Magnetic Properties of Polymer Matrix Nanocomposites on a Basis of Metal Carboxylates

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Summary: Metallopolymer nanocomposites on the bases of cobalt and iron acrylates as well as their cocrystallites have been obtained and characterized. Microstructure of the materials consists of both agglomerated and individual nanocrystallites which are homogeneously distributed in the polymer matrix. Mean crystallite size is 7-14 nm. All the composite materials exhibit soft magnetic properties at room temperature. The magnetic parameters are controlled by the intrinsic magnetic properties of the constituents and agglomeration of the particles.

Keywords: magnetic; metallopolymer nanocomposites; nanocrystallites

Introduction

Nanomaterials attract substantial scientific and technological interest due to their optical, magnetic and electronic properties and to possible application in catalysis, molecular and nanoelectronics.[1] Such materials exhibit phenomena such as giant reluctance, anomalous great magnetic calorific effect, etc. Much effort has been put into development of new methods for processing composites with controlled size and shape of the resulting particles. We elaborated a convenient way of preparing metal nanoparticles stabilized with a polymer matrix.[2-5] It comprises; (i) thermal transformation of metal-containing monomers; i.e., compounds comprising a metal equivalent and a polymerisable group containing multiple bonds, (ii) thermolysis of these compounds, which involves transformations typical of the consequence of three main macrostages occurring at different temperatures. They comprise dehydration of initial monomers, solid-state (co)polymerization of the dehydrated monomers and (iii) subsequent decarboxylation of the polymer to form nanoparticles stabilized with a

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polymer matrix.

In this work we report on the study of the magnetic properties of the metallopolymer nanocomposites based on iron and cobalt acrylates and their cocrystallites.

Experimental

The Fe(III) acrylate, $[Fe_3O(CH_2{=}CHCOO)_6OH]\cdot 3H_2O$ ($FeAcr_6$) and Co(II) acrylate, $Co(CH_2{=}CHCOO)_2]\cdot H_2O$ ($CoAcr_2$) were prepared by an exchange reaction between metal hydroxide or carbonate and an excess of unsaturated carboxylic acid according to a procedure described in.[6] The Fe(III)-Co(II) acrylate (Fe_2CoAcr) complex with nominal composition: $[Fe_3O(CH_2CHCOO)_6OH][Co(CH_2CHCOO)_2]_{1.5}\cdot 3H_2O$ was prepared by coprecipitation of $[Fe_3O(CH_2CHCOO)_6OH]\cdot 3H_2O$ and $Co(CH_2CHCOO)_2]\cdot H_2O$ salts from an alcoholic solution at Fe/Co = 2. For the Fe_2CoAcr complex we found the following contents (wt.%): Fe, 17.0; Co, 9.1. The respective calculated contents (wt.%) were: Fe, 17.08; Co, 9.12 and the Fe/Co = 1.98. Thermal transformations of the complexes in a self-generated atmosphere and under static non-isothermal conditions were studied at T_{exp} = 613 to 663 K.

X- ray phase analysis was performed at room temperature with the application of a Philips PW 1050 diffractometer, using Cu K_{α} radiation. The magnetic properties were measured using an Oxford Instruments Vibrating Sample Magnetometer (VSM).

Polymer Matrix Nanocomposite Processed by Pyrolysis of $CoAcr_2$

The topography peculiarities of the solid phase product comprises its dispersion and specific surface ($S_{sp,f}$), which is produced in the course of the thermal transformation. In our case the $S_{sp,f}$ increases from 20.2 m^2/g ($S_{sp,o}$) to 24.1(623 K)-42.1 m^2/g (663K). In the end of $CoAcr_2$ decomposition at 663 K the mass loss is 48%. The main product is CoO phase with mean crystalline size, measured by the Sherrer method, 7.4 nm (Fig.1). Selected loops, obtained at 5 K and 300 K in the field range ±1.1 T, are shown in Fig. 2. The loops are closed and symmetrical about the origin. The coercivity values are 0.08 T and 0.03 T for temperatures 5 K and 300 K, respectively. It can be seen that hysteresis loop recorded at 300 K shows behaviour typical of a material with preferential ferromagnetic ordering. At low temperatures the shape of the magnetisation curves changes considerably. The high field susceptibility (dM/dH), which is a slope of the linear portion of M=f(H) curve, increases five times with the decrease of temperature from 300 to 5 K. Thus, at low temperatures, besides of the ferromagnetic part, a substantial contribution from the antifferomagnetic CoO phase is observed.

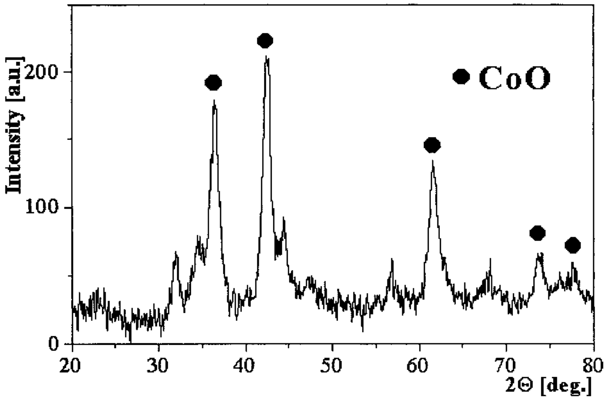

Fig. 1. X-ray diffraction pattern for the product of $CoAcr_2$ decomposition.

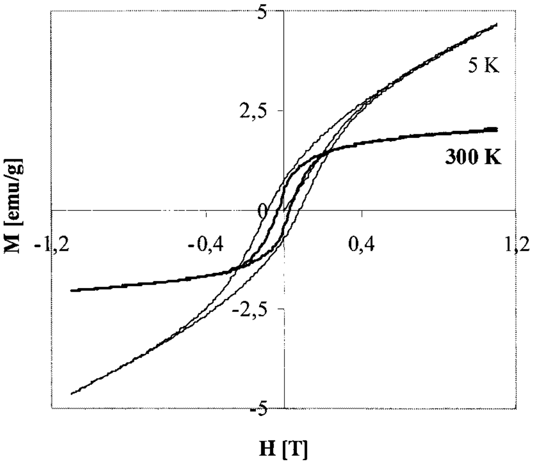

Fig. 2. Selected hysteresis loops for the product of $CoAcr_2$ decomposition, recorded at 5 and 300 K (±1.1 T).

The temperature dependence of the magnetisation M(T), measured in a field of 1 T, is shown in Fig. 3. The magnetisation decreases rapidly from 4.48 emu/g down to 1.98 emu/g for temperatures of 5 K and 300 K, respectively. The latter value (1.98 emu/g) is much higher than the 0.02 emu/g, which has been reported for the 560 nm particles of the CoO measured in the same field.[7] Moreover the Néel temperature (T_N= 293 K) of the CoO phase is not seen on the M(T) curve. These observations point to the presence of an additional ferri-/ferromagnetic phase in the material with its Curie point above the room temperature. We suppose that the shape of the M(T) curve results from the contribution of at least two phases: ferromagnetic and antiferromagnetic, as well as the wide distribution of the particle sizes and their agglomeration. Magnetisation versus temperature, in the field of 0.005 T, measured in zero field cooling (ZFC) and field cooling (FC) regime, is shown in Fig. 4. The continuous increase of the M_{ZFC} with temperature and a wide gap between M_{ZFC} and M_{FC} curves indicate the presence of strong interactions between agglomerated particles. The negative values of ZFC magnetisation we attribute to the influence of the diamagnetic organic matrix.[8]

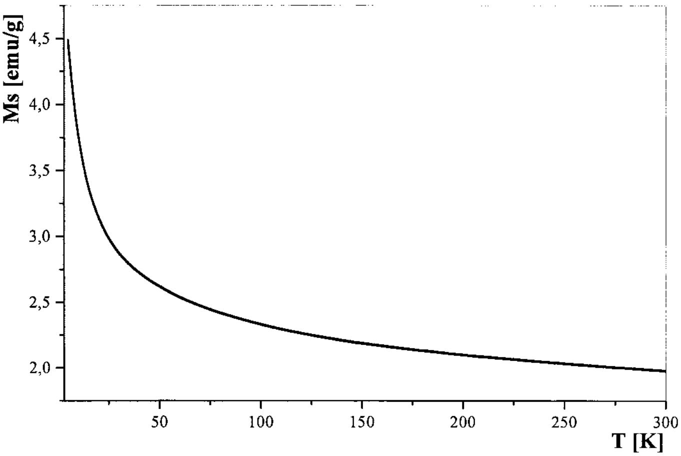

Fig. 3. Magnetisation versus temperature in a field of 1 T, for the product of $CoAcr_2$ decomposition.

Polymer Matrix Nanocomposite Processed by Pyrolysis of $FeAcr_6$

After the thermal transformation of $FeAcr_6$ the value of $S_{sp,f}$ do not substantially changes and is close to 15 m^2/g. Decomposition of the $FeAcr_6$ at 663K (mass loss 55.5%) leads to the formation of the Fe_3O_4 phase (Fig. 5). Mean crystalline size of the crystallite is 12.5 nm. The hysteresis loops were recorded at 5 K and 300 K in the field range ±1.1 T. The loops are closed and symmetrical about the origin. The coercivity values are 0.008 T and 2.73 mT for temperatures 5 K and 300 K, respectively. In Fig. 6. the temperature dependence of the magnetisation M(T), measured in a field of 1 T, shows typical ferromagnetic behaviour. The magnetisation decreases from 25.66 to 21.82 emu/g for temperatures of 5 K and 300 K, respectively. These values are much smaller than 98 and 92 emu/g which have been reported for the bulk magnetite obtained in the same field.[9]

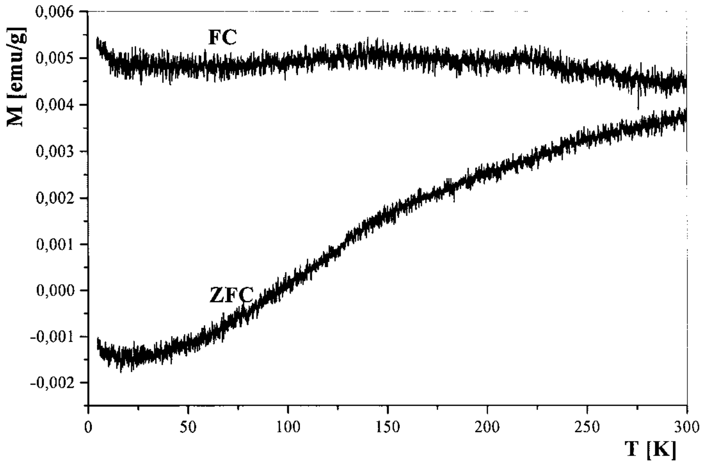

Fig. 4. Magnetisation versus temperature in a field 0.005 T after ZFC and during FC, for the product of $CoAcr_2$ decomposition.

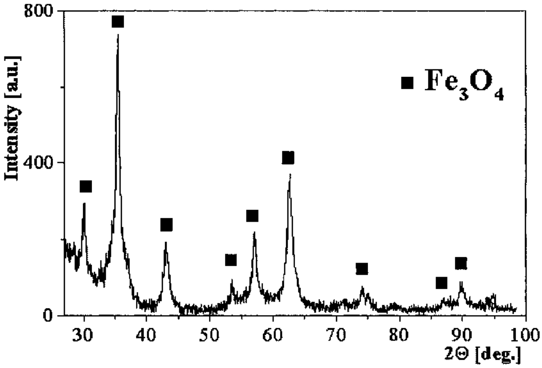

Fig. 5. X-ray diffraction pattern for the product of $FeAcr_6$ decomposition.

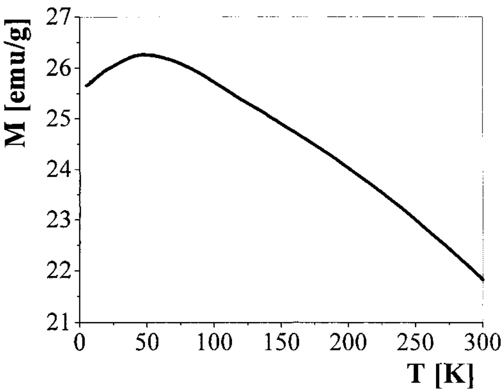

Fig. 6. Magnetisation versus temperature in a field of 1 T, for the product of $FeAcr_6$ decomposition.

We suppose that reduced magnetisation is an effect of small size of magnetite particles and canted spin structure of surface atoms.

Polymer Matrix Nanocomposite Processed by Pyrolysis of Fe_2CoAcr

For Fe_2CoAcr no change in both the dimensions of particles and $S_{sp,f}$ is observed at the end of the thermal decomposition. Crystalline phases, which were found in the fully processed product of thermal decomposition of Fe_2CoAcr at 643 K (mass loss 42%) are ferrimagnetic Fe_3O_4, $CoFe_2O_4$ and antiferromagnetic CoO (Fig. 7). The mean size of the crystallites is 14 nm. The hysteresis loops were recorded in a temperature range of 5-300 K, in ±1.1 T applied field. Selected loops, obtained at 5 K and 300 K are shown in Figure 8. Below 200 K the loops are open and shifted towards negative magnetic field. 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.[10] These configurations, in our case, become frozen at temperatures below 200 K. Both, the coercivity and remanence decreases, over 200 K, showing room temperature values of 0.035 T and 7.49 mT, respectively.

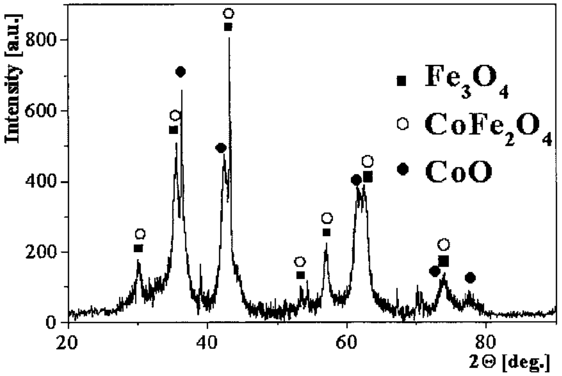

Fig. 7. X-ray diffraction pattern for the product of Fe_2CoAcr decomposition.

In Figure 9 the magnetic moment versus temperature is shown after ZFC and in the course of $2x10^{-3}$ T FC. The measurements of the magnetisation versus temperature after ZFC indicate continuous increase of this parameter. The drop of ZFC magnetisation to negative values we attribute to the influence of the diamagnetic organic matrix. FC curves indicate small decrease of the magnetisation with increasing temperature. The difference in the shapes and positions of the both curves is related to the strong irreversible processes, origin of which at this stage can not be fully explained. They may arise from magnetic interactions within the particles, between the particles or the particles and polymer matrix.[11]

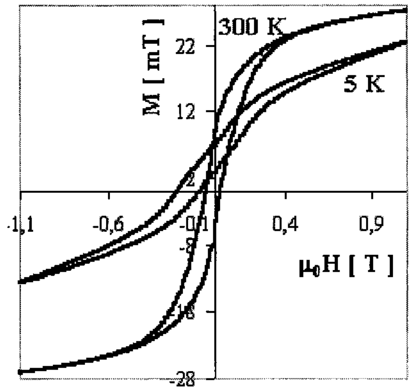

Fig. 8. Selected hysteresis loops for the product of Fe_2CoAcr decomposition, recorded at 5 and 300 K (±1.1 T).

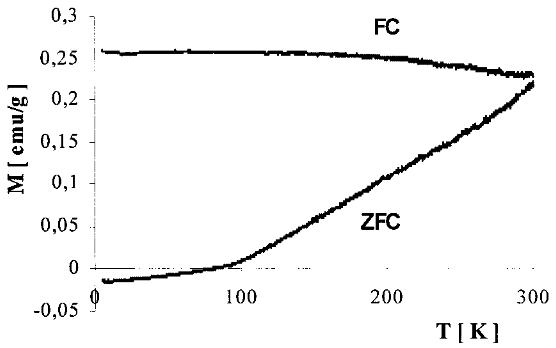

Fig. 9. Magnetisation versus temperature in a field 2×10^{-3} T after ZFC and during FC, for the product of Fe_2CoAcr decomposition.

Conclusions

Mixed metal oxides particles embedded in a polymer matrix, having uniform size and distribution, were successfully synthesised by pyrolysis of iron and cobalt acrylates. Crystalline phases, which were found in the fully processed product of thermal decomposition of Fe_2CoAcr at 643 K (mass loss 42%) were: ferrimagnetic Fe_3O_4, $CoFe_2O_4$ and antiferromagnetic CoO. In the product of $CoAcr_2$ decomposition at 643 K (mass loss 48%) the main product was CoO phase. Decomposition of the $FeAcr_3$ at 663K (mass loss 55.5%) led to the formation of the Fe_3O_4 phase. Microstructure of the materials consisted of both agglomerated and individual crystallites, which were homogeneously distributed in the polymer matrix. Mean crystalline size of the Fe_2CoAcr, $FeAcr_3$, $CoAcr_2$ crystallites were: 14, 12.5 and 7.4 nm, respectively. All the composite materials exhibited soft magnetic properties at room temperature. The magnetic properties depended on the intrinsic magnetic properties of the constituents and agglomeration of the particles. Negative values of the ZFC magnetisation curves, measured for Fe_2CoAcr and $CoAcr_2$ decomposition products, can point to substantial influence of the diamagnetic organic matrix on the magnetic properties.

Acknowledgement

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[1] A.D. Pomogailo, A.S. Rozenberg, I.E. Uflyand, *Metal nanoparticles in polymers*, 2000, Khimiya, Moscow.
[2] E. I. Aleksandrova, G. I. Dzhardimalieva, A. S. Rozenberg, A. D. Pomogailo, *Russ. Chem. Bull.* **1993**, *42*, 264.
[3] A. S. Rozenberg, E. I. Aleksandrova, G. I. Dzhardimalieva, A. N. Titkov, A. D. Pomogailo, *Russ. Chem. Bull.* **1993**, *42*, 1666.
[4] A.S. Rozenberg, G.I. Dzhardimalieva, A.D. Pomogailo, *Polym. Adv. Technol.*, **1998**, *9*, 527.
[5] A.D. Pomogailo, V.G. Vlasenko, A.T. Shuvaev, A.S. Rozenberg, G.I. Dzhardimalieva, *Colloid J.*, **2002**, *64*, 472.
[6] G.I. Dzhardimalieva, A.D. Pomogailo, V.I. Ponomarev, L.O. Atovmyan, Yu.M. Shulga, A.G. Starikov, *Bull. Acad. Sci. USSR, Div. Chem. Soc.*, **1988**, *38*, 1346.
[7] Liyng Zhang, Desheng Xue, *J. Mater. Sci. Lett.*, **2002**, *21*, 1931.
[8] M. Ławecka, M. Leonowicz, A. Ślawska-Waniewska, K. Racka, G.I. Dzhardimalieva, A.S. Rosenberg, A.D. Pomogailo, *J. Alloys and Comp.*, **2003**, in print.
[9] Z. Kakol, J. M. Honig, *Phys. Rev. B*, **1989**, *40*, 9090.
[10] R. H. Kodama, *J. Magn. Magn. Mater.*, **1999**, *200*, 359.
[11] M. Ławecka, M. Leonowicz, M. Kopcewicz, A. Ślawska-Waniewska, J. Kozubowski, G.I. Dzhardimalieva, A.S. Rosenberg, A.D. Pomogailo, *Acta Physica Polonica* A, **2002**, *102*, 317.