Introduction

Organogels constitute a diverse group of gelled materials in which a network of self-assembled molecules forms a thermally reversible gel upon cooling, immobilizing a non-aqueous liquid. These viscoelastic structures form through non-covalent associations of gelator molecules at low concentrations (i.e., often <1%). The aggregated molecules form superstructures, often long fibers, which entangle or form pseudo-cristalline regions, immobilizing the liquid largely by surface tension and forming a gel of variable consistency (Terech & Weiss, 1997; Van Esch & Feringa, 2000). The networks formed are reminiscent of macromolecular gels and polymers. However, their thermoreversibility and nucleation involving one-dimensional crystal growth distinguish organogels from materials like cross-linked polystyrene (Mukkamala & Weiss, 1996).

Traditional applications of organogels include gelation of flammable solvents, aerogel formation, and media for nonaqueous reactions (Abdallah & Weiss, 2000; Van Esch & Feringa, 2000). However, there is considerable interest in the potential uses of organogels across various industries. For example, the ability of these materials to self assemble on the nano-scale and to solubilize lipophilic guest molecules makes them useful in purification and separation processes, as media for non-aqueous synthesis or reactions, and in drug delivery. In addition, the sharp temperature and moisture sensitivities of many organogels make them useful in sensing and controlled release scenarios. The wide-ranging uses of organogels include environmental clean-up, safe transport of flammable liquids, aerogel formation, ingredients in lubricants and coatings, and pharmaceutical and food technologies uses (Abdallah & Weiss, 2000; Terech & Weiss, 1997; Van Esch & Feringa, 2000). In the food industry, attempts are being made to apply the principles of organogelation (Bot & Agterof,
to structure oils without the need for high levels of saturated or *trans* fatty acids, which have recognized implications for cardiovascular disease risk. There is also active research in using organogels to minimize oil migration in composite food products and for enhanced stability and delivery of lipophilic bioactive molecules. However, it remains a significant challenge to identify appropriate food-grade organogelator molecules.

Organogelator molecules have relatively low molecular weights compared to the molecules that form the gel networks in typical hydrogels. Some organogelators include derivatives and metal salts of fatty acids (Uzu, 1975; Terech et al., 1994) and steroids (Mukkamala & Weiss, 1996), amino-acid type molecules (Hanabus et al., 1997; Okabe et al., 2004), carbohydrate amphiphiles (Friggeri et al., 2002), and organometallic compounds (Terech et al., 1987; Terech, et al., 1992). These molecules are amphiphilic in nature and self-assemble in hydrophobic liquids when an appropriate balance between solubility and aggregation forces exists (Terech & Weiss, 1997). Aggregation occurs primarily through dipolar interactions, specific intermolecular hydrogen bonding, and metal co-ordination bonding (Terech & Weiss, 1997). The nature of both the solvent and gelator influence organogel formation and morphology (Terech et al., 2000). In fact, a fine balance between aggregation and dissolution forces is critical in the formation of an organogel and the identification of organogelator-solvent combinations capable of forming these gels remains a challenge and an area of considerable activity (Hanabus et al., 1997; Terech & Weiss, 1997). There is still much to learn in identifying suitable gelator-solvent combinations (Terech & Weiss, 1997).

Hydroxystearic acid (hydroxy octadecanoic acid, HSA) is a well known organogelator molecule. Studies with its isomers (Eloundou et al., 2005; Marton et al., 1941; Tamura et al., 1994; Terech et al., 1994, Terech et al., 2000) and other fatty acids (Daniel & Rajasekharan, 2003) have led to a greater understanding of the relationships between molecular structure and organogel formation and structure. 12-hydroxy octadecanoic acid (12-HSA) in particular is commonly used in cosmetics as well as lubricating greases and coatings (Terech et al., 2000; Marton et al., 1941). The hydroxylated fatty acid is formed through the hydrogenation of castor oil, a material rich in ricinoleic acid (12-hydroxy, 9-octadecenoic acid). In organic solvents, 12-HSA forms long, rigid fibers through hydrogen bonding, and these fibers then are linked together in crystalline monoclinic domains (Terech & Weiss, 1997).

HSA organogel research has served as a model for further exploration of organogels (Terech & Weiss, 1997). For example, in our quest to identify new organogelator molecules, we turned to 12-hydroxy, 9-*trans*-octadecenoic acid (ricinelaic acid, REA). REA is a derivative of 12-HSA and has a similar molecular structure. Given the *trans* configuration of the double bond on carbon 9, it was hypothesized that the molecule would physically align in a similar manner as the saturated molecule, 12-HSA. Our lab was the first to report on the ability of REA to act as an organogelator. (Wright & Marangoni, 2006; Wright & Marangoni, 2007). This chapter
summarizes our current understanding of REA gelation of vegetable oils, including the influence of temperature and concentration on gel formation, microstructure, and stability.

**Experimental Procedures**

**Materials and Sample Preparation**

Ricinelaidic acid (REA, >99 % purity, Nu-Chek Prep, Elysian, MN) was blended with refined, bleached, and deodorized canola oil (CO, Bunge, Toronto, Canada), unrefined sesame oil (Sunfresh Ltd., Toronto, Canada), and diacylglycerol oil (ENOVA, ADM Kao LLC, Decatur, IL) at 0.1–5.0 wt% levels. The samples were heated to 80°C, mixed vigorously, and held at 80°C for 10 minutes prior to subsequent experiments. The melting temperature of REA was determined by differential scanning calorimetry (DSC) using a Q-1000 calorimeter (TA Instruments Water-LLC, New Castle, DE); 8–10 mg of sample was hermetically sealed in an aluminum pan, crystallized at 5°C for 24 hours, and then heated at a rate of 5°C/minute. The peak melting temperature was determined using the software provided with the instrument.

**Gelation Behavior**

Phase diagrams were constructed using the aforementioned blends of REA and CO, unrefined sesame oil, and diacylglycerol oil. Vials containing 1 mL of the blends were held at temperatures between –10 and 50°C. After 24 hours, the vials were inverted and the self-standing ability of the samples was assessed visually. Depending on appearance, samples were described as “liquid”, “thickened liquid”, “clear gel”, “translucent-opaque gel”, or “fat-like”.

Gelation times ($t_{gel}$) were determined for the REA-CO samples by recording the time when the material was self-standing in an inverted vial. For the 0.5, 1.0, and 5.0% REA-CO samples at 5°C, gelation was also monitored by small deformation rheology using an AR 2000 rheometer (TA instruments, Mississauga, ON, Canada). Oscillatory stress sweeps (0.15% strain and 1 Hz) were performed periodically (i.e., every 14 minutes) after loading the samples at 80°C into a temperature controlled aluminum recessed end concentric cylinder (1 mm spacing between cylinders and 2000 µm gap).

**Gel Microstructure and Rheological Properties**

Gel microstructure was visualized by bright field and polarized light microscopy using an Olympus BH microscope (Olympus, Tokyo, Japan). Small samples (∼15 mg) of the gels were placed on glass microscope slides and gently covered with glass cover-slips. Slide temperature was maintained using a Linkham LTS350 cold stage (Linkam Scientific Instruments Inc., Surrey, England). Digital images of the partially and fully polarized specimens were acquired using a Sony XC75 CCD camera and LG-3 capture board (Scion Corporation, Frederick, USA).
Gel microstructure was also studied using a Rigaku MultiFlex X-Ray Diffractometer (RigakuMSC Inc., The Woodlands, TX). Glass holders with sample wells (0.5 mm depression) were loaded with hot sample and held for 1, 7, 14, and 28 days at 5, 15, 20, and 25°C. Sample temperature during analysis was maintained by placing a Peltier plate at the desired temperature directly beneath the sample holder. Angular scans was performed at 0.5 degree per minute from 1 to 30° 2θ using a Cu source X-ray tube at 40 kV and 44 mA. Background subtractions, to remove liquid oil scattering, and peak detection/labeling were performed using the MDI Jade 6.5 software.

Characteristic small deformation dynamic rheological parameters of the gels were determined after 1, 7, 14, and 28 days at temperatures between 5 and 35°C. Three mL of each sample was placed in a 4 mL vial at the desired temperature and, after the specified time, loaded onto the temperature-controlled flat plate of the AR2000 rheometer (TA instruments, New Castle, DE) and storage moduli in the linear viscoelastic region ($G'_{LVR}$) were determined. A 6 cm, 2 degree acrylic cone with truncation gap of 66 µm was used. Strain sweeps were performed from $6.0 \times 10^{-3}$ to 2.0% at a frequency of 1 Hz. Frequency sweeps from 0.1 to 10 Hz were also performed after 24 h, using a controlled strain of 0.1%.

Results and Discussion

Phase Behavior and Gelation

The 24 hour phase diagrams for REA with canola oil (REA-CO) and sesame oil (REA-sesame) are shown in Fig. 4.1. In the case of the REA-CO system (1A), four phases were identified, according to the visual appearance of the samples. These were fat-like (i.e., the material appeared more polycrystalline than gel-like), nontransparent gel (i.e., gels ranged from slightly translucent to completely opaque), clear gel (i.e., self-standing gel was completely transparent) and liquid (i.e., no thickening or gelation was observed).

The minimum REA concentration at which gelation occurred was 0.5%. A clear gel formed at this concentration at 5°C, but not at 10°C. According to Fig. 4.1.A, the concentration and temperature range at which a clear gel formed was narrow. By 1%, the gels were slightly cloudy. With increasing REA content, increased opacity was observed. By 3.5%, the samples were gelled, but opaque. Gel appearance depended more on concentration than temperature, i.e., within each concentration, sample opacity was similar across the temperature range where setting occurred. Larger changes in the appearance of the samples were observed with increasing temperature. Similarly, there was no transition region in the upper temperature range for gelation. For example, a clear gel was not observed for the 2% sample around 25°C, nor was an opaque-gel observed for the 4% sample around 40°C.

The peak melting temperature of pure REA is 50.3 ± 0.1°C, while the maximum gelation temperature was 35°C with 5% REA. Maximum gelation temperatures
generally do not correspond to the melting temperatures of the neat gelators (Terech & Weiss, 1997). According to the Van’t Hoff equation, some of the REA will be solubilized in the oil phase, thereby lowering the melting temperature of the gels versus pure REA. Even above the solubility limit, gelation will be dependent on having a threshold REA concentration, which results in enough organized molecules to form a space-filling network capable of entrapping canola oil. Also, based on the similarities of REA to HSA, hydrogen bonding is expected to play a critical role in the aggregation of REA molecules into the long network strands. Hydrogen bonding between hydroxyl groups causes HSA aggregation in organic solvents (Terech et al., 1994). Since the strength of hydrogen bonding decreases with increasing temperature, this may also partially limit REA aggregation at higher temperatures.

**Fig. 4.1.** Phase diagram for REA-canola oil (A) and REA-sesame oil (B). Fat-like (i.e., the material appeared more crystalline than gelled), Nontransparent gel (i.e., gels ranged from slightly translucent to completely opaque), Clear gel (i.e., self-standing gel was completely transparent), Liquid (i.e., no thickening or gelation observed), and Thick liquid (i.e., liquid was visibly thickened, but self-standing gel was not observed).
Solvent nature, polarity, and the presence of co-surfactants can influence the aggregation of organogelator molecules (Terech & Weiss, 1997). To investigate the influence of solvent on REA gelation, phase diagrams were constructed using unrefined sesame oil and diacylglycerol oil. The phase diagram for REA with the sesame oil is shown in Fig. 4.1.B. Comparing Figs. 4.1.A and 4.1.B shows that the upper limits for REA gelation were lower for sesame oil than with canola oil. Unrefined sesame oil contains relatively higher levels of free fatty acids, sterols, and tocopherols than RBD canola oil (AOCS, 1996). Each of these compounds contains hydroxyl groups with the potential to participate in hydrogen bonding and therefore impede REA self-assembly. In addition, sterols and tocopherols contain large ring structures that may sterically interfere with the ability of REA to aggregate. A clear gel was never observed with sesame oil. However, a fifth type of phase was apparent, i.e., some samples were visibly thickened, but not gelled (thick liquid). This behavior represented a transition between the formation of a non-transparent gel and a liquid sample. No such intermediary phases were observed with the canola oil samples.

The phase behavior was also studied for REA with diacylglycerol (DAG) oil. However, no thickening or gelation was observed after 24 hours (data not shown). DAG oil is prepared from canola and soybean oils. It differs from natural seed oils, including canola oil and sesame oil, in that it is made up of diacylglycerol molecules (as the name implies), rather than triacylglycerols. In a DAG molecule there is a free hydroxyl group on the glycerol backbone, which is otherwise esterified to a fatty acid in a triacylglycerol. This high number of hydroxyl groups in the DAG oil was correlated with a lack of REA gelation. This lends further evidence to the fact that hydrogen bonding is critical to REA gelation.

Gelation times for the REA-CO blends are shown in Table 4.A. The concentration dependence of REA gelation is evident. Even after several months at 5°C, no gelation was observed below 0.5% REA. At 0.5% a gel was observed after 20.5 hours. With 1% REA, \( t_{gel} \) decreased dramatically to roughly 11 minutes. With increasing concentration, an exponential decrease in \( t_{gel} \) was observed at 5°C. Within each temperature studied, concentration had a significant influence on \( t_{gel} \) (\( P < 0.05 \)). However, for each concentration above 1%, significantly higher values of \( t_{gel} \) were not observed until above 20°C. For concentrations of 2% and above, \( t_{gel} \) was independent of temperature, up to 20°C. Above 20°C, a dramatic increase in \( t_{gel} \) was observed for the gels, indicating the existence of a different gelation regime.

Gelation behavior at 5°C was also monitored by small deformation rheology. Fig. 4.2 shows the changes in the storage modulus (\( G' \)) during gelation of the 0.5, 1.0, and 5.0 % REA blends at 5°C. With 1.0 and 5.0 % REA, gelation occurred rapidly at 5°C. The samples quickly reached a maximum in the storage modulus \( G' \), \( \approx 24,000 \) Pa and \( \approx 65,000 \) Pa, respectively). Such sharp sol-to-gel transitions are characteristic of “strong” organogels, which demonstrate solid-like viscoelastic behavior (Terech & Weiss, 1997). In contrast, the most dilute sample (0.5%) gelled gradually
Table 4.A. Gelation Times ($t_{gel}$, s)* for 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 % REA-canola Oil Blends Between 5 and 40°C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>0.5%</th>
<th>1.0%</th>
<th>2.0%</th>
<th>3.0%</th>
<th>4.0%</th>
<th>5.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>7,4025 ± 4512</td>
<td>660 ± 91 a</td>
<td>446 ± 12 a</td>
<td>341 ± 6 a</td>
<td>290 ± 38 a</td>
<td>207 ± 59 a</td>
</tr>
<tr>
<td>10</td>
<td>ng</td>
<td>886 ± 80 b</td>
<td>458 ± 49 a</td>
<td>326 ± 41 a</td>
<td>306 ± 36 a</td>
<td>265 ± 35 a</td>
</tr>
<tr>
<td>15</td>
<td>ng</td>
<td>3359 ± 993 c</td>
<td>353 ± 5 a</td>
<td>227 ± 4 b</td>
<td>187 ± 6 a</td>
<td>145 ± 8 a</td>
</tr>
<tr>
<td>20</td>
<td>ng</td>
<td>ng</td>
<td>517 ± 24 a</td>
<td>342 ± 4 a</td>
<td>224 ± 27 a</td>
<td>190 ± 6 a</td>
</tr>
<tr>
<td>25</td>
<td>ng</td>
<td>ng</td>
<td>1819 ± 28 b</td>
<td>1693 ± 46 c</td>
<td>1136 ± 240 b</td>
<td>795 ± 75 b</td>
</tr>
<tr>
<td>30</td>
<td>ng</td>
<td>ng</td>
<td>ng</td>
<td>Ng</td>
<td>2959 ± 475 c</td>
<td>1638 ± 125 c</td>
</tr>
<tr>
<td>35</td>
<td>ng</td>
<td>ng</td>
<td>ng</td>
<td>Ng</td>
<td>ng</td>
<td>ng</td>
</tr>
<tr>
<td>40</td>
<td>ng</td>
<td>ng</td>
<td>ng</td>
<td>Ng</td>
<td>ng</td>
<td>ng</td>
</tr>
</tbody>
</table>

*Time when material was self-standing in inverted vial
Mean ± standard deviation (n=6)
ng indicates no gelation after 24 hours
Within each column, different superscript (a–c) indicates significant difference (P <0.05)

Fig. 4.2. Changes in storage modulus ($G'$, Pa) of 0.5, 1.0 and 5.0% REA-canola oil blends during gelation at 5°C (0.15% strain, 1 Hz).
in a manner more typical of “weak” gel-like systems, which possess liquid-like viscoelastic properties (Terech & Weiss, 1997). An increase in $G'$ was observed throughout the duration of the experiment, reaching a $G'$ of $\sim 370$ Pa after 68 hours.

**24-Hour Gel Rheology and Scaling Relationships**

Fig. 4.3 shows the storage modulus in the linear viscoelastic region ($G'_{LVR}$, Pa) for samples of the 0.5, 1.0, 2.5, 4.0 and 5.0% REA-CO gels after 24 hours at 5, 10, 20 and 30°C.

REA concentration had a significant influence on gel elasticity at each temperature studied (Figs. 4.3.A–4.3.D, $P<0.05$). In contrast, Figs. 4.3.E–4.3.H show that storage temperature was only significantly correlated with gel elasticity at the

![Image of Fig. 4.3](image-url)

**Fig. 4.3.** Influence of REA concentration (0.5, 1.0, 2.5, 4.0 and 5.0%) and gelation temperature (5, 10, 20 and 30°C) on the 24 hour linear viscoelastic region storage modulus ($G'_{LVR}$, Pa) for REA-CO gels.
1.0% REA level (P=0.01). Above 1.0% REA, there was no significant effect of temperature on $G'_{LVR}$ for the gels that formed (P>0.05). This trend correlates with similar trends in the REA-CO phase diagram (Fig. 4.1). Within each region where gelation occurred, only 1 type of phase was observed across all temperatures. Therefore, both gel appearance and strength depended more on concentration than on temperature. Comparing $t_{gel}$ for the 2–5% REA-CO gels, indicates significant changes only above 20°C. However, based on the REA concentrations in Fig. 4.3.G and 4.3.H, there is no evidence from $G'_{LVR}$ that a change in gelation mechanism around 20°C resulted in a change in network elasticity. To further explore this and to identify differences in gel microstructure across the temperature range studied, the scaling relationship between $G'_{LVR}$ and REA concentration are shown in Fig. 4.4 for 5, 10, 15, 20 and 25°C.

For HSA organogels, the elastic modulus scales with concentration in a power-law fashion. According to Fig. 4.3, this scaling behavior was observed for the REA-CO gels at each temperature, suggesting that, regardless of concentration, within each temperature, the gel structure is similar. However, comparing the scaling exponents in Fig. 4.4, similar values were observed at 5, 10, 15 and 20°C, but not at 25°C (2.69, 3.12, 2.36, and 3.16 vs 8.18, P<0.05). The values observed between 5 and 20°C are within the range of those reported for HSA-solvent gels in the literatures (i.e., 1.89–3.87) (Eloundou et al., 2005; Terech et al., 2000). The change in scaling exponent observed at 25°C coincides with differences in $t_{gel}$, i.e., increases in gelation time for the 2, 3, 4 and 5% gels above 20°C. However, this change is primarily the result of a low $G'_{LVR}$ for only the 2% sample at 25°C (Fig. 4.4.D). Differences in gelation time and the scaling exponent at 25°C may suggest differences in gelation

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**Fig. 4.4.** Scaling relationships between $G'_{LVR}$ and REA concentration (wt%) for REA-CO gels formed at 5, 10, 15, 20 and 25°C.
mechanism and structure compared with the gels at the lower temperatures, particularly at lower concentrations. Any potential differences in gelation mechanism did not translate into differences in $G'_LVR$ for the 4 or 5% REA gels (i.e., Figs. 4.3.G and 4.3.H) between 5 and 30°C.

**Gel Microstructure**

When neat REA crystallizes, it forms large spherulitic microstructures made up of thick, needle-like structures (Fig. 4.5.A). A significantly different network is observed for the CO gels. During gelation, the REA molecules aggregate into long, thin, fibers that intertwine and cluster, immobilizing the liquid oil. The polarized light micrographs of the REA gels in Figs. 4.5.B and 4.6 show the networks of long birefringent REA fibers characteristic of organogels (Terech & Weiss, 1997). According to Fig. 4.6, some of the fibers exceed $\sim 800 \mu m$ in length. Also Fig. 4.6.A nicely shows the edges between two clusters of fibers.

![Fig. 4.5. Partially polarized light micrographs of neat REA (A) and 3% REA-canola oil (B) after 1 day at 25°C. Magnification bar represents 100 μm.](image)

![Fig. 4.6. Polarized light micrographs of 1.5% REA-CO gel at 4, 10, and 40× magnification after 24 hours at 20°C. Magnification bars represent 100 μm.](image)
Gel microstructure was systematically studied for the REA-CO samples using partially polarized light microscopy. Fig. 4.7 shows the 0.5, 1.0 and 5.0% gels at 5°C. Images of the gels at 2 and 5% REA, but at higher temperatures (15, 20, and 25°C) are shown in Fig. 4.8.

**Fig. 4.7.** Partially polarized light micrographs for 0.5% (A, D, G), 1.0% (B, E, H) and 5.0% (C, F, I) REA-canola oil gels after 1 (A, B, C), 7 (D, E, F) and 28 (G, H, I) days at 5°C. Magnification bars represents 100 µm.

**Fig. 4.8.** Partially polarized light micrographs of 2 (A, B, C) and 5% (D, E, F) REA-canola oil gels after 1 day at 15 (A, D), 20 (B, E), and 25°C (C, F). Magnification bar represents 100 µm.
The influence of REA concentration on gel microstructure is apparent after 24 hours in Fig. 4.7 A (0.5%), B (1%) and C (5%). At 0.5% REA, the networks were difficult to visualize. Only when the samples were flooded with light and partially polarized could any structure be seen. At higher concentrations, more of the individual strands were apparent and clusters of the strands were evident. According to Fig. 4.8, the nature of the REA fibers was influenced by REA concentration. The fibers in the 5% gels (Figs. 4.8.D–4.8.F) were longer and thicker than those at 2% (Figs. 4.8.A–4.8.C). Also, smaller and circular structures (~5–10 µm) were observed, on occasion, in the gels examined in this study (i.e., in the 2, 3, 4 and 5% gels at 15, 20 and 25°C). However, this type of structure is most apparent in the 2% REA-CO gels (Figs. 4.8.A–4.8.C).

There were no apparent differences in microstructure between 15, 20 and 25°C, in the case of the 3, 4 (data not shown) and 5% REA-CO gels. However, for the 2% REA-CO gels in Figs. 4.8.A–4.8.C, temperature did influence gel microstructure. At 25°C (Fig. 4.8.C), the fibers were shorter and more difficult to visualize than at 15 and 20°C (Figs. 4.8.A and 4.8.B). A similar microstructure was observed for the clear 0.5% REA-CO gel at 5°C (Fig. 4.7.A). According to Fig. 4.1, 5°C was the upper temperature limit of gelation for the 0.5% REA-CO blend and 25°C was the upper temperature limit of gelation for the 2% gel. Of the gels formed at 15, 20 and 25°C, the 2% sample at 25°C was also the least opaque of the gels.

**XRD**

Powder X-ray diffraction (XRD) was used to explore the structure of the REA gels in both the small and wide angle regions. The XRD patterns for neat REA and the 5% REA-CO gel after 24 hours at 5°C are shown in Fig. 4.9. The peaks identified in

![Fig. 4.9. Powder X-ray diffraction patterns for neat REA (A) and 5.0% REA-canola oil gel (B) after 24 hours at 5°C. Numbers 1-6 refer to spacings for neat REA: 43.28, 15.16, 4.41, 3.99, 3.86, and 3.71 Å, respectively.](image-url)
Fig. 4.9 correspond to those for neat REA, and spacings for the REA-CO samples are shown in Table 4.B.

The patterns for the neat REA and REA organogels are similar, suggesting a relationship between the molecular packing in the neat and gel phases. Both neat REA and the gel had small angle reflections, which roughly correspond to the 001 and 003 planes. This is similar to neat HSA, which shows characteristically intense (001) and (003) reflections that shift to different extents depending on the solvent. HSA organogels consist of randomly distributed long fibers, interconnected through junction zones, i.e., monoclinic crystalline domains. The fibers themselves are made up of fatty acid dimers formed through hydrogen bonding between the hydroxyl groups at C12 and carboxyl groups that are aligned head to head (Terech et al., 1994). The small angle reflections observed for the REA gels suggest the presence of dimers (i.e., ~ peak at 41 Å) and a structure similar as HSA gels. Crystallinity is evidenced

<table>
<thead>
<tr>
<th>Days</th>
<th>0.5% Spacings (Å)</th>
<th>1.0% Spacings (Å)</th>
<th>5.0% Spacings (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>nd</td>
<td>nd</td>
<td>40.5 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>14.8 ± 0.0</td>
<td>4.4 ± 0.0</td>
<td>4.0 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>4.0 ± 0.0</td>
<td>3.9 ± 0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.8*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>40.8 ± 1.3</td>
<td>41.1 ± 0.8</td>
<td>42.7 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>14.78*</td>
<td>14.9 ± 0.1</td>
<td>15.0 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>4.4 ± 0.0</td>
<td>4.0 ± 0.0</td>
<td>3.9 ± 0.0</td>
</tr>
<tr>
<td>28</td>
<td>41.1 ± 1.0</td>
<td>40.7 ± 1.3</td>
<td>41.7 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>14.9 ± 0.0</td>
<td>14.9 ± 0.1</td>
<td>14.9 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>4.4*</td>
<td>4.4 ± 0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.0*</td>
<td>4.0 ± 0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.9 ± 0.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

nd: no peak detected

* Indicates spacing was only detected in one replicate

Spacings (Å) for neat REA: 43.28 ± 0.001, 15.16 ± 0.01, 4.41 ± 0.00001, 3.99 ± 0.00001, 3.86 ± 0.001, 3.71 ± 0.0001
by the presence of the short Bragg spacings. Neither small nor wide angle reflections were observed for the 0.5 and 1.0% REA-CO gels after 24 hours at 5°C. This is likely related to equipment sensitivity issues at low solids, as gelation was observed and structure was evident by microscopy.

There was a shift towards slightly higher peak positions in the gel phase versus neat REA (for example, 43.28 Å for neat REA versus 40.54 Å for the gel). Shifts and peak broadening can occur when liquid molecules are included in the network strands (Terech & Weiss, 1997). For example, HSA aerogel structures (formed by the evaporation of the organic solvents from organogels) have slightly, but consistently higher values of d-spacings than neat HSA (Terech et al., 1994). In our case, a shift towards smaller spacings in the REA gels was observed, indicating a different and more closely packed arrangement of the REA dimers within the strands than in the neat crystalline state. The properties of the solvent strongly influence the shape and dimensions of organogelator assemblies (Abdallah & Weiss, 2000). These results point to differences between gelator aggregation in organic solvents versus vegetable oil. REA also exhibits polymorphism (data not shown). Differences in REA polymorphic behavior between the neat and gel phases may also explain the differences observed.

Powder XRD was also used to study differences in the REA-CO gels formed at higher temperatures, i.e., 15, 20 and 25°C. In this case, peaks corresponding to the (001) and (003) reflections and Bragg spacings were again observed for the gels (data not shown). However, there was more variability associated with these determinations and no trends with respect to peak position and concentration or temperature. Also, in several samples, a double peak around the (003) position was observed, indicating the existence of multiple structures within the gel network, a characteristic absent from the gels at 5°C.

**Frequency Sweeps**

To study the nature of the REA-CO gels formed at different temperatures after 24 h, frequency sweeps were performed. These results are shown in Fig. 4.10.

In all cases, the initial storage modulus (G′) was greater than the loss modulus (G″). The 0.5% gel behaved differently than the more concentrated samples. Fig. 4.10.A shows that G′ was frequency dependent and a cross-over point was observed for the 0.5% gel at ~4 Hz. A strong frequency dependence of G′, tan(δ) >1, and a cross-over point where G″ exceeds G′ are characteristics of entangled polymeric solutions (Tosh et al., 2004).

A slight positive slope for G′ is consistent with the presence of a weak gel. This was observed for the 5.0% sample at 5, 20 and 30°C (Figs. 4.10.D–4.10.F). At 5°C, the 1.0 and 3.0% gels showed a relatively higher frequency dependence, although tan(δ) was less than one and no cross-over points were observed for these gels (Figs. 4.10.B and 4.10.C). These 5°C results suggest that, while the 0.5% gel consists of entangled fibers, the 1.0, 3.0, and 5.0% gels are stabilized by junction zones between the fibers. Similarly, the 5% samples at 20 (Fig. 4.10.E) and 30°C (Fig. 4.10.F) had behavior consistent with the presence of a weak gel stabilized by junction zones. Each
sample demonstrated a small frequency dependence of $G'$ and $G''$ and had tan delta values < 1. Recall that 35°C was around the upper temperature range for gelation with 5% REA. According to Fig. 4.10, $G'$ and $G''$ were significantly less at 35°C (Fig. 4.10.F) versus 5 and 20°C (Fig. 4.10.E) ($P<0.05$). However, the differences in $t_{gel}$ above and below 20°C did not correlate with large differences in the gel’s frequency response for the 5% gels. In terms of visual appearance, the gels at 5, 20 and 35°C were also similar (data not shown).

The fact that entangled fibers versus junction zone stabilization are suggested for the 0.5% versus 1, 3, and 5% gels, respectively, is consistent with the XRD and microscopy data. Little, if any, birefringence is observed for the 0.5% gels after 24 hours (Fig. 4.7.A) and no diffraction peaks were observed in the wide-angle region (refer to Table 4.B). At higher concentrations, both the light microscopy and XRD analysis indicate the presence of crystallinity, which is expected in the junction zones between REA fibers (i.e., the microcrystalline domains).
REA-CO Gel Stability with Time

After 7 days at 5°C, changes were observed in the opacity of the 0.5 and 1.0% gels, i.e., the 0.5% gel changed from a clear to a cloudy gel after 7 days and the 1.0% sample changed from a cloudy to a more opaque gel. Visible changes were not observed in the 0.25 and 5.0% samples during 28 days storage, i.e., the 0.25% sample remained liquid and the 5.0% appeared “fat-like” throughout. The most significant change in gel microstructure was observed for the 0.5% sample between 7 and 28 days (Fig. 4.7.D versus 4.7.G). After 28 days, an increase in the number and thickness of fibers were evident in the 0.5% sample. The 0.5, 1.0 and 5.0% gels had similar networks as visualized by microscopy after 28 days, although the gels differed substantially in terms of their visual appearance; the 0.5, 1.0 and 5.0% gels appeared as a cloudy gel, an opaque gel, and fat-like, respectively.

Changes in gel elasticity and microstructure at 5°C in the region of the apparent transition temperature of 20°C (i.e., around room temperature) were determined. Fig. 4.11 compares the $G'_LVR$ for the gels after 1, 7 and 28 days at 5, 15, 20, and 25°C.

Significant increases in $G'$ were observed for the 1.0 and 5.0% samples in time ($P<0.05$), although not for the 0.5% gels ($P=0.16$) (Fig. 4.11.A). These results indicate continued setting and/or restructuring of the gels. The observed increases in gel opacity and changes in microstructure of the 0.5% sample also indicate the dynamic nature of the gels. Similarly, Table 4.B shows that changes were observed

![Fig. 4.11. Storage modulus in the linear viscoelastic region ($G'_LVR$) for the 0.5, 1 and 5% REA-CO gels at 5°C (A) and the 2, 3, 4, and 5% REA-CO gels at 15 (B), 20 (C), and 25°C (D) after 1, 7, and 28 days.](image)
in the scattering properties of the gels during storage. After 1 day, no scattering was observed for the 0.5 and 1.0% gels. However, after 7 days, peaks in the small-angle region were detected, suggesting the presence of more REA dimers. In addition, wider angle reflections were detected in the 1.0% gel after 28 days.

Although more order was observed for the dilute gels, there were no significant trends in the XRD patterns for the 5.0% gels during storage at 5°C or higher (P>0.05). The positions of the ∼41 and ∼15 Å peaks neither increased nor decreased over time for the 5.0% gel at 5°C (Table 4.B). Similarly, the interplanar spacings were not significantly different after 28 days (P>0.05). The 2 and 5% REA-CO gels at 15, 20, and 25°C appeared to increase in opacity over time (data not shown), although there also was no evidence of microstructural changes either from microscopy or by XRD (data not shown). Overall, these results indicate continual reorganization of the REA gels at 5°C, leading to an increase in the microcrystalline domains, which may be likened to retrogradation in polysaccharide gels. Evidence for continual structuring at the higher temperatures was less conclusive.

Conclusion

The hydroxylated fatty acid ricinelaicid acid (12-hydroxy-9-trans-octadecenoic acid, REA) is an organogelator molecule, capable of gelling triacylglycerol-based vegetable oils, depending on temperature, concentration and oil purity. Gelation occurred with as little as 0.5% (w/w) REA. Reduced gelation tendency was correlated with the presence of potential hydrogen-bonding moieties in the oils. REA concentration also had a significant influence on gelation kinetics and gel rheology. At 5°C, the 0.5% canola oil gel behaved like a weak, viscoelastic network composed of entangled strands. Between 1.0 and 5.0% REA, solid-like, viscoelastic gels were formed at 5°C. Between 5 and 30°C, REA concentration had a significant influence on gel elasticity (P<0.05), whereas temperature had a relatively lesser influence on gel rheology. Differences were observed in the scaling exponent of $G'_1$VR with concentrations above 20°C. These were correlated with significant differences in gelation time, also at 20°C. Values for gelation time indicated a change in behavior below 2% REA and above 20°C.

The 5% REA gels at 5, 20 and 35°C displayed similar microstructures and behaved like weak gels stabilized by junction zones. Most of the gels studied (i.e., the 2, 3, 4, and 5% gels at 15, 20 and 25°C) consisted of long, thin fibrous REA strands. Polarized light microscopy revealed that the gels were formed through the interactions of long, thin and birefringent fibers. However, at 25°C, the 2% gel was characterized by more transient and circular entities. Structural analysis using XRD indicated the presence of repeating REA dimers and increasing order with REA concentration and gel storage time. Increases in gel opacity, birefringence, XRD scattering, and fiber clustering were observed for the dilute gels during storage at 5°C. However, with 28 days of storage at higher temperatures, there were no apparent changes detected in the 2 and 5% gel microstructure by microscopy or XRD, despite increases in gels opacity.
References


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