PARTIAL RECOVERY OF WAX GEL STRENGTH: QUANTITATIVE AND QUALITATIVE ANALYSES

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Abstract

Waxy components in a crude oil start to precipitate when the surrounding temperature is lower than wax appearance temperature (WAT). While the wax deposition can be initiated during the flow, wax gel formation occurs primarily under static conditions. When the wax gel develops within a relatively short time, certain pressure is needed to overcome the yield strength of the gel along the pipeline for restart. It was found that paraffinic components contribute to the evolving gel strength continuously while the oil is cooled below pour point (PP). Gel strength depends on wax amount and wax composition in the gel network. It has been reported that the gel properties depend on various factors: temperature, cooling rate, cooling time, shear history, and a diverse combination of factors. This study explores gel strength by stress exertion below the PP followed by further cooling. Model oil used in this study was prepared by mixing mineral oil and well-characterized wax. The measurements of WAT and PP were performed using the ASTM methods. A controlled-stress rheometer equipped with a cone-and-plate geometry and a Peltier plate device was employed to determine the yield stress and the measurement of creep response. The cooling was scheduled after applying stresses in the creep range. Yield behavior was compared after applying varying stresses and cooling to lower temperatures.

Key words: wax, gel strength, yield stress, creep compliance

Introduction

High molecular paraffinic waxes in a crude oil start to precipitate when the surrounding temperature is lower than the wax appearance temperature (WAT). Pour point is another important characteristic temperature usually determined by ASTM D97 (1), which represents a transition from flow to no flow. Flow discontinuity occurs in due to either wax deposition or wax gel formation. While the wax deposition can be initiated during flow, wax gel formation occurs primarily under static conditions caused by either planned or emergency shutdown. When the wax gel develops within a relatively short time, certain level of pressure application upstream is necessary to overcome the yield stress of the gel along the pipeline for restart (2, 3). Various rheological studies of gelled waxy oil have been published. Boger and coworkers (4, 5) discussed the existence of three definite characteristic responses, which they categorized as elastic, creep and fracture when the gel was subjected to shear. In the elastic region, the gel strength is fully recovered after sufficiently low shear is applied to the gel regardless of duration time over which the shear is applied. Prior to the static yield stress (the point at which the gel fractures), a creep region is observed, in which the gel strength is partially recovered once the applied stress is released. The gel yields at shorter times, when higher shear is applied. In case of fracture, the gel breakage occurs when the loading stress is high enough to deform the gel network.

Singh et al.(6) pointed out that various factors, such as wax/oil ratio (wax amounts), molecular weight of the wax, cooling rate and mechanical shear history, affect wax precipitation and deposition characteristics including gelation temperature. In particular, they reported that when shear is applied to waxy oils, the gelation temperature is depressed, with a greater reduction at higher shear rates. They also compared the effect of cooling rates on the gelation temperatures, showing that slower cooling rates resulted in greater reductions in yield stresses. Venkatesan et al. (7) examined the yield stresses with different cooling rates in both quiescent and shear conditions. Highest yield value was observed in quiescent condition with slowest cooling rate. Under shear application, the yield stress increase was observed with the highest cooling rate. Lopes da Silva and Coutinho (8) explained that the gelation measurement is obtained from the initial network development with low level of cross linking.

Building weaker gel would be favorable to the restart process. Deo et al. (9) presented that the restart pressure was decreased when they applied the certain pressure during gel formation in a laboratory-scale flow loop. Ekweribe et al. (10) showed that restart pressures decreased when increasing pressures were applied during gel formation. Both results were obtained by pressure induction into the pipeline at temperatures higher than WAT. The pressure application at a temperature above WAT suppresses the gel formation if the pressure induces mechanical shear on the gel. The yield strength of the gel being cooled with shear is important for restart considerations.

In this study, we examine the gel strength behavior by measuring a static yield stress at different temperatures and creep test combined with secondary cooling.

Experiment

Model oil

Model oil was prepared by using a well-characterized wax and white mineral oil. The carbon number distribution of wax is shown in Figure 1. This study used 5 wt.% wax in oil.

WAT and Pour point

Modified ASTM methods were used to determine WAT and pour point using a temperature-controlled bath and a cell-type jacket for coolant circulation. Temperature in the cooling bath was set to 10 ^{o}C, 0 ^{o}C and -5 ^{o}C to determine both the WAT and the pour point. The measurement was carried out at 3 ^{o}C intervals at first and then in narrower temperature intervals as the measurements got closer to the target. The pour point was defined as the temperature 1^{o}C higher than the temperature of no-flow observation. The pour point measurement was repeated. The results were presented in Table 1.

Rheometer measurement

A controlled-stress rheometer (AR 500, TA instruments, Inc) equipped with a cone-and-plate geometry and a Peltier plate device was employed to determine the yield stress and the measurement of creep response. Cooling was scheduled after various applications of stresses in the creep range. Yield stress was determined by the ramping stress rate at 1 Pa/sec. Gap setting was 48 micrometer and cone angle is 2°.

Results and Discussion

Yield stress and creep response

Yield stress was determined by stress ramping rate of 1 Pa/sec. The sample was heated to 50°C in an oven and was loaded in the rheometer with the plate at 35°C. In the rheometer, the sample was heated to 55°C heating for 10 minutes, and the cooling run was begun. Cooling rate was fixed for all measurements. The static yield stress values of 195-215 Pa at 5°C and 115-135 Pa at 10°C are observed. Creep yield was also examined with different creep stresses at 5°C and 10°C. Compliance responses measured at 5°C are shown in Figure 2 and creep yield values are presented in Table 2. Lower stress values resulted in longer time to break the waxy gel as expected.

Yield stress after creep application at same temperature

Yield stress was determined after creep stresses were applied until the creep compliance response reached a certain value that was chosen before the gel fracture occurred. Creep compliance showed three different regions as shown in Figure 3. Gel breakage or fracture was observed by cone rotation after the compliance values increased exponentially. Additional creep recovery test confirmed that the gel strength recovered partially after creep stress was released before gel fracture occurred. This study examined the creep effect on the static yield stress. Table 3 presents the yield stress results after creep stresses, 150 Pa and 100 Pa, applied differently. In instances when stresses were applied to the gel until the compliance value reached 1e-4 (1/Pa) with 150 Pa and 1.4e-4 (1/Pa) with 100 Pa, the static yields were 205 Pa and 199 Pa. These values were within the measured yield stress values of 195-215 Pa at 5°C. However, with the creep compliances of 2e-4 (1/Pa) in 150 Pa creep stress, 1.6e-4 (1/Pa) and 2.4e-4 (1/Pa) in 100 Pa creep stress, lower static yield values of 190 Pa, 187 Pa and 168 Pa were obtained. Lower yield stresses were obtained after creep stress was applied to higher compliance values at same temperature, which indicated a gel strength loss.

Combined effect of creep application and secondary cooling

The gel strength was examined by secondary cooling combined with different magnitude of creep stress compliance. Figure 3 shows the creep compliance during creeping the gel at 90 Pa at 10°C. Creep stress of 90 Pa was applied to the gel (10°C) differently in the compliance range of 1e-4 to 5e-4 (1/Pa). Creep applied gel at 10°C was cooled down again to 5°C before yield stress measurement. Yield values obtained are presented in Table 4. In the cases of creep application in the compliance range of 1e-4 (1/Pa) to 4e-4 (1/Pa) at 10°C, the static yield values measured at 5°C were higher than the yield stress values without creep application (247-278 Pa with creep versus 195-215 Pa without creep). The creep stress contributes to the increase of compactness of the initial gel network resulting in stronger gel formation after secondary cooling. Other case of creep compliance up to 5e-4 (1/Pa), the beginning of exponential increase, resulted in lower yield value (172 Pa) than the yield without creep. This compliance value, 5e-4 (1/Pa) (see Figure 3) resulted in the partial loss of gel strength, which resulted in less static yield value at 5°C. Similar observations were made when creep stress was applied at 15°C. The gel strength increase at 5°C (266 Pa) was observed in case of creep stress with 50 Pa up to 9e-4 (1/Pa) compliance. The compliance values recorded before gel fracture increased at lower temperature. In other cases of the creep stress application just before the cone rotation of rheometer, 50 Pa up to 1e-2 (1/Pa) and 30 Pa up to 1e-3 (1/Pa) at 15°C, the yield stress values at 5°C were much lower (83 Pa and 51 Pa). As a reference value, the yield stress at 5°C was 10-15 Pa after gel fracture by cone rotation at 15°C.

Conclusion

Gel strength was examined by measuring the static yield stress, creep response and yield stress combined with secondary cooling after creep stress application. The static yield stress increased with decreasing temperatures. In creep test, yielding time was dependent on the magnitude of creep stresses. When the yield stress was measured after applying the creep stress at the same temperature, the yield stress values decreased after increasing the magnitude of creep compliance. Gel strength after creep stress application and secondary cooling was also explored. While the gel strength after secondary cooling was lower when the gel fracture initiated, the gel strength dramatically increased when stresses in the creep range were applied prior to secondary cooling. This study provides insight to various scenarios which may exist during gel formation along the pipeline. Previous studies confirm that the initial pressure induction during the gel formation resulted in lower restart pressures. However this study shows evidence of gel strength increases when the pressure is applied at temperatures below PP.

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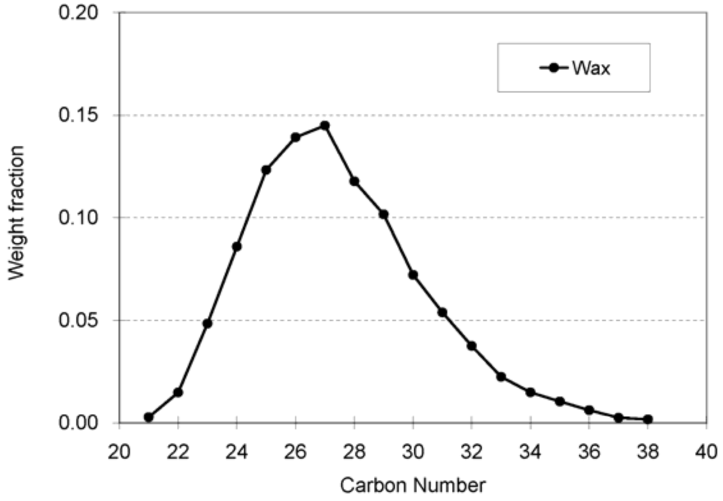

Figure 1. Carbon number distribution measured by SIMDIS.

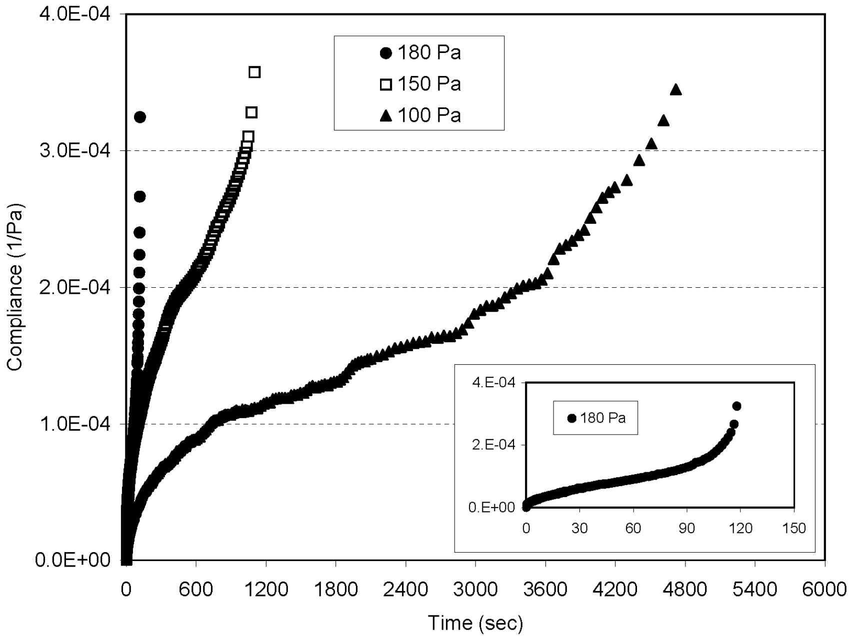

Figure 2. Compliance behaviors when the various creep stresses were applied at 5 °C.

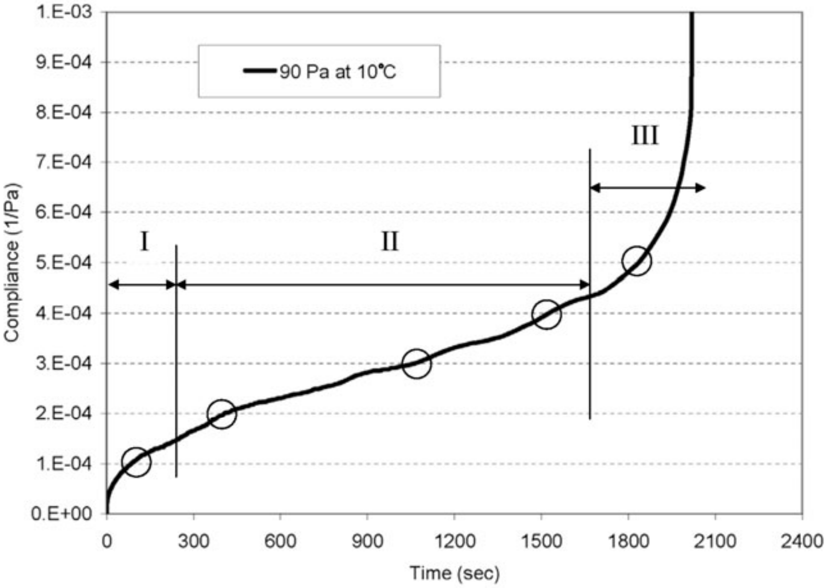

Figure 3. Compliance response when the creep stress of 90 Pa was applied to 5 wt.% wax gel at 10 °C.

Table 1. WAT and PP data of 5 wt.% wax model oil measured by modified ASTM methods (D2500 and D97) at different temperatures.

Cooling bath temperature	10 °C	0 °C	-5 °C
WAT	31 °C	34 °C	35 °C
PP	21 °C	22 °C	23 °C

Table 2. Creep responses of 5 wt.% of wax model oil. Longer time was required when the less creep stress was applied at certain temperatures. Deviation values were added when the tests were carried more than two times.

Temperature	Creep stress	Time to break the gel
5 °C	180 Pa	2 min
	150 Pa	20 min
	100 Pa	100 ± 10 min
10 °C	100 Pa	4 ± 1 min
	90 Pa	34 min
	70 Pa	59 min

Table 3. Yield stresses of 5wt.% wax gel measured at the ramping rate of 1 Pa/sec after creep stresses were applied until the certain compliance values were reached at 5 °C

Creep stress	Creep compliance (1/Pa)	Ramping yield after creep
150 Pa	1e-4	205 Pa
150 Pa	2e-4	190 Pa
100 Pa	1.4e-4	199 Pa
100 Pa	1.6e-4	187 Pa
100 Pa	2.4e-4	168 Pa

Table 4. Combined effect of creep application and secondary cooling in various compliance values followed by ramping yield stresses

Initial Temperature	Creep stress	Creep compliance (1/Pa)	Decreased Temperature	Ramping yield
10 °C	90 Pa	1e-4	5 °C	260 Pa
10 °C	90 Pa	2e-4	5 °C	278 Pa
10 °C	90 Pa	3e-4	5 °C	247 Pa
10 °C	90 Pa	4e-4	5 °C	259 Pa
10 °C	90 Pa	5e-4	5 °C	172 Pa
15 °C	50 Pa	9e-4	5 °C	266 Pa
15 °C	50 Pa	1e-2	5 °C	83 Pa
15 °C	30 Pa	1e-3	5 °C	51 Pa