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ORIGINAL ARTICLE

Research on the rheological properties of a silicone oil-based ferrofluid

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Abstract

To study the overall rheological characteristics of the silicone oil-based ferrofluid, a chemical co-precipitation method was adopted for preparation, and transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM) were used for characterization. The average size of Fe_3O_4 magnetic particles was 10.4 nm and the saturation magnetization of the ferrofluid was 5.98 emu/g. Then, the fluidity, magnetoviscous effect and viscoelasticity of the ferrofluid were studied using a rotational rheometer. The results showed obvious shear thinning of the silicone oil-based ferrofluid under an external magnetic field, and the yield stress of the ferrofluid could not be accurately obtained by fitting the flow curve with an H–B model at a continuous shear rate. A strong magnetoviscous effect could be observed at different shear rates and temperatures. The magnetoviscous parameter *R* increased with the increase of temperature and its variation decreased with the increase of shear rate. Moreover, based on the magnetic particle chain model and the viscosity–temperature characteristics of the base carrier liquid, different mechanisms of temperature influence on the magnetoviscous effect were analyzed. Finally, a discussion of the microstructure evolution mechanism of the ferrofluid in the modulus changing with frequency was presented through the viscoelastic analysis of the silicone oil-based ferrofluid.

Keywords Ferrofluid · Rheological properties · Magnetoviscous effect · Viscoelasticity

1 Introduction

Ferrofluid (FF) is a new kind of synthetic nanoscale functional material [1]. It is a colloidal solution formed by magnetic solid particles of size about 8–15 nm, uniformly dispersed in the base liquid with the help of a surfactant. It can still maintain a stable system under the action of gravity field or magnetic field without precipitating [2]. Ferrofluid was first prepared by NASA in the early 1960s to solve the sealing problem of spacesuits and applied in actual working conditions, which opened the door for the research and exploration of ferrofluid around the world [3]. So far, water-based, kerosene oil-based, machine oil-based, silicone oil-based, perfluoropolyether-based and other ferrofluids have been used [4]. Due to its unique fluidity and magnetic properties under an applied magnetic field, ferrofluid can be applied in machinery, electronics, aerospace and other fields, and has shown great application potential in many basic fields such as biomedicine, chemical industry, environmental protection and medical treatment [5, 6].

Ferrofluids have been widely used in recent years. One of the most important theoretical bases for these applications is the rheological theory of ferrofluids [7]. Early in 1968, Rosensweig [8] used a cone–plate viscometer to measure the viscosity of ferrofluids in the experiment. It was the first time that the magnetic induction change of the viscosity of ferrofluids was observed through an experiment, and it was soon defined as the magnetoviscous effect. Shliomis [9] proposed a theoretical model of the magnetoviscous effect for

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non-interacting ferrofluids systems. The model can only be used to quantitatively predict the behavior of highly diluted fluids without considering the effect of temperature. Pinho et al. [10] set up an experimental device to study the magnetoviscous effect of ferrofluids under oscillating conditions. In terms of the microstructure of ferrofluids, Genes and Pincus [11] pointed out in their study that the particles in ferrofluids could form chains and cluster structures under the interaction of a magnetic dipole force, which makes the ferrofluids system change from a stable colloidal system to a thixotropic system. Zubarev [12] proposed and optimized a double-dispersed chain structure model to describe the rheological properties of ferrofluids when chain agglomeration occurs in ferrofluids. In addition, with the development of applications, the research focus of ferrofluids rheology has shifted to complex rheological properties such as viscoelasticity [13], yield [14] and thixotropy [15].

Silicone oil-based ferrofluids have attracted much attention because the base liquid is a silicone oil with good chemical stability, corrosion resistance, high temperature resistance, low volatility and change of viscosity weakly affected by temperature. Furthermore, silicone oil-based ferrofluids, with admirable viscosity–temperature properties and excellent physical and chemical properties, have a unique potential in aerospace, especially in sealing and space damping [16]. Chen et al. [17] prepared a stable silicone oil-based ferrofluid using ethoxy-terminated polydimethylsiloxane as the surfactant and the prepared ferrofluid has good thermal stability and strong magnetism, with a saturation magnetization of 257.8Gs and a magnetic susceptibility of 0.027. They also found that the ferrofluid has the characteristics of shear thinning, and the viscosity changes little with temperature. Bo Le et al. [18] employed the chemical co-precipitation method and selected tetraethyl orthosilicate and silane coupling agent A1120 for synergistic coating of magnetic particles, resulting in a silicone oil-based ferrofluid with a saturated magnetization intensity of 2.51×10^{-2} T. They subsequently investigated the viscosity–temperature curve of the silicone oil-based ferrofluid. They found that the rate of viscosity change for the silicone oil-based ferrofluid was only 13cP/℃, which was 20 times lower than the aforementioned two fluids, demonstrating excellent viscosity–temperature characteristics. Li et al. [19] prepared a silicone oil-based ferrofluid-doped multiwalled carbon nanotube (MWNT) and studied its viscosity and magnetoviscous effect and found that MWNT could significantly improve its viscosity. Currently, research has been mainly focused on the influence of magnetic particles, silicone surfactants on the magnetic properties, viscosity, and stability of silicone oil-based ferrofluids. These studies have provided a brief analysis of shear-thinning behavior, magnetoviscous effects, viscosity–temperature characteristics, and viscoelastic properties from the perspective of viscosity changes. However, there is limited research on the micro-mechanisms underlying the overall rheological properties of silicone oil-based ferrofluids, particularly regarding the changes in the microstructure during the force application process. Given the incomplete understanding of the micro-mechanisms of rheology in silicone oil-based ferrofluids, limited experimental studies, and poor reproducibility, especially regarding the investigation of microstructural changes, it is necessary to conduct in-depth research on the comprehensive rheological properties of silicone oil-based ferrofluids.

Therefore, the rheological properties of the silicone oil-based Fe_3O_4 ferrofluid prepared were tested comprehensively with the Anton Paar Physica MCR 302 rotational rheometer in this study, and the shear-thinning mechanism was analyzed. Especially, the magnetoviscous effect of the silicone oil-based ferrofluid at different temperatures and shear rates was compared, and the influence mechanism of temperature and shear rate on the magnetoviscous effect was explained. Moreover, the microscopic mechanism of viscoelasticity was investigated.

2 Materials and methods

2.1 Materials

Ferric chloride ($FeCl_3 \cdot 6H_2O$) and ferrous sulfate ($FeSO_4 \cdot 7H_2O$) were purchased from China Pharmaceutical (Group) Shanghai Chemical Reagent Company. Aqueous ammonia (25%), silane coupling agent KH550 ($C_9H_{23}NO_3Si$), and modified silicone ($(CH_2)_2(CH_3)_2SiO(SiO(CH_3)_2)_nSi(CH_3)_2(CH_2)_2$) were purchased from Shanghai Maclin Biochemical Technology Co., LTD. All chemicals were of analytical grade without further purification. Deionized water was used throughout the experiments.

Experimental instruments include the LP10002B electronic scale, DZKW-4 electric thermostatic water bath, D-8401-WZ multi-kinetic electric stirrer, PHS-3C pH meter, DZF-6050AB vacuum drying oven, MEICO Fisher Scientific, and Anton Paar Physica MCR 302 rotational rheometer.

2.2 Preparation of the ferrofluid

Fe_3O_4 nanoparticles were prepared by the unprotected gas chemical co-precipitation method. The chemical equation of co-precipitation is as follows:

$$2Fe^{3+} + Fe^{2+} + 8OH^- \rightarrow Fe_3O_4 \downarrow + 4H_2O.$$

Considering the oxidation of ferrous ions, the precipitation reaction was carried out at the ratio of Fe^{2+}: $Fe^{3+} = 1{:}175$. After 0.200 mol $FeCl_3 \cdot 6H_2O$ and 0.115 mol $FeSO_4 \cdot 7H_2O$ were weighed, they were dissolved in 200 ml deionized water and placed in a water bath with stirring at a constant speed and heating up to 60℃. Then, 140 ml ammonia was added with constant stirring for half an hour to produce black Fe_3O_4 magnetic particles.

The temperature of the water bath containing the magnetic particle solution of Fe_3O_4 was raised to 80℃. Modified silicone oil with carboxyl group and silane coupling agent KH550 was used as a surfactant to improve settling stability and reduce aggregation, and after a certain amount of addition, the solution was stirred and covered for 1 h. The coated magnetic particles were separated from the mixed solution with magnets and then washed with deionized water to pH = 7. After washing, the particles were dried for 8 h in a vacuum drying oven at 75℃. Finally, the modified coated Fe_3O_4 magnetic particles were mixed with organosilicone oil, and the silicone oil-based Fe_3O_4 ferrofluid was obtained by rapid stirring and ultrasonic dispersion.

2.3 Characterization

The morphology of coated, modified Fe_3O_4 magnetic particles was observed using transmission electron microscope (TEM), as shown in Fig. 1. It can be seen from the figure that the magnetic nanoparticles coated with surfactants were spherical with an average particle size of 10.4 nm, and there was no significant aggregation observed. This indicates that the coating of surfactants does not alter the particle size and morphology of the magnetic nanoparticles. However, despite the surfactant coating preventing particle aggregation, there is still a slight tendency for aggregation among a small number of particles. This phenomenon can be attributed to the bad coating efficiency, as well as the small size of the magnetic particles and their high surface energy.

The magnetic properties of the silicone oil-based Fe_3O_4 ferrofluid were characterized by a vibrating sample magnetometer (VSM) at room temperature. Its magnetic hysteresis curve is shown in Fig. 2. It can be seen that the curve is smooth, without hysteresis, remanence and coercivity, confirming the superparamagnetism of the silicone oil-based Fe_3O_4 ferrofluid. The saturation magnetization of the ferrofluid was 5.98 emu/g and the weight fraction (wt%) of the particles in the ferrofluid can be calculated as 9.2%, showing good magnetic properties.

2.4 Rheological parameter

Considering the environmental conditions of silicone oil-based ferrofluids in sealing applications and the magnetoviscous effect and dynamic viscoelasticity in the simulated sealing application conditions, the commercial Anton Paar Physica MCR 302 rotary rheometer was selected to carry out rheological study on the prepared silicone oil-based ferrofluid in this study. The rheological equipment is presented in Fig. 3a, b. During the test, the parallel plate rotor (PP20, Anton Paar Co.) measuring tool with a diameter of 19.995 mm was used and maintained a 0.2 mm gap thickness for all the experiments between the two plates. So the volume of the ferrofluid sample controlled for each experiment was $0.25\pi d^2 h = 0.063$ ml. The variable magnetic field from 0 to a maximum of 692 kA/m was generated by the magnetorheological device (MRD) unit manufactured using the Anton Paar formula. The Peltier temperature control system and the water cycle temperature control system was used to rapidly raise and drop the temperature at the same time and keep a constant temperature. The precision of temperature control was set to ± 0.01℃ in the measurement process, as

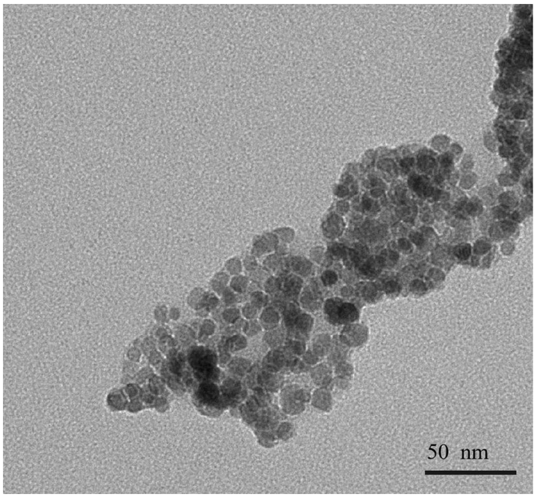

Fig. 1 TEM morphology of the modified Fe_3O_4 magnetic nanoparticles

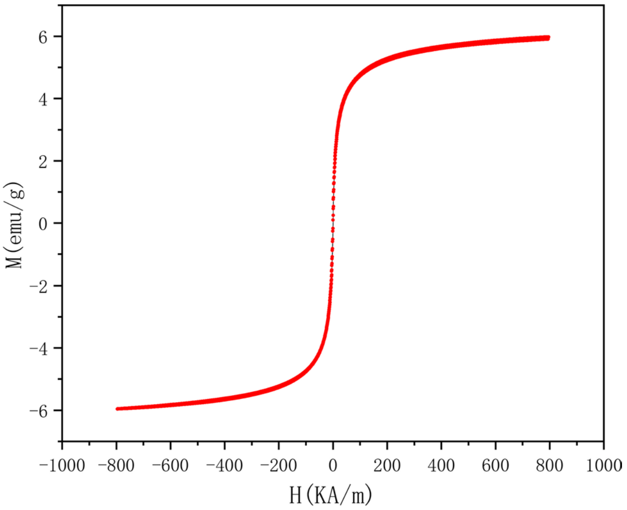

Fig. 2 VSM magnetic hysteresis curve of the silicone oil-based ferrofluid

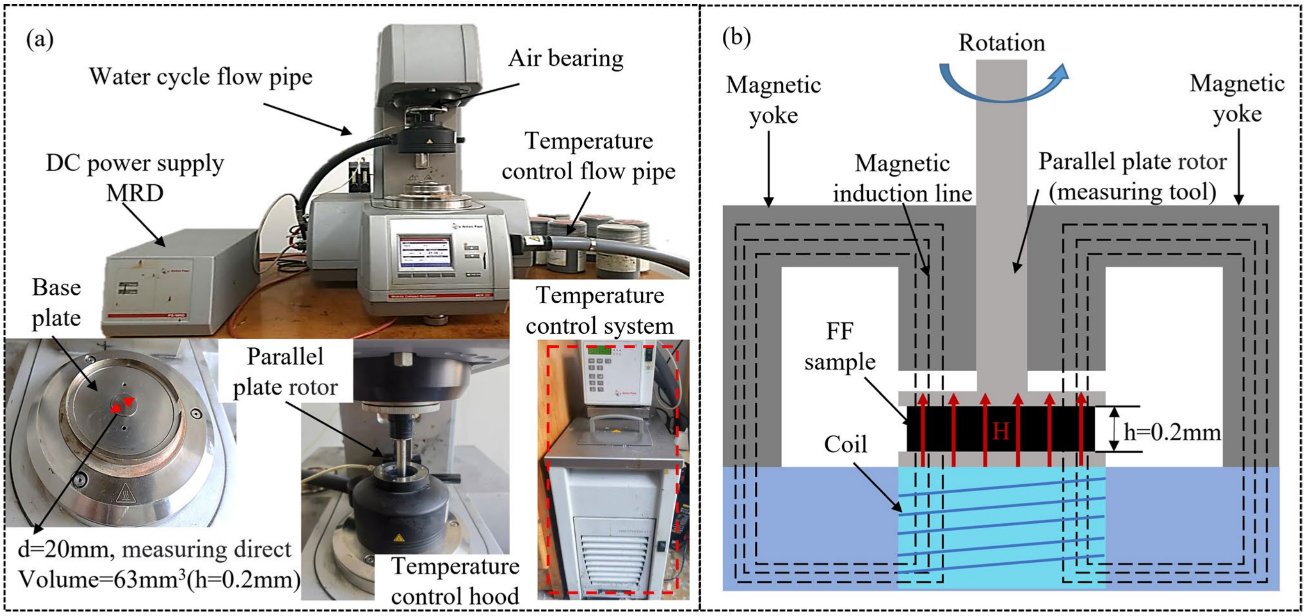

Fig. 3 Rheological measurement setup: **a** Rotary rheometer (Anton Paar MCR 302) and **b** Schematic diagram of rheological measurement and magnetic field direction

in Fig. 3a. During the experimental process, the ferrofluid sample was placed between the parallel plate rotor and the base plate. The testing magnetic field was generated by a coil fixed underneath the rheometer's bottom plate, as shown in Fig. 3b. The magnetic field passed through the parallel plates in the usual manner and the parallel plate were overlaid with a magnetic yoke to ensure the approximate homogenous field and perpendicular field lines with respect to the plate. The shear rate range for the rheological testing was 0–100 s^{-1}, while the magnetic field varied from 0 to 250 mT. In the viscoelastic testing, a fixed strain of 1% was used.

3 Results and discussion

3.1 Shear flow curve

The shear stress and shear rate curves of the prepared silicone oil-based ferrofluid under different magnetic fields are shown in Fig. 4. The slope of the curve is defined as the viscosity of the ferrofluid. When the magnetic field is set to 0 mT, the shear stress of the prepared silicone oil-based ferrofluid increases with the increase of the shear rate, and the slope is constant, showing an obvious linear relationship. Therefore, it can be considered that the viscosity of the ferrofluid is not affected by the shear rate under the condition of no magnetic field, which shows a Newtonian fluid behavior. When the magnetic field is applied, the shear stress of the ferrofluid at a low shear rate is significantly enhanced compared with that with no magnetic field, and increases with the increase of the shear rate, because the magnetic particles form a strong chain structure along the magnetic direction under the action of an external magnetic field. Nevertheless, the shear stress of the ferrofluid under a high shear rate is not much different from that under no magnetic field, because the internal chain structure of the ferrofluid under a high shear rate is destroyed and many small chain structures are formed, similar to the internal structure under no magnetic field. This indicates that the magnetic field plays a major role at low shear rates and the shear rate plays a major role at

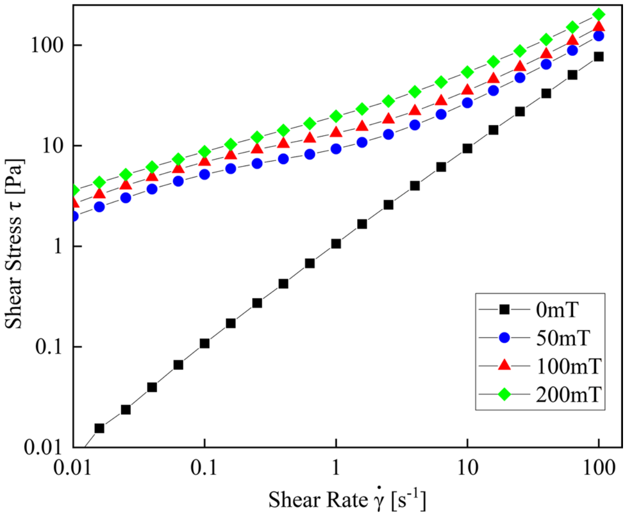

Fig. 4 Flow curves of the silicone-based ferrofluid under different magnetic fields

high shear rates under the influence on the internal structure of the ferrofluid. In addition, with the intensity of the applied magnetic field increased from 0 to 200 mT, the flow curve shows a nonlinear trend and moves upward, and the slope of the curve changes with the change of shear rate, which indicates the size and fluid resistance of the magnetic field induced structure increase with the increase of the magnetic field. It also means a stronger energy loss resulting in an increased shear stress of the ferrofluid, because the value of shear stress depends on the formation of weak structures between particles in a low magnetic field environment [20]. When the magnetic field is enhanced, a stronger and more compact chain or column structure is formed between the particles, and the collision between the particles is more intense under the shear action, which leads to the increase of stress. At the high intensity magnetic field of 200 mT, the nonlinear trend becomes very obvious, which shows that the unique shear rheological properties of the ferrofluid are different from those of Newtonian fluids, also known as the properties of non-Newtonian fluid.

The viscosity of the ferrofluid as a function of the shear rate is shown in Fig. 5. Compared with the stable viscosity of the ferrofluid without magnetic field, under the magnetic field, the viscosity of the ferrofluid decreases with the increase of the shear rate, which is the phenomenon of shear thinning. As the shear rate increases, the internal microstructure of the ferrofluid caused by the magnetic field is damaged, and a part of it is divided into a single particle, which leads to a decrease of viscosity and the phenomenon of shear thinning. As can be seen from the figure, with the increase of the shear rate, the viscosity changes more slowly and eventually becomes stabl, similar to that under no magnetic field at a certain shear rate. The results are the same as shown in Fig. 4.

The yield stress of the ferrofluid is very important for its application. It is commonly obtained by fitting with simple shear flow constitutive models, such as Einstein model, Bingham model, Carson model and Herschel–Bulkley (H–B) model. Since the ferrofluid shows the characteristics of non-Newtonian fluid, the H–B model [21] is used to fit the flow curve of the silicone oil-based ferrofluid. The mathematical expression of the H–B model is as follows:

$$\tau = \tau_{H-B}(H) + K\dot{\gamma}^{n}, \tag{1}$$

where $\tau_{H\text{-}B}(H)$ is the yield stress generated by the ferrofluid under the magnetic field strength H, K is the viscosity coefficient, and n is the flow index. The fitting results are shown in Fig. 6, and the flow curves under 50 mT, 100 mT, and 200 mT magnetic fields were fitted, respectively. The H–B model coefficients obtained from the fitting are shown in Table 1. It can be obtained from the table that the yield stresses of the samples under three different magnetic field intensities are 5.24 Pa, 7.28 Pa and 8.26 Pa, respectively. In addition, the flow index is all less than 1, indicating the shear-thinning characteristic of the silicone oil-based ferrofluid, which is consistent with the above analysis.

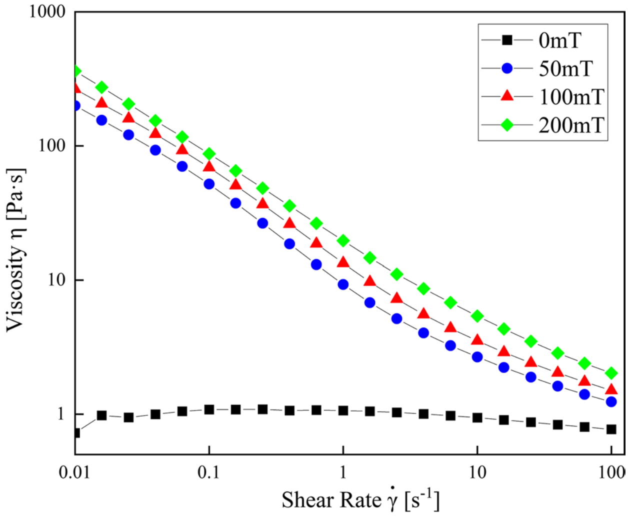

Fig. 5 The viscosity change of the ferrofluid with the intensity of a magnetic field under different shear rates

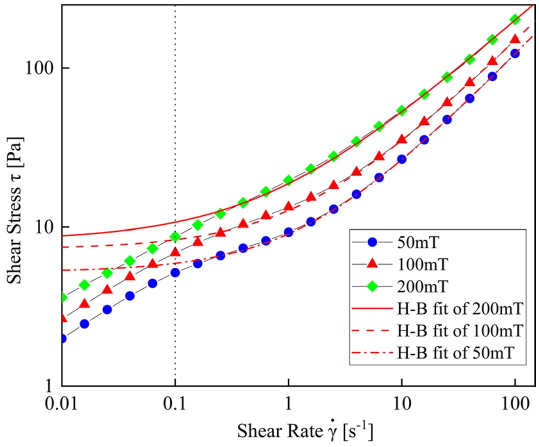

Fig. 6 The flow curves of the ferrofluid in three magnetic fields and the fit curves of the H–B model

Table 1 H–B model fitting parameter values of flow curves of three different magnetic fields

Magnetic fields	$\tau_{H\text{-}B}$/(Pa)	K	n
50 mT	5.24	3.84	0.74
100 mT	7.28	5.43	0.71
200 mT	8.26	10.50	0.63

The experimental data highly coincide with the fitting curve in Fig. 6. However, when the shear rate is less than $0.1s^{-1}$, the shear stress significantly decreases instead of converging to a constant value as predicted by the H-B model. This indicates the presence of a slow relaxation mechanism in the internal structure of the ferrofluid. In the static state, the ferrofluid forms large-scale columnar structures that are aligned in parallel along the direction of the magnetic field, as shown in Fig. 7a. These columnar structures are not disrupted at very low shear rates, while a significant number of side chains laterally attached to the inter-columnar bridges may cause slow relaxation, as shown in Fig. 7b. Due to the relatively loose internal structure of the ferrofluid and the relatively weak connections between the side chains and columns, the detachment and movement of the side chains result in an increase in fluid dynamic resistance at relatively low shear rates, exhibiting stress relaxation behavior. Similar phenomena resembling a soft glassy state [22], characterized by sluggish non-diffusive relaxation, have been observed in various colloidal systems [23]. Based on the above discussion, it can be concluded that accurately determining the yield point under continuous shear rates or shear rates is nearly impossible. Therefore, the use of the H-B model for fitting the yield stress of the ferrofluid is not sufficiently accurate, and caution should be exercised when using it for quantitative analysis, taking into account the fitting errors involved.

3.2 The magnetoviscous effect

The ferrofluids have a special rheological property of anisotropy under magnetic field. The magnetoviscous effect refers to the effect of viscosity of the ferrofluids changs with the magnetic field, which is the unique rheological property of the ferrofluids. In this study, the rotational rheometer was used to set different constant shear rates, and the change curves of the viscosity of the ferrofluid with the change of the magnetic field intensity were observed by changing the magnetic field intensity, so as to analyze the characteristics of the ferrofluid. According to the temperature control system of the rheometer, the magnetoviscous effect of the silicone oil-based ferrofluid under a series of temperature environments and four different shear rates was studied and the magnetoviscous curves are shown in Fig. 8.

From Fig. 8, we find that the silicone oil-based ferrofluid shows shear-thinning characteristics at all temperatures. The magnetoviscous effect has the same trend and decreases with the increase of the shear rate. Moreover, when the external magnetic field is continuously enhanced, the viscosity of the ferrofluid under the four shear rates shows a rapid upward trend at the lower magnetic field intensity range (< 50kA/m). This is because under the action of the external magnetic field, the particles inside the ferrofluid react quickly and arrange in the direction of the magnetic field to form a chain-like or drop-like structure, which increases the shear resistance and thus shows an increase in the viscosity of the ferrofluid. With the increase of the magnetic field, the viscosity of the ferrofluid increases due to the effect of "magnetic torque" [24]caused by the offset of magnetic moment, but the growth rate slows down and finally tends to be stable in the range of high magnetic field strength (100-250kA/m). Because the number of particles inside the ferrofluid is certain, the number of chain structures formed and the torque generated also maintain certain. And then under the continuous and stable shear action, these particles finally reach equilibrium with the magnetic field action, showing that the viscosity of the ferrofluid no longer increases with the increase of the magnetic field strength.

In addition, we can also see from the figure that under the same magnetic field and shear rate changes, the overall apparent viscosity of the silicone oil-based ferrofluid decreases with the increase of temperature, and the change range is also narrowing and gradually reaches the saturation state. The main reason is that silicone oil has good

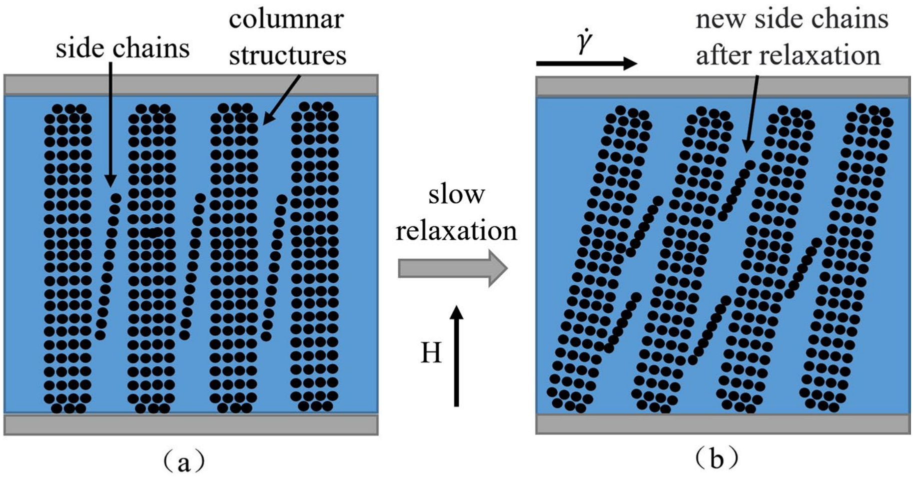

Fig. 7 The schematic diagram of slow relaxation mechanism of the ferrofluid at relatively low shear rates. **a** Microstructure of the ferrofluid in the static state under a certain magnetic field; **b** Microstructure of the ferrofluid after slow relaxation

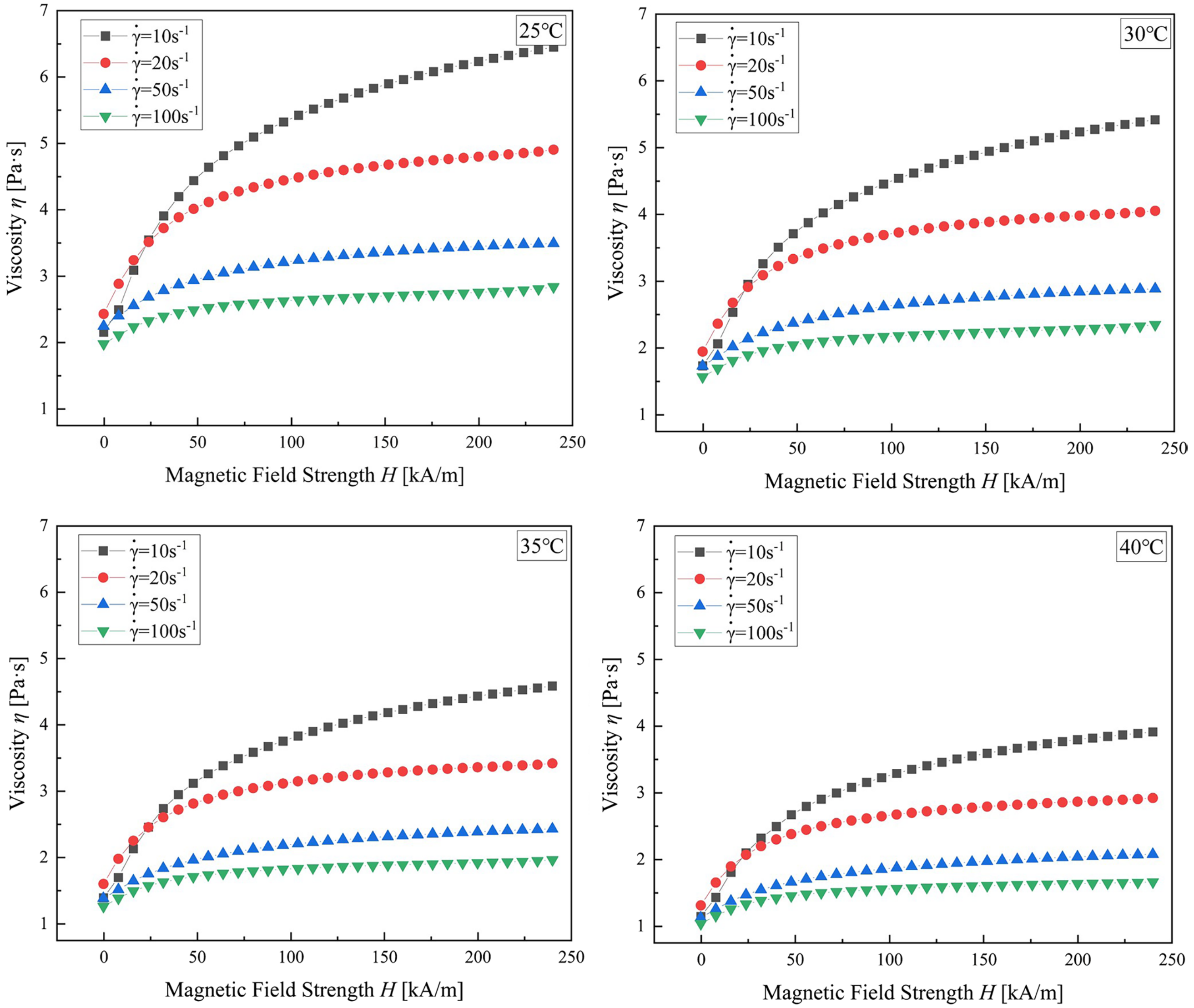

Fig. 8 The curves of viscosity of ferrofluid with the intensity of magnetic field under four shear rates at different temperatures

viscosity–temperature characteristics, and the ferrofluid prepared with silicone oil as the base liquid also has high-quality viscosity–temperature characteristics, that is, the viscosity change of the ferrofluid is less affected by temperature. The universality of the magnetic properties of this silicone oil-based ferrofluid is further demonstrated by the results in Fig. 8.

3.3 Influence of temperature on the magnetoviscous effect

To further verify the influence of temperature on the magnetoviscous effect of the silicone oil-based ferrofluid, the magnetoviscous parameter R was used as the reference quantity to explore the influence mechanism at high and low shear rates. R is usually used to quantify the degree of the magnetoviscous effect, which represents the relative change in viscosity under the magnetic field. The magnetoviscous parameter *R(H)* can be expressed as follows:

$$R(H) = \frac{\eta_H - \eta_0}{\eta_0}, \tag{2}$$

where η_H is the viscosity of the silicone oil-based ferrofluid under the magnetic field strength H, and η_0 is the viscosity of the silicone oil-based ferrofluid without the magnetic field.

The magnetoviscous curves and the relationship between the magnetoviscous parameter R and the magnetic field H of the silicone oil-based ferrofluid at different temperatures at high shear rates (100s^{-1}) are shown in Figs. 9 and 10, respectively. It can be seen from the two figures that the silicone oil-based ferrofluid tested at

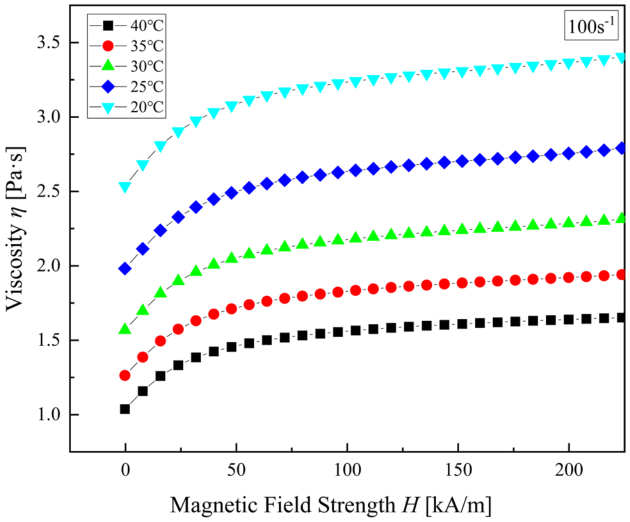

Fig. 9 The magnetoviscous curves of the silicone oil-based ferrofluid at different temperatures at a shear rate of 100 s^{-1}

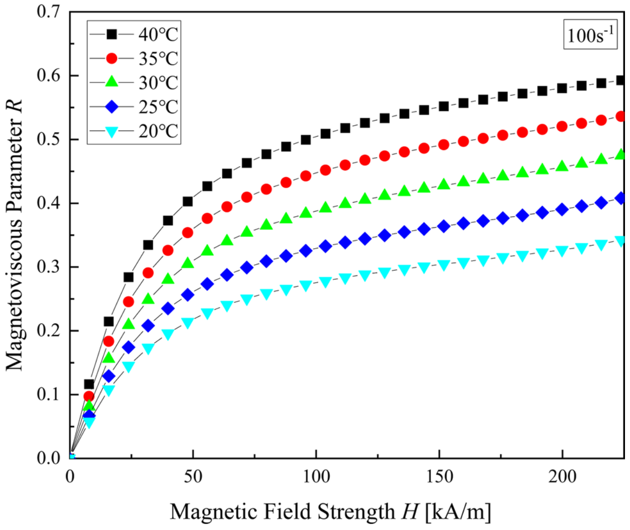

Fig. 10 The relationship between the magnetoviscous parameter and the magnetic field strength of the silicone oil-based ferrofluid at different temperatures at a shear rate of 100s^{-1}

each temperature shows the same trend of magnetoviscous properties, consistent with the results obtained above. At the same temperature, R increases with the increase of the magnetic field strength and eventually tends to be stable. This is because at the high shear rate of 100s^{-1}, most of the chain structure formed between the magnetic particles in the silicone oil-based ferrofluid is destroyed, which can be considered that there is no chain structure inside the ferrofluid. Therefore, the magnetoviscous effect is mainly caused by the interaction between the magnetic moment and the non-magnetic moment of the single magnetic particle in the ferrofluid under the magnetic field. At this point, the magnetic particles in the unit volume reach equilibrium under magnetic torque and viscous torque, as shown in the formula:

$$\mu_0 M \times H = 6\phi\eta_C\left(\omega_P - \omega_C\right), \tag{3}$$

where μ_0 is the magnetic permeability, M is the saturation magnetization of the ferrofluid, H is the magnetic field strength, η_C is the viscosity of base carrier liquid, ω_P is the angular velocity of particle rotation, and ω_C is the angular velocity of base carrier liquid under vortex flow [25]. When the magnetic moment ($\mu_0 M \times H$) of magnetic particles increases with the increase of the magnetic field, and the viscosity η_C of the silicone oil as the base carrier liquid remains unchanged, the angular velocity difference (ω_P-ω_C) between the liquid–solid phases of the ferrofluid increases according to Eq. (3). Thereby, the magnetoviscous effect will be enhanced, as shown by R increasing with the increase of the magnetic field intensity H. Moreover, the motion of the magnetic particles is completely bound by the magnetic field when the magnetic field strength increases to a certain value, at which the magnetoviscous effect tends to saturate.

Under the same magnetic field, the viscosity of the silicone oil-based ferrofluid decreases with the increase of temperature, the magnetoviscous parameter R increases with the increase of temperature, and the maximum value of R is positively correlated with temperature. This is because the saturation magnetization M of the silicone oil-based ferrofluid is basically unchanged under the constant magnetic field. Since the viscosity η_C of the silicone oil as the base carrier liquid decreases with the increase of temperature, the angular velocity difference between the two phases (ω_P-ω_C) will increase to balance with the magnetic moment according to Eq. (3), which ultimately shows that the magnetoviscous parameter R increases with the increase of temperature. Otherwise, the ferrofluid shows macroscopic magnetoviscous characteristics, because the magnetic moment and the viscous moment cancel each other out. The magnetic moment is not affected by temperature, so the change of the magnetically induced viscosity (η_H-η_0) is approximately constant. The zero-field viscosity η_0 decreases with the increasing temperature due to the viscosity–temperature properties of the silicone oil. Therefore, according to Eq. (2), the maximum value of R increases with the increasing temperature, which is the same as concluded from the above analysis.

The magnetoviscous curves at different temperatures and the relationship between the magnetoviscous parameter R and the magnetic field H are shown at a lower shear rate ($10/20/50\text{s}^{-1}$) in Fig. 11. It can be seen that at the three low shear rates, the ferrofluid exhibits the same trend of magnetoviscous effect as at a high shear rate, and the mechanism is the same. In addition, at a low shear rate, the magnetic particles form anisotropic chain-like and columnar

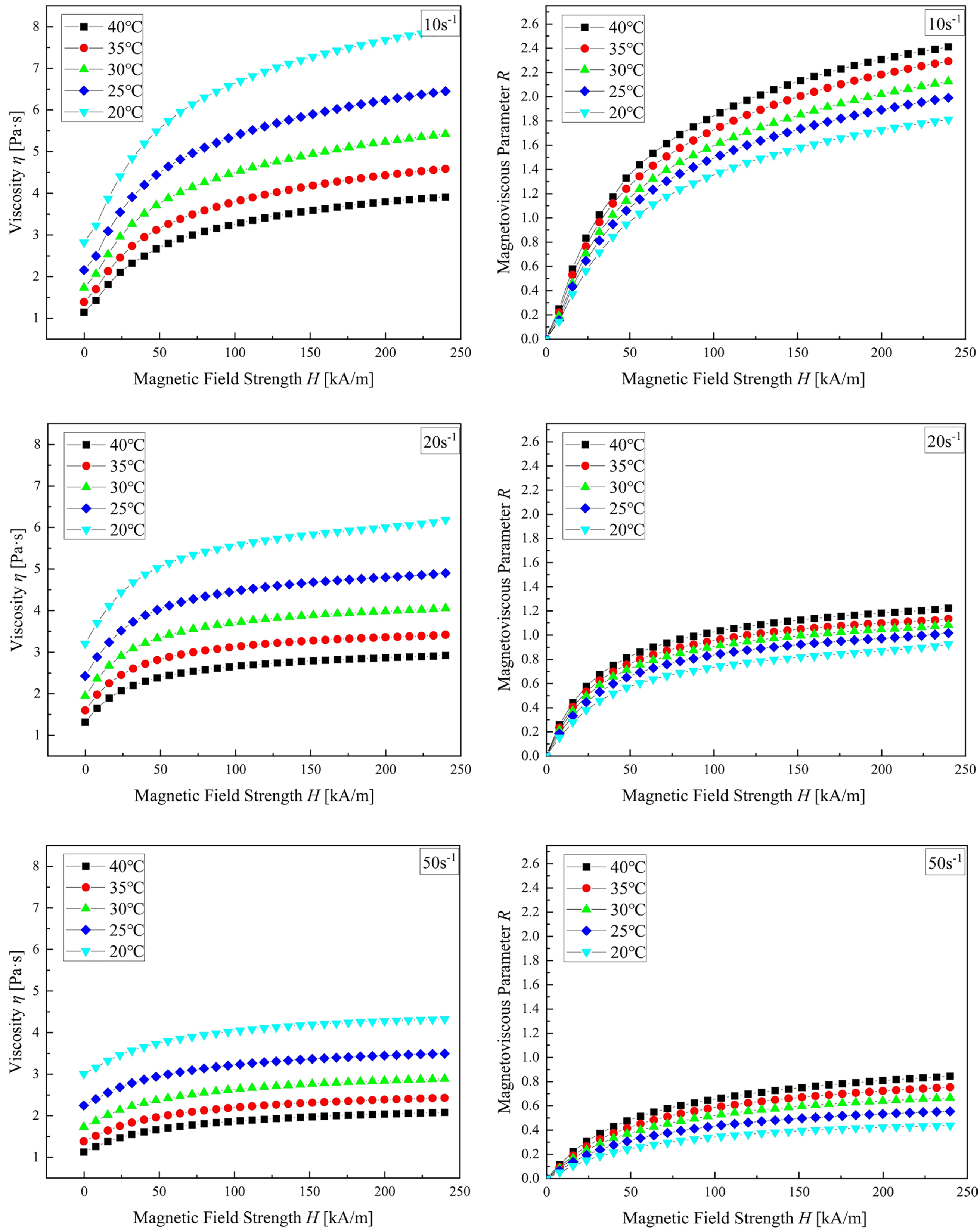

Fig. 11 The magnetoviscous curves and the curves of relationship between the magnetoviscous parameter and the magnetic field at different temperatures

microstructure under the magnetic field, causing the magnetic field viscosity η_H to increase with the increase of the magnetic field, while the zero magnetic field viscosity η_0 can be considered as unchanged under the influence of the base carrier liquid, so the viscosity increment (η_H-η_0) increases with the increase of the magnetic field. Therefore, according to Eq. (2), the magnetoviscous parameter R increases with the increase of the magnetic field strength at the same temperature. However, the increase of the shear rate only results in the destruction of the chain or columnar structure inside the ferrofluid, and then in the reduction of the variation of the magnetoviscous effect as shown in Fig. 11.

We can also see from Fig. 11 that the zero magnetic field viscosity η_0 of the ferrofluid decreases with the increase of temperature. Since the interaction between particles in the ferrofluid is very weak at zero magnetic field, this phenomenon is mainly determined by the viscotemperature properties of the base carrier liquid of the ferrofluid. Under the strong magnetic field, the changes of magnetic field viscosity η_H of the ferrofluid with temperature is similar to that of the zero magnetic field viscosity η_0. According to the theory of Zubarev chain structure model of the ferrofluid, the relationship between the average chain length and temperature T in the shear flow of ferrofluid can be obtained as follows:

$$\bar{\mathrm{n}} \propto \mathrm{e}^{\frac{1}{T}}, \tag{4}$$

where e is the constant associated with the magnetic and flow field parameters [26]. With the increase of temperature, the free energy E_f of the chain structure inside the ferrofluid is increased, the chain length distribution function g_n is narrowed, and the average chain length of the structure is decreased, so that the viscosity increment (η_H-η_0) of the ferrofluid due to the magnetic field decreases. According to the quantitative relationship, the change in the zero magnetic field viscosity η_0 of the ferrofluid is smaller than that of the magnetic field viscosity η_H of the ferrofluid. Therefore, according to Eq. (2), the magnetoviscous parameter R increases with the increase of temperature under the same magnetic field at a low shear rate, which is in correspondence to the R–H curve in Fig. 11.

3.4 The study of viscoelasticity

With complexity, the internal microstructure of the ferrofluids behaves differently under different rheological test conditions, such as aggregation and relaxation behaviors, which make the ferrofluids show both the viscosity of ordinary fluid and the elasticity of traditional solid materials, that is, unique viscoelastic characteristics.

The modulus of the ferrofluids is an important parameter for the study of viscoelasticity. The variation trends of the storage modulus G' and loss modulus G" of silicone oil-based magnetic liquid in the linear viscoelastic region under different magnetic fields with frequency are shown in Fig. 12. The closed symbols indicate the storage modulus and the open symbols indicate the loss modulus. It can be observed in Fig. 12 that the storage modulus and loss modulus increase with the increase of the magnetic field, which can be attributed to the field-sensing structure formed by the magnetic particles. When the magnetic field is applied to the ferrofluid in the static state, the internal magnetic particles will be arranged in parallel along the direction of the magnetic field and form a large columnar structure. However, the internal columnar structure will be split into a single-chain structure when the applied stress exceeds its yield stress, which is manifested as an increase in the viscosity of the ferrofluid, and then this internal structural change leads to an increase of the loss modulus G". Besides, with the increase of frequency, the magnetic particles inside the ferrofluid will vibrate, and when some particles have no time to relax, the response of the overall modulus will be generated, and then this part of the response will be stored, leading to the increase of the storage modulus G'.

The frequency scan curves of general structured liquids can be divided into two types. In the first type, the loss modulus is always larger than the storage modulus. In the second type, both the storage modulus and the loss modulus increase with frequency, and a region appears where the storage modulus is greater than the loss modulus, so the curves intersect twice. The width of the "crossing" region depends on the number and size of the structures formed in the liquid [27]. For the ferrofluids, the frequency scan curve is the second type. The closed symbols indicate the storage modulus and the open symbols indicate the loss modulus. In

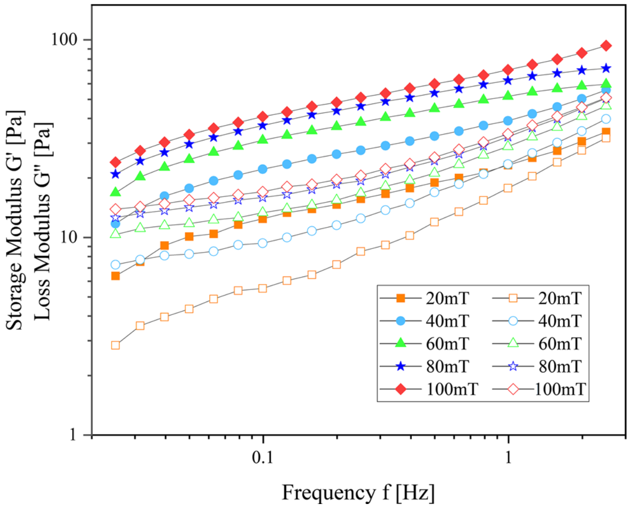

Fig. 12 The positional relationship of storage modulus and loss modulus with frequency under different magnetic fields

the case of low frequency, the storage modulus G' is close to the loss modulus G", It can be inferred from the trend that at a lower frequency (less than 0.01Hz), G" > G', due to the fact that the internal microstructure of the ferrofluid is not destroyed but in a relatively relaxed state, where the energy loss is mainly viscous loss. When the oscillation frequency reaches 0.01Hz, the first intersection point of the storage modulus G' and the loss modulus G" appears, which marks the formation of a large columnar structure. At this time, the corresponding frequency is the liquid–solid transition frequency of the ferrofluid, and the characteristic relaxation time of the internal structure of the ferrofluid can be obtained by taking the inverse of this frequency. However, after the first intersection point, the increase of oscillation frequency is G" < G'. The part microstructure of the ferrofluid cannot reach the relaxation state in time, resulting in the energy growth of the elastic part of the ferrofluid and then a significant increase of the storage modulus G'. At this time, the ferrofluid exists in a solid state dominated by elasticity. When the frequency increases to near 10Hz, the two modulus curves intersect again. The glass transition [28] occurs in the interior of the ferrofluid, which represents the existence of more intense energy loss inside, and then the ferrofluid is kept in a fluid state dominated by viscosity.

4 Conclusion

In this paper, a silicone oil-based ferrofluid was prepared by the chemical co-precipitation method. The average size of Fe_3O_4 magnetic particles was 10.4 nm and the saturation magnetization of the ferrofluid was 5.98 emu/g, which were characterized by TEM and VSM. The flow characteristics, magnetoviscous effect and viscoelasticity of the ferrofluid were studied by rotational rheometer. From the flow curve, an obvious shear-thinning phenomenon was found and non-Newtonian fluid characteristics of the silicone oil-based ferrofluid under the external magnetic field were shown. The yield stress of the ferrofluid under three different magnetic field intensities of 50 mT, 100 mT and 200 mT was 5.24 Pa, 7.28 Pa and 8.26 Pa respectively, which was obtained through the H–B model fitting the flow curve. However, at the continuous shear rate, it was not possible to accurately obtain the yield stress of the ferrofluid by fitting the flow curve with the H–B model. In addition, a strong magnetoviscous effect could be observed at different shear rates and temperatures, and the magnetoviscous parameter R increased with the increase of temperature and its variation decreased with the increase of shear rate. The microscopic mechanism of the temperature influence on the magnetoviscous effect at higher and lower shear rates corresponded to the two microscopic constituent units of single particles and chain structure based on the viscoelastic properties of the base liquid, respectively. Finally, a discussion on the microstructure evolution mechanism of ferrofluid in the process of modulus changing with frequency was presented through the viscoelastic analysis of silicone oil-based ferrofluid, and thus the experimental results were explained.

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Data availability The data that support the findings of this paper are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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