

FMR STUDY OF $\gamma\text{-Fe}_2\text{O}_3$ MAGNETIC NANOPARTICLES EMBEDDED IN A POLY(ETHER-ESTER) MULTIBLOCK COPOLYMERS (PEN-BLOCK-PTMO) AND (PTT-BLOCK-PTMO)

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Abstract. Samples containing $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) magnetic nanoparticles dispersed at concentrations of 0.1 wt.% and 0.3 wt.% in two different polymer matrixes, poly(ether-ester) multiblock copolymers (PEN-block-PTMO) and (PTT-block-PTMO), have been prepared. The filler was in form of solid grains with typical size of 10 nm, assembled in 10 μm agglomerates. The samples have been characterized by XRD and TEM technique. The ferromagnetic resonance (FMR) measurements have been carried out at room temperature for all four samples. It was found that the magnetic nanoparticles were homogenously dispersed in the matrixes. Intense resonance absorption line with a slightly asymmetric lineshape, arising from $\gamma\text{-Fe}_2\text{O}_3$ has been recorded. FMR spectra of the studied samples have different intensities, resonance fields and linewidths. The resonance lines were centered in $H_f=3050$ to 3270 Gs magnetic field range, while the registered linewidths were in $\Delta H=1020$ to 1090 Gs range. It has been observed that type of the matrix could play an important role in the behavior of the FMR spectra.

1. INTRODUCTION

The interest in materials based on iron oxides has been continuing since times of ancient civilizations, due to their physical properties (mainly magnetic behavior) and a broad range of applications. In the last twenty years the most interesting aspects of these materials are concerned with magnetic nanoparticles phase of these compounds because

of their extraordinary physical properties as well as potential applications in nanotechnology. An extensive literature on iron-oxide nanostructures and their nanocomposites attests to vast technological importance of these materials, e.g. [1-8]. Polymers or copolymers with magnetic fillers (nanocomposite materials) are finding a widening range of applications. Magnetic nanoparticles embedded in the above matrices are providing a lot of

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new information about critical phenomena in the underlying structures [2,4,9-12]. In addition, such materials have made important contributions to fundamental studies in nanoscale physics such as quantum tunneling of magnetization, spin reversal mechanisms in single-domain particles and quantum size effects [13-16]. Temperature dependence of the ferromagnetic resonance (FMR) spectra of $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) magnetic nanoparticles embedded at low concentration in copolymer have shown a strong influence on the matrix freezing processes and on the magnetic interactions between nanoparticles [12]. Thus a new sensitive method for study of a wide range of interesting properties of different matrices at the nanolevel is possible. Room temperature FMR investigation of copolymer matrices with embedded magnetic nanoparticles at different concentrations has shown a large diversity between them [11]. It is believed that FMR could provide a simple method of characterization of the materials containing magnetic nanoparticles.

In this paper we report preparation of polymer samples containing $\gamma\text{-Fe}_2\text{O}_3$ magnetic nanoparticles dispersed at concentrations of 0.1 wt.% and 0.3 wt.% and their FMR study at room temperature. Two kinds of polymer matrices were used: multiblock poly(ether-ester) copolymer (PEN-block-PTMO) and (PTT-block-PTMO). Magnetic properties of these samples will be investigated and analyzed.

2. EXPERIMENTAL

The $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (with an average diameter of 10 nm) in an agglomerate state have been used to prepare two kinds of polymer composites by "in situ" synthesis. Nanoparticles were initially deagglomerated and dispersed in ethylene glycol (EG) and trimethylene glycol (n-propylene glycol, PG) in concentrations 1 wt.% and 3 wt%.

2.1. Preparation of nanocomposites based on a poly(ether-ester) multiblock copolymer (PEN-block-PTMO).

The PEN-block-PTMO copolymer with $\gamma\text{-Fe}_2\text{O}_3$ was prepared by melt polycondensation of dimethyl 2,6-naphthalenedicarboxylate (DMN), ethylene glycol (EG), and poly(tetramethylene ether) glycol (PTMEG) in the presence of zinc acetate and antimony oxide as catalysts and phenolic antioxidant IRGANOX 1010 (Ciba Geigy) as stabilizers.

In the first step $\gamma\text{-Fe}_2\text{O}_3$ in the ethylene glycol were grinded and stirred for 5 min at 20000 rpm. In the second step the dispersion was sonicated for 5 min (Sonoplus – Homogenissator HD 2200). The first step of dispersing and the second step were repeated six times. Finally, the system has been dispersed for 30 min to ensure stable distribution of $\gamma\text{-Fe}_2\text{O}_3$ in the glycol matrix. Subsequently, all substrates were introduced into the reactor, were the two-stage process of multiblock poly(ether-ester) copolymer (PTMO-block-PEN) synthesis proceeded with continuous mixing.

In the first stage, the trans-esterification process of DMN with EG was carried out under atmospheric pressure in the temperature range of 150-190 °C. The progress of the reaction was monitored by the amount of distilled methanol in reaction relative to the theoretical amount. In the second stage, the trans-esterification of di(2-hydroxyethylene) naphthalate with PTMEG and the polycondensation were performed. The process of polycondensation proceeded at 200-280 °C under a pressure of 0.1 hPa and it was carried out until the desirable torque value was achieved. The polymer composite filled with $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles was extruded from the reactor by compressed nitrogen in the form of a filament. The obtained in this way sample designated as I contains 0.1% magnetic nanofiller, while sample designated as I' contains 0.3% nanofiller.

2.2. Preparation of nanocomposites based on a poly(ether-ester) multiblock copolymer (PTT-block-PTMO)

The PTT-block-PTMO copolymer with $\gamma\text{-Fe}_2\text{O}_3$ was prepared by melt polycondensation of dimethyl terephthalate (DMT), n-propylene glycol (PG), and poly(tetramethylene ether) glycol (PTMEG) in the presence of tetrabutyl orthotitanate as catalyst and a IRGANOX 1010 as stabilizer. In a first step, the PG and $\gamma\text{-Fe}_2\text{O}_3$ were grinded and stirred for 5 min at 20000 rpm. In the second step, the dispersion was sonicated for 5 min (Sonoplus – Homogenissator HD 2200). These two steps were repeated six times. Finally, the system has been dispersed for 30 min. to ensure homogeneous distribution of $\gamma\text{-Fe}_2\text{O}_3$ in the glycol matrix. Subsequently, all substrates were introduced into the reactor, were the two-stage process of multiblock poly(ether-ester) copolymer (PTMO-block-PTT) synthesis proceeded with continuous mixing.

In the first stage, the trans-esterification process of DMT with TG was carried out under atmospheric

pressure in the temperature range of 150-190 °C. The progress of the reaction was measured by the amount of distilled methanol in reaction relative to the theoretical amount. In the second stage, the trans-esterification of di(2-hydroxytrimethylene) terephthalate with PTMEG and the polycondensation were performed. The process of polycondensation proceeded at 200-260 °C under the pressure of 0.1 hPa and it was carried out until the desirable torque value was achieved. The polymer composite filled with γ -Fe₂O₃ nanoparticles was extruded from the reactor by compressed nitrogen in the form of a filament. The obtained in this way sample designated as II contains 0.1 wt.% magnetic nanofiller, while sample designated as II' contains 0.3 wt.% nanofiller.

Ferromagnetic resonance measurements were carried out on a conventional X-band ($\gamma=9.5$ GHz) Bruker E 500 spectrometer with 100 kHz magnetic field modulation. The measurements were performed at room temperature. A square-shaped sample of 3.5×3.5 mm² cut out from a polymer sheet was attached to a sample holder made of a quartz rod 4 mm in diameter. The sample holder was accommodated in the center of the TE₁₀₂ cavity, i.e., at local maximum of the microwave magnetic component H_1 and in the nodal plane of the electric component E_1 . Prior to the measurements, samples have been magnetized by a steady magnetic field of 15 kGs to saturate any existing domain structure.

3. RESULTS AND DISCUSSION

Scherrer equation has been used to estimate an average size of γ -Fe₂O₃ magnetic nanoparticle. The calculated average size of a nanoparticle from the X-ray line broadening was about 10 nm. The SEM (Scanning Electron Microscopy) has been used to determine morphology of the prepared samples. It was observed that the magnetic nanoparticles were organized in agglomerates with an average length of about 10 μ m. For magnetic nanoparticles kept in a suspension the SEM technique confirmed that their dispersion in a polymer was homogenous.

Fig. 1 presents the FMR spectra of all four samples registered at room temperature. To check on the level of homogeneity of nanoparticles in a given polymer, few different parts of a large polymer filament were studied by the FMR method. The calculated FMR parameters from these different parts were the same within the experimental errors, proving a very good homogeneity of nanofiller. Although slightly asymmetrical and very intense line was registered for all four samples, the observed FMR spectra were different and strongly dependent on concentration of magnetic nanoparticles as well as on the kind of polymer matrix. Additionally, samples have been frozen for a short time to liquid nitrogen temperature. After reheating these samples back to room temperature their FMR spectra did not show any differences with thermally non-treated samples.

Table 1. The obtained values of the linewidth ΔH , resonance field H_{res} , relative integrated intensity I_{int} and effective γ -factor for γ -Fe₂O₃ nanoparticles embedded in polymer matrixes (samples I, I', II, and II') and, for comparison, embedded in a multiblock poly(ether-ester) copolymer (PET-block-PTMO) matrix (last four lines) [11].

Sample designation	Resonance field H_{res} [Gs]	Linewidth ΔH [Gs]	Relative intensity I_{int}	g_{eff}
Sample I (0.1%)	3260(1)	1020(5)	1.0	2.072
Sample I' (0.3%)	3253(1)	1070(5)	3.0	2.078
Sample II (0.1%)	3209(1)	1148(5)	5.6	2.105
Sample II' (0.3%)	3225(1)	1155(5)	5.2	2.094
0.1% solid	2992(10)	1213(5)	1.0	2.259
0.1% solution	3222(10)	1079(5)	6.3	2.098
0.3% solid	3073(10)	1376(5)	3.0	2.199
0.3% solution	3272(10)	1274(5)	13.6	2.066

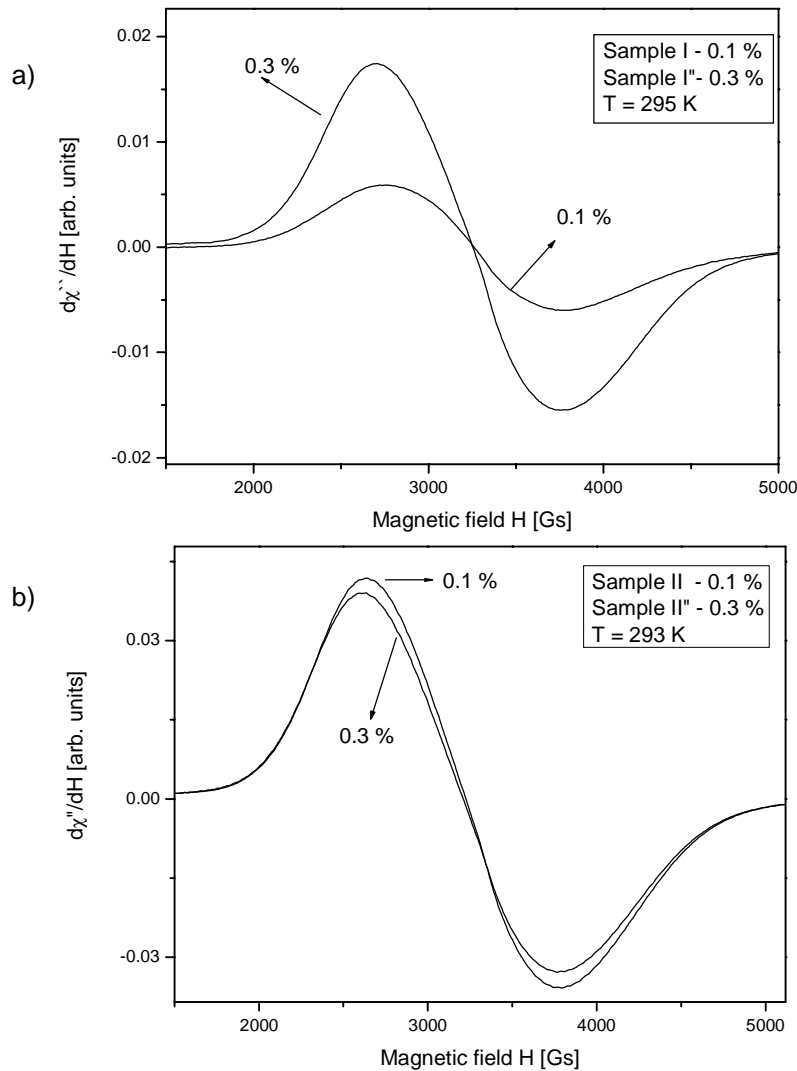


Fig. 1. FMR spectra of four investigated samples at room temperature (a) samples I and I', and (b) samples II and II'.

The FMR spectra of maghemite nanoparticles could be properly characterized by using the following three parameters: H_L , H_R , and $H_{res} = (H_L + H_R)/2$, where they are positions of the left peak, the right peak of the line and the effective resonance field, respectively [2]. Table 1 shows the values of the resonance field H_{res} , the peak-to-peak linewidth $\Delta H = H_R - H_L$ and the relative integrated intensities $I_{int} = A \cdot \Delta H^2$ (where A is the line amplitude) for all studied samples. The obtained values of the resonance field indicate that the agglomerates are of very small sizes and we have to do practically with the superparamagnetic resonance. Comparison of the resonance fields obtained for samples I and II but differing in concentration shows that they are slightly shifted by -7 Gs and 16 Gs, respectively. Also the

linewidths display differences equal to 50 Gs and 7 Gs, respectively (see Table 2). The intensity is greater for the sample with greater concentration of the $\gamma\text{-Fe}_2\text{O}_3$ filler for samples I but an opposite effect is observed for both samples II (Fig. 1, Table 1). These changes with increasing concentration of magnetic nanofillers are smaller than observed for the multiblock poly(ether-ester) copolymer (PET-block-PTMO) [11]. Increasing filler concentration shifts the resonance line towards higher magnetic fields while the linewidth and the intensity are increasing. The ratio of the integrated intensities is close to the 3 for samples I, what suggests that the magnetic interactions has not changed essentially. The integrated intensities are very close for both samples II despite the threefold

difference in maghemite concentration. Thus kind of matrix is also very important for the interactions between magnetic nanoparticles (Tables 1 and 2). Usually for greater agglomerate a stronger magnetic entity is formed and its FMR spectrum displays a strong shift of the resonance line towards lower magnetic fields (down to near zero field) and the line is broadened considerably [17]. For the γ -Fe₂O₃ nanoparticles, with sizes \sim 2.5 nm, embedded in a polyethylene, the FMR line with a linewidth of $\Delta H=400$ Gs, centered at $g\sim 2.07$, has been recorded [2]. Almost similar parameters have been obtained for greater in size particles dispersed in a sol-gel silicate glass [17], and the resonance field is similar to what has been registered for samples I and I'. The simulation of the FMR spectra of iron oxide in non-magnetic matrices has shown that the intensity and the linewidth increases strongly with increasing size of the nanoparticles. For nanoparticles with an average size of 10 nm the FMR spectrum was almost the same as that obtained in this work [18].

If the ferromagnetic nanoparticles are not well separated, the spin of a nanoparticle is subjected to the following total magnetic field:

$$H_{\text{tot}} = H_{\text{dem}} + H_{\text{app}} + H_{\text{dip}} + H_{\text{dip}}', \quad (1)$$

where the first term represents the demagnetization field, the second term the applied external magnetic field, the third term the dipole field from the neighboring nanoparticles and the last term the dipole-dipole interaction between agglomerates. The collective spin of agglomerates is affected by an additional magnetic field, which broadens the FMR line and shifts it towards lower or higher magnetic fields. The magnetic resonance condition in that case could be written as:

$$h\nu = g \mu_B H_{\text{tot}}, \quad (2)$$

where h is Planck constant, ν is macrowave frequency, and μ_B is Bohr magneton. For magnetic nanoparticles of smaller sizes the last term in Eq. (1) is dominating. Using a simplified approach it could be shown that the magnetic field acting on the magnetic centers is given by the relation:

$$H_{\text{dip}} = \sum_i [(3\cos^2\theta_i - 1)/r_{ij}^3] \mu_i, \quad (3)$$

where θ_i is an angle between magnetic momentum and applied magnetic field, r_{ij} is the distance between magnetic center and other agglomerates, and μ_i is magnetic momentum of agglomerates. It is supposed that the main factor responsible for the observed differences between different ma-

Table 2. The relative position of resonance field to $g=2$ and relative linewidths (relative to sample I). For comparison, the same parameters have been calculated for maghemite nanoparticles embedded in a multiblock poly(ether-ester) copolymer (PET-block-PTMO) matrix and are given in the last four lines [11].

Sample designation	ΔH_{res} [Gs]	$\delta\Delta H$ [Gs]
Sample I (0.1%)	117	0
Sample I' (0.3%)	123	50
Sample II (0.1%)	168	128
Sample II' (0.3%)	152	135
0.1% solid	385	193
0.1% solution	155	59
0.3% solid	304	356
0.3% solution	105	254

trixes is the change of the geometrical coefficient, $f=(3\cos^2\theta_i - 1)$, and if an average angle $\langle\theta\rangle$ is introduced, than:

$$H_{\text{dip}} = (3\cos^2\langle\theta\rangle - 1) \sum_i \mu_i / r_{ij}^3. \quad (4)$$

Now it will be assumed, for simplicity, that the magnetic momentum and concentration of agglomerates are the same in different matrixes. Using data from Table 2, we can obtain: $\langle f \rangle = 117(\text{sample I}) / 168(\text{sample II}) \sim (3\cos^2\langle\theta\rangle - 1) / (3\cos^2\langle\theta+\Delta\theta\rangle - 1)$. From this estimation is seen that the angle $\langle\theta\rangle$ is smaller than $\langle\theta+\Delta\theta\rangle$. It follows that in the PTT-block-PTMO copolymer matrix the magnetic centers are more easily oriented by an external magnetic field than in the other copolymer. The magnetic dipole interactions are stronger for sample II and the increased concentration of dipoles could influence essentially the integrated intensity what is observed for sample II'. The new parameter f could be a usefully characteristic of a given matrix but more FMR measurements are needed to relay on it.

In conclusion, intense FMR spectra (similar to superparamagnetic spectra) were recorded for all four samples of γ -Fe₂O₃ in two polymer matrixes and the positions of resonance field, linewidths and the intensities have shown a strong dependence on filler concentration as well as on type of polymer matrix. The internal magnetic field is signifi-

cantly greater in samples with greater degree of agglomeration. The increasing magnetic nanoparticles contents could ensure a stronger magnetic dipole interaction which in certain types of matrix (with greater mechanical hardness) could provide that the FMR spectra are changing in an unusual way.

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