Core-shell typed polymer coated-carbonyl iron suspensions and their magnetorheology

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Abstract. In order to resolve aggregation and sedimentation problem of carbonyl iron (CI) for magnetorheological (MR) fluids, polymer coated composite magnetic particles (CIPMMA) were synthesized via a dispersion polymerization method using CI dispersions in methyl methacrylate monomer, and then adopted the product as a dispersed phase of MR fluids. Especially, to improve mechanical property of the coated poly(methyl methacrylate) (PMMA) onto CI microspheres, a cross-linking method was adopted in this study. Flow and viscoelastic properties of the MR fluids were analyzed via a rotational rheometer equipped with a magnetic field supplier using a parallel plate measuring system.

1. Introduction
Magnetorheological (MR) fluid, which is a suspension of magnetically susceptible particles dispersed in a nonmagnetic suspending medium, has been investigated by many research groups [1, 2]. It is regarded as a smart material with controllable properties by an external magnetic field, which is abruptly transformed within milliseconds from a fluid-like to solid-like state under an applied magnetic field, by showing changes of its rheological characteristics such as yield stress and shear viscosity [3-6]. When magnetic field is applied to MR fluids, randomly dispersed magnetic particles are being oriented with a chainlike structure in the direction of magnetic field, which can be deformed and then broken by hydrodynamic drag as they are subjected to the shear force [7, 8]. Therefore, MR fluids have many industrial applications such as dampers, shock absorbers and brakes so as to control resistance due to the tuneable rheological properties and their fast response time [9-11].

For the high performance engineering application, both high yield stress and colloidal dispersion are essential in MR fluids [12]. Among various magnetic materials, pristine carbonyl iron (CI) has been extensively investigated as a MR material regarding MR characteristics due to its high magnetization properties in certain magnetic field strength [13]. However, the CI based MR suspensions are known to possess several drawbacks such as dispersion non-uniformity and sedimentation of the CI particles due to the large density difference. In order to improve this problem, dispersants were added in MR fluids to improve dispersion stability [14-16]. In other ways, magnetic particles were coated with polymer or monodispersed polymer cores were coated with magnetic particle to lower density of the magnetic particles [17-19].

In this study, to improve dispersion stability of the MR fluids, core-shell typed polymer coated-CI composite particles via an encapsulation method with poly(methyl methacrylate) (PMMA) [20] are
introduced. The polymer coated composite magnetic particles (CIPMMA) were synthesized via a dispersion polymerization method using CI dispersants in methyl methacrylate monomer, and then adopted as dispersed phase of MR fluids. Especially, to improve mechanical property of the coated PMMA onto CI microspheres, a cross-linking method was adopted using ethylene glycol dimethacrylate (EGDMA) as a crosslinker in this study. MR properties were analyzed via a rotational rheometer equipped with a magnetic field supplier using a measuring system of parallel plate geometry.

2. Experimental

2.1. Preparation

We used carbonyl iron (CI) (standard CD grade, BASF, Germany) particles whose average particle size and density are 2.57 µm and 7.86 g/cm³, respectively. Initially, the CI surface was modified by methacrylic acid (MAA, Junsei, Japan) for 4h to induce easy polymerization reaction on the CI surface. The modified CI particles were then dispersed in methanol containing poly(vinyl pyrrolidone) (PVP) (Aldrich, USA, Mw = 1,300,000 g/mole) as a stabilizer. Methyl methacrylate (MMA) (Dongyang Chem. Co., Korea) monomer and 2, 2-azobisisobutyronitrile (AIBN) (Junsei, Japan) as a radical initiator were dissolved in the reaction system. The AIBN was used after being recrystallization in acetone. In addition, ethylene glycol dimethacrylate (EGDMA) (Aldrich, USA) was used as a cross-linking agent of PMMA. The mass ratio of CI to MMA was 2.0. The temperature was increased up to 55 ºC, and the dispersion polymerization was continued for 24 h under the nitrogen purging. After the polymerization, the crosslinked CIPMMA was separated by magnet and washed with distilled water and methanol to remove PVP, unreacted monomer, and PMMA oligomers. Finally, the CIPMMA composite particles were dried at 60 ºC in oven.

2.2. Characterization

External and internal morphology of the produced particle was observed using scanning electron microscope (SEM) (Hitachi S-4300) and transmission electron microscope (TEM). The MR fluids were then prepared by dispersing the crosslinked CIPMMA particles into lubricant oil (Yubase 8, SK Co. Korea). Rheological properties with and without external magnetic field were investigated using a commercial rotational rheometer (MCR 300, Anton-Paar, Germany) with the MR device (MRD 180, Physica, Stuttgart, Germany) which can generate a homogeneous magnetic field. The MR properties were measured in both steady and oscillatory shear modes.

3. Results and discussion

3.1. Morphology of magnetic particles

Figure 1. (a) SEM images (inset: pure CI) (b) TEM images of PMMA-coated CI particles
Surface morphology of the cross-linked CIPMMA particles was observed by SEM. Figure 1(a) shows the SEM images of both pure CI and PMMA coated CI particles. The surface of the synthesized cross-linked PMMA-coated CI particles becomes smooth compared to pure CI, indicating that the polymers were encapsulated onto the CI surface as a result of the coating process. It also indicated that the coated particles have spherical shape while showing similar size with pure CI.

The internal structure of the PMMA coated CI particle was shown in Fig. 1(b) which represented TEM image of cross sectioned core-shell particles using an epoxy mold. The CIPMMA particles were found to have about 50nm of PMMA coated layer, of which the PMMA layer was partially sectioned due to difference of hardness between CI and PMMA during microtoming.

3.2. Thermal property of CIPMMA magnetic particles
The encapsulation was also characterized using thermal gravimetry analyzer (TGA). Figure 2 shows thermal degradation of cross-linked CIPMMA magnetic particles with N₂ purging. It displayed typical degradation curve of the dispersion polymerized PMMA, which shows multistep degradation due to solubility difference as PMMA molecular weight, between 150 and 450. The final weight loss is estimated to be about 13 wt% which implies the content of PMMA in CIPMMA particles. The density of the CI/PMMA composite at 20°C was measured to be 4.7 g/cm³ via a gas pycnometer, which is about half of the density of pristine CI.

![Cross-linked CIPMMA composite](image)

Figure 2. Thermal degradation curve of CIPMMA composite particles

3.3. Magnetorheological properties of MR fluids
The MR properties were characterized via a rotational rheometer equipped with a magnetic field supplier using a measuring system of a parallel plate. Figure 3 shows shear stress as a function of shear rate for the CI and CIPMMA based MR fluids under different external magnetic field strengths ranging from 0 to 342kA/m. Both of pure CI and CIPMMA based MR fluids behave typical Bingham fluids with yield stresses under external magnetic fields, while they behave like Newtonian fluids without a magnetic field, implying the formation of chain structure and the increase of magnetic interaction between the particles. It was also clearly shown that the shear stresses increased for the entire shear rate region with the increase in magnetic field strength, indicating the increase of magnetic dipole moment with increase of magnetic field strength. Although the yield stress of the PMMA encapsulated CI particle based MR fluid was indicated to be smaller than that of the CI based MR fluid because the polymer shell reduces the particle interaction, the CIPMMA based MR fluids exhibit enough yield stresses for their industrial application. Furthermore, the CIPMMA based MR fluids show more stable Newtonian behaviour at 0kA/m magnetic field, indicating that the encapsulation of magnetic particle offers colloidal stability into MR fluids.
Viscoelastic behaviour of the MR fluids was also analyzed in the oscillatory shear mode. Figure 4 shows storage modulus of pure CI and CIPMMA based MR fluids as a function of angular frequency. It was found that the storage modulus was frequency independent for both CI and CIPMMA based MR fluids, implying the solid-like properties of MR fluids.

The relationship between shear stress and the applied magnetic field strength (H) is presented in Figure 5 which shows shear stresses of CI and CIPMMA based MR fluid at each magnetic field strength. With the increase in magnetic field strength, the shear stresses were increased. When considering yield stresses of MR fluids at intermediate field strengths, yield stress can be predicted by various factors [21]:

$$\sigma_y = \varphi \mu_0 M_s^{1/2} H^{3/2}$$

where is the volume fraction of the magnetic particles, $\mu_0$ the permeability of free space, $M_s$ magnetic-field saturation, and $H$ is the magnetic field strength. The relationship between yield stress and magnetic field strength exhibits that yield stress increases in proportion to $H^{3/2}$. This prediction of a $3/2$ power law for the field-dependence has been confirmed experimentally and we can also confirm in Fig. 5, in which there was a trend for the slope of stress based on the field to start to decline in a high magnetic field strength range.

3.4. Sedimentation and re-dispersion of MR fluids
Although the yield stress of MR fluids decreases due to the encapsulation of magnetic particles, the encapsulation has advantages in industrial application because it can enhance the dispersion stability of the suspension. In Fig. 6, the sedimentation ratio of CI and CIPMMA based MR fluid was compared to each other, in which the sedimentation curve of pure CI based MR fluid displayed faster sedimentation than PMMA encapsulated CI based MR fluid due to the density difference between pure CI and CIPMMA particles. After most particle settled down, the pure CI based MR fluid showed a lower level particle height than that of the CIPMMA based MR fluid, indicating that the CIPMMA particle possesses larger effective volume than pure CI in the medium oil. It was also confirmed that the CIPMMA could be easily re-dispersed after removing magnetic fields due to their surface properties.

4. Conclusion
In this study, magnetic CI particles were encapsulated by cross-linked PMMA via in-situ dispersion polymerization. The surface morphologies and cross-sectional images were examined by SEM, TEM. Due to not only decrease of absolute contents of CI with polymer coating but also reduction of the particle interaction because of the polymer shell, the yield stress of CIPMMA composite particle based MR fluid was lower than that of pristine CI based MR fluid. Despite slight lower yield stress and modulus of the MR fluids, it was found that the encapsulation process of magnetic particles improve the sedimentation and dispersion quality.

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