Magnetorheological carbonyl iron particles doubly wrapped with polymer and carbon nanotube

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To improve magnetorheological (MR) characteristics of carbonyl iron (CI) microparticles, we introduce two-step CI coating procedures with poly(methyl methacrylate) (PMMA) and multiwalled carbon nanotube (MWNT) for the first time. Core(CI)-shell(PMMA) (CI-PM) structured composite magnetic microbeads were synthesized by dispersion polymerization first, showing improved dispersion stability and sedimentation quality. However, its magnetic strength was decreased compared with that of pristine CI-based MR fluid. To enhance its magnetic strength, the core-shell type CI-PM particles were wrapped with MWNT via ultrasonication. Rheological properties of their MR fluid were measured by a rotational rheometer with a magnetic field supplier. The CI-PMMA-MWNT (CI-PM-NT) particles were found to show better flow and dynamic rheological properties compared to those from CI-PM particles while density of the CI-PM-NT particles was not much different from that of CI-PM, implying that sedimentation stability of the CI-PM-NT particles was also being kept. © 2009 American Institute of Physics. [DOI: 10.1063/1.3058674]

I. INTRODUCTION

Magnetorheological (MR) fluids, suspensions of magnetic particles in nonmagnetic fluid, exhibiting a continuous, rapid, and reversible change from fluidlike to solidlike behavior when subjected to sufficiently strong magnetic field, have drawn much attention due to their controllable characteristics and wide range of applications such as active controllable dampers, shock absorbers, brakes, and others.1–4 The mechanism is known that each irregularly dispersed particle makes chain structure under external magnetic field strength, thus demonstrating increased yield stress, shear viscosity, and modulus of the MR fluids.5,6 However, particle suspension stability against settling, large field-induced yield stress, and low shear viscosity without magnetic field are still to be improved. Many kinds of magnetic particles for MR fluids have been modified via diverse strategies to satisfy industrial demands as MR fluids.7–10 To improve the sedimentation stability, we have adopted various coating techniques, since the coating technology has become prevalent due to favorable morphology and effective decrease in density, corresponding to an abated sedimentation problem. We prepared carbonyl iron (CI) particles with poly(methyl methacrylate) (PMMA) by dispersion polymerization. As the polymer coated surface of the CI particles, their corrosion, abrasion properties, and sedimentation stability were enhanced but their magnetic properties were observed to be decreased.11,12 Recently, magnetic response of carbon nanotubes have been applied in various areas.13,14 In order to utilize magnetic properties of the carbon nanotube (CNT) for MR fluids, we wrapped multiwalled carbon nanotube (MWNT) bundles onto PMMA coated CI particles via physical method of ultrasonication.15 And then we analyzed not only rheological properties but also magnetic response properties of the MR fluids when dispersed in lubricant oil under applied external magnetic fields.

II. EXPERIMENTAL

Magnetic carbonyl iron particles (CI, standard CD grade, BASF, Germany), whose average particle size and density are 4.25 μm and 7.91 g/cm³, respectively, were used and modified as a disperse phase of MR fluid in this study. The doubly wrapped CI particles were prepared by two steps. Firstly, pristine CI particles were wrapped with polymer via a dispersion polymerization,11,12 in which the CI surface was modified by methyl acrylic acid (MAA) for inducing the polymerization reaction on the CI surface. The surface modified CI was dispersed in methanol containing poly(vinyl pyrrolidone) (PVP) as a stabilizer. MMA monomer and a radical initiator of 2, 2-azobisisobutyronitrile (AIBN) were dissolved in the reaction system. The polymerization was proceeded for 12 h at 60 °C. After the polymerization, the CI particles were coated with PMMA (CI-PM). And then products were separated by a magnet and washed with methanol in order to remove PVP, unreacted MMA, and PMMA oligomers. The CI-PM particles were dried at 60 °C oven and their density was measured to be 4.56 g/cm³ by a pycnometer. Secondly, a MWNT (Hanwha Nanotech Co., Korea) with a diameter of 10–15 nm, length 5–15 μm, and over 95% purity synthesized by thermal chemical vapor deposition method was used for MWNT coating. Prior to its use, to remove impurities while functionalizing MWNT into MWNT-COOH, it was treated in a mixed acid solution consisting of concentrated H₂SO₄ and HNO₃ (3 mol:1 mol) at 60 °C using an ultrasonic bath for 1 h and then stirred for 12 h followed by reflux process. After that, the mixture was
filtered using membrane, washed with di-water until the pH value became 7, and then dried in a vacuum oven at 60 °C for 24 h.\textsuperscript{16}

Prepared both CI-PM particles and MWNT-COOH were sonicated together in methanol with cetyl trimethylammonium bromide (CTAB) as a surfactant in order to stabilize the nanotubes against van der Waals attractive force. Concentrations of both surfactant and MWNT were 0.3 and 0.02 wt %, respectively. Reaction was performed at 25 °C for 48 h and then MWNT wrapped CI-PM particles (CI-PM-NT) were separated using a magnet and washed with methanol in order to remove unreacted MWNT.\textsuperscript{15} The CI-PM-NT particles were dried at 60 °C in a vacuum oven and their density was measured to be 4.22 g/cm\textsuperscript{3} by a pycnometer. Their morphology was examined by scanning electron microscopy (SEM).

To prepare the MR fluid, these magnetic particles were dispersed in lubricant oil (YUBASE3, density of 0.8299 g/cm\textsuperscript{3}, SK Energy Co., Korea) in this work, the concentration of both CI-PM and CI-PM-NT particles in lubricant oil was set to be 20 vol %. MR characterizations were performed at 25 °C via a rotational rheometer (MCR 300, Physica, Germany) equipped with a MR device (MRD 180). A parallel-plate measuring system (diameter of 20 mm) which was made of nonmagnetic metal to prevent the occurrence of radial magnetic force components on the shaft of the measuring system was used at 1 mm gap distance.\textsuperscript{17} A homogeneous magnetic field direction was applied perpendicular to the shear flow direction.

III. RESULTS AND DISCUSSION

Figure 1 shows morphological characteristics of (a) pristine CI, (b) CI-PM, and (c) CI-PM-NT particles. The size and coarse surface of CI particles became larger and smoother, respectively, as shown in Fig. 1(c) compared with Figs. 1(a) and 1(b). Moreover, Fig. 1(c) distinctly indicates that the MWNT bundles were well settled on the CI-PM surface. Figure 1 also shows that all of CI, CI-PM, and CI-PM-NT particles possess polydispersity. Note that it has been reported that monodisperse particle suspension performed better MR characteristics.\textsuperscript{18} Densities of the CI-PM (4.56 g/cm\textsuperscript{3}) and CI-PM-NT (4.22 g/cm\textsuperscript{3}) particles have been tremendously decreased compared with that of pristine CI particles (7.91 g/cm\textsuperscript{3}). Therefore, from both results of density change and particle surface morphology change, we can conclude that the PMMA and MWNT coating on CI particles can improve sedimentation and redispersion of the MR fluid because the double coating with PMMA and MWNT not only prevents cake formation for the CI particles but also reduces rust for the CI particles and protects the device from abrasion.

On the other hand, the relationship between the storage modulus (\(G'\)) of the MR fluid and applied magnetic field strength (\(H\)) is presented in Fig. 2. The measurements were conducted by increasing 0.171 kA/m of magnetic field strength per second up to 342 kA/m at fixed both strain (10\textsuperscript{−3} %) in a linear viscoelastic condition and angular frequency (10 l/s). It is found that coated layers of the CI slowed magnetic response time of the MR fluid compared with that of the pristine CI particle, in which the response time can be estimated based on the critical point where the slope of storage modulus suddenly changed in Fig. 2. However, the response time of the MWNT wrapped CI-PM became slightly faster than that of CI-PM due to magnetic characteristics of the MWNT such as 94 A/m for CI, 118 A/m for CI-PM-NT, and 128 A/m for CI-PM. Above the critical magnetic field strength, the storage modulus of both CI-PM and CI-PM-NT rapidly increased compared with the slope of the CI. It may be related with the fact that the applied magnetic field strength was disturbed by the polymer coated layer on the CI. But over the critical point, the applied magnetic field strength strongly affects the CI directly even through the polymeric layer covered the CI particles. Furthermore, it was also observed that the storage modulus of the CI-PM-NT was always higher than that of the CI-PM over all applied magnetic field range. Also, the storage modulus of both CI-PM and CI-PM-NT indicates an increasing tendency with increasing applied magnetic fields, indicating that both CI-PM and CI-PM-NT represent the remarkable elastic properties of the MR fluids.

Figure 3 represent changes of shear stress (\(\tau\)) for MR fluids of CI-PM and CI-PM-NT as a function of shear rate under four different external magnetic field strengths ranging from 0 to 343 kA/m. The shear stress leveled up in the en-
tire shear rate region with an increase of magnetic field strength. These steady shear behaviors were induced due to solidlike chain formation of the dispersed magnetic particles in which the magnetic moments of the particles are parallel to the field direction caused by applied magnetic field. Moreover, the enhancement of shear stress with increased magnetic field strength is a typical characteristic of the MR fluids implying internal structure change, i.e., formation of the robust chain structure of magnetized particles. On the other hand, apparent yield stress can be obtained by extrapolating the shear stress values at zero shear rate. The yield stresses at the 343 kA/m are 3.9 kPa for the MR fluid of CI-PM-NT and 2.9 kPa for the MR fluid of CI-PM, respectively, strongly indicating that as the MWNT wrapped outer surface of the polymer layer in the CI-PM, magnetic properties of the CI-PM-NT became slightly higher, thus enhancing its MR characteristics.

IV. CONCLUSIONS

Carbonyl iron (CI) particles were doubly wrapped with PMMA and MWNT via both dispersion polymerization and ultrasonication methods. The MWNT coated CI-PM particle not only improves shear stress in a broad shear rate range with improved yield stresses but also maintains sedimentation stability without particle density change. In addition, as we wrapped outside surface of CI-PM with MWNT, it was found that the magnetic response time of the CI-PM-NT particles became faster.

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FIG. 3. Shear stress for both CI-PM (filled symbol) MR fluid and CI-PM-NT (open symbol) MR fluid as a function of shear rate under four different external magnetic field strengths of \( H=0, 86, 171, \) and 343 kA/m.