



Combined effect of shearing and cooling rate on the rheology of organogels developed by selected gelators



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ABSTRACT

In this study we investigated the combined effect of shearing and cooling rate in the rheology of organogels developed in high oleic safflower oil by (*R*)-12-hydroxystearic acid (HSA), its primary amide derivative [(*R*)-12-hydroxyoctadecanamide, HOA], and the *N*-octadecyl derivative of HOA [(*R*)-*N*-octadecyl-12-hydroxyoctadecanamide, OHOA]. The experimental set up to develop the organogels involved: 1). The use of quiescent (0 s^{-1}) or shearing (300, 600, and 1200 s^{-1}) conditions during cooling the gelator solutions (2%) just until achieving the gelator's melting temperature (T_M) in the vegetable oil, to then continuing the cooling under static conditions until achieving $15\text{ }^\circ\text{C}$. The use of cooling rate protocols involving a constant cooling rate of $1\text{ }^\circ\text{C}/\text{min}$ (CR_1) or $10\text{ }^\circ\text{C}/\text{min}$ (CR_{10}) in the shearing and static stages, or variable cooling rates in each stage (i.e., VR_{1-10} or VR_{10-1}). The elasticity of the organogels (G') was measured while cooling under static conditions, once the systems achieved $15\text{ }^\circ\text{C}$, and after 60 min at this temperature. The rheological results obtained at $15\text{ }^\circ\text{C}$ showed a cooling rate and molecular weight-dependent effect of shearing on G' . We propose that the molecular relaxation time of gelator molecules, and its increase as molecular weight increases and as temperature decreases, plays an important role on the gelator's susceptibility to go through a shear induced crystallization process. Therefore, high molecular weight molecules like OHOA (551.97 Da) would remain stretched by shearing longer times than HSA (300.49 Da) and HOA (299.49 Da). Thus, when shearing was applied while cooling at the higher cooling rate (i.e., CR_{10} and VR_{10-1}), the stretched OHOA molecules would lead to the development of mesophase precursors that upon further cooling under quiescent conditions, crystallize developing a well-structured organogel. In contrast, stretched low molecular weight molecules (i.e., HSA and HOA) with shorter relaxation time would dissolve back to the isotropic state during cooling. Additionally, the rheological results of HSA and HOA organogels suggested that the shear induced crystallization process might be dependent on the gelator polarity also. These results show that the application of shear and the extent of its application as temperature decreases until achieving T_M , have important implication on the self-assembly of gelator molecules, and therefore in the organization and rheology of the three-dimensional crystal network of the organogel.

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1. Introduction

Organogelation is a useful and novel alternative to structure vegetable oils without the use of *trans* and/or saturated fats, providing useful and novel functional properties to food systems (Co & Marangoni, 2012; Dassanayake, Kodali, & Ueno, 2011; Marangoni & Garti, 2011; Rogers et al., 2014), cosmetics (Morales, Gallardo, Clarés, & García, 2009), and drug delivery systems (Jibry, Sarwar, & Murdan, 2006). Through this technology, low molecular weight gelators (LMOG) self-assemble developing supramolecular structures that physically trap apolar solvents (i.e., vegetable oils), providing the liquid phase with structure and viscoelastic properties.

For food systems, the use of organogelation would allow a significant reduction of saturated fatty acids and the elimination of *trans*-fatty acids from food formulations, and subsequently from the diet. The formulation and production of *trans*-free food products are encouraged due to the well-established link of *trans* fats' consumption with higher risk of coronary heart disease and type II diabetes (Ascherio, Katan, Zock, Stampfer, & Willett, 1999; Risérus, Willett, & Hu, 2009; Salmerón et al., 2001). On the other hand, although the relationship of an intake rich in saturated fat to a higher risk for atherosclerotic cardiovascular disease is controversial (Siri-Tarino, Sun, Hu, & Krauss, 2010), the consumers' response has been to move away from products high in saturated fatty acids.

The variety of LMOG (molecular weight < 3000 Da) is extremely wide, i.e., cholesteryl anthraquinone derivatives, sterols, *n*-alkanes, lecithin, sorbitan monostearate, fatty acids, amines, amides. Nevertheless, the relationship between the molecular structure of an LMOG, its gelling

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capability, and the particular physical properties of its gels (i.e., rheological properties) is not evident a priori. This regardless different groups have conducted some systematic studies with the objective of providing insights into the factors that establish these relationships (Abraham et al., 2012; Mallia, George, Blair, & Weiss, 2009; Mallia & Weiss, 2014; Toro-Vazquez et al., 2013). Within this context we have previously established that the introduction of a primary or a secondary amide group into the *R* enantiopure form of the 12-hydroxystearic acid (HSA) molecule, resulted in the formation of LMOGs that crystallize in the vegetable oil as fibrillar or acicular spherulites (Toro-Vazquez et al., 2013). This, in contrast to HSA that crystallizes as fibers. Additionally, we observed that although the organogels formed by the primary and secondary amides show higher rheological properties than HSA organogels, its behavior had a significant cooling rate dependence. This rheological behavior was clearly associated with the effect of cooling rate on the spherulites size, and its subsequent effect in fiber interpenetration between vicinal spherulites (Toro-Vazquez et al., 2013). Nevertheless, in that study the organogels were developed under static conditions. Tailoring the gelator's capacity to structure the liquid apolar phase and the resulting organogels physical properties (i.e., melting temperature, viscoelasticity, and thixotropic behavior), requires the understanding of the effect of external thermodynamic and mass transfer conditions on the gelation of well-defined gelator chemical structures.

Adjusting the thermodynamic driving force to achieve nucleation and crystal growth (i.e., supercooling) is an efficient alternative to modify the rheological properties of soft materials like organogels (Li & Liu, 2010; Wang, Liu, Xiong, & Li, 2006; Yuan, Liu, Li, & Xu, 2011). Through the application of different extent of supercooling, the nucleation and crystal growth rate of gelators, and also the growth mechanism (i.e., fibers or spherulitic) might be modified. Consequently, the micro-topology of the crystal network in the organogel, e.g., from a multi-domain network with mutually exclusive spherulites into interconnecting fibrillar network, can be modified through supercooling (Wang et al., 2006; Yuan et al., 2011). On the other hand, experiments done in our laboratory showed that the application of a continuous shear (i.e., 600 s^{-1}) during organogelation of candelilla wax in safflower oil, resulted in the formation of a sol-type system in contrast with gels developed under quiescent conditions (Chopin-Doroteo et al., 2011). Similar results had been observed when shear rates between 50 and 2000 s^{-1} were applied to 5% monoglyceride solutions in vegetable oil (Da Pieve, Calligaris, Co, Nicoli, & Marangoni, 2010), the development of 2% and 8% monoglyceride organogels in canola oil applying 100 rpm (using an overhead mechanical stirrer) just for 1 min at $40\text{ }^{\circ}\text{C}$ (Lopez-Martinez, Charó-Alonso, Marangoni, & Toro-Vazquez, 2015), and in the development of 2.5% HSA canola oil organogels with the application of continuous oscillatory shear (Co & Marangoni, 2013). In contrast, applying shear (i.e., 600 s^{-1}) during cooling of 3% CW solutions in safflower oil just until achieving $52\text{ }^{\circ}\text{C}$ (i.e., a temperature above the crystallization and melting temperature for CW in the vegetable oil), and then allowing the organogel to form under static conditions at $5\text{ }^{\circ}\text{C}$, resulted in enhanced nucleation and crystal growth (Alvarez-Mitre, Morales-Rueda, Dibildox-Alvarado, Charó-Alonso, & Toro-Vazquez, 2012). These organogels showed higher rheological properties compared with the organogels developed under quiescent conditions or with the application of continuous shear. This was explained considering that the application of shearing just until achieving metastable conditions, enhanced nucleation through the development of flow-induced liquid structures. Tentatively, this enabled the formation of permanent (i.e., branching) and transient junction zones among crystals favoring the development of a viscoelastic three-dimensional crystal network (Alvarez-Mitre et al., 2012). Based on these results we hypothesized that the use of shear and the extent of its application as temperature decreases (i.e., supercooling increases) have important implication on the self-assembly of gelator molecules, and

therefore in the organization of the three-dimensional crystal network of the organogel.

Within this framework, our primary objective was to investigate the combined effect of shearing ($0, 300, 600,$ and 1200 s^{-1}) and cooling rates ($1\text{ }^{\circ}\text{C}/\text{min}$ and $10\text{ }^{\circ}\text{C}/\text{min}$) on the rheological properties of organogels developed in safflower oil by selected gelator molecules. The gelators investigated were HSA, (*R*)-12-hydroxyoctadecanamide (HOA) and (*R*)-*N*-octadecyl-12-hydroxyoctadecanamide (OHOA). The HOA and OHOA were obtained by systematic modification of the parent molecule, to study how these chemical modifications alter their gelation ability as affected by the external conditions applied. Thus, HOA is the corresponding primary amide of HSA, and OHOA (i.e., a secondary amide) is the *N*-octadecyl derivative of HOA (Fig. 1).

HSA is a very efficient gelator of a variety of apolar liquids including vegetable oil (Co & Marangoni, 2013; Marangoni & Garti, 2011), widely available in large quantities in the *R* enantiopure form from hydrogenation of castor oil (Maskaev et al., 1971; Terech, Pasquier, Bordas, & Rossat, 2000; Terech, Rodriguez, Barnes, & McKenna, 1994). Given the gelling properties and simplicity of the molecule, HSA provides a useful structural platform from which a variety of derivatives can be made easily, some with gelling properties in apolar liquids like HOA and OHOA (Mallia et al., 2009; Toro-Vazquez et al., 2013). Then, these gelators provide a useful set of molecules to study the relationship between the molecular structure of LMOG's, and the effect of shearing and cooling rate (i.e., supercooling) on the rheological properties of organogels. To develop the organogels, shearing was applied during cooling of the gelator solutions (2% wt/wt) from their isotropic phase just until achieving a temperature nearby the melting temperature of the gelator in the vegetable oil. Then, cooling was continued under static conditions until achieving $15\text{ }^{\circ}\text{C}$.

2. Materials and methods

2.1. Materials

We obtained high oleic safflower oil from a local manufacturer (Coral Internacional, San Luis Potosí, Mex.). As determined by HPLC the major triacylglycerides (TAGS) in the vegetable oil were OOO ($65.65\% \pm 0.15\%$), LOO ($16.26\% \pm 0.04$), and POO ($8.58\% \pm 0.04$), and as minor TAGS: StOO ($2.64\% \pm 0.01\%$), LLO ($2.25\% \pm 0.02\%$), POL ($1.70\% \pm 0.11$), StLL ($0.87\% \pm 0.05\%$), and LLL ($0.46\% \pm 0.01\%$) (O = oleic acid; L = linoleic acid; St = stearic acid; P = palmitic acid). The *R* enantiopure form of 12-hydroxystearic acid (CAS: 106-14-9) was obtained from Sigma-Aldrich Company (St. Louis, MO, USA) with a purity of 99% and was used as received. The primary amide, (*R*)-12-hydroxyoctadecanamide (HOA), and secondary amide, (*R*)-*N*-octadecyl-12-hydroxyoctadecanamide (OHOA), utilized as gelators were synthesized from the 12-HSA following slight modifications of the methodology described by Mallia et al. (2009). The melting point of the HOA was $112.65\text{ }^{\circ}\text{C}$, and for OHOA $107.54\text{ }^{\circ}\text{C}$. The infrared spectrum (diamond) for the gelators showed bands at the following wave numbers (cm^{-1}), HOA: 3409, 3302, 3210, 2914, 2848, 1652, 1617, 1470, 1416, and OHOA: 3323, 2917, 2948, 1634, 1563, 1466, and 1373. The mass spectrometry spectrum, obtained with a gas chromatographer (Agilent Technology, model 6890) coupled with a selective mass detector (Agilent Technology model MS 5973N) and a DB-5HT capillary column showed a purity above the 99.5%.

2.2. Crystallization and melting profiles of the neat gelators and gelator solutions

The crystallization and melting profiles of the neat and 2% solutions (wt/wt in the vegetable oil) of HSA, HOA, and OHOA were determined using a DSC Q1000 from TA Instruments (New Castle, DL, USA). A sample (2–8 mg) of the neat gelators or their solutions was sealed in aluminum hermetic pans, heated up to a temperature $10\text{ }^{\circ}\text{C}$ to $15\text{ }^{\circ}\text{C}$ above the

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