# The Yielding of Waxy Crude Oils

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The yielding process of statically cooled waxy crude oil was examined in detail. Three direct measurements—a controlled stress test, a creep−recovery test, and an oscillatory test—were employed using a controlled stress rheometer to investigate the yielding of two distinctly different statically cooled waxy crude oils. The results showed that yielding of waxy crude oil occurs by an initial elastic response, followed by viscoelastic creep and a final fracture. A model with an elastic-limit yield stress, a static yield stress, and a dynamic yield stress was introduced to describe the yielding process. The three yield stresses were determined by means of different techniques. The effect of the time scale in different measurements on the three yield stresses was studied. It was shown from both the creep−recovery and oscillatory tests that the elastic-limit yield stress was independent of the time scale. The static yield stress was found to be dependent on the time scale in the three tests. The dynamic yield stress measured only with the controlled stress test was also found to be dependent on the time scale of the yielding. Good reproducibility can be obtained in these tests by strictly controlling the thermal and shear history of the samples.

## Introduction

Waxy crude oil has been produced for many decades around the world. The wax, contained in the oil, imparts various complex non-Newtonian and nonlinear characteristics to the flow properties of the oil, including the particular yielding behavior. Significant problems of increased drag, wall deposition, and blocked lines have been experienced in the pipeline transport of waxy crude oils (Gill and Russell, 1954; Perkins and Turner, 1971; Uhde and Kopp, 1971; Herring, 1974; Sifferman, 1979; Irani and Zajac, 1982; Wardhaugh and Boger, 1987). The yielding property of the waxy crude oils is directly related to the start-up and restart operations of pipeline transportation systems.

Wardhaugh and Boger (1991) have qualitatively described the yielding of waxy crude oils in detail. The results obtained in their work using the vane technique for yield stress measurement (Nguyen and Boger, 1985) for Australian waxy crudes indicate that three features should be quantified—the elastic response, creep, and the sudden and dramatic failure (fracture), as shown in Figure 1. This description is in agreement with the three yield stress model, proposed by Kraynik (1990) and Bonnecaze and Brady (1992) for electrorheological fluids. The transition between elastic response and creep (point A in Figure 1) corresponds to the first yield stress, or the elastic-limit yield stress ($\tau_e$); the stress at the starting point of the fracture (i.e., point B) corresponds to the second (or the static) yield stress ($\tau_s$); the third (or the dynamic) yield stress ($\tau_d$) (which was not determined in Wardhaugh and Boger's work) can be measured after the structure of the sample is ultimately broken through sustained shear (after point C). The experimental results from controlled stress, creep−recovery, and oscillatory testing are presented in this paper to support and quantify the above description.

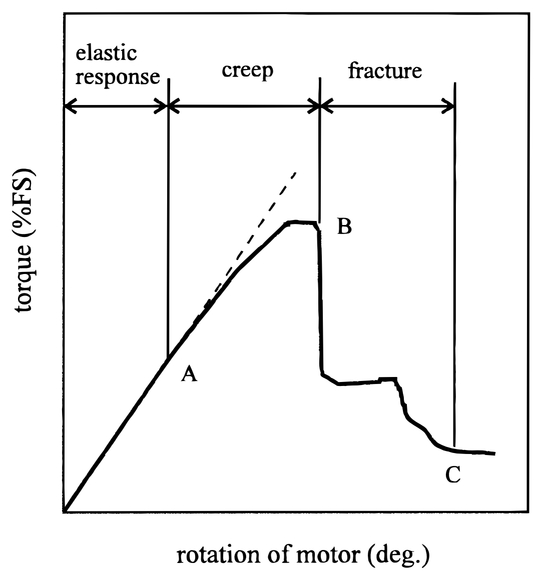


**Figure 1.** Yielding process of waxy crude oil: vane technique (Jackson-Hutton crude oil at 10 °C; Wardhaugh and Boger, 1991).

The dynamic yield stress is not a material property relating to the yielding process because it is obtained from extrapolation of the broken shear stress−shear rate data (as illustrated by $\tau_d$ in Figure 2a). The elastic-limit yield stress, the stress at which the viscoelastic creep starts, and the static yield stress, which is the stress at the starting point of fracture, are the stress values relating to the yielding process and may be considered to be two true yield stresses. The dynamic yield stress is actually an imagined parameter which

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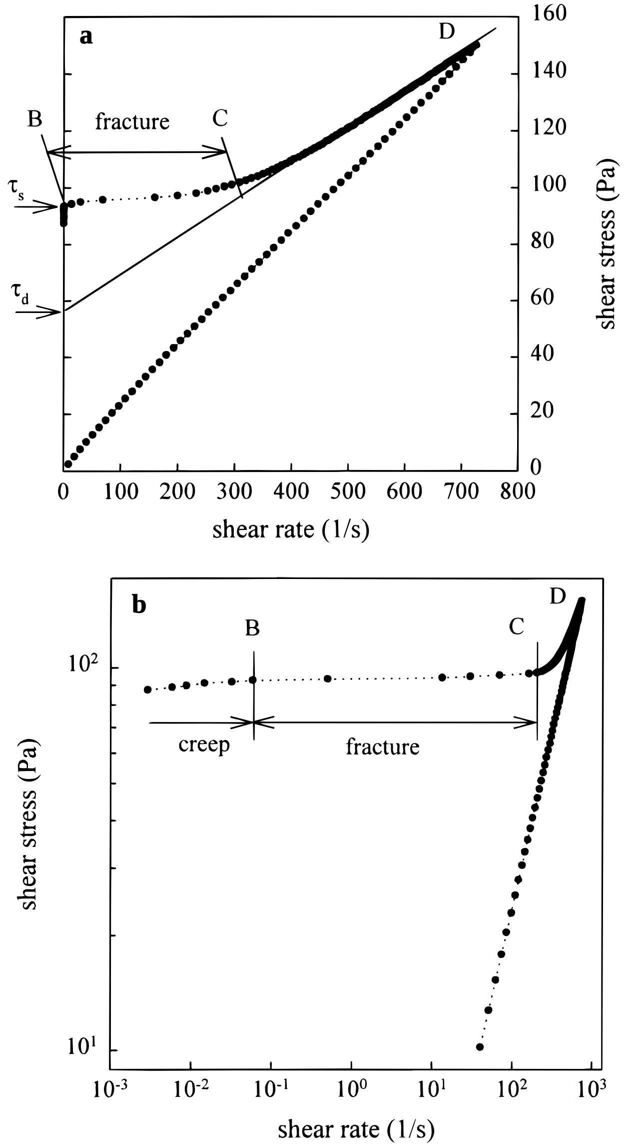


**Figure 2.** Controlled stress test: (a) difference between the static and dynamic yield stresses (DH19, 16 °C); (b) fracture process (DH19, 16 °C).

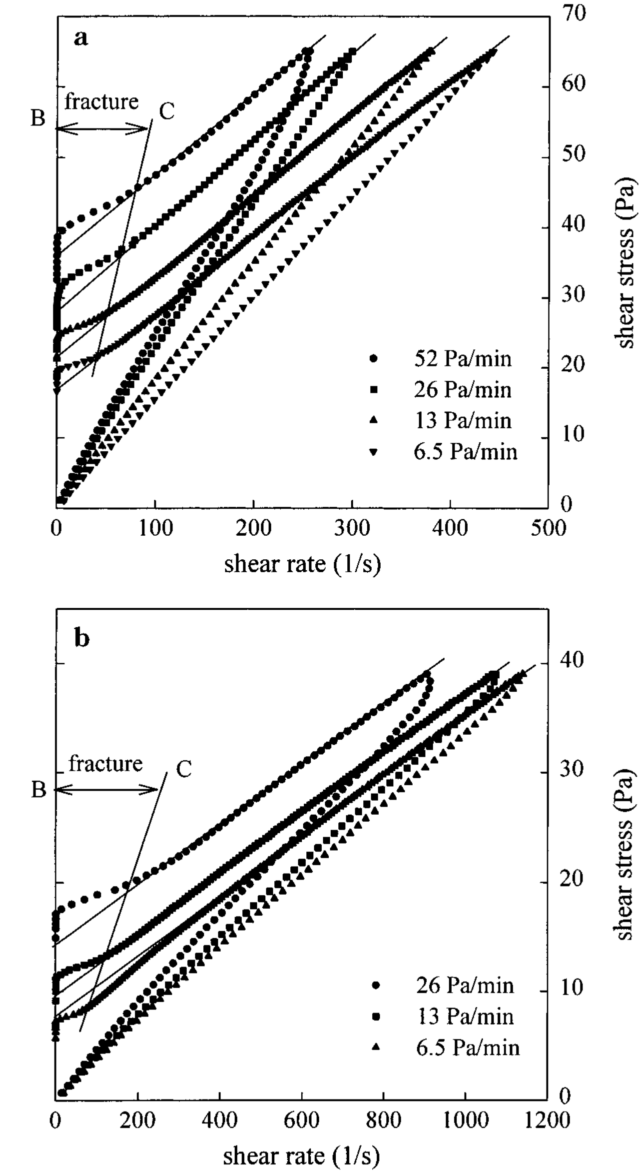


**Figure 3.** Controlled stress test: (a) effect of stress loading rate (DH19, 20 °C); (b) effect of stress loading rate (BO, 20 °C).

can be used in describing the oil properties at the final sheared state and has no relation to the yielding itself. Both the elastic-limit and static yield stresses are dependent on the strength of the interlocking network of wax crystals in the oils before the structure is disturbed, while the dynamic yield stress is related to the concentration and size of the wax particles in the oils after the structure is completely destroyed.

Engineers are most interested in the static yield stress ($\tau_s$), the stress value when the fracture occurs, as this stress value effectively determines the pump capacity required to initiate flow and ensure pipeline restart. Although static yield stress can be easily obtained from a simple direct measurement—a controlled stress test, as shown in Figure 2a,b—it cannot be directly applied to pipeline design since this measured static yield stress strongly depends on the time scale of the measurement, i.e., the stress loading rate in this test, as shown in Figure 3a,b for the two oils. Similar effects have also been reported by Ronningsen (1992) for a North Sea waxy crude oil. The dependence of the static yield stress on the stress loading rate may be attributed to the viscoelastic creep process in yielding. Complete understanding of the entire yielding process is no doubt necessary for the successful application of the measurement results from the rheometer to the design of a real pipeline system.

It appears that a reliable method for determining the true yield stresses of waxy crude oil would be from direct measurements employing a controlled stress rheometer, in which a shear stress is applied and the strain or shear response is measured. The wax structure which is unrecoverable after breakdown without temperature cycling will not be significantly disturbed prior to yielding in the tests; thus, a true material property can be obtained. Note that, although the vane technique used by Wardhaugh and Boger (1991) is nominally a shear-controlled instrument, the movement of the vane in the yielding is not, in fact, constant. The vane does not move while the torque keeps increasing in the initial stage of yielding (before creep), which makes this technique somewhat similar to the stress-controlled technique in this stage; thus, the elastic response can be recorded. In this work, further understanding of the yielding behavior of waxy crude oil was obtained from three direct measurements performed with a controlled stress cone-and-plate rheometer. It is shown that the elastic-limit yield stress, which is independent of the time scale of the measurements, can be evaluated by creep–recovery or oscillatory tests, while the static yield stress, which is dependent on the time scale, can be determined by each of the three methods. The dynamic yield stress, which is also dependent on the time scale of yielding, can be measured only with the controlled stress test. Even for the statically cooled waxy crude oils, good reproducibility can be obtained in these tests by strictly controlling the thermal and shear history of the samples.

## Review of the Concept of Yield Stress and Its Measurement for Waxy Crude Oils

The yield stress concept was first introduced by Bingham and Green (1919) for a class of fluids known as viscoplastic fluids. After the initial work, many different equations have been proposed to describe the relationship between shear stress and shear rate for different viscoplastic materials (Nguyen and Boger, 1983, 1992). In all those models, the yield stress was simply defined as the minimum stress required to produce a shear flow. The material was thought to be in a solidlike state when the applied stress was less than the yield stress. In other words, the yield stress was thought to be a transition between the elastic solidlike and viscous liquidlike behavior. The yield stress value for these models was measured by extrapolating the dynamic shear stress–shear rate data to the zero shear rate limit. The difference between the end of the elastic behavior and the start of the viscous behavior was described as early as in 1958 by Houwink in a two yield stress model, in which the elastic behavior, the plastic behavior, and the viscous flow were distinguished (Houwink, 1958). The three yield stress model used in this paper was initially proposed by Kraynik (1990) for electrorheological fluids and further discussed by Bonnecaze and Brady (1992).

The early measurements of a yield point for waxy fuel oils and waxy crude oils were performed with capillaries or large pipelines (Gill and Russell, 1954; Davenport and Russell, 1960; Davenport and Somper, 1971; Knegtel and Zeilinga, 1971; Verschuur et al., 1971; Nguyen and Boger, 1985; Ronningsen, 1992). Both capillary and model pipeline techniques have now been rejected due to the uncertainties arising from the known effects of stress concentration, compressibility of the pipe and the oil, diffusion of the wax-free oil, and contraction of the oil (Gill and Russell, 1954; Davenport and Russell, 1960; Davenport and Somper, 1971; Perkins and Turner, 1971; Verschuur et al., 1971; Smith and Ramsden, 1978; Wardhaugh and Boger, 1991). Rotational viscometers with concentric cylinders, parallel plates, a cone-and-plate, or vanes have also been used to study the yielding of waxy crude oils (Davenport and Somper, 1971; Perkins and Turner, 1971; Sifferman, 1979; Keentok, 1982; Nguyen and Boger, 1985; Titkova and Yanovsky, 1988; Wardhaugh and Boger, 1991; Ronningsen, 1992). However, no standard test for determining the yielding quantity of waxy crude oils has been adopted by the petroleum industry because of the very poor repeatability in any given instrument and the poor reproducibility between the different tests. One of the reasons for the poor repeatability and poor reproducibility is that the yield values, along with all other rheological properties of waxy crude oils, strongly depend not only on what the sample is experiencing, i.e., temperature and shear rate, but also on what the sample has experienced, i.e., thermal and shear history. Even small variations in any of the test conditions or history can cause a marked difference in the measurement results. Another important reason for the poor repeatability is that there are various confusing definitions of the yield stress due to a lack of understanding of the complicated yielding process. In addition, the usual instrumental effects such as wall slip, instrument inertia, damping characteristics of the rotation body, and sensitivity to external disturbance have also been identified as the possible sources of the poor repeatability of results (Wardhaugh and Boger, 1991; Nguyen and Boger, 1992).

## Experimental Section

**Crude Oil Samples and Pretreatment.** Initially, a waxy crude oil DaiHung19 (DH19), supplied by Broken Hill Pty. Ltd. (BHP), was used in the tests. The pour point of DH19 is 32 °C. The conditioning treatment prior to testing involved heating the 10 mL samples to 95 °C for 15 min while stirring in a sealed beaker, cooling the samples to 65 °C for 20 min, and storing the samples in a 65 °C waterbath. 95 °C is actually the oil temperature at the production well head and should be high enough to remove all the waxy structure memory since the wax disappearance temperature (WDT) of this oil is about 65 °C. No wax was found to precipitate during either the cooling from 95 to 65 °C or the isothermal holding at 65 °C in the waterbath as the wax precipitation temperature (WPT) of this oil is 60 °C.

Another waxy crude oil, Beatrice oil (BO) supplied by the British Petroleum Co., was also used to repeat some controlled stress tests. The BO sample has a pour point of 27 °C, WDT of 60 °C, and WPT of 55 °C. The thermal pretreatment involved heating the samples to 85 °C for 15 min to erase any possible waxy structure, cooling the samples to 60 °C for 20 min, and holding the samples in a waterbath at 60 °C.

After the pretreatment process, a sample was loaded with a plastic pipet from the sealed beaker in the waterbath into the rheometer, which had been preheated to the starting temperature of the testing (65 °C for DH19 and 60 °C for BO). The rheometer was then statically cooled from the starting temperature to a testing temperature according to the programmed cooling process for each oil. The cooling program for DH19 involved cooling the sample from 65 to 45 °C in 2 min, 45 °C to the final testing temperature (16 or 20 °C) at the cooling rate of 2 °C/min, and holding at the testing temperature for 5 min before testing. The program for BO involved cooling from 60 to 45 °C in 1.5 min, 45 °C to the testing temperature (20 °C) at 2 °C/min, and holding at the testing temperature for 5 min before testing. Each test was then isothermally performed at the testing temperature.

**Instrument.** A computer-interfaced controlled stress rheometer (Carri-Med CSL 100), fitted with truncated cone-and-plate geometry (4 cm diameter, 1′59″angle and 53.3 $\mu$m truncation), was used in the tests. A solvent trap was applied to avoid the possible evaporation of the oil during testing. In theory, several kinds of measurements can be performed in the rheometer to determine the yield values. However, the shear-induced methods are not recommended for waxy crude oils because even the smallest shear rate in steady flow could lead to deformations large enough to damage the wax structure prior to the testing, such as in stress relaxation tests. No true yielding properties can then be measured in shear-induced methods since the destroyed waxy structure cannot be recovered without temperature cycling.

A cone-and-plate geometry rheometer offers major advantages in characterization of non-Newtonian and time-dependent fluids since the shear stress as well as the shear rate is effectively uniform throughout the material for small cone angles. Such a stress distribution ensures the simultaneous yielding of the entire sample, avoiding the errors produced by partial yielding, such as those which occur in pipelines and in a concentric cylinder rheometer. Furthermore, the small volume of the sample used in the cone-and-plate geometry makes it possible to control the temperature and thermal history more precisely, compared to the concentric cylinder and vane geometries which use more sample and have problems in temperature control.

**Measurements.** Three stress-induced direct measurements—controlled stress test, creep—recovery test, and oscillatory test—were employed. The details of each test procedure are discussed together with the results in the next section.

## Results and Discussion

**Controlled Stress Test.** This is basically a "hysteresis-loop" method often used in the study of thixotropic fluids. The controlled stress testing result for DH19 at 16 °C is displayed in Figure 2a on linear coordinates. The data were obtained by applying stress and measuring the shear rate. The applied stress increases linearly from 0 to 150 Pa in 5 min and then decreases back to zero in 1 min. No data can be recorded in the up curve before the shear rate reaches 0.002 83 $s^{-1}$, which is the resolution limit of the rheometer for this test. The initial part of the up curve almost coincides with the zero shear rate axis. A clear deviation occurs at a shear stress of 92.7 Pa, indicated by point B. A dramatic increase of the shear rate following this deviation point is represented by an approximately horizontal segment which ends at point C at a shear rate of about 300 $s^{-1}$. The curve becomes finally a rising incline ending at point D. The curve segment between C and D can be roughly described with the Bingham equation, although it has a slight upward curvature, which is attributed to shear thinning. The down curve is approximately a straight line crossing the origin with a slight upward curvature as well.

The same data are also plotted on logarithmic coordinates in Figure 2b, in which the data before and during the fracture are displayed more clearly. Correspondingly, the transition points B, C, and D are also indicated. The shear rate at point B is 0.0578 $s^{-1}$. From point B to C, the shear rate increases 3—4 orders of magnitude from 0.0578 to about 300 $s^{-1}$, while the shear stress only has a slight increase from 92.7 to about 100 Pa. The creep region before point B is a slightly rising incline while the C—D segment, which represents the shear thinning process after the yielding, is a sharply rising curve.

Point B is identified as the starting of the fracture since the horizontal segment between B and C in both figures definitely represents a fracture process. The stress at the starting point of the fracture may then be identified as the fracture stress, or the static yield stress, as defined by Kraynik (1990). The curve segment between C and D together with the entire down curve may be used to exhibit the final broken state of the oil when the microstructure is totally destroyed in the sample. The extrapolated zero-shear rate stress of the up curve from data between C and D, according to the Bingham equation, may be determined as the dynamic yield stress. The dynamic yield stress must be determined from the up curve since the oil is thixotropic at the final sheared state. This thixotropy is exhibited by the hysteresis loop between the C—D curve segment and the down curve.

Due to the resolution of the rheometer, the shear rate in the elastic deformation and initial creep regions cannot be recorded, as the shear rate in those regions is very low. Thus the elastic-limit yield stress cannot be determined from this measurement. The data recorded before point B in Figure 2b show that the shear rate increases gradually with the increasing shear stress during the creep process.

The controlled stress test has been used for many years in the indirect measurement of the yield stress, i.e., extrapolation using a linear or nonlinear constitutive equation. As shown in Figure 2a, the extrapolated yield stress $\tau_d$, i.e., the dynamic yield stress, is completely different from the static yield stress $\tau_s$, which means the indirect measurement cannot be used to determine the true yield stresses for waxy crude oil. Direct measurement of the yield stress from low shear stress—shear rate data was suspect in the classic one-yield-stress model due to the lack of results at sufficiently low shear rate (Nguyen and Boger, 1983). After introducing the yielding model with three sequential steps, this measurement is now used as a direct method for the static yield stress since the shear rate during the fracture process is reasonably high and thus can be detected by the rheometer.

**Effect of Stress Loading Rate.** The time scale of the measurement in the controlled stress test is expressed in term of the stress loading rate, the rate at which the stress was increased. The different controlled stress testing curves at different stress loading rates are displayed in Figure 3a,b for DH19 and BO, all at 20 °C. In Figure 3a, the stress is applied from 0 to 65 Pa at four different rates of 52, 26, 13, and 6.5 Pa/min. In Figure 3b, the stress loading rate is 26, 13, and 6.5 Pa/min respectively between 0 and 39 Pa. The measured static and dynamic yield stresses for both oils are plotted in Figure 4, in which a similar dependence on the stress loading rate is observed for two oils. The up curves under different stress loading rates in both parts a and b of Figure 3 become parallel after fracture, with similar slopes and different intercepts. The down curves are approximately straight lines crossing the origin for both oils.

Figure 4 shows that a lower stress loading rate, corresponding to a longer time scale for the creep process in yielding, causes a lower static yield stress as well as a lower dynamic yield stress. When the stress loading rate decreases from 52 to 6.5 Pa/min, the static yield stress of DH19 decreases from 38.7 to 18.9 Pa and the dynamic yield stress of DH19 decreases from 36.1 to 16.7 Pa. Similarly, when the stress loading rate decreases from 26 to 6.5 Pa/min, the static yield stress of BO decreases from 17.1 to 7.2 Pa while the dynamic yield stress of BO decreases from 14.1 to 6.9 Pa. The relationships between the stress loading rate and the

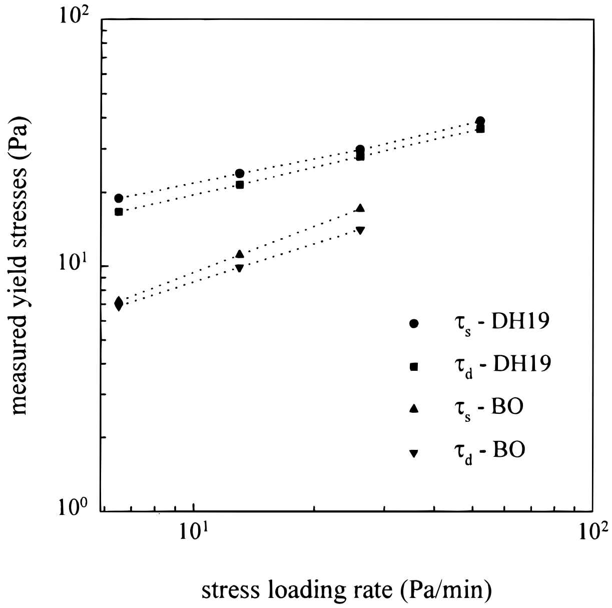


**Figure 4.** Dependence of the measured yield stresses on stress loading rate (DH19 and BO, 20 °C).

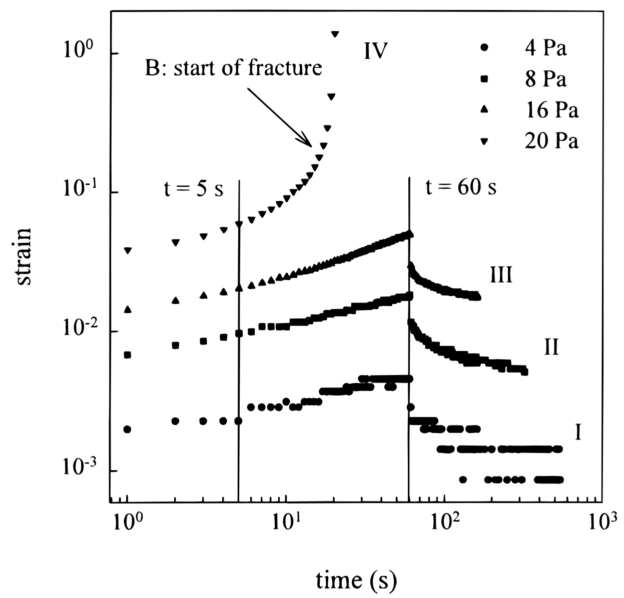


**Figure 5.** Creep−recovery test: different responses under different applied stresses (DH19, 20 °C).

static or dynamic yield stress for both oils are almost perfectly straight lines on logarithmic coordinates. The slopes and the intercepts of the relationship lines are, however, oil dependent. There also exists a slight slope difference between the $\tau_s$−stress loading rate and the $\tau_d$−stress loading rate relationships for both oils.

Based on a similar conclusion obtained from the measurement of a North Sea waxy crude oil, Ronningsen (1992) suggested that the static yield stress might become arbitrarily low at sufficiently low rates of stress loading. Since the results from the creep−recovery and oscillatory tests to be discussed demonstrate that the elastic-limit yield stress is independent of the time scale of the measurement, it is believed that the elastic-limit yield stress is the lowest limit of the static yield at the infinitely low stress loading rate in the controlled stress test. The dependence of the dynamic yield stress on the stress loading rate indicates that the final state of wax particles is also influenced by the yielding process. The parallelism of the high shear rate segment in the up curves for both DH19 and BO indicates that the Bingham plastic viscosities at the final broken state for both oils are independent of the time scale of the yielding. However, the apparent viscosity at the final state depends on the time scale of the yielding since the dynamic yield stress changes with the stress loading rate.

The dependence of the static yield stress on the stress loading rate may imply that the pump pressure required to initiate a pipeline flow not only is controlled by the strength of the wax structure of the oil in the pipeline but also is dependent on how quickly the pipeline is started. Since a lower stress loading rate leads to both a lower static and a lower dynamic yield stress, it is then recommended that the pump pressure in starting or restarting a pipeline transporting waxy crude oil should be increased as slowly as possible, since a slower operation will require a lower pump pressure not only in initiating the flow but also in transporting the oil in the final broken state after the restart.

**Creep−Recovery Test.** Creep−recovery tests were performed by imposing different constant stresses on fresh aliquots of DH19 oil at 20 °C for a creep time of 1 min and then removing the stress abruptly while recording the resulting strain recovery over time, as shown in Figure 5 on logarithmic coordinates. Curve I represents the strain over time during creep and recovery processes with an applied constant stress of 4 Pa. Complete strain recovery after the stress is removed indicates that the applied stress is below the elastic limit and the sample responds as an elastic solid, with no irreversible deformation. Curves II and III represent the strain responses over time with applied stresses of 8 and 16 Pa, respectively. Partial recovery of the strain after the stress of 8 or 16 Pa is removed indicates that both elastic and plastic deformation are involved in the creep. With the stress of 8 or 16 Pa, the microstructure in the oil degrades gradually from the initial solidlike state to a viscoelastic state. Curve IV represents another distinctly different state, a completely unrecoverable state, where fracture is observed shortly after the stress of 20 Pa is applied to the sample. The structure degrades from the initial elastic solidlike state to the viscoelastic state and finally to the viscous state in less than 10 s. The yielding process of DH19 waxy crude oil may thus be identified to occur in the sequence of elastic deformation, viscoelastic creep, and final fracture. The final range of curve IV after the starting point of fracture represents the oil state in the fracture process. Since the waxy structure in the oil is shear degrading during the fracture, the strain increases dramatically over time after the fracture starts even when the stress is fixed.

Two stress transitions can be determined from the results in the creep−recovery test. The first is between curves I and II, and the other is between curves III and IV. The first transition may be defined as the elastic-limit yield stress ($\tau_e$). An applied stress lower than this stress will only produce an elastic recoverable deformation, while a higher stress will cause creep with both recoverable and unrecoverable deformations in the given creep time. The second transition is actually the static yield stress ($\tau_s$). A stress higher than this transition will break the structure very quickly while a lower stress will not destroy the structure in a reasonable time. From the results presented, the elastic-limit yield stress is determined between 4 and 8 Pa, and the static

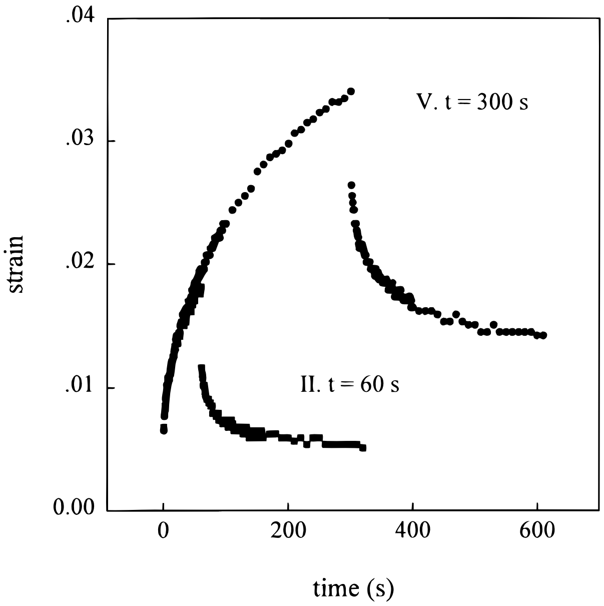


**Figure 6.** Creep−recovery test: effect of creep time (DH19, 20 °C).

yield stress is determined between 16 and 20 Pa. Both the elastic-limit and static yield stresses measured in the creep−recovery test are true material properties related to yielding because no extrapolation from higher shear rate, i.e., after yielding, is involved in their determination.

**Effect of Creep Time.** It must be mentioned that the two yield stresses determined above are based on measurements with an applied stress time of 1 min. The effect of the creep time, which represents the time scale of the creep−recovery testing, on the two measured yield stresses can be observed by carefully studying the creep curves at different applied stresses. Curve I in Figure 5 shows that the strain under a stress of 4 Pa increases initially with time and reaches a maximum at about 35 s. After that the strain remains constant and does not change with time, which means the extension of the creep time will not increase the strain response any more under the stress of 4 Pa. A complete strain recovery will always occur after the applied stress of 4 Pa is removed. In other words, the lower limit of the measured elastic-limit yield stress does not change with a change of the time scale of the creep−recovery test.

Curves II−IV show that the strain responses increase with time when the applied stress is higher than the elastic-limit yield stress. For the same creep time, a higher applied stress causes a higher strain. In Figure 6, the same stress of 8 Pa, which is also higher than the elastic-limit yield stress, is applied to two identical samples with different creep times. The results demonstrate that the final strain response is influenced by the creep time: a longer creep time causes a higher final strain. Also, a higher unrecoverable strain is observed with a longer creep time, which means more plastic deformation is involved in a longer creep. The microstructure in the oil during creep is thus concluded to be influenced by both the stress and creep time, providing the stress is higher than the elastic-limit yield stress. The end of the creep, which is also the start of the fracture, may then occur at a lower stress if the creep time is longer, and *vice versa*. As shown by curve IV in Figure 5, the fracture occurs 10 s after a stress of 20 Pa is applied. If the stress was removed after only 5 s of application to the sample, no fracture would occur and a partial strain recovery would be observed to follow the creep. A higher applied stress is then necessary to produce a fracture with a creep time of 5 s. The measured static yield stress will thus be higher than 20 Pa, with a creep time of 5 s. On the other hand, if the stress time was extended to sufficiently long, a fracture transition would be observed under the stress of 8 or 16 Pa since the strains under these stresses keep increasing over time while the unrecoverable strain can be observed even with a stress time of 1 min. However, no fracture can be observed under the stress of 4 Pa with any extended stress time since a mechanical equilibrium can be reached shortly after the application of the stress, as shown by the constant strain between 35 and 60 s in curve I.

Good reproducibility for the creep−recovery test is demonstrated by the coincidence of the two curves in Figure 6 during the creep process.

**Oscillatory Test.** This is a popular technique used in the study of the viscoelasticity of polymer systems. Usually, the testing is performed in a linear region to record true viscoelastic properties for the tested samples. Several methods for determining the shear yield stress from low-frequency dynamic data have also been proposed (Petrellis and Flumerfelt, 1973; Vinogradov et al., 1982; Yang et al., 1986; Franck, 1988; Wardhaugh and Boger, 1991; Nguyen and Boger, 1992). In our work, oscillatory testing was employed using the Carri-Med rheometer to investigate the yielding of the DH19 waxy crude oil at 20 °C by applying the torque oscillation at a fixed low frequency (1 Hz) and measuring the strain response in both linear and nonlinear regions (Figure 7a), from which the storage modulus ($G'$) and the loss modulus ($G''$) during the entire yielding process can be determined (Figure 7b). The amplitude of the oscillation was increased linearly from 1 to 65 Pa. At a frequency of 1 Hz the testing with small stress amplitude is in the linear region; thus, the true structural properties before yielding can be observed. The oscillatory testing is also performed in the nonlinear region to record the destruction process, i.e., the yielding.

The initial linear stress−strain relationship before point A in Figure 7a with the stress amplitude less than 10.1 Pa indicates an elastic behavior for the sample. The stress−strain relationship follows Hooke's law. The strain recovers after each oscillation in this region. The approximately constant $G'$ and $G''$ before A in Figure 7b indicate that the interlocking waxy network in the oil is not destroyed when the stress amplitude is lower than 10.1 Pa. The sample may be thought of as a true elastic solid before the microstructure has any damage. When the stress amplitude increases to greater than 10.1 Pa, $G'$ and $G''$ decrease gradually with increasing amplitude, indicating a creep response in which both elastic and plastic strains are involved, represented also by the deviation of stress−strain curves from the linear relationship. The elastic-limit yield stress may be determined to be between 5.6 and 10.1 Pa. An oscillatory stress with an amplitude higher than the elastic-limit yield stress will cause creep, which will partially damage the waxy structure, if the stress is not sufficiently high to produce fracture. After point B, a sudden increase of the strain occurs together with sharp drops of $G'$ and $G''$, indicating the fracture process of the waxy network. Another important change around B is that $G'$ becomes lower than $G''$ after B, which also

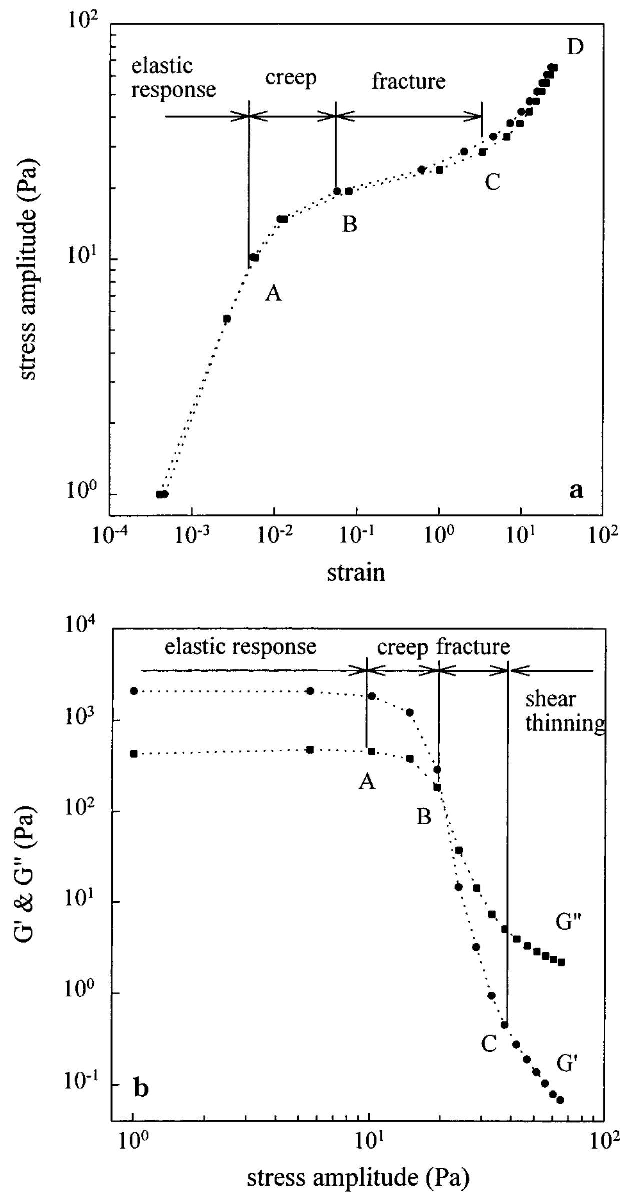


**Figure 7.** Oscillatory test: (a) stress vs strain relationship during the yielding process (DH19, 20 °C, 1 Hz); (b) $G'$ and $G''$ during yielding (DH19, 20 °C, 1 Hz).

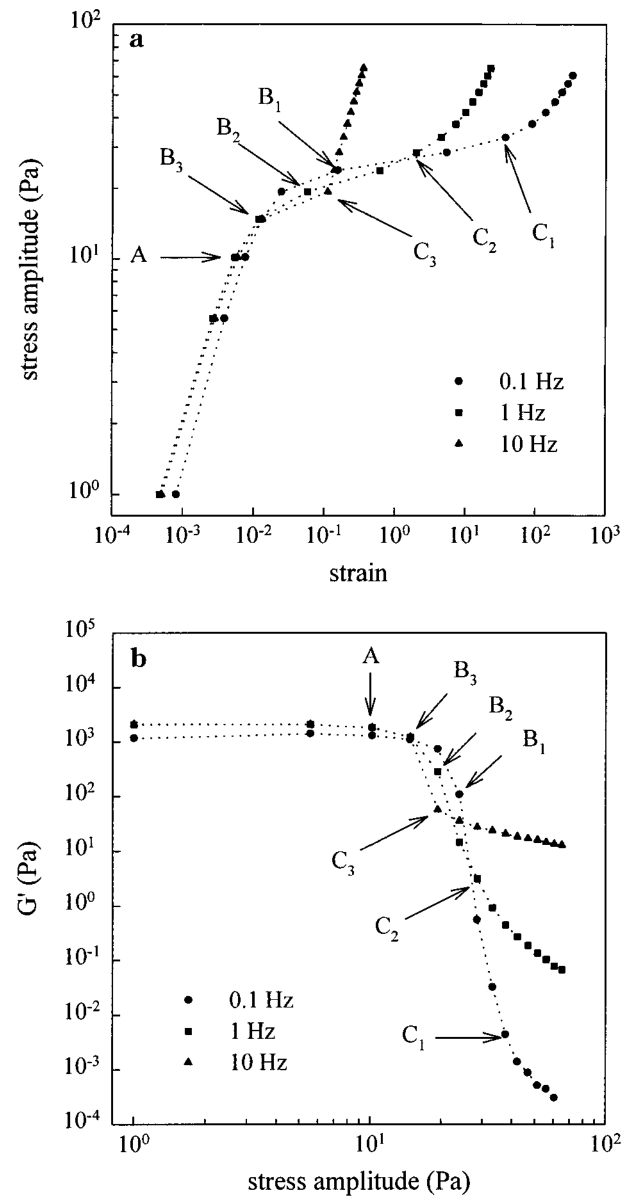


**Figure 8.** Oscillatory test: (a) effect of frequency on stress vs strain relationship during and after yielding (DH19, 20 °C); (b) effect of frequency on $G'$ during and after yielding (DH19, 20 °C).

indicates a change of the oil sample from solidlike to liquidlike. Point B may be identified as the starting point of the fracture. The static yield stress may then be determined to be between 19.1 and 23.9 Pa. Oscillation with a stress amplitude higher than the static yield stress will destroy the waxy structure completely. The oil after the destruction displays a typical viscous behavior, with very high strain responses and $G'$ much lower than $G''$, as displayed by the final range of the curve after point C. Two identical runs were performed to ensure the reproducibility and the reliability of the test.

**Effect of Frequency.** The frequency, representing the time scale of the oscillatory test, is changed from 0.1 to 10 Hz to evaluate the effect on the measured yield stresses. The stress−strain relationship during testing at three frequencies is shown in Figure 8a on logarithmic coordinates. $G'$ in three tests are compared in Figure 8b. It is shown that the measurements at different frequencies give similar strain and $G'$ responses in the small stress amplitude regions, represented by the segments before point A, indicating that the elastic response is independent of the time scale. The strain in the elastic range thus only depends on the stress amplitude. The figure also shows that the transitions from the elastic behavior to creep occur at the same stress level (point A) at different frequencies, although creep subsequently develops along different tracks. The elastic-limit yield stress may then be determined as frequency independent.

In both figures, "B" indicates the start of the fracture while "C" is the end of the fracture, as in other figures in this paper. Subscripts 1−3 are used to represent the testing with frequencies of 0.1, 1, and 10 Hz, respectively. The creep processes in the three tests are then displayed by the curve segments between A and B. The static yield stresses are between 23.9 and 28.4 Pa for 0.1 Hz, between 19.3 and 23.9 Pa for 1 Hz, and between 14.7 and 19.3 Pa for 10 Hz. A lower static yield stress is observed with a higher frequency, which may be explained by the fact that more vibration in the testing, corresponding to a higher frequency, causes more damage to the waxy structure. The waxy structure therefore is destroyed more quickly at a higher frequency. The differences between $G'$ after point C at different frequencies indicate that the change of the time scale also causes a change of the oil property at the final broken state; this is similar to that observed in the controlled stress test, in which the final apparent viscosity after yielding is dependent on the stress loading rate.

The results from both oscillatory and controlled stress tests indicate that the rheological properties of oils, such as viscosity, $G'$ and $G''$, at the final broken state are also shear history dependent. This dependence, together with shear-thinning, thixotropy, and thermal history dependence, attributed to the wax structure in the oil, makes waxy crude oils a complicated material from the viewpoint of rheology.

**Comparison of Three Techniques.** The entire yielding process of DH19 waxy crude oil was successfully recorded by both creep−recovery and oscillatory tests. The yielding process recorded in both techniques is in good agreement with that described qualitatively by Wardhaugh and Boger (1991). In the controlled stress test, only the fracture process and partial creep process can be observed. The elastic response and the initial creep segments cannot be recorded in the controlled stress test since the shear rate in these ranges is lower than the resolution of the rheometer. Although the entire yielding process can also be recorded using the vane technique, the vane technique is not available for the quantitative measurement of yield stresses at this stage since the relatively large sample volume used in testing makes it very difficult to exactly control the thermal history of the samples. The three techniques used in this paper all are stress controlled, while the vane technique described by Nguyen and Boger (1985) is shear controlled. The difference between the results from shear-controlled and stress-controlled methods is that the stress drops sharply after the start of fracture in the shear-controlled testing, as indicated by point B in Figure 1 while the strain (or shear rate) in the stress-controlled testing increases dramatically when fracture starts, as indicated by point B in Figures 2a, 5, and 7a. Due to the degrading of the structure during the yielding, after fracture a much lower stress is sufficient to keep the oil rotating while a stress higher than (or the same as) the static yield stress will cause significantly higher strain and shear rate.

The results shown in Figures 3a, 5, and 7 are from three techniques studied in this paper for DH19 waxy crude oil with identical thermal and shear histories. The values of $\tau_s$ can be directly determined from each testing and so are the values of $\tau_e$ from the creep−recovery and oscillatory tests. The values of $\tau_d$ in the controlled stress test are extrapolated from the high shear rate range after the fracture, which is after point C in Figure 3a, according to the Bingham equation. Because of the time scale dependence of the static yield stress, it is meaningless to compare directly the measured static yield stresses from different methods with each other since the time scale is totally distinct in the different tests. The measured elastic-limit yield stress from different tests, however, should be comparable since it is not influenced by the characteristic time of the tests. The elastic-limit yield stress was determined between 4 and 8 Pa from the creep−recovery test and between 5.6 and 10.1 Pa from the oscillatory test. The results from different techniques are in a reasonably good agreement. The controlled stress test may be the most expedient, since the static yield stress can be determined in a single run of this test, while only a range of values can be obtained for the static yield stress in both creep−recovery and oscillatory tests. The creep−recovery test is very time-consuming as yield stresses can only be determined after several runs.

It was inevitable that some lighter distillate in the oils evaporated during the pretreatment, cooling, and even testing process. The evaporation caused the final testing samples to be more viscous than the original oil in the drum. However, this difference would not affect the understanding of the yielding process of the oils or the trend of various factors on the yielding. The testing results are comparable if the pretreatment, the cooling, and the testing are conducted by the same procedures for each oil. The reproducibility can be guaranteed by controlling all related factors of each process.

**Application of Three Yield Stresses in Pipeline Transportation of Waxy Crude Oils.** The test results from three different direct measurements for a statically cooled DH19 waxy crude oil have verified the usefulness of the three-yield-stress model in describing the yielding process of waxy crudes. Most of the previous works in this field, based on the one-yield-stress model, were focused on the determination of the one unique yield stress and the application of this unique yield stress to the design and calculation of pipelines. The model with one yield stress has been shown in this paper to be oversimplified for the yielding of waxy crude oil. This simplification will definitely cause some miscalculation. It is clear now that the different yield stresses should be used in different stages of yielding for the shear stress−shear rate relationship calculation. For example, the elastic-limit yield stress should be used to determine if the yielding could start. The waxy microstructure will not be disturbed at positions where the stress is kept below the elastic limit. The static yield stress can be used to determine if fracture occurs. The oil structure at positions where the stress is between the elastic limit and the static yield stresses will decay over time (creep), meanwhile the static yield stress itself decreases over time at these positions. Fracture occurs at any points where the stress is higher than the static yield stress. After the fracture, the dynamic yield stress should be used in the calculation of the shear stress−shear rate relationship. Both the static and dynamic yield stresses are time-scale dependent, which means they depend on the yielding history. The history dependence of the static and dynamic yield stresses suggests that these two yield stresses could be different from position to position both radially and axially and from time to time at the same position. It is then necessary to exactly determine the stress history, not only shear history, for each oil particle at any time during the pipeline restart operation for the successful prediction and calculation.

## Conclusions

The yielding of waxy crude oils is a complex process. It consists of three successive steps: elastic response, creep, and fracture. One yield stress is not sufficient to describe this process. A model with three yield stresses has an extensive range of application and can be generally accepted for waxy crudes.

The best method to determine the true yield stresses of waxy crude oils is direct measurements employing a controlled stress rheometer. In a controlled stress rheometer, the measurement of the static yield stress can be produced by the controlled stress test, creep–recovery test, and oscillatory test, while the elastic-limit yield stress can be evaluated by creep–recovery and oscillatory tests. The dynamic yield stress can be extrapolated from high shear rate data after fracture to the zero-shear rate limit in the controlled stress test.

The elastic-limit yield stress, which is the minimum limit of the pump pressure required to initiate flow in a pipeline, is independent of the time scales of the measurements, and thus independent of the techniques as well. The static yield stress is controlled by not only the strength of the wax structure in the oils but also the time scale of the yielding. The measured static yield stress from the rheometer can only be applied to the design with the information of the time scale of the measurement. The dynamic yield stress, which is also influenced by the time scale of the yielding, may be used in the calculation of the pressure–flow rate relationship when the oil is flowing in an equilibrium state after fracture.

With strict temperature and history control, all three tests concerning the yielding values for the statically cooled oil are found to have reasonably good reproducibility.

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## Nomenclature

$G'$ = storage modulus (Pa)
$G''$ = loss modulus (Pa)
$\tau_d$ = dynamic yield stress (Pa)
$\tau_e$ = elastic-limit yield stress (Pa)
$\tau_s$ = fracture stress or static yield stress (Pa)

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