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Colloidal dispersibility of fatty acid-capped iron nanoparticles and its effect on static and dynamic magnetorheological response

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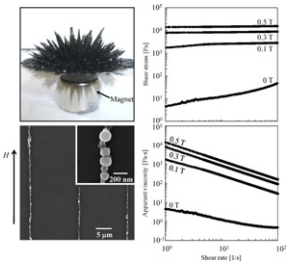
HIGHLIGHTS

- Colloidal dispersibility of concentrated suspensions containing iron nanoparticles.
- n-Octanoic acid controls the flocculated structures of nanoparticles in mineral oil.
- The effect of suspension stability on the magnetorheological response was discussed.
- Pair potential energies between the suspended nanoparticles were calculated.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein we report colloidal dispersibility of concentrated suspensions containing fatty acid-capped iron nanoparticles and its influence on the static and dynamic magnetorheological (MR) response. The amount of fatty acid absorbed on the surface controls the non-field dispersion state as well as weakly and strongly flocculated structure of the nanoparticles. Both yield stress at $B = 0.5$ T of an applied magnetic field is ca. 14–16 kPa Because the flocculated structure has a negligible effect on the field-dependence yield stress, the non-field dispersion state mainly determines the turn-up ratio; the ratio of the yield stress at $B = 0.5$ T to shear stress (at 1 s^{-1}) at $B = 0$. The dynamic measurements indicate that the two dispersion states are different in the field-induced aggregation structures. A viscoelastic linear region appears for a weakly flocculated suspension, and does not for a strongly flocculated suspension. Additionally, the colloidal stability for the two dispersion states is discussed in terms of pair potential energy.

1. Introduction

Magnetorheological (MR) fluids are a class of smart materials whose rheological behavior can be reversibly changed from a fluid-like to a solid-like state depending on the magnitude of the applied magnetic field [1]. Typically, MR fluids are non-colloidal suspensions composed of micron-sized iron particles in a nonpolar medium such as silicon or mineral oil. These iron particles, which typically have average diameters of ~5 μm or more [2–4], are subject to anisotropic attractive forces between the induced magnetic dipoles along an external magnetic field, and tend to align along the field, forming chains, which provide an elastic response [5,6].

Magnetic nanoparticles dispersed in colloidal MR fluids are of both scientific and practical interests because sedimentation and abrasion problems associated with the micron-sized particles will be greatly reduced [7–9]. On the other hand, colloidal suspensions with fine magnetic nanoparticles such as ferrofluids (approximately 10 nm in diameter) exhibit a weak MR effect [10,11] because Brownian forces dominate the magnetic forces. To enhance the MR effect (i.e., to form strong chain structures), a high dipolar

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parameter (λ), which is defined as the ratio of the dipolar interaction to thermal energies, is necessary [12]. The dipolar interaction energy between two magnetic particles with radius a is proportional to a^3. Hence, λ becomes sufficiently high ($\lambda > 1000$) when the particle diameter exceeds ~70 nm under the appropriate magnetic field at room temperature. López-López et al. have reported that particle size has a negligible influence on the MR response when the average diameter exceeds 100 nm [13]. Recently, we have observed that suspensions containing iron nanoparticles (approximately 100 nm in diameter) exhibit a clear MR effect and a good stability against sedimentation [14]. Such relatively large nanoparticles have potential in colloidal MR fluid applications. In addition, magnetic nanoparticles with high volume fractions are preferable because standard chain models predict that the field-induced yield stress is proportional to the volume fraction (Φ) [6]. In case of the micron-sized MR fluids, the volume fraction is typically 20 vol% or more [2–4].

Nevertheless, few works have reported the MR behaviors of concentrated suspensions of magnetic nanoparticles because increasing the volume fraction without significantly increasing the suspension viscosity (i.e. the formation of strongly flocculated or aggregated states) is experimentally difficult. On the other hand, magnetic particles may be deflocculated in a nonpolar oil by physically preventing a close approach due to steric hindrance of an adsorbed surfactant or polymeric species [15–18]. Additionally, it may be possible to tailor the interparticle forces and consequently, the suspension stability (or suspension structure). Although suspension stability may be related to the field-induced suspension structure and ultimately responsible for the MR response, most studies on MR fluids have not focused on the relative influence of suspension stability on the MR effect.

Herein we report the MR behaviors associated with suspension stability for concentrated magnetic nanoparticles. The amount of added fatty acid (n-octanoic acid: $C_7H_{15}COOH$) controls the suspension stability. Both weakly and strongly flocculated suspensions are successfully prepared using iron nanoparticles approximately 100 nm diameters [14] and a particle volume fraction of 20 vol%. Through static and dynamic MR measurements, the influences of suspension stability on the MR effect are investigated. Additionally, the suspension stability is analyzed in terms of pair potential energies where a simple sum of the steric hindrance interaction of the absorbed fatty acid and the van der Waals attractive interactions as well as the surface roughness of the oxide shell are used to calculate the pair potential energy.

2. Experimental

2.1. Materials

Iron nanoparticles were synthesized by the arc-plasma method, which is described elsewhere [14], under reduced conditions of Ar + 75%H_2 with a total pressure of 101 kPa After synthesizing 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 a relatively long time (5 h). This procedure coated the iron nanoparticles with a thin oxide layer, allowing the nanoparticles to be handled. Nitrogen gas adsorption based on the BET multipoint method indicated the specific surface area (SSA) of the iron core/oxide shell iron nanoparticles was 7.21 m^2/g. The calculated equivalent diameter (d) was 106 nm [$d = 6/(\rho \times SSA)$ where ρ is the density, which is 7870 kg m^{-3} for pure iron]. The core/shell nanoparticles had a high saturation magnetization [14].

The carrier liquid and surfactant were mineral oil (guaranteed reagent grade, Nacalai Tesque, Japan) and n-octanoic acid ($C_7H_{15}COOH$; extra pure grade, Tokyo Chemical Industry Co., Ltd., Japan), respectively. Table 1 lists their physical features.

Table 1
Physical features of the solvent and additive.

	Unit	Mineral oil	n-Octanoic acid
Number of carbons	[−]	26	8
Chemical formula		C_xH_y	$C_7H_{15}COOH$
Molar mass (MW)	[g/mol]	350.0[a]	144.2
Boiling point	[°C]	> 300	238
Chain size (δ)	[nm]	3.2[b]	1.1[b]
Density (ρ)	[10^6 g/m^3]	0.84	0.91
Viscosity	[mPa s]	27.71 ± 0.07[c]	6.10 ± 0.02[c]

[a] Molar mass of the mineral oil was measured using GC-TOF/MS.
[b] Assumed a completely stretched conformation.
[c] Viscosity was measured using a cone-plate rheometer (RheoStress600, HAAKE, Germany) at 293 K. Plate diameters were 50 mm and the gap distance was fixed at 52 μm.

2.2. MR fluids

The MR fluids were prepared as follows. To remove physisorbed water on the surfaces, the nanoparticles were dried overnight under a vacuum. A planetary centrifugal mixer (AR-100, THINKY, Japan) was used to coat the dried particles with n-octanoic acid as well as to disperse the coated nanoparticles in mineral oil. Each step took 10 min. Finally, the mixture was immersed in an ultrasonic bath for 1 h to ensure homogeneity. The solid concentration of the MR fluids was set to 20 vol%. To minimize the apparent viscosity of the suspension, the optimum additive content was determined by varying the concentration of n-octanoic acid from 0 to 5.0 mass% of the total mass of the iron nanoparticles.

The adsorbed amount of n-octanoic acid on the nanoparticles was estimated from the measured carbon content of the sample using a total organic carbon analyzer (TOC-V; Shimadzu, Japan). Samples were prepared as follows. First, nanoparticles coated with n-octanoic acid were mixed with toluene and treated in an ultracentrifuge at 10,000 rpm for 5 min Then the supernatant was discarded, and the residue was dried in a vacuum for 12 h. The resulting dry powder was used in the measurements.

2.3. Magnetorheology

MR responses of the prepared fluids were measured at 293 K using a parallel-plate rheometer (RheoStress600, HAAKE, Germany) attached to an electromagnetic system (MR-100N, EKO Instruments, Japan) where the plates had a diameter of 20 mm and a fixed gap distance of 500 μm. A magnetic flux was applied perpendicular to the shear flow direction. Current control regulated the generated magnetic flux from 0 to 0.5 T.

To obtain reproducible results, the fluids were pre-sheared for 120 s at a large shear rate ramp (0–150 s^{-1}). Pre-shearing was immediately ramped down from 150 to 0 s^{-1}. Then the fluids stood for 60 s to ensure equilibrium. Finally, two different experiments, steady-state and dynamic (oscillatory) measurements, were conducted. In the steady-state measurements, the shear rate increased from 1 to 100 s^{-1}, and the MR behaviors were characterized using the Herschel–Bulkley (HB) model [8]. The relation between shear stress (σ) and shear rate (γ) in the HB model is given as

$$\sigma = \sigma_y + K(\gamma)^n \quad (1)$$

where σ_y is the yield stress, which was estimated by fitting the experimental data to the equation. K and n are model parameters.

In the dynamic measurements, an oscillatory shear stress was applied with an amplitude between 10^{-1} and 10^4 Pa at a constant frequency of 1 Hz The elastic or storage modulus (G') and