Section A-Research paper

SYNTHESIS AND DIELECTRIC PROPERTIES STUDY OF NICKEL FERRITE DOPED POLYANILINE

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Abstract:

Nickel ferrite ($NiFe_2O_4$) was prepared by co-precipitation technique and polyaniline-nickel ferrite (PANI- $NiFe_2O_4$) composites were prepared by in-situ chemical oxidative polymerization method with different weight percentages. Samples were characterized to understand their thermal properties such as TGA and DSC, electrical such as AC and DC conductivity and dielectric properties. The surface morphology and average grain size was investigated by scanning electron microscope analysis. Oxidizing agent played vital role to change conducting polyaniline to dielectric. This kind of behavior encouraged to study their dielectric properties. Results of dielectric studies showed that ferrites doped polyaniline may suitable for energy storage device and applications.

Key words: Ferrites/PANI, Oxidizing agent, AC and DC conductivity, Dielectric behavior.

Introduction:

All are probably aware that the study of polymeric materials is a fast-developing field and may also help in achieving breakthroughs in the development of new materials. The idea behind this is, to develop polymeric materials for technological applications. Here materials interact with each other and it is important to consider the effect of one, when designing a material [1]. In recent years, there has been a lot of interest in using materials viz. metals (silver, gold), carbon, and polymer (especially conductive polymers) due to their different uses in optical, mechanical, chemical, and electronic systems. The conducting polymer, polyaniline, has been gaining attention recently not just because it is easy to synthesize but also due to its affordability and high environmental stability. The material has a very high electrical conductivity and many more [2]. These can be synthesized in different ways, including electrochemical polymerization, rapid mixing and dilute solutions, interfacial polymerization and chemical oxidative polymerization and they are also become hard or soft depending upon the process and materials. One of the best ways to make good quality polymeric material is by using an in-situ and ex-situ chemical oxidative polymerization method. This process involves using a suitable oxidizing agent, catalyst

and monomer and in a common synthesis method, the yield of the conductivity of various polymers depends upon the oxidant. Analogous to most other polymer material, Polyaniline (PANI) conductivity is may maximize using an in-situ chemical oxidative polymerization method with suitable an oxidizing agent. The interaction between monomer and oxidizing agent is very significant to make best quality and technological suitable polymer. Ferrites are ceramic materials usually appearing in dark grey or black. They are incredibly hard and brittle. When we talk about ferrites, we refer to them as magnetic materials mainly made of oxides composed of ferric ions, which makes them show ferromagnetic behavior. AFe_2O_4 ferrospinels, where A can be Ni, Cu, Mg or Co. to name a few, are extremely relevant in the field of magnetic materials as they fit a diverse range of uses. Additionally, these ferrite materials are inexpensive and can be found in numerous devices like microwaves, transformers cores, magnetic memories, isolators, and noise filters [3]. Nickel ferrite ($NiFe_2O_4$) is one of the prominent ferrite. It has been extensively studied due to its high electromagnetic performance, excellent mechanical hardness, chemical stability, high coercivity, and moderate saturation magnetization, ferrites are at high frequency shows low-loss and are soft magnets [4,5]. Therefore, we have attempted to fabricate the nickel ferrite doped polyaniline composites. Nickel ferrite is considerably studied because of its simple and well controlled synthesis technique, which have a great influence on the electrical, structural, and magnetic properties of the composites [6]. In this present work tried to study how oxidizing agents, ferrites, and polyaniline all interact with each other and influences the behavior of electricity. It sought to show how a change in conductivity could be achieved. In the near future, work will be done on the magnetism of these elements to further exploit their technological potential.

2. EXPRIMENTAL

2.1: Materials:

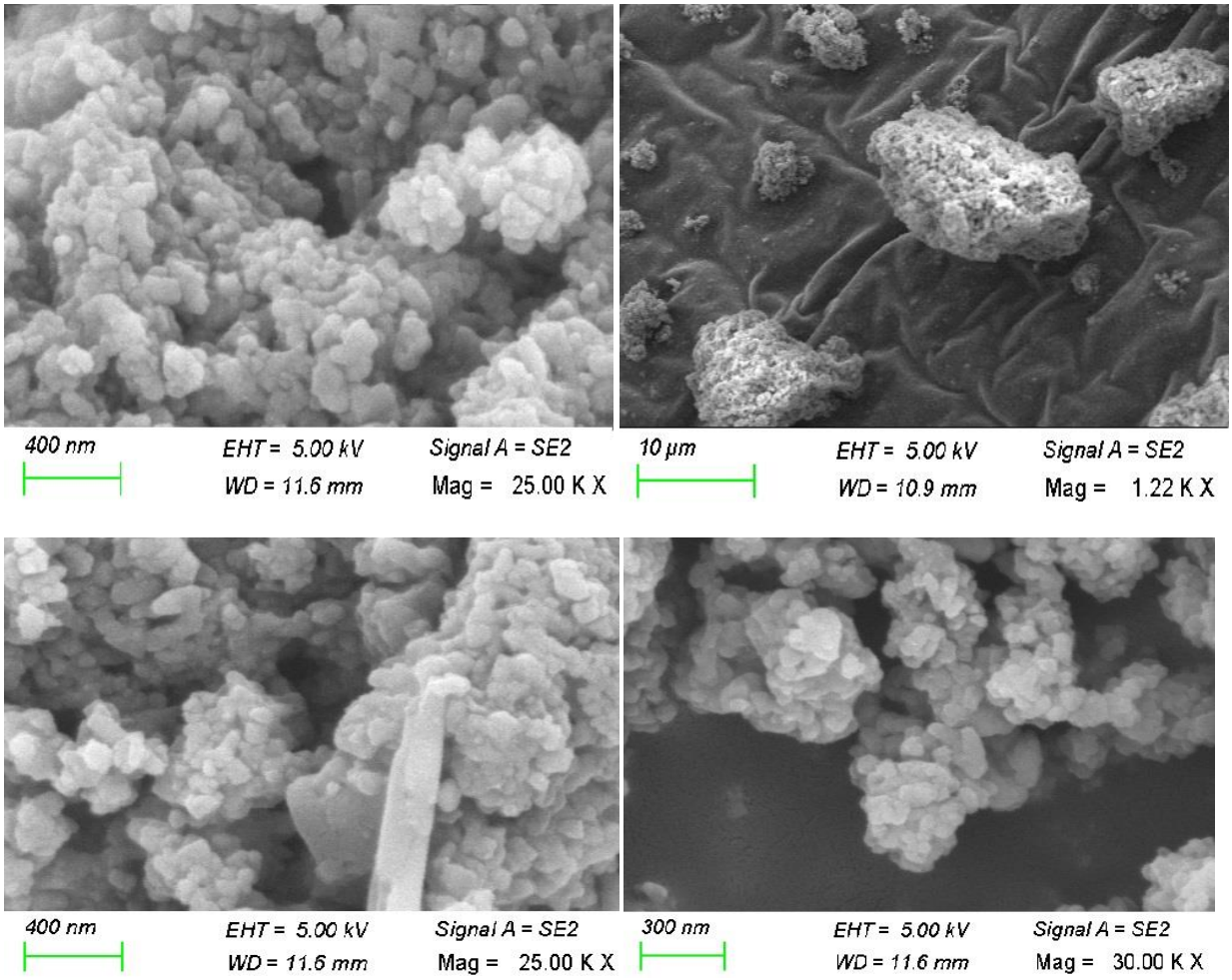
To carry out the synthesis process, all the chemicals and substances used were of analytical grade (AR). Double distilled water was also utilized. The $NiFe_2O_4$ was synthesized by utilizing the coprecipitation route. Pure polyaniline was synthesized by using aniline, ammonium dichromate, and hydrochloric acid. Using the in-situ chemical oxidative polymerization method polyaniline (PANI) and composites of different compositions (PANI / $NiFe_2O_4$) have been prepared. All the chemicals and substances were used of analytical grade (AR). Distilled water was used in the complete synthesis process. NiFe2O4 was synthesized by the co-precipitation route. Pure polyaniline was synthesized by using aniline, ammonium dichromate, and hydrochloric acid. Polyaniline (PANI) and composites of different compositions (PANI / $NiFe_2O_4$) have been synthesized using in-situ chemical oxidative polymerization method $(NH_4)_2Cr_2O_7$ (ammonium dichromate) as an oxidizing agent.

2.2: Preparation of PANI/ $NiFe_2O_4$composites:

PANI/ $NiFe_2O_4$ composites sample was prepared by using in-situ chemical oxidative polymerization root. The PANI/ $NiFe_2O_4$ composites were prepared with different weight % of $NiFe_2O_4$ (10, 20, 30, 40 & 50 wt%). The aniline (0.25M) was dissolved in 100ml double distilled water and HCl (1N) is also dissolved in 100ml double distilled water and added together and kept stirring after that adds ammonium dichromate (0.25M) drop wise and the $NiFe_2O_4$ same slowly add to the above mixture with vigorous stirring at normal room temperature for 8hours to the end of the reaction. The PANI/ $NiFe_2O_4$ solution is collected by filtration and the collected sample dries in the oven at 80 ^oC for 12h to get constant mass. In this way, five different PANI/ $NiFe_2O_4$ composites with different weight percentages of $NiFe_2O_4$ (10, 20, 30, 40 & 50wt %) in polyaniline have been synthesized. The desired Polymer composites materials are used for the structural and conductivity studies [7-10].

3. RESULT AND DISCUSSION:

3.1. Scanning Electron Microscope:



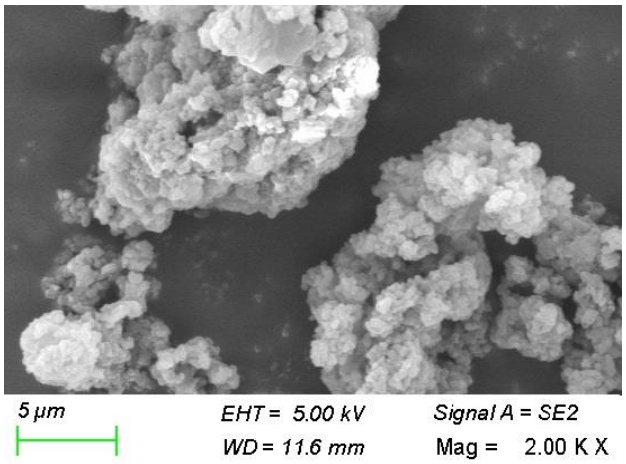


Figure: 1. SEM images (a) PANI/ $NiFe_2O_4$ (10%), (b) PANI/ $NiFe_2O_4$ (20%), (c) PANI/ $NiFe_2O_4$ (30%), (d) PANI/ $NiFe_2O_4$ (40%), (e) PANI/ $NiFe_2O_4$ (50%).

Scanning electron microscope is used study about surface morphology and particle size of the synthesized sample. Figure 1 illustrates micrographs of pure PANI, Nickel ferrite/PANI and their composites of 10%, 20%, 30%, 40% and 50% weight percentage and from the images it is observed irregular shapes and the porous nature of the synthesized samples. According to images the surface of these nanocomposites was rough and the nanocomposites have more or less spherical morphology. Moreover, the diameter of the particle is about 20nm and it can also be seen that PANI can reduce the aggregation of the nanoparticles due to the repulsive force between the magnetic nanoparticles and PANI. From the line intercepting method it can be concluded that the average particle size of PANI / $NiFe_2O_4$ composites may vary from 25-30nm.

3.2. AC Conductivity:

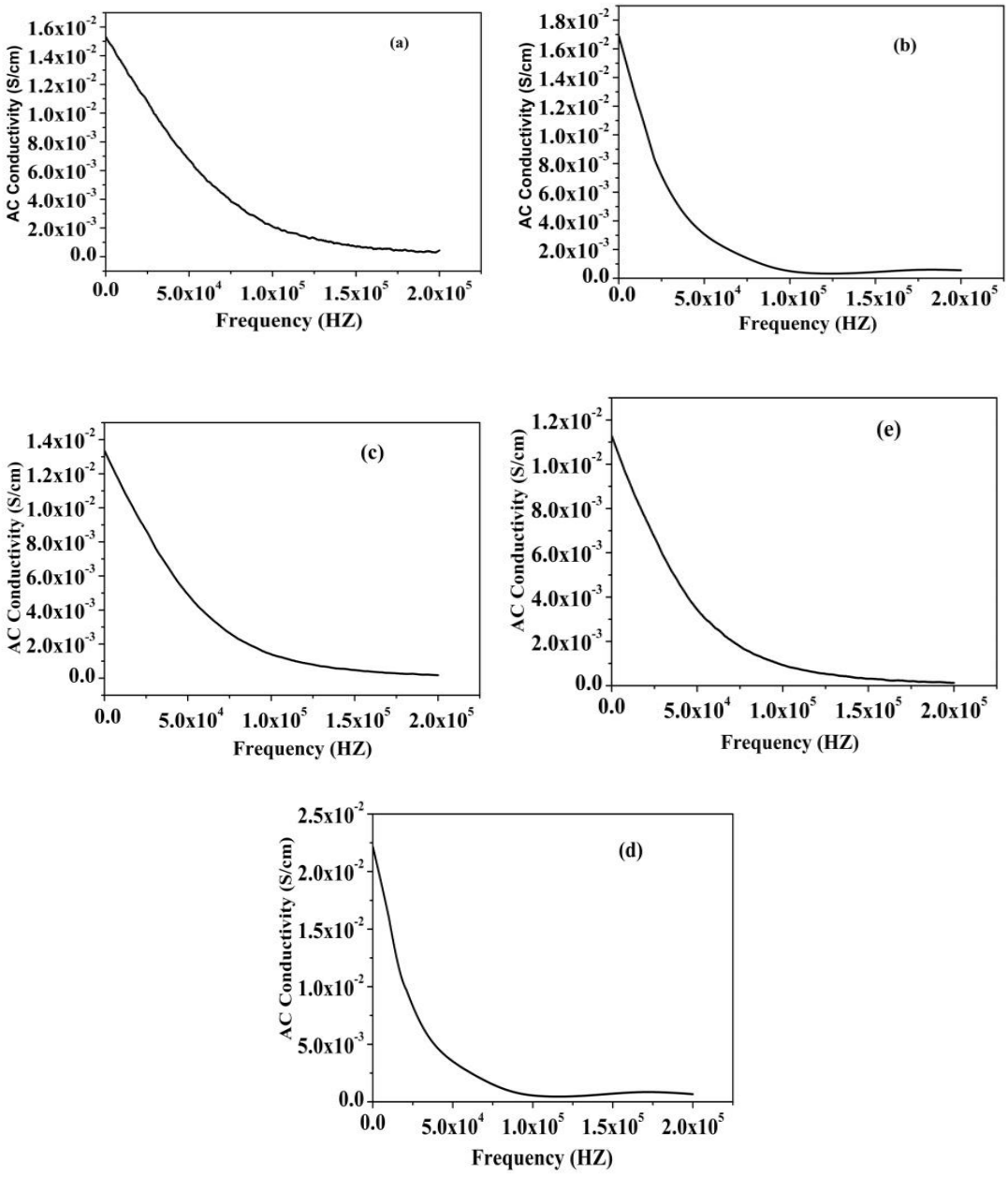


Figure: 2 AC conductivity (a) PANI/ $NiFe_2O_4$ (10%), (b) PANI/ $NiFe_2O_4$ (20%), (c) PANI/ $NiFe_2O_4$ (30%), (d) PANI/ $NiFe_2O_4$ (40%), (e) PANI/ $NiFe_2O_4$ (50%).

The frequency dependent electrical conductivity of composites is shown in Figure 2. It is observed that the conductivity is high at low frequency, as frequency increases the conductivity decreases gradually and at higher frequency conductivity remains constant [11-12]. In frequency dependent AC conductivity here frequency is showing that there may be charge carrier which

can be transported through polymer chain. The frequency dependent of AC conductivity is the solution of interface charge polarization and intrinsic electric dipolar polarization.

3.3. DC conductivity:

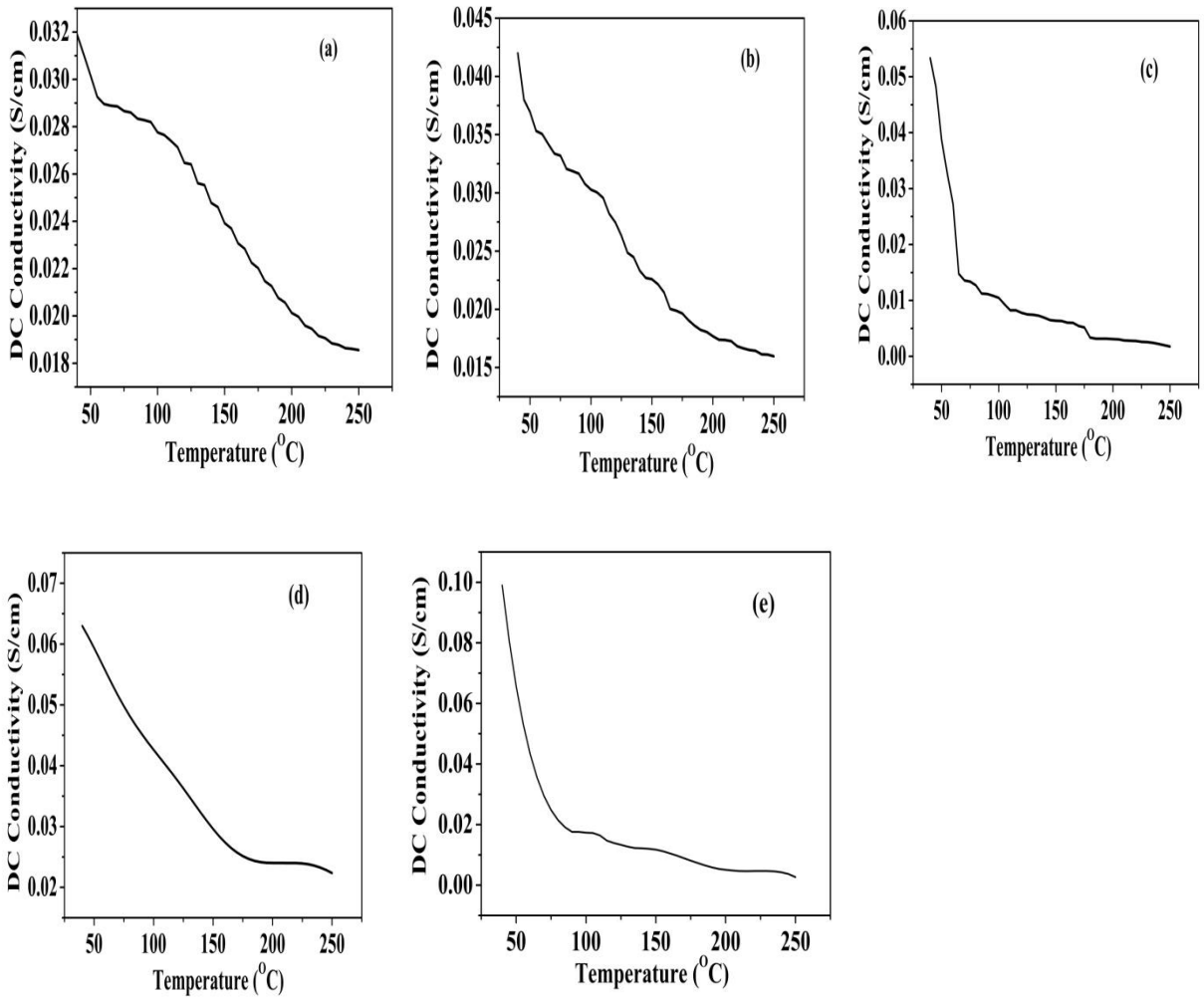


Figure: 3 DC conductivity (a) PANI/ $NiFe_2O_4$ (10%), (b) PANI/ $NiFe_2O_4$ (20%), (c) PANI/ $NiFe_2O_4$ (30%), (d) PANI/ $NiFe_2O_4$ (40%), (e) PANI/ $NiFe_2O_4$ (50%).

Figure 3 shows the DC conductivity of the PANI/ $NiFe_2O_4$ (10, 20, 30, 40, 50 wt %), composites were measured as function of temperature to study the charge transport mechanism. Temperature dependent DC conductivity of PANI/ $NiFe_2O_4$ (wt %) was studied in the temperature range 50 to 250 ^{o}C. DC conductivity of PANI/ $NiFe_2O_4$ composites is high at low temperature and as

temperature increases the conductivity decreases gradually. The incorporation of $NiFe_2O_4$ nanoparticles impressively affects the conductivity of PANI/ $NiFe_2O_4$ composites [13].

3.4. Dielectric constant:

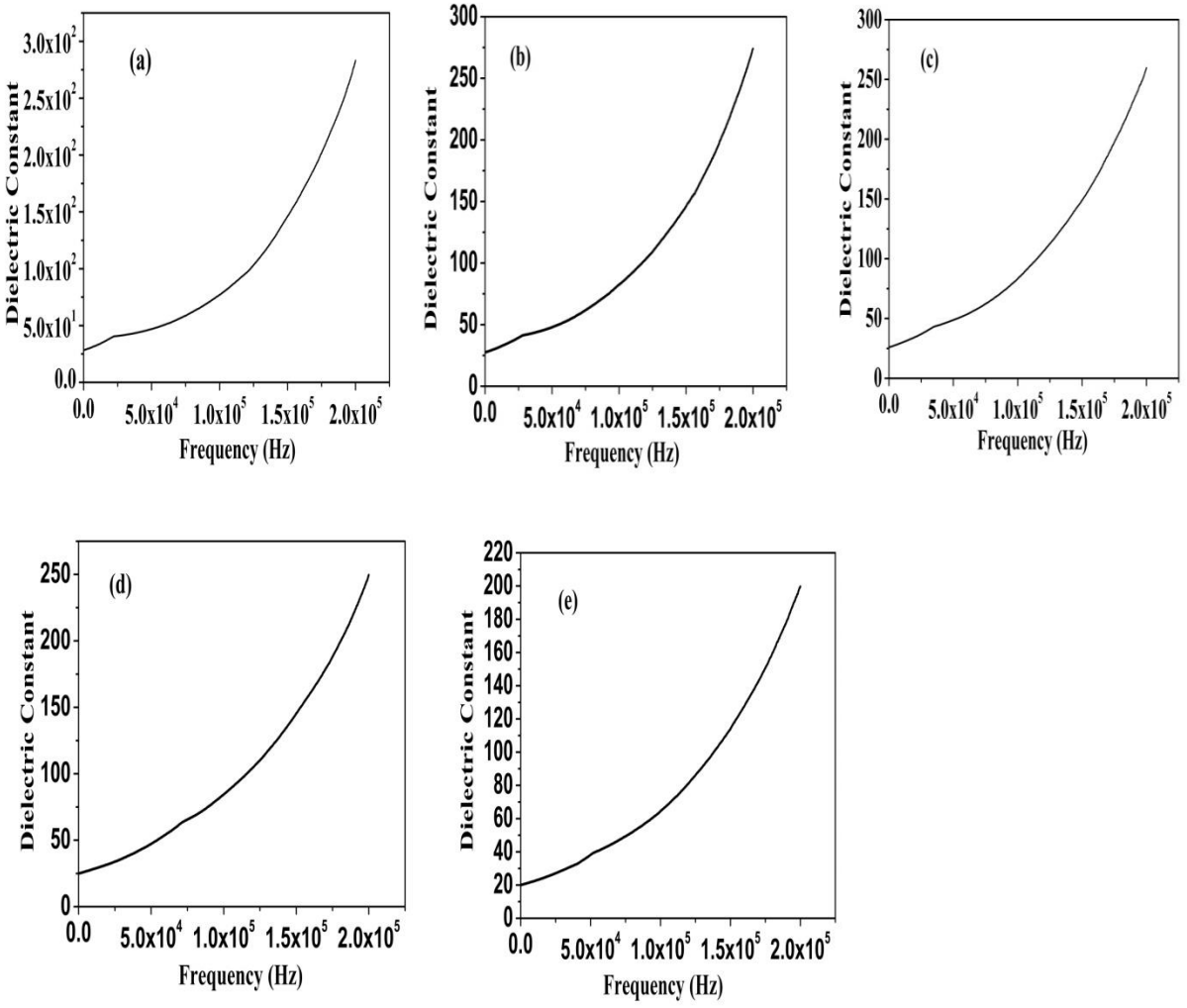


Figure. 4 Dielectric constant of (a) PANI/ $NiFe_2O_4$ (10%), (b) PANI/ $NiFe_2O_4$(20%), (c) PANI/ $NiFe_2O_4$(30%), (d) PANI/ $NiFe_2O_4$(40%), (e) PANI/ $NiFe_2O_4$(50%).

The frequency-dependent dielectric constant is shown in Figure 4. The ionic, electronic, and dipolar polarizations are affects the dielectric constant of the material and it may change the dielectric property of the sample. According to the effect of that the synthesized material may show the value of dielectric constant [14-16]. The dielectric constant value is unvarying at low

frequency and as gradually frequency increases dielectric constant also increases. The abrasion against dipole motion drops due to an increase in frequency dielectric constant also increases.

3.5. Dielectric Loss:

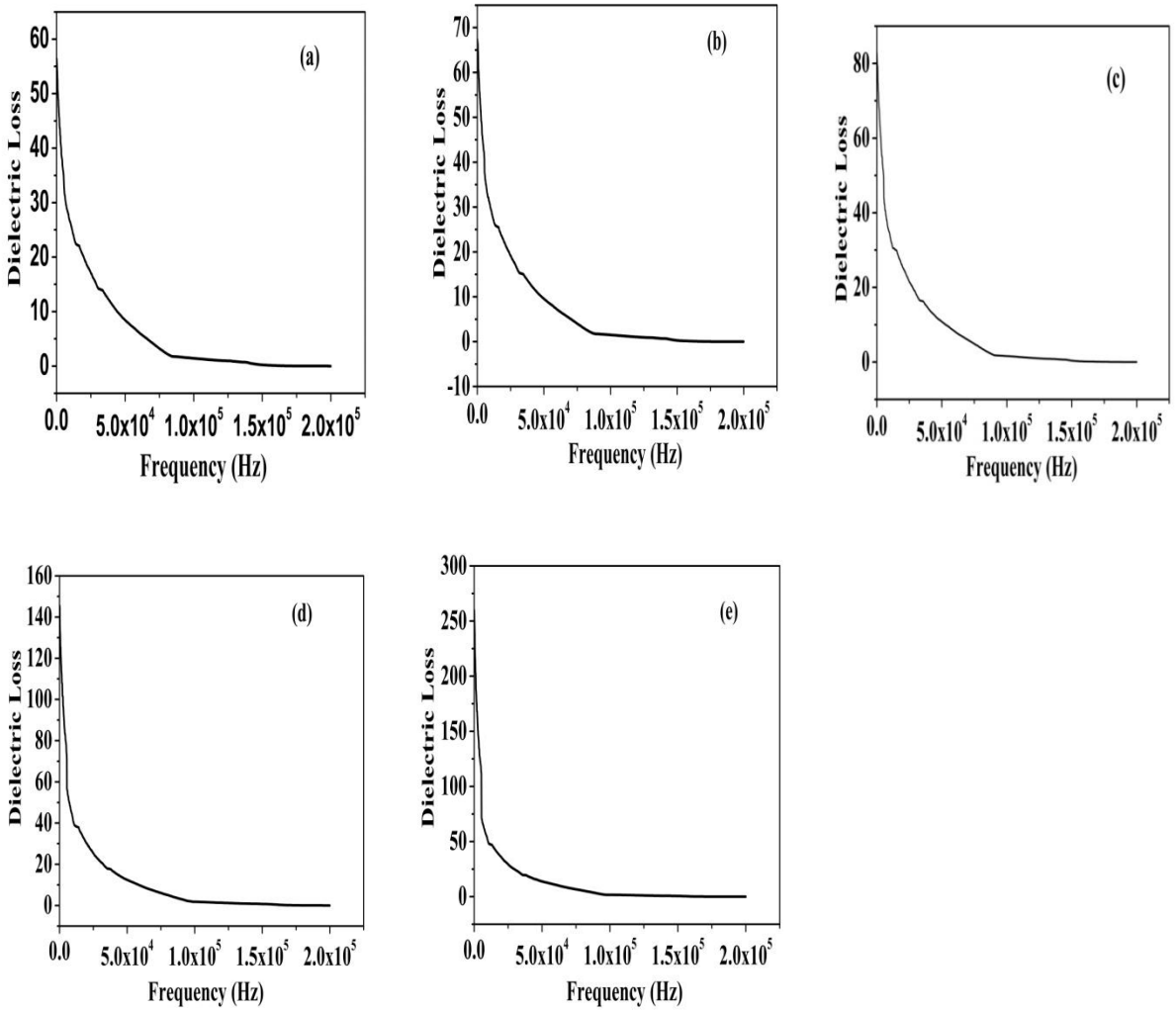


Figure. 5 Dielectric loss of (a) PANI/ $NiFe_2O_4$ (10%), (b) PANI/ $NiFe_2O_4$ (20%), (c) PANI/ $NiFe_2O_4$ (30%), (d) PANI/ $NiFe_2O_4$ (40%), (e) PANI/ $NiFe_2O_4$ (50%).

The analysis revealed that the PANI/ $NiFe_2O_4$ composites exhibited the frequency dependent dielectric losses; although the figure 5 shows that the dielectric loss changes with frequency as increasing the frequency dielectric loss deceases and reaches a low value at high frequency part. The figure clearly showed that the dielectric loss is high at low level frequency may be attributed to high resistivity caused by grain boundary and near constant at high region of frequency [20]. The frequency increases dielectric loss deceases due to space charge polarization [17]. The

PANI/ $NiFe_2O_4$ composites were showing the less dielectric losses that revealed the PANI/ $NiFe_2O_4$ composites suitable for electronic applications such as fabrication of capacitors [21].

3.5. TGA-DSC:

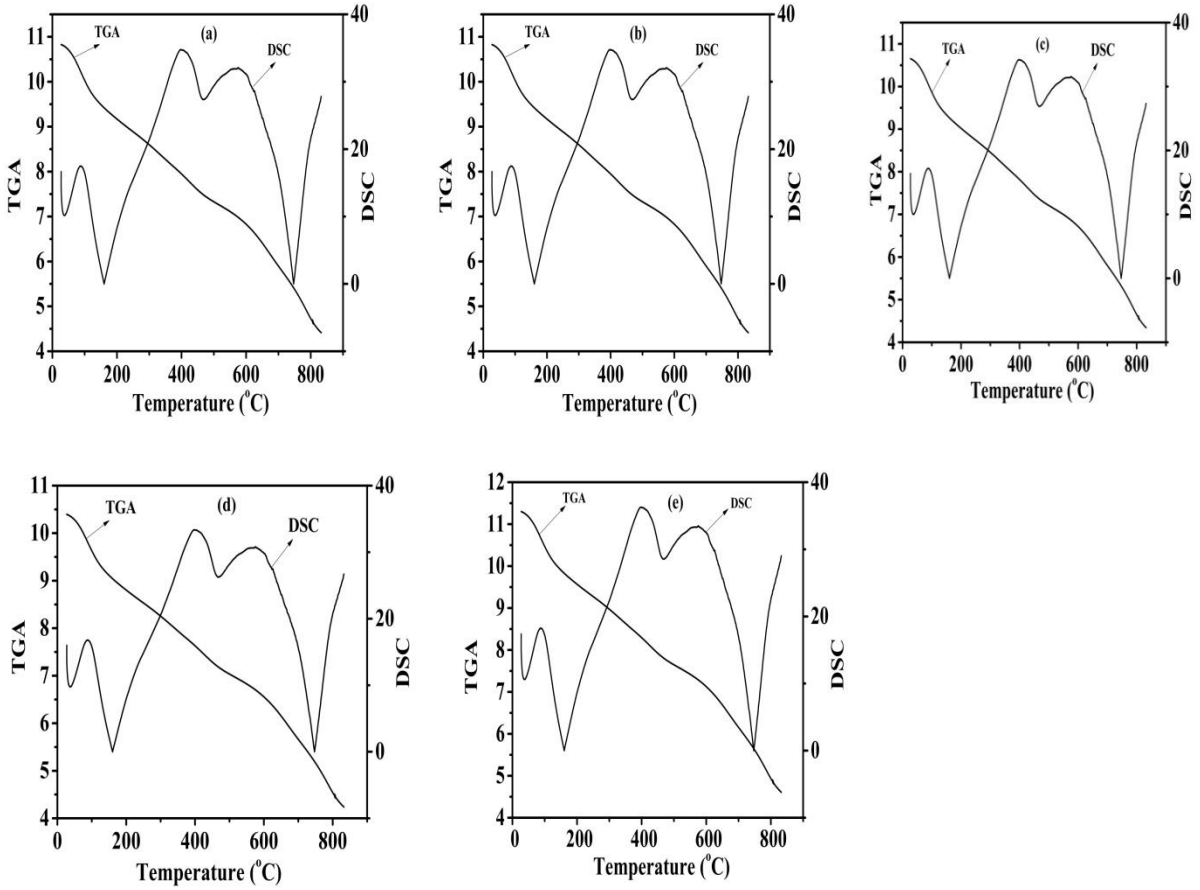


Figure: 6 TGA-DSC of (a) PANI/ $NiFe_2O_4$ (10%), (b) PANI/ $NiFe_2O_4$ (20%), (c) PANI/ $NiFe_2O_4$ (30%), (d) PANI/ $NiFe_2O_4$ (40%), (e) PANI/ $NiFe_2O_4$ (50%).

Figure 6 shows the thermal stability of PANI / $NiFe_2O_4$ (10, 20, 30, 40, 50 wt %) while PANI and the composites decompose over the measured temperature range 0 to 800 ^oC. The thermo gram of PANI in the figure shows the three stage weight loss. The initial weight loss at lower temperatures (less than 60 °C) is due to after drying the PANI some amount of moisture may retain in the matrix and that may cause weight loss. The second weight loss in the range of 100-115 ^oC is due to the loss of acidic anions that compensate for the positive charge of the PANI chains [17]. The third weight loss, which starts at about 420 °C, can be attributed to the decomposition of the PANI chains after the suspension of the doping anions. This could be due to the interaction between and PANI chains ferrite particles. Three exothermic peaks at about 96oC, 385 ^oC and 555 ^oC and two endothermic peaks at about 170oC and 730oC can be seen in the DSC curve [18

Samples	Weight loss% first step	Weight loss% second step
PANI/$NiFe_2O_4$ 10%	**9.5**	**4**
PANI/$NiFe_2O_4$ 20%	**9.5**	**4.3**
PANI/$NiFe_2O_4$ 30%	**9.3**	**4.5**
PANI/$NiFe_2O_4$ 40%	**9**	**4.8**
PANI/$NiFe_2O_4$ 50%	**9.5**	**5.1**

4. Conclusion:

In the present research polyaniline composites with (10, 20, 30, 40, and 50%) of $NiFe_2O_4$ in PANI have been synthesized. Ammonium dichromate is used as oxidizing agent and the samples synthesized by in-situ chemical oxidative polymerization technique. Characterizations of the prepared samples were performed using SEM, AC, DC, TGA, and DSC technique. The prepared samples surface morphology and particles size was investigated by SEM analysis the average grain size is about 25-30nm. The result of AC conductivity decreases with increasing frequency. The DC conductivity is high at low temperature and as temperature increases the conductivity decreases gradually. The dielectric constant increases with increase in the frequency. The frequency increases dielectric loss decreases. Dielectric properties of PANI/ $NiFe_2O_4$ composites are useful in many device applications.

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