ISSN (Print) 1226-1750
ISSN (Online) 2233-6656
Journal of Magnetics 28(1), 77-83 (2023)
https://doi.org/10.4283/JMAG.2023.28.1.077

Research on Synthesis and Rheological Properties of Silicone Oil-based Ferrofluid with Dual Surfactants

Hongchao Cui[1,2,3]*, Jiahao Xu[1,2], Jiajia Zhang[1,2], Jingjing Lu[1,2], and Zhenkun li[1,2]*

[1]*School of Mechanical, Electronic and Control Engineering, Beijing Jiaotong University, Beijing 100044, PR China*
[2]*Key Laboratory of Vehicle Advanced Manufacturing, Measuring and Control Technology (Beijing Jiaotong University), Ministry of Education, Beijing 100044, PR China*
[3]*Beijing Key Laboratory of Flow and Heat Transfer of Phase Changing in Micro and Small Scale, School of Mechanical, Electronic and Control Engineering, Beijing Jiaotong University, Beijing 100044, China*

(Received 3 August 2022, Received in final form 11 January 2023, Accepted 20 January 2023)

Ferrofluids as a new kind of nano-functional material, possessing both magnetism of solid material and fluidity of liquid material, thus, they have extensive scientific research and engineering application value. To avoid the defects of conventional non- or single silane coupling agent in silicone oil-based ferrofluid preparation, TEOS and KH-792 were introduced as surfactants to modify Fe_3O_4 magnetic nanoparticles (MNPs). Silicone oil modified by carboxylic acid was used as based liquid because of improved compatibility with surfactants. Silicone oil-based ferrofluid was prepared by high-energy ball milling method, and its rheological properties were studied. The saturated magnetization of the silicon oil based ferrofluid was 142.71 Gs. When external magnetic field was applied, the MNPs formed a chain structure in the microscope. The viscosity of ferrofluid increased with magnetic field and the shear stress rose with shear rate. The viscosity decreased steeply with increasing temperature and shear rate. The viscosity of silicone oil-based ferrofluid was 950 mPa·s at 25 °C and can vary from 2044 mPa·s at 5 °C to 465 mPa·s at 40 °C. The ferrofluid transformed from a Newtonian fluid at zero magnetic field to a shear-thinning pseudoplastic Bingham fluid when an external magnetic field was applied. The viscosity varied from 1.37 to 2.38×10^5 mPa·s at zero shear rate. While, when magnetic field varied from 0 kA/ rose to 160 kA/m, the viscosity increased obviously and this phenomenon became more pronounced as the shear rate decreased. When magnetic field intensity was higher than 64 kA/m, the viscosity increased slowly with increasing shear rates and viscosity curve was close to a straight line at 100 s^{-1}. This study expands the idea of exploring the synthesis of ferrofluids with mixed surfactants. Silicone oil-based ferrofluid is expected to have unique application prospects in the aerospace field, especially in space damping, sealing and biomedicine.

Keywords : ferrofluid, silicone oil-based ferrofluid, dual surfactant, rheological properties, synthesis

1. Introduction

As a new type of nano-functional material, ferrofluids possess many unique properties. Their applications have been extended from machinery, electronics, energy, chemical, environment, and biomedical to aerospace, military, and other fields. With the application expansion, working conditions of ferrofluids become more and more complex, new demands are placed on the performance, while conventional ferrofluids can no longer satisfy. Compared with traditional ferrofluids, silicone oil-based ferrofluid possesses unique viscosity-temperature properties, temperature resistance, low volatility, stable chemical properties, long service life, and other advantages, especially suitable for extreme environmental conditions. The preparation and performance study of silicone oil-based ferrofluid have become a hot research topic. Silicon oil surfactant ethoxy terminated polydimethylsiloxane (EtO-PDMS) was used to modify the Fe_3O_4 nanoparticles [1]. The Fe_3O_4 nanoparticles were first coated with a SiO_2 layer by hydrolysis of tetraethoxysilane. Then, by the active hydroxyl groups on SiO_2 surface, silicon oil surfactant was covalently grafted onto Fe_3O_4 nanoparticle surface. Silicon oil-based ferrofluid was prepared with oleic acid as surfactant [2], viscosity properties were investigated by a rotating viscometer and a torsional oscillation cup

---

*Corresponding author: Tel: +01051684006
Fax: +8651684006, e-mail: hccui@bjtu.edu.cn,
e-mail: zhkli@bjtu.edu.cn

viscometer, respectively. Bai *et al.* [2, 3] prepared $Fe_3O_4@SiO_2$ core-shell magnetic particles by hydrolysis method, which was coated by silane coupling agent A1120 and dispersed in dimethyl silicone oil. Serrano [4] dispersed magnetic particles coated by SiO_2 in silicon oil to prepare magnetorheological fluid, and rheological behavior in static and sinusoidal fields as disturbances were studied. A silicon surfactant of α,ω-(3-aminopropyl) polydimethylsiloxane and a polydimethylsiloxane polymer was used to prepare silicone oil-based ferrofluid in Jong-Hee Kim's [5] research. MNPs were synthesized by chemical co-precipitation with multi-walled carbon nanotube (MWNT) of 0.5 wt%. Then, silane coupling agents N-(2-aminoethyl)-3-aminopropyltrimethoxysilane was used to modify the MNPs [6]. Results showed that MWNT significantly increased the viscosity of ferrofluid. Wang [7] investigated $CoFe_2O_4$ nanoparticles grown on multi-walled carbon nanotubes (MWCNTs) by ultrasonic-assisted. The obtained MWCNTs/$CoFe_2O_4$ was adopted to fabricate a uniform magnetorheological fluid (MRF). It revealed that the designed MRF suspension exhibited typical MRF features with increasing viscosity, shear stress, yield stress, storage modulus, and loss modulus depending on the applied magnetic fields. Mesoporous Fe_3O_4 nanospheres were synthesized by the solvothermal method and applied in preparation of MRF. The MRF exhibited a rapid and reversible transition from a liquid-like to a solid-like state under the action of an external magnetic field, and showed enhanced sedimentation stability [8]. Uniform Fe_3O_4 submicron spheres assembled by tiny nanocrystals were fabricated via a facile one-step solvothermal strategy. The formed MRF with excellent sedimentation stability behaved as a Newtonian fluid without an external magnetic field and turned into Bingham behavior under the action of magnetic field [9]. Sodium dodecyl benzene sulfonate and oleic acid were used as surfactants to modify soft magnetic carbonyl iron particles The particles were dispersed in dimethyl silicone oil to produce mechanical magnetorheological fluid [10]. Duan [11] modified two kinds of magnetic particles with different surfactants in combination: sodium laurate and silane coupling agent, ethyl orthosilicate and poly-ethoxysiloxane, respectively, and then dispersed them in silicone oil by ultrasound to prepare ferrofluid. Ashtiani [12] summarized magnetorheological fluid produced by micron-scale particles dispersing in silicone oil, and rheological properties were also studied. The micron-scale particles, such as Fe, carbonyl iron, iron oxide or $Fe_{76}Cr_2Mo_2Sn_2P_{10}B_2C_2Si_4$ amorphous metal alloy particles were coated with stearic acid, silicon or sterol. Rabbani [13] dispersed micron carbonyl iron powder into silicone oil and added stearic acid and palmitic acid respectively to improve the stability of MRF. Hollow MNPs were synthesized and then dispersed in silicon oil to prepare MRF with a volume concentration of 10 %, which was proved to be Bingham fluid by flow curve experimental study [14]. Anupama [15] added non-surfactant $Ni_{0.5}Zn_{0.5}Fe_2O_4$ synthesized by hydrothermal method into silicone oil, dispersed them by mechanically stirring and ultrasonic for 15 min to prepare MRF with concentrations of 10 %, 20 %, and 40 %, respectively.

At present, magnetic particles modified by silicon surfactants are often used to prepare MRF, and MRF is very different from ferrofluid. The magnetic particles in MRF are micrometer scale, while in ferrofluid are nanometer scale. Ferrofluid requires lasting uniform and stable suspension, while MRF does not need to be kept in a long-term stable suspension, and magnetic particles can precipitate from the based liquid. In the preparation of silicon oil-based ferrofluid, hydrocarbon surfactants such as acid or a single silane coupling agent are mostly used to modify Fe_3O_4. The compatibility of hydrocarbon surfactants and silicone oil is poor, while magnetic particles tend to precipitate from based liquid, then solid-liquid two phase is formed. A single silane coupling agent is prone to form $Fe_3O_4@SiO_2$ core-shell structure, which will reduce not only magnetic properties, but also suspension performance, and then affect the rheological properties. The lesser volume fraction of stable suspended magnetic particles the lower saturation magnetization. In this paper, two kinds of silane coupling agents were used to improve surface modification performance of magnetic particles and suspension stability in silicone oil, and the rheological properties were investigated.

2. Materials and Experiments

2.1. Materials

Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and ferric trichloride ($FeCl_3 \cdot 6H_2O$) were purchased from Xilong Scientific Co., Ltd. Absolute ethyl alcohol and ammonium hydroxide (25 %) were procured from Beijing Chemical Industry Group Co., Ltd. The silane coupling agents TEOS (Tetraethyl orthosilicate) and KH-792 (*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane) were obtained from Beijing Chemical Industry Group Co., Ltd and Yangzhou Wanhe Chemical Co., Ltd respectively. Carboxylic acid modified silicone oil was purchased from Shin-Etsu. The purity grade of the chemicals was analytical reagent (AR) and used as received without further purification. Deionized water with a resistivity of 18.2 MΩ·cm filtered by an ultrapure water machine (PSDK2-20-C) in the lab.

2.2. Experiments

Considering Fe^{2+} will partially oxidize into Fe^{3+} in a non-protective atmosphere, adjusted mole ratio of Fe^{2+}: Fe^{3+} to 1:1.75 and dissolved them in deionized water. 25 % ammonia as precipitant was added into the mixed solution at 60 °C with stirring, Fe_3O_4 MNPs were formed by co-precipitation [16, 17]. Washed Fe_3O_4 MNPs with deionized water to pH=9 and dispersed the particles in anhydrous ethanol, heat up to 65 °C, TEOS and KH-792 were added into the flask, proceed moderate coating for 2 hours with continuous stirring. Collected the modified Fe_3O_4 MNPs by a magnet, the modified Fe_3O_4 MNPs were obtained after washing, filtering, and vacuum drying.

The dried magnetic particles (g) were mixed with silicone oil (mL) in a ratio of 1:10. Intermittent cycle cooling was adopted to prevent oxidation of magnetic particles due to temperature increase during ball milling. With 30 minutes of ball milling and 20 minutes of intervals, it usually took 12 to 30 such cycles, and the process may last 6 h to15 h. Then took out the mixture and placed in a magnetic field to settle and remove the large particles. The upper black and bright gloss homogeneous suspension liquid was silicone oil-based ferrofluid. Magnetic peaks appeared under the action of an external magnetic field, degradation and sedimentation did not occur even prolonged exposure to gravity field, centrifugal field, and magnetic field.

2.3. Characterization

The magnetic property was carried out by vibrating sample magnetometer (VSM) of model 8604 from Lakeshore Company. The maximum magnetic field of 1T, the sensitivity was 1.2×10^{-7} emu/g, and the test temperature was 25 °C. An inverted microscope, Olympus gx41, with a magnification of 100x-1000x was used to observe the microstructure of silicone oil-based ferrofluid directly with and without an external magnetic field. Anton Paar's MCR302 magnetic rheometer with 19.995 mm plate diameter, 1.995° cone angle and 0.084 mm measurement gap was used in the experiment to measure the magnetic-viscosity characteristics of the ferrofluid. The sample volume was 0.1 ml. The magnetic field measurement range was 0-160 kA/m and the temperature range was 0-40 °C.

3. Results and Discussion

3.1. Magnetic properties

Fig. 1 shows the micrographs of diluted silicone oil-based ferrofluid observed by microscope in and absence of magnetic field, the objective magnification was 1000X. From the micrographs, when there is no magnetic field, the magnetic particles in ferrofluid show uniform suspension and dispersion due to irregular Brownian thermal motion. When an magnetic field was applied, the magnetic particles began to rearrange themselves along the direction of magnetic field lines to form a particles chain structure from their original random state [18]. The larger the external magnetic field was, the more magnetic particles arranged in the direction of magnetic field line. The longer the chain structure was, the more stable the structure was. This is also the cause of viscosity increase of ferrofluid in magnetic field.

Ferrofluid shows magnetic property due to magnetic particles were magnetized and rearranged when an external magnetic field is applied, but ferrofluid itself does not present magnetism without magnetic field. When the magnetic field is removed, the ferrofluid immediately loses its magnetism. Fig. 2 are magnetization curves of Fe_3O_4 MNPs and silicone oil-based ferrofluid. The saturation magnetization of synthesized Fe_3O_4 MNPs without modification was 70.04 emu/g, and slightly reduced to 57.41 emu/g after modification because of nonmagnetic silane coupling agents. The silicone oil-based ferrofluid gradually magnetized and increased with

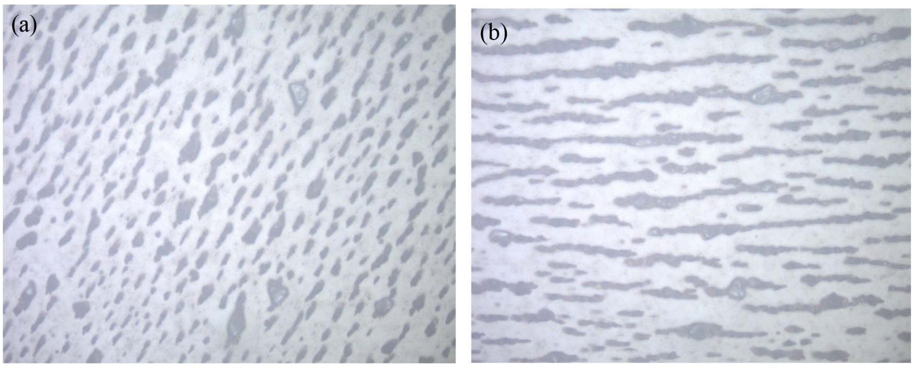

Fig. 1. (Color online) The distribution of magnetic particles without (a) and with (b) magnetic field.

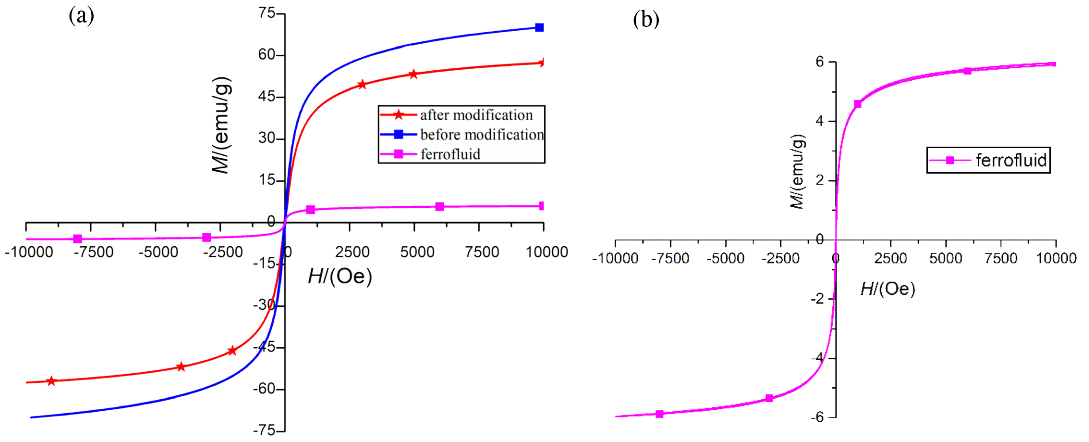

Fig. 2. (Color online) Magnetization curve of Fe_3O_4 MNPs and silicone oil-based ferrofluid.

the rise of the magnetic field. It was basically saturated when the magnetic field reached to 8000 Oe and the saturation magnetization was 5.98 emu/g from Fig. 2(b). When saturation reached, even improve magnetic field, the magnetization intensity of ferrofluid did not increase significantly. The magnetization curves are approximately S-shaped, showed no remanence, no coercivity and without hysteresis phenomena. The initial magnetic susceptibility was above zero calculating by $\chi = M/H$, which indicated that silicone oil-based ferrofluid was superparamagnetic. The density is 1.90 g/ml, and saturation magnetization was 142.71Gs calculated by the formula $M_S = 4\pi\rho\sigma_S$. Because the based liquid is non-magnetic and the magnetism is mainly provided by Fe_3O_4 magnetic particles. Due to the ratio of magnetic particles and silicone oil being 1:10, the magnetism of the synthesized magnetic liquid was significantly reduced.

3.2. Flow curves

Fig. 3 shows the flow curve of silicone oil-based ferrofluid, and the top left corner was a zoomed-in view of the shaded portion shown in the square. It can be seen from the figure that shear stress increased with the increase of shear rate. Without the magnetic field, the flow curve was a straight line with a fixed slope across zero, and the slope was the value of flow viscosity, which indicates that ferrofluid was a Newtonian fluid at zero magnetic field. When an external magnetic field was applied, the shear stress in the flow curve increased as the magnetic field strength increase and viscosity was no longer a constant value.

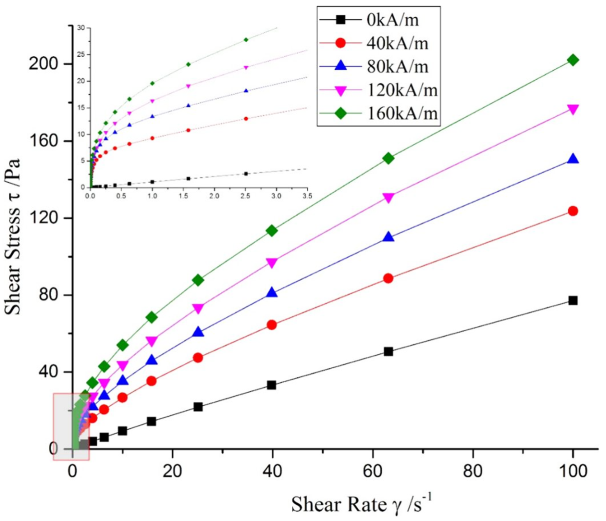

Fig. 3. (Color online) Flow curve of ferrofluid.

3.3. Magnetoviscous effects

Fig. 4 shows the relation of ferrofluid viscosity with shear rate in different magnetic fields. From the figure, it can be seen at 25 °C, the viscosity of ferrofluid at zero magnetic field was a straight line parallel to the X axis, indicating that the viscosity basically did not change with shear rate, which was consistent with Newtonian fluid characteristics, and the average viscosity was about 950 mPa·s. When magnetic field was applied, the viscosity of ferrofluid was significantly different from that at zero magnetic field. Firstly, viscosity shown an exponential decrease with increasing shear rate. Secondly, the greater the magnetic field strength at the same shear rate, the greater the viscosity. Viscosity decreased with increasing shear rate indicating that the ferrofluid was a pseudo-plastic fluid. The viscosity at zero shear rate varied from 1.37 to 2.38 × 10^5 mPa·s, with a 10^2 magnitude decreased compared to zero magnetic field viscosity of 950 MPa·s. The viscosity of ferrofluid increased with the enhancement of magnetic field, indicating that the magnetic particles in

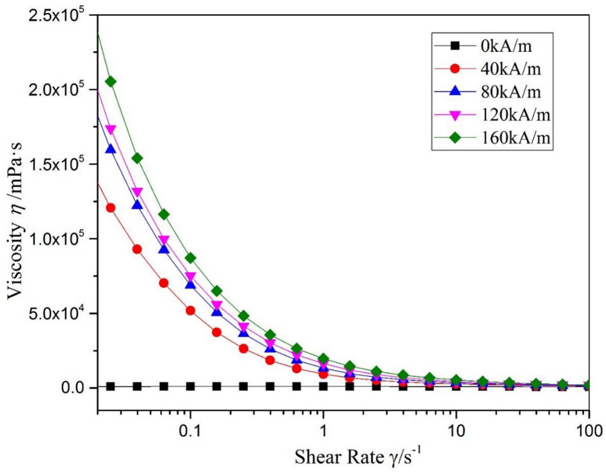

Fig. 4. (Color online) Relationship between viscosity and shear rate in different magnetic fields.

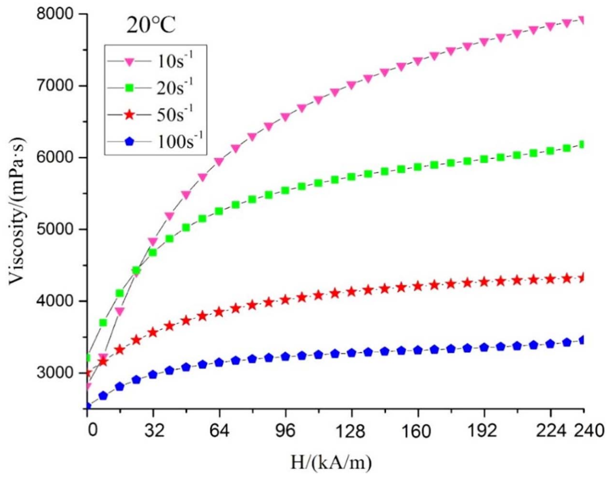

Fig. 5. (Color online) The relationship between the viscosity of the ferrofluid and the magnetic field strength at different shear rates.

ferrofluid show a chain-like structure or columnar structure when the magnetic field was applied. The force between the chain segments enhanced, and the frictional resistance increased when the chain segments move, which was macroscopically expressed as an increase in viscosity. As the shear rate increased, the chain structure or column structure was destroyed and shear thinning occurred. Therefore, in contrast, the viscosity decreased with increasing shear rate, which also indicated that silicone oil-based ferrofluid was nolonger a Newtonian fluid under the action of external magnetic field, but a shear-thinning pseudoplastic Bingham fluid.

Fig. 5 shows the relationship between the viscosity of ferrofluid and magnetic field strength at different shear rates. As the magnetic field enhanced, the magnetic particles in the ferrofluid started to arranged regularly from the random structure of Brownian motion. As the magnetic field was enhanced, the magnetic particles took on a highly ordered three-dimensional ring or mesh-like structure. The stress to be overcome to cut off this structure became larger, which is expressed as an increase in viscosity.

When the external magnetic field increased from 0 to 160 kA/m, the viscosity increased significantly, and this phenomenon presented more significant with the decrease of the shear rate. When the magnetic field strength was higher than 64 kA/m, the increasing trend of viscosity slowed down and tended to be linear. A nonlinear fit to the magnetic viscosity curve was performed and the fitting equation was,

$$\eta = y_0 + A_1(1 - e^{(-H/t_1)}) + A_2(1 - e^{(-H/t_2)}) \quad (1)$$

The parameters at different shear rates were shown in Table 1.

The solid icons in Fig. 6 were the experimental value curves, and the hollow icons were the fitted curves. From

Table 1. Fitted parameters of viscosity at different shear rates

Shear rate (s^{-1})	10	20	50	100
y_0	2732.03591	3222.8954	3002.47351	2533.94899
A_1	3576.89344	4645.98839	587.88041	5.74645E16
t_1	0.27548	6.81506	0.20777	2.77774E14
A_2	10298.37327	2016.74594	858.74937	582.7521
t_2	8.56362	0.18882	0.77179	0.16917

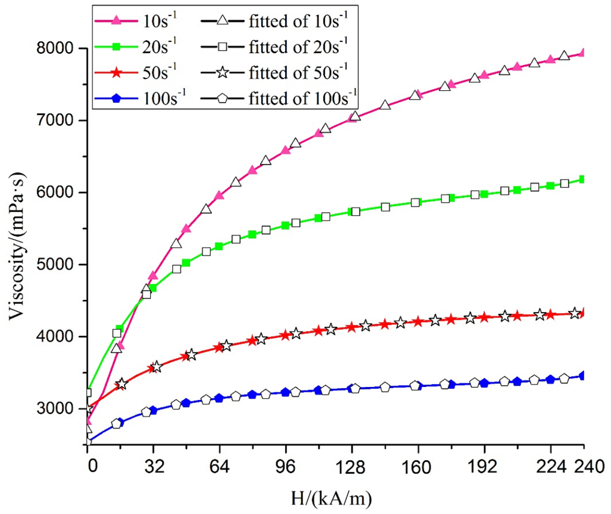

Fig. 6. (Color online) Non-linear fitted curve of magnetic viscosity curve.

the figure, it can be seen that the fitted values and the theoretical values basically overlap together, and the fitted equation and parameters were reasonable. The fitted curve can be used to calculate the ferrofluid viscosity at different shear rates.

3.4. Viscosity-temperature characteristics

The viscosity-temperature curve of silicone oil-based ferrofluid in different magnetic fields were shown in Fig. 7. From the viscosity-temperature curve, it can be seen that viscosity decreased with increasing temperature in both the case of zero magnetic field and applied magnetic field. The viscosity was 950 mPa·s at 25 °C and can vary from 2044 mPa·s at 5 °C to 465 mPa·s at 40 °C. The viscosity in different applied magnetic field exhibit the same law. The difference was that at the same temperature, the viscosity increased with the increase of magnetic field, which was consistent with the mechanism of magnetoviscous effect. When the magnetic field was applied, the magnetic particles in ferrofluid will be arranged into a chain-like structure along the magnetic line. Force and frictional resistance between the chain segments became stronger with magnetic field. The macroscopic manifestation was an increase in viscosity. At the same time, at low temperature, the molecular chains of the based liquid exhibit a random cross-linked structure with mutual constraints and hold-ups between them. The magnetic particles in ferrofluid performed random Brownian motion between molecular chains of based liquid. When the temperature increased, the spacing between molecular chains of based liquid expanded by the energy provided by external thermal field. The chain structure or network structure was stretched and the intermolecular force was weakened. On the other hand, magnetic particles gained kinetic energy at high temperatures. Thermal movement "frees" the particles from the binding system between molecular chains of the original based liquid. More individual magnetic particles were released and internal friction between chain segments was reduced [19]. This will not only lead to a decrease in the viscosity of ferrofluid, but its saturation magnetization will also increase in magnetic field.

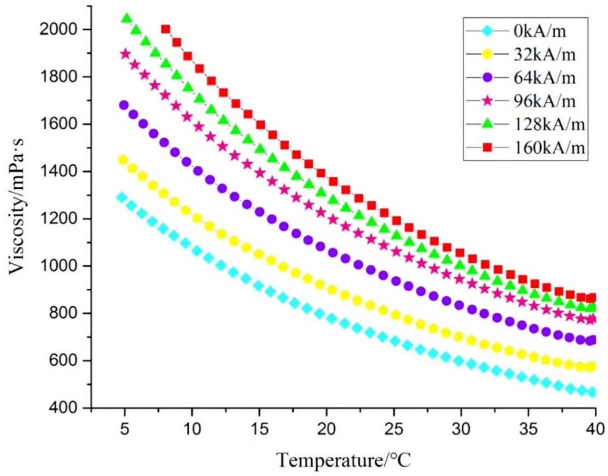

Fig. 7. (Color online) Viscosity-temperature curve of silicone oil-based ferrofluid in different magnetic fields.

4. Conclusions

Silicone oil-based ferrofluid was prepared by dual surfactant of TEOS and KH-792 silane coupling agents, and its rheological properties were studied. The saturated magnetization was 142.71Gs. The viscosity increased with the increase of external magnetic field, and decreased steeply with the growth of temperature and shear rate. The viscosity was 950 mPa·s at 25 °C and can vary from 2044 mPa·s at 5 °C to 465 mPa·s at 40 °C. When magnetic field was applied, Newtonian fluid turned to shear-thinning pseudoplastic Bingham fluid, and viscosity varied from 1.37 to 2.38×10^5 mPa·s at zero shear rate. When the magnetic field rose from 0 kA/m to 160 kA/m, the viscosity increased obviously and this phenomenon was more significant with the decrease of shear rate. When magnetic field was higher than 64 kA/m, the viscosity increased slowly with increasing shear rates and viscosity curve was close to a straight line at 100 s^{-1}.

Acknowledgments

This study has been supported by the Fundamental Research Funds for the Central Universities (2022JBMC032), Beijing Natural Science Foundation (2222072), Foundation of Key Laboratory of Vehicle Advanced Manufacturing, Measuring and Control Technology (Beijing Jiaotong University), Ministry of Education, China (M21GY1300050), and National Major Instrument Research and Development Program of Natural Science Foundation of China (51927810).

Data Availability Statements: All data generated or analyzed during this study is included in this published article.

Conflicts of Interest: The authors declare no conflict of interest.

References

[1] H. J. Chen, Y. M. Wang, J. M. Qu, R. Y. Hong, and H. Z.

Li, Appl. Surf. Sci. **257**, 10802 (2011).

[2] S. Wang, C. Yang, and X. Bian, J. Magn. Magn. Mater. **324**, 3361 (2012).

[3] L. Bai, Z. Zhang, L. Xu, N. Di, and D. Li, J. Funct. Mater. **11**, 018 (2017).

[4] R. Agustín-Serrano, F. Donado, and E. Rubio-Rosas, J. Magn. Magn. Mater. **335**, 149 (2013).

[5] J. H. Kim, K. B. Park, and K. S. Kim, Composites Research **30**, 41 (2017).

[6] W. Li, Z. Zhang, and D. Li, Smart Mater. Struct. **28**, 065023 (2019).

[7] F. Wang, Y. Ma, H. Zhang, J. Gu, J. Yin, X. Jia, H. Zhang, Y. Wang, X. Fu, and R. Yu, J. Mol. Liq. **324**, 115103 (2021).

[8] G. Wang, J. Geng, X. Qi, T. Du, Y. Zeng, R. Yu, M. Yuan, H. Peng, H. Li, and C. Chen, J. Mol. Liq. **336**, 116389 (2021).

[9] G. Wang, J. Geng, T. Guo, X. Qi, R. Yu, Z. Zhang, Y. Wang, Z. Wang, Z. Li, and P. Li, Ceram. Int. **48**, 29031 (2022).

[10] D. Wang, X. Liu, L. Wang, Y. Ren, and Q. Zhang, Open. Mec. Eng. J. **9**, 682 (2015).

[11] P. Duan, Master, Beijing Jiaotong University, Beijing (2014).

[12] M. Ashtiani, S. Hashemabadi, and A. Ghaffari, J. Magn. Magn. Mater. **374**, 716 (2015).

[13] Y. Rabbani, M. Ashtiani, and S. H. Hashemabadi, Soft Matter. **11**, 4453 (2015).

[14] J. S. An, W. J. Han, and H. J. Choi, Colloids Surf., A. **535**, 16 (2017).

[15] A. V. Anupama, V. Kumaran, and B. Sahoo, Powder Technol. **338**, 190 (2018).

[16] S. Slimani, C. Meneghini, M. Abdolrahimi, A. Talone, J. P. M. Murillo, G. Barucca, N. Yaacoub, P. Imperatori, E. Illes, M. Smari, E. Dhahri, and D. Peddis, Appl. Sci-Basel. **11**, 5433 (2021).

[17] M. J. Eskandari and I. Hasanzadeh, Mat. Sci. Eng. B. **266**, 115050 (2021).

[18] Y. Huang, D. C. Li, F. Li, Q. S. Zhu, and Y. Xie, Opt. Commun. **338**, 551 (2015).

[19] Z. Li, J. Yao, and D. Li, J. Magn. Magn. Mater. **424**, 33 (2017).