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Short communication

Fabrication of *p*-aminobenzoic acid grafted carbonyl iron/polyindole composite particles and their magnetorheological response

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ABSTRACT

To improve the dispersion stability of magnetic microspheres, polyindole (PIn) was adopted as a shell material to encapsulate micro-spherical carbonyl iron (CI) core particles using 4-aminobenzoic acid as a grafting agent. The coated morphology of the CI/PIn particles was observed by scanning electron microscopy and the coating was confirmed by Fourier transform infrared spectroscopy. The magneto-rheological (MR) properties were examined using a rotational rheometer equipped with a plate-to-plate geometry and different magnetic field strengths. The improved dispersion stability of the CI/PIn particle-based MR fluid was confirmed using a Turbiscan.

Introduction

Magnetorheological (MR) fluids are phase tunable smart engineering materials that exhibit a rapid phase change from liquid-like in the absence of a magnetic fluid to solid-like under an applied magnetic field, implying that these fluids have a viscoelastic modulus that changes under the application of a magnetic field [1–5]. The phase transition occurs very fast, in the range of several to dozens milliseconds, and its shear viscosity changes by several orders of magnitude under an applied magnetic field. Such outstanding and controllable properties of MR fluids have attracted attention for a wide range of engineering applications, where active vibration control or torque transmission is required. Typical examples include clutches, dampers, control valves, brakes, and artificial joints. On the other hand, the use of this material is limited by the density mismatch between the particle and dispersing fluid, corrosion of the particle, weakness in the thermal and chemical stability, etc. Other fields of involving the use of magnetic fields include applications in chemical sensing [6] and haptic displays [7]. On the other hand, the chemical stability, sedimentation, corrosion and aggregation of particles, and thermal stability over a wide temperature range require improvement before they can have wider engineering applications.

MR fluids are normally produced by mixing magnetic particles and a non-magnetizable carrier fluid. The dispersing magnetic particles are on a micrometer scale size with high saturation magnetization and are usually carbonyl iron (CI). CI is a highly purified iron produced by the chemical decomposition of iron pentacarbonyl, and is a well-known MR material for its superior saturation magnetization, optimal particle size, and low magnetic hysteresis [8,9]. Nevertheless, improvement in the dispersion stability still remains. To overcome this drawback, a range of methods have been introduced, including adding fillers or submicron size additives to the CI-based MR suspension, such as guar gum [10], carbon nanotubes [11], clay [12], and silica nanoparticles [13]. The dispersed fillers and additives locate among the CI particles, which prevent the caking phenomenon. Some additives also increase the yield stress of MR fluids with their synergistic magnetic properties. In addition, coating low density polymers onto the surface of CI particles is another way of improving their sedimentation problem with high density [14–16]. The coated polymer decreases the density gap of dispersing media and magnetic particles, thereby elevating the dispersion stability. The coated polymer also inhibits the corrosion and oxidation of the CI microspheres by encapsulating the core [17].

In this study, conducting polymeric polyindole (PIn), having a π-conjugated structure, was adopted as a shell material. Such a coating method with conducting polymers as the shell material has also been attempted using polyaniline [16] and polypyrrole [18]. The PIn was introduced with its superior thermal stability compared to the above-mentioned two conducting polymers, while possessing high chemical stability and redox activity [19]. Previously, there have been other researches of coating polymer onto CI core, using PABA as a grafting agent [20]. This is the first

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time that PIn has been coated onto CI instead of being prepared as an inorganic/organic composite material. The core–shell morphology was analyzed and the magnetic properties, MR characteristics, thermal stability, and dispersion stability were analyzed.

Experimental

Materials and synthesis

CI microspheres (CC grade, BASF, Germany) were used as a core part. A 5 g sample of CI microspheres was dispersed in 100 ml of deionized water with ultrasonication. 4-Aminobenzoic acid (PABA, 1 g, Junsei Chemical, Japan) was then added to the CI dispersion and stirred at 5 °C for 3 h. The PABA-modified CI was then washed with excess deionized water to remove the remaining PABA from the particles. Subsequently, 4 g of ammonium persulfate (APS, Daejung Chemical, Korea) pre-dissolved in 0.1 M HCl (aq) (Junsei, Japan) was placed into a 3-neck reactor at a temperature of 15 °C. The indole monomer was dispersed in a small amount of ethanol and added drop-wise to the reactor. Polymerization was maintained for 12 h with vigorous stirring. Finally, the reacted PIn-coated CI particles were precipitated and washed with ethanol and water to remove the unreacted monomers and oxidant. The extracted particles were dried in a vacuum oven for 24 h.

Characterization

The coated rough surface morphology of the CI/PIn microspheres was observed by high resolution scanning electron microscopy (HR-SEM, SU8010, HITACHI, Japan). The density of the synthesized CI/PIn particles was measured using a pycnometer (Accupyc 1330, Gas pycnometer, USA). The chemical structure of the CI/PIn microspheres was characterized by Fourier transform infrared (FT-IR, VERTEX 80v, Bruker, Germany) spectroscopy over the range, 4000–400 cm^{-1}. Two different MR fluids, one with pure CI particles and the other with CI/PIn particles, were fabricated by dispersing particles in silicone oil (100 cSt) with a 50 wt% particle concentration. A steady shear rotational test was performed for two MR fluids with a plate-to-plate type geometry (PP20) using a rotational rheometer (MCR 300, Anton Paar, Austria). The transmission percentage was measured as a function of time for 1400 min, using a Turbiscan (Turbiscan Classic MA2000, Formulaction, France) to measure the sedimentation stability. All experiments were conducted at room temperature (25 °C).

Results and discussion

Fig. 1 compares SEM images of the pure CI particles and PIn-coated CI/PIn particles/Pure CI (Fig. 1(a)) has a smooth surface, whereas the PIn-coated particles (Fig. 1(b)) have a rough PIn coating layer. SEM revealed the successful encapsulation of the CI core with PIn. The density of the core–shell particle measured using a pycnometer decreased from 7.86 g/cm^3 for the pure CI particle to 7.3 g/cm^3 for the CI/PIn particles.

FT-IR spectroscopy was carried out to confirm the coating more accurately, as shown in Fig. 2 for 3 samples of CI (dashed line), PIn (dashed and double dotted line), and CI/PIn particles (solid line). The samples were ground with KBr into a disk type pellet and compressed under high pressure. The CI particles appeared to be almost neat with a single broad peak in the finger-print region, whereas the CI/PIn showed similar peaks to PIn, except for the finger print region. The main characteristic peaks included the N-H stretching bond peak at 3418 cm^{-1}, aromatic C=C stretching bond peaks between 1650–1500 cm^{-1}, aromatic C—N stretching bond peak at nearly 1450 cm^{-1}, and out-of-plane deformation of C—H bond ay approximately 740 cm^{-1}. As reported elsewhere [21], the FT-IR result of the CI/PIn showed the indole characteristic peak, confirming that PIn had been coated successfully on the CI particles.

The MR characteristics of CI/PIn particles were measured using a rotational rheometer with a PP20 geometry in controlled-shear-rate (CSR) mode. Fig. 3 shows the shear stress plotted as a function of the shear rate. Both the shear stress and shear viscosity increase by inducing a stronger magnetic field strength, which means that stronger magnetic particle chains form in an increased magnetic field strength. The stress of the CI/PIn-based MR fluid was higher than that of pure CI-based MR fluid when the magnetic field was not applied (Fig. 3) [22]. This is the opposite tendency compared to the case of the applied magnetic field strength because the coated particles have a lower shear stress and viscosity than the pure CI particle. This is because of the difference in surface morphology. As shown in Fig. 1, the coated particles have a rough surface compared to the pure particles, causing additional friction with each other and leading to flocculation in a bridged formation with the nearby particles. In contrast, when the magnetic field was applied, the shear stress of CI/PIn MR fluid was lower than that of the pure CI-based MR fluid at every magnetic field strength due to the decrease in saturation magnetization of the CI/PIn particles.

In addition, it can be also noted that due to electro-responsive property of the PIn with its conducting characteristics, these CI/PIn particles could show electrorheological (ER) behavior under an applied electric field. This ER phenomenon of phase change with chain alignment between a liquid-like and solid-like phase arose from the field-induced polarization of CI/PIn particles relative to an insulating silicone oil. The conducting polymeric shell PIn, having a π-conjugated electron system is the main source of this behavior, and this local distribution of electron leads to induce of ER effect when electric field is applied [23]. The alignment of CI/PIn chain

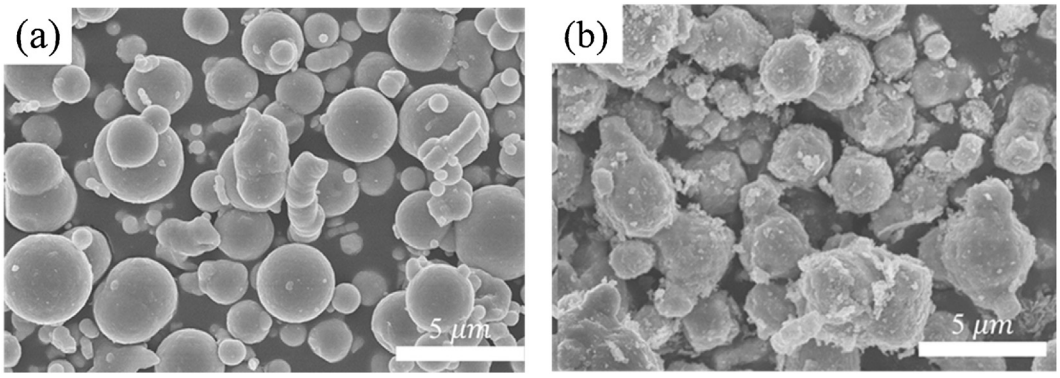

Fig. 1. SEM images of comparing the surface morphology of pure CI core particle (a) and PIn coated CI/PIn particles (b).

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