

Improved thermooxidation and sedimentation stability of covalently-coated carbonyl iron particles with cholesteryl groups and their influence on magnetorheology

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ABSTRACT

Sedimentation of particles in magnetorheological suspensions represents a crucial problem that concerns their efficient long-term application in practice. Prepared carbonyl iron (CI) microparticles coated with a low density substance, cholesteryl chloroformate, via a two-step reaction and immersed in silicone oil, exhibit three positive aspects: (1) the CI particle modification increased the compatibility between the particles and the silicone oil resulting in improved long-term stability (reduction in sedimentation); (2) the coating provided the particles with enhanced thermal stability in the oxygen atmosphere; and (3) rheological measurements proved a promising magnetorheological performance at different particle weight fractions.

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1. Introduction

Magnetorheological (MR) fluids are basically two-phase systems consisting of ferromagnetic or ferrimagnetic particles and a liquid non-magnetizable medium [1–8]. In the absence of an external magnetic field, particles are randomly dispersed. However, after the application of an external magnetic field, the magnetic dipoles induced in the particles enable them to orient along the magnetic field streamlines and create internal structures. The presence of such structures causes an abrupt change of the rheological properties (viscosity and viscoelastic moduli) over several orders of magnitude [9–13]. This phenomenon is reversible immediately after switching-off the magnetic field. Thus, such MR fluids find perspective application, for example, as dumping systems or torque transducers [14,15]. Furthermore, such suspensions can be successfully applied as magnetoresistors in various devices, due to their electro-conducting character [16–25].

Unfortunately, MR fluids exhibit some shortcomings such as particle sedimentation and poorer oxidation stability. Magnetic particles usually settle very quickly when dispersed in a fluid, due to the different densities of both media. Oxidation decreases

the magnetization saturation of the particles and thus the MR performance. Many studies have dealt with the improvement of sedimentation and oxidation stability [26–28]. An improvement of the long-term stability can be made by adding various surfactants, fillers or thixotropic agents or using bidispersed and bimorphic MR fluid [29–32]. Both shortcomings can be substantially attenuated by the compact coating of magnetic particles with a low density and non-oxidizing substance. This results in a partial decrease in particle density and an enhanced mutual compatibility between the particles and the carrier liquid that reflects in improved MR performance [33–39].

The aim of this study is to apply such a procedure to carbonyl iron (CI) particles. First, the CI particles were functionalized with reactive silane, and subsequently, the surface of the particles was coated with cholesteryl groups. Thermal and sedimentation stability as well as the rheological properties of MR fluids based on such modified CI particles were investigated under steady shear flow to document improved MR performance.

2. Materials and methods

2.1. Materials

Carbonyl iron microparticles (ES grade) consisting of >97% of iron particles produced by BASF (Germany), solvent tetrahydrofuran (THF) by (POCH, Poland), (3-aminopropyl)triethoxy silane,

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cholesteryl chloroformate (both Sigma Aldrich, USA), and triethylamine (Fluka, Switzerland) were used as received.

2.2. Modification of CI microparticles with (3-aminopropyl)triethoxy silane

CI particles were first treated with 0.5 M HCl for 1 h in order to activate the surface and obtain reactive OH groups on the surface. Then, the particles were washed with water, ethanol, and acetone. Finally, the powder was dried from residues for 6 h under a vacuum. The bulk of the 100 g of surface-activated particles was put into the 3-neck flask with 250 ml of toluene. The particles were stirred under 350 rpm, and 3.5 ml of (3-aminopropyl)triethoxy silane was added. Then, the reaction mixture was stirred at 110 °C for 8 h. Finally, the CI particles functionalized with (3-aminopropyl)triethoxy silane (CI-NH₂) were washed with toluene, ethanol, and acetone and dried for 24 h under a vacuum. A schematic illustration of the functionalization of CI particles with silane is presented in Scheme 1. As the result of the preceding procedure, CI particles with amino groups on the surface were obtained.

2.3. Preparation of CI microparticles functionalized with cholesteryl groups

The bulk of the 5 g of CI-NH₂ particles was added into a 250 ml 3-neck flask, which was three times evacuated and backfilled with argon. Dry THF was added under an argon atmosphere and sonicated for 10 min. Then, 0.76 mmol of ethylenetriamine was transferred to the flask followed by dropwise adding of a solution of 0.76 mmol of cholesteryl chloroformate in 10 ml of dry THF, keeping the temperature of the reaction mixture below 5 °C. The reaction mixture was then slowly warmed up to room temperature and stirred overnight under an argon atmosphere. Finally, the reaction mixture was heated up and refluxed for an additional hour. The prepared CI particles coated with cholesteryl groups (CI-chol) were filtered, washed with acetone, and dried for 24 h under a vacuum. The whole process is sketched in Scheme 2.

2.4. Characterization of the prepared particles

The morphologies of bare CI and CI-chol particles were studied using a scanning electron microscope (SEM, VEGA II LMU, Tescan Ltd., Czech Republic) with an operating voltage of 30 kV. FT-IR spectra of the prepared samples were obtained from a Nicolet FT-IR spectrometer (Nicolet Magna-550 Spectrometer, USA) in the region of 4000–700 cm⁻¹. The magnetic properties of particles were determined using a vibration sample magnetometer (VSM, EG&G PARC 704, Lake Shore, USA) at room temperature.

2.5. Suspension preparation and rheological measurement

Bare CI and CI-chol particles were suspended in silicone oil (Lukosiol M 200, viscosity $\eta_c = 194$ mPa s, density $d_c = 0.970$ g cm⁻³, relative permittivity $\epsilon = 2.89$, loss factor $\tan \delta = 0.0001$, Chemical Works Kolín, Czech Republic) with 40, 60, and 80 wt.% particle concentrations. The suspensions were mechanically stirred before each measurement. The rheological properties under an external

magnetic field in the range 0–300 mT were investigated using a rotational rheometer Physica MCR501 (Anton Paar GmbH, Austria) equipped with a Physica MRD 180/1T magneto-cell. The true magnetic flux density was measured using a Hall probe, and the temperature was checked with the help of an inserted thermocouple [40]. Rheological measurements at temperature 25 °C were performed using an Anton Paar Viscotherm VT2 circulator with a temperature stability ± 0.02 °C.

2.6. Sedimentation stability and redispersibility

Sedimentation stability of the bare CI and CI-chol based suspensions was determined at room temperature by UV-vis-spectrometer (Shimadzu, Japan), using values of transmittance at 600 nm.

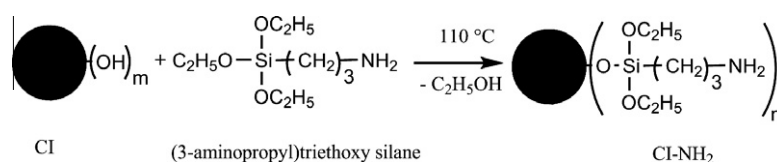
Furthermore, redispersibility measurements were performed according to the ASTM-D5-05a standard method, when the standard needle penetrates to the suspension with fixed velocity 10 mm s⁻¹, and the stiffness is recorded by analytical balance (ABJ 120-4 KERN, Germany) with 0.1 mg accuracy. Similar procedure was also applied by other research group [32].

3. Results and discussion

3.1. FTIR spectra of modified CI particles

As described in the preceding section, the surface of CI particles was modified using a two-step synthesis. The surface of CI particles was first modified by reaction with (3-aminopropyl)triethoxy silane. The role of triethoxy silane was to react with hydroxyl groups present on the CI surface and thus enable covalent modification of CI surface by functional amino groups, which can be subsequently used for further reactions. Transformation of CI into CI-NH₂ particles was investigated by FT-IR spectra (see Fig. 1). As can be seen from the FTIR spectra, bare CI particles (Fig. 1a) did not exhibit any characteristic bands due to their composition consisting of more than 97% of iron particles; only one broad peak was visible probably because of the 3% of unknown residue. (3-aminopropyl)triethoxy silane (Fig. 1c) exhibited characteristic vibration for C–N at 1441 cm⁻¹ [41] and the absorption of C–H aliphatic at 1388 cm⁻¹, respectively [42]. Other characteristic bands are at 1285 cm⁻¹ for Si–CH₂ [43], 1165 cm⁻¹ for C–O, and 1072 cm⁻¹ for O–Si [44]. On the other hand, in the FTIR spectra of CI-NH₂ particles (Fig. 1b), a characteristic C–O stretching vibration from triethoxy groups at 1212 cm⁻¹ and Si–O vibrations at 1100 cm⁻¹ were observable [45]. These absorptions were shifted to higher wavenumbers in comparison with the absorptions of (3-aminopropyl) triethoxysilane due to the presence of the CI particles [12]. In addition, C–H vibrations from alkyl groups appeared in the 2800–3000 cm⁻¹ region.

The modified CI particles, with covalently-bonded cholesteryl groups on the surface of the CI particles, were also characterized (and the modification was confirmed) by FTIR spectra (see Fig. 2). As can be seen in FTIR spectra, an increase in maxima of C–H vibration bands from cholesteryl group in the 2800–3000 cm⁻¹ region was observable after its covalent bonding to the CI surface. In addition, new bands appeared at 1818 cm⁻¹ and 1258 cm⁻¹. The



Scheme 1. Modification of the carbonyl iron particles with (3-aminopropyl)triethoxy silane.

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