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Crystallization, microstructure and polymorphic properties of soybean oil organogels in a hybrid structuring system

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ABSTRACT

Organogels are semi-solid systems where the liquid phase is immobilized for three-dimensional network self-sustained formed by structuring agents capable to hold a larger quantity of liquid oil. The use of these structuring agents or crystallization modifiers, as specific triacylglycerols, emulsifiers and high molecular weight - high melting point lipids, have been recognized as the main alternative for obtaining low saturated fats for food formulation. The aim of this work was to evaluate the crystallization, microstructure and polymorphism properties of hybrid soybean oil (SO) organogels, formulated with 6% (w:w) of structuring agents through a centroid simplex system added singly, in binary or ternary association of candelilla wax (CW), sorbitan monostearate (SMS) and fully hydrogenated palm oil (FHPO). The thermal behavior, crystallization kinetics, physical stability by temperature cyclization, microstructure and polymorphism were evaluated. FHPO and CW increased the stability and ability to form crystalline networks in organogels, while SMS accelerated the crystallization process. The structuring agents increased the initial and final crystallization temperatures, even as the melting temperatures and the enthalpy values of organogels. Time-temperature cyclization (cyclization 1: 5 °C/48 h + 35 °C/24 h + 5 °C/24 h; cyclization 2: 35 °C/48 h + 5 °C/72 h) showed that all the systems resulted in firm and stable organogels, except when SMS or FHPO were used singly. CW promoted formation of denser crystalline networks with higher solids content, quick crystallization onset and higher melting points that indicates adequate thermal resistance; while FHPO increased the solid content although it was effective to obtain organogels only at the cooling temperature (5 °C). The binary interaction of FHPO + CW increased the thermal resistance of organogels; and the interactions among SMS + CW and SMS + CW + FHPO although it was effective to obtain organogels. Regardless of the presence and proportions of structuring agents, organogels were characterized by beta polymorphism.

1. Introduction

Modification of the physical properties of lipid matrices has proven to be a strategic alternative for the processing of foods high in fat aiming at obtaining healthier products, with lower saturated fatty acids and free from trans fatty acids. In this context, a new range of lipidic structuring agents has been shown to be effective in obtaining a three-dimensional network capable of immobilizing liquid oil, leading to the formation of lipid bases with distinct macroscopic characteristics as an alternative to conventional structurants high in saturated fatty acids or trans fatty acids. The products of this technological advance have been called organogels or oleogels (Marangoni & Garti, 2011; Patel &

Dewettinck, 2016; Peyronel, 2018).

The structuring agents used for organogel production are characterized as lipid materials capable of retaining a large amount of liquid oil and can be classified into two systems: self-assembly systems and crystal particle systems. The former involves molecular-level self-organization in the oil phases and can be represented by macromolecules or low molecular weight compounds such as sorbitan monostearate, monoacylglycerols, phytosterols, and waxes. The latter forms colloidal crystal networks from triacylglycerols, which limits the solubility of the molecules with a higher melting point upon cooling leading to nucleation events. Thus, the crystals grow and interact with each other through non-covalent forces, forming a continuous three-dimensional

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network. After complete crystallization, the crystals aggregate to form increasingly larger clusters from weak bonds, giving rise to the final macroscopic characteristics (Co & Marangoni, 2012; Dassanayake, Kodali, & Ueno, 2011; Pernetti, van Malssen, Flöter, & Bot, 2007).

Recently, Hwang, Kim, Singh, Winkler-Moser, and Liu (2012), Jang, Bae, Hwang, Lee, and Lee (2015), Lim, Hwang, and Lee (2017), Rocha et al. (2013), Silva et al. (2018), Godoi et al. (2019) studied the formation of organogels through the addition of candelilla wax (CW) and reported that lower CW concentrations (minimum 0.5%) allowed obtaining firm organogels with higher melting point and thermal resistance, as a function of the structurant agent concentration. When compared to other waxes used to obtain organogels (such as carnauba wax and beeswax), CW is the most promising due to the characteristics of hardness and high stability during gel storage (Lim et al., 2017).

In contrast, Garbolino, Bartoccini, and Flöter (2005), Pérez-Martínez et al. (2019), Sagiri et al. (2016) and Singh, Pramanik, Ray, and Pal (2015) evaluated the formation of organogels containing sorbitan monostearate (SMS) and reported that this structuring agent led to an increase in the crystal network density, affecting the viscoelastic properties, especially when used in higher concentrations (above 10%), in addition to delaying the transition from polymorphic forms in lipid matrices.

Regarding the crystal particle system, fully hydrogenated oils have shown the potential to increase the consistency and thermal resistance of lipid systems, as reported by Klok, Walstra, and van Vliet (2000), Oliveira, Ribeiro, dos Santos, Cardoso, and Kieckbusch (2015); de Oliveira et al. (2011), Omonov, Bouzidi, and Narine (2010).

The combination of crystal particles and self-assembled structures has shown great potential for the formation of organogels. Several authors have studied the combination between these hybrid systems and CW and SMS, CW and FHPO, or SMS and FHPO (Oliveira, Ribeiro, dos Santos, Cardoso, & Kieckbusch, 2015; Pérez-Martínez et al., 2019; Singh, Pramanik, Ray, & Pal, 2015; Stahl, Buscato, Grimaldi, Cardoso, & Ribeiro, 2018).

Organogels can be applied in foods as water-in-oil emulsions stabilizers, controlled release of pharmaceutical and nutraceutical products, as structuring agents to minimize the migration of liquid oil in the multi-components system and to guarantee texture and consistency with lipid materials without trans fatty acids (Chaves, Barrera-Arellano, & Ribeiro, 2017). The polymorphic habit can direct in the food application. According to the literature data, the SO shows, preferably, the β polymorphic form due to the low variability of triacylglycerols and low content of palmitic acid being indicate the application in food products with greater hardness and lower aeration. In contrast, the FHPO is characterized by β' polymorphic form due to the long-chain triacylglycerols present whose application is directed to margarine, shortenings, and emulsified products (Gunstone, 2005; Oliveira, Ribeiro, dos Santos, Cardoso, & Kieckbusch, 2015). Due to the versatility and thermic reversibility of organogels made with candelilla wax, is possible that the systems can be used in food application to reduce saturated fats in ice cream and margarine, for example (Morales-rueda, Dibildox-Alvarado, Charó-Alonso, & Toro-Vazquez, 2009; Si, Cheong, Huang, Wang, & Zhang, 2016; Toro-Vazquez et al., 2007).

The materials used as structuring agents in this study consisted of ingredients usually produced in the food industry, which makes its use economically viable and versatile. Thus, this study aimed to evaluate the structuring properties of organogels made with SO alone or in binary and ternary mixtures with CW, SMS, and FHPO, which constitutes a promising hybrid system concerning the crystallization, microstructure, and polymorphism characteristics of the final system, for application in the most diverse lipid-based foods.

2. Material and methods

2.1. Materials

Refined soybean oil (SO) supplied by Cargill Foods, fully hydrogenated palm oil (FHPO) supplied by SGS Agriculture and Industry, Sorbitan monostearate (SMS - Span 60) purchased from Sigma Aldrich (USA) and candelilla wax (CW) provided by Koster Keunen (USA) were used. The raw materials exhibited the following fatty acids composition: SO (C18: 1–25.38%, C18: 2–51.51%, C16: 0–11.05%), FHPO (C16: 0–43.77%, C18: 0–53.60%), and the following iodine values: HPO – 0.56 I₂/100 g/, and SO – 28 I₂/100 g (Godoi et al., 2019).

2.2. Methods

2.2.1. Organogel preparation

The SO was heated to 80 °C and the structuring agents were mixed without pretreatment or previous alteration with magnetic stirring for 3 min until complete dispersion in the liquid phase. The samples were transferred to 50 mL glass beakers and kept in a static condition at 5 °C for 24 h, for structuring and stabilization. Then, the temperature was raised to 25 °C and the organogels were kept at this temperature for 24 h. The lipid system was composed of mixtures containing SO and the structuring agents FHPO, SMS, and CW, with a total structurant concentration of 6% (w/w), previously determined (Godoi et al., 2019; Godoi, Barrera-Arellano, & Ribeiro, 2017). A simplex-centroid design with seven experiments (samples 1–7) and three additional experiments (samples 8–10) for model validation were used (Cornell, 2002; Neto et al., 2001) (Table 1).

2.2.2. Crystallization kinetics

The samples were prepared according to Section 2.2.1 and placed in a liquid state in a dry bath system (Peltier Tcon 2000, Duratech, USA) at 70 °C for 1 h and analyzed by isothermal crystallization. The solid content (SC) was determined at 25 °C (± 0.5 °C) at 1 min of intervals, in triplicate, using a low-resolution nuclear magnetic resonance (NMR) spectrometer Bruker pc120 Minispec, with temperature control by a thermostatic bath (± 0.5 °C) (Wassell & Young, 2007).

Characterization of crystallization kinetics for organogels is performed at 25 °C and was evaluated the induction period (t_{ind}) – referent to the beginning of crystal formation, when the system shows some quantity (minimum 1%) of solid content– and the maximum solid content (SC_{max}) observed during the time of analysis, defined by the specific characteristic in each sample, until to stabilize the SC (when do not occur an increase in SC or when a little decrease in SC occur). Induction time is graphically attained and reflects the time needed for a

Table 1

Centroid simplex design for structuring agents: Coded and real values.

Organogels	Structuring agents (mass proportion)					
	Coded values			Real values		
	CW	SMS	FHPO	CW	SMS	FHPO
1	1	0	0	6%	0	0
2	0	1	0	0	6%	0
3	0	0	1	0	0	6%
4	1/2	1/2	0	3%	3%	0
5	1/2	0	1/2	3%	0	3%
6	0	1/2	1/2	0	3%	3%
7	1/3	1/3	1/3	2%	2%	2%
8	2/3	1/6	1/6	4%	1%	1%
9	1/6	2/3	1/6	1%	4%	1%
10	1/6	1/6	2/3	1%	1%	4%

CW: Candelilla wax, SMS: Sorbitan monostearate, FHPO: Fully hydrogenated palm oil.

stable nucleus of critical size to be formed in liquid phase (Marangoni, 1998). For all the organogels, to standard the results, the time of analysis was 40 min, enough time to stabilize the solid content.

2.2.3. Thermal behavior

The thermal analysis was performed in a differential scanning calorimeter (DSC) TA Q2000 coupled to an RCS90 Refrigerated Cooling System (TA Instruments, Waters LLC, New Castle) according to the AOCS method Cj 1–94, with adaptations (AOCS, 2009) using Universal V4.7A for data processing (TA Instruments, Waters LLC, New Castle). The analysis conditions were: sample weight: 10 mg; crystallization and melting curves: 10 min (100 °C); 100 °C to –60 °C (10 °C/min); 10 min at –60 °C; and –60 °C to 100 °C (10 °C/min), respectively.

The results were evaluated for the following parameters: initial temperatures of crystallization and melting (T_i), peak temperatures of crystallization and melting (T_p), enthalpy of crystallization and melting, and crystallization and melting enthalpy (ΔH) (Campos, 2005; Godoi et al., 2019; Rocha et al., 2013).

2.2.4. Physical stability by temperature cyclization

Approximately 40 mL of sample was placed in 50 mL glass beakers. Two temperature cyclizations were studied, representing the exposure of organogels to different temperatures after removal from the refrigeration condition. First cyclization: the organogels were stored at 5 °C for 48 h for complete crystallization, and then at 35 °C for 24 h before visual analysis. Soon after, they were stored at 5 °C for 24 h and visualized again. Second cyclization: the organogels remained at 35 °C for 48 h before visual analysis, and then subjected to refrigeration temperature (5 °C) for 72 h, followed by a further visualization (Garcia, Gandra, & Barrera-Arellano, 2013).

The organogels were classified according to Godoi et al. (2019), as follows: To be classified as totally liquid (1), the material should be oil-like, flowing easily when the content of the beaker is poured or subjected to force (faced down, five soft beats are exerted on the beaker toward the surface of support surface); for classification as a weak gel (2), the material should be viscous, with the slower flow when the beaker is subjected to gravitational force or when the content of the beaker is poured; for classification as a medium gel (3), the material should have a visual gel characteristic, but with an easy flow when the beaker content is poured or subjected to gravitational force; to be classified as a firm gel (4), the material should visually present as a gel, without flow when the beaker content is poured, but with a slow flow when subjected to gravitational force; for classification as a firm gel (5), the material should not flow when the beaker content is poured or subjected to force.

2.2.5. Microstructure

Organogels were evaluated by polarized light microscopy (PLM). With the aid of a capillary tube, a drop of the previously fused sample was placed on a glass slide at 80 °C, covered with a coverslip and stored in a BOD chamber at 5 °C for 24 h and then 25 °C for 24 h before analysis. The microstructure of the organogels was evaluated using a polarized light microscope (Model BX51, Olympus America Inc., United States), coupled to a digital video camera (Media Cybernetics) with four different visual fields of the slide for each sample (Toro-Vazquez et al., 2013).

2.2.6. Polymorphism

The organogels were kept at 5 °C for 24 h and subsequently at 25 °C for 24 h before analysis, which was performed at 15 °C to ensure the solid condition in the moment of analysis. The polymorphic habit of the organogels was determined by X-ray diffraction according to the AOCS method Cj 2–95 (AOCS, 2009). The determinations were made in a Philips diffractometer (PW 1710) using Bragg-Bretano geometry (θ :2 θ) with Cu-K α radiation (λ = 1.54056 Å, 40 KV, and 30 mA). The measurements were obtained with steps of 0.02° in 2 θ and acquisition time

of 2 s, with scans from 2 to 40° (scale 20). The identification of the crystalline forms was carried out from the characteristic short spacings of the crystals (Chopin-Doroteo et al., 2011; Dassanayake et al., 2011; Yap, Man, & Man, 1989).

2.3. Statistical analysis

Data from crystallization kinetics and the thermal behavior were subjected to analysis of variance (ANOVA) using the STATISTICA software version 8 (StatSoft Inc., Tulsa, OK, USA). Multiple regression models were applied for the analytical response of the initial temperature of crystallization and maximum solids content (HARE, 1974). The model coefficients, significance levels, determination coefficients, and analysis of variance were also determined using the STATISTICA software version 8 (StatSoft Inc., Tulsa, OK, USA). Tukey's test was used for comparisons between means, with a significance level of 5% ($p \leq 0.05$).

3. Results and discussion

3.1. Crystallization kinetics

Crystallization kinetics is a parameter that can directly influence the final structure of fats and application decisions (De Graef, Dewettinck, Verbeken, & Foubert, 2006). The main parameters obtained by crystallization kinetics include the induction time (t_{ind}) corresponding to the onset of crystal growth, and the maximum solids content (SC_{max}) obtained after the isothermal stabilization of the lipid base (Ribeiro et al., 2015). The results of these parameters for the organogels studied are shown in Table 2 and the isothermic curves were in Fig. 1

The highest SC_{max} value was observed for the organogels made with CW or FHPO isolated. This occurs due to the presence of FHPO, which is composed of high-melting triacylglycerols as reported by de Oliveira et al. (2011). In this study, FHPO led to changes in the crystallization profile of palm oil with an increase in consistency and reduction of t_{ind} . Similarly, CW exhibited higher SC_{max} and reduced t_{ind} because hentriacontane is its major constituent, an n-alkane that guarantees the self-assembled structure, and long-chain fatty acids, which contribute to the increase in SC (Alvarado et al., 2012; Chopin-Doroteo et al., 2011; De Oliveira et al., 2015; Toro-Vasquez, Charó-Alonso, Pérez-Martínez, & Morales-Rueda, 2011) which is commonly observed for waxes, as also reported by Martini, Carelli, and Lee (2008) who observed an increase in SC_{max} and a ~ 15 min reduction of crystallization time t_{ind} of anhydrous milk fat.

Both the organogels made with FHPO isolated and those made with

Table 2
Crystallization kinetics parameters of organogels.

Organogels	t_{ind}	SC_{max}
1	2.66 ± 0.57 _d	5.28 ± 0.21 _a
2	4.66 ± 1.15 _{cd}	3.03 ± 0.24 _d
3	17.66 ± 1.15 _a	5.63 ± 0.08 _a
4	5.66 ± 0.57 _{bc}	3.36 ± 0.19 _{cd}
5	6.33 ± 0.57 _{bc}	4.43 ± 0.11 _b
6	8.33 ± 0.52 _b	1.63 ± 0.15 _f
7	7.00 ± 1.00 _{bc}	2.30 ± 0.10 _e
8	4.66 ± 0.57 _{cd}	3.66 ± 0.13 _c
9	5.66 ± 1.15 _{bc}	2.42 ± 0.23 _c
10	19.66 ± 0.57 _a	4.05 ± 0.14 _b

t_{ind} : period of induction; SC_{max} : maximum solid content. Same letters for the same columns indicate that there are no significant differences between the means evaluated by Tukey's test ($p \leq 0.05$). 1) CW, 2) SMS, 3) FHPO, 4) CW + SMS, 5) CW + FHPO, 6) SMS + FHPO, 7) 1/3 CW + 1/3 SMS + 1/3 FHPO, 8) 2/3 CW + 1/6 SMS + 1/6 FHPO, 9) 2/3 SMS + 1/6 CW + 1/6 FHPO, 10) 2/3 FHPO + 1/6 CW + 1/6 SMS. CW: Candelilla wax, SMS: Sorbitan Monostearate, FHPO: Fully hydrogenated palm oil.

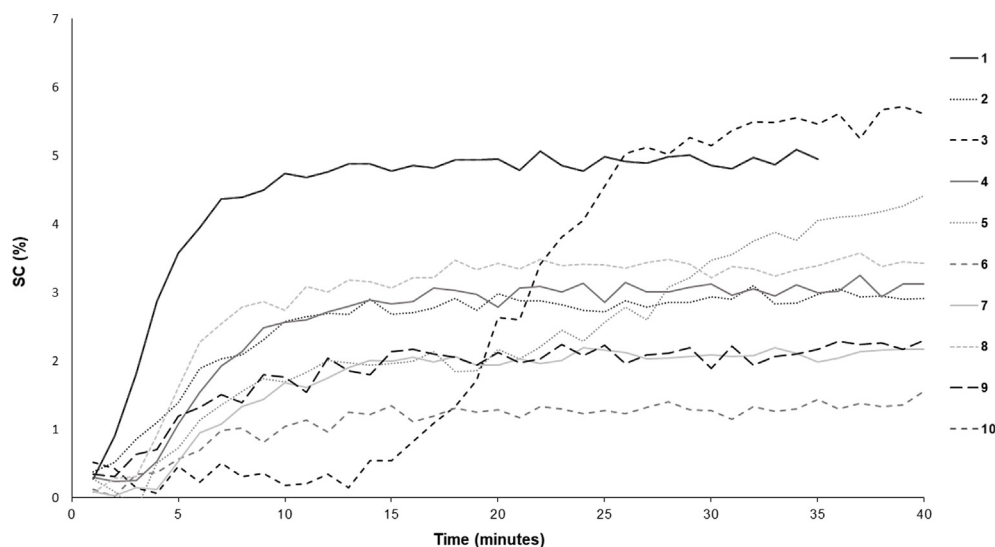


Fig. 1. Isothermal crystallization curves of organogels. 1) CW, 2) SMS, 3) FHPO, 4) CW + SMS, 5) CW + FHPO, 6) SMS + FHPO, 7) 1/3 CW + 1/3 SMS + 1/3 FHPO, 8) 2/3 CW + 1/6 SMS + 1/6 FHPO, 9) 2/3 SMS + 1/6 CW + 1/6 FHPO, 10) 2/3 FHPO + 1/6 CW + 1/6 SMS. CW: Candelilla wax, SMS: Sorbitan monostearate, FHPO: Fully hydrogenated palm oil.

the ternary mixture containing mostly FHPO exhibited the highest t_{ind} , while the organogels made with CW had the lowest t_{ind} demonstrating the ability to accelerate the crystallization process, which was impaired by FHPO despite the considerable increase in SC_{max} . The addition of SMS was able to accelerate the onset of crystallization for the organogel containing FHPO and the ternary mixture with the highest FHPO concentration, which can provide greater thermal and physical stability to the crystal network, as reported by Peyronel and Marangoni (2014).

The multiple regression coefficients were calculated from the experimental data of SC_{max} determined by the crystallization kinetics at 25 °C. The statistical model for SC_{max} of the organogels is shown in Fig. 2. The regression analysis showed that the data best fit the cubic model, and the responses indicated that all the structuring agents contributed with SFC_{max} as a function of the concentration used.

The use of FHPO alone, followed by the addition of CW led to the formation of organogels with higher SC_{max} , and the binary combination of these structurants resulted in $> 4SC_{max}\%$. In turn, ternary mixtures with lower SMS concentrations exhibited the highest SC_{max} .

The model robustness was demonstrated by the mean R-squared ($R^2 = 0.96$) and comparison between $F_{calculated}$ and $F_{tabulated}$ values, with $F_{calculated} > F_{tabulated}$ ($14.352 > 4.757$) confirming the significance of the model (Neto et al., 2001).

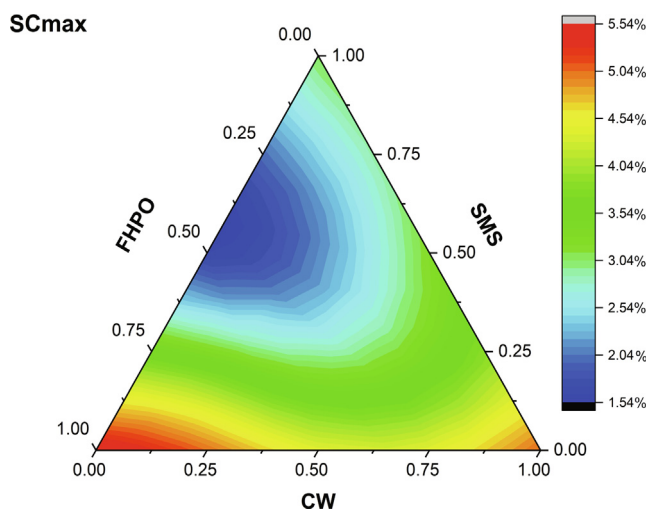


Fig. 2. Triangular diagram of SC_{max} at 25 °C. $R^2 = 0.96$. CW: Candelilla wax, SMS: Sorbitan Monostearate, FHPO: Fully hydrogenated palm oil.

3.2. Thermal behavior

The thermal behavior parameters of the organogels are shown in Table 3. The crystallization behavior showed that CW and SMS used alone resulted in higher onset crystallization temperatures (T_{ic}) of the organogels (45.51 and 45.94 °C, respectively), while lower T_{ic} was observed when these structuring agents were used in similar concentrations. In contrast, the FHPO used alone had a lower T_{ic} when compared to the other structuring agents, with a value of 21.99 °C, and similar T_{ic} (21.91 °C), when associated with SMS, while higher T_{ic} was observed when FHPO was associated with CW, which increased by 18 °C, with T_{ic} of 39.88 °C.

Sorbitan esters, such as SMS, can affect the trisaturated and disaturated triacylglycerols, thus the higher onset crystallization temperatures may be associated with the crystallization of SMS with trisaturated and disaturated triacylglycerols from SO (Domingues et al., 2015; Oh, McCurdy, Clark, & Swanson, 2005; Ribeiro et al., 2015; Takeuchi, Ueno, & Sato, 2002; Domingues, 2013). Among the ternary mixtures, the organogel with equal concentrations of structuring agents presented lower T_{ic} when compared to SMS and CW, and higher T_{ic} when compared to FHPO alone, showing a synergistic effect of the structuring agents on this parameter.

For the melting behavior of the systems, the addition of CW and SMS isolated resulted in similar initial melting temperature (T_{if}), about 12 °C, which was higher than that observed for the system with the addition of FHPO, until the complete melting of the solid materials, as demonstrated by the peak temperature 2 (T_{p2}). The binary mixtures showed that the SMS + FHPO blend resulted in the lowest T_{if} , which was about 8 °C lower than the combination of CW + SMS, which indicates less thermal stability due to the presence of FHPO. Among the ternary mixtures, organogels with the higher SMS concentrations (2% and 4%) were characterized by lower peak temperatures (T_p) indicating a negative effect of this structuring agent on the melting temperature of organogels when compared to the other formulations.

Multiple regressions were used to calculate the coefficient model generated for the thermal behavior T_{ic} , which indicates the beginning of the formation of crystal network in the organogel. The equation was adjusted cubic model, which provided the interaction between the variables for the effect of the acceleration or delay of the onset crystallization. The proposed model was validated according to ANOVA and F test ($F_{calculated} > F_{tabulated}$; $6.635 > 5.192$) (Neto et al., 2001). The diagram generated by the statistical model (Fig. 3) allowed concluding that the higher onset crystallization temperatures in the ternary combinations resulted in higher CW and lower FHPO concentration.

Table 3
Thermal behavior parameters of organogels.

Organogels	Crystallization					
	T_i (°C)	T_{p1} (°C)	T_{p2} (°C)	ΔH_1 (J/g)	ΔH_2 (J/g)	T_f (°C)
1	45,51 ± 0,19 _a	34,88 ± 0,11 _a	−26,66 ± 24,72 _b	7,37 ± 1,92 _{ab}	12,67 ± 1,61 _a	−59,97 ± 0,08 _{bc}
2	45,94 ± 0,07 _a	14,24 ± 0,37 _b	−44,05 ± 0,36 _b	2,15 ± 0,28 _b	13,35 ± 0,36 _a	−59,91 ± 0,22 _{bc}
3	21,99 ± 0,08 _b	20,53 ± 5,76 _{ab}	−43,36 ± 1,52 _b	8,60 ± 3,40 _a	14,05 ± 0,55 _a	−60,23 ± 0,45 _{bc}
4	38,41 ± 0,02 _{ab}	23,61 ± 5,76 _{ab}	−43,03 ± 1,05 _{ab}	5,03 ± 1,63 _{ab}	12,94 ± 0,64 _a	−59,79 ± 1,01 _c
5	39,88 ± 0,26 _a	19,74 ± 0,50 _{ab}	−44,85 ± 0,30 _b	5,05 ± 0,14 _{ab}	14,60 ± 0,42 _a	−60,88 ± 0,43 _{ab}
6	21,91 ± 0,19 _b	14,82 ± 0,23 _b	−22,53 ± 0,18 _a	2,60 ± 0,01 _b	10,16 ± 0,24 _a	−56,11 ± 0,10 ^a
7	37,05 ± 0,12 _{ab}	14,12 ± 0,14 _b	−44,52 ± 0,17 _b	4,42 ± 0,03 _b	10,37 ± 0,06 _a	−55,71 ± 0,47 _c
8	41,72 ± 0,77 _a	24,43 ± 11,43 _{ab}	−45,19 ± 0,15 _b	6,16 ± 0,98 _{ab}	16,70 ± 0,23 _a	−60,55 ± 0,23 _c
9	44,74 ± 1,37 _a	12,01 ± 1,62 _b	−33,57 ± 16,17 _{ab}	2,61 ± 0,26 _b	12,75 ± 4,40 _a	−58,12 ± 3,20 _{ab}
10	32,59 ± 13,40 _{ab}	26,42 ± 7,37 _{ab}	−44,74 ± 0,82 _b	6,33 ± 1,77 _{ab}	15,80 ± 2,80 _a	−60,63 ± 0,12 _c
Melting						
1	−39,06 ± 0,57 _a	−27,94 ± 0,02 _a	50,14 ± 0,06 _b	53,3 ± 0,07 _a	2,90 ± 1,38 _a	68,10 ± 3,31 _a
2	−38,23 ± 1,00 _a	−28,52 ± 0,34 _a	51,12 ± 0,51 _b	50,21 ± 0,77 _a	0,30 ± 0,07 _a	60,43 ± 1,35 _a
3	−34,43 ± 6,51 _a	−27,37 ± 1,68 _a	38,45 ± 3,95 _{ac}	5,03 ± 9,08 _a	12,94 ± 1,71 _a	59,76 ± 5,94 _a
4	−34,99 ± 7,31 _a	−27,19 ± 1,42 _a	44,95 ± 1,05 _{bc}	44,14 ± 9,6 _a	1,69 ± 5,24 _a	56,62 ± 1,01 _a
5	−39,69 ± 0,40 _a	−24,20 ± 0,62 _a	40,71 ± 0,38 _{bc}	54,19 ± 0,58 _a	2,09 ± 0,10 _a	55,25 ± 2,12 _a
6	−40,29 ± 0,54 _a	−25,12 ± 0,42 _a	36,79 ± 0,09 _{ac}	55,58 ± 3,54 _a	2,84 ± 0,14 _a	57,74 ± 0,13 _a
7	−44,22 ± 1,71 _a	−26,03 ± 0,06 _a	34,10 ± 0,09 _{ac}	56,85 ± 0,02 _a	2,48 ± 0,11 _a	54,26 ± 0,23 _a
8	−41,14 ± 1,37 _a	−25,63 ± 0,19 _a	43,33 ± 5,08 _{bc}	57,29 ± 0,48 _a	2,06 ± 1,88 _a	61,63 ± 3,09 _a
9	−41,87 ± 1,94 _a	−25,60 ± 0,33 _a	28,68 ± 0,07 _a	52,81 ± 0,26 _a	1,32 ± 0,06 _a	57,63 ± 0,85 _a
10	−39,53 ± 1,68 _a	−26,65 ± 3,02 _a	43,46 ± 4,22 _{bc}	52,98 ± 6,56 _a	2,91 ± 1,35 _a	58,72 ± 4,46 _a

T_i : Initial temperature of crystallization/melting; T_p : Peak temperature; T_f : Final temperature of crystallization/melting; ΔH_1 : Enthalpy of peak 1; ΔH_2 : Enthalpy of peak 2. 1) CW, 2) SMS, 3) FHPO, 4) CW + SMS, 5) CW + FHPO, 6) SMS + FHPO, 7) 1/3 CW + 1/3 SMS + 1/3 FHPO, 8) 2/3 CW + 1/6 SMS + 1/6 FHPO, 9) 2/3 SMS + 1/6 CW + 1/6 FHPO, 10) 2/3 FHPO + 1/6 CW + 1/6 SMS. CW: Candelilla wax, SMS: Sorbitan Monostearate, FHPO: Fully hydrogenated palm oil.

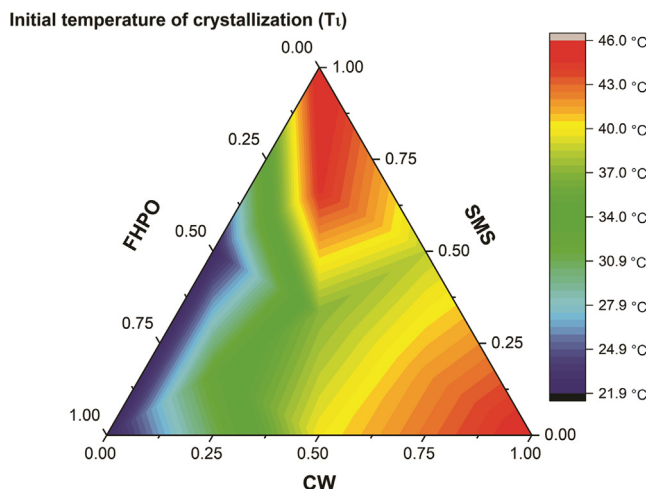


Fig. 3. Triangular diagram of initial temperature of crystallization (T_{ic}) of organogels. $R^2 = 0,89$. CW: Candelilla wax, SMS: Sorbitan Monostearate, FHPO: Fully hydrogenated palm oil.

3.3. Physical stability for temperature cyclization

The gel firmness was assessed visually using a photographic record and a standardized scale, aiming to verify the resistance of organogels to temperature fluctuations (Garcia et al., 2013; Godoi et al. 2019).

In the first cyclization in Table 4, according to the visual analysis and classification on the firmness scale, the organogels 1 (CW), 4 (CW + SMS), 5 (CW + FHPO), 6 (FHPO + SMS), 7 (ternary mixture with equal structuring agents concentrations), 8 (ternary mixture with a higher CW concentration) and 10 (ternary interaction with a higher FHPO concentration) were stable and firm at the temperature used for static crystallization (5 °C) and when subjected to the highest temperature (35 °C) demonstrating the thermal resistance of these organogels. This effect is probably due to the composition of CW and its specific crystallization profile, which corroborates the results for the low t_{ind} and high SC_{max} and T_i crystallization, with a mean value of

Table 4
Classification of organogels according temperature cyclization.

Organogel	Cyclization 1		Cyclization 2	
	Stage 1 (5 °C/48 h + 35 °C/24 h)	Stage 2 (5 °C/ 24 h)	Stage 1 (35 °C/ 48 h)	Stage 2 (5 °C/ 72 h)
1	5	5	5	5
2	1	1	1	2
3	3	5	2	3
4	4	5	5	5
5	5	5	5	5
6	5	5	1	5
7	5	5	3	5
8	5	5	5	5
9	1	5	2	5
10	5	5	1	5

Samples: 1 (CW), 2 (SMS), 3 (FHPO), 4 (CW + SMS), 5 (CW + FHPO), 6 (SMS + FHPO), 7 (1/3CW + 1/3FHPO + 1/3SMS) 8 (2/3CW + 1/6SMS + 1/6FHPO) 9 (2/3SMS + 1/6FHPO + 1/6CW) 10 (2/3 FHPO + 1/6SMS + 1/6CW). CW: Candelilla wax, SMS: Sorbitan Monostearate, FHPO: Fully hydrogenated palm oil.

45.51 °C, which was higher than that used in this analysis (maximum 35 °C) (Godoi et al., 2019).

In addition, the organogels 2 (SMS) and 9 (ternary mixture with higher SMS concentration) were viscous, but flowed easily due to the insufficient amount of SMS for the formation of the crystal network, with high solubility in the continuous phase, regardless of the temperature. In the combination CW + SMS, as observed in the crystallization kinetics and thermal behavior, that the SMS reduced the effectiveness of CW as a structuring agent, which may also have interfered with the gel formation. On the other hand, the organogel 3 (FHPO) was firm, flowing on the surface when the beaker content was poured, which indicates an incomplete crystallization. When returning the organogels to cooling temperature (5 °C), only the organogel 2 (SMS) remained liquid, while the organogel 9 (ternary mixture with higher SMS concentration) was thermoreversible.

Concerning the second cyclization, only the organogels 1 (CW), 4

Table 5
Polymorphic habit obtained by ray-x diffraction.

Organogels	Shorts spacings (Å)	Polymorphic habit
1	4,04–3,61	β'
2	–	Liquid
3	4,28–3,76	β'
4	4,01–3,69	β'
5	4,05–3,68	β'
6	–	Liquid
7	4,06–3,73	β'
8	4,05–3,65	β'
9	–	Liquid
10	–	Liquid

1) CW, 2) SMS, 3) FHPO, 4) CW + SMS, 5) CW + FHPO, 6) SMS + FHPO, 7) 1/3 CW + 1/3 SMS + 1/3 FHPO, 8) 2/3 CW + 1/6 SMS + 1/6 FHPO, 9) 2/3 SMS + 1/6 CW + 1/6 FHPO, 10) 2/3 FHPO + 1/6 CW + 1/6 SMS. CW: Candellila wax, SMS: Sorbitan monostearate, FHPO: Fully hydrogenated palm oil.

(CW + SMS), 5 (CW + FHPO), and 8 (2/3CW + 1/6SMS + 1/6FHPO) were firm when subjected to 35 °C for 48 h, while the others required a reduction in temperature (5 °C) for the gel formation. The organogel 2 did not form a completely firm gel, even at a lower temperature (Table 4). The organogels that remained firm after exposure to 35 °C for 48 h showed crystallization temperature ranging from 37 °C to 45 °C and t_{ind} of approximately 5 min, thus the maintenance of the static temperature for 48 h influenced the crystal formation and stabilization and the crystal network formed.

CW showed a greater capacity for formation and maintenance of the crystal network, even at higher temperatures, besides its greater thermal resistance as observed in the DSC. The SMS, with onset crystallization temperature close to 49 °C, was able to form crystal structures but did not result in a stable network in the concentration used, regardless of temperature. In contrast, FHPO presented the onset crystallization temperature of approximately 45 °C, which was also observed in the cyclization temperature, in which firmer organogels were formed only when subjected to the refrigeration temperature. This cyclization methodology was previously used by Silva, Arellano, and Martini (2018) in margarine produced with organogels containing candellila wax. Thus, high thermal resistance and thermoreversible behavior were observed in products containing organogel as a lipid phase when compared to commercial margarine, without phase separation and rare oil exudation.

3.4. Polymorphism

As can be seen in Table 5 and Fig. 4, the polymorphic habit β' was found for organogels made with CW and FHPO alone, in binary mixtures of CW + FHPO and CW + SMS, and in the ternary mixtures in organogel 8 (mostly CW). The SMS alone, the FHPO + SMS blends, and

the other ternary mixtures did not result in crystallinity detectable by the X-ray diffraction, demonstrating that SMS cannot induce the formation of the crystalline phase under the conditions of the analysis, besides being a potent crystal stabilizer, delaying, for example, the polymorphic transitions in cocoa butter, which justifies the use of this emulsifier in lipid bases (Ribeiro et al., 2015; Smith, Bhagga, Talbot, & Van Malssen, 2011). Therefore, the degree of crystallinity of the system depended on the presence of CW. The polymorphic habit β' is characteristic of CW, as also reported by Chopin-Doroteo et al. (2011) with diffraction peaks of 4.07–4.14 Å and 3.65–3.74 Å, a result similar to that obtained in this study.

According to the literature, SO crystallizes in the form β , due to the low variability of TAGs and low palmitic acid levels, being the polymorph for applications in products of greater hardness and low aeration. On the other hand, palm oil is characterized by the form β' , which is the same polymorphic habit of FHPO and CW, due to the concentration of long-chain triglycerides (50–52C) that are arranged as β' (Foubert, Van De Walle, Dewettinck, & Dijkstra, 2007; Oliveira, Ribeiro, & Kieckbusch, 2015) which justifies the polymorphic habits observed in this study.

3.5. Microstructure

The different molecular packaging reflects on the morphological characteristics and the density of the crystalline network formed what defines the macroscopy behavior of the fat as texture, appearance and functionality. The lipid composition and the crystallization conditions and the solid fat content can influence the morphological forms of the crystals, factors that can be observed in the analysis of microscopy under polarized light (Rashid, Kamarulzamani, & Omar, 2016). A general relationship exists between the structure of a fat and its physical and sensory properties, as spreadability and the melting sensation in the mouth depend on the mechanical strength of this crystalline network (Ribeiro, Basso, Grimaldi, Gioielli, & Gonçalves, 2009). Anyway, when organogels are evaluated, is possible to observe, besides the conventional crystals, the three-dimensional networks formed by the organogelators and their interactions in microscopic scale considering the final product characteristics. These results for the organogels formulated were in Fig. 5.

When the structuring agents alone were mixed with SO, the organogel containing CW exhibited a more structured highly visible three-dimensional network, in the form of platelets (Chopin-Doroteo et al., 2011; Sánchez-Becerril et al., 2018). This structure showed a greater immobilization capacity of the liquid phase, which may influence the mechanical resistance in the tests of hardness and a higher complex module (G') in the rheological behavior, confirming the correlation between the microstructure of the organogel and its mechanical resistance, according to the results our research group (Godoi et al., 2019).

In contrast, the use of SMS alone provided few crystals, always in a

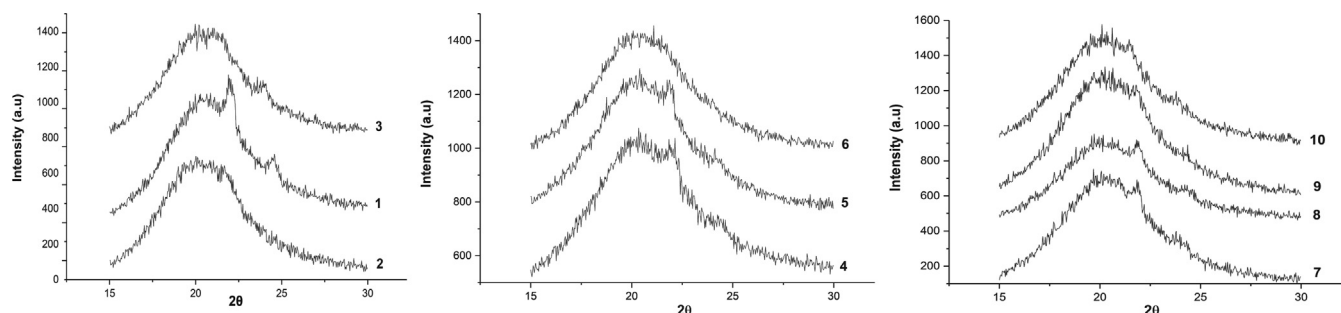


Fig. 4. Diffractions peak showing the polymorphic habit of organogels. 1) CW, 2) SMS, 3) FHPO, 4) CW + SMS, 5) CW + FHPO, 6) SMS + FHPO, 7) 1/3 CW + 1/3 SMS + 1/3 FHPO, 8) 2/3 CW + 1/6 SMS + 1/6 FHPO, 9) 2/3 SMS + 1/6 CW + 1/6 FHPO, 10) 2/3 FHPO + 1/6 CW + 1/6 SMS. CW: Candellila wax, SMS: Sorbitan monostearate, FHPO: Fully hydrogenated palm oil.

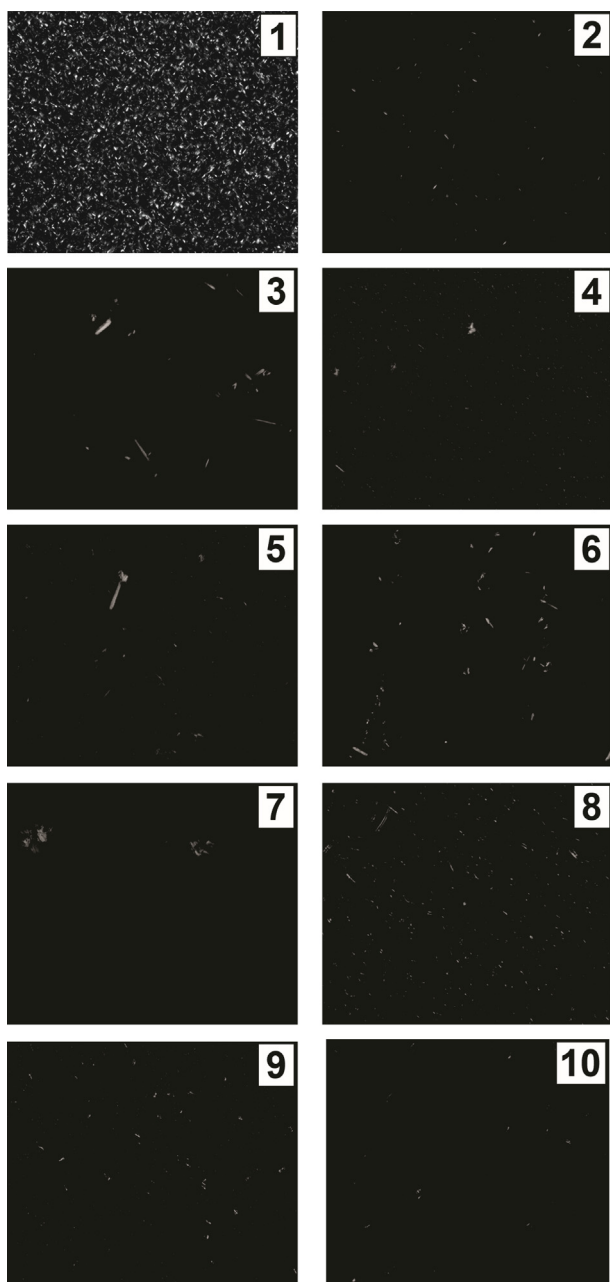


Fig. 5. Micrographs of organogels at 25°C with 40x. 1)CW, 2) SMS, 3) FHPO, 4) CW+SMS, 5) CW+ FHPO, 6) SMS+ FHPO, 7) 1/3 CW+ 1/3 SMS+ 1/3 FHPO, 8) 2/3 CW+1/6 SMS+1/6 FHPO, 9) 2/3 SMS+1/6 CW+1/6 FHPO, 10) 2/3 FHPO +1/6 CW + 1/6 SMS. CW: Candellila wax, SMS: Sorbitan monostearate, FHPO: Fully hydrogenated palm oil.

tubular and elongated shape, characteristic of this structuring agent. However, as observed in the thermal behavior and crystallization kinetics, the amount of SMS used was insufficient to form a dense and structured network, as also observed by [Swe and Asavapichayont \(2018\)](#) who reported that SMS structuring molecules formed vesicular tubules, followed by association, requiring a concentration of at least 18% to form the three-dimensional network.

The addition of FHPO alone led to the formation of dispersed needle-shaped crystals. Although triacylglycerols generally crystallize into spherulite-type crystals that correspond to the aggregation of crystal lamellae and grow radially from the same central nuclei, eventually they crystallize like needles and discs, depending on the cooling conditions or the melting characteristics of the sample. Thus, palm oil

can present as spherulites or needles, as observed in the present study, with smaller and isolated crystals when associated with other structuring agents ([Marangoni & Rosseau, 2002](#); [De Oliveira et al., 2015](#)).

Concerning the binary combinations (4, 5, and 6), a microstructure pattern characteristic of CW was observed. Needle-shaped crystals were observed in the organogels 4 and 5, probably due to the presence of FHPO. In the SMS + FHPO blend (organogel 6), although there was no formation of crystals, some needle-type crystals were observed, characteristic of FHPO and small spherical crystals, representing the SMS crystals, as also observed by [Barbosa, Cardoso, Ribeiro, Kieckbusch, and Buscato \(2018\)](#).

In ternary mixtures, which are unprecedented in the literature, crystals characteristic of CW was observed, mainly in the micrographs of organogel 8, which contained the higher concentration of this structuring agents, while the other micrographs showed dispersed crystals, without characterizing a typical crystal network. This effect is consistent with the results of the X-ray diffraction analysis, which demonstrated that the organogels 2, 6, 9, and 10 were liquid, with no crystalline phase.

4. Conclusion

The CW was effective for the formation of a dense three-dimensional crystal network, with an increase in the solids content, rapid onset of crystallization and high melting point, which indicates adequate thermal and mechanical resistance of the organogels. The FHPO improved the higher solids content of SO with a lower melting point, forming organogels only under refrigeration temperatures. Improved effects were observed when FHPO was combined with CW, increasing the thermal and mechanical resistance of the organogel. On the other hand, besides not contributing to the increase in the solids content, SMS did not form a firm organogel when subjected to high (35 °C) or low temperatures (5 °C). However, when used in combination, mainly in binary or ternary mixtures with CW, it behaved as a crystallization accelerator. Among the ternary mixtures, the organogel 8, containing a higher CW concentration, showed a greater capacity for immobilization of the oil phase, indicating a stronger bond strength, thus higher stability of the crystal network in the presence of CW, forming a stable and firm organogel for all temperatures and conditions studied, with the CW determining the thermal behavior of the system. The use of CW, SMS and FHPO, combined in organogels, led to a predominance of the polymorphic habit β' , which can expand the possibilities of application of the organogels studied in margarines, spreads and shortenings reducing the saturated fatty acids, without trans fatty acids, keeping the physical characteristics of these products, where gloss and uniform surface coverage are needed.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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