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ORIGINAL PAPER

Time, Temperature, and Concentration Dependence of Ricinelaidic Acid–Canola Oil Organogelation

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Abstract Canola oil (CO) gels were formed using ricinelaidic acid (REA), a hydroxylated fatty acid, and the time, temperature, and concentration dependence of the resulting gel structure was studied using small-deformation rheology, light microscopy, and powder X-ray diffraction (XRD). Between 5 °C 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'_{LVR} with concentration above 20 °C, which were also correlated with significant differences in gelation time at 20 °C. However, the 5% gels at 5 °C, 20 °C, 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 °C, 20 °C, and 25 °C) consisted of long, thin, fibrous REA strands, although at 25 °C, the 2% gel was characterized by more transient and circular entities. During 28 days' storage, there were no apparent changes detected in gel microstructure by microscopy or XRD, despite increases in the gel's opacity.

Keywords Organogels · Ricinelaidic acid · Canola oil · Time–temperature dependence · Stability · Gel rheology

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Introduction

Organogels are a diverse class of materials in which a network of self-assembled molecules immobilizes an organic liquid, forming a thermally reversible gel upon cooling. Traditional applications for organogels include gelation of flammable solvents, aerogel formation, and media for nonaqueous reactions [1, 2]. However, there is increasing interest in applying the principles of organogelation in various arenas, including food applications [3, 4], where the ability to structure oils without the need for high levels of saturated or trans fatty acids would be advantageous.

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 [5, 6]. Studies using isomers of hydroxystearic acid [hydroxy octadecanoic acid (HSA)], a well-known organogelator molecule [7–11], and other fatty acids [12] have permitted a better understanding of the relationship between molecular structure and organogelation, and organogel formation and structure, in general. HSA, specifically, forms long, rigid fibers through hydrogen bonding, and these fibers are then linked with each other in crystalline monoclinic domains [6]. We recently reported [13] for the first time on the gelation of vegetable oils by 12-hydroxy-9-trans-octadecenoic acid [ricinelaidic acid (REA)], a derivative of HSA. REA was found to gel vegetable oils, depending on concentration, temperature, and the presence of hydrogen bonding moieties in the oils. Figure 1 shows the 1-day phase diagram for REA–canola oil (CO) [13].

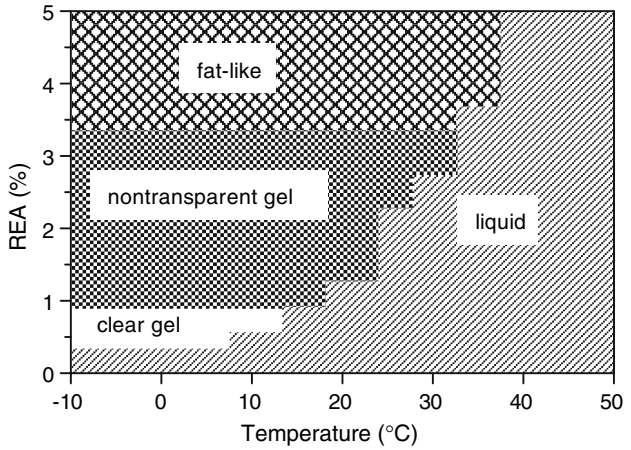

Fig. 1 Phase diagram for ricinelaidic acid–canola oil (REA-CO) after 1 day. Phases are described as: fat-like (i.e., the material appeared more crystalline than gelled), nontransparent gel (i.e., gels ranged from slightly translucent to completely opaque), and clear gel (i.e., self-standing gel was completely transparent and liquid (i.e., no thickening or gelation observed)

Above a critical concentration of ~0.5% (w/w REA), canola oil gelation occurred at 5 °C. In a very limited region, a clear gel was observed. However, above 0.75% REA, the resultant gels ranged from translucent to opaque or ''fat-like'' in appearance. Gelation times, i.e., the time when the material was self-standing in an inverted vial (t_{gel}) were determined. At each temperature, REA concentration had a significant influence on t_{gel} ($P < 0.05$). Between 2% and 5% REA, t_{gel} was independent of temperature up to 20 °C and decreased dramatically above this temperature ($P < 0.05$), indicating a change in gelation behavior [13].

Gel microstructure at 5 °C was studied for the 0.5%, 1.0%, and 5.0% REA-CO gels after 1, 7, and 28 days using polarized light microscopy (PLM), small-deformation rheology, and powder X-ray diffraction (XRD). PLM revealed networks composed of long, thin, birefringent fibers, the size of which depended on REA concentration and storage time. Gel strength was characterized using the storage modulus in the linear viscoelastic region (G'_{LVR}) and was found to be highly dependent on concentration at 1 day ($P < 0.05$). According to XRD, the gel solids consisted of REA dimer-sized units, with increasing order evident at higher REA concentrations. During 28 days, increases in gel opacity, birefringence, G'_{LVR}, and intensity of XRD scattering peaks indicated continued structuring of the gels in time at 5 °C [13].

In this paper, we report on the structure and stability of the REA-CO organogels at temperatures above 5 °C in order to better understand the influence of temperature and concentration on gel microstructure and stability.

Materials and Methods

REA (>99% purity, Nu-Chek Prep, Elysian, MN, USA) was blended with refined, bleached, and deodorized CO (Bunge, Toronto, Canada) at 0.5–5.0 wt% levels. The samples were heated to 80 °C, mixed vigorously, and held at 80 °C for 10 min prior to subsequent experiments.

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

Gel microstructure was visualized using bright-field and PLM with 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 coverslips. Slide temperature was maintained using a Linkham LTS350 cold stage (Linkam Scientific Instruments, 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, MD, USA).

Gel structure was also studied using a Rigaku MultiFlex X-Ray Diffractometer (RigakuMSC, The Woodlands, TX, USA). Glass holders with a sample well (0.5-mm depression) were loaded with hot sample and held for 1, 7, and 28 days at 15 °C, 20 °C, 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 were performed at 0.5° per minute from 1–30° 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.

Results and Discussion

Influence of Temperature and Concentration on Gel Rheology at 24 h

Figure 2 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 h at 5 °C, 10 °C, 20 °C, and 30 °C.

REA concentration had a significant influence on gel elasticity at each temperature studied (Fig. 2a–d, $P < 0.05$). In contrast, Fig. 2e–h shows that storage temperature was only significantly correlated with gel elasticity at the 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. This trend correlates with similar trends in the REA-CO phase diagram (Fig. 1). Within each region where gelation occurred, only one type of phase was observed across all temperatures. Therefore, both gel appearance and strength depended more on concentration than on temperature. When gelation times (t_{gel}) were compared for the 2–5% REA-CO gels [13], significant changes were only observed above 20 °C. However, based on the concentrations presented in Fig. 2g and h, there was no evidence from G'_{LVR} that a change in

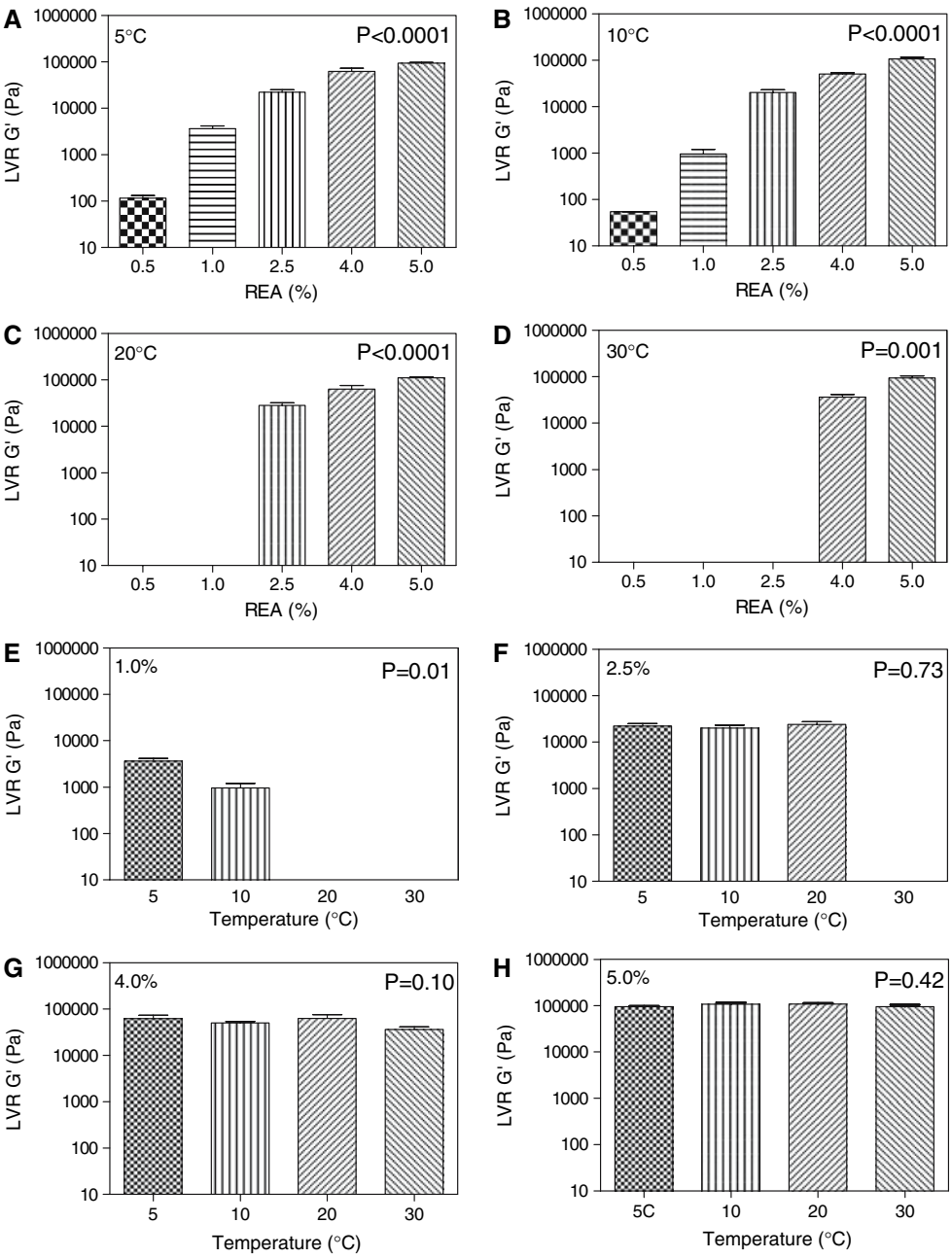

Fig. 2 Influence of ricinelaidic acid (REA) concentration (0.5%, 1.0%, 2.5%, 4.0%, and 5.0%) and gelation temperature (5 °C, 10 °C, 20 °C, and 30 °C) on the 24-h linear viscoelastic region storage modulus (G'_{LVR}, Pa) for REA-CO gels

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 relationships between G'_{LVR} and REA concentration are shown in Fig. 3 for 5 °C, 10 °C, 15 °C, 20 °C, and 25 °C.

For HSA organogels, the elastic modulus scales with concentration in a power-law fashion [7, 11]. According to Fig. 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 was similar. However, comparing the scaling exponents in Fig. 3, similar values were observed at 5 °C, 10 °C, 15 °C, 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 °C and 20 °C were within the range of those reported for HSA-solvent gels in the literature (i.e., 1.89–3.87) [7, 11]. The change in scaling exponent observed at 25 °C coincided with differences in t_{gel}; (i.e., increases in gelation time for the 2%, 3%, 4%, and 5% gels above 20 °C) [13]. However, this change was primarily the result of a low G'_{LVR} for only the 2% sample at 25 °C (Fig. 3d). Differences in gelation time and the scaling exponent at 25 °C may suggest differences in gelation mechanism and structure compared with 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., Fig. 2g, h) between 5 °C and 30 °C.

To study the nature of the gels formed at different temperatures, 24-h frequency sweeps were conducted on the 5% REA-CO gels at 5 °C, 20 °C, and 35 °C. These results are shown in Fig. 4.

At 5 °C, the 0.5% REA-CO gel demonstrated a strong frequency dependence of G' and G'' and had a tan delta > 1 and a crossover point where G'' exceeded G', suggesting the presence of an entangled network [13]. In contrast, Fig. 4 shows that, at 5 °C, 20 °C, and 35 °C, the 5% REA-CO gel behavior was more consistent with the existence 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. Around the upper temperature range for gelation with 5% REA (i.e., 35 °C, Fig. 4c), G' and G'' were significantly less than at 5 °C and 20 °C ($P < 0.05$). Therefore, 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 °C, 20 °C, and 35 °C were also similar (data not shown).

Structure and Stability of 2–5% REA-CO Gels at 15 °C, 20 °C, and 25 °C

Gel elasticity and microstructure were studied for the 2–5% gels in the region of the apparent transition temperature of 20 °C (i.e., around room temperature). Figure 5 compares the G'_{LVR} for the gels after 1, 7, and 28 days at 15 °C, 20 °C, and 25 °C.

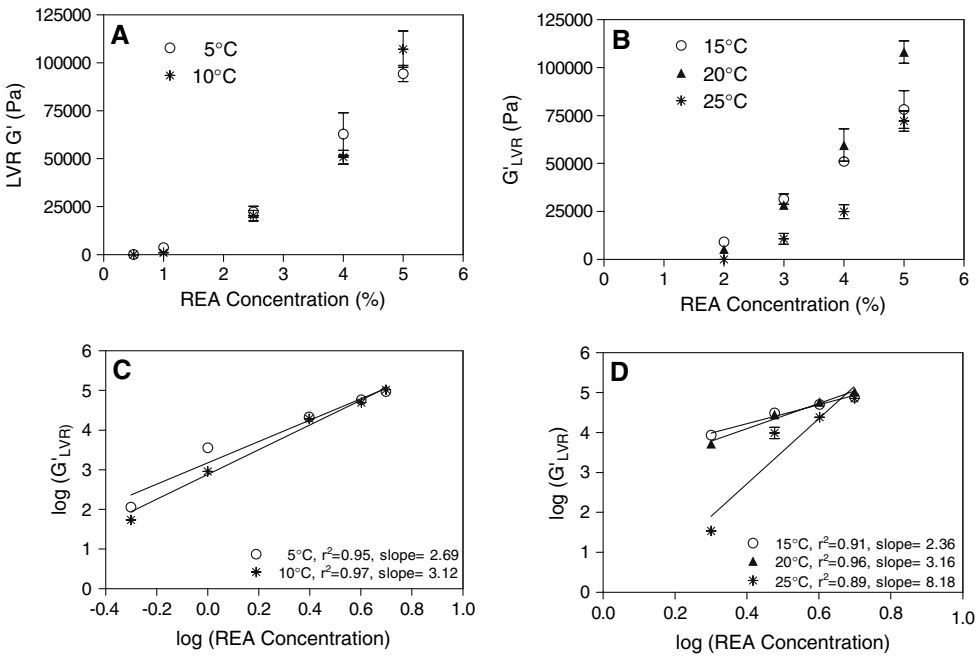

Fig. 3 Scaling relationships between G'_{LVR} and ricinelaidic acid (REA) concentration (wt%) for REA–canola oil (CO) gels formed at 5 °C, 10 °C, 15 °C, 20 °C, and 25 °C

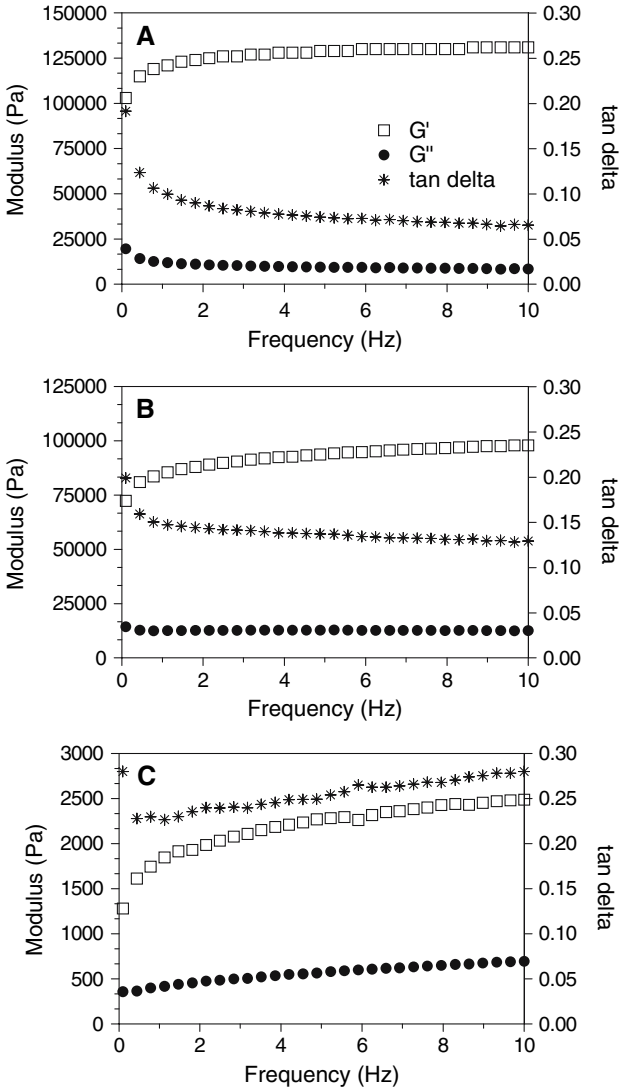

Fig. 4 Storage (G') and loss (G'') moduli and tan delta of 5% ricinelaidic acid–canola oil (REA-CO) gels after 1 day at 5 (**a**), 20 (**b**), and 35 °C (**c**) during frequency sweeps (0.1–10 Hz)

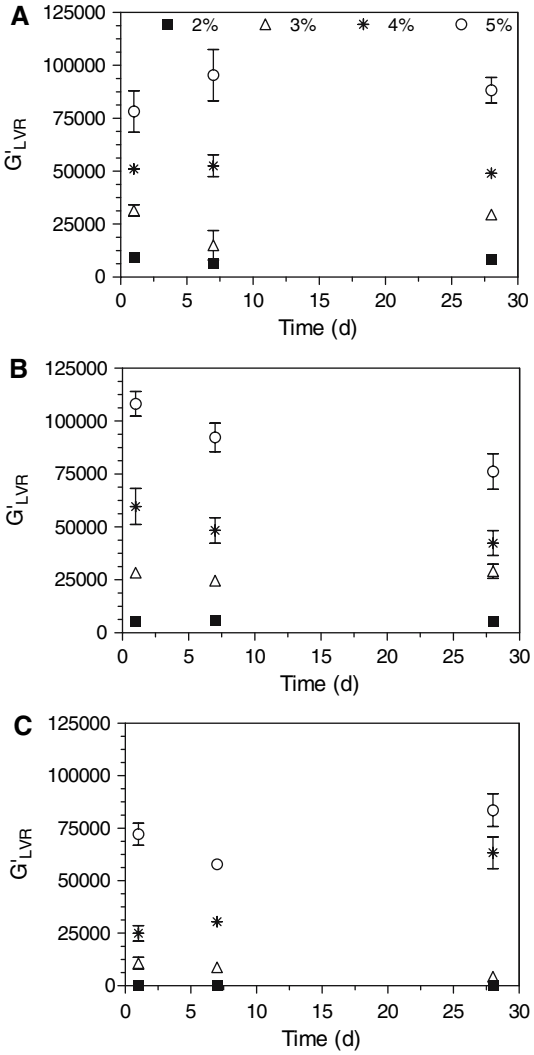

Fig. 5 Storage modulus in the linear viscoelastic region (G'_{LVR}) for the 2%, 3%, 4%, and 5% ricinelaidic acid–canola oil (REA-CO) gels after 1, 7, and 28 days at 15 °C (**a**), 20 °C (**b**), and 25 °C (**c**)

At each temperature, a higher REA concentration resulted in gels with higher values of G'_{LVR} ($P < 0.05$). However, no consistent trends were observed with respect to storage time. Only in the case of 20 °C storage of the 5% sample (Fig. 5b) was a significant change (i.e., a decrease) in G'_{LVR} observed during storage ($P < 0.05$). In all other cases, the REA-CO gels at 15 °C, 20 °C, and 25 °C were stable. In contrast, increases in G'_{LVR} were observed for 1% and 5% REA-CO gels stored at 5 °C [13]. According to visual inspection (data not shown), at higher REA concentrations, the gels in this study were qualitatively more opaque and ''fat-like'' versus ''gel-like,'' and the gels increased in opacity during the 28 days of storage. To visualize changes in network microstructure, the 2%, 3%, 4%, and 5% gels were imaged using light microscopy. Figure 6 compares partially polarized light micrographs of neat REA and 3% REA-CO after 1 day at 25 °C.

When neat REA crystallizes, it forms large, spherulitic microstructures made up of thick, needle-like structures (Fig. 6a). A very different network is observed for CO gels. During gelation, REA molecules aggregate into long, thin, fibers that intertwine and cluster, immobilizing the liquid oil. Figure 6b shows that these strands, which themselves demonstrate birefringence [13], form a dense network with regions of birefringence. Figure 7 shows the partially polarized light micrographs for the 2% and 5% REA-CO gels after 1 day at 15 °C, 20 °C, and 25 °C.

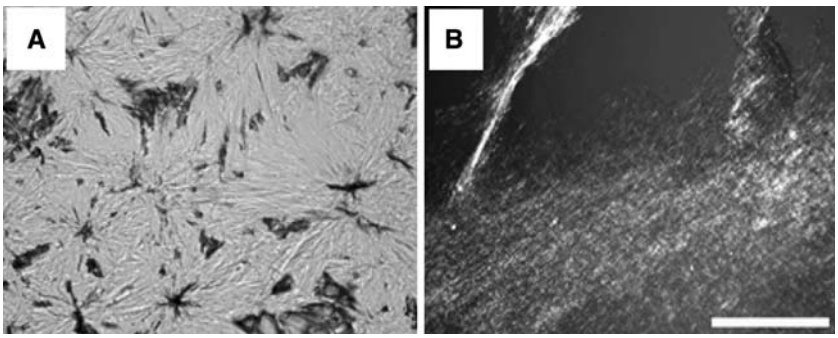

Fig. 6 Partially polarized light micrographs of neat ricinelaidic acid (REA) (**a**) and 3% REA–canola oil (CO) (**b**) after 1 day at 25 °C. *Magnification bar* represents 100 μm

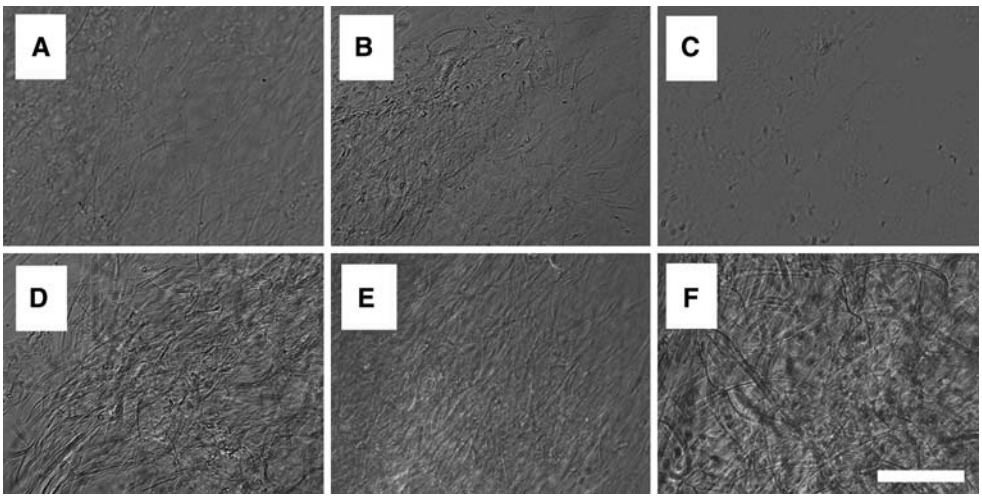

Fig. 7 Partially polarized light micrographs of 2% (**a–c**) and 5% (**d–f**) ricinelaidic acid–canola oil (REA-CO) gels after 1 day at 15 °C (**a**, **d**), 20 °C (**b**, **e**), and 25 °C (**c**, **f**). *Magnification bar* represents 100 μm

According to Fig. 7, the nature of the REA fibers that formed was influenced by REA concentration. The fibers in the 5% gels (Fig. 7d–f) are longer and thicker than those at 2% (Fig. 7a–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 °C, 20 °C, and 25 °C). However, this type of structure was most apparent in the 2% REA-CO gels.

There were no apparent differences in microstructure between 15 °C, 20 °C, 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, temperature had an influence on gel microstructure. At 25 °C (Fig. 7c), the fibers that formed were shorter and more difficult to visualize than at 15 °C and 20 °C (Fig. 7a, b). A similar microstructure was observed for the clear 0.5% REA-CO gel at 5 °C [13]. According to Fig. 1, 5 °C is the upper temperature of gelation for the 0.5% REA-CO blend, and 25 °C is the upper temperature limit of gelation for the 2% gel. Of the gels formed at 15 °C, 20 °C, and 25 °C, the 2% sample at 25 °C was also the least opaque of the gels throughout the study. In general, the gels increased in opacity and crystalline appearance over time. Despite this, there were no apparent changes in gel microstructure according to microscopy. Previously, when the clear 0.5% weak gel increased in opacity at 5 °C, there was a corresponding increase in the size and number of REA fibers, although this was not the case for the 1% REA-CO gel at 5 °C, which also increased in opacity [13].

Powder XRD was used to study differences in the REA-CO gels formed at 15 °C, 20 °C, and 25 °C. At 5 °C, small-angle reflections that corresponded to the approximate size of REA dimmers (i.e., ~41 Å) were observed for the 5% gels after 1 day, as were reflections in the wider angles, suggesting crystallinity [11]. At lower concentrations, the roughly 41 Å reflection was only apparent after 7 days and the Bragg spacings only after 28 days. At the higher temperatures used in this study, peaks corresponding to the (001) and (003) reflections and Bragg spacings were observed. However, there was more variability associated with these determinations and no trends with respect to peak position and concentration, temperature, or storage time (data not shown). Also, in several samples, a double peak around the 003 position was also observed, indicating the existence of multiple structures within the gel network, something that was not seen in the gels at 5 °C [13]. Although visually the REA-CO

gels at 15 °C, 20 °C, and 25 °C appeared to increase in opacity, there was no evidence of clear structural changes either from microscopy or by XRD.

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