Magnetorheological Properties of Aqueous Ferrofluids

Yongbo YANG*, Lin LI†, Guang CHEN*, and Weihua LI**

*School of Mechanical and Aerospace Engineering, Nanyang Technological University
50 Nanyang Avenue, Singapore 639798

**School of Mechanical, Materials, and Mechatronic Engineering, Faculty of Engineering, University of Wollongong, NSW 2522, Australia
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The nanosized magnetite particles were synthesized by means of a coprecipitation method and used to prepare the aqueous ferrofluids with various volume fractions. The magnetorheological properties of the aqueous ferrofluids have been investigated as a function of magnetic field. Under steady-state shear, the apparent viscosity for all of the ferrofluids exhibited a shear thinning behavior. But the Bingham model was invalid since the ferrofluids did not show a yield stress before they began to flow. However, the shear stress increased linearly with shear rate after a critical shear rate, showing a Bingham-like behavior. A Bingham-like yield stress, which was obtained by extrapolating the shear stress to the zero shear rate, increased with both the volume fraction of magnetic particles and the strength of magnetic field. The Bingham-like viscosity was approximately independent of the magnetic field at a given volume fraction of magnetic particles, but increased with the volume fraction under a given magnetic field. In the strain sweep experiment at an angular frequency of 10 rad/s, a transition from a gel-like state to a sol-like state was observed and a chain model has been proposed to qualitatively explain the mechanism of the transition. From the frequency sweep tests, it was found that there existed a plateau of storage modulus $G'$, which was independent of frequency but dependent on the volume fraction. A scaling law has been proposed to correlate the $G'$ plateau with the volume fraction.

1. INTRODUCTION

Ferrofluids are colloidal suspensions of nanosized ferromagnetic or ferrimagnetic particles in a carrier liquid.1) They are also called magnetic fluids because they respond to an external magnetic field to change their rheological properties.1) Due to unique magnetically-responsible rheological properties, ferrofluids have been an attractive area of research since 1980’s. A number of research works have focused on synthesis of novel nanoparticles for ferrofluids, formulation and characterization of ferrofluids, and development of technological applications using ferrofluids.2,3) Dampers are one of the typical applications of ferrofluids. More interestingly, biocompatible magnetic fluids have been attempted to be used for magnetic drug targeting or controlled drug delivery.4) It is expected that ferrofluids will continue to be an active area of research.

Due to small sizes of magnetic particles, particle agglomeration is one of the main issues for the preparation of a stable magnetic fluid. Magnetic particles in ferrofluids can be usually stabilized against agglomeration by coating with an appropriate surfactant. The surfactants for the surface coating of magnetic particles can be organic long molecules such as oleic acid, perfluoropolyether acid, and tetramethylammonium hydroxide (TMAOH).5) An appropriate coating not only gives a better stability of magnetic particles in a carrier liquid, but is also able to modify the surface properties of magnetic particles. For example, a coating with a biocompatible surfactant may result in a biocompatible magnetic fluid.6,7)

Similar to magnetorheological (MR) fluids, under a magnetic field the chain-like structures are formed from the magnetic particles and aligned in the direction of the magnetic field.6,7) This phenomenon was demonstrated by Hayes and Hwang using the water-based ferrofluids.8) Jones and Niedoba observed that the number of chains per unit volume increased monotonically with the applied field.9) Furthermore, simulations and theoretical modeling have shown that the aggregation of the particles can strongly affect the magnetization behavior of the systems.10,11)

The formation of the chain-like structures and their alignment in a magnetic fluid are the key factors controlling the rheological properties. When a steady-state shear stress is applied, if the chain structures cannot be destroyed at low shear rates and they are able to resist against the shear deformation until a critical shear stress, the

† To whom correspondence should be addressed.
Tel: +65-6790 6285, Fax: +65-6791 1859, E-mail: mlli@ntu.edu.sg
fluid will show a so-called yield stress and the Bingham model may be applicable if the shear stress of the fluid increases linearly with shear rate after the yield stress. When the Bingham model is valid, the fluid will show a shear thinning behavior as \( \eta_a = \tau_B / \dot{\gamma} + \eta_B \) where \( \eta_a, \tau_B, \eta_B, \) and \( \dot{\gamma} \) are the apparent viscosity, the Bingham yield stress, the Bingham viscosity, and the shear rate respectively. When \( \dot{\gamma} \to \infty, \eta_a \) will become close to \( \eta_B \) showing a shear-rate independent viscosity (but it is not Newtonian viscosity). For a magnetic fluid to behave like a magnetic fluid or a Bingham-like fluid, the chain-like structure formed under a magnetic field must be broken down by the steady-state shear flow applied.

The magneto-rheological properties of MR fluids have been extensively studied. However, the Bingham model is not always valid for all of MR fluids with microsized magnetic particles. Similarly, the validity of the Bingham model has not been proved for ferrofluids with nanosized magnetic particles. We believe that the validity of the Bingham model for a magnetic fluid is dependent on how a chain-like structure is formed under a magnetic field to give the fluid a certain “stiffness”. If the stiffness has to be developed under a steady-state shear flow, the magnetic fluid will not be a real Bingham fluid.

In the present work, we synthesized the ferrous magnetite nanoparticles coated with a surfactant, tetramethylammonium hydroxide (TMAOH), and characterized their morphological and magnetic properties. Furthermore, the synthesized magnetic particles were used to prepare three aqueous ferrofluids with different volume fractions (0.04 to 0.14) of magnetic particles. Under a steady-state shear, the viscosity of the ferrofluids was investigated under different magnetic fields. Then, the validity of the Bingham model was examined.

On the other hand, the dynamic measurements were conducted and the dynamic rheological properties of the magnetic fluids were studied. A schematic model is proposed to explain the transition between the formation and destruction of a chain-like structure under dynamic deformation. Furthermore, a scaling law is found, which is able to correlate the elasticity of the fluid with the volume fraction.

### 2. EXPERIMENTAL

#### 2.1 Synthesis and Characterization of Nanosized Magnetic Particles

All of the chemicals used in this work were purchased from Sigma-Aldrich and used as received. Following the literature, the nanosized magnetite particles were synthesized by means of a precipitation reaction in de-ionized (DI) water. The reaction occurred upon mixing FeCl₂ and FeCl₃ in a molar ratio of 1:2 in a sodium hydroxide solution. The detailed procedure is given as follows. 2.7 g ferric chloride (FeCl₃ • 6H₂O) and 1.0 g ferrous chloride (FeCl₂ • 4H₂O) were dissolved in 100 mL dilute acid solution (HCl, 0.5 M). A sodium hydroxide solution (100 ml, 2 M) was also prepared. All the solutions were heated to 70 °C, and the iron salt solution was then added into the basic solution and stirred for 30 min. The Fe₃O₄ precipitates were formed and isolated from the solution by a strong magnet. 80 ml of DI water was added into the precipitate and it was ultrasonicated for 15 min for re-dispersion of the particles. 40 ml of 1.0 M tetramethylammonium hydroxide (TMAOH) was added to the Fe₃O₄ precipitate and stirred for 120 min. The precipitate was settled down again by a strong magnet and washed several times with DI water until pH = 7.9. The precipitate was then isolated by centrifugation for 15 min at 4,000 rpm. A small amount of the precipitate was dried in nitrogen at 65 °C for the density measurement.

The morphology and particle size distribution of the coated magnetic nanoparticles were observed by transmission electron microscopy (TEM, Joel, JEM-2010) under a voltage of 200 kV. The magnetic property of the dried particles was measured by a vibrating sample magnetometer (VSM, Lakeshore 7,300) at room temperature.

#### 2.2 Preparation of Ferrofluids

By knowing the density of the magnetic particles, the aqueous ferrofluids of three volume fractions \( \phi = 0.04, 0.07 \) and 0.14 were prepared either by adding water or by water evaporation.

#### 2.3 Magnetorheological Measurements

The magnetorheological properties of ferrofluids were measured using a parallel-plate MR rheometer (USD 200, Paar Physica Co.) at a temperature of 25 ± 0.5 °C. The rheometer was equipped with a built-in solenoid coil to generate a homogeneous magnetic field perpendicular to the shear flow direction. According to the parameters provided by Paar Physica Co., the magnetic induction \( B \) is proportional to the coil current \( I \). The measuring geometry was a 10 mm diameter parallel-plate set with a gap of 1.0 mm. A sample of volume 0.4 ml was filled between the two plates before the measurements. To prevent the sample from dehydration, silicon oil of viscosity 0.05 Pa•s was placed to the outer circumference of the liquid sample.

Two operating modes, steady-state shear and dynamic shear,
were used for characterizing the magnetorheological properties of the ferrofluids. In a steady-state shear test, after the sample was loaded on the rheometer, it was initially sheared at 100 s\(^{-1}\) for 2 min in order to obtain a uniform dispersion of particles for the reproducible results. In the dynamic shear tests of both strain sweep and frequency sweep, similarly, each sample was initially oscillated at the frequency \(\omega = 10\ \text{rad}/\text{s}\) and strain amplitude \(\gamma_0 = 10\%\) for 4 min in order to acquire repeatable results. When a magnetic field is required, a direct current can be applied to the built-in electromagnet.

3. RESULTS AND DISCUSSION

3.1 Morphology and Magnetism of Synthesized Magnetic Particles

As presented in Fig. 1, the magnetic nanoparticles, measured by TEM, are roughly spherical with diameters about 13 nm, which are considerably uniform. The magnetization saturation of the particles was about 46 emu/g, which is about half of the pure bulk magnetite and it is close to that of the magnetic particles synthesized by coprecipitation method.5)

3.2 Magnetorheological Properties under Steady-state Shear

Figure 2(a) illustrates the shear stress \(\tau\) as a function of shear rate \(\dot{\gamma}\) for the sample of volume faction \(\phi = 0.04\) at various magnetic fluxes (0 to 0.288 Tesla). \(\dot{\gamma}\) was increased logarithmically from 0.1 to 400 s\(^{-1}\). At a given magnetic field, it is observed that the shear stress increases quickly within a small range of shear rate. On the other hand, the stress-shear rate curve shifts to a higher level with increasing the strength of magnetic field. However, the so-called Bingham behavior is not exactly applicable for all of stress-shear rate curves. If we only look at the stress-shear rate behavior after the small range of the shear rate, each curve is very much like a Bingham curve after the yield stress. By extrapolating the shear stress to the zero shear rate, an “imaginary” yield stress can be obtained. As this “imaginary” yield stress is dependent on the

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![Fig. 1. TEM micrograph of Fe\(_3\)O\(_4\) nanoparticles coated with as surfactant TMAOH.](image1)

![Fig. 2. Shear stress \(\tau\) as a function of shear rate \(\dot{\gamma}\) at 6 different magnetic fluxes with the volume fraction: (a) \(\phi = 0.04\), (b) \(\phi = 0.07\), (c) \(\phi = 0.14\).](image2)
magnetic strength or the volume fraction, it can be conveniently used as one of measures for the rheological features of a ferrofluid. It has been widely used in MR or ER fluids. The similar behavior has been observed for the other volume fractions ($\phi = 0.07$ and $0.14$) as shown in Figs. 2(b) and 2(c).

If we apply the following Bingham model$^{22)}$ only for the linear portion of the stress-shear rate curve at high shear rates,\[ \tau = \tau_y + \eta_B \dot{\gamma} \quad (1) \]
the imaginary Bingham yield stress, $\tau_y$, can be obtained, which is the same value as that obtained by extrapolating the shear stress to the zero shear rate. Here, the slope $\eta_B$ can be still called the Bingham plastic viscosity. The values of $\tau_y$ and $\eta_B$ obtained are listed in Table I, and $\tau_y$ is plotted against the magnetic flux $B$ in Fig. 3.

From Table I, it is found that the Bingham plastic viscosity $\eta_B$ of the ferrofluids is insensitive to the magnetic field, which is similar to the behavior of ER fluids under different electric fields.$^{22),23)}$ However, $\eta_B$ depends strongly on the volume fraction $\phi$.

As shown in Fig. 3, the imaginary Bingham yield stress $\tau_y$ shows an increasing trend with the volume fraction and/or the magnetic field strength. For the samples with small volume fractions of $0.04$ and $0.07$, the dependence of $\tau_y$ on the magnetic field can be approximately expressed by a linear equation:

$$\tau_y = a + bB \quad (2)$$

where $a$ and $b$ are constants, and $B$ is the magnetic flux. However, Eq. (2) is invalid for the sample of $\phi = 0.14$. At this high volume fraction, the particle agglomerations may take place to form bigger particles that could withstand higher stresses.

The apparent viscosity is defined as $\eta_{app} = \tau / \dot{\gamma}$ and shown in Fig. 4. $\eta_{app}$ keeps reducing with increasing $\dot{\gamma}$, indicating a shear thinning behavior over the whole range of $\dot{\gamma}$. If Eq. (1) can be applied, the apparent viscosity is then expressed as

$$\eta_{app} = \tau / \dot{\gamma} = \tau_y / \dot{\gamma} + \eta_B \quad (3)$$

As $\eta_B$ is the slope of each straight line, which is a constant, $\eta_{app}$ will be a decreasing function of shear rate. With increasing shear rate, $\eta_{app}$ will be gradually approaching to $\eta_B$. Thus, $\eta_B$ is known to be the minimum or limit value of the apparent viscosity. However, we were not able to measure the minimum viscosity experimentally due to the limitation of a plate rheometer.

### 3.3 Magnetorheological Properties under Oscillatory Shear

The microstructure of a complex fluid being formed as a result of deformation history can be reflected in the rheological properties of the fluid. Dynamic shear tests with small...
amplitudes can be sensitive to detecting of subtle structural changes even on a nanometric scale, which are evolved during a deformation process.24)

### 3.3.1 Under strain amplitude sweep

To study the effect of shear strain on the dynamic viscoelastic moduli of the ferrofluids, a series of experiments in strain amplitude sweep mode were carried out. Figure 5 shows the plots of storage modulus $G'$ and loss modulus $G''$ against the strain amplitude $\gamma$ at $B = 0.150$ T and frequency $\omega = 10$ rad/s for the samples with different volume fractions.

All of the samples behave in a similar pattern over the whole strain range. At a given volume fraction, both $G'$ and $G''$ show a strain-independent plateau at low strain amplitudes, which is similar to linear viscoelasticity. $G'$ is much greater than $G''$, indicating that there exists an elastically dominant structure or a solid-like behavior. However, with increasing the volume fraction, the height of the $G'$ plateau increases while the $G'$ plateau becomes narrower. This indicates that the strain range for the linear viscoelasticity is narrowed by increasing the volume fraction. Thus, a less stable structure formed from magnetic particles can be expected in a higher volume fraction sample. With further increasing strain amplitude, $G'$ begins to decrease whereas $G''$ begins to increase. As a result, a crossover of $G'$ and $G''$ appears. Beyond the $G'$ and $G''$ crossover, both $G'$ and $G''$ decrease monotonously with increasing strain amplitude, but $G'$ becomes smaller than $G''$, indicating a viscous liquid behavior. In the vicinity of the $G'$ and $G''$ crossover point, there is a clear peak in $G''$, which is an indicative of the maximum dissipation of energy during the period of destroying the elastic structure. In addition, it is found that the $G'$ and $G''$ crossover point shifts to the lower strains with increasing the volume fraction, implying a stronger but more brittle structure formed from a higher volume fraction initially.

The transition from the solid-like behavior to the liquid like one is very much similar to the gel-sol transition observed in many gelling materials.25) In the case of Fig. 5, the shear strain amplitude is the controlling parameter for the gel-sol transition.

The rheological behavior of the ferrofluids under a magnetic field is similar to that of an ER fluid under an electric field.22) The fumed silica suspensions also have the similar transition phenomenon of $G'$ and $G''$ in the strain-sweeping oscillation.26) Based on the aforementioned similarity and the chain structures of magnetic particles of MR fluids under magnetic fields,26) the mechanism involved in the strain amplitude sweep process can be considered by the construction and destruction of chain structures.22,26,27) A series of schematic diagrams of chain structures are proposed in Fig. 6 (a) to (e) to explain the mechanisms in the different regions of deformation.

As illustrated in Fig. 6(a), under a magnetic field, the longer chains represented by the solid circles are formed as a parallel framework, which contributes to the majority of the elastic modulus $G'$. The shorter chains are represented by the grey circles and the free particles (wandering in the water) are represented by empty circles, which contribute to $G''$. In a static equilibrium, the chain framework structure holds all the magnetic particles and the water tightly, so that the ferrofluid would behave like a gel. At very small strains below a critical strain $\gamma_{cr}$, as shown in Fig. 6(b), the chain framework can withstand the small shear stress caused by the small strains, and the chain framework remains the same as that in the static equilibrium. Thus, both $G'$ and $G''$ remain constant with $G' > G''$.

![Fig. 5. Dependence of dynamic moduli $G'$ and $G''$ on strain $\gamma$ at $B = 0.150$ T and $\omega = 10$ rad/s for three samples.](image)

![Fig. 6. A schematic model for the structural changes during an oscillatory strain sweep process under a magnetic field: (a) in the static equilibrium status, (b) both $G'$ and $G''$ keep in plateaus, (c) $G'$ keeps in the plateau, $G''$ increases, (d) $G'$ starts decreasing, $G''$ keeps on increasing, (e) both $G'$ and $G''$ decrease.](image)
When $\gamma_0 > \gamma_{c*}$, some of the long chains are broken down into short ones, so that the number of the short chains increases (Fig. 6(c)), causing the increase in $G''$ and the decrease in $G'$. Subsequently, the gel-sol transition at which $G'$ is equal to $G''$ is shown. With further increasing the shear strain, the chain framework formed from the long chains is destroyed greatly and at the same time the shorter chains and free particles increase, resulting in a continuous decrease in $G'$ and an increase in $G''$ (Fig. 6(d)). Eventually, a complete destruction of the chain framework and a fine dispersion of magnetic particles are reached at large strains, and a viscoelastic liquid is obtained (Fig. 6(e)).

3.3.2 Under frequency sweep

In a frequency sweep mode at a small strain amplitude $\gamma_0 = 0.1 \, \%$, the effect of volume fraction on $G'$ was examined at a given magnetic flux (0.230 Tesla). The results are shown in Fig. 7(a). The application of the small strain amplitude ensured the non-destruction of the chain structures formed. In Fig. 7(a), each $G'$ curve shows a frequency-independent plateau in the region of $\omega < \omega_{c*}$. $\omega_{c*}$ is defined as a critical frequency below which $G'$ starts being approximately independent of frequency. It is observed from Fig. 7(a) that $\omega_{c*}$ is lower for the sample with a lower volume fraction $\phi$.

The $G'$ plateau is very similar to a rubbery plateau of polymer, which is an indication of formation of a 3D network.27) Similarly to polymers, we may also consider that a 3D structure is formed from the ferrous particles or particle aggregates in a ferrofluid and it can be rheologically observed only in a range of appropriate frequencies (or time). Thus, the height of the $G'$ plateau is directly proportional to the network’s density. A higher plateau indicates a denser and more elastic network. However, it should be noted that the chains of particles can be formed under the magnetic field to “connect” two plates of the rheometer as illustrated in Fig. 6 to contribute to the elasticity, but a polymer-network like 3D structure is not really formed because it would not be possible to form some bridges or chains of particles in the lateral direction (i.e., the direction perpendicular to the magnetic field). But, the concept of 3D is still useful here because one can consider that there are many chains formed in the vertical direction, which is a 3D structure. And the number of the chains per area has a similar meaning to the network’s density.

The shift of $\omega_{c*}$ to the higher frequency with increasing volume fraction can be explained as follows. It should be true that it takes a shorter time to observe (or detect) a more elastic structure while it takes a longer time to observe (or detect) a more viscous structure. Since a lower frequency is equivalent to a longer time, it is reasonable to take a longer time (i.e., a lower frequency) to observe a structure with a lower $G'$, which is formed from a smaller volume fraction.

The height of the $G'$ plateau, $G'_p$, is plotted against volume fraction $\phi$ in Fig. 7(b). In the log-log scale, $G'$ shows a linear relationship with $\phi$, from which a scaling relation is obtained:

$$G'_p \propto \phi^\alpha$$

where $G'_p$ is the $G'$ plateau height in Pa. $\alpha = 4.62$ is the power index obtained from curve fitting. The scaling laws have been widely used for many physical functions of polymeric systems.28) For example, the equilibrium modulus $G_{eq}$ of a polymeric gel is scaled with polymer concentration $c$ as $G_{eq} \propto c^z$, where the scaling exponent $z$ has a value between 1.9 and 2.7, depending on the gel type.28) Although the scaling relation in Eq. (4) is very similar to the scaling law

![Graph](image-url)

Fig. 7. (a) Dependence of $G'$ on frequency for the ferrofluids of three volume fractions at $B = 0.23\, T$ and strain amplitude $\gamma_0 = 0.1 \, \%$. (b) A scaling relation between plateau modulus $G'$ and volume fraction $\phi$ at $B = 0.23\, T$ and $\gamma_0 = 0.1 \, \%$. 

(i.e., $G_\infty \sim c^n$) for polymeric gels, it is noted that the scaling exponent in Eq. (4) is much larger than the $z$. Thus, we may conclude that the ferrofluids are more sensitive to a change in volume fraction of magnetic particles than polymeric gels. We have not found any reports dealing with this kind of scaling relations for ferrofluids. There is no doubt that the scaling relation is useful in predicting the relation between the elastic property and particle volume fraction for ferrofluids.

4. CONCLUSIONS

In the present study, we synthesized the nanosized magnetite particles using a coprecipitation method. The synthesized nanoparticles were stabilized by a surfactant, tetramethylammonium hydroxide (TMAOH), in order to prevent the particles from agglomeration. The aqueous ferrofluids with three volume fractions (0.04, 0.07, and 0.14) were prepared from the nanoparticles. The magnetorheological properties of the ferrofluids have been investigated using a parallel-plate rheometer under different external magnetic fields.

Under steady-state shear, the apparent viscosity depends both on magnetic field and shear rate. The Bingham model was invalid for all of the ferrofluids studies, but a Bingham-like viscosity was observed at high shear rates. By assuming that the ferrofluids followed the Bingham model, the nominated (or imaginary) Bingham yield stress and the nominated (imaginary) Bingham yield stress were obtained. The nominated Bingham yield stress increased approximately linearly with the magnetic field. However, the Bingham plastic viscosity is found to be insensitive to the magnetic field for a given volume fraction.

Under oscillatory shear, the ferrofluids behaved viscoelastically, showing a gel-like characteristic at sufficiently small strains and a sol-like behavior at high strains. The gel-sol transition region was observed by increasing shear strain. A chain structure model has been proposed to explain the above changes.

Finally, the frequency-independent $G'$ plateau was observed in a broad range of frequency for all the volume fractions studied at a magnetic flux of 0.23 Tesla and a small shear strain of 0.1 %. A scaling law, $G'_p \propto \phi^{4z}$ has been obtained, where $G'_p$ is the height of the $G'$ plateau and $\phi$ is the volume fraction.

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