

Low coercive field and conducting nanocomposite formed by Fe₃O₄ and poly(thiophene)

R.A. Silva^a, M.J.L. Santos^a, A.W. Rinaldi^b, A.J.G. Zarbin^d, M.M. Oliveira^d, I.A. Santos^c,
L.F. Cótica^e, A.A. Coelho^f, A.F. Rubira^a, E.M. Giroto^{a,*}

^aGrupo de Materiais Poliméricos e Compósitos, Departamento de Química, Universidade Estadual de Maringá, Avenida Colombo 5790, 87020-900 Maringá, PR, Brazil

^bFaculdade de Ciências Exatas e Tecnologia, Universidade Federal da Grande Dourados, 79804-970 Dourados, MS, Brazil

^cGrupo de Materiais Especiais, Departamento de Física, Universidade Estadual de Maringá, Avenida Colombo 5790, 87020-900 Maringá, PR, Brazil

^dGrupo de Química de Materiais, Departamento de Química, Universidade Federal do Paraná, CP 19081, 81531-990 Curitiba, PR, Brazil

^eDepartamento de Física, Universidade Estadual do Centro Oeste, CP 3010, 85040-080 Guarapuava, PR, Brazil

^fGrupo de Preparação e Caracterização de Materiais, Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, CP 6165, 13083-970 Campinas, SP, Brazil

Received 22 February 2007; received in revised form 6 September 2007; accepted 14 October 2007

Available online 24 October 2007

Abstract

Magnetite and poly(thiophene) composites have been produced by in situ monomer oxidation. Fourier transform infrared (FTIR) and X-ray diffraction (XRD) confirmed the presence of Fe₃O₄ as particle agglomerates ranging from 15 to ca. 54 nm in size. Transmission electron micrographs (TEMs) revealed a face-to-face structure in both the pure magnetite and the nanocomposite. Typical superparamagnetic (ferrimagnetic) curves have been observed, whereas the relatively weak magnetic field employed in measurement, 200 Oe, was sufficient to split the curves completely. Zero field cooling (ZFC) and field cooling (FC) curves coincide only above room temperature, indicating that the characteristic blocking temperature (T_B) for superparamagnetic particles in this assembly is above room temperature.

© 2007 Elsevier Inc. All rights reserved.

Keywords: Poly(thiophene); Nanocomposite; Magnetite; Superparamagnetic

1. Introduction

Conducting and magnetic compounds find a number of applications in batteries, sensors, displays, and conversion energy devices [1–6]. Recently, poly(thiophenes) have attracted much attention due to their chemical stability in air/humid environments. Inorganic inclusions in polymeric materials provide mechanical robustness [7], thermal stability [8], and enhanced optical [9], magnetic [10,11] and electrical [12] properties. Experiments have shown that nanoscale inclusions bring about phenomena that contribute to new material properties. However, studies of how the properties are altered are still ongoing and there is

no definite conclusion on the effect of nanosized inclusions on polymeric systems yet. Some experiments have shown that interesting properties such as dimensional quantum effect [13,14], transport [15], and magnetic properties [16] may result from the inclusion of nanoparticles. In addition, the preparation of nanocomposites in many cases allows finding a better cost–benefit relation, which is generally associated to the interactions between inclusions and polymer (synergism phenomenon). These interactions may affect the molecular dynamics of the polymer, which results in altered physical properties. Among the inorganic loads, carbonates, sulfates, and metallic oxides are the most commonly used compounds [17,18]. Recently, we demonstrated the electrodeposition of semiconducting poly(*o*-anisidine)/ γ -Fe₂O₃ (maghemite) thin films using an aqueous alkaline medium containing ferrous sulfate and

*Corresponding author. Fax: +55 44 2635784.

E-mail address: emgirotto@uem.br (E.M. Giroto).

o-anisidine [19]. Concerning the magnetite phase, Deng and colleagues [20] reported on conducting and magnetic core-shell nanoparticles (80 nm) formed by Fe₃O₄ and poly(aniline). In addition, Wang and colleagues [21] used an inverse miniemulsion method to synthesize Fe₃O₄-poly(acrylamide) nanosize particles (ca. 100 nm) and pointed out their superparamagnetic behavior. Zaitsev and colleagues [22] reported on the properties of polymer-coated magnetite nanoparticles synthesized by seed precipitation polymerization of methacrylic acid and hydroxyethyl methacrylate in the presence of magnetite nanoparticles. It has been shown that the inclusion of magnetite particles into a hydrophilic polymeric shell increases the stability of the dispersion and decreases the influence of the stabilizing agent on the magnetic and structural properties of the magnetite particles.

In all the previous cases, differences between the various materials were observed. These differences were substantial in some cases and more subtle in others, presumably deriving from the sensitivity of the systems to preparation method details and the resulting structure in both cases. This considered, it seemed worthwhile preparing and investigating a series of nanocomposite systems as thoroughly as possible. The present contribution is one of a series of such studies. Here, we present a simple chemical route for preparing a nanocomposite formed by magnetite (Fe₃O₄) and poly(thiophene). First, the magnetite nanoparticles were prepared through an oxidation–reduction method as described earlier [20]. Afterwards, the nanocomposites were prepared via monomer polymerization in an organic solution containing dispersed Fe₃O₄ and anhydrous iron chloride. Particularly in this case, the objective was to produce a material with electronic conductivity and magnetic properties similar to those of the parent oxide or polymer, but with a better cost–benefit relation.

2. Experimental

Fe₃O₄ particles were synthesized through an oxidation–precipitation method [20]. A mixture of 35 g of poly(ethylene glycol) (10 000 g mol⁻¹, Sigma) and 3.0 g of FeSO₄·6H₂O (Synth) was dissolved in 140 mL of distilled water. The mixture was kept under reflux and vigorous stirring for 6 h. After dropping 20 mL of H₂O₂ (Merck) 1%, the mixture had its pH adjusted to 13 with NaOH 3.0 mol L⁻¹ and was stirred for 6 h at 50 °C. The magnetic fluid was then separated by centrifugation followed by vigorous washing with distilled water. The final product (a dark-brown powder) was dried at 70 °C for 48 h.

The nanocomposite was prepared by stirring 0.4 g of the Fe₃O₄ particles in 50 mL of dried acetonitrile (Acros) for 15 min. Next, 10 mL of distilled thiophene (Acros) was added and the dispersion was stirred for 20 min. Excess anhydrous FeCl₃ was then added and the recipient was sealed. The mixture was vigorously stirred for 24 h. The final product was filtered and washed with distilled water.

The brown powder was dried at 50 °C for 72 h and stored under N₂.

Fourier transform infrared (FTIR) spectra of the samples prepared in KBr pellets were made in a Bomem spectrophotometer, model MB-100. Quantitative analysis of iron was made through atomic absorption spectrometry (AAS) with a Varian Spectra A10Plus model flame spectrometer equipped with deuterium lamp and air acetylene burner. The instrumental parameters were as follows: wavelength 372.0 nm, slit width 0.2 nm, lamp current 282.0 mA, fuel flow rate 0.015 L min⁻¹. Transmission electron micrographs (TEMs) were made in a JEOL 120KV instrument. The samples were suspended in water and allowed to settle for 15 min for observation. Then, a drop of the supernatant dispersion was placed onto a carbon film supported by a copper grid. X-ray diffraction (XRD) measurements were made in Shimadzu XD-3A, model VG-108R with CuK α radiation. Magnetic characterization was performed with a commercial superconducting quantum interference device (SQUID) magnetometer. The curves of magnetization (*M*) vs. field (*H*) (–60 kOe; +60 kOe) of the PT-Fe₃O₄ composite and the magnetite compound at room temperature (300 K) were studied. The curves of magnetization vs. temperature were measured following the field cooling (FC) and zero field cooling (ZFC) protocols.

3. Results and discussion

FTIR spectra of Fe₃O₄, pure poly(thiophene) (PT) and the nanocomposite (PT-Fe₃O₄) particles are shown in Fig. 1. The poly(thiophene) prepared in a different medium (Fe₃O₄ powder was added to the solution for the synthesis of PT-Fe₃O₄) is different from pure poly(thiophene); thus, its FTIR spectrum should not be the same. The differences rely mainly on band shifts and/or the appearance of bands deriving from either chemical and/or physical interactions. According to the literature [23,24], the magnetite band at ca. 573 cm⁻¹ is due to iron oxide lattice deformations and that at 895 cm⁻¹ is due to OH groups bound to the oxide particle surface due to water adsorption. The latter does not appear in the pure-Fe₃O₄ spectrum due to the drying process used after synthesis, which must have reduced the amount of adsorbed water. The PT band at 782 cm⁻¹, the main characteristic peak, was assigned to the out-of-plane C–H angular deformation of thiophene [25]; the signal at 688 cm⁻¹ was assigned to C–S stretching. These signals are also observed in the nanocomposite spectrum. However, they are shifted to higher wavenumbers (C–H shifted to 788 cm⁻¹ and C–S signal shifted to 682 cm⁻¹) as compared to those of pure PT. Although it is difficult to assign some bands and band shifts to specific interactions, these shifts suggest that iron oxide might be interacting with the conducting polymer chains strongly. This fact was also observed for similar materials [19,20]. Regarding the quantitative analysis, atomic absorption spectrometry showed 9.63% (wt/wt) iron species (ca. 13.3% Fe₃O₄).

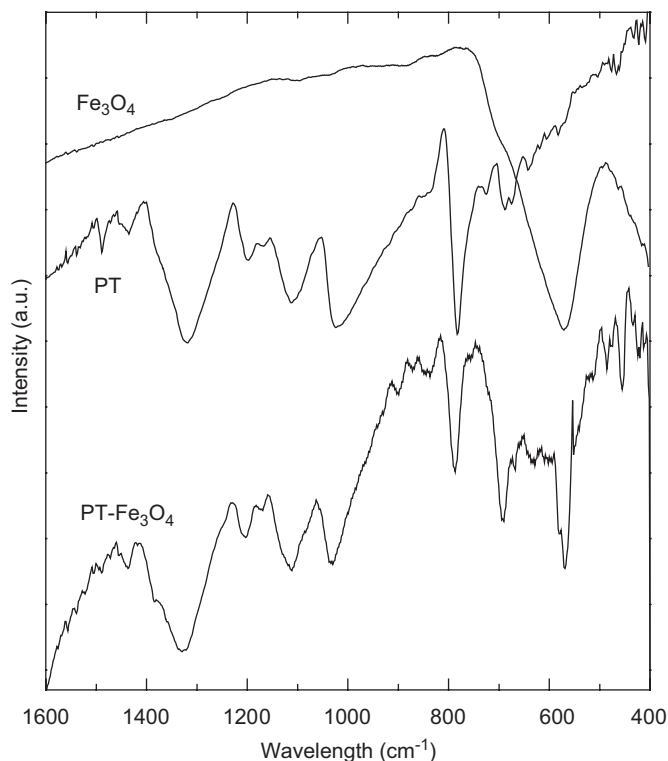


Fig. 1. KBr pellet FTIR spectra of poly(thiophene) (PT), Fe_3O_4 , and PT- Fe_3O_4 composite.

Fig. 2 shows the TEM images of both magnetite and the PT- Fe_3O_4 composite. According to Fig. 2a and b, the magnetite sample is formed by faceted nanoparticle agglomerates. In these images, the agglomerate sizes vary from 15 to 54 nm. The composite images (Fig. 2c and d) show that the iron oxide nanoparticles are embedded in a polymeric mass, which evidences the intimate contact between the two phases. Apparently, the morphology and shape of the composite agglomerates did not change, but agglomerate size is large, as may be seen in Fig. 2(c) and (d). Because the iron oxide particles are superimposed onto the agglomerate core, i.e., the boundary limit of each nanoparticle is diffuse, it is not possible to measure the size of each individual iron oxide particle in magnetite and the composite by TEM images accurately.

Fig. 3 shows the XRD pattern of the PT- Fe_3O_4 composite, as well as those of the Fe_3O_4 compound and pure PT. The main Fe_3O_4 compound peak patterns are at $2\theta = 30.3^\circ$, 35.6° , 43.3° , 53.7° , and 57.3° , and they show a spinel structure (space group $Fd\bar{3}m$) characteristic of magnetite. The pure PT pattern presents a peak with a very large linewidth broadening at ca. 20° . All the peaks found in the Fe_3O_4 compound pattern and in the pure PT pattern are also observed in the PT- Fe_3O_4 composite pattern, indicating that the composite contains Fe_3O_4 and polymer. However, in the PT- Fe_3O_4 composite pattern,

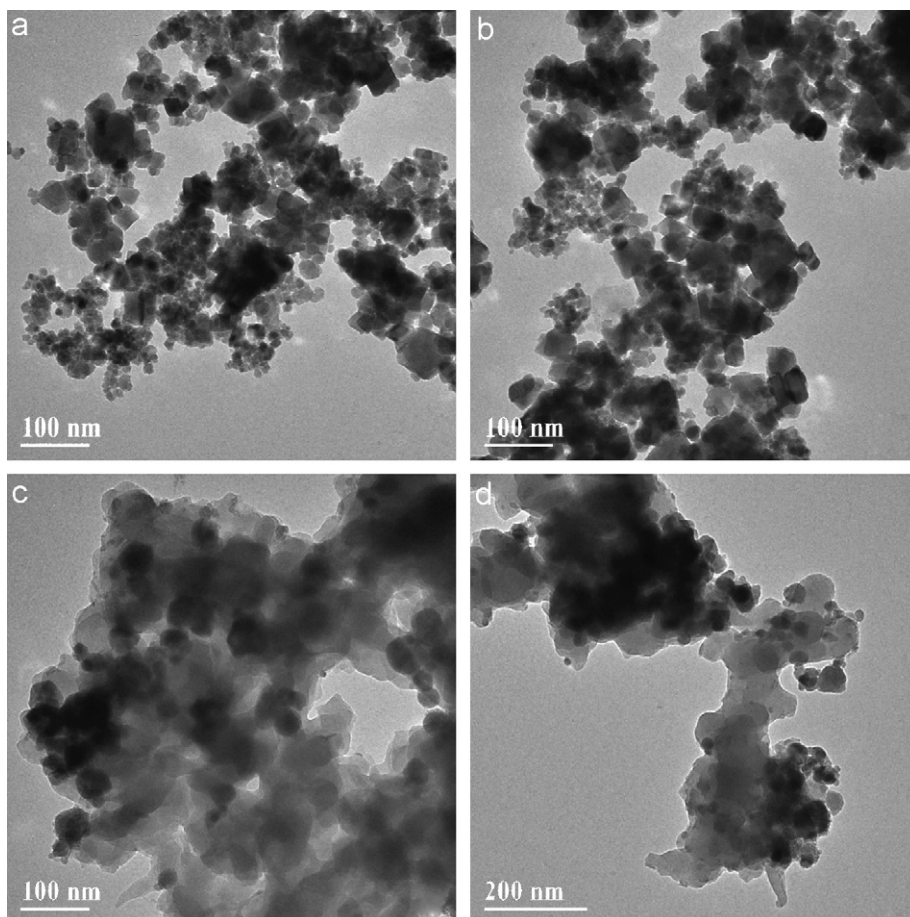


Fig. 2. TEM images of magnetite (a, b) and magnetite/poly(thiophene) nanocomposite (c, d).

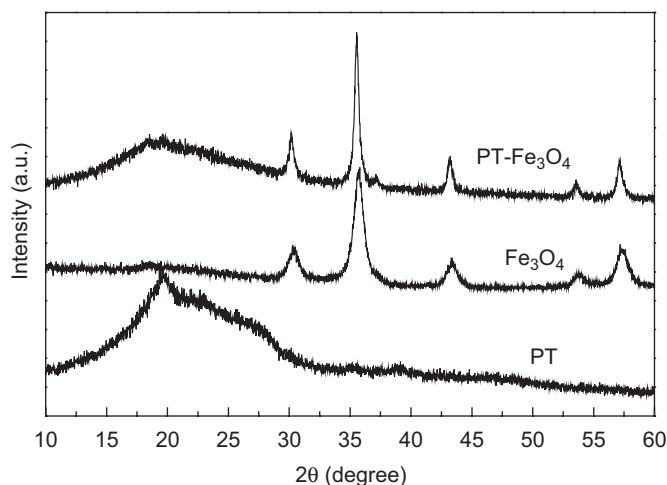


Fig. 3. X-ray diffraction pattern of poly(thiophene) (PT), Fe₃O₄, and PT-Fe₃O₄ samples.

the magnetite peaks present a linewidth broadening smaller than that of the Fe₃O₄ compound. This decrease in linewidth broadening is an indication of the iron oxide particle crystallite size growth with the addition of the conducting polymer. The mean crystallite sizes for the PT-Fe₃O₄ composite and the Fe₃O₄ compound, calculated from linewidth broadening relative to a metallic silicon standard by using Scherrer's formula, were around $d = 30$ and 10 nm, respectively. A possible reason for the increase in crystallite size (from Fe₃O₄ to PT-Fe₃O₄) is the addition of FeCl₃ for polymerizing poly(thiophene). Fe³⁺ ions attach to Fe₃O₄ particles, thus increasing grain and crystallite sizes. The 10–30 nm crystallite size is a common value for superparamagnetic iron oxide nanoparticle monodomains [26].

It is worth noting that the experimental sample preparation route provided a composite with characteristics between those of poly(thiophene) and those of one of the most important iron oxide family materials, magnetite, Fe₃O₄ [27]. Magnetite has a cubic inverted spinel-like (A_2BO_4) ferric oxide ($Fd - \bar{3}m$ space group) with vacant B sites and two distinct sub-lattices (A and B in the spinel structure), which gives origin to a ferrimagnetic ordering in this compound at room temperature [28]. In this way, the intimate contact between poly(thiophene) and magnetite may produce some composites with interesting mismatched functional properties and combined polymer electrical and iron oxide magnetic properties.

To investigate the magnetic properties of the Fe₃O₄ compound and the PT-Fe₃O₄ composite, their magnetic field dependence (M vs. H curves) was investigated by using a SQUID magnetometer. A superparamagnetic-like behavior may be observed for 300-K curves, Fig. 4(a) and (b). Nevertheless, a close inspection of the M vs. H curves indicates the hysteretic behavior of both samples. This corroborates previous works that reported ferrimagnetic ordering of Fe₃O₄ nanoparticles [29,30]. The magnetic

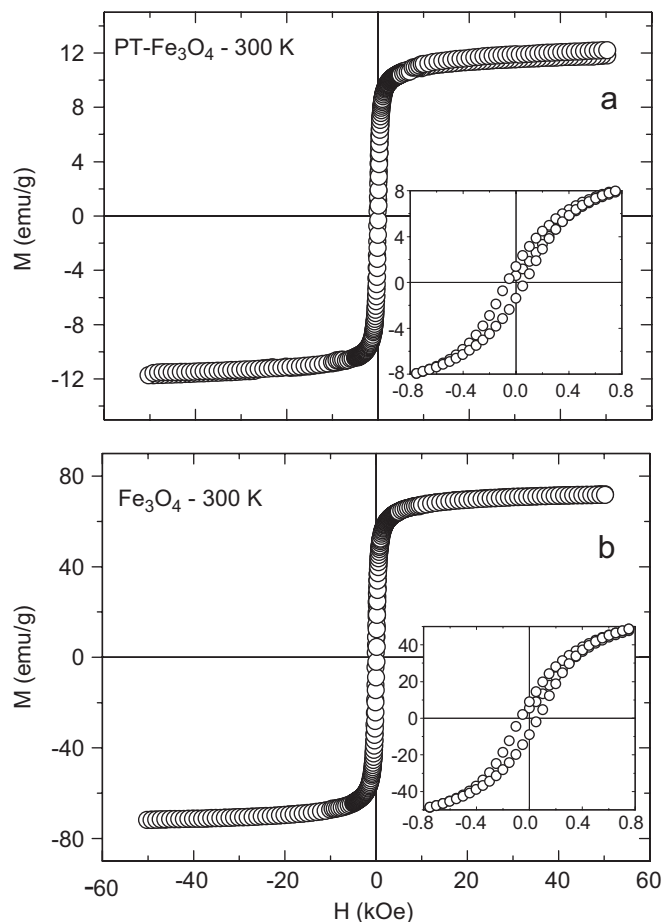


Fig. 4. Magnetization curves of (a) PT-Fe₃O₄ and (b) Fe₃O₄ samples at 300 K. Inset: low field magnetization curves at 300 K.

saturation and coercive fields of 72 emu g^{-1} (at 50 kOe) and 70 Oe found for the Fe₃O₄ compound are in accordance with the values reported in the literature [29,30]. The coercive field of the PT-Fe₃O₄ composite is about the same as that of the Fe₃O₄ compound, i.e., 70 Oe. At this point, it is worth mentioning that the difference observed in crystallite size seems not to be sufficient to change coercivity [31,32]. A remarkable alteration of the saturation magnetization (12 emu g^{-1}) of the PT-Fe₃O₄ composite was observed in comparison with that shown by the Fe₃O₄ compound. This remarkable reduction in the saturation magnetization was also observed in Fe₃O₄ encapsulated by polyacrylamide [21]. These characteristics, i.e., low coercivity and saturation magnetization, which could be exploited in electromagnetic interference (EMI) shielding applications, may be explained considering the polymer coating in these samples. It contributes to hinder the exchange interaction between the magnetic sublattices of the magnetic core (Fe₃O₄) in the oxide-polymer composite. Taking into account this magnetic ordered behavior, and to shed some light on the magnetic behavior of the studied samples, FC and zero field cooling (ZFC) measurements were employed in our analysis. The

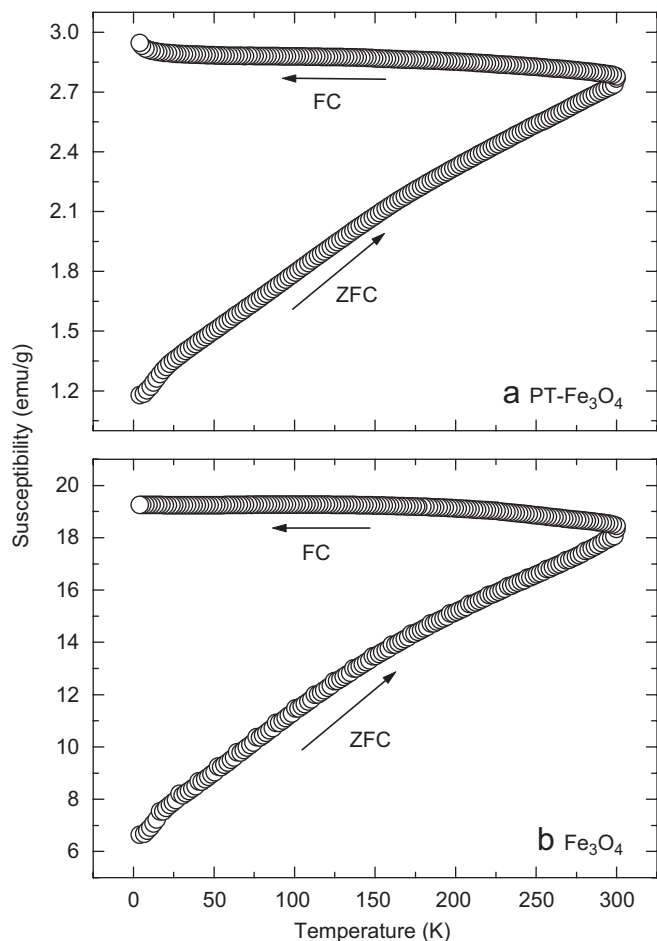


Fig. 5. The ZFC and FC curves for (a) PT-Fe₃O₄ and (b) Fe₃O₄ samples.

FC/ZFC magnetization measurements of the PT-Fe₃O₄ composite and the Fe₃O₄ compound FC/ZFC magnetization measurements are shown in Fig. 5(a) and (b), respectively. Diversely from the superparamagnetic-like behavior reported in the literature for polymer-coated magnetic nanoparticles, typical magnetic ordered curves were observed for these samples, whereas the relatively weak magnetic field employed in measurement, i.e., 200 Oe, was sufficient to completely split the curves. ZFC and FC curves coincided only above room temperature, which indicates that the characteristic blocking temperature (T_B) of possible superparamagnetic particles in this assembly is above room temperature. Furthermore, the behavior shown by magnetization and FC/ZFC curves generally implies a large particle size distribution and nanoparticle anisotropy.

4. Conclusions

Due to a common ion effect, stable and dispersed Fe₃O₄ nanoparticles solvated by Fe³⁺ were obtained. The Fe³⁺ present on the surface of Fe₃O₄ nanoparticles not only prevented nanoparticle agglomeration but also polymerized the thiophene monomer. The nanocomposite particles

thus formed do not have the core-shell structure shown by other similar systems, but rather form faceted small agglomerates. The present study has shown that composite material polymerization techniques have potential in the development of EMI shielding applications. Magnetic studies have shown that the magnetically ordered states of both magnetite and composite samples are highly affected by a large particle size distribution. The composite has low coercive field, which means that it may be made into electric-magnetic shielding materials. With the proper selection of the iron oxide and the conducting polymer, the composite properties may be improved many-fold for its application as electric-magnetic shielding materials.

Acknowledgments

The authors thank Fundação Araucária de Apoio ao Desenvolvimento Científico e Tecnológico do Paraná (Contract nos. 8772 and 7437), Conselho Nacional de Desenvolvimento Científico e Tecnológico-CNPq (PIBIC/UEM), and PROFIX/CNPq (Project no. 541058/01-0) for financial support. The authors also thank IQ-Unicamp for XRD measurements and Centro de Microscopia Eletrônica-UFPR for TEM images. R.A.S., M.J.L.S., A.W.R., and M.M.O. thank CAPES for fellowships, A.J.G.Z. thanks CNPq and Rede de Materiais Nanoestruturados for the financial support.

References

- [1] H. Kawaguchi, Prog. Polym. Sci. 25 (2000) 1171–1210.
- [2] O. Kalinina, E. Kumacheva, Macromolecules 32 (1999) 4122–4129.
- [3] R.H. Marchessault, P. Rioux, L. Raymond, Polymer 33 (1992) 4024–4028.
- [4] R.F. Ziolo, E.P. Giannelis, B.A. Weinstein, M.P. Ohoro, B.N. Ganguly, V. Mehrotra, M.W. Russel, D.R. Huffman, Science 257 (1992) 219–223.
- [5] A. Dhanabalan, S.S. Talwar, A.Q. Contractor, N.P. Kumar, S.N. Naranq, S.S. Major, K.P. Muthe, J.C. Vyas, J. Mater. Sci. Lett. 18 (1999) 603–606.
- [6] G.R. Pedro, Adv. Mater. 13 (2001) 163–174.
- [7] Y.C. Ou, F. Yang, Z.Z. Yu, J. Polym. Sci. B: Polym. Phys. 36 (1998) 789–795.
- [8] J. Zhu, F.M. Uhl, A.B. Morgan, C.A. Wilkie, Chem. Mater. 13 (2001) 4649–4654.
- [9] D.E. Fogg, L.H. Radzilowski, B.O. Dabbousi, R.R. Schrock, E.L. Thomas, M.G. Bawendi, Macromolecules 30 (1997) 8433–8439.
- [10] P.C. Morais, R.B. Azevedo, D. Rabelo, E.C.D. Lima, Chem. Mater. 15 (2003) 2485–2487.
- [11] C. Castro, J. Ramos, A. Millan, J. Gonzalez-Calbet, F. Palacio, Chem. Mater. 12 (2000) 3681–3688.
- [12] H. Du, Y. Cao, Y.B. Bai, P. Zhang, X.M. Qian, D.J. Wang, T.J. Li, X.Y. Tang, J. Phys. Chem. B 102 (1998) 2329–2332.
- [13] H. Weller, Adv. Mater. 5 (1993) 88–95.
- [14] M.L. Steigerwald, L.E. Brus, Acc. Chem. Res. 23 (1990) 183–188.
- [15] C. Joly, M. Smaih, L. Porcar, R.D. Noble, Chem. Mater. 11 (1999) 2331–2338.
- [16] J. Ramos, A. Millan, F. Palacio, Polymer 41 (2000) 8461–8464.
- [17] C.O. Oriakhi, J. Chem. Educ. 77 (2000) 1138–1146.
- [18] D.C. Schnitzler, M.S. Meruvia, I.A. Hümmelgen, A.J.G. Zarbin, Chem. Mater. 15 (2003) 4658–4665.

- [19] L.H.M. Fonseca, A.W. Rinaldi, A.F. Rubira, L.F. Cótica, S.N. de Medeiros, A. Paesano Jr., I.A. Santos, E.M. Giroto, *Mater. Chem. Phys.* 97 (2006) 252–255.
- [20] J.G. Deng, C.L. He, Y.X. Peng, J.H. Wang, X.P. Long, P. Li, A.S.C. Chan, *Synth. Met.* 139 (2003) 295–301.
- [21] Z.Z. Xu, C.C. Wang, W.L. Yang, Y.H. Deng, S.K. Fu, *J. Magn. Magn. Mater.* 277 (2004) 136–143.
- [22] V.S. Zaitsev, D.S. Filimonov, I.A. Presnyakov, R.J. Gambino, B. Chu, *J. Colloid Interf. Sci.* 212 (1999) 49–57.
- [23] M. Kryszewski, J.K. Jeszka, *Synth. Met.* 94 (1998) 99–104.
- [24] G. Sócrates, *Infrared and Raman Characteristic Group Frequencies*, third ed., Wiley, 2001, p. 325 (Chapter 22).
- [25] S. Hotta, M. Soga, N. Sonoda, *Synth. Met.* 26 (1988) 267–279.
- [26] M. Shinkai, H. Honda, T. Kobayashi, *Biocatalysis* 5 (1991) 61–69.
- [27] R. Zboril, M. Mashlan, D. Petridis, *Chem. Mater.* 14 (2002) 969–982.
- [28] R.M. Cornell, U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses* VCH Verlagsgesellschaft mbH, Weinheim, 1996, p. 137 (Chapter 6).
- [29] Z.B. Huang, F.Q. Tang, *J. Colloid Interf. Sci.* 275 (2004) 142–147.
- [30] B.D. Cullity, *Introduction to Magnetic Materials*, Addison-Wesley, Reading, MA, 1972.
- [31] V. Kusigerski, M. Tadic, V. Spasojevic, B. Antic, D. Markovic, S. Boskovic, B. Matovic, *Scripta Mater.* 56 (2007) 883–886 and references therein.
- [32] C. Balasubramaniam, Y.B. Kholam, I. Bannerjee, P.P. Bakare, S.K. Date, A.K. Das, S. Bhoraskar, *Mater. Lett.* 58 (2004) 3958–3962 and references therein.