Magnetic and Conducting Properties of Composites of Conducting Polymers and Ferrite Nanoparticles

Ignacio Muñoz Resta[1], Gabriela Horwitz[1], Matías Lanús Mendez Elizalde[1], Guillermo A. Jorge[2], Fernando V. Molina[1], and P. Soledad Antonel[1]

[1]Instituto de Química Física de Materiales, Ambiente y Energía (INQUIMAE), Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina.

[2]Instituto de Ciencias, Universidad Nacional de General Sarmiento, Los Polvorines, Provincia de Buenos Aires, Argentina.

Composites of ferromagnetic $CoFe_2O_4$ nanoparticles and two conducting polymers (polyethylenedioxythiophene -PEDOT- and polypyrrole -Ppy-) were prepared and characterized. Both synthesis were performed by monomer polymerization in presence of a dispersion of the magnetic nanoparticles, at different monomer:$CoFe_2O_4$ molar ratios. For PPy-composites, both the coercive field and the applied field required to reach the maximum magnetization decrease as the polymer content increases. For PEDOT-composites, the remanence ratio increases as the polymer content increases, indicating the presence of interactions related to the amount of polymer present. Electrical conductivity measurements indicate that, for both types of composites, a high polymer content gives rise to high electrical conductivity. These results indicate that the composite properties can be modulated by varying the polymer identity and the monomer:$CoFe_2O_4$ molar ratio.

***Index Terms*—conducting materials, ferrites, magnetic analysis, magnetic nanoparticles**

I. Introduction

In recent years, there has been a growing interest in composites formed by magnetic nanoparticles (MNP) embedded in a polymer matrix [1]-[3]. Magnetic nanomaterials (MNM) have a high interest not only by their very important applications in data storage, but also due to the intrinsic interest on the magnetic properties in the nanoscale [4],[5]. Conducting polymers (CP) are well known due to their interesting chemical, mechanical and optical properties leading to a high number of proposed applications [6]-[8]. A number of MNP-CP composites have been proposed, based on polypyrrole (PPy) [9],[10], poly(ethylenedioxithiophene) (PEDOT) [11] and poly(aniline) (PANI) [12],[13]. The use of CP gives rise to materials with properties that would be difficult to obtain with the individual components, since they have both high magnetic susceptibilities and high conductivity, and can be use in many applications [14],[15]. Among MNM, $CoFe_2O_4$ is highly interesting since it is a hard material from the magnetic point of view (is ferromagnetic at room temperature), has a high coercive field and moderate saturation magnetization and, in addition, displays excellent chemical stability [16],[17]. $CoFe_2O_4$-PPy and $CoFe_2O_4$-PEDOT composites have not received much attention in the literature; for example, Murillo et al [18] prepared $CoFe_2O_4$-PPy nanocomposites by a microemulsion method, obtaining materials that exhibit superparamagnetism or ferromagnetism depending on the grain size. However, little attention was given to the analysis of the magnetic behavior.

In this work, $CoFe_2O_4$-PPy and $CoFe_2O_4$-PEDOT composites have been prepared by a wet chemical method, with in situ monomer polymerization. The composites were characterized by SEM and TEM observation, IR Spectroscopy, DC magnetization and conductivity measurements.

II. Materials and Methods

AR grade chemicals and high purity water from a Milli-Q system were employed throughout.

A. Synthesis of $CoFe_2O_4$ nanoparticles

The synthesis of $CoFe_2O_4$ nanoparticles (NP) was performed following Antonel et al [3]. Briefly, 22.25 mL of a solution containing 0.450 M $FeCl_3.6H_2O$ and 0.225 M $CoCl_2.6H_2O$ (2:1 Fe(III)-Co(II) molar ratio), in 0.4 M HCl, was added dropwise to 200 mL of 1.5 M NaOH, keeping the pH adjusted at 12, under constant high speed stirring; the synthesis temperature was set at 80º C. Dark brown $CoFe_2O_4$ NP precipitated immediately after the first drops of the cationic solution. The reaction media was maintained at 80º C, at high speed stirring, for 2 h. The $CoFe_2O_4$ NP were separated by centrifugation at 15000 G and washed with Milli-Q water, repeating the cycles of washing-centrifugation until neutral pH of the supernatant was reached. Finally, the $CoFe_2O_4$ NP were dried using a vacuum oven at 40º C during 24 h.

B. Synthesis of $CoFe_2O_4$-PPy composites

The synthesis of $CoFe_2O_4$-PPy composites was performed following Guo et al [9], with some modifications, for different values of the pyrrole (Py):$CoFe_2O_4$ molar ratio r_{Py}: 0.5; 1; 2; 5; 10. First, 100 mg of $CoFe_2O_4$ were added to 50 mL of MilliQ water. This mixture was subjected to ultrasound treatment and vigorous mechanical stirring, for 30 minutes, to disperse the NP. Then, *p*-toluensulfonic acid (*p*-TSA) and Py monomer (according to the desired r_{Py}) were added, in a molar ratio 1:1, keeping the reaction mixture for 1 h in the same conditions. Finally, ammonium persulphate (APS), in a ratio 1:1 with respect to Py, was added. After that, the mixture was maintained for 1.5 h always under ultrasound treatment and mechanical stirring. The black precipitate obtained was separated by centrifugation at 15000 G, during 10 min at 17º C, washed with ethanol and MilliQ water to remove the excess of reactants and oligomers (by-products of the polymerization reaction), and dried at room temperature for 24 h.

C. Synthesis of $CoFe_2O_4$-PEDOT composites

The synthesis of $CoFe_2O_4$-PEDOT composites was performed following Ohlan et al [11], with some modifications. First, $CoFe_2O_4$ NP were added to a 0.1 M

dodecylbenzenesulfonic acid (DBSA) solution (used both as protecting agent and acid media), in a $CoFe_2O_4$:DBSA molar ratio of 0.33. Under ultrasound treatment and strong mechanical stirring for 30 minutes, a brown emulsion was obtained. Then, ethylenedioxithiophene (EDOT) monomer (in molar ratios with respect to $CoFe_2O_4$, r_{EDOT}, of 2; 3.5; 5; 10) was added keeping the reaction mixture for 1 h in the same conditions. Finally, APS, in a molar ratio of 1:1 with respect to EDOT, was added, and the reaction mixture was kept 3 h always under ultrasound treatment and mechanical stirring. The obtained product was demulsified by treating it with an equal volume of isopropyl alcohol. The blue precipitate obtained was separated by centrifugation at 15000 G, during 10 minutes, at 17º C, washed with ethanol and MilliQ water to remove the excess of reactants and oligomers. Finally, the pellets were dried at room temperature for 24 h. To study the influence of the reactants concentration on the composite properties, a synthesis with r_{EDOT} = 10, but with all the concentrations 3 times higher was also performed.

D. Characterization of $CoFe_2O_4$ nanoparticles and $CoFe_2O_4$-polymer composites

1) X-ray diffraction (XRD)

X-Ray powder diffraction analysis of the NP was performed with a Philips X-Pert diffractometer using Cu Kα radiation.

2) Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS)

The particle size and morphology were studied using a Transmission Electron Microscope Philips EM 301. SEM and SEM-EDS analysis were performed using a Zeiss Supra 40 Gemini microscope.

3) Fourier Transform Infrared Spectroscopy (FTIR)

The infrared (IR) measurements of composites, NP and polymers were performed using a FTIR Nicolet 8700 spectrometer, in the range 400-4000 cm^{-1}. For each sample, 32 scans were accumulated.

4) Magnetic properties

Magnetization curves at room temperature were recorded with a Lakeshore 7400 Vibrating Sample Magnetometer.

5) Conductivity measurements

The conductivity of the different samples was measured on pressed circular pellets (1 cm diameter) using a Teq-03 potentiostat (S. Sobral, Buenos Aires, Argentina) under computer control. A known current was applied and the potential difference was measured and averaged during 120 s; the resistance was determined for different applied currents and potentials and the conductivity determined following Ohm's laws. The pellet thickness was measured with a caliper.

III. Results and Discussion

XRD patterns of the $CoFe_2O_4$ NP (not shown) are fully coincident with the expected inverse spinel structure.

Fig. 1 shows TEM (left) and SEM (right) images of $CoFe_2O_4$ nanoparticles.

FIG. 1 HERE

As it can be seen, the NP have a nearly spherical shape and from TEM images, the particle diameters were measured, with the aid of the ImageJ software [19]; the resulting histogram is shown in the inset of Fig. 1, revealing a good monodispersity. The average particle diameter, d_p, is (17.3 ± 1.0) nm. SEM-EDS analysis reveals a Fe:Co molar ratio of 2:1 confirming the compositon of the NP.

In Fig. 2, TEM (a) and SEM (b,c) images of 1:2 $CoFe_2O_4$-PPy composite are presented. For other r_{Py} values the images are very similar, so they are not shown here.

FIG. 2 HERE

In Fig. 2(a) the dark spots correspond to $CoFe_2O_4$ NP, while the lighter areas correspond to the polymer. Comparing with TEM images of pure $CoFe_2O_4$ NP (fig. 1), it is evident that the presence of PPy favors the dispersion of the NP. In the SEM images of Fig. 2, the dark areas correspond to the polymeric matrix, whereas $CoFe_2O_4$ nanoparticles are observed as bright spots. From TEM images of all the synthesized composites, the particle sizes were determined, ranging between (6.1 ± 0.5) nm and (8.0 ± 0.7) nm, which are somewhat smaller than the original size, but nearly independent of r_{Py}. This decrease occurs during the composite preparation, due to the presence of *p*-TSA, which favors the acidic dissolution of metal oxides. In a synthesis with poly(vinilypirrolidone) (PVP, commonly used as protecting agent for NP), a marked decrease in the particle diameter was also observed (SEM/TEM not shown), so the use of this protecting agent, at least in the synthetic conditions used here, does not prevent NP dissolution.

Fig. 3 shows SEM images of $CoFe_2O_4$-PEDOT composites of different PEDOT:$CoFe_2O_4$ molar ratios.

FIG. 3 HERE

From Fig. 3(a), it is clear that high CP content favors the dispersion of the NP, as they are observed as bright spots, well dispersed in the polymeric matrix. In (b) and (c) there is a marked change in the composite morphology, since more NP are observed and they appear to be larger than those observed in (a). In this case, it seems that the NP are covered by polymer; as a result, they look larger than pure $CoFe_2O_4$ NP. At this point, it is worth to mention that these NP act as catalyst for EDOT polymerization, since the polymerization yield increases significantly when they are present in the polymerization medium. This fact is in accordance with SEM results: for low r_{EDOT}, the polymer is produced preferably around $CoFe_2O_4$ NP; for higher r_{EDOT}, first the monomer polymerizes around the NP, then the CP grows further giving rise to a homogeneous polymeric matrix with the NP dispersed uniformly. This fact was also observed in a previous work [20], for $CoFe_2O_4$-PANI composites.

Unfortunately, there are no TEM images of $CoFe_2O_4$-PEDOT composites available at present, so the particle diameters cannot be reported. However, from SEM images (not shown) of $CoFe_2O_4$ NP subjected to the composite preparation procedure in absence of EDOT, it was noticed that the nanoparticle diameter does not decrease significantly after the polymerization process. This fact suggests that DBSA is effective as a protecting agent.

From IR Spectroscopy (not shown) for both composites, the typical bands for polymers and NP are present. That means

that the composites have been successfully synthesized. Algún comentario sobre interacciones?

Fig. 4 shows the magnetization, *M*, hysteresis loops as a function of applied field, *H*, for pure $CoFe_2O_4$ NP and $CoFe_2O_4$-PPy composites.

FIG. 4 HERE

In (a), the magnetization is referred to the composite mass, thus the curves have smaller *M* values as the contents of MNP decreases. The curve for the bare particles is similar to others reported in the literature [3],[16],[21], showing hysteresis which reveals ferromagnetic behavior.

In order to better analyze the differences between the magnetization loops for the different composites, in (b) the relative magnetization, M/M_{max}, (where M_{max} is *M* at $H = 1$ T) is presented in the low *H* regime. As it can be seen, both the coercive field, H_c, and the applied field required to reach M_{max} decrease as the polymer content in the composite increases. A first decrease in H_c (with respect to bare nanoparticles) is observed for $r_{Py} = 0.5$, which could be attributed to the reduction in the particle size. For higher polymer contents, although the particle diameter remains essentially constant, H_c decreases as r_{Py} increases. This behavior was also observed by Prasanna et al [12], with $CoFe_2O_4$-PANI composites. A possible explanation is that the coercivity is dependent on surface anisotropy and interparticle interactions [22] so, the coating with PPy could affect the net anisotropy (*K*):

$$K = K_b + \left(6/d\right) K_s \quad (1)$$

K_s results from low coordination symmetry for spin-orbit couplings at the surface of NP; K_b is the bulk anisotropy and *d* is the particle diameter. K_s could be reduced due to the polymeric coverage. According to the Stoner-Wohlfarth theory, H_c of a single domain particle is proportionally related to the anisotropy:

$$H_c = \left(2K/\mu_0 M_s\right) \quad (2)$$

where μ_0 is the vacuum permeability. The decrease in K_s, resulting from the particle coverage by the PPy shell, reduces the effective magnetocrystalline anisotropy (*K*) and therefore decreases H_c.

In Fig. 5 the relative magnetization, M/M_{max}, as a function of *H* is presented, in the low applied fields regime, for $CoFe_2O_4$ NP and $CoFe_2O_4$-PEDOT composites.

FIG. 5 HERE

It is worth to mention that for these composites, the saturation magnetization (in emu/g of material) also decreases as the polymer content increases. In Fig. 5 it can be observed that both the remanence ratio (M_r/M_{max}) and the applied field needed to reach M_{max} increase with r_{EDOT}, indicating the presence of interactions related to the amount of CP present. So, this result suggests the presence of magnetic interactions between the MNP and the polymer matrix. As discussed elsewhere [20], the Stoner- Wohlfarth theory is not consistent with this behavior; dipolar interactions could possibly explain that. Also, such behavior has been previously attributed [20] to a RKKY-like coupling of isolated polymer spins with the MNP mediated by the polymer conduction electrons. Further work is ongoing to elucidate the origin of the observed effect. Other interesting result is that for $r_{EDOT} = 10$, H_c increases about 0.015 T when all the reactants concentrations increase three times (see Fig. 5). For higher concentration of reactants, the polymerization yield was increased, that is, more polymer is present in the composite. An increase in H_c could be attributed, in this case, to mechanical strains originated by the polymer shell [18] (magnetomechanical coupling). Although these matters are subject of further research, the different behavior observed in the magnetization curves for both type of polymers is promising for different applications.

Finally, the electrical conductivities were measured for both types of composites. In the case of PPy, the conductivity increases from 1×10^{-5} S/cm, for $r_{Py} = 0.5$ to 1×10^{-2} S/cm for $r_{Py} = 5$; further increases in r_{Py} does not change substantially the resulting conductivity. On the other hand, for PEDOT composites, the conductivity increases from 3×10^{-5} S/cm, for $r_{EDOT} = 5$ to 1×10^{-3} S/cm for pure PEDOT. In this case, also the electrical conductivity depends on r_{EDOT}. The decrease in the electrical conductivity with a decrease in the polymer content is due to the reduction in the amount of conducting material. In both cases, composites with acceptable electrical conductivity were obtained.

IV. Conclusions

$CoFe_2O_4$-CP composites with good magnetic and conducting properties were obtained. It was found that the magnetic behavior depends on the $r_{monomer}$ and on the polymer identity. Moreover, the presence of interactions between the MNP and the polymer matrix could be detected. It can be concluded that the magnetic properties of $CoFe_2O_4$-CP nanocomposites can be modulated not only through the polymer identity but also by the monomer:$CoFe_2O_4$ ratio.

Acknowledgment

The authors gratefully acknowledge funding from the Universidad de Buenos Aires, the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Agencia Nacional de Promoción Científica y Tecnológica, all of Argentina. G. J., F. V. M. and P. S. A. are members of the Carrera del Investigador Científico of CONICET.

References

[1] A. Caprile, M. Coïson, F. Fiorillo, P. Kabos, O. M. Manu, E. S. Olivetti, M. A. Olariu, M. Pasquale, and V. A. Scarlatache, "Microwave behavior of polymer bonded iron oxide nanoparticles," *IEEE Trans. Magn.*, vol 48, no. 11, pp. 3394-3397, 2012.

[2] H. J. Choi, I. B. Jang, J. Y. Lee, A. Pich, S. Chattacharya, and H.-J. Adler, "Magnetorheology of synthesized core-shell structured nanoparticle," *IEEE Trans. Magn.*, vol. 41, no. 10, 2005.

[3] P. S. Antonel, G. Jorge, O. E. Perez, A. Butera, A. Gabriela Leyva, and R. M. Negri, "Magnetic and elastic properties of $CoFe_2O_4$-polydimethylsiloxane magnetically oriented elastomer nanocomposites", *J. App. Phys.*, vol. 110, pp. 043920(8), 2011.

[4] D. L. Leslie-Pelecky, and R. D. Rieke, "Magnetic properties of nanostructured materials," *Chem. Mater.*, vol. 8, pp. 1770-1783, 1996.

[5] T. Ozdemir, D. Sandal, M. Culha, A. Sanyal, N. Z. Atay, and S. Bucak, "Assembly of magnetic nanoparticles into higher structures on patterned magnetic beads under the influence of magnetic field," *Nanotechnology*, vol. 21, pp. 125603(6pp), 2010.

[6] P. Chandrasekhar, "Conducting Polymers, Fundamentals and Applications: A Practical Approach", 1st. ed., 1999 (New York: Springer).

[7] L. Lizarraga, E. M. Andrade, and F. V. Molina, "Swelling and volume changes of polyaniline upon redox switching," *J. Electroanal. Chem.*, vol. 561, pp. 127-135, 2004.

[8] P. S. Antonel. E. Völker, and F. V. Molina, "Sequence-length distribution dependence of photoluminescence quenching as studied by fluorescence measurements and Monte Carlo simulations," *Polymer*, vol. 53, pp. 2619-2627, 2012.

[9] A. Guo, K. Shin, A. B. Karki, D. P. Young, R. B. Kaner, and H. Thomas Hahn, "Fabrication and characterization of iron oxide nanoparticles filled polypyrrole nanocomposites," *J. Nanopart. Res.*, vol. 11, pp. 1441-1452, 2009.

[10] C. S. Priya, and G. Velraj, "Synthesis and characterization of nano and micro copper doped conducting polymer," *Mater. Lett.*, vol. 77, pp. 29-31, 2012.

[11] A. Ohlan, K. Singh, A. Chandra, and S. K. Dhawan, "Microwave absorption behavior of core-shell structured poly(3,4-ethylendioxythiophene)-barium ferrite nanocomposites," *Applied Mat. & Interf.*, vol. 2, no. 3, pp. 927-933, 2010.

[12] G. D. Prasanna, H. S. Jayanna, A. R. Lamani, and S. Dash, "Polyaniline/$CoFe_2O_4$ nanocomposites: A novel synthesis, characterization and magnetic properties," *Synth. Met.*, vol. 161, pp. 2306-2311, 2011.

[13] S. Xuan. Y.-X. J. Wang, J. C. Yu, and K. C.-F. Leung, "Preparation, characterization, and catalytic activity of core/shell Fe_3O_4@polyaniline@Au nanocomposites," *Langmuir*, vol. 25, pp. 11835-11843, 2009.

[14] L. Yongbo, G. Chen, Q. Li, G. Qiu, and Z. Liu, "Facile synthesis, magnetic and microwave absorption properties of Fe_3O_4/polypyrrole core/shell nanocomposite," *J. Alloys Comp.*, vol. 509, pp. 4104-4107, 2011.

[15] L. G. Paterno, M. A. G. Soler, F. J. Fonseca, J. P. Sinnecker, E. H. P. C. Sinnecker, E. C. D. Lima, M. A. Novak, and P. C. Morais, "Layer-by-layer assembly of bifunctional nanofilms: surface-functionalized maghemite hosted in polyaniline," J. Phys. Chem. C, vol. 113, pp. 5087-5095, 2009.

[16] Y. I. Kim, D. Kim, and C. S. Lee, "Synthesis and characterization of $CoFe_2O_4$ magnetic nanoparticles prepared by temperature-controlled comprecipitation method," *Physica B: Cond. Matter*, vol. 337, pp. 42-51, 2003.

[17] E. Mazarío, P. Herrasti, M. P. Morales, and N. Menéndez, "Synthesis and characterization of $CoFe_2O_4$ ferrite nanoparticles obtained by an electrochemical method," *Nanotechnology*, vol. 23, pp. 355708(6pp), 2012.

[18] N. Murillo, E. Ochoteco, Y. Alesanco, J. A. Pomposo, J. Rodriguez, J. González, J. J. del Val, J. M. González, M. R. Britel, F. M. Varela-Feria, and A. R. de Arellano-López, "$CoFe_2O_4$-polypyrrole (PPy) nanocomposites: new multifunctional materials," *Nanotechnology*, vol. 15, pp. S322-S327, 2004.

[19] W. Rasband, 2012, *ImageJ* (Bethesda, Maryland, USA: National Institute of Health, Research Services Branch).

[20] F. M. Berho, P. S. Antonel. G. Jorge, and F. V. Molina, "Enhancement of remanence ratio and coercivity in nanostructured $CoFe_2O_4$-poly(aniline) composites," not published.

[21] Y. Qu, H. Yang, N. Yang, Y. Fan, H. Zhu, and G. Zou, "The effect of reaction temperature on the particle size, structure and magnetic properties of coprecipitated $CoFe_2O_4$ nanoparticles," *Mater. Lett.*, vol. 60, pp. 3548-3552.

[22] K. H. Wu, Y. M. Shin, C. C. Yang, W. D. Ho, J. S. Hsu, "Preparation and ferromagnetic properties of $Ni_{0.5}Zn_{0.5}Fe_2O_4$/polyaniline core-shell nanocomposites," *J. Polym. Sci Part A: Polym. Chem.*, vol. 44, pp. 2657-2664, 2006.

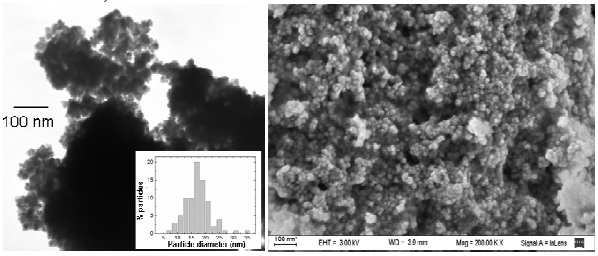

Fig. 1. TEM (left) and SEM (right) images of $CoFe_2O_4$ nanoparticles. Inset: particle size histogram.

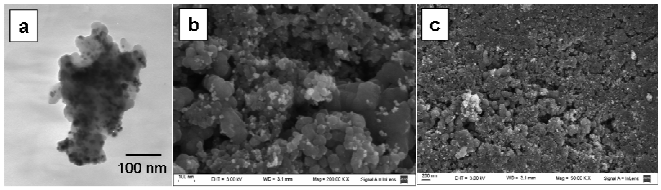

Fig. 2. TEM (a) and SEM (b,c) images of $CoFe_2O_4$-PPy composite, r_{Py} = 2.

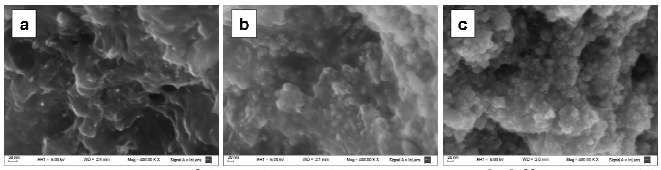

Fig. 3. SEM images of $CoFe_2O_4$-PEDOT composites, with different r_{EDOT}. (a) 10; (b) 5; (c) 2.

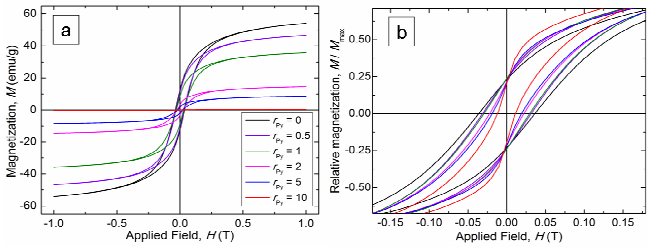

Fig. 4. (a) Magnetization, *M*, per gram of material, as a function of the applied field, *H*, for pure $CoFe_2O_4$ and $CoFe_2O_4$-PPy composites. (b) Relative magnetization, M / M_{max}, for pure $CoFe_2O_4$ and $CoFe_2O_4$-PPy composites, in the low applied fields regime.

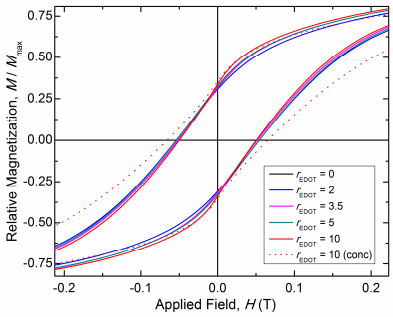

Fig. 5. Relative magnetization, M / M_{max}, for pure $CoFe_2O_4$ and $CoFe_2O_4$-PEDOT composites, in the low applied fields regime. Note: the red dot curve (r_{EDOT} = 10 (conc)) corresponds to a composite with r_{EDOT} = 10, synthesized with all the reactants concentrations three times higher than r_{EDOT} = 10, red full curve.