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Dimorphic magnetorheological fluid with improved rheological properties

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ABSTRACT

A type of dimorphic magnetorheological (MR) fluid was prepared by adding wire-like iron nanostructures into the conventional carbonyl iron based MR fluid. The Fe nanowires were synthesized through reducing Fe^{2+} ion with excessive sodium borohydride in aqueous solution. The rheological behaviors of the dimorphic MR fluids were measured with a rotational rheometer and the sedimentation properties were also studied in this work. It was found that the Fe wires additives can greatly enhance the stress strength of the dimorphic MR fluids comparing with the conventional MR fluids. The sedimentation of the dimorphic MR fluids was also mitigated greatly.

1. Introduction

Magnetorheological (MR) fluid is a type of smart materials with micro-sized soft magnetic particles suspended in a hydraulic or silicone oil carrier fluid [1]. The rheological properties of the MR fluids such as the yield stress and their apparent viscosity can be controlled rapidly and continuously by varying the applied magnetic field [2]. As a consequence of these behaviors, MR fluids are valuable materials for technological applications such as clutches, damping devices, brakes, antiseismic protection, etc. [3,4].

The sedimentation property and the achievable yield stress are two important factors to evaluate MR fluids. Due to the density mismatch between the magnetic particles and the carrier fluids, the particle sedimentation caused by gravitational forces comes to be a serious drawback when the MR fluids are used. Many studies have been done to solve this problem. Coating the magnetic particles with organic polymers [5,6] is the most commonly used method, which can decrease the density of the particles and then the density difference between the particles and the carrier decreases. Cheng et al. [7] employed *N*-glucose ethylenediamine triacetic acid (GED3A) which can form a network configuration via hydrogen bonds in water to coat the carbonyl iron (CI) particles and got a reduced sedimentation rate. Besides the coating method, introducing additives into the MR fluids can also improve their stability. During the past decades, many additives such as magnetic nanoparticles [8,9], surfactants [10,11], organoclay particles [12,13] or thixotropic agents [14,15] were applied in preparing high performance MR fluids. Most of these products show great sedimentation stability. Unfortunately, the yield stress is reduced in comparison to the non-doped MR fluids.

The yield stress is very important for the MR fluids due to the requirement of engineering application. The spherical CI particles based MR fluids can receive high yield stress because the CI particles have high saturation magnetization. Thus the spherical CI particles have been widely used as the dispersed phase of the conventional MR fluids. Very recently, Lopez-Lopez et al. [16] found that the magnetic fibers could not only improve the sedimentation of the MR fluids but also enhance the Bingham yield stress in comparison to the conventional MR fluids based on spherical particles. By dispersing iron microwires into silicone oil, Bell and coworkers [2] found that the rod-shaped microwires could increase the yield stress and enhance the MR performance. However, due to the high wetted area and wire-to-wire interactions among the wires [17], the iron loading could not be as high as the spherical particles. As a result, the yield stresses of the solely wire-based MR fluids are smaller than that of the commercial MR fluids. Therefore, the combination of spherical CI particles and magnetic iron nanowires may lead to novel MR fluids with high yield stress and sedimentation stability.

To improve the settling properties and enhance the yield stress of the MR fluids, dimorphic MR fluids, which are composed of both Fe nanowires and microspheres, is prepared. The CI weight percent of the as-formed hybrid MR fluids is same to the conventional MR fluid. The Fe nanowires were synthesized via a simple redox reaction in aqueous solution with $NaBH_4$ as the reducing agent and Fe^{2+} ion as the starting substance [18]. The magnetorheological properties of the dimorphic MR fluids with different weight percentage of Fe

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nanowires show that such additives can greatly improve the stability and the yield stress value of the MR fluids.

2. Experimental details

2.1. Reagents

Analytical grade iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), sodium borohydride ($NaBH_4$), stearic acid and absolute alcohol were used. All reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. CI particles (model CN) were bought from BASF, Germany.

2.2. Synthesis of Fe nanowires

Typically, $NaBH_4$ was dissolved in 100 mL deionized water with the concentration of 1.2 mol/L and then added into 200 mL of 0.05 mol/L $FeSO_4 \cdot 7\ H_2O$ solution within two minutes while the reaction system being vigorously stirred. The temperature was maintained at 30 °C for 30 min. The resulting fluffy black precipitates were separated and collected by a magnet. After being washed with water and absolute ethanol several times, the samples were dried at 50 °C under vacuum for 12 h.

2.3. Preparation of dimorphic MR fluids

Spherical CI particles with an average diameter of 3.5 μm were used as the main dispersed phases. Silicone oil with a viscosity of 0.168 Pa s was used as the carrier fluid and stearic acid with 3 wt% of the mass of CI was utilized as a surfactant for producing stable dispersions. In order to investigate the influence of these Fe nanowires on the MR fluids, both the conventional and the dimorphic MR fluids with the same weight ratio of CI particles were prepared (Table 1). Moreover, magnetic suspensions with different weight ratios of Fe nanowires were also prepared.

2.4. Characterization and rheological measurement

The crystalline structures of the as-synthesized Fe wires and the raw CI particles were characterized by X-ray diffraction (XRD) with CuK_α ($\lambda = 0.154178$ nm) radiation on a Philips X-Pert diffractometer at room temperature. X-ray photoelectron spectra (XPS) were measured on an ESCA Laboratory MKII instrument with AlK_α radiation as the exciting source at a pass energy of 70 eV. The morphology of the samples was examined by field emission scanning electron microscope (FE-SEM) (JEOL, JSM-6700F) and transmission electron microscope (TEM) (Hitachi model H-800). The magnetic hysteresis loops were measured by a superconducting quantum interference device (SQUID, MPMSXL5) magnetometer at 300 K. To investigate the magnetorheological properties of the MR fluids, rheological measurements were taken using an Anton Parr Physical MCR301 rheometer with a magnetorheological device. A parallel-plate measuring system (PP20) with a diameter of 20 mm and a standard testing gap of 1 mm was employed. The temperature was maintained at 25 °C throughout the test. A magnetic flux density of up to 0.5 T was used for the fluids in this study.

Table 1
Compositions of MR fluid samples.

Sample no.	1	2	3	4	5	6	7
CI dosage (wt%)	60	60	60	60	0	0	0
Nanowires dosage (wt%)	0	2	4	6	2	4	6

3. Results and discussion

3.1. Characterization of Fe nanowires and carbonyl iron

The XRD patterns of the CI particles and the as-prepared Fe wires are given in Fig. 1. All the diffraction peaks can be indexed as body-centered cubic Fe [space group, *Im*3*m* (2 2 9)] which is consistent with the reported data (JCPDS card no. 06-0696). No impurity peaks are observed in XRD pattern of the Fe wires. However, small quantities of iron particles on the surface were inevitably oxidized during the processes of washing and drying due to the high activity of the iron nanoparticles. XPS was further employed to characterize the as-prepared Fe wires (Fig. 2). It is found that a considered amount of O, which may existed on the surface of Fe wires, is presented. Here, the presence of element O indicates the existence of the thin oxidation layer. The amount of the iron oxide is so small that it cannot be detected by XRD.

The general morphology of the products was examined by SEM and TEM. Fig. 3a reveals that the as-prepared product consists of a large quantity of wire-like nanostructures. The synthesized Fe wires are randomly entangled and the diameter ranges from 60 to 90 nm. As shown in the TEM image, the Fe nanowires are composed of

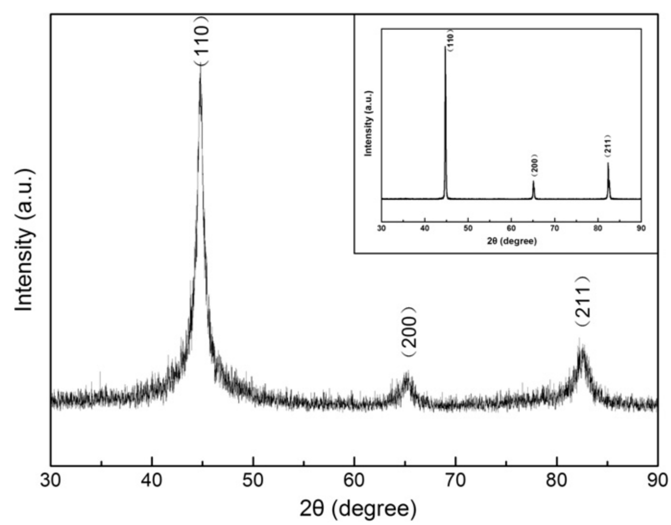

Fig. 1. XRD patterns of the Fe nanowires, the inset is the XRD patterns of CI.

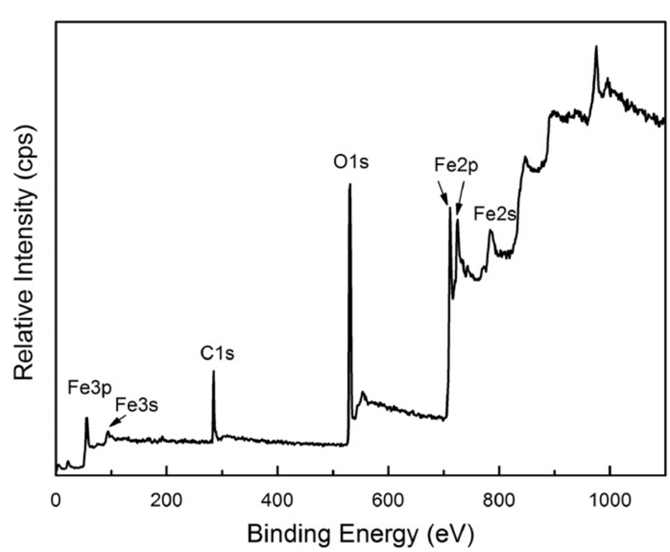

Fig. 2. XPS spectrum of the Fe nanowires.

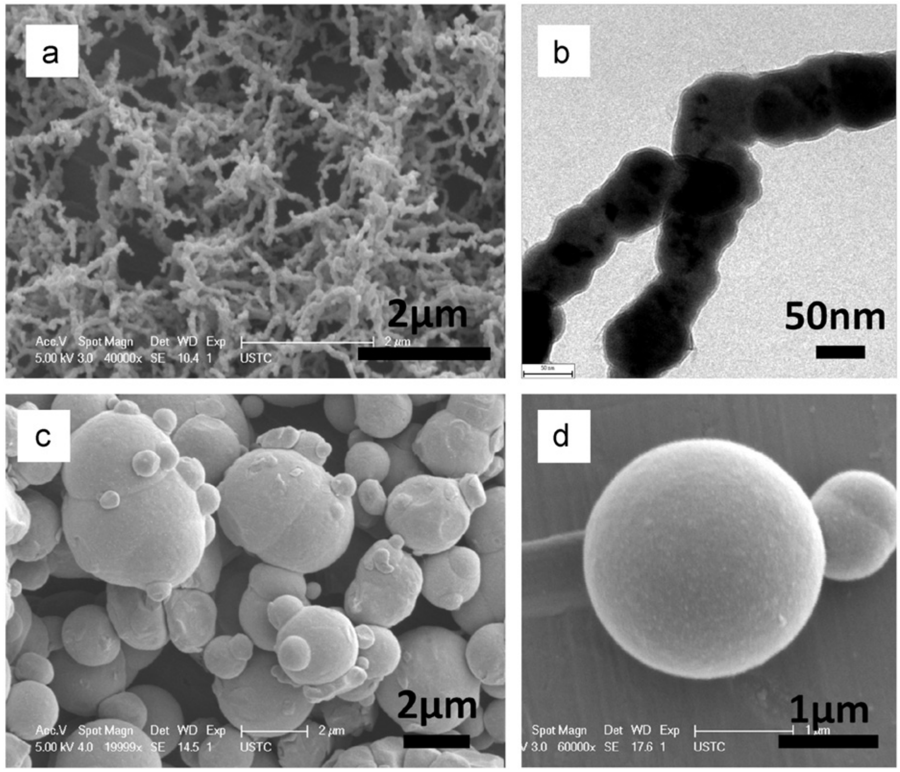

Fig. 3. SEM (a) and TEM (b) images of the wire-like Fe nanostructures, SEM (c,d) images of CI particles in different magnifications.

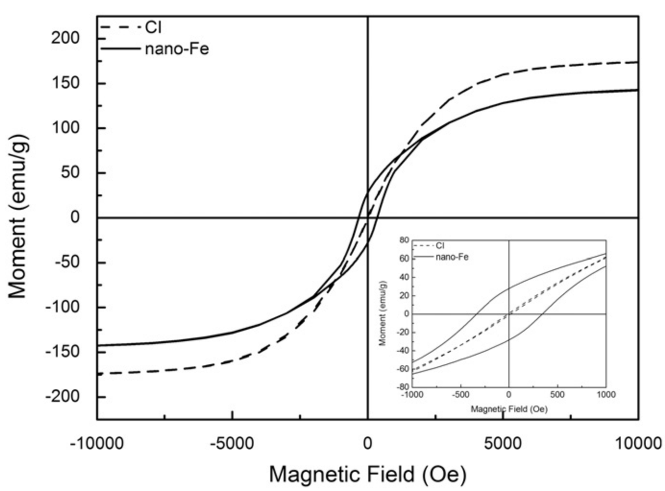

Fig. 4. M–H curve of the nanowire Fe samples at 300 K.

many nanoparticles and they are not single crystals. The broad nature of the XRD patterns also supports our observation. Moreover, the Fe nanowires are not very uniform and the lengths range from several micrometers to several hundred micrometers. Comparatively, the morphology of the CI particles is generally spherical and the average diameter is about 3.5 μm.

3.2. Magnetic properties

The as-prepared Fe nanowires show a typical ferromagnetic behavior. Fig. 4 shows the magnetic hysteresis loop of the products measured at room temperature. The saturated magnetization (M_s), remnant magnetization (M_r), and coercivity (H_c) values are 142.3, 27.95 emu/g and 0.35 kOe, respectively. Meanwhile, the CI used here exhibits soft magnetic property and the saturated magnetization is about 173.7 emu/g. Here, the ferromagnetic characteristic of the Fe wires should be attributed to the 1D structure and their big surface anisotropy. Moreover, the lower M_s of the Fe wires may be due to the thin oxidation layer existed on the surface.

3.3. Magnetorheological behavior

Due to their special nanostructure, the Fe wires based MR fluid exhibited a high yield stress and MR performance. In this work, the Fe wires were introduced into the conventional CI based MR fluids and a series of dimorphic MR fluids (Table 1) were prepared. The effects of the wire-like additives on the magnetorheological characteristics of MR fluids were systematically investigated. The MR fluids were sheared at a constant shear rate of $100\ s^{-1}$ at zero field for half a minute to distribute the particles uniformly [15], and then the desired magnetic field was applied to test the flow curve (shear stress *vs.* shear rate) and the viscosity curve (viscosity *vs.* shear rate).

Here, dimorphic MR fluids with different weight ratio of Fe wires (0, 2, 4 and 6 wt%) were tested (keep the weight ratio of CI spheres (60 wt%) as a constant). Fig. 5 gives the tested curves of the MR fluid (sample 4, with 6 wt% weight ratio of Fe wires and 60 wt% weight ratios of CI spheres). It shows that the shear stress increases with the shear rate and magnetic field strength, which indicates the particular structures formed by the particles within fluid under the applied magnetic field are continuously broken by a shear deformation until $100\ s^{-1}$ [5]. The shear stress under applied magnetic fields is 2–3 orders of magnitude higher than that in the absence of the magnetic field. In addition, the viscosity of the sample increases rapidly when the magnetic field is applied and the sample presents a solid-like state in appearance. The fluids show an obvious "shear thinning" behavior with increasing of the shear rate at specified magnetic fields. Other samples being tested have the same tendency as sample 4. As a result, the dimorphic MR fluid shows a typical MR behavior.

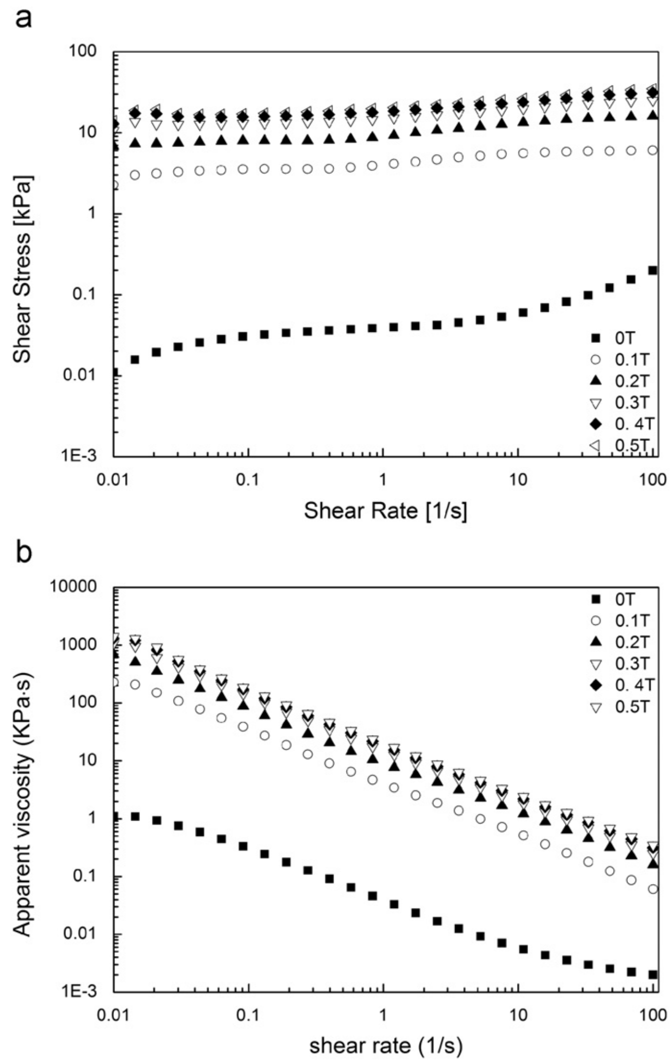

Fig. 5. (a) Flow curve (shear stress *vs.* shear rate) of MR fluid containing 6 wt% Fe nanowires (b) viscosity curve (viscosity *vs.* shear rate) of MR fluid containing 6 wt% Fe nanowires.

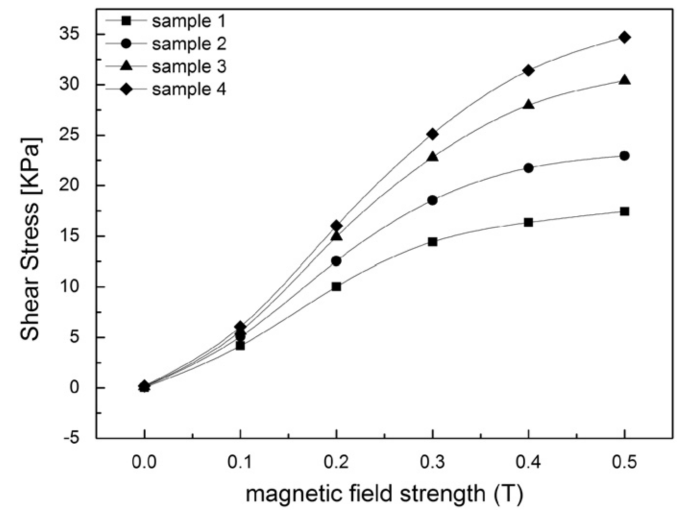

Fig. 6. Shear stresses as a function of the magnetic field for MR fluids containing different weight ratio of Fe nanowires.

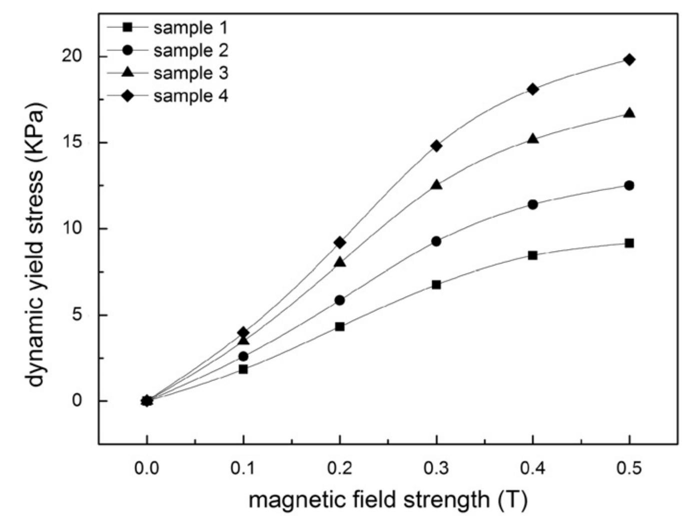

Fig. 7. Dynamic yield stresses as a function of the magnetic field for MR fluids containing different weight ratio of Fe nanowires.

Fig. 6 shows the plot of shear stress as a function of magnetic flux density at a shear rate of 100 s^{-1}. It also demonstrates that the shear stress increases with the magnetic field strength. It is worth mentioning that the shear stress of the dimorphic MR fluid is much higher than that of the conventional CI based MR fluid containing the same weight ratio of CI and no Fe wires. For fluid containing 6 wt% magnetic nanowires with and without spherical CI particles, the shear stress is 34.71 KPa and 373.8 Pa, respectively. Meanwhile, under the same magnetic field strength (0.5 T), the shear stress of the conventional MR fluid is only 17.44 KPa. It can be calculated that the shear stress of the dimorphic MR fluid is even higher than the sum of the shear stresses of the conventional CI based MR fluid and the Fe nanowires based ferrofluid (Fig. 6). These results indicate that the Fe wire-like products can greatly improve the stress strength of MR fluids. In addition, under the same magnetic field strength (0.5 T) and the same shear rate (100 s^{-1}), the shear stresses of the MR fluids containing 2, 4 and 6 wt% of Fe nanowires are 22.96, 30.41 and 34.71 KPa, respectively. It implies that the shear stress increases with the weight ratio of Fe nanowires.

The values of the dynamic yield stress are obtained by fitting the Bingham equation [16]

$$\tau = \tau_{yB} + \eta_{pl}\dot{\gamma}$$

where τ is the shear stress, τ_{yB} is the dynamic yield stress, η_{pl} is the plastic viscosity and $\dot{\gamma}$ is the shear rate. The plot of the dynamic yield stress as a function of the magnetic field strength is shown in Fig. 7. It is found that the dynamic yield stress also increases with the weight ratio of the Fe nanowires, which consists with the Fig. 6 that the additional Fe nanowires can greatly improve the MR effect.

In Ngatu's report, the dimorphic MR fluids could only maintain the level of yield stress by substituting part of the spherical particles with nanowires [17]. Here, the Fe nanowires and CI spherical particles show a synergistic effect on improving the performance of the MR fluid. The large enhancement effect in our experiments may be attributed to the increment of the solid friction among the magnetic particles [16]. Under externally applying a magnetic field, the CI spherical particles and the Fe nanowires combine together to form complicated dendrite-like networks, so that the as-formed chain or column structures become more robust. These structures are very difficult to be broken to form flowing MR fluid, thus the dynamic yield stress is higher than that of the conventional CI based MR fluid [19].

Fig. 8 shows the sedimentation tests of the MR fluids. We determined sedimentation percentage [2] of both the dimorphic

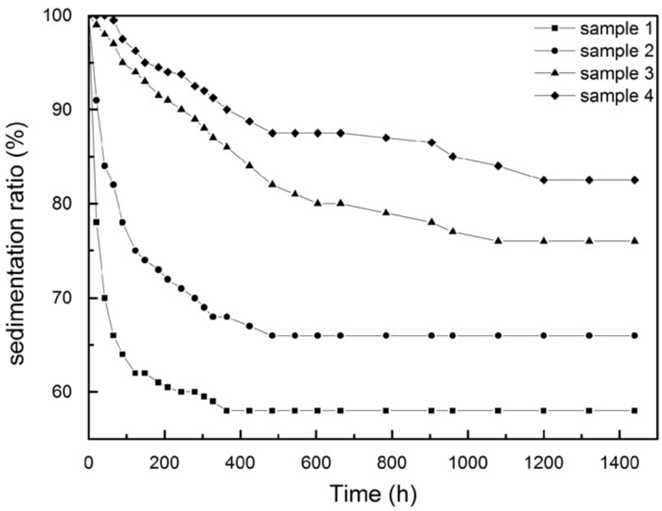

Fig. 8. Sedimentation percentages as a function of time for MR fluids containing different weight ratio of Fe nanowires.

fluids and the conventional MR fluids so as to make comparisons.

$$\text{Sedimentation percentage} = \frac{\text{Volume of supernatant fluid}}{\text{Total volume of MR fluid}} \times 100\%$$

For fluids containing wire-like iron products, they displayed reduced sedimentation to a certain degree when they settled to their equilibriums. For example, the dimorphic fluid with a wires loading of 6 wt% shows a significant sedimentation percentage decrease of 24% compared to suspensions without nanowires. The difference in the sedimentation rate of the two types of fluids can be mainly attributed to the entanglement of the nanowires, because the complicated networks restrict the motion of the wires and the CI particles [2]. The loose sediments formed by the nanowires play a supporting role, so the sedimentation percentage of the MR fluid with Fe wires is much smaller. Besides, the increase of the solid friction should also be responsible for the improvement of the sedimentation performance. It increases the flowing resistance of the suspension and results a slow sedimentation rate.

4. Conclusions

In summary, a type of dimorphic MR fluids was prepared by adding Fe nanowires into the conventional CI based MR fluids. These fluids remain behaving as the typical MR fluids, however, the shear stress and the dynamic yield stress were markedly increased and the sedimentation stability of the MR fluid was also significantly improved compared with the conventional MR fluids. These may be attributed to the complicated networks formed by the wires and the increase of solid friction among the magnetic particles.

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