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Magnetic Properties of Polypyrrole Doped with Iron

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In this study the incorporation of small contents of iron species in polypyrrole was investigated by means of magnetization measurements. The incorporation was performed by the addition of $FeCl_3$ to the solution during the chemical polymerization with a mass ratio of $[monomer]/[Fe^{3+}] = 10$. Comparison was made between polypyrrole pellets with and without the addition of iron and showed an increase in the saturation magnetization and in the ferromagnetic properties of polypyrrole when iron is present in the material. This increase in the magnetic properties probably occurs due to an effective increase in local polarization of the polymer's polarons.

Keywords Conducting polymers; ferromagnetism; polypyrrole

Introduction

Conducting polymers (CPs) offer potential applications in the domain of composite materials, separation membranes, actuators, supercapacitors, molecular motors, and electronic and electro-optic devices [1,2]. Recently, conducting polymer composites (CPP), with both electrical and ferromagnetic properties, have become one of the most active research areas. A particular interest has been emerging in the preparation of composites consisting of magnetic nanoparticles (NPs) embedded in a conducting polymer matrix, such as polypyrrole and polyaniline, exhibiting all-in-one magnetic, electrical and optical properties [3–6].

Additional control and design of magnetic nanoparticles was achieved by the development of nanoparticles covered with polymer layers. Encapsulation of metal nanoparticles into CPs results in hybrid organic–inorganic nanocomposites with enhanced thermal stability, electrochemical, magnetic and optical properties. Also, the properties of such polymer-coated metal composite materials are strongly dependent on particle size and shape [7–9].

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Various CP-metal/metal oxide composites have been synthesized with different methodologies. Reddy *et al*. have studied core–shell nanocomposites prepared with Fe_3O_4 nanoparticles and poly (3,4-ethylenedioxythiophene) (PEDOT) [10]. Parvatikar *et al*. have synthesized WO_3–PANI composites and found improved electrical conductivity, higher than that observed for pure PANI [11]. These composite systems can also be used as sensors for gases [12] or glucose [13]. Dey *et al*. reported that a TiO_2–PANI nanocomposite with high dielectric constant can be used in an integrated electronic circuit, such as capacitors and gate oxides [14]. Finally, Pana *et al*. proposed that the hybrid core-shell Fe/Au nanoparticles with PPy composites are superparamagnetic, as the magnetization of the investigated nanocomposites measured against an increasing and decreasing magnetic field showed no hysteresis loop [15].

Considering the above, the aim of this article is to present the synthesis and characterization of the magnetic behavior of polypyrrole modified with small contents of iron species, as, nowadays, it is very attractive to discover a magnetic semiconductor at room temperature in which the properties can be easily controlled by the preparation variables.

Experimental

All reagents were analytical grade and the monomer was distilled before synthesis. Polypyrrole was chemically synthesized in a solution of 0.1 M HCl (Quimis) at 298 K under constant stirring using 0.1 M Pyrrole (Aldrich) and 0.1 M $(NH)_2S_2O_8$ (J. T. Baker) as oxidant. The procedure used was to dissolve the monomer in HCl solution for 10 minutes and then add the oxidant drop by drop. After 2 hrs of polymerization, the powder formed was filtered under a vacuum and dried for 48 hrs at 323 K. This sample was named Sample A. To prepare the composites, $FeCl_3$ (Aldrich) was added to the $(NH)_2S_2O_8$ solution, which was then added to the monomer solution using the process described above. The mass ratio [monomer]/[Fe^{3+}] was 10. This sample was named Sample B. Following this, pellets were obtained by uniaxial pressing of the powders at 2,817 bar for 3 minutes.

The sample composition was measured using an Atomic Absorption Spectrometer in a graphite furnace, model Spectra AA240FS. The magnetization measurements were performed using a Quantum Design SQUID Magnetometer, model MPMS – 5S. The latter data were collected in an applied magnetic field range from −1 kOe to 50 kOe, as the curves are symmetrical, up to 300 K.

Results and Discussion

The iron content was calculated from atomic absorption data as 3 ppb and 82 ppb, for samples A and B, respectively. The content of iron in sample A could be explained by air-particle contamination.

Figures 1 and 2 show the magnetization versus field for samples A and B at 300 K and 5 K, respectively. The results were similar to those observed in poly(3-methylthiophene) and poly(3-hexylthiophene) pellets [16,17]. The diamagnetic contribution was subtracted from curves presented in these figures to facilitate the visualization of magnetic behavior. The addition of iron species increased the magnetization saturation twofold, as can be seen in Figure 1. The same feature was found for those data measured at 5 K. One possible explanation for this

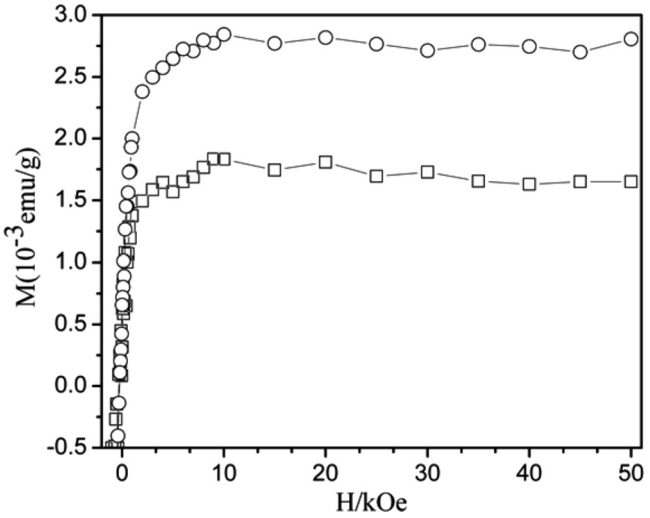

Figure 1. Magnetization versus applied magnetic field at 300 K for Sample A (open squares) and Sample B (open circles). The diamagnetic contribution was subtracted.

phenomenon is that the presence of iron species bound to the polymer backbone locally polarizes polarons producing an increase in the effective saturation magnetization as proposed by Das Sarma [18]. This interpretation is supported by the calculation of the saturation magnetization for sample B at 300 K. Sample B was prepared using 4.7×10^{-3} g and with 82 ppb of iron, which results in 1.5×10^{-9} g of incorporated iron. Considering that the iron species are metallic iron (217.6 emu/g) [19] this content of incorporated iron has a magnetization saturation of 3.4×10^{-7} emu. Comparing samples A and B, the increase of saturation

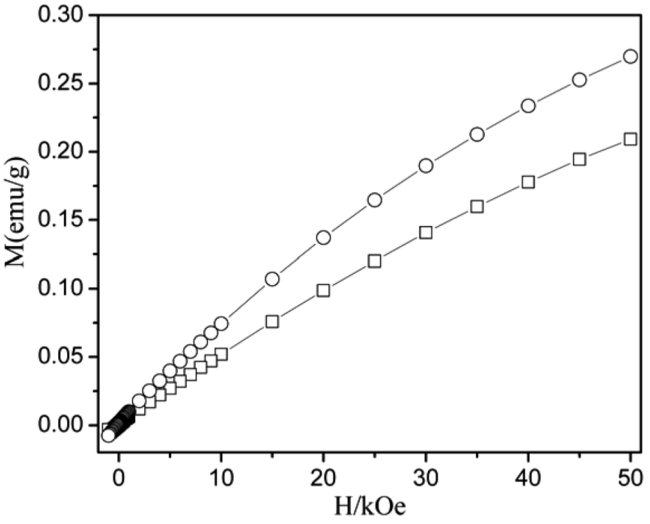

Figure 2. Magnetization versus applied magnetic field at 5 K for Sample A (open squares) and Sample B (open circles). The diamagnetic contribution was subtracted.

magnetization is approximately 1.5×10^{-3} emu/g and about 7×10^{-6} g of iron is required for this, which is larger than that found in the sample by an order of magnitude of a three. Therefore, it is not possible that the increase in the saturation magnetization comes solely from the incorporation of iron species into the sample. This can then be seen as evidence that there is an interaction among the iron species and the conducting polymer charge carriers.

Figure 3 shows the spontaneous magnetization as a function of the temperature for samples A and B. In this measurement, samples were cooled from 300 K to 5 K without an applied magnetic field. At 5 K, a magnetic field of 50 kOe was applied for 3 minutes and then removed. After this, data were collected for raising the temperature at 2 K/min. The main characteristic of this kind of measurement is to show the intrinsic ferromagnetism of the samples. As one can see, for both samples, increasing the temperature causes a decrease in magnetization, which is expected. The value of magnetization for sample B is higher than for sample A, showing that sample B has a ferromagnetism higher than sample A, as the addition of iron increases the effective magnetization of polarons, as described above for the magnetization versus field curves [20,21].

Another way to show the influence of iron in the material properties is to analyze the magnetization versus field curves, considering the diamagnetic contribution, at 300 K, which is presented in Figure 4. In this way, we can calculate the magnetic susceptibility from the fit of the curve slope, at the high field linear part, using the equation below (1) and assuming it is independent of temperature:

$$M = \chi_D H \tag{1}$$

where M is magnetization, H is the applied field and χ_D the magnetic susceptibility [22].

The results of the fitting are $\chi_D = -4.7 \times 10^{-7}\,\text{emu}\,\text{g}^{-1}\,\text{Oe}^{-1}$ and $\chi_D = -3.0 \times 10^{-7}\,\text{emu}\,\text{g}^{-1}\,\text{Oe}^{-1}$ for samples A and B, respectively. This means that the addition

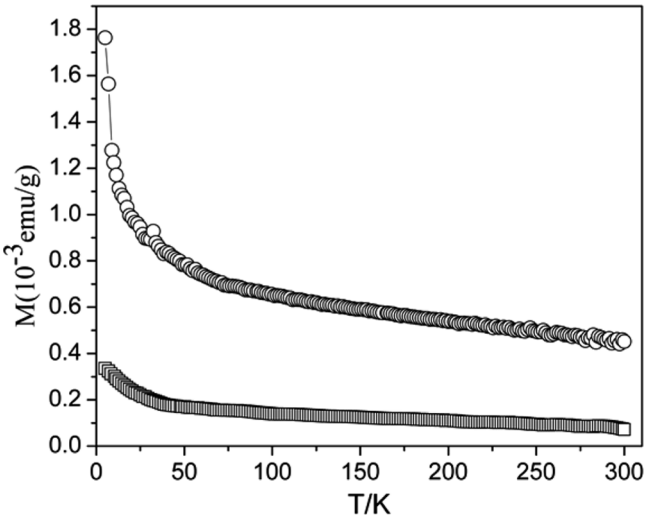

Figure 3. Thermoremanence obtained for Sample A (open squares) and Sample B (open circles).

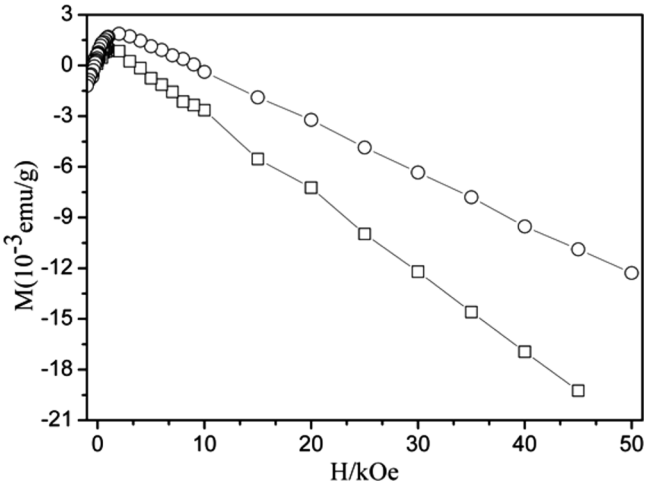

Figure 4. Magnetization versus applied magnetic field at 300 K with diamagnetic contribution for Sample A (open squares) and Sample B (open circles).

of iron in the polymer backbone causes a decrease in the diamagnetic contribution of the system. Considering that the magnetic susceptibility of sample A is smaller than that of sample B, this provides evidence that the ferromagnetic portion has increased.

In summary, the results presented here illustrate that there is an interaction among iron species and charge carriers in the polymer chains.

Conclusions

The addition of small contents of iron in the polymer backbone was successfully carried out by directly adding $FeCl_3$ to the polymerization solution without any further treatment. This was confirmed by atomic absorption, as the amount of iron species in the polymer synthesized without addition of $FeCl_3$ in the polymerization solution was 3 ppb and the amount of these species in the material polymerized in the presence of $FeCl_3$ was 82 ppb.

Although the content of iron in the polymer backbone was small, the magnetic properties were significantly modified, as observed in the curves of magnetization versus applied field and thermoremanence. One possible explanation is related to the interaction of the polymer's polarons with the iron species; as the former has an intrinsic local orientation, the presence of iron species could change this orientation. This proposition was illustrated by the results of magnetic susceptibility, as the addition of iron species increased the magnetic susceptibility of the polypyrrole sample.

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