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FMR study of γ-Fe_2O_3 magnetic nanoparticles in a multiblock poly(ether-ester) copolymer matrix

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Four samples containing γ-Fe_2O_3 magnetic nanoparticles dispersed at a concentration of 0.1 % (samples I and I′) and 0.3 % (samples II and II′) in a polymer matrix have been prepared. The polymer filler was in two forms: as solid-state grains (samples I and II) and as a liquid solution in trichloromethane (samples I′ and II′). The typical size of the magnetic nanoparticles was 10 nm. The samples were characterized by XRD and TEM spectroscopy. Ferromagnetic resonance (FMR) measurements were carried out at room (RT) and liquid nitrogen (LNT) temperatures for all four samples. An intense resonance absorption line from γ-Fe_2O_3 was recorded, with a slightly asymmetric line shape. The FMR spectra at RT and LNT are almost the same, as could be expected for the composite matrix. For samples II and II′, the resonance lines are centred at H_r = 3039(10) Gs and H_r = 3197 (10) Gs, respectively, with linewidths of ΔH = 1289(5) Gs and ΔH = 1364(5) Gs, respectively. For samples I and I′, the following values of resonance line parameters were obtained: H_r = 3172(10) Gs for sample I′, and H_r = 2958(10) Gs for sample I, with linewidths of ΔH = 1279(5) Gs and ΔH = 1200(5) Gs, respectively. In both cases the resonance field for samples obtained from a solid state filler is shifted to lower magnetic fields as compared to samples made from a suspension filler, which suggests stronger ferromagnetic interactions in these materials.

Key words: *magnetic nanoparticle; ferromagnetic resonance*

1. Introduction

Iron oxides, especially maghemite (γ-Fe_2O_3), in the form of nanoparticles, are very interesting materials not only due to their potential applications (high density mag-

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netic recording [1]), but also due to the possibility of rich fundamental research in magnetism, e.g. superparamagnetism or the quantum tunnelling of magnetization [2–4]. Nanocomposite materials with magnetic fillers are gaining a widening range of applications [5]. For example, magnetic nanoparticles embedded in polymer matrices have excellent potential for electromagnetic devices like those used for electromagnetic interference suppression [6]. FMR measurements give information about local magnetic properties and, in principle, about the nature of spin–spin interactions, the distribution of internal fields, or about spin–spin correlation [7–9].

The aim of this paper is to report the preparation of samples of γ-Fe_2O_3 magnetic nanoparticles dispersed at a concentration of 0.1 % and 0.3 % in a polymer matrix of (PTMO–block–PET), and to present the results of their characterization by the SEM and FMR methods.

2. Experimental

Two forms of γ-Fe_2O_3 nanoparticles were used to prepare the polymer composite: one as a solid powder (samples designated as I and II) and the other as a suspension of nanoparticles dispersed in trichloromethane so as to prevent phase separation (samples designated as I′ and II′).

The basic components used in the synthesis were: ethanediol (ethylene glycol), purchased from BASF (Germany); dimethyl terephthalate (M_n = 194 g/mol), supplied by Elana S.A. Toruń (Poland); α,ω-dihydroxy-polyoxytetramethylene (M_n = 970 g/mol), produced by Du Pont (USA).

The nanocomposites were obtained by *in situ* polycondensation in a molten state, where nanoparticles were introduced into the polymer during its synthesis. The whole process was carried out in an acid resistant steel reactor equipped with a controlled heating system and a horseshoe stirrer with perpetual torque measurement. As the polymer matrix, a multiblock poly(ether-ester) copolymer (PEE) was used. In the first step of preparation, an appropriate amount of γ-Fe_2O_3 nanoparticles were dispersed in ethanodiol (ED) by means of shear force (ultra-high speed stirrer) and ultrasonication (Sonoplus-Homogenisator), in order to ensure a homogeneous distribution of the nanofiller in the matrix. All substrates were introduced into the reactor, in which a two-stage process of PEE synthesis was accompanied by continuous mixing. In the first stage, the transesterification of dimethyl terephthalate (DMT) with ED under atmospheric pressure and at a temperature between 150 and 190 °C was carried out. The progress of the reaction was measured by the amount of distilled methanol in relation to the theoretical amount. In the second stage, the transesterification of di(2-hydroxy-tetramethylene) terephthalate with α,ω-dihydroxy-polyoxytetramethylene (PTMEG) and polycondensation were performed. Polycondensation proceeded at 200–260 °C under the pressure of 0.1 hPa and was carried out until the desirable torque value of the stirrer was achieved. The polymer composite filled with γ-Fe_2O_3 nanoparticles was extruded from the reactor by compressed nitrogen in the form of a filament.

Four samples were synthesized in the same way. The samples I and I′ contained 0.1 wt. % of the nanofiller, and samples II and II′ contained 0.3 wt. % of the nanofiller. The nanofiller used in samples I and II was in the form of a solid powder, and in the samples I′ and II′ it was in the form of a suspension of γ-Fe_2O_3 nanoparticles in trichloromethane.

The nanomaterials were prepared using nanocrystalline iron oxide (γ-Fe_2O_3) as the starting material, which was synthesized by the fusion of magnetite with small amounts of Al_2O_3 and CaO (3 wt. %).

After reduction, nanocrystalline iron was obtained, while the promoter oxides remained in the oxidised states. The role of the additives (CaO, Al_2O_3) was to stabilise a well-developed nanocrystalline iron oxide structure. To avoid oxidation, the sample was subsequently passivated with nitrogen containing traces of water vapour. X-ray diffraction (XRD) measurements were then performed on a Philips X Pert powder diffractometer using $CoK_{\alpha1}$ radiation. The mean size of iron crystallites was estimated from the width of the main reflections of the diffractogram using the Scherrer equation, which yielded an average value of 10 nm. The specific surface area and the pore distribution of the carburised sample were measured using low-temperature nitrogen adsorption (Micromeritics, ASAP), yielding 180 m^2/g and 5.5 nm for the specific surface area and the average pore diameter, respectively. The analysis of the SEM images showed an almost homogenous distribution of fine graphite fibres with similar shape and size and with diameters below 1 μm.

Ferromagnetic resonance measurements were carried out using a conventional X-band (v = 9.43 GHz) Bruker E 500 spectrometer, with 100 kHz magnetic field modulation. The measurements were performed at room temperature. A square-shaped 3.5×3.5 mm^2 sample, 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 centre of the TE_{102} cavity, i.e., at the local maximum of the microwave magnetic component H_1, and in the nodal plane of the electric component E_1. Prior to measurements, the samples were magnetized with a steady magnetic field of 16 kG in order to saturate any domain structure.

3. Experimental results and discussion

The crystalline sizes of the magnetic phases grown by the reduction of γ-Fe_2O_3 powder were estimated from the broadening of prominent diffraction lines using the Scherrer equation: $d = 0.89\ \lambda/\beta\cos\theta$, where λ, β, θ and d are the wavelength of radiation, line broadening, angle of diffraction, and particle size, respectively. The average size of magnetic particle of γ-Fe_2O_3, estimated from X-ray line broadening, was about 10 nm.

The morphologies of the prepared samples and magnetic powders were studies by Scanning Electron Microscopy (SEM). Figure 1 presents SEM pictures of solid-state γ-Fe_2O_3 magnetic nanoparticles with concentrations of 0.1 % and 0.3% and of solution (0.1%) in a polymer matrix, respectively. The magnetic nanoparticles are organized in agglomerates of particles having a maximum length of about 10 μm for sample I (Fig. 1a) and 20 μm for sample II (Fig. 1b). For magnetic nanoparticles kept in suspension and embedded in the polymer, their homogenous dispersion in the matrix was observed by the SEM technique (Fig. 1c).

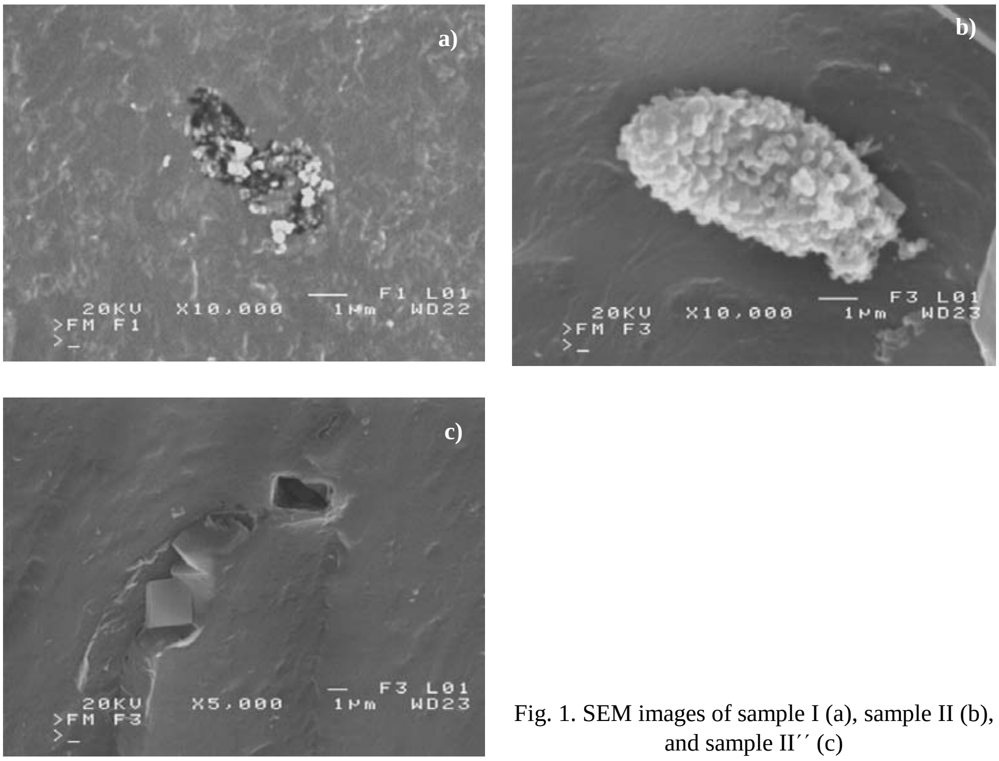

Fig. 1. SEM images of sample I (a), sample II (b), and sample II′′ (c)

Figure 2 presents the FMR spectra of all four samples. A slightly asymmetrical and intense line is observed for the samples. For all investigated samples, the recorded FMR spectra were similar, the resonance fields roughly the same and magnetic nanoparticles in aggregates or agglomerates were dispersed homogeneously in polymer matrices. Additionally, magnetic nanoparticles in nanocomposites were frozen to liquid nitrogen temperature. In this case, the FMR spectra of non-frozen and frozen samples did not yield any essential differences – the intensities, linewidths, and resonance fields were exactly the same.

For a proper description of the FRM spectra of γ-Fe_2O_3, the parameters H_L, H_R, and $H_{\mathrm{res}} = (H_L + H_R)/2$ have been introduced, being the left, the right peak positions of the line, and the effective resonance field position, respectively [10]. Table 1 shows the values of the peak-to-peak linewidth $\Delta H = H_R - H_L$, the positions of the resonance field H_{res}, and the relative integrated intensities $I_{\mathrm{int}} = A\Delta H^2$ (A is the peak-to-peak amplitude) for all samples. A comparison of the resonance fields obtained for samples I and II (solid state filler) with analogous fields for samples I′ and II′ shows that they are strongly shifted (over 200 Gs) and their linewidths display an opposite temperature dependences. The intensities are greater for samples obtained from γ-Fe_2O_3 filler in the form of suspension. Increasing filler concentration shifts the resonance line to higher magnetic fields, while its linewidth and intensity increase (Table 1).

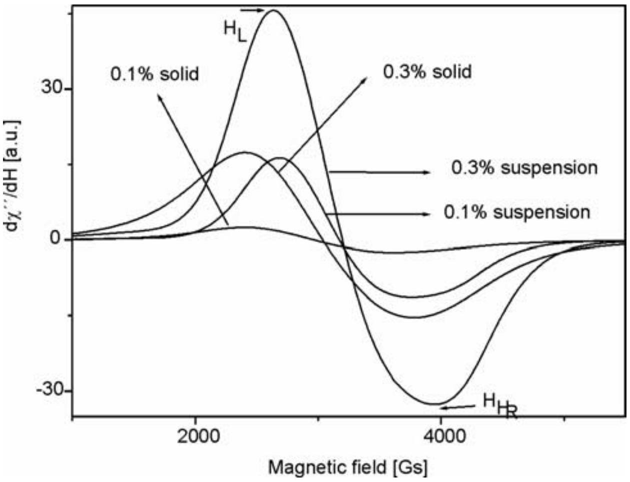

Fig. 2. FMR spectra of the investigated samples at room temperature

For γ-Fe_2O_3 nanoparticles, with sizes ~2.5 nm, embedded in polyethylene, an FMR line with the linewidth of $\Delta H = 400$ Gs, centred at $g \sim 2.07$, has been recorded [10]. A simulation of the FMR spectra for iron oxide has shown that the intensity and linewidth increase strongly with increasing nanoparticle size. For 10 nm nanoparticles the FMR spectrum is almost the same as that obtained in this work [4].

Table 1. The linewidths ΔH, resonance field H_{res}, integrated intensities I_{int}, and g-factors of γ-Fe_2O_3 nanoparticles in the polymer matrix

Sample	Resonance field H_{res} [Gs]	Linewidth ΔH [Gs]	Intensity I_{int} [a.u.]	g_{eff}
I	2992(10)	1213(5)	1.0	2.259
I′	3222(10)	1079(5)	3.0	2.098
II	3073(10)	1376(5)	6.3	2.199
II′	3272(10)	1274(5)	13.6	2.066

With decreasing temperature, the resonance field of magnetic nanoparticles is shifted to lower magnetic fields, the linewidth increases, and the integrated intensity decreases [2, 4, 7]. Samples synthesized from solid-state magnetic nanoparticles have a blocking temperature shifted toward higher values, which is opposite to that seen for samples obtained from filler in a suspension form.

If the ferromagnetic nanoparticles are not well separated, the spin of a nanoparticle is subject to the following total magnetic field [11]:

$$H_{\text{tot}} = H_{\text{dem}} + H_{\text{app}} + H_{\text{dip}} + H'_{\text{dip}}$$

where the first term represents the demagnetisation field, the second term the applied external magnetic field, the third term the dipole field originating from the neighbouring nanoparticles, and the last term the dipole-dipole interaction between aggregates. The collective spins of agglomerates could recognize an additional magnetic field, which broadens the FMR line and shifts it in the direction of lower magnetic fields.

4. Conclusions

Intense FMR spectra were recorded for all four samples of γ-Fe_2O_3 in polymer matrix. FMR studies confirmed that the agglomerates are distributed homogeneously in the polymer matrix. Cooling samples to liquid nitrogen temperature did not influence the FMR spectra. The resonance field, linewidth, and intensity strongly depend on filler concentration and on the form of the magnetic nanoparticles (solid or suspension) used to fill the polymer matrix. Solid magnetic nanoparticles more easily build conglomerates of great sizes in the polymer matrix than those being in a suspension form. The internal magnetic field is significantly greater in the former type of samples. This field decreases with increasing filler concentration; that trend is the same for samples formed by magnetic nanoparticles in a suspension form.

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