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Electrical and Magnetic Properties of Polyaniline-Nickel Ferrite Composites

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ABSTRACT: Polyaniline-Nickel ferrite composites with different weight percent of $NiFe_2O_4$ (10, 30 and 50 wt %) were prepared via interfacial polymerization using ammonium persulphate as an oxidant, whereas $NiFe_2O_4$ was synthesized by combustion route. The prepared samples were characterized using some techniques such as FTIR, XRD and SEM. FTIR spectra revealed the formation of some interactions between polyaniline and $NiFe_2O_4$ particles. XRD reveals the crystalline phase of composites. The AC conductivity is studied as a function of frequency at room temperature in the frequency range 10 Hz to 10^6 Hz. The AC conductivity increases as the frequency increased. The magnetic properties of the samples were measured at room temperature using vibrating sample magnetometer (VSM) in the field range -15000 G to +15000 G. The composites show ferromagnetic behavior.

Key Words: Polyaniline, Nickel ferrite, Composites, Conductivity, Magnetic saturation.

I. INTRODUCTION

Conducting polymers have attracted much interest because of their many promising technological applications [1]. Among all, polyaniline is one of the most widely used conducting polymers because of its ease to synthesis, low density, low cost, good processability, excellent environmental stability, and high electrical conductivity [2- 6]. Polyanilne has also been used in many applications such as electromagnetic interference (EMI) shielding, light-emitting diodes, rechargeable battery, chemical sensor, corrosion devices and microwave absorption [7–10].

Many kinds of materials can be used as magnetic part of the composite materials, such as γ-Fe_2O_3 [11], $ZnFe_2O_4$ [12, 13], $CoFe_2O_4$ [14], Co_3O_4 [15] and $BaFe_{12}O_{19}$ [16]. Among magnetic materials, the spinel ferrites exhibitremarkable magnetic properties particularly in radio-frequency region, physical flexibility, high electrical resistivity, mechanical hardness and chemical stability [17]. $NiFe_2O_4$ is an important magnetic ferrite which has been found its extensive applications in diverse areas such as permanent magnets, recording media, Ferro fluids and gas sensors.

In this paper, $NiFe_2O_4$ particles were prepared by combustion route, and Polyaniline-$NiFe_2O_4$ composites were then synthesized via interfacial polymerization method using ammonium persulphate as an oxidizing agent. The structure and morphology of the polyaniline, $NiFe_2O_4$ particles and polyaniline-$NiFe_2O_4$ composites have been investigated through FTIR, XRD and SEM. The frequency dependence of AC conductivity investigated in the frequency range 10 Hz to 10^6 Hz. Themagneticpropertiesaremeasuredusingvibratingsample magnetometer (VSM) at room temperature in the field range of +15000G to -15000G.

II. EXPERIMENTAL

All chemicals used for synthesis are analytical reagent (AR) grade. Aniline and hydrochloric acid have been purchased from Aldrich chemicals. Aniline was double distilled before use. Ammonium persulphate is purchased from Qualigens. Nickel ferrite particles were synthesized by combustion route. Double distilled water was used throughout the work.

As prepared nickel ferrite was used for preparation of polyaniline composites. The samples so obtained are crushed finely in the presence of acetone medium in agate mortar and processed into circular pellets of 10 mm diameter and thickness varying from 1 to 2 mm by applying a pressure of 90 MPa using a hydraulic press. For conductivity measurements, the pellets are coated with silver paste on either side of the surfaces to provide better electrical contacts.

Synthesis of Polyaniline. The synthesis of polyaniline was based on mixing aqueous solution of aniline, hydrochloride and ammonium persulphate at room temperature, followed by the separation of polyaniline hydrochloride precipitate by filtration and drying. Aniline hydrochloride (equimolar volumes of aniline and hydrochloric acid) is dissolved in double distilled water in a volumetric flask to 100 ml of solution. Ammonium persulphate (0.25M) was dissolved in water also to 100 ml solution and then kept for 1 hour at room temperature (25^{o}C), then mixed in a beaker, stirred mechanically and left at rest for complete polymerization. After 24 hours the polyaniline precipitate is collected on a filter, washed with 0.2M HCl and similarly with acetone. Finally, the resultant polyaniline hydrochloride powder is dried in air and then vacuum at 60^{o}C to achieve a constant mass.

Synthesis of $NiFe_2O_4$ particles (Combustion route). Nickel ferrite particles were prepared by, known quantity of nickel salt and iron salt was mixed thoroughly and is grounded well with polyvinyl alcohol in 1:5 in a pestle and mortar. The reaction mass was transferred in to crucible initially burnt in an electrical oven for complete evolution of the fumes.

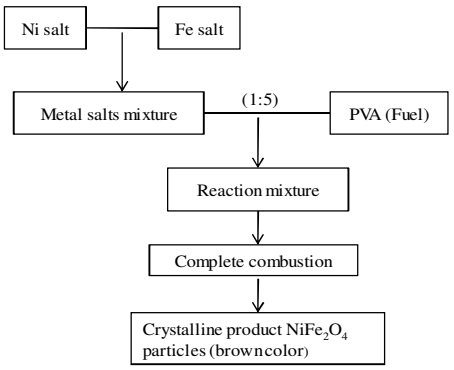

Fig. 1. Flow chart: Synthesis of $NiFe_2O_4$ Particles.

The resultant residue was heated continuously for complete combustion. The reaction was completed within 30 minutes to form brown colored crystalline $NiFe_2O_4$ is formed. On cooling to room temperature carbon impurities in the ferrite sample is removed by treating with acetone. The carbon flowts on the acetone is decanted and evaporated the acetone. The various steps involved in chemical synthesis of $NiFe_2O_4$ particle is shown in flow chart (figure 1).

Synthesis of Polyaniline-$NiFe_2O_4$ composites. The Polyaniline-$NiFe_2O_4$ composites were prepared via interfacial polymerization method with different weight percentage of $NiFe_2O_4$ (10, 30 and 50 wt %). One gram of aniline was dissolved in 40 ml of $CHCl_3$. 0.1M ammonium persulphate was dissolved in 1M HCl and the $NiFe_2O_4$ particles are added to the above mixture of aqueous and organic phase. After 5 minutes dark green precipitate formed slowly at the interface and then gradually diffused into 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 vacuum oven at 40^{o}C for 36 hours. The dried polymer composite sample was used for structural characterization and further used to study the electrical and magnetic properties.

III. CHARACTERIZATION

The above synthesized samples were structurally and morphologically characterized by using different techniques like FTIR, XRD and SEM. The FTIR spectra of samples were recorded on ThermoNicolet, Avatar 370 spectrometer in KBr medium at room temperature. The X-ray diffraction patterns of the prepared samples were obtained by employing Bruker AXS D8 advance X-ray diffractometer using CuK_α radiation (λ=1.5418A^{o}) in the 2θ range 20^{o} to 80^{o}. The surface morphplogy ofpolyaniline, $NiFe_2O_4$ particles and polyaniline-$NiFe_2O_4$ composites were studied by using Joel model JSM-6390 LV scanning electron microscope (SEM). To measure the AC conductivity, the pellets of the prepared samples were coated with silver paste on either side was held between two nominally spring loaded copper plates and the AC parameters were measured using N4L-PSM 1735 NumetriQ programmable LCR meter in a frequency range 10 to 10^6 Hz. The magnetization measurements were carried out at room temperature using vibrating sample magnetometer (VSM) Lakeshore VSM-7410 with a maximum field of -15000 G to +15000 G.

IV. RESULTS AND DISCUSSION

A.Infrared spectra

The IR spectra of $NiFe_2O_4$ particles, polyaniline and polyaniline-$NiFe_2O_4$ (10, 30 and 50 wt %) composites are shown in figure2.

Figure 2(a) shows IR spectra of polyaniline.The characteristic peaks of polyaniline occur at 1564, 1478, 1301, 1244, 1137, 808 and 702 cm^{-1}. The peaks at 1564 and 1478.15 $cm^{-1}$are attributed to the characteristic C-C stretching of the quinoid and benzenoidrings, the peaks at 1301 and 1244 cm^{-1} are assigned to C-N stretching of the benzenoid ring, the broad peak at 1137 cm^{-1}which is described as electronic-like band is associated with vibration mode [18] and the peak at 808 and 702 cm^{-1} are attributed to the out of bending of N-H and C-H bond in aromatic rings respectively. The IR spectra of $NiFe_2O_4$ particles (Fig. 2b), the main peak at 546 $cm^{-1}$is due to intrinsic stretching vibrations of metal at tetrahedral site andthe peak at 468 $cm^{-1}$is due to octahedral-metal stretching vibrations. The IR spectra of polyaniline-$NiFe_2O_4$ (10, 30 and 50 wt %) composites (fig.2 c-e) shows the peaks of the composites shift to higher frequencies. This indicates that there is some interaction between $NiFe_2O_4$ particles and polyaniline backbone.

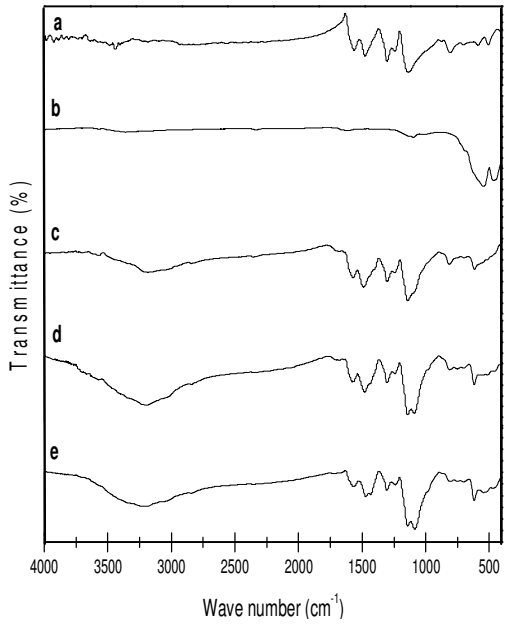

Fig. 2. FTIR spectra of (a) Polyaniline, (b) $NiFe_2O_4$ particles and (c-e) polyaniline-$NiFe_2O_4$ composites.

B.X-ray diffraction

The XRD pattern of polyaniline (Fig. 3a) shows two broad peaks centered at $2\theta=20.7^o$ and 25.29^o, which are ascribed to the periodicity parallel and perpendicular to the polymer chains, respectively [19-21].

The XRD pattern of $NiFe_2O_4$ particles (Fig 3b), the prominent peaks at $2\theta= 32.90^o$, 35.38^o, 43.00^o, 53.79^o, 57.23^o, 63.76^o, 75.31^o and 79.43^o corresponds to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (6 2 2) and (4 4 4) crystal planes. All the peaks match with the characteristic reflection of $NiFe_2O_4$ (JCPDS Card No.10-0325). The XRD patterns of polyaniline-$NiFe_2O_4$ composites (Fig. 3c-3e) exhibit both the characteristic peaks of $NiFe_2O_4$ and the broad diffraction of polyaniline. These results confirm the formation of polyaniline-$NiFe_2O_4$ composites.

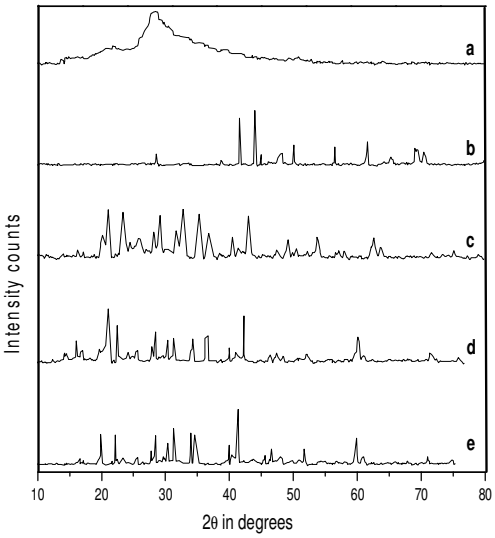

Fig. 3. XRD patterns of (a) Polyaniline (b) $NiFe_2O_4$ and (c-e) polyaniline-$NiFe_2O_4$ composites.

C. SEM analysis

The surface morphology of polyaniline-$NiFe_2O_4$ (10, 30 and 50 wt %) composites was investigated by means of SEM.

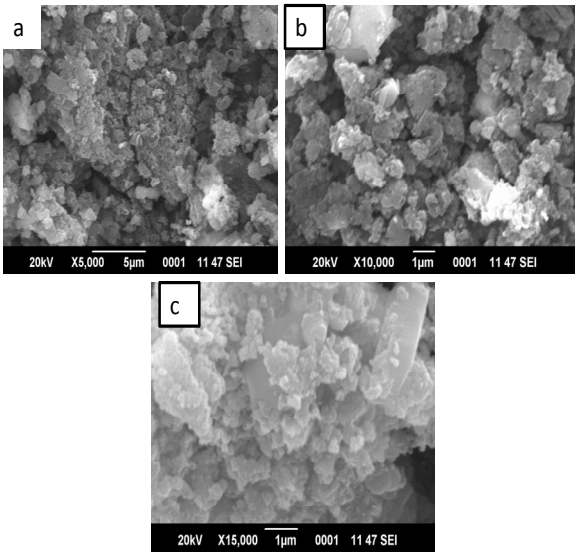

Fig. 4. SEM micrographs of polyaniline-$NiFe_2O_4$ (10, 30 and 50 wt %) composites

Figure 4(a-c) gives the SEM micrographs of polyaniline-$NiFe_2O_4$ composites, suggesting that the polyaniline is deposited on the surface of $NiFe_2O_4$ particles.

V. ELECTRICAL PROPERTIES

Figure 5(a and b) shows the variation of AC conductivity as a function of frequency for the polyaniline and polyaniline-$NiFe_2O_4$ (10, 30 and 50 wt %) composites. From the fig 5(a) it is seen that the conductivity of polyaniline remains constant up to 10^4 Hz after that there is increase in conductivity at higher frequencies. Figure 5(b) shows the conductivity of polyaniline-$NiFe_2O_4$ composites, it is seen that the conductivity increases gradually for all the composites. Increased conductivity may be due to increased charge polarization [22]. Among the composites, 30 wt% shows the higher conductivity.

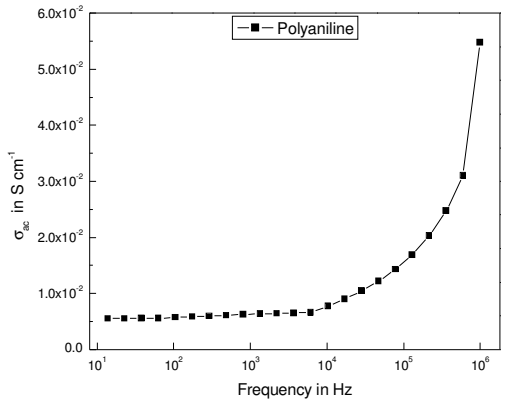

Fig. 5a. Variation of AC conductivity with frequency for Polyaniline.

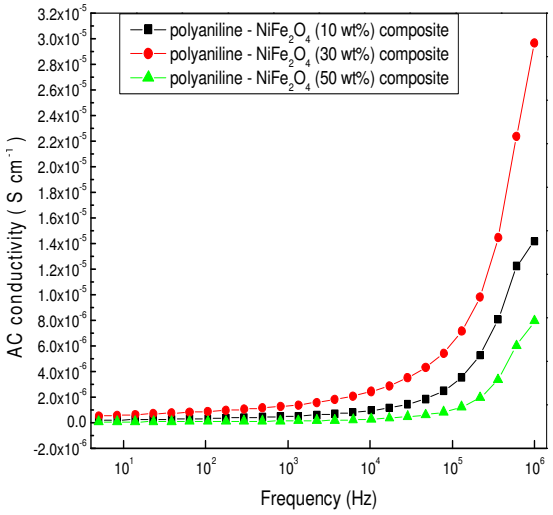

Fig. 5b. Variation of AC conductivity with frequency for Polyaniline-$NiFe_2O_4$ composites.

VI. MAGNETIC PROPERTIES

Figure 6 (a-e) shows room temperature magnetization curves for Polyaniline, $NiFe_2O_4$ and Polyaniline-$NiFe_2O_4$composites. It has been found that polyaniline show diamagnetic behavior whereas $NiFe_2O_4$ particles and polyaniline-$NiFe_2O_4$ composites show ferromagnetic behavior. The saturation magnetization (M_S) of polyaniline-$NiFe_2O_4$ (10, 30 and 50 wt %) composites increase in ferrite % in the polymer matrix. Among the composites, 30 wt% show low saturation magnetization value of 0.97 emu g^{-1}. The saturation magnetization (M_S), Remanent magnetization (M_R) with Coercive field (H_C) for the samples are listed in table1.

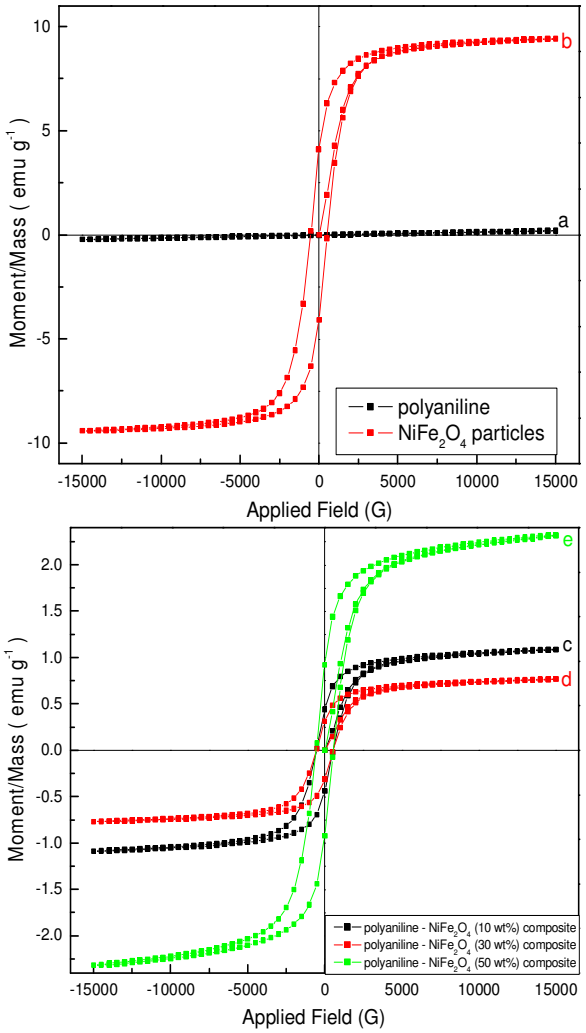

Fig. 6. Magnetization curves for (a) Polyaniline, (b) $NiFe_2O_4$ and (c-e) Polyaniline-$NiFe_2O_4$ composites.

Table 1: Magnetic parameters of Polyaniline, $NiFe_2O_4$ particles and polyaniline-$NiFe_2O_4$ composites.

Samples	M_S in emu g^{-1}	M_R inemu g^{-1}	H_C in G
Polyaniline	0.69	$8.31x10^{-3}$	-
$NiFe_2O_4$ particles	9.43	4.09	525.39
Polyaniline-$NiFe_2O_4$ (10 wt%) composite	1.09	0.44	533.50
Polyaniline-$NiFe_2O_4$ (30 wt%) composite	0.97	0.36	529.38
Polyaniline-$NiFe_2O_4$ (50 wt%) composite	2.32	0.92	551.37

VII. CONCLUSIONS

In summary, $NiFe_2O_4$particles and polyaniline-$NiFe_2O_4$ composites have been successfully synthesized by combustion route and an interfacial polymerization respectively. FTIR and XRD analysis shows there is some interaction between polyaniline and $NiFe_2O_4$ particles. The AC conductivity increased with increased frequency, the composites with 30 wt% of $NiFe_2O_4$ in polyaniline show high conductivity. The magnetic parameters such as saturation magnetization and coercivity of composites were found to be depended on the wt % of $NiFe_2O_4$ particles in polyaniline. The composites showferromagnetic nature.

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