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Surface modification of iron particles with polystyrene and surfactants under high-energy ball milling

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ABSTRACT

Metal–polymer composites are widely used in many applications including efficient microwave absorbing materials. Interface makes up a great fraction in the composite bulk and may significantly affect the functional properties of the composite. In this work, we have modified the surface of iron particles with polystyrene and fluorine-substituted/alkyl carbon acids by wet mechanochemical treatment. The study was performed by means of Fourier-Transform Infrared (FT-IR) spectroscopy, Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy and X-ray Photoelectron Spectroscopy (XPS). It is shown that wet mechanochemical treatment is accompanied by chemisorption of the surfactant molecules on the iron particle surface through the formation of the carboxylate derivatives and catalytic dehydrogenation resulting in the formation of condensed polyaromatic structures. Surface modification of particles with polystyrene is observed in all cases regardless of the presence and type of surfactant in the milling environment. Stable binding of polystyrene with the particle surface is achieved by different ways, including binding through the oxygen-containing groups, covalent bonding with the polyaromatic structures and/or tails of the chemisorbed fluorine-substituted acid. As-formed organic layers stabilize the metal particles preventing them from oxidation and agglomeration and increase their chemical compatibility with polymer matrices in subsequent fabrication of the metal–polymer composites.

1. Introduction

Metal–polymer composites attract researchers' attention due to their use in various fields of electronics, including microwave application devices [1–3]. Such composites offer a lot of advantages, among which are cost effectiveness, flexibility, lightweight, etc. [4]. To develop improved metal–polymer composite materials a better understanding of the chemistry and structure of the metal–polymer interface is needed since the interface makes up a great part in the composites and significantly affects the functional properties of the devices. Much research is being carried out for providing the chemical compatibility in the metal–polymer interface. A variety of experimental techniques can be used to chemically modify the metal surface by different functional groups. One of the most effective and promising ways is high-energy ball milling of metal powder in an organic environment, whose chemical composition is close to that of further organic matrix [5]. Surfactant additives are used to affect significantly both size and shape of the metal particles. Recently, the chemical structure of the surface layers grown on the surface of iron particles under the mechanochemical synthesis in the presence of polystyrene and surfactant molecules (stearic and perfluorononanoic acids) has been studied [6]. It has been shown by means of NEXAFS and XPS techniques that the surfactant-assisted mechanical milling makes for the flake-shaped particles covered with the layer of surfactant molecules chemisorbed. However, it has not been definitely clarified whether the surface modification of the metal particles with the polystyrene molecules takes place, since NEXAFS and XPS spectroscopies are not capable of distinguishing the contributions from different compounds containing double carbon–carbon bonds. The double bonds observed in NEXAFS spectra could be assigned to both polystyrene and various products of dehydrogenation of organic environment, which are formed on the iron surface under the mechanochemical synthesis. This point is of key importance as the surface modification with the polystyrene fragments favors better compatibility with the polymer matrix in the subsequent fabrication of the metal–dielectric composites. Besides, it has been not clear from the NEXAFS and XPS data if the surfactant molecules retain their structure unchanged under mechanical milling or the chemisorbed layer contains only the products of their partial destruction.

To better understand the chemical structure of the as-formed organic layers, a complementary study of the surface layer constituents was required. FT-IR spectroscopy is the most appropriate and helpful technique in this case because it allows one to distinguish different

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functional groups [7], in particular the contributions from polystyrene and various products of the dehydrogenation and destruction of polystyrene and surfactant molecules. Comparison of FT-IR spectra of the milling environments with the components of the surface layers will clarify a number of important items related to the surface modification mechanism.

In this paper, Fourier-Transform Infrared (FT-IR) spectroscopy was used as main experimental technique to study the chemical structure of the surface layer of iron particles formed under mechanical milling of Fe powder in the polystyrene- and surfactant-containing environment. FT-IR results complementary by NEXAFS and XPS data would allow us to study a possibility of chemical modification of the iron particle surface with the polystyrene fragments, mechanisms of such modification and main processes occurring during wet mechanochemical treatment of iron particles with the presence of polystyrene and surfactant molecules.

2. Experimental

2.1. Synthesis and materials

The samples were fabricated by mechanical milling of the Fe powder (99.98%) in the polystyrene (Sigma-Aldrich) solution in *p*-xylene. The starting Fe powder particles had a stone-like shape and the size of less than 5 μm. Mechanical milling was performed in a planetary ball mill Fritsch P7. Vials and balls were made of the hardened steel. The sum weight of Fe and polystyrene in the starting mixture was 10 g with the Fe/polystyrene ratio of 80:20 vol.%. The reaction mixture was prepared immediately in the vial. The total amount of *p*-xylene was 20 g. Polystyrene was preliminarily dissolved in the heated distilled *p*-xylene (10 g) and then transferred quantitatively into the vial with an additional 10 g of solvent. After that the iron powder (9.673 g) was loaded into the vial with an appropriate surfactant (3 wt.%) if that was the case, the concentration of surfactant being indicated with respect to the solvent weight (20 g). Stearic acid ($C_{17}H_{35}COOH$) and perfluorononanoic acid ($C_8F_{17}COOH$) were added into the milling mixture for the samples designated as *PS* + *SA* and *PS* + *PFNA*, respectively. For the samples synthesized with the mixture of surfactants (*PS* + *SA* + *PFNA*), stearic and perfluorononanoic acids were added into milling liquids in the ratio of 1.9:1.1 wt.%, respectively. The sample synthesized without any surfactant will be referred to as *PS*. The mixtures were mechanically milled for 24 h. Due to the forced air-cooling the temperature of vials did not exceed 60 °C during milling.

2.2. Sample preparation

After the milling the vials were cooled to the room temperature and the powder was separated by decantation. The precipitate was boiled in 10 ml of *n*-hexane for 1 min and then ultrasonicated for 15 min. This procedure was repeated five times with decantation of the solvent and its replacement for a new portion, preventing the precipitate from its contact with air. The synthesis procedure was described in detail elsewhere [6].

For a long-term protection from atmospheric oxidation the precipitate was stirred under a layer of hexane with 1 g of melted paraffin, and then the solvent was evaporated at 90 °C. The same rinsing procedure was used to remove thoroughly paraffin layer served as conserving shell for the powder surface.

2.2.1. Preparation of samples for FT-IR characterization

The FT-IR study was carried out on i) chemisorbed organic layers on the metal powders, and ii) liquids, in which the mechanochemical synthesis was performed. Below, the first ones will be denoted as "extracts", the second ones —as "liquids". The chemisorbed layers were separated from the particles as follows. A portion of the powder (500 mg) was completely dissolved in 5 M HCl (10 ml). Then 5 ml of CCl_4 was added, and the blend was thoroughly mixed to extract the maximum quantities of the surface layer organic constituents. After the decomposition of the mixture into different fractions, 3.5 ml of its non-aqueous fraction was taken and dropped onto the ZnSe crystal for the FT-IR analysis. The spectra were measured after CCl_4 had been completely evaporated. The weight of the non-volatile components of the chemisorbed layers for different samples varied from 4 mg to 8 mg. The "extracts" films deposited on a silicon substrate were also studied by the Raman spectroscopy.

The samples of "liquids" for the FT-IR study were deposited onto the ZnSe crystal and dried until complete evaporation of the solvent *p*-xylene, after which the non-volatile components were studied. It should be noted that an addition of a stearic acid into the milling mixture results in the formation of stable sols of the dispersed particles, while there were no sols in the case of the *PS* and *PS* + *PFNA* sample. As for the sols, the measured spectra relate to both the milling environment components and the constituents of the surface layers of the sol fine particles.

2.3. Measurements

2.3.1. FT-IR characterization

FT-IR spectra were measured with an Excalibur Varian 3100 FT-IR spectrometer using a PIKE Technologies Attenuated Total Reflection (ATR) accessory (ZnSe crystal). ATR operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample in ATR mode. The spectra were collected in the range of 650–4000 cm^{-1} with a resolution of 2 cm^{-1}. The measured spectra were normalized to the total reflectance intensity beyond the spectral features.

2.3.2. Raman spectroscopy characterization

Raman spectra were acquired with a Horiba LabRam HR800 spectrometer using a He–Ne laser operating at a wavelength of 632.8 nm and input power not exceeding 20 mW at the sample surface.

2.3.3. NEXAFS characterization

The NEXAFS spectra were acquired at the RG-PGM dipole beamline at BESSY II, Helmholtz-Zentrum Berlin. The beamline uses the plane-grating monochromator with the 400 lines/mm and 1200 lines/mm gratings to select photon energies in the range from 30 to 1500 eV with a resolving power of up to $E/\Delta E = 100.000$. A detailed description of the beamline can be found elsewhere [8]. All the X-ray absorption spectra were measured under ultrahigh vacuum conditions ($\sim 5 \times 10^{-10}$ Torr).

The NEXAFS data were acquired in a total electron yield (TEY) mode by measuring the sample drain current with varying photon energies. The energy resolution was equal to ~80 meV for the range of the C K edge. The measured spectra were analyzed using the procedure described in detail in [9]. The spectra were normalized to the incident photon flux recorded as TEY signal from the clean gold film deposited onto the tungsten substrate fixed at the manipulator holder. The C K edge absorption spectral features were calibrated with respect to the energy position of the $C1s \rightarrow \pi^*(C{=}C)$ resonance of the measured absorption spectrum of highly-oriented pyrolytic graphite to be at 285.35 eV [10].

For the analysis, the powder suspension in hexane was dropped onto a rough copper substrate immediately before loading into the spectrometer vacuum chamber. The reference NEXAFS spectra were measured for pure substances prepared as thin films deposited on a copper substrate from their solutions in appropriate solvents (polystyrene in toluene; perfluorononanoic and stearic acids in heptane). To simulate the NEXAFS spectra for the mixtures the measured reference spectra were then summed up according to the proportions of the corresponding pure substances in the milling environment.