



Influence of ethyl cellulose in a multicomponent mixture (sorbitan monopalmitate-vegetable oils) on physicochemical properties of organogels

Influencia de etilcelulosa en una mezcla multicomponente (monopalmitato de sorbitan-aceites vegetales) sobre las propiedades fisicoquímicas de organogeles

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Received: August 22, 2019; Accepted: November 14, 2019

Abstract

The modification of vegetable oils from liquid to solid state gel type is achieved by organogelation, where the first phenomenon experienced is nucleation that can be spectrophotometrically evaluated and obtain thermodynamic properties. The objective of this work was to evaluate the solid formation from nucleation to macroscopic properties of the mixture: sorbitan monopalmitate and ethyl cellulose in canola, olive and coconut vegetable oils. Nucleation kinetics, solid growth analysis, oscillatory rheology characterization, thermal properties by differential scanning calorimetry and microstructural formation by optical microscopy were evaluated. Non-isothermal nucleation kinetics indicated short induction times for canola and prolonged ones for coconut. The inclusion of ethyl cellulose involved a more compact solid formation in the systems without modifying the growth parameters, the coconut organogel was more sensitive to thermal changes. Non-isothermal nucleation kinetics are useful for determining the thermodynamic properties of organogels and the closest to thermodynamic equilibrium, being decisive the inclusion of ethyl cellulose, which does not influence formation speed and solid growth. The multicomponent gels obtained showed that the structural differences depend on the concentration of the mixture that includes ethyl cellulose, presenting more compact structures and thereby more resistant gels.

Keywords: Nucleation, organogelation, ethyl cellulose, vegetable oils.

Resumen

La modificación de aceites vegetales de estado líquido a sólido tipo gel, se logra por organogelación, el primer fenómeno experimentado es la nucleación que puede evaluarse espectrofotométricamente y obtener propiedades termodinámicas. El objetivo de este trabajo fue evaluar la formación sólida desde nucleación hasta propiedades macroscópicas de la mezcla: monopalmitato de sorbitan y etilcelulosa en aceites vegetales de canola, oliva y coco. Se evaluaron cinéticas de nucleación, análisis de crecimiento sólido, caracterización por reología oscilatoria, propiedades térmicas por calorimetría diferencial de barrido y formación microestructural por microscopía óptica. Las cinéticas de nucleación no isotérmica indicaron tiempos de inducción cortos para canola y tiempos prolongados en coco. La inclusión de etilcelulosa involucró una formación sólida más compacta en los sistemas, sin modificar los parámetros de crecimiento el organogel de coco resultó más sensible a cambios térmicos. Las cinéticas de nucleación no isotérmica son útiles para establecer las propiedades termodinámicas de organogeles y el más cercano al equilibrio termodinámico, siendo determinante la inclusión de etilcelulosa; misma que no influye en velocidad de formación y crecimiento sólido. Los geles obtenidos mostraron que las diferencias estructurales dependen de la concentración de la mezcla que incluye etilcelulosa, presentando estructuras más compactas y geles más resistentes.

Palabras clave: Nucleación, organogelación, etilcelulosa, aceites vegetales.

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Tel. 52- 618-8186936 ext 111
<https://doi.org/10.24275/rmiq/Alim801>
issn-e: 2395-8472

1 Introduction

The organogels are defined as semi-solid materials resulting from the immobilization of an organic liquid in a three-dimensional network formed by a gelling or structuring agent (organogelator) that is randomly entangled in the form of fiber or platelet (Toro-Vazquez *et al.*, 2013).

The conversion of oils into gels generally involves altering the chemical characteristics of the liquid, (Daniel and Rajasekharan, 2003). The organic liquids involved in the elaboration of organogels have specific characteristics, such as their chemical composition. Several vegetable oils have been used to obtain organogels, for instance canola oil is a vegetable oil that contains 7.49% saturated fatty acids (SFA) and 92.51% of polyunsaturated fatty acids (PUFA) (Kim *et al.*, 2014); olive oil, 13.29% of SFA, 81.28% of monounsaturated fatty acids (MUFA) and 5.43% of PUFA (Utrilla *et al.*, 2014); and coconut oil than

contains 93.33% of SFA, 5.33% of MUFA and 2% of PUFA (USDA, 2018). These vegetable oils are an example of oils with different saturated and unsaturated fatty acid levels, whose function is to act as solvents.

Most supramolecular gels consist of two parts, namely the solvent and the gelator, however, the concept of multi-component supramolecular gels, in which more than one component is added to the solvent, offers a facile way (e.g., by changing the ratio of the different components) to tailor the properties of the gel. The simplest multi-component gels consist of two components added to the solvent and are the most widely studied to date (Buerkle and Rowan, 2012). Solvent-gelator interactions play a key role in mediating organogel formation, which determines the macroscopic properties of the gel (Zhu and Dordick, 2006).

An ideal gel has an almost pure elastic response behavior. The elastic modulus should be much higher than the viscous modulus and independent of frequency.

Table 1. Fatty acids composition of the vegetable oils.

Fatty Acid	Canola %	Olive %	Coconut %
C6:0	-	-	0.23±0.00 ^a
C8:0	-	-	4.04±0.01 ^a
C10:0	-	-	4.02±0.02 ^a
C12:0	-	-	38.76±0.13 ^a
C14:0	0.04±0.00 ^b	-	17.96±0.07 ^a
C16:0	4.06±0.00 ^c	10.55±0.01 ^b	14.13±0.10 ^a
C16:1	0.20±0.00 ^b	0.78±0.01 ^a	0.13±0.00 ^c
C17:0	0.02±0.03 ^c	0.06±0.00 ^b	0.09±0.00 ^a
C17:1	0.14±0.00 ^a	0.10±0.00 ^b	-
C18:0	1.78±0.00 ^c	3.48±0.03 ^b	4.53±0.05 ^a
C:18:1 TRANS	-	-	0.38±0.01
C:18:1 CIS	59.76±0.05 ^b	77.14±0.05 ^a	12.47±0.31 ^c
C:18:2 TRANS	3.24±0.00 ^a	1.90±0.00 ^b	
C18:2 CIS	19.23±0.05 ^a	4.51±0.04 ^b	
C18:3	9.05±0.06 ^a	0.68±0.01 ^c	2.92±0.06 ^b
C:20	0.61±0.00 ^a	0.41±0.00 ^b	0.13±0.00 ^c
C:20:1	1.23±0.00 ^a	0.24±0.00 ^b	0.06±0.00 ^c
C:20:2	0.06±0.00 ^a	-	-
C22:0	0.33±0.00 ^a	0.11±0.00 ^b	-
ΣSFA	6.87±0.05 ^c	14.66±0.01 ^b	83.94±0.40 ^a
ΣMUFA	61.35±0.05 ^b	78.27±0.03 ^a	13.05±0.33 ^c
ΣPUFA	31.77±0.11 ^a	7.10±0.05 ^b	2.99±0.06 ^c
Σ Total	100	100	100

Abbreviations SFA: saturated fatty acids; MUFA: monounsaturated fatty acids; PUFA: polyunsaturated fatty acids.

Table 2. Kinetic and thermodynamic parameters of organogels obtained through non-isothermal nucleation adapted to the Fisher-Turnbull model.

Organogel	EC%-SMP%	t_i (min)	T_i (°C)	$\Delta T(T_m - T_n)$	J (min ⁻¹)	ΔG_n (J/nucleus)
Canola	0-10	15.29±0.05 ^c	37.5±0.70 ^a	42.5±0.70 ^b	0.0654±0.00 ^a	-2.27E-26± 4.08E-27 ^a
	0-12	15.41±1.53 ^c	31.0±1.41 ^b	49.0±1.41 ^a	0.0651±0.00 ^a	-2.32E-26± 3.49E-27 ^a
	4-10	19.74±0.12 ^b	35.5±2.12 ^{ab}	44.50±2.12 ^{ab}	0.0506±0.00 ^b	-1.75E-26±1.52E-27 ^a
	4-12	19.43±0.31 ^b	37.5±0.70 ^a	42.50±0.70 ^b	0.0514±0.00 ^b	-1.76E-26±8.70E-27 ^a
	8-10	22.58±0.01 ^{ab}	36.5±0.70 ^a	43.50±0.70 ^b	0.0448±0.00 ^b	-1.26E-26±1.09 E-27 ^a
	8-12	20.58±0.11 ^a	39.5±0.70 ^a	40.50±0.70 ^b	0.0485±0.00 ^b	-1.16E-26±1.14E-27 ^a
Olive	0-10	18.41±0.11 ^a	32.0±0.00 ^{cd}	48.0±0.00 ^{ab}	0.0542±0.00 ^b	-4.53E-26±7.67E-27 ^a
	0-12	15.51±0.49 ^{ab}	29.5±0.70 ^d	50.5±0.70 ^a	0.0645±0.00 ^{ab}	-3.73E-26±7.35E-27 ^a
	4-10	17.58±0.11 ^{ab}	33.5±0.70 ^{bc}	46.50±0.70 ^{bc}	0.0568±0.00 ^{ab}	-1.84E-26±1.45E-27 ^a
	4-12	16.91±1.76 ^{ab}	38.5±0.70 ^a	41.50±0.70 ^d	0.0594±0.00 ^{ab}	-1.80E-26±3.58E-28 ^a
	8-10	18.50±0.00 ^a	33.5±0.70 ^{bc}	46.50±0.70 ^{bc}	0.0540±0.00 ^b	-2.98E-26±9.27E-27 ^a
	8-12	14.83±0.70 ^b	35.5±0.70 ^b	44.50±0.70 ^c	0.0675±0.00 ^a	-2.26E-26±1.31E-27 ^a
Coconut	0-10	17.66±2.35 ^{cd}	35.5±2.12 ^a	44.5±2.12 ^a	0.0571±0.00 ^{ab}	-3.74E-26±3.38E-26 ^a
	0-12	16.91±0.35 ^d	30.0±0.00 ^a	50.0±0.00 ^a	0.0591±0.00 ^a	-3.57E-26±3.06E-26 ^a
	4-10	23.83±0.46 ^a	31.5±2.12 ^a	48.50±2.12 ^a	0.0419±0.00 ^c	-1.75E-26±5.54E-28 ^a
	4-12	19.41±0.35 ^{bcd}	35.0±1.41 ^a	45.00±1.41 ^a	0.0515±0.00 ^{abc}	-1.52E-26±5.94E-28 ^a
	8-10	22.41±0.12 ^{ab}	30.5±0.70 ^a	49.50±0.70 ^a	0.0447±0.00 ^{bc}	-1.46E-26±4.23E-27 ^a
	8-12	21.58±0.35 ^{abc}	34.5±0.70 ^a	45.50±0.70 ^a	0.0468±0.00 ^{abc}	-1.46E-26±3.98E-27 ^a

Abbreviations: sorbitan monopalmitate (SMP), ethyl cellulose (EC), induction time (t_i), nucleation rate (J), nucleation-free energy change (ΔG_n).

However, when gel networks are formed with imperfections, the response of the polymer gel depends on frequency, i.e., both the storage and loss moduli increase with frequency. The polymer gel can be tested at various time scales by using the oscillation mode in rheological experiments. At low frequencies, both the gel and polymer solution are rearranging by the Brownian motion. Thus, the measured properties are dominated by the elastic deformation equilibrium of the gel network (Zhang *et al.*, 2018). Numerous oleogelator systems have now been identified with great promise for mimicking the physical characteristics of traditional fats, and several of these systems have also shown to be effective fat replacers in certain food systems. However, the range of physical properties, which can be achieved using oleogelators, are often fairly limited due to either the nature of the gelator or the process/conditions necessary to achieve gelation. In this regard, ethyl cellulose (EC) offers a unique set of physical and chemical properties as an oil-structuring agent, allowing the resulting oleogels to be used in a wide variety of applications. More specifically, the polymeric nature of EC produces gels with unique properties that can be tuned and altered to specific requirements (Davidovich-Pinhas *et al.*, 2016). Ethyl

cellulose has the ability to modify the crystallization behavior of a low molecular weight oleogelator, while increasing the plasticity of the polymer network, to form a synergistic oleogelator system (Gravelle *et al.*, 2017).

The gelation process that involves EC and gel properties are similar to those of polymer hydrogels, being the nature of the solvent the main difference (Gravelle *et al.*, 2016). The EC has a semicrystalline structure with crystalline domains within an amorphous background (Davidovich-Pinhas *et al.*, 2014a), therefore, this characteristic is important because the self-assembly of crystalline particles or fibrils are created from a low molecular weight gelator (Garti and Marangoni, 2011).

The gelation of edible oils using EC is achieved by dispersing the polymer in the liquid oil and heating above the glass transition temperature of EC. This temperature is approximately 140 °C, but it has been found to depend on the polymer molecular weight (Davidovich-Pinhas, *et al.*, 2014b). The gelation mechanism and gel structure of EC-based oleogels are not fully understood and therefore, it is not easy to explain the origin of this behavior (Davidovich-Pinhas *et al.*, 2014a). Additionally, these types of gels arise upon the formation of non-covalent junction

zones, and are thus termed ‘physical’ gels. Physical gels are characterized by a unique network behavior arising from the nature of the junction zones, which can fluctuate in size, number, position, and time, and are also strongly affected by environmental conditions. Such systems exhibit interesting gelation kinetics, which never achieves a final equilibrium state due to secondary chain extension, formation or breaking of junction zones, and rearrangement or stacking of the already formed junction zones (Lefebvre and Doublier, 1998).

Eventually, depending on the proper interaction between solute-solute and solvent-solute, the gelation (Patel, 2017) and the existence of larger assemblies occur as a result of the increase in hydrophobic interactions (Sánchez-Juárez *et al.*, 2019). The phenomena of the formation of fat crystal networks are similar to the colloidal gel formation (Sciortino *et al.*, 2005; Lu and Weitz, 2013). Those primary particles assemble together to form aggregates, which leads to the formation of a complex network of particles in the solution. Similarly, in the formation of organogels as in the case of fat crystallization, the nucleation starts either because of the mass transfer or heat transfer in the system, where the stable nuclei start to form through aggregation of crystallites. The growth of primary particles occurs until they attach to each other, which ultimately lead to the complex cluster formation that is dispersed into the liquid oil (Joshi *et al.*, 2018). Gelator combinations may modify the structural arrangements of the gel network, which could thus influence the functional properties of the bulk material. Polymer gelators may be particularly amenable to this strategy, as plasticizing agents are regularly used to manipulate the intermolecular junction zones of such networks. In a recent study, it was investigated the effect of incorporating the polymer oleogelator ethyl cellulose into a structured oleogel with a 7:3 mixture of stearyl alcohol (SO) and stearic acid (SA); the addition of EC reduces the brittleness and increases the plasticity of the bulk material, demonstrating the ability of EC to modify the crystallization behavior of a low molecular weight oleogelator (Gravelle *et al.* 2017). The use of surface active molecules as sorbitan monopalmitate (hydrophobic non-ionic molecule) could be favorable to the ethyl cellulose gels systems because it may form solid fiber matrix in non polar solvents under cooling (Kantaria *et al.*, 1999).

Davidovich-Pinhas *et al.* (2015) have characterized the effects of surfactant addition on the mechanical strength of ethyl cellulose/canola oil

oleogels in order to examine the role of both the “head” and “tail” groups on the final gel properties. They observed that the interaction behavior could arise from an additional organized structure formation in the presence of surfactant molecules, which can self-assemble due to their amphiphilic nature. The presence of surface-active species such as high-melting monoglycerides assists in promoting the nucleation by forming stable nuclei, which can act as a template for other TAG molecules to grow on. The segregated crystalline phase thus formed organizes into flocs, which are linked together via weak forces to form a continuous network (Patel, 2015). Consequently, the objective of this work was to relate the influence of the conditions of formation of the first solid nucleus with the macroscopic properties of the material (rheological and thermal) in a multicomponent mixture using edible oils (canola, olive and coconut), sorbitan monopalmitate, with and without ethyl cellulose.

2 Materials and methods

2.1 Materials

Sorbitan monopalmitate (SMP) and ethyl cellulose (EC) at viscosity 10 cP, molecular weight 28.6 Kda, 5% in toluene/ethanol 80:20 v/v and 48% ethoxyl, were obtained from Sigma Aldrich (St. Louis MO., USA), and three vegetable oils (canola, olive and coconut) were bought at local supermarket of Durango (Durango, Mexico), stored at (20 °C) until use.

2.2 Methods

2.2.1 Fatty acid profile determination

Methylation of the fatty acids in vegetable oils was performed as described (AOAC 969.33 method), analyzed by gas chromatography using a Hewlett Packard 6890 Series (Palo Alto, CA, USA) with a flame ionization detector (FID) and an auto-sampler 6890 m and Supelco SP2560 capillary column (100 m × 0.25 mm). Temperatures of the injection port was maintained at 250 °C and at the detector was maintained at 300 °C. The identification of fatty acids was performed according to the retention time, and the elution pattern showed the FAME standards (Supelco 37 FAME mix). The quantification was performed by integrating the area under the curve of peaks and was expressed as the percentage of

total fatty acid present in the sample. Additionally, the amounts of saturated fatty acids (SFAs), mono-unsaturated fatty acids (MUFAs), and polyunsaturated fatty acids (PUFAs) were calculated.

2.2.2 Preparation of organogels

Organogels with EC were obtained as follows: oils were heated to 140 °C and separately EC was added up to 4 and 8% (w/w); the mixture was stirred for 10 min, and allowed to cool at 80 °C to add SMP up to 10 and 12% (w/w) for each concentration of EC, remaining under stirring during 20 min. Organogels without EC were only heated to 80 °C and the SMP was added at 10 and 12% and kept that way for 20 min, after all the samples were placed in glass tubes and stored 24h at 5 °C.

2.2.3 Non-isothermal nucleation kinetics

Kinetics of non-isothermal nucleation of organogels was performed in a Jenway 6705 spectrophotometer (OSA, UK), controlling the temperature with a Techian water bath (OSA, UK), starting at 80 °C up to approx. 18 °C. Before starting the kinetics the sample was maintained at 80 °C for 20 min. After this time the measurement started in the spectrophotometer from 80 °C, generating a temperature differential ($\Delta T/\Delta t$) induced by the water bath and measuring the 550 nm absorbance every 10s for 60 min (Toro-Vazquez and Gallegos-Infante, 1996; Terech *et al.*, 2000). The induction time of nucleation (t_i), nucleation rate (J) and nucleation free energy (ΔG_n) were determined by the use of Fischer-Turnbull model already described (Rogers and Marangoni, 2009) as follows:

$$J = \frac{1}{ti} \quad (1)$$

The cooling rate (ϕ) as the temperature change ratio $\Delta T(T_0 - T_i)$ with respect to the change in time (i.e., $\Delta t = (t_0 - t_i)$)

$$\phi = \frac{\Delta T}{\Delta t} \quad (2)$$

The determination of effective supercooling (β), which incorporates a thermodynamic component: supercooling in nucleation (ΔT_c) and a kinetic component in the form of a non-isothermal nucleation induction time (ϕ)

$$\beta = \frac{\Delta T_c}{\sqrt{2\phi}} \quad (3)$$

The determination of the previous time-dependent supercooling parameters finally provides the nucleation-free energy

$$\Delta G_n = \frac{mk\beta}{(\Delta T)^2} \quad (4)$$

2.2.4 Modeling and analysis according to the Avrami equation

The Johnson-Mehl-Avrami equation was used to modelling the spectrophotometrical data by the use of following equation:

$$q(t) = \exp(-k * t^N) \quad (5)$$

This is known as the Avrami equation, where (N) is the exponent of Avrami, (k) is an associated constant with the global phase transition speed, (t) the time and $q(t)$ is the fraction without crystallizing at the time (t) (Avrami, 1939). An integer value of N represents the formation of bar-shaped crystals (1-D), disc-shaped crystals (two-dimensional 2-D) and spherical crystals (3-D), respectively. A non-integer value indicates the formation of irregularly shaped crystals. The parameters N and K were determined through a non-linear regression by the use of Rosenbrock and Quasi-Newton method into Statistica software, v 12.0 (StatSoft, OK, 2013). The model was tested for each processing condition of the organogels.

2.2.5 Polarized light microscopy

Micrographs of organogels were obtained through an AxioLab Carl Zeiss polarized light optical microscope (Champaign, IL) equipped with a color digital video camera (AxioCam ERC 55). The obtained images were analyzed by Zen 2.3 Lite image software (Germany). Samples of gels were placed prior to analysis and tested at room temperature (25 °C) on the glass slide, obtaining micrographs on the 40X lens and magnification 400X of the samples under all processing conditions.

2.2.6 Rheological tests

Dynamic rheology test was performed with a controlled strain rheometer Discovery Hybrid Rheometer 3 (TA Instruments, USA) equipped with parallel plate geometry (diameter 40 mm and gap 1500 μ m) with a Peltier system for the thermal control of the sample. Preliminary strain sweep tests were carried out to determine the linear viscoelastic regime (LVR): in this region a frequency sweep test was

performed in the frequency range $0.01\text{--}100\text{ rad s}^{-1}$ at $25\text{ }^{\circ}\text{C}$, and a temperature sweep in the range of $18\text{--}90\text{ }^{\circ}\text{C}$ and $90\text{--}18\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C min}^{-1}$. Each sample was prepared independently and the results presented are the average values of the rheological properties measured for each one.

2.2.7 Differential Scanning Calorimetry (DSC)

The thermal properties of the organogels were measured with a TA Instruments Differential Scanning Calorimetry (DSC), Model Q2000 with a refrigerated cooling system RCS90 (New Castle, DE, USA). The instrument was calibrated with indium, 8–10 mg of organogel samples were weighted into aluminum pans and sealed hermetically. A heating cycle was performed ($8\text{ to }80\text{ }^{\circ}\text{C}$, at $10\text{ }^{\circ}\text{C min}^{-1}$). Thermograms were analyzed with the software provided with the equipment. Analyses were performed in two replicates.

2.2.8 Statistical analysis

All experiments were performed by two replicates and data analyzed by standard statistics methods ANOVA in the software Statistica (Data Analysis Software system, StatSoft, Inc, Tulsa – USA) v.7.

3 Results and discussion

3.1 Non-isothermal nucleation kinetics

Data obtained into the non-isothermal kinetics experiments are shown in Figure 1. Nucleation start is defined as the point at which curves rise from the base line, this time was shorter in the canola organogel, followed by olive and coconut. However, the inclusion of the EC polymer in the mixture showed a differentiated nucleation mechanism that involved longer times to carry out the nucleation, influencing the different triglyceride mixtures present in the oils. Specifically, the content of saturated fatty acids in the oils, canola ($6.87\pm0.05\%$), olive ($14.66\pm0.01\%$) and coconut ($83.94\pm0.40\%$) have influenced longer induction times, as well as the available interactions of the gelling molecule and the lipid. Thus, oil polarity and unsaturation degree exert effect on its ability to form H-bonds with organogelator molecules (Gravelle *et al.*, 2016). They showed that increase concentration of EC, leads to a organogels' assembly with low degree of self-supported crystalline structure (Figure

2). This result is opposite to reported by Cerqueira *et al.* (2017). This can be explained from the fact that EC forms a hydrogen bond stabilized polymer network in the oil, however the presence of SPM inhibits the interaction between EC and oil, diminishing the hydrogen bond and alter the balance between polymer-solvent and polymer-polymer interactions in the system plays a major role on the network structure and gel properties (Davidovich-Pinhas *et al.*, 2015).

The parameter of thermodynamic guiding force (ΔT) is the difference between the equilibrium melting temperature of the material (T_m) and the nucleation temperature (T_n). This difference of temperature (i.e., $T_m - T_n$) induces major mobility in canola oil in comparison to coconut and olive oils. However, it is not sufficient for the generation of the first solid core despite having the greatest molecular movement impulse; although the temperature differential is larger by including the EC in the mixture, it originated the largest number of nuclei per minute (J) in organogels with olive oil.

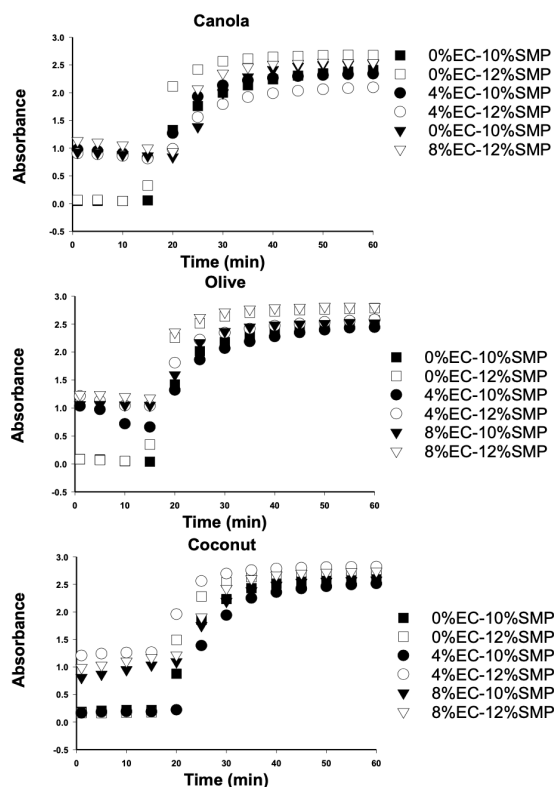


Fig. 1. Change in solid content as a function of time for the non-isothermal.

Coconut oil begins the formation of nuclei at a longer time, propitiating an explanation related to the majority composition of saturated fatty acids $83.94 \pm 0.40\%$ given that the triacylglycerols often crystallize in one of the metastable states because they have lower activation energy of nuclei formation. At the molecular level, the more saturated and uniform are the TAGs, more stable is the polymorphic form formed upon nucleation, while the presence of a kink such as cis-unsaturated fatty acids results in the formation of less stable polymorphic forms (Grotenhuis *et al.*, 1999; Cisneros *et al.*, 2006).

3.2 Modeling and analysis according to the Avrami equation

Parameters of Avrami model are shown into the Table 3. Organogels made with olive oil and higher concentration of EC and SMP showed high k value. According to results shown in table 3, the parameter (N) of the Avrami model predicts a 1D growth in the organogels assuming a formation from sporadic nuclei (e.g., needles, bars) because the number of nuclei increases linearly with time at all processing conditions of organogels. Although N should be an integer, fractional values are usually obtained, even in cases where the model fits well. Deviations

from integer values for N have been explained as simultaneous development of two or more types of crystals, or similar crystals from different types of nuclei (i.e., sporadic vs. instantaneous). At all tested conditions, organogels displayed the same behavior with good fitting to the Avrami model and non-integer values, independently of the type of oil and type of mixture. An exception was the condition involving coconut oil and EC4% -SMP10% with N value of 2.68 ± 0.71 that could indicate differences in crystal growth geometry and the type of nucleation, because it is a function of the number of dimension in which growth take place, reflecting the details of fat crystal nucleation and growth mechanism (Cristian, 1975). Despite the good fit of the Avrami model, this value is contrary to the morphology shown in the micrography, where N value resembles a plastic fat, since it is greater than 2, attributable probably to the presence of coconut oil showing an order similar to the packing of a plastic grease, which may lead to a granular microstructure composed of a large number of small and more dense crystals.

Generally, low values of N and high values of k are associated with an increased rate of crystallization and a more instantaneous nucleation process with shorter induction times, which in turn, would yield smaller and more numerous crystals (Meng *et al.*, 2014).

Table 3. Parameters of rate and crystal growth in organogels from the Avrami model.

Organogel	EC%- MPS%	k (min^{-1})	N	R^2
Canola	0-10	0.0001295 ± 0.00^a	1.27 ± 0.01^a	0.99
	0-12	0.0001316 ± 0.00^a	1.30 ± 0.02^a	0.96
	4-10	0.0154787 ± 0.01^a	1.46 ± 0.07^a	0.98
	4-12	0.0101120 ± 0.01^a	1.71 ± 0.42^a	0.98
	8-10	0.0022822 ± 0.00^a	1.94 ± 0.01^a	0.98
	8-12	0.0278446 ± 0.02^a	1.33 ± 0.17^a	0.95
Olive	0-10	0.0056292 ± 0.00^b	1.65 ± 0.10^a	0.98
	0-12	0.0001316 ± 0.00^b	1.46 ± 0.03^a	0.97
	4-10	0.0083574 ± 0.01^b	1.81 ± 0.50^a	0.98
	4-12	0.0269681 ± 0.01^b	1.30 ± 0.07^a	0.97
	8-10	0.0529352 ± 0.02^{ab}	1.10 ± 0.21^a	0.92
	8-12	0.09893854 ± 0.03^a	1.00 ± 0.08^a	0.97
Coconut	0-10	0.0114379 ± 0.01^a	1.67 ± 0.50^a	0.97
	0-12	0.0000403 ± 0.00^a	1.55 ± 0.03^a	0.97
	4-10	0.0003759 ± 0.00^a	2.68 ± 0.71^b	0.98
	4-12	0.0433361 ± 0.00^a	1.2 ± 0.04^a	0.98
	8-10	0.0067232 ± 0.01^a	1.78 ± 0.33^a	0.99
	8-12	0.0133901 ± 0.01^a	1.58 ± 0.31^a	0.97

Abbreviations: sorbitan monopalmitate (SMP), ethyl cellulose (EC), velocity (k), dimensionality of growth (N).

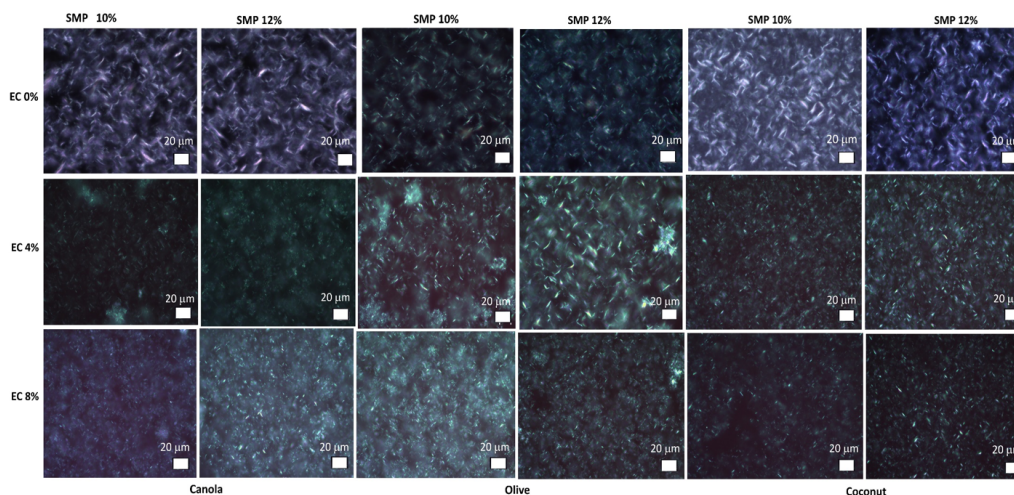


Fig. 2. Optical light microscopy polarized in dark field of organogels with mixtures (ethyl cellulose (EC) - sorbitan monopalmitate (SMP) in Canola, Olive and Coconut oil organogels.

This behavior was presented only in olive oil systems, indicating an instant nucleation process, while the other two oils show the formation of crystalline growth as a sporadic nucleation with similar crystals of different types of nuclei.

3.3 Polarized microscopy

The morphology arrangement was studied for a better understanding of the influence of EC concentration in organogel formation as a mixture using SMP. The morphology of solids was observed under a polarized light microscope. Figure 2 shows the increase of birefringence at lower concentrations of EC. The changes in the crystalline morphology are related to the concentrations of the mixture and the type of oil; in addition, the arrangement is fibrillar needle type, corresponding to what was predicted through the Avrami model. There is a marked difference in the fibers of organogels since the polymer is not included, given that the size is much greater regardless of the oil, the size of the fiber decreased proportionately with increased EC concentrations. However, the solid formation had a very long needle shape, which is a desirable feature for gel formation (Terech and Weiss, 1997 Burkhardt *et al.*, 2009).

When a crystalline structure was not observed, it was associated to the cooling of the phase of the solution, which resulted in reduced solubility of the gellant in the solvent and, consequently, a reduction of affinity with the solvent (vegetable oil). Such spacings are possibly due to the fact that hydrogen bonds are

not available for gelation; however, between these spacings is where the needle-like fibers are observed. This is a product of the gelator molecules that come out of the solution for aggregates, interacting through junctions and points to form a three-dimensional network that immobilizes the liquid components. This formation is related to the effect exerted by the SMP, characterized by the formation of rods with increasing tubular length (Jibry *et al.*, 2006).

3.4 Rheological Properties

3.4.1 Frequency sweep (ω)

All samples were analyzed in the regimen of the linear viscoelastic region (LVR). In organogels that involve the use of EC polymer, it has been demonstrated the strong influence of the solvent composition on the mechanical properties of organogels, therefore, the influence of solvent polarity can be attributed to the presence/absence of chemical species capable of forming hydrogen bonds with the polymer network (Gravelle *et al.*, 2016). About the influence of SMP into the system, it has been reported that it forms a viscous solutions in edible oils whose viscosity increases when increasing the concentration of the gelator, where the threshold concentration to form a gel is 10%, causing a firm and opaque gel (Murdan *et al.*, 1999). The SMP behavior was modified by adding EC polymer. Obtained organogels with SMP and EC showed higher G' 's. Regardless of the type of oil used and concentrations of the mixture, its behavior was gel type (i.e., $G' > G''$) (see Figure 3).

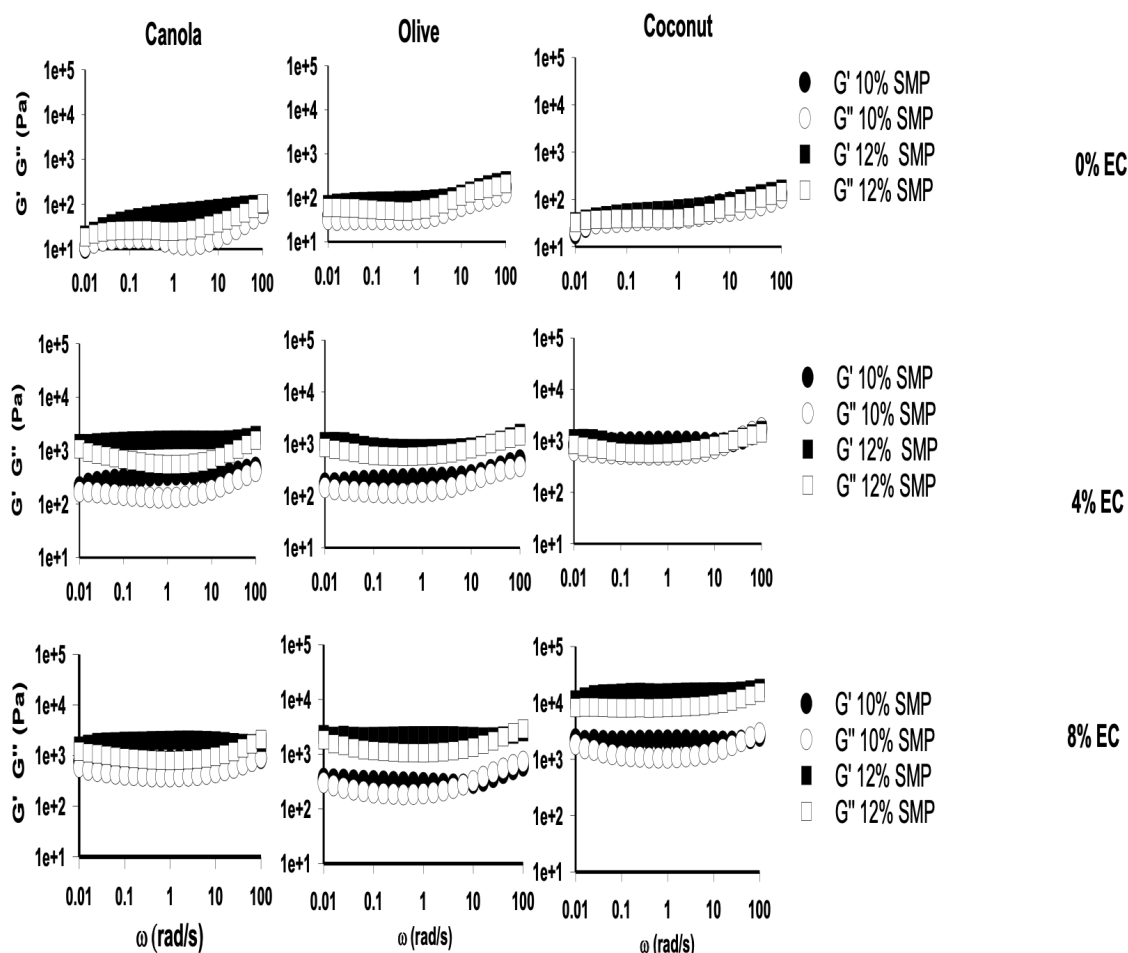


Fig. 3. Dynamic viscoelastic properties: Storage modulus (G') and loss modulus (G'') for canola, olive and coconut oil organogels added with ethyl cellulose (EC) over a frequency range of 0.01 to 100 rads^{-1} at 25 °C.

However, the difference between values of G' and G'' was minimum for coconut oil SMP and EC organogels, and higher for organogels obtained with canola oil. These behaviors could be related with the hydrophilic interactions between SMP, EC and vegetable oils that stabilize polymer network and increase mechanical properties of the gel network. However, this increase is related with the type of vegetable oil, Laredo *et al.*, (2011) demonstrated that the use of oil with high level of insaturation render strong gels, similar results have been reported by Dey *et al.* (2011) and Zetzl *et al.* (2012) and they agree with the results found into the present work.

Data were adjusted to the power law ($G' = K\omega^n$) and obtained parameters are shown in Table 4. These results indicate the influence of the oil, SMP and EC in the mechanical behavior of oleogels. Several reports about the influence of EC/oil (Laredo *et*

al., 2011; Gravelle *et al.*, 2018) have shown higher resistance of gel with increase concentration of EC, and no influence with the type of vegetable oil. These results were opposite to the found in the present work a possible explanation about the influence of vegetable oil could be done by the use of solubility theory, it has reported that in oleogel systems, which are structured via hydrogen bonds, the hydrogen bonding δ_h parameter of Hansen solubility theory alone can dominate the “quality” of the combined solvent (Rogers and Marangoni, 2016). This behavior was demonstrated by Gravelle *et al.* (2018) for EC/oils blends, showing that higher mechanical properties are obtained when δ_h distance between the elements of the blend were shorter. Thus, following this idea, the presence of SMP in the blend modifies the mechanical structure of the obtained oleogels in combination with EC and vegetable oil.

Table 4. Power-law model $G' = K\omega^n$ parameters calculated for describing the behavior of G' values in canola, olive coconut oils organogels.

Organogel	Mixture EC-SMP%	Parameter (K) Pas ⁿ	Parameter n	R ²
Canola	0-10	44.56±4.29 ^k	0.09±0.03bcd	0.95
	0-12	67.55±11.92 ^{ijk}	0.09±0.04 ^{bcd}	0.95
	4-10	308.50±61.64 ^{hi}	0.14±0.04 ^{bcd}	0.96
	4-12	480.93±28.48 ^{fgh}	0.24±0.04 ^{bcd}	0.94
	8-10	1086.04±9.33 ^e	0.11±0.00 ^{bcd}	0.9
	8-12	4246.70±72.46 ^c	0.06±0.01 ^{cd}	0.95
Olive	0-10	58.32±3.38 ^{jk}	0.21±0.15 ^{bcd}	0.98
	0-12	64.34±2.98 ^{ijk}	0.29±0.03 ^{ab}	0.99
	4-10	291.32±82.95 ^{hjj}	0.21±0.05 ^{bcd}	0.99
	4-12	440.81±2.57 ^{gh}	0.27±0.06 ^{abc}	0.99
	8-10	190.10±39.54 ^{ijk}	0.25±0.06 ^{bcd}	0.98
	8-12	701.93±56.69 ^f	0.26±0.03 ^{abc}	0.98
Coconut	0-10	62.74±18.14 ^{ijk}	0.14±0.00 ^{bcd}	0.99
	0-12	51.54±20.34 ^{jk}	0.24±0.04 ^{bcd}	0.99
	4-10	686.12±49.54 ^{fg}	0.18±0.00 ^{bcd}	0.94
	4-12	3733.31±126.42 ^j	0.04±0.01 ^d	0.97
	8-10	5561.50±75.60 ^b	0.18±0.00 ^{bcd}	0.93
	8-12	8496.35±144.65 ^a	0.46±0.01 ^a	0.94

Abbreviations: sorbitan monopalmitate (SMP), ethyl cellulose (EC).

Obtained results show that more elastic gels are those made with coconut oil, even without the mixture (EC-MPS), which is reflected in the larger differences of K followed by canola and olive. This mechanical characteristic is attributed to the oil chemical composition, viz. in coconut the interaction is exerted by the components of the oil, mostly saturated fatty acids (83.94±0.40%), while in canola oil, rich in PUFA (31.77±0.11%) and in olive oil, rich in MUFA (78.27±0.03%).

3.4.2 Temperature sweep

The organogels made with canola, olive and coconut oils at all experimental conditions of MPS and EC showed a sol-gel phase transition at temperatures ranging from about 42 to 47 °C, (Figure 4). It was observed a sinusoidal or stepped increase in Tan δ with temperature increase; consequently, this behavior indicated the formation of an additionally organized structure formed by the gellant SMP (Davidovich-Pinhas *et al.*, 2015). Stepped sol-gel transitions have been associated with the formation of secondary structures, such as helices (Braudo *et al.*, 1991; Miyoshi *et al.*, 1996), double helices (Mangione *et al.*, 2003) and crystallization (Rocha *et al.*, 2013). The

nature of these structures in organogels with EC is not fully understood, however, the ability of surfactants to self-assemble and create a crystal structure in the presence of hydrocarbon chains is already known (Sánchez *et al.*, 2011).

Depending on the interfacial structure of the fibers (or networks), several interactions can develop between adjacent fibers at the nodes (or junction zones) of the networks, showing in this way that the sol-gel temperatures are dependent on concentration of the structuring agent and type of oil. The sol-gel transition was estimated as the temperature at which the transition occurs between the loss modulus and storage modulus, that is, the crossover temperature ($G' = G''$) (Figure 5).

Sol-gel transition is the same regardless of the type of oil used. The addition of the polymer increases this temperature considerably; however, there is no statistically significant difference between the inclusion of 4 and 8% of EC, whose temperature range was 54-59 °C, achieving a transition to a lower temperature by not including the polymer at 48-52 °C. The change of sol-gel influences all the factors involved in the elaboration of materials, whose temperature intervals are shorter in this transition for the organogel with coconut oil between 41 and 46 °C.

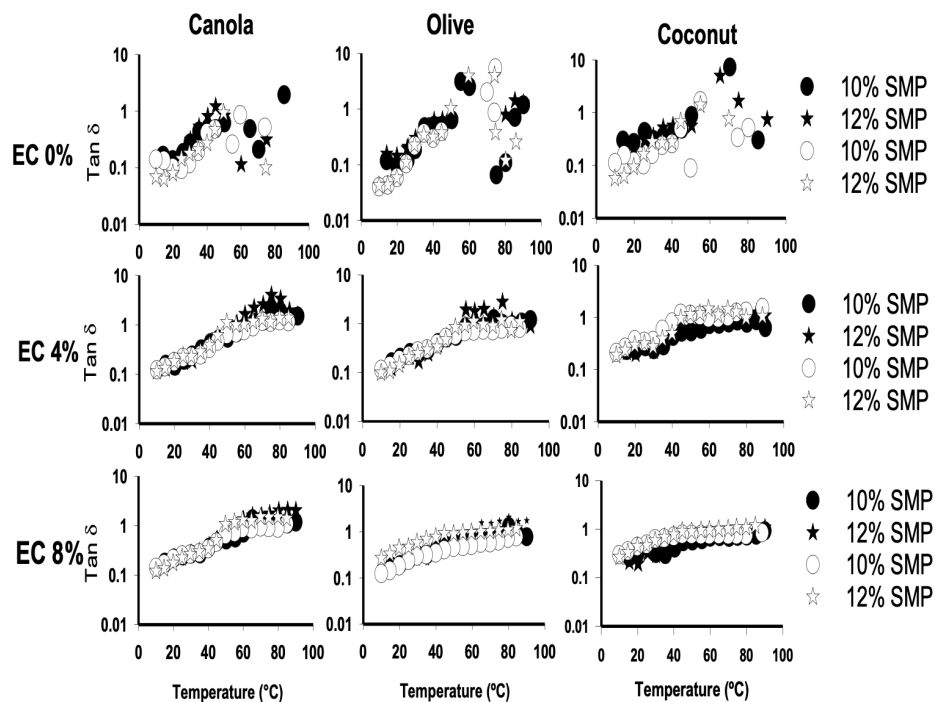


Fig. 4. Temperature sweep. Tan delta for heating (full symbols) and cooling (empty symbols) for canola, olive and coconut oil organogels added with ethyl cellulose (EC).

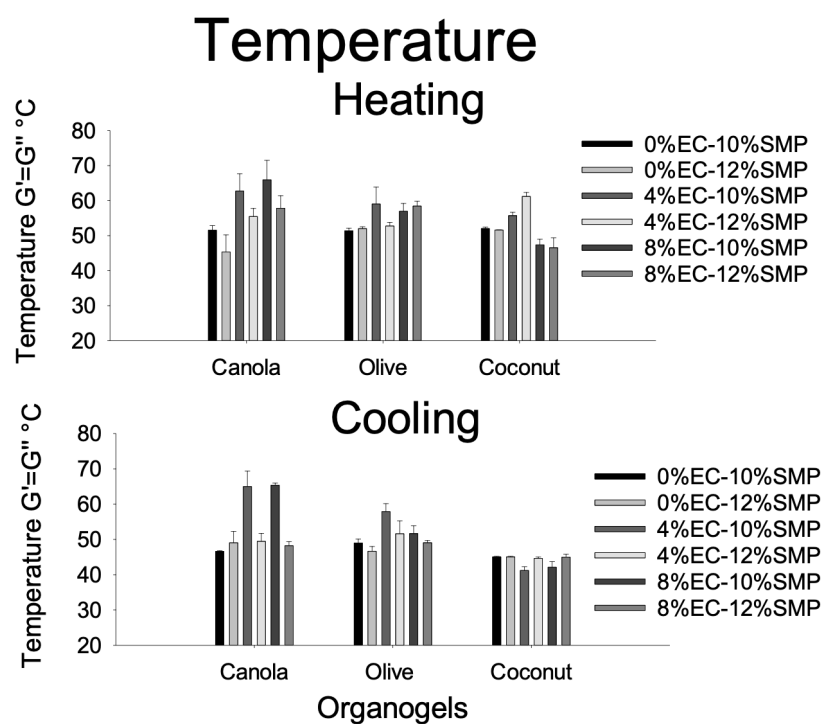


Fig. 5. Temperature $G' = G''$ in heating and cooling from a temperature sweep in canola, olive and coconut oils organogels added with ethyl cellulose (EC).

Organogels with olive and canola oils experience this transitions in a range of temperatures between 49 and 56 °C, but without statistical difference between them. The mixture used suggests that at a lower concentration of the gellant, this temperature tends to be higher, suggesting that the concentration used influences the transition temperature of the materials regardless of the concentration used of the polymer.

3.5 Differential scanning calorimetry (DSC)

In the present study, surfactant characteristics were observed for the determination of the thermodynamic properties of organogels. Specifically, in the melting process of the material, at a range of 8-90 °C in a single heating cycle, it was observed the impact of the polymer on the different mixtures of organogels.

The start of melting was observed at higher temperatures for organogels from olive oil, following by canola and coconut oils. This behavior could be related to the structural arrangement shown by canola and coconut oils that retards absorption of heat caused by the heating to which they are subjected and to the

distribution of non-covalent bonds in the materials. The EC polymer is determinant for such effects and although it is not added in the mixtures, this start is an indication of a higher T onset. Therefore, EC is an inducer of the most important thermal transition regardless of the type of oil, but depending on the concentration used of the polymer in any of the concentrations used.

The maximum temperature or the temperature considered as that from the maximum peak that refers to the point of complete melting of the material has significance in the type of oil and the presence of EC. Such behavior reflects that there is a higher temperature (T_m) and a greater thermal resistance in those organogels made with olive oil followed by the ones with canola and coconut oils, who showed the lowest melting T (i.e., the lowest thermal resistance and the highest sensitivity to heat absorption). The end of structure loss is influenced by the type of oil and concentration of polymer, being the highest T for canola, followed by olive and coconut oils. The materials without polymer have the lower T end; also it was observed higher T end with higher polymer concentration.

Table 5. Thermal parameters (Temperature of melting- T_m , enthalpy of melting ΔH).

Organogel EC-SMP%	Start (°C)	Onset (°C)	T_m (°C)	Stop (°C)	ΔH_m (J g ⁻¹)
Canola					
0-10	38.39±0.19 ^a	40.45±0.95 ^a	46.94±0.02 ^a	52.63±0.14 ^b	1.43±0.00 ^b
0-12	37.18±0.10 ^a	40.18±0.73 ^a	46.54±0.14 ^{ab}	52.49±0.04 ^b	1.31±0.18 ^b
4-10	30.96±1.85 ^b	33.33±0.62 ^{bc}	45.41±0.14 ^{ab}	52.03±0.09 ^b	1.75±0.00 ^b
4-12	26.92±0.15 ^b	32.01±0.60 ^c	44.73±0.98 ^b	54.95±0.22 ^a	1.44±0.07 ^b
8-10	31.43±0.19 ^c	28.82±0.91 ^d	45.61±0.39 ^{ab}	54.98±0.15 ^a	2.76±0.51 ^a
8-12	32.67±0.65 ^b	35.67±0.04 ^b	46.45±0.27 ^{ab}	52.21±0.35 ^b	1.96±0.26 ^{ab}
Olive					
0-10	41.83±1.05 ^a	42.09±0.70 ^a	46.91±0.84 ^a	50.01±0.45 ^b	0.80±0.25 ^c
0-12	40.34±0.04 ^{ab}	41.53±0.40 ^{ab}	47.46±0.59 ^a	49.94±0.45 ^b	1.92±0.28 ^{ab}
4-10	33.34±0.40 ^c	38.53±0.07 ^{cd}	46.64±0.00 ^a	51.92±0.04 ^a	1.80±0.02 ^{ab}
4-12	32.31±0.04 ^c	39.11±0.27 ^c	46.56±0.31 ^a	51.54±0.00 ^a	2.06±0.41 ^{ab}
8-10	33.35±1.90 ^c	37.17±0.33 ^d	46.78±0.19 ^a	51.89±0.19 ^a	2.52±0.13 ^a
8-12	37.4±0.19 ^b	40.10±0.6 ^{bc}	46.46±0.12 ^a	51.39±0.09 ^a	1.41±0.03 ^{bc}
Coconut					
0-10	35.41±0.19 ^a	35.86±0.74 ^{ab}	44.00±0.16 ^a	49.12±0.09 ^c	1.00±0.08 ^a
0-12	35.44±0.04 ^a	38.81±1.42 ^a	44.42±0.50 ^a	48.73±0.15 ^{bc}	1.28±0.00 ^a
4-10	34.80±0.34 ^b	35.54±0.52 ^b	43.64±0.12 ^a	50.25±0.60 ^{bc}	0.75±0.02 ^a
4-12	34.34±0.50 ^b	35.63±0.64 ^b	43.45±0.71 ^a	52.95±0.04 ^a	1.33±0.40 ^a
8-10	32.18±0.08 ^c	34.87±0.14 ^b	44.41±0.62 ^a	50.68±0.80 ^b	1.57±0.80 ^a
8-12	32.11±0.04 ^c	33.36±0.51 ^b	44.12±0.62 ^a	48.90±0.09 ^c	1.66±0.45 ^a

Abbreviations: sorbitan monopalmitate (SMP), ethyl cellulose (EC).

The area under the curve of the materials has an equal behavior in the organogels of canola and olive oils, being different for coconut, where it is smaller. However, the addition of polymer (EC) indicates that there is no difference in this parameter between 0 and 4%, but if it increases to 8% of EC, following the pattern as the concentration increases, this value is also increasing. Similar behavior was observed in organogels with sesame oil and sorbitan monostearate (Singh *et al.*, 2015).

Conclusions

Non-isothermal nucleation kinetics obtained by a simple test (e.g., spectrophotometrically) was a useful tool to determine the thermodynamic properties from the origin of the organogel (i.e., nucleation). These parameters indicate what type of oil is capable of initiating the phenomenon at longer or shorter times and which is more favorable and closer to the thermodynamic equilibrium, emphasizing that for this case the inclusion of ethyl cellulose is determinant. However, this inclusion does not modify the speed of formation and directionality of nuclei growth according to the Avrami model, indicating an instant nucleation process in olive oil systems, while canola and coconut oils systems show the formation of crystalline growth as a sporadic nucleation with similar crystals of different types of nuclei. The multicomponent gels obtained showed that the structural differences depend on the concentration of the mixture, presenting more compact structures at higher concentrations of ethyl cellulose according to their microstructure, where the crystals are closer ones and the inclusion of EC limits their growth by an inhibitory effect of the SMP gelling agent.

Acknowledgements

Author M. Garcia-Andrade is very thankful for graduate scholarship and the financial support received from the Basic Science Program, grant number 241241 from CONACyT (National Council of Science & Technology), Mexico.

Nomenclature

C	Centigrade
k	crystal growth rate
K	consistency index (Pa.sn)
DSC	differential scanning calorimetry
EC	ethyl cellulose
T_m	equilibrium melting temperature of material, °C
G'	elastic or storage modulus, Pa
$q(t)$	fraction without crystallizing at the time
n	flow behavior indices (dimensionless)
H	hours
T_i	induction time, minutes
t_0	initial time, minutes
LVR	linear viscoelastic region
Min	minutes
N	avramy exponent
Pa	pascal, $N \cdot s^{-2}$
J	rate nucleation: nucleus per minute
SMP	sorbitan monopalmitate
S	Seconds
T	Time
G''	viscous or loss modulus, Pa
W	Weight

Greek symbols

ΔG_n	change free energy nucleation
ϕ	cooling rate
ΔT	temperature differential
Δt	time differential
β	Supercooling
$\tan \delta$	tangente delta

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