RHEOLOGY OF WAXY OILS

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Abstract. *It is well known that below the crystallization temperature the rheology of waxy oils changes from Newtonian to an extremely complex non-Newtonian behavior, which is shear-rate and temperature-history dependent. Along the last decades a lot of effort has been put into obtaining reliable rheological measurements from different oils so as to understand the yielding of waxy oils as well as the effects of shear and temperature histories on rheological properties, such as viscosity, yield stress, storage and loss moduli. In this paper we examine in detail the related literature, discussing the main reasons for some disagreements concerning the history effects on the flow properties of waxy oils. In addition, we performed temperature ramps and stress-amplitude-sweep tests and compared the results obtained with the main trends observed, highlighting the effects of cooling and shear on the microstructure and consequently on the rheological properties of these oils.*

Keywords: *rheology, waxy oils, paraffin, gelation, rheometry*

1. INTRODUCTION

The oil production in deepwater and ultra-deepwater has been growing fast over the last years. In this kind of activity, the oil undergoes a rapid temperature drop, from the high temperatures at the reservoir to around 4 °C at the sea floor in these depths. During the shutdown and restart of production of waxy crude oils, this change in temperature becomes critical due to paraffin crystallization, which leads to a gelation process (as seen in Fig. 1), causing a radical transformation in the rheological behavior of these oils. This phenomenon complicates the design and operation of a pipeline system (Chang et al., 1999), particularly with respect to the prediction of the rheological properties of waxy crude oils at low temperatures, and has been widely related as one of the most important problems inherent to its processing.

From the literature we know that a simple Newtonian liquid at higher temperatures converts into a highly complex non-Newtonian material below the crystallization temperature (T_c), the temperature at which a sharp increase in viscosity is observed (Wardhaugh and Boger, 1987; Wardhaugh and Boger, 1991; Webber, 1999). Rheological characterization of these oils is very difficult, once the flow properties depend not only on the temperature and shear applied during the tests, but also on the shear and thermal histories experienced by the sample during cooling. Therefore, Wardhaugh and Boger [1987 and 1991] established a methodology in order to perform a meaningful rheological characterization. They showed that strict control of shear and temperature histories is necessary to obtain reproducible results in rotational rheometers. Moreover, Boger and associates [1991, 1998 and 2000] observed a complex yielding process and used a three-yield-stress model to describe it.

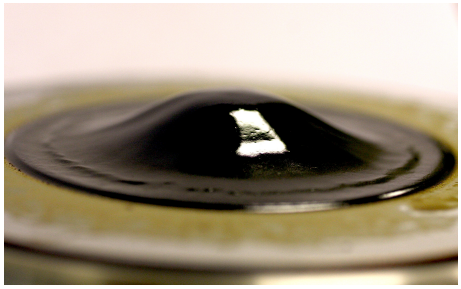


Figure 1. Gelled waxy oil sample at 4 °C.

Over the last decades, many researchers have been working in understanding the microstructure and rheology of waxy oils, considering the importance of determining the flow properties of these materials under different circumstances. Considerable progress has been made although some disagreements concerning the history effects on the flow properties of waxy oils still exist because of the complexity involved. Thus, more investigation in this subject is needed.

In this paper we performed a review of the related literature and a detailed discussion of history effects on microstructure and rheology. In addition, we carried out temperature ramps and stress-amplitude-sweep tests so as to clarify the main reasons of the disagreements mentioned above.

2. THE EXPERIMENTS

A pretreated waxy crude oil was used to carry out the rheological measurements. The pretreatment consisted on heating the crude oil at 60 °C for 1 h and then for 3 h at 50 °C in order to achieve a stable composition. The pretreated crude oil was separated and stored in five closed bottles. Before each rheological measurement a sample of one bottle was heated at 50 °C for 30 min to erase the oil "memory" by redissolving the wax crystals.

In order to perform the rheological characterization we use an AR-G2 rheometer from TA instruments, with smooth and cross hatched parallel plates and a range of gaps from 0.5 to 3mm. The set of tests performed includes temperature ramps and stress-amplitude-sweep. In the temperature ramps, the oil is cooled down from 50 °C to 4 °C under different cooling rates and subjected to different shear rates during cooling, and reheated back to 50 °C. At the end of the test we obtain information on how the viscosity varies with the temperature.

Since the oscillatory tests and flow curves are performed at 4 °C, the first step is to fix a "history" of the sample, i.e. fixing the cooling rate and shear rate during cooling. These tests serve to investigate the postcooling flow properties of waxy oils. Stress-amplitude-sweep tests consist on applying a fix oscillatory frequency, for a large range of stress amplitudes, and measuring both the storage and loss modulus responses of the sample.

3. RESULTS AND DISCUSSION

Figure 2(a) presents the main parameters involved in a temperature cycling, i.e. cooling and heating ramps. As previously mentioned, temperature ramps consist on cooling the sample, from 50 °C to 4 °C, and reheating it back to 50 °C, with a fixed cooling rate (which we name $\dot{T}_h$) and fixed shear rate (called $\dot{\gamma}_h$). The subscript "h" always refers to the history of the material. The Newtonian behavior, i.e. the linear part of the curve, can be observed until the crystallization temperature T_c, where the viscosity increases drastically. The viscosity reaches its maximum, η_{h0}, at the lowest temperature, and then decreases as the samples is reheated. At the reheating path we can observe a dissolution temperature T_d, above which the oil restores its simple Newtonian behavior. It is important to highlight that WAT cannot be measured with a rheometer, so that it is not shown in this graph, though it was measured with a calorimeter and has a value of 35 °C.

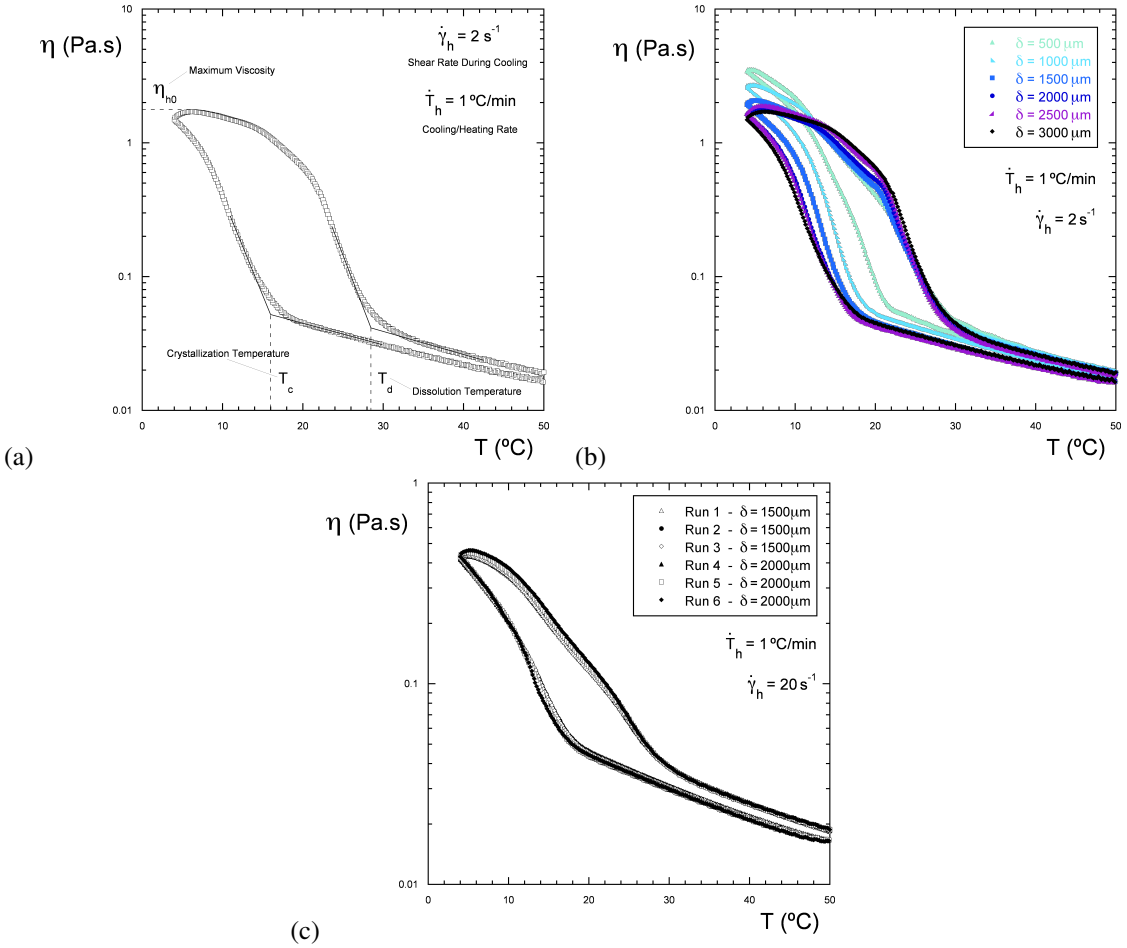


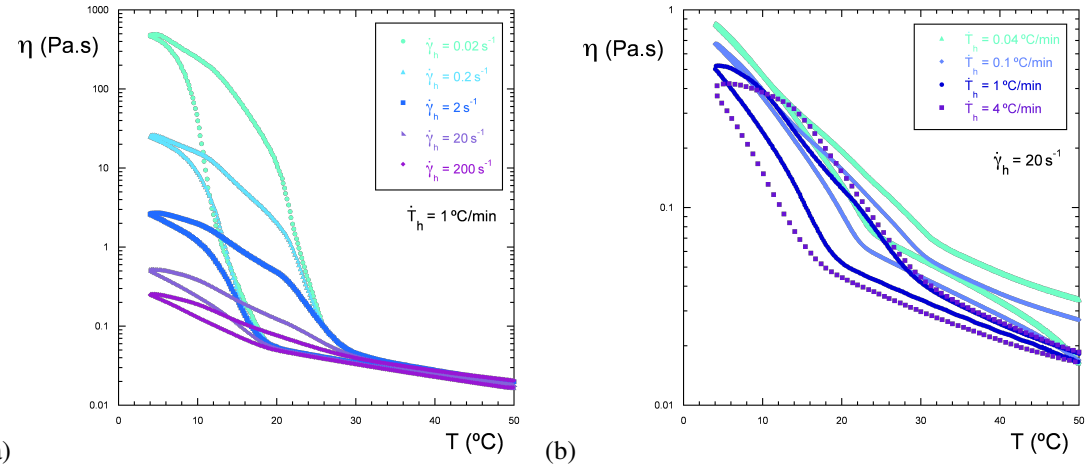
Figure 2. Temperature ramps: (a) Main Parameters; (b) Effect of gap; (c) Repeatability

In Figure 2(b) it is shown how the viscosity varies with gap changes. For the smallest gap, of 500μm, we obtained the higher viscosity η_{h0}. As the gap is increased, we can observe that the maximum viscosity decreases, until we reach an "ideal gap", where the results stop varying with the gap change. For instance: in this case, for a cooling rate of 1 °C/min and a shear rate during cooling of $2s^{-1}$, we see that with a gap of 2000μm we obtain the same result as for gaps of 2500μm and 3000μm, so that 2000μm is large enough. We verified that the ideal gap depends on the shear rate applied during cooling; it seems that higher $\dot{\gamma}_h$ generates smaller wax crystals.

Once we have established the ideal gap for each shear rate, we verified the repeatability of the tests with large enough gaps. As we can see in Fig.2(c), we obtain the exact same result for six runs of this kind of teste. As one can also note that, in this case, for a shear rate during cooling of $20s^{-1}$, a gap of 1500μm is enough.

From these graphs we can conclude that the "ideal gap" for a test depends on the shear rate applied during cooling and that the gap must be large enough to ensure reliable data.

With the ideal gap set, we can investigate the effect of shear rate during cooling and cooling rate on the microstructure, as shown in Figures 3(a) and 3(b), respectively.

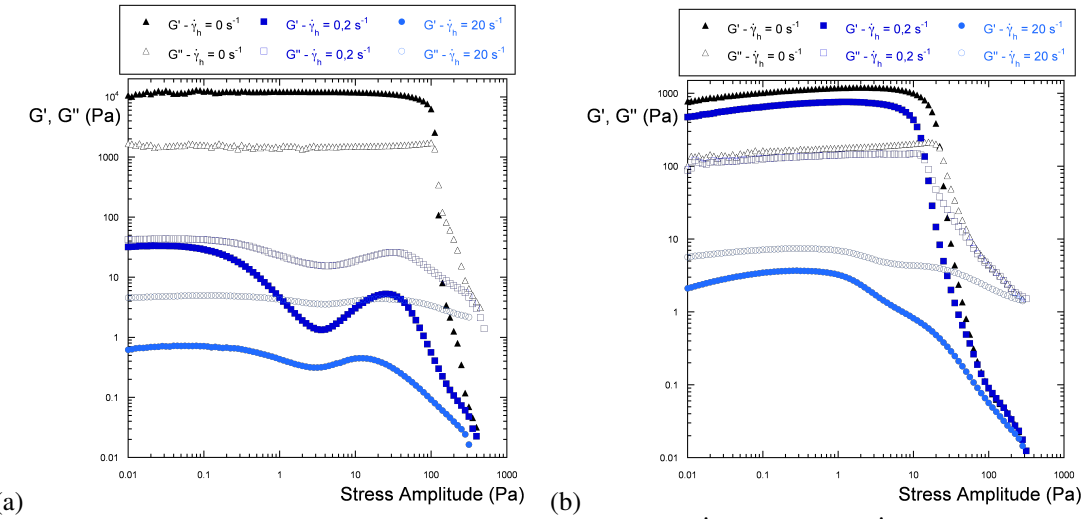


(a) (b)

Figure 3. Temperature Ramps: (a) Effect of shear rate during cooling ; (b) Effect of cooling/heating rate.

In Fig. 3(a) it can be observed the effect of shear rate on these ramps. As expected, smaller shear rates lead to much higher viscosities, in a clear shear thinning behavior. However, from this figure it can be noted that both T_c and T_d were not affected by altering the shear rate during cooling/heating. On the other hand, increasing the cooling rate during temperature cycling causes T_c, T_d and η_{h0} to decrease (Fig. 3(a)). This suggests that unlike the cooling rate that promotes an increase in average crystal length when decreased, the shear rate does not affect nucleation and growth of wax crystals but only the macroscopic structure that is developed from the interaction of growing crystals.

Once the investigation of flow properties during cooling is finished, we can move on to the stress-amplitude-sweep tests, which are performed in order to investigate the yielding of gelled waxy oils. In stress-amplitude-sweep tests we fix a "history" to the sample, by fixing the cooling rate $\dot{T}_h$ and the shear rate during cooling, $\dot{\gamma}_h$. These tests are performed at 4 °C.



(a) (b)

Figure 4. Stress sweep tests with fixed cooling rate: (a) $\dot{T}_h$ = 0.1 °C; (b) $\dot{T}_h$ = 1 °C.

On the graphs above it is shown the effect of the shear rate during cooling on the postcooling flow properties of the oil. For this purpose, the cooling rate had to be fixed for each set of tests.

In Figure 4(a) and 4(b) it is possible to see that, as expected, applying a shear rate to the sample during cooling leads to a less elastic behavior of the sample (G" > G'), and also that as $\dot{\gamma}_h$ is increased, the levels of both G' and G" decrease, which can be explained by the breakdown of the gelled structure. The difference between both graphs is that for the same $\dot{\gamma}_h$ of $0.2s^{-1}$ two different behaviors can be observed: for a $\dot{T}_h$ = 1 °C(fig. 4(b)) we observe a more elastic behavior of the sample (G'>G") and that the curve is almost the same as for the statically cooled sample ($\dot{\gamma}_h = 0s^{-1}$). However, the corresponding curve in Fig. 4(a) shows G" higher than G', and at much lower levels than for the non-sheared sample. It is worth noting here that smaller cooling rates imply more time of test. From this we can conclude that even a small shear, when applied for long enough time, causes damage to the structure.

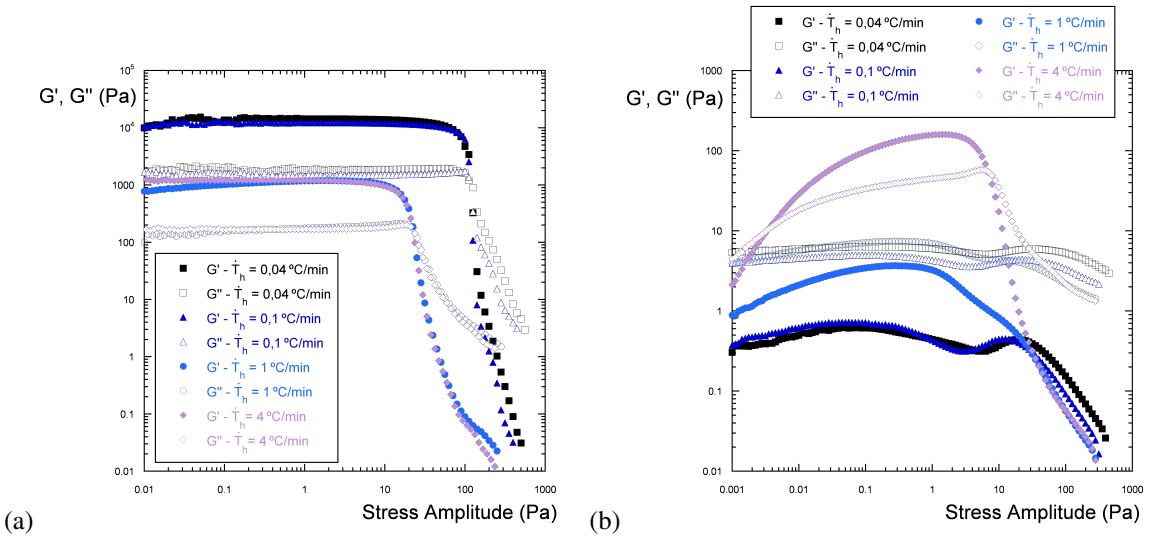


Figure 5. Stress sweep tests with fixed shear rate during cooling: (a) $\dot{\gamma}_h = 0s^{-1}$; (b) $\dot{\gamma}_h = 20s^{-1}$.

Figures 5(a) and 5(b) show the effect of the cooling rate on the postcooling flow properties for samples submitted to shear and not. For statically cooled samples we can observe the same behavior for all cooling rates: more elastic behavior (G' > G") and the consequent presence of a yield stress. It is also noticible that increasing the cooling rate causes both G' and G" to decrease, together with a decrease in the yield stress. On the other hand, observing the curves for a sample sheared during cooling, a different trend is shown: by increasing the cooling rate, both G' and G" increase too. It is noteworthy that only for $\dot{T}_h$ = 4 °C/min a more elastic behavior is observed and that yield stress appears. This curious fact can be illustrated by the fact that higher cooling rates mean less time of test, and in this specific case, less time of shearing, so that the sample does not get damaged enough that a more viscous behavior can be noted. Another comment that has to be made is the following: at the very beginning of the test, for small stress amplitudes, one can note that G" > G'. This occurs because the sample is not yet partially destroyed. As it structures along the test, G' becomes higher than G" and both moduli increase.

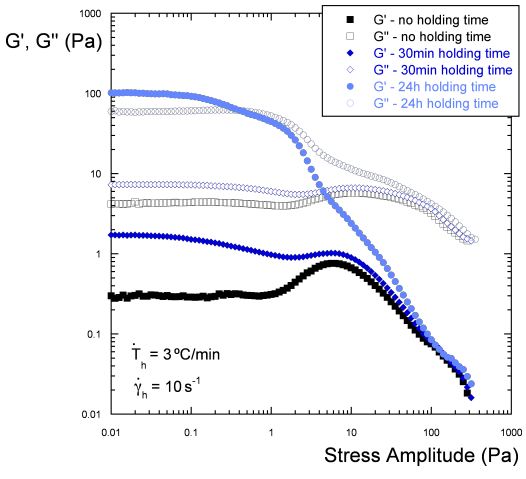


Figure 6. Stress sweep tests, after a preshear of $10s^{-1}$ for 30 minutes.

With respect to the holding time, after a preshear of $\dot{\gamma} = 10s^{-1}$ for 30 minutes, we verified that only for large enough holding times, of approximately one day, the microstructure can rebuild, and only partially.

4. FINAL REMARKS

An extremely complex rheological behavior including shear-rate and temperature-history effects on post-cooling flow properties was shown for a pretreated waxy crude oil. From the results it can be noted that above T_c waxy oils exhibit a Newtonian behavior, while below T_c they are highly non-Newtonian, with their behavior strongly depending on the thermal and shear rate histories. It was shown that increasing the shear rate during cooling, $\dot{\gamma}_h$, does not affect crystallization and dissolution temperatures (T_c and T_d), but causes a strong increase in the maximum viscosity, while on the other hand, decreasing the cooling rate, $\dot{T}_h$, causes a slight increase in viscosity but a strong increase of the T_c, indicating that the cooling rate affects the nucleation and growth of wax crystals.

Regarding the postcooling flow properties of waxy oils, it was observed that not only the magnitude of the shear rate during cooling affects the structure, but also the time of shear applied, which is directly related to the cooling rate. In addition, it will be shown that as previous related, waxy oils are not thixotropic materials since they are irreversible with a period of standing. However, waxy oils can recover the original structure if a temperature cycling is performed without any change in the composition, and can partially rebuild after shear when enough holding time. More detailed information will be presented at the conference.

5. ACKNOWLEDGEMENTS

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