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Strain amplitude dependence of shear modulus in heavy oils: Rheometer versus tension/compression technique

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ABSTRACT

Although heavy oils are an enormous resource and a common seismic monitoring target, their geophysical properties remain poorly understood. The shear modulus is of particular interest, because under the right conditions, these oils can transmit S-waves. However, there is a large uncertainty on how to measure the shear modulus of heavy oils. The use of the rheometer, common in chemical engineering applications, has been proposed as a good alternative to tension/compression techniques. Rheometers are an attractive alternative for measuring the shear modulus because of their widespread use and availability. In order to test the validity of the rheometer as a method to measure the shear modulus of heavy oils for geophysical applications, we tested two samples using techniques familiar to geophysics (tension/compression and ultrasonic) and compared the results with the rheometer measurements. We noticed a difference in the measured shear modulus between the two techniques. The samples showed a solid-like behavior when tested in the tension/compression equipment while behaving liquid-like in the rheometer. Both measurements were done in the linear regime (in which there is no change in modulus with amplitude), indicative of the potential presence of two linear viscoelastic regimes (LVRs) at different amplitudes. We developed a model that explains the presence of the two LVRs for heavy oils with a large content of resins and asphaltenes and at temperatures that allows the formation of large aggregates. We analyzed the presence of the two LVRs in terms of the weak interaction that appeared between aggregates when subjected to small-amplitude strains, resulting in a solid-like behavior; those weak interactions were not present when the sample was subjected to larger strains resulting in a liquid-like behavior.

INTRODUCTION

Even though heavy oils constitute the largest contributor to oil reserves in the world, they still remain one of the least understood fluids in the reservoir by geophysicists. Many heavy-oil reservoirs are characterized using seismic data; in particular, time-lapse (4D) seismic methods have been introduced to facilitate the monitoring of enhanced oil recovery (EOR) methods, which are often, if not always, required in these reservoirs. The success of seismic and other acoustic monitoring techniques is based on the ability of geophysicists to accurately model the P- and S-wave propagation through actual and potential rock-fluid scenarios that will be encountered during EOR operations. It is essential, therefore, to translate these scenarios into changes in the elastic properties that govern wave propagation (bulk modulus, shear modulus, and density); this is a goal of rock-physics modeling. Rock-physics models estimate the elastic properties of the rock-fluid system from its components, usually divided into two parts: mineral grains and pore fluids. The grains comprising the rock are either treated as a uniform solid, for example, sandstone or limestone, or they can be treated as a combination of minerals such as quartz, calcite, and dolomite. On the other hand, fluids are usually divided into gases (i.e., methane and CO_2) and liquids (water and crude oil). Regardless of how the rock-physics models divide the components, all are based on the assumption that the properties of the individual components are well known. This last statement is far from the truth in the case of heavy oils.

It is usually understood that fluids are not capable of supporting shear stress; heavy oils and all their heavier relatives, however, behave acoustically different from the rest of the fluids in the reservoir, allowing the transmission of S-waves below a certain temperature or above a certain frequency. Thus, depending on the condition, heavy oils can behave as liquids or solids, a property called *viscoelasticity.*

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Geophysicists working with the analysis of seismic data in heavy oil reservoirs must face this fact and consider the shear modulus of the heavy oil in their analysis. Authors such as Ciz and Shapiro (2007), Gurevich et al. (2008), Ke et al. (2010), and Makarynska et al. (2010) develop rock-physics models that include the viscoelastic behavior of heavy oils in their estimation of the elastic properties. Nonetheless, a limitation in those models is the uncertainty in the effective shear modulus of heavy oils. Moreover, there is uncertainty about how to measure this modulus. Wolf et al. (2008) raise that concern, emphasizing the author's limitation in model S-wave behavior because of the lack of appropriate rock-physics models and, moreover, the lack of experimental data to calibrate them. This constitutes a definite gap in rock-physics models that estimate the elastic properties of heavy oils. The work presented here attempts to fill this gap, in particular by trying to determine how we can reliably measure the shear modulus of heavy oils.

It has been demonstrated (Batzle et al., 2006b; Hasan, 2010) that the shear modulus of heavy oils is highly dependent on temperature, composition, and frequency. Frequency dependency adds a major difficulty to the problem because the data we study are obtained at different frequencies. Laboratory acoustic experiments are usually performed at ultrasonic frequencies (on the order of megahertz) whereas seismic data are collected in the range of 10–100 Hz, vertical seismic profiles (VSPs) at approximately 30–120 Hz, and sonic logs at 10–30 kHz. To provide a complete picture of the shear modulus of heavy oils, we need to account for the properties at different frequencies.

Frequency dependency of the shear modulus of heavy oils, also called frequency dispersion, has been measured (Batzle, 2006a), but it lacks extensive characterization because of the difficulty of measuring shear properties at different frequencies. Measuring elastic properties at high frequencies, which has been done for many years, is much simpler and robust than measuring the same properties at low frequencies. Low-frequency measurements of bulk heavy oils bring many complications. One technique used at the Colorado School of Mines consists of a tension/compression system that deforms or compresses the sample over a frequency range from 3 to 3000 Hz. The equipment works well for solid or solid-like samples, but it cannot be used for liquid-like samples. An alternative method used to measure the shear modulus of heavy oils at low frequencies is the rheometer.

The rheometer constitutes a convenient way of measuring the shear modulus of oil samples because the equipment is widely available and much data have been published. A rheometer typically can measure the shear modulus in a frequency range of 0.01–100 Hz, providing insight into the low end of the frequency range, where seismic field data are acquired. Several authors, Behura et al. (2007), Hinkle et al. (2008), Rojas (2008), Bazyleva et al. (2010), and Hasan (2010) measure the shear modulus of heavy oils with the rheometer, but none offer insight into how comparable these measurements are with what has been measured at ultrasonic measurement frequencies and with tension/compression techniques at seismic frequencies. The lack of verification of the rheometer as an adequate technique to measure the shear modulus of heavy oils at low frequencies has created hesitation and reluctance to its use. The focus of our work is to thoroughly understand rheometer measurements, compare them with tension/compression results, and ascertain if the two techniques measure the same shear phenomena. Ensuring that the two techniques are measuring the same properties is crucial before the rheometer can be widely used for geophysical applications.

The major question in the use of the rheometer for geophysical applications is related to the strain amplitudes used. The minimum strains measured by the rheometer are on the order of 10^{-4} whereas strain amplitudes in geophysical acoustic measurements, including laboratory measurements, are on the order of 10^{-6}–10^{-7}. Linear viscoelasticity theory states that for linear materials, if measurements are done in the linear viscoelastic regime (LVR), all techniques should be consistent because their elastic properties should be independent of amplitude. As far as we know, the work we present here constitutes the first effort to compare the two low-frequency techniques (rheometer and tension/compression) and ultrasonic techniques simultaneously and to demonstrate how the measurements relate over the broad frequency range.

Comparisons between rheometer and ultrasonic measurements are done by Rojas (2010), but because of the large gap in frequencies between the two techniques, a clear validation is not obtained. As a result of the different strain magnitudes used in the rheometer and tension/compression technique, a comprehensive inquiry of how the strain amplitude changes the structure of heavy oils and consequently the shear modulus will be central to this analysis. We provide theories and evidence of the structural changes occurring in the heavy oil that affect the shear modulus when measured using different amplitudes. The insights we provide in this work have important implications for how we measure and interpret the shear behavior of heavy oils with geophysical data. In order to understand and explain the results of this work, we must incorporate concepts and references from different sciences (i.e., construction, chemical engineering, and chemistry) that have worked with either similar materials or techniques but in a completely different context.

We begin by providing a short explanation of viscoelasticity and a summary of heavy-oil characteristics that are relevant to our work. We then describe modifications to the tension/compression technique that allow for testing of soft samples. We next compared the rheometer and tension/compression technique for two samples, and then we discuss a model of the shear behavior of heavy oils with varying amplitudes. Literature examples demonstrate similar behavior for materials that differ from heavy oils. Before summarizing the implications and conclusions of this work, we describe another mechanism that influences the rheometer measurements.

Theory of viscoelasticity

Viscoelastic materials exhibit characteristics of solids and fluids. A solid is defined as a material that responds to Hooke's law (Lakes, 2009), which means that the stress is proportional to the strain. In contrast, a fluid under shear stress responds linearly with the rate of strain, and the constant of proportionality is the viscosity. Viscoelastic materials exhibit time or frequency dependence and require a time function to describe the behavior. Heavy oils are viscoelastic materials.

Of particular interest in the oil industry is the study of materials under sinusoidal load. *Sinusoidal load* is the basis of many geophysical acoustic methods such as seismic, VSP, crosswell tomography, and sonic logs, among others. In this case, the stress varies sinusoidally with time:

$$\sigma(t) = \sigma_0 \sin(2\pi f t), \tag{1}$$

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where t is time, σ is stress, and f is frequency (in hertz). The strain ε response of a linearly viscoelastic material is also sinusoidal in time, but the response will lag the stress by a phase angle δ as

$$\varepsilon(t) = \varepsilon_0 \sin(2\pi f t - \delta). \tag{2}$$

As a result of the phase lag between stress and strain, the modulus M must be treated as a complex number (Lakes, 2009):

$$M^* = M' + iM'', \tag{3}$$

$$M' = \frac{\sigma_0}{\varepsilon_0} \cos \delta, \tag{4}$$

and

$$M'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta. \tag{5}$$

The modulus typically is either Young's modulus E or shear modulus G depending on the type of loading: compressional, or shear. The real part G' of the shear modulus is also called the storage modulus, whereas the imaginary part G'' is called the loss modulus because it is related to the loss of energy in the form of heat. In terms of molecular deformation, when a material is subject to force, part of the energy is stored by the material and allows the material to return to the same configuration when the force is released. The "loss" part of the deformation changes the material's configuration in an irreversible manner. In terms of seismic waves, when the wave perturbs the molecules, part of the energy is transmitted and part is lost in changes to the molecular configuration. Solids and liquids can be defined based on the relative magnitude of their storage and loss modules. A material with zero storage modulus is considered a "liquid" ($G' = 0$); in contrast, a material with a zero loss modulus is considered a "solid" ($G'' = 0$). Hence, viscoelastic materials are referred to as having a "solid-like" behavior when their storage modulus is larger than their loss modulus $G' > G''$, and a "liquid-like" behavior when their loss modulus is larger than their storage modulus ($G'' > G'$).

Heavy-oil characteristics

Hydrocarbons are considered "heavy oils" when their American Petroleum Institute (API) gravities are less than 20°. There are descriptive terms to refer to various specific ranges of API gravity, such as extra-heavy oils, tar, pyrobitumen, and asphalts, among others, but in our work, we use the term heavy oils to refer to all hydrocarbons with an API gravity of less than 20°. Heavy oils have high molecular weight, with composition so complex that individual components are difficult to identify. These oils are often described in terms of solubility through saturates, aromatics, resins, and asphaltenes (SARA) fractions. SARA fractionation is based on separating the heavy oil in fractions soluble to different solvents (Wu et al.,). SARA fractions separate the heavy oil in terms of polarity, which is the tendency of molecules to interact with surrounding molecules as a result of an imbalance of the electric charge. Polarity increases from saturates to asphaltenes, asphaltenes being the most polar fraction. Evidence of the increased polarity of asphaltenes and resins relative to aromatics and saturates has been expressed in terms of the dipole moment, dielectric constant, or conductivity, as shown by several authors (Goual and Firoozabadi, 2002; Chow et al., 2004; Evdokimov and Losev, 2010). There is also molecular weight, which generally increases from saturates to asphaltenes, but this property can exhibit significant overlap.

Resins and asphaltenes are the fractions with the highest polarity and tend to interact and form aggregates. These asphaltene aggregates are often called asphaltene colloids or micelles in the literature. The attraction between molecules is so strong in these aggregates that they bond together almost permanently because it requires much energy to reverse the process; aggregates are therefore effective in increasing viscosity and shear modulus. The aggregates tend to be rigid structures, not flexible like polymers of large chains. Besides the strong molecular bonds formed between resin and asphaltene molecules, secondary interactions between aggregates also exist. This secondary interaction is referred to as aggregate association, which is a weaker or temporary interaction between aggregates. These associations can transmit forces and alter the mechanical properties of the material. Still, these associations are weak enough and can break, for example, during an experiment (Witten and Pincus, 2004). At rest, aggregates form a network that immobilizes the fluid (or solvent), and the system behaves like an elastic solid under low stress. As the force applied to the material is increased, a yield point is reached, and the network breaks apart causing the system to begin to flow and the viscosity of the material to decrease (Hiemenz and Rajagopalan, 1997).

METHODS: SHEAR PROPERTIES OF HEAVY OILS AT LOW FREQUENCIES

The experimental work here consists of comparing shear measurements from two samples, which are solid-like at the testing temperature, using three different techniques: ultrasonic, tension/compression, and rheometer. The two samples were collected from outcrops in the Unites States: Asphalt Ridge (GP029) from Utah and Uvalde (GP007) from Texas. For reference, Table 1 lists the API gravity and SARA analysis of the samples. Tests performed on GP029-Asphalt Ridge were done at −6.5°C and for GP007-Uvalde at 30°C; temperatures were selected to ensure that samples showed viscoelasticity, closer to solid-like behavior. The solid-like behavior was needed in order to perform the tension/compression experiments.

We briefly explain the rheometer measurements and tension/compression techniques, in particular, the aspects relevant to this investigation. These two techniques come from different disciplines because the rheometer is mainly used by chemical engineers, whereas the tension/compression technique is used by geophysicists. Even though these techniques come from different disciplines,

Table 1. SARA analysis and API gravity of samples.

	Oil composition (wt%)				API gravity
Sample	Saturates	Aromatics	Resins	Asphaltenes	Density (g/cm^3)
GP007	2.24	26.38	23.47	47.91	−5.00 (1.118)
GP029-1	16.06	31.78	45.45	6.70	14.03 (0.972)
GP029-2	18.14	31.17	44.21	6.49	14.03 (0.972)

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they are based on the same theory; they differ in the geometry, physical state of the samples, and amplitudes used.

Rheometer measurements

A rheometer measurement involves a simple technique to measure shear properties of heavy oils at low frequency. The rheometer has an upper rod connected to a geometry that constitutes the upper piece and at the bottom, there is a Peltier plate that provides temperature control. Different geometries are available and are selected depending on the viscosity of the sample. For this work, the sample is placed between two plates and a sinusoidal force is imposed by the upper rod displacing the sample; when the force is released, the response of the sample is recorded by the same rod. It is considered simple because it does not require much time for sample preparation (minutes) compared with the tension/compression technique in which sample preparation can take up to a week. The rheometer is also considered to be "standard" because such equipment is amply available and there is wide experience among chemical engineers who have studied many types of materials for many years.

The rheometer used in this work can measure the dynamic elastic properties at frequencies between 0.01 and 100 Hz, covering the seismic frequency range. The equipment used for this work is the AR-G2 from TA Instruments, using parallel plates of 8-mm diameter. The rheometer measures the magnitude of the strain and the phase lag between the stress and the strain, from which it calculates the storage and loss modulus through equations 4 and 5.

The steps to perform rheometer measurements depend on the specific equipment, but it is always important to perform the initial calibration steps recommended by the manufacturer. The more important calibration steps are: equipment inertia, geometry inertia, zero-gap, oscillatory, and rotational mappings. Enough time is needed to allow the sample to achieve equilibration temperature and to release normal force. Finally, a detailed quality control of the results needs to be done. In particular, close attention needs to be paid to the comparison of the measured phase lag (raw phase) and the corrected phase (delta). The equipment performs automatic corrections resulting from inertia (for low-viscosity samples) and equipment/motor compliance (for high-viscosity samples). These corrections, however, cannot be too large, or the results are unreliable.

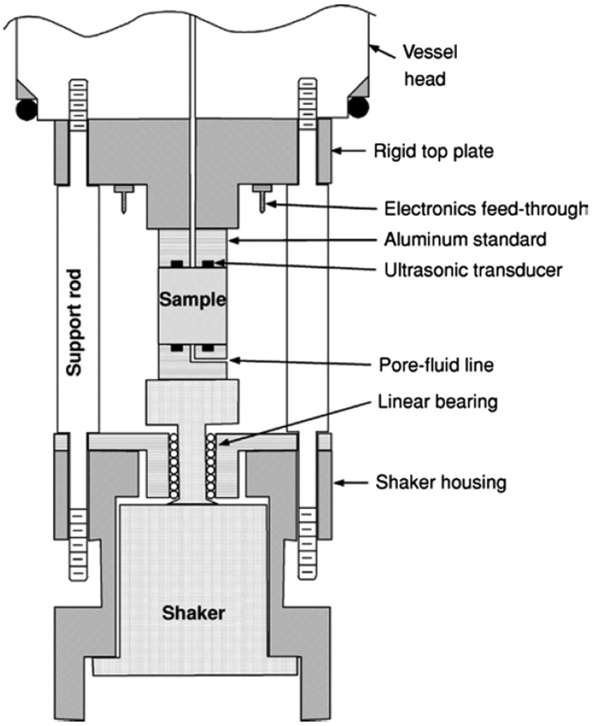

Figure 1. Schematic representation of the tension/compression equipment from Batzle et al. (2006b). The sample is fixed to the upper rigid plate and the shaker below. A sinusoidal signal is sent to the shaker at different frequencies, and strains are measured by gauges attached to the outside of the sample and the aluminum standards.

Tension/compression measurements

Other researches (Spencer, 1979; Batzle et al., 2006a) develop techniques to measure the elastic properties of solid materials (i.e., rocks) at wide frequency ranges, including the seismic frequency range. However, only limited results have been reported in measuring soft samples at low frequencies because of limitations of the technique (Spencer, 2013). The tension/compression technique used here consists of applying axial deformation to the sample and measuring the resulting strain. Measured frequencies can be between 3 and 3000 Hz, but the actual range of valid measurements depends on properties of the sample and the quality of equipment shielding. Strain amplitudes are kept in the 10^{-6}–10^{-7} range and are a trade-off between measurements at low amplitudes (seismic amplitudes) and interfering noise levels. The sample has to be in cylindrical shape, and horizontal and vertical strain gages are attached to the sides of the sample. Aluminum pieces are attached to the ends of the sample with vertical and horizontal strain gauges attached. Ultrasonic crystals can also be included at the end of the sample to measure ultrasonic velocities. At every frequency, the vertical and horizontal strain is measured at every gauge. Using the known Young's modulus of the aluminum, the applied stress can be calculated. With the stress and measured vertical strains of the sample, the Young's modulus of the sample is calculated. Poisson's ratio is calculated as the ratio of the horizontal to vertical strains, and using Young's modulus and Poisson's ratio, the shear modulus is calculated. These values are calculated at every tested frequency. Figure 1, from Batzle et al. (2006b), shows a schematic representation of the tension/compression equipment, and additional details about the experimental procedure can be found in Das (2010) and Batzle et al. (2006b).

In addition to strong dependence of the elastic properties on frequency, heavy oil properties have a strong dependence on temperature. This introduces the need to assure a constant temperature during the length of the experiment; this was achieved by the introduction of a more rapid acquisition system and a temperature-control bath. In the following sections, we summarize the advances made during our work in order to measure the elastic properties of soft samples at low frequencies. We begin with changes in the acquisition system and calibration, and we finish with sample preparation and temperature control.

Acquisition system

In the Center for Rock Abuse (CRA) at Colorado School of Mines, data were previously collected using digital oscilloscopes. These oscilloscopes had a limited number of channels but poor dynamic range. We also used a bank of phase-lock amplifiers controlled by a MATLAB program; these amplifiers were accurate but slow, had low reliability, and developed communication issues. A complete sweep of frequencies and channels took several hours. The new acquisition system used for this work was developed based on high-accuracy digitizers (National Instruments); it allowed for a reduction in the acquisition time and is more stable. This system performs amplitude and phase measurements, calculates standard deviations, allows for variable amplitude, stores waveforms for each frequency, and filters signals working with up to 12 channels simultaneously. Calibration of the new acquisition system was performed for amplitude and phase measurements using a standard material: polyethylene ether ketone (PEEK). A comparison between ultrasonic and the tension/compression setup with PEEK is shown in Figure 2. Young's modulus is calculated at low frequencies directly from stress-strain measurements. The modulus at ultrasonic frequency is derived from compressional and shear velocities assuming an isotropic material. The noise spikes at low frequencies result from spurious electromagnetic impulses and are enhanced for these bench-top measurements because of a lack of shielding (the assembly was outside of the steel vessel). A good match between low-frequency and ultrasonic measurements is obtained, but a small dispersion is observed. PEEK properties can vary between manufacturers, and we did not have that information for the PEEK used in this test. A review of published values provides a range to the static Young's modulus of the PEEK between 3.6 and 3.95 GPa. Some of the values reported are: from AZO Materials, 3.76–3.95 GPa; from Performancefiber.com, 3.6 GPa; and from Xin et al. (2012), 3.7 GPa; all of these values show a good match to the measured values with the tension/compression setup. Those values are shown in Figure 2 for the results of the tension/compression and ultrasonic techniques.

Soft sample preparation

Measuring elastic properties of soft samples (heavy oils) at low frequencies presents a major challenge. Spencer (2013) conducts low-frequency measurements on jacketed bitumen-saturated sands using displacement sensors, and Batzle, et al. (2006b) measure a heavy-oil sample at low frequency, attaching strain gauges to the surface of the heavy oil after it was molded into a cylinder shape (see Figure 3 from Behura et al., 2007). The Batzle et al. (2006b) procedure was possible because of the extreme high viscosity and density of the sample (API-5) at room temperature. The majority of the heavy oils of commercial interest, however, have lower viscosity at room temperature, which makes the process of attaching strain gauges impractical, if not impossible.

For this reason, the first and major requirement was the need to use a jacket to contain the heavy oil. The jacket, which is made of a material resistant to high temperatures (Kapton) and flexible enough to allow contraction and deformation of the sample, is attached to the aluminum standard. The jacket material has to be "softer" that the material being tested at all times during the experiment. Strain gauges are attached to the exterior of the jacket or positioned inside the jacket with wires through the jacket. For heavy oils, the samples are heated above the liquid point and poured into the jacket. The heating temperature should be kept at less than 100°C to avoid loss of volatile material. After cooling, the upper part of the sample is capped with another aluminum standard. Aluminum standards can contain ultrasonic crystals to allow for ultrasonic measurements in the sample. Results shown in this paper for sample GP029-Asphalt Ridge were obtained using gauges attached to the jacket. An example of a similar jacket is shown in Figure 4. In this figure, the strain gauges are inserted through the jacket. Either in the exterior or interior configuration, the jacket and strain gauges have a Young's modulus that is several orders of magnitude lower than does the sample at the tested temperature to ensure that the properties of the jacket and gauges do not contaminate the measured strains of the sample. Because of the large strain amplitudes expected in heavy oils, foil gauges must be used to measure the heavy oil instead of the more sensitive semiconductor gauges used to measure the low strain amplitudes of the aluminum standards.

Temperature control

A chromel-alumel thermocouple is inserted through the jacket to measure the temperature inside the sample. Measurements were conducted inside a steel vessel equipped with a temperature bath that allowed constant low temperatures for a long period of time.

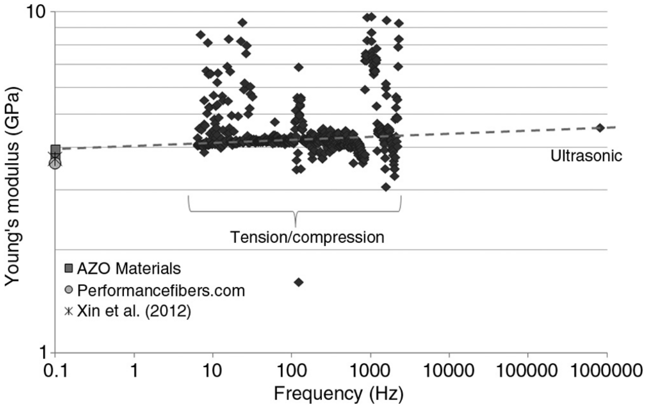

Figure 2. Young's modulus of PEEK at intermediate and ultrasonic frequencies collected outside the steel vessel in tension/compression. Even with the presence of noise, consistency exists between the low frequency and the ultrasonic results. Minor dispersion is observed and expected for the sample. Published static values (zero frequency) of the PEEK Young's modulus, plotted at 0.1 Hz for display, indicate a good match with measured values at higher frequencies.

Figure 3. Heavy-oil (GP007-Uvalde) sample with semiconductor strain gages attached to the surface (from Batzle et al., 2006b).

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Samples were placed inside the steel vessel for 24 h prior to testing to ensure that the temperature had equilibrated throughout the sample. Temperature measurements were taken periodically throughout the duration of the experiments. Dynamic elastic measurements were kept to a short time (less than 5 min) because the heat induced by the components of the equipment and the strain gages increased the temperature during the experiment. After each experiment, the temperature was allowed to equilibrate before acquiring additional data.

RESULTS: COMPARISON AMONG RHEOMETER, TENSION/COMPRESSION, AND ULTRASONIC MEASUREMENTS, SOLID-LIQUID TRANSITION DUE TO STRAIN AMPLITUDE

Figure 5 shows the shear modulus of the heavy oil for the GP029-Asphalt Ridge sample using the three techniques. A significant difference between rheometer and tension/compression results can be seen as compared with a general Cole-Cole dispersion model. Here, rheometer results were obtained using a large gap to reduce the increased viscosity near the surface of the rheometer plates. This means that the gap between parallel plates is set to a large value to avoid the increased shear modulus observed at the liquid-solid interfaces between the plates and the sample. In a yet-unpublished paper, we show that when the distance between the plates in the rheometer is reduced, the shear modulus increases. A similar result is obtained for sample GP007-Uvalde in which, as shown in Figure 6, the measurements do not match the expected trend from the Cole-Cole dispersion model (the continuous line in the figure). The difference between the tension/compression and the rheometer is believed to be caused by the larger strain amplitude used by the rheometer.

In addition, when comparing the same results of the tension/compression with rheometer measurements performed at small gaps, the two data sets get closer, showing a more consistent match (Figures 7 and 8).

Figure 4. Example of jacket design to measure elastic properties of soft samples. The jacket is made of Kapton, a material resistant to heat and flexible enough to allow deformation of the soft sample. The jacket is attached to an aluminum standard with six pairs of gauges, three vertical and three horizontal, inserted in the jacket. The jacket used for the experiment shown in this work had outside gauges attached to the surface of the jacket.

DISCUSSION: AMPLITUDE-DEPENDENT SOLID-LIKE TO LIQUID-LIKE TRANSITION DUE TO AMPLITUDE

Heavy oils with a large content of resins and asphaltenes can form aggregates under certain conditions. These aggregates are internally chemically bonded due to the presence of polar molecules such as asphaltenes and resins, whereas aromatic and saturate fractions act as a background or solvent to the high-polarity molecules. Each aggregate is composed of many molecules attached to others

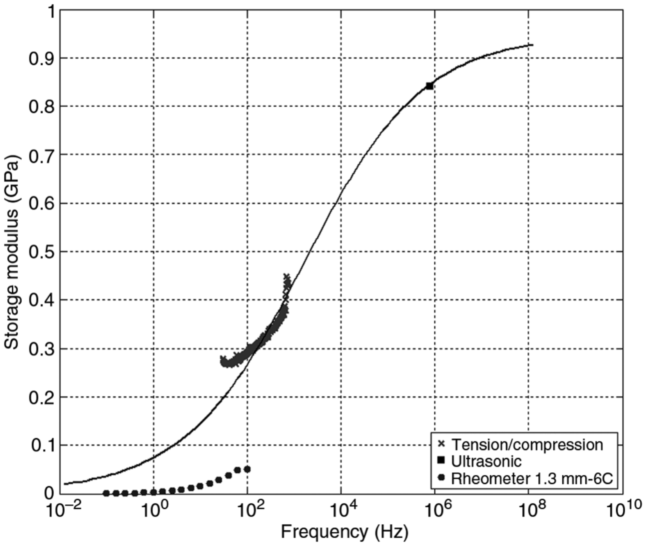

Figure 5. Storage modulus (G') versus frequency for sample GP029-Asphalt Ridge from three different techniques, with a Cole-Cole dispersion model for reference (continuous line, alpha = 0.68). The rheometer raw data shown correspond to values measured using a large gap (1.3 m). The tension/compression tests used external gauges.

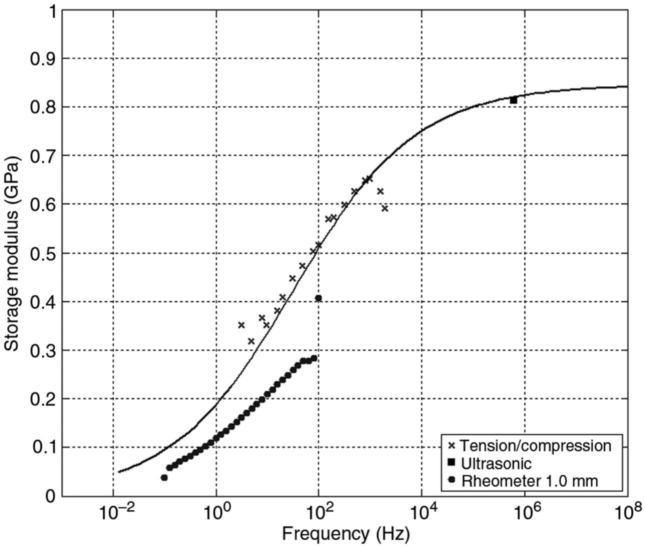

Figure 6. Storage modulus (G') versus frequency for sample GP007-Uvalde with rheometer data acquired using a large gap (1 mm). In this case, the rheometer data do not match the expected Cole-Cole dispersion model (continuous line, alpha = 0.66).

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by strong intermolecular forces. If the sample is kept at a low energy level (low temperature or low strain), physical interparticle forces between aggregates become important and cause aggregates to associate and form networks that give a solid-like behavior to the heavy oil. The interparticle physical forces are much weaker than the intermolecular chemical bonds forming the aggregates. Therefore, as long as the level of energy of the sample is kept low, these structures exist. When shearing the sample at a low strains (low amplitudes), these structures do not break but rather stretch and deform. This secondary attraction between aggregates in heavy oils has not been proposed before, and we introduce it here as a plausible mechanism that explains its shear behavior at different strain amplitudes.

This behavior is represented by Figure 9a, in which the material acts solid-like, and if the amplitude is slightly changed, the shear modulus remains constant and the material is in an LVR. When the amplitude is increased (Figure 9b), the weaker bonds are broken and the aggregates are separated and act like a suspension of polar aggregates (asphaltenes and resins) in a solvent (aromatics and saturates). The material still behaves linearly, and a second LVR develops. If the amplitude is increased further (Figure 9c), aggregates begin to break and a nonlinear behavior appears. The change with amplitude between in Figure 9a and 9b has not been previously proposed for heavy oils, but it has been critical for other materials, as is discussed in the next section. It is important to emphasize that the change in shear modulus between the two LVRs is less than one order of magnitude, which contrasts with much larger changes observed in the literature for other materials. The model shown in Figure 9 raises a major issue when comparing data from the rheometer with data from tension/compression, ultrasonic techniques, or geophysical field measurements because the heavy oil studied in these tests are under different strain regimes.

Multiple linear viscoelastic regimes reported in the literature

Even though the presence of multiple LVRs has not been reported for heavy oils, it is well known for other materials such as fresh cement paste. Ramachandran and Beaudoin (2000) show the presence of two LVRs for a cement paste as an example of its typical behavior with strain. Similarly, Chougnet et al. (2007) explain that aggregates under no deformation tend to form a single continuous phase and the material acts solid-like, but when the strain is increased, the material acts liquid-like. For two different aggregate materials, they show that two LVRs occur in the shear modulus. The change between the two LVRs are described as an amplitude-dependent solid-like to liquid-like transition. Figure 10 shows the results of Chougnet et al. (2007) who emphasize that for the first LVR, G' (storage) is larger than G'' (loss), which corresponds to a solid-like behavior. In the second LVR at larger amplitudes, G'' is larger than G', corresponding to a liquid-like behavior. Heymann et al. (2002) also measure similar results for spheres of polymer particles in concentrated suspensions. At low stress (low strains), the suspension behaves solid-like and shows a quasi-linear viscoelastic regime. Upon increasing the stress (and strain), they report a sharp transition to liquid-like behavior and a secondary LVR appears. In samples tested in our work, the strain magnitude or range of magnitudes where the transition occurs is unknown because the limitation of the equipment did not allow measurement of the shear modulus between 10^{-4} and 10^{-6} strain amplitude.

Rheometer versus tension/compression: Liquid-like to solid-like transition due to confinement versus solid-like to liquid-like transition due to amplitude

At the beginning of this section, we give comparisons of different results from the rheometer at large gaps and those of the tension/compression tests and explained this behavior as a solid-like to liquid-like transition related to amplitude. Figures 7 and 8, however, show a much

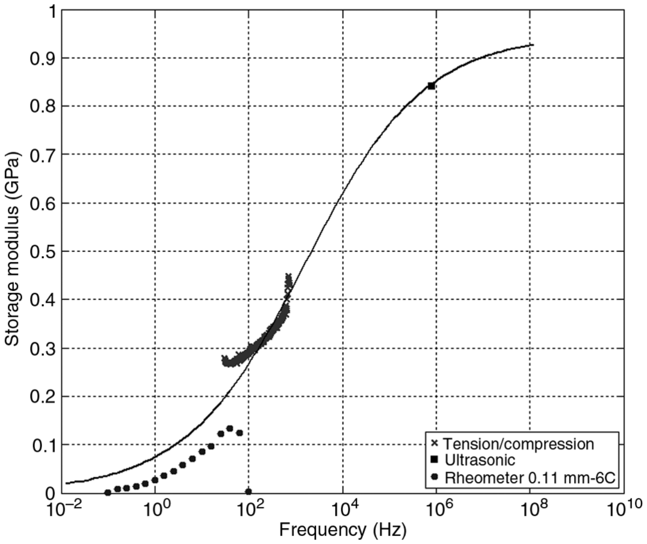

Figure 7. Storage modulus (G') versus frequency for sample GP029-Asphalt Ridge from three different techniques and the Cole-Cole dispersion model (continuous line, alpha = 0.68). In these experiments, the three techniques show a close match when compared here with the rheometer results measured at a small gap (0.11 mm).

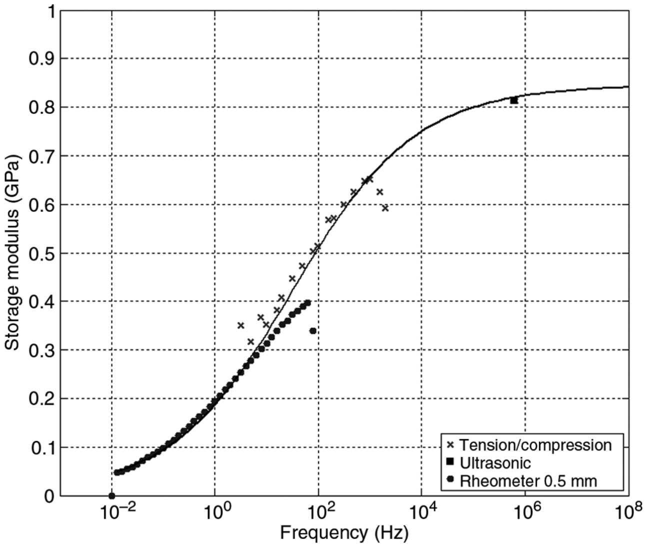

Figure 8. Shear modulus (G') versus frequency (Hz) for the GP007-Uvalde sample at 30°C for the three techniques and using a small gap (0.5 mm) in the rheometer. Data for tension/compression and ultrasonic taken from (Batzle et al., 2006b). A good match of the data is obtained consistent with the Cole-Cole model (continuous line, alpha = 0.66). Compare with Figure 6.

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more consistent match when comparing the tension/compression results with rheometer results obtained using a smaller gap.

Because of the configuration of the rheometer, two plates (upper and lower) are in contact with a small amount of sample creating two liquid-solid interfaces. The two solid-liquid interfaces in the rheometer produce an increase in the modulus of the heavy-oil sample as we reduce the gap between the parallel plates, changing the sample from a liquid-like behavior to a solid-like behavior. In other words, an increase in the shear modulus results from confinement between the plates. In contrast, when we compare the tension/compression with the rheometer, a change from a solid-like behavior to a liquid-like behavior occurs when the heavy oils are subjected to larger strains. Basically, this results in a decrease in the shear modulus in the presence of high amplitude. These two effects are in opposition and compensate each other when we compare the tension/compression results with the rheometer measurements at smaller gaps.

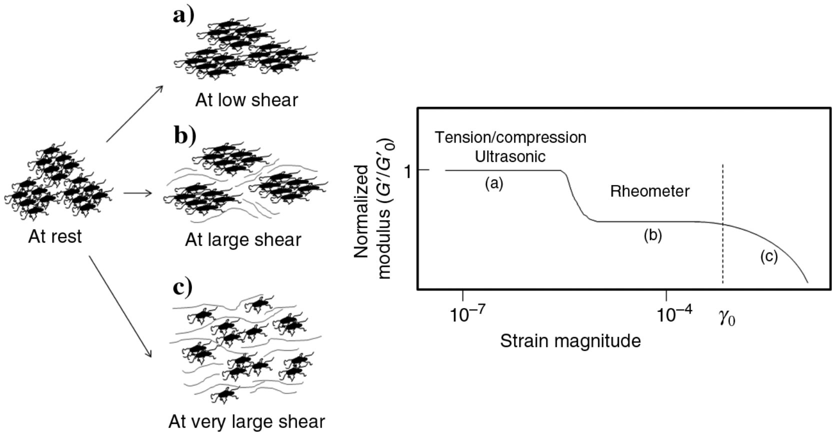

Figure 9. Schematic representation of heavy-oil behavior under different shear amplitudes. The left side shows a representation of the molecular behavior, and the right side shows the corresponding expected shear behavior with strain amplitude. (a) At low shear: aggregates form weak bonds that deform behaving solid-like. (b) At large shear: bonds between aggregates are broken, and the heavy oil acts liquid-like. (c) Intermolecular bonds are broken, aggregates break, and a nonlinear behavior develops.

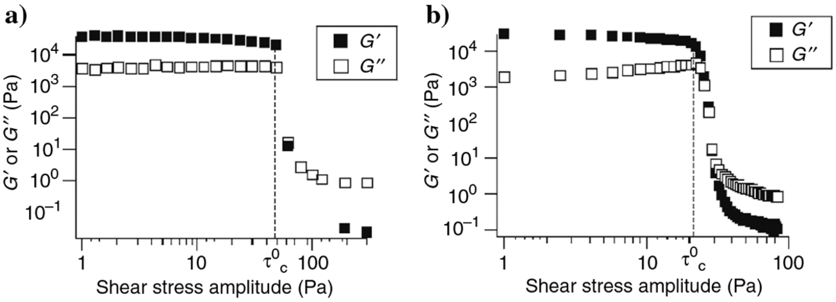

Figure 10. Shear moduli (G' and G'') versus stress amplitude for two different materials at 1 Hz: (a) cement and (b) silica suspension (Chougnet et al., 2007). Two LVRs are observed: the first one at low stresses showing a solid-like behavior ($G' \gg G''$) and a second one at large stresses showing a liquid-like behavior ($G'' \gg G'$).

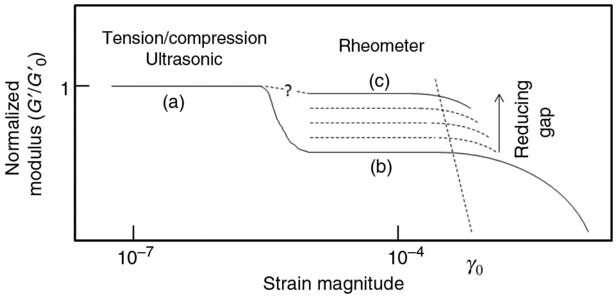

Figure 11. Extension of Figure 9 (right) adding the appearance of an "equivalent" solid-like LVR (c) in the rheometer after reducing the gap thickness.

Rheometer measurements when gaps are large cause a transition from solid-like to liquid-like because amplitudes are large. If the gap in the rheometer is reduced significantly where the sample is "confined," a transition from liquid-like back to solid-like is imposed on the sample, explaining why a better match between the two techniques is obtained at small gaps. Figure 11 further illustrates these changes. At low strains (Figure 11a), in the tension/compression technique, the sample has a high modulus. When subjected to large strains in the rheometer, however, the sample reaches a secondary LVR with lower modulus (Figure 11b). As we reduce the gap in the rheometer, the modulus increases with confinement between two solid surfaces. As the gap is reduced further, the modulus could reach a value that is comparable with that measured at lower strains (Figure 11c) in the tension/compression technique. The reduced gap moved the sample to a similar shear regime similar to that measured at low strains in the tension/compression equipment (Figure 11a).

The LVR at reduced gaps is similar to the solid-like state measured by the tension/compression technique, but it is not equivalent. In the rheometer, the confined properties are a function of the nature of the solid surface material and the nature of the interaction between the specific heavy oil and that surface (wettability). Therefore, it is not a property of the sample itself.

CONCLUSIONS

An important finding of this work is the effect of amplitude on the shear modulus of heavy oils. The increased shear-modulus values measured by the tension/compression technique at low amplitudes in comparison with the much lower shear modulus values measured by the rheometer at higher amplitudes are an indication of two potential LVRs present in the heavy oil at different amplitudes.

When rheometer measurements are performed at small gaps, a solid-like behavior of the heavy oil can be achieved from confinement between the two solid surfaces. The increase in shear modulus almost reaches the values measured at much lower amplitudes in the tension/compression technique. Hence, the lowering of the shear modulus under

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higher amplitudes in the rheometer is reversed under confinement between the two solid surfaces of the rheometer plates. However, because the increase in confinement depends on the nature of the solid surfaces of the rheometer and not only on the properties of the sample, the magnitude measured under confined conditions (rheometer) can be similar to that at low amplitude (tension/compression); these, however, are not equivalent and should not be considered as an alternative for measuring the properties of the heavy oil.

The rheometer has been proposed as an alternative technique to measure soft samples under shear because the handling of soft samples in the tension/compression technique has many complications. However, there have always been doubts about the validity of the rheometer results when amplitudes are higher, and our present work confirms those doubts. The rheometer is an appropriate technique for measuring the properties of heavy oils for engineering applications, when the flow is constant at high shear rates. Also, it could be argued that at high temperatures, such as those present in thermal EOR methods, the heavy-oil dynamic shear modulus measured with the rheometer will be close to that measured by the seismic because the heavy oil is in a liquid-like state. At colder reservoir conditions, such as in colder regions, e.g., Canada or Alaska, however, the seismic waves measure the heavy oil in a solid-like state because of the low temperatures of the reservoir and low amplitudes of the seismic waves. Under these conditions, trying to predict the behavior of the seismic waves from heavy-oil properties measured in the rheometer will likely give erroneous results. This implies that the use of the rheometer for geophysical characterization of heavy oils is limited and must be done with considerable care.

We recommend extending the work of handling soft samples in the tension/compression technique, which allows a better understanding of the heavy oil properties at low amplitudes. There is also a possibility that in the future rheometers will be able to measure lower amplitudes and a better comparison could be made. Even in this case, however, the rheometer measurements are still influenced by the confinement between two solid surfaces and thus alter the heavy oil elastic properties.

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