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Rheological Measurement of Waxy Crude Oil under Controlled Stress Rheometer: Determination of the Setting Parameters

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Abstract: Rheological measurements are essential in transporting crude oil, especially for waxy crude oil. A lot of rheological measurements have been conducted to determine various rheological properties of crude oil including the viscosity, yield strength, Wax Appearance Temperature (WAT), Wax Disappearance Temperature (WDT), storage modulus and loss modulus, amongst others, by using a controlled stress rheometer. However, a standard procedure to determine the correct parameters for rheological measurement is still unavailable in the literature. The paper proposes a set of procedures to systematically determine the setting parameters including the angular frequency range, geometry gap determination and also the equilibrium time prior to the rheological measurements of waxy crude oil. The correct parameters settings will produce a more reliable and repeatable results of the rheological properties.

Key words: Waxy crud oil, angular frequency, geometry gap

INTRODUCTION

Currently, the efforts to overcome depleted crude oil production are focusing on heavy crude oil production by using Enhanced Oil Recovery (EOR) technology and exploring new oil-reservoirs at more severe locations i.e., deep water fields (Martinez-Palou *et al.*, 2011). EOR technique proposes enhanced recovery methods to effectively lift up higher fractions of crude oil from the reservoirs. Exploring new oil-reservoirs at deep water field is challenging due to low sea-bed temperature which can be as low as 4°C (Ribeiro *et al.*, 1997), high pressure (>10,000 psi shut-in pressure), high temperature (>350°F) and complex fluid with flow assurance difficulties (Olson, 2008). At present, one of common EOR technique is to reduce heavy oil viscosity by forming Oil in Water (O/W) emulsion. Both EOR and deep water explorations, amongst others, are known to have flow assurance problems, including hydrate formation, wax deposition and crude oil emulsions. To solve these problems, rheological studies of the crude oil are required in order for the facilities to be designed and installed appropriately.

For instance, W/O emulsion viscosity measurement done by Ronningsen (1995) for North Sea Crude Oils showed that viscosity of the emulsion varies significantly according to the fluid systems. Meriem-Benziane *et al.* (2012) measured rheological properties of 4 light crude oil

types and the O/W emulsions under a rheometer using a cone and plate geometry. The results from continuous flow measurements over a shear rate range of 0-130 sec⁻¹ (at 20°C) showed that the viscosities for all the crude oil types linearly increase with the shear rate showing shear thickening behaviour and quasi-Newtonian rheological behaviour. In addition, from the experimental results, it was concluded that water contents and the nature of crude oils strongly affects the rheological and physical stability of the emulsions. Rheological measurement of a heavy crude oil from Husky Energy-Lloydminster, Canada using a cone and plate geometry was conducted by Hasan *et al.* (2010) at a temperature range from 25-75°C. The results show that over the shear rate range, Non-Newtonian shear thinning behaviour was observed, contradicting to the observations documented by (Barnes, 2000). However, this result is consistent with that of (Ghannam *et al.*, 2012; Aomari *et al.*, 1998). Another rheological study on heavy crude oil under the rheometer by ramping the shear rate from low to high and back to the low shear rate showed that the heavy crude oil exhibit thixotropic behaviour (Ghannam *et al.*, 2012). The degree of thixotropy is higher as the temperature is increased. (Aomari *et al.*, 1998) conducted a strain sweep measurement at a frequency 1 Hz over the strain range of 10⁻²-10³% to determine the strength of dispersant structure of the fluid, storage (G') and loss (G'') modulus. Frequency sweep measurement was then performed to

determine cross over point at which the G' value overlap the G'' value. The authors found that the inverse points or critical fractions above which the emulsion is reversed from W/O to O/W emulsion were 0.84 and 0.88 for the two light crude oil samples. Frequency sweep measurements between a frequency of 1 and 40 Hz under various temperatures (-20-20°C) were conducted by Pierre *et al.* (2004). Pseudo plastic behaviour was observed for the heavy crude oil used without any yield stress. A yield stress measurement was done by Ghannam *et al.* (2012) using a stress ramp method at various temperature (25, 45 and 65°C). The stress was applied to the sample from 0.09-4 Pa and the shear stress against shear strain was plotted. The yield stress was the stress at which the sample starts flowing (shear rate > 0). In other work, stress sweep of 100-10,000 mPa (at frequency 1 Hz) was done using parallel plate geometry (35 mm) with gap of 2 mm to determine viscoelastic region of crude oil emulsion (Fingas and Fieldhouse, 2009). All rheological properties were measured within this region. Geometry diameter and gap utilized were 40 mm and 600 μm , respectively (Pierre *et al.*, 2004).

Based on existing literature available, various rheological measurements have been conducted to assess similar rheological parameter i.e., G' , G'' , linear visco-elastic region, yield stress, viscosity, thixotropy, etc. However, no standard procedure has been proposed to correctly set the parameters in order for the rheological measurements to be conducted. These procedures are very important in order for reliable results to be obtained (Ghannam *et al.*, 2012; Pierre *et al.*, 2004), (Fingas and Fieldhouse, 2009). Moreover, rheological measurement procedures may be specific for each fluid system as indicated in the work done by Ronningsen (1995). Hence, different rheological measurement procedures may be required for each fluid system.

This study aims to propose the procedures to determine the setting parameters for rheological measurements of waxy crude oil.

METHODOLOGY

A waxy crude oil from South East Asia region is utilized in this study. Controlled stress rheometer AR-G2 was used for all rheological measurements using a 40 mm cross hatched plate geometry to minimize apparent wall slip phenomena. A solvent trap was used to minimize evaporation of the light end components from the sample for all the rheological measurements and maintain the stability of the sample composition. The measurements procedures in this work are as described below.

Non-newtonian region, WAT and WDT: Two rheological measurements were first conducted to determine the gelled temperature, Newtonian and Non-Newtonian

regions of the sample as well as the Wax Appearance Temperature (WAT) and the Wax Disappearance Temperature (WDT). The sample was sheared at a constant rate of 0.1 and 100 sec^{-1} from an initial temperature (T_i) of 45°C, a temperature well above the anticipated WAT, to a low temperature (T_o) of 15°C, at constant cooling rate of 1°C min^{-1} . Once it reached T_o , the sample was heated back to T_i at same rate. The test was known as a thermal cycle test (Marchesini *et al.*, 2012).

Gap determination and linear visco-elastic (LVE) region:

Measurement gap is an important parameter in any rheological measurements such that continuum assumption is valid within the gap. The rule of thumb dictates that the measurement gap is to be 10 times the particle size in order for gap-independent results to be obtained (Barnes, 2000). To determine the correct gap for the rheological measurement, the sample was subjected to a thermal cycle test (Marchesini *et al.*, 2012) under a shear rate of 100 sec^{-1} at 4 different gaps (300, 500, 700 and 900 μm) within the temperature range of 45-15°C. After thermal cycle test, the sample is subjected to a strain sweep from 0.01-200% at a frequency of 10 rad sec^{-1} at the gap defined previously to determine the LVE region.

Inertia dominated region: Inertia dominated region is a region where the inertia of the equipment strongly affects the rheological measurement. It can be observed as an artificial increasing of viscosity or storage modulus. Misinterpretation and inaccurate analysis could result without indentifying the inertia-dominated data.

Tas the inertia torque formula shown below for controlled stress (CMT) rheometer should be greater than 10:

$$\frac{T}{T_s} = \frac{Ik_s \omega}{\eta} \quad (1)$$

It can be seen from the formula that the minimum viscosity would result in a maximum torque ratio (other parameters are kept constant) indicating that the minimum viscosity would give a maximum torque limit above which will be the inertia dominated region. Alternatively, inertia dominated region can also be determined by observing delta and raw phase angle of the sample during measurement following their correlation as below:

$$\text{Raw Phase} \times \text{Inertia correction} = \text{delta } (\delta) \quad (2)$$

The measurement will not be affected at all by system inertia when the inertia correction factor is equal to 1 or

when the sample fully dominates the measurement. When system inertia start to take part in the measurement, the contribution of the sample will be less and thus, the inertia correction factor will be <1 .

A frequency sweep test was conducted to determine the region. The sample was subjected to a frequency sweep of 0.01-20 rad sec at the temperature below (15°C) and above (45°C) the WAT of the crude oil sample; i.e., when the sample exhibits Newtonian and non-Newtonian behavior. In addition, the strain should be set within the LVE region of the sample such that the elastic and loss moduli are independent of the stress and strain applied and are only functions of frequency.

Response time of the sample: Another important parameter to be considered for the rheological measurements especially for waxy crude oil is the response time of the sample. It is the time required by the sample to regain stability under the given conditions (Mazzeo, 2012). If equilibrium time allowed is shorter than the response time of the sample, the measurement results would be highly influenced by the shear history of the sample.

To achieve the purpose, a time sweep test was suggested by Mazzeo (2012) to determine the response time of the sample. The test is conducted at a frequency 10 rad sec^{-1} and a constant strain of 0.5%, i.e., within the LVE region and at two measurement temperatures: 45°C (Newtonian region) and 15°C (Non-newtonian region) for 15 min.

RESULTS AND DISCUSSIONS

Rheological measurements have been performed using the procedures described in the previous sections and the results are explained below.

Non-Newtonian region, WAT and WDT: Two thermal cycle test were first conducted to determine the Newtonian and Non-Newtonian regions as well as WAT and WDT. These results are presented in Fig. 1 and 2.

The results showed that at low shear rate, only Non-newtonian region was observed. However, it was obvious that there were sudden viscosity changes on both cooling and heating curves. These changes were observed at temperature below 20 and above 30°C , respectively. The noisy result at temperature above 30°C was believed due the low shear rate and sample's viscosity so that the measurement becomes very sensitive to any external disturbance.

At high shear rate, typical Arrhenius temperature dependent of Newtonian fluid were observed at approximately temperature above 20 and 30°C for the cooling and heating curves, respectively while non-newtonian regions were observed below these temperatures. The two temperatures were known as WAT (the cooling curve) and WDT (the heating curve), respectively. Below WAT, the sample would have higher viscosity value under low shear rate than with high shear rate. It is because high shear rate promotes finer wax crystal formation than low shear rate such that it reduces the viscosity. From these experiments, it was clear that the measurement temperature range covers both Newtonian and non-newtonian regions of the sample. In addition, higher applied shear rate would significantly reduce the noise (less sensitive to external disturbance) that was shown as non-Newtonian-like behaviour (Fig. 1).

Gap determination and linear visco-elastic (LVE) region:

From the thermal cycle test, as shown in Fig. 3, the viscosity data varies according to the measurement gaps. WAT and WDT for all the measurements were found to be around 22 and 34°C (good agreement with previous

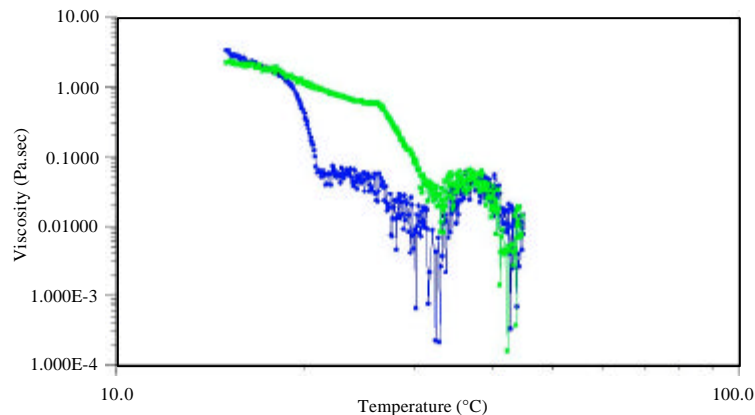


Fig. 1: Thermal cycle test result at the shear rate of 0.1 sec^{-1}

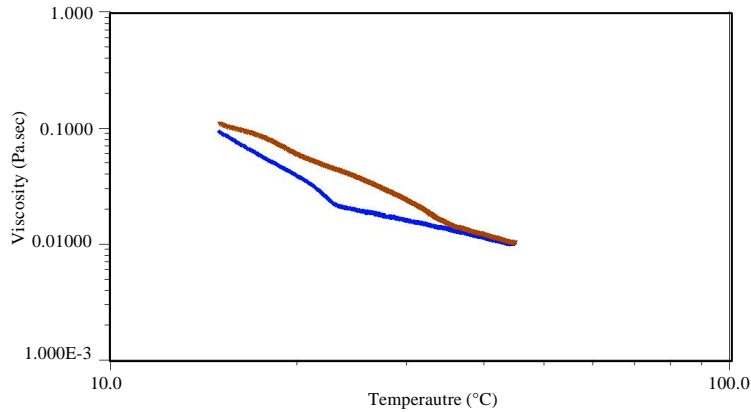


Fig. 2: Thermal cycle test result at the shear rate of 100 sec⁻¹

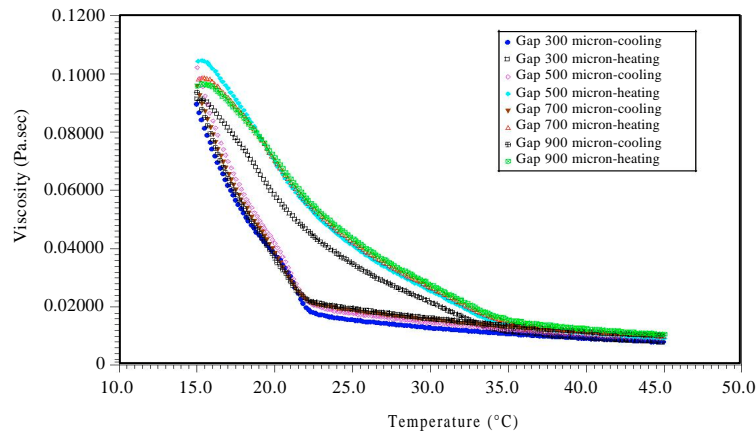


Fig. 3: Thermal cycle test at 4 different gaps

results), respectively indicating that the WAT and WDT are independent of the gap setting. In Newtonian region, the viscosity value at the gap of 300 μm was the lowest. At the gap settings of 700 and 900 μm, the viscosity values were in agreement. Within the non-newtonian region, the viscosity values for all the four gaps were in agreement to each other except for the gap setting of 300 μm when the sample is subjected to heating where the viscosity is significantly lower.

For both Newtonian and non-Newtonian range (above and below WAT) the viscosity values at the gap settings of 700 and 900 μm were very close to each other indicating that the gap of 700 μm is the minimum gap to ensure gap independent results. From this result, independent gap result can be achieved at gap 700 μm.

However, it should be noted that this gap is valid under the applied shear rate of 100 sec⁻¹ and temperature cooling/heating rate of 1°C/min. Different combinations of

shear rate and cooling/heating rate may produce different results (Marchesini *et al.*, 2012).

In this measurement, viscosity difference on Newtonian region (Arrhenius sector) during heating and cooling processes were very small (negligible) compare to the work done by Marchesini *et al.* (2012) for all the measurement gap settings. It indicated that there was no significant irreversible mechanical degradation on the sample and hence, rheological measurements can be done on the same sample in series.

Strain sweep measurement in Fig. 4 showed that linear G' values exist at strain 0.1-2% and thus, this region is the LVE region of the sample. The intersection between G' and G'' appears at strain above 10% followed by dramatic increased on the raw phase angle. It indicated that the sample was completely broken down.

Inertia dominated region: In order to determine inertia dominated region, a Newtonian fluid was subjected to a

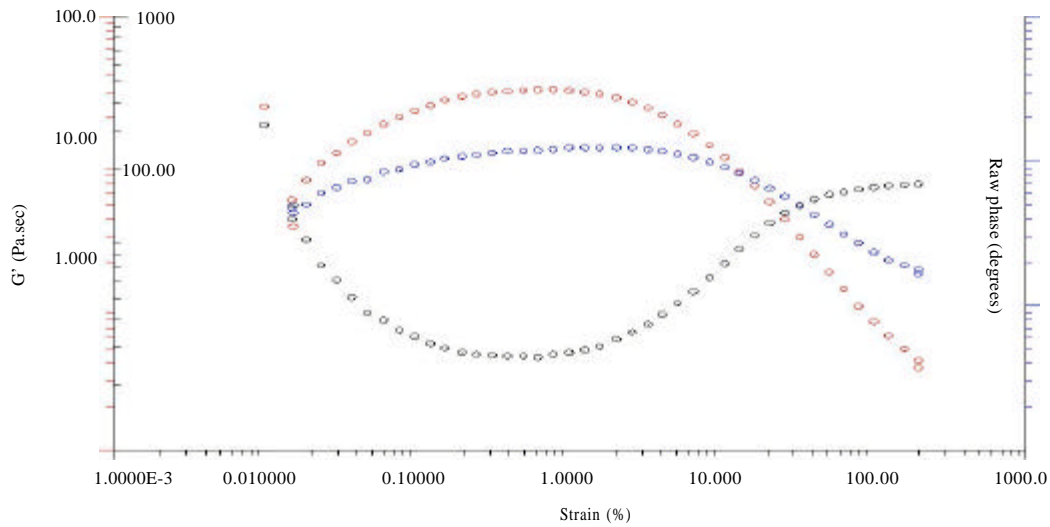


Fig. 4: Strain sweep measurement at non-Newtonian region (15°C)

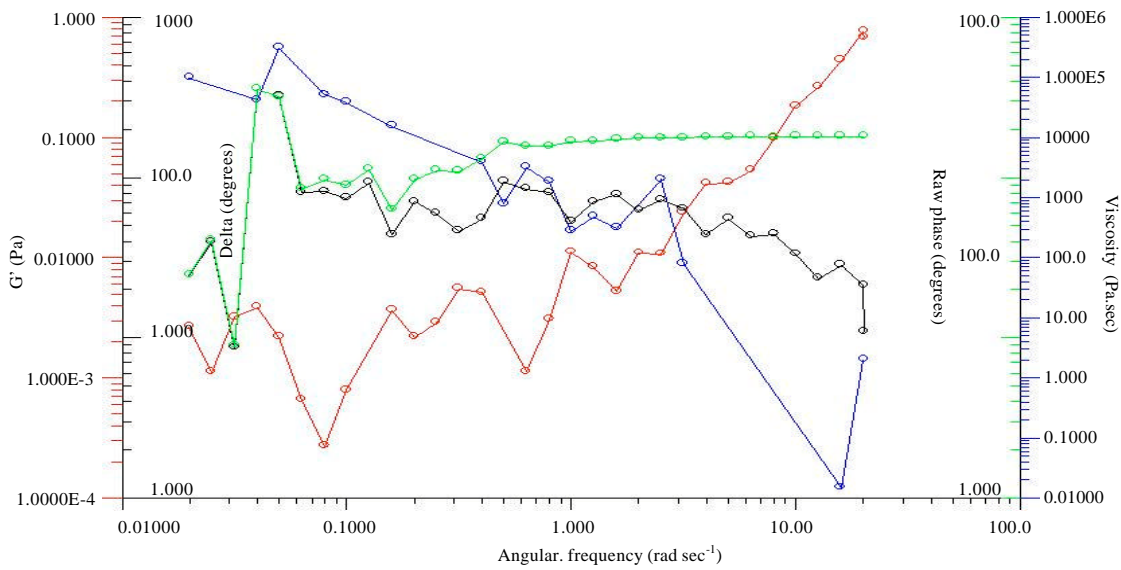


Fig. 5: Frequency sweep measurement at temperature above WAT (Newtonian region)

frequency sweep measurement as described in the previous section at gap of 700 m as determine previously. For a Newtonian fluid, a constant viscosity value is anticipated over the applied frequency range or otherwise the result is highly influenced by the system inertia. The elastic modulus should also be zero.

Results from the frequency sweep measurements on the sample at both Newtonian (above WAT) and non-Newtonian regions (below WAT) are presented in Fig. 5 and 6, respectively. Within the Newtonian region, it can be seen that delta values start to deviate from raw phase angle at 0.05 rad sec⁻¹ and become significant at

0.3 rad sec⁻¹ onwards. As indicate by Eq. 2, the results implied that the system inertia start to dominate the measurement at frequency above 0.3 rad sec⁻¹ and hence, this region should be avoided. The raw phase angle was found to be above 150° for almost all the measurement range due to the Newtonian behavior.

Within the non-newtonian region, almost all raw phase angles were below 150°C indicating that the sample was not broken down. A linear G' value was observed at frequency from 0.04-0.2 rad sec⁻¹ indicating that the sample was at its visco-elastic region. Decreasing viscosity trend displays shear thinning behavior of the

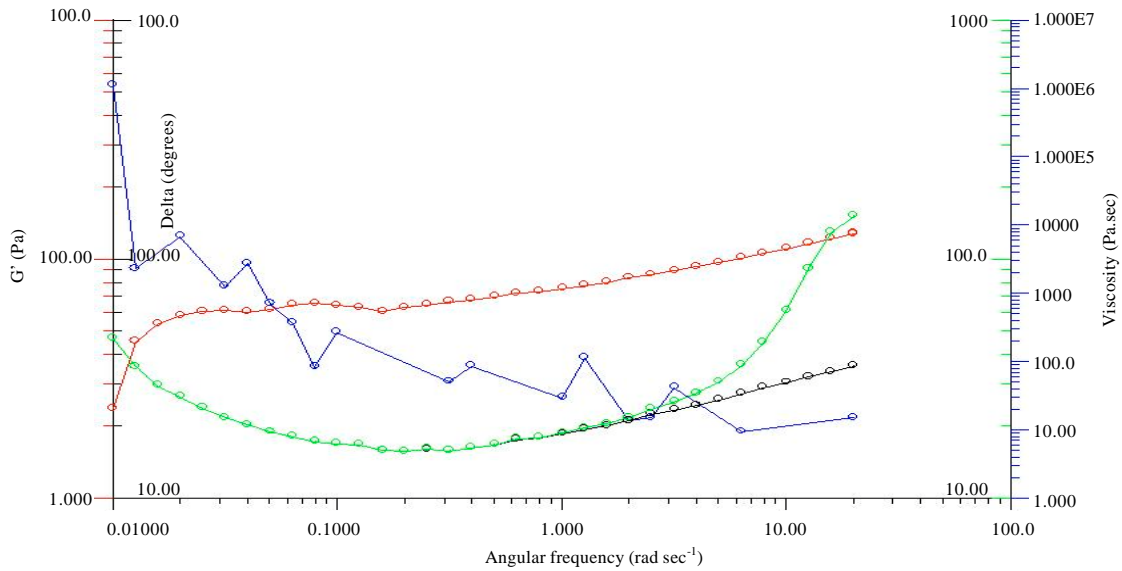


Fig. 6: Frequency sweep measurement at temperature below WAT (non-Newtonian region)

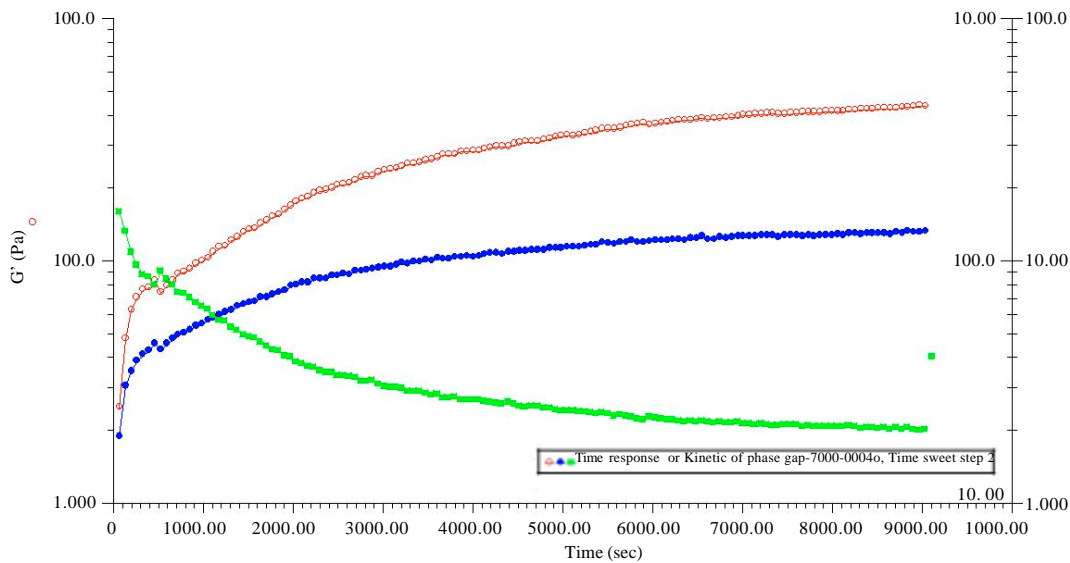


Fig. 7: Time sweep result

sample. Delta values were found to start deviate from the raw phase angle at frequency 2 rad sec⁻¹ indicating that system inertia took part in the measurement. Significant deviation was observed starting at frequency 10 rad sec⁻¹ above which is inertia dominated region.

Response time of the sample: A time sweep was applied to the waxy crude sample to determine the time response at which the sample regains its structure (Mazzeo, 2012). This set is crucial in order to determine the correct equilibrium time on the conditioning step of the

measurement. The result is presented in Fig. 7. The G' and G'' is taken as an indicator of the stability of the crude sample with an equilibrium value indicating that the sample is stable.

It can be observed that at gelled condition (15°C) even with 900 sec of time duration, the sample was found to still be unstable. However, it is not practical to wait until the sample to become completely stable. Hence, it is reasonable to consider the response time at the point at which slope of the gradual curve changes is significantly decreased. In this case, the point was at approximately

360 sec. It should be noted that the sample was subjected to a temperature ramp from 45-15°C under an imposed shear rate of 100 sec⁻¹ before being subjected to the time sweep measurement. Hence, it can be concluded that the sample required an equilibrium time as long as 360 sec after the temperature ramp step before any other measurements can be taken.

Within the Newtonian region at 45°C, the raw phase angle was all above 150° and highly scattered indicating that the data is inertially dominated and hence not be presented.

CONCLUSION

A series of rheological measurements have been done for a waxy crude oil from South East Asia region. From thermal cycle test, the results showed that the WAT and WDT of the crude oil are 22 and 34°C, respectively and are independent of the gap setting. The appropriate gap for any rheological measurements to be conducted on this sample is 700 µm. The thermal cycle test also provide an evident that the sample has no irreversible mechanical degradation due to the temperature ramping and applied shear rate, hence, the sample can be subjected to a series of rheological measurement. Strain sweep measurement result display LVE region of the sample at strain 0.1-2%. Frequency sweep measurements showed that rheological measurement on the sample within Newtonian region should be conducted within the frequency range of 0.01-0.3 rad sec⁻¹. At temperatures below WAT (non-Newtonian region), the measurements should be performed within the frequency range of 0.01-10 rad sec⁻¹ for minimum inertia effects. Decreasing viscosity trend during frequency sweep measurement represent shear thinning behavior of the sample. Time sweep measurements confirmed that the crude oil sample needs an equilibrium time as long as 360 sec in order to regain a stable structure. The systematic protocols proposed in this study provide critical parameter values that are important in order for a reliable rheological measurements to be conducted. The protocols may be applied to any other crude oil rheological measurements as preliminary measurement.

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