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**Large amplitude oscillatory shear (LAOS) rheology of candelilla wax/canola oil oleogels**  
**Reología de cizalla oscilatoria de amplitud grande (LAOS) de oleogeles de cera de candelilla/aceite de canola**

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Received: May 9, 2022; Accepted: June 8, 2022

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### Abstract

Candelilla wax (CW) was added in 5, 6 and 7% w/w to canola oil (CO), heating the mixtures to 90 °C, and cooling down to room temperature, to obtain CW/CO oleogels. The nonlinear viscoelastic properties of the oleogels were addressed using large amplitude oscillatory shear (LAOS) methods. To this end, Fourier analysis of the stress-time response was carried out to extract information on high-harmonic oscillatory moduli. The results showed that nonlinearities were expressed for moderate strain deformations, of the order of 1-15%. In particular, nonlinearities quantified in terms of the harmonic contributions were stronger for the elastic response (about 85-125%) than for the viscous response (less than 40%). In contrast, the mechanical response was essentially harmonic for small amplitude values, indicating the absence of nonlinearities and hence the dominance of linear viscoelastic response. Interestingly, the viscoelastic response was also linear for large strain deformation (>100%). The results reported in the present study demonstrated the viability of LAOS method for obtaining invaluable insights regarding the nonlinear mechanical response of edible oleogels made with natural waxes.

*Keywords:* Candelilla wax; Oleogels; nonlinear viscoelasticity; LAOS; Fourier analysis; High harmonics.

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### Resumen

Oleogeles de cera de candelilla (CW)/aceite de canola (CO) fueron formados añadiendo 5, 6 y 7% de CW a CO, calentando las mezclas a 90 °C y dejándolas enfriar a temperatura ambiente. Se estudiaron las propiedades viscoelásticas no lineales de los oleogeles mediante la técnica de cizalla oscilatoria de amplitud grande (LAOS). Para ello, se realizó un análisis de Fourier de la respuesta esfuerzo-tiempo para obtener información acerca de los módulos oscilatorios altamente-armónicos. Los resultados señalaron que deformaciones moderadas, del orden de 1-15%, produjeron no-linealidades. En particular, las no-linealidades cuantificadas en términos de las contribuciones armónicas fueron más fuertes para la respuesta elástica (alrededor del 85-125%) que para la respuesta viscosa (menos del 40%). En contraste, la respuesta mecánica fue esencialmente armónica para valores de amplitudes pequeñas, indicando la ausencia de no-linealidades, y por lo tanto de una respuesta viscoelástica lineal dominante. Interesantemente, la respuesta viscoelástica también fue lineal a deformaciones grandes (> 100%). Los resultados reportados en este estudio muestran la viabilidad del método LAOS para obtener introspecciones valiosas acerca de la respuesta mecánica no-lineal de oleogeles comestibles hechos con ceras comestibles.

*Palabras clave:* Cera de candelilla; Oleogeles; Viscoelasticidad no-lineal; LAOS; análisis de Fourier; Armónicos altos.

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<https://doi.org/10.24275/rmiq/Bio2816>

ISSN:1665-2738, issn-e: 2395-8472

## 1 Introduction

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Edible oleogels are bi-continuous structures formed by liquid oil and a gelling agent. After cooling, the gelling agent forms a self-assembled, 3D networks into the oil bulk to obtain a semisolid structure. In this way, the resulting material can be easily handled, incorporated and mixed into more complex food structures. Oleogels exhibit the important characteristic of thermo-reversibility between phases obtained by heating/cooling cycles, allowing their applicability over a relatively wide range of temperatures (Rogers *et al.*, 2008). Nutritionally, oleogels have been proposed as alternatives for additives to develop trans-free products for the food industry (Toro-Vazquez *et al.*, 2011; García-Andrade *et al.*, 2020), and in potential applications for the pharmaceuticals and cosmetics industries (Mattice and Marangoni, 2018; Wang *et al.*, 2022).

The process of oleogelation can be classified into three main mechanisms: the formation of self-assembled fibrillar structures, polymer gelation and network formation of crystalline particles (Co and Marangoni, 2012; Hwang *et al.*, 2012). Natural waxes have the potential of gelling via the formation of 3D network structures. Rice bran (Zulim Botega *et al.*, 2013), carnauba and sunflower (Öğütçü and Yilmaz, 2015), shellac (Patel *et al.*, 2013) waxes are instances of natural gelling agents that can be used in food and cosmetic products. In particular, candelilla (*Euphorbia cerifera* and *Euphorbia antisiphilitica*) wax (CW) is considered as a Generally Regarded as Safe (GRAS) food additive by the Food and Drug Administration (FDA; regulations 21CFR, 175.105, 175.320, 176.180) and is permitted as a food glazer by the European Food Safety Authority (EFSA; E 902). Besides, CW can be incorporated into food with no limitation other than current good manufacturing practice (FDA regulation 184.1976). The basic composition of CW is 49-50% n-alkanes (29-33 carbons), 20-29% high-molecular esters, 12-14% alcohols and sterols, and about 7-9% free acids. Toro-Vazquez *et al.* (2007) showed that CW has the ability to form relatively inexpensive oleogel structures with thermal stability. Furthermore, CW is a product from semi-desert regions of northern Mexico and the southwestern USA, and there is a growing interest in promoting its commercialization for boosting regional economic activity. On the other hand, canola oil is widely used for food

preparation given its high content of unsaturated fats. Canola oil contains a significant fraction (9-11%) of polyunsaturated omega-3 fat, as well as phytosterols (about 0.9% by weight) with the ability to reduce cholesterol in the bloodstream. In this way, the canola oil is quite suitable for the preparation of edible oleogels for applications in, e.g., bakery and confectionery products.

The viscoelasticity of oleogels based on natural waxes plays an important role in applications. Oleogels are commonly used as additives to improve the textural properties of foods, cosmetics and pharmaceuticals. For instance, spreadability is a desirable property for applications in cosmetics and foods (Hwang *et al.*, 2013). Also, mixability is required for obtaining acceptable properties in food products where oleogels are used for the substitution of traditional (e.g., lard) fats (Mert and Demirkesen, 2016). In this regard, an accurate characterization of oleogels viscoelasticity would help in designing products with prescribed textural properties and mechanical responses. Toro-Vazquez *et al.* (2007) reported that the CW concentration increased the oleogel elasticity, maybe through the formation of a more compact 3D network. Morales-Rueda *et al.* (2009) characterized the rheological response of CW/dotriacontane organogels, reporting that results from fixed-gap analysis should be taken with some caution. Patel *et al.* (2013) found that the rheological response of shellac-based oleogels was comparable to oleogels obtained using commercial crystal starters. Alvarez-Mitre *et al.* (2012) found that shearing plays an important role in the structuring of CW oleogels during the cooling process. Wijarnprecha *et al.* (2018) reported that both, viscoelastic moduli and hardness, rose with increasing rice bran wax fraction. Rodriguez-Hernandez *et al.* (2021) used oscillatory tests to show that mixed CW oleogels with ethylcellulose are rheologically close to commercial shortening agents. Liu *et al.* (2022) used rheological tests to explore the effect of the stigmasterol concentration on the structure and formation of edible oleogels.

The results reported so far on the rheological response of wax-based oleogels were obtained on methods based on small-amplitude strain deformations (SAOS). However, in practice, oleogels are usually subjected to large strain deformations that can lead to important variations in the viscoelastic response. Motivated by this fact, methods based on large amplitude oscillatory strain (LAOS) have been envisioned for the accurate characterization

of complex soft materials (Ewoldt *et al.*, 2008). In principle, LAOS would provide valuable information on the nonlinear viscoelasticity of oleogel systems (Macias-Rodriguez and Marangoni, 2018). In recent years, LAOS analysis has found interesting applications for the characterization of food structures, including wheat dough (Alvarez-Ramirez *et al.*, 2019a), maize masa (Alvarez-Ramirez *et al.*, 2019b) and konjac glucomannan solutions (Ma *et al.*, 2020). It has been pointed out that LAOS methods have important potential for obtaining insights into the functionality and mechanical response of lipid-based materials during their application process (Macias-Rodriguez and Marangoni, 2017). Joyner (2021) highlighted the potential of LAOS methods as a valuable tool for investigating food structure-function-texture relationships, and the links with sensory attributes. Despite of the potential of LAOS methods for food analysis and processing, few studies are reporting the application of LAOS methods for the characterization of nonlinear viscoelasticity of oleogels. Aguilar-Zarate *et al.* (2019) showed that lecithin can modify the thickening response of ethylcellulose oleogels. Interestingly, it was shown that the lecithin fraction can be used as a control variable for matching the nonlinear thickening response of model fats (e.g., lard). Yazar and Rosell (2022) pointed out that the large-strain viscoelasticity of oleogels is a determinant factor for applications in bakery products. Zhang *et al.* (2022) used LAOS analysis for tuning the viscoelastic response of oleogel-in-water emulsions and showed that the oleogel fraction played an important role in the strain thinning behavior of the emulsion.

The present work aimed to apply large amplitude oscillatory strain to candelilla wax/canola oil oleogels to gain insights regarding their nonlinear viscoelasticity, including shear-thickening and energy dissipation rates for large strain deformations. In particular, the effect of the CW concentration in the linear and nonlinear oleogel viscoelasticity was explored. The issue is of practical importance since the CW concentration determines the structural stability of the 3D network formed during the cooling process (Toro-Vazquez *et al.*, 2007). Pérez-Martínez *et al.* (2019) showed that CW oleogels had massive breaking of junction zones during large-amplitude shearing, causing the loss of regularity in the crystal network and a decrease of the elasticity. In this way, a LAOS analysis should provide valuable insights on the effect of the CW concentration in the nonlinear mechanical response of the oleogel. Results in this

line are of prime importance to prepare oleogels with viscoelasticity similar to that of commercial shortenings (Rodríguez-Hernández *et al.*, 2021).

## 2 Materials and methods

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### 2.1 Materials

Micronized high purity candelilla wax (CW; CAS No. 8006-44-8; melting point 68.5-72.5 °C) was purchased from Multiceras S.A. de C.V. (Monterrey, State of Nuevo Leon, Mexico). Canola oil (CO; Aceite Maravilla®) was purchased from WalMart S.A. de C.V. (Mexico City, Mexico). The typical CO composition is 6%-14%  $\alpha$ -linolenic acid, 50%-65% oleic acid, and < 7% of saturated fatty acids (Ghazani and Marangoni, 2013).

### 2.2 Preparation of oleogels

Toro-Vazquez *et al.* (2011) reported a tight characterization of the conditions required to form a CW/CO oleogel. CW concentrations below 5 g/100 g produced weak oleogels, while concentrations higher than 7 g/100 g led to oleogels with low malleability. In this way, CW was mixed with CO at three different levels (5, 6 and 7 g/100 g). The mixtures were heated at 90 °C, with continuous stirring (model BDC1850, Cafra Lab Solutions, ON, Canada) at 150 rpm for 10 min. Then, the heated mixture was cooled down to room temperature overnight (18±1 °C). CW/CO oleogel samples were stored at 4 °C until required for analyses.

### 2.3 Rheological measurements

Measurements were conducted with a Physica MCR 300 rheometer (Physica Meßtechnik GmbH, Stuttgart, Germany) under strain-controlled mode. A plate-plate serrated geometry (gap 1.0 mm, 50.0 mm diameter) was used to eliminate slip effects. Samples (~5.0 g) were placed in the measuring framework and left to rest for 5 min at 25 °C for allowing structure recovery. To avoid instabilities and water evaporation, the edges of the measuring geometry were covered with mineral oil. Temperature regulation and tracking were achieved with a Physica TEK 150P temperature control system. The rheological measurements were made in triplicate to check reproducibility and consistency.

Frequency sweep measurements (0.01 to 100 Hz) were performed followed by large amplitude oscillatory shear (LAOS) measurements for strain amplitude range between 0.01 and 1000% at a frequency falling within the linear viscoelastic region (LVR). Also, a forward-backward temperature sweep (20-80-20 °C) was performed at 1 Hz, 1% strain amplitude and temperature rate of 10 °C/min. The storage ( $G'$ ) and loss ( $G''$ ) moduli were provided by the equipment software (US200/32 V2.50). Transient (i.e., relaxation) effects were reduced by discarding the first 100 cycles.

#### 2.4 Fourier-domain analysis

Oscillatory strain/stress disturbances are commonly used for assessing the mechanical response of materials. In practice, a harmonic oscillatory strain disturbance of the form

$$\gamma(\omega t) = \gamma_0 \sin(\omega t) \quad (1)$$

is applied to excite the dynamic response. In this way, the shear stress response is oscillatory  $\tau(t; \omega, \gamma_0)$ , which may contain high-order harmonic components. An approach based on the Fourier series allows the representation of the shear stress signal as

$$\tau(t; \gamma_0) = \gamma_0 \sum_{n \text{ odd}} [G'_n(\gamma_0) \sin(n\omega t) + G''_n(\gamma_0) \cos(n\omega t)] \quad (2)$$

In the above expression,  $G'_n(\gamma_0)$  and  $G''_n(\gamma_0)$  can be seen as  $n$ th-order storage and loss moduli, respectively. Materials that exhibit linear mechanical response satisfy  $G'_n(\gamma_0) = 0$  and  $G''_n(\gamma_0) = 0$ , for  $n > 1$ . However, this case is rarely found in practice as many practical materials display non-linear mechanical responses. Under small amplitude oscillatory shear (SAOS), the first-harmonics components should dominate the overall mechanical response. This implies that  $|G'_1(\gamma_0)| \gg |G'_n(\gamma_0)|$  and  $|G''_1(\gamma_0)| \gg |G''_n(\gamma_0)|$ , for all  $n > 1$ . However, materials are commonly subjected to relatively large amplitude oscillations, where nonlinear moduli can be displayed in the form of harmonic distortion. In such a case, the traditional approach based on the storage and loss moduli provides a limited characterization of the mechanical response.

The characterization of high-order harmonic moduli is a suitable approach for the characterization of signals with nonlinear distortion. Hyun *et al.* (2002) and Ewoldt *et al.* (2010) proposed the following ratios

for quantification of the harmonic distortion:

$$I_{n/1}(\gamma_0) \equiv I_n(\gamma_0)/I_1(\gamma_0), n > 1 \quad (3)$$

The ratio  $I(n/1)(\omega, \gamma_0)$  provides a measure of the contribution of the  $n$ th-harmonic component relative to the fundamental component. Ewoldt *et al.* (2008) also introduced measures of nonlinear viscoelasticity based on local material response of a cycle response. In terms of the Fourier decomposition Eq. (1), one has

$$G'_M(\gamma_0) \equiv \left. \frac{d\tau}{d\gamma} \right|_{\gamma=0} = \sum_{n \text{ odd}} n G'_n(\gamma_0) \quad (4)$$

and

$$G'_L(\gamma_0) \equiv \left. \frac{\tau}{\gamma} \right|_{\gamma=\pm\gamma_0} = \sum_{n \text{ odd}} (-1)^{(n-1)/2} G'_n(\gamma_0) \quad (5)$$

Here,  $G'_M(\gamma_0)$  is the dynamic modulus estimated at minimum strain for which instantaneous strain rates are maximized, and  $G'_L(\gamma_0)$  is a large strain dynamic modulus. For linear mechanical response, the above measures are reduced and coincide with the storage moduli (i.e.,  $G'_M(\gamma_0) = G'_L(\gamma_0) = G'(\gamma_0)$ ).

The effect of nonlinearities in the viscosity characteristics is given by

$$\eta_M(\gamma_0) \equiv \left. \frac{d\tau}{d\dot{\gamma}} \right|_{\dot{\gamma}=0} = \frac{1}{\omega} \sum_{n \text{ odd}} n (-1)^{(n-1)/2} G''_n(\gamma_0) \quad (6)$$

and

$$\eta_L(\gamma_0) \equiv \left. \frac{\tau}{\dot{\gamma}} \right|_{\dot{\gamma}=\pm\dot{\gamma}_0} = \frac{1}{\omega} \sum_{n \text{ odd}} G''_n(\gamma_0) \quad (7)$$

In this case,  $\eta_M(\gamma_0)$  and  $\eta_L(\gamma_0)$  reflect the viscosity values measured at minimum and maximum strain rates, respectively. Based on these quantities, the nonlinear elasticity is given as the strain-stiffness ratio:

$$S(\gamma_0) = \frac{G'_L(\gamma_0) - G'_M(\gamma_0)}{G'_L(\gamma_0)} \quad (8)$$

Strain-stiffening nonlinear effects are present when  $S(\gamma_0) > 0$ . In contrast, strain-softening nonlinearity appears when  $S(\gamma_0) < 0$ . Similarly, the shear-thickening ratio is taken as

$$T(\gamma_0) = \frac{\eta_L(\gamma_0) - \eta_M(\gamma_0)}{\eta_L(\gamma_0)} \quad (9)$$

It has been shown that intra-cycle shear-thickening behavior is found when  $T(\gamma_0) > 0$ , and shear-thinning behavior when  $T(\gamma_0) < 0$  (Hyun *et al.*, 2011).

The parameters  $S(\gamma_0)$  and  $T(\gamma_0)$  are also known as fluidizing ratio and the thickening ratio, respectively (Faber *et al.*, 2017). Indeed, the former ratio quantifies the extent of the transition from an elastic solid gel into a flowing fluid. On the other hand, the second ratio describes the resistance to flow.

### 2.5 Time-domain analysis

The Lissajous plot is given by  $\tau(t; \gamma_0)$  versus  $\gamma(t)$ , and corresponds to a limit cycle in the stress-strain plane. On the other hand, the energy dissipation coefficient along the trajectory of a stress-strain limit cycle is given by the path integral (Ewoldt *et al.*, 2010)

$$\varphi(\gamma_0) = \frac{\oint_H \tau(\omega t) d\gamma(\omega t)}{4\tau_{\max}\gamma_0} \quad (10)$$

Here,  $\tau_{\max}$  denotes the highest value of the stress values. The parameter  $\varphi(\gamma_0)$  can be seen as the ratio of the energy dissipated in one cycle ( $\oint_H \tau(\omega t) d\gamma(\omega t)$ ) relative to the energy dissipated if the response was purely elastic,  $4\tau_{\max}\gamma_0$ . Hence,  $\varphi(\gamma_0) = 0$  for purely elastic material, and  $\varphi(\gamma_0) = 1$  for purely plastic material. In general, one has that  $\varphi(\gamma_0)$  varies in the range (0,1).

The harmonic distortion (HD) provides an index of the nonlinearities affecting the viscoelastic system. The first harmonic mode in a given signal is given by (see Eq. (1))

$$\tau(t; \gamma_0)_{FH} = \gamma_0[G'_n(\gamma_0)\sin(\omega t) + G''_n(\gamma_0)\cos(\omega t)] \quad (11)$$

The harmonic distortion can be defined as follows:

$$HD(\gamma_0) = \frac{\int_0^T |\tau(t; \gamma_0) - \tau(t; \gamma_0)_{FH}| dt}{\int_0^T |\tau(t; \gamma_0)| dt} \quad (12)$$

where  $T = 2\pi/\omega$  is the base period of the harmonic oscillation. For linear mechanical response, one finds that  $\tau(t; \gamma_0) = \tau(t; \gamma_0)_{FH}$ , such that the harmonic distortion is  $HD(\gamma_0) = 0$ . In general, one has that  $HD(\gamma_0) \in (0, 1)$ .

### 2.6 Statistical analysis

All experiments were done in triplicate and the statistical analysis of was subjected to analysis of variance and Tukey's test using the Statgraphics 7 (Statistical Graphics Corp. Manugistics Inc., Cambridge, MA). The data were reported as means $\pm$ S.D.

## 3 Results and discussion

### 3.1 Linear viscoelasticity

Small amplitude oscillatory strains (SAOS) frequency sweeps provide information on linear viscoelasticity. Frequency sweeps of the CW/CO oleogels at the three different candelilla wax concentrations are shown in Figure 1. The presence of wax crystals is not necessarily sufficient to achieve oleogel formation. Leading researchers in the field (Toro-Vazquez *et al.*, 2007; Doan *et al.*, 2015) have shown that several factors are involved to obtain a wax-based oleogel. The wax ability to form a 3D crystalline network is at the heart of the oleogel formation. This requires a minimal wax concentration, which for candelilla wax is about 4-5 g/100 g (Toro-Vazquez *et al.*, 2011). It should be stressed that although important advances have been obtained, the mechanisms involved in the oleogel formation via waxes have not been completely elucidated. Novel techniques, such as small-angle x-ray (SAXS) scattering (Trujillo-Ramirez *et al.*, 2022) are increasingly explored in recent years. It has been postulated that the melted wax components (e.g., alkanes and esters) are homogeneously dispersed in the oily phase. Upon cooling, crystal growth extends in the oil bulk to form a fractal network with the ability to trap the dispersed phase (Doan *et al.*, 2015; Trujillo-Ramirez *et al.*, 2022). One has that  $G' > G''$  over the whole frequency range, indicating that the oleogels had a well-consolidated 3D network formed by the candelilla wax crystallization in the canola oil continuous phase (Toro-Vazquez *et al.*, 2007; Doan *et al.*, 2015). The storage modulus was about tenfold the loss modulus in all the frequency range.  $G'$  and  $G''$  values were practically constant up to about 0.04 Hz which was considered the upper limit of the linear viscoelastic region. The viscoelastic parameter became slightly frequency-dependent above 0.04 Hz, with the magnitude of moduli increasing as a fraction of candelilla wax in the oleogel increased, indicative that the further addition of wax crystals led to the formation of a stronger 3D network (Co and Marangoni, 2012). The weak dependence of the storage and loss moduli with the frequency indicates that the 3D network formed by CW crystals is structurally stable.

### 3.2 Strain amplitude sweeps

Strain amplitude sweep of the CW/CO oleogel samples was performed as a preliminary analysis for assessing LAOS analysis. The experimental results for three different CW concentrations are exhibited in Figure 2. The value of the storage and loss moduli was nearly constant for small strain amplitudes up to about 0.04%. In this way, the mechanical response of the oleogels was linear for small oscillatory disturbances below this strain% value. As already observed in the frequency sweeps in Figure 1,  $G' > G''$  which pinpoints the predominantly solid-like nature of the oleogels for small strain values. This effect can be ascribed to the consolidated 3D network induced by the crystallization process of the candelilla wax (Toro-Vazquez *et al.*, 2007; Co and Marangoni, 2012). The increase of the strain amplitude led to important variations in the storage and loss moduli. The storage modulus exhibited a monotonous decrease behavior, which suggests the disruption of the elastic characteristics of the oleogel structure. A sharp decay in the storage modulus occurred at a strain% of about 0.4 for the three candelilla wax fractions. In contrast, the behavior loss modulus was not monotonous, exhibiting a small bump (weak strain overshoot) for strain values of about 0.08-0.8%. Hyun *et al.* (2002) postulated that this behavior can be explained by the jamming of solid particles dispersed in the continuous phase, which do not align along the flow direction. Similar results were reported for semi-solid materials, like chili pastes where aggregation of particles was not discarded as a mechanism of rheological behavior (Medina-Torres *et al.*, 2021). For strain values above about 1% the decay of the storage modulus was greater than that of the loss modulus with a cross-over between the moduli occurring. The fast decay of the viscoelasticity moduli suggests a reorganization of the oleogels microstructure providing them with an enhanced fluidity, which in turn reflects a shear-thinning trend of the material for relatively high strain amplitudes. The transition from a solid-like (i.e.,  $G' > G''$ ) to a liquid-like (i.e.,  $G' < G''$ ) behavior occurred for strain values of about 3-8% for the three candelilla wax fractions. Overall, the behavior of the oscillatory storage and loss moduli for variations of the strain amplitude indicated the presence of nonlinear mechanisms governing the mechanical response of the CW/CO oleogels.

### 3.3 Temperature sweeps

Forward and backward temperature sweeps tests were conducted to assess the CW/CO oleogels melting/gelation pattern (Figure 3). In general, the temperature sweeps exhibited a continuous decrease in the storage and loss moduli during the heating process. This process suggests that the melting of the CW induces a continuous disassembling of the 3D network formed by CW wax crystals dispersed in the CO continuous phase (Toro-Vazquez *et al.*, 2007; Co and Marangoni, 2012; Doan *et al.*, 2015). Li (2002) showed that this behavior indicates a gelation mechanism that does not include the formation of secondary structures or conformational transitions, but only the formation of a 3D network with a certain order extent (i.e., negative entropy change). That is, wax-based gelling is an entropy-driven process where the CW fractions (e.g., alkanes and esters) undergo spontaneous solidification without the mediation of energy-requiring conformational adjustments of the molecular structure. The cooling (i.e., gelation) of the dispersion led to a continuous increase in the storage and loss moduli. However, the pattern was different from that shown in the melting process. The moduli remained nearly constant for decreasing temperatures up to 46-50 °C. At this temperature, a fast increase in the storage and loss moduli was observed, indicating the fast formation of the crystalline 3D network. The starting temperature for the gelation process (i.e., the sol-gel transition temperature) increased with the fraction of the CW, being 46 °C for 5% CW to about 51 °C for 7% CW. The gel point temperature, taken as the temperature where  $G' = G''$ , was practically unaffected by the fraction of CW. This temperature was about 42-43 °C for the three cases shown in Figure 3. This temperature indicates the consolidation of the oleogel microstructure to form a predominantly solid-like material.

### 3.4 High harmonic contribution

The application of a strain harmonic signal to the CW/CO oleogels led to a stress response signal containing high-harmonic components. The magnitude of such high-harmonic moduli can be taken as a measure of the nonlinearities affecting the viscoelasticity of the material. In this way, Figure 4.a presents the variation of the ratio  $I_{3/1}(\omega, \gamma_0)$  concerning the strain magnitude  $\gamma_0$  (see Eq. (3)). Commonly, this index is taken as a measure of high-harmonic deformation of response signals (Ewoldt *et*

*al.*, 2008). For small values of the strain, the index  $I_{3/1}(\omega, \gamma_0) \approx 0$ , indicates that the response stress signal was scarcely affected by nonlinear effects. That is, the viscoelastic response was linear for small strain amplitude values, up to approx. 0.5%, which is in line with the used practice of taking small strain amplitude values for assessing the linear mechanical response of oleogels (Zetzl *et al.*, 2014; Rogers *et al.*, 2014). Nonlinear effects were present for higher strain amplitude values, as expressed by a huge increase of the index  $I_{3/1}(\omega, \gamma_0)$ , which achieved values of approx. 0.8 for 5% CW, and 0.95 for 7% CW over the region 1-100% strain values. Interestingly, the index  $I_{3/1}(\omega, \gamma_0)$  decreased for higher strain amplitude values.  $I_{3/1}(\omega, \gamma_0)$  decreased to small values for strain values of 1000%. This suggests that the mechanical response of the oleogels was essentially linear for very large values of  $\gamma_0$ , an effect that can be attributed to the high fluidity of the oleogels induced by the disruption of the oleogel microstructure. On the other hand, the value of the index  $I_{3/1}(\omega, \gamma_0)$  increased with the CW fraction, meaning that increasing the dispersed crystalline phase would increase the strength of the nonlinear mechanisms involved in the viscoelasticity of the CW/CO oleogels. Jamming of particles and increased friction between solid particles could be involved in the increased nonlinearities as the crystalline fraction was increased.

The individual high-harmonic contributions to elastic and viscous effects were evaluated using the indices  $I'_{3/1}(\gamma_0)$  and  $I''_{3/1}(\gamma_0)$ , where

$$I'_{3/1}(\gamma_0) = |G'_3(\gamma_0)/G'_1(\omega, \gamma_0)| \quad (13a)$$

$$I''_{3/1}(\gamma_0) = |G''_3(\gamma_0)/G''_1(\omega, \gamma_0)| \quad (13b)$$

The results are shown in Figures 4.b and 4.c. The individual indices exhibited a pattern similar to that of the overall index in Figure 4.a. However, the high-harmonic contribution was more salient for elastic mechanisms. The maximum value of the storage index  $I'_{3/1}(\gamma_0)$  was in the range 0.8-0.9, while the maximum value of the viscous index was in the range 0.3-0.4. These results indicate that the elasticity had larger nonlinear contributions to the viscoelasticity of the CW/CO oleogels.

### 3.5 Strain-stiffness and shear-thickening ratios

Further information on the nonlinear viscoelasticity of the CW/CO oleogels were drawn from the strain-stiffness  $S(\gamma_0)$  and shear-thickening  $T(\gamma_0)$  ratios

(Figure 5). The index  $S(\gamma_0)$  exhibited positive values for strain amplitudes up to 100% for 5% CW, and about 30% for 6% and 7% CW. This means that the oleogels exhibited a strain-stiffening behavior for small and moderate strain amplitudes, a behavior commonly displayed by many soft biological materials (Storm *et al.*, 2005). For high strain amplitude values, the parameter  $S(\gamma_0)$  exhibited a sharp drop, showing small negative values. This shows that the stiffness of the oleogels became essentially linear for high strain amplitudes, in line with the results shown in Figure 4.

On the other hand, the parameter  $T(\gamma_0)$  showed negative values over the whole range of strain values, indicating that the viscous behavior was intra-cycle shear-thinning. This effect could be ascribed to the disruption of the 3D network by shear forces (Acevedo and Marangoni, 2010) and the alignment of CW crystals along the oscillatory flow direction (Hyun *et al.*, 2002). Interestingly, the behavior of  $T(\gamma_0)$  is non-monotonous, showing a maximum value at about 10-20% strain amplitude. That is, the more visible nonlinear effects in the viscous behavior of the CW/CO oleogels were displayed for moderate strain amplitude values near the crossover transition (see Figure 2). The effect was more noticeable and statistically significant ( $p < 0.05$ ) as the CW fraction was increased, an expected feature as an increased number of particles in a soft material would lead to jamming effects and increased particle-particle interactions.

### 3.6 Energy dissipation rate

Figure 6 presents the Lissajous curve geometry for the three scrutinized CW fractions (5, 6 and 7%). For small strain amplitudes, up to approx. 1%, the Lissajous curve exhibited a rectangular-like shape. In turn, this shape indicates that the oleogel microstructure is energetically capacitive, which is in line with the strain sweep tests where the storage modulus predominated over the loss modulus (i.e.,  $G' \gg G''$ ). Elasticity mechanisms were weaker as the strain amplitude was increased, and this effect is reflected by the shape of Lissajous curve for moderate (10%) and large (100%) strain amplitude values. The Lissajous curve in the transition region (about 10%) exhibited a convex meniscus, which is related to the transition from a solid-like material to a fluid-like material. The increased oleogel fluidity for large strain amplitude values (see Figure 5) led to Lissajous curves with an elliptic-like shape. In turn, this behavior is consistent with a viscoelastic fluid with dominant viscous (i.e., dissipation) effects (Ewoldt *et al.*, 2008).

The stress overshoot exhibited in the reversal points of the Lissajous curve could be attributed to yield stress effects in the mechanical response of the oleogel (Alvarez-Mitre *et al.*, 2012). As the strain oscillation was reversed, the yield of the oleogel microstructure induced a delay in the directionality of the stress response.

The parameter  $\varphi(\gamma_0)$  provides a way for quantifying the energy dissipation characteristics of the oleogel microstructure. Figure 7.a shows the behavior of  $\varphi(\gamma_0)$  for the strain amplitude  $\gamma_0$ , for the three different CW fractions. The rate of energy dissipation showed a decreasing trend for small strain amplitudes (up to 2-3%). Subsequently, the parameter  $\varphi(\gamma_0)$  presented a minimum at strain amplitude values of about 10-20%. Interestingly, the position of this minimum agrees with the crossover shown by the first-order viscoelasticity moduli (see Figure 2). The minimum energy dissipation rate implies that the nonlinear behavior observed in the transition from a solid-like behavior to a liquid-like behavior is linked to mechanisms linked to the storage and dissipation of mechanical energy, and not necessarily to the rearrangement of particles in the bulk of the oily continuous phase. It is suggested that the accumulation of mechanical energy led to the excitation of nonlinear oscillation moduli, in agreement with nonlinear resonance reported for mechanical systems (Vakakis and Gendelman, 2001). The further increase of the strain amplitude increased the rate of energy dissipation. The dissipation of mechanical energy is linked to frictional effects, which are strengthened with increased fluidity of the oleogel.

### 3.7 Harmonic distortion

The harmonic distortion  $HD(\gamma_0)$ , defined as in Eq. (12), is a further measure of nonlinear deviations from a purely harmonic behavior. Figure 7.b presents the variation of the harmonic distortion as a function of the strain amplitude. The value of  $HD(\gamma_0)$  was less than 10% for strain amplitudes up to 0.1%, signifying that the viscoelastic response was essentially linear. However, the harmonic distortion showed an important increase with the strain amplitude. The value of  $HD(\gamma_0)$  increased to achieve a maximum value (100-125%) for strain amplitudes in the range from 2% to 8%. For higher strain amplitudes, the harmonic distortion decreased to nearly zero values for strain amplitudes larger than 100%. This result corroborates the already discussed observation that CW/CO oleogels exhibit a linear viscoelastic

response for large deformations. In turn, such a feature is important in practice given that oleogels are commonly used as shortening agents (Mert and Demirkesen, 2016; Puşcaş *et al.*, 2020) for which uniform spreadability is a desirable characteristic. On the other hand, the harmonic distortion increased with the CW fraction, with maximum values of about 90% for 5% of CW, and about 125% for 7% of CW. That is, the nonlinear viscoelasticity mechanisms gained further importance as the amount of CW crystals increased. However, statistically significant differences ( $p < 0.05$ ) were not observed for moderate strain values, mainly for concentrations of 5 and 6%.

## Conclusions

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The use of large amplitude oscillatory shear (LAOS) rheology for characterizing the nonlinear mechanical response of CW/CO edible oleogels led to the following conclusions: a) Linear viscoelasticity response can be guaranteed for SAOS with strain amplitudes non-higher than about 0.04%. In this case, the mechanical response was predominantly harmonic, which implies that stress response can be described by linear models. b) Nonlinearities effects arise for moderate strain amplitude values, from 0.05% to 10%. Nonlinear effects were predominantly dominated by elasticity mechanisms, suggesting that large shear forces disrupted and possibly led to the breakage of the 3D network responsible for the oleogel stability. c) Strain stiffness was expressed as the dominant nonlinear characteristic of candelilla wax oleogels, which indicates that the oleogel response closely resembled that of melted plastic. d) The increase of candelilla wax concentration accentuated to the nonlinear viscoelastic response, an effect that might be ascribed to the formation of a more robust 3D network. Overall, the results in this work showed that the approach based on LAOS tests is viable for gaining insights into the nonlinear viscoelasticity of edible oleogels. Information obtained on the nonlinear nature of the oleogel viscoelasticity should lead to guidelines for improving the design of food structuring agents (e.g., shortening agents).

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