

# Mössbauer Investigation of Highly Dispersed Iron Particles in Crazed Porous Polymers

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**Abstract.** Formation and stability of highly dispersed iron particles in crazed porous polymer matrices were studied. The iron–polymer composites obtained were characterized by different morphologies and dimensions of iron particles. The phase content of the iron constituent in a composite studied by Mössbauer spectroscopy was shown to depend on the type of the iron salt and the method of introduction of the initial reagents into a polymer.

**Key Words:** crazing, iron–polymer composites, Mössbauer spectroscopy.

## 1. Introduction

Materials containing iron nanoparticles are of interest for high-density magnetic recording. In view of that, the preparation and stabilization of iron particles with controlled dimensions is an important problem. One way of nanoparticle stabilization is the synthesis of iron particles inside polymer matrices. There are several approaches for the synthesis of iron particles in a polymer, e.g. thermo-chemical decomposition of iron carbonyl in polymer melts [1], electrochemical reduction inside solvent swollen polymer matrix [2], and ion implantation [3]. The main disadvantages of the known approaches are oxidation and destruction of the polymer matrix under the influence of temperature or of the  $\text{Fe}^+$  ion beam [1, 3], a relatively high cost of polymers which are capable of swelling [2], and poor mechanical properties of such composites.

In this paper, an alternative approach to the preparation of iron–polymer composites based on commercial polymers is proposed. Here, the reduction of iron ions is carried out *in situ* within nanometre-sized pores of a polymer obtained via solvent crazing [4]. Solvent crazing is the transition of glassy and semicrystalline polymers in a highly dispersed and oriented state upon uniaxial stretching in the presence of adsorptionally active media. Earlier, highly dispersed particles of nickel, copper and silver were introduced into porous

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polyethylene, isotactic polypropylene, poly (ethylene terephthalate), and poly (vinyl chloride) films using solvent crazing. It is important that the reduction of metal particles in crazed polymer was carried out without destruction of the polymer film. Those metal–polymer composites were shown in [5, 6] to be characterized by a high level of mutual dispersion of thermodynamically incompatible components and by good mechanical properties.

The objective of this work was to investigate the formation and stability of iron particles inside crazed porous films of high-density polyethylene by Mössbauer spectroscopy, X-ray diffraction and scanning electron microscopy (SEM).

## 2. Experimental

Commercial films of isotropic high-density polyethylene (HDPE) ( $\overline{M}_w = 200000$ , thickness 75  $\mu\text{m}$ ) were used as initial materials. To obtain porous samples, the films of HDPE were stretched up to 200% in the presence of isopropanol with a rate of 5 mm/min using hand-operated clamps. In this case craze nucleation and growth proceed via the mechanism of delocalized solvent crazing [7], i.e. throughout the bulk of the sample. The as-received porous HDPE matrices were characterized by their effective volume porosity, which was estimated by the changes in geometrical size of the polymer under crazing. Its value was  $\sim 40$  vol.%. The average diameter of the polymer pores evaluated using the method of pressure-driven liquid permeability was 6 nm.

We studied the development of iron particles as a result of chemical reduction of ammonium iron(II) sulfate hexahydrate,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , and iron(III) chloride hexahydrate,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , using sodium boron hydride,  $\text{NaBH}_4$ , as a reducing agent. The concentration of water–alcohol solutions of the initial reagents was 0.1 mol/l (the content of alcohol was 20 vol.%).

Low-molecular-weight substances were introduced into polymer matrices using two approaches:

- I First, a porous structure of the polymer was obtained by deforming the polymer film in iron-free isopropanol. Then, streams of the metal salt and reducing agent proceeded to the polymer using counter-current diffusion. In this case, driving force of the reagent diffusion to the reaction front was provided by precipitation and removal of the as-formed substance from the reaction sphere. The reduction time was 1 h. After reduction the samples were washed in distilled water and dried in the isometric state at 100°C during 2 h in the atmosphere of argon.
- II Pores were created and filled simultaneously during the deformation of the polymer film in the water–isopropanol solution of an iron salt. Then, the filled polymer film was stored in the solution of  $\text{NaBH}_4$  to reduce iron.

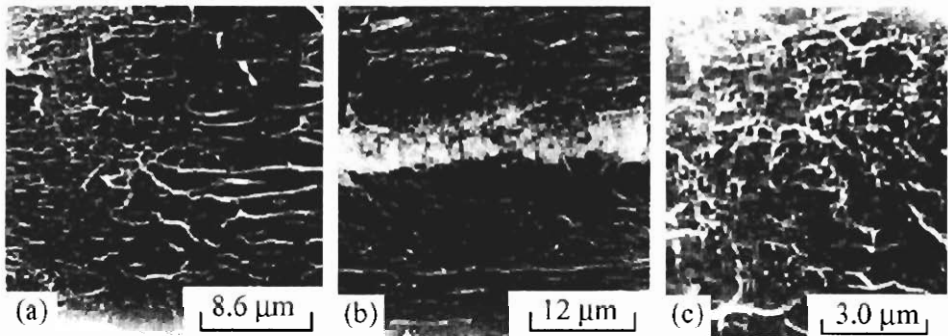


Figure 1. SEM-micrographs of (a) the initial porous HDPE matrix and iron-containing composites obtained by (b) method I and (c) method II.

The content of the iron introduced into the film was determined gravimetrically. In this work, composites containing up to 40 wt.% of iron were obtained.

The phase composition of the iron-polymer samples was studied by absorption Mössbauer spectroscopy. Mössbauer spectra were measured with a Perseus spectrometer working at constant velocities; the control and adjustment of the transducer velocity were performed by a laser interferometer. A standard  $\gamma$ -source of  $^{57}\text{Co}$  in the matrix of metallic rhodium with the activity of 0.6 GBk (a product of Cyclotron Co., Ltd., Obninsk, Russia) was employed. In this work, isomer shift values are related to  $\alpha$ -Fe at room temperature.

X-ray diffraction analysis of samples was performed with a DRON-3M diffractometer using  $\text{MoK}_\alpha$  radiation (Zr filter). The average crystallite size was estimated using Scherrer's formula.

The morphology of composites obtained was examined with a Hitachi S-520 scanning electron microscope. Samples were prepared using the procedure of brittle fracture in liquid nitrogen and plating with a platinum-palladium alloy.

### 3. Results and discussion

After reduction, the iron-polymer composite films become dark-gray. X-ray investigation of samples obtained by method I shows that they contain metallic iron. Peaks of  $\alpha$ -Fe with the lattice distance of  $d_{110} = 2.02(1) \text{ \AA}$  and  $d_{200} = 1.43(1) \text{ \AA}$  (2.0268 and 1.4332  $\text{ \AA}$  [8]) are observed in their diffraction patterns. The average diameter of iron crystallites is 40(5) nm for different preparation conditions. Samples obtained by method b do not show any peaks in X-ray patterns.

SEM micrographs of the initial HDPE crazed film (a) and iron-HDPE composite films obtained via methods I (b) and II (c) are presented in Figure 1. It can be seen that the structure of the initial crazed HDPE film represents a system of co-penetrating pores. In the composite obtained via method II, the spherical particles with the dimension of 0.1  $\mu\text{m}$  are discretely and uniformly distributed within the porous polymer matrix. When the counter-current diffusion approach

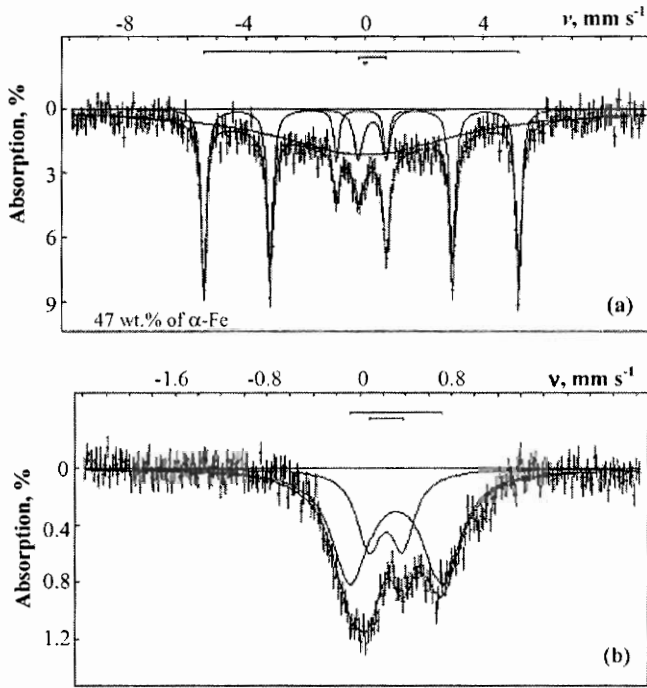
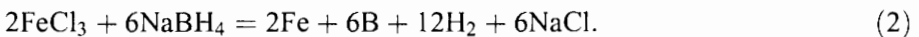
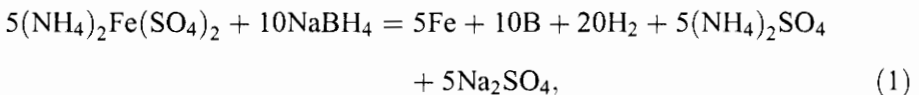


Figure 2. Mössbauer absorption spectra of the iron-containing HDPE composites obtained by (a) method I and (b) method II.

(method I) is used, spherical particles with a diameter of 0.2–0.4  $\mu\text{m}$  form a layer with a thickness of 4–6  $\mu\text{m}$  inside a polymer. It is important to stress that the structure of the original porous matrices is unchanged after the reduction of iron inside a polymer.

It is known [9] that chemical reduction of metals from their salts by  $\text{NaBH}_4$  gives a mixture of products. However, X-ray diffraction and microscopic investigations of metal–polymer composites do not allow us to determine amorphous admixtures that are produced during the reduction process within a polymer film. For example, reduction of iron by  $\text{NaBH}_4$  can be described by the following reactions:



From the literature data [9], 3.5 to 10 wt.% of boron is obtained in these processes. In reaction (2), 5 to 10 wt.% of iron(III) hydroxide is also formed owing to the high pH (pH = 11) of an aqueous  $\text{NaBH}_4$  solution.

The composite film was found to change its color immediately from dark-gray to yellow-brown after the removal of the reducer excess, which is connected with the oxidation of highly dispersed iron particles in air and with the formation of different iron oxo-, hydroxo-derivatives. It was not possible to avoid iron oxidation even by drying and storing the iron-polymer composite films in the inert atmosphere of argon.

Mössbauer spectroscopy is a very informative technique for the analysis of iron-polymer samples. It allows one to confirm the presence of metallic iron in a polymer and to estimate the amount of admixture of other iron-containing phases. Mössbauer spectra of the samples obtained are presented in Figure 2. For a sample received via method a (Figure 2(a)) we found a sextet of  $\alpha$ -Fe and a doublet related to Fe(III) compounds. The content of  $\alpha$ -Fe depends on the type of iron salt used and varies from 20 to 60 wt.%. The amount of Fe(III) compounds increases when we use  $\text{FeCl}_3$ . There is also an extended absorption background in the spectrum that is difficult to explain. Due to the layer distribution of highly dispersed iron particles within HDPE the chemical composition of samples remains constant even during storage of the composites in the presence of air for 3 months. Apparently, a thin oxide film that prevents penetration of oxygen molecules into the layer is obtained on the surface of the iron layer within a polymer.

Mössbauer absorption spectrum of the iron-polymer sample obtained by method II (Figure 2(b)) differs completely from that of the sample obtained by method I. This spectrum can be presented as a superposition of two doublets with isomer shifts  $\delta_1 = 0.33(1) \text{ mm} \cdot \text{s}^{-1}$  and  $\delta_2 = 0.24(1) \text{ mm} \cdot \text{s}^{-1}$  and quadrupole splitting values  $\Delta_1 = 0.79(1) \text{ mm} \cdot \text{s}^{-1}$  and  $\Delta_2 = 0.29(1) \text{ mm} \cdot \text{s}^{-1}$ . These Mössbauer parameters correspond to oxo-compounds of Fe(III) with octahedral and tetrahedral coordination of the metal, respectively [10]. There are no  $\alpha$ -Fe lines in the spectrum that can be explained by rapid oxidation of highly dispersed iron particles, discretely distributed within the porous HDPE matrix, by water and alcohol (Figure 1(b)).

Thus, iron nanoparticles are formed in pores of a crazed polymer during reduction of  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  ions by sodium boron hydride. The nanoparticles are extremely reactive, so that their oxidation by solvents or oxygen starts immediately after their formation. Aggregation of metallic particles decreases the oxidation rate. In addition, these aggregates are covered by a layer of oxidation products protecting the metallic nuclei from further oxidation. The aggregates are well visible in micrographs and have bigger sizes as compared to the size of iron crystallites. In the case of a low concentration of iron nanoparticles in a polymer (if method II is applied), aggregation is not possible and each nanoparticle is oxidized completely. Micrographs show big particles (see Figure 1(c)) consisting of insoluble iron oxidation products.

We were unable to stabilize iron nanoparticle with super-paramagnetic properties—stable particles were too big. Nonetheless, crazed porous polymers

seem to be promising as templates for synthesis and stabilization of iron nanoparticles and preparation of composite materials with different distributions of metallic particles inside a polymer. Particle sizes can be diminished by introducing surfactants and other additives during the synthesis, which would cover iron particles immediately after their formation and protect them from oxidation.

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