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Differential Scanning Calorimetry contribution to a better understanding of the aging of gelled waxy crude oils

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Abstract. Below Wax Appearance Temperature (WAT), waxy crystals appear within the crude oil and make it viscous with yield stress and shear thinning properties. Particular attention has been paid during the past works on different parameters such as temperature, pressure, shear history, etc. Another important parameter is the holding time of the sample once it has gelled and left at rest under isothermal conditions. Actually, the network of waxy crystals is known to change with time. This phenomenon has been particularly observed in the case of deposit that is expected to harden. The set of rheological tests and calorimetric analysis that were performed on a real waxy crude oil confirm that a gel formed with waxy crystals may evolve with time and that the extent of this phenomenon depends on the thermo-mechanical past of the sample. Actually, a strengthening of the gel during holding time is observed in the case of fast cooling because the sample gets supersaturated. Aging takes place through isothermal crystallization that lasts a few minutes. The results have also shown that slowly cooled samples do not lead to any aging.

1 Introduction

Crude oils are mixtures of hydrocarbons among which waxes constitute a particular group of challenging compounds. They are composed of n-alkanes that have a low solubility at low temperatures. Below the so called Wax Appearance Temperature (WAT), they precipitate out in submicronic orthorhombic crystallites that form larger overlapping platelets or needles. A 3-D network stabilized by Van der Waals forces develops and is a major issue for the transportation of waxy crude oils. The network of waxes traps a large amount of non-precipitated oil and leads to deposits that reduce the flow capacity of pipelines or even plug them with a gel in the worst cases (Vinay *et al.*, 2005, 2006; Wachs *et al.*, 2009). Particular attention has been paid to characterize the wax deposit (hardness, melting point, heat of fusion, etc.) and the gel (yield stress, compressibility, rheology, crystallinity (Coutinho and Ruffier-Méray, 1999; Lorge *et al.*, 1997, etc.) but few papers have been published concerning their aging. Indeed, the network of waxy crystals is known to significantly change with time. This phenomenon has been particularly observed in the case of deposits which are said to get harder and richer in heavier n-alkanes (Creek *et al.*, 1999; Hsu *et al.*, 1994). The evolution of the deposit composition is mainly attributed to a diffusion process during which the heavy

n-paraffin components diffuse into the deposit layer while the light n-paraffin components diffuse out of it. The threshold size is called the Critical Carbon Number (CCN; Quan *et al.*, 2015). The involved mass transfer is supposed to be driven either by temperature or composition gradients. Ostwald ripening has been also mentioned as a second possible aging mechanism in the absence of any gradient (Hollander *et al.*, 2001; Lopes da Silva and Coutinho, 2004). In this case, the large crystals grow at the expenses of the melting of smaller ones of higher energy. X-ray diffraction and cross polar microscopy were employed to evidence the increase in size of the crystals by Coutinho *et al.* (2003). These authors also used Differential Scanning Calorimetry (DSC) to investigate the aging of wax deposit: the thermograms they obtained did not show any detectable heat change under isothermal conditions. According to them the heat of the melting (small crystals) and of the recrystallization (thickening of large crystals) are balanced, which is consistent with the process of Ostwald ripening. The aging behavior of the waxy gels has been even more rarely analyzed than deposits. One example can be found in Lopes da Silva and Coutinho (2007). It is based on rheological properties of different gels that have been used to follow the kinetics of their isothermal crystallization. According to this study, Avrami model (Avrami, 1939) appeared to well describe the related isothermal structure development. In this case, the authors did not imply Ostwald ripening but only isothermal crystallization without any induction time.

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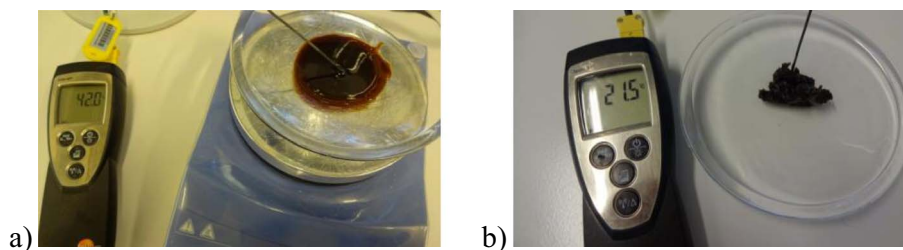


Fig. 1. a) Liquid aspect of the studied waxy crude oil above 40 °C and b) solid like aspect below 40 °C.

The obtained crystallization rates and resulting morphology were found to strongly depend on temperature that is to say on the degree of super-cooling. Faster crystallizations were observed for lower temperatures and were characterized by the presence of crystallized needles. On the contrary, slower crystallizations were observed for higher temperatures and were characterized by the presence of crystallized platelets. These findings illustrate how isothermal crystallization may concern waxy gels. Anyhow previous results were obtained on quenched samples with very fast cooling that are different from field conditions. To further investigate this complex subject, we followed the aging of waxy crude oils gelled with various cooling rates (from 0.1 to 30 °C/min). Both DSC and rheology were used, results are successively discussed in the present paper.

2 Materials and methods

2.1 Samples

The waxy crude oil that has been studied has a WAT of 40 °C. It appears like a solid below 40 °C and like a liquid above (cf. Fig. 1). This waxy crude oil is referenced as crude oil S in the remaining part of the paper.

2.2 Rheology

Rheological tests have been carried out on the controlled stress rheometer AR2000, *TA Instruments*. In order to limit slipping effect, a roughened plate and plate geometry was chosen. Thermal control (± 0.1 °C) was guaranteed with the Peltier device of the rheometer. Homogeneous temperature of the sample was favored using a small gap (300 μm). The diameter of the rotating plate was 4 cm. Oscillatory tests have been applied with a frequency of 10 Hz and a strain of 0.1. The significant advantage of this measurement is that it does not damage the sample and allows its characterization without destroying it. On this purpose, care was taken to evaluate it in the linear domain of the product. Many authors use smaller frequencies than 1 Hz as recommended by Li *et al.* (2009) to avoid interfacial artefacts. Anyhow it was decided to select the high frequency of 10 Hz in order to decrease the duration of the oscillation cycle and make it compatible with the kinetics of the aging of the sample in its initial step. Frequency sweeps from 5×10^{-4} to 50 Hz were made on two extreme representative samples (statically cooled and dynamically cooled (50 s^{-1}) from 60 to 30 °C). The cooling rate applied was -1 °C in order to respect equilibrium thermal conditions. The resulting spectra (cf. Fig. 2) show that for both cases no inertial artefact could be observed, which validates the choice of 10 Hz frequency.

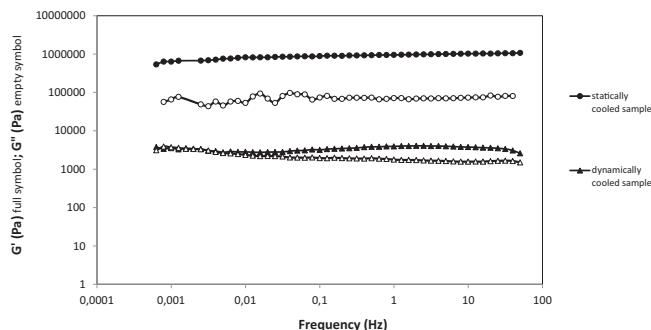


Fig. 2. Frequency sweeps obtained at 30 °C on two extreme representative samples showing their low frequency dependence of the tested range (samples cooled from 60 to 30 °C at -1 °C/min without any isothermal holding time after cooling).

2.3 Differential Scanning Calorimetry (DSC)

Calorimetric analysis has been performed on Mettler Toledo DSC 1. Samples of crude oil are weighed (7 mg) in sealed aluminum crucibles. The calibration of the DSC apparatus was performed with ultra-pure indium.

To investigate the ability of the crude oil to crystallize, DSC analyses have been performed with a cooling step from 80 °C down to -80 °C at -5 °C/min. This step was followed by a heating one from -80 °C up to 80 °C at $+5$ °C/min. The involved heat flows have been plotted (cf. Fig. 3). They show that waxy components start to crystallize below 40 °C which is consistent with the given WAT of the furnished crude oil. The appearance of crystals has been confirmed by optical microscopy at ambient temperature. It was realized between crossed polarizer and analyzer and display spherulites with a diameter of 15 μm (cf. Fig. 4). The thermographs also show that the sample contains tiny water droplets as described by Dalmazzone *et al.* (2009). This topic is out of scope of the present paper that focuses on isothermal aging of waxy crude oils without paying attention to water influence.

3 Results and discussion

During a potential shutdown during transportation, the produced fluid may reach the surrounding temperature and get gelled due to waxy crystallizations. Once isothermal conditions are fulfilled, the resulting structure may keep on developing. This phenomenon is called aging. Two cases of aging have been studied: the one that follows a quiescent cooling and the one that is subsequent to a dynamic cooling. The quiescent cooling is related to the upstream part of the

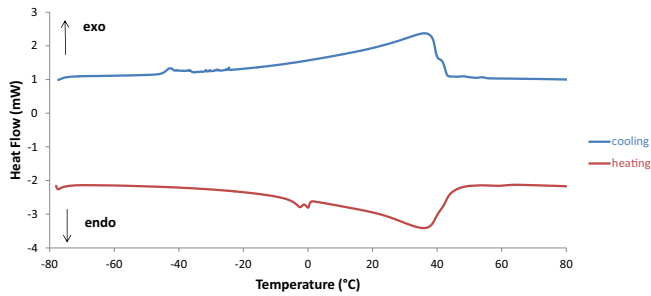


Fig. 3. Heat flow profile of crude oil S.

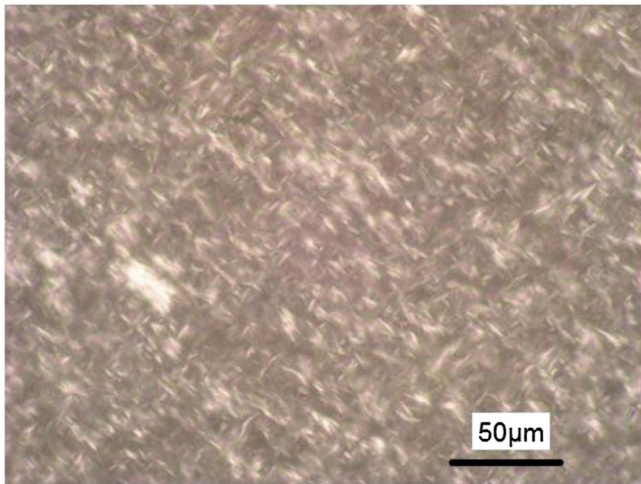


Fig. 4. Optical microscopy on tested crude oil, polarizer and analyser crossed at ambient temperature.

pipeline that is cooled once the shutdown occurs while the dynamic cooling is related to the downstream part of the pipeline that is cooled down under flow. Both scenarios have been studied and both comprise an isothermal holding time without any shear. Several cooling rates have been investigated.

3.1 Aging phenomenon after quiescent cooling – rheological results

3.1.1 Influence of cooling rate on the rheological properties of the waxy gel

The first scenario of aging has been studied in the case of quiescent cooling that is to say a cooling during which the sample is not submitted to any shear rate. Several cooling rates were applied. To assess the strength of the resulting structure, the elastic modulus G' of the sample has been measured with oscillatory tests. Its value has been plotted as a function of cooling rate in Figure 5. Results clearly demonstrate that the elastic modulus of the crude oil S decreases when the cooling rate increases. Several explanations can justify this behavior. Actually, cooling rate is known to impact the size of crystals which in turn influences the strength of the gel. This phenomenon is quite complex as it is not systematic. It seems to depend on the

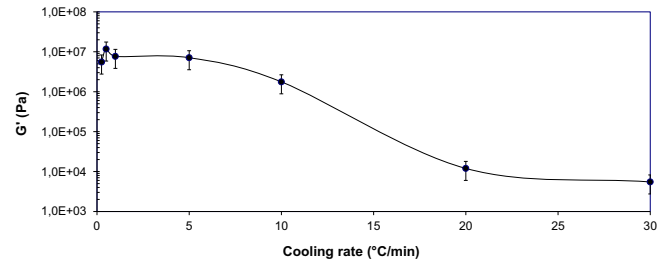


Fig. 5. Influence of cooling rate on the elastic modulus of crude oil S statically cooled from 60 to 30 °C without any holding time after cooling.

composition of the crude oil, especially on the presence of solids that can modulate crystals morphology (Yang *et al.*, 2015). In most cases reported in the literature, higher cooling rates lead to smaller crystals promoting more consistent gels (Cawkwell and Charles, 1989; Hénaut *et al.*, 1999; Russell and Chapman, 1971). Anyhow the reverse tendency has also been mentioned (Chang *et al.*, 2000; Ronningsen, 1992). Apart from morphological reasons, thermal equilibrium conditions can also be considered: when the cooling rate is higher than the rate of precipitation, crystals have not enough time to form and the sample is supersaturated (Venkatesan *et al.*, 2005) leading to a less consistent gel.

3.1.2 Influence of cooling rate on the aging of the waxy gel

To check the hypothesis of crystallization delay, the oscillatory moduli have been measured after different periods of holding time. This treatment should allow the sample to catch up with crystallization. Therefore previous experiments have been repeated and followed by different isothermal rests. During these periods, the moduli have been continuously measured. As it does not damage the sample, the rheological measurement of the moduli appears as a good method to assess the structuration with time. The responses of the samples cooled at -1 °C/min and -10 °C/min are shown in Figure 6. The curves display that the moduli of the slowly cooled sample (-1 °C/min) do not evolve with time and immediately reach a plateau. On the contrary, it takes roughly 2 min for the quickly cooled sample (-10 °C/min) to achieve the plateau level of moduli and finish the structuration.

These results confirm the hypothesis of crystallization delay when a higher cooling rate than precipitation rate is applied. It seems that for given experimental conditions a critical equilibrium cooling rate has to be considered. Consistently, Venkatesan *et al.* (2005) identified a cooling rate not to exceed in order to remain in the equilibrium cooling rate regime. In their study, the highest admitted cooling rate was 10 °C/min. In the same manner, Lin *et al.* (2011) restricted their cooling rates to 0.1 °C/min and 0.75 °C/min to respect equilibrium cooling conditions. According to Paso *et al.* (2005), the non-equilibrium cooling conditions are related to the density of nuclei present in the fluid as expected by homogeneous nucleation theory.

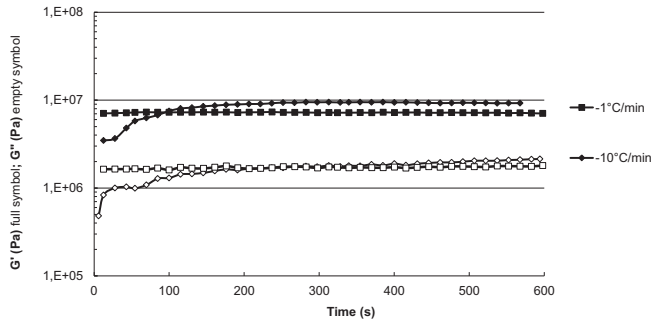


Fig. 6. Elastic (G') and viscous (G'') moduli during holding time of crude oil S statically cooled from 60 to 30 °C.

The results also display that the storage and the loss moduli evolve in the same manner during isothermal holding time for cooled sample at -10 °C/min: the aging strengthens both the viscous and elastic properties of the waxy crude oil. This behavior was not observed by Luthi (2013) on a waxy crude oil. This author noticed a significant increase of the storage modulus during aging times while the loss modulus remained constant. No further explanation is given. It seems that different aging mechanisms may exist and influence differently the structural properties of the sample. It can be expected that an aging accompanied by the appearance of crystals lead to an increase in viscosity and elasticity whereas the one due to Ostwald ripening with moderate change in morphology may influence more strongly the elasticity of the network than the viscosity of the evolving gel.

It can be noticed in that for the two statically cooled samples, the storage modulus is much higher than the loss one, showing the strong relationship between G' and the gelled structure. For the rest of the study, this parameter has been selected to quantify the evolving of the gel.

In order to better understand the influence of the cooling rate on the subsequent aging, the evolution of the elastic modulus has been plotted for different holding times and different cooling rates (cf. Fig. 7). The curves confirm that when slowly cooled, the sample usually does not demonstrate any delay in the crystallization so that the elastic modulus is quite high even in the first period of the holding time. On the contrary, a fast cooling (above 10 °C/min for crude oil S) leads to a delay in the crystallization, the sample is supersaturated and forms crystals during the holding time. These additional crystals seem to appear mostly in the first 2 min of the holding time as the increase in the elastic modulus is not significant afterward.

The above analysis clearly evidences that the evolution of the elastic modulus G' during the holding time comes from an isothermal crystallization process and not a thermal delay. Actually for the largest cooling rates, we verified that the thermal steady state in the sample was fully reached. The time evolution of the mean temperature was calculated in the gap at the end of the cooling process (from 60 to 30 °C), during the holding time and for different cooling rate, as illustrated in Figure 8. Even for a large cooling rate (30 °C/min), less than 15 s are required to reach the steady state, *i.e.*, the final temperature of 30 °C in this case.

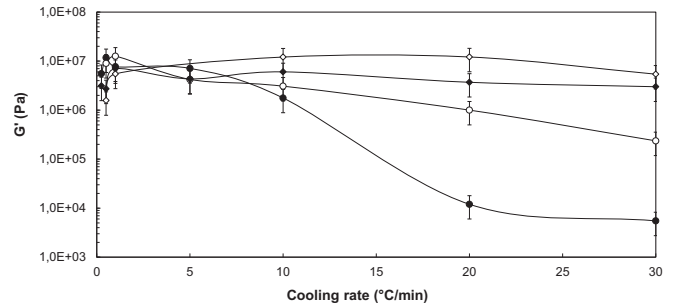


Fig. 7. Influence of cooling rate and holding time on the elastic modulus of crude oil S statically cooled from 60 to 30 °C without any holding time after cooling ($-●-$), with an holding time of 10 s ($-○-$), with an holding time of 2 min ($-◆-$), and with an holding time of 3 h ($-◇-$).

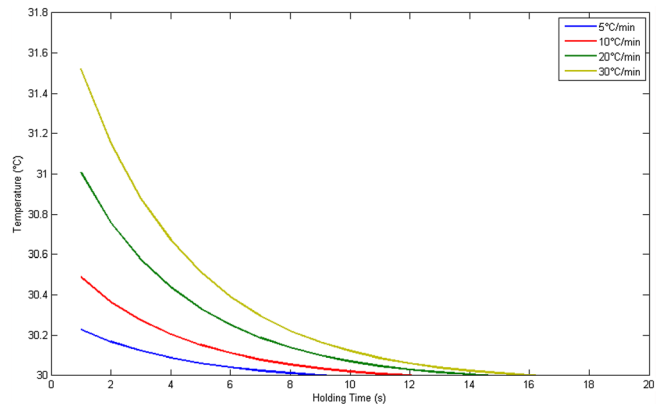


Fig. 8. Time evolution of mean temperature in the gap during holding time for different cooling rate.

Since G' is still evolving for about 2 min during the holding time, thermal effects cannot explain G' variations during holding time, and is mainly due to the crystallization process as explained before.

3.2 Aging phenomenon after dynamic cooling – rheological results

3.2.1 Influence of cooling rate on the rheological properties of the waxy gel

The second type of aging has been studied in the case of dynamic cooling that is to say a cooling during which the sample is submitted to a shear rate. To do so, the crude oil S been cooled down from 60 to 30 °C under a shear rate of 50 s $^{-1}$. Several cooling rates were applied. As for previous samples, the strength of the resulting structure has been quantified using the elastic modulus G' measured with oscillatory tests. Results are shown in Figure 9. They display the exact opposite tendency of the statically called sample: in the case of samples cooled under shear, the elastic modulus increases when the cooling rate increases. This behavior can be justified with the impact of the shear rate on the formation of the waxy network. The applied shear rate is

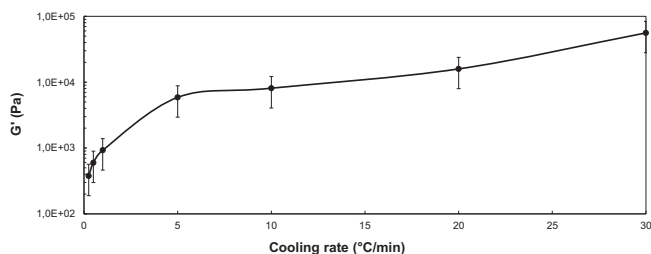


Fig. 9. Influence of cooling rate on the elastic modulus of crude oil S dynamically cooled under 50 s^{-1} from 60 to 30 °C without any holding time after cooling.

supposed to align the forming particles in the direction of flow, which weakens the 3D structure. This phenomenon was previously observed by [Cazaux et al. \(1998\)](#) analyzing a flowing waxy crude oil under flow. A lower cooling rate implies that the sample S is submitted to the shear stress for a longer time and as a result its elastic modulus decreases. This tendency has been observed by [Lin et al. \(2011\)](#), who attributed the decrease in yield stress for the dynamically samples to the resulting smaller and less interconnected crystals. Anyhow it seems that this dependency is not monotonic ([Paso, 2014](#)). Actually a moderate shear rate may aggregate wax crystals and contribute to an increase in gel strength. This was visually confirmed by [Venkatesan et al. \(2005\)](#) with a Linkam flow cell on a waxy fluid cooled under 0.1 rad/s compared to one cooled under 1 rad/s. In fact the gel strength of a gelled waxy crude oil seems to be the resulting of amount, size, shape and interconnecting of waxy crystals whose evolutions are not monotonic. This complex morphology and its effect on yield stress were recently explained by [Andrade et al. \(2018\)](#) for statically cooled samples with respect to thermal history.

3.2.2 Influence of cooling rate on the aging of the waxy gel

In order to study the influence of the holding time after a dynamic cooling, a sample of waxy crude oil S has been cooled and left at constant temperature for at least 3 h. During this period of rest, the moduli have been continuously measured to see how the sample evolves. The results obtained for -1 °C/min and for -10 °C/min have been plotted in [Figure 10](#), because they illustrate the two possible patterns. Actually, when slowly cooled, the moduli of the sample are low and do not evolve with time: the sample is not supersaturated, components that were expected to crystallize have been formed and no more crystals can appear. The low value of moduli is due to the applied shear rate during the long period of cooling. When quickly cooled, the waxy components did not have time to all crystallize. The sample is supersaturated and therefore can still evolve during the holding time. Due to the appearance of new crystals under quiescent conditions, the moduli increase and both G' and G'' reach a high plateau. Again the storage modulus is higher than the loss modulus, particularly for the sample enriched in waxy crystals at rest.

In order to better understand the influence of the cooling rate on the subsequent aging of dynamically cooled

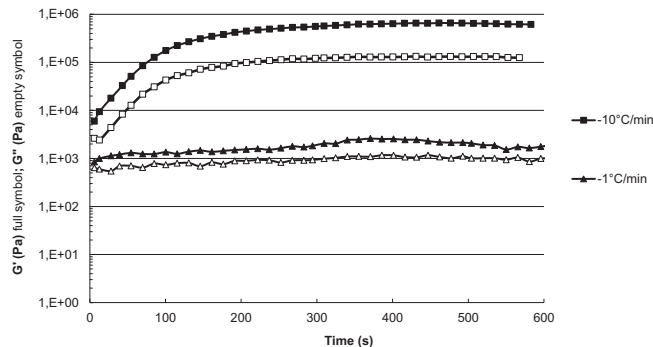


Fig. 10. Elastic and viscous moduli during static holding time of crude oil S dynamically cooled under 50 s^{-1} from 60 to 30 °C.

waxy crude oils, the evolution of the elastic modulus has been plotted for different holding times and different cooling rates (cf. [Fig. 11](#)). The curves confirm that when slowly cooled, the sample does not demonstrate any delay in the crystallization so that the elastic modulus remains low even after a long holding time. On the contrary, a fast cooling (above 5 °C/min for crude oil S) leads to a delay in the crystallization, the sample is supersaturated and crystals still form during the isothermal holding time. These additional crystals seem to appear mostly in the first 2 min of the holding time as beyond this time, the elastic modulus increases only slightly. As the new crystals are formed in quiescent conditions the resulting elastic modulus tends to reach the value of the statically cooled sample but remains lower due to the existence of permanently sheared crystals.

3.3 Differential Scanning Calorimetry (DSC) results

The DSC has been further applied to observe if crystallization would occur during an isothermal holding time. Actually isothermal crystallization can easily be depicted because it is an exothermal process. However, the inconvenient of the method is that it can only address statically cooled sample as no shear can be applied in the DSC apparatus. Therefore the waxy crude oil S was statically cooled from 80 to 30 °C in the DSC with different cooling rates. The cooling rates were chosen to be in the same range as the ones used in the rheological tests. When at 30 °C, the sample is left under 30 °C and heat flow is measured. The resulting amount of waxy crystals is quantified with the enthalpy required to completely melt them. The enthalpy is assessed by the melting peak integration. The obtained values have been plotted as a function of the cooling rates in [Figure 12](#). Different cases can be distinguished: The first one corresponds to the scenario without any holding time after cooling. In this case, the amount of crystallized waxes is higher when the cooling rate is lower. A plateau for the amount of crystals is reached for cooling rates lower than 1 °C/min : these peculiar thermal conditions allow the complete gelation of the sample. The crude oil does not get supersaturated due to the imposed equilibrium conditions. Reversely, when quickly cooled, the waxes do not have enough time to fully crystallize. The corresponding melting peaks are small and lead to weak

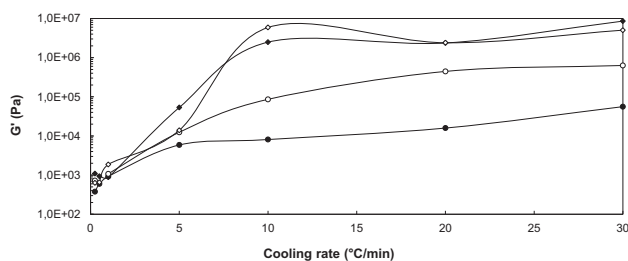


Fig. 11. Influence of cooling rate and holding time on the elastic modulus of crude oil S dynamically cooled under 50 s^{-1} from 60 to 30 °C without any holding time after cooling (—●—), with an holding time of 10 s (—○—), with an holding time of 2 min (—◆—), and with an holding time of 3 h (—◇—).

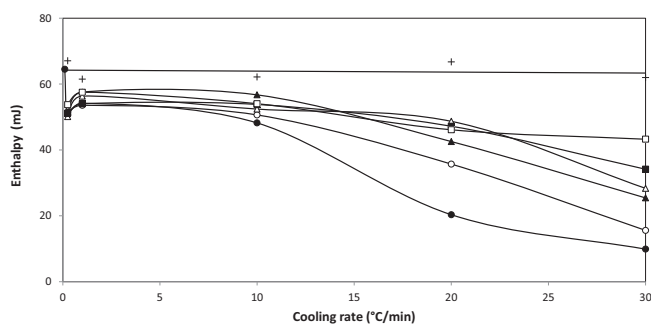


Fig. 12. Influence of cooling rate and holding time on the melting enthalpy of crude oil S cooled from 80 to 30 °C without any holding time after cooling (—●—), with an holding time of 10 s (—○—), with an holding time of 30 s (—▲—), with an holding time of 45 s (—△—), with an holding time of 1 min (—■—), with an holding time of 2 min (—□—), and with an holding time of 5 min (+).

enthalpy. The resulting sample is supersaturated. During the subsequent holding times in isothermal conditions, crystals form from the saturated solution and the crude oil ages. Results show that it takes roughly 5 min to catch up with the entire crystallinity.

4 Conclusion

The set of rheological tests and calorimetric analysis that were performed on waxy crude oil S confirm that a gel formed with waxy crystals may evolve with time and that the extent of this phenomenon depends on the thermo-mechanical past of the sample. Actually, a strengthening of the gel during holding time is favored in the case of fast cooling because the sample gets supersaturated. This is valid for statically and dynamically cooled samples.

It has been shown that the aging resulting from an isothermal crystallization takes place in a short period. It is complete after a few minutes. This is opposite to the slow evolution sometimes observed on large volumes of waxy crude oils due to a thermal delay or a slow structural change (Ostwald ripening, molecular diffusion).

The results have also shown that slowly cooled samples do not lead to any aging, *i.e.*, the gel structure of a slowly cooled sample does not evolve during the isothermal holding time:

- For a gel formed under a slow and static cooling, its maximum structure is reached at the end of the cooling because all waxy components have crystallized.
- For a gel formed under a slow and dynamic cooling, all crystals have also been formed during the cooling, but its maximum structure is weaker because formed under shearing conditions.

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