

FMR STUDY OF POLYMER COMPOSITES WITH NANOCRYSTALLINE IRON-CARBON FILLERS

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Abstract. Three kinds of nanocrystalline materials: Fe/C, Fe₃C/C, and Fe/Fe₃C have been prepared by carburization of nanocrystalline iron and characterized by using XRD and SEM methods. The nanoparticles were next applied as fillers in polymer nanocomposites using the polycondensation reaction (*in situ*) in poly(ether-ester) matrix with two different concentrations: 0.1 wt.% and 0.3 wt.%. The ferromagnetic resonance (FMR) has been applied to the study of the magnetic interactions in these nanocomposites at room temperature. FMR measurements have shown two types of spectra originating from magnetic agglomerates, the one iron carbide (Fe₃C) and the other from α -iron. New parameters are introduced to describing the FMR spectra of strongly interacting magnetic nanoparticles. The FMR spectra depend strongly on the sample preparation process as well as on the concentration of magnetic nanoparticles, which strongly influence the magnetic interactions between them.

1. INTRODUCTION

In recent years polymer nano-composites have attracted great interest, both in industry and in science, because they often exhibit remarkably improved material properties when compared with virgin polymer or conventional micro and macro-composites. This improvement can include high moduli, increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability in the case of biodegradable polymers. Magnetic nanocrystallines embedded in various matrices have been widely reported in the literature due to their diverse usage in many technological applications including catalysis, magneto-optics, magneto-sensor electronics, magneto-opti-

cal devices, etc. [1–5]. Particular attention has been paid to systems containing various magnetic nanoparticles which reveal unique mechanical, electrical, thermal and optical properties as a result of nanofiller – matrix interaction [2,3,5-8]. Nanocomposites filled with carbon nanotubes or fibers are often used in optoelectronics [9,10]. The ferromagnetic resonance (FMR) technique has been fruitfully exploited as a sensitive method for the study of magnetic nanoparticles dispersed in different non-magnetic matrices where the magnetic interaction was very intense and essentially modified the physical properties of the matrix [11-14].

This report is an account of the FMR study of magnetic nanoparticles systems: α -Fe/C, Fe₃C/C or α -Fe/Fe₃C, applied as nanofillers (at two different

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concentrations: 0.1 wt.% and 0.3 wt.%) in polymer nanocomposites produced using polycondensation reaction (*in situ*) in poly(ether-ester) matrix. The characteristic FMR spectra of the above magnetic nanoparticles in a non-magnetic matrix could supply important information about the matrix and the magnetic interaction among nanoparticles.

2. EXPERIMENTAL

The procedure of sample preparation has been described elsewhere [15]. Magnetic nanocrystalline α -Fe/C, $\text{Fe}_3\text{C}/\text{C}$, or α -Fe/ Fe_3C samples were obtained by carburisation of nanocrystalline iron with ethylene.

The mean crystallite size of iron crystallites, as determined by X-ray diffraction (Philips X'Pert equipment) and calculated using the Scherrer equation, was found equal to 17 nm.

Preparation of nanocrystalline carbon materials was performed in a thermobalance, enabling to survey the sample mass increase. Before each carburisation process all samples were reduced in the thermobalance under hydrogen flow (40 l/h), in order to remove the thin oxide passivation layer. The reduction process was carried out polythermally in rising temperature from 20 to 500 °C until the mass of the sample stabilized.

The carburisation of the samples of nanocrystalline iron was performed under ethylene (40 l/h) or ethylene – hydrogen mixture (2:38 l/h) flow, at atmospheric pressure, at a constant temperature in the range of 370 – 550 °C. Three kinds of samples were prepared:

- 1) $\text{Fe}_3\text{C}/\text{C}$ samples were obtained by carburization of nanocrystalline iron under ethylene at 550 °C.
- 2) α -Fe/ Fe_3C samples were obtained by carburization under ethylene – hydrogen mixture at 370 °C. The process led to an increase of mass equal to 0.04 gC/gFe, which corresponds to about half of value of the mass increase necessary to obtain the stoichiometric Fe_3C (0.072 gC/gFe).
- 3) To prepare the α -Fe/C sample nanocrystalline iron was initially carburised under ethylene – hydrogen mixture at 400 °C to obtain cementite (Fe_3C) and carbon deposit. The sample was next reduced under hydrogen at 450 °C. In this way cementite was reduced to iron and the resulting sample contained only iron and carbon.

The phase composition of the samples after the carburization or carburization and hydrogenation processes was determined using XRD analysis with CuK_α radiation (X'Pert, Philips).

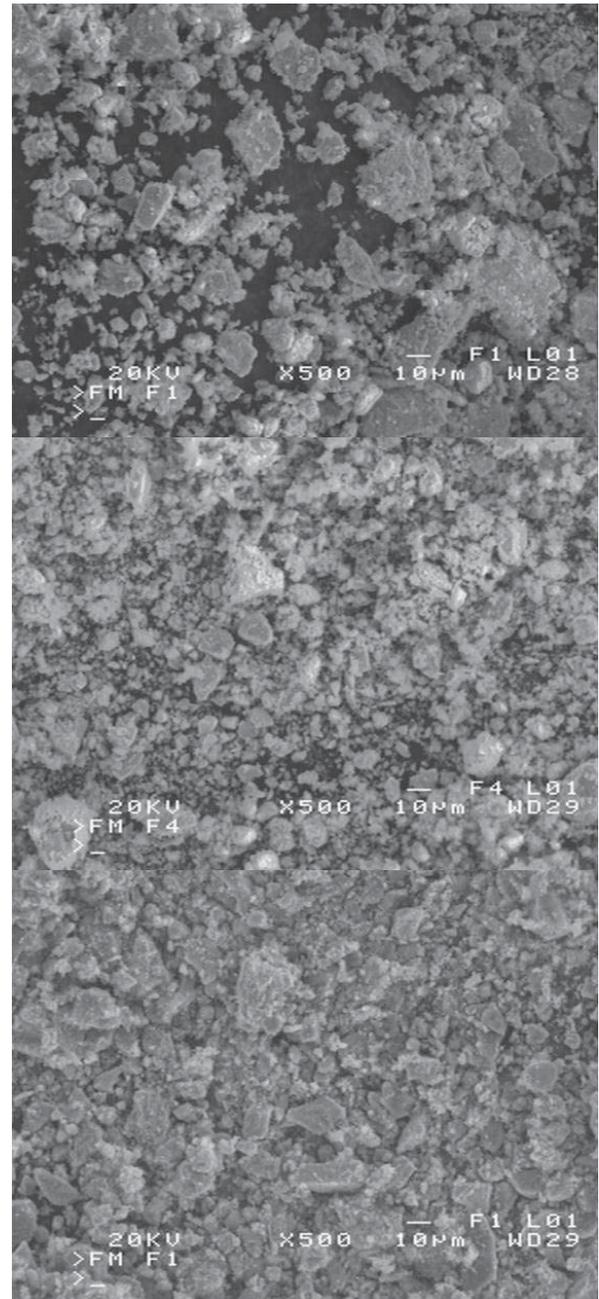


Fig. 1. SEM pictures of used nanofillers: (a) α -Fe/C; (b) α -Fe/ Fe_3C ; (c) $\text{Fe}_3\text{C}/\text{C}$.

For the preparation of polymer nano-composites the following substrates have been used:

- dimethyl terephthalate (DMT) supplied by ELANA S.A., Poland,
- ethylene glycol (ED) supplied by BASF, Germany
- and α,ω -dihydroxy-polytetraoxymethylene (PTMEG) from Du Pont, USA.

The polymer nanocomposite samples containing nanocarbon materials were obtained by an *in situ* polycondensation method. The nanofillers have been introduced into the reaction mixture during the synthesis of multiblock poly(ether-ester) copolymers based on poly(ethylene terephthalate) (PET) and polyoxytetramethylene (PTMO).

A given amount of filler (appropriate to obtain a concentration of 0.1 or 0.3 wt.% of filler in the composite) was first dispersed in ethanediol (ED) using mixing tools: ultrasonic (Homogenisator HD 2200, Sonoplus) and high – speed (Ultra-Turrax T25, > 20000 s⁻¹) stirrers. The suspension thus obtained was next introduced into the polycondensation reactor (Autoclave Eng. Inc., USA). The detailed description of the whole process of nanocrystalline carbon materials-polymer nanocomposites preparation the detailed description of the synthesis has been presented previously [11]. The polymer composite samples were characterized using scanning electron microscopy (SEM - DSM-962, Leo Zeiss Jena).

FMR absorption spectra were recorded using a conventional X-band spectrometer BRUKER type E 500, with a magnetic field modulation of 100 kHz. The magnetic field was scaled with a usual NMR technique. As usual, the field derivative of the microwave power absorption (dP/dH) was recorded as a function of dc field. The resonance field, H_r , was defined as the value of the applied field, at which the dP/dH curve intersects a baseline. The intensity of the FMR signal was calculated by double integration of the FMR curves. The sample, containing about 10 mg of polymer, was placed into 5 mm diameter quartz tubes.

3. RESULTS AND DISCUSSION

The objective of using the *in situ* poly-condensation as a method of polymer nanocomposites preparation was to obtain a homogeneous distribution of nanofiller in polymer system by dispersing it in the liquid substrate. The whole polymerisation process was carried out in the same way as in the case of undoped polymer. The SEM pictures showed agglomerates of magnetic nanoparticles of different sizes (Fig. 1) before the filling of the polymer. The magnetic nanoparticles agglomerates were formed in the following sizes: α -Fe between 1-50 μm , α -Fe/ Fe_3C 1-20 μm and Fe_3C 1-30 μm . Smaller sizes of agglomerates were obtained for the mixed state samples. Additionally, in the sample containing Fe/C nanofiller a certain amount of fibrous struc-

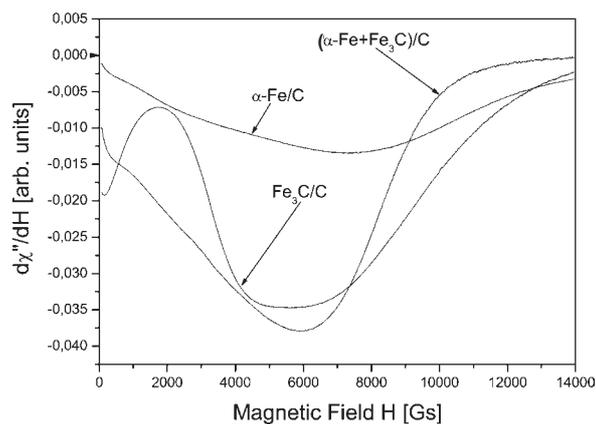


Fig. 2. FMR spectra of α -Fe/C, α -Fe/ Fe_3C , and $\text{Fe}_3\text{C}/\text{C}$ nanofillers.

tures was observed. The following filler concentrations in polymer composites were prepared for the FMR study: sample I – 0.1% α -Fe/ Fe_3C , sample II – 0.3% α -Fe/ Fe_3C , sample III – 0.1% α -Fe/C, sample IV – 0.3% α -Fe/C, sample V – 0.1% $\text{Fe}_3\text{C}/\text{C}$ and sample VI – 0.3% $\text{Fe}_3\text{C}/\text{C}$.

The XRD spectra of α -Fe/C and $\text{Fe}_3\text{C}/\text{C}$ samples showed characteristic peaks suggesting that the system is dominated by one phase with different intensities connected with an increased concentration of the magnetic nanoparticles in the polymer matrix. Samples I and II display coexistence of XRD spectra of α -Fe/C and $\text{Fe}_3\text{C}/\text{C}$ compounds.

Fig. 2 presents the FMR spectra for all types of used fillers at room temperature. The FMR spectra of α -Fe/C are similar to these obtained earlier [13], while more intense FMR spectra of Fe_3C are the same as in [16]. The superposition of FMR spectra from α -iron and iron carbide has created an intense and broad resonance line shifted to lower magnetic fields. The collection of magnetic nanoparticles and agglomerates is subjected to an additional magnetic field, which broadens the FMR line and shifts it to lower magnetic fields. Thus the resonance condition is changed to $h\nu = g\mu_B(H_{\text{app}} - H_{\text{int}})$, where μ_B is Bohr magneton, H_{app} is the external applied magnetic field and H_{int} is an internal magnetic field produced by the magnetic interactions. As magnetic nanoparticles are not well separated, the spin of a

Table 1. FMR parameters for investigated samples and comparison with literature data.

Compound	H_r [mT]	H_p [mT]	ΔH [mT]	I_p	c	Ref.
(α -Fe+F ₃ C)/C - 0	~30	591(1)	~630	-0.3799		
0.1% (α -Fe+F ₃ C)/C	~70	503(1)		-0.00076	0.14 %	
0.3% (α -Fe+F ₃ C)/C	~40	527(1)		-0.00187	0.39 %	
α -Fe/C	27(1)	620(1)	814(1)			[12]
75%Fe+25%Fe ₃ C	95(1)	600(1)	812(1)			
57%Fe+43%Fe ₃ C	26(1)	580(1)	695(1)			
38%Fe+62%Fe ₃ C	91(1)	450(1)	635(1)			
19%Fe+81%Fe ₃ C	220(1)	470(1)	603(1)			
12%Fe+88%Fe ₃ C	258(1)	400(1)	666(1)			
60%Fe+40%Fe ₃ C	30(1)	530(1)	706(1)			[17]
α -Fe/C	~0	748(1)	~850	-0.1500		
0.1 % α -Fe/C	~20	518(1)		-0.00108	0.35%	
0.3 % α -Fe/C	~10	534(1)		-0.00147	0.50%	
Fe ₃ C/C	~200	566(1)	~680	-0.346		
0.1 % Fe ₃ C/C	~250	388(1)		-0.00044	0.06%	
0.3 % Fe ₃ C/C	~235	415(1)		-0.00165	0.27%	
Fe ₃ C/C in wax	250(1)	480(1)				[16]
72% Fe ₃ C+28%C	130(1)	530(1)	413(1)			[13]
88% Fe ₃ C+12%C	195(1)	600(1)	702(1)			
83% Fe ₃ C+17%C	215(1)	600(1)	685(1)			

nanoparticle is subjected to the following total magnetic field:

$$H_{int} = H_{dem} + H_{app} + H_{dip} + H'_{dip}, \quad (1)$$

where the first term represents the demagnetization field (H_{dem}), the third term the dipole field from the neighboring nanoparticles (H_{dip}) and the last term the dipole-dipole interaction between agglomerates (H'_{dip}). The FMR resonance line originating from α -iron displays the largest shift, with increasing linewidth, compared to other samples and this could suggest stronger magnetic interactions. The α -Fe is involved in a strong ferromagnetic exchange interaction with the highest transition temperature to the paramagnetic state (at about 1000K), while for iron carbide $T_c=488$ K. On the other hand, as evidenced from Figs. 1a and 1c, the agglomerates containing α -iron are greater in size thus explaining a very wide and less intense FMR spectrum. Two new parameters are introduced for the description of the FMR spectra of strongly magnetic nanoparticles in agglomerate state: the position of

the peak H_p and its relatively intensity I_p . Table 1 presents the parameters obtained and their comparison with literature data. An attempt of fitting such spectra could produce large errors and the introduction of new parameters could hint at trends in the system doped by magnetic nanoparticle agglomerates.

Fig. 3 shows the FMR spectra for all six investigated samples, I to VI. The FMR spectra of all these samples are similar to corresponding spectra of appropriate fillers (Fig. 2). The intensity I_p and the position H_p of the FMR spectra strongly depend on the concentration of the magnetic agglomerates in a non-magnetic matrix (Table 1). The resonance field H_r is influenced slightly by the concentration of the magnetic agglomerate which suggests that the dipole interaction between agglomerates H'_{dip} (1) is playing an important role in the formation of an internal magnetic field H_{int} . The dependence of the linewidth on the filler concentration is evident - the linewidth is narrower for samples with lower filler concentration. A greater change is observed in the

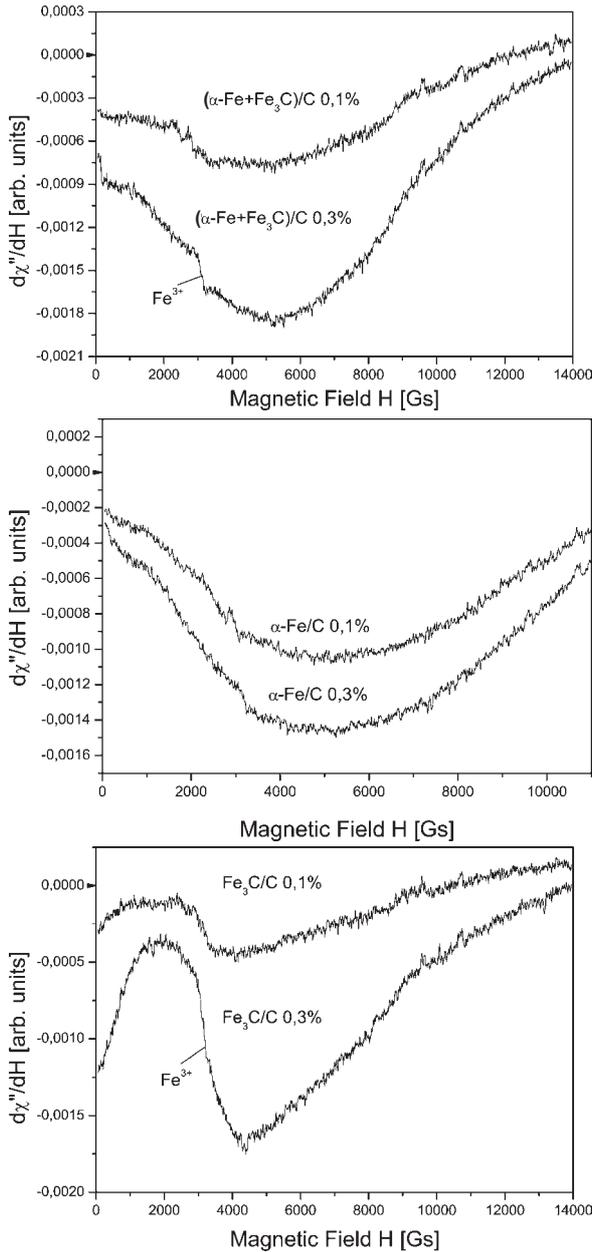


Fig. 3. FMR spectra at room temperature of polymer composites containing 0.1 wt.% and 0.3 wt.% nanofiller: (a) α -Fe/ Fe_3C ; (b) α -Fe/C; (c) Fe_3C /C.

intensity of the FMR spectra: with an increase in the concentration of magnetic particles the intensity the resonance signal increases. To describe better the observed changes and gain insight into physical processes involved, two new parameters, H_p and I_p , have been introduced. The parameter H_p accounts for the main part of the line broadening and it could be determined from the FMR trend of

linewidth behaviour. The second introduced parameter, I_p , is the amplitude of the FMR peak and the ratio $C = (H_p/H_{p0})^2 / (I_p/I_{p0})$ depends on concentration and reveals something about the magnetic interaction. Table 1 presents the concentration of the magnetic nanofillers in polymers matrix obtained by using the above formula. For the samples I, II, V, and VI good agreement is found between the estimated concentration of the magnetic nanoparticles from this formula and from masses of compounds used, while essential differences are observed for samples IV and V (Table 1). By changing the concentration of iron carbide in polymeric matrix in samples IV and III this ratio increases $C_{IV}/C_{III} = 1.4$ times only while for samples I, II this ratio is $C_{II}/C_I = 2.8$ and $C_{VI}/C_V = 4.5$ for samples V and VI. It is indeed strange that $(C_{IV}/C_{III} + C_{VI}/C_V)/2 = 2.95$, which is almost the value of introduced magnetic nanoparticles (a triple increase of concentration).

A more complicated spectra observed for the samples with iron carbide could be produced by two different types of iron ions (at Fe(1) and Fe(2) crystallographic positions) placed in two different sublattices, with magnetic moments $\text{Fe}(1) = 1.98 \mu_B$ and $\text{Fe}(2) = 1.74 \mu_B$, and a lower value of concentration is obtained using the introduced FMR parameters with above formula (Table 1). The broad FMR lines arising from magnetic agglomerates are analyzed more easily by the introduction of the new parameters because the errors are smaller by taking into account the correlation between the linewidth and intensity.

4. CONCLUSION

The FMR spectra of the polymer composites obtained strongly depended on the type of nanofiller as well as on the concentration of the magnetic nanoparticles. New parameters were introduced for description of the FMR spectrum of strongly interacting nanoparticles in agglomerates. A good agreement is obtained between the FMR line shift and magnetic aggregate concentration in the polymer matrix. The observed small change of the position of the FMR resonance line due to different concentrations of magnetic material is suggested to be produced by different dipole-dipole interaction between agglomerates placed in the internal magnetic field. The strong exchange magnetic interaction has displayed a strong influence on the intensity and the linewidth of the FMR nanocomposite spectra, especially for the matrix filled by α -iron nanoparticles.

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