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Magnetorheology of dimorphic magnetorheological fluids based on iron nanorods

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Abstract. The aim of this paper is to document suitability of partial substitution of magnetic carbonyl iron (CI) microspheres with iron nanorods to obtain dimorphic magnetorheological (MR) suspensions with comparable MR performance to conventional MR suspensions exclusively based on (CI) microspheres while the sedimentation stability is considerably improved. The morphology of CI and iron nanorods was analyzed via scanning electron microscopy and transmission electron microscopy, respectively, and magnetic properties via vibrating sample magnetometry. The steady shear flow and small-amplitude dynamic oscillatory shear measurements were carried out to confirm effective MR performance. The sedimentation test showed positive role of dimorphic composition of dispersed phase on the sedimentation stability.

1. Introduction

Magnetorheological (MR) suspensions are generally two-phase systems, in which micrometer-sized ferro- or ferrimagnetic multi-domain particles are suspended in a variety of carrier liquids like silicone or mineral oils [1,2]. It is worth to mention here, that MR suspensions differ from so called ferrofluids which contain nanometer-sized magnetizable particles [3]. The most important feature of MR suspensions is their ability to change viscosity in several orders of magnitude (in controllable way) during milliseconds upon the application of an external magnetic field. In the absence of magnetic fields (off-state) they behave as conventional dispersions. The application of large enough field induces a dipole moment in each suspended particle causing the particles to form columnar structures, parallel to the applied field. The formed chain-like or columnar structures restrict the motion of the fluid and, thereby, increase the elastic characteristics of the suspension. The use of MR suspensions in real systems is based on the simultaneous application of magnetic field, and shear, oscillatory or pressure driven force [4-6]. Although the mechanical loading evokes rupturing of created internal structure, the field-induced attractive forces cause “self healing” of particles alignment until the moment, when hydrodynamic forces overcome the field-induced magnetic ones and suspension starts to exhibit yielding behavior. Once the external field is removed, the columnar structures rapidly break under flow and the system immediately returns to its liquid character.

Although a large amount of various studies have been performed by now, the comprehensive qualities are still far from their wider commercialization because of large sedimentation of magnetic particles in the absence of frequent mixing due to predominant gravity forces; *i.e.*, density mismatch between dispersed particles and carrier medium. Moreover, once settled, the residual magnetic



attractions and attraction forces between particles make re-dispersion difficult, which results in much lower MR effect of the system in time. Following the purpose of overcoming these limitations, several approaches such as the coating of magnetic particles with polymers [7,8], or the addition of surfactants [9], have been used. However, the addition of some non-magnetic portion can lead to reduction of field-responsive behavior of MR suspension. Recently, experimental investigation with conventional carbonyl iron (CI) spherical microparticles based MR suspension where part of the CI were replaced with magnetic wire-like nanoparticles has been performed [10,11]. Such nanoparticles play, in the so called dimorphic MR suspensions, a role of steric repulsion between the CI microparticles resulting in improved stability against their rapid sedimentation while the yield stress for dynamic applications is still maintained additionally or even higher due to the friction occurring between fibers.

In this paper, dimorphic MR suspension based on partially substituted CI spherical microparticles with iron nanorods was prepared and its MR performance as well as sedimentation stability was compared with MR suspension of the same magnetic portion loading based exclusively on CI microparticles.

2. Experimental

2.1. Materials

Carbonyl iron particles (HS grade, BASF, Germany) were selected as the main magnetic agent. The material characteristics of HS grade of CI are following: spherical shape of particles with the average size of about 2 μm , non-modified surface, and content of α -iron > 98%.

For the synthesis of iron nanorods, 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 %) all produced by Sigma-Aldrich (St Louis, USA), and cetyltrimethylammonium bromide (CTAB, purity % 98%) obtained from Lach-Ner (Neratovice, Czech Republic) were used. All chemical were used without further purification.

2.2. Synthesis of iron nanorods

Iron nanorods were prepared following procedure [12], with a minor modification. Briefly, 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 were added into the solution. Then, the formed mixture was transferred to an autoclave which was properly sealed, heated for 10 h at 120 $^\circ\text{C}$, and after that cooled down to room temperature naturally. The precipitated iron nanorods were collected on the filter, rinsed with distilled water and ethanol several times, and then dried at 80 $^\circ\text{C}$ under decreased pressure for 24 h.

2.3. Morphology

The morphology of CI particles was observed with scanning electron microscopy (SEM, VEGA II LMU, Tescan Ltd., Czech Republic) operated at 30 kV. Further, iron nanorods were examined using transmission electron microscopy (TEM; JEOL 1200, JEOL Ltd, Japan).

2.4. Magnetic properties

The magnetization curve of individual particles morphology was ascertained using a vibration sample magnetometer (VSM, EG&G PARC 704, Lake Shore, USA). The external magnetic field was swept from +800 to -800 $\text{kA} \cdot \text{m}^{-1}$ and then back to 800 $\text{kA} \cdot \text{m}^{-1}$. Measurements were carried out at room temperature.

2.5. Rheological properties

Two MR suspensions with the same particle concentration of 40 wt% in silicone oil (Fluid 200, Dow Corning, USA; $\eta \approx 108 \text{ mPa} \cdot \text{s}$) were prepared. The first one contained just 40 wt. % of microspherical CI particles only while the second was dimorphic MR suspension containing 35 wt. % of CI and 5 wt. % of iron nanorods. MR characteristics for both MR suspensions were measured using a

rotational rheometer Physica MCR 502 (Anton Paar GmbH, Austria) with a Physica MRD 170/1T magneto-cell. The true magnetic flux density in the range $0 - 438 \text{ kA}\cdot\text{m}^{-1}$ was measured using a Hall probe (FH 51, MAGNET-PHYSIK Dr Steingroever GmbH, Germany) and the temperature was set to 25°C . The parallel-plate geometry with a diameter of 20 mm and gap of 1 mm was employed.

All the steady flow measurements in the controlled shear rate mode were performed in the shear rate range $0.1 - 300 \text{ s}^{-1}$. The oscillatory measurements were carried out through dynamic strain and frequency sweeps. Strain sweeps were performed in the strain range of 10^{-5} to 0.1 at a fixed angular frequency of $6.28 \text{ rad}\cdot\text{s}^{-1}$ in order to get the position of the linear viscoelastic region (LVR). Afterwards, the viscoelastic moduli were obtained from the frequency sweep tests (1 to $100 \text{ rad}\cdot\text{s}^{-1}$) at fixed strain amplitude in the LVR. All the oscillatory measurements were performed in the controlled shear rate mode too. During each run under a magnetic field, the MR suspension was firstly sheared ($\dot{\gamma} = 100 \text{ s}^{-1}$) at zero field for 60 s to destroy previously formed structures and after the measurement the system was completely demagnetized.

2.6. Suspension stability test

Stability of MR suspensions consisted of 40 wt. % of dimorphic magnetic particles and microspherical CI particles only in silicone oil was examined by a sedimentation ratio test. The settling of the macroscopic phase boundary between the concentrated suspension and the relatively clear oil-rich phase was measured as a function of time for 24 hrs. Afterwards, the sedimentation ratio is defined as the height of particle-rich phase relative to the total suspension height.

3. Results and discussion

3.1. Characterization of prepared particles

The size and shape of microspherical CI particles (a) and iron nanorods (b) are shown in SEM and TEM images, respectively (Figure 1). These pictures clearly demonstrate the micrometer size of spherical CI particles on the one hand and nanometer size of rod-like iron particles with the geometric aspect ratio, L/D , ranging from 5 to 9 on the other hand.

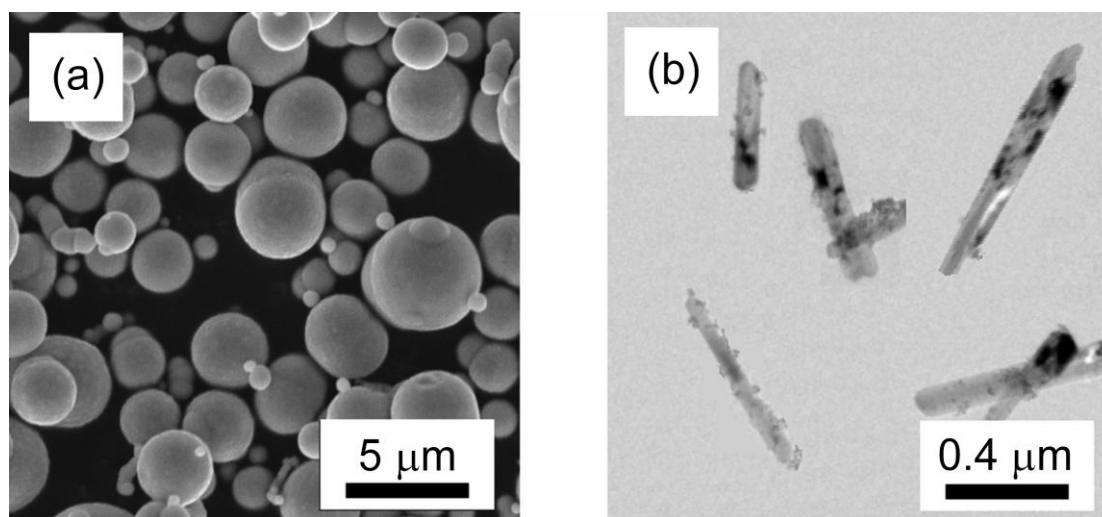


Figure 1. SEM and TEM images of (a) microspherical CI particles and (b) iron nanorods

The magnetization curve measurements of the microspherical CI particles and iron nanorods are depicted in Figure 2. The saturation magnetization of iron nanorods is expectedly lower in comparison with microspherical CI particles. However, iron nanorods in the dimorphic system more likely

contribute particularly to the better MR suspension sedimentation stability and as filler between the microsphere contacts than main magnetic agent.

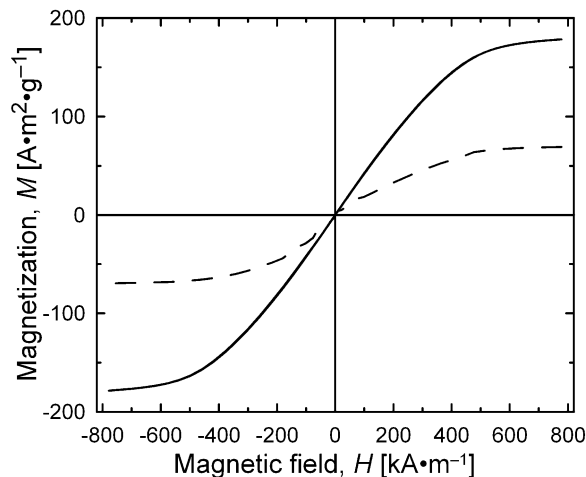


Figure 2. Magnetization curves of microspherical CI particles (solid line) and iron nanorods (dashed line)

3.2. Suspension stability

Moreover, other properties including sedimentation stability also significantly participate in the overall performance of MR suspensions and thus should be well balanced. Figure 3 illustrates the stability test for model MR suspension containing 40 wt. % of the microspherical CI particles only and dimorphic MR suspension having 5 wt. % from overall 40 wt. % substituted with iron nanorods. The dimorphic MR suspension apparently exhibits better suspension stability than that based on the microspherical CI particles only suspension, which is probably due to the increased solid friction within the suspension, *i.e.*, magnetic nanorods adsorb onto the CI microparticles through magnetostatic interactions imparting to the iron particles a brush-like effect. 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 in the MR suspension [13].

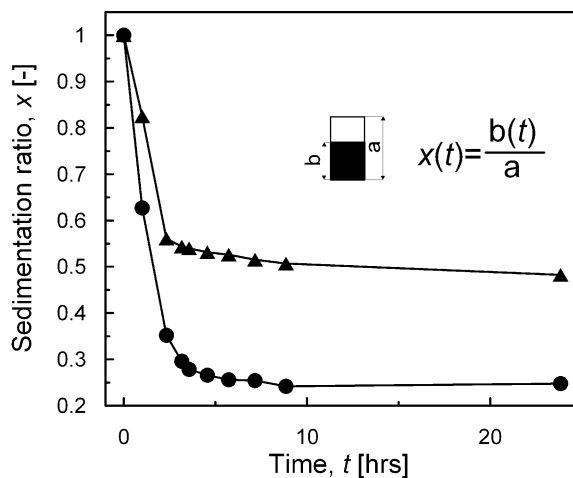


Figure 3. Sedimentation ratio of MR suspensions (40 wt. %) based on microspherical CI particles only (●) or dimorphic (▲) particles dispersed in silicone oil

3.3. MR performance

The steady shear flow of microspherical CI particles only and dimorphic particles system based MR suspensions (40 wt. %) were investigated to evaluate the influence of the magnetic dispersed phase composition on the MR performance (Figure 4). The off-state shear stress, τ_0 , of dimorphic MR suspensions would increase with the presence of the magnetic nanofiber content within the system due to the residual magnetization as illustrated in reference [10], which would consequently negatively influence the MR performance expressed as $e = (\tau_M - \tau_0)/\tau_0$, where τ_M is an on-state shear stress of the suspension in external magnetic field. Nevertheless, the magnetic iron nanorods used within the dimorphic MR suspension under investigation do not exhibit too high shape anisotropy and their concentration is not excessively high at the same time to increase the off-state shear stress. Hence, in the absence of magnetic field, both types of MR suspensions exhibit nearly Newtonian behavior. In the presence of magnetic field, both systems show Bingham plastic behavior indicating that the magnetic particles were aligned into the chain-like structure sufficiently rigid to withstand certain deforming stresses without any external manifestation of flow. Typically for both MR suspensions, the shear stress increased for the entire shear rate region with the increase of external magnetic field intensity [2,3].

When magnetic field is applied, the magnetic iron nanorods are probably polarized in the contact region between two micrometer spherical CI particles, where the saturation area is expected [14]. This leads to the stronger inter-particle interactions between such CI particles. Evidently from Figure 4, both MR suspensions have approximately the same values of shear stress under the same magnetic field intensity and thus it can be concluded that although the dimorphic system contains less amount of micrometer-sized CI particles representing main component in chain-like structure formed, its MR performance is comparable to the conventional CI particles based system of the same concentration due to the improved contact area between CI particles in the chain-like structure generated under the application of external magnetic field.

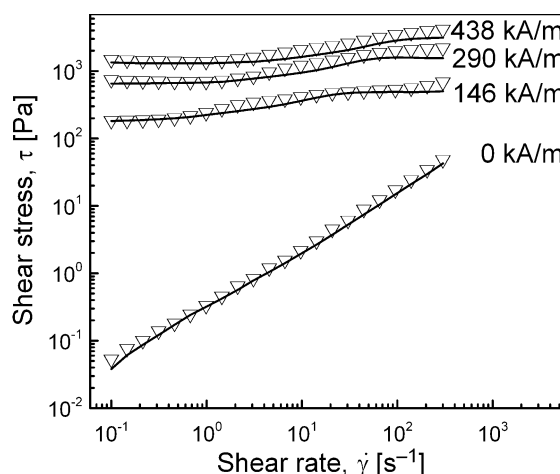


Figure 4. The shear stress, τ , vs. shear rate, $\dot{\gamma}$, dependence for 40 wt. % suspension of micro-spherical CI particles only (lines) and dimorphic system (∇) particles in silicone oil under various magnetic fields applied

The formation of internal organized chain-like structures under external magnetic field application is undoubtedly aligned with the change of viscoelastic characteristics. The storage, G' , and loss, G'' , moduli provide quantitative information about the magnetically induced structures in a wide range of time and frequency [7]. The dependence of G' and G'' on the angular frequency, ω , within the LVR ($\gamma = 2 \times 10^{-4}$ in our experiments) for 40 wt. % dimorphic MR suspension under magnetic field intensities of 0 and $438 \text{ kA}\cdot\text{m}^{-1}$ are included in Figure 5. Without the application of an external

magnetic field, both moduli grow in the whole frequency range and G' slightly dominates over G'' probably due to a quite high total particle loading in the suspension. When a magnetic field is applied, however, G' becomes significantly higher due to the internal structure formation than G'' and both moduli increase rapidly in several orders of magnitude from their off-state value especially at lower angular frequencies. Moreover, G' is constant or increases slightly over wide range of driving frequencies. This illustrates a typical behavior of stiff three-dimensional network formed by magnetized particles within MR suspension which is sufficiently strong to transmit the elastic forces in such systems [15].

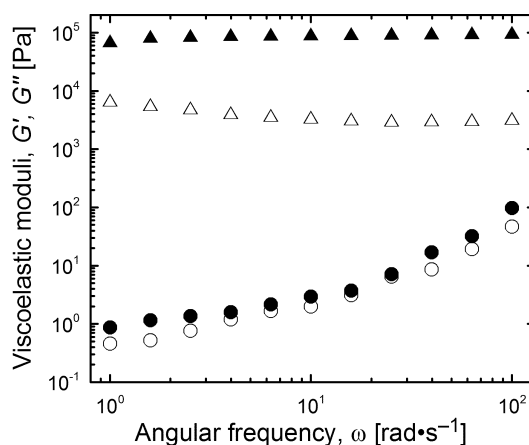


Figure 5. Storage, G' , (solid) and loss, G'' , (open) moduli as a function of the angular frequency, ω , in the various magnetic fields applied for 40 wt. % dimorphic MR suspension. The symbols for magnetic flux density ($\text{kA}\cdot\text{m}^{-1}$): (\blacksquare, \square) 0; and ($\blacktriangledown, \triangledown$) 438

4. Conclusions

A novel dimorphic MR suspension based on partially substituted micrometer-sized spherical CI particles with iron nanorods was prepared and an experimental investigation has been performed to elucidate the effect of such partial substitution on the overall MR performance as well as sedimentation stability. The dimorphic MR suspension shows typical MR characteristics including Newtonian behavior in the off-state and high values of yield stresses which are fully comparable at given external magnetic field with conventional MR suspension of the same overall concentration based on CI microparticles. In addition, the viscoelastic characteristics of dimorphic MR suspension confirmed the strong elastic behavior within the LVR due to the compact chain-like structures formed under an applied external magnetic field. Apart from promoting a comparable MR performance with microspheres-based MR suspension, the dimorphic MR suspension also exhibits better sedimentation stability due to brush-like effect of iron nanorods presented on CI microspheres.

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