

On Dimorphic Magnetorheological Fluid with Improved Oxidation and Chemical Stability under Oscillatory Shear

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Abstract

The aim of this contribution is to prepare such a dimorphic MR fluid for which sedimentation stability, oxidation and chemical stability will be enhanced in comparison with the common MR fluids, while at the same time preserving the MR effect at its fullest practical applicability. A dimorphic MR fluid exhibiting these properties was prepared in two consequent steps. The first step involved the partial substitution of carbonyl iron (CI) spherical microparticles with Fe rod-like particles synthesized via a surfactant-controlled solvothermal method. Doing so improved sedimentation stability in comparison with the application of mere CI particles. In the second step both spherical CI and Fe rod-like particles

were coated with a polysiloxane layer through the hydrolysis-condensation polymerization of tetraethylorthosilicate. This ensured better oxidation and chemical stability balance with an acceptable decrease in the MR effect. This effect is still markedly better than that based on Fe_3O_4 particles.

Keywords: Magnetorheological fluid, Dimorphic system, Chemical stability, Oxidation, Polysiloxane, Sedimentation

PACS

- 47.65.Cb Magnetic fluids and ferrofluids
- 83.80.Hj Suspensions, dispersions, pastes, slurries, colloids
- 82.70.Kj Emulsions and suspensions
- 83.60.Np Effects of electric and magnetic fields
- 47.57.ef Sedimentation and migration

1 Introduction

Magnetorheological (MR) fluids are intelligent systems that undergo a tunable and reversible transition from liquid to solid-like state under the presence of an external static magnetic field [1]. This unique property enables their applications as e.g. vibration dampers, brakes, clutches and control valves [2]. Conventional MR fluids are suspensions of usually spherical micron-sized magnetic particles dispersed in a non-magnetic carrier liquid. Under an applied magnetic field, the originally randomly distributed particles magnetize and position themselves parallel with the field streamlines into anisotropic chain-like structures spanning the suspension. This is outwardly manifested by the generation of large yield stress and enhanced pseudoplasticity. Generally, there are still some limitations, the full or partial elimination of which enables wider utilization of MR fluids. Hence, current research on MR fluids is focused on: sedimentation stability and redispersion of the magnetic particles as well as durability of the MR fluids, typically attributed to their weak chemical stability and the oxidation of their magnetic particles.

As a result of low sedimentation stability, various approaches including the use of viscoplastic media [3], the coating of magnetic particles with polymers [4, 5], or the addition of surfactants [6] have been tried. It has been recently determined through experiments that the substitution of spherical particles with magnetic fibers increases both the sedimentation stability and the MR activity, owing to the solid friction between fibers [7, 8]. This result was also supported by a theoretical model [9]. However, the particle loading is limited to lower values due to the high wetted area and strong fiber-to-fiber interactions. More recently, dimorphic systems of partially substituted micron-sized particles with rod-like nanoparticles have been developed [10, 11]. Dimorphic MR fluids enable to suppress particle sedimentation while their MR activity is comparable with monomorphic, spherical, particle-based MR fluids.

As mentioned, a lack of durability represents another major limitation of MR fluids. This problem is well expressed by the term 'in-use-thickening' [12], characterized by an increase of the off-state viscosity of the system over time. This adverse phenomenon is caused by fragmentation of the brittle oxide layer formed continuously on the surface of magnetic particles [13]. The coating of magnetic particles with a protective surface layer seems to be an effective way to enhance the durability of MR fluids [14, 15].

For improving the properties of MR fluids (sedimentation stability, oxidation and chemical stability), a dimorphic MR fluid composed of carbonyl iron (CI) microspheres and iron (Fe) rod-like nanoparticles, both polysiloxane-coated, was prepared. The effect of the applied magnetic field on the MR properties under oscillatory shear was investigated for a wide range of magnetic flux densities (from 0 to 263 mT). In addition, both types of particles were polysiloxane-coated, and their stability against oxidation and chemical resistance compared to uncoated particles was investigated.

2 Experimental

2.1 Materials

CI (HS grade, BASF, Germany) particles were selected as the main magnetic agent. For the synthesis of Fe rod-like nanoparticles, Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, purity $\geq 98\%$), sodium hydroxide (NaOH, purity $\geq 98\%$), hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 64–65 %) produced by Sigma–Aldrich (St. Louis, USA), and cetyltrimethylammonium bromide (CTAB, purity = 98 %) obtained from Lach–Ner (Neratovice, Czech Republic) were used. Chemicals for the polysiloxane coating of the magnetic particles, namely tetraethylorthosilicate (TEOS, purity = 98 %), absolute ethanol (purity $\geq 99.5\%$) and aqueous ammonia (NH_3 , 25 wt%), were produced by Sigma–Aldrich (St. Louis, USA). All the chemicals were used without further purification.

2.2 Synthesis of rod-like Fe particles

Rod-like Fe particles were prepared following the report [16], with a minor modification. 1 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL of distilled water, and 1 g of NaOH, 4 mL of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, and 0.73 g of CTAB as a structure determining agent were added into the solution. The homogenized mixture was transferred to a 100-mL Teflon-lined autoclave and filled with distilled water up to 50 % of the total volume. The autoclave was sealed, heated for 10 h at 120 °C, and then cooled down to room temperature. The suspension of formed Fe rod-like particles was filtered. The precipitate was then rinsed with distilled water and ethanol several times and then dried at 80 °C in a vacuum for 24 h.

2.3 Preparation of magnetic particles coated with polysiloxane

The composite particles formed by both CI and Fe rod-like particles as a core and polysiloxane as a shell were prepared by hydrolysis–condensation polymerization of TEOS via a modified Stöber method [17], as schematically indicated in figure 1. Briefly, magnetic particles were dispersed in a mixture of TEOS and ethanol. The final thickness of the polysiloxane surface layer was controlled by the magnetic particle/TEOS ratio. An ammonia solution was added slowly into the suspension to accelerate both the hydrolysis and condensation processes of the TEOS. The reaction was vigorously stirred for 24 h. After cooling the mixture to room temperature, magnetic particles encapsulated with polysiloxane were separated by a magnet and rinsed several times with ethanol and then with distilled water to remove unreacted monomer and polysiloxane oligomers. The obtained particles were then dried at 80 °C in a vacuum for 24 h. The effectiveness of this procedure, i.e. the full coating of the particles with a polysiloxane shell, will be discussed later (see Sections 3.1 and, 3.2).

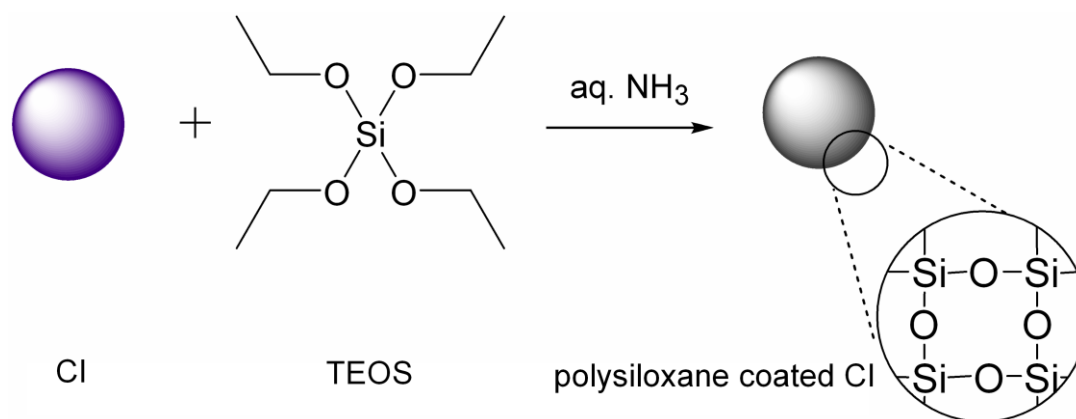


Figure 1. Schematic illustration of the encapsulation of magnetic particles with polysiloxane.

2.4 Characterization and MR measurement

The structural analysis of the uncoated CI particles and prepared Fe rod-like particles was carried out with an X'Pert PRO (Philips, the Netherlands) diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.540598 \text{ \AA}$) and a scanning rate of 4° min^{-1} for the recording data in the range of $2\theta = 15^\circ - 90^\circ$. The morphology of the magnetic particles before and after polysiloxane coating was examined via transmission electron microscopy (TEM, JEOL 1200, JEOL Ltd., Japan) and scanning electron microscopy (SEM, VEGA II LMU, Tescan, Czech Republic) with an accelerating voltage of 30 kV. The SEM microscope was also equipped with an energy-dispersive X-ray spectroscope (EDS) for surface elemental analysis of the samples. The magnetic properties of the samples were measured at room temperature using a vibrating sample magnetometer (VSM, Lakeshore, USA) at the magnetic field of $796 \text{ kA} \cdot \text{m}^{-1}$. In order to examine the resistance to thermal oxidation, thermogravimetric analysis (TGA, TA Instruments Q500, USA) under air atmosphere at a heating rate of $5^\circ \text{C} \cdot \text{min}^{-1}$ was used. To observe the resistance to corrosion by acids, the same amounts of uncoated and polysiloxane-coated CI particles were dispersed in a hydrochloric acid solution of concentration $0.05 \text{ mol} \cdot \text{L}^{-1}$, and the pH values of the solutions as a function of time were recorded.

Two MR fluids with the same particle concentration (40 wt%) in silicone oil (Dow Corning, Fluid 200, USA, $\eta \approx 100 \text{ mPa}\cdot\text{s}$) were prepared. The first one contained 40 wt% uncoated CI particles only while the second was dimorphic MR fluid containing 35 wt% of CI and 5 wt% of Fe rod-like particles both coated with polysiloxane (weight contribution of the polysiloxane shells can be neglected with respect to its volume and weight). Both fluids formed well-dispersed systems for the period of the experiment. The MR characteristics of the fluids under investigation in oscillatory shear were determined using a rotational rheometer Physica MCR 501 (Anton Paar GmbH, Austria) with the Physica MRD 180/1T magneto-cell at 25 °C. True magnetic flux density (not the one indicated by software calculations only) was measured using a Hall probe, and temperature was checked with the help of an inserted thermocouple [18]. Magnetic flux density (MFD) does not attain a constant value along the diameter (20 mm) of the measured sample. This was carefully measured and documented in the official report of the Anton Paar company. This implies that maximum magnetic flux density used in all measurements did not exceed $300 \text{ mWb}\cdot\text{m}^{-2}$ in order to ensure acceptable homogeneity of a magnetic field perpendicular to a parallel-plate measuring system. The small-strain oscillatory tests were carried out through dynamic strain and frequency sweeps. The strain sweeps were performed in the applied strain range of 10^{-5} to 1 at a fixed angular frequency of $2\pi \text{ rad}\cdot\text{s}^{-1}$ under a magnetic field with the aim of determining the position of the linear viscoelastic region (LVR). LVR position depends on the strength of an applied magnetic field. With an increasing value of MFD the position of LVR was moved to higher values of strain. The time periods of the individual runs respected the frequency values at which the experiments were carried out, i.e. the lower frequency value the longer time period to ensure steady regime during the measurements. The constant values of strain were maintained by the rheometer within the whole range of frequencies measured. Afterwards, the viscoelastic moduli were obtained from frequency sweep tests (1 to $100 \text{ rad}\cdot\text{s}^{-1}$) at a fixed

strain amplitude in the LVR ($\gamma = 1 \times 10^{-4}$). First, the individual suspensions were mechanically stirred. Then, prior to each measurement when a new magnetic field was imposed, the residual internal structures were destroyed by continuous shearing ($\dot{\gamma} = 100 \text{ s}^{-1}$) for 1 min. The temperature during the experiment was maintained at 25 °C using a closed water circuit (Viscotherm VT2). After each run an even distribution of the material studied across the whole circles of both plates was checked. During the measurements no tendency to a stick-slip regime was observed.

3 Results and Discussion

3.1 Characterization of CI and Fe rod-like particles

The XRD patterns of the CI particles and synthesized Fe rod-like particles are shown in figure 2. All the diffraction peaks in the spectrum of CI spherical particles can be indexed as body-centered cubic Fe. On the other hand, the peaks in the spectrum of Fe rod-like particles are in good correspondence with the goethite mineral with orthorhombic crystalline structure.

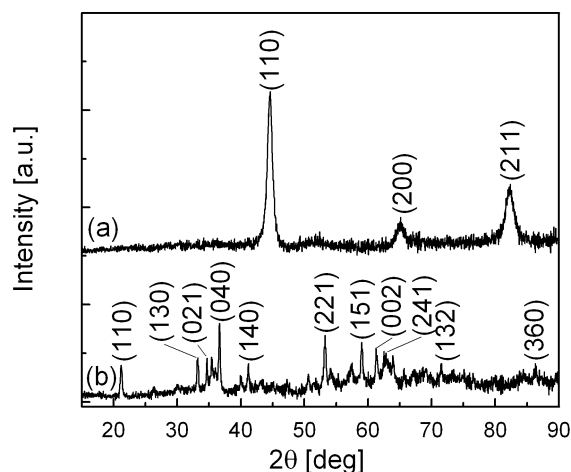
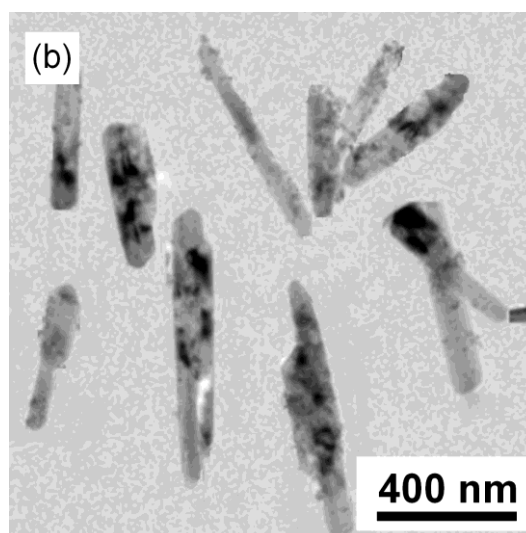
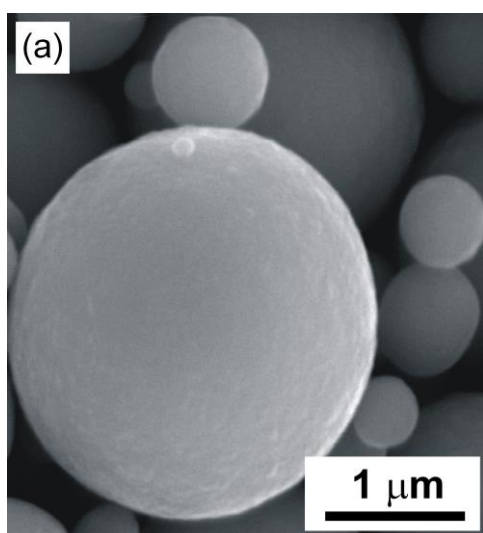


Figure 2. XRD patterns of CI spherical particles (a) and Fe rod-like particles (b).

The general morphology of uncoated CI particles, Fe-rod-like particles, the mixture of CI particles with Fe rods in a ratio used for the preparation of MR fluid, and the CI particles

coated with polysiloxane as well as their EDS spectra are depicted in figure 3. CI particles have a spherical shape (Figure 3) with average particle size $D = 0.75 \pm 0.56 \mu\text{m}$ (obtained from image analyses of SEM pictures). On the other hand, Fe particles of goethite mineral structure prepared via solvothermal method have a rod-like shape with the length $L = 590 \pm 185 \text{ nm}$ and a diameter $D = 135 \pm 42 \text{ nm}$. Thus, the geometric aspect ratio, L/D , of prepared Fe rod-like particles ranges from 2 to 8. As can be further seen, the nanometer-sized Fe rod-like particles are assembled on the surface of micron-sized CI particles of spherical shape in the dimorphic system (Figure 3b), probably due to the residual remanence. Under a magnetic field, rod-like particles will arrange in the voids and fill the gaps between microsphere chain-like structures [10]. To improve the oxidation and chemical stability, magnetic particles were coated with a polysiloxane layer. The polysiloxane prepared via the hydrolysis–condensation polymerization of TEOS formed polyhedral agglomerates on the surface of the magnetic particles (Figure 3c). The EDS analysis (Figure 3d) proved the existence of an elemental form of silicon on the surface of the magnetic particles, thereby indicating a successful coating process.



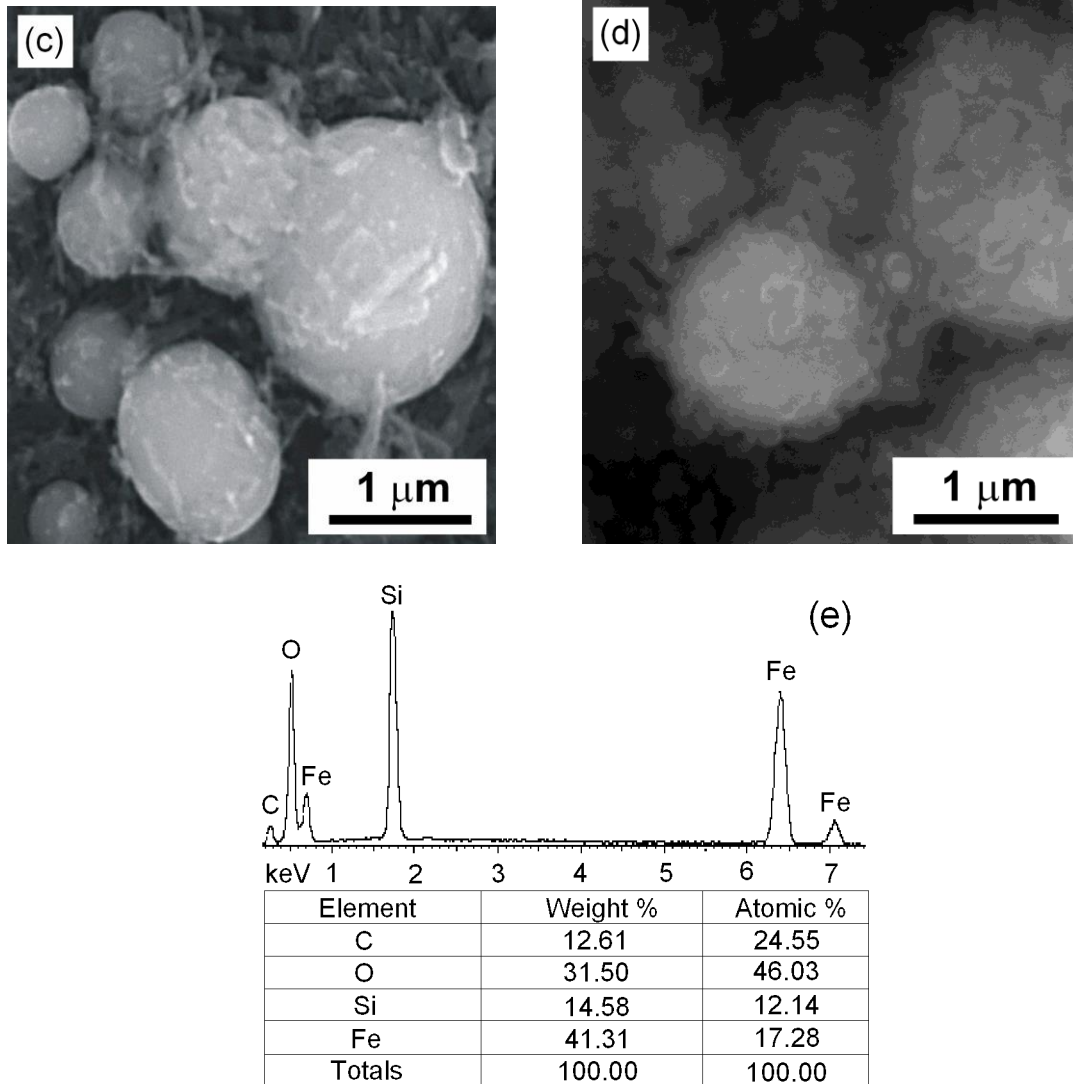


Figure 3. SEM and TEM images of uncoated CI particles (a), Fe rod-like particles (b), a mixture of CI particles and Fe rod-like particles (c), CI particles coated with polysiloxane (d), and an EDS analysis of the surface of the coated particles (e).

The magnetization curves as a primary characterization of MR fluids are shown in figure 4 for uncoated and polysiloxane-coated variants of CI particles, Fe rod-like particles and dimorphic MR fluids. The magnetization curves for dry powders (Fig. 4a) were further analyzed by applying the Langevin equation [19]:

$$M(H) = M_s * \left[\frac{1}{\tanh\left(\frac{m * \mu_0 * H}{k * T}\right)} - \frac{1}{\left(\frac{m * \mu_0 * H}{k * T}\right)} \right] \quad (1)$$

where M_s is the saturation magnetization, m is the magnetic moment, μ_0 is the magnetic permeability of free space ($4\pi * 10^{-7}$ Henry·m⁻¹), H is the magnetic field, k is the Boltzmann constant ($1.38 * 10^{-23}$ J·K⁻¹), and T is the temperature in Kelvin.

The magnetic particles diameter, d , assuming the shape of the particles to be spherical can be calculated as:

$$d = \left(\frac{6 * m}{\pi * M_s} \right)^{\frac{1}{3}} \quad (2)$$

After the application of Langevin equation for magnetization curves of dry powders, a saturation magnetization of 228.2 ± 3.7 and 82.9 ± 1.5 A·m²·g⁻¹ were obtained for uncoated CI and Fe rod-like particles while 135.8 ± 0.7 and 16.9 ± 0.2 A·m²·g⁻¹ for coated variants of CI and Fe rod-like particles respectively. Thus, as could be expected, the non-magnetic polysiloxane shell layer decreases the magnetization properties. Notice that the values of the saturation magnetization obtained by application of the Langevin equation are higher than those obtained from the experimental magnetization data due to the incompleting saturation state of the samples in the magnetic field used for the experiment. Moreover, the initial susceptibility for the Fe rod-like (goethite mineral structure) particles is lower in comparison to that of uncoated CI (body-centered cubic Fe) spherical microparticles (Fig. 4a). This feature is given due to the chemical structure of both types of particles. However, the contribution of Fe rod-like particles in the dimorphic system profits especially in the better MR fluid sedimentation stability and as the filler between the microsphere contacts. Evidently, the presence of the non-magnetic polysiloxane shell layer decreases not only the magnetic properties but also causes the occurrence of hysteresis loop. Nevertheless, the

necessity to use particles with as high saturation magnetization as possible for the corresponding intensive MR effect is not the only criterion for the preparation of efficient MR fluids. The magnetic diameter of uncoated CI particles (obtained from eq.2) is $0.59 \pm 0.06 \mu\text{m}$, which is in quite good correlation with SEM results. Furthermore, slightly decreased initial susceptibility after the polysiloxane coating of particles is observed also in the magnetization curves of dimorphic MR fluids (Fig. 4b). Other properties such as sedimentation stability, oxidation and chemical stability, also significantly participate in the overall performance of MR fluids. All these properties should be well balanced. However, the values of magnetization themselves obtained for polysiloxane-coated CI particles are still sufficient [20].

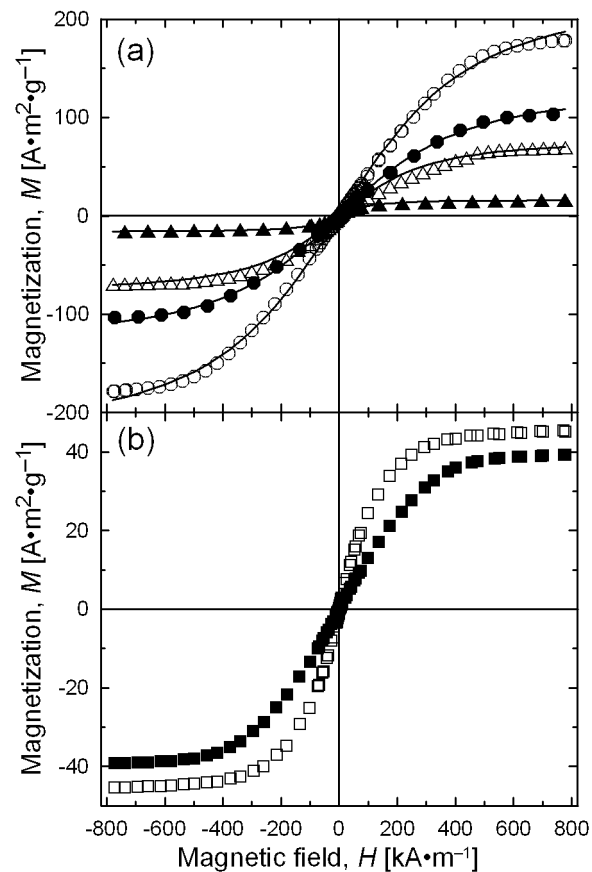


Figure 4. Magnetization curves of uncoated (○) and coated (●) CI particles, uncoated (△) and coated (▲) Fe rod-like particles (a), and uncoated (□) and polysiloxane-coated (■) particles based dimorphic MR fluids (b). Solid lines are applications of Langevin equation.

3.2 Influence of polysiloxane coating on the oxidation and chemical stability

For practical applications of MR fluids it is very important to improve their durability by suppressing the oxidation and chemical decomposition of magnetic particles. Surprisingly, despite their importance these aspects have attracted relatively little attention so far. The thermal oxidation resistance of the samples before and after polysiloxane coating is shown in figure 5. In comparison with uncoated CI particles having an increase of over 30 % due to the formation of iron oxides on their surface and a sharp weight increase at about 460 °C, the polysiloxane-coated CI particles evidently show much lower weight increase (by about 10 %) and severe oxidation occurred at much higher temperatures (570 °C). This proves the improved thermal oxidation resistance of coated CI particles. The TGA curve of uncoated Fe rod-like particles shows characteristic conversion of goethite to hematite with dehydroxylation between 230 and 290 °C [21]. The more pronounced weight loss of polysiloxane-coated Fe rod-like particles (below 150 °C) compared to uncoated ones is presented. This weight loss can be attributed to possible adsorbed moisture in the polysiloxane shell layer. However, the weight loss due to the conversion of goethite to hematite is not so high compared to uncoated Fe rod-like particles. Further weight reduction above 340 °C is caused by polysiloxane shell layer degradation.

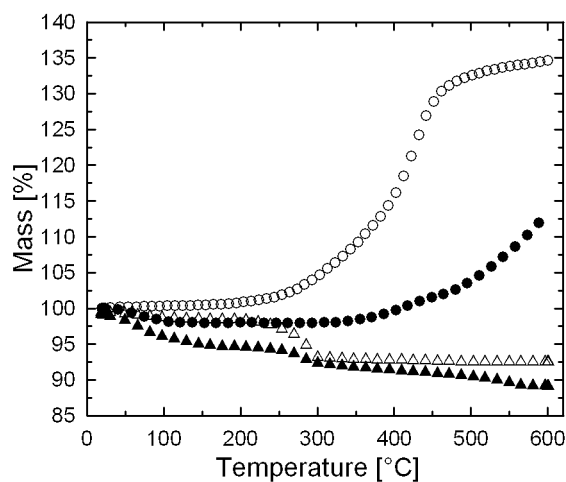


Figure 5. TGA curves of uncoated (○) and coated (●) CI particles, and uncoated (△) and coated (▲) Fe rod-like particles.

The courses of pH values of dispersions of uncoated and polysiloxane-coated CI and Fe rod-like particles in HCl over time were used to compare the anti-acid corrosion properties (Figure 6). The pH value of the uncoated CI particles-based dispersions increases rapidly due to the reaction between the iron presented in particles and the HCl acid. The reaction was accompanied by intensive bubble generation and a linear increase in pH. In contrast to the CI particles, the corrosion of Fe rod-like particles is much slower probably due to the presence of homogenous crystals in the structure of goethite, which are less easily attacked by protons of HCl [22]. The pH value of the dispersions with polysiloxane-coated particles increased only slightly during the tested period (16 times lower slope) and only a few bubbles appeared, which indicated the compact coating of particles with anti-acid corrosion layer.

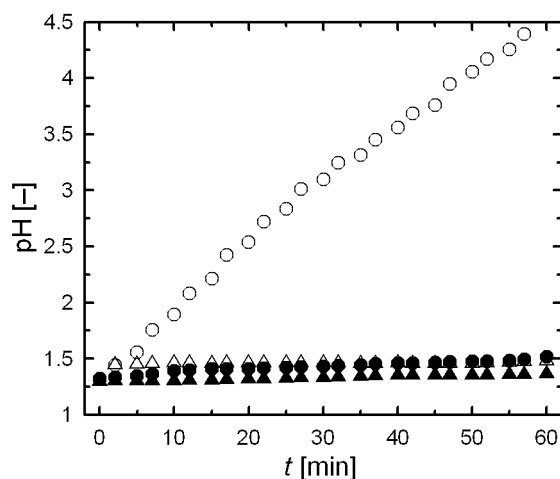


Figure 6. Resistance to corrosion by acids of uncoated (○) and polysiloxane-coated (●) CI particles and uncoated (△) and polysiloxane-coated (▲) Fe rod-like particles.

3.3 MR measurements of viscoelastic properties

The MR systems in practical applications operate usually in oscillatory mode. This implies that oscillatory shear tests represent an effective way to study the dynamic characteristics (such as complex viscosity, η^* , storage, G' , and loss, G'' , moduli representing elastic and viscous response in the system, respectively) of microstructures formed within the MR fluid [23]. Figure 7 shows viscoelastic moduli in dependence on angular frequency for all three studied MR systems with the same total particle concentration of 40 wt%; i.e. uncoated spherical CI particle-based MR fluid, a dimorphic system containing 35 wt% of CI and 5 wt% of Fe rod-like particles, and dimorphic MR fluid with both types of particles coated with polysiloxane. The G' is a little bit higher than G'' in spherical CI and dimorphic MR fluid containing uncoated particles (Figure 7a), probably due to the lower wettability of dispersed particles exhibiting high surface energy to silicone oil used in contrast to a carrier liquid having low surface energy. Compatibility and, consequently, a better liquid-like character of MR fluid is reached after coating the particles with polysiloxane in a dimorphic system. When the magnetic field is applied (Figure 7b), a high G' appears, which is associated with the field-induced chain-like structures within the fluid, and G' is typically at least one order of magnitude higher than G'' . The storage modulus, G' , under applied magnetic field is 2–3 orders of magnitude higher than that in the absence of the field. Dimorphic MR fluid containing uncoated particles exhibits the strongest internal structures as the Fe rod-like particles fill the contact region between CI microspheres. Thus, the Fe rod-like particles and CI microspheres show a synergistic effect in improving the MR performance, as also observed for other dimorphic MR fluids [10]. Not surprisingly, the weakest internal structure is exhibited by the dimorphic MR fluid with polysiloxane-coated particles, as polysiloxane layer is not magnetic (Figure 4).

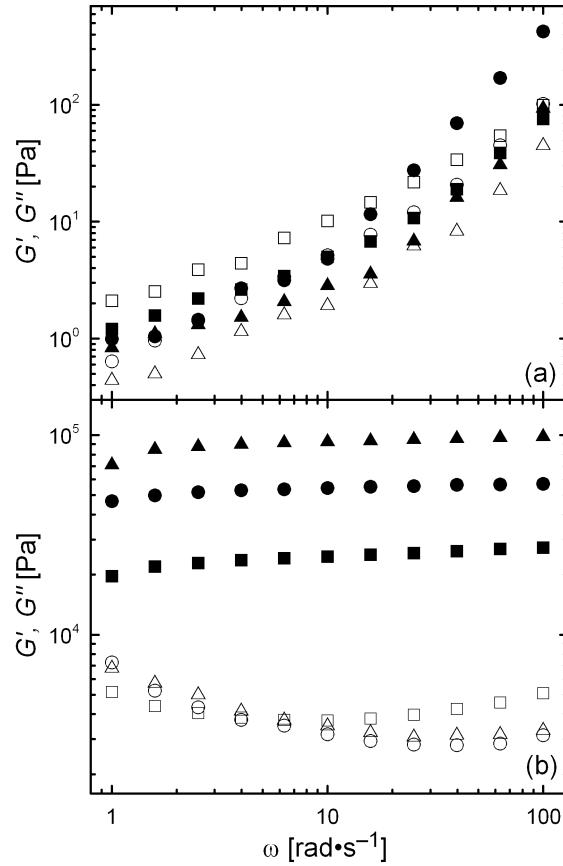


Figure 7. Storage, G' , (solid) and loss, G'' , (open) moduli as a function of angular frequency, ω , under $0 \text{ mWb}\cdot\text{m}^{-2}$ **(a)** and $266 \text{ mWb}\cdot\text{m}^{-2}$ **(b)** magnetic flux densities. MR fluid with 40 wt% uncoated spherical CI (●, ○), dimorphic fluid containing 35 wt% of CI + 5 wt% of Fe rod-like particles (▲, △), dimorphic fluid with both types of particles (35 wt% CI and 5 wt% Fe rod-like) coated with polysiloxane (■, □).

Even so, the dimorphic MR fluid with polysiloxane-coated particles still exhibits sufficient MR performance according to the magnetosweep test depicted in figure 8. The complex viscosity, η^* , of all three MR fluids studied increases rapidly with an applied magnetic field indicating a solid-like state appearance.

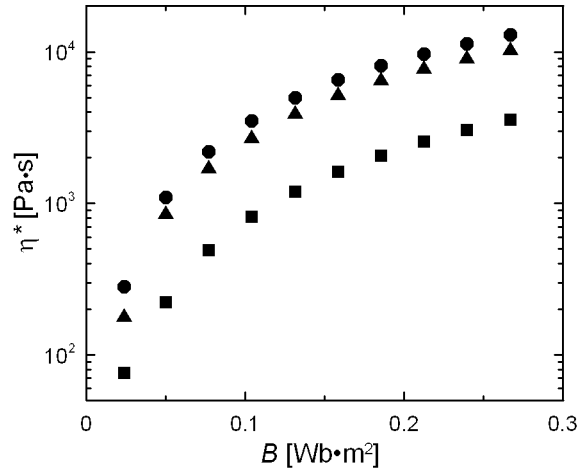


Figure 8. The dependence of complex viscosity, η^* , on the magnetic flux density, B , at $\omega = 2\pi \text{ rad}\cdot\text{s}^{-1}$ for 40 wt% of MR fluid of uncoated spherical CI (●), dimorphic fluid containing 35 wt% of CI + 5 wt% of Fe rod-like particles (▲), dimorphic fluid with both types of particles coated with polysiloxane (■).

3.4 Sedimentation behaviour

The stability of all three MR fluids was examined by a sedimentation ratio test based on the observation of sedimentation velocity (Figure 9). In this method, MR fluids were placed into test cylinders, and the settling of macroscopic phase boundary between the concentrated fraction and the relatively clear oil-rich phase was measured for 24 h. Then, the sedimentation ratio represents the height of the particle-rich phase relative to the total MR fluid height. Obviously from figure 9, the dimorphic system improves the sedimentation stability regardless of particle coating. The rod-like particles probably increase the solid friction within the fluid, resulting in the increased flow resistance of the suspension as was proved also in figure 7a with G' dominating G'' . The addition of nanorods moreover contributes to the formation of soft sediments by avoiding short-range attractions between the large CI particles and thus allows easy redispersion of particles [24]. Further improvement in sedimentation stability was obtained after the polysiloxane coating of particles contained in the dimorphic

MR fluid. This increased stability can be attributed to their improved wettability to silicone oil [15].

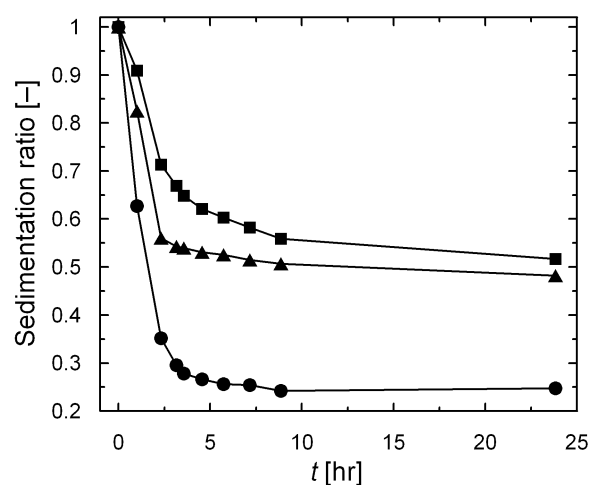


Figure 9. Sedimentation ratio/time dependence of 40 wt% of MR fluid based on uncoated CI (●), dimorphic fluid containing 35 wt% of CI + 5 wt% of Fe rod-like particles (▲), dimorphic fluid with both types of particles coated with polysiloxane (■).

4 Conclusions

A novel type of dimorphic MR fluid was prepared by partial substitution of CI spherical microparticles with Fe rod-like particles fabricated via a simple surfactant-controlled solvothermal synthesis. This substitution considerably increased the sedimentation stability compared to spherical particle-based MR fluid as well as the MR behavior in the presence of an external magnetic field. Further, both types of magnetic particles in the dimorphic fluid were coated with polysiloxane through the hydrolysis–condensation polymerization of TEOS. The polysiloxane surface layer highly improved both the resistance to thermal oxidation and the resistance to corrosion by acids. Moreover, the coating enhanced also the wettability of magnetic particles to silicone oil used as a carrier liquid. This was reflected in lower off-state viscosity and further improvement in sedimentation stability compared to uncoated spherical particle-based MR fluid and a dimorphic system with uncoated magnetic particles. These

improvements highly compensate for a decrease in magnetization of the dimorphic MR fluid with coated particles.

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