Mössbauer study of a Fe$_3$O$_4$/PMMA nanocomposite synthesized by sonochemistry

H. Martínez · L. D'Onofrio · G. González

Abstract Magnetite nanoparticles of 10 nm average size were synthesized by ultrasonic waves from the chemical reaction and precipitation of ferrous and ferric iron chloride (FeCl$_3$· 6H$_2$O y FeCl$_2$· 4H$_2$O) in a basic medium. The formation and the incorporation of the magnetite in PMMA were followed by XRD and Mössbauer Spectroscopy. These magnetite nanoparticles were subsequently incorporated into the polymer by ultrasonic waves in order to obtain the final sample of 5 % weight Fe$_3$O$_4$ into the polymethylmethacrylate (PMMA). Both samples Fe$_3$O$_4$ nanoparticles and 5 % Fe$_3$O$_4$/PMMA nanocomposite, were studied by Mössbauer spectroscopy in the temperature range of 300 K–77 K. In the case of room temperature, the Mössbauer spectrum of the Fe$_3$O$_4$ nanoparticles sample was fitted with two magnetic histograms, one corresponding to the tetrahedral sites (Fe^{3+}) and the other to the octahedral sites (Fe^{3+} and Fe^{2+}), while the 5 % Fe$_3$O$_4$/PMMA sample was fitted with two histograms as before and a singlet subspectrum related to a superparamagnetic behavior, caused by the dispersion of the nanoparticles into the polymer. The 77 K Mössaubuer spectra for both samples were fitted with five magnetic subspectra similar to the bulk magnetite and for the 5 % Fe$_3$O$_4$/PMMA sample it was needed to add also a superparamagnetic singlet. Additionally, a study of the Verwey transition has been done and it was observed a different behavior compared with that of bulk magnetite.

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Abbreviations

PMMA	Polymethylmethacrylate
XRD	X-ray diffraction
Fe_3O_4	Magnetite
IS	Isomer shift
QS	Electrical quadrupole splitting
HF	The hyperfine magnetic field
SP	Superparamagnetic

1 Introduction

In recent years, the synthesis and analysis of materials in the nanometer scale has been an area of intense study. Nanostructured materials often exhibit chemical, electrical, magnetic and optical properties different from those of bulk materials. There is a great interest in iron oxides because of its importance in the technology of magnetic information storage, magnetic resonance imaging and ferrofluids, Skomski [1], Bahadur and Giri [2] and Neuberger et al. [3]. At room temperature bulk magnetite (Fe_3O_4) has an inverse spinel structure with eight Fe^{3+} ions in tetrahedral sites (A) and sixteen $Fe^{2.5+}$ ions in octahedral sites (B). Above the Verwey temperature, $T_V \sim$ 120 K, magnetite has a cubic spinel structure, with lattice parameter $a_0 \sim 8.397$ Å and the O atoms arranged in a face centered—cubic (fcc) lattice. The lattice can accommodate Fe^{3+} on the tetrahedral site (A) and Fe^{3+} and Fe^{2+} on the octahedral site (B) in antiparallel arrangement, yielding ferrimagnetic order below T_C (Curie's temperature, $\approx$860 K). Below the temperature T_V, 120 K, there is a change from cubic to orthorhombic structure, a lower symmetry structure, and a more complex Mössbauer spectrum is observed, and can be fitted by at least five subspectra due to 3d electron localization, leading to discrete Fe^{2+} and Fe^{3+} spectral contributions of the B sites, [4, 5]. In this work, we study the Mössbauer Spectroscopy of magnetite nanoparticles embedded in a polymeric matrix of PMMA because it allows a good dispersion of nanoparticles in the polymeric matrix, and a superparamagnetic behavior can be observed.

2 Experimental

Magnetite nanoparticles (Fe_3O_4) included in PMMA were synthesized by the reaction of iron chloride salts ($FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$) with pH = 10. The reaction process was done in an ultrasound equipment (Fisher, Model 150 W), at a fixed frequency of 20 KHz for 15 min. In this period of time a solution NH_3 (10 ml) was added to keep the a pH = 10 and thus ensure the formation of nanoparticles Fe_3O_4.

The formation of Fe_3O_4 nanoparticles was according to the following reaction:

$$FeCl_{2(aq)} + 2FeCl_{3(aq)} + 8NH_{3(aq)} + 4H_2O + Ultrasound \rightarrow Fe_3O_{4(sol)} + 8NH_4Cl_{(aq)}$$
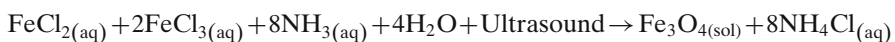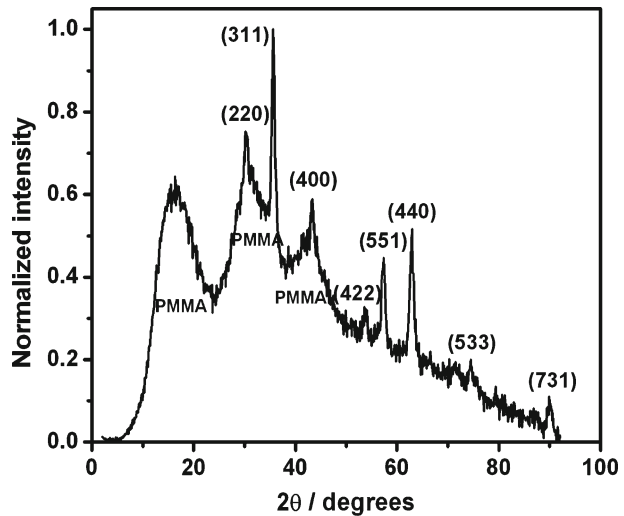
Fig. 1 XRD of synthesized
5 % Fe_3O_4/PMMA

The product was centrifuged and washed with distilled water so that all the NH_3 disappeared from the obtained nanoparticles. To incorporate these nanoparticles into the polymer, the PMMA (120.000 MW), was dissolved in acetone, and the magnetite powder was dispersed in this solution using the same conditions of the sonochemical synthesis. The relative amount of iron ions and PMMA was calculated in order to obtain 5 % weight Fe_3O_4 in PMMA. The polymer solution and the nanoparticles were subjected to ultrasonic irradiation for 15 min at a frequency of 20 KHz.

XRD measurements were performed using a Bruker D8 powder diffractometer using CuK_α ($\lambda = 0.1548$ nm). The XRD allowed us to identify the precipitate as magnetite, with an average particle size of 10 nm as deduced from the Scherrer formula for the crystallite size.

The Mössbauer spectra were obtained using a source of ^{57}Co in a Rh matrix, a driving unit running in the triangular symmetric mode for velocity and a multichannel analyzer (Wissel Instruments). The measurements were performed both at room temperature and at liquid nitrogen temperature. The fitting parameters are: the isomer shift (IS) calibrated with α-Fe, the electrical quadrupole splitting (QS) and the hyperfine magnetic field (HF).

3 Results and discussion

The XRD pattern of 5 % magnetite/PMMA is shown in Fig. 1, and the pattern of nanoparticles magnetite is shown in Fig. 2. The indexation was done by reference to the magnetite in bulk proving the presence of magnetite only. Also it is seen that the peaks are broadened indicating that the sample is composed of small crystals, where peaks broadening are inversely proportional to grain size. An average grain size of 10 nm was found using the Scherrer equation.

While magnetite and maghemite are indistinguishable by XRD, the Mossbauer spectroscopy is a useful tool to differentiate unambiguously these iron oxides. The

Fig. 2 XRD of bulk Fe_3O_4
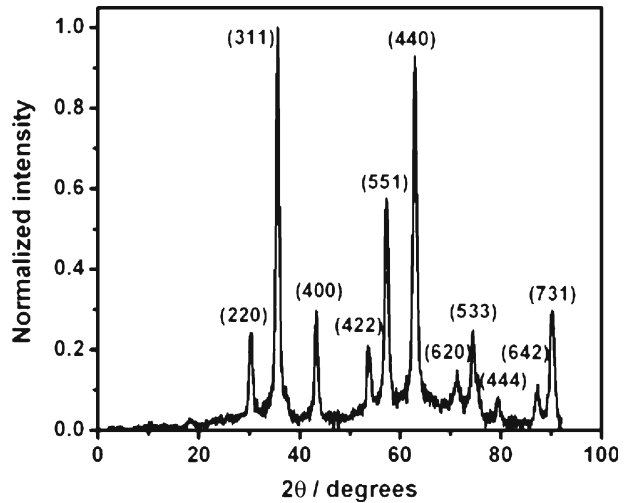
Fig. 3 Williamson-Hall plot for the 10 nm Fe_3O_4 nanoparticules
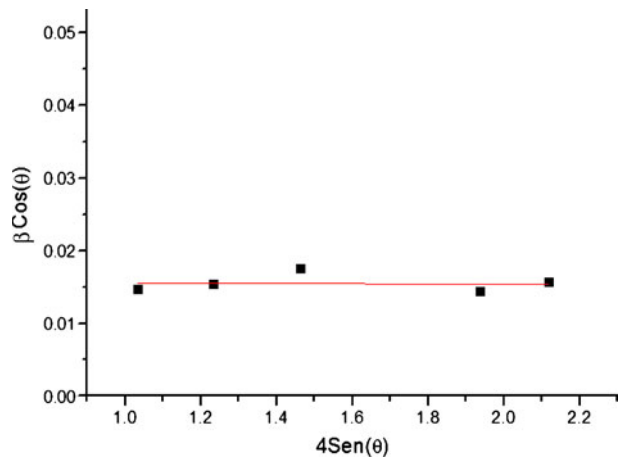
HF values at room temperature for magnetite are slightly lower than those of the maghemite. Vandenberghe et al. [6].

By Hall Williamson analysis the grain size and the microdeformation (ε) were calculated. The average particle size obtained from Fig. 3 was (10 ± 2) nm, and the microdeformation $\varepsilon = 4.2 \times 10^{-5}$ with respect to the magnetite in bulk.

The TEM micrograph of Fig. 4 corresponds to the 5 % Fe_3O_4/PMMA sample, and it shows the crystallites of magnetite with a nearly spherical morphology. The electron diffraction pattern in Fig. 4, shows intense rings corresponding to the same families of planes that characterize Fe_3O_4.

Figure 5 shows a histogram of sizes of magnetite nanoparticles obtained from microscopy analysis. The particle distribution histogram was obtained counting 250 particles from the micrograph. The solid line corresponds to the log—normal distribution fit, and give us an average particle size of 11 nm and a standard deviation $\sigma = 0.22$.

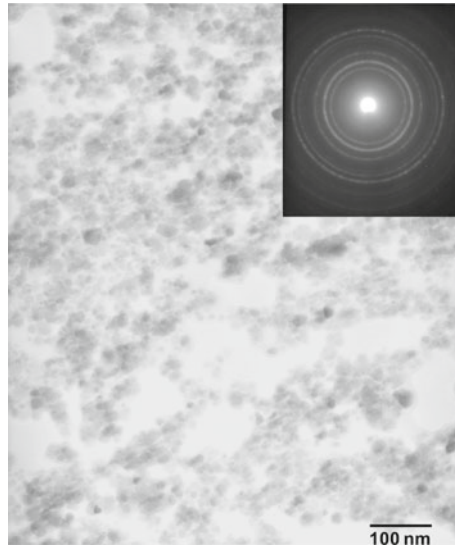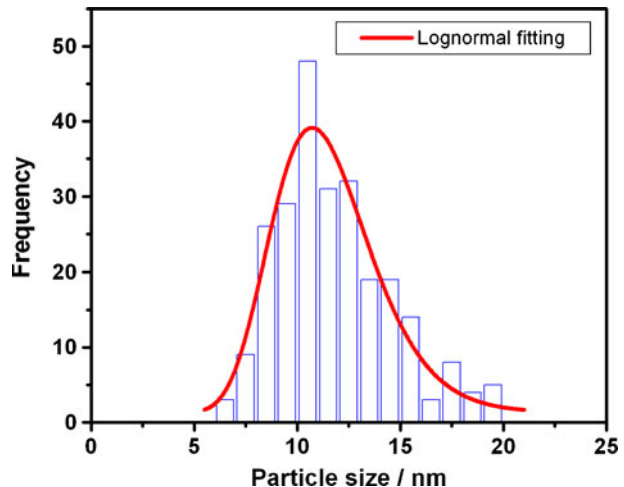**Fig. 4** TEM micrograph of 5 % de Fe_3O_4/PMMA sample

Fig. 5 Particle size distribution histogram and lognormal fitting

In Fig. 6 is shown the Mössbauer spectra recorded at 300 K of Fe_3O_4 nanoparticles and 5 % Fe_3O_4/PMMA nanocomposite. At 300 K the spectrum was fitted with two histogram for magnetite; in the case of magnetite nanoparticles, one histogram for tetrahedral sites with IS = 0.29 mm/s, QS = 0.00 and HF = 47.2 T and one histogram for octahedral sites with IS = 0.52 mm/s, QS = 0.00 and HF = 45.8 T. These value of hyperfine fields obtained represents a field magnetic mean, which is caused by the size distribution of nanoparticles in the sample. For the 5 % Fe_3O_4/PMMA was fitted, as in the case previous, with two histograms for tetrahedral and octahedral sites and a singlet; whose values were: for tetrahedral sites IS = 0.28 mm/s, QS = 0.00 and HF = 45.8 T and one for octahedral Sites with IS = 0.52 mm/s, QS = 0.00 and T in HF = 44.2 T, addition one singlet caused by the presence of nanoparticles of magnetite

Fig. 6 Mössbauer spectrum at 300 K, (**a**) Fe_3O_4 nanoparticules, (**b**) 5 % Fe_3O_4/PMMA

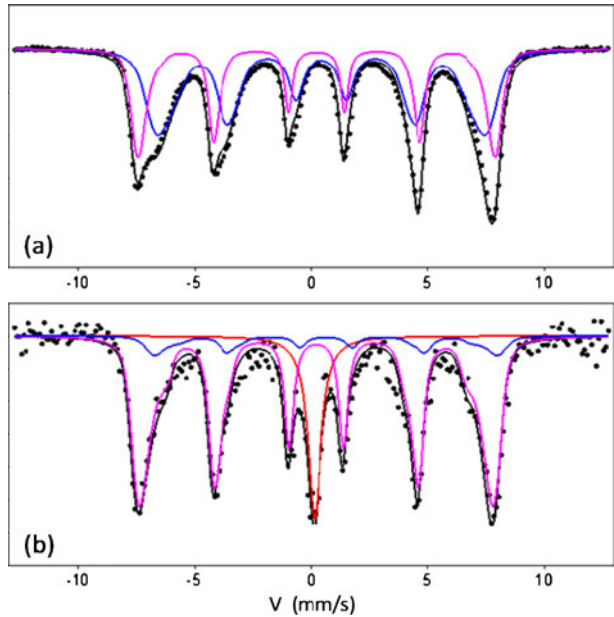**Fig. 7** Mössbauer spectrum at 77 K, (**a**) Fe_3O_4 nanoparticules, (**b**) 5 % Fe_3O_4/PMMA
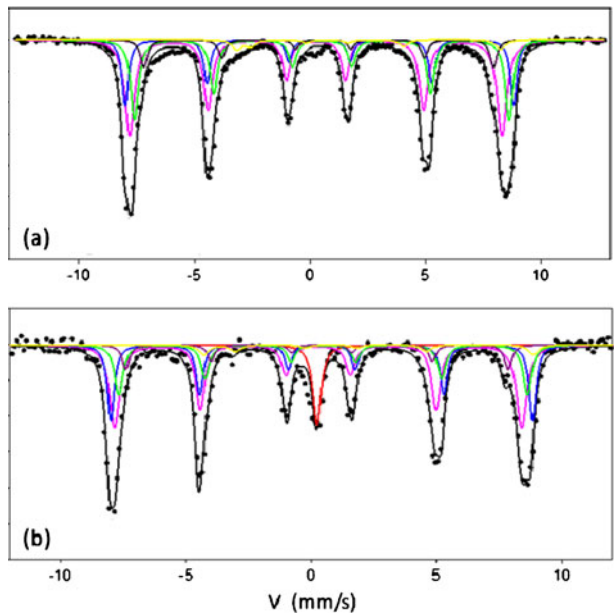
present in the sample, with hyperfine parameters of IS = 0.23 mm/s, QS = 0.00 and HF = 0.00 T. The singlet that is observed in the sample is due to the super-paramagnetic behavior (SP) caused by the inclusion of the magnetite obtained by sonochemistry in the PMMA. The PMMA allows for less interaction of the magnetite

Table 1 Mössbauer parameters of Fig. 7

Name	SUBESPECTRO	DI (mm/s)	QS (mm/s)	CH (Tesla)
Nanoparticules of Fe_3O_4	Tetra. (A) Fe^{3+}	0,33	0,00	50,0
	Oct. (B) Fe^{3+}—I	0,47	0,00	52,2
	Oct. (B) Fe^{3+}—II	0,52	−0,01	50,3
	Oct. (B) Fe^{2+}—I	0,48	−0,19	46,9
	Oct. (B) Fe^{2+}—II	1,62	1,80	32,5
5 % Fe_3O_4/PMMA	Tetra. (A) Fe^{3+}	0,34	0,00	50,4
	Oct. (B) Fe^{3+}—I	0,45	0,00	52,1
	Oct. (B) Fe^{3+}—II	0,50	−0,01	50,6
	Oct. (B) Fe^{2+}—I	0,33	−0,19	47,3
	Oct. (B) Fe^{2+}—I	1,51	1,50	40,8
	Singulete (SP)	0,32	0,00	0,00

Fig. 8 Mössbauer spectrum at 110 K of the 5 % Fe_3O_4/PMMA sample
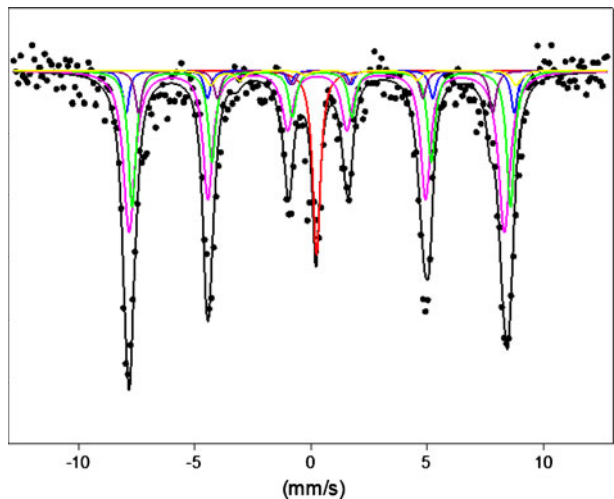
nanoparticles, in contrast to case of the nanoparticles without polymer since these are agglomerated due to the strong magnetism between these nanoparticles.

The Mössbauer spectrum at 77 K of Fig. 7a, for magnetite nanoparticle, is fitted with five sextets [3], one of them represents the tetrahedral sites of Fe^{3+} and the other four the distinction between Fe^{2+} and Fe^{3+} in the octahedral sites. The sample 5 % magnetite/PMMA, was fitted with five sextets similar to the previous case, but in addition we can observe the appearance of one singlet caused by the distribution of the magnetite nanoparticles in the polymer producing a slight separation of the nanoparticles, this happens due to the magnetism of the magnetite is very strong which makes the nanoparticles are held together. The values of parameters hyperfine shows in the Table 1. The fit of magnetite at 77 K is difficult to perform because a distinction must be made between Fe^{2+} and Fe^{3+}, although there are recent publications [4, 7], reported only in bulk magnetite at 77 K.

Figure 8 shows the 5 % magnetite/PMMA sample at 110 K, and we can observe the presence of a Verwey transition, therefore Mössbauer spectrum was fitted with six subspectra similar to the case of this sample at 77 K, and whose values of the hyperfine parameters are reported in Table 2. It has to be noted that the

Table 2 Mössbauer parameters of Fig. 8

Name	SUBESPECTRO	DI (mm/s)	QS (mm/s)	CH (Tesla)
5 % Fe_3O_4/PMMA	Tetra. (A) Fe^{3+}	0,34	0,00	50,2
	Oct. (B) Fe^{3+}—I	0,46	0,00	51,5
	Oct. (B) Fe^{3+}—II	0,50	−0,01	49,8
	Oct. (B) Fe^{2+}—I	0,31	−0,19	47,4
	Oct. (B) Fe^{2+}—I	1,50	1,50	40,8
	Singulete (SP)	0,33	0,00	0,00

Verwey transition is still observed at this temperature. Dénes Szabó et al. [7] assume that the transition disappears. However, at 77 K and 110 K the sample was fitted with five subspectra due to the suffering change of the magnetite structure, which causes a slight distortion, passing from a cubic symmetry to a monoclinic symmetry, Muxworthy and McCleallanda [8].

Pasternak et al. [9], Rozenberg et al. [10], reported a Tv behavior with Pressure, in which the value of T_V in absence of pressure is consistent with our results. These authors attributed the nature of this transition as due to distorted—cubic- insulater, Rozenberg et al. [10].

4 Conclusions

The sonochemical synthesis method described above provides a simple way to prepare nanoparticles of Fe_3O_4 and 5 % of Fe_3O_4/PMMA nanocomposites. For the analysis of Willamson—Hall and Scherrer equation the average grain size of the magnetite of nanoparticles is (10 ± 2)nm and the microdeformation of $4,21 \times 10^{-5}$ with respect to the magnetite in bulk, so we can say that the microstrain is very small. For Mössbauer spectroscopy the hyperfine magnetic field value (CH) is smaller than in the case of magnetite in bulk, this is due to the presence of magnetite nanoparticles. The Fe_3O_4 nanoparticles included in the PMMA showed a singlet superparamagnetic (SP) because the superparamagnetic polymer acted as a dispersant. At 77 K Mössbauer spectras of Fe_3O_4 nanoparticles were fitted with five sextets, of which, one represents the Fe^{3+} tetrahedral sites and the other four the distinction between (Fe^{2+} y Fe^{3+}) of octahedral sites. The 5 % Fe_3O_4/PMMA sample, additionally shows a singlet corresponding to the size distribution present in this sample. Regarding the transition of Verwey this is not suppressed, observed in both fitted as in the case 77 K and 110 K, suggesting a change in the crystal structure of the magnetite.

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