Two-step Surface Modification of Iron Particles for Magnetorheological Fluid†

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Abstract

We propose a two step modification of iron nanoparticles, including is pre-oxidation to grow the thin oxide layer with nanoscale roughness and subsequent fatty acid capping, for preparing colloidal magnetorheological (MR) fluids. The solid loading of the iron nanoparticles was 15 vol%, and a fatty acid of oleic acid was used as surfactant. We demonstrate the prepared MR fluid displays a good redispersibility and significant field-dependence yield stress when we add the adequate amount of oleic acid to the fluid. Additionally, dynamic measurements were performed to investigate field-induced aggregation structures.

KEY WORDS: (Magnetorheological fluid), (Magnetorheological response), (Iron nanoparticles), (Oleic acid), (Colloidal stability), (Redispersibility)

1. Introduction

Magnetorheological (MR) fluid is a class of smart fluid, whose rheological response can be rapidly and reversibly changed when subjected to an external magnetic field (MR effect) [1–4]. Because the conventional MR fluids are suspensions of non-colloidal magnetic particles dispersed in lubricant oils, they have drawbacks for being adopted in designing MR devices. One problem is abrasion, as MR fluids are used for polishing medium as well. Another problem is gravitational sedimentation of the micron-sized particles. The initial operation of MR devices is needed as well as the redispersion. Several methodologies including addition of additives such as polymers, thixotropic agents, and fillers have been investigated to prevent this deficiency [5, 6].

Replacing the micron-sized particles by submicron or nano-sized particles may solve these problems associated with the micron-sized particles [7]. Nevertheless, few works have reported the concentrated suspensions of magnetic nanoparticles because increasing the solid volume fraction into non-polar oil phase without increasing the viscosity is difficult. Additionally, the iron nanoparticles react violently in the atmosphere due to their huge specific surface area.

Recently, we have reported that iron nanoparticles, of which size was ca. 100 nm, synthesized by the arc plasma method are potential candidates for preparing MR fluids [8–10]. The iron nanoparticles were pre-oxidized to grow a thin passivating oxide (< 2 nm) around the iron core, allowing the nanoparticles to be handled in the atmosphere. Besides the formation of a thin oxide layer, the physical structure of the thin oxide shell was of interesting in terms of colloidal stability. During the pre-oxidized process, the thin oxide layer with nanoscale roughness was grown on the iron particles surface [8]. With these properties in mind, we calculated the pair potential energies between the suspended iron nanoparticles with nanoscale roughness, and concluded that the roughness was responsible for the colloidal stability [9]. Over 100 nm in particle size, however, a surfactant coating is necessary to control the colloidal dispersibility because van der Waals attraction energy is much bigger than thermal energy (k_BT) in this scale size. Then, we found an adequate addition of oleic acid into silicone oil including the iron nanoparticles reduced their apparent viscosity [10]. Hence, we report the influence of oleic acid coating on steady and dynamic MR response for concentrated suspensions of the iron nanoparticles with nanoscale roughness. We also demonstrate the redispersibility of the prepared MR fluids in the development of MR devices.

2. Experimental

Iron particles were fabricated by the arc-plasma method described elsewhere [8]. After fabrication of pure iron nanoparticles, pre-oxidation was carried out under N_2+2%O_2 with a total pressure of 101 kPa at room temperature for 5 h. The specific surface area of the iron

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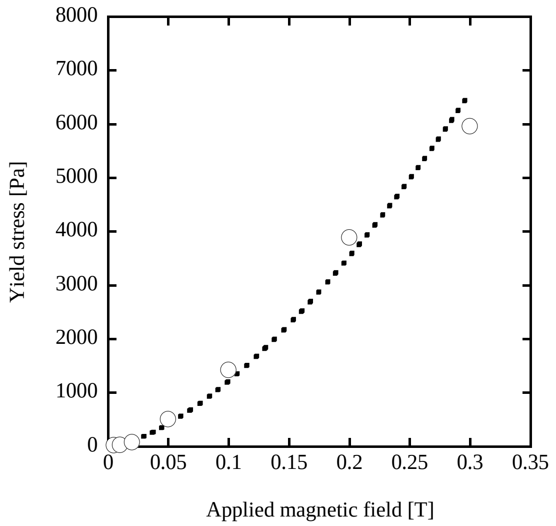


Fig. 1 Yield stresses as functions of the applied magnetic field for MR fluids containing 2.7 mass% oleic acid. Dotted line corresponds to the best fit of Eq. (1).

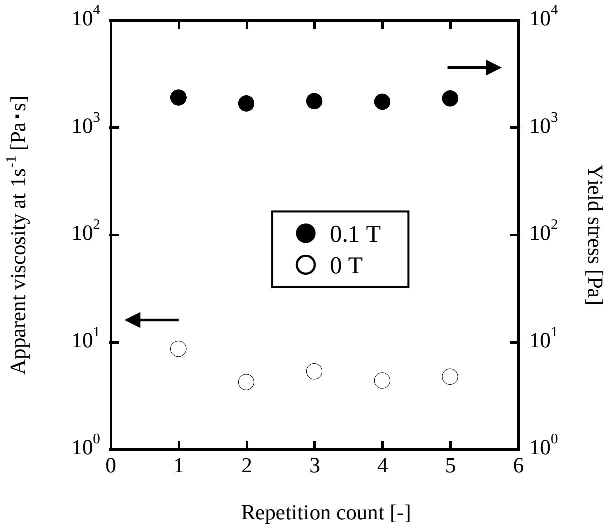


Fig. 2 Redispersibility test for the MR fluid. The added amount of oleic acid was 2.7 mass%.

nanoparticles was 7.2 m^2/g determined by nitrogen gas adsorption based on the BET multipoint method. The equivalent diameter is calculated to be 106 nm [8, 9]. The carrier liquid was silicone oil (KF96-50cs, Shin-Etsu Chemical, Japan), and the surfactant was oleic acid (Kanto Chemical, Japan).

The MR fluids were prepared as follows. The iron nanoparticles were coated with oleic acid using a planetary centrifugal mixer (AR-100, THINKY, Japan) for 10 min. Then, the modified nanoparticles were mixed with silicone oil by means of the planetary centrifugal mixer for 10 min. The solid concentration of MR fluids was set to 15 vol%. Added amount of oleic acid was from 0 to 7.1 mass% of the total mass of the iron nanoparticles in order to evaluate the effect of the oleic acid coating on MR responses.

MR responses of the prepared fluids were measured at 293 K using a parallel-plate rheometer (RheoStress600, HAAKE, Germany) attached with the electro-magnetic system (MR-100N, EKO Instruments, Japan). The diameter of the plates was 20 mm and the gap distance was fixed at 0.5 mm. Magnetic flux from 0 to 0.1 T was applied perpendicular to the direction of the shear flow. In the dynamic measurements, an oscillatory shear stress was applied with amplitude in the range 10^{-1}–10^{4} Pa at a constant frequency of 1 Hz. The storage modulus (G') and the loss modulus (G'') was measured.

3. Results and Discussion

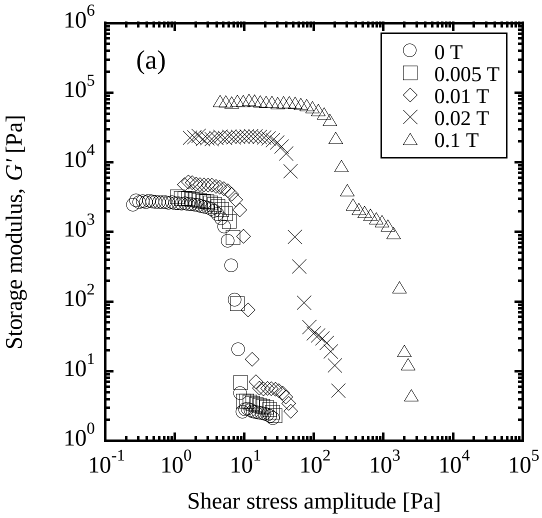
We have investigated the effect of oleic acid addition on the MR fluids viscosity without an external magnetic field [10]. The relationship between the apparent viscosity at a shear rate of 1 s^{-1} and the added amount of the oleic acid was measured. Briefly, adding from 1.4 to 3.3 mass% gave the relatively low viscosity of ca. 10 Pa·s. Below 1.4 mass%, the viscosity drastically increases because iron particles aggregates and the suspensions are unstable. Above the optimum concentration region, the excess addition of oleic acid, the viscosity is slightly increased. Thus, the present study confirms that nanoparticles covered with the oleic acid are suitable for colloidal MR fluids.

When σ_y is the yield stress, σ_0 is the yield stress in a zero magnetic field, and b and n are fitting parameters, the relation between the applied field (H) and yield stress can be evaluated by fitting the experimental data to Eq. (1).

$$\sigma_y = \sigma_0 + bH^n \qquad (1)$$

Figure 1 demonstrates the yield stress as a function of applied magnetic field strength for MR fluids of 2.7 mass% oleic acid addition. Dotted lines indicate the best fit to Eq. (1). According to the theoretical model of MR fluids associated with the magnetic field dependency of yield stress [3], n is 1.5 if the field is lower than the saturation magnetization of a suspended magnetic particle. Strong aggregation reduces the average dipole–dipole force between the particles due to the mean particle–particle distance [11]. Then, the parameter n should be below the theoretical value. The n value in this study is 1.53 and is approximately equal to the theoretical value. The dipole–dipole interactions are much larger than the interparticle van der Waals attractive or Brownian forces.

In order to evaluate the fluid redispersibility, the effect of on-off repetition of applied magnetic field on the fluid viscosity. After apparent viscosity of the fluid under zero magnetic field was measured, MR response at 0.1 T of the applied magnetic field was monitored. This operation was repeated 5 times. **Figure 2** shows apparent viscosity at shear rate of 1 s^{-1} and yield stress at 0.1 T, respectively. The prepared MR fluid showed the good reversibly change when subjected to an external magnetic field.



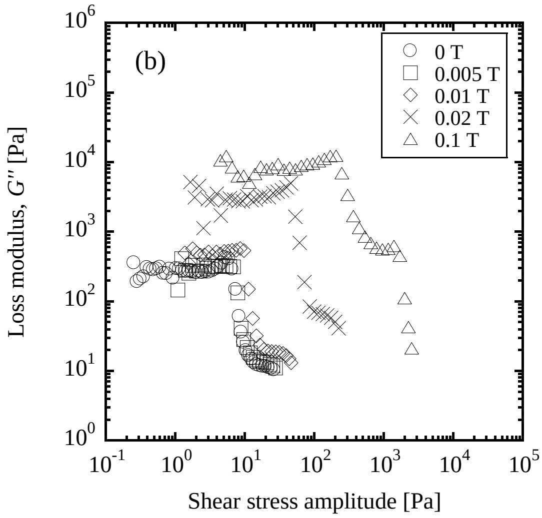


Fig. 3 (a); Storage and (b); Loss modulus of the suspension containing 7.1 mass% oleic acid as a function of the shear stress amplitude.

Further experiments on dynamic magnetorheology were performed for the stabilized suspension with 7.1 mass% amount of the oleic acid. The storage modulus *G'* and loss modulus *G''* was measured for the MR fluid. **Figure 3** shows the *G'* and *G''* as a function of the amplitude of shear stress in the presence of applied magnetic flux density. A viscoelastic linear region appears in *G'* and *G''* at low shear stresses. In this region, the internal structure of the suspension is ordered. When shear stresses are larger than a critical point, the viscoelastic moduli decrease drastically, indicating a nonlinear viscoelastic response. It should be noted that the *G'* is considerably stronger than *G''* for any field applied as shown in Fig. 3a and Fig. 3b. The *G'* and *G''* increased depending on the strength of applied magnetic flux density. These results indicate that robust chain-like structures of the iron particles can be formed in the suspension under the magnetic field applied.

4. Conclusion

Iron-based MR fluid, which consisted of oleic acid coated iron nanoparticles dispersed in silicone oil have been successfully prepared. We confirmed that two step modification of iron particles, i.e. pre-oxidation to grow the thin oxide layer with nanoscale roughness and subsequent fatty acid capping, was effective to obtain the low viscous suspensions. We then demonstrated colloidal dispersibility of oleic acid-capped iron nanoparticles and its effect on steady and dynamic MR response. When an adequate amount of oleic acid was added, the MR fluid displayed a good redispersibility and significant field-dependence yield stress. The dynamic measurements indicated that robust chain-like structures of the iron nanoparticles could be formed in the suspension.

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