Study on Rheological Properties of Nanofluids

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Abstract: Based on the previous research on the rheological properties of nanofluids by many scholars at home and abroad, to solve the problem that the viscosity of conventional polymer water control agents is large and cannot meet the demand for increasing production capacity in the process of tight gas reservoir exploitation, this paper takes self-made nanofluids as the research object, tests the rheological properties of self-made nanofluids by rheological experiment, and systematically studies the effects of concentration, temperature and shear action on the viscosity of nanofluids, and the dynamic viscoelasticity and thixotropy of nanofluids were discussed. The results show that the rheological type of nanofluid belongs to power-law fluid, but it is related to the shear rate. The viscosity of nanofluids increases with the increase of concentration; when the temperature increases, the viscosity of nanofluids decreases and the fluidity increases; under the shear action, the viscosity of nanofluid changes very little and has good shear resistance; the dynamic viscoelastic test shows that the storage modulus G’ of the nanofluid is larger than the loss modulus G”, showing elastic characteristics; the thixotropy test shows that when the shear rate is accelerated, the viscosity decreases with time, and when the shear rate is slowed down, the viscosity recovers rapidly with time, which has good thixotropy. The research results provide an important theoretical basis for further research on the application of nanomaterials in tight oil and gas reservoirs.

1. Introduction
Nanofluid is a brand-new functional fluid, which is a kind of suspending liquid of ultramicro particles [1-5] formed on account of a certain liquid and being added nanoparticles according to a certain formula and ratio. It has attracted the attention of many experts and scholars at home and abroad due to its low degree, small size, low energy consumption, no pollution and wide application. Therefore, to make nanofluids better applied in the field, it is of great significance to study their rheological properties.

Viscosity is a key index for studying the rheological properties of fluids [6-7], and that’s why many domestic and foreign scholars have carried out studies on the viscosity of nanofluids. Yu Li, Bian Yongning, et al [8,10,12,17,18] found that the larger the volume fraction of nanoparticles combined with the lower temperature, the higher the viscosity of the nanofluid; Pang Dongshan, Gu Chunyuan, et al [9,14] revealed that the reason for the increase in the viscosity of nanofluids lies in the increase in the concentration of nanoparticles. When the shear rate is less than the critical shear rate value, the viscosity of the nanofluid does not change much, but when the shear rate is greater than the critical shear rate value, the viscosity of the nanofluid increases rapidly and the viscosity of the low-concentration nanofluid increases faster. Mo Ziyong, Wu Zhangyong, et al [11] reckoned that the fluid state of the nanofluid differs when the shear rate is changed. Ouyang Xinwang, Wu Zhangyong, et al [13] believed that the viscosity of nano TiN fluid changes inversely with the stirring time in the
early stage, while the viscosity decreases to a fixed value in the later stage and does not change with the extension of the stirring time. Song Zhengzheng, Wu Zhangyong, et al [15] found that the rheological properties of Nano-B4C water-based nanofluids have a greater relationship with the type and particle size of the dispersant. Su Chengyan, Huang Wende, et al [16] discovered that the more stearic acid in the modified nano-calcium carbonate, the lower the viscosity of the CaCO3/DOP system. The viscosity of the nanofluid could even increase to 790% due to the presence of nanoparticles. ApmannKevin [20] considered that the increase in the concentration of nanoparticles can lead to an increase in their viscosity as well as the increase in the size of nanoparticles can reduce the viscosity of nanofluids.

As mentioned before, scholars have conducted much researches on the rheological properties of nanofluids due to their low viscosity, small size, low pollution, low energy consumption and wide application in the oil sector. However, there are few studies on the application of the rheological properties of nanofluids in exploiting tight gas reservoirs. Therefore, in order to solve the problem that the viscosity of conventional polymer water-controlling agents cannot meet the demands of increasing productivity during the exploitation of tight gas reservoirs, this paper analysed the influence of the concentration, temperature and shear rate on the viscosity of nanofluids, and discussed the dynamic viscoelastic and thixotropic properties of nanofluids, taking self-made nanofluids as the research object, and thus providing a reference for the application of nanofluids in tight gas reservoirs.

2. Experiment

2.1 Materials and Experimental Instruments

Materials used in the experiment: modified silicone oil nanofluid, (self-made, colourless, and doorless) whose main components are modified silicone oil, deionized water, emulsifier, low-molecular alcohol, and electrolyte, the mass ratio is 11.19:78.30:6.82:3.02:0.67, and median diameter is of 5.37 nm, Zeta potential 47.93 mV.

Instruments used in the experiment: Rheometer (Model MCR102, AntonPaar, Austria)

2.2 Method

2.2.1 Rheological Types of Nanofluids

Prepare different concentrations of nanofluids at the temperature of 30 °C and the shear rate of 0.01 s⁻¹ ~ 1000s⁻¹, according to the experimental requirements. Then, test the relationship between shear stress and shear rate. Finally, determine the rheological type of the self-made nanofluids according to the relationship.

2.2.2 Analysis on Influencing Factors of Nanofluid Viscosity

(1) Prepare 0.2%, 0.4%, 0.6%, 0.8%, 1.0%, 6.25%, 25%, 50%, 75%, 100% concentration nanofluids with deionized water, use coaxial cylinder measurement unit (CC27 (open system)) to measure the viscosity of nanofluids at different concentrations at a constant temperature of 30°C and a shear rate of 7.34 s⁻¹, then discuss how the viscosity of nanofluids changes with concentration;

(2) Use a coaxial cylinder measuring unit (CC32 (closed system)) to measure the viscosity of the 100% concentration nanofluid, in the temperature range of 30 °C ~ 70 °C, under the condition of a shear rate of 7.34s⁻¹, furthermore, and then discuss the change rule of nanofluid viscosity at different temperatures;

(3) Use a coaxial cylinder measuring unit (CC27 (open system)) to continuously shear the 100% nanofluid at a shear rate of 1000s⁻¹ for 1 h, and discuss the effect of shear on the viscosity of the nanofluid.

2.2.3 Research on the Viscoelasticity and Thixotropic Properties of Nanofluids

1) Viscoelasticity
Under the condition that the angular frequency range of the dynamic oscillating experiment is 100 ~ 0.1 rad/s, the cone-plate measuring unit (CP50) is used to carry out the dynamic viscoelastic experiment of the nanofluid solution. To begin with, the linear viscoelastic region is scanned in the strain amplitude range of 0.01% to 100% to be assured, furthermore, the best experimental strain amplitude is determined in the linear viscoelastic region, and the dynamic oscillation experiment is performed with the strain amplitude as a fixed value. The specific experimental steps are as follows:

a) Find out the linear viscoelastic region: set the frequency to 1.0 Hz, the strain (amplitude) is between 0.01 and 100%, obtain the relationship curve of the dynamic modulus ($G'$ and $G''$) with the strain (amplitude), and finally, determine the linear viscoelastic area of the nanofluids through the storage modulus $G'$ platform area.

b) Test dynamic modulus: The variation range of the oscillation angular frequency is 100 ~ 0.1 rad/s, and the relationship curve between the dynamic modulus of nanofluid and the angular frequency is obtained through the test.

2) Thixotropic properties

The thixotropy of nanofluids was tested based on the thixotropic loop method.

First, increase the shear rate continuously from 1 s$^{-1}$ to 1000 s$^{-1}$, and measure the change of its stress with the shear rate; then decrease gradually from 1000 s$^{-1}$ to 1 s$^{-1}$, and measure the change of its stress with the shear rate; finally, the obtained closed curve of shear rate and shear stress is called a thixotropic loop. And then analyse the thixotropic property of the nanofluid based on the thixotropic loop.

3. Results and Discussion

3.1 Determine the Type of Self-Made Nanofluid

The relationship between shear rate and shear stress of 100% concentration nanofluids is shown in Figure 1. Under the shear rate of 0.01 ~ 1000 s$^{-1}$, it meets with the power-law model and fits it with the formula $\tau = K\gamma^n$, where $\tau$ refers to shear stress (Pa), $K$ consistency coefficient (Pa·sn), $\gamma$ shear rate (s$^{-1}$), and $n$ Power law index (when $n$≤1, it became pseudoplastic fluid; when $n$≥1, it became swelling plastic fluid; when $n$=1, it became Newtonian fluid). When the shear rate is less than 117s$^{-1}$, the rheological law of the nanofluid follows $\tau = 0.0032\gamma^{1.0255}$. Figure 1 shows $R^2$=0.9976,
indicating that the model has a good fit for the rheological curve of the nanofluid. On the contrary, when the shear rate is greater than 117 s\(^{-1}\), the rheological law of the nanofluid follows \( \tau = 0.0003 \gamma^{1.5461} \), as shown in Figure 1, \( R^2=0.9983 \). Under the action of the change of the shear rate, as the viscosity of the nanofluid fluctuates, the consistency coefficient \( K \) increases to 0.0003, indicating that the nanofluid is a power-law fluid.

3.2 The Influence of Concentration, temperature, and Shear Action on the Viscosity of Nanofluid

After analysis, the main factors that affect the viscosity of the nanofluid are 1) concentration; 2) temperature; 3) shear rate.

1) Concentration

Use deionized water to prepare 0.2%, 0.4%, 0.6%, 0.8%, 1.0%, 6.25%, 25%, 50%, 75%, 100% concentration of nanofluid, adopt the coaxial cylinder measurement unit (CC27 (Open system)) to measure the viscosity of nanofluids at different concentrations at a constant temperature of 30°C and a shear rate of 7.34 s\(^{-1}\), and discuss how the viscosity of nanofluids changes with concentration.

The experimental results are shown in Figure 2. After testing, it was found that the viscosity of the 0.2% to 100% concentration nanofluid was stable at 0.822 mPa\(\cdot\)s to 3.193 mPa\(\cdot\)s. When the concentration of nanofluid is less than 25%, that is, the viscosity of the nanofluid with a concentration of 0.2% ~ 6.25% is very close, and as the concentration of nanofluid increases, the viscosity of the nanofluid shows an overall upward trend.

2) Temperature

Adopt a coaxial cylinder measuring unit (CC32 (closed system)) to measure the viscosity of the 100% concentration nanofluid, under the condition of a shear rate of 7.34 s\(^{-1}\), in the temperature range of 30°C ~ 70°C, and then discuss the change rule of nanofluid viscosity at different temperatures.
The experimental results are shown in Figure 3. The viscosity of the nanofluid will decrease as its temperature rises, and the decrease will gradually decrease. When the temperature is between 64.8°C and 70°C, the viscosity of the nanofluid will be 1.58 mPa·s fluctuates slightly. When the temperature is 30°C, the viscosity of the nanofluid is 3.2 mPa·s; when the temperature rises to 70°C, the viscosity of the nanofluid drops to 1.58 mPa·s. When the temperature of the nanofluid rises by itself, the nanofluid molecules in the microscopic state will accelerate when heated, which will weaken the interaction force between internal molecules. While in the macroscopic state, the fluidity of nanofluid is enhanced, which reduces the viscosity of nano-fluid, and the viscosity decreases about 51% from 30°C to 70°C. This indicates that nanofluids are easier to inject into the formation when their fluidity is enhanced by temperature.

3) Shear action

Adopt a coaxial cylinder measuring unit (CC27 (open system)) to shear continually 100% concentration nanofluid at a shear rate of 1000 s⁻¹ for 1 h, and then the influence of shear on the viscosity of the nanofluid is discussed.
The experimental results are shown in Figure 4. When the nanofluid is sheared at a shear rate of 1000 s\(^{-1}\) for 1 h, the viscosity value fluctuates slightly. In the initial 10 min, the viscosity of the nanofluid was maintained at 10.7 mPa·s; the viscosity of the nanofluid was maintained at 10.8 mPa·s between 10 min and 40 min; while between 40 min and 60 min, the viscosity of the nanofluid was maintained at 10.9 mPa·s. In summary, when shearing for 1 h at a shear rate of 1000 s\(^{-1}\), the viscosity of the nanofluid fluctuates very little, only 2%. Thus, the effect of high shear action on the viscosity of the nanofluid is not significant.

3.3 Viscoelastic and Thixotropic Properties of Nanofluids

1) Dynamic viscoelasticity

a) Find out the linear viscoelastic region

The strain variation interval adopted in the experiment is 0.01% ~ 100%. And the cone-plate measuring unit (CP50) is used to measure the change of the storage modulus \(G'\) of the nanofluid solution in this variation interval. The experimental results are shown in Figure 5.

![Figure 5 Variation curve of nanofluid storage modulus with strain](image)

The size of the nanofluid storage modulus \(G'\) remained unchanged in the strain range of 0.01% to 0.14% (Figure 5). When the strain is greater than 0.14%, the size of the storage modulus \(G'\) of the nanofluid decreases as the strain increases. Therefore, the plateau range of the change of the storage modulus \(G'\) of the nanofluid is 0.01% ~ 0.14%, that is, the linear viscoelastic region of the nanofluid.

b) Test dynamic modulus

The linear viscoelastic region of the nanofluid solution is 0.01% ~ 0.14% in Figure 5, therefore, the fixed strain is set as 0.1% while the pulsatance change range is 100 ~ 0.1 rad/s. Then the cone-plate measuring unit (CP50) is used to conduct a dynamic oscillating test to measure the law of dynamic modulus of the nanofluid with the variation of angular frequency to determine the dynamic viscoelasticity of the nanofluid.
The experimental results shown in Figure 6 show that in the measured oscillating angular frequency range, both the storage modulus and loss modulus of the nanofluid solution decrease with the decrease of the angular frequency. In the range of angular frequency of 0.1 ~ 100 rad/s, $G'$ is greater than $G''$, nanofluids will exhibit its elastic characteristics.

2) Thixotropic properties

In order to study the thixotropy of nanofluids, a coaxial cylinder measuring unit (CC27 (open system)) was used to measure the shear stress changes of nanofluids in the shear rate range of 1 ~ 1000 s$^{-1}$. The thixotropic loop shown in Figure 7 is obtained.

In the upward loop (white box), the shear stress of the nanofluid increases in a power-law mode with the increase of the shear rate; in the descending loop (black square), the shear stress of the nanofluid gradually decreases with the decrease of the shear rate.

From the overall view of the thixotropic loop, the two curves of the upward loop and the downward loop overlap. The area of the thixotropic loop enclosed by the upward loop and the downward loop is very small (almost no), which indicates that the viscosity of nanofluid can be quickly restored to meet the construction requirements after being subjected to shearing action. Thus, it can be concluded that the nanofluid has good thixotropy.
4. Conclusions

(1) The rheological type of nanofluid is a power-law fluid, the change of whose rheological law has a certain relationship with the shear rate.

(2) The viscosity of the nanofluid shows an upward trend with the increase of the concentration of the nanofluid. When the concentration of the nanofluid is less than 25%, the viscosity is maintained at about 0.854 mPa·s; when the concentration is greater than or equal to 25%, the viscosity is between 1.007 mPa·s and 3.193 mPa·s. When the concentration is 100%, it is only 3.193 mPa·s. When the temperature increases from 30°C to 70°C, the viscosity of the nanofluid decreases, that is, the viscosity of the nanofluid decreases with the increase in temperature, besides this, the viscosity eventually drops by about 51%. The effect of high shear on the nanofluid viscosity was not obvious, and its viscosity was maintained at 10.8 mPa·s with an up and down fluctuation of 0.1 mPa·s.

(3) In the range of angular frequency 0.1 ~ 100 rad/s, nanofluid has certain elastic characteristics. After the nanofluid is subjected to shear action, its viscosity can quickly recover as well as it has superior thixotropy, which fully meets the needs of the mine.

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