Oscillatory Rheology and Surface Water Wave Effects on Crude Oil and Corn Oil Gels with (R)-12-Hydroxystearic Acid as Gelator

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Supporting Information

ABSTRACT: The mechanical properties of films of gels composed of a crude oil or corn oil and (R)-12-hydroxystearic acid are described using oscillatory rheology and water-surface waves. The integrity of these gel films are contrasted with those of neat oil films subjected to the same types of mechanical testing. The oil-based gels are thixotropic, and we quantify their post-recovery yield. A simple model is proposed to describe the loss of integrity when the gels are subjected to high amplitude surface waves. Our technique provides a novel method for quantifying the role of dynamic surface perturbations on the mechanics of viscoelastic films, providing an illustrative model system for testing coagulants and dispersants designed to mitigate oil spills.

INTRODUCTION

Crude oil and other chemical spills continue to produce long-term and perhaps permanent damage to the environment.1 Spills may occur during extraction of oil from the ground, at refineries, at storage facilities, and during transportation of refined products.2 Remediation of crude oil spills is a very complex process and may require one or more methods, such as dispersion, solidification, digestion by microorganisms or skimming.2 Although it is not possible to mitigate completely the deleterious effects of a spill, chemical methods, including dispersion through the use of polymeric surfactants3 or superabsorbent polymers,4 offer attractive options. However, the process of dispersal does not permanently remove the oil from the environment; for this reason, there is increasing interest in the design and use of materials that efficiently trap crude oil as a mechanism to minimize environmental impact.

Gels composed of a liquid and a low molecular-mass organic gelator (LMOG) are a class of self-assembled systems that form when the LMOGs aggregate via van der Waals, intermolecular H-bonding, or π–π stacking (in the case of gelator having aromatic moieties) into rodlike objects (e.g., fibers, strands, nanotubes, or tapes).5 Some LMOGs are known to be able to solidify selectively an oil phase from a mixture of oil and water.6 Examples of such gelators include amino acid amphiphiles,6a closed-chain saccharides,6b and dialkanoate derivatives of saccharides.6c However, many factors may affect the ability of an LMOG to coagulate and gel crude oil selectively.

(R)-12-hydroxystearic acid (HSA) is known to be a very efficient gelator of a wide variety of liquids7 and has been used industrially as a lubricant and to modify the properties of bulk polymers.8 Here, we report the properties of gels employing HSA as the gelator and a crude oil or a vegetable oil as the liquid component. Corn oil was selected arbitrarily to show that the methodology employed is applicable to other liquids that might be spilled. These studies are complemented by measurements of the mechanical effects on them measured by rheology and by water-surface waves on films of the gels and the liquids in the absence of the gelator. HSA is an efficient, low molecular-mass gelator that forms helical fibrillar aggregates and gelates aromatic liquids, alkanes, carbon tetrachloride, chloroform, acetone, ethanol and silicone oil.9 In a previous report, the crystal lattice of HSA in its gelated state has been tentatively assigned to be monoclinic, in which four HSA molecules are packed in a “head-to-head” arrangement.10 The hydroxyl groups on the chiral centers of HSA are connected by unidirectional hydrogen bonding sequences in their 1-dimensional (1D) fibers.10 The gel melting temperatures (Tmel) and stabilities (as indicated by the period between when the gels were prepared in sealed containers and when they underwent visually detected phase separation after being left at ~24 °C) of 2 wt % HSA in n-alkane gels are known to increase slightly upon increasing the chain length of the liquid from hexane to decane. The HSA gels with both crude oil and corn oil are found to exhibit reversible mecano-responses (i.e., they are thixotropic),9 and they are the materials used throughout this work.

EXPERIMENTAL SECTION

A BK Precision Function Generator, Crown PSA-2 Self-Analyzing Amplifier, Stanford Research System model SR830 DSP lock-in amplifier and shear accelerometer (PCB Piezotronics, model J 35B68, voltage sensitivity = 102.5 mV/g, frequency range = 1–8000 Hz, output bias level = 14.9 V) were used to detect the oscillating frequency of waves generated by a Vibration Test System VTS 100-8 shaker through the use of a custom built Teflon trough (7.5 cm × 2.5 cm × 4.5 cm; 80 cc capacity). The sinusoidal parametric driving amplitude is directly related to the voltage signal of an accelerometer that is mounted parallel to the oscillation direction. Using the output voltage and the calibration characteristics of the accelerometer, we calculate
the linear amplitude of the trough over a frequency range of 15—30 Hz.

Polarized optical micrographs (POMs) were recorded on a Leitz 585 SM-LUX-POL microscope equipped with crossed polarizers, a Leitz 350 heating stage, a Photometrics CCD camera interfaced to a computer, and an Omega HH503 microprocessor thermometer connected to a J-K-T thermocouple. Samples for POM analyses were flame-sealed in 0.4 or 0.5 mm path-length, flattened Pyrex capillary tubes (VitroCom, Inc.). Rheological measurements were made using an Anton Paar MCR 301 stress-controlled rheometer with a Peltier based temperature controller with parallel plates (25 mm diameter) with a nominal gap of d = 0.5 mm. Data were collected and analyzed using Rheoplus/32 Service V3.10 software.

Materials. HSA (Arizona Chemicals) was purified as reported (mp, 80.2–80.3 °C (lit.,11 80.5–81.0 °C)).9 Corn oil (Mazola) and crude petroleum oil (Surrogate, SO-20111116-MPDF-003, A0064A-OL-OIL, supplied by British Petroleum) were used as received. Water was purified by passing through LT Technology CF 101 and CF102 cartridge filters, a SANITRON UV water purifier, and by reverse osmosis that was monitored by Hydro and Ecodyne controllers.

Preparation of HSA—Corn Oil Gels. Weighed amounts of corn oil and 1 wt % of HSA were placed into a screw capped sample vial and the mixture was heated at ca. 80 °C until a solution/sol was obtained. The vial was then placed directly into an ice—water bath for 10 min and allowed to return to room temperature.

Preparation of HSA—Crude Oil Gels. A mixture of 2, 5, or 10 wt % HSA was added to the crude oil and stirred at 45–50 °C for 10 min. The resulting sol was left undisturbed at 25 °C for 1 h.

Preparation of HSA in Crude Oil “Aged” Gels. Aliquots (1.0 g) of 2, 5, or 10 wt % HSA in crude oil gels, prepared as above, were placed in scintillation vials (7 mL; o.d., 17 mm; i.d., 13 mm; and height 54 mm; height of the gel = 9 mm) and weighed before and after being left open to the air for 1 week.

Figure 1. Log—log frequency sweeps (0.1% strain, A and B) and strain sweeps (1.0 rad/s, C and D) for a 10 wt % HSA in corn oil gel (A and C) and 10 wt % HSA in crude oil gel (B and D) at 25 °C. G′, ■; G″, red ●.

Deposition of 10 wt % HSA—Crude Oil Gels on Water. HSA (1 g) and crude oil (10 g) were mixed and heated to 45–50 °C for 10 min to form a solution/sol. About 5 g of the sol were placed on ~80 mL of an ice—water mixture within the Teflon chamber and the mixture was left there undisturbed at 24 °C for 24 h (during which time the ice melted) to obtain a ~0.2 cm layer of the gel on water.

Deposition of 1 and 10 wt % HSA—Corn Oil Gels on Water. The same procedure as described above was employed on HSA (100 mg or 1 g) and corn oil (10 g) that were heated initially to 80 °C to form a clear solution/sol. The layer thicknesses were ~0.2 cm.

RESULTS AND DISCUSSION

Rheological and POM Studies of HSA in Crude Oil Gels. In the present study, gels of 1 and 10 wt % HSA in corn oil and 2, 5, and 10 wt % HSA in crude oil have been investigated in a rheometer and in a wave trough over water, so that their comportment under different forms of disturbance can be compared with each other and with the neat liquids (i.e., in the absence of HSA).

Frequency sweep studies (ω = 0.1–100 rad/s at 0.05% strain) of the gels at 25 °C indicate that the storage modulus (G′) and loss modulus (G″) values are independent of the applied frequency within the linear viscoelastic regions (LVRs) (Figure 1 and Figures S1–S3); the samples are true gels. The mechanical strength of the gels decreased upon decreasing the HSA concentration in both oils. For example, at 1 rad/s; G′ ≈ 55 and 250 kPa for 1 and 10 wt % HSA in corn oil gels (Figure 1 and Figure S1), respectively, and G″ ≈ 0.5, 15, and 27 kPa for 2, 5, and 10 wt % HSA in crude oil gels, respectively. Figures S4–S6 show strain sweeps for the corresponding 1 and 10 wt % HSA in corn oil gels and the 2, 5, and 10 wt % HSA in crude oil gels. Rheological properties of a gel material are independent of strain up to yield strain, and beyond yield strain the rheological behavior is nonlinear. At a frequency of 1 rad/s, the yield strain for the 1 wt % HSA in corn oil gel was at 2.6% strain, a value more
than two times larger than that of the gel with 10 wt % HSA (Figure 1C and Figure S4 and S7). For HSA in crude oil gels, the largest yield strain was observed for 2 wt % HSA; that value is nearly two times larger compared to the measured yield strains for gels comprising 5 and 10 wt % HSA in crude oil (Figure 1D and Figure S6). The rheologically determined quantity tan(δ) = G″/G′ determines the relative elasticity of viscoelastic materials; tan(δ) values less (greater) than unity indicate a more solid- (liquid-) like behavior, respectively. The lower tan(δ) observed for 1 wt % HSA in corn oil compared to that for 10 wt % HSA in corn oil is indicative of a higher relative elastic modulus for the lower HSA concentration gels (Figure S7). Interestingly, a similar correlation was observed for HSA in crude oil gels.

The POM image of a freshly prepared 10 wt % HSA in crude oil gel (Figure 2A) shows fibillar assemblies. Because the appearance of the gel did not change markedly after being “aged”, Ostwald ripening is not important in these systems (Figure 2B). Distinct fibillar textures were not observed for 1 and 10 wt % HSA in corn oil gels (Figures S8 and S9).

The percentage weight loss from about 1 g each of 2, 5, and 10 wt % HSA in crude oil gels was measured after they were kept at 25 °C for 1 week in the air (Table S1). Increasing the concentration of HSA in a crude oil gel decreases the evaporation of volatiles from the crude oil. We hypothesize that the more extensive self-assembled fibillar networks (SAFINs) at higher HSA concentrations decreases the rate at which the crude oil diffuses to the air interface as a result of increased interfacial interactions between the gelator fibers and the liquid surfaces at the micrometer (or submicrometer) distance scales.

The mechanical properties of the aged HSA in crude oil gels were studied using rheology at 25 °C. Frequency sweeps at 0.1% strain (Figures S10–S12) indicate that, like the fresh samples, the aged ones remain gels. The G′ values for the 10, 5, and 2 wt % gels at 1 rad/s were ca. 240, 30, and 0.2 kPa, respectively; aging strengthened the 10 and 5 wt % gels and weakened the 2 wt % gel for reasons that are not clear at present. The similarity between the corresponding strain sweeps of the fresh and aged HSA in crude oil gels (Figures S13–S15) indicates that evaporation of volatiles in the crude oil does not significantly affect the linear viscoelastic regime. This conclusion is consistent with the observation of little change in the appearance of the fresh gel after aging it (Figure 2).

Surface Wave Dynamics of Multiphasic Fluid/Gel Layers: Corn Oil, HSA–Corn Oil Gels, Crude Oil, and HSA–Crude Oil Gels. Fluids and even granular materials that are sinusoidally accelerated exhibit linear and nonlinear surface waves. We utilize these waves to explore the stability of the thin fluid and gel films found in Figures 3 and 4. Corn and crude oil (both in a neat state and with HSA added) are placed on the surface of a water bath resulting in continuous thin films (h ∼ 0.2 cm). Through vertical sinusoidal acceleration, parametric surface wave states are generated. The amplitude of the sinusoidal acceleration is slowly increased while maintaining a constant frequency. Breaking amplitudes are calculated using the peak heights of the fluid at which the continuity of the corn oil or crude oil layer was lost (Tables 1 and 2).

Table 1 summarizes the breaking amplitudes and drop sizes at different applied frequencies for the crude oil layer deposited on water. At the breaking amplitudes, droplets similar to those for crude oil layer were observed (Figure 4B). For both oils, the sizes of the droplets appeared to be independent of applied frequency over the range investigated (Table 1). At an applied frequency of ∼20 Hz, the breaking amplitude of corn oil as well as crude oil deposited on water was 0.04 mm, but the observed droplets of crude oil were larger (0.2–0.7 cm in diameter; Table 2) compared to those from the corn oil layer (0.1–0.3 cm in diameter; Table 2). At an applied frequency of ∼25 Hz, similar breaking amplitudes and droplet sizes were observed from the corn oil and crude oil layers. At this point, there are insufficient data to correlate the specific dependence of
the perturbations on the droplet sizes because the latter are expected to change with factors such as film thickness, interfacial interactions, and liquid viscosity.

In the experiments conducted with a corn oil layer on water, droplets of ~0.1–0.5 cm diameter were formed at the breaking amplitudes (Figure 3B). The sizes of the droplets have been measured directly from photographs similar to that in Figure 3B. We assume that all are on the surface. We found no evidence that new droplets were formed over the periods of the experiments (~20 min). In essence, there was no evidence for agglomeration of smaller droplets into larger ones. Increasing the amplitude created inhomogeneities in the oil layer thickness which facilitate breakage of the layer at a critical shaking amplitude (especially, where the layers are thinnest; Figure 5).

Several investigations of the conditions needed to break a layer, form stable layers, or prepare continuous jets (when one liquid was added to a second immiscible liquid, leading to the generation of droplets) have been reported.\textsuperscript{13,14} For example, droplets were formed in a microfluidic device upon injection of an immiscible 15 wt % aqueous solution of tripotassium phosphate into capillaries containing a continuous aqueous phase of 17 wt % of aqueous polyethylene glycol.\textsuperscript{13} On the basis of the formation of droplets at the breaking amplitudes of layers, we suggest that the dynamics of formation and stability of an oil layer on the surface of water depend mainly on the relative magnitudes of the viscous forces and velocity at the interface between the liquids.\textsuperscript{13} The externally imposed velocity field and shear rate at large distances from a drop of corn oil or crude oil within the vicinity of an existing drop increase interfacial tension that generates drops of different dimensions.\textsuperscript{13}

To understand the effect of gelation on the response of the oils to surface wave action, aliquots of the gels were deposited on water and the amplitude of the shaking, as quantified by the accelerometer, was slowly increased as before at a constant frequency until the gel layers yielded. For a 1 wt % HSA in corn oil gel (Figure 6A), the amplitude of the waves at which the layer was broken was 0.09 mm at 20 Hz (Figure 6B). The breaking amplitude was increased to 0.2 mm for the 10 wt % HSA corn oil gel (Figures S16 and S17). As described before and shown in Figure 3B, the breaking amplitude of a ~0.2 cm corn oil layer on water was 0.04 mm. Similarly, the breaking amplitude of a ~0.2 cm thick layer of a 10 wt % HSA in crude oil gel on water was found to be 0.1 mm at 20 Hz (Figure 7). Here again, no droplets were observed at the breaking amplitude, and the layer was irreversibly broken into large fragments that remained on or near the water surface. At 20 Hz applied frequency, the breaking

Table 1. Summary of Breaking Amplitudes and Droplet Sizes at Different Applied Frequencies for Crude Oil Deposited on Water

<table>
<thead>
<tr>
<th>applied frequency, Hz</th>
<th>breaking amplitude, mm</th>
<th>droplet diameters, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.04</td>
<td>0.2–0.7</td>
</tr>
<tr>
<td>25</td>
<td>0.03</td>
<td>0.1–0.3</td>
</tr>
<tr>
<td>30</td>
<td>0.03</td>
<td>0.2–0.3</td>
</tr>
</tbody>
</table>

Table 2. Summary of Breaking Amplitudes and Droplet Sizes at Different Applied Frequencies for Corn Oil on Water

<table>
<thead>
<tr>
<th>applied frequency, Hz</th>
<th>breaking amplitude, mm</th>
<th>droplet diameters, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.4</td>
<td>0.06</td>
<td>0.1–0.5</td>
</tr>
<tr>
<td>15.2</td>
<td>0.05</td>
<td>0.1–0.5</td>
</tr>
<tr>
<td>20.3</td>
<td>0.04</td>
<td>0.1–0.3</td>
</tr>
<tr>
<td>25.3</td>
<td>0.02</td>
<td>0.1–0.5</td>
</tr>
</tbody>
</table>

Figure 5. Schematic cartoon of the shaking trough in cross section with a thin corn or crude oil layer placed on the surface of water and vertically oscillated at a fixed frequency and amplitude. The thin layers remain continuous until a critical amplitude, $A_c$, (as shown in the dashed box), when the oil layer becomes unstable and breaks into droplets on the surface of the water.

Figure 6. An ~0.2 cm layer of a 1 wt % HSA–corn oil gel deposited on water (A) before applying wave action and (B) at the breaking amplitude (0.09 mm and 20 Hz). Space bar = 1 cm.
amplitude of the neat crude oil layer deposited on water was 0.04 mm (Figure 4B).

The difference between the droplets observed at the breaking amplitudes of the neat oil layers and the solid-like chunks of the layers from the gels is clearly a manifestation of the much greater elasticity within the HSA gels. Upon increasing the amplitudes, the gel layers on water experience increased strain on the crests, leading to breakage of the gel (Figure 8). To understand better how the different perturbations affect the gels, the trough and rheology studies were compared.

From the strain sweep analysis, the storage modulus ($G'$) value of 10 wt % HSA in crude oil gel ($G' = 300$ kPa at LVR, 1 rad/s and 25 °C; Figure 1) is about five times larger than that of the 1 wt % HSA in corn oil gel ($60$ kPa at LVR, 1 rad/s and 25 °C; Figure 1), whereas the yield strain of the 10 wt % HSA in crude oil gel is about 7 times smaller than that of the 1 wt % HSA in corn oil gel. The breaking amplitude of 1 wt % HSA in the corn oil gel and the 10 wt % HSA in crude oil gel were nearly same (0.1 mm at 20 Hz). This observation indicates the lack of a direct relationship between the $G'$ values of the gels and their breaking amplitudes. Although the exact height of the waves at the breaking amplitudes has not been determined, we speculate that the gels may be in their linear viscoelastic regimes at the 20 Hz frequency employed. Additional experiments to examine this hypothesis are planned for the future.

**Thixotropic Properties of HSA in Crude Oil Gels.** The possibility that the gels from HSA in the two oils are thixotropic was explored. In other studies with organogels composed of LMOGs with structures very similar to that of HSA, ($R$)-12-hydroxyxteramide and ($R$)-12-hydroxy-N-(ω-hydroxyalkyl)-octadecanamides, we have observed extensive viscoelastic recovery after the cessation of destructive strain; the gels are thixotropic.\(^{16}\) There, it was found that the value of the destructive strain did not change the % of recovery. However, the breaking amplitudes of the gels may not be directly compared with the thixotropic properties described here if our assumption is correct that destructive strains were not applied in the trough experiments at the breaking amplitudes. In the thixotropic experiments, rheological measurements were conducted on fresh HSA in crude oil gels at 25 °C under initial conditions at which they were in their linear viscoelastic regimes (i.e., a strain of 0.1% and angular frequency of 1 rad/s) for 150 s to establish baseline values for $G'$ and $G''$. Figure S18 shows the evolution of $G'$ and $G''$ for the 10 wt % HSA in crude oil gel after applying a 30% strain, a condition that leads to loss of its viscoelasticity. Then, the original conditions were reapplied in order to monitor the recovery of the viscoelastic properties. Approximately 75% of the original $G'$ value, from 228 000 Pa to 170 000 Pa, was recovered eventually. After application again of the 30% destructive strain, only about 70% of the previous $G'$ value was recovered, and similar recoveries were observed in subsequent cycles (Figure 9).

![Figure 7. A ∼0.2 cm layer of a 10 wt % HSA—crude oil gel on water (A) before applying wave action and (B) at the breaking amplitude (0.1 mm at 20 Hz). Scale bar = 1 cm.](image)

![Figure 8. Schematic cartoon of the shaking trough in cross section with a thin corn or crude oil gel layer placed on the surface of water and vertically oscillated at a fixed frequency and amplitude. We anticipate that capillary waves are suppressed due to the viscoelasticity of the gel layer and that, at the critical amplitude, $A_c$, the gel layer will either crack or break up near the pinning boundary condition as shown in the dashed box.](image)

![Figure 9. $G'$ (■) and $G''$ (red ●) values at 25 °C for a 10 wt % HSA in crude oil gel as a function of time and application of different strains and frequencies. Linear viscoelastic region (LVR): $\gamma = 0.1\%$, $\omega = 1$ rad/s. Destructive strain (DS): $\gamma = 30\%$, $\omega = 1$ rad/s. Rotational strain was kept at 0% for 0.05 s before changing from the DS to LVR conditions.](image)
\[
\ln \left[ -\ln \left( \frac{G'(\infty) - G'(t)}{G'(\infty) - G'(0)} \right) \right] = m \ln t - m \ln \tau
\]

(1)

From the \(G'\) values for the first cycle in Figure S21 and eq 1, \(\tau\) was calculated to be 55 ± 4 s (\(R^2 = 0.98\); Figure S19).

Figure S20 shows the evolution of \(G'\) and \(G''\) after applying a 30% strain to the 5 wt % HSA in crude oil gel, conditions that lead to loss of its viscoelasticity. After application of the non-destructive conditions, ~82% of the original \(G'\) value, 14 700 Pa, was recovered. However, in subsequent destruction-recovery cycles, virtually no additional losses to the value of \(G'\) were detected (Figure S21). From analyses of data from the average \(G'\) values of 4 consecutive recovery curves (Figure S21), \(\tau\) was calculated to be 53 ± 9 s (Figure S22). Figure S26 shows the evolution of \(G'\) and \(G''\) after applying a 30% strain to the 2 wt % HSA in crude oil gel. Only ~44% of the original \(G'\) value was recovered for this sample (from 440 to 246 Pa). From the \(G'\) values of the recovery curves (Figure S23), \(\tau\) was calculated to be \(\tau = 73 \pm 40\) s (\(R^2 = 0.84\); Figure S24). Similar \(\tau\) values of ~50 s, observed for the 5 and 10 wt % HSA in crude oil gels, show that the recovery times are not acutely dependent on the concentration of HSA, at least within this concentration range. Considerably larger error in \(\tau\) value, 73 ± 40 s obtained for 2 wt % HSA in crude oil gel may be due may be the mechanically weaker nature of the 2 wt % HSA in crude oil gel.

Also, rheological measurements were conducted on HSA in corn oil gels at 25 °C. The initial conditions were in their linear viscoelastic regimes (i.e., a strain of 0.05% and angular frequency of 1 rad/s) for 150 s to establish baseline values for \(G'\) and \(G''\).

Figure S25 shows the evolution of \(G'\) and \(G''\) for the 10 wt % HSA in corn oil gel after cessation of the application of 100% strain, a condition that leads to loss of its viscoelasticity. Eventually, ~75% of the original \(G'\) value, 300 kPa, was recovered. After application again of the 100% destructive strain, only about 90% of the previous \(G'\) value was recovered, and similar losses were observed in subsequent cycles (Figure S26). From the \(G'\) values for the average of the first three cycles in Figure S26 and eq 1, \(\tau\) was calculated to be 17 ± 4 s (\(R^2 = 0.99\), Figure S27). A somewhat greater degree of thixotropic recovery (>99% of \(G'\)) was observed for a 1 wt % HSA in corn oil gel after the cessation of the destructive strain (Figure S28), although its \(\tau\) value, 15 ± 3 s (\(R^2 = 0.99\), Figure S29), was very similar to that of the 10 wt % gel. We suspect that the higher degree of recovery of the 1 wt % than that of the 10 wt % is related to the \(G'\) and \(G''\) values. The less extensive SAFIN of the 1 wt % gel is weaker and, thus, more easily reconstituted.

Thixotropic experiments were also conducted on the corresponding aged gels. By contrast, only ~25%, ~60%, and ~25% of the initial \(G'\) values were recovered after destruction, respectively, of the 2, 5, and 10 wt % aged gels (Figures S30–S32). These observations, that the volatile components of crude oil are necessary to maintain viscoelasticity, are important to the design of systems to recover oil from spills.

**CONCLUSIONS**

Possible correlations between the mechanical properties of molecular gels composed of crude oil or corn oil and HSA have been explored using oscillatory rheology and surface waves on water. POM studies indicate that the SAFINS of HSA in corn oil (1 and 10 wt %) and 10 wt % HSA in crude oil gel have fiberlike networks. Frequency sweep studies of the gels at 25 °C indicate that the \(G'\) and \(G''\) values are independent of the applied frequency at LVR. The mechanical strength of the gels decreased upon decreasing the HSA concentration in both oils. The \(G'\) value of 10 wt % HSA in crude oil gel is five times larger than that of the 1 wt % HSA in corn oil gel, whereas the yield strain of the 10 wt % HSA in crude oil gel is about 7 times smaller than that of the 1 wt % HSA in corn oil gel. The sizes of the droplets that appear at the breaking amplitudes for the thin films (0.2 cm) of corn oil or crude oil deposited on water were independent of the applied frequency. Breaking amplitudes calculated for a 1 and 10 wt % HSA corn oil gel were 0.09 mm and 0.2 mm, respectively, at 20 Hz. Upon increasing the amplitude, the gel layers on water experienced increased strain on the crests, leading to breakage of the gels. Similarly, the breaking amplitude of a ~0.2 cm thick layer of a 10 wt % HSA in crude oil gel on water was ~0.1 mm at 20 Hz.

In addition, the HSA in crude oil and HSA in corn oil gels exhibit thixotropic properties. They recover a large part of their viscoelasticity within seconds after the cessation of destructive shear strains. The thixotropic recovery for the 10, 5, and 2 wt % HSA in crude oil gels after application a \(\gamma\) ~30% strain were ~75, ~82, and ~44%, respectively, based on the original \(G'\) value. The thixotropic recovery for 10 wt % HSA in corn oil gel was ~75% based on the original \(G'\) value. Thixotropic recovery values decreased to ~25, ~60, and ~25%, respectively, for the aged 10, 5, and 2 wt % gels. The observation that the volatile components of crude oil are necessary to maintain viscoelasticity is important to the design of systems to recover oil from spills. In the future, we will adopt a room temperature gelation protocol by dissolving HSA in small amounts of ethanol or methanol to avoid the need for heating and cooling. We have found that this methodology does work with other gellers; in future investigations it will be explored with crude oil (and vegetable oil) in future investigations.


