

Structure and Magnetic Properties of Polymer Matrix Nanocomposites

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Structure and magnetic properties of the thermal decomposition products of Fe(III)Co(II) acrylate complex were analysed. The crystalline phases, which were found in the fully processed material, at 643 K, were Fe₃O₄, CoFe₂O₄, and CoO and had a mean particle size of about 30 nm. In the intermediate stages of the thermolysis iron was present in a form of Fe^{III} (trivalent low-spin iron), Fe²⁺ (divalent high-spin iron), and Fe₃O₄. The coercivity and remanence were measured versus temperature in the range of 5–300 K, in 1.1 T applied field. Both, M_H and M_r , decreased showing room temperature values of 0.038 T and 7.49 mT, for coercivity and remanence, respectively. At temperatures below 200 K the hysteresis loops were asymmetrical, opened and shifted towards negative field values.

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1. Introduction

Thermal transformation of metal-containing monomers is a unique technique, which allows producing nano-sized particles stabilised in a polymer matrix [1]. This method involves solid state polymerisation of the initial monomer followed by decarboxylation of the metal-containing fragments of polymers. Metal

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formed in the last reaction can be oxidized by CO_2 or H_2O . The composite material can be in a form of $\text{MOr}(\text{CH}_2\text{CHCOO})_p - x(\text{CH}_2\text{CH})_x (\text{CHCHCOO})_q - y(\text{CHCH})_y$, where M is transition metal. The composition of the composite material depends on the temperature and time of thermal decay [1]. The thermal decomposition products of metal acrylates such as Fe (III), Fe (II), Co(II), Ni(II) can be used for the production of ferromagnetic materials.

In the present study the formation and structure of nanocomposites processed by thermolysis of the complex:

$[\text{Fe}_3\text{O}(\text{CH}_2\text{CHCOO})_6\text{OH}][\text{Co}(\text{CH}_2\text{CHCOO})_2]_{1.5} \cdot 3\text{H}_2\text{O}$ has been investigated.

2. Experimental

Thermal transformation of the Fe(III)Co(II) acrylate complex was performed. The following specimens were analysed:

Sample 1 — precursor (the Fe(III)Co(II) acrylate complex);

Sample 2 — product of a thermal decomposition at 493 K, weight loss, $\Delta m = 25.1\%$;

Sample 3 — product of a thermal decomposition at 643 K, weight loss, $\Delta m = 37.3\%$;

Sample 4 — product of a thermal decomposition at 643 K, weight loss, $\Delta m = 42\%$ (longer annealing time).

X-ray phase analysis was performed at room temperature with the application of a Philips PW 1050 diffractometer, using $\text{Cu } K_\alpha$ radiation. For the Mössbauer spectroscopy the $^{57}\text{Co}^*$ -in-Rh source was used. The specimens were tested at different temperatures in the range of 80 to 370 K. For the TEM investigations a Philips EM 300 microscope, operating at 100 kV, was used. Magnetic measurements were carried out using a PAR-155 and Oxford Instruments vibrating sample magnetometers.

3. Results

The X-ray diffraction pattern of the precursor material revealed a very complex crystalline structure, which was not analysed at this stage. In the specimen, which was annealed at 493 K ($\Delta m = 25.1\%$), crystalline phases were not found. After the thermolysis at 643 K, ($\Delta m = 37.3\%$), the only phase, which was detected was Fe_3O_4 . After a longer annealing at this temperature ($\Delta m = 42\%$) CoO , Fe_3O_4 , and CoFe_2O_4 phases were found, however, the crystallographic parameters for cubic inverse spinels CoFe_2O_4 and Fe_3O_4 are very similar. Some unidentified reflections were also present (Fig. 1).

The TEM investigations for sample 4 proved the existence of metallic particles, which were distributed in a polymer matrix. A mean size of the particles was

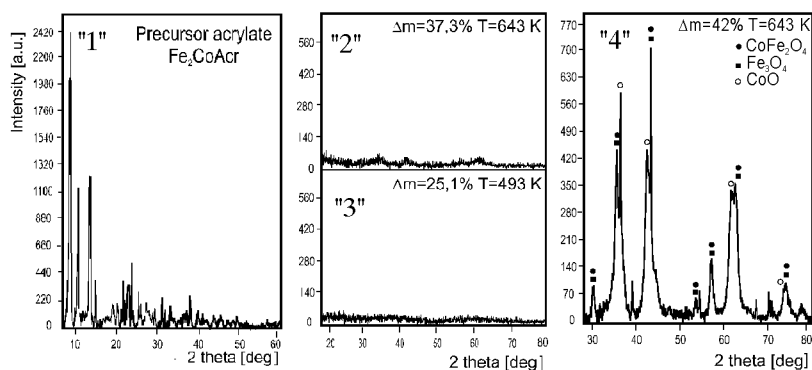


Fig. 1. X-ray diffraction patterns for the precursor complex 1 and for the samples 2, 3 and 4.

30 nm, however, at this stage we are unable to state whether these particles are mono- or polycrystalline.

The Mössbauer spectra, which were recorded at 295 K, are shown for all the samples in Fig. 2a. For the precursor acrylate a presence of Fe^{III} only was apparent from the spectrum. In the course of annealing at 493 K a reduction of the Fe^{III} to Fe^{2+} occurred which is represented in Fig. 2a for sample 2 by an additional doublet. On increasing the annealing temperature up to 643 K (sample 3) the reduction of Fe^{III} proceeded further. For sample 4 the Fe_3O_4 appeared, which was evidenced from the values of the two sextets representing hyperfine fields of trivalent iron in the tetrahedral sites (A) as well as trivalent and divalent iron in the octahedral sites (B). The values of those fields were 48.68 T and 45.866 T, respectively. We suppose that the effect from cobalt ferrite, CoFe_2O_4 , was included in the Fe^{III} spectrum. The results of low temperature Mössbauer spectroscopy for sample 4 are shown in Fig. 2b. In these spectra: Fe^{III} , Fe^{2+} , Fe_3O_4 , CoFe_2O_4 components were detected. The values of hyperfine fields for CoFe_2O_4 , in sites A and B, were 49 T and 52 T, respectively [2].

The hysteresis loops were recorded in a temperature range of 5–300 K, in 1.1 T applied field. Below 200 K the loops were open and shifted towards negative magnetic field. The shift increased with decreasing temperature. This behaviour we attribute to the strong irreversible magnetic processes, which at temperatures below 200 K, could not produce a continuous closed loop in a presence of low external magnetising field. However, we cannot exclude some additional contribution to this phenomenon from the effect associated with “freezing” of disordered surface spins of nanoparticles, which are bonded to the organic molecules [3]. These configurations, in our case, become frozen at temperatures below 200 K.

In Fig. 3a the coercivity and remanence are plotted versus temperature in the range of reversible magnetisation processes, i.e. over 200 K. Both the M_Hc and M_r decreased showing room temperature values of 0.035 T and 7.49 mT for

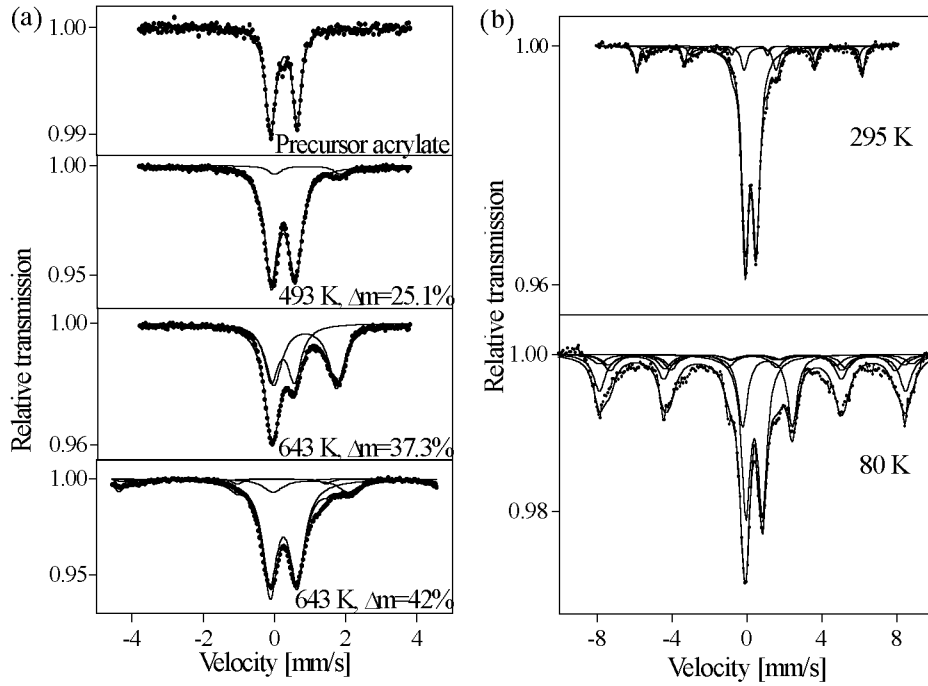


Fig. 2. The 295 K Mössbauer spectra for all the samples investigated (a) and the 295 K and 80 K spectra for the specimen 4 (b).

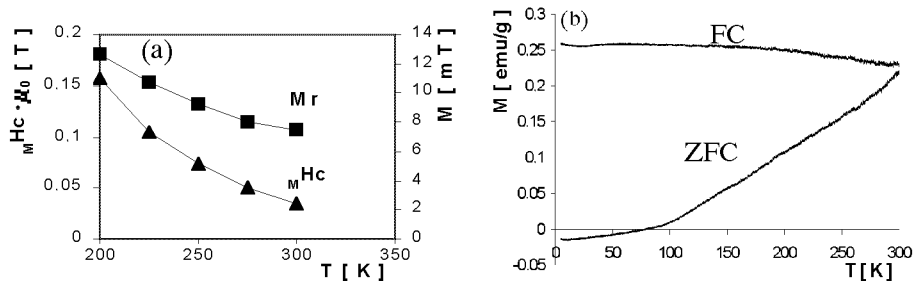


Fig. 3. The coercivity M_Hc and remanence M_r versus temperature for sample 4 (a), and magnetisation versus temperature after ZFC and during FC for sample 4 (b).

the coercivity and remanence, respectively. In Fig. 3b the magnetisation versus temperature is shown after zero field cooling (ZFC) and in the course of 2×10^{-3} T field cooling (FC). The measurement of the magnetisation versus temperature after ZFC indicated continuous increase in this parameter. The curve changes its slope at around 100 K, which may indicate changes in a magnetic structure of the material, which contains two magnetic phases. FC led to a small decrease in magnetisation

with increasing temperature. The difference in the shapes and positions of both the curves is related to the strong irreversible processes, origin of which at this stage cannot be fully explained. They may arise from magnetic interactions within the particles, between the particles or the particles and polymer matrix.

4. Summary

Crystalline phases, which were found in the fully processed material (643 K, $\Delta m = 42\%$), were ferrimagnetic Fe_3O_4 and CoFe_2O_4 , and antiferromagnetic CoO . At the intermediate stages of the transformation iron was present in a form of Fe^{III} , Fe^{2+} and Fe^{3+} , Fe^{2+} in Fe_3O_4 . The microstructure of the material consisted of 30 nm polycrystalline metallic particles, which were homogeneously distributed in the polymer matrix. The precursor acrylate as well as sample 2 (493 K, $\Delta m = 25.1\%$) were nonmagnetic. The room temperature coercivity and remanence values for sample 4 were 0.038 T and 7.49 mT, respectively.

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