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Control of Magnetic Particle Size in Ferrofluid and Its Effect on Rheological Properties

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Abstract

Rheological properties are the theoretical basis and the key to common problems in ferrofluid applications, therefore they are expected to be adjustable to satisfy different technical requirements through altering the microstructure of ferrofluid during the process of preparation. In this paper, Four ferrofluid samples with different magnetic particle size were prepared by controlling the concentration of precursor solution during co-precipitation process and the rheological properties of these samples were investigated. These samples exhibited field-controlled rheological properties. Eternal magnetic field would enhance the formation of microstructures, resulting in an increase of viscosity. While with the increase of shear rate, microstructures tended to be destroyed, causing viscosity to decrease. There were two opposing mechanisms of the influence of precursor solution concentration. On one hand, the reduction of the precursor solution concentration would produce primary magnetic particles of smaller size. But on the other hand, the surfactant became insufficient to completely coat the magnetic particles because of an increased specific surface area, causing the magnetic particles to aggregate and form secondary clustering structures which strongly enhanced the magnetoviscous effect and weakened the viscoelastic effect.

Keywords: Ferrofluid, Rheology, Magnetoviscous effect, Viscoelastic effect

1 Introduction

Ferrofluid (also called magnetic fluid) exhibits liquid behavior coupled with ability to response to external magnetic field [1], thus has been extensively applied in many devices, such as seals [2, 3], sensors [4, 5] and shock absorbers [6].

Rheological properties are theoretical base and the key to common problems in ferrofluid applications. For example, rheological properties of ferrofluid would affect the resistance torque of seals [7], the transmittance of optical devices [5], the damping performance of shock absorbers [6], the accuracy of sensors [4, 5] and the thermal properties of heat transfer devices [8]. Take ferrofluid seal as an example, which is most widely used in practical. Under various working conditions, in consideration of equipment power and response time, resistance torque of ferrofluid seal is often required to be small enough,

stay within a certain range with the change of external environment, and remain stable after long duration of use [9, 10]. And the most important factor affecting resistance torque is the viscosity of ferrofluid [11–13]. Therefore, it is necessary to figure out the rheological properties of ferrofluid before the design process, so that we could select appropriate type of ferrofluid according to different application requirements by adjusting conditions during preparation and post-processing.

There are many factors that affect the rheological properties of ferrofluid, including the type, shape, volume fraction and size distribution of magnetic particles, the type of carrier fluid, the amount of surfactant, the additives etc. Shahnazian et al. found out that the yield stress of the cobalt based ferrofluid is stronger than that of the magnetite based ferrofluid [14], and ferrofluid with nanodisc particles showed higher yield stress compared with ferrofluid with spherical nanoparticles under high magnetic field strength [15]. Wu et al. [16] added plant-virus-derived nanotube into commercial ferrofluid and

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observed a dramatic enhancement in magnetoviscosity and a suppression of shear thinning. López-López et al. [17] compared the rheological properties of ferrofluids constituted by CoNi nanospheres and nanofibers and found out that the curvature of the yield stress vs magnetic field curves was negative in the case of nanosphere ferrofluid, while it was positive in the case of nanofiber ferrofluid, which may be due to the existence of strong interparticle solid friction in the case of nanofiber ferrofluids. Felicia et al. [18] investigated the effect of multiwalled carbon nanotubes (MWCNTs) on the magnetorheological properties of ferrofluid, the results showed that the shear resistant plateau observed in a pure ferrofluid disappears when 0.5 wt% of MWCNT is incorporated, and the yield stress values of the composite system are slightly smaller than that of the pure system.

The particle size distribution of magnetic particles in ferrofluid has a significant influence on rheological properties, since it affects magnetic moment of magnetic particles [19], which would change the strength of the magnetic dipole interaction between particles, thus exerts an important influence on the formation of aggregates in ferrofluid [20–22]. Iskakova et al. [23] analyzed the effect of interaction between chains on their size distribution theoretically and estimated the influence of interaction between the chains on the size distribution as well as on the mean number of the particles in the chain. Thurm et al. [24] used a magnetic separation device to obtained ferrofluid sample with different fraction of larger particles and found out that the larger particles showed strong, magnetic field induced interparticle interactions and formed chain-like structures, which in turn dominate the flow behavior. Wang et al. [25] investigated the influence of polydispersity in the particle size by Langevin molecular dynamics simulations and found that the average aggregate size formed by large particles decreased when the volume fraction of small particles increased. Chand et al. [26] studied the effect of size distribution on viscoelastic properties of ferrofluid and conclude that the size distribution and the dipole-dipole interaction have contributed most to form the magnetically induced chain structures. Nowak et al. [27] compared the rheological behavior of three biocompatible ferrofluids with different hydrodynamic diameter and core composition, the results revealed that multicore ferrofluids showed strong magnetoviscous effect and the effect was approximately three times stronger when hydrodynamic diameter is only approximately twice as large. Wu et al. [28] investigated the rheological properties of ferrofluid with different particle size experimentally and analyzed the mechanical characteristics by molecular dynamic simulation, pointing out that the strong magnetorheological effect was originated from the strong assembling microstructure under external magnetic field. Our team has also conducted research on this field, ferrofluid sample was processed by applying a magnetic field gradient to obtain samples with different fractions of large particles, results showed that sample enriched with large particles exhibited a stronger magnetorheological effect [29].

Meanwhile, particle size distribution is a factor that could be controlled relatively conveniently during the preparation process.

Therefore, in this work we chose to control the size distribution of magnetic particles in ferrofluid by controlling the concentration of precursor solution during chemical co-precipitation process, and obtained 4 different ferrofluid samples. Then their rheological properties were investigated to figure out the influence of different factors. So that we could determine how key parameters in ferrofluid applications, such as resistance torque, would change with environmental factors and how we should adjust the preparation processes and post-processing procedures to obtain ferrofluid with desired microstructure that could satisfy application requirements.

2 Preparation and Characterization
2.1 Preparation of Ferrofluid Samples
Ferrofluid samples were prepared by chemical co-precipitation. During co-precipitation, the formation of nanoparticles could be divided into two processes, the nucleation process and the growth process [30]. The key to both processes was the degree of supersaturation, it had a significant impact on the nucleation rate and growth rate of the crystal, thus could be regarded as the driving force of co-precipitation reaction. Therefore, we changed the concentration of the precursor solution in co-precipitation process to control the degree of supersaturation and obtained 4 ferrofluid samples with different particle size distribution, the preparation process of ferrofluid samples was shown in Figure 1.

The detailed procedure was as follows:

(1) 54.06 g $FeCl_3 \cdot 6H_2O$ and 22.72 g $FeCl_2 \cdot 4H_2O$ was dissolved in a certain amount of deionized water.
(2) The solution was stirred by 400 r/min in a 45 ℃ water bath, 150 mL ammonia was added into the solution and reacted for 30 min.
(3) The precipitated magnetic particles were washed by deionized water until the supernatant water pH=7.
(4) Carrier liquid(kerosene) and surfactant(oleic acid) were mixed with the washed magnetic particles, and the mixture was stirred by 400 r/min in a 80 ℃ water bath for 60 min.
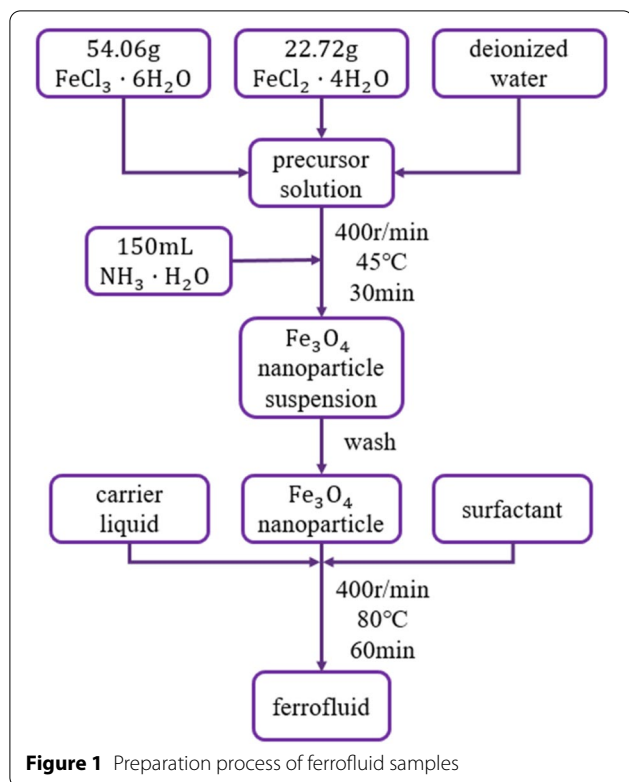(5) The residual liquid was poured out.

Figure 1 Preparation process of ferrofluid samples

Figure 2 Magnetic properties of ferrofluid samples

3.1 Flow Curves of Ferrofluid Samples

The dependence of shear stress and viscosity on shear rate of ferrofluid samples under different external magnetic fields was shown in Figure 4.

According to the results, ferrofluid samples behaved as Newtonian fluid without external magnetic field, while

During the preparation process, the volume of deionized water used to dissolve $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ was 300 mL, 350 mL, 400 mL and 500 mL, respectively, and the samples were named No. 1 Ferrofluid Sample, No. 2 Ferrofluid Sample, No. 3 Ferrofluid Sample, and No. 4 Ferrofluid Sample, respectively.

2.2 Magnetic Properties of Ferrofluid Samples

The magnetization characteristics of ferrofluid samples were characterized by VSM. The magnetization curves were shown in Figure 2. All the samples exhibited super-paramagnetic property and the saturation magnetization of these samples was 42.41 emu/g, 41.14 emu/g, 41.73 emu/g, and 40.90 emu/g, respectively. There was no much difference between these samples, indicating that with the same volume concentration of magnetic particles, the particle size distribution differences caused by different concentration of precursor solution during the preparation process had little influence on the magnetic property of ferrofluid.

3 Measurement and Discussion of Rheological Properties

The rheological properties of different ferrofluid samples were investigated using the Anton Paar MCR 302 rheometer as shown in Figure 3.
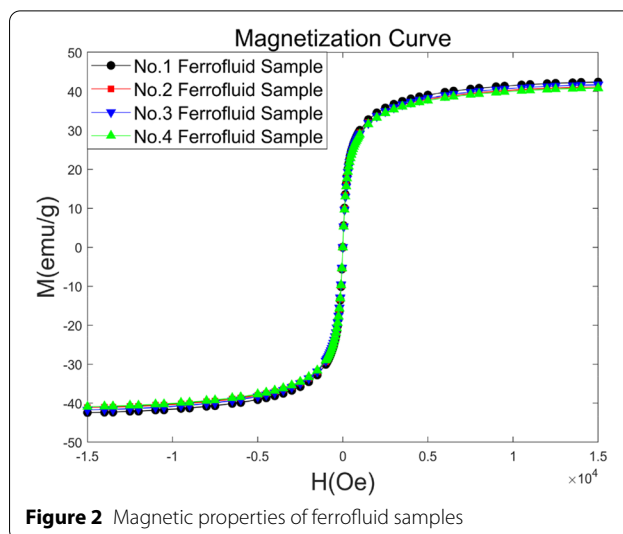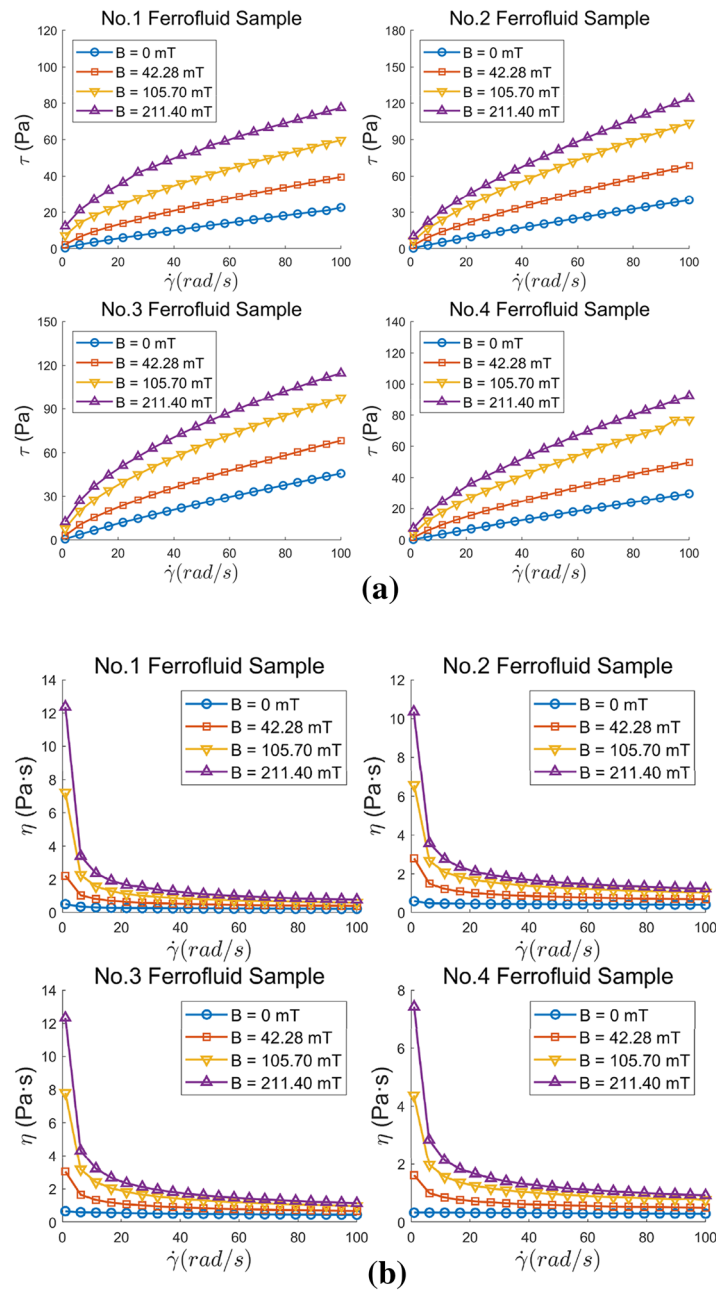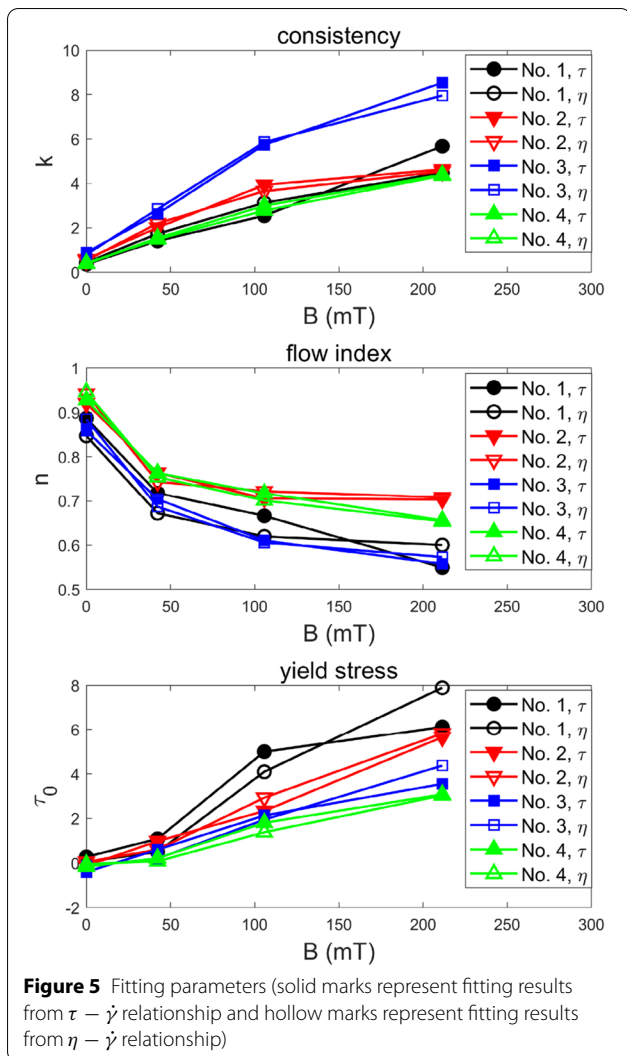

Figure 3 MCR 302 rheometer

Figure 4 Dependence of shear stress (**a**) and viscosity (**b**) on shear rate of ferrofluid samples under different external magnetic fields

exhibited non-Newtonian fluid properties under external magnetic field, which indicated formation of microstructures. For each sample, under different external magnetic field strength, with the increase of shear rate, shear stress increased but the increase rate decreased gradually, viscosity decreased and gradually reached a stable value. There was an intercept on the y axis, indicating that ferrofluid samples had a yield stress. Furthermore, for the same ferrofluid sample, shear stress and viscosity would increase with the strength of external magnetic field.

Because the sample showed a shear thinning effect and had a yield stress, we chose Herschel-Bulkley fluid model to fit the data. Herschel-Bulkley fluid model was as follows:

$$\tau = \tau_0 + k\dot{\gamma}^n, \tag{1}$$

Figure 5 Fitting parameters (solid marks represent fitting results from $\tau - \dot{\gamma}$ relationship and hollow marks represent fitting results from $\eta - \dot{\gamma}$ relationship)

$$\eta = \tau_0 \dot{\gamma}^{-1} + k\dot{\gamma}^{n-1}, \qquad (2)$$

where τ was shear stress, $\dot{\gamma}$ was shear rate, τ_0 was yield stress, η was viscosity, k was consistency, and n was flow index.

The fitting parameters were plotted in Figure 5. Results for $\tau - \dot{\gamma}$ relationship and $\eta - \dot{\gamma}$ relationship were very close, verifying the reliability. For the same ferrofluid sample, with the increase of the external magnetic field, the consistency increased, showing the magnetoviscous effect of ferrofluid, while the flow index decreased and the deviation from 1 grew gradually, indicating a stronger non-Newtonian rheological property. Moreover, the gradual increase of yield stress indicated the presence of more complicated aggregates in ferrofluid.

3.2 Magnetoviscous Effects of Ferrofluid Samples

As we could see from Figure 6, for all ferrofluid samples, the relative change of viscosity increased with external magnetic field strength, and decreased with shear rate. Besides, the magnetoviscous effect became weaker from No. 1 Ferrofluid Sample to No. 3 Ferrofluid Sample, and then rebounded at No. 4 Ferrofluid Sample.

This was due to the influence of two opposing mechanisms. On one hand, with the reduction of precursor solution concentration, the size of primary magnetic particles produced by chemical co-precipitation reaction got smaller, resulting in a weaker magnetoviscous effect. On the other hand, as the primary magnetic particle size decreased, the specific surface area of particles increased, causing the surfactant, which was of the same amount in different preparation process, to be insufficient to completely coat the magnetic particles. Therefore, the aggregation phenomenon became more intense, more secondary clustering structures were formed, thus increased the effective magnetic particle size and leaded to an enhanced magnetoviscous effect. The combined effect of two mechanisms resulted in the trend that the magnetoviscous effect gradually weakened from No. 1 Ferrofluid Sample to No. 3 Ferrofluid Sample but then rebounded at No. 4 Ferrofluid Sample.

3.3 Viscoelastic Properties of Ferrofluid Samples

The amplitude sweep curves of different ferrofluid samples were shown in Figure 7. According to Figure 7, for all samples, under different magnetic fields, storage modulus tended to experience a plateau and then decayed by power law, while loss modulus went through a plateau at first, then increased to a peak, finally decayed by power law with a smaller decay index than the storage modulus. With the increase of external magnetic field, the storage modulus and loss modulus both increased.

There was an intersection point between storage modulus and loss modulus (not obvious at B = 21.14 mT) at a critical shear strain, parameters of the intersection points were shown in Figure 8. When shear strain was less than the critical shear strain, storage modulus was greater than loss modulus, i.e., the sample exhibited solid-like rheological properties. When the shear strain was greater than the critical shear strain, storage modulus was less than loss modulus, i.e., the sample exhibited liquid-like rheological properties. Therefore, the intersection point of two moduli could be treated as a transition point from solid-like behavior to liquid-like behavior for ferrofluid samples. With the increase of applied magnetic field, the transition modulus increased, and the transition shear stain decreased.
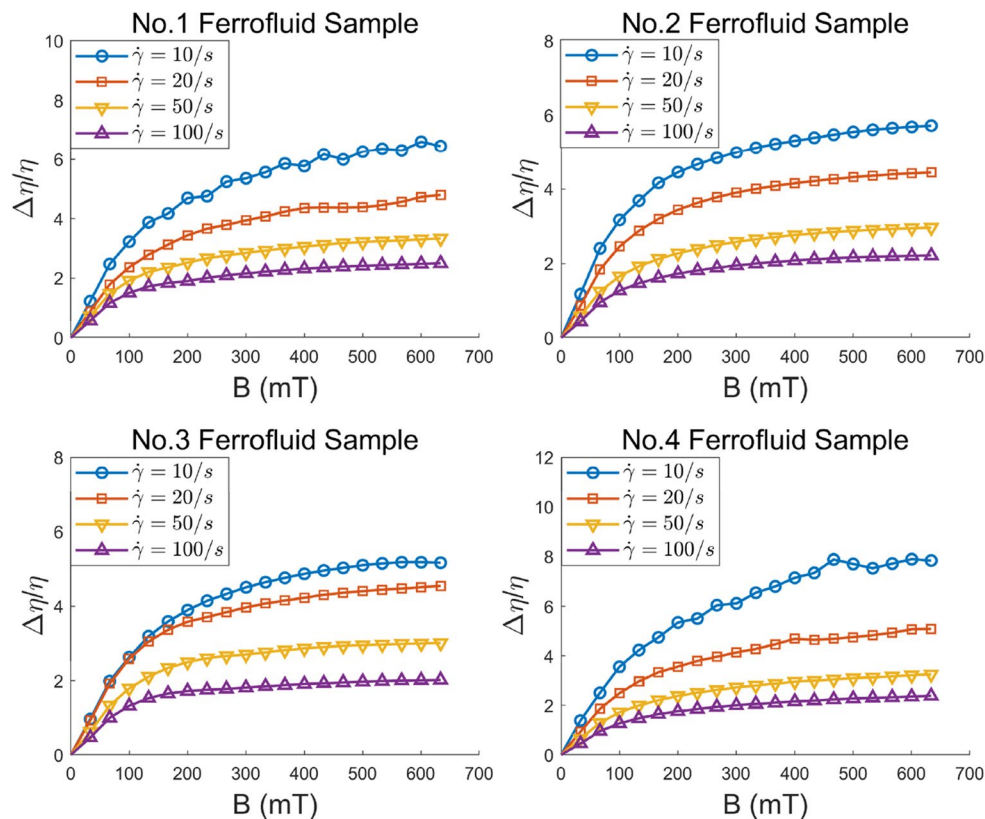
Figure 6 Dependence of viscosity on magnetic field strength of ferrofluid samples under different shear rates

The critical shear strain and the modulus at intersection both increased at first and then decreased from No. 1 Ferrofluid Sample to No. 4 Ferrofluid Sample. This could be explained by the microscopic point of view. When the shear strain was small, there were long microstructures formed in ferrofluid, which spanned across the gap of rheometer's measuring cell. Therefore, the sample exhibited solid-like behaviors. However, when the amplitude of shear strain increased to the critical strain, the microstructure across the gap was destroyed, so the sample showed liquid-like behavior. According to the analysis in the part of magnetoviscous effect, the effective particle size from No. 1 Ferrofluid Sample to No. 4 Ferrofluid Sample decreased at first and then increased. Hence, with the volume fraction of magnetic particles remained unchanged, particles of smaller effective size were more likely to form structures that were long enough to span across the gap.

4 Conclusions

In this work, we prepared 4 ferrofluid samples with different particle size distribution by controlling the precursor solution concentration during the chemical co-precipitation process and then investigated the rheological properties of these samples, including flow curves, magnetoviscous effects and viscoelastic properties to figure out the influence of magnetic field, shear rate and precursor solution concentration.

The research results were as follows:

(1) Ferrofluid exhibited field-controlled rheological properties, which could be explained by the formation and destruction of the magnetic microstructures in ferrofluid.
(2) Ferrofluid behaved as non-Newtonian fluid under external magnetic field and the flow behavior could be described by Herschel-Bulkley fluid model.
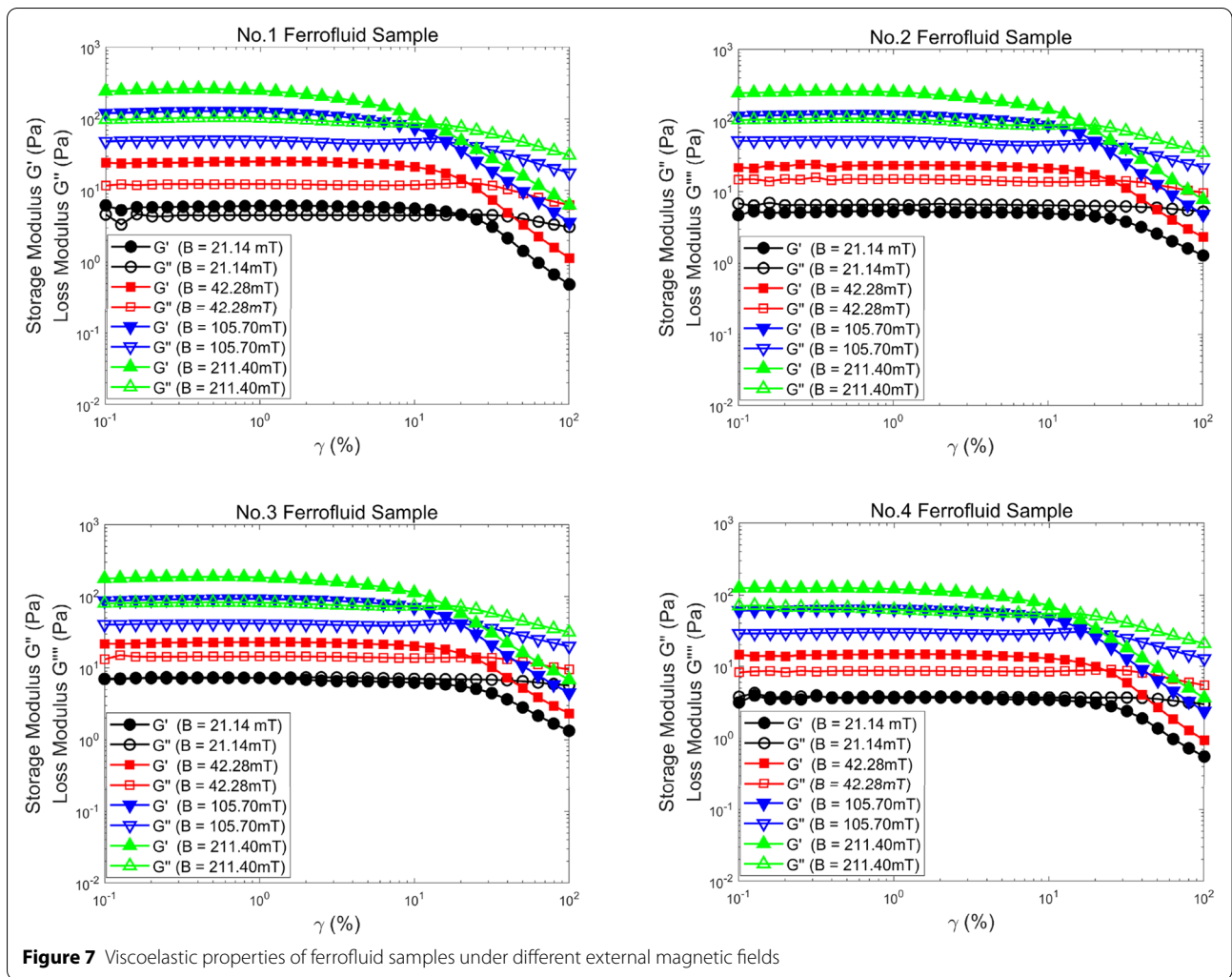
Figure 7 Viscoelastic properties of ferrofluid samples under different external magnetic fields

(3) When the small angle oscillating load was applied, ferrofluid exhibited a transition from solid-like behavior to liquid-like behavior with the increase of shear strain.

(4) With the increase of external magnetic field strength, the viscosity of ferrofluid increased gradually. This was due to the formation of aggregates which impeded the flow and resulted in the increase of the apparent viscosity.

(5) The introduction of shear flow would promote the destruction of aggregates in ferrofluid, causing the viscosity to decrease thus showing shear thinning effect.

(6) The influence of precursor solution concentration affected the rheological properties in two opposing mechanisms. With the reduction of the precursor solution concentration, the size of the magnetic particle produced by chemical reaction got smaller. But at the same time, the surfactant was insufficient to completely coat the magnetic particles due to an increased specific surface area, causing the particles to aggregate and form clusters of larger effective size which strongly enhanced the magnetoviscous effect and weakened the viscoelastic effect.
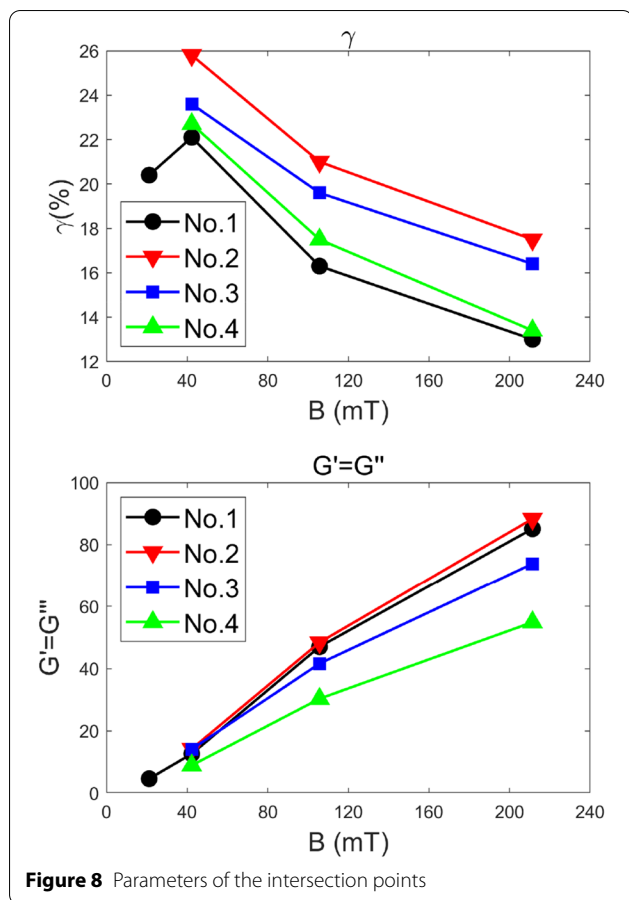
Figure 8 Parameters of the intersection points

Author contributions
SC was in charge of the whole experiment and wrote the manuscript; DL was the mentor of SC, and provided critical discussion during manuscript preparation. All authors read and approved the final manuscript.

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Competing interests
The authors declare no competing financial interests.

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