Preparation and Characterization of MR fluid consisting of Magnetite Particle coated with PMMA

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Abstract. To improve physical characteristics of MR fluid, we synthesize magnetite nanoparticles (MNP) in shape of magnetic core- poly(methyl methacrylate) (PMMA) polymeric shell by atomic transfer radical polymerization. Prepared MNPs-PMMA which possesses a density lower than that of pure MNPs were characterized by FT-IR, XPS and TEM. Synthesized MNP-PMMA based MR fluid which was dispersed in non-magnetic medium lubricant oil (Yu-base 8) with 10 vol% was prepared. Rheological properties such as shear viscosity, shear stress and storage modulus were measured by both static and dynamic tests using a rotational rheometer with various external magnetic field strength applied.

1. Introduction

Magnetorheological (MR) fluids, which consist of either ferro- or ferri-magnetic particles with a size on the order of sub to several microns dispersed in a nonmagnetic fluid medium, are considered as smart particle suspensions because they have readily controllable characteristics by an external magnetic field. When exposed to an external magnetic field, the fluid transforms from a freely-flowing liquid-like state to a solid-like state as quickly as a flash, because the dispersed magnetic particles attract each other to form fibril structures aligning along the applied magnetic field direction, consequently inhibiting the fluid flow. That makes a change of rheological properties of the MR fluids such as an improvement of yield stress, shear viscosity and storage modulus with external magnetic field strength [1-3]. In addition, soft magnetic materials such as magnetite (Fe₃O₄) are more reversible to control rheological properties of the MR fluids than hard magnetic materials due to be relatively easy to be magnetized and demagnetized. These characteristics of the MR fluids allow their engineering applications such as active controllable dampers, position controllers, clutches and shock absorbers. However, their some problems which are sedimentation and abrasion by high density and rigid surface of magnetic particles need to be improved for practical engineering applications [4-6]. Generally, dispersants have been added in MR fluids to improve dispersion stability. In addition, either magnetic particles were coated with polymers or monodispersed polymer cores were coated with magnetic particle to lower the density of magnetic particles [7-9]. In this study, to improve sedimentation and abrasion problems caused by high density and rigid surface of magnetic particles, we synthesized PMMA/magnetite nanoparticle composites by atomic transfer radical polymerization (ATRP) method [10-14]. Synthesized PMMA/magnetite composites (MNP-PMMA) in shape of magnetite core - PMMA shell were observed to possess lower density and be softer than pure magnetite particles. Some drawbacks of the MR fluids such as sedimentation and abrasion of magnetic particles are improved by using PMMA/magnetite composites.

2. Experimental

2.1. Materials
Ferric chloride hexahydrate (FeCl₃·6H₂O, 98%), ferrous sulfate heptahydrate (FeSO₄·7H₂O, 99%), oleic acid (OA), methanol, 3-chloropropionic acid (CPA, 98%), 2,2-dipyridyl (bpy, 99%) and copper(I)
bromide (CuBr, 98%) were purchased from Aldrich, USA, while methy mathacrylate (MMA), n-hexane and ammonium hydroxide (NH₄OH) were from DC Chemical Co., LTD, Korea.

2.2. Synthesis of magnetic Fe₃O₄ nanoparticles
The magnetite nanoparticles (MNP) were produced by co-precipitation of an aqueous Fe³⁺/Fe²⁺ solution with a base [15]. Ferric chloride hexahydrate (FeCl₃·6H₂O, 98%) and ferrous sulfate heptahydrate (FeSO₄·7H₂O, 99%) were dissolved in distilled water and heated to 60 °C. Then ammonium hydroxide and oleic acid (OA) (Aldrich, USA) were added rapidly under stirring for 30min. Temperature was then decreased to room temperature (25 °C). After 6h, the precipitates were washed several times with distilled water and methanol. After being dried in the vacuum oven at 80 °C, the dark brown powder was obtained.

2.3. Immobilized initiator on MNPs surface
Prepared MNPs which were stabilized by OA were mixed with hexane. The mixture was sonicated for 1 hour in order that the MNPs were well dispersed in hexane. Initiator CPA was added in the solution with stirring and sonication. After 1 day, the precipitate was separated from mixture using a centrifuge (at 5000rpm, for 15min). They were washed with hexane several times to remove the excess initiator (CPA). After being dried in the vacuum oven at 80 °C, the dark brown MNPs-CPA in which the initiator CPA was immobilized on the surface of MNPs were obtained.

2.4. Surface initiated atomic transfer radical polymerization of MMA
Prepared MNPs-CPA were dispersed in toluene and then were sonicated for 1 hour. MMA monomer, CuBr and bpy were added in the mixture and then the mixture was sealed in glass reactor under vacuum. The final mixture was purged with nitrogen for 1 hour and was agitated with a mechanical stirrer at 300 rpm speed. Surface initiated ATRP was carried out at 80 °C with stirring for 1day. After reaction, the precipitate was washed with toluene using a centrifuge and a magnet. After washing several times, the precipitate were dried in vacuum oven at 80 °C. The red brown powder, PMMA coated MNPs with core (MNPs)–shell (PMMA) structure, was obtained.

2.5. Characterizaiton
Fourier transform infrared (FT-IR) spectra were obtained by using VERTEX 80v vacuum FT-IR spectrometers (Bruker Optics, USA). The spectrum was taken between 400cm⁻¹ and 4000cm⁻¹ and 16scan at resolution of 8cm⁻¹. X-ray photoelectron spectroscopy (XPS) was performed with Axios (Phillips, USA). Transmission electron microscopy (TEM) was performed with Philips CM200 (Phillips, USA) at 120kV. Rheological properties of the MR fluid were characterized by using MCR300 rheometer (Physica, Germany) with the MR device (MRD 180). The steady shear rotation test was perform with the shear rate range from 10⁻² s⁻¹ to 10³ s⁻¹ and the dynamic test was perform with the frequency range from 10⁻¹ Hz to 10¹ Hz.

3. Results and discussion
3.1. Preparation MNPs-PMMA particle
Figure1 shows the FT-IR spectra of (a) MNPs-OA, (b) MNPs-CPA, (c) MNPs-PMMA and (d) pure PMMA. In curves (a), the strong absorption band between 590cm⁻¹ and 630cm⁻¹ was corresponded to the Fe-O bond of Fe₃O₄ and the strong band around 3400cm⁻¹ was attributed to O-H bond. It was conformed that the MNPs were synthesized by co-precipitation of an aqueous Fe³⁺/Fe²⁺ solution. Two peaks around 2930cm⁻¹ and 2850cm⁻¹ were attributed to the asymmetric CH₂ stretch and the symmetric CH₃ stretch, respectively. There are the picks around 1660cm⁻¹ which were characteristic of C=O double bond stretching. These results indicate that the oleic acid has been coated on the surface of MNPs. In curve (c), the strong absorption band around 1090cm⁻¹ was corresponded to the C-O-C ether stretch. It was conformed that PMMA has been coated on the surface of MNPs.
As shown in Figure 2 (a), there are some picks at 284eV, 530eV and 710eV which are attributed C 1s, O 1s and Fe 2p respectively. In figure (b) which is the C 1s core level spectrum of MNPs-OA, there are two picks at 284.9eV and 287.8eV that are attributed to C-C/C-H and COOH. It means that the oleic acid is coated onto MNPs. New pick was observed at 200eV in figure (c) that is attributed to Cl 2p. As shown figure (d) which is the C 1s core level spectrum of MNPs-OA, three pick are observed at 285.4eV, 286.8eV and 288eV which are attributed to C-C/C-H, C-Cl and COOH. It was conformed that initiators are immobilized on the surface of MNPs by observing the C-Cl.

Figure 3 is TEM images of MNPs (a), (d) MNPs-OA, (b), (e) MNPs-CPA and (c), (f) MNPs-PMMA. As shown in figure 3 (a) ~ (c), MNPs-OA, MNPs-CPA and MNPs-PMMA have practically spherical shape and uniform particle size of 8~15nm. It is difficult that the PMMA coating layers of MNPs-PMMA were found, because of only small contrast difference between PMMA and background and particles are severely aggregated. In addition, as shown in Figure 3 (d) ~ (f), we could find more clearly that MNPs-PMMA aggregates are smaller than others. The MNPs which have very high surface energy are aggregated to reduce their surface energy. Since the MNPs were coated with PMMA, surface energy of the MNPs was reduced. It was also confirmed that the MNPs-PMMA was less aggregated than MNPs-OA and MNPs-CPA as given in Fig. 3.

3.2. Rheological properties of MR fluids

MR fluids (10 vol%) was prepared by dispersing synthesized MNP-PMMA in non-magnetic medium oil of Yu-base 8, and then their rheological properties were measured by both static and dynamic tests using a rotational rheometer. Figure 4 shows their relation which was obtained by the rotation test, between shear rate and shear stress for different external magnetic field strength. MR fluids act as like general suspensions without a magnetic field of which the shear stress increases with a shear rate. However, once the external magnetic field is applied to MR fluids, MR fluids behave like a Bingham fluid with yield stress.
This is the reason why the magnetic particles moving freely in the medium make particle chains or particle cluster by polarization force between particles, which is induced by an applied external magnetic field. As shown in Fig. 4, the shear stress at low shear rate increased with augmenting external magnetic field between 100mA and 1999mA. The polarization force between particles increases with increasing external magnetic field strength. Increased polarization force between particles makes strong particle chains or particle clusters in the MR fluid. Yield stress at low magnetic field drastically increases with increased magnetic field strength. On the other hand, at high magnetic field the yield stress rarely increases with magnetic field strength. At low applied fields, the shear stress of the MR fluids increases with increased external magnetic field. In intermediate fields, the contact or polar region of each particle saturates, thus reducing the rate of increase of the shear stress with increasing field. At high fields, the shear stress reaches a limiting value due to completely saturated particles [16]. In addition, the shear stress is independent of shear rate until critical shear rate, because the particle chains which are formed by an external magnetic field are maintained by repeated creation and destruction of the particle chain until the critical shear rate reaches. On the other hand, shear stress is dependent of shear rate above the critical shear rate because the destruction of particle chains is superior to their creation above critical shear rate region.

Figure 4. Shear stress of MR fluid with various external magnetic field strength.

Figure 5 shows the relation between shear viscosity and shear rate. It is confirmed that shear viscosity at low shear rate increases as the external magnetic field strengths increase. In addition, shear thinning behaviour of which shear viscosity decreases with increased shear rate is shown. Figure 6 represents the storage modulus with frequency. It was carried out with increasing frequency at linear viscoelastic region.
Before the test, we found the linear viscoelastic region of the MR fluid through amplitude sweep test in which the storage modulus is measured with changing the strain at a fixed frequency (10Hz). The applied external magnetic field induces polarization force between particles, and induced polarization force between particles becomes strong with external magnetic field strength, so that storage modulus increases with magnetic field strength. As shown figure 6, storage modulus of the MR fluid as similar as shear viscosity and shear stress were increased with external magnetic field strength but the increase of storage modulus was insignificant in high magnetic field strength. Storage modulus are observed to be independent of frequency, indicating that the MR fluid changes from liquid like to solid like mainly by the applied external magnetic field.

4. Conclusion
The MNPs-PMMA composites, which are magnetite core-PMMA shell type, were synthesized by the ATRP. They were observed to possess quite uniform particle size and less aggregation compared with MNPs-OA and MNPs-CPA. Rheological properties of the MR fluids prepared with synthesized MNPs-PMMA and non-magnetic medium Yu-base 8 with 10 volume% were measured by both static and dynamic tests using a rotational rheometer with various external magnetic field strength. Shear stress, shear viscosity and storage modulus of the MR fluids increased with applied external magnetic field strength.

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\[\text{Figure 6. Storage modulus of MR Fluid with various external magnetic field strength.}\]