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Original Paper

Study on the thixotropy and structural recovery characteristics of waxy crude oil emulsion

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A B S T R A C T

Waxy crude oil emulsion has thixotropic properties at the temperature near gel point, which is a macro-mechanical characterization of the structure failure and recovery of waxy crude oil emulsion. In this paper, the thixotropic behaviors of waxy crude oil emulsion near gel point were studied using hysteresis loop formed by stress linear increase and decrease, as well as the structural recovery characteristics. The influence of the loading conditions and water content on the thixotropy of waxy crude oil emulsion were analyzed with hysteresis loop area. The concept of "structural recovery" was introduced to study the degree of structural recovery after different stewing, and influencing factors were taken into account. Results have shown that for waxy crude oil emulsion, the failure to fully restore of the structure after lysis is the cause of the formation of hysteresis loop, and the loading conditions will not affect the strength of thixotropy and the degree of structural recovery. Additionally, the dispersed phase droplets weaken the thixotropy and structure recovery characteristics of waxy crude oil emulsion, and the greater the water content, the weaker the thixotropy. The findings can help to better understand the safe and economic operation of waxy crude oil-water pipeline transportation.
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1. Introduction

With the development of global oil and gas exploitation to the deep sea, the ocean has become the main battlefield of oil and gas exploitation. In the production of offshore oilfield, waxy crude oil and water flow together in the pipeline. Due to the low-speed shear of the wellbore and pipeline and the high-speed shear of the pump and throttle valve, it is easy to form a water-in-oil (W/O) emulsion (Umar et al., 2016). Meanwhile, the resin and asphaltenes in crude oil are natural surfactants, which promote the formation of crude oil emulsion with good stability (Mirshekar et al., 2020).

Most of the crude oil produced in offshore oilfield is high wax crude oil (Chen et al., 2018 Zhang et al., 2013), which has complex rheological properties including thixotropy (Jiang et al., 2005 Struchkov et al., 2020). Due to the existence of dispersive droplets and the synergy between droplets and wax crystals, the thixotropic characteristics of W/O emulsions are more complicated than that of single crude oil. In addition, due to accidents or planned maintenance of equipment, the shutdown is inevitable. Along with the pipeline shutdown, the fluid temperature drops rapidly. When the fluid temperature drops below the wax appearance temperature (WAT) of crude oil, wax crystals will precipitate in the W/O emulsion system. With the wax crystals increase, a spatial network is formed by the interaction of wax crystals. At this point, the dispersed phase droplets are enclosed within the spatial structure (Sun and Zhang 2016). When a shearing is applied to the spatial structure, the skeleton of the network is destroyed, and then the liquid crude oil and dispersed droplets will be released. On the other hand, the shearing effect will cause the deformation of dispersed droplets, resulting in that the flow resistance and apparent viscosity of the gel system decreases. As the shearing effect is reduced or stopped, the gelling structure will gradually recover, that is, the system showed thixotropy. Due to the thixotropy of W/O waxy crude oil emulsion gelling system, when the pipeline restarts, it is necessary to ensure that the flow rate continues to increase until reach the steady state, otherwise it will lead to the secondary condensation accident. In other words, the

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thixotropic property of W/O waxy crude oil emulsion gelling system is an important parameter for the calculation of shutdown-restart and pumpability evaluation for high waxy crude oil-water pipeline (Abedi et al., 2019 Sun et al., 2016).

At present, most of research on the rheology of crude oil emulsions pay attention to the description and prediction of viscosity (Zadymova et al., 2017 Talal et al., 2015), the distribution of dispersed phase particle size (Alade et al., 2019 Chen et al., 2005) and the interface properties (Guo et al., 2013 Leebyn et al., 2017). In addition, there are also some reports on the viscoelasticity of the time-dependent rheological behavior of waxy crude oil emulsions (Feng et al., 2019 Ionescu et al., 2020). However, there are few studies on the thixotropic and recovery properties of waxy crude oil emulsions (Nikitin and Saychenko 2018). For the crude oil system, its thixotropic properties refer to time-dependent effect of the apparent viscosity reduction under constant shear stress or shear rate, and the viscosity will gradually recover when the shear stress or shear rate is relieved (Bao and Zhang 2017). Cheng et al. found that hysteresis loop is one of the typical thixotropic characteristics (Cheng 1987). In the past, the thixotropic properties of waxy crude oil and its emulsions mainly focused on the shear stress attenuation behavior under constant shear rate loading (Yao et al., 2016 Taraneh 2016), and established some mathematical models (Teng and Zhang 2013; Shranish et al., 2016 Hamadi et al., 2020). In addition to that, many other loading patterns and factors have also been applied to thixotropy research, such as the linear shear rate loading (Teng and Zhang 2013; Razavi and Karazhiyan 2008 Han et al., 2015), the linear change of shear rate or the influence of dispersed phases (Cakmak et al., 2017; Perissinotto et al., 2019 Huang et al., 2020). However, there is a lack of research on the hysteresis characteristics of waxy crude oil and its emulsion under stress loading and the subsequent system recovery characteristics after stress release.

In this paper, the thixotropic properties of W/O waxy crude oil emulsion near the gel point were studied by using the hysteresis loop. Using the hysteresis loop area as the representative quantity, the thixotropic characteristics of W/O waxy crude oil emulsion and the influencing factors of the structural recovery characteristics are analyzed. The specific research is as follows: First, the experimental section is setup, including the preparation of waxy crude oil emulsion, determination of the gelling conditions and loading methods, the thixotropy experiments, and structural recovery experiments. Then, based on the hysteretic loop curve, the thixotropic and structural recovery characteristics of the waxy crude oil emulsion were analyzed.

2. Experimental section

2.1. Experimental instruments

The thixotropy of waxy crude oil and its emulsion is tested HAAKE MARS III rheometer (Germany). Z41 coaxial cylinder is selected as the measuring system, and HaakeEA25 program-controlled water bath (Germany, accuracy is ±0.1 °C) is used as the temperature control system. The gel point is measured by SYD-510 petroleum product instrument produced by Shanghai Changji Geological Instrument Co., Ltd. The wax precipitation characteristics are measured by the TA2000/MDSC2910 modulated differential calorimetry scanner. The emulsion is prepared by RW20 agitator produced by IKA Company of Germany, and a 45° inclined paddle with four blades is selected. The water bath used for preparing emulsion is German HAAKEA25, and its temperature control precision is 0.1 °C.

2.2. Treatment of waxy crude oil

Daqing crude oil (wax content is 20.54 wt%, wax precipitation temperature is 36.66 °C, the gel point at 50 °C is 33.3 °C, the density at 20 °C is 862.3 kg/m^3) is used as the crude oil sample. In order to make the experimental data comparable, it is necessary to eliminate the shear and thermal history of waxy crude oil (Chen 2016). The specific method is as follows: crude oil is sub-packed into grinding bottles (100 mL) and sealed as experimental oil samples. Then experimental oil samples were put into a water bath, heated to 80 °C and maintained the temperature for 2 h. Then, take out the oil samples and put them in a thermostatic chamber for more than 48 h. The oil sample obtained after the above operation is the base oil sample for preparing the emulsion.

2.3. Preparation of W/O waxy crude oil emulsion

In order to prepare stable W/O waxy crude oil emulsion, the preparation conditions are important. Firstly, dehydrated crude oil and deionized water are weighed respectively according to the mass ratio, and immediately poured into a beaker of 250 mL. After that, at the preparation temperature of 45 °C, the stirring speed is set to 800 r/min and the stirring time is 20 min. During the procedure, dispersed phase water was added into the Daqing crude oil for three times, and the adding time was 0, 7 and 14 min respectively. After the above operation is completed, stable W/O emulsions with water content of 10%, 20%, 30% and 40% are prepared successfully. It should be noted that the preparation temperature of emulsion should be selected above the WAT, so as to avoid destroying the formed wax crystal structure, and then affecting the measurement results of emulsion rheology (Li et al., 2016). In addition, the preparation temperature of emulsion should not be too high. The increase of preparation temperature will lead to the decrease of interfacial viscosity, resulting in the weakening of interfacial membrane strength and the deterioration of emulsion stability (Shan and Wei 2017).

2.4. Experimental methods

2.4.1. Determination of the gelation time of W/O waxy crude oil emulsion

In order to determine the formation time of emulsion gelation structure, the small amplitude oscillation time scanning experiment was carried out on Daqing crude oil at 34 °C, and the time corresponding to the increase rate of storage modulus less than 1‰ is taken as the time needed for the gel structure to be fully formed. The experimental result is shown in Fig. 1. From Fig. 1, it can be concluded that the full formation time of gel structure for Daqing crude oil is 40 min. In other words, during the thixotropy test, the W/O waxy crude oil emulsion must be kept at a constant temperature for 40 min to ensure that the gel structure is formed.

2.4.2. Determination of the loading stress of W/O waxy crude oil emulsion

As is known that the W/O waxy crude oil emulsion near the gel point is a gelation system, in which the dispersed droplets are wrapped by wax crystals (Wang et al., 2016). Because of the interaction of wax crystal and dispersed droplets, the structural strength of crude oil emulsion gel system is enhanced compared with pure crude oil under the same conditions. To evaluate the structural strength of gel system and determine the stress loading conditions, a small oscillating stress scanning experiment was carried out under the maximum water content and minimum experimental temperature. The specific procedure is as follows: (1) 40 mL of the prepared W/O waxy crude oil emulsion was immediately put into

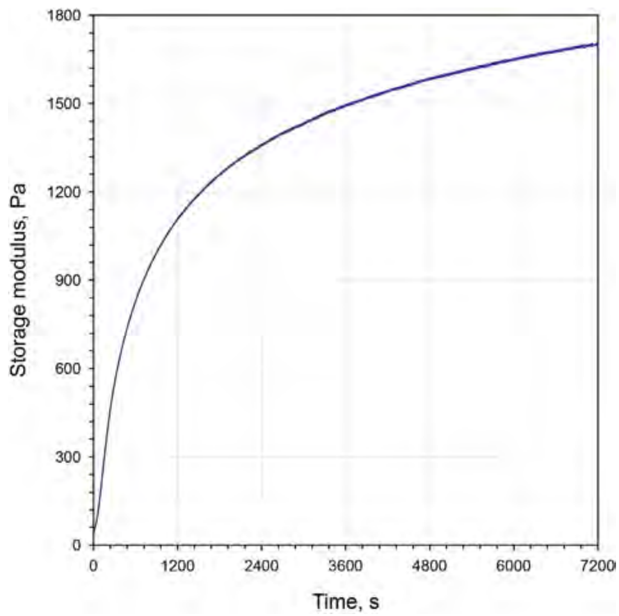

Fig. 1. Storage modulus-time curve of Daqing crude oil at 34 °C.

the measuring cylinder of the rheometer with the preheating temperature of 45 °C; (2) the test sample was static cooled from 45 °C to 34 °C at the rate of 0.5 °C/min; (3) the constant temperature remained for 40 min; (4) After the gelation structure was fully formed, the small oscillating stress scanning experiment was carried out.

Fig. 2 shows the experimental curves of Daqing crude oil at water content of 40% and 34 °C. The yield of the system is defined when the storage modulus decreases rapidly, and the yield stress of the test oil sample in this experiment is 110 Pa. Considering the description of the yield, cracking and recovery process of the gel structure, the maximum loading stress is determined to be 140 Pa in this study. The stress loading conditions at other experimental temperatures are also determined by this method.

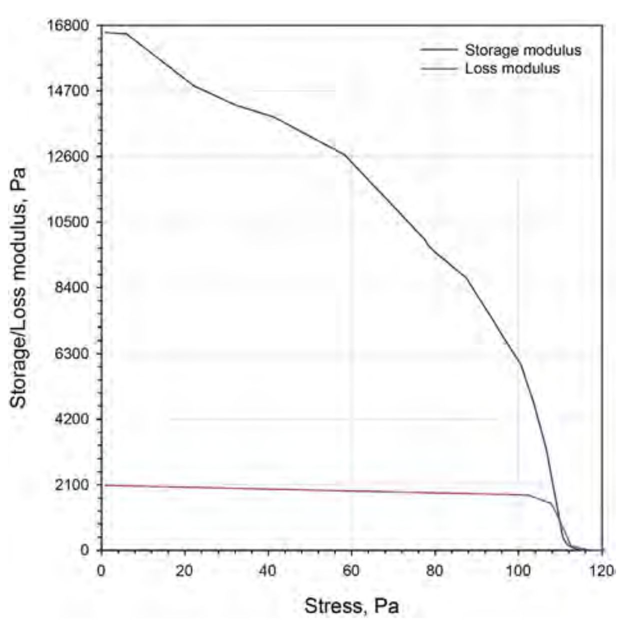

Fig. 2. Stress scanning curve of Daqing crude oil emulsion at 34 °C.

2.4.3. Thixotropy experiment of W/O waxy crude oil emulsion

Taking the experiment condition at 34 °C as an example, the thixotropy experiment is as follows: (1) 40 mL of the prepared W/O waxy crude oil emulsion was immediately put into the measuring cylinder of the rheometer with the preheating temperature of 45 °C; (2) The test sample was static cooled from 45 °C to 34 °C at the rate of 0.5 °C/min; (3) The constant temperature remained for 40 min; (4) After the gelation structure is fully formed, it is loaded under the mode of linear increase of shear stress and linear decrease to form hysteresis loop, and the variation relation of the applied shear stress with time satisfies Eq. (1); (5) The shearing process was repeated three times in a row to form three hysteresis loops, and data points were recorded every 0.1s in the experiment.

$$\begin{cases} \tau = \dfrac{d\tau}{dt} t & 0 \le t \le t_1 \\ \tau = \dfrac{d\tau}{dt}(2t_1 - t) & t_1 \le t \le 2t_1 \end{cases} \tag{1}$$

where, τ is shear stress, Pa; $\frac{d\tau}{dt}$is the change rate of shear stress, Pa/s, which are 0.125 Pa/s, 0.25 Pa/s, 0.5 Pa/s, 1.0 Pa/s and 1.5 Pa/s respectively; t_1 is the rise time of shear stress, s, which are 1120 s, 560 s, 280 s, 140 s and 93 s respectively.

2.4.4. Structural recovery experiment of W/O waxy crude oil emulsion

In order to investigate the recovery of waxy crude oil and its emulsion, take the experiment process at 34 °C as an example. After the thixotropic experiment in 2.4.3 section, the experimental sample was kept at a constant temperature for 30 min. Then three hysteresis loops were formed according to the loading mode of thixotropy experiment. After that, the above shear loading was repeated after standing for another 30 min and 60 min, respectively. In the experiment, data points were recorded every 0.1 s.

3. Results and discussion

3.1. Hysteresis loop curve

Thixotropic characteristics of pure crude oil and its emulsions with four water cuts were tested under stress loading at five shear stress change rates near the gel points (34 °C and 36 °C). Fig. 3 shows the hysteresis loop curves of three systems (structure complete formation, stand at constant temperature for 30 min, stand at constant temperature for 60 min) at 34 °C, water content of 40% and shear stress change rate of 1.0 Pa/s. Because the gelled structure has a certain strength near gel point, the oil sample is in a creep process at the initial stage of loading, which is shown in Fig. 3 that the shear rate does not increase with the increase of shear stress.

As for the creep-yield process of gelled crude oil, Hou et al. believed that the criterion for determining whether the gelled crude oil system has yield flow is not the yield stress but the yield strain, that is, the strain generated under the action of a certain external force reaches and exceeds the yield strain, and the gelled crude oil system will yield and flow (Hou and Zhang 2007). In this study, as shown in Fig. 3, in the early stage of the experiment, a relatively low shear stress is applied to the gel system to produce strain. With the continuation of shear action, when the strain accumulation reaches the yield strain, the system structure begins to crack and flow, showing a curve in Fig. 3 that the shear rate increases rapidly. It should be noted that the corresponding shear stress is the yield stress under the corresponding loading condition, and the corresponding time is the yield time. As shown in Fig. 3,

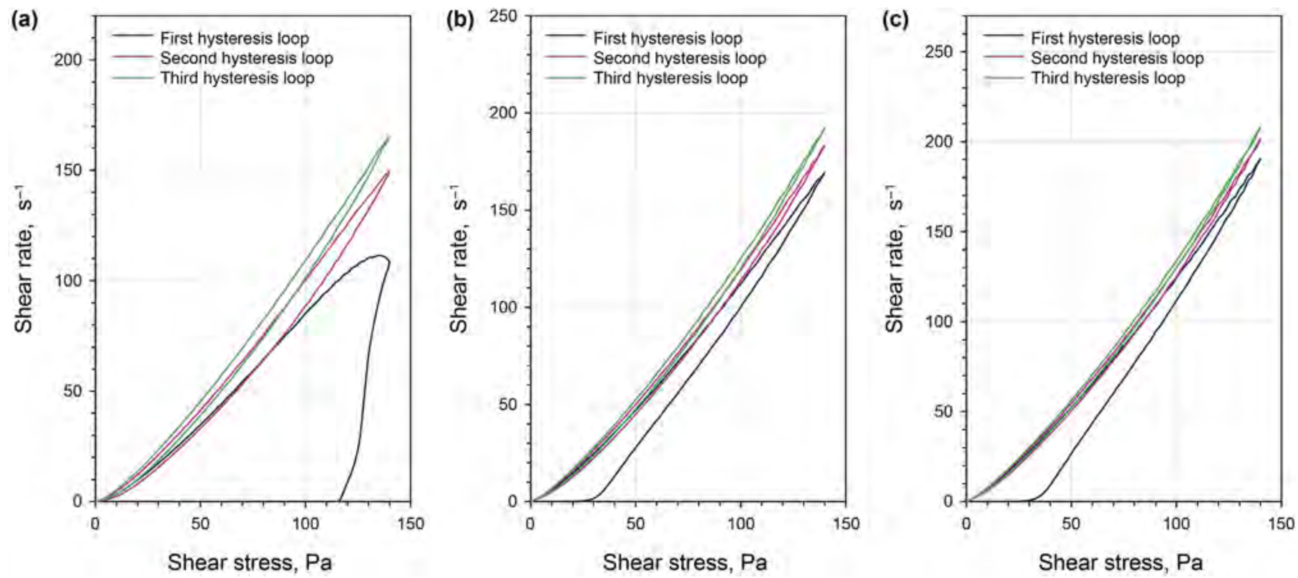

Fig. 3. Hysteresis curve of stress loading at 34 °C, water content 40% and shear stress change rate 1.0 Pa/s: (a) Complete formation of system structure; (b) Stand at constant temperature for 30 min; (c) Stand at constant temperature for 60 min.

then the shear rate goes up with the shear stress increasing gradually, but the shear rate does not increase uniformly. The reason for above phenomenon is that the increase of shear stress is accompanied by the decrease of apparent viscosity due to structural cracking. At the stage when the structure begins to crack after yielding, the shear rate increases rapidly because the cracking rate of the structure is relatively large. It can be seen that during the downward process of the gradual decrease of shear stress, it is the result of the joint action of the reduction of shear stress and the increase of apparent viscosity caused by the structure recovery. Since the recovery rate of the W/O waxy crude emulsion gel system is generally relatively slow, there is no stage of the rapid decrease of shear rate.

In this experimental loading process, the cracking of W/O waxy crude emulsion gel system was not fully recovered in time, which caused the upward curve and downward curve not to coincide, and formed a hysteresis loop under stress loading condition. The area of hysteresis loop indicates the thixotropy of the system (Li et al., 2011). With the continuous cyclic loading, the hysteresis loop area gradually decreases and moves away from the shear stress axis. However, from the second ring, the area of hysteresis loop has been very small, and the thixotropy of W/O waxy crude emulsion gel system has been greatly weakened at this time, which indicates that the gel structure has been damaged to a great extent after a reciprocating shear, and it is also a manifestation of the slow recovery rate of the gel structure.

In order to study the structural recovery of W/O waxy crude oil emulsion gel system, after shear action, the gel system was set at 34 °C for 30 min and 60 min, respectively, and then shear was repeated. The experimental results were shown in Fig. 3. Comparing Fig. 3a–c, the stress loading when the gelled system reaches yield is obviously different. It can be seen that the yield stress is the highest when the gel system is completely formed as shown in Fig. 3a, and the yield stress is the lowest when the system is stationary at constant temperature for 30 min. This indicated that after standing at 34 °C, the gel structure recovered somewhat, but it could not be completely recovered in a short time. In addition, the case for 60 min standing was better than that of standing for 30 min, but the structure could not be completely recovered either.

In addition, the second and third hysteresis loops of the three gel systems all moved away from the shear stress axis. It can be seen that the areas of the second ring and third ring in Fig. 3a decrease in turn and are significantly smaller than that of the first ring. In Fig. 3b and c, the upward curve and downward curve of the second ring and third ring almost coincide. It shows that the gelled structure is seriously damaged after the first hysteresis loop shear, and the structure recovery after standing at a constant temperature is fragile.

As is known to us, under different loading conditions, the yield stress and yield time corresponding to the deformation reaching the yield strain are also different. Fig. 4 is the first hysteresis loop curve of W/O waxy crude oil emulsion with 36 °C and water content of 40% under different shear stress change rates. The experimental results show that with the decrease of shear stress increasing rate, the yield stress decreases and the corresponding yield time increases. This is because the smaller the increasing rate of shear

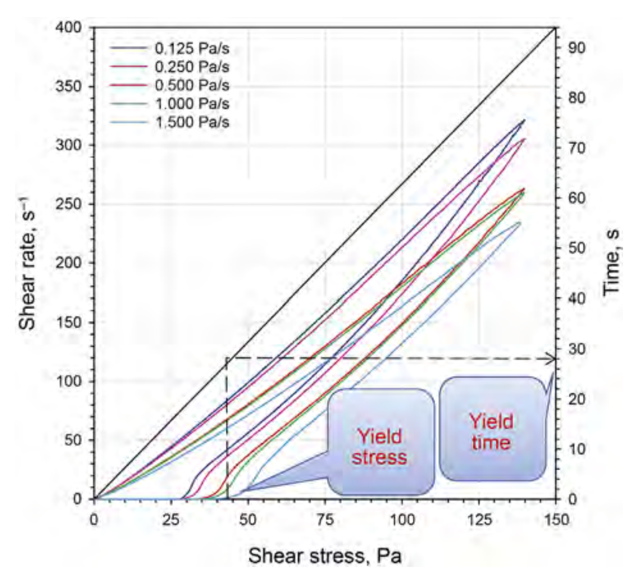

Fig. 4. First hysteresis loop curve under the loading conditions of 36 °C, 40% water content and different shear stress change rates.

stress, the longer the duration of shear action at the same level, resulting in the increased strain. Therefore, when the strain accumulation reaches the yield strain, the corresponding stress value will decrease relatively and the yield time will increase relatively.

3.2. Analysis of thixotropy and recovery characteristics of W/O waxy crude oil emulsion gelling system

The hysteresis loop area can characterize the thixotropy of gel structure (Li et al., 2011). In this paper, the hysteresis loop is divided into several infinitesimal trapezoids, and its area can be obtained by summing the infinitesimal trapezoids (Tárrega et al., 2004). On this basis, the influence of the shear stress change rate and water content on hysteresis loop curve is also analyzed.

3.2.1. Influence of shear stress change rate on thixotropy and recovery characteristics of W/O waxy crude oil emulsion gelling system

In order to analyze the influence of shear stress change rate on thixotropy, the hysteresis loop areas of W/O waxy crude oil emulsion gelling system under three structural conditions: (1) loading after the structure is completely formed; (2) loading after standing at a constant temperature for 30 min after shearing; (3) loading after standing at a constant temperature for 60 min after shearing. Fig. 5 shows the first hysteresis loop area of the gelled system under three structural conditions.

In Fig. 5, it shows that under the same water content, there is little difference in the area of the first hysteresis loop at different shear stress change rates, and its change trend under three structural states is consistent. Therefore, it can conclude that the shear stress change rate has little effect on thixotropy of waxy crude oil emulsion gel system.

In addition, as is known that the structural recovery is one of the main rheological properties of thixotropic materials. In order to characterize the structural recovery characteristics of W/O waxy crude oil emulsion gel system under constant temperature and static conditions, the concept of structural recovery degree is quoted in this paper, as shown in Eq. (2).

$$r = \frac{S}{S_0} \times 100\% \tag{2}$$

where, r is the structural recovery degree of hysteresis loop, %; S is the area of hysteresis loop obtained by shear loading after the system was subjected to static temperature after shear until its structure was recovered, $\mathrm{Pa \cdot s^{-1}}$; S_0 is the area of hysteresis loop obtained by shear loading after the structure of system is completely formed, $\mathrm{Pa \cdot s^{-1}}$.

According to Eq. (2), the experimental data are counted. Figs. 6 and 7 are the structural recovery curves of the first hysteresis loop and second hysteresis loop after standing at constant temperature at 36 °C with different water cuts, respectively. From the results, it can be seen that the recovery degree of the W/O waxy crude oil emulsion gel system undergoing the same shear process is different under different constant temperature standing time conditions. Obviously, the recovery degree of the W/O waxy crude oil emulsion gel system after standing for 60 min is higher than that after standing for 30 min. In addition, the W/O waxy crude oil emulsion gel system with the same water cut and structural recovery condition has little difference in structural recovery degree under different shear stress change rates. Therefore, the loading conditions have no effect on the structural recovery degree of W/O waxy crude oil emulsion gel system. All the experimental data in this paper are consistent with this conclusion.

3.2.2. Influence of water content on thixotropy and recovery characteristics of W/O waxy crude oil emulsion gelling system

In order to investigate the effect of water cut on thixotropic characteristics of W/O waxy crude oil emulsion gel system, the curves of the first, second and third hysteresis loop areas of three gel systems with different water contents were compared. Fig. 8 shows the results of the first, second and third hysteresis loop areas changing with water contents at 36 °C. It should be noted that 0.5 Pa/s is taken as the shear stress change rate.

It can be seen from the curves that at the same temperature and shear stress change rate, the hysteresis loop areas of the three systems decrease with the increase of water content. It shows that the existence of dispersed droplets weakens the strength of gelled system, resulting in a weaker thixotropy. The reason is that in W/O waxy crude oil emulsion gel system, dispersed water droplets are wrapped in wax crystal structure (Zhao 2018). With the increase of water content, the volume fraction of pure crude oil decreases, and the wax crystal content in the system spontaneously decreases, resulting in the decrease of structural strength. Once shear is applied to it, the thixotropy decreases.

In addition, in order to investigate the effect of water content on the structural recovery characteristics of W/O waxy crude oil emulsion gel system, the curves of structural recovery degree with water content under the same shear stress change rate were compared, as shown in Fig. 9. It should be noted that 0.5 Pa/s is taken as the shear stress change rate.

It can be seen from Fig. 9 that the structure of waxy crude oil

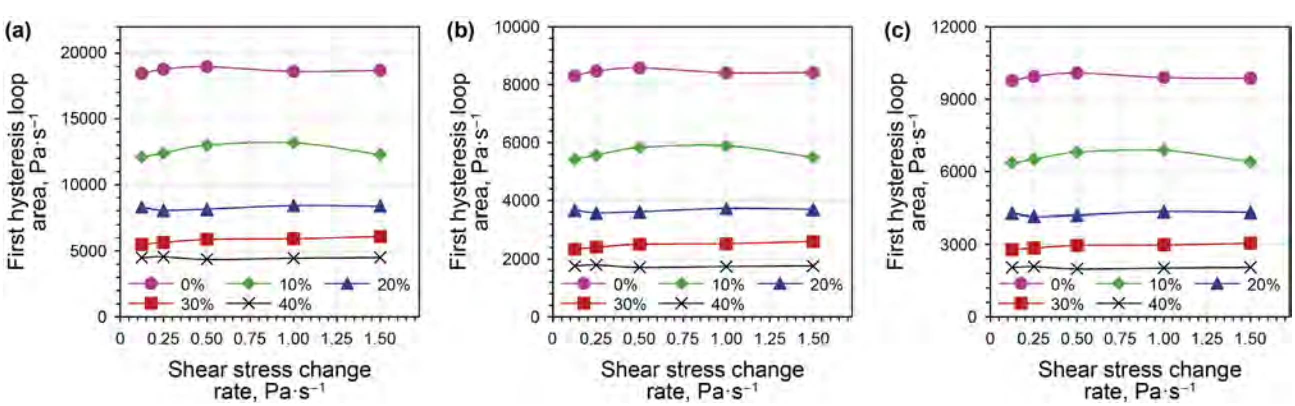

Fig. 5. The curve of the first hysteresis loop area with shear stress change rate at 36 °C and different water content: (a) Complete formation of system structure; (b) Stand at constant temperature for 30 min; (c) Stand at constant temperature for 60 min.

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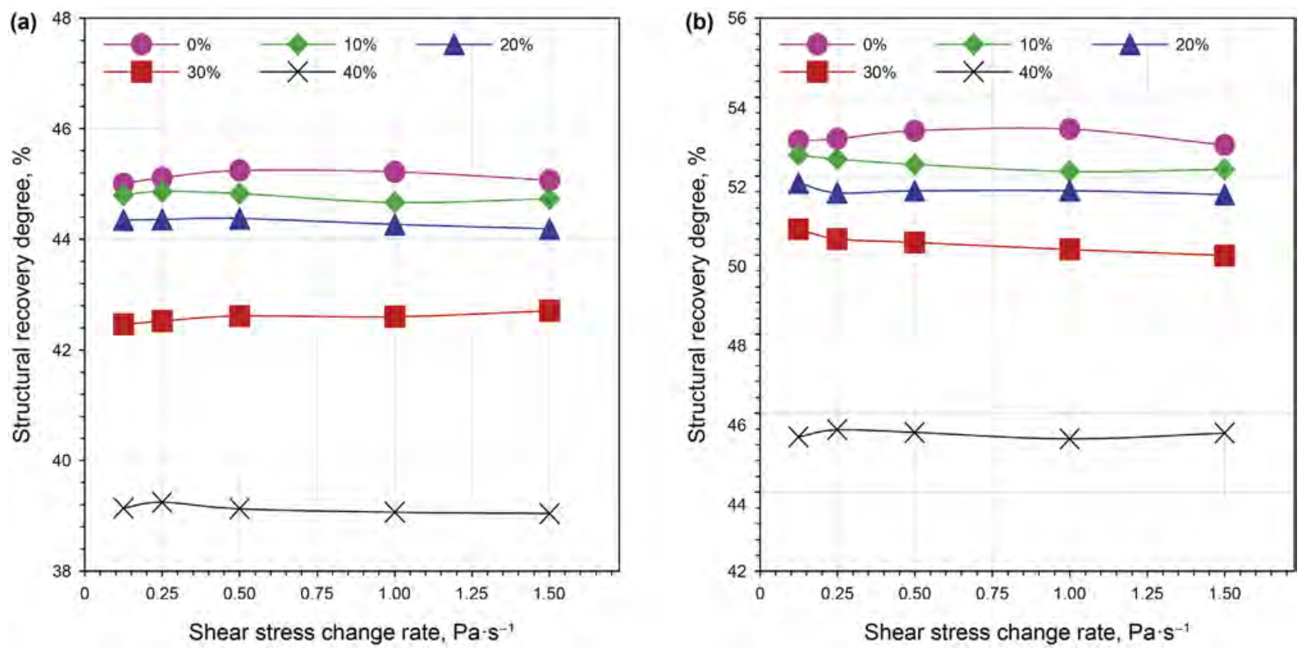

Fig. 6. Structure recovery curve of the first hysteresis loop after standing at constant temperature at 36 °C with different water cut: (a) Stand at constant temperature for 30 min; (b) Stand at constant temperature for 60 min.

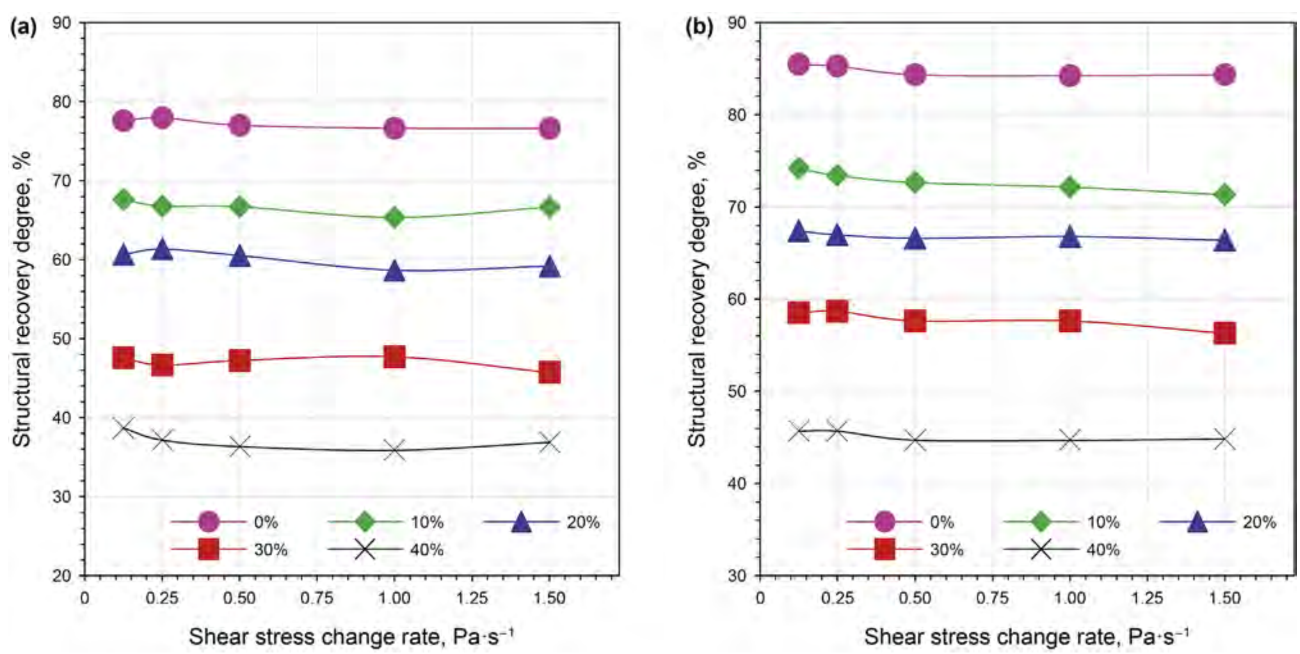

Fig. 7. Structure recovery curve of the second hysteresis loop after standing at constant temperature at 36 °C with different water cut: (a) Stand at constant temperature for 30 min; (b) Stand at constant temperature for 60 min.

emulsion was recovered in different degrees after the constant temperature standing for 30 min and 60 min. Meanwhile, the latter has a stronger degree of structural recovery, but it is still not completely recovered. In other words, as Zhao said (Zhao 2018), the structure of wax crystal in crude oil can only be partially recovered after being destroyed. In addition, it can also be seen that the structural recovery degree decreases with the increase of water content. The reason is that although the wax crystal structure can partially recover in W/O waxy crude oil emulsion gelling system, the dispersed droplets have no structure recovery characteristics.

4. Summary and conclusions

In this paper, the thixotropic characteristics near the gel point of W/O waxy crude oil emulsion gel system are studied by using the loading mode that shear stress increases linearly and decreases

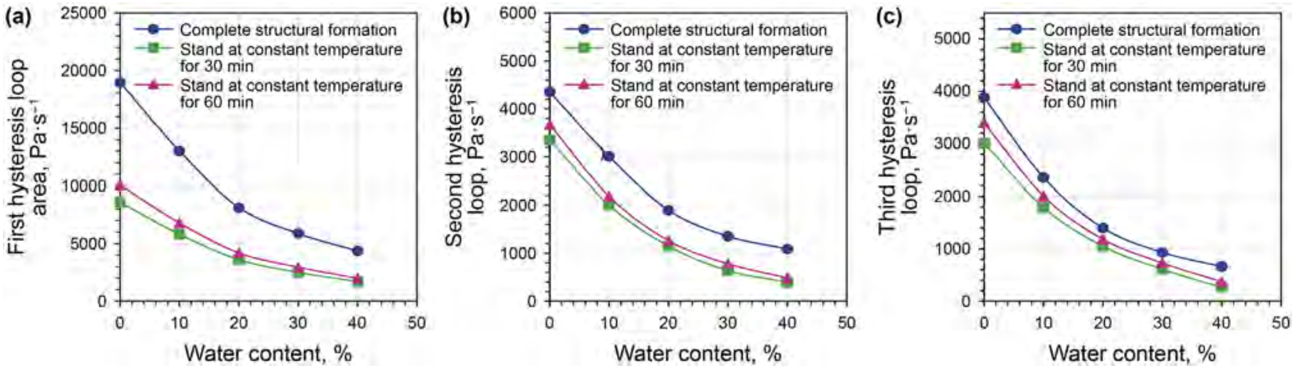

Fig. 8. The curves of the first, second and third hysteresis loop area with water content at 36 °C and 0.5 Pa/s: (a) First hysteresis loop; (b) Second hysteresis loop; (c) Third hysteresis loop.

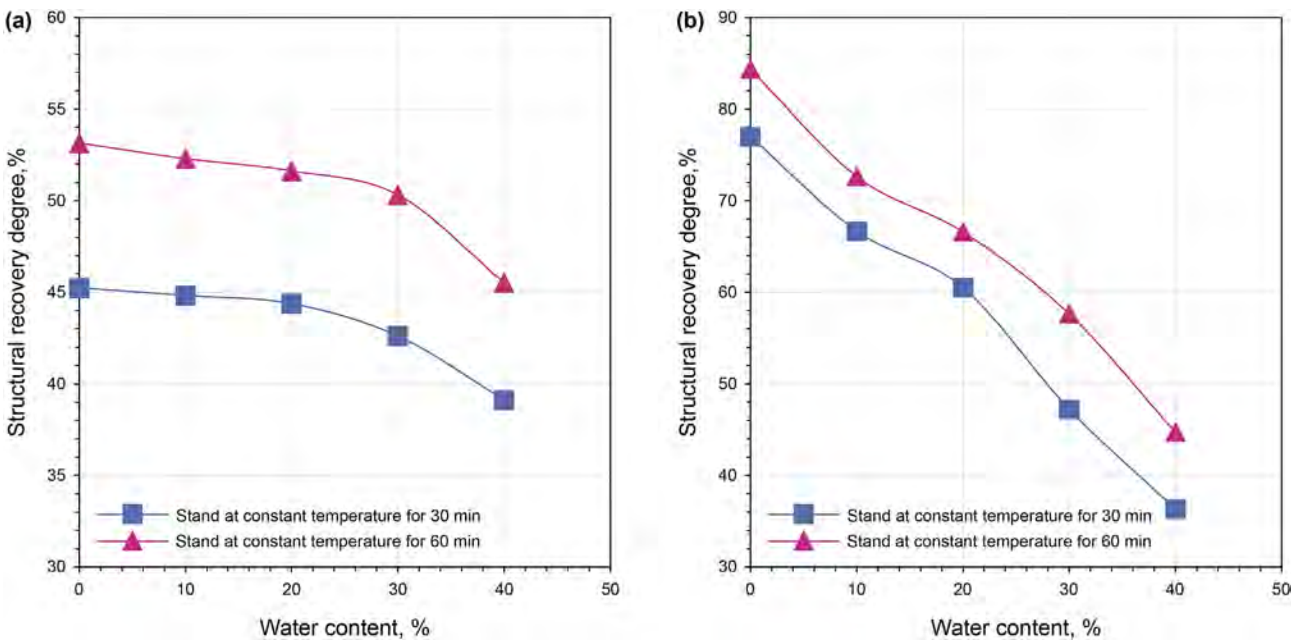

Fig. 9. Structural recovery curves of the first and second hysteresis loops after standing at constant temperature at 36 °C and 0.5 Pa/s: (a) First hysteresis loop; (b) Second hysteresis loop.

linearly to form hysteresis loop. Taking the area of hysteresis loop as the characterization quantity, the thixotropic characteristics and the influencing factors of structural recovery characteristics of W/O waxy crude oil emulsion gel system were analyzed.

- Because the structure of gelled system has a certain strength near the gel point, the oil sample is in a creep process at the initial stage of loading, and then shows an upward process of increasing shear rate. After that, the oil sample undergoes a downward process of shear rate reduction caused by shear stress reduction. The upward curve and downward curve form a hysteresis loop under stress loading.
- Under different shear stress change rate, the area of hysteresis loop and degree of structural recovery are basically unchanged, that is, the shear stress loading conditions have no effect on thixotropy and structural recovery degree of waxy crude oil emulsion gel system.
- The area of hysteresis loop and degree of structural recovery decreases with the increase of water content, which indicates that the existence of dispersed droplets weakens the thixotropy of gelled structure.

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Nomenclature

r	The structural recovery degree of hysteresis loop
S	The area of hysteresis loop obtained by shear loading after the system was subjected to static temperature after shear until its structure was recovered

S_0 The area of hysteresis loop obtained by shear loading after the structure of system is completely formed
t_1 The rise time of shear stress
τ Shear stress
$\frac{d\tau}{dt}$ The change rate of shear stress

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Availability of data and material

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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