Sedimentation Characterization of Gelatin Added Bidisperse Magnetorheological Fluids Containing Nanoparticles

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Abstract. In this paper, the bidisperse magnetorheological (BMR) fluids containing micron carbonyl iron (CI) particles, nanoscale magnetite (Fe\textsubscript{3}O\textsubscript{4}) and gelatin were prepared. Gelatin was used as a coating layer to improve stability of bidisperse particles and restrict the oxidation of Fe\textsubscript{3}O\textsubscript{4}. Under the effect of magnetic field, Fe\textsubscript{3}O\textsubscript{4} particles were attached at the end of CI chains and filled into the interspace of micron CI particles, which influences the interactions among BMR fluids. Some groups with different concentrations and mass fractions of gelatin and Fe\textsubscript{3}O\textsubscript{4} were considered to reveal the sedimentation characterization of BMR fluids. The BMR fluids showed enhanced dispersion stability.

1. Introduction
Magnetorheological (MR) fluids, composed of micron soft magnetic particles dispersed in nonmagnetic carrier liquid, have rapidly and reversibly transformed between fluid-like and solid-like state under the effect of magnetic field [1, 2]. Therefore, MR fluids have been widely used in many engineering applications, such as dampers, brakes, torque transducers, and shock absorbers [3-5]. However, the urgent problem is the aggregation and sedimentation of micron CI particles, which can seriously reduce the magnetism and rheological properties of MR fluids.

To mitigate sedimentation of CI particles, many surface-modification CI particles were synthesized to prevent large particles from aggregation, such as lipophilic coating, organic coating and nanoparticles [6-8]. Nanoparticles Fe\textsubscript{3}O\textsubscript{4}, due to their tiny size, will be attached at the end of CI chains and filled into the interspace of micron CI particles to influence the interactions among dissimilar particles. However, Fe\textsubscript{3}O\textsubscript{4} particles are susceptible to oxidation at elevated temperatures and lose their magnetism.

In this study, magnetic micron CI and nanoscale Fe\textsubscript{3}O\textsubscript{4} particles were coated with gelatin layer to restrict the oxidation of Fe\textsubscript{3}O\textsubscript{4} and improve stability of bidisperse particles. Furthermore, the sedimentation characterization of various gelatin-based BMR fluids is measured to improve the dispersion stability of conventional MR fluids.

2. Experimental methods

2.1. BMR fluids materials and synthesis
Soft micron magnetic CI particle (average diameter 3.5 μm) was purchased from Zhixing Science and Technology Nantong Co. Ltd. And nanoscale magnetic Fe₃O₄ (average diameter 20 nm) were prepared by the co-precipitation method.

The preparation process of gelatin-coated BMR fluids is as follows: first, the mixture of solution containing soft CI, Fe₃O₄ and gelatin was dissolved in deionized water and heated to 55°C for 30 min, in which the CI and Fe₃O₄ surfaces were coated with gelatin layer. And then magnetic particles were separated by a magnet and washed by distilled water. Finally, appropriate amounts of gelatin coated magnetic particles were poured into mixture of polyolefins synthetic oil, sodium chloride and some additives, which was stirred for 40 min at 60°C. After ultrasonic oscillation, the BMR fluids were poured into graduated cylinders for investigation of sedimentation characterization.

2.2. Sedimentation characterization
The stabilities of the MR fluids and BMR fluids were checked by qualitative observations of the sedimentation which occurs when placing them into graduated cylinders without magnetic field. Furthermore, this experiment was performed at room temperature. The sedimentation characterization is a significant fact for the properties of BMR fluids and can be qualitative estimated from sedimentation ratio \( \beta \) obtained by equation (1):

\[
\beta = \left( \frac{H - h}{H} \right) \times 100\%
\]

where, \( H \) and \( h \) represent the initial height and residual height in the measuring cylinder after sedimentation of the BMR fluids, respectively. Figure 1 shows the schematic diagram of observation method.

3. Results and discussion
3.1. Theories and analysis
Figure 2 shows the schematic diagram of additive added BMR fluids, in which some Fe₃O₄ particles are attached to soft CI particles surfaces, others are suspended into polyolefins synthetic oil-additives solvent. Under the effect of magnetic field, due to dipolar interactions, Fe₃O₄ particles are attached at the end of CI chains and filled into the interspace of micron CI particles, which influences the interactions among BMR fluids. The field induced linear structure based gelatin-coated BMR fluids is shown in figure 3. For BMR fluids, Interactions can be mainly classified as van der Waals force, Brownian force, repulsive force and magnetic force [9].
Figure 3. Field induced linear structure based gelatin-coated BMR fluids

The magnitude of the van der Waals force generally decreases with the increase of intermolecular distance $h$. In this work, the dispersity of gelatin coated BMR fluids is superior to the previous reports [10, 11]. The gelatin coated layer was selected herein for its better viscosity and stability to restrict the oxidation of Fe$_3$O$_4$. In addition, as we coated outside surface with gelatin, it was found that the aggregation and sedimentation of large magnetic particles were significantly prevented due to the decrease of particles interaction. The pair interaction for two dissimilar particles of radius $R_1$ and $R_2$, respectively, can be calculated by Equation (2) [12]:

$$F_v = - \frac{A_{12} R_1 R_2}{6h} \frac{R_1 R_2}{R_1 + R_2}$$  \hspace{1cm} (2)

where, the Hamaker constant $A_{12}$ is therefore given by:

$$A_{12} = \left( \frac{1}{A_1^2} - \frac{1}{A_2^2} \right)^2$$  \hspace{1cm} (3)

The Hamaker constants of BMR fluids containing micron CI and nanoscale Fe$_3$O$_4$ particles are $A_1 = 7.24 \times 10^{-20}$J, $A_2 = 1.0 \times 10^{-19}$J, and $A_{12} = 2.22 \times 10^{-21}$J, respectively.

Brownian motion force has an important effect on preventing the aggregation of micron particles, which can be obtained by Equation (4):

$$F_B = \zeta \cdot \sqrt{\frac{12 \pi R \mu k_B T}{\Delta t}}$$  \hspace{1cm} (4)

where, $\zeta$ is the random number of Gaussian distribution, $R$ is the average radius of two dissimilar particles, $k_B$ is Boltzmann constant, $\mu$ is dynamic viscosity, $T$ is thermodynamic temperature and $\Delta t$ is time step.

Figure 4. Schematic illustration for the magnetic force induced by dissimilar dipoles

Without loss of generality, magnetic force can be described by the interaction of induced dipoles. Figure 4 shows schematic diagram for the magnetic force induced by dissimilar dipoles. Dipole moment of a magnetic particle is given by:

$$m = \frac{4}{3} \pi R^3 \chi H$$  \hspace{1cm} (5)

$\chi$ is the magnetic permeability of BMR particles, $H$ is the applied magnetic strength. The magnetic potential energy between dipoles $i$ and $j$ can be expressed:

$$W_{m_i m_j} = m_i \cdot B = \frac{\mu_0}{4 \pi r^3} \left[ m_i \cdot m_j - \frac{3(m_i \cdot r_0)(m_j \cdot r_0)}{r^3} \right]$$  \hspace{1cm} (6)
where, \( \mathbf{r}_{ij} \) is a relative positive vector between the dissimilar dipoles, and \( \mathbf{r}_0 \) is a unit vector of \( \mathbf{r}_{ij} \).

And hence the magnetic force between dipoles \( i \) and \( j \) is:

\[
F_{m_{ij}} = \nabla W_{m_{ij}} = \frac{3\mu_0}{4\pi r_{ij}} [m_i \cdot m_j - 3(m_i \cdot \mathbf{r}_0)(m_j \cdot \mathbf{r}_0)]
\]

Therefore, sum of magnetic forces exerted by the surrounding magnetic particles can be given by:

\[
F_m = \sum_{j \neq i} \frac{3\mu_0}{4\pi r_{ij}} [m_i \cdot m_j - 3(m_i \cdot \mathbf{r}_0)(m_j \cdot \mathbf{r}_0)]
\]

For BMR dispersions, the stability effect can be improved as a consequence of repulsion. The repulsion for per magnetic particles induced by other particles is given by Equation (9):

\[
F_R = \sum_{j \neq i} F_0 \exp \left[ -B \left( \frac{r_{ij}}{2R} \right)^2 \right] \hat{r}_{ij}
\]

Combined with Equations (2), (4), (8) and (9), the total interaction force for BMR fluids can be written as:

\[
F_\sigma = F_v + F_\beta + F_m + F_R
\]

According to Equation (10), the magnetic and repulsion force would be a major factor in describing dispersity behavior for BMR fluids. And nanoscale \( \text{Fe}_3\text{O}_4 \) increases the dipolar interaction between CI particles, which prevents the aggregation and sedimentation of larger particles.

3.2. Sedimentation results

To study the effect of gelatin coating and nanoscale \( \text{Fe}_3\text{O}_4 \) on the properties of MR fluids, some samples were prepared in the experiments. First, the details of the index and concentrations (wt\%) of gelatin in CI-based MR fluids are showed in table 1. Figures 5 and 6 show the sedimentation images in various concentrations of gelation and sedimentation ratio as a function of time for samples with different conditions in CI-based MR fluids, respectively. It should be noted that, sedimentation ratio increases rapidly during the initial 25 days, then gradually tends to become steady. 40 days later, the sedimentation ratio of MR-1, MR-2, MR-3, MR-4 and MR-5 is 42.5\%, 35.1\%, 24.3\%, 17.2\% and 28.0\%. It is obvious that, the concentration of gelatin significantly affects sedimentation ratio of CI-based MR fluids, and the sedimentation ratio for MR-4 is lower than 20\%, which is superior to many MR fluids included in the literature [13].

| Index | MR-1 | MR-2 | MR-3 | MR-4 | MR-5 |
|-------|------|------|------|------|------|
| Concentration | 0 % | 5.0% | 10.0% | 15.0% | 20.0% |

Figure 5. Sedimentation images in various concentrations of gelation in CI-based MR fluids
Additionally, magnetic nanoparticles have been considered as additives in the MR-4 suspensions, because they can prevent large particles from aggregation based on random Brownian motion. The details of the index and mass fractions (%) of nanoscale Fe₃O₄ in BMR fluids are showed in Table 2. Figures 7 and 8 show the sedimentation images in various mass fractions of nanoscale Fe₃O₄ and sedimentation ratio as a function of time for samples with different conditions in BMR fluids, respectively. It can be seen that the status of each sample will no longer change after 34 days and the sedimentation ratios are 14.2%, 11.5%, 10.3% for BMR-2, BMR-3 and BMR-4, which has better stability than those without nanoscale Fe₃O₄. In particular, the number of nanoparticles attached to the CI chains and filled into the interspace of CI particles increases with the increase in the mass fraction of Fe₃O₄ particles, in such BMR system. Thus, the sedimentation characterization has been further improved.

Table 2. Four samples of BMR fluids

| Index  | BMR-1 | BMR-2 | BMR-3 | BMR-4 |
|--------|-------|-------|-------|-------|
| Mass fraction | 0  | 2.0%  | 4.0%  | 5.0%  |

Figure 6. Changes of Sedimentation ratio with time for CI-based MR fluids

Figure 7. Sedimentation images in various mass fractions of Fe₃O₄ in BMR fluids

Figure 8. Changes of Sedimentation ratio with time for BMR fluids
4. Conclusion
The BMR fluids containing CI particles, nanoscale Fe$_3$O$_4$, gelatin coating and polyolefins synthetic oil are synthesized. Gelatin is used as a coating layer to improve the stability of bidisperse particles and restrict the oxidation of Fe$_3$O$_4$. Fe$_3$O$_4$ particles attached at the end of CI chains and filled into the interspace of micron CI particles influence the interactions among BMR fluids and reduce the aggregation of larger particles. As a result, the sedimentation characterization of the gelatin-based BMR fluids is measured, which shows that adding a certain concentration of gelatin (15.0wt%) and mass fraction of Fe$_3$O$_4$ (5.0%) significantly improves the dispersion stability of BMR fluids.

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References
[1] Klingenberg D J, Ulicny J C and Golden M A 2007 J. Rheol. 51 883-93.
[2] Rwei S P, Ranganathan P, Chiang W Y and Wang T Y 2017 J. Magn. Magn. Mater. 443 58-66.
[3] Park B J, Fang F F and Choi H J 2010 Soft Matter 6 5246-53.
[4] Niranjan M, Jha S and Kotnala R K 2014 Mater. Manuf. Process. 29 487-92.
[5] De Vicente J, Klingenberg D J and Hidalgo-Alvarez R 2011 Soft Matter 7 3701-10.
[6] Fang F F, Choi H J and Seo Y 2010 ACS Appl. Mater. Interfaces 2 54-60.
[7] Arief I and Mukhopadhyay P K 2017 J. Alloy. Compd. 696 1053-58.
[8] Jonsdottir F, Gudmundsson K H, Dijkman T B, Thorsteinsson F and Gutfleisch O 2010 J. Intell. Mater. Syst. Struct. 21 1051-60.
[9] Ngatu G T and Wereley N M 2007 Ieee Trans. Magn. 43 2474-76.
[10] Liu X H, Wang L F, Lu H, Wang D D, Chen Q Q and Wang Z B 2015 Mater. Manuf. Process. 30 204-9.
[11] Leong S A N, Mazlan S A, Samin P M, Idris A and Ubaidillah 2016 Proc. 6th Nanoscience and Nanotechnology Symposium.
[12] Patel R 2011 J. Magn. Magn. Mater. 323 1360-63.
[13] Fang F F and Choi H J 2010 Colloid Polym. Sci. 288 79-84.