Magnetorheological characteristics of carbon nanotube wrapped carbonyl iron particles

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Abstract. Carbonyl iron (CI) based magnetorheological (MR) fluid exhibits serious dispersion defect in general due to large density mismatch between CI particles and continuous medium, which restricts further MR application. Thus, various strategies were explored either to reduce the density or to prevent CI particle aggregation. Among them, polymer coating technology becomes more prevalent due to favorable morphology obtained and effective decrease in density by introducing polymeric shell; nevertheless, coating polymer on the surface of CI particles is always influenced by the selected grafting agent, mole ratio of reactant or the temperature of reaction. In this work, considering self-assembling trend of carbon nanotube (CNT) which exhibits similar density with polymer but better magnetic property due to the iron catalyst, we constructed a dense nest composed of CNT on the surface of CI particles by using 4-aminobenzoic acid (PABA) as a grafting agent under sonication. Thickness and morphology of the CNT nest were found to be related with sonication duration via SEM/TEM images. MR performances (yield stress behavior, shear viscosity) of the CI/CNT particles based MR fluid were investigated via controlled shear rate and controlled shear stress methods. Finally, sedimentation observation was checked to be improved.

1. Introduction
Magnetorheological (MR) fluids consisting of magnetic particles dispersed in nonmagnetic fluids are being regarded as smart/intelligent engineering materials, since they are free-flowing liquids under normal condition with out magnetic field but immediately become solid-like when exposed to an external magnetic field [1-5]. During this process, the rheological properties (yield stress, apparent viscosity, and storage modulus et. al) are altered. Therefore, MR fluids, along with their electrically analogous electrorheological (ER) fluids, attract considerable attentions in widespread engineering applications of designing damper, torque transducer or polishing devices [6-10]. Exploring superior MR materials which can promote their further engineering application is in progress, and various magnetic species or alloys have been investigated [11-16]. So far, much attention has been focused on carbonyl iron (CI) particles (CD grade, BASF Germany, average particle size: 4.25 µm; density: 7.91 g/cm³) which are considered as an excellent candidate for MR fluid due to the superior magnetic properties as well as their appropriate size [17-20]. Nevertheless, CI based MR fluid has not been widely applied in designing MR devices as expected because serious sedimentation problem caused by large density mismatch between CI particles and medium oil affects the operation of MR test as well as the re-dispersion. Thus, plentiful efforts (introducing sub-micro additives or polymer coating technology) have been paid on preventing CI particles’ contact or decreasing density of CI particles to
improve the sedimentation rate indirectly. A mass of sub-micro fillers (carbon nanotube, graphite nanotube, fumed silica et al) have been introduced into CI based MR suspension, in which the interspaces of CI particles are occupied, by which way restrains the direct contact of CI particles, consequently sustains the stability of MR fluid [21-24]. Additionally, when exposed to a magnetic field, the produced chain-like structure undergoes a chain rupture and reformation process, adding fillers can donate to repairing the deformed chain structure under an external shear field. However, we have to regard the influence of size dimension, morphology of additives as well as the affinity with CI particles on improving this problem. Therefore, modifying CI particles to reduce the density mismatch with continuous oil comes to front. Coating polymer on the surface of CI particles has become popular due to the produced favorable core-shell structure along with the apparently decreased density for CI/polymer composite particles [17, 25, 26]. However, coating polymers on the surface of CI particles is not a facile process in spite of using versatile functional grafting agents. Failing to select an optimal grafting agent may lead to a very thin coating layer even a failure in coating. In addition, the mole ratio among monomer, initiator or stabilizer as well as the reaction temperature also plays a critical role in affecting the final shell product. Taking into account of the above mentioned complicated procedures, we have to seek a new strategy based on the coating technology. Concurrently, carbon nanotubes (CNT) have been extensively studied as filler materials for fabricating polymer/CNT nanocomposites which exhibit synergistic mechanical, electrical, and thermal properties. Chemical functionalization of CNT with carboxyl/amino group (COOH/NH₂-CNT) or physical adsorption of dispersants onto the wall of CNT has been developed to enhance the dispersibility of CNT in solvent [27]. In addition, CNT exhibits unique self-assembling trend [28], therefore, in this work we tried to construct a dense nest of CNT on the surface of CI particles with the aid of using 4-aminobenzoic acid (PABA) as a grafting agent. Anther two principal reason of choosing CNT as the shell material for coating CI particles may lie in two main aspects. On the hand, the density of CNT is similar with that of polymer; on the other hand, the existence of magnetic iron catalyst within CNT wall may contribute to better magnetic properties, which does not occur in polymer coating systems. The thickness and morphology of CNT nest were investigated by alternating sonication duration. MR performances (yield stress behaviour, viscosity) of CI/CNT particles based MR fluid were studied via controlled shear rate and controlled shear stress methods. Finally, sedimentation of the produced particles was checked.

2. Experimental

2.1. Preparation of CI/CNT composite particles

Initially, the grafting agent, 4-aminobenzoic acid (PABA) was dispersed in distilled-water at 60°C for 2h. Raw CNT was chemically pre-treated to obtain COOH-CNT [29]. Then, a certain amount of CI particles (CD grade, BASF, Germany) were dispersed in this solution and underwent sonication for 15 minutes to modify the surface. After removing the excess PABA by washing with di-water, the PABA modified CI particles were added to reactor, in which a dispersion of COOH-CNT (0.1 wt% of CI particles) in di-water was predispersed. The reaction was kept with sonication at room temperature under vigorous stirring in order to avoid sedimentation due to the large density of CI particles. At first, the color of reaction dispersion is absolute black due to the dispersed CNT in di-water, as time goes on, the liquid turns to be light brown, at last becomes transparently brown. Meanwhile, CI particles change its color from initial silver grey to complete black which suggests the successful wrapping of COOH-CNT. Therefore, the majority COOH-CNT was adsorbed to the surface of CI particles, leaving minority COOH-CNT with very short chain dispersed in water which may cause the transparently brown liquid because sonication process will cut COOH-CNT long chains into very small parts. This assumption was proved by holing the transparent brown liquid in vial still for about 1 month, after which the liquid became completely transparent but left a very thin black layer at bottom which was considered to be short COOH-CNT. The fabricated CI/CNT particles were separated from the residual COOH-CNT dispersion using a magnet and washed with di-water and methanol separately.
Finally, the sample was dried in vacuum oven at 60°C for 24 hours. Here, in order to obtain densely coated CNT nests and perfect spherical profile along the surface of CI particles, different sonication duration (12, 24 hours) was performed with preserved other reaction condition.

2.2. Characterization of CI/CNT composite particles

Both surface morphology and cross section view of fabricated CI/CNT particles were detected by Scanning Electron Microscope (SEM, S-4300, Hitachi Japan) and Transmission Electron Microscope (TEM, Philips CM200), respectively. The sampling for TEM view was done by an initial moulding of particles in epoxy bath, a following nano-scaled cutting by using an ultramicrotome (UMT) as well as a final dropping on a copper grid. Density of the synthesized CI/CNT particles was examined by using pyconometer. In order to prepare MR fluid, the fabricated CI/CNT particles were dispersed in lubricant oil (Yubase 8, SK Corp. Korea) with a particle concentration of 20vol%. Magnetorheological measurements (controlled shear rate/CSR mode and controlled shear stress/CSS mode) were performed using a rotational rheometer (MCR 300, Physica, Stuttgart, Germany) with the magnetorheological device (MRD 180, Physica, Stuttgart, Germany). A parallel-plate measuring system with a diameter of 20 mm and a gap of 1 mm was made of non-magnetic metal to prevent the occurrence of radial magnetic force components on the shaft of the measuring system. The magnetic field direction was set to be perpendicular to the flow direction. To control temperature of the device and the sample, a water circulator was adopted to the MRD 180, and the temperature was set at 25 °C for all tests.

3. Results and discussion

3.1. Morphology of CI/CNT particles and influence of sonication duration on morphology

Figure 1 indicates the morphology of pristine CI particles and COOH-CNT (the inset picture) used in this experiment. It is clear that most CI particles are spherical and polydisperse with considerably smooth surface. Chemically treated COOH-CNT with an average diameter of 15 nm gives serious aggregation. After immersing PABA modified CI particles in COOH-CNT dispersion with sonication, obvious change in surface appearance is visible as indicated in Fig. 2. A dense layer composed of huge CNT is found to wrap CI particles leading to a considerably rough surface compared with that of the pure CI particles. As pointed with white arrow head, there seems to be a nest-like shell which connects two adjacent CI particles. Innumerable CNT piled together thus formed a firm network overspreading the whole surface of CI particles. Besides this, compared with the compactly aggregated CNT nest, there is some single CNT standing at the surface towards the outside. It is worthy to notice that the length of CNT here seems to be shorter than that of pure COOH-CNT, which may be attributed to the sonication. In order to track the role of PABA as grafting agent, an additional experiment without employing PABA was made. Unfortunately, there is no any apparent CNT layer around the CI particle, consequently confirming that PABA take crucial function in joining hydrophilic CI particles and CNT networks. On knowing that PABA possesses a carboxyl group (COOH) and an amino group (NH$_2$), we assume that an amide functional group may form between PABA modified CI and COOH-CNT, besides this, the non-covalent bond appeared between adjacent –COOH functionalized CNT may also help producing the network of CNT [28, 30]. Anyway, a further study in either FT-IR or XPS spectra is necessary to confirm this prediction.
In order to observe the internal structure within CNT nest as well as the coating thickness, we examined the cross section view for an individual CI/CNT particle via TEM as indicated in Fig. 3. The black block represents CI core particle, while the rest fibril part is CNT. There is no apparent leakage between CI particles and CNT shell. The CNT close to the surface of CI particles seems to aggregate probably due to the overlap of multi-layer of CNT shell. Therefore, in this region, dense CNT nest was constructed, consequently revealing that the coating thickness of CI particles was about 100 nm as pointed in the picture. The CNT extending out over the surface exhibits relative straight shape with an average size of about 11 nm. This result is well coincided with that of Fig. 1. In order to coat CNT nest as dense as possible on the surface of CI particles, the effect of sonication duration was examined. When the COOH-CNT is dispersed in di-water without using any other dispersant, sonication will contribute to break CNT agglomerates leading to homogeneous CNT dispersion as well as a chemical banding between carboxyl and amino group [31, 32]. Thus, we set sonication duration for 12 hr and 24 hr to observe the difference. Figure 4 is a SEM image taken for the CI/CNT particles sonicated for 24 hours. Unfortunately, compared with the apparent nest structure found by sonicatoring for 12 hr, the expected more dense CNT nest did not appear. We find, although the surface becomes rougher than pure CI particle which is possibly caused by the initial coating of CNT, plenty of short CNT segments rather than long ones were observed. This may be attributed to the vigorous long term-sonication which may cut the long CNT into short ones, by which way the formed CNT nest gets broken up. The interspace of adjacent CI particles was filler of short CNT segments. Thus, the CNT within the interspaces may suffer less influence from sonication than that of loaded on the surface of CI particles. In this experiment, the chemical interaction produced between PABA modified CI and COOH-CNT as well as the noncovalent bond appeared within –COOH functional groups of adjacent CNTs was assumed to be the driving force to construct CNT network [21]. Although we can not decide the optimal sonication duration, excess sonication does have a negative effect on coating.

3.2. The MR characterization of CI/CNT particles based MR fluid

MR characterization was performed at magnetic field strengths ranging from 0 to 343kA/m. Yield stress was investigated via two modes: controlled shear rate (CSR) and controlled shear stress (CSS). The CSR mode is the most common way to obtain a yield stress by shearing the sample over a range of shear rate, then plotting the shear stress as a function of shear rate as shown in Fig. 5 [33, 34]. The intersection on the stress axis is then taken as dynamic yield stress demonstrating that any stress below this is insufficient to cause the sample to flow [35]. In this system, the dynamic yield stress is extrapolated to be about 0.89 kPa, 3.5 kPa and 11.8 kPa, corresponding to the strength of magnetic field of 86, 171 and 343kA/m. In addition, when the magnetic field is present, all of shear stress curves shift upwards and represent a wide plateau range over the whole region of applied shear rate which may be caused by the robustly formed columns via strong dipole-dipole interaction among the adjacent magnetic particles. Compared with the above dynamic yield stress, static yield stress was also investigated via CSS approach which starts testing in rest state and increases the stress to a critical value at which the sample starts to flow [36]. Figure 6 describes the change of viscosity as a function of shear stress, in which viscosity initially holds its value at low shear rate region then falls abruptly and finally approaches to a constant value at high shear stress. The static yield stress develops below which there is no real macroscopic flow. From the point marked with arrow head, all curves indicate

**Figure 3.** TEM image of fabricated CI/CNT particles with mild sonication for 12 hr. **Figure 4.** SEM image of fabricated CI/CNT particles with mild sonication for 24 hr (other reaction condition is same).
about 4 decade drop in viscosity. Thus, the value of this point can be considered as static yield stress which is about 1.02 kPa, 5.31 kPa and 13.9 kPa separately. Actually, the sample is undergoing creep behavior below this stress; however we just assume that it is static.

3.3. Investigation on sedimentation problem

Finally, sedimentation problem was examined. The density for synthesized CI/CNT particles is 6.42 g/cm$^3$ which is much smaller that pure CI particles (7.91 g/cm$^3$). Obviously, the density mismatch between dispersed particles and medium oil (0.85 g/cm$^3$) is reduced, thus an improved sedimentation rate should be expected [17, 26, 37]. Figure 7 indicates the sedimentation ratio for the CI/CNT suspension and pure CI suspension as a function of time. In this method, the settling of macroscopic phase boundary between concentrated suspension and supernatant liquid was observed. We notice that initially, CNT wrapped CI particles settle down more slowly than that of pure CI particles at the same time duration. As time goes by, after most particles settle completely, compared with the nearly transparent supernatant of pure CI suspension, CNT wrapped CI suspension exhibits obscure phase, in which many CI/CNT particles still suspended in the medium oil. Actually, when we prepared the MR fluid and operated MR test, the CI/CNT particles dispersed more easily in medium and homogeneously re-dispersed MR fluid can also be achieved by momently mild shaking. The improved sedimentation and easy redispersion can be attributed to the reduced density along with the rough surface. Compared with the smooth surface of pure CI particles, the rough surface of CI/CNT particles is available to produce much friction force with medium oil, evidently, this may help to postpone the settling of particles, thus reduce the sedimentation rate.

4. Conclusions

In this work, we focused on fabricating unique spherical CI/CNT particles with densely coated CNT network by using PABA as grafting agent basing on the CNT’s self-assembling principle. The perfect core-shell morphology as well as the coating thickness was confirmed via SEM/TEM view. Long-term sonication was not favored to construct much denser CNT nest on the surface of CI particles. Although the possible mechanism of forming CNT nest was assumed, further physical characterization should be continued. In the case of MR
characterization, both dynamic yield stress and static yield stress were investigated. Finally, sedimentation was observed to be improved by the reduced density along with easy redispersity. Working on coating more densely CNT shell on the surface of CI particles which leads to improved sedimentation is in progress.

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