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SHEAR HISTORY AS THE MAIN POINT TO DETERMINE THE MECHANICAL BEHAVIOR OF WAXY OILS

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Abstract. *Waxy crude oil is a complex mixture of hydrocarbons that includes paraffins. During production, the oil at high temperature in the reservoir loses heat to the surrounding and the paraffins crystalize. These solid crystals suspended in the material provide a non-Newtonian behavior to the fluid. The shear and thermal histories imposed to the waxy oil affect the crystallization process, the final morphology of the crystals and finally the mechanical behavior of the material at low temperatures. Recent studies have showed that the equilibrium flow curve of waxy oils is a function of the highest shear rate imposed to the material (Mendes et al. 2015; Geri et al. 2017). In the current work, the effect of the shear history in the flow curve of a model waxy oil is revisited by carrying out controlled shear rate experiments in a rotational rheometer. The experiments consisted of imposing different shear rate plateaus to the material during different times. It was observed that the equilibrium depends on a combination of the shear rate and on the time this shear rate is imposed, in other words, the total shear strain imposed to the material is the key point to determine the influence of the shear history on the rheological behavior of waxy oil.*
Keywords: *Waxy crude oil, paraffins, total shear strain, shear rate.*

1 INTRODUCTION

Waxy crude oil is a complex mixture of hydrocarbons consisting of paraffins, aromatics, naphthenes, asphaltenes and resins. The crude oil in the reservoirs are at high temperatures (70 to 150 °C) and high pressures (50 to 100 MPa), in these conditions all the components are dissolved in the oil and the material behaves as a Newtonian fluid (Venkatesan et al. 2005). During production and transportation, the crude oil flows in pipelines that are in contact with the seabed; a low temperature environment (around 4 °C). Due to the heat loss for the environment the temperature of the material decreases during the transportation. At low temperatures the solubility of high molecular weight components in the oil is decreased and especially the n-paraffins tend to precipitate as crystal structures. (Singh et al. 2000; Venkatesan et al. 2003). These crystals provide a non-Newtonian behavior to the fluid, tend to deposit in the inner surface of pipelines and are responsible for the structure the material, giving a solid-like behavior to the crude oil, when the flow is interrupted. High pressures are usually required for gel breakage and flow restart. In the case of overestimated pressures during the restart of the gelled oil flow, pipeline damage and material leakage may occur (Magda et al. 2013; de Oliveira e Negrão 2015).

In recent works, it has been shown that the breakage of the material structure seems to be irreversible, in other words, the structure of the material can only be recovered if the paraffins are dissolved (heating the material) and crystallized again (due to the cooling) at the same condition. Tarcha et al. (2015) show that after the breakage, if kept in the same temperature, the material does not structure again even after some hours of observation. In a more detailed paper, Mendes et al. (2015) propose that the rheological behavior of waxy oils after the breakage is a function of the highest shear rate experienced by the material. The authors claim that waxy oils behave as a typical thixotropic material when flowing with a shear rate below the shear rate used during the cooling or below the highest shear rate experienced by the material. But when submitted to a higher maximum shear rate, it can be observed some irreversible changes in the material. In other words, the irreversibility of the structure caused by the highest shear rate leads to a reduction in the apparent viscosity of the material. Similar behavior was observed in a recent paper (Geri et al. 2017), according this point of view, the material flow curve is a function not only of the shear rate but also of the highest shear rate experienced by the material.

In the current work, the influence of the shear history on the mechanical behavior of waxy oils is revisited. By means of rheological experiments it is shown that the key point to understand the rheological behavior of the material is not the highest shear rate but the total shear strain imposed to the material.

2 MATERIALS AND METHODS

Materials

The material used in experimental tests is a model oil composed of 95 wt.% of mineral oil (Sigma Aldrich-330779) and 5 wt.% of white paraffin wax with a melting point between 58 and 62 °C (Sigma Aldrich-327212). The sample formulation was carried out adding the solid paraffin to mineral oil and inserting the mixture into a heat oven at 60 °C for 2 hours for complete dissolution of paraffin.

In the experimental tests, the DHR-3 rotational rheometer (TA Intruments, USA) with direct shear stress and indirect shear rate control was used. The temperature control of the rheometer was performed by the Peltier electronic base and a thermostatic bath. The geometry used was a 40 mm diameter, 1.998° cone with truncation gap of 63 μm .

Methods

With the main objective of relating the rheological behavior of paraffinic oils to the total shear undergone by the material, rheometric tests were performed with shear rate levels. Before each rheometric experiments, the oil was heated to a high enough initial temperature, Ti=60 °C, in order to dissolve all the paraffin in the oil (Mendes et al. 2015a; Geri et al. 2017;).

For better repeatability, a pre-test was developed which contains the following steps:

i) the sample is placed in the oven at 60 °C along with the syringe and the needle for 30 minutes in order to fully dilute the paraffin;

ii) the sample is then inserted into the rheometer using the syringe;

iii) the paraffinic oil is maintained for 15 minutes at 50 °C with a shear rate of 50 s^{-1} to ensure that the sample is homogenized and the oil temperature along the measuring plates is constant;

iv) the sample is then cooled statically from 50 to 4 °C for 46 minutes, i.e., with a cooling rate of 1 K/min;

v) finally, at the final temperature, the sample is kept at rest for 1 hour to complete build-up of the structure at the final temperature.

The pre-test assures same thermal and shear histories for all the samples. Then procedures 1 and 2 were performed:

a) Procedure 1: The first experiment was performed with three consecutives steps of shear rate: 100, 500 and 100 s^{-1}, each lasting 30 minutes. The objective is to verify the influence of the maximum shear rate on the sample behavior;

b) Procedure 2: The second experiment was carried out by imposing a plateau of 100 s^{-1} for 90 min. In this procedure it is analyzed the possibility of the sample presenting the same rheological behavior of procedure 1, but without the influence of the maximum shear rate.

To facilitate understanding of the test guidelines, Figure 2.1 shows a flowchart of the pre-test followed by procedures 1 and 2. In which the pre-test step with a total duration of 151 minutes is presented, and the experiments 1 and 2 with duration of 90 minutes. In the flowchart one can observe that the pre-test defined above will be the same for both experiments.

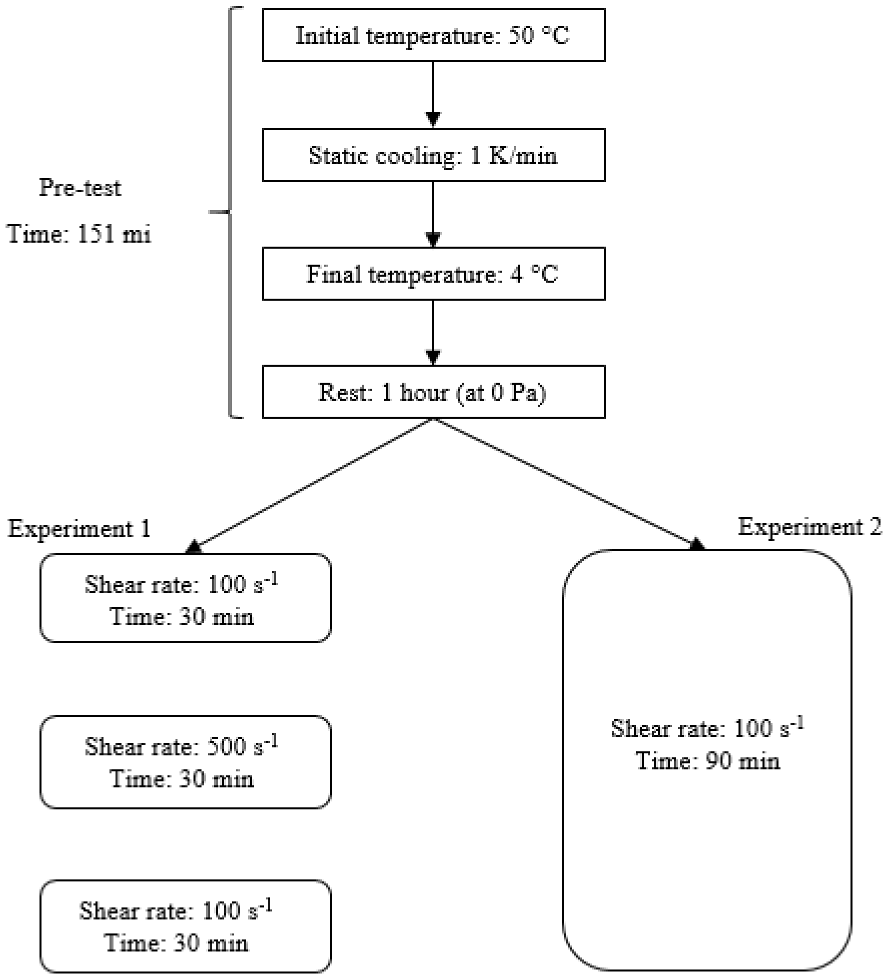

Figura 2.1. Flowchart of the methodology applied in the tests performed.

3 RESULTS

In Figure 3.1 one can observe the rheometric results of the imposed shear rate and the shear stress measured as a function of time for both procedures. Curve E1 represents the result of the Procedure 1. It can be seen that by applying a shear rate of 100 s^{-1} during the first 30 minutes, there is a decrease in shear stress and the steady state is not reached. When applying a shear rate of 500 s^{-1} for 30 minutes, the fluid again does not reach equilibrium. However, by applying the shear rate to 100 s^{-1} it seems that the paraffin oil sample reaches equilibrium almost immediately with the beginning of this step. In the Procedure 2 (curve E2) the shear rate plateau of 100 s^{-1} was applied for 90 minutes. It can be observed that the material does not reach the steady state. It should be noted that although the E2 curve approaches the E1 curve, the behavior of the sample at the end of the experiments is similar, but the shear stress value of E2 (12.5 Pa) is higher than that of E1 (10.9 Pa).

In this way, it can be observed that the E2 curve tends to approximate the E1 curve. Thus, possibly if the test had continued for a longer time, the response presented by the E2 curve would reach equilibrium and the same value as the E1 curve.

To evaluate this hypothesis, both experiments were performed again, but increasing the total duration to 700 minutes. Figure 3.2 shows the results of the imposed shear rate and the shear stress measured as a function of time for both experiments. It can be seen that the sample tested with the three plateaus of shear rate exhibited the same behavior of the previous test throughout the experiment. However, curve E2, in which the plateau is kept constant at 100 s^{-1} during all the experiment, takes longer compared to curve E1 but also reach the equilibrium. Which means that in both cases, the same final rheological behavior is obtained independently of the highest shear rate experienced by the sample.

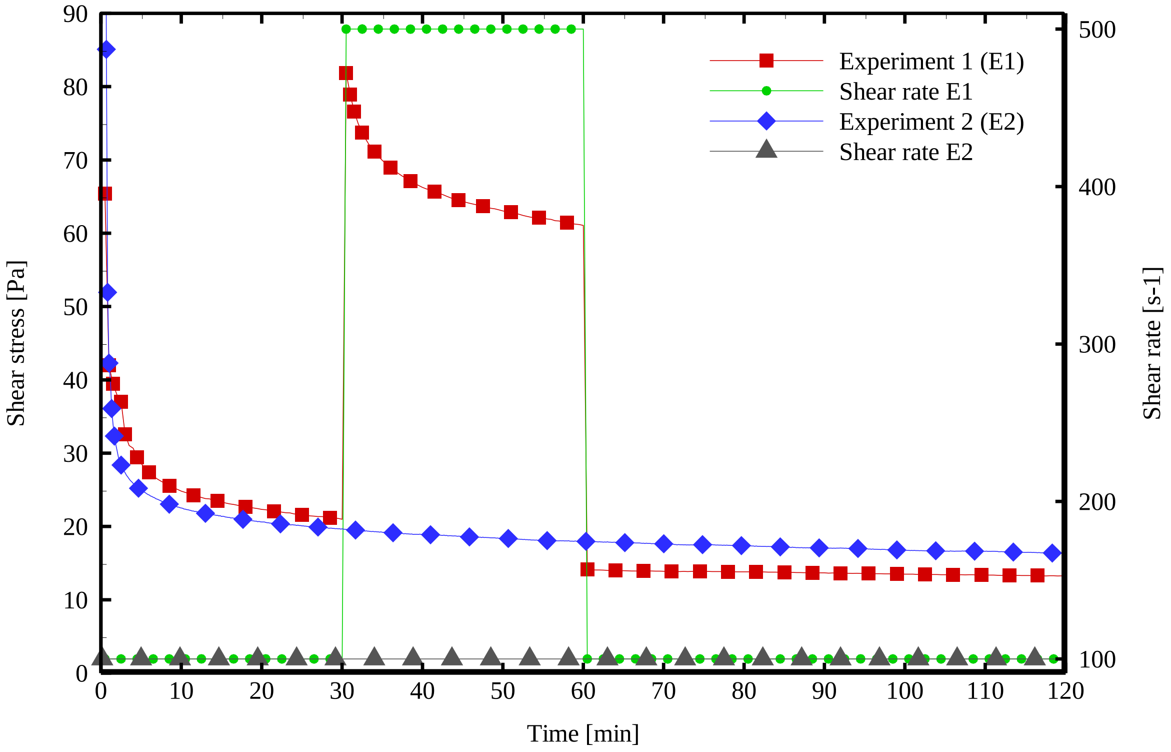

Figure 3.1. Imposed shear rate and measured shear stress as a function of time. First experiment was performed with three plateau of shear rate 100, 500 and 100 s^{-1}. The second experiment was performed just imposing a plateau of 100 s^{-1}.

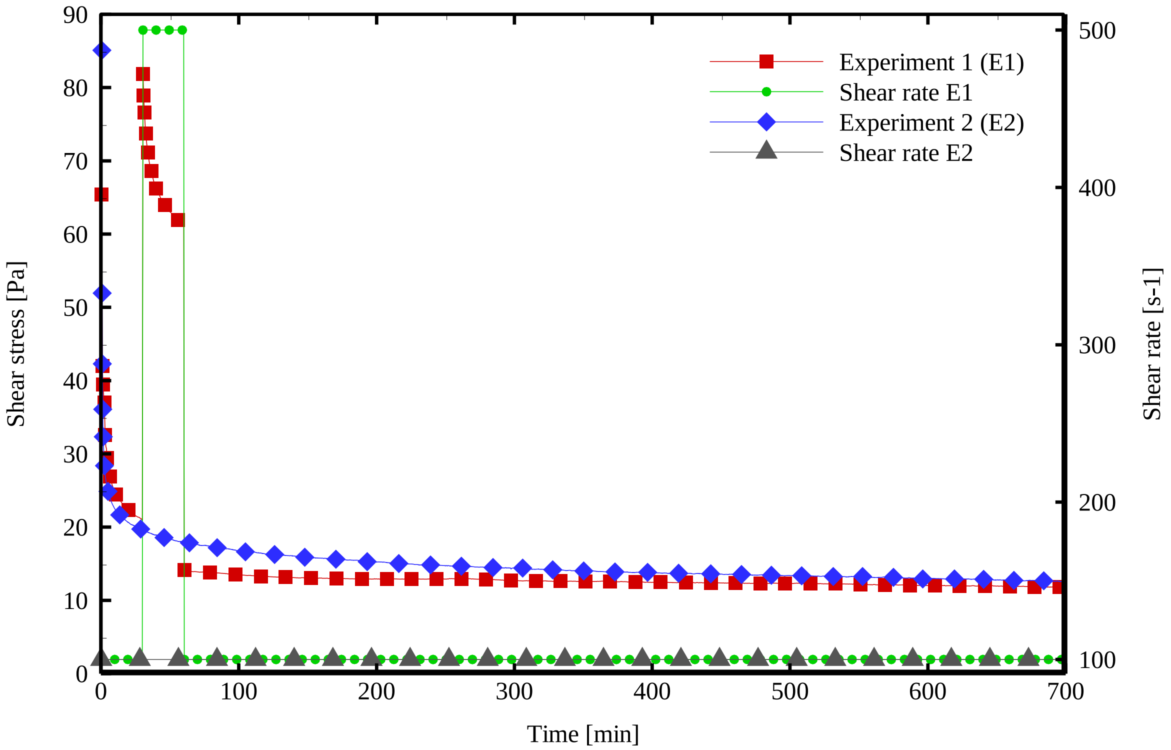

Figure 3.2. The same result presented in Figure 1, but now if the extended time of experiment.

Similarly, the previous result of the shear stress measured as a function of the total shear imposed on the material can be analyzed, as can be seen in Figure 3.3. Note that both curves present approximately the same results when the shear rate 100 s^{-1} is imposed on the material. The 500 s^{-1} plateaus does not significantly affect the posterior behavior of the material. Comparing Figure 3.2 and Figure 3.3, it can be concluded that the higher shear rate (in this case, 500 s^{-1}) imposed on the material only causes the material to reach equilibrium more quickly. However, the main point to analyze the rheological behavior and to achieve the equilibrium of the paraffinic oil is the total deformation established during the shear history of the material, not the highest shear rate experienced by the material.

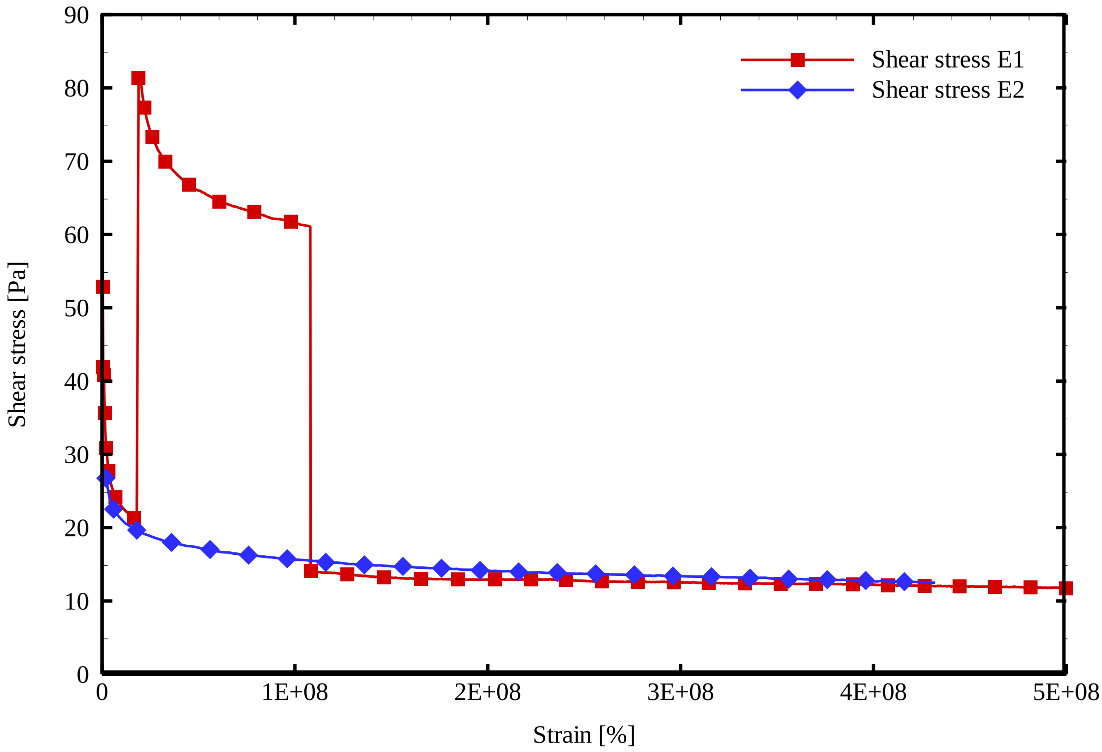

Figure 3.3. Shear stress as a function of shear strain for the same experiments showed in Figure 4.2.

4 CONCLUSIONS

The rheological behaviour of waxy oils at low temperature has been recently described as a function of the highest shear rate that was imposed to the material. Mendes et al. (2015) observed that these materials behave as a classical thixotropic fluid when the fluid flows with a shear rate below its cooling shear rate or the maximum shear rate it has ever experienced. Once the material is submitted to one new maximum shear rate, the behavior changes irreversibly. Similar behavior was reported by Geri et al. (2017).

In the present work, it was shown that the impact of the shear history on the rheological behavior of the material can be better understood from the point of view of the total deformation experienced by the material due to the shear. Based on results obtained with waxy model oil, one can conclude that the same final rheological condition can be obtained with different maximum shear rates imposed to the material since the total strain of the material is the same. In other words, the main point to be observed in the shear history is not only the magnitude of the maximum shear rate imposed to the material, but also the time that this shear rate was imposed. In that point of view, one can get the same rheological behavior for a waxy oil if the material experienced a low shear rate during a long period of time or also if it was imposed a higher shear rate to the material during a shorter period of time. If the total deformation experienced by the material is the same, the final rheological behavior seems to be similar.

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