

MAKING OF POLYMERS CONTAINING MAGNETIC NANOPARTICLES ASSISTED BY SUPERCRITICAL CARBON DIOXIDE

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In this work we deal with introduction of Co and Fe-containing compounds assisted by supercritical carbon dioxide (sc-CO₂) into polyarylate (PAR), polystyrene (PS), siloxane (SIEL and SKTN) and ultrahigh density polyethylene (PE) matrices with follow-up making of magnetic nanoparticles. Metal-polymeric nanocomposites have been produced by metal reduction and were characterized by gravimetric, FTIR, SAXS, SEM and TEM methods.

INTRODUCTION

Synthesis of metal-polymeric nanomaterials has attracted much attention in the latest years. Owing to their small size metal particles exhibit some unusual magnetic, catalytic, and biological properties untypical for large particles. In this work for making of metal-polymeric nanomaterials we used three different methods. In the first method samples of Fe₂O₃-containing nanoparticles stabilized in the bulk of the siloxane matrix were synthesized by the standard procedure for preparing materials "clusspol" [1]. The underlying idea of this method is the thermal decomposition of metal-containing compounds (MCC) in polymer dissolved in mineral oil. We used oligomer of siloxane caoutchouc without mineral oil, because SIEL and SKTN are viscous liquid. The way in which the MCC were introduced into siloxane caoutchouc ensured the decomposition of the precursor without additional supply of the MCC in order to provide for the homogeneity of the resulting nanoparticles in both composition and size. In second method we used cryochemical synthesis for making metal-polymeric nanoparticles in the samples which preliminary were treated by supercritical CO₂. At last in third method first step consisted in diffusion of a MCC from solution in sc-CO₂ into the polymeric matrix. The second step included the reduction of metal by heating of the sample. The method of impregnation from solution in sc-CO₂ has several advantages: (a) the matrix tends to prevent an agglomeration of metal particles; (b) sc-CO₂ shows high penetrability into polymers; (c) it is possible to control the solvent power and the impregnation rate and therefore to control the composition and morphology of the obtained materials. In the present work we described the conditions of impregnation of different polymeric matrices and following thermal transformations of MCC in a polymeric matrix, and morphology of the synthesized metal-polymeric materials.

I - MATERIALS AND METHODS

Materials

Aminoimines and their Fe- and Co-chelate complexes (hexafluorodiiminates HFDI) were synthesized according to [2]. Monoacetylferrocene (MAF), Co and Fe acetylacetonates were purchased from "Aldrich" and used without additional purification. The Fe₂O₃ nanoparticles

were manufactured by the thermo destruction of $\text{Fe}(\text{CH}_3\text{COO})_3$ at 280-300°C. The flow rate of an inert gas (argon) was controlled in order to provide for rapid and full removal of the ligands and solvent from the reaction sphere. The PS films with a thickness of $30 \pm 2 \mu\text{m}$ and PAR (polyester of bis-phenol A and tere-isophthalic acids) film with a thickness of $39 \pm 2 \mu\text{m}$ were performed by casting from their chloroform solution on to cellophane substrate. The PE powder (GUR 4120) was received from “Hoechst”.

Experimental set-up

A syringe pressure generator, valves and capillaries from “High Pressure Equipment Company” were applied to making of pressure in a custom-made stainless-steel cell (Fig. 1) with a reaction volume $\sim 10 \text{ cm}^3$.

Impregnation procedure

A metal-containing complex and magnetic stirrer were loaded in to the cell. The film sample with the square of several cm^2 were placed on a wire-mesh. Then the cell was closed and pressurized up to 6 MPa, heated up to desired temperature and pressurized to working pressure. The runs were carried out in two temperature-pressure steps: the first step is solvation of the complex in sc CO_2 and second one is the impregnation of polymer matrix. After completion of a run the cell was decompressed and the film was weighed by OHAUS AP250D electronic balance (the accuracy of 10^{-5} g).

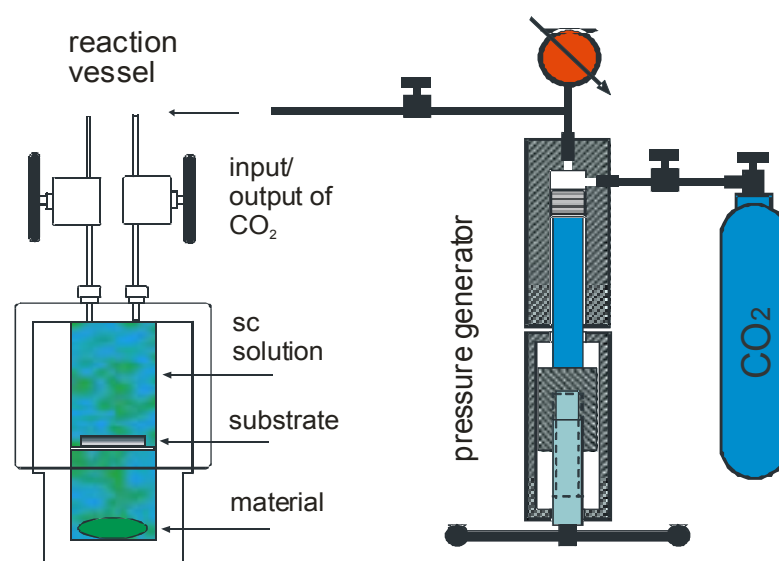


Fig. 1. Experimental set up

Reduction of metal

Reduction of a metal was carried out under CO_2 - atmosphere in the cell at the temperature of 220°C for 2-4 hours or in a horizontal furnace at a heating rate of 5°C/min. After that they were cooled, weighed and placed into an ampoule filled with argon to prevent any subsequent chemical processes.

Spectral Measurements

The FT-IR spectra were recorded by a Nexus “Thermo Nicolet” spectrometer. The size distribution of metal particles in films was determined using an automated small-angle X-ray diffractometer “Amur-K” (Cu K_α radiation, $\lambda = 1.54 \text{ \AA}$), operating at the accelerating potential of 30 kV and the anode current of 30 mA. SEM investigations were proceeded on “Zeiss” DSM 962 scanning electron microscope by standard technique. The sizes of the Fe-containing nanoparticles were determined using transmission electron microscopy (TEM) on a JEM-100B

Jeol instrument. The test sample was UV-dispersed in aqueous alcohol, and the dispersed powder was spread over a copper grid coated by a graphite film. The X-ray patterns were recorded from powdered and compacted samples on a DRON-3 diffractometer ($CuK_{\alpha 1}$ radiation, scan rate 2 deg/min). The diffraction peak positions were determined accurate to $\pm 0.05^\circ$. EPR spectrum was measured using Varian E-4 X-range spectrometer by room temperature.

II - RESULTS AND DISCUSSION

We synthesized polymer nanocomposites containing Fe_2O_3 nanoparticles in SIEL and SKTN matrixes. TEM was employed to verify the existence of the nanoparticles in the composites; representative micrographs for the series of the samples synthesized are demonstrated in Fig. 2.

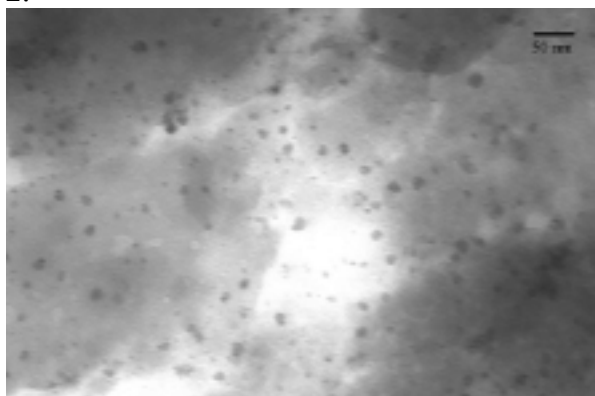


Fig. 2. TEM micrograph of a sample containing Fe_2O_3 nanoparticles stabilized in SKTN.

The compositions of all of the synthesized nanoparticles were determined using X-ray powder diffraction. The diffraction maxima associated with the metal-containing component, although having lower intensities and larger widths, were indexed well enough. The X-ray diffraction pattern for a sample of Fe_2O_3 in SKTN matrix displayed strong reflections Fe_3O_4 (JCPDS card no. 16-239) and Fe_2O_3 (JCPDS card no. 24-72). And for Fe_2O_3 nanoparticles in SIEL matrix composition are analogous. Nanoparticles Fe_2O_3 in SKTN matrix are superparamagnetic, because hysteresis of microwave absorption was not detected (see Fig. 3).

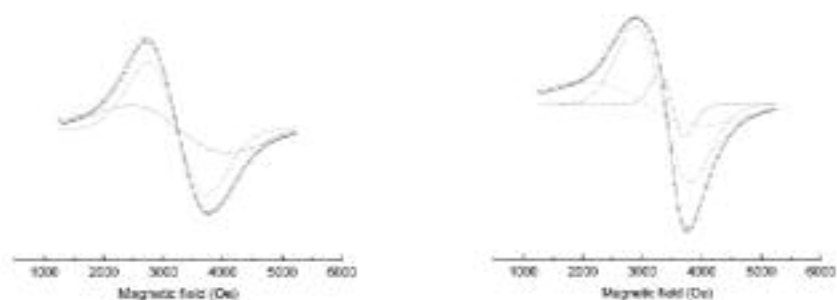


Fig. 3. EPR spectrum for nanoparticles of Fe_2O_3 in SIEL and SKTN matrixes

As followed from our experiments, the iron(III) diiminate had minimum impregnation ability into PAR (0.5 wt % in comparison with 1.5 wt % for Co diiminate) perhaps due to a larger size of molecule. The impregnation effectivity depends also on swelling ability of polymeric matrix (~ 10 wt % for PAR, ~ 9 wt % for PS and $\sim 2-3$ wt % for PE at $38^\circ C$ and 12.5 MPa). The monoacetylferrocene is more effective impregnant may be due their good solubility in $sc-CO_2$ (near 10 wt % into PAR and PS and ~ 4 wt % into PE).

The FT-IR spectra (Fig. 4) confirm the presence of diiminate in PAR films after impregnation (the $\nu(\text{NH})$ band at 3300 cm^{-1} for Fe(III)-HFDI). After heating, the $\nu(\text{NH})$ band disappears and the $1200\text{-}1300\text{-cm}^{-1}$ region of $\nu(\text{CF}_3)$ vibrations becomes identical to that of a polymer. At the same time, the final weight gains are smaller than the weights of pure iron impregnated into films. Special previous experiments showed that PAR does not lose weight and does not color when heated under the same conditions. So we can assume that a fraction of the complex is evaporated with heating. After heating, the film color strengthens and the surface acquires metallic luster.

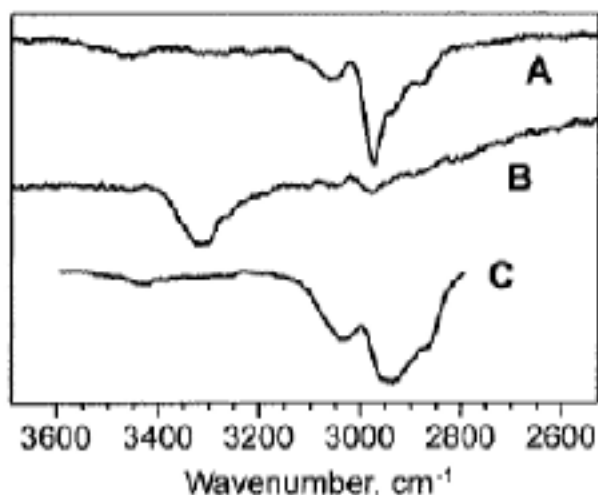


Fig. 4. FT-IR spectra of (a) initial, (b) impregnated with Fe(III)-HFDI, and (c) impregnated and heated polyarylate samples. The band at 3300 cm^{-1} corresponds to $\nu(\text{NH})$ of Fe(III)-HFDI.

Size of the metallic clusters into the polymers was in the interval from 5 to 60 nm (from SAXS data). As example Fig. 5 demonstrates the particles size for MAF into PE. One can see that particles size distribution had a maximum near 20 nm (diameter of the particles).

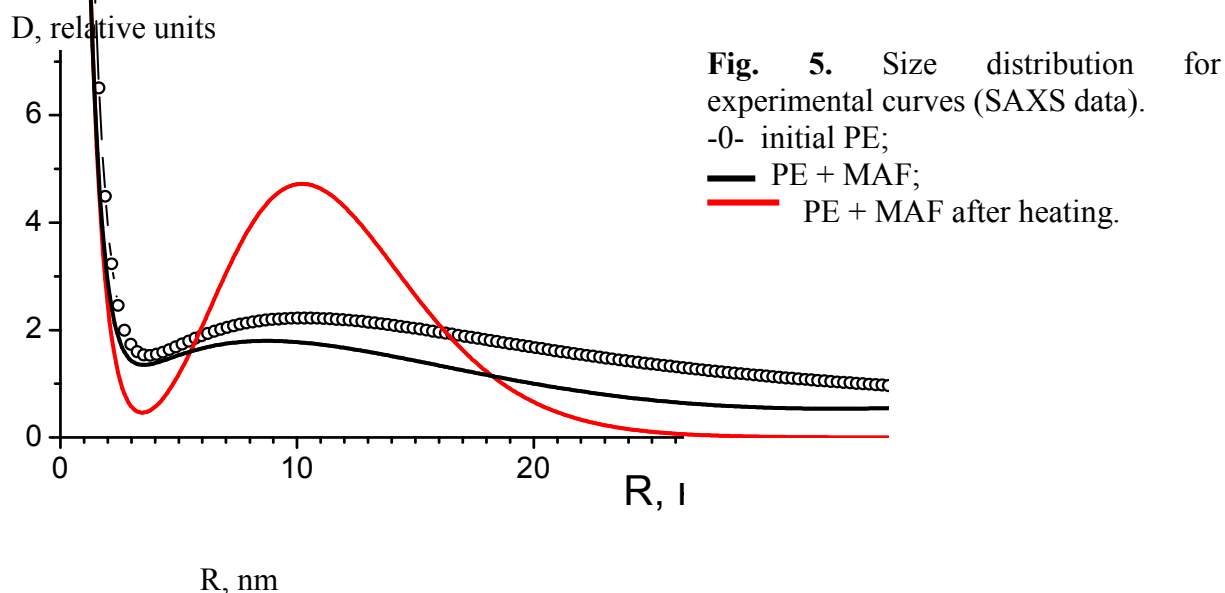


Fig. 5. Size distribution for experimental curves (SAXS data).
 -○- initial PE;
 — PE + MAF;
 — PE + MAF after heating.

CONCLUSIONS

Making of polymers containing magnetic nanoparticles was studied by several different methods. First method consisted in thermal decomposition of metal-containing compounds in polymer dissolved in mineral oil. Second method included cryochemical synthesis for making

metal-polymeric nanoparticles in the polymeric samples which preliminary were treated by supercritical CO₂. And third method embraced the supercritical technology. The diffusion of metal-containing compounds (iron and cobalt carbonyls and diiminates) dissolved in supercritical carbon dioxide into different polymers (polyethylene, polyarylate, polystyrene) films were investigated. Some physical characteristics of polymeric films have been studied. The impregnation was confirmed by the FT-IR spectroscopic data. Thermal reduction of metal ions was investigated. Transformations of the metal-containing complexes in the polymer films were studied by different analytical methods. The iron and cobalt contents in polymeric films were nearly several weight %. The FT-IR and ESCA spectroscopic studies showed that metal-containing complexes interact with functional groups of the polymers. Subsequent thermal reduction of metal in air results in thermal degradation with ligand decomposition and enrichment of the surface with metal atoms. According to the SAXS data, the size distribution of metal-containing particles ranges from several to hundreds nanometers.

ACKNOWLEDGEMENTS

This work was supported by the Russian Foundation for Basic Research (projects no. 05-03-33046, 04-03-39012, 04-03-32311, 04-03-08143) and NATO project SfP 977998. The authors are also grateful to Russian Academy of Sciences (programs of Division of Chemistry and Material Sciences "Creation of new metallic, ceramic, glass, polymeric and composite materials" and "Creation and investigation of macromolecules and macromolecular structures of new generation") for financial support. Authors thanks also V.V.Volkov, E.V.Shtykova, K.A.Dembo and S.V.Amarantov for SAXS measurements.

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