

Synthesis, characterization and magnetic properties of polyaniline/ γ -Fe₂O₃ composites

SYED KHASIM*, S C RAGHAVENDRA¹, M REVANASIDDAPPA², K C SAJJAN³,
MOHANA LAKSHMI and MUHAMMAD FAISAL

Department of Physics, ¹Department of E&CE, ²Department of Chemistry, PES School of Engineering,
Bangalore 560 100

³Department of Physics, Veerasaiva College, Bellary 583 101, India

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Abstract. Conducting polyaniline/ γ -Fe₂O₃ (PANI/FE) composites have been synthesized using an *in situ* deposition technique by placing fine-graded γ -Fe₂O₃ in a polymerization mixture of aniline. The composites are characterized by using scanning electron microscopy (SEM), X-ray diffraction (XRD) and infrared (IR) spectroscopy. The electrical properties such as d.c. and a.c. conductivities are studied by sandwiching the pellets of these composites between the silver electrodes. It is observed that the conductivity increases up to a composition of 20 wt.% of γ -Fe₂O₃ in polyaniline and decreases thereafter. The initial increase in conductivity is attributed to the extended chain length of polyaniline, where polarons possess sufficient energy to hop between favourable sites. Beyond 20 wt.% of γ -Fe₂O₃ in polyaniline, the blocking of charge carrier hop occurs, reducing conductivity values. The magnetic properties such as hysteresis characteristics and normalized a.c. susceptibility are also measured, which show a strong dependence on content of γ -Fe₂O₃ in polyaniline. Because of superparamagnetic behaviour of these composites, they may find extensive technological applications, especially for absorbing and shielding applications in microwave frequencies.

Keywords. Conducting polymers; conductivity; polarons; polyaniline composites, γ -Fe₂O₃.

1. Introduction

Among various conducting polymers, polyaniline (PANI) is a unique and promising candidate for potential applications because of its stability in air and solubility in some organic solvents (Angalopoulos *et al* 1988; Cao *et al* 1992). It also exhibits dramatic changes in its electronic structure and physical properties on protonation (Mexiang Wan *et al* 1991, 1992). Conducting polymer composites are, in fact, synthesized by mixing a suitable composition of conducting polymer with one or more insulating materials so that their desirable properties are combined successfully (Raghavendra *et al* 2003; Murugendrappa *et al* 2005; Syed Khasim *et al* 2005; Basavaraja *et al* 2007). Over the last few years, composites of special category termed 'nanocomposites' have been studied with growing interest. These materials are especially important as they combine the properties of conducting polymers and nanoparticles (Hanemann 2010).

The addition of nanoinorganic nanoparticles to polymers allows the modification of polymer's physical properties as well as the implementation of new features in the polymer matrix. The properties of nanocomposites of

this kind are strongly dependent on concentration of oxide nanoparticles (Hanemann 2010).

Recently PANI has attracted much attention for its magnetic behaviour as it exhibits high spin density (Mexiang Wan and Zhou 1992). In fact, Yoshizawa *et al* (1992, 1993) reported that ferromagnetic spin-spin interaction was observed in poly(*m*-aniline). The composite materials based on nano-sized magnetic particles have been of great interest to researchers due to their possible applications in microwave absorption, bio analytical sensors, refrigeration and high-density information storage (Shull *et al* 1992; Xiao *et al* 1993; Vijayanad *et al* 2007; Wang *et al* 2008; Lia Stanciu *et al* 2009; Singh *et al* 2010). These composites are often prepared by dispersing magnetic materials in a non-magnetic matrix.

In this paper, we report on the preparation of nanocomposites of conducting polymers (polyaniline) and iron oxide (γ -Fe₂O₃), so that the resulting hybrid composite exhibits both conducting as well as ferromagnetic properties.

2. Experimental

2.1 Synthesis of polyaniline/ γ -Fe₂O₃ composites

All chemicals of analytical grade procured from Sigma-Aldrich were used for the synthesis of polyaniline/

*Author for correspondence (skhasim@rediffmail.com)

γ -Fe₂O₃ (PANI/FE) composites. γ -Fe₂O₃ powder in the form of fine particles with an average particle size of 750 nm is synthesized by usual oxalate precursor method.

The 0.1 M aniline monomer is dissolved in 1 M HCl to form polyaniline. Fine-graded pre-sintered γ -Fe₂O₃ powder (with 10, 20, 30, 40 and 50 wt.%) is added to the polymerization reaction with vigorous stirring in order to keep γ -Fe₂O₃ powder suspended in the solution. To this reaction mixture, 0.1 M aqueous ammonium persulphate, which acts as an oxidant, is added slowly dropwise with continuous vigorous stirring for 4–6 h at 0–5°C. Polymerization of aniline is allowed to take place over fine-graded γ -Fe₂O₃ particles. The resulting precipitate is filtered under suction and washed with distilled water until the filtrate becomes colourless. Acetone is used to dissolve any unreacted aniline. After washing, the precipitate is dried under dynamic vacuum at 60–80°C for 24 h. The obtained composite is grinded into a fine powder in smooth agate mortar in the presence of acetone medium. The composite powder is pelletized to required dimensions and copper electrodes are placed using silver paste for conductivity measurements.

Apart from pure polyaniline, polyaniline/ γ -Fe₂O₃ composites with different wt.% values (10, 20, 30, 40 and 50 wt.%) of γ -Fe₂O₃ in polyaniline have been synthesized.

The powder morphology of PANI and its composites sintered in the form of pellets are investigated using Philips XL-30 ESEM scanning electron microscope. The X-ray diffraction pattern of the sample is recorded on Philips X-ray diffractometer using CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The IR spectra of the samples are recorded on the Perkin-Elmer (model 783) IR spectrometer in KBr medium at room temperature in the region 4000–450 cm⁻¹. The dc conductivity of PANI and PANI/FE composites are measured by using two-probe method at two fixed temperatures, viz. 50 and 100°C. The a.c. conductivity of PANI and PANI/FE composites are measured using the Hewlett-Packard impedance analyser 4192-A at room temperature. Magnetic hystereses of pre-magnetized PANI/FE composites are recorded on a cathode ray oscilloscope (CRO) using high-field hysteresis loop tracer and different parameters are calculated. A.C. susceptibility measurements were carried out using double coil setup at switching frequency of 263 Hz.

3. Results and discussions

3.1 Scanning electron microscopy

Figure 1(a, b) shows the SEM micrograph displaying surface morphology of conducting PANI and PANI/FE composites synthesized by chemical oxidative method. It is seen from the micrograph (figure 1a) of PANI that the surface is smooth and homogeneous. Figure 1(b) shows

the micrograph of PANI/FE-50 (polyaniline with 50 wt.% of γ -Fe₂O₃) composite, which reveals the presence of γ -Fe₂O₃ homogeneously distributed throughout the polymeric sample. Typical dimensions of γ -Fe₂O₃ particles distributed in the matrix are of the order of 750 nm, as measured by SEM.

3.2 X-ray diffraction

Figure 2(a) shows X-ray diffraction pattern of PANI. Careful analysis of XRD pattern of PANI suggests that it exhibits a semicrystalline behaviour. The broad peak between $2\theta = 22^\circ$ and 28° is the characteristic peak of PANI (Mexiang Wan *et al* 1994).

X-ray diffraction pattern of PANI/FE-50 composite is shown in figure 2(b). It is observed by comparing the XRD pattern of composite with that of γ -Fe₂O₃. The prominent peaks corresponding to $2\theta = 32.55^\circ$, 35.67° , 49.58° , 54.13° and 62.44° are due to (220), (311), (400), (422) and (511) planes of γ -Fe₂O₃, respectively. By comparing the XRD patterns of the composite and γ -Fe₂O₃, it is confirmed that γ -Fe₂O₃ retains its structure even though

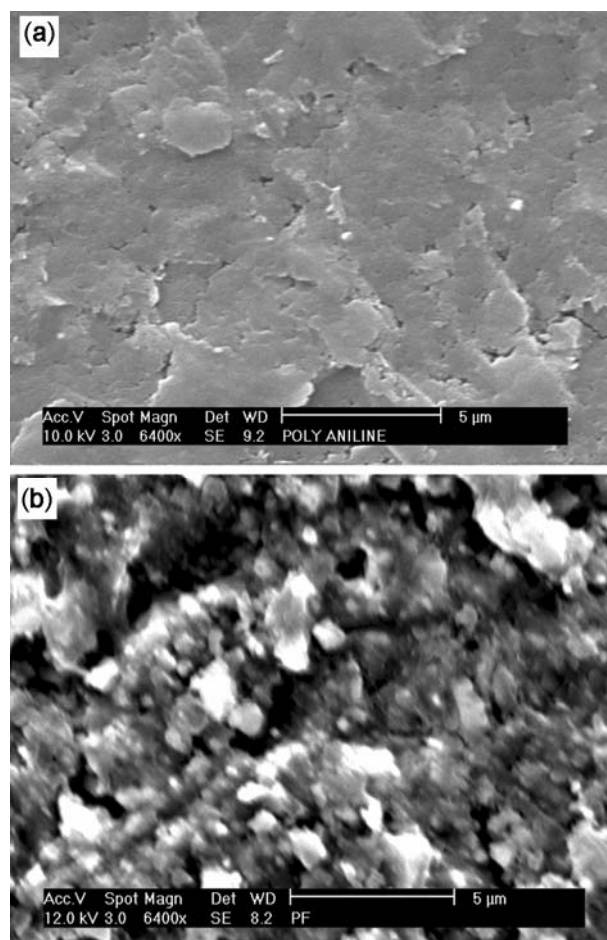


Figure 1. Scanning electron micrographs of (a) polyaniline and (b) polyaniline/ γ -Fe₂O₃ composite (with 50 wt.% of γ -Fe₂O₃ in PANI).

it is dispersed in PANI during the polymerization reaction. Hence it is reasonable to believe that FE in the composite is responsible for the ferromagnetic properties of the composites.

3.3 Infrared spectroscopy

Figure 3(a) shows the IR spectra of pure PANI, with prominent peaks at 1559 cm⁻¹ (C=N stretching in quinoid ring of PANI), 1485 cm⁻¹ (C=C stretching in benzenoid ring of PANI and C-C of *para*-substituted benzene), 1299 cm⁻¹ (C-N stretching \leftarrow C-C stretching), 1243 cm⁻¹ (C=N stretching \rightarrow C-C stretching) and 1131 cm⁻¹ (C-N stretching \rightarrow C-C stretching).

The IR spectra of PANI/FE composite is shown in figure 3(c). No significant differences in the position of characteristic peaks are observed in PANI/FE composites when compared with that of pure PANI and pure FE (figure 3(b)). The characteristic peak in FE at 3443 cm⁻¹ is shifted to 3439 cm⁻¹ in the composite and the peaks due to PANI (1559 cm⁻¹) and FE (1595 cm⁻¹) appear as a single peak at 1591 cm⁻¹ in the composite. The characteristic peaks of PANI at 1299 and 1132 cm⁻¹ appear at 1299 and 1135 cm⁻¹ in the composite. Some of the characteristic peaks of FE at 1351, 1129 and 555 cm⁻¹ disappear in the composite. The shift in the characteristic IR frequencies of PANI and FE in the composite clearly suggests the formation of composite due to substantial interaction between the polymer chain and FE. The chain

structure of composite suggests that it retains both conducting and ferromagnetic functions due to formation of structural chains between PANI and FE.

3.4 Conductivity

The d.c. conductivity of these samples at two different temperatures were measured using two-probe method and a.c. conductivity measurements were done using 4192-A HP impedance analyser.

Figure 4(a, b) shows the variation of d.c. and a.c. conductivity with different wt.% values of FE in PANI. In both figures, it can be observed that the values of conductivities increase up to certain concentration of FE in PANI and decreases thereafter. The initial increase up to 20 wt.% is attributed to the extended chain length of PANI where polarons possess sufficient energy to hop between favourable localized sites. As the wt.% of FE increases beyond 20%, the partial blocking of charge carrier hop occurs and as a result conductivity decreases. Similar behaviour was observed in polyaniline/TiO₂ composites (Shi-Jian *et al* 2000).

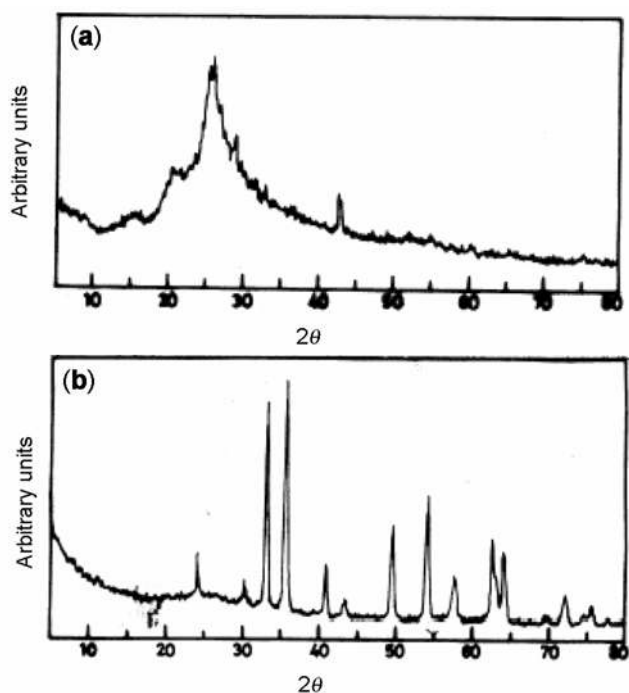


Figure 2. XRD spectra of (a) polyaniline and (b) polyaniline/ γ -Fe₂O₃ composite (with 50 wt.% of γ -Fe₂O₃ in PANI).

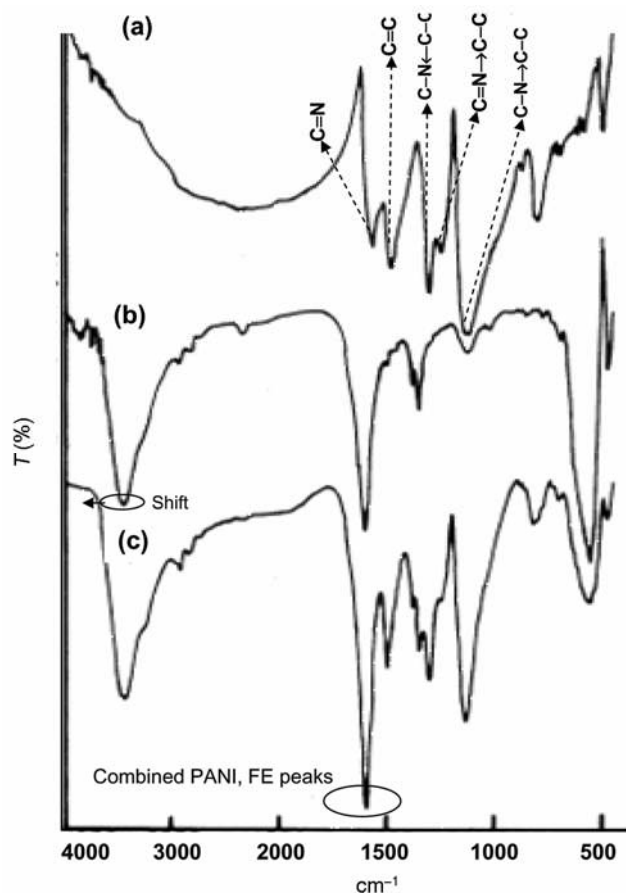


Figure 3. Infrared spectra of (a) polyaniline, (b) γ -Fe₂O₃ and (c) polyaniline/ γ -Fe₂O₃ composite (with 50 wt.% of γ -Fe₂O₃ in PANI).

The same observation could possibly be explained on the basis of percolation theory (Tanioka *et al* 1982), which predicts that at a particular concentration (critical concentration) of conducting polymer and oxide particles, a full conducting path is formed for the flow of current, as a result of which the conductivity rises.

3.5 A.C. Susceptibility

The variation of normalized susceptibility as a function of temperature for γ -Fe₂O₃ and PANI/FE composites with different wt.% values of γ -Fe₂O₃ in PANI is shown in figure 5. The susceptibility of these composites decreases with increasing temperature. It can be observed that a transition peak at 232°C is observed for γ -Fe₂O₃, at which point the material makes a transition from the ferromagnetic to the paramagnetic state. In case of PANI/FE

composites, no clear transition is observed, but to some extent the samples with 40 and 50 wt.% of γ -Fe₂O₃ in PANI seem to exhibit transition peaks in the temperature range of 125–175°C. In case of composites with 10, 20 and 30 wt.% of γ -Fe₂O₃ in PANI, the curve of normalized susceptibility plotted as function of temperature cannot be expressed by Curie–Weiss law given by

$$\chi = C/(T - \theta),$$

where C is the Curie constant and θ the Weiss constant.

The PANI/FE composite displays super-paramagnetic behaviour.

3.6 Magnetic hysteresis

From magnetic hysteresis measurements, it is observed that γ -Fe₂O₃ exhibits a saturation magnetization of

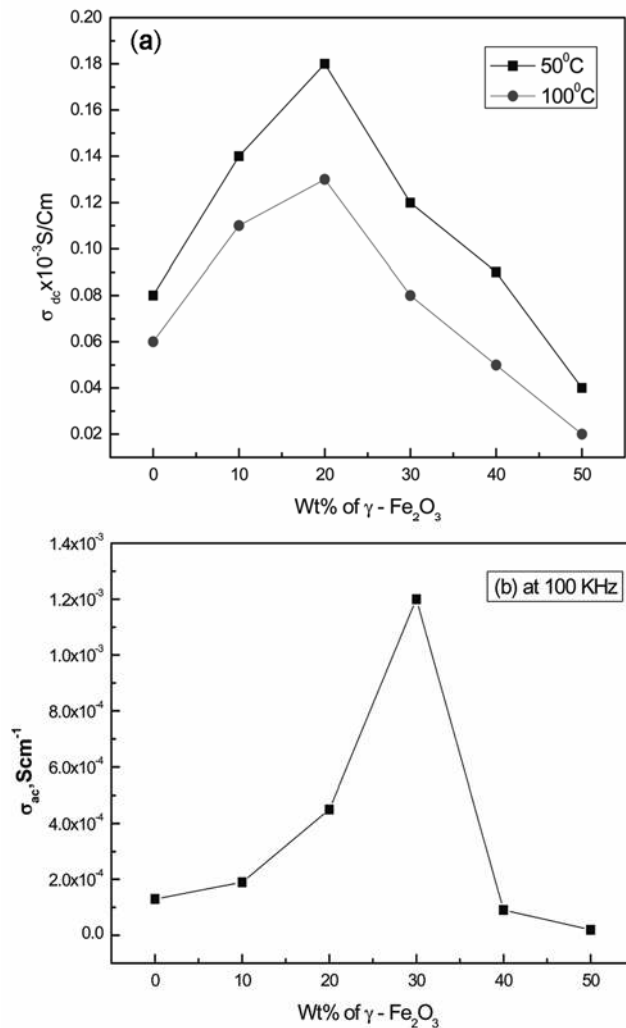


Figure 4. Variation of (a) d.c. conductivity as a function of wt.% of γ -Fe₂O₃ in PANI and (b) a.c. conductivity as a function of wt.% of γ -Fe₂O₃ in PANI at 100 kHz.

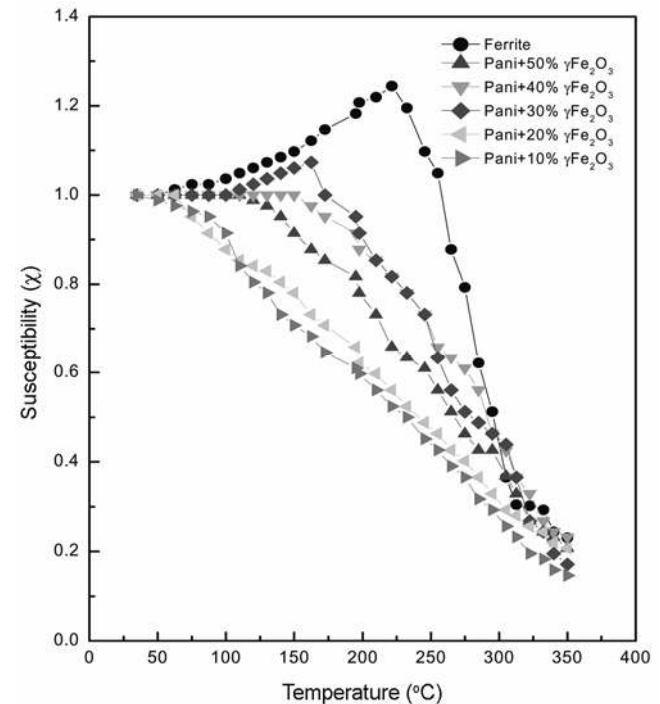


Figure 5. Variation of normalized susceptibility as a function of temperature for polyaniline/ γ -Fe₂O₃ composites.

Table 1. Values of saturation magnetization, remnant induction and coercive field for polyaniline/ γ -Fe₂O₃ composites.

Wt.% of γ -Fe ₂ O ₃ in polyaniline	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
10	12	5	45
20	18	9	47
30	34	21	82
40	48	32	97
50	127	83	273

1845 emu g⁻¹, remnant induction M_r value of 1475 emu g⁻¹ and coercive field value of $H_c = 1200$ –1700 Oe. In case of PANI/FE composites at the values of saturation magnetization, remnant induction and coercive field are given in table 1.

Some of the authors (Mexiang Wan *et al* 1998) have reported saturation magnetization values of $M_s = 8$ –20 emu g⁻¹ and coercive field $H_c = 0$ in PANI composites, which exhibit conducting and ferromagnetic functions. The composites used in the present investigation yield better results than previous reports using polyaniline composites.

4. Conclusions

The conducting polyaniline/ γ -Fe₂O₃ composites with both conducting and ferromagnetic properties have been synthesized successfully. SEM micrograph clearly reveals the homogeneous distribution of γ -Fe₂O₃ in polyaniline matrix. The XRD studies confirm the presence of γ -Fe₂O₃ phase in the composites. The shift in characteristic IR frequencies of polyaniline and γ -Fe₂O₃ in composite suggest the formation of composite with conducting and ferromagnetic functions.

A marked increase in the conductivity is observed for a critical concentration, which needs further investigation and in-depth understanding. The composites exhibit very good magnetic properties such as hysteresis characteristics and a.c. susceptibility. Because of both conducting and ferromagnetic functions, these composites may find application in microwave frequencies as absorbing and shielding materials.

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