Magnetic susceptibility investigation of magnetic nanoparticles in styrene-divinylbenzene mesoporous template

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Abstract

In this study, dynamical susceptibility (DS) was used to investigate magnetite-based composites. The field dependence of peaks observed in the DS curves was analyzed within the picture of an asymmetric double well potential for the relaxation of the magnetic moment associated to the magnetite nanoparticle. Parameters obtained from the analysis of the DS data indicate that different magnetite structure, build up from isolated nanoparticles, explains the features observed in the susceptibility curves.
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In recent years the technique known as high gradient magnetic separation (HGMS) has been attracting a great deal of attention [1–6]. Applications of such technique span from cell separation [1] to removal of actinides from wastewater [2]. The HGMS technique uses nanosized magnetic particles, which are surface coupled to target species for latter removal using a high gradient magnetic field device [3,4]. Magnetite (Fe_3O_4) nanoparticles, surface-coated either with non-specific [5] or specific [6] molecular layers, have been widely used in HGMS. Magnetic nanoparticle in micron-sized polymeric templates, once physically and chemically engineered, is an excellent candidate to support cleanup remediation technologies addressed to water oil spill in natural environments using HGMS-based processes. This study reports on the magnetic characterization of magnetite-based composites using dynamical susceptibility (DS) measurements. The template used in the preparation of the composite samples was the mesoporous styrene-divinylbenzene (Sty-DVB) copolymer.

The composite preparation uses a four-step experimental procedure [7]. Briefly, the mixture containing the ferrous aqueous solution (bath solution) and the micron-sized polymeric sphere is first stirred at room temperature. Second, the polymer particles were separated by filtration and washed thoroughly with water. Third, the oxidation of the ferrous ion was performed in alkaline medium following the standard recipe used in the synthesis of magnetite micro-crystals from ferrous ion in aqueous solution [8]. Fourth, the obtained black composite was filtered, washed with water until the pH of the eluent was neutral, and dried. At any particular concentration of the bath solution the above-described procedure can be performed N times in order to obtain the N-cycle composite samples with increasing amount of magnetic material.

The present investigation is focused onto two 2-cycle composite samples, prepared using different bath solution concentrations (5 and 30 mmol/l). Increasing the ferrous concentration in the bath solution leads to the increase of the magnetite nanoparticle size [7]. The two 2-cycle composite samples, namely, 5 mmol/l (5M2C) and 30 mmol/l (30M2C) were used in the magnetic susceptibility measurements. The experimental setup consists of a Robinson oscillator operating in the megahertz region (2–10 MHz). The room-temperature DS data (real and imaginary components) were taken at different external fields (0–4 kG). Fig. 1 shows two representative DS imaginary component of samples 5M2C and 30M2C, at 150 and 3000 G. All the DS curves were fitted for two peaks (P1 and P2), as

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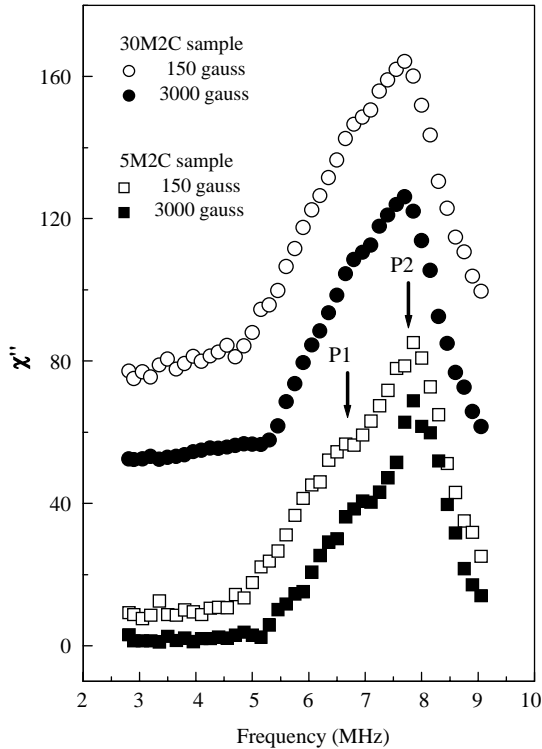*E-mail address:* ruiz@fis.unb.br (A.F.R. Rodriguez).

Fig. 1. Typical imaginary component of the susceptibility of samples 30M2C and 5M2C, at 150 and 3000 G.

Fig. 2. Field dependence of the susceptibility peak shift associated to sample 30M2C. Solid lines represent the best fit according to Eq. (2).

indicated in Fig. 1. Regarding the sample 30M2C, symbols in Fig. 2 represent the field dependence of DS peaks P1 and P2. Similar behavior was observed in the field dependence of the DS peak positions in sample 5M2C (data not shown). The data analysis will be focused on the two main features (P1 and P2) of the DS curves.

In the polymeric template, magnetite nanoparticles stick together building up agglomerates that, in general, show chain-like structures [9]. The close contact of the individual nanoparticles in a chain-like structure gives rise to a system which is, from the magnetic point of view, very similar to a system of a finite cluster of spins coupled to an infinite magnetically ordered cluster of spins. The DS associated to the nanoparticle system follow the Debye form, $\chi(\omega) = \chi_0(1 - i\omega\tau)^{-1}$, with the typical Néel relaxation time, $\tau = \tau_0 \exp(v/kT)$. However, application of an external field deforms the symmetrical double well potential. Under the asymmetrical double well potential the relaxation of the magnetic moment is $\tau = \tau_0 \exp(v/kT) \operatorname{sech}(E/2kT)$, where v and E are the barrier energy height and the asymmetry parameter, respectively. Therefore, the imaginary component of the susceptibility curve peaks at frequencies given by $f(V, E) = f_0 \exp(-v/k) \times \cosh(E/2kT)$. While v describes the magnetocrystalline
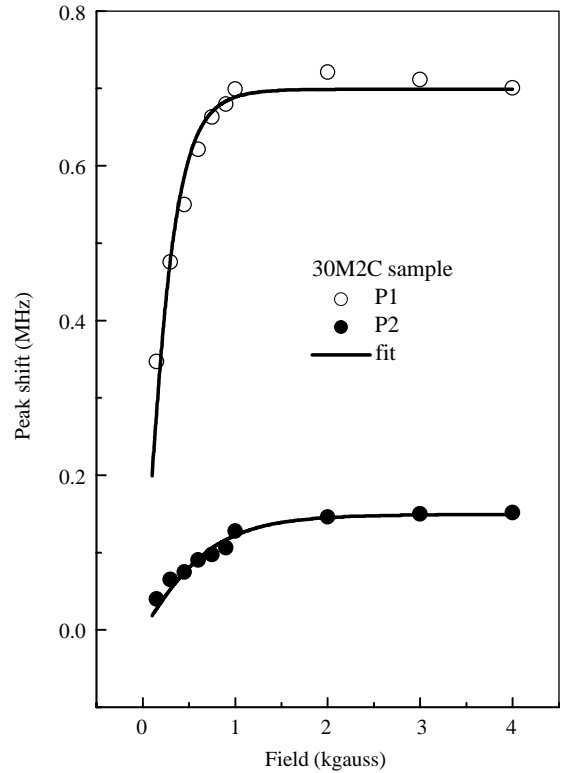
anisotropy (KV), E is due to the interaction between the nanoparticle magnetic moment (μ) and the applied field (H). Regarding the polydispersity in particle volume (V), the barrier height (v) and the asymmetry parameter (E) need to be described using distribution functions. The lognormal distribution function, $P(V)$, has been widely used to describe size polydispersity, while a flat distribution function, $G(E)$, has been used to describe the asymmetry parameter [10]. Then, the field dependence of the peak frequency (f_P) reads

$$f_P(H) = \int \int f(V, E)P(V)G(E)\, dE\, dV. \qquad (1)$$

A flat distribution for $G(E)$, however, does not describes the data shown in Fig. 2. In contrast, the non-flat distribution $G(E) = \operatorname{sech}^{\beta}(E/2kT)$, with $\beta = 3$, has been proved to be an excellent choice. Using the non-flat description Eq. (1) is reduced to

$$f_P(H) = \int A \exp(-KV/kT) \tanh(E/2kT)P(V)\, dV. \qquad (2)$$

Solid lines in Fig. 2 represent the best fit of the experimental data according to Eq. (2). At this point two aspects of the non-flat distribution, $G(E)$, should be

emphasized. Firstly, from the mathematical point of view Eq. (2) is exactly obtained from Eq. (1), as long as $G(E) = \text{sech}^3(E/2kT)$. Secondly, from the physical point of view the non-flat distribution function $G(E)$ deviates very little from the Boltzmann distribution function. In other words, the good agreement between the data and the model proposed above, which uses the non-flat distribution function, indicates that the asymmetry parameter (E) may follow a classical distribution function. Though empirical the present approach represents a step forward as compared to the use of a flat distribution function.

Except for the scale factor A, four independent parameters can be obtained from the fitting of the data shown in Fig. 2, namely, the mean particle diameter, diameter dispersion, anisotropy, and magnetization. Parameters obtained from the fitting showed in Fig. 2 are in excellent agreement with data obtained from transmission electron microscopy (TEM) and from the literature [11]. The TEM data of sample 30M2C gives 20.1 nm and 0.22 for the mean particle diameter and diameter dispersion, respectively. The fitting showed in Fig. 2 was performed with 19.9 nm and 0.22 for the mean particle diameter and diameter dispersion, respectively. Furthermore, the anisotropy values obtained from our DS analysis of sample 5M2C were 1.2×10^5 and $1.6 \times 10^5 \, \text{erg/cm}^3$ for peaks P1 and P2, respectively. For sample 30M2C, however, we found the same value of anisotropy associated to both DS peaks ($1.6 \times 10^5 \, \text{erg/cm}^3$). The anisotropy values we found from the fitting procedure can be compared to the reported anisotropy value for bulk magnetite at room temperature ($1.9 \times 10^5 \, \text{erg/cm}^3$) [11]. Finally, we found from the fitting of the data shown in Fig. 2 that the magnetization associated to peaks P1 and P2 are different from one another by a factor of 2.3 and from the bulk value reported for magnetite, suggesting that different magnetic structures are related to the susceptibility curves presented in Fig. 2. More detailed investigations of such magnetic structures are presently in progress and will be the issue of future publications.

In summary, magnetite-based composite samples were investigated using DS measurements. Comparison of the particle size profile from DS and TEM measurements highlights the capability of susceptibility measurements in assessing the mean size and size dispersion of magnetic nanoparticles in polymeric templates. In addition, the field dependence of the susceptibility peak allows determination of the magnetocrystalline anisotropy values associated to magnetite nanoparticles. Finally, observation of distinct magnetization values associated to P1 and P2 peaks suggests the presence of different magnetic structures build up from isolated magnetite nanoparticles.

References

[1] H. Honda, A. Kawasabe, A. Shinkai, T.J. Kobayashi, J. Ferment. Bioeng. 86 (1998) 191.

[2] A.D. Ebner, J.A. Ritter, H.J. Ploehn, R.L. Kochen, J.D. Navratil, Sep. Sci. Technol. 34 (1999) 1277.

[3] L.P. Sun, M. Zborowki, L.R. Moore, J.J. Chalmers, Cytometry 33 (1998) 469.

[4] S. Kurinobu, J. Uesugi, Y. Utumi, H. Kasahara, IEEE Trans. Magn. 35 (1999) 4067.

[5] J.W.M. Bulte, L.D. Ma, R.L. Magin, R.L. Kamman, C.E. Hulstaert, K.G. Go, T.H. The, L. Deleij, Magn. Reson. Med. 29 (1993) 32.

[6] H. Iinuma, K. Okinaga, M. Adachi, K. Suda, T. Sekine, K. Sakagawa, Y. Baba, J. Tamura, H. Kumagai, A. Ida, Int. J. Cancer 89 (2000) 337.

[7] D. Rabelo, E.C.D. Lima, A.C. Reis, W.C. Nunes, M.A. Novak, V.K. Garg, A.C. Oliveira, P.C. Morais, Nano Lett. 1 (2001) 105.

[8] S.B. Couling, S. Mann, J. Chem. Soc. Chem. Commun. 0 (1985) 1713.

[9] P.C. Morais, R.B. Azevedo, L.P. Silva, D. Rabelo, E.C.D. Lima, Phys. Status Solidi (a), in press.

[10] P.C. Morais, A.L. Tronconi, K. Skeff Neto, J. Appl. Phys. 55 (1984) 3744.

[11] K.P. Belov, Sov. Phys. Usp. 36 (1993) 380.