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FMR STUDY OF MAGNETIC NANOPARTICLES EMBEDDED IN NON-MAGNETIC MATRICES

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Samples containing small amounts of magnetic nanoparticles (α-Fe/C, Fe_3C/C, γ-Fe_2O_3, Fe_3O_4 and Ni/C) embedded in various non-magnetic matrices, such as polymer, concrete or wax, have been studied by using the ferromagnetic resonance (FMR) method in the 4–300 K temperature range. Generally, an intense resonance line was recorded at all temperatures. All FMR parameters strongly depends on temperature, reflecting reliance on dynamic processes influenced by concentration of magnetic nanoparticles, agglomeration state, type of matrix characterized by its physical properties (presence of critical points) and the kind of used fine particles. The temperature gradient of the resonance field, ($\Delta H_r/\Delta T$), was introduced that is connected with reorientation processes of the correlated spin system. The value of this parameter usually increases over one order of magnitude in low temperatures range and straightforwardly shows matrix's phase transitions, e.g. to a spin glass state or other freezing processes present in the matrix. It is believed that after large statistics of experimental data is collected it could be a useful and simple method of characterization of different type of materials.

INTRODUCTION

The oxides containing 3*d* transition metals with their strongly correlated spin system has been the subject of intense studies for many years. Electronic and magnetic properties of fine magnetic particles embedded at low concentration in different non-magnetic matrices could be used for manufacturing of new generations of functional materials (Dorman *et al.*, 1997; Koksharov *et al.*, 2000; Skumryev *et al.*, 2003; Berry & Curtis, 2003; Dutta *et al.*, 2004; Guskos *et al.*, 2006c; Guskos *et al.*, 2008e; Guskos *et al.*, 2008f; Guskos *et al.*, 2008g; Zezin *et al.*, 2007; Castel *et al.*, 2007; Tang *et al.*, 2008; Maryniak *et al.*, 2009). Small amount of iron or iron oxide magnetic nanoparticles embedded in a non-magnetic matrix could be a very sensitive indicator of the magnetic dipole-dipole interaction (Koksharov *et al.*, 2000; Guskos *et al.*, 2006c; Guskos *et al.*, 2008e; Guskos *et al.*, 2008f; Guskos *et al.*, 2008g; Maryniak *et al.*, 2009; Guskos *et al.*, 2009h). It was shown that small amount of nanoparticles could shift significantly the melting and polymer-glass transitions temperatures (Maryniak *et al.*, 2009; Majszczyk *et al.*, 2006; Guskos *et al.*, j). The resonance field (H_r) *vs.* temperature dependence ($\Delta H_r/\Delta T$ gradient) has shown a very intense change which could be associated with the spin reorientation processes inside the matrix. Interestingly, for similar matrices a drastically different behavior was observed for different kind of magnetic nanoparticles (Narkiewicz *et al.*, 2004; Guskos *et al.*, 2005a; Guskos *et al.*, 2005b; Guskos *et al.*, 2006d). Theoretically it could be described by using magnetization dynamics in Landau-Lifshitz-Gilbert formulation (Dudek *et al.*, 2008).

The aim of this report is to review works of our group devoted to the study of small concentration of magnetic nanoparticles used as filler in different non-magnetic matrices. We are interested in magnetic properties of the resulting nanocomposites by registering ferromagnetic resonance (FMR) spectra and static magnetization at various temperatures. The concentration dependence of magnetic properties at different temperatures could be very useful for better understanding of the reorientation processes and matrix influences *via* magnetic dipole-dipole interaction at the nanosize scale. These experimental data could also be very valuable for those working in application of the functional materials.

RESULTS AND DISCUSSION

Figures 1, 2, 4 and 6 present FMR spectra of small amounts of magnetic nanoparticles in different agglomerated states in non-magnetic matrices (in this case polymers).

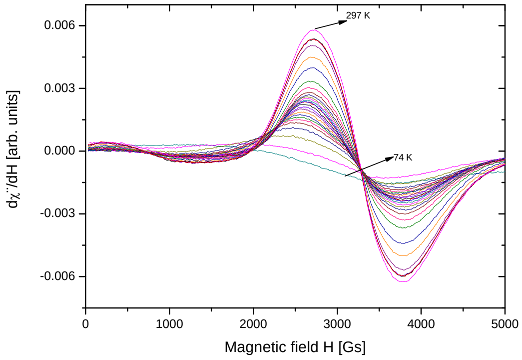

Fig.1. FMR spectra of γ-Fe_2O_3 embedded in PTT-block-PTMO copolymer at concentration of 0.1 %

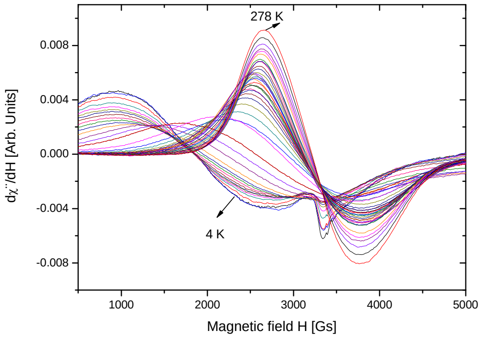

Fig.2. FMR spectra of γ-Fe_2O_3 embedded in PTT-block-PTMO copolymer at concentration of 0.3%.

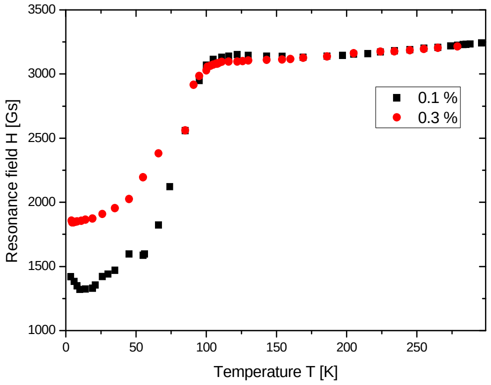

Fig.3. Temperature dependence of the resonance field $H_r(T)$ of γ-Fe_2O_3 embedded in PTT-block-PTMO copolymer at concentration of 0.1% and 0.3%.

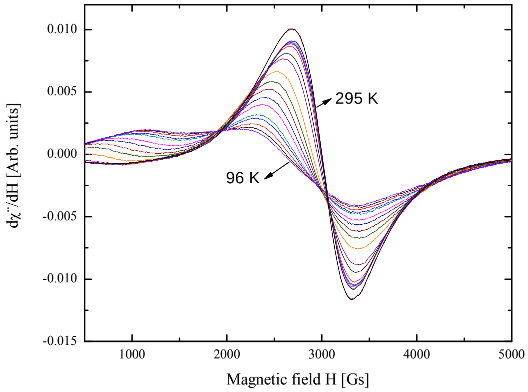

Fig.4. FMR spectra of 0.25% Ni/C in PBT-block-PTMO copolymer.

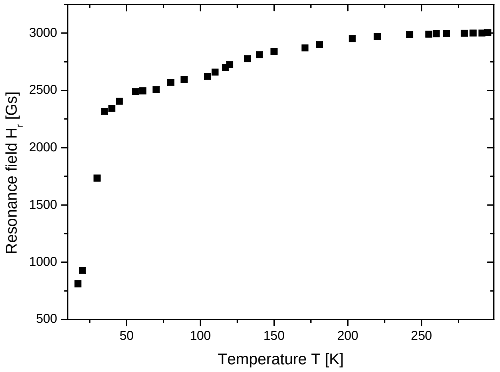

Fig.5. Temperature dependence of the resonance field $H_r(T)$ for 0.1%Fe_3C/C in PET-block-PTMO copolymer.

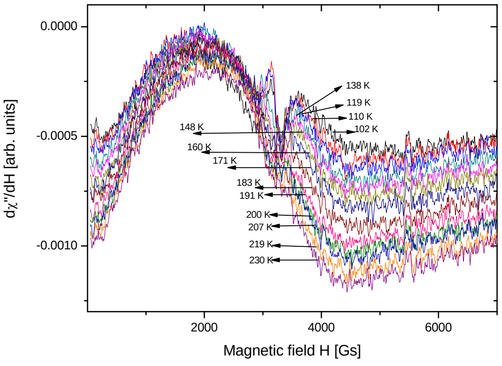

Fig.6. FMR spectra of 0.1%Fe_3C/C in PET-block-PTMO copolymer.

Strong magnetic correlated spin system in an agglomerated state (α-Fe, Fe_3C) produces a broad, intense and strongly shifted FMR line (Fig.6). The ferromagnetic coupled system γ-Fe_2O_3 in a different agglomerated state displays a very intense resonance FMR line (Fig.1 and 2) with about two times smaller linewidth that shifts with decreasing temperature what is especially evident at low temperatures (Fig.3). The temperature dependence of the FMR spectrum is essentially different for small and large in size agglomerates. The very small concentration of magnetic nanoparticles Ni/C (Ni is covered by carbon) has shown a very intense line with about two times smaller value of the linewidth than sample with γ-Fe_2O_3. A strongly shifted resonance line is seen at low temperatures (Fig.3 and Fig.5). The blocking temperature is higher for samples with smaller sizes of agglomerates of magnetic nanoparticles. It could be deduced from the temperature dependence of the *dc* magnetic susceptibility observed for small values of applied magnetic field (Guskos *et al.*, 2006c; Guskos *et al.*, 2008e; Guskos *et al.*, 2008f; Guskos *et al.*, 2008g).

In this report we concentrate on newly introduced FMR parameter, $\Delta H_r/\Delta T$, which plays a very important role in the reorientation processes of correlated spin systems. The resonance condition strongly depends on internal magnetic field formed by a coupled spin system. The resonance condition is the following: $h\nu = g\mu_B(H_0 - H')$, where $H' = H_{dem} + H_{dip}$(inter-agglomerate)$+H_{dip}$(intra-agglomerate). Macroscopic size of an agglomerate produces the gradient $\Delta H_r/\Delta T \sim 0.08$ mT/K (Guskos *et al.*, 2010i) which is similar to the value measured for assemble of many smaller agglomerates in the high temperature range (see Table 1). On the other hand, very small agglomerates of Ni have produced greater value and the dipole interaction that could influence the value of an internal magnetic field. The same character is observed for low temperatures (Table 1). These processes could be very important in changing the physical properties of a matrix, especially they could shift the critical point in the polymer, e.g. melting, and α-, β-, γ-relaxations (Maryniak *et al.*, 2009; Majszczyk *et al.*, 2006). Magnetic nanoparticles at small concentration could form an additional bonding term which might shift the melting point to higher temperatures. They could also change significantly the mechanical properties of concrete (Blyszko *et al.*, 2008).

Table 1. The values of the $\Delta H_r/\Delta T$ for Ni/C in PBT-block-PTMO(I) and Fe_2O_3 in PET-block-PTMO (II) and PTT-block PTMO (III) (for solution and solid magnetic nanoparticles with greater sizes of agglomerates - Fe_2O_3).

Sample designation	$\Delta H_r/\Delta T_{(<160\ K),}$ [mT/K]	$\Delta H_r/\Delta T_{(160-95\ K),}$ [mT/K]	$\Delta H_r/\Delta T_{(70-50\ K),}$ [mT/K]	$\Delta H_r/\Delta T_{(>41\ K),}$ [mT/K]	Reference
0.1% Ni/C-I	0.13(1)	0.95(1)	0	6.56(2)	[11]
0.25% Ni/C-I	0.12(1)	0.14(1)	0.34(1)	6.15(2)	[13]
0.1% Fe_2O_3-II	0.002(1)	0.002(1)	0.08(1)	0.08(1)	[6]
0.3% Fe_2O_3-II	0.13(1)	0.13(1)	0.65(1)	0.65(1)	[6]
0.1% -Fe_2O_3-II	0.007(3)	0.007(3)	0.09(1)	0.09(1)	[6]
0.3% -Fe_2O_3-II	0.07(1)	0.07(1)	0.79(1)	0.79(1)	[6]
0.1%- Fe_2O_3-III	0.058(5)	0.058(5)	3.5(1)	0.98(7)	[6]
0.3%- Fe_2O_3-III	0.078(5)	0.078(5)	1.9(2)	0.57(3)	[6]

In summary, the FMR method could be a very important tool for characterization of different materials. Addition of small amount of magnetic nanoparticles could change the physical properties of a doped matrix. This method could be more useful if large sets of experimental data are collected.

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