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Characterization and Rheological Properties of Waxy oils

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ABSTRACT

The characterization of wax crystal and waxy crude oils were carried out with NIR and DSC. Effects of temperature and cooling rates on the rheological properties of waxy oils were studied. The interpretation of the rheological data was related with the crystal growth and microstructure the oil system.

INTRODUCTION

Petroleum wax can be found in the majority of crude oils. At high temperatures, the waxes are in the molten state, and the crude oils normally behave like Newtonian liquids. When the temperature drops below Wax Precipitation Temperature (WPT), solid wax crystals precipitate out of oils. Very low amount of solid wax (1–4% in weight) might be enough for the formation of gel below WPT.[1, 2] Wax precipitation and deposition occurring due to oil cooling in cold-environment may give rise to a variety of problems during oil production, transportation, and storage.

This paper deals with the relationship between rheology and structure of waxy crude oils. The precipitation of wax causes the particular rheological behaviors such as yield stress, shear thinning behavior and dependence on the shear and thermal histories [2] [3] [4] [5]. Thus several rheogical techniques were applied, including temperature scan of oscillation and viscosity and yield stress.

EXPERIMENTAL

Materials

The wax supplied by Champion Technologies was used in this study. The original waxes comprised a distribution of chain length from $C_{27}H_{56}$ to $C_{42}H_{86}$ and centered around 35 carbons, which was provided from Gas Chromatograph/Mass Spectroscopy (GC/MS) analysis. Model waxy oil samples were prepared by dissolving waxes in decane (99%) in a tightly sealed vial at 70°C.

Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry (DSC) measurements of original wax and model waxy oils were performed with Perkin- Elmer Pyris 7 DSC thermal analyzer system, which was calibrated with an indium standard before use. The samples were cooled at varying rates from 70 °C to -10 °C and then heated back to 70 °C at the same rate.

Near Infrared (NIR) Spectroscopy

NIR Spectra of waxy oils during cooling were carried out on a FT-NIR spectrometer (Bruker Optics) equipped with a fiber optic sampling probe for transflectance measurements. The path length of the probe was 2mm. The spectral range was set 12800-3900cm^{-1} with a resolution of 2cm^{-1}. 32 scans were performed for each spectrum and averaged.

Rheological measurements

The rheology measurements of the model waxy oil were performed by shear or oscillatory measurements with the parallel plate geometry (Physica MCR301 Rheometer). Temperature was controlled by a Peltier device within ±0.1°C. After loading the sample on the bottom plate, the top plate was lowered to the desired gap height. Before collecting data, the samples were allowed to temperature equilibrate for 10 min. To decrease evaporation, a solvent trap was used. 5 ml sample sealed in a vial was heated at 80 °C for at least 2 hours, to melt the existing paraffin crystals. The samples are loaded on the rheometer plate with a hot pipette.

RESULTS AND DISCUSSION

Wax crystallization

Differential Scanning Calorimetry (DSC) and NIR were applied to study wax crystallization. The DSC can describe wax crystallization in mass, however NIR would indicate the wax crystal growth in dimension.

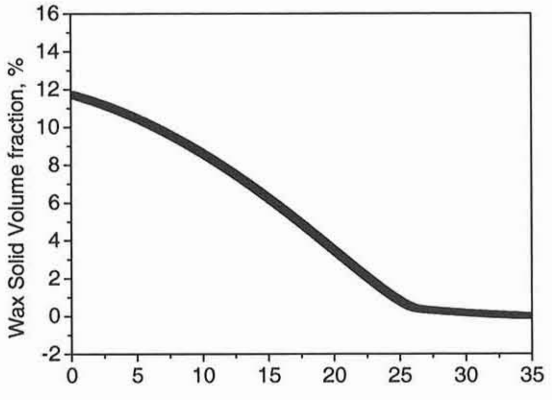

Figure 1. Volume fraction of solid wax in model waxy oils (20%) measured by DSC at cooling rate 2°C/min

The DSC crystallization is expressed in terms of solid wax fraction crystallized. The DSC crystallization for the case of 20% paraffin in decane is plotted in Fig. 1, with wax solid volume fraction as the function of temperature. It is obvious that with the temperature going down, the amount of precipitated wax starts to increases from the onset temperature around 30°C. Even at 25°C, the solid wax has very low value of only 0.8% (volume).

NIR spectroscopy could gain information about the physical state of particles in the solution. Due to scattering, the NIR spectra will display a baseline elevation depending on the size and the number of particles.

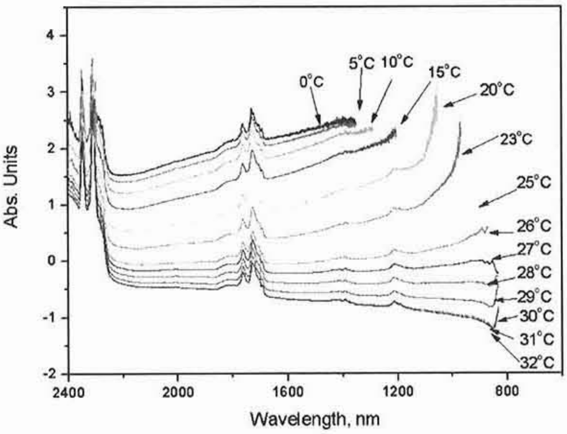

Figure 2: Spectra of model waxy oils (20%) at cooling rate 0.5°C/min illustrating the baseline elevation due to the growth of wax crystals.

The Spectra of model waxy oil (20% paraffin in decane) were recorded during cooling at varying cooling rates. Fig. 2 displays spectra of model waxy oils (20%) at cooling rate 0.5°C/min. The lowest spectrum is that of oil system above Wax Precipitation Temperature (WPT). As the cooling of oils, the baseline is shifted upwards due to scattering by the formation and growth of wax crystals. And the larger particles are formed, and the higher is the baseline elevation.

The absorbance at 1600nm for wax oils in the temperature range 40-0°C was plotted in Fig. 3. It is clear to see that the absorbance unit increases as temperature goes down from 40°C to 0°C. With the decreasing of cooling rates, absorbance unit also increases. Generally, the crystals formed at low cooling rate are longer in length than those crystallized at high cooling rate. Moreover the long crystals lean to enlace and form large aggregations and therefore strong net-structure, which are exhibited with viscosity and viscoelasticity to discuss below.

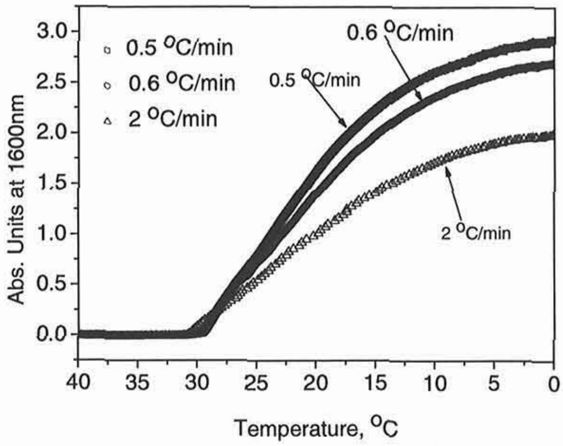

Figure 3. Absorbance at 1600nm of model waxy oils (20%) at three cooling rates as the function of temperature

Temperature Scan Oscillation

Viscoelastic properties of waxy model fluids during the cooling process were investigated by rheometric measurements. Temperature scan of oscillation for model waxy oils of concentrations from 5% to 25% by 5% step were carried out with the strain fixed at 0.05% and the cooling rate at 2 °C/min. All oscillation tests of model waxy oils are carried out under fixed 0.05% strain to make sure that the investigated behavior lies within the linear viscoelastic range. The storage modular G' and the loss modular G'' at frequency 1 Hz are shown in Fig. 4 with respect to temperature from 40°C to 0°C.

For model waxy oils of concentrations 20%, the storage and the loss moduli start to increase around 27.3 °C, which may be named Wax Precipitation Temperature (WPT). When the temperature is above the Wax Precipitation Temperature, a finite value of the loss modulus is obtained, which indicates the Newtonian behavior. When under the cloud point, the presence of solid paraffin crystals causes the formation of random interaction networks among the growing paraffin crystals and imparts a solid-like mechanical response to the fluid, which is characterized by the sharp increase of both storage and loss moduli G' and G''.

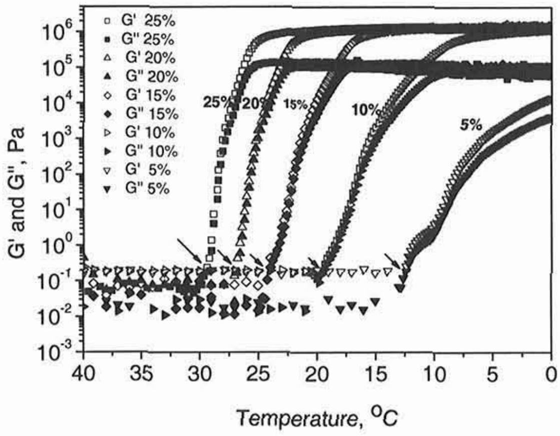

Figure 4. Temperature Scan of Oscillation of model waxy oils of concentration from 5% to 25% cooled at 2°C/min

The crossing point of the moduli occurs at 26.0°C which one may call the 'gelation temperatures', confirming the formation of a continuous paraffin crystal interaction network. As the temperature is further lowered, the interaction among the wax crystals increases, which is reflected in an increase in the storage modulus G'. At 25°C, the storage moduli reach very high values, of the order of 10^5–10^6 Pa. For other model waxy oils of other concentrations, their oscillation behaviors with respect to temperature are similar with concentration 20%.

Temperature Scan Viscosity

The wax melts and dissolves in the matrix oil above the wax precipitation temperature. Therefore, a Newtonian behavior is obtained for the model waxy oil, characterized with viscosity increase slowly with temperature. It is in agreement with the most adequately used Arrhenius equation, which is expressed in a simple exponential form as following[3],

$$\mu = Ae^{Ea/RT} \tag{1}$$

where μ is the Newtonian dynamic viscosity, *A* is a constant dependent on the entropy of activation of flow, *Ea*, is the activation energy of viscous flow, *R* is the universal gas constant, and *T* is the absolute temperature.

After the wax precipitation point, the precipitation of solid wax crystals dispersed in the continuous phase causes the increase of viscosity. As the temperature is further lowered, the degree of interaction among the wax crystals increases and induces the formation of random interaction networks among the growing paraffin crystals which is characterized by the sharp increase of viscosity.

Viscosities of waxy model fluids during the cooling process were investigated. Temperature scan of viscosity for model waxy oils of concentrations from 5% to 25% were carried out at a fixed shear rate and the cooling rate at 2 °C/min. The viscosity at shear rate 100 s^{-1} with respect to temperature from 50°C to 0°C is shown in a plot of $\ln \eta$ against 1/T, Fig. 5. For different concentrations model waxy oils, their viscosity behaviors with respect to temperature are similar. For model oil concentration of 20%, above temperature 28.8°C, the curve of $\ln \eta$ against 1/T shows a linear behavior, obeying with the Arrhenius equation. The WPT is indicated by an arrow where it departs from the Arrhenius behavior in the curve. The viscosities are very low of the order of 0.7-2x10^{-2} Pa.s. The activation energy of viscous flow, *Ea* can be obtained from the slope of the linear curve. Moreover the values of *Ea* for the five concentration are in the range 9.8-10.4KJ/mol and in agreement with values reported by Rønningsen et al. [3]

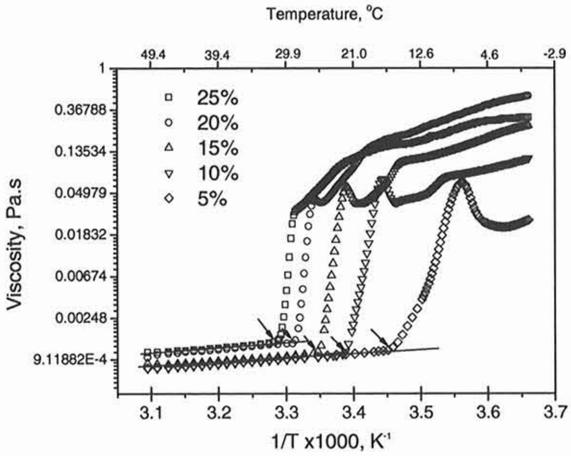

Figure 5. Temperature Scan of Viscosity of model waxy oils from concentration 5% to 25%

As temperature drops, solid wax suspends in the oil, the viscosity and *Ea* increase sharply, characterized with the large slope of the curve of $\ln \eta$ against 1/T. At 25.9°C, the formation of the continuous paraffin crystal interaction network rigid network causes a slippage between sample and the wall of measuring plate, the viscosity starts to drop.

Yield Stress

Yield stress is an important property to evaluate the waxy oil fluids. Yield stress is the upper limit of shear stress before flow occurs. It is also the stress value at which point the range of reversible elastic deformation ends and range of irreversible deformation or viscoelastic- viscous flow begins. When the waxy oil fluid are subjected to a oscillation shear below a certain critical value (yield stress), they exhibit high and nearly constant storage modulus G'. Upon increasing the shear stress above the critical value, a sharp decrease of storage modulus G' is observed indicating fracturing of the material.

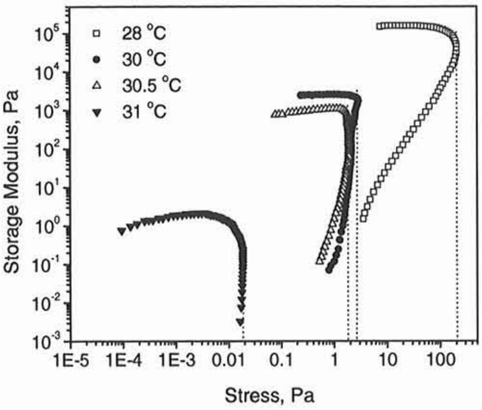

Figure 6. Determination of Yield Stress from stress creep curve of storage modulus

After allowing the sample to anneal at constant temperature under no stress for 15 min, the stress sweep measurements were then performed and the storage and loss moduli data were collected at a frequency of 0.1 Hz. The typical storage modulus versus oscillation stress behavior of model oil around WPT with cooling rate 0.5°C/min is shown in Fig. 6. The yield stress is indicated by a vertical segment of the modulus versus stress plot. The storage modulus versus stress plots exhibit a nearly linear response (constant value of the storage modulus independent of the stress) up to a certain critical shear stress (yield stress). With further increase in shear stress, the storage modulus drops sharply. The yield stress increases from the point where a sharp reduction in storage modulus occurs with the decrease of temperature.

Yield stresses at different cooling rates are shown in Fig. 7. The yield stress obtained at low cooling rates behaviors higher value due to longer crystals formed and stronger crystals interaction.

CONCLUSIONS

The DSC and NIR measurements indicated that the crystals formed at low cooling rate are longer in length than those crystallized at high cooling rate. And very low value of solid wax in model oil can form a strong net-structure.

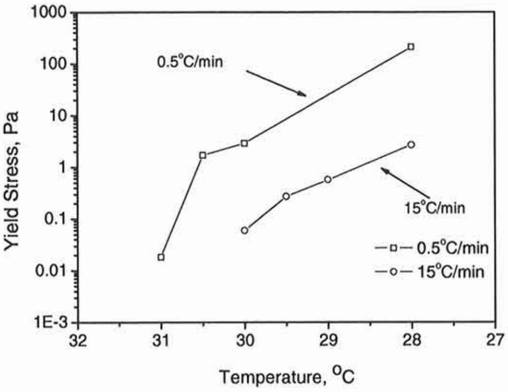

Figure 7. Yield Stress verse Temperature & Cooling Rate

From temperature scan of oscillation and viscosity, with the dropping of the temperature, the interaction among the wax crystals increases, which is reflected in an increase in the storage modulus G' and viscosity.

The yield stress obtained at low cooling rates behaviors also higher value due to longer crystals formed and stronger crystals interaction.

ACKNOWLEDGEMENTS

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