# Preparation, Structural and Dielectric Properties of Polyaniline-Nickel Ferrite Composites

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## Abstract

Conducting polyaniline-nickel ferrite ($PANI/NiFe_2O_4$) composites are synthesized by employing interfacial polymerization method. The composite has been synthesized with various compositions (10, 30 and 50 wt %) of nickel ferrite in PANI. The prepared samples were characterized by FTIR, and the dominant peaks confirmed the formation of $PANI/NiFe_2O_4$ composites. The surface morphology of these composites is studied with scanning electron microscope (SEM) and thermogravimetric analysis (TGA). The ac conductivity ($\sigma_{ac}$) and dielectric properties of these composites is investigated in the frequency range of $10^2$ Hz to $10^6$ Hz. The conductivity of composites found constant up to $10^5$ Hz thereafter increased with increasing frequency.

**Keywords:** Polyaniline, $NiFe_2O_4$, FTIR, Scanning electron microscope, Conductivity, Dielectric properties.

## INTRODUCTION

Conducting polymers are attractive materials because they have a wide range of functions from insulators to metals and retain their mechanical properties of polymers and also have many promising technological applications [1-3]. Among the conducting polymers, polyaniline (PANI) gets a great deal of attention due to its good

environmental stability, easy synthesis and widely used in many applications such as electromagnetic interference shielding, rechargeable batteries, chemical sensors, corrosion protection coatings, and microwave absorbing materials [4-8].

Many kinds of materials can be used as magnetic part of the composite materials, such as $ZnFe_2O_4$ [9], $CoFe_2O_4$ [10], $BaFe_{12}O_{19}$ [11], $\gamma$-$Fe_2O_3$ [12] and $Co_3O_4$ [13]. Among magnetic materials, the spinel ferrites exhibit remarkable magnetic properties particularly in radio frequency region, physical flexibility, high electrical resistivity, mechanical hardness and chemical stability [14]. $NiFe_2O_4$ is an important magnetic ferrite which has been widely used as gas sensor [15], catalysts [16], and absorbent materials [17] and so on.

In the present work, $NiFe_2O_4$ particles were chosen as a magnetic source due to their scientific and technological applications, which was prepared by combustion route. The polyaniline/nickel ferrite (PANI/$NiFe_2O_4$) composites (with 10, 30 and 50 wt % of $NiFe_2O_4$ in PANI) have been synthesized via interfacial polymerization. The effect of $NiFe_2O_4$ particles with respect to the electrical properties of PANI/$NiFe_2O_4$ composites is discussed on the basis of the structure characterization and morphology analysis.

## EXPERIMENTAL

### Materials:

All the chemicals and reagents used were of analytical grade. Double distilled water was used throughout the work. Nickel ferrite (Synthesized by combustion method) is used for the preparation of polymer composites and ammonium persulphate was purchased from Qualigens; Aniline was double distilled before use and Hydrochloric acid was purchased from Aldrich chemicals. Polyaniline (PANI) and polyaniline-nickel ferrite composites of different compositions (PANI/$NiFe_2O_4$) have been synthesized by employing interfacial polymerization using ammonium persulphate as an oxidizing agent.

### Preparation of PANI/$NiFe_2O_4$ composites:

PANI/$NiFe_2O_4$ composites were prepared with different weight % of $NiFe_2O_4$ (10, 30 and 50 wt %). The details are as follows: 0.5 g of aniline is dissolved in 20 ml of chloroform ($CHCl_3$), 0.1 M ammonium persulphate is dissolved in 1.0 M HCl & the $NiFe_2O_4$ same is slowly added to the above mixture of aqueous and organic phase. After 5 minutes, dark-green precipitate is formed slowly at the interface and then gradually diffused into the aqueous phase. After 24 hours, the entire aqueous phase was filled homogeneously with dark-green color film, organic layer observed shows orange color due to the formation of aniline oligomers. The aqueous phase was then collected and washed with ethanol and water to remove the unreacted aniline. The residue of polymer thus obtained is purified and dried in a vacuum oven at $40^0C$ for 36 hours. In this way three different PANI/$NiFe_2O_4$ composites with different weight

percentage of nickel ferrite (10, 30 and 50) in polyaniline have been synthesized. The dried polymer composite samples are used for the structural and conductivity studies.

## Characterization Techniques:

The IR spectra of all the samples are recorded on ThermoNicolet, Avatar 370 IR spectrometer in KBr medium at room temperature. The surface morphology of the samples has been studied by employing scanning electron microscope (SEM) Joel Model JSM-6390 LV. TGA thermograms of samples were recorded under oxygen atmosphere and in temperature range 40-730$^0$ C and at a heating rate of 10$^0$ C/min using Perkin Elmer STA 6000 thermal analyzer. The ac conductivity measurements were carried out using N4L-PSM 1735 NumetriQ programmable LCR meter in a frequency range 10$^2$ to 10$^7$ Hz.

## RESULTS AND DISCUSSION

### Fourier transmission infrared spectroscopy:

The FTIR spectra measurement is carried out to study the molecular structure of the PANI and PANI/NiFe$_2$O$_4$ composites.

**Fig. 1a** shows the FTIR spectra of pure PANI. The characteristic absorption peaks are found to be at 1564.06 cm$^{-1}$, 1478.15 cm$^{-1}$, 1301.22 cm$^{-1}$, 1244.06 cm$^{-1}$, 1137.88 cm$^{-1}$, 808.32 cm$^{-1}$, 702.21 cm$^{-1}$, 588.23 cm$^{-1}$ and 507.96 cm$^{-1}$. The band at 1564.06 cm$^{-1}$ C=N quinoid stretching mode of vibration, 1478.15 cm$^{-1}$ C=C stretching mode of vibration of the benzenoid ring, 1301. 22 cm$^{-1}$ C–N bonds of aromatic amines, 1244.06 cm$^{-1}$ C–N stretching of the benzenoid ring, 1137.88 cm$^{-1}$ corresponds to C–O–C stretching of excess oxidant, 808.32 cm$^{-1}$ is due to the C–H vibration of the benzenoid ring and bands at 588.23 cm$^{-1}$ and 507.96 cm$^{-1}$ are due to stretching out of the plane.

**Fig. 1b** shows FTIR spectra of PANI/NiFe$_2$O$_4$ (10 %) composites. It is observed that the peak around 1575.16 cm$^{-1}$ is due to the C=N quinoid stretching mode of vibration and that at 1491.04 cm$^{-1}$ corresponds to C=C stretching of the benzenoid ring, 1299.89 cm$^{-1}$ for C–N stretching, 1140.53 cm$^{-1}$ corresponds to C–O–C stretching of excess oxidant, 816.72 cm$^{-1}$ and 616.51 cm$^{-1}$ is due to stretching out of plane.

**Fig. 1c** shows FTIR spectra of PANI/NiFe$_2$O$_4$ (30 %) composites. The peak observed at 1577.36 cm$^{-1}$ corresponds to the quinoid-stretching mode of vibration, 1479.03 cm$^{-1}$ for stretching of the benzenoid ring, 1301.19 cm$^{-1}$ for bonds of aromatic amines, 1140.34 cm$^{-1}$ for C–N stretching mode of the benzenoid unit, 1088.69 cm$^{-1}$ for C–NH–C is a secondary amine vibration, 812.93 cm$^{-1}$ for vibration of the benzenoid ring and 618.99 cm$^{-1}$ is due to stretching out of plane.

**Fig. 1d** shows FTIR spectra of PANI/NiFe$_2$O$_4$ (50 %) composites. The peak at 1567.89 cm$^{-1}$ corresponds to the C=N quinoid stretching mode of vibration, 1472.91 cm$^{-1}$ is due to stretching of the benzenoid ring, 1303.11 cm$^{-1}$ corresponds to C–N

bonds of aromatic amines, at 1241.84 cm$^{-1}$ is due to C–N stretching, at 1139.98 cm$^{-1}$ to C–O–C stretching of excess oxidant, the peak at 1084.81 cm$^{-1}$ to S–O stretching of vibration, at 808.63 cm$^{-1}$ is attributed to C–C and C–H of the benzenoid ring, at 619.21 cm$^{-1}$ of the aromatic ring and 546.99 cm$^{-1}$ is a M-O stretching due to rotational vibration of the molecules, which confirms formation of the composites.

From the **figures 1a-1d**, it is observed that the introduction of NiFe$_2$O$_4$ particles in PANI causes positive shifting of the FTIR peaks and considerably decreases the relative intensities of the composites, in comparison with pure PANI, which confirms the formation of PANI/NiFe$_2$O$_4$ composites.
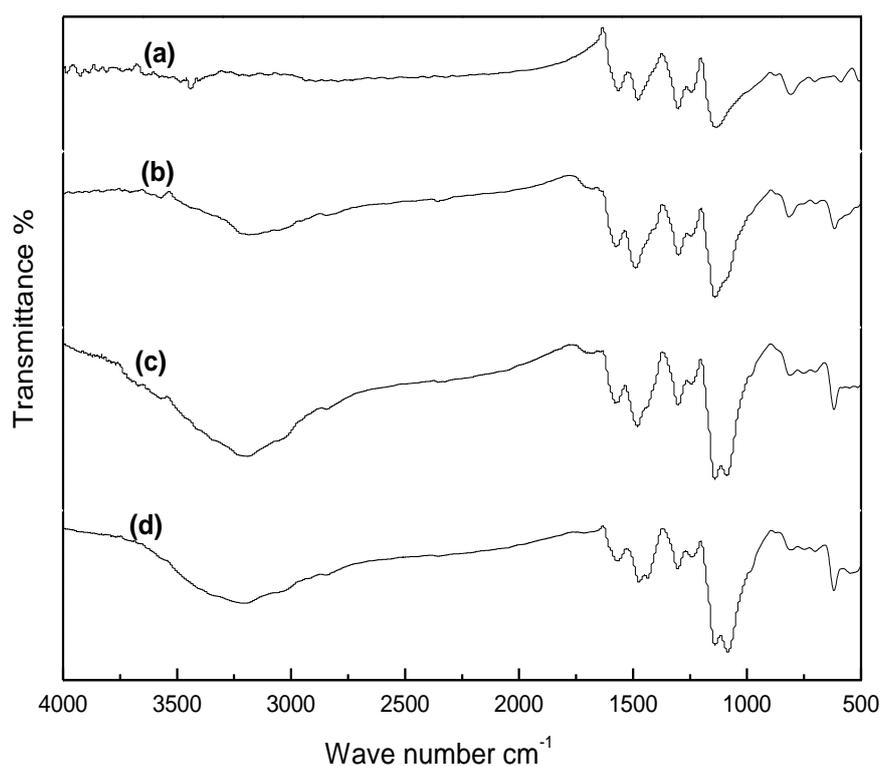


**Figure 1:** FTIR spectra of pure PANI (a) and PANI/NiFe$_2$O$_4$ composites of 10 wt % (b), 30 wt % (c) and 50 wt % (d).

**Scanning Electron Microscopy:**

**Figure 2a** shows that scanning electron microscopic (SEM) image of pure PANI which is of a highly agglomerated granular structure and the grains are well interconnected with each other. The average grain size was calculated by linear intercept method, found to be about 2-4 μm. **Fig. 2b** shows the SEM image of PANI/NiFe$_2$O$_4$ (50 wt %) composites which are agglomerated and irregular in shape.

The average grain size is found to be 866 nm. **Fig. 2c** shows the SEM image of PANI/NiFe$_2$O$_4$ (30 wt %) composites which are highly crystalline and have greater agglomeration. The average grain size is found to be 693 nm. **Fig. 2d** shows the SEM image of PANI/NiFe$_2$O$_4$ (50 wt %) composites which are highly agglomerated and irregular in shape. The average grain size is found to be 794 nm.
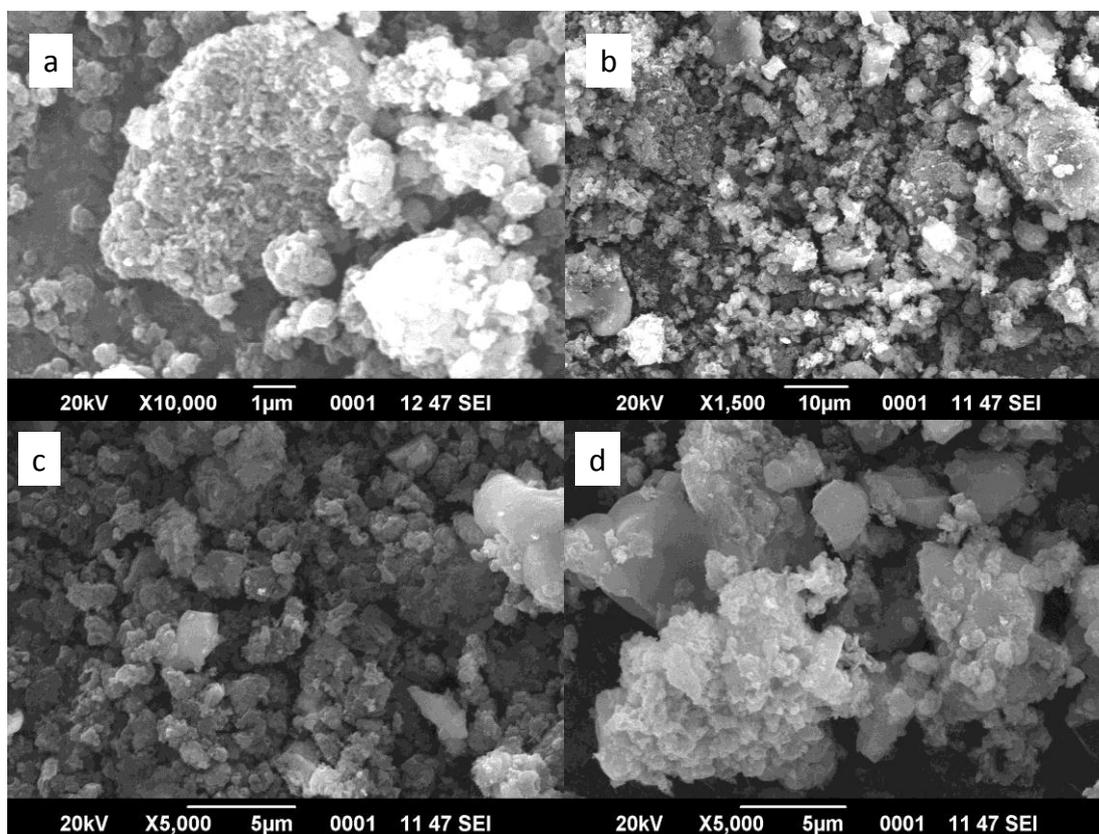


**Figure 2:** SEM images of pure PANI (a) and PANI/NiFe$_2$O$_4$ composites of 10 wt % (b), 30 wt % (c) and 50 wt % (d).

**Thermogravimetric analysis:**

**Figure 3** shows thermogravimetric analysis (TGA) for PANI and PANI/NiFe$_2$O$_4$ composites. All curves show a three step weight loss. The initial weight loss at lower temperature ranging from $70^0$ C to $121^0$ C is due to the loss of water molecules retained in PANI matrix after drying [18]. The second weight loss ranging from $121^0$C to $280^0$C is attributed to the loss of dopant from PANI chains. The third weight loss is higher than $280^0$ C is attributed to the thermal degradation of PANI. This reveals that the thermal stability of the composites is higher than that of pure PANI. This may be due to the interaction between NiFe$_2$O$_4$ particles and PANI chains [19].
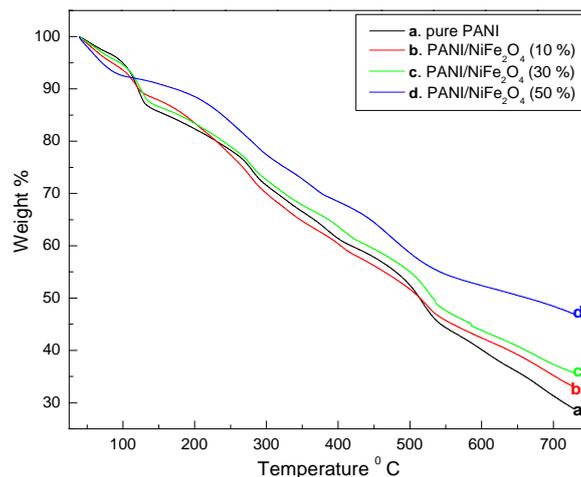
**Figure 3:** TGA of pure PANI (a) and PANI/NiFe$_2$O$_4$ composites

of 10 wt % (b), 30 wt % (c) and 50 wt % (d).

**Conductivity and dielectric measurements:**

The frequency dependent electrical conductivity ($\sigma_{ac}$) of PANI and PANI/NiFe$_2$O$_4$ composites is shown in **Figure 4**. At higher frequencies beyond $10^5$ Hz, the conductivity increases with increasing frequencies, obeys universal power law. The conductivity is almost constant up to $10^5$ Hz and then conductivity increases because of the contribution of polarons. The increasing conductivity at higher frequencies is attributed to charge motion in the crystalline regions and this supports the presence of isolated polarons and bipolarons in this region [20, 21]. Among all composites 30 wt % shows high conductivity of $2.97 \times 10^{-5}$ Scm$^{-1}$ at $10^6$ Hz due to dipole polarization.
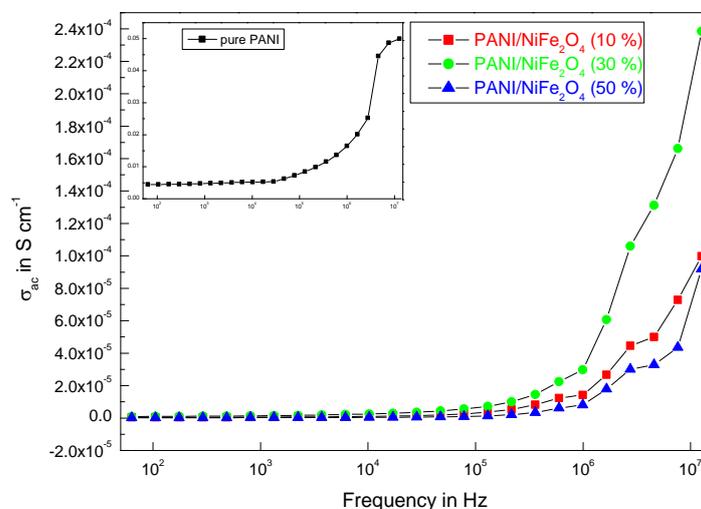


**Figure 4:** Frequency dependence AC conductivity of PANI/NiFe$_2$O$_4$ composites. (*Inset*: Frequency dependence AC conductivity of pure PANI).

**Figure 5** shows the variation of real dielectric constant $\varepsilon'$ (the real part of complex permittivity) as a function of frequency for pure PANI and PANI/NiFe$_2$O$_4$ composites at different weight percentage. The value of $\varepsilon'$ is quite high at low frequency and decreases with increase in frequency for all composites. At higher frequencies the value of $\varepsilon'$ remains constant for all the composites and after $10^6$ Hz frequency exhibits low value plateau, which is due to Debye-like relaxation [20]. Among all composites 30 wt % shows high value of real permittivity due to dielectric relaxations.
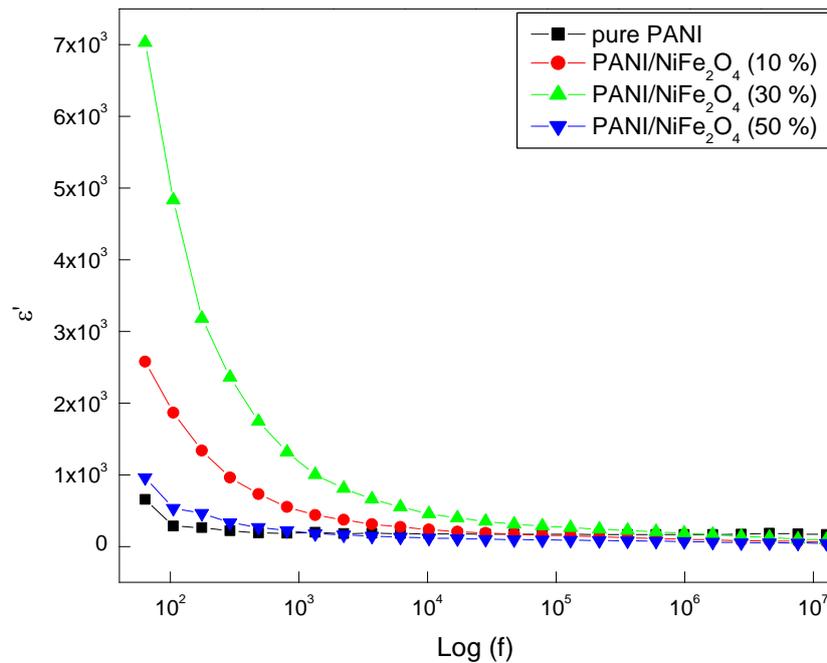


**Figure 5:** Frequency dependence of real dielectric constant

of PANI and PANI/NiFe$_2$O$_4$ composites

**Figure 6** shows the variation of imaginary dielectric constant $\varepsilon''$ (the imaginary part of complex permittivity) with frequency for pure PANI and PANI/NiFe$_2$O$_4$ composites at different weight percentage. At low frequency the value of $\varepsilon''$ is quite high and its value decreases with increasing frequency. After $10^4$ Hz frequency, $\varepsilon''$ exhibits low value plateau. This may be due to electric charges being displaced inside the polymer [22].
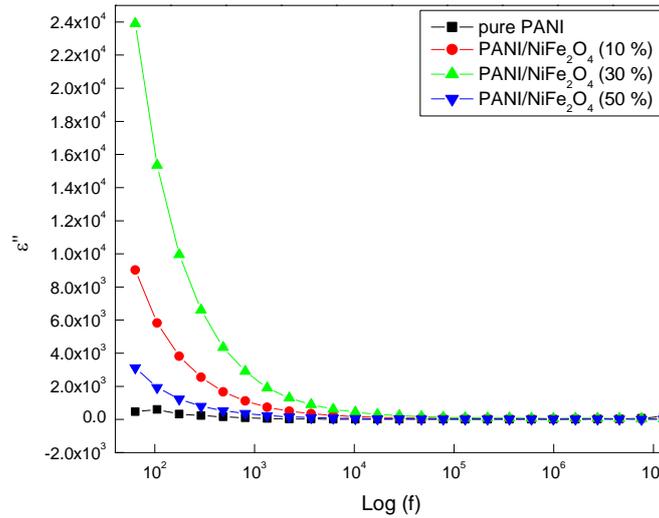
**Figure 6:** Frequency dependence of imaginary dielectric constant of
PANI and PANI/NiFe$_2$O$_4$ composites

**Figure 7** shows the variation of dielectric loss with frequency for PANI and
PANI/NiFe$_2$O$_4$ composites at room temperature. The dielectric loss of pure PANI and
PANI/NiFe$_2$O$_4$ composites decreases with increase in frequency. The dielectric loss
curves characterized by peak appearing at a characteristic frequency at $10^2$ Hz to $10^3$
Hz for 30 and 50 wt % of PANI/NiFe$_2$O$_4$ composites suggest the presence of relaxing
and non-relaxing dipoles in composites. Pure PANI and PANI/NiFe$_2$O$_4$ (10 %)
composites does not show relaxations. At higher frequencies PANI and
PANI/NiFe$_2$O$_4$ composites exhibit almost zero dielectric loss suggests that these are
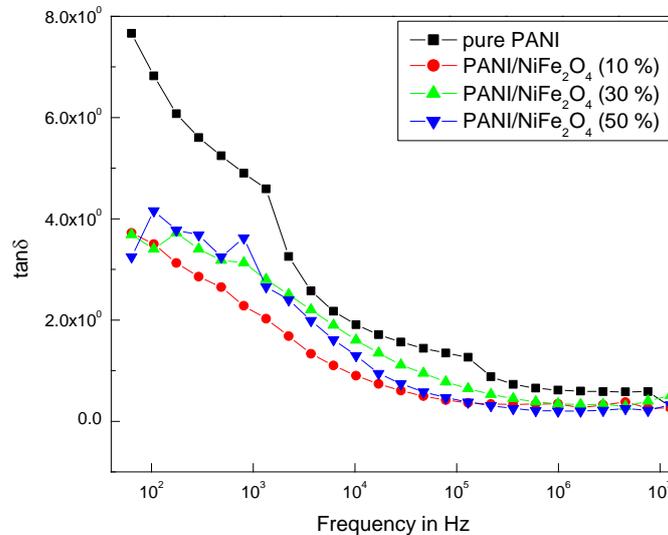lossless materials at frequencies beyond $10^7$ Hz.



**Fig. 7** Frequency dependence of dielectric loss of PANI and PANI/NiFe$_2$O$_4$
composites at room temperatures.

**CONCLUSION:**

- In the present research, polyaniline composites with different wt % of $NiFe_2O_4$ in PANI have been synthesized by interfacial polymerization using ammonium persulphate as an oxidizing agent.
- The result of FT-IR spectroscopy the peaks are shifted towards the higher frequency indicating there is some interaction between PANI and $NiFe_2O_4$ particles.
- The SEM studies show that the polyaniline composites are agglomerated and granular in morphology.
- The results of TGA showed that $NiFe_2O_4$ particles enhanced the thermal stability of the $PANI/NiFe_2O_4$ composites.
- The results of AC conductivity obey the power law. AC conductivity increases at higher in frequencies because of hopping of polarons from one localized states to another localized state.
- The dielectric properties of $PANI/NiFe_2O_4$ composites are large at lower frequencies and decrease steeply with increasing frequency.

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