Shear modulus of heavy oils, rheometer vs. tension/compression techniques: Solid to liquid transition due to strain amplitude effects

Patricia E. Rodrigues and Michael L. Batzle, Colorado School of Mines

Summary

Unlike other fluids, heavy oils have a shear modulus and can propagate shear waves. Several techniques can be used to extract this important property. In this work we explain how the large amplitudes used in the rheometer affect the shear properties of heavy oils and therefore limits the use of this technique for geophysical acoustic applications. This conclusion is reached by comparing the shear properties of heavy oils measured with the rheometer to geophysical techniques (ultrasonic and tension/ compression). The effect of amplitude is due to the aggregate characteristics of heavy oils that at small strains form networks with solid-like behavior but at large strains, these networks can break having liquid like behavior. This solid to liquid transition due to amplitude is commonly seen in other materials like cement paste and silica suspensions.

Introduction

Even though heavy oils constitute the largest component of oils reserves in the world, they still remain one of the least understood fluids in the reservoir by geophysicists. The study of wave propagation in heavy oil reservoir for design acquisition, monitoring of enhanced Oil recovery (EOR) operations or interpretation, usually goes through rock physics modeling with the purpose of predicting the elastic properties of the rock. Rock physics models predict the reservoir elastic properties from the properties of the pure components, assuming that these are well known. This assumption is not true for heavy oils. One aspect that makes heavy oils particularly complicated is its viscoelasticity; which means that depending on the temperature and frequency heavy oils are capable of propagating shear waves (Batzle, et al. 2004; Hasan 2010). Viscoelasticity is not a characteristic of the other fluids in the reservoir. This viscoelasticity also implies that the heavy oil shear behavior shows an important dependency on frequency. Frequency dependency introduces complications: measurement of elastic properties at ultrasonic frequencies is well known and fairly simple when compared to tension/compression techniques at low frequencies. The complication is even greater when we try to measure soft samples like many of the commercial heavy oils. In 2013, Rodrigues and Batzle, showed some preliminary results about the use of the rheometer as an alternative technique to measure the shear modulus of heavy oils at low frequencies. The rheometer, a technique well known and extensively used by chemical engineers, allows measurement of liquid-like samples at frequencies between 0.01 to 100 Hz which are in the range of seismic frequencies. The rheometer is a convenient way to measure heavy oils and, if valid, could help to accelerate the understanding of heavy oils shear behavior. Several authors such as Hinkle et al. (2008), Rojas et al. (2008), Hasan (2010), and Behura et al. (2007) have measured the shear modulus of heavy oils with the rheometer but no one has reported insight on how comparable these measurements are to what has been measured at ultrasonic frequencies and with tension/compression techniques at seismic applications frequencies. Rodrigues and Batzle (2013) showed preliminary results indicating that the rheometer had good potential to be used in the geophysical acoustic characterization of heavy oils. However, further experiments and tests were needed to better understand the results obtained. The main concern about the rheometer is the large strain amplitudes used in comparison to amplitudes used in geophysical acoustic applications (between two or three orders of magnitude smaller). Here, we provide theories of the structural changes occurring in the heavy oil that affects the shear modulus when measured at different amplitudes. The insights we provide in this work are new to geophysics and have important implications on how we measure and interpret the shear behavior of heavy oils with geophysical data. We begin this paper providing a summary of heavy oil characteristics that are relevant to our work. We will then describe modifications done to the tension/compression methodology in order to allow for testing of soft samples. Results are shown for two samples, followed by discussion providing a model of the shear behavior of heavy oils with amplitude. Finishing with implications and conclusions of our work.

Heavy oil characteristics

Hydrocarbon fluids are considered "heavy oils" when their API gravity is below 20 (or 22.3 for the World Energy Council). There are descriptive terms to refer to specific ranges of API gravity like extra-heavy oils, tar, pyrobitumen and asphalts among others, but in our work we will use the term "heavy oils" to refer to all hydrocarbons with API < 20°. Heavy oils have high molecular weight with compositions so complex that individual components are difficult to identify using standard analytic techniques. As a result, these oils are often described in terms of solubility through "SARA" fractions. SARA (Saturates, Aromatics, Resins and Asphaltenes) fractionation is the technique used to separate the heavy oil in fractions soluble to different solvents. SARA fractions separate the heavy oil in terms of polarity, which is the tendency of molecules to interact with surrounding molecules due to an imbalance of the electric charge. Polarity increases from saturates to asphaltenes, asphaltenes being the most polar fraction. Resins and asphaltenes with the highest polarity tend to interact and form aggregates or macromolecules not seen in simple liquids. The attraction between molecules is so strong in these aggregates that they can bond together permanently. Aggregates are therefore effective in increasing viscosity and shear modulus, and tend to be rigid structures, not flexible like polymers with large chains. Besides the strong molecular bonds formed between resins and asphaltenes, secondary interactions between aggregates also exist. This weaker secondary interaction is referred as "aggregate association". These associations can transmit forces and

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alter the mechanical forces of the material (Witten and Pincus 2004). At rest, aggregates form a network that immobilizes the fluid (or solvent), and the system behaves as an elastic solid under low stress (Hiemenz and Rajagopalan 1997). The secondary attraction between aggregates in heavy oils has not been reported before and we introduce it here as a plausible mechanism that explains its shear behavior at different strain amplitudes, as it will be shown below.

Methodology

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

Table 1. SARA analysis and API gravity of samples

	Oil Composition (wt%)				API
Sample	S	A	R	Asp	Gravity
GP007	2.2	26.4	23.4	47.9	-5.00
GP029	17.1	31.5	44.8	6.5	14.03

Rheometer measurements: The equipment used for this work is the AR-G2 from TA Instruments using parallel plates with 8 mm diameter. The rheometer measures the magnitude of the strain and the phase lag between the stress and the strain and calculates the storage and loss modulus. Specific steps to perform rheometer measurements are published by the manufacturer, but what is always important is to perform the initial calibration steps as a detailed quality control of the results.

Tension/compression measurements: Several investigators have developed models and techniques to measure the elastic properties of hard materials at wide frequency ranges, including lower frequencies in the range of seismic data (Spencer 1979; Batzle, et al. 2006a). The tension/compression technique consists of applying axial deformation to the sample and measuring the resulting strain at frequencies between 3 to 3000 Hz. Amplitudes are kept in the 10^{-6}-10^{-7} range, and are a tradeoff between measurements at low amplitudes characteristic of seismic data and interfering noise levels. A detailed description of the experimental procedure can be found in Das (2010) and Batzle, et al. (2006b). A new acquisition system, and temperature control system were needed in order to work with soft samples.

Soft samples preparation: Batzle, et al. (2006b) measured a heavy oil sample at low frequency attaching strain gages to the surface of the heavy oil after it was molded into a cylinder. The major modification from this that we needed for softer samples was the 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 an aluminum standard. Strain gages with pre-attached wires can either be attached to the jacket, or positioned inside the jacket with wires through the jacket and sealed. The heavy oil is heated and poured into the jacket. Heating should be kept below 100C to avoid loss of material; 100C is the temperature below which the pyrolysis tests show minimal production of hydrocarbons. After cooling, the upper part of the sample is capped with another aluminum standard. After the sample is cooled to room temperature, epoxy is added to seal the upper binding between the jacket and the aluminum standard. A thermocouple is inserted through the jacket and sealed to be able to measure the temperature inside the sample. Experiments were kept to a very short time, since the heat induced by the components of the equipment and the strain gages increased the temperature during the experiment. After each experiment, temperature was allowed to equilibrate before acquiring additional data.

Results: Rheometer vs. tension/compression and ultrasonic measurements

Figure 1 shows the shear modulus of the heavy oil from three techniques for the GP029. As it can be seen, there is a significant difference between rheometer and tension/ compression results when compared using a Cole-Cole dispersion model. Rheometer results shown were taken using a large gap to reduce the effects from the surfaces of the geometry plates. A similar result is obtained for sample GP007 when comparing the tension/compression results to the rheometer measurements obtained at large gaps (Figure 2). The difference between the tension/ compression and the rheometer data can be explained by changes in the sample due to the larger strain amplitude used in the rheometer. This phenomenon is a solid to liquid transition due to amplitude, and explained in the next section.

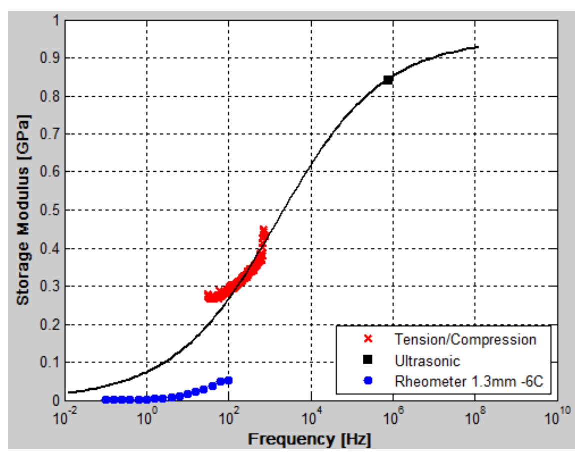

Figure 1. Storage modulus (G') vs. frequency for sample GP029 from different techniques and Cole-Cole model. Rheometer data was measured at 1.3mm gap thickness ("bulk").

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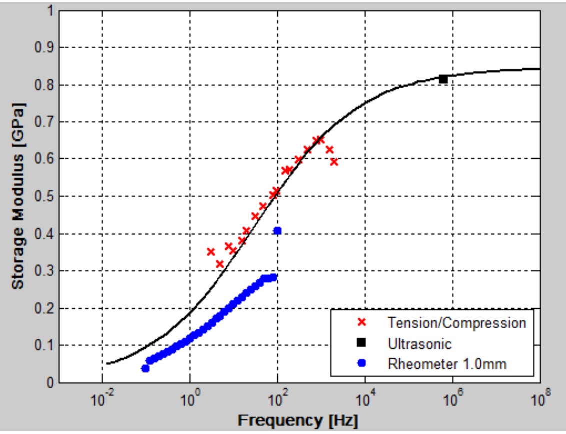

Figure 2. Storage modulus (G') vs. frequency for sample GP007 at 1 mm gap thickness ("bulk") for the rheometer results.

Discussion of results: Solid to liquid transition due to amplitude - nonlinearity

Heavy oils act as aggregates, and these are internally chemically bonded due to the presence of polar molecules such as asphaltenes and resins. Each aggregate is composed of many molecules attached to others by strong intermolecular forces. If the sample is kept at a low energy level, physical inter-particle forces between aggregates become important and cause aggregates to associate and form networks that give a solid-like behavior to the heavy oil. The inter-particle 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 persist. When shearing the sample at low strains (low amplitudes), the association between the aggregates do not break, but rather stretch and deform. This behavior is represented by (a) in Figure 3, the material acts like a solid. From this point, if the amplitude is *slightly* reduced or increased the shear modulus is constant and the material is in a linear viscoelastic regime (LVR). When the amplitude is increased substantially (b), 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 (c), aggregates begin to break and a non-linear behavior appears. This change in shear state with amplitude has not been previously measured or proposed for heavy oils to our knowledge.

Even though the presence of multiple LVR has not been reported for heavy oils, it is well known for other materials like fresh cement paste. Ramachandran & Beaudoin (2000) shows the presence of two LVR for a cement paste as an example of typical behavior of cement suspensions with strain. Chougnet et al. (2007) emphasize the fact that for the first LVR the G' (storage) is larger than the G" (loss), which corresponds to a solid-like behavior, while in the second LVR at larger amplitudes, G" is larger than G' corresponding to a more liquid-like behavior.

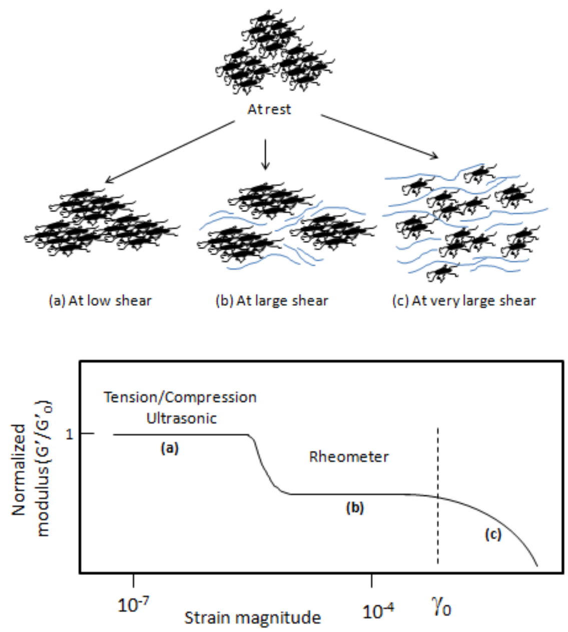

Figure 3. Schematic representation of heavy oil behavior under shear at different amplitudes. Upper image shows a representation of the molecular behavior, and the lower image shows the corresponding expected shear modulus with strain amplitude.

Opposing effects: amplitude vs. confinement effects

We saw previously the difference of the results from the "bulk" rheometer measurement in contrast to the "bulk" tension/compression measurements. However, when comparing the same results of the tension/compression to rheometer measurements performed at small gaps ("confined") the two data sets get very close and in some cases reach an almost perfect match (Figure 4 and Figure 5). The presence of the two solid-liquid interfaces in the rheometer has a measurable effect on the shear modulus of the heavy oil sample. This effect produces an increase of the modulus as we reduce the gap between the parallel plates, changing the behavior of the sample from a liquid-like behavior to a solid-like behavior. This effect is called liquid to solid transition due to amplitude (or solidification). On the other hand, there is a change from a solid-like behavior to a liquid-like behavior when the heavy oils are subjected to larger strains in the rheometer. These two effects are somewhat contradictory and seem to compensate for each other when we compare the tension/compression results with the rheometer measurements at smaller gaps ("confined").

In other words, rheometer measurements done in the "bulk" sample (large gaps), cause a transition from solid to liquid due to the increased amplitudes, but if the gap in the rheometer is reduced significantly where sample is "confined", a transition from liquid back to solid is forced in the sample, explaining the better match between the two techniques obtained at small gaps. Figure 6 illustrates these changes. At low strains (a) in the tension/compression technique, the sample has a high modulus, when subjected

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to large strains in the rheometer, the sample reaches a secondary LVR with lower modulus (b). As we reduce the gap in the rheometer, the modulus increases due to the confinement effect. As the gap is reduced further, the modulus could (or not) reach a value that is comparable to that measured at lower strains (c). The magnitude of moduli measured in LVR at reduced gaps is similar to the solid-like state measured by the tension/compression technique. These measurements are not equivalent since 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 the surface (wettability).

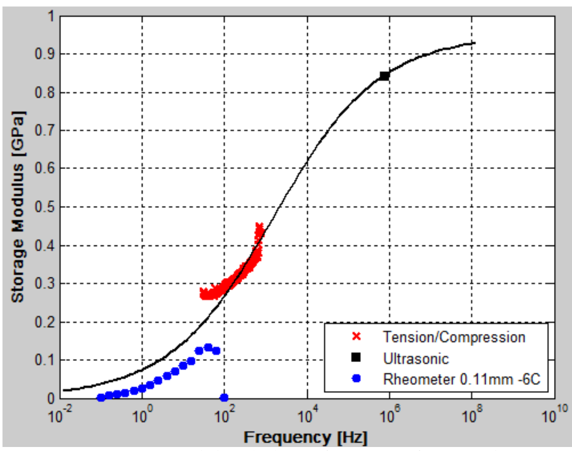

Figure 4. Storage modulus (G') vs. frequency for sample GP029 from three different techniques and Cole-cole model. Compared to the rheometer results at a small "confined" gap (0.11 mm).

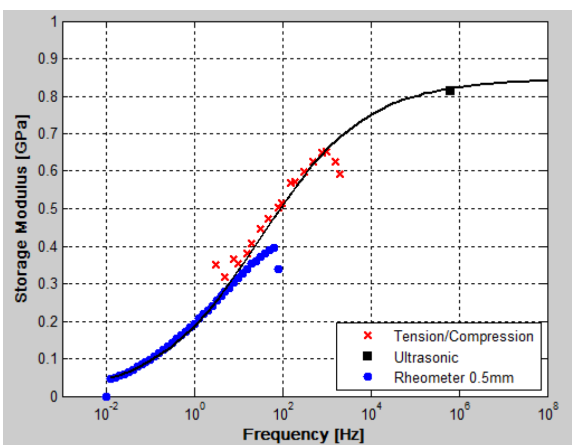

Figure 5. Shear modulus (G') vs. frequency (Hz) for the GP007 sample, using three techniques and 0.5 mm "confined" gap thickness. Tension/compression and ultrasonic data from (Batzle, et al. 2006b).

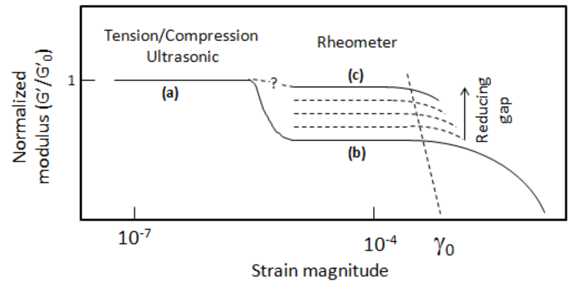

Figure 6. Modification to Figure 3 adding the appearance of an "equivalent" solid-like LVR (c) with the rheometer after reducing the gap thickness.

Implications on geophysics experimental work

Our present work confirms the concerns that the higher amplitudes of the rheometer can affect the measured properties of heavy oils. The rheometer is an appropriate technique to measure the properties of heavy oils for engineering applications, in which there is a constant flow at high shear rates. However, seismic waves will measure the heavy oil like a solid due to the initial 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 with the rheometer will likely give erroneous results.

Conclusions

Heavy oils are aggregates that at rest or at low shear, behave as a solid due to weak inter-particle forces between the aggregate. As strain amplitude is increased the weak bonds are broken and the heavy oil behaves liquid-like. This indicates that two linear viscoelastic regimes can be present in the heavy oil at different amplitudes. However, when rheometer measurements are performed at reduced gaps, a solid-like behavior of the heavy oil can be achieved due to confinement between the two solid surfaces and the increased values almost match the tension/compression results.

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EDITED REFERENCES

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