

# Chemical Synthesis, Characterization, and Direct-Current Conductivity Studies of Polypyrrole/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> Composites

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**ABSTRACT:** The *in situ* polymerization of pyrrole was carried out in the presence of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> to synthesize polypyrrole/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> composites by a chemical oxidation method. The polypyrrole/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> composites were synthesized with various compositions, including 10, 20, 30, 40, and 50 wt %  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in pyrrole. The polypyrrole/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> composites were characterized with X-ray diffractometry and infrared spectroscopy. The surface

morphology of these composites was studied with scanning electron microscopy. The direct-current conductivity was studied from 40 to 200°C. The dimensions of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles in the matrix had a greater influence on the conductivity values. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2797–2801, 2007

**Key words:** composites; conducting polymers; polypyrroles

## INTRODUCTION

In recent years, the electrical and optical properties of conducting polymers synthesized by electrochemical polymerization have been studied in great detail. Considerable attention has been paid to the polymers of five-membered heterocycles such as polypyrrole (PPy), polythiophene, and polyacetylene because they can substitute for conductors and semiconductors in a wide variety of electric and electronic devices. The features of conducting polymers, such as reversibility, availability in film form, and good environmental stability, enhance their potential use in practical applications.

One of the most widely studied conducting polymers, PPy, can be obtained chemically or electrochemically. The electrochemical polymerization of pyrrole has been extensively studied because it is easily obtained in the form of freestanding films and has good environmental stability and conductivity. PPy has many technological applications as secondary batteries,<sup>1–3</sup> electrochromic display devices,<sup>4,5</sup> light-emitting diodes,<sup>6,7</sup> capacitors,<sup>8,9</sup> sensors,<sup>10–12</sup> and enzyme electrodes.<sup>13–15</sup>

Electrical transport in polymeric materials<sup>16,17</sup> has become an area of increasing research interest because these materials have great potential for solid-state devices. Similarly, conducting polymer composites have attracted considerable interest in recent years because of their numerous applications in a variety of electric

and electronic devices. Conducting polymer composites with some suitable compositions of one or more insulating materials have led to desirable properties.<sup>18</sup> These materials are especially important because of their bridging role between the world of conducting polymers and that of nanoparticles. For the application of conducting polymers, knowing how these conducting polymer composite will affect the behavior in an electric field is a longstanding problem and of great importance. The discovery of doping in conducting polymers has led to further dramatic increases in the conductivity of such conjugated polymers to values as high as 10<sup>5</sup> S/cm.

PPy is one of the most attractive polymers and has some special electrical properties. These properties originate from the fact that PPy is an intrinsically conducting polymer and can be synthesized to have conductivities up to 1000 S/cm which approaches the conductivity of metals. Most practical types of PPy have conductivities in the range of 1–100 S/cm. Mixed-metal oxides with iron oxide as their main component are known as ferrites. They are classified into four groups on the basis of the crystal structure:<sup>19</sup> (1) spinels, (2) hexagonal ferrites, (3) garnets, and (4) orthoferrites. Many ferrites exhibit a spinel structure. The ferrosinels have the general chemical formula MFe<sub>2</sub>O<sub>4</sub>, where M is a divalent metal ion and Fe is a trivalent iron ion. The structure of ferrites can be regarded as an interlocking network of positively charged metal ions (Fe<sup>3+</sup> and M<sup>2+</sup>) and negatively charged divalent oxygen ions (O<sup>2-</sup>).<sup>20</sup> They have the crystal structure of a mineral spinel (MgAl<sub>2</sub>O<sub>4</sub>). Many spinels exhibit remarkable electrical, magnetic, and other physical characteristics.<sup>21</sup> In

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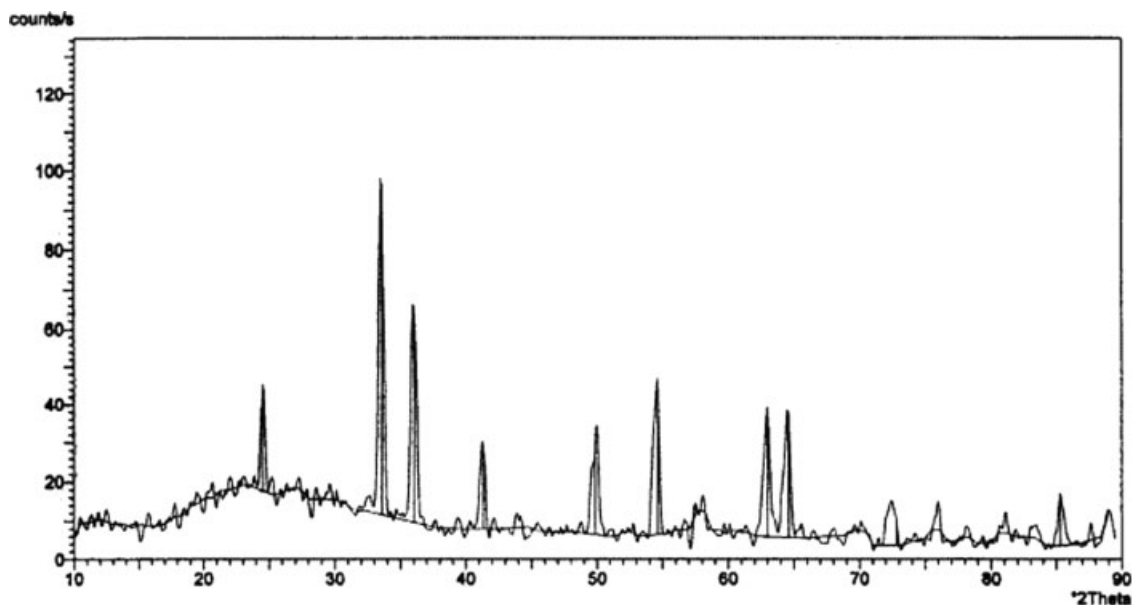


Figure 1 X-ray diffraction pattern of PPy with 50 wt %  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

this work, we report a study on the morphology and direct-current (dc) conductivity of PPy/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> composites. The samples were also characterized with X-ray diffraction and infrared spectroscopy.

### EXPERIMENTAL

Analytical-reagent-grade pyrrole was purified by distillation under reduced pressure. Distilled pyrrole (0.03M) was added to a solution of 0.06M ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], and the reaction mixture was stirred continuously at a constant temperature (5°C) to obtain PPy. About 0.8 g of ferrous ammonium sulfate

(analytical-reagent-grade) was dissolved in 50 mL of water containing 10 mL of dilute hydrochloric acid (1 : 1). About 1–2 mL of concentrated nitric acid was added to the solution, and then the solution was boiled gently until the solution turned yellow. Then, 200 mL of water was added and boiled again. To the boiling solution, a 1 : 1 NH<sub>3</sub> solution was added in a slow stream until it became a slight excess. The boiling was continued for another 2 or 3 min, and the precipitate was allowed to settle down. The supernatant liquid was colorless. The clear, supernatant liquid was decanted through Whatman no. 41 filter paper. The precipitate was thoroughly washed with a hot 1% ammonium

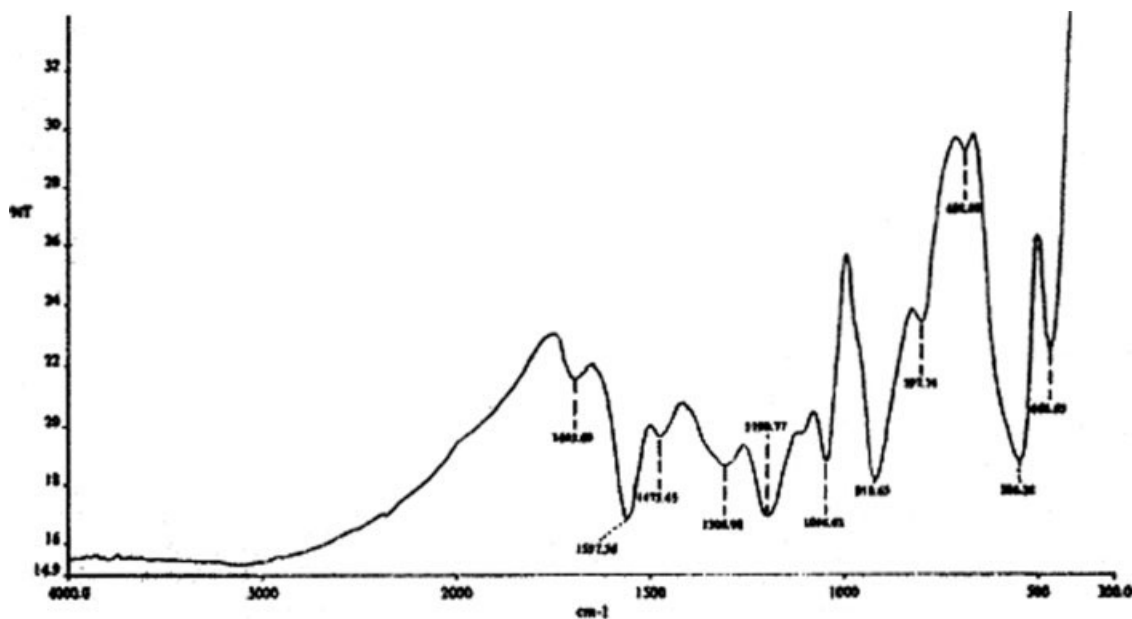
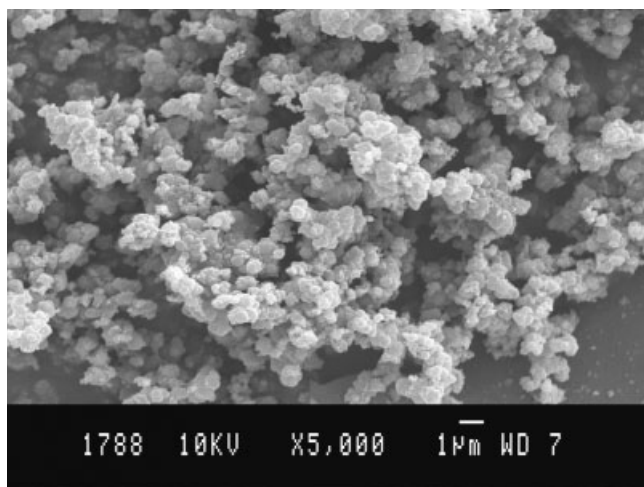


Figure 2 Infrared spectroscopy of PPy with 50 wt %  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> ( $T$  = transmittance).



**Figure 3** SEM micrograph of PPy with 50 wt %  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

nitrate solution until the solution filtrate was free from chloride ions and then dried at 120°C in a hot air oven. The yield of ferrous hydroxide was about 92%. The obtained precursor was mixed with poly(ethylene glycol) in a weight ratio of 1 : 5 and grounded well in a pestle and mortar. The resultant solids were poured into an alumina boat and heated in air to about 400°C with a burner. Poly(ethylene glycol) initially melted, then frothed, and finally ignited to form  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. After it cooled to room temperature, no impurities of carbon were observed in the final residue of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> powder so obtained was tested for ferromagnetic behavior with a bar magnet. This reaction may be called a self-propagating combustion reaction and strongly resembles the combustion reaction used for the preparation of SnO<sub>2</sub>. The obtained  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> powder was ball-milled for an hour and sintered at 700°C for 5–6 h. The resultant powder after sintering was used for the preparation of PPy/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> composites.

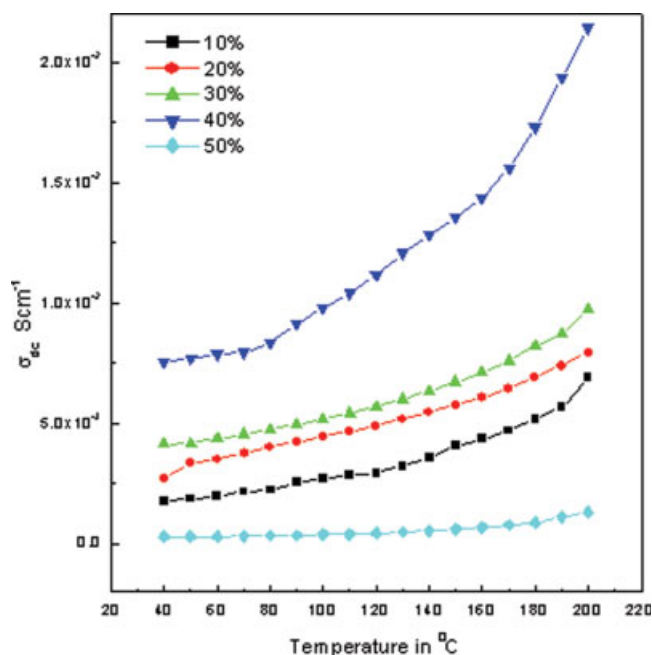
The 0.03M pyrrole monomer was dissolved in 100 mL of distilled water. The finely graded, presintered  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> powder synthesized with the aforementioned technique was added in weight percentages of 10, 20, 30, 40, and 50 to the polymerization reaction mixture with vigorous stirring to keep the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> powder suspended in the solution. To this reaction mixture, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, as an oxidant, was added slowly dropwise with continuous vigorous stirring for 4–6 h at 0–5°C. The polymerization of pyrrole took place over finely graded  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles. The resulting precipitate was filtered under suction and washed with distilled water until the filtrate became colorless. Meanwhile, the precipitate was tested to ensure that there were no free SO<sub>4</sub><sup>2-</sup> ions in the filtrate with a dripping BaCl<sub>2</sub> solution. Methyl alcohol was used for washing again. After the washing, the precipitate was dried under a dynamic vacuum at 60–80°C for 24 h to get the resulting composites. The resulting product

was filtered and washed thoroughly with methanol (CH<sub>3</sub>OH) and was dried *in vacuo* at room temperature. These composites were pressed in the form of pellets 1 cm in diameter. In this way, five different PPy/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> composites with different weight percentages of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (10, 20, 30, 40 and 50) in PPy were synthesized.

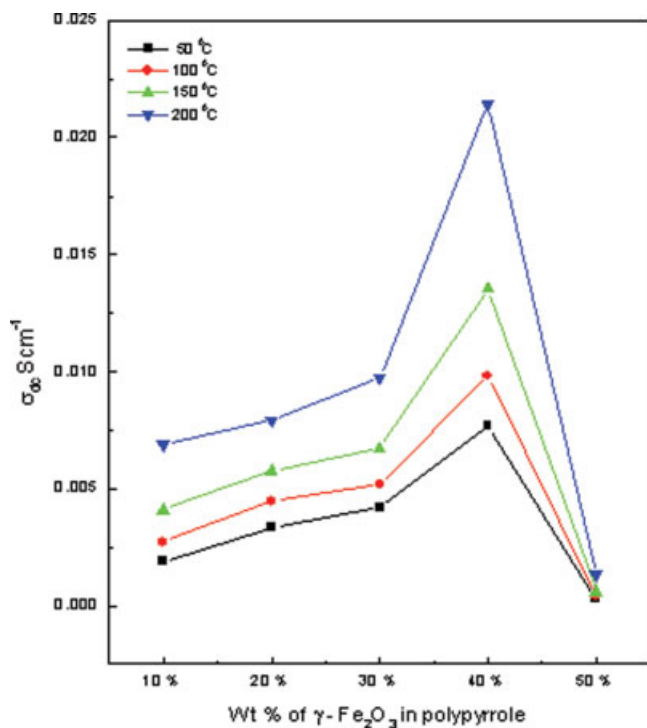
The X-ray diffraction patterns of these samples were recorded on a Philips X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the  $2\theta$  range of 20–80°. The infrared spectra of these samples were recorded on a PerkinElmer model 783 infrared spectrometer in a KBr medium at room temperature. The scanning electron microscopy (SEM) images of the PPy/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> composite (50 wt %) were investigated with a Philips XL 30 ESEM scanning electron microscope. The dc conductivity of these composites was measured by the two-probe technique with a laboratory-made setup in the temperature range of 40–200°C.

## RESULTS AND DISCUSSION

The X-ray diffraction pattern of the PPy/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> composites (50 wt %  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in PPy) is shown in Figure 1. The spectra of the composites show the distribution of the crystalline phase of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in PPy and prominent peaks at  $2\theta$  values of 33.57, 36.03, 54.62, 62.99, and 64.56° with relative intensities of 100, 66.18, 45.63, 38.87, and 37.62% and with  $d$ -spacings of 2.66, 2.49, 1.67, 1.47, and 1.44 Å, respectively. These prominent peaks are due to the (220), (311),



**Figure 4** Variation of the dc conductivity ( $\sigma_{dc}$ ) as a function of temperature for the PPy/ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> composites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 5** Variation of the dc conductivity ( $\sigma_{dc}$ ) as a function of the weight percentage of  $\gamma\text{-Fe}_2\text{O}_3$  in PPy at different temperatures. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

(400), and (511) planes of  $\gamma\text{-Fe}_2\text{O}_3$ , respectively. The spectra of this composite also reveal that  $\gamma\text{-Fe}_2\text{O}_3$  retained its structure even though it was dispersed in the polymerization reaction of pyrrole.

The infrared spectra of the PPy/ $\gamma\text{-Fe}_2\text{O}_3$  composite with 50 wt %  $\gamma\text{-Fe}_2\text{O}_3$  is shown in Figure 2. The important peaks that can be observed in this composite in infrared spectra are at 1693, 1554, 1475, 1306, 1199, 1040, 918, 805, 682, 544, 464, and 384  $\text{cm}^{-1}$ . By careful observation of the infrared spectra, we have found that some of the characteristic stretching frequencies are considerably shifted toward the higher frequency side. The typical peaks are located at 1693, 1554, 1040, and 554  $\text{cm}^{-1}$ . These data suggest that there is a Vanderwall type of interaction between the polymeric chain and  $\gamma\text{-Fe}_2\text{O}_3$ .

Figure 3 shows an SEM photograph of PPy/ $\gamma\text{-Fe}_2\text{O}_3$  composites of powder formed with 50 wt %  $\gamma\text{-Fe}_2\text{O}_3$ . It shows clusters of spherical particles and a chain pattern, with the chains connecting the nanosized  $\gamma\text{-Fe}_2\text{O}_3$  particles. As the concentration of  $\gamma\text{-Fe}_2\text{O}_3$  is increased further above the critical concentration, the chain pattern becomes less and less visible, and clusters of spherical patterns are observed. This may be due to the lower concentration of nanosized particles that are interacting with the polymer chain. A small variation in the particle dimensions of  $\gamma\text{-Fe}_2\text{O}_3$  so dispersed in PPy has also been observed. These particle dimensions varied from

720 to 910 nm in length and from 170 to 190 nm in width as SEM images were taken.

Figure 4 shows the variation of the dc conductivity as a function of temperature for all the composites, and Figure 5 shows the variation of the dc conductivity as a function of the weight percentage of  $\gamma\text{-Fe}_2\text{O}_3$  in PPy at different temperatures. In all the composites, the conductivity increases with respect to the temperature, forming multiple phases of conductivity. The values of the conductivity increase up to 40 wt %  $\gamma\text{-Fe}_2\text{O}_3$  in PPy and decrease thereafter. This may be due to the extended chain length of PPy, which facilitates the hopping of charge carriers when the concentration of  $\gamma\text{-Fe}_2\text{O}_3$  is as high as 40%. This point is a percolation threshold, and the composites obey percolation theory. Furthermore, a decrease in the conductivity can be observed after 40 wt % and can be attributed to the distribution of  $\gamma\text{-Fe}_2\text{O}_3$  particles of larger grain sizes, which are partially blocking the hopping of charge carriers. Charge trapping in PPy and blends is a general universal feature of these materials.<sup>22,23</sup>

## CONCLUSIONS

Efforts have been made to synthesize PPy/ $\gamma\text{-Fe}_2\text{O}_3$  composites to tailor their properties. Detailed characterizations of the composites have been carried out with X-ray diffraction, SEM, and infrared techniques. The results of dc conductivity show a strong dependence on the weight percentage of  $\gamma\text{-Fe}_2\text{O}_3$  in PPy.

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