STRUCTURE AND MAGNETIC PROPERTIES OF POLYMER MATRIX NANOCOMPOSITE PRODUCED BY PYROLYSIS OF Fe(III) ACRYLATE COMPLEX

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ABSTRACT

Structure and magnetic properties of ferromagnetic polymer matrix – nanocomposites, processed by thermal decomposition of Fe (III) acrylate complex, were studied. X-ray and Mössbauer spectroscopy showed that the product obtained by pyrolysis of the acrylate at 663 K consisted of 13 nm crystallites of magnetite (Fe_3O_4) and a phase containing Fe^{III} (trivalent low - spin iron). TEM microstructural studies revealed presence of agglomerates, up to 25 nm in size, of magnetite as well as individual crystals randomly distributed in amorphous polymer matrix. The static magnetic properties of the sample are dominated by the interparticle magnetic interactions and glass-type freezing effects.

1. INTRODUCTION

Growing interest in new processing techniques follows rapid development of nanomaterials. Nanosize inorganic particles can be produced within polymer matrix, where they can be randomly distributed in entire volume or deposited as a monolayer. Low stability of colloidal solutions is one of the main drawbacks of the processing of such nanocomposites [1]. This problem can be overcomed by polymerization in solid phase of metallo-organic complexes, followed by decarboxylation of fragments containing metal. The metal can be further oxidized by reaction with CO_2 or H_2O. Composite material processed in this way can be in a form of $MO_r(CH_2CHCOO)_{p-x}(CH_2CH)_x(CHCHCOO)_{q-y}(CHCH)_y$, where M – is the transition metal. Phase composition of the pyrolysis product depends on the processing temperature and time [2].

In this study the structure and magnetic properties of the nanocomposite processed by thermal decomposition of $[Fe_3O(CH_2{=}CHCOO)_6]OH{\bullet}3H_2O$ complex have been investigated. The main product in the material is magnetite ($Fe_{3(1-\delta)}O_4$). In this phase a structural transformation, occurs at a Verwey temperature Tv=119 K. Above this temperature the cubic unit cell of magnetite consists of two sublattices, Fe^{3+} is located in tetrahedral (A) and octahedral (B) positions and Fe^{2+} in the octahedral position. In the position B an electron jump occurs between pairs Fe^{3+} and Fe^{2+}. Below Tv the magnetite has monoclinic structure and the electron jump does not occur. Whether the Verwey transition is observed or not, depends on the stoichiometry parameter δ, i.e. number of pairs in the B site as, well as magnetite particle size [3].

2. EXPERIMENTAL DETAILS

Iron (III) acrylate complex $[Fe_3O(CH_2{=}CHCOO)_6]OH{\bullet}3H_2O$ was prepared by reaction of acrylic acid with $Fe(OH)_3$ [1]. Subsequently the material was subjected to thermal decomposition. The following specimens were investigated:

- Starting iron (III) acrylate complex, ($FeAcr_3$),

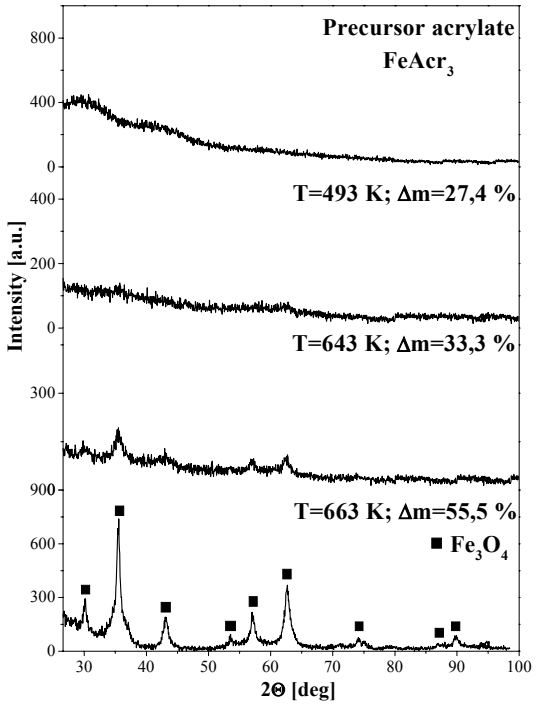
- Product of thermal decomposition of the starting complex at a temperature 493 K, mass loss Δm=27.4 %,
- Product of thermal decomposition of the starting complex at a temperature 643 K, mass loss Δm=33.3 %,
- Product of thermal decomposition of the starting complex at a temperature 663 K, mass loss Δm=55.5 %,

X-ray phase analysis was done using Philips 1040 diffractometer, and CuKα radiation. The Mössbauer spectroscopy was performed in a temperature range of 80 - 300 K, using ^{57}Co* in –Rh source. The isomer shift is related to the αFe standard. The electron microscopy analysis was performed by means of a transmission electron microscope (TEM) JEM 1200 EXII. The magnetic properties were evaluated using Oxford Instruments VSM. The magnetic measurements were done for the specimen annealed at 663K, having mass loss Δm=55.5 %. The hysteresis loops were recorded within temperature range of 5 - 300 K, in external magnetic fields of ± 1.1 T and ± 0.6 T. Measurements of magnetisation versus temperature for the zero field cooled (ZFC) and field cooled (FC) specimens were done in a field of $5 \cdot 10^{-3}$ T. The magnetisation versus temperature was measured in a field of 1 T.

3. RESULTS & DISCUSSION

Structural and microstructural analysis

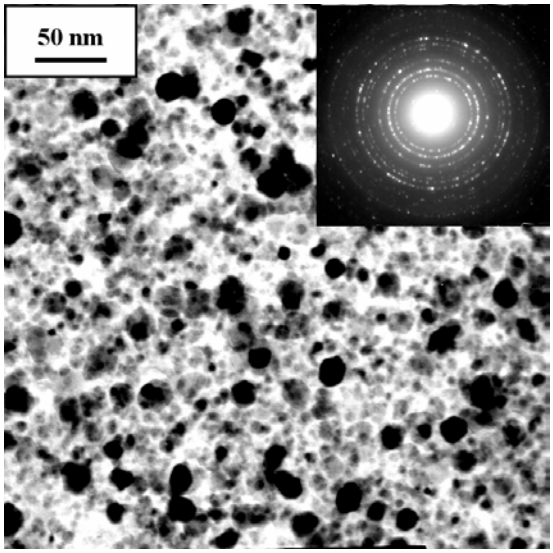
X-ray phase analysis, performed for the starting acrylate $FeAcr_3$ and a product of its decomposition at 493 K showed amorphous structure. After the thermolysis at 643 K, (Δm=33.3 %), the only phase, Fe_3O_4, was detected. After longer annealing, at 663 K (Δm=55.5 %), the contents of the Fe_3O_4 phase increased (Fig. 1).



"**Fig. 1.** Diffraction pattern of the starting acrylate and nanocomposites processed at: 493 K (Δm=27.4 %), 643 K (Δm=33.3 %) and 663 K (Δm=55.5 %)".

The X-ray diffractogram of the fully annealed sample showed peaks typical for both magnetite and maghemite (γ - Fe_2O_3). Due to the broadening of the observed reflections, no clear distinction between two iron oxide structures could be made from X-ray data. However,

lack of reflections in our study, in the angle range of 2Θ= 20°-27°, suggests that γ - Fe_2O_3 phase does not exist in our material [4]. The mean crystallite size of the magnetite, calculated using the Scherrer formula, is 13 nm. The TEM observations proved the existence of nanocrystalline particles randomly distributed within amorphous matrix. One can observe a wide distribution of their sizes, which suggests that beside the individual crystallites agglomerates of several crystals are also present (Fig. 2).

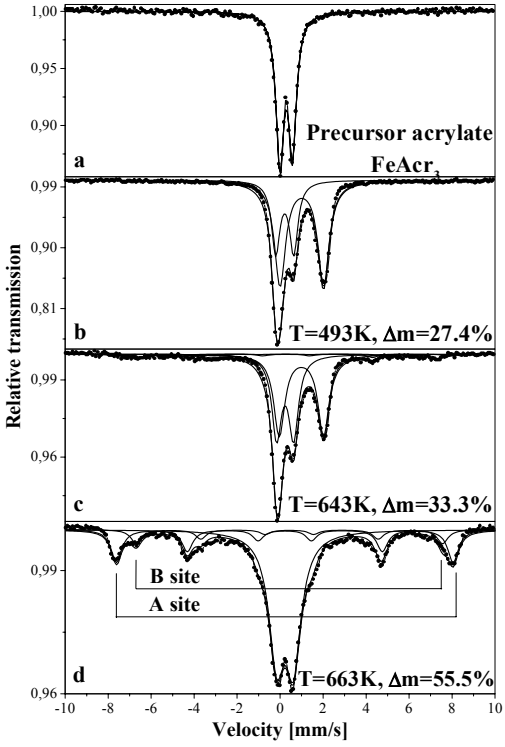


”**Fig. 2.** TEM microstructure and electron diffraction pattern of the nanocomposite processed at 663 K, (Δm=55.5 %)”.

Room temperature Mössbauer spectra for the starting acrylate and specimens annealed at different temperatures are shown in Fig. 3. The Mössbauer parameters of these spectra are collected in Table 1.The spectrum analysis of the starting material shows the existence of trivalent low - spin iron (Fig. 3a). In the course of annealing at 493 K partial reduction of Fe^{III} to divalent - high spin (Fe^{2+}) occurs. In Fig. 3b one can see an additional doublet showing large quadruple splitting, resulting from Fe^{2+}. Increase of the annealing temperature to 643K brings about decrease of the Fe^{2+} content from 66.5 % down to 49.6 %; and a new phase, magnetite, which spectral contributions is about 7 %. This fact is evidenced by values of hyperfine fields, 49 and 45.3 T, in A and B sites respectively (Fig. 3c). Further annealing, at 663 K, causes further increase of the magnetite content up to about 35 %, leading also to the complete disappearance of the phase containing Fe^{2+} (Fig. 3d). One can also notice, that in distinction to the bulk magnetite the relative intensities of Mössbauer lines corresponding to the B site (Fe^{3+}, Fe^{2+}) are much smaller than those at the A site (Fe^{3+}) that points to the non-stoichiometric structure of the magnetite. We assume that this is an effect of partial only filling of vacancies of Fe ions in B location, which leads to reduced number of the Fe^{2+} - Fe^{3+} pairs responsible for jumps of electrons. The idea of the non-stoichiometry of the magnetite is further supported by a low value of the hyperfine fields, especially in the B site (48.6 T (A), 44.3 T (B)), in relation the reported in the literature values for the stoichiometric magnetite (48.6 T (A), 46.0 T (B)) [5].

”**Table 1.** Parameters of Mössbauer spectra at 295 K”.

Sample / annealing conditions	δ (IS) [mm/s]	QS [mm/s]	Hhf [T]	Iron forms	Relative procentage of iron [%]
Precursor $FeAcr_3$	0.184	0.617	0	Fe^{III}	100
T=493 K; Δm=27.4 %	0.945 0.110	2.128 0.878	0 0	Fe^{2+} Fe^{III}	66.5 33.5
T=643 K; Δm=33.3 %	0.927 0.131 0.086 0.186	2.165 0.831 0 0	0 0 49.0 45.3	Fe^{2+} Fe^{III} Fe^{3+} (A) Fe^{3+}, Fe^{2+} (B)	49.6 43.5 1.4 5.5
T=663 K; Δm=55.5 %	0.117 0.106 0.321	0.778 0 0	0 48.6 44.3	Fe^{III} Fe^{3+} (A) Fe^{3+}, Fe^{2+} (B)	65.4 24.2 10.4

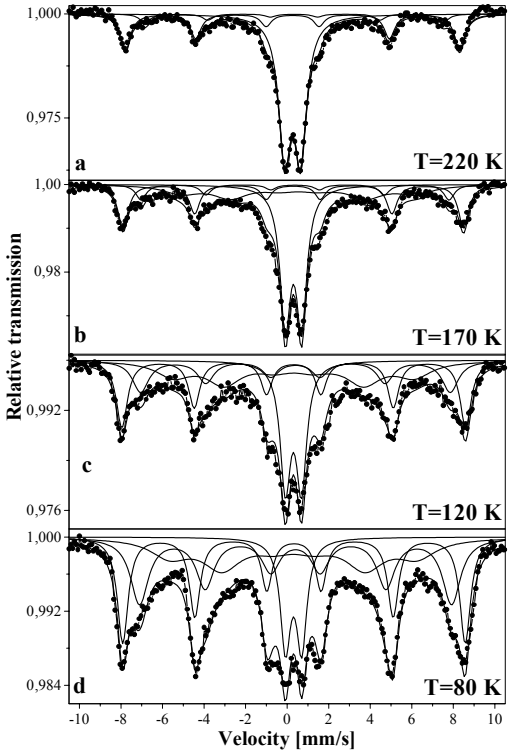


”**Fig. 3.** Mossbauer spectra recorded at 295 K, for all specimens”.

In Fig. 4 the Mossbauer spectra for the acrylate annealed at 663K are shown. The spectra were recorded at temperatures 220, 170, 120 and 80 K, respectively. Detailed parameters are collected in Table 2. Analysis of the spectrum obtained at 220K shows a presence of the same phases as detected at room temperature (Fig. 4a). Relative percentage of the Fe^{III} phase is somewhat lower, about 63 %, whereas the amount of Fe_3O_4 increases up to 37.4 %. Further lowering of the measurement temperature, down to 170 K, results in appearance of a new six-line spectrum, which comes from an unidentified phase (Fig. 4b). This spectral component does not correspond to any known equilibrium phases, which contain iron and oxygen or carbon. The value of the hyperfine field for this phase is 35 T. One can also notice substantial decrease of the amount of the phase containing Fe^{III} and slight drop of the magnetite content. At 120 K the relative percentage of the phase containing Fe^{III} is only a half of the amount existing at 170 K; instead a substantial increase of the magnetite and slight increase of the other unidentified phase contents are observed (Fig. 4c). Analysis of the spectra recorded at 80 K evidences further decreasing amount of the phase containing Fe^{III} and increase of the magnetite content. The values of hyperfine fields representing Fe_3O_4 in tetrahedral and octahedral sites are 51.2 T and 46.6 T, respectively. The hyperfine field representing the unidentified phase is 37 T. A monotonic decrease of the content of the phase containing Fe^{III}, from 65.47 % to 13 %, at 300 K and 80 K respectively, accompanied by increasing amount of magnetite suggests the existence of superparamagnetic particles of magnetite (Fig. 4d). These results may also arise from wide distribution of magnetite particle size and their partial agglomeration. Apparently the room temperature doublet, resulting from small, superparamagnetic crystallites of the magnetite phase, is included in the doublet representing Fe^{III}.

”**Table 2.** Parameters of Mössbauer spectra at 220, 170, 120, 80 K”.

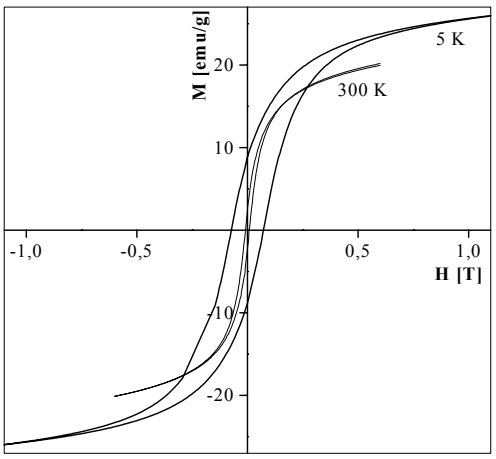
Sample annealed at T= 663 K Δm=55.5%	δ (IS) [mm/s]	QS [mm/s]	Hhf [T]	Iron forms	Relative procentage of iron [%]
T=220 K	0.153	0.764	0	Fe^{III}	62.6
	0.147	0	50.0	Fe^{3+} (A)	29.9
	0.210	0	44.5	Fe^{3+}, Fe^{2+} (B)	7.5
T=170 K	0.188	0.785	0	Fe^{III}	40.0
	0.181	0	50.9	Fe^{3+} (A)	25.9
	0.265	0	46.0	Fe^{3+}, Fe^{2+} (B)	9.2
	0.421	0	35.0		24.9
T=120 K	0.186	0.778	0	Fe^{III}	22.8
	0.203	0	51.4	Fe^{3+} (A)	29.1
	0.284	0	46.3	Fe^{3+}, Fe^{2+} (B)	20.2
	0.208	0	36.0		27.9
T=80 K	0.195	0.782	0	Fe^{III}	13.1
	0.214	0	51.2	Fe^{3+} (A)	30.1
	0.289	0	46.6	Fe^{3+}, Fe^{2+} (B)	31.3
	0.187	0	36.9		25.7



”**Fig. 4.** Mossbauer spectra, recorded at 220 K, 170 K, 120 K and 80 K, for the specimen annealed at 663 K (Δm=55.5 %)”.

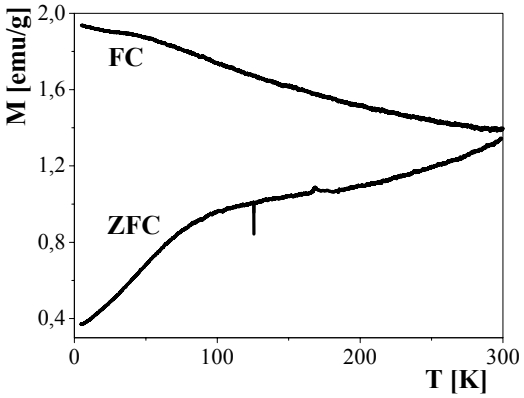
Magnetic properties

In the sample obtained at 663 K the hysteresis loops, recorded at temperatures 5 K and 300 K, are shown in Fig. 5. The loops exhibit a large high field susceptibility and the magnetization does not saturate in the field applied. The coercivity at 5 K is around 73 mT and reduces to 8 mT at room temperature.



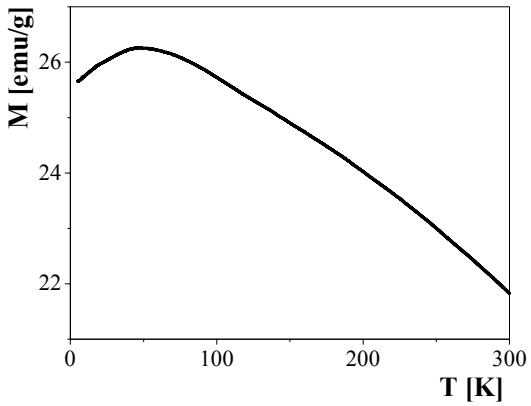
”**Fig. 5.** Hysteresis loops for the specimen annealed at 663 K (Δm=55.5 %), recorded at 5 and 300 K”.

The ZFC and FC curves, measured in a field of 5 mT, are presented in Fig.6. The irreversibility is observed in the whole temperature range. This fact along with the lack of maximum in ZFC curve show that the transition of particles to a superparamagnetic state is not seen and the magnetic behaviour of the sample is dominated by the interparticle interactions. The stronger $M_{ZFC}(T)$ dependence observed at $T < 80$ K indicates that presence of an additional low temperature freezing process.



"**Fig. 6.** ZFC and FC curves versus temperature, for the specimen annealed at 663 K (Δm=55.5 %), recorded in a field of $5x10^{-3}$ T".

This is confirmed by the measurements of the ZFC magnetization versus temperature in the field of 1 T shown in Fig. 7. The initial increase of the magnetization, observed in the temperature range of 4-50 K, results from a random freezing of certain spins during the cooling process, which do not achieve the full alignment with the external field at the lowest temperatures. The freezing process observed can be: (i) of a spin-glass type and appear in the partly disordered surface layers of particles due to their topological disorder and competing ferro- and antiferromagnetic interactions or (ii) of a cluster-glass character due to a freezing of randomly oriented particles forming agglomerates and coupled by magnetic interactions. The low temperature value of the sample magnetization (magnetic particles + diamagnetic matrix) is 26.2 emu/g. Considering that the magnetization of the magnetite is 98 emu/g [6] and that the magnetization of the sample studied does not reach the saturation at 1 T it can roughly be estimated that the mass fraction of the magnetic phase in the sample obtained at 663 K is $p \geq 25\%$. However the created magnetite nanocrystals are not of a very good quality since in any of the M(T) curves we do not observe a characteristic deflection point at ~120 K which is a characteristic feature of a stoichiometric Fe_3O_4 and corresponds to a Verwey transition.



”**Fig. 7.** Magnetisation versus temperature, measured in external field 1 T, for the specimen annealed at 663 K”

4. CONCLUSIONS

Thermal decomposition of metal-organic complexes enables in-situ processing of nanosize particles distributed in polymer matrix. Pyrolysis of $[Fe_3O(CH_2{=}CHCOO)_6]OH{\bullet}3H_2O$ complex at 663 K, leads to the formation of nanocomposite material consisting of: 34.6 % magnetite nanoparticles and the phase containing Fe^{III}. Lower annealing temperatures bring about formation of phases containing: Fe^{III} and Fe^{2+} as well as Fe_3O_4. Microstructure of the final product consists of crystallites, having about 12 nm in size, and their agglomerates. The observed magnetic behaviour of the sample is dominated by the agglomerates in which the particles are coupled by the magnetic interactions, off-stoichiometric structure of the magnetite particles as well as spin-canting effecs.

ACKNOWLEDGEMENTS

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