dwivedi
Amity School of Engineering and Technology, Rajasthan

Deepshikha Rathore
Amity School of Engineering and Technology, Rajasthan

kritivaid@gmail.com, umeshkudwivedi@gmail.com, deep.nano@gmail.com

Abstract. Nickel and Copper ferrite of different compositions have been synthesized by wet co-precipitation technique. The synthesized samples were annealed at 800ºC for 4 hours and characterized by X-Ray Diffraction (XRD) analysis. The XRD pattern confirms the formation of a cubic structure with the crystalline size for nickel ferrite 23nm and copper ferrite 37nm. The composite has been synthesized with the various compositions (10wt% and 30wt%) of nickel ferrite and copper ferrite with pH values 6, 8 and 10 in LDPE. The Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectrum (EDAX) confirms the homogeneous mixing of the composite material. The dielectric measurement has been carried out as a function of frequency at room temperature in the range of 1Hz-8MHz. The dielectric behaviour of Nickel ferrite and Copper ferrite based LDPE composite results decrease in dielectric constant and dielectric loss factor with the increase in frequency.

Keywords: Low-Density Polyethylene, Nickel ferrites, Copper ferrite, X-Ray Diffraction, Scanning Electron Microscopy, Dielectric properties.

1. Introduction

Low-density polyethylene (LDPE) is one of the excellent thermoplastic materials used in the industrial, electrical and mechanical fields because of its low dielectric loss, low cost, high dielectric strength, low moisture, and chemical resistant. LDPE consists of one or two per 1000 carbons which change the properties of the material [1]. LDPE has a large distribution of crystalline size and therefore having a melting point of around 100ºC-110ºC. For decades insulating polymers have been widely used in power cables and further LDPE is considered as the best polymer most commonly used in the insulation of cables [2] [3]. Polymers are made electrically conductive by the addition of ferrites as there are insulating oxides and have a variety of properties compared to other materials [4]. With excellent technological importance of ferrites, their electrical and magnetic properties also exhibit dielectric properties that allow the passing of electromagnetic waves through it [5] [6]. Ferrites are mainly made up of a combination of oxides of metals like nickel, copper, nickel ferrite (NiFe₂O₄) and copper ferrite (CuFe₂O₄), these ferrites have a counter spinel structure and having typical ferromagnetic properties. The
Ferrite material is being synthesized by various techniques such as co-precipitation method, hydrothermal technique. Nickel ferrite and copper ferrite are one of the most important spinel ferrites because of their fascinating magnetic and electrical equity along with good chemical and thermal stabilities. Copper ferrite (CuFe₂O₄) is an inverse spinel ferrite in which the tetrahedral (A) sites are occupied by ferric ions, and octahedral (B) sites are occupied by ferric and copper ions [7][8]. Apart from synthesis, pH value has a significant role in the characterization of properties for ferrites as they bring variation or modification in properties of the material [9]. In the present work-study, the dielectric properties have been carried out because of numerous applications of ferrites because of their lightweight, low cost, and compatibility in electrical circuits and Power Electronics [10]. Nickel ferrite and Copper ferrite are chosen as a source because a layer of ferrite materials can increase the operational life of the polymer and other properties as compared to the normal operation of the polymer. LDPE/NiFe₂O₄ and LDPE/CuFe₂O₄ composites with 10wt% and 30wt% at different pH value of 6, 8, and 10 are studied in this work; there is still a scope of more research in the present work hence the work carried out in the present study is a step in this direction. The present paper is arranged schematically as follows.

In section 2 outlines of the experimental XRD, SEM and EDAX set up is given which provide the detail of the process which has been followed to take up the present work. In section 3 the experimental, result and discussion of dielectric for Low-density polyethylene based nickel ferrite and copper ferrite composite has been carried out and final closure is explained in section 4.

2. Experimental
The nickel ferrite and copper ferrite have been prepared by the wet co-precipitation technique.

Starting Chemicals:
- Ferric nitrate (Fe(NO₃)₃.9H₂O)
- Nickel nitrate (Ni(NO₃)₂.6H₂O)
- Copper nitrate (Cu(NO₃)₂.6H₂O)
- Ammonia solution (NH₃)

The nickel nitrate (Ni(NO₃)₂.6H₂O with 2.9077g and Ferric nitrate (Fe(NO₃)₃.9H₂O) with 8.085g of weight stoichiometrically are dissolved separately in a minimum amount of double-distilled water, then 300ml of the solution is formed[11]. The solution then divided into three different beakers and stirred continuously for 30 minutes using magnetic stirrer attached with hot plate, with continuous stirring ammonia solution is added dropwise to maintain pH value of 6, 8 and 10. The product is kept at room temperature and then washed thrice with distilled water to eliminate unwanted impurities and the residual surfactant from the prepared sample. The solution is kept in the mantle at a temperature of 80°C for 7 hours, due to the continuous evaporation of water the mixed solution gets transform sol into a gel and then gel completely dried and the solution becomes viscous and finally crushed into powder form. The powder form then annealed in a muffle furnace at 800°C for 4 hours and cooled slowly down to room temperature.

During the experiment, the solvent Xylene C₆H₄(CH₃)₂ of 106.17g/mol is taken from Fisher scientific and heated up to the temperature 85°C before mixing LDPE granules. When the LDPE granules dissolved into the xylene solvent in few hours, then it swelled and turned from white color to odorless later LDPE solution is mixed with Nickel ferrite and Copper ferrite with 10wt% and 30wt% by the melt mixing process. The synthesized sample annealed at 800°C for 4 hours and characterized by X-Ray Diffraction analysis, the structural characterization of nickel ferrite and copper ferrite are made through the XRD Diffraction technique in the 2θ range of 20 to 79.960 deg. The XRD pattern is recorded at room temperature using CuKα λ=1.54060 Å radiation[12]. The slow scan of selected diffraction peaks is carried out in step size of 0.0260, measurement time 51.76s, measured temperature 25°C, standard and generator setting 40mA, 45KV.
3. Results and discussions

3.1. XRD of nickel ferrite
The XRD pattern of nickel ferrite of prepared samples are calcinated at 800ºC for 4 hours, the calcinated samples shows the reflection peaks at (220), (311), (400), (422), (511), (440), (533) which indicates the presence of NiFe₂O₄ having cubic structure. The obtained peaks are well-matched with standard JCPDS card number 44-1485, with sharp and strong peaks reflecting the purities and crystalline of NiFe₂O₄. No secondary phase has been detected of annealed XRD samples. The lattice parameter is calculated as \( a = 8.31 \text{Å} \) and crystallite sizes are found to be 23nm from the maximum intensity peak (311) using Debye Scherrer formula. The crystallite size has been estimated from the XRD pattern using Scherrer’s relation.

\[
D = \frac{0.9\lambda}{B \cos \theta}
\]

Where \( D \) is the Grain size, \( \lambda \) the wavelength of X-ray (1.5406 Å), \( B \) is the full width at half maxima of diffraction peak [13].

![XRD of nickel ferrite](image1.jpg)

**Figure 1.** Nickel ferrite XRD

3.2. XRD of copper ferrite
XRD pattern of copper ferrite (CuFe₂O₄) of prepared samples are calcinated at 800ºc for 4hours, calcinated samples shows the reflection peaks at (220), (311), (400), (420), (422), (404), (440), (600) and indicates the presence of copper ferrite (CuFe₂O₄) with Tetragonal structure and are well-matched with JCPDS number 72-1174. The lattice parameter is calculated as \( a = 8.30 \text{Å} \) and crystallite sizes are found to be 37nm from maximum intensity peak (311) using Debye Scherer formula.

![XRD of copper ferrite](image2.jpg)
Table 1. Structure parameters of nickel ferrite and copper ferrite sample

| Sample   | Angle 2θ | Lattice constant | d spacing | Crystalline size |
|----------|----------|------------------|-----------|------------------|
| NiFe$_2$O$_4$ | 35.76   | 8.31Å            | 2.50Å     | 23nm             |
| CuFe$_2$O$_4$ | 35.84   | 8.30Å            | 2.50Å     | 37nm             |

3.3. **SEM for nickel ferrite**

The morphology is performed using scanning electron microscopy (SEM) using BRUKER® spectrometer for nickel ferrite. The samples are coated with gold for avoiding the charging effect. SEM images are taken at different magnifications. The nickel ferrite with or without the composition of LDPE exhibit in the micrographs and showing the even distribution and presences of a large number of crystals with uniform distribution size, as shown in Figure 3 with 1µm for nickel ferrite and figure 4 of LDPE/nickel ferrite composition with 30 µm.
3.4. **EDAX of nickel ferrite**

The EDAX spectroscopy is performed for the chemical composition and purity using BRUKER® spectrometer for Nickel ferrite and through EDAX the elemental analysis confirms the homogeneous mixing of Ni, Fe and O atoms shown in Figure 5.

![Figure 5. Nickel ferrite EDAX](image-url)
3.5. SEM for copper ferrite

The morphology is performed using scanning electron microscopy (SEM) using BRUKER® spectrometer for copper ferrite with or without LDPE and the samples are coated with gold for avoiding charging effect. SEM images are taken at different magnification which shows the formation of multigrain agglomerations consisting of fine crystallites with almost spherical agglomerated in bigger shapes and sizes shown in Figure 6 and Figure 7.

![Figure 6. SEM of Copper Ferrite](image1)

![Figure 7. SEM of LDPE/Copper Ferrite](image2)

3.6. EDAX of copper ferrite

The EDAX spectroscopy is performed for the chemical composition and purity using BRUKER® spectrometer for copper ferrite and through EDAX the elemental analysis confirms the presence of Cu, Fe and O shown in Figure 8.

![Figure 8. EDAX of Copper Ferrite](image3)
3.7. Dielectric constant

To quantify the dielectric measurements, the samples of LDPE/NiFe$_2$O$_4$ and LDPE/CuFe$_2$O$_4$ with pH value 6, 8 and 10 of wt%10 and wt%30 are cut into pellets and are electroded using the silver paste on both the sides for an electric contact and dried for 3 hours. The dielectric measurements are taken by employing LCR meter with the frequency range from 1Hz to 8MHz. The two electrodes placed on the top and bottom of the sample. Top and bottom electrode set as working and the ground electrode. All the electrical measurements, dielectric constant, tan delta are measured at room temperature for all samples [14].

The dielectric constant of samples are be calculated using the equation, \( \epsilon_r = \frac{c \cdot d}{\varepsilon_0 \cdot A} \)

where, \( A= \) area of sandwiched structure, \( c= \) capacitance, \( d= \) thickness, \( \epsilon_0= \) absolute permittivity[15].

3.7.1. Dielectric constant for LDPE based nickel ferrite and copper ferrite weight percentage (10%) pH (6, 8, 10) Figure 9 shows the variation of Dielectric constant of nickel ferrite based LDPE and figure 10 of Copper Ferrite based LDPE with various pH (6, 8, 10) by weight percentage (10%) values versus frequency from 1 Hz to 8MHz. On the study of figures, it is found that for all composition the dielectric constant increases in low frequency, remains more or less constant between 1MHz to 5MHz and then decreases rapidly at higher frequencies. The dielectric constant is decreasing by the presence of ions and can be explained that the dielectric constant in ferrites attributes to 4 types of polarization which influence the dielectric properties and with further increase in frequency, the electrons change their direction of motion rapidly. Among all composites, NiFe$_2$O$_4$/LDPE pH (10) and CuFe$_2$O$_4$/LDPE pH (10) show high value from region 1Hz to 8MHz. Due to dielectric relaxation after 5MHz frequency exhibit low value may be due to electric charges being displaced inside the LDPE.

![Figure 9. Dielectric constant for nickel ferrite Weight percentage (10%) pH (6, 8, 10)](image)

![Figure 10. Dielectric constant for copper ferrite Weight percentage (10%) pH (6, 8, 10)](image)

3.7.2. Dielectric constant for LDPE based nickel ferrite and copper ferrite weight percentage (30%) pH (6, 8, 10) Figure 11 shows the variation of Dielectric constant of nickel ferrite based LDPE and copper ferrite based LDPE with various pH (6, 8, 10) of weight percentage (30%) values versus frequency from 1Hz to 8MHz. On the study of figures, it is found that for all composition the dielectric constant increases till 1MHz, remains more or less constant between 1MHz to 5MHz and then decreases rapidly at higher frequencies. Among all composites, nickel ferrite pH 6 in figure 11 shows the high value of dielectric

![image]
constant. As per figure 12 copper ferrite pH6 shows the higher dielectric value among others. A small notching peak in Copper ferrite pH6, pH8, and pH10 till 1MHz suggest the presence of relaxing and nonrelaxing dipoles in composite and then results indicate constant dielectric with minor surges then deviated towards 8MHz.

Figure 11. Dielectric constant for nickel ferrite
Weight percentage (30%) pH (6, 8, 10)

Figure 12. Dielectric constant for copper ferrite
Weight percentage (30%) pH (6, 8, 10)

3.7.3. Tan Loss for LDPE based nickel ferrite and copper ferrite weight percentage (10%) pH (6, 8, 10) Figure 13 shows the variation of dissipation factor of composite which starts decreasing at low frequency then sudden spike appears up to the value 0.07 till a frequency of 1MHz and then sudden drop thereafter gradual increase of dissipation factor till 8MHz. The nickel ferrite based LDPE with pH10 having a lower dielectric loss, the dielectric loss curve characterized by peak appearing at 1MHz. As per figure 14 copper ferrite based LDPE a spike in pH6 and pH10 appears up to the value of 0.06 and follows the same pattern that of nickel ferrite whereas dissipation factor for copper ferrite pH8 continuously decreases with increase in frequency.

Figure 13. Tan Loss for nickel ferrite
Weight percentage (10%) pH (6, 8, 10)

Figure 14. Tan for copper ferrite
Weight percentage (10%) pH (6, 8, 10)
3.7.4. **Tan Loss for LDPE based nickel ferrite and copper ferrite weight percentage (30%) pH (6, 8, 10)** Figure 15 shows the variation of dissipation factor of composite which starts increasing sharply up to the value 0.08 till a frequency of 1MHz and then sudden drop, thereafter gradual increase of dissipation factor till 8MHz. Only in case of nickel ferrite pH6 decrease in dissipation factor is seen at low frequency till 0.5MHz. It measures the loss of electrical energy from the applied electric field at different frequencies. The value of dielectric loss tangent is less in nickel ferrite pH10 as compared with other composites. As per figure 16 copper ferrite based LDPE a spike in all composites up to the value of 0.06 and follow the same pattern that of nickel ferrite.

![Figure 15. Tan Loss for nickel ferrite](image1)

![Figure 16. Tan for copper ferrite](image2)

4. **Conclusion**

In the present research, LDPE based nickel and copper ferrite composite with varying pH value at 6, 8, 10 weight 10wt% and 30wt% have been successfully synthesized. The powder XRD results show that NiFe₂O₄ have a cubic structure and CuFe₂O₄ have a tetragonal structure. The lattice parameters are calculated for NiFe₂O₄ is 8.31Å and CuFe₂O₄ is 8.30Å for annealed samples. The average crystalline size is found to be 23nm for NiFe₂O₄ and 37nm for CuFe₂O₄. The SEM indicated the uniform distribution of large particles. The EDAX shows the presence of Cu, Fe, and O in CuFe₂O₄ and Ni, Fe, and O in NiFe₂O₄. The dielectric properties of LDPE based Nickel and copper ferrite composite with 10wt% and 30wt% by varying pH value to 6, 8 and 10 has been determined at frequency 1Hz to 8MHz. Results show that the dielectric constant decreases with an increase in frequency. All dielectric parameters are changing with the addition of ferrite with LDPE, with increase concentration leads to an increase in dielectric loss factor. The LDPE based composite ferrite can enhance the operational life and electrical properties as per this research and there is still a scope of more research in this present area for future aspects.

**References**

[1] Nayeemuddin, Quadri S A M N 2019 Low density polyethylene/zinc ferrite nanocomposite prepared for structural, morphology and electrical studies *International Journal of Recent Technology and Engineering* **8** 1C

[2] Ilona P, Petru V N, Cristina S, Frank W, Sandra S 2018 Polyethylene nanocomposites for power cable insulations *Polymers* **11** 24

[3] Dao N L, Lewin P, Hosier I L, Swingler S G 2010 A comparison between LDPE and HDPE cable insulation properties following lightning impulse ageing *IEEE International Conference on Solid*
Dielectrics 10 5567944

[4] Satyanarayana G, Nageswara G R, Vijaya K B 2018 Structural, dielectric and magnetic properties of Al$^{3+}$ and Cr$^{3+}$ substituted Ni-Zn-Cu ferrites Journal of Nanoscience and Technology 4 487 - 491

[5] Raju P, Ramesh T, Murthy S R 2015 Ferrite + polymer nanocomposites for EMI applications International Journal of ChemTech Research 7 3 1343 - 1350

[6] Teyssedre G, Laurent C 2013 Advances in high-field insulating polymeric materials over the past 50 IEEE Electrical Insulation Magazine 29 26-36

[7] Valenzuela R 2012 Novel applications of ferrites physics research international 2012 591839

[8] Mahmoud G N, Elias B S 2012 Crystalization in spinel ferrite nanoparticles Intechopen 14

[9] Elsayed E M, Rashad M M, Khalil H F Y, Ibrahim I A, Hussein M R, ElSabahh M M B 2015 The effect of solution pH on the electrochemical performance of nanocrystalline metal ferrites MF$_2$O$_4$ (M=Cu, Zn, and Ni) thin films Applied Nanoscience 6 4 485 - 494

[10] Cullity B D, Graham C D 2009 Introduction to Magnetic Materials 2nd Wiley

[11] Farid M T, Ahmad I, Aman S, Kanwal M, Murtaza G, Ali I, Ahmad I, Ishaq M 2015 Structural, electrical and dielectrical of Ni$_x$Co$_{1-x}$N$_{y}$Fe$_{2-y}$O$_5$, nano ferrite synthesized by sol-gel method Digest Journal of Nanomaterials and Biostructures 10 265-275

[12] Kesavamoorthi R, Vigneshwaran A N, Vijayalakshmi S, Ramachandra C R 2016 Synthesis and characterization of nickel ferrite nanoparticles by sol-gel auto combustion method Journal of Chemical and Pharmaceutical Sciences 9 160 - 162

[13] Farah T M N 2015 Preparation and study dielectric properties of Copper-nickel ferrite nanoparticles by hydrothermal method Disala Journal for Pure Science 11 43-59

[14] Ravi G K, Vijaya K K, Venudhar Y C 2012 Electrical conductivity and dielectric properties of copper doped nickel ferrites prepared by double sintering method International Journal of Modern Engineering Research 2 177-185

[15] Tamboli A M, Rathod S M, Rabbani G 2017 Effect on dielectric properties of nanocrystalline spinel ferrite material due to substitution of Cu$^{2+}$ in Co Ni International Journal of Electronics, Electrical and Computational System 6 243-253