Dispersion control of magnetic nanoparticles for functional fluids†

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1. Introduction

Current magnetorheological (MR) fluids are non-colloidal dispersions of micron-sized magnetic particles in a carrier liquid such as silicone oil. Under an applied magnetic field, MR fluids alter their rheological properties, rapidly and reversibly. Such magnetic-field tunable rheological behavior of MR fluids is the base in many smart actuation systems [1]. The MR fluids stability against aggregation and settling of micron-sized magnetic particles is an intrinsic hindrance for many practical applications. Several studies based on interfacial chemistry have been done to improve this problem. Surface modification of magnetic particles with surfactants or polymers is a common sense approach that prevents aggregation by means of steric repulsion. In order to avoid particle settling, however, a thickening carrier liquid using additive (fumed silica [2] or organoclay [3], for instance) is required. Nano-sized magnetic particles are capable of homogeneous dispersion into the oil phase without aggregation and settling. Hydrophilic oxide magnetic particles are difficult to disperse into conventional silicone oils due to a poor interaction of the oil with particle surfaces. A colloidal dispersion system should be then developed. Generally, principle phenomena in developing colloidal dispersion system are dissolving additives in liquid, adsorption of additives on particles and wetting of the particles by liquid [4]. Liquid must dissolve additives so that they become uniformly distributed and have wettability with the liquid. Although oleic acid ($C_{18}H_{34}O_2$) can be adsorbed on the surface of oxide particles [5], fabrication of MR fluid using oleic acid has not been reported because oleic acid and silicone oil are mutually-immiscible. In this work, we have investigated the influences of oleic acid as a surface-active substance on the dispersibility into oil phase and the MR response.

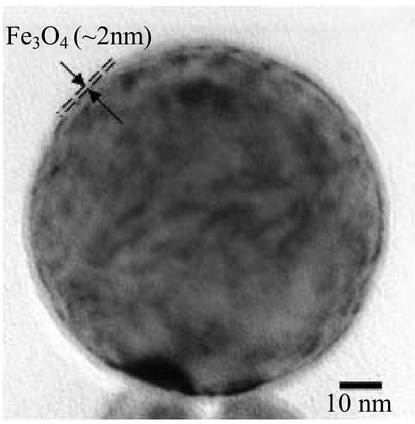

Fig. 1 TEM image of a Fe nanoparticle

2. Method

Crystalline Fe nanoparticles which used a magnetizable matrix were fabricated via an arc-plasma method [6]. The nanoparticles had a spherical shape with about 100 nm in size and were covered with 2 nm thin oxide layer as shown in **Fig. 1**.

MR fluids were prepared as follows. The Fe nanoparticles were coated with oleic acid (Kanto Chemical, Japan) by means of planetary centrifugal mixer (AR-100, THINKY, Japan) during 10 min. Then, either non-modified or the modified Fe nanoparticles were mixed with silicone oil (KF96-50cs, Shin-Etsu Chemical, Japan) using the planetary centrifugal mixer for 10 min. Additive amount of oleic acid was 0–11 wt%. The solid concentration of MR fluids was set to 1–15 vol%.

MR responses of the fluids were measured at 293 K using a parallel-plate rheometer (RheoStress600, HAAKE, Germany) attached to 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 was applied perpendicular to the direction of the shear flow from 0 to 0.3 T.

3. Results and Discussion

Influence in the dispersibility on MR effects was firstly investigated by using the non-modified and modified Fe nanoparticles. Additive amount of oleic acid was 3.0 wt%. **Figure 2** shows shear stress versus shear rate relationship with and without internal magnetic flux for 15 vol% MR fluids.

With respect to the surface-modified nanoparticles, the shear stress of the dispersions increased with strengthening magnetic fields. Additionally, the MR fluid behaves as a Bingham fluid which is generally monitored in micron-sized MR fluids. The yield stress at 0.3 T of the applied magnetic field was ca. 5.9 kPa, indicating significant turn-up ratio (=1150, refers to the difference between off-state apparent viscosity and on-state yield stress) of the modified

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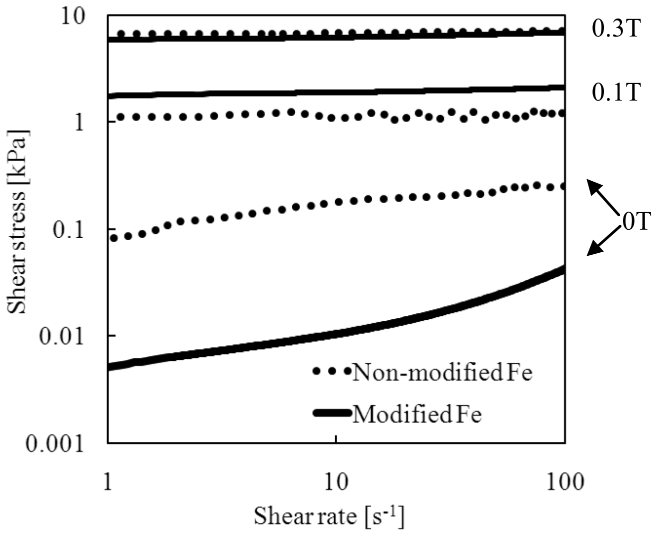

Fig. 2 Shear stress versus shear rate relationship with and without magnetic flux for 15 vol% MR fluids

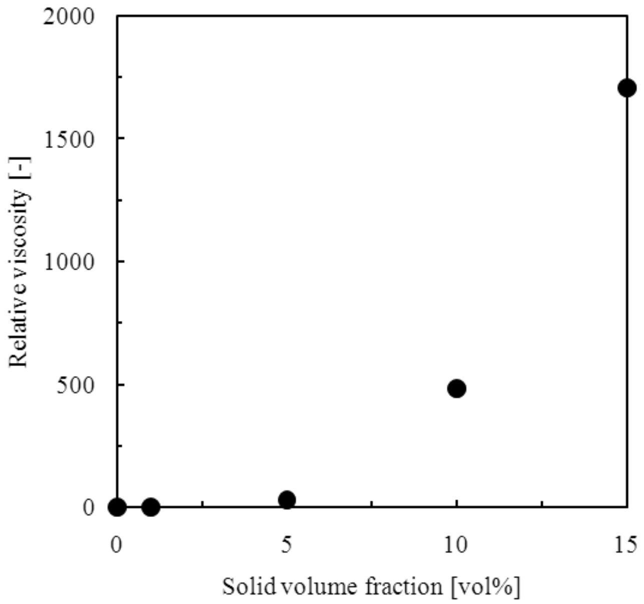

Fig. 3 Relative viscosity as a function of solid volume fraction without internal magnetic field

nanoparticles dispersions. It should be noted that oleic acid is effective to control dispersibility of the nanoparticles into the silicone oil. Hence, resulting MR fluids clearly verifies a large MR effect.

In contrast, a slight turn-up ratio (=82) was observed for the non-modified nanoparticles fluid. The shear stress of the non-modified based fluid at the off-state field is ten times larger than that of the modified dispersions. This result indicates that the non-modified nanoparticles formed aggregates in the oil phase spontaneously due to entropically unfavorable interaction between the oil and the nanoparticles. Obviously, the most illustrative expositions of the interparticle attraction between nanoparticles are volume fraction dependency of relative viscosity in **Fig. 3.** Above 5 vol% of solid volume fraction, the relative viscosity increased, dramatically. Surface distance between nanoparticles for 5 vol% MR fluid calculated from the Woodcock equation [7] is ca. 100 nm. Actually, the distance basically agrees with interaction distance of a hydrophobic attraction force [8].

It is commonly believed that there is an optimal amount of added dispersant. That is, incomplete coverage or excessive addition of dispersant leads to particles aggregation. **Figure 4** demonstrates the effect of additive amounts of oleic acid on off-state apparent viscosity. The fluid showed the lowest viscosity with the 3.0 wt% addition.

4. Conclusions

We have found that the adequate addition of oleic acid into silicone oil including the magnetic nanoparticles dramatically reduced their apparent viscosity and was a key to develop colloidal dispersion system. Additionally, the resulting fluid clearly demonstrated a large MR effect.

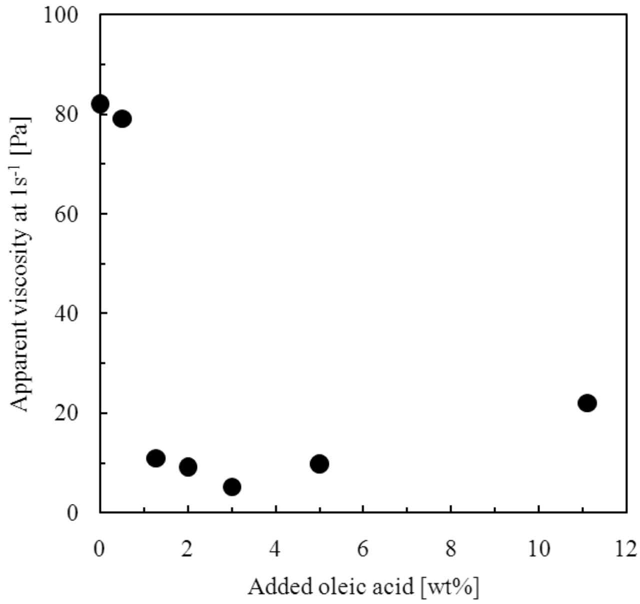

Fig. 4 Off-state apparent viscosity of MR fluids with various amount of oleic acid

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