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Study on Viscoelastic Behaviors of Waxy Crude Water-in-Oil Emulsion

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Abstract

Emulsion of waxy crude oil is one of the common states in the subsea pipeline. At low temperatures in offshore environment, waxy crude oils with water could form the crude oil emulsion gel of oil-in-water emulsion. Thus, the waxy crude oil emulsion viscoelastic behavior for deep sea transportation and restarting pipeline safety is particularly important. By means of MASIII HAAKE rheometer which is produced by German company, waxy crude oil emulsion viscoelastic behavior is explored at different volumetric water contents and different shear stresses. By analyzing the rate of change of shear rate in the initial stage, the influence rules of viscoelastic properties were summarized, with the change of volumetric water content and the applied shear stress and based on the experimental results, the law of emulsion is explained from the micro level. It is proposed that brittle fracture exists between wax crystals, and flexible fracture was found in the interaction between water droplets and wax crystals.

Keywords

Waxy Crude Oil Emulsion, Viscoelastic Behavior, Brittle Fracture, Flexible Fracture

1. Introduction

With the global strategic oil basis to the deep sea, oil and water mixed transportation technology has great application value in the submarine pipeline. In oil-water flow, waxy crude oil and water form water-in-oil emulsion, compared with waxy crude oil, under low temperature conditions, oil production is complex in deep sea, because waxy crude oil emulsion more easily forms gel structure. Similarly, if the pipe is stopped because of the plan or accident, crude oil or emulsion will form a gel structure in the process of conveying emulsion or oil to the ground with pipeline. To restart, we must make the pump start-up pressure can overcome the yield stress of the waxy crude oil or emulsion gel in the pipeline, in order to ensure the smooth start of the pipeline [1]. Before

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reaching the yield stress, the crude oil mainly exhibits viscoelastic properties. Thus, viscoelastic behavior of waxy crude oil and its emulsion gel, for the safety of deep sea transport and the pipeline shutdown and restart, is especially important.

The rheological properties of waxy crude oil itself are complex. There is an interaction between the emulsion liquid system of waxy crude oil, for example, interaction between inner phases and outer phases, droplets and droplets [2]-[6]. At present, the viscoelastic behavior of emulsion gel of waxy crude oil is mainly through the study of the small amplitude oscillation experiment. Visintin *et al*. [7], and Sun Guangyu [8] analysed viscoelastic by small amplitude oscillatory experiments. In order to simulate the viscoelastic process of field pipeline restarting, based on the experiment, the viscoelastic properties of waxy crude oil emulsion are studied by the method of applying constant shear stress in this paper. We study the viscoelastic properties from two aspects: one is the different volumetric water contents; the other is the different loading stresses. The influence rules of viscoelastic properties are summarized. According to this rule, the contribution of wax crystal and liquid drop to the viscoelastic properties is revealed. Based on the experimental results, the law of emulsion is explained from the micro level. It is proposed that brittle fracture exists between wax crystals, and flexible fracture was found in the interaction between water droplets and wax crystals.

2. Experimental

2.1. Experimental Apparatus and Experimental Samples

Experimental instruments are mainly MARSIII rheometer produced by German HAAKE companies, and used its Z41 coaxial cylinder measurement system. Rheometer equipped with A40 controlled water bath with temperature controlling precision of 0.1˚C produced by German HAAKE companies. Used for the preparation of emulsion instrument is RW20 strong and digital mixer produced by the German IKA company, its speed range is from 0 r/min to 2400 r/min.

The properties of matter of waxy crude oils used in the experiments are shown in **Table 1**. In order to ensure the repeatability and comparability of the experimental data, the experimental oil samples were pretreated to eliminate the "memory" effect of the crude oil, and the specific steps are as follows: 1) Barrels of oil should be proper heated and adequately stirred, stirring can make the recombinant and light components mix evenly, then pour it into grinding mouth bottle seal preservation; 2) Will be filled oil sample grinding mouth bottle placed in constant temperature water bath in, static heated to 80˚C and constant temperature for 2 hours, then get under the condition of room temperature static cooling more than 48 hours, to eliminate the "memory" effect of history, as the basic oil sample experimental [9].

In this paper, the crude oil is high wax oil, which is characterized in that the temperature dropped to below the temperature of wax precipitation point will appear wax crystal. If the temperature of making emulsion is below the temperature of wax precipitation point, it will affect its comparability of the result of viscoelasticity measurement [10]. The preparation temperature should select the temperature above the wax precipitation point. And the higher the temperature is, the worse emulsion stability is [10]. Therefore, in order to obtain the stable wax emulsion, the experimental setup temperature is 55˚C, the methods of making emulsion is to divide the required water into two equal portions first, then pour one of them into the oil at the start of timekeeping, five minutes later pour another one. Before preheating the water, avoid temperature difference of the water and the oil is too large, which has great influence on the rheological behavior. After repeated tests, the crude oil and water could form a stable water-in-oil emulsion at the lowest 700 r/min speed stirring. And the lowest in the 700 r/min speed stirring, so stirring speed of 700 r/min is chosen, each stirring for 5 minutes, then the total mixing time is

Table 1. The physical properties of the oil sample.

Physical parameters	*Parameter value*
Density of 20˚C (kg/m^3)	865.5
Condensation point (˚C)	33.4
Wax precipitation point (˚C)	40
Wax content (wt%)	15.5

10 minutes. Due to the type of impeller affect physical properties of emulsion directly [11]. Therefore, stirring paddle of 4 leaves and 45 degrees inclined blades and 250 ml beaker are used in this experiment in this paper. The required emulsion volume is 60 ml in this experiment. The mixing paddle is placed in the middle of the liquid.

2.2. Experimental Program

The viscoelastic properties of waxy crude oil emulsion are studied by the method of applying constant shear stress in this paper. The viscoelastic-yield behavior of waxy crude oil has been studied. Compared with the crude oil, emulsion viscoelastic properties are more complex. Because of the existence of water-drops, the viscoelastic of waxy crude emulsion gels are not only related to the wax crystal structure, but also to the strength of interfacial film between water droplets and crude oil. It is proposed that brittle fracture exists between wax crystals, and flexible fracture was found in the interaction between droplets and wax crystals, through the changing law of the change rate of shear rate in this paper.

The prepared fresh emulsion was quickly and accurately poured into rheometer measuring tube, then reduce the temperature to 35˚C at the cooling rate of 0.5˚C/min. Before the experiment measuring the time scan is required, which this can measure the time of the sufficient formation of the gel structure of crude oil, it is 45 minutes. Changing new emulsion and repeating the above operation, then 45 minutes later, the measurements were carried out with the method of applying constant shear stress.

Under the above conditions, different volumetric water content of emulsion of 10%, 20%, 30%, 40%, 50% need to be prepared. The emulsions of these water contents are carried out with applying different constant shear stresses. These constant shear stresses are 80 Pa, 90 Pa, 100 Pa, 110 Pa and 120 Pa separately.

3. Results and Discussion

At different volumetric water content, the shear rate will go through the following stages: 1) Rapid increase in shear rate; 2) The shear rate is increased by a rapid increase to a gentle increase; 3) Gentle increase stage. With increasing volumetric water content, shear rate value of gentle stage is low. The change of shear rate at the initial stage also changes with the change of water content. Specific changes will be analyzed in the following. Under the constant shear stress of 80 Pa, the variation of shear rate with different water content is shown in **Figure 1**. The tendency of experimental datas of the other four groups with constant shear stress is the same as the tendency of the following.

In order to explore the viscoelastic properties of wax crude oil emulsion, the initial stage of the experimental data will be analysed carefully. The initial stage means that the main properties are viscoelastic. After repeated several experiments, the first 20 seconds of the experimental dates are analysed in this paper. By calculating the change rate of shear rate of the first 20 s, the changing law of the change rate of shear rate at the same shear stress and different volumetric water content are showed in **Figure 2**. The changing law of the change rate of shear rate at the same volumetric water content and different shear stress is showed in **Figure 3**.

Under the constant shear stress of 80 Pa, the curve of change rate of shear rate—time is shown in **Figure 2(a)**. When the volumetric water content is more than 30%, the rate of change of shear rate increases firstly and then decreases, and the higher water content is, the lower the change rate of shear rate is at the initial point, the peak

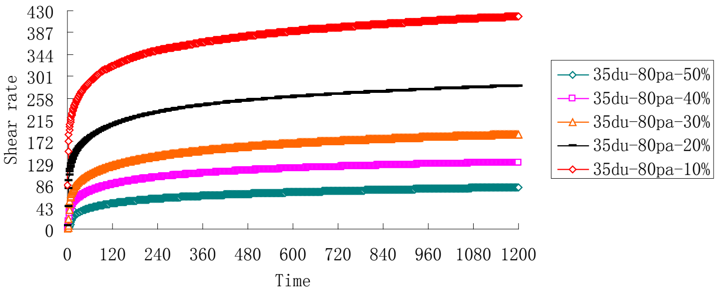

Figure 1. The variation of shear rate with different volumetric water content at 80 Pa.

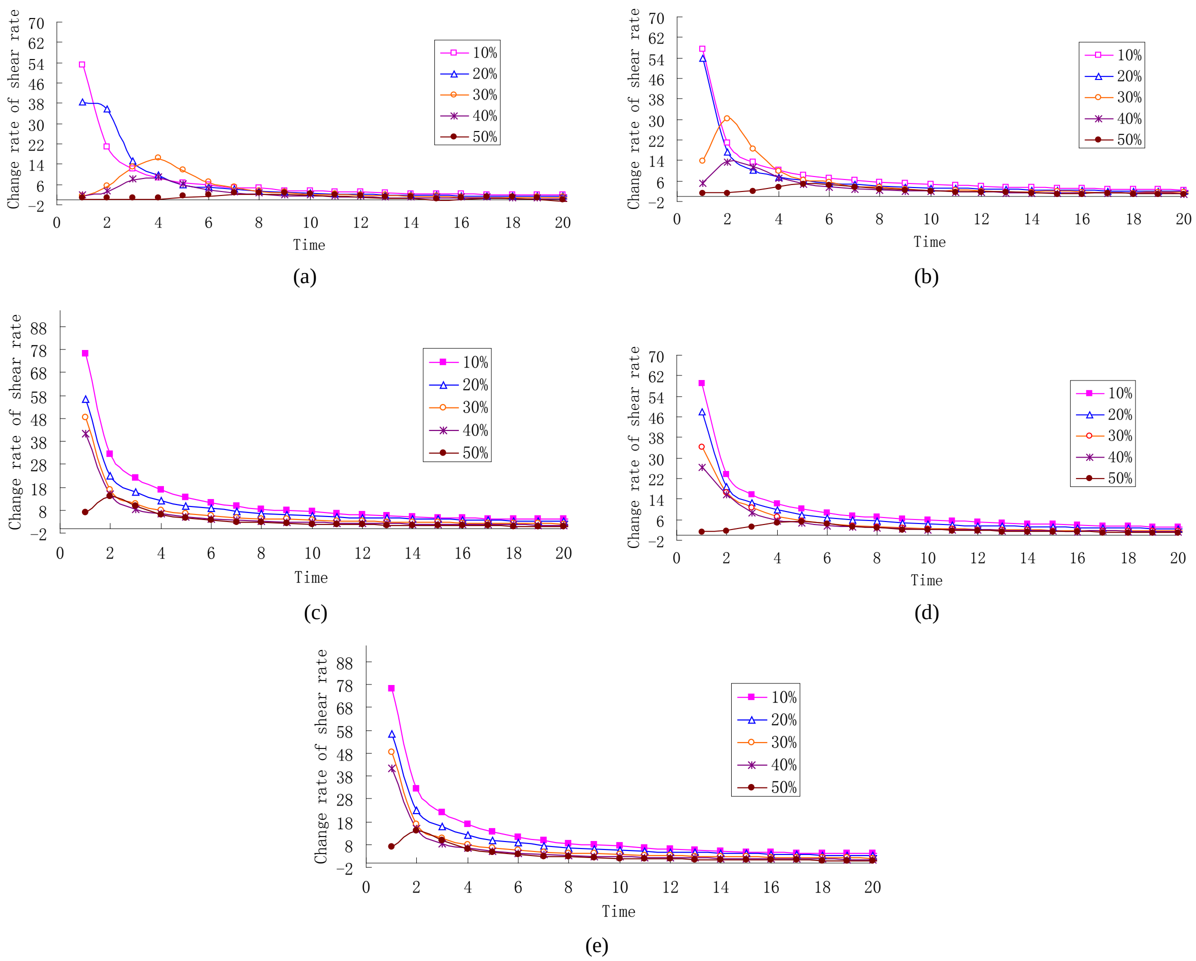

Figure 2. The curve of the change rate of shear rate at the same shear stress and different volumetric water content. (a) 80 Pa; (b) 90 Pa; (c) 100 Pa; (d) 110 Pa; (e) 120 Pa.

and the balance, the gentler the change rate of shear rate rise and decline. Wherein, the water content of 20% is the transition stage, which curve is between the water content of 10% and the water content of 30%. As shown in **Figure 2(b)**, with the applying constant shear stress becomes 90 Pa, the curve of water content of 20% is similar to the water content of 10%, and it locates below curve of the water content of 10%, when the water content is not less than 30%, the time of peak value appears in advance and the peak value increases obviously. Analogously, as shown in **Figure 2(c)**, **Figure 2(d)**, the curves of the water content of 30% and 40% are similar to the water content of 10% and successively arranged downwardly. As shown in **Figures 2(c)-(e)**, when the water content is 50%, the time of peak value appears in advance and the peak value increases gradually.

When the water content is 10%, the changing law of the curve is shown in **Figure 3(a)**. With the increase of water content, the smaller the constant shear stress appears a peak value in this curve firstly. When the water content is 50%, as shown in **Figure 3(e)**, all curves appear peak values, and the greater the applied constant shear stress is, the sooner peak values appears, the greater the value at the peak is.

Investigate its reason, Visintin has been proposed that water droplets are gradually covered with wax crystals, due to the adsorption of wax crystals on the droplet interface, then the gel structure is formed with the droplets wrapped in three-dimensional network of wax crystals. Recently, by studying the creep-recovery characteristics of mock oil emulsion, Haj-shafiei *et al*. [12] found that a large proportion of the deformed emulsion gel could be recovered at high water content, because the droplet itself has elasticity. By contrast, when the water content is low, because the structure of water droplets wrapped by wax crystal network structure is more brittle, crude oil emulsion gel is prone to non recoverable deformation. Based on previous studies, it is confirmed Visintin [7], Haj-shafiei [12] like Sun Guangyu [8] and other researchers' discoveries are right by analyzing the experimental

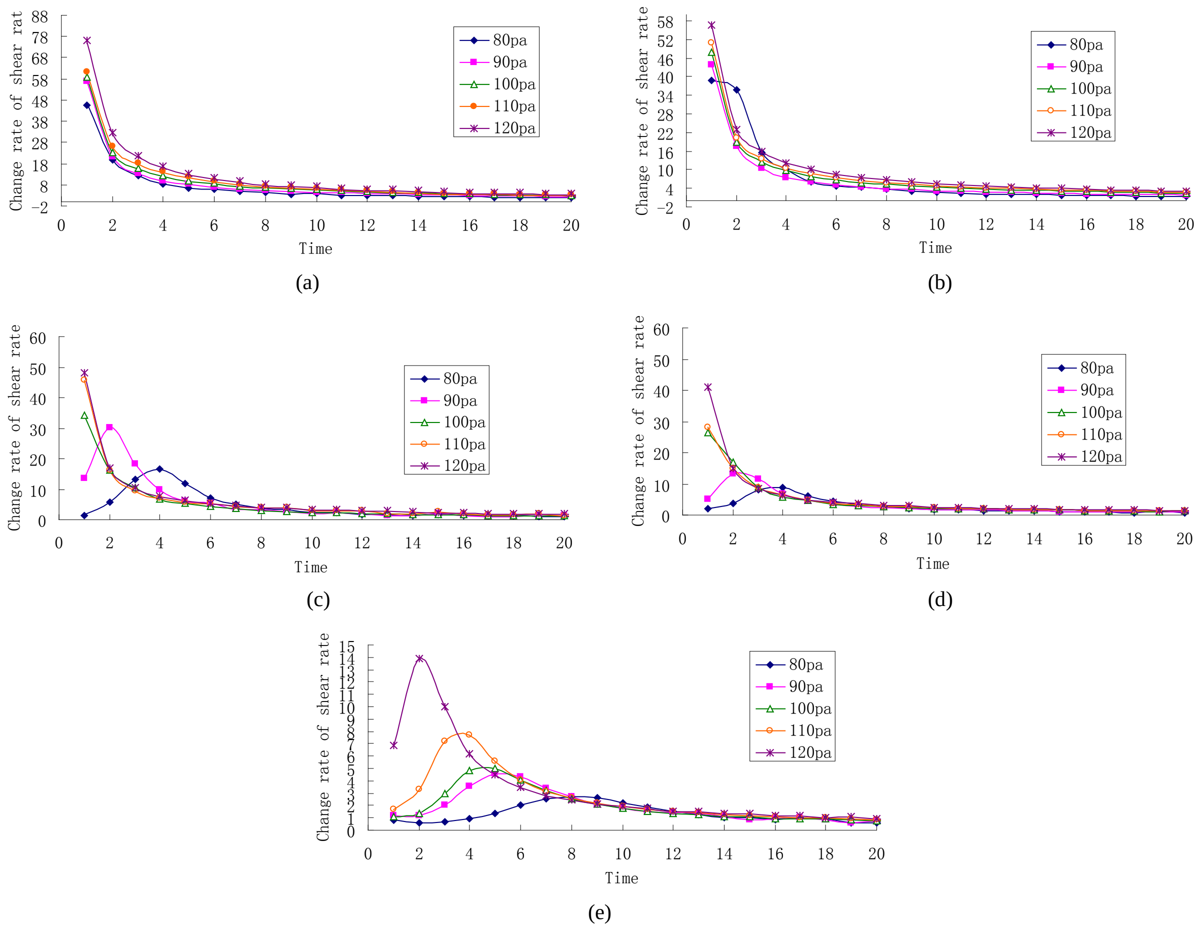

Figure 3. The curve of the change rate of shear rate at the same volumetric water content and different shear stress. (a) 10%; (b) 20%; (c) 30%; (d) 40%; (e) 50%.

data, at the same time, it is also found that the three-dimensional network structure of space between the wax crystals are prone to brittle fracture, wax crystals attached to the water droplets surface are prone to flexible fracture by applying shear stress, because of elastic effect of interfacial film between wax crystals and water droplets.

As shown in **Figure 4(a)**, when the volumetric water content is low, available area of the water droplets surface which wax crystal can be attached to is reduced, the majority of wax crystals are the same as wax crystals in crude oil. Spatial three-dimensional network structure is formed between wax crystals, when the shear stress is greater than a certain value, the network structures appear brittle fracture, then damage rate is greater than the recovery rate, therefore the change of shear rate decline rapidly at the beginning, eventually tend to balance. As shown in **Figure 4(b)**, when the volumetric water content is higher, the majority of wax crystals will be attached to the surface of the droplets, and the droplets are wrapped in three-dimensional network of wax crystals. Because of elastic effect of interfacial films between wax crystals and water droplets, when applied to certain force a period of time, small part of the structure appears brittle fracture first, resulted in the increase of the change rate of shear rate. Since most of them are attached to the surface of the droplets, due to the limit of interfacial films, so that the rate of destruction becomes slow, after a while, slowly tend to balance. When the shear stress is greater than the interfacial film elasticity, it will also make wax crystals structure attached to the surface of the droplets to destroy rapidly.

4. Conclusions

The viscoelastic properties of waxy crude water-in-oil emulsion are studied by the method of applying constant

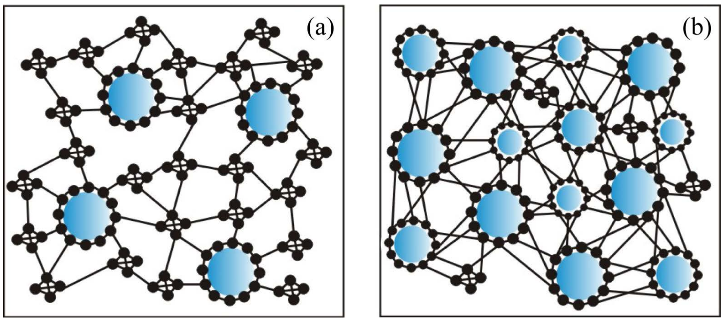

Figure 4. Schematic diagram of waxy crude oil emulsion gel at different volumetric water content.

shear stress in this paper. The change rate of shear rate is analyzed at the initial stage in each of experimental data. The main conclusions are as follows:

1) Each shear stress corresponds to a critical water content. When it is less than the critical water content, the change rate of shear rate showed a trend that first step decreases rapidly and then slowly. When it is more than the critical water content, the change rate of shear rate showed a trend of increasing firstly and then decreasing; and peak value with the increasing of water content decreases; the trend of increasing firstly and then decreasing also becomes more slowly with the water content increasing.

2) Similarly, each water content corresponds to a critical shear stress. When it is greater than the critical shear stress, the change rate of shear rate presents decreasing rapidly at first and then decreasing slowly, and finally tends to zero; when it is less than the critical shear stress, the change rate of shear rate presents increasing at first and then decreasing, finally tends to zero, and the peak value decreases with the decreasing of shear stress, and the trend of increasing firstly and then decreasing with the increasing of shear stress is becoming more and more slow.

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