Colloids and Surfaces A 540 (2018) 53–66

Contents lists available at ScienceDirect

Colloids and Surfaces A

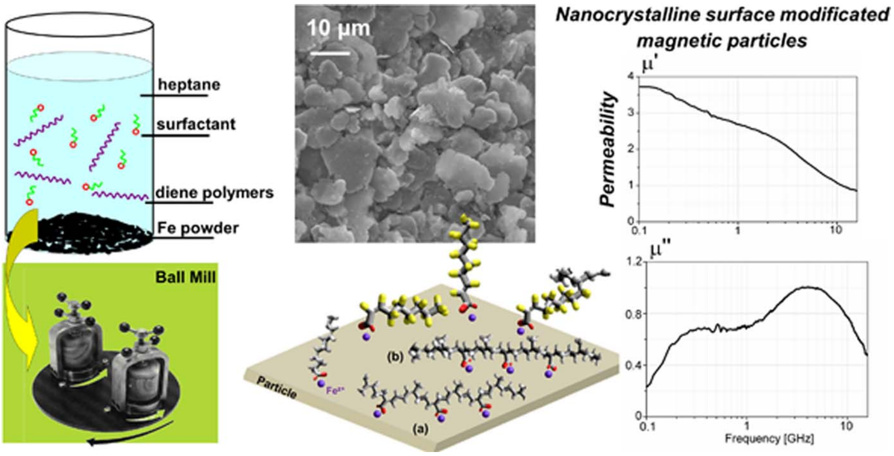
journal homepage: www.elsevier.com/locate/colsurfa

Chemical modification of Fe powders under surfactant-assisted ball milling in polydiene solutions

Alexander V. Syugaev[a,*], Alena N. Maratkanova[a], Svetlana F. Lomayeva[a], Anatoly A. Shakov[a], Dmitry A. Petrov[b], Stanislav Yu. Bobrovskii[b], Boris V. Senkovskiy[c,d], Konstantin N. Rozanov[b]

[a] Physical-Technical Institute UB RAS, 132 Kirov Street, 426000 Izhevsk, Russia
[b] Institute for Theoretical and Applied Electromagnetics RAS, 13 Izhorskaya ul., 125412 Moscow, Russia
[c] II Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, 50937 Köln, Germany
[d] St. Petersburg State University, 7/9 Universitetskaya nab., 199034 St.-Petersburg, Russia

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Surfactant-assisted ball milling
Surface modification
Fe powder
Diene polymers
Particle characterization
Magnetodielectric composites

ABSTRACT

Composite materials are of great importance for both science and technology. In this work, the high-energy ball milling of carbonyl iron in the presence of polydienes of various structures (*cis*-polybutadiene, *cis*- and *trans*-polyisoprene) and surfactants (perfluorononanoic and stearic acid) is used to chemically modify the bulk and surface of iron particles. A comprehensive study of the particles was performed with the use of various experimental techniques. Mechanochemically activated iron surface favors the processes of decomposition and transformation of organic molecules that make up the milling medium, resulting in the accumulation of carbides in the particles bulk and the formation of modified organic layer on the surface. The composition and thickness of the modified layer as well as the arrangement of organic molecules in it was shown to be sensitive to variations in the chemical structure of the initial diene polymer and the type of surfactant added. The as-grown layers inhibit corrosive destruction of the resulting particles. Platelet-shaped particles prepared by surfactant-assisted ball milling can be used as fillers for magnetodielectric composites with high permittivity and permeability values.

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[*] Corresponding author.
E-mail address: syual@mail.ru (A.V. Syugaev).

https://doi.org/10.1016/j.colsurfa.2017.12.063
Received 18 October 2017; Received in revised form 20 December 2017; Accepted 26 December 2017

1. Introduction

Magnetodielectrics, including iron-resin composites, are considered as promising materials for the use in various technical applications, in particular, as microwave absorbing materials [1–4]. The easiest way to produce such composites is physical mixing of pure iron powders and resin followed by warm curing in order to melt the resin and make it flow around the iron particles. The resin insulation provides electrical resistivity and minimizes eddy current loss.

To improve compatibility between insulating matrix and iron particles, the particle surface may be chemically modified with different polymer and/or surfactant molecules. Currently, surface modification is successfully used to stabilize and improve the properties of particles [5–11]. As-formed layer of organic molecules on the particle surface can also provide better adhesion of the particles with the polymer matrices, which is important in the development of composite materials [12,13]. In addition, the modified layer on the surface of the particles would significantly enhance their corrosion resistance in various aggressive media being potentially used for their real operation. One of the simplest and most successful ways of chemical modification of the particles is their surfactant-assisted ball milling in organic solution containing corresponding polymer [14–17]. Besides, the use of surfactants under milling of iron may facilitate the formation of platelet-shaped particles and then provide desirable magnetic properties of magnetodielectrics under certain conditions (milling time, amount surfactants, ball to powder ratio, etc.) [18].

As compared to more equilibrium ways of organic layer synthesis, such as chemical solution deposition or chemical vapor deposition, mechanochemical treatment is characterized by (i) stronger adsorption of organic molecules on mechanochemically activated surface; (ii) possible modification of the surface with even relatively inert substances, such as paraffin and Teflon; (iii) stronger transformation of the substance in the surface layer [18–23]. The rate of conversion/decomposition of organic molecules, including polymers and surfactants, is particularly high when treating catalytically active particles, for example, iron particles known as an active catalyst for the dehydrogenation of organic molecules [18,24,25]. The structure of the as-formed organic film may be very sensitive to variations in the molecular structure of the starting polymer. For example, the influence of substituents in the main chain or *cis-trans* isomerism is not clear so far. To get deeper insight into this matter, a comparative study was carried out on the layers formed under mechanochemical modification of iron with unsaturated polymers, similar in their chemical structure (*cis*-polybutadiene, *cis*- and *trans*-polyisoprene). In this work, simultaneous modification of iron particles with both polymer and surfactant (perfluorononanoic acid, stearic acid) is also studied. Surfactant additives are commonly used to assist the milling process [17] and prepare the particles of platelet shape [24]. This approach of simultaneous modification of metal particles with polymers and surfactants has been recently shown to be rather promising [26].

The work was focused on studying the effect of the chemical structure of diene polymer and surfactant on the structure of modified layer formed under mechanical milling of iron as well as the effect of this layer on the properties of the as-prepared powders, including corrosion resistance and microwave performance. Within the scope of this study, the following tasks were carried out: (i) the fabrication and structural characterization of chemically-functionalized iron particles by means of surfactant-assisted ball-milling of iron powder in polydiene-containing solution; (ii) thorough analysis of the modified organic layer formed on the iron particles under ball-milling in organic solutions; (iii) detailed analysis of the changes induced in the particle bulk by the destruction of organic molecules at interfaces; (iv) study of the protective properties of the chemically modified layers of iron particles; (v) study of the microwave characteristics of the composites comprising the modified particles.

2. Experimental

Mechanochemical treatment of carbonyl iron (99.98%) was performed in a planetary ball mill Fritsch P7 (720 rpm, G-force 25 g) equipped with the vials (45 cm^3) and balls (16 pcs, 12 mm dia.) made of the hardened steel. Milling was carried out in polydiene (*cis*-polyisoprene, *trans*-polyisoprene, *cis*-polybutadiene) solutions in heptane. Surfactants (perfluorononanoic acid $C_8F_{17}COOH$ and mixture of stearic acid $C_{17}H_{35}COOH$ with perfluorononanoic acid in the proportion of 5:1) were added into the milling mixture when it was the case. The second surfactant has been previously shown to be a good choice for preparing the magnetodielectric composites with the improved microwave performance [27]. Besides, the powders were milled in the surfactant solutions in heptane (without polymer additives).

The volume ratio of iron to polymer was 4:1 in all cases with the sum weight of the load being 10 g. The milling was carried out in the vials fully filled with the solutions of polymer (1.5 wt.%) and surfactant (3 wt.%) in heptane at the ball-to-powder mass ratio of 11:1. After milling for 24 h, the powder was washed in boiling hexane. Wet powder was blown dry with argon to evaporate the solvent and then placed in a container filled with argon.

The powders prepared in solutions of *cis*-polyisoprene, *trans*-polyisoprene and *trans*-polybutadiene were denoted as *c-PI*, *t-PI*, *PB*, respectively. The powders prepared by surfactant-assisted ball milling with perfluorononanoic acid were denoted as *c-PI/FA*, *t-PI/FA*, and *PB/FA*. The powders prepared with the mixture of stearic and perfluorononanoic acids were designated as *c-PI/MA*, *t-PI/MA*, and *PB/MA*. The powders obtained in the surfactant solutions but without polymer were designated as *MA* and *FA*. Additionally, the samples of sols (*PB/FA**, *PB/MA**) formed under surfactant-assisted ball milling in polybutadiene solution were measured.

The secondary electron microscopy (SEM) images were acquired with a microscope VEGA 3 LMH (TESCAN). The particles were dropped from their suspension in *n*-hexane onto a copper substrate. Structural characterization of the powder bulk was performed by means of X-ray diffraction (XRD) analysis at a Rigaku diffractometer with a CoK_α source (1.79 Å) using graphite monochromator. The Mossbauer spectra were measured at room temperature with a SM2201DR spectrometer in the constant acceleration mode with ^{57}Co source embedded in the Cr matrix.

X-ray absorption spectra (XAS) at the Fe K edge (7112 eV) were measured at the DORIS III synchrotron radiation storage ring at the HASYLAB/DESY, beamline A1, using a Si(111) double crystal monochromator. Being sensitive to the local atomic structure up to 5–10 Å around an absorbing atom, XAS is a very informative tool to study the mechanically milled powders with no long-range order. XANES (X-ray absorption near-edge structure) and EXAFS (Extended X-ray absorption fine structure) techniques analyze oscillations just beyond (~50 eV) and above (up to 1000 eV) the ionization edge, respectively [28,29]. XAS spectra were measured with the use of both transmission and total electron yield (TEY) modes. The EXAFS data analysis was performed according to the conventional procedure by applying IFEFFIT code [30]. The phase shifts and backscattering amplitudes were calculated using the FEFF8 code [31]. It should be remembered that the uncertainty in the bond length that can be achieved with the EXAFS analysis is about 1–3% whereas the accuracy in the determination of coordination number is about 10–30%, as it is strongly correlated with the Debye-Waller factor.

The XANES spectra at the C K (285 eV), Fe $L_{2,3}$ (721 and 708 eV, respectively) and F K (692 eV) absorption edges were acquired at the Russian-German beamline (RGBL) at the BESSY II, HZB Berlin GmbH. The XANES spectra were obtained in a TEY mode by measuring the drain current from the sample changing the incident photon energy. The powder particles were dropped from their suspension in *n*-hexane onto a copper substrate. The polarization-dependent XANES spectra were obtained by changing the orientation of the substrate coated with