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# Dielectric and magnetic properties of conducting ferromagnetic composite of polyaniline with $\gamma$-$Fe_2O_3$ nanoparticles

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ABSTRACT

The present paper reports the synthesis of conducting polyaniline polymer composite with nanoclusters of ferrite ($\gamma$-$Fe_2O_3$) particles in the presence of dodecylbenzene sulfonic acid in aqueous medium through electrochemical and chemical oxidative polymerization. Different formulations have been prepared to study the effect of ferrite constituent on the electrical and dielectric properties of polyaniline nano-composite. Vibrating sample magnetometer (VSM) studies and electrical conductivity measurements have revealed that conducting polymer composite has a saturation magnetization ($M_s$) value of 48.9 emu $g^{-1}$ and conductivity of the order of 0.13 S $cm^{-1}$. The particle size of $\gamma$-$Fe_2O_3$ was found in the range of 8–15 nm as analyzed by transmission electron microscopy (TEM). Fourier transform infrared spectroscopy (FTIR) results have shown the presence of characteristic band stretching of Fe—O band at 630 and 558 $cm^{-1}$, indicating the presence of $\gamma$-$Fe_2O_3$ in the polyaniline matrix which is in agreement with the electrochemical results. Dielectric measurements have shown decreasing trend of dielectric constant with the increase of $\gamma$-$Fe_2O_3$ particles in the polymer matrix while shielding effective (SE) of −11.2 dB was achieved for the polymer composite in 8.2–12.4 GHz (X-band) frequency range. The characterization of the composite was further carried out by X-ray diffraction, UV–vis and thermal gravimetric analysis (TGA).



## 1. Introduction

Electronically conducting polymers are the novel class of synthetic metals with wide spread application in number of technological devices like EMI shielding and electrostatic charge dissipation [1–5], sensors [6–8], organic light emitting diodes [9–11] and polymer solar cells [12,13]. The prospects of conducting organic magnetic materials have inspired much interest where lightweight, flexibility, moderate conductivity and magnetization are required. Deliberate modifications in chemical and super molecular structure of polymer matrix by incorporating nano-ferromagnetic particles can lead to the formation of conducting ferromagnetic materials which can be suitably designed for high tech applications. Among different conducting polymers, polyaniline has been chosen because of its unique structure, containing an alternate arrangement of benzene rings and nitrogen atoms. The polyaniline exists in four forms namely leucoemeraldine (fully reduced form), emeraldine base (50% oxidized and 50% reduced form), pernigraniline (fully oxidized form) and conductive emeraldine salt. In recent years much research attention has been paid to the conducting polymer composites with one or more magnetic materials so that polymer possesses both electrical as well as magnetic properties. For the absorption of electromagnetic radiations, ferrites are incorporated in the polymers as they possess high magnetization values which make them useful at higher frequencies [14–16]. Many attempts to produce the colloidal polyaniline composite containing the ferrite have been made using the different charge carriers for doping the polymer [17–23]. However, the resultant polymer composites lose its conductivity and have low magnetization value.

Nanostructures of polyaniline-$Fe_3O_4$ nanoparticle composites were also prepared in the presence of $\beta$-naphthalene sulfonic acid as a dopant that shows a magnetization value of 6 emu $g^{-1}$ [24]. US Patent 6,764,617 claims a formation of conductive ferromagnetic composition comprising sulfonated lignin or a sulfonated polyflavonid or derivatives thereof and ferromagnetic iron oxide particles [25].

The present work deals with electrochemical and chemical oxidative polymerization of the aniline with nanosized $\gamma$-$Fe_2O_3$ particles with dodecyl benzene sulfonic acid (DBSA) as dopant and

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reports the effect of γ-$Fe_2O_3$ on the electrical, magnetic, dielectric and shielding properties of the resultant conducting polyaniline-γ-$Fe_2O_3$ nano-composite. Electrochemical studies were carried out using cyclic voltammetric technique in order to see the incorporation of γ-$Fe_2O_3$ nanoparticles in the conducting polyaniline matrix. Beside this, characterization of the polymer composite has been carried out by FTIR spectroscopy, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA)

## 2. Experimental

### 2.1. Synthesis of the γ-$Fe_2O_3$ nanoparticles

The magnetic nanoparticles of γ-$Fe_2O_3$ were synthesized by coprecipitaion method. The aqueous solution of 1.0 M $FeCl_2 \cdot 4H_2O$ and 2.0 M $FeCl_3$ were mixed together and precipitated by adding ammonium hydroxide solution with continuous stirring for 2–3 h by maintaining the pH at 10–11 [26]. The precipitated ferrite particles are filtered out and washed thoroughly with distilled water. γ-$Fe_2O_3$ particles so obtained are dried at 120 ± 1 °C in vacuum oven. The formation of γ-$Fe_2O_3$ nanoparticles were confirmed by X-ray diffraction pattern.

### 2.2. Synthesis of polyaniline composite with γ-$Fe_2O_3$

Chemical oxidative polymerization of aniline was carried out in the presence of nanoferrite particles in aqueous medium. 0.3 M DBSA and γ-$Fe_2O_3$ were homogenized by using the ART-Miccra D-8 ($N^0$-10956) homogenizer at 10500 rpm for 2–3 h. To this 0.1 M of aniline (An) was added and supersonic stirring was continued for 1 h to form an emulsion. The oxidant ammonium peroxidisulfate (0.1 M) was added drop-by-drop keeping the temperature of the reactor at −2.0 °C with vigorous stirring for 5–6 h to the above emulsion. The green polymer precipitate so obtained was treated with isopropyl alcohol under vigorous stirring for 2–3 h. The resulting precipitate was then filtered and washed thoroughly and dried at 60–65 °C in a vacuum oven. Several composition of the polymer composite having different weight ratio of monomer to ferrite An:γ-$Fe_2O_3$::2:1(PC21), 1:1(PC11), 1:1.5(PC115), 1:2(PC12) are also synthesized in DBSA medium to check the effect of ferrite constituents in the polymer matrix. Beside this, for comparison of results, polyaniline doped with DBSA (PD13) without ferrite particles is also synthesized using emulsion polymerization.

### 2.3. Electrochemical polymerization

The electrochemical polymerization of 0.1 M aniline in 0.3 M DBSA was carried out at 0.8 V on platinum electrode vs. SCE reference electrode. The polymer film growth was also studied by cycling the potential between −0.20 and 0.95 V on Pt electrode at a scan rate of 20 mV $s^{-1}$. Prior to polymerization, the solution was deoxygenated by passing argon gas through the reaction solution for 30 min. Electrochemical growth study of aniline in the presence of γ-$Fe_2O_3$ particles were also studied on platinum electrode in DBSA medium.

### 2.4. Characterization

The conductivity of the powder pellet of the sample polyaniline-γ-$Fe_2O_3$ composite was measured by four-probe method using Keithley programmable current source and nanovoltmeter attached to digital temperature controller and APD Cryo cooler. The magnetic measurements of the ferrite as well as conducting PANI–γ-$Fe_2O_3$ composite were carried out using vibrating sample magnetometer (VSM), Model 7304, Lakeshore Cryotronics Inc., USA. Thermogravimetric analysis of the polymer and composite were carried on a Mettler Toledo TGA 851e. FTIR spectra were recorded on Nicolet 5700 and UV–vis absorption studies were carried on Shimadzu 1601 Spectrophotometer. Three-electrode cell geometry was used in all the electrochemical experiments, where Pt was used as working electrode as well as counter electrode and SCE was used as reference electrode. An Auto lab PGSTAT30 (Ecochemie, Utrecht, The Netherlands) potentiostat/ galvanostat interfaced with a personal computer was used in all the electrochemical measurements. The particle size and the morphology were examined using a Transmission electron microscopy (TEM, JEOL JEM 1011) and the samples were deposited on carbon coated nickel grids. Permittivity and dielectric loss measurements were carried out on an Agilent E8362B Vector Network Analyzer in a microwave range of 8.2–12.4 GHz (X-band), using 15.8 mm × 7.9 mm × 6 mm copper sample holder connected between the waveguide flanges. To avoid air gap the above sample holder is modified with a groove of 1.5 mm on each side having 3 mm depth.

## 3. Result and discussion

The emulsion polymerization of aniline to polyaniline in the presence of γ-$Fe_2O_3$ particles may bring certain changes in the properties of polyaniline because conduction mechanism in polyaniline involves protonation as well as ingress of counter anions in the polymer matrix to maintain charge neutrality. Protonation and electron transfer in polyaniline leads to formation of radical cations by an internal redox reaction, which causes the reorganization of electronic structure to give two semiquinone radical cations. In the doping process, ingress of anions occurs to maintain charge neutrality in the resultant doped polyaniline matrix. In situ emulsion polymerization of aniline in the presence of γ-$Fe_2O_3$ constituents resulted in the formation of ferromagnetic conducting polymer. In order to avoid phase segregation, the γ-$Fe_2O_3$ nanoparticles were functionalized with the surfactant DBSA that ensure its compatibility with the polymer.

The electrochemical polymerization of aniline with DBSA in aqueous medium was carried out using cyclic potential sweep method by switching the potential from −0.20 to 0.95 V vs. SCE at a scan rate of 20 mV $s^{-1}$. The rise in current value at 0.78 V in the first cycle corresponds to the oxidation of aniline leading to generation of anilinium radical cations (Fig. 1). In the subsequent cycles, new oxidation peaks appear which indicates that these radical cations undergo further coupling to form benzenoid structure and combination of benzenoid and quinoid structure. The peak current increases continuously with successive potential scans to build up electroactive polyaniline on the electrode surface.

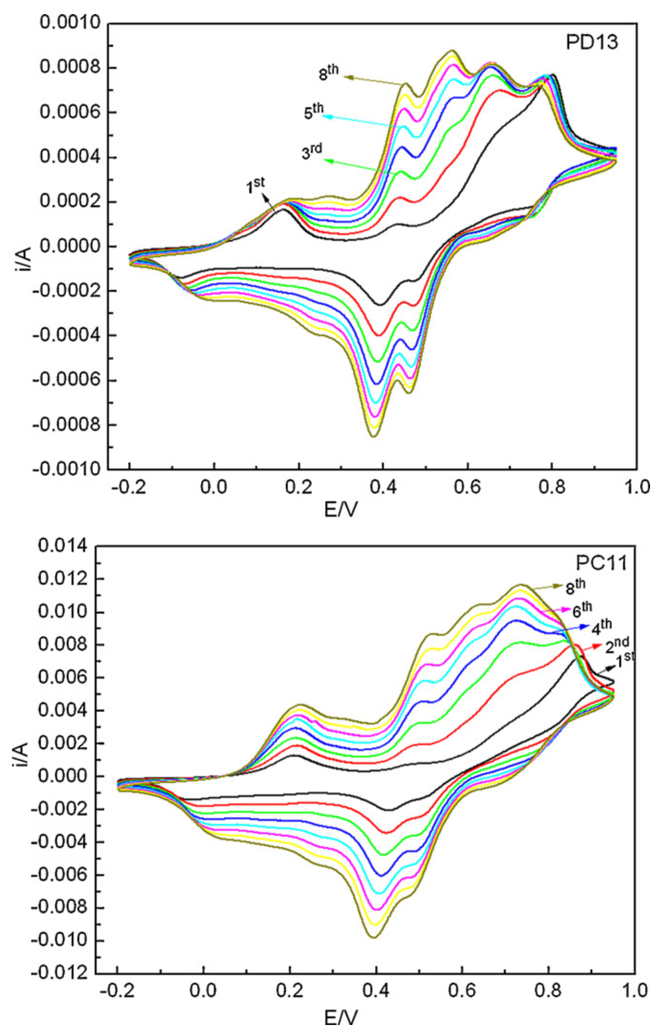


**Fig. 1.** Electrochemical growth behavior of aniline in DBSA medium (PD13) and aniline in DBSA medium containing ferrite particles (PC11) on cycling the potential between −0.2 and 0.95 V, taking eight successive scans, on platinum electrode vs. SCE at a scan rate of 20 mV $s^{-1}$.