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MAGNETIC PROPERTIES OF POLYANILINE MAGNETIC IRON OXIDE COMPOSITES

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Abstract

Magnetic iron oxide (Fe_3O_4) was prepared by the simple approach of sol–gel process using ferrous ammonium sulphate as precursor. Conducting polyaniline- Magnetic iron oxide (PANI/ Fe_3O_4) composites were synthesized by in-situ polymerization technique in sulphuric acid medium with ammonium persulphate as oxidizing agent in the presence synthesized particles of Fe_3O_4 as reinforcing filler in different concentrations so as to study the effect of filler particles on magnetic behaviour of the conducting polyaniline. The synthesized composites were characterized by XRD, FTIR, UV-VIS and SEM analysis. The X-ray diffraction (XRD) pattern and scanning electron microscopy (SEM) image show that crystalline Fe_3O_4embedded into polycrystalline PANI to form crystalline composites. Fourier transform infrared (FTIR) and ultraviolet visible (UV-VIS) spectroscopy show that Magnetic iron oxide particles get electro statically bound to the specific sites of polyaniline, thereby modifying torsional degrees of freedom of the composites system. VSM study reveals that PANI/ Fe_3O_4 composites show ferromagnetic with filler concentration dependant variation of saturation magnetization (Ms), coercive field (Hc) and remnant magnetization (Mr).

Keywords: conducting polymers; polyaniline; Magnetic iron oxide Fe_3O_4; composites; VSM.

1. Introduction

Interest in the development of the new inorganic organic composites has grown in recent years due to a wide range of potential applications of these materials [1, 2]. Polymer-based composites represent a new concept in the development of systems exhibiting functional properties resulting from the synergistic interaction between the disperse phase and the matrix. In our particular case, the many properties of conducting polymers like non-corrosiveness, light weight, mechanical strength, and

the possibility to tune electrical conductivity can be utilized along with magnetic properties of ferrite particles to make multifunctional structures.

One important class of hybrid materials is that in which the organic fraction is composed of conducting polymers, such as polyaniline, polypyrole or polythiophene [3, 4].Polyaniline (PANI) is known as one of the most promising conducting polymers due to of preparation, excellent environmental stability, better electronic properties, electrochemical properties and its applications in electrochromic display, electrocatalysis, rechargeable batteries, sensors and biosensors [5-8]. Polyaniline has a variety of oxidation states and three different states of them are usually referred to in the literature: leucoemeraldine base, emeraldine base (EB) and pemigraniline base. Emeraldine base is the most attractive one because it can be doped with protonic acid to become emeraldine salt (ES) and the conductivity of the ES is increased.

Iron oxides, as the main ferromagnetic material, can offer great potential applications in different area such as ferrofluids, colour imaging, magnetic refrigeration, detoxification of biological fluids, and magnetically controlled transport of anti-cancer drugs, magnetic resonance imaging and magnetic cell separation [7]. Polymer composite PANI- Fe_3O_4 exhibits some novel properties such as improved electrical conductivity, improved magnetic properties etc. Various co-workers have reported studies on electrical and magnetic properties of PANI- Fe_3O_4 polymer composites [8-9].

The present paper has to be revealed the synthesis of PANI- Fe_3O_4 polymer composites with different weight percentage of Fe_3O_4 with PANI, their characterizations by various spectral studies such as UV-visible, FT-IR, florescence and XRD. Magnetic properties of these polymer composites were studied by VSM techniques. The morphology of these polymer composites was studied by SEM.

2. Experimental

2.1. *Materials and methods*

Aniline (99%), ferrous ammonium sulphate and NH_3 (ammonia) were purchased from Merck. Aniline was distilled before use for polymerization. Ammonium persulphate (APS) (99%) was purchased from Qualigens Fine Chemicals. Other supplement chemicals were of AR grade and used as received.

The FTIR spectra of the composites were recorded on a Shimadzu FTIR-8101A spectrophotometer between 400 and 4600 $cm.^{-1}$. UV-visible spectra were recorded by UV-1800 Shimadzu double beam spectrophotometer. X-ray diffract grams were recorded on a Philips PW1710 automatic X-ray diffractometer. SEM micrographs were scanned by JEOL JSM-6380 A. The magnetization measurements were carried out using vibrating sample magnetometer (VSM) model Oxford Maglab 14T.

2.2. Synthesis of Magnetic iron oxide (Fe_3O_4)

Magnetic iron oxide (Fe_3O_4) were prepared by the simple approach of sol–gel process in which requisite amount of ferrous ammonium sulphate (precursor) was added to starch solution and then stirred the solution for 30 minutes. Prepared solution was hydrolysed by NaOH under constant stirring at room temperature for 2 hours. The solution was kept overnight and then filtered using membrane filtration assembly, washed using deionised water and ethanol to remove the impurities and then dried at 80^0C in hot air oven. Dried sample was treated at different temperatures in order to maintain the stability of compound.

2.3 Synthesis of PANI- Magnetic iron oxide (Fe_3O_4) polymer composite

Polyaniline composite with Magnetic iron oxide (Fe_3O_4) was synthesized by chemical oxidation method. In-situ polymerization of the monomer (aniline) was initialled by drop wise addition of the oxidizing

agent (ammonium persulphate) in acidic solution of 1 M H_2SO_4, using doubly distilled water under constant stirring at 0-4°C. During this stirring for one hour Magnetic iron oxide (Fe_3O_4) in weight ratio of 5% was added for synthesizing the composite. The ratio of monomer to oxidizing agent was kept as 1:1. After complete addition of the oxidizing agent the reaction mixture was kept under constant stirring for 8-10 hours. The precipitated polymer was filtered and washed with double distilled water and methanol until the filtrate was colourless. Finally the precipitate was dried in an oven at 70°C for 12 hours. Then precipitate polymer composite was powdered finely.

2. Results and Discussion

The synthesized purified magnetic iron oxide (Fe_3O_4) was shiny black in colour, while composite was found to be blackish green in colour. The composite are soluble in solvents such as DMF, DMSO while insoluble in almost all other organic solvents.

UV-visible spectra of polyaniline- Magnetic iron oxide (PANI/ Fe_3O_4) composites in DMF solvent are shown in figure 1. It is seen obviously from curve of PANI that two strong absorptions around 330 and 660nm respectively, assigned for π-π* transition and the transition of benzenoid rings into quinoid rings corresponding to bipolaronic band [11].

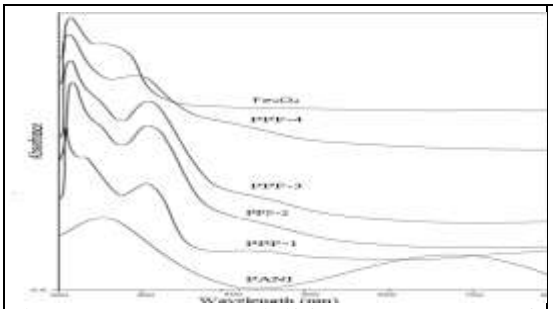


Figure 1: UV-visible spectra of Polyaniline, pure metal oxide Fe_3O_4 and polymer composites PANI- Fe_3O_4

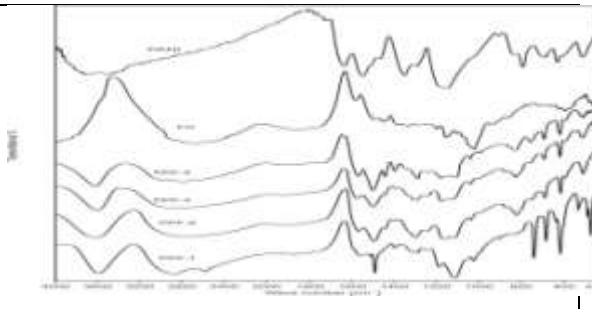


Figure 2: IR spectra of newly synthesized Polyaniline, pure metal oxide Fe_3O_4 and polymer PANI- Fe_3O_4 (PPF) composites.

From the figure, one can see that the spectra of polyaniline-Magnetic iron oxide (PANI/ Fe_3O_4) composites show hypsochromic shift. This trend

indicates an increase in band gap through about by an increase in the torsion angle between C-N-C plane and the plane of benzene ring, thus decreasing the conjugation, which may be due to the addition of the Fe_3O_4particles which twist the torsion angle. It is observed that there is bipolaronic band shift significantly from 660nm to shorter wavelength side with incorporation of Fe_3O_4particles. It is suggested that the change in delocalization of electrons in PANI structure (i.e. variation in energy gap between HOMO and LUMO) has taken place with incorporation of Fe_3O_4particles in PANI.

The IR spectral studies revealed that polyaniline and its composites gave rise to nearly similar pattern of spectra. Fig.2 shows the IR spectra of polyaniline, pure Fe_3O_4 and their composites. Table 1 has given the IR spectral data. Broad absorption band appeared in the region 3433-3400 cm-1 may be assigned to the stretching vibrations of N-H groups exhibiting intermolecular hydrogen bonding [12]. A sharp strong peak at 1556 cm-1 may be ascribed to aromatic skeletal ring. The bands obtained at 2889-2800 cm-1 suggest the C-H stretching vibrations of ethylene ($-CH_2$). The bands obtained at 1624-1600 cm-1 suggest the C-N stretching vibrations of quinonoid ring. The bands obtained at 1492-1424 cm-1 suggest the C-N stretching vibrations of benzenoid ring. A sharp strong peak at 1168-1100 cm-1 may be ascribed to vibration bands of dopent ions. The paradisubstituted aromatic rings indicating polymer formation by the bands appeared at 826-802 cm-1. The presence of sharp and strong band at 592-588 cm-1 indicates the presence of Fe-O stretching vibrations. This indicates the formation of polymer composites [13].

The XRD spectra of polyaniline, pure Fe_3O_4 and PANI- Fe_3O_4 polymer composite samples have shown in Fig.3. All the strong and sharp diffraction peaks in the pattern can be indexed to the face centred cubic phase of Fe_3O_4, with the cell constant a = 7.67 A^0, which are consistent with the values reported in the literature (JCPDS No.79-0419).

The main peaks at 2θ = 35.5^0, 56.4^0 and 62.3^0 are characteristics of Fe_3O_4 broad peak at about 2θ = 25^0 in composite is the characteristic peak of PANI.

The crystalline particle size can be determined by Scherer's formula (D=k λ/β *Cos θ) Where, λ is X-ray wavelength (1-54056A°), θ_B is Bragg's diffraction angle and B is reflection broadening as full width at half maximum intensity. Average sizes of Fe_3O_4 particle which is found to be 98 nm [14].

Fig.4 shows SEM photographs of polyaniline, pure Fe_3O_4 and their composites. The SEM photographs of polyaniline-Fe_3O_4 composite (PPF-1) shows less crystalline structure showing spherulites and more amorphous character with less closed packed surface having deep pits. The morphology of polyaniline-Fe_3O_4 composite thus identified by SEM as crystalline as well as amorphous or transition between crystalline and amorphous.

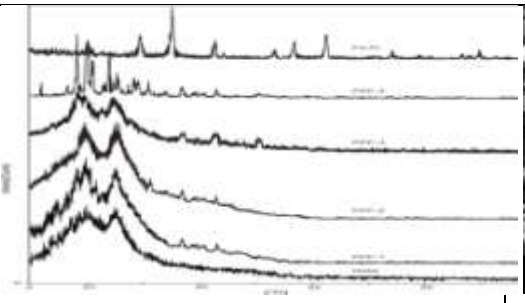
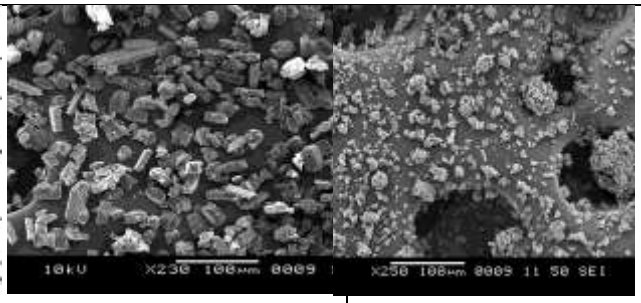


Fig.3 : XRD spectra of polyaniline, pure metal oxide $Fe_3O_4$and polymer PANI- Fe_3O_4 composite



SEM Micrographs of (a) Fe_3O_4 and (b) PANI- Fe_3O_4 polymer composites (PPF-1)

3.1 Magnetic properties

On the basis of VSM study polyaniline composites with Fe_3O_4 viz PPF-1 to PPF-4 show hysteresis loop as they are ferromagnetic [15]. Figure 8, 9 shows the hysteresis measurements performed at room temperature for Fe_3O_4 and Polyaniline-Fe_3O_4 composites. The hysteresis loop of Fe_3O_4 at room temperature shows a ferromagnetic behavior with

high saturation magnetization (Ms) 97.5 emu/g, remnant magnetization (Mr) 19.5emu/g and coercivity (Hc) 500 Oe respectively.

It has been observed that the magnetic polymer composite show a finite coercivity at room temperature. This indicates that the composites are in the ferromagnetic regime having magnetization (Ms) 77.25 - 88.26 emu/gm, retentivity remain constant 10.0 emu/gm and coercivity 354-365 Oe respectively. Magnetic properties of pure Fe_3O_4 and polyaniline magnetic iron oxide composites are shown in table 1.

Conclusions

1. New Polyaniline magnetic iron oxides composites were successfully obtained by in-situ polymerization of aniline in the presence of magnetic iron oxides particles. The synthesis method is a simple one and has a great potential for the commercial applications. Samples morphology is evident from SEM pictures. FTIR analysis confirms the interaction between polyaniline and Fe_3O_4 respectively.
2. Reinforcement of magnetic iron oxide on polyaniline matrix gives ferromagnetic material may be applicable in MRI.

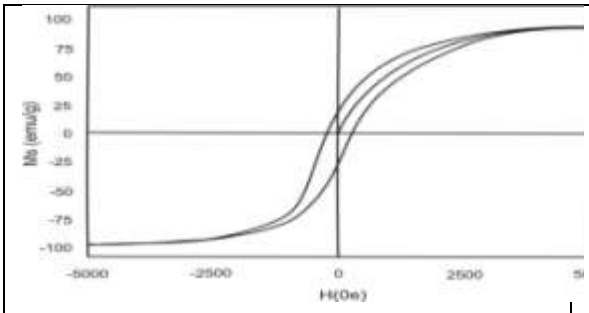


Figure 5: Hysteresis loop of pure Fe_3O_4

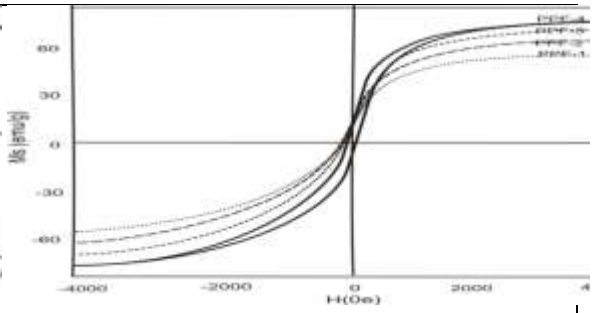


Figure 6: Hysteresis loop of polymer composite PPF-1- 4

Table 1: Magnetic parameters of Fe_3O_4, PANI and PANI/ Fe_3O_4 composites

Materials	*Ms (emu/g)*	*Mr (emu/g)*	*Hc (Oe)*	*SQR*
Fe_3O_4	64	20.5	360	0.32
PANI	25	5.7 $x10^{-3}$	----	22.8 x 10^{-3}
PPF-1	37.52	5.5	225	0.14
PPF-2	39.08	7.5	235	0.18
PPF-3	41.56	8.8	238	0.21
PPF-4	48.45	10.5	240	0.21

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