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Polymer-coated magnetic carbonyl iron microparticles and their magnetorheological characteristics

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Abstract−We review core/shell structured magnetic carbonyl iron (CI)/polymer hybrid particles fabricated with various polymeric systems and their magnetorheological (MR) characteristics when dispersed in non-magnetic suspending medium. Their morphology and magnetization properties are compared with those from different fabrication methodologies. Rheological characteristics of the MR fluids, exhibiting improved dispersion stability compared to the pure CI based MR fluid, are presented along with their potential engineering applications.

Key words: Magnetic Material, Carbonyl Iron, Magnetorheological Fluid, Encapsulation, Core-shell

INTRODUCTION

Magnetorheological (MR) fluids, colloidal suspensions of soft ferro-/ferri-magnetic particles in nonmagnetic medium, have been considered as one of smart and intelligent materials which can be rapidly and reversibly transformed from a fluid-like to a solid-like state within milliseconds by showing dramatic and tuneable changes in rheological properties under an external magnetic field [1-4]. It can be also noted that these characteristics are reversible. MR fluids are usually made up of the magnetically susceptible material as a dispersed phase and non-magnetisable suspending oils such as silicone oil, mineral oil, lubricant and grease as a medium oil [5-11]. In the absence of an external magnetic field strength, the magnetizable particles are randomly distributed and the MR fluid behaves similarly to a Newtonian fluid. When a certain magnetic field strength is imposed, the dispersed particles build up the chain-like structure in the field direction due to an induced magnetic dipole-dipole interaction, as shown schematically in Fig. 1. Thus, during this process, their rheological properties (yield stress, apparent viscosity, and storage modulus etc.) are being rapidly altered. This property of the MR suspensions has been employed in many engineering applications such as active controllable dampers, torque transducers, clutches, magnetoresistors, magnetic field sensors, ultrafine polishing technology and position controllers [12-14].

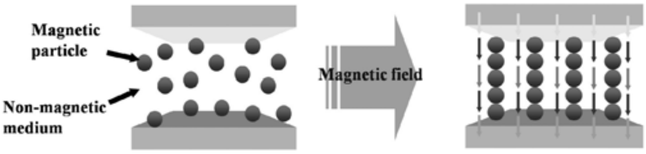

Fig. 1. Schematic diagram of the microstructure change of the MR fluid.

Therefore, MR suspensions, along with their electrically analogous electrorheological (ER) fluids, [15-18] have attracted considerable attention in both academia and industry since their first discovery. The electro-responsive ER fluids, composed of electrically polarizable particles of 1-100 μm sizes, exhibit fascinating field-induced rheological properties as like MR suspensions including a rapid and reversible change in suspension microstructures under an applied electric field strength up to several kV/mm. These include inorganic non-metallic, organic, and polymeric semiconducting materials such as polyaniline [19], polypyrrole [20], poly(p-phenylene) [21], poly(naphthalene quinone radicals) [22] and their composites with clays [23] or carbon nanotubes [24] with volume fractions of 0.05-0.5 dispersed in insulating oils such as mineral or silicone. However, it is well known that compared to the ER fluids, MR suspensions possess several merits for industrial applications such as large yield stress, low voltage power, and less sensitivity to contaminants.

Particles for MR suspensions such as maghemite, magnetite, chromium dioxide, iron and carbonyl iron should be magnetized under an external magnetic field, meaning that ferromagnetic, ferrimagnetic, and paramagnetic materials can be in general used as a dispersed phase of MR suspensions. Among various magnetic MR materials, carbonyl iron (CI) has been widely used as a magnetizable particle for the MR fluids due to its high magnetic permeability, soft magnetic property and common availability [25-27]. However, sedimentation of the CI particles due to the large density mismatch with the medium oil and difficulties in re-dispersion after caking has been regarded as a serious drawback. Therefore, many researchers have made great efforts to improve the dispersion stability and re-dispersion after solidification in the pure CI-based MR system. Generally, adding a dispersion stabilizer and modifying the particles are widely known as the way to improve the dispersion stability in the suspension system [28,29]. Adding sub-micron sized fillers (carbon nanotubes, graphite nanotube, fumed silica and organoclay etc.) have been proven to be an effective method to increase dispersion stability by occupying interspaces of the CI particles with additives to restrain the direct contact of CI particles, consequently sustaining the stability of MR fluid. However, we have to regard the in-

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[‡] This paper is dedicated to Professor Jae Chun Hyun for celebrating his retirement from Department of Chemical and Biological Engineering of Korea University.

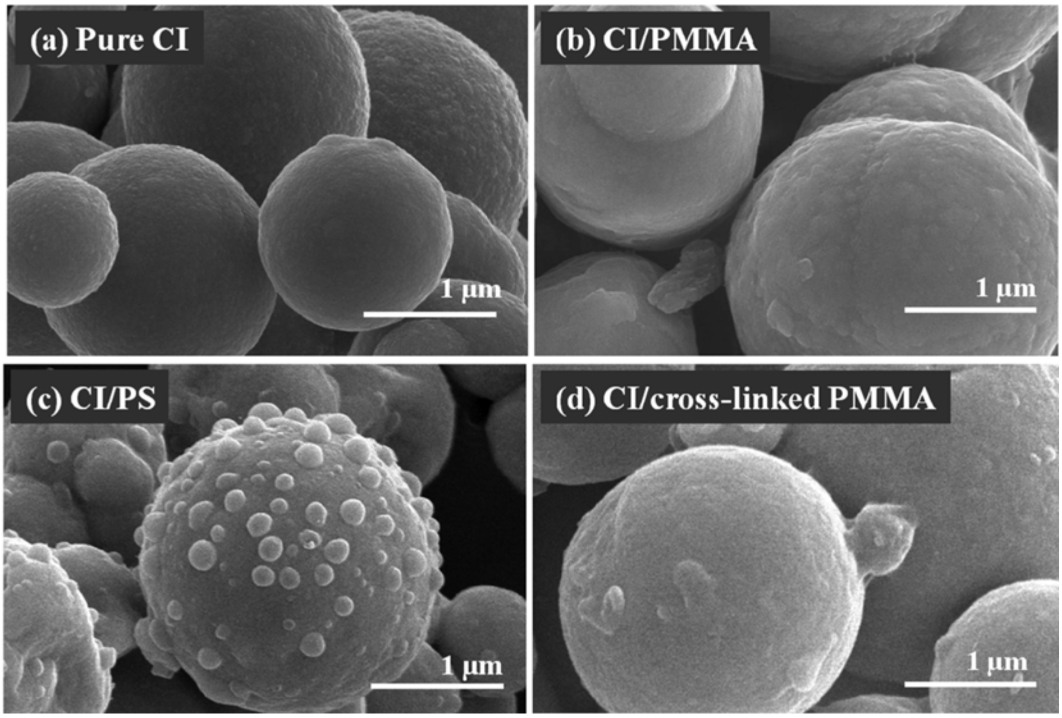


Fig. 2. SEM images of polymer encapsulated CI particles by dispersion polymerization.

fluence of size dimension, morphology of additives as well as the affinity with CI particles on improving this problem. Note that recently nano-sized CI particles have been found to exhibit synergistic effects on MR performance [30].

Concurrently, the polymer encapsulation technique has been considered as one of the advanced methods in the MR system, because it can reduce the particle density and enhance the electrostatic repulsion of CI particles [31]. Also, the polymer coating is a good way to prevent chemical oxidation of the CI surface. Several methods to encapsulate particles with polymers including grafting, in-situ polymerization, and solvent evaporation have been reported. In addition, it can be also noted that such core-shell structured ER materials have been also reported for various advantages using conducting polyaniline either as a core or a shell [32-35].

In this article, we briefly review synthesis and magnetorheological properties of the core/shell structured CI/polymer hybrid particles which are being adopted as magnetic particles for the MR fluid. Various methods to prepare the polymer coated CI particles are summarized. Also, their experimental results such as the particle morphology and rheological characteristics of the composite particle based MR fluids are presented.

IN-SITU POLYMERIZATION METHOD

The most common way to cover particles with polymer is to polymerize directly the appropriate monomer on the surface of particles using various in-situ polymerization methods such as dispersion polymerization and emulsion polymerization in the presence of the core particles. In recent reports, the CI microspheres were encapsulated with the polymers which can be easily polymerized by a radical polymerization method. For example, the CI microsphere was coated with poly(methyl methacrylate) (PMMA) using dispersion polymerization [36,37], in which the CI microspheres were dispersed in the medium followed by polymerization of methyl methacrylate in the CI microspheres-suspended phase. Acrylic acid or methacrylic acid was used to enhance compatibility between methyl methacrylate and the CI particles. For chemical stability, the polymer was even cross-linked using a cross-linking agent [38]. The styrene was also used instead of methyl methacrylate to have polystyrene (PS) coating [39].

As shown in Fig. 2, the polymer-coated CI particles maintain the spherical shape of pure CI particles even after the encapsulation process. Nonetheless, it is well known that the surface morphology depends on the hydrophobicity or solubility. In the case of CI/PS, the surface morphology was observed to be much different from that of the CI/PMMA hybrid particles, because the polystyrene has less affinity for the carbonyl iron and lower solubility to the methanol which was used as a medium for the dispersion polymerization. It can be also noted that the PS particles are usually smaller than the PMMA particles if they are fabricated by dispersion polymerization using methanol as a medium. Because the solubility of PS to methanol was much different with that of PMMA, PS particle growth was limited to 1 micron in methanol while PMMA particle grew to 6 microns. It is due to the process and speed of nuclear and growth during polymerization. Also, because the affinity between PS and CI is smaller than that between PMMA and CI, the attached interfacial area of PS and CI becomes smaller. Even the PS was attached on the CI surface with a hemispherical shape while the coated PMMA layer had even surface in the CI/PMMA composites. Mostly, the surface of CI particles with a polymer encapsulation method becomes smoother than that of pure CI particles. In addition, the particle size increased from 1-6 microns of pure CI to

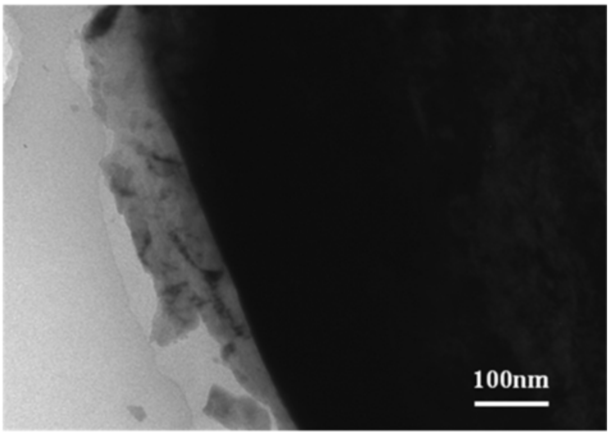


Fig. 3. TEM images of CI/PMMA core/shell particle by dispersion polymerization.

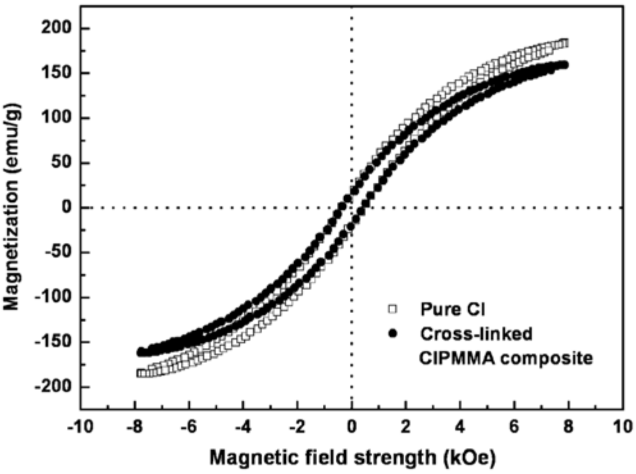
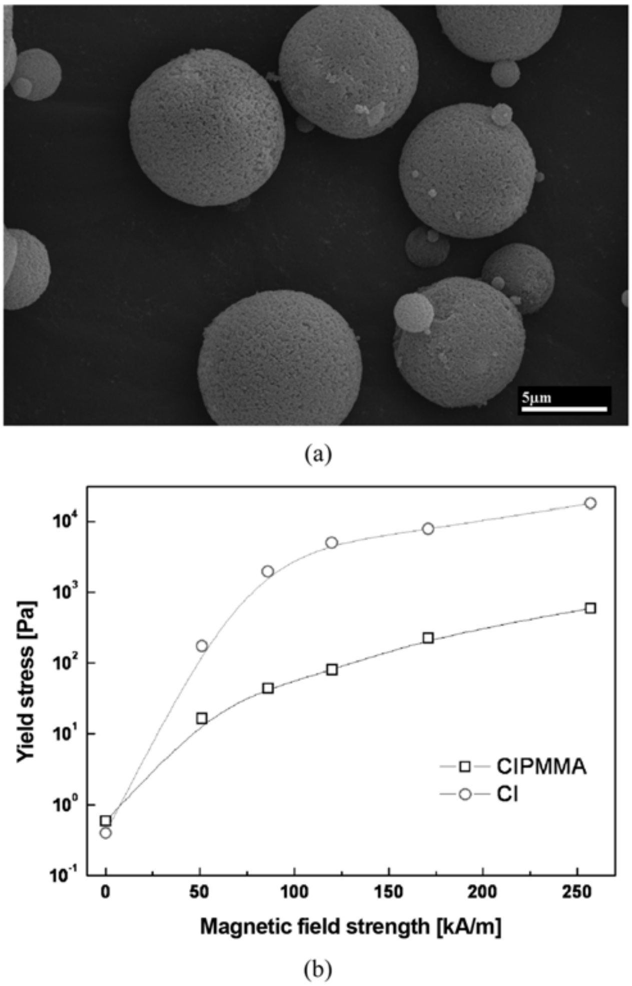


Fig. 4. VSM curve of CI/PMMA particles (reprint from [38] with permission from Wiley).



(a)

(b)

Fig. 5. SEM images (a) of CI/PMMA particles by suspension polymerization and yield stress (reprint from [40] with permission from IEEE); (b) of the particle based MR fluid as function of external magnetic field strength.

be the range of 3-8 microns. The thickness of the polymer-coated layer was observed to be up to 100 nm by TEM as shown in Fig. 3. Because the polymeric coated layer is not much thick, the magnetization saturation of the polymer encapsulated CI is also not much lower than that of pure CI. In Fig. 4, the typical magnetization curve of CI/polymer composite is displayed. Saturated magnetization value of the CI/polymer was observed to be slightly lower than that of the pure CI. This explains why the yield stress value of the composite particles based MR fluids is preserved to be similar to the pure CI based MR fluid.

On the other hand, in a different way, the suspension polymerization method was also introduced [40]. In this case, the morphology and size were regarded to usually depend on the stabilizer and its contents and the surfactant used. Recently, the PMMA was encapsulated onto the CI microparticles via a suspension polymerization method for the MR application. The result of the work shows that morphology and size of the microparticles were remarkably changed from those of the pristine CI when the poly(vinyl alcohol) and triblock copolymer, PEG-PPG-PEG, were used as a stabilizer and a co-stabilizer, respectively. Because of the contents of polymer in the product particles, they have much lower magnetization value, thus resulting in a lower yield stress of the core-shell structured composite based MR fluids. Fig. 5 shows the external morphology of the CI/PMMA particles coated via a suspension polymerization method and the flow behavior of the composite based MR fluids with application of external magnetic field. As shown in Fig. 5(a), the core-shell particles possess 5-8 micron size and small particle-wrapped surface morphology. Fig. 5(b) displays that the composite based MR fluids sow a typical flow behavior of the common MR fluids, showing that the shear stress increases in a whole range of shear rate with the increase of external magnetic field strength. However, the MR performance of the composite materials became lower than that of pristine CI based MR fluid, because of reduced magnetic property of the saturation magnetization.

SOLVENT EVAPORATION METHOD

The solvent evaporation method is considered as one of the advanced techniques for encapsulating the core particles with polymers because it has been widely used for various polymer systems with appropriate corresponding solvents. In addition, the method can also easily control the coating thickness and polymer contents by using various solvents and various stabilizers. In this system, two different solvents of both a good solvent and a non-solvent for the polymers are used. Therefore, the solubility, molecular weight of polymer, and affinity between polymer and carbonyl iron can affect the encapsulation quality. Recently, the polymer-encapsulated CI via solvent evaporation methods was reported using several different polymers including poly(vinyl butyral) (PVB) [41], polystyrene (PS) [42] and polycarbonate (PC) [43].

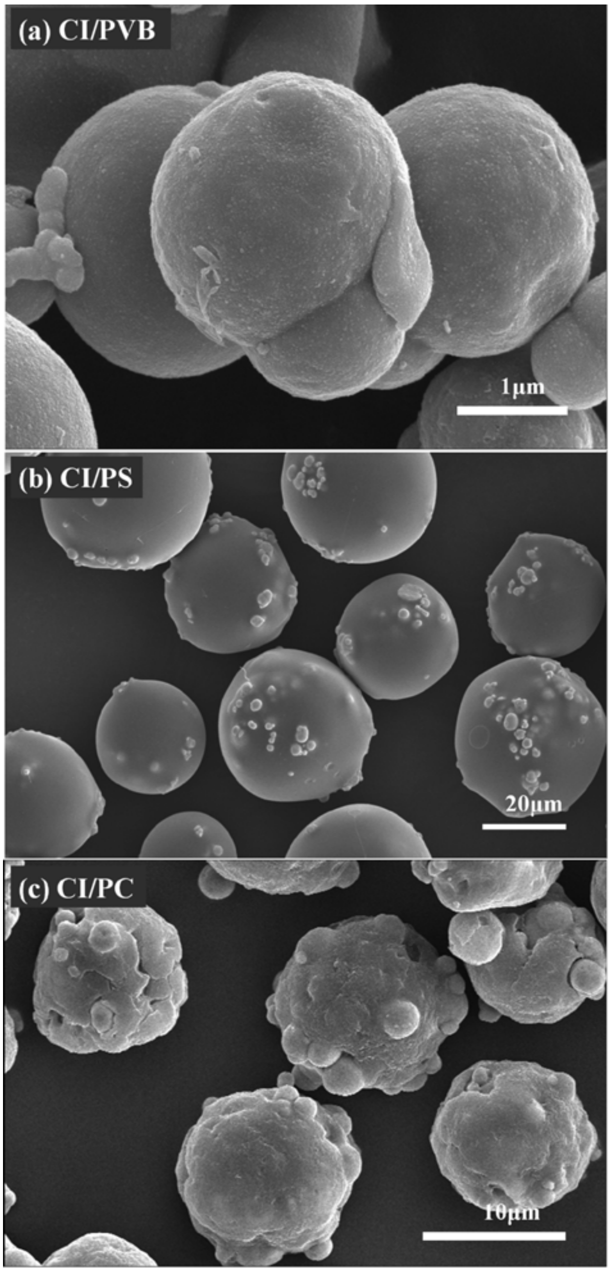


Fig. 6. SEM images of polymer encapsulated CI particles by solvent evaporation ((a) reprint from [41] with permission from AIP; (b) reprint from [42] with permission from Wiley; (c) reprint from [43] with permission from IEEE).

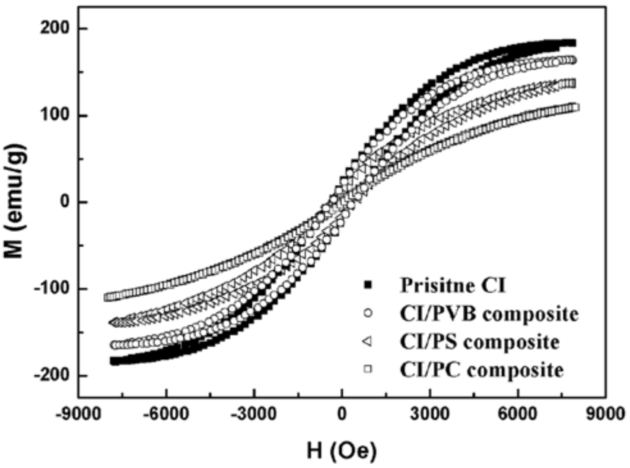
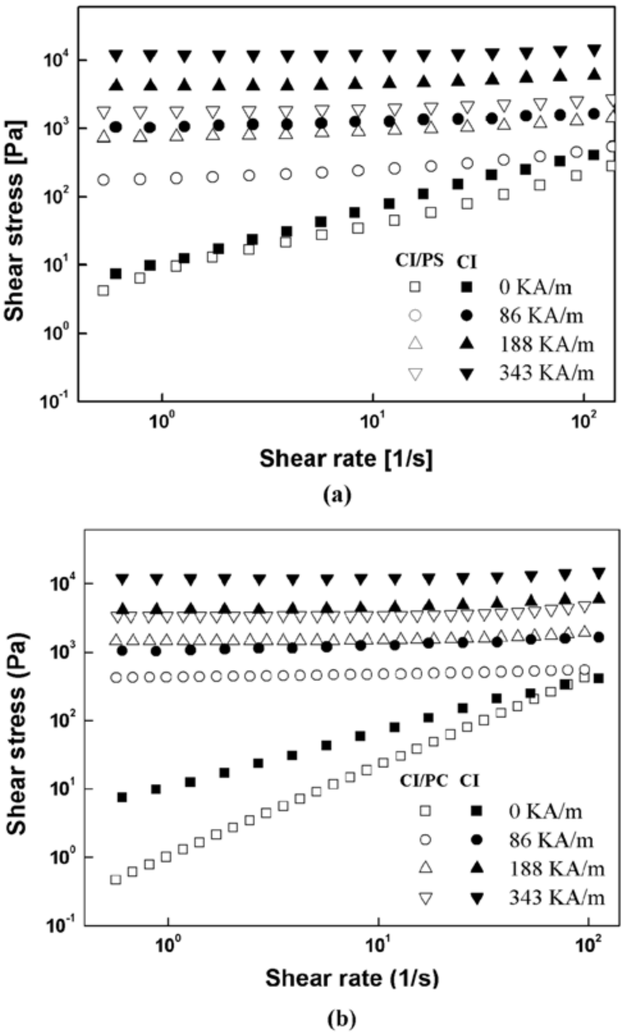


Fig. 7. VSM curve of polymer encapsulated CI particles by solvent evaporation.

Fig. 6 shows the morphology of the polymer-encapsulated CI using a solvent evaporation method. Although the same encapsulation method was used, each particle has a different size and morphology. In the case of the PS/CI system, the average size was observed to be about 35 microns with considerably rough surface morphology, while the PC/CI particles have 13 microns of average size and quite bumpy surface morphology due to the embedded CI particles. In addition, the CI/PVB particles have almost similar size with that of the pristine CI with smoother surface morphology. For these systems, distilled-water was used as a non-solvent and a different solvent was used as a solvent in each system. In the case of PS, chloroform was used as solvent and CI was dispersed into the polymer solution phase. For the PC, the toluene was used as solvent. Chloroform was evenly used for the PVB system. However, the wettability between PVB solution and CI was different because CI particles were firstly dispersed in aqueous phase. In other words, the solubility and wettability mainly affect the encapsulation process.

As presented above, the magnetic properties strongly depend on the CI contents in the composite particles. Three systems, CI/PS, CI/PC and CI/PVB, possess 72 wt%, 49 wt%, and 83 wt% of CI, respectively. Relatively, the magnetization shows also similar tendency. Fig. 7 displays the vibrating sample magnetometer (VSM) data of the polymer-coated CI systems via a solvent evaporation method. It indicated that all systems show magnetic characteristics of soft magnetic materials like pure CI. However, the magnetization curves also displayed that the saturation values were much different from that of pristine CI and were proportional to the CI content. However, the polymer coating was not found to influence the magnetorheological behavior seriously. Densities of both CI/PC and CI/PS were measured to be 3.2 g/cm^3 and 4.3 g/cm^3, respectively, indicating that the density of polymer-coated CI is much lower than that of pure CI (7.8 g/cm^3). Therefore, the sedimentation became slow compared to pure CI based MR fluid, although the sedimentation still appears to be due to the density mismatch between composite magnetic particles and medium. If the CI/polymer-based MR fluid is laid without any force for a month, many particles settle down forming a cake. However, if the MR fluid is shacked again, the particles in the fluids are easily re-dispersed while the CI based MR fluid has difficulty to be re-dispersed after the settling and forming



(a)

(b)

Fig. 8. Flow curve with external magnetic field of CI/PS (a) (reprint from [42] with permission from Wiley); and CI/PC (b) based MR fluids (reprint from [43] with permission from IEEE).

a cake of the CI in the fluid.

Fig. 8 shows the shear stress curve of two different systems, CI/PS (a) and CI/PC (b), as a function of shear rate with the increase of magnetic field strength. The polymer-coated CI based MR fluids have a very typical MR behavior. With the increase of the magnetic field strength, the shear stresses levelled off for the entire shear rate region. Both MR fluids exhibited the Bingham plastic behavior with a nonvanishing yield stress under a magnetic field, implying the formation of stable chain structures of magnetized particles, which is much different for many ER fluids. Also, it indicated that the yield stress of polymer-coated CI based MR fluids was lower than that of pure CI based MR fluid. However, it represented that the value is not exactly dependent on the magnetization value of the particles, because the particle size and distance between CI particles are different from each other. Also, the surface morphology may affect the MR response because of the packing density difference. In other words, the controlling coating thickness and morphology become very important for the MR properties because the yield stress is strongly related with the strong dipole-dipole interaction among the adjacent magnetic particles.

Concurrently, biopolymeric guar gum has been also applied to coat CI particles via either ball milling method or precipitation method showing a strengthening effect [44].

MAGNETORHEOLOGICAL CHARACTERISTICS

The rheological behavior of pure CI based MR fluids has been widely investigated by many researchers. Because of the large and distinct magnetization value of the magnetic CI microspheres, it usually shows high yield stress behavior in proportion to the volume percent of CI particles, much higher than any typical ER fluids. The response of shear stress with shear rate in a steady shear flow shown as Fig. 8 is a typical yield stress behavior [45]. When the shear force is applied to the chain structures made of induced dipole particles, the microstructure is being deformed, inclined and broken, with hydrodynamic flow occurring when the shear stress (τ) becomes greater than yield stress (τ_y). The Bingham fluid equation given below has been used as the simplest, yet physically realistic, constitutive relationship descriptive of the steady shear behaviour of MR fluid [46].

$$\begin{aligned} &\tau = \tau_y + \eta\dot{\gamma}, && \tau \geq \tau_y \\ &\dot{\gamma} = 0 && \tau < \tau_y \end{aligned}$$

Polymer-coated CI based MR fluids also exhibit similar yield behavior of pure CI based MR fluids with a smaller yield stress value compared to that of the pure CI based MR fluids. The magnetorheological characteristics of the polymer-encapsulated CI based MR fluids show that the yield stress value is relevant to the thickness of shell layer and the contents of polymer. The in-situ polymerization method for encapsulation makes relatively thin coating layer so that the encapsulated CI based MR fluids exhibit similar yield stress value with pure CI based MR fluids. Fig. 9 shows the stress curve of pure CI and CI/PMMA based MR fluids. As shown in Fig. 8, the CI/PMMA based MR fluid exhibits similar yield stress with that of pure CI based MR fluid. The effect of coating thickness was also

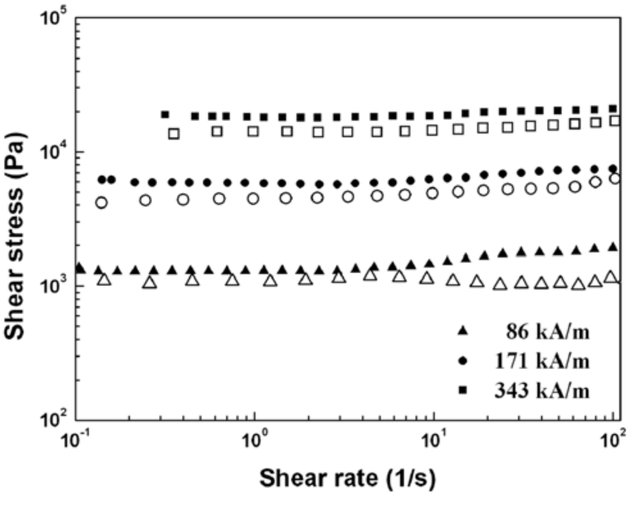


Fig. 9. Flow curve with external magnetic field of CI (closed symbol) and CI/PMMA by dispersion polymerization (open symbol) (reprint from [47] with permission from Elsevier).

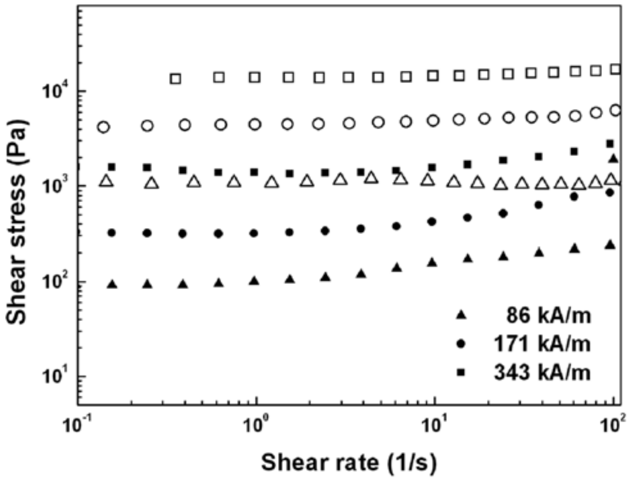


Fig. 10. Flow curve with external magnetic field of CI/PMMA-1 (open symbol) and CI/PMMA-3 (closed symbol) based MR fluids.

reported by using CI/PMMA particles with different PMMA coating layer [47].

Fig. 10 shows the shear stress of CI/PMMA particle based MR fluids with different PMMA content. CI/PMMA-1, 2 and 3 were fabricated with 2 : 1, 1 : 1 and 1 : 2 of CI:MMA content ratio, respectively. The PMMA content in CI/PMMA-1, 2, 3 was measured to be 19.2 wt%, 32.3 wt%, and 40.2 wt%, respectively. The density of each sample was measured to be 5.73, 4.85, and 4.1 g/cm^3. Fig. 10 shows that the yield stress of CI/PMMA-3 based MR fluids was much lower than that of CI-PMMA-1 based MR fluid, indicating that the PMMA content affected the yield stress of the MR fluid because the absolute amount of CI was different and the distance between CI particles became different.

This Bingham fluid characteristic is very typical for various MR fluids, while various deviations from the Bingham fluid behavior have been reported for ER fluids. Instead of the increase of shear stress, a decrease of shear stress has been observed at a low shear region; and then above a critical shear rate, the shear stress increases with shear rate. Such complex behavior was successfully fitted using a six-parameter model constitutive rheological equation [48].

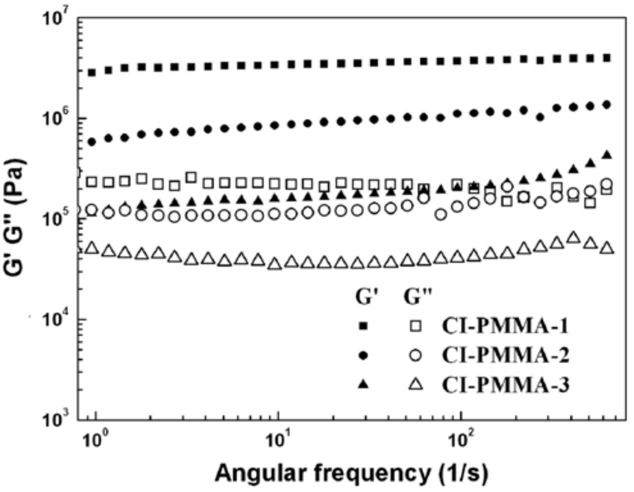


Fig. 11. Modulus of CI/PMMA based MR fluids with 171 kA/m of magnetic field strength as a function of frequency for different MMA concentrations.

MR characteristics can also be measured by measuring the viscoelastic modulus which is directly related with the interaction between the magnetic particles, which is an oscillatory shear flow. Fig. 11 shows the oscillatory flow behavior of MR fluids for different coating thickness under the magnetic field strength of 171 kA/m. Storage modulus of the MR fluids increased and became more frequency independent as the coating thickness decreased. The difference between storage and loss moduli increased when the concentration of MMA decreased, indicating that the solid-like property was reduced. On the other hand, it can be also noted that to improve not only sedimentation drawback but also MR performance, a commercial grease has been adopted as a dispersing medium [49].

CONCLUSIONS

We have briefly reviewed various MR materials based on encapsulated carbonyl iron with polymers such as PMMA, PS and PVB. Polymer encapsulation is a novel method to fabricate organic-inorganic hybrids that provides enhanced surface properties and dispersion stability. Both in-situ polymerization and solvent evaporation methods were introduced as the encapsulation technique, finding that the contents of encapsulating polymer proportionally affect not only magnetization of the CI but also their MR characteristics.

ACKNOWLEDGMENTS

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NOMENCLATURE

τ : shear stress
τ_y : yield stress
η : shear viscosity
$\dot{\gamma}$: shear rate

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