Obtenção e caracterização de organogéis de óleo de soja estruturados com cera de canade-açúcar e suas frações solúveis em etanol à quente

Obtention and characterization of soybean oil organogels structured with sugarcane wax and its hot ethanol soluble fractions

Obtención y characterización de organogeles producidos con cera de caña de azúcar y sus fracciones solubles en etanol caliente

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Resumo

A cera de cana (SCW) foi fracionada usando etanol quente e um sistema de lavagem simples, as frações obtidas solúveis (SSCW) e insolúveis (ISCW) foram usadas para produzir organogéis cristalizados em duas temperaturas diferentes (5 e 25°C) nas concentrações de 1, 2, 3 e 4% (m/m). A pesquisa avaliou o comparamento dos organogéis obtidos da cera de canade-açúcar (e suas frações), todos os organogéis foram avaliados quanto à sua microestrutura, comportamento térmico, comportamento reológico e resistência mecânica. Todas as amostras de organogel foram avaliadas quanto à estabilidade em uma estufa BOD com temperatura controlada (a 5, 25 e 35°C), e o comportamento térmico para os organogéis de SCW, SSCW e ISCW foi diferente. A variação de entalpia passou de 118,87 para 129,63 e 85,65J/g para as frações. Os organogéis obtidos a partir desses materiais foram algo semelhantes durante a cristalização (TPeak de 42,83, 37,19 e 36,23°C, respectivamente), a variação da cristalização e da entalpia de fusão apresentou histerese, como observado para outros organogéis de ceras. Os organogéis de SSCW foram significativamente mais difíceis do que os obtidos com SCW e ISCW. As micrografias dos organogéis mostraram uma rede mais organizada presente no organogel da SSCW quando comparada com a SCW que foi mais organizada que os

organogéis da ISCW. A diferença na microestrutura observada explica a diferença no comportamento mecânico dos organogéis formados com frações solúveis e insolúveis em etanol quente da cera de cana de açúcar.

Palavras-chave: Organogéis; Cera de cana; Morfologia de cristais; Reologia; Dureza.

Abstract

Sugarcane wax (SCW) was fractionated using hot ethanol and a simple washout system, the obtained fractions soluble (SSCW) and insoluble (ISCW) were used to produce organogels crystallized at two different temperatures (5 and 25°C) at the concentrations of 1, 2, 3 and 4% (w/w). The laboratory research evaluated the behavior of organgels obtained from sugarcane wax (and its fractions), all organogels were assessed due to its microstructure, thermal behavior, rheological behavior and mechanical resistance. Samples were visually assessed for stability at a controlled temperature oven (at 5, 25 and 35°C), and the thermal behavior for SCW, SSCW and ISCW were different. The enthalpy variation changed from 118.87 to 129.63 and 85.65 J/g for the fractions. Organogels obtained from these materials were somewhat similar during crystallization (TPeak of 42.83, 37.19 and 36.23°C respectively), crystallization and melting enthalpy variation presented hysteresis as observed for other waxy organogels. SSCW organogels were significantly harder than the obtained with SCW and ISCW. Micrographs of the organogels showed a more organized network present on SSCW organogel when compared with SCW that was more organized than ISCW organogels. The difference on the microstructure observed explains the difference on the mechanical behavior of organogels formed with sugarcane wax hot ethanol-soluble and insoluble fractions.

Keywords: Organogels; Sugarcane wax; Crystal morphology; Rheology; Hardness.

Resumen

Se fraccionó la cera de caña de azúcar (SCW) usando etanol caliente y un sistema de lavado simple, las fracciones obtenidas solubles (SSCW) e insolubles (ISCW) se usaron para producir organogeles cristalizados a dos temperaturas diferentes (5 y 25°C) a las concentraciones de 1 , 2, 3 y 4% (p/p). Se evaluó la estabilidad de todas las muestras de organogel en una camara a temperatura controlada (a 5, 25 y 35°C), y el comportamiento térmico para SCW, SSCW e ISCW fue diferente. La variación de entalpía cambió de 118.87 a 129.63 y 85.65 J / g para las fracciones. Los organogeles obtenidos de estos materiales fueron algo similares durante la cristalización (TPeak de 42.83, 37.19 y 36.23°C respectivamente), la cristalización y la variación de la entalpía de fusión presentaron histéresis como se observó para otros organogeles de ceras. Los organogeles SSCW fueron significativamente más duros que los obtenidos con SCW e ISCW. Las micrografías de los organogeles mostraron una red más organizada presente en el organogel SSCW en comparación con SCW que estaba más organizada que los organogeles ISCW. La diferencia en la microestructura observada explica la diferencia en el

comportamiento mecánico de los organogeles formados con cera de caña de azúcar fracciones solubles e insolubles en etanol calientes.

Palabras clave: Organogeles; Cera de caña de azúcar; Morfología cristalina; Reología; Dureza.

1. Introduction

Organogels are described as a system where two continuous phases coexist, a solid organogelator and an immobilized continuous phase that is an organic solvent (Abdallah et al., 1999), they are called organogels because of their gel-like behavior and differing from hydrogels the immobilized phase is an organic component (Rogers, 2009)

Due to its microstructure as a three-dimensional network (Abdallah & Weiss, 2000), they are considered as self-sustaining, which makes them an interesting material for studies, but also show their potential for food application.

Organogels has been presented as "the fat for the future" (Hughes et al., 2009; Pernetti, van Malssen, Flöter, et al., 2007; Rogers et al., 2009a), even though they have a long way until being a potential application to achieve an industrial application.

Many of the materials that have the ability to form organogels, also called organogelators, are not edible, as 12-hydroxystearic acid (Rogers et al., 2008, 2009b), or implicate in higher costs for future possible uses for example; cholesterol (Almeida & Bahia, 2006) or γ -oryzanol at high concentration (Bot et al., 2008).

Because of it the use of edible already approved materials as organogelators are important to produce organogels that are easier to be used as potential food application. The most common organogelators are acylglycerols (Lupi et al., 2012), fatty acids, fatty alcohols (Rogers et al., 2009b), mixtures of γ -oryzanol and cholesterol (Bot et al., 2008), mixtures of lecithin and sorbitan tristearate (Pernetti, van Malssen, Kalnin, et al., 2007), mixtures of fatty acids and fatty alcohols (Pernetti, van Malssen, Flöter, et al., 2007).

Waxes which are mixtures of fatty acids, fatty alcohols and minor components such as alkanes (Parish et al., 2002), are potential materials to be used as organogelators for edible organogels (also known as oleogels), some studies had been performed using vegetable waxes as organogelators such as; candelilla (CLW), carnauba (CRW), rice bran (RBW), sugarcane (SCW) and sunflower (SFW) (Alvarez-Mitre et al., 2012; Daniel & Rajasekharan, 2003; Dassanayake et al., 2009; Rocha et al., 2013; Toro-Vazquez et al., 2007) all of them presented the ability to form organogels at different concentrations and conditions.

The process to produce organogels is simples and usually the same for any

organogelators passing through the heating of the continuous phase followed by the addition of the organogelator and posterior crystallization the process has been reported various times at the literature (Morales-Rueda, Dibildox-Alvarado, Charó-Alonso, & Toro-Vazquez, 2009; Patel & Dewettinck, 2016; Rocha et al., 2013).

Also organogels present an important role at the future of fat structure, once called "the fat the future" (Rogers et al., 2009a), even with so many years at the moment there are no products that are structured using organogels, but the feasibility had been evaluated several times for icecream (Zulim Botega et al., 2013), margarine (Chaves et al., 2020; Hwang et al., 2014), cookies (Jang et al., 2015; Mert & Demirkesen, 2016; Yılmaz & Öğütcü, 2015) and some other products such as meat emulsions (Lupi et al., 2014).

The potential of sugarcane wax had been already been studied (Rocha et al., 2013), the idea that some of the components of the material should have a better ability to form organogels lead to the idea of wax fractioning to isolate some of the components, once soybean oil is soluble in hot ethanol the use of the same solvent aimed to collect a fraction with similar polarity that should be compatible (Terech, 1992) and possibly could change the amount needed to gelation (Dassanayake et al., 2012) and also improve the quality of the organogels, specially hardness as reported previously at literature the polarity of organogelators and their continuous phases is relevant to such quality (Hwang et al., 2015).

The objective of this laboratory research was to determine the behavior of organgels obtained from sugarcane wax and organogels obtained at the same conditions using fractions of a simple washout fractionating method using hot ethanol. Organogels were compared due to its microstructure, thermal behavior, rheological behavior and mechanical resistance.

2. Material and Methods

An experimental design were elaborated and the research separated at four parts the first was to acquire and prepare the raw materials, after the acquisition the second step was to prepare the wax fractions at a third step the organogels samples were prepared and finally the samples were evaluated at the final fourth step. The research was based on acquisition of qualitative and also quantitative data from several analytical methods (Pereira et al., 2018; Severino, 1996).

2.1. Material and Sample Preparation

Refined soybean oil (SO) (Cargill Alimentos S.A., Mairinque, SP, Brazil) was purchased from the local market, clarified and purified sugarcane wax (SCW) was kindly donated by Usina São Francisco (Sertãozinho, SP, Brazil) and anhydrous ethanol (Merck, Germany), was purchased at the local market.

2.2. Fractioning of Waxes

An amount of 1 l of anhydrous ethanol was added to 500 g of SCW and boiled under reflux for 30 minutes and a hot ethanol soluble fraction (SSCW) diluted at the ethanol was separated as a supernatant, the residue was washed with another 11 of anhydrous ethanol and the ethanol supernatant separated and added to the first fraction the fractioning was performed according to Gandra (2006). The fractionating process presented a yield of 55% for the soluble and 43% for the insoluble fractions (ISCW). Both fractions were dried under vacuum and milled.

The thermal properties of SCW and the fractions were measured and are presented in Table 1 (the obtained results were similar to those obtained by Gandra (2006), fatty acids and fatty alcohols compositions are described in Table 2 (Gandra, 2006; Lopes, 2010).

Property	SCW	SSCW	HSCW
Melting point (°C)	78.3	75.8	79.4
Acidity value (mg KOH/g)	23.2	34.19	18.2
Iodine value (g/100g)	22.3	42.3	17.2
Saponification value (mg KOH/g)	79.1	113.3	93.6

Table 1. Physical Properties of sugar cane wax (SCW) and its fractions.

(Gandra, 2006)

	Fat	Fatty Acids % (w/w)		Fatty Alcohols % (w/w)		
	SCW	SSCW	HSCW	SCW	SSCW	HSCW
16:0	22.5	29.6	39.6	-	-	-
18:3	3.3	14.1	2.5	-	-	-
18:1 e 18:2	7.1	13.8	8.7	-	-	-
18:0	3.9	4.6	4.3	-	-	-
20:0	1.6	1.6	2.0	-	-	-
22:0	2.1	1.2	2.0	-	-	-
24:0	4.1	2.6	3.5	3.2	1.4	4.6
26:0	2.9	2.6	2.2	10.4	15.7	19.8
28:0	24.8	12.0	18.1	58.5	59.5	51.1
29:0	2.0	-	-	0.8	2.1	6.1
30:0	10.1	12.3	8.3	15.6	10.7	8.8
32:0	5.4	2.3	4.1	7.6	5.2	3.1
34:0	5.3	2.2	4.1	1.0	-	-

Table 2. Fatty acids and fatty alcohols Composition of sugar cane wax (SCW) and its fractions.

(Gandra, 2006; Lopes, 2010)

2.3. Organogels Preparation

Organogel samples were prepared firstly heating soybean oil up to 80 °C under stirring and SCW, SSCW or ISCW solid wax was slowly added (1, 2, 3 and 4% w/w) and mixed up to its complete dissolution. After complete dissolution, the mixture was kept under agitation without heating for 3 min. The samples were put inside 50 ml glass beakers and stored at 5 or 25 °C for 24 hours to static crystallization and kept at 25 °C temperature up to perform the analysis.

Two temperatures were used for static crystallization aiming to achieve evaluate the effect of different supercooling at the formation of different crystallization polymorphs (Himawan et al., 2006) although it was not possible to evaluate the cooling rates due to processing conditions it is known that with the lower temperature a faster crystallization is expected.

3. Methods

3.1. Visual stability

Organogel liquid samples at (1, 2, 3 and 4% w/w), were put inside glass tubes and conditioned at the studied temperatures of 5 and 25°C for static crystallization for 24 hours. The crystallized samples were kept at 5, 25 and 35°C for 7 days and visually assessed for oil exudation of phase separation at first, third and seventh days. The aimed temperatures ideally represent refrigeration (5°C) and room temperature (25°C) while above 35°C sugarcane organogels showed no stability as reported by Rocha et. al. (2013), meaning that there is no point in evaluating the samples at temperatures above 35°C.

3.2. Crystallization and Melting Behavior of Organogels

The crystallization and melting thermograms were determined by differential scanning calorimetry (DSC) using a TA Instruments model Q2000 (TA Instruments, New Castle, DE, USA). Samples of organogels (10mg) were placed in aluminum hermetic pans and weighted.

The samples were heated at 100°C and maintained at this temperature for 15 minutes before the samples were cooled to -40°C at 10°C/min. Samples were kept at this temperature for 30 minutes and then again heated to 100°C at 10°C/min, as evaluated by Rocha et. al. (2013).

The thermal parameters (TOnset, TEndset, TPeak, Δ H) were calculated for cooling (crystallization) and heating (melting) sweeps using Universal Analysis software (TA Instruments, New Castle, DE, USA).

The average of 3 measures was used to perform parameters calculation.

3.3. Hardness (Compression/Extrusion)

Hardness of SCW, SSCW and ISCW organogels (1, 2, 3 and 4 %w/w) were evaluated by compression/extrusion measurements using a texture analyzer Stable Micro Systems model TA-XT2i (Godalming –UK) using a head cross speed of 1.0 mm/s, 30 ml of the gels were conditioned in 50 ml glass beakers glass recipients and compressed using an acrylic cylinder probe (25mm diameter and 35 mm high) up to 15 mm height at the temperature of 25°C.

The average of 4 measurements of the maximum force measured at any depth was considered as the result.

3.4. Polarized light microscopy

Micrographs of organogels (4 %w/w) were obtained under polarized light microscope Olympus System Microscope model BX 51 (Olympus America Inc. Center Valley, PA, USA) equipped with a digital camera model Olympus EX300 (Olympus America Inc. Center Valley, PA, USA).

Samples were melted at 80 °C and a small drop put over a heated glass slide and covered with a glass coverslip. The glass slides were crystallized on at 5 and 25°C for 24 hours and analyzed at 25°C. Samples were treated using Image cell Sens Standard 1.7.1. (Olympus, USA).

3.5. Scanning Electronic Microscopy (SEM)

Morphology of 4% (w/w) samples were analyzed by SEM, using a TM3000 Microscope (Hitachi, Japan). All samples were crystallized at 50 μ l aluminum pans at controlled temperature, after complete crystallization all samples were washed out by immersion at an Acetone:Chloroform 1:1 (v:v) for 6 hours and dried at low pressure at room temperature using a vacuum chamber.

Samples were directly observed using an acceleration of 15 kVA and an increase of 1000x.

3.6. Statistical analysis

The results were evaluated by analysis of variance (ANOVA) and significant differences (p < 0.05) between the treatments were determined by Tukey test. Statistical analysis was performed using the software Statistica (Data Analysis Software system, StatSoft, Inc, Tulsa-USA) version 7.0.

4. Results and Discussion

4.1. Visual stability

SCW organogel samples crystallized at 25°C were stable for 7 days at all studied conditions (5, 25 and 35°C) at all concentrations, the same material crystallized at 5°C did not present the same stability presenting a small oil exudation after 3 days at 35°C up to the seventh day.

At Figure 1A, it was possible to observe that the ISCW organogel at 1% (w/w) did not form a stable phase after 3 days at 25°C, with the increase of the amount of wax the samples

became just one phase as shown in Figure 1B for 4% (w/w) organogel samples.

Figure 1. Organogel samples crystallized at 25°C at (a) SCW, (b) SSCW and (c) ISCW (A) after 3 days at 25°C; (A) 1% (w/w), (B) 4% (w/w) and (C) SSCW organogel at 4% (w/w) crystallized at 5°C after 7 days at 35°C.



The SSCW organogels at 4% (w/w) presented oil exudation after 3 days at 35°C at both crystallization conditions (5 and 25°C) as shown in Figure 1C, the oil exudation was not visible for SSCW samples at lower concentrations. All other samples that formed a visually continuous phase did not show oil separation. The results are similar to those observed by Rocha et. al. (2013) for organogel samples produced using SCW and also candelila wax.

Based on polarity it is possible to explain why the ISCW showed lower stability specially compared to the SSCW, with polarity similar to the studied soybean oil. If we observe the polarity table presented by Hwang et. al. (2015), it is the expected behavior with similar polarity the organogels are expected to be more stable and organized, and at the present study the same behavior was observed.

4.2. Thermal Analysis

The thermal properties of SCW, SSCW and ISCW were measured, the Figure 2A shows the crystallization of the waxes and it is possible to observe that the waxes presented changes on the crystallization behavior especially the peak temperature, 67.88°C for SCW changed to 54.98 and 66.89°C for SSCW and ISCW respectively. The enthalpy variation changed from 118.87J/g for SCW to 129.63J/g for SSCW and decreased to 85.65J/g for ISCW.

Figure 2. (A) Crystallization thermogram for 4% (w/w) organogels of SCW (full lines), SSCW (dashed line) and ISCW (dotted line); (B) Melting thermogram for 4% (w/w) organogels of SCW (full lines), SSCW (dashed line) and ISCW (dotted line).



The melting behavior was presented in Figure 2B and allows to observe that organogels from SCW and ISCW presented very similar peaks (although with different intensities) while SSCW was different. The measured peak temperature for melting was 61.91°C for SCW, 60.77 and 65.41°C for SSCW and ISCW respectively. The enthalpy variation changed from 121.70J/g for SCW to 132.27J/g for SSCW and decreased to 87.21J/g

for ISCW.

The crystallization thermogram for ISCW also indicates that this fraction is, a concentrate of some of the wax components, as expected, presenting a narrower and pronounced peak which for thermal analysis represents pure components (Campos, 2005), allowing to see that this fraction presents a higher uniformity.

At SSCW thermogram a wider peak is presented, but without the presence of the higher peak that is present on the SCW and were pronounced for ISCW, such difference should be due to chemical composition, according to Gandra (2006), the ISCW presented an increase from 22.5 to 39.6% of the amount of palmitic acid when compared with SCW and also presented a decrease of the amount of fatty alcohols from 21 to 18% (w/w), also SSCW presented 59.5% of octacosanol compared with 51.1% of ISCW, but also the SSCW presented an increase of the fatty alcohols content from 21 to 25% compared with SCW (Gandra, 2006; Vieira, 2003).

Sample	Tonset (°C)	T _{Endset} (°C)	Τ _{Max} (° C)	ΔH (J/g)				
Crystallization								
SCW	46.75ª	15.82 ^b	42.83ª	3.53ª				
SSCW	41.89 ^c	14.20 ^c	37.19 ^b	3.44 ^a				
ISCW	44.94 ^b	18.20 ^a	36.23°	2.20 ^b				
Melting								
SCW	59.50ª	77.29ª	72.62 ^b	0.88 ^a				
SSCW	49.22 ^b	78.44 ^a	69.92°	0.42 ^c				
ISCW	58.17 ^a	78.15 ^a	73.88ª	0.62 ^b				

 Table 3. Results of the thermal analysis of organogels developed with SCW, SSCW and ISCW.

*Same letters indicate that there is no significant difference between samples at the same column (p>0.05).

The 4% (w/w) organogels samples obtained with each of the waxes were also evaluated and the crystallization and melting thermograms presented in Figure 2A and 2B respectively. The calculated thermal parameters are presented in Table 3, they allow to observe that compared with the SCW organogel, both fractions presented a change on enthalpy variation (Δ H), for melting, this difference should be related to the separation of

components of each fraction. The effect was not observed for the crystallization, SCW and the SSCW organogels presented no statistical difference, only ISCW organogel presented a statistically different enthalpy variation, it was also possible to observe that the enthalpy variation for melting was significantly different between all organogel samples.

Enthalpy variation for crystallization and melting showed a hysteresis for all organogels samples, such effect according to Abdallah, Lu, & Weiss (1999), is due to the presence of an exothermic event of dissolution of the organogelator during the heating of the sample Rocha et al. (2013), observed the same effect for SCW organogels and the present work using the same wax and its fractions observed the same effects.

4.3. Mechanical Properties

Hardness (compression/extrusion)

The samples at a concentration of 1, 2, 3 and 4% (w/w) of each of the studied organogelators SCW, SSCW and ISCW were analyzed and the results are shown in Table 2.

As expected the samples obtained with higher amounts of waxes were significantly harder than the organogels with lower concentrations, except for ISCW that did not show significant difference with the increase of wax concentration.

Crystallization temperature showed a significant influence on the hardness of the organogels for SCW and SSCW while it did not influence the hardness of the organogels obtained with the ISCW.

Hardness tests are handy to evaluate changes in physical behaviour of wax organogels (Dassanayake et al., 2009; Rocha et al., 2013; Toro-Vazquez et al., 2007), and for this case it was possible to observe that a higher crystallization temperature resulted at an increased mechanical hardness of the organogels for SCW and SSCW, such increase of hardness that was observed is probably caused by an increase in the organization of the organogel network, that should be the result of a smaller supercooling that allow the crystals to change their polymorphism (Himawan et al., 2006; Morales-Rueda, Dibildox-Alvarado, Charó-Alonso, Weiss, et al., 2009) and achieve a more stable polymorph.

4.4. Polarized light microscopy

Micrographs of the organogels obtained with all three waxes allowed to observe the network formed by the organogelators.

Figure 3. Polarized light micrographs of SCW organogels obtained at (A) 5° C and (B) 25° C, SSCW organogels obtained at (C) 5° C and (D) 25° C and ISCW organogels obtained at (E) 5° C and (F) 25° C.



Figure 3A shows the organogel developed with 4% (w/w) of SCW at 5°C while Figure 3B shows the same material crystallized at 25°C. At both images it is possible to observe the presence of needle-like crystals that should represent a bi-dimensional view of the network that keeps the liquid phase immobilized, we can notice that the crystals on Figure 3A are slightly smaller than the observed on Figure 3B, 3.8 ± 0.7 and 4.2 ± 0.9 µm respectively, but it is possible to observe a higher organization of them at Figure 3B.

The organogels obtained with SSCW at 4% (w/w), at 5°C are shown in Figure 5C and

 25° C on Figure 3D. On Figure 3C it is possible to observe a lot of crystals so small that measured around $2.0 \pm 0.3 \mu$ m and at Figure 3D it is possible to observe a large amount of crystals with the average size of $3.5 \pm 0.7 \mu$ m.

For ISCW organogels the micrograph of the organogels at 4% (w/w) as shown in Figure 3E and 3F, shows a large difference among the materials obtained at 5 and 25°C. On Figure 3E the organogel was obtained at 5°C and it is possible to observe an organized structure with crystals of $5.1 \pm 1.1 \mu m$, while on Figure 3F the observed crystals were larger $(7 \pm 1.8 \mu m)$ and also a smaller organization on the network was observed, being possible to observe crystals that were not part of the network.

The observation using polarized light microscopy corroborated the results obtained for mechanical properties, a more organized network as seen in Figure 3B and Figure 3D are correlated with a higher mechanical resistance. The observed structures were similar to those observed to candelilla wax (Blake et al., 2014; Dassanayake et al., 2012; Morales-Rueda, Dibildox-Alvarado, Charó-Alonso, Weiss, et al., 2009), rice bran wax (Dassanayake et al., 2012), carnauba wax (Dassanayake et al., 2009) organogels, meaning that the organogels should also present similar behavior.

4.5. Scanning Electronic Microscopy (SEM)

At Figure 4B, 4D and 4F (where the 25°C organogels are presented), it is possible to observe that the SCW and its fraction organogels are indeed a three-dimensional network at a rupture point (the material suffered a volume reduction due to the removal of the liquid oil).

Figure 4. SEM micrographs of SCW organogels obtained at (A) 5° C and (B) 25° C, SSCW organogels obtained at (C) 5° C and (D) 25° C and ISCW organogels obtained at (E) 5° C and (F) 25° C.



Once the measure of the cells was not possible once the material was modified, the structure of the material can be observed as a really organized structure of a foam-like network, as observed in the literature (Ema et al., 2006), such authors used SEM of polymeric foams and it was possible to observe the resemblance among their material and the studied

organogel samples.

The type of foam is indeed a question to be observed, the literature shows that waxy organogels formed closed cell foams, that immobilize the liquid phase as a physical barrier (Miyazaki et al., 2011), but once we compare the images obtained in this study with the ones from EMA et. al., (2006), the material is more similar to an open cell foam, a less stable structure that keeps the immobilized liquid oil due to chemical interactions (such as steric hindrance), making the material less stable to oil exsudation once it is not physically kept inside a cell.

Although SCW and SSCW organogels presented similar structures the ISCW organogel presented a different structure with the presence of some loose crystals.

Comparing SCW organogel (Figures 4B) with SSCW organogel (Figures 4D), crystallized at 25°C it is possible to observe the presence of open cells at the foam structure.

The same organogels crystallized at 5°C, shown in Figure 4 (A, C and E), it is possible to observe that there are no different among the SCW and SSCW organogels, while ISCW organogel formed a structure with no open cells, just a few pores where visible at the surface. The structure was indeed similar to those observed by (Rogers et al., 2009b).

The observed structure was similar at polarized light microscopy and SEM allows to observe that the higher crystallization temperature of 25°C formed a more organized structure.

5. Final Considerations

The performed analysis allows concluding that SCW presented the ability to act as an organogelator and that the SSCW presented a better potential for this application, while the ISCW fraction did not. SSCW produced harder organogels and better-organized networks as verified using microscopy.

Organogels produced using SSCW were harder than the obtained using SCW, probably due to the chemical composition and its interactions with the immobilized phase (soybean oil).

The thermal behavior observed on DSC, especially the enthalpy variation was similar to the results for hardness and rheology, where the samples that presented higher enthalpy values were also harder and the sample of ISCW organogels that presented a really lower enthalpy variation was not able to form proper organogels.

Although sugarcane wax is not yet a commercial product, its potential as

organogelator has been evaluated and confirmed, for the next steps a better understanding of how organogels behave under shear during food processing should allow the inclusion of organogels structured food at our shelves.

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References

Abdallah, D. J., Lu, L., & Weiss, R. G. (1999). Thermoreversible Organogels from Alkane Gelators with One Heteroatom. *Chemistry of Materials*, *11*(10), 2907–2911. https://doi.org/10.1021/cm9902826

Abdallah, D. J., & Weiss, R. G. (2000). n -Alkanes Gel n -Alkanes (and Many Other Organic Liquids). *Langmuir*, *16*(2), 352–355. https://doi.org/10.1021/la990795r

Almeida, I. F., & Bahia, M. F. (2006). Evaluation of the physical stability of two oleogels. *International Journal of Pharmaceutics*, *327*(1–2), 73–77. https://doi.org/10.1016/j.ijpharm.2006.07.036

Alvarez-Mitre, F. M., Morales-Rueda, J. A., Dibildox-Alvarado, E., Charó-Alonso, M. A., & Toro-Vazquez, J. F. (2012). Shearing as a variable to engineer the rheology of candelilla wax organogels. *Food Research International*, *49*(1), 580–587. https://doi.org/10.1016/j.foodres.2012.08.025

Blake, A. I., Co, E. D., & Marangoni, A. G. (2014). Structure and Physical Properties of Plant Wax Crystal Networks and Their Relationship to Oil Binding Capacity. *Journal of the American Oil Chemists' Society*, *91*(6), 885–903. https://doi.org/10.1007/s11746-014-2435-0

Bot, A., Adel, R., & Roijers, E. C. (2008). Fibrils of γ-Oryzanol + β-Sitosterol in Edible Oil Organogels. *Journal of the American Oil Chemists' Society*, 85(12), 1127–1134. https://doi.org/10.1007/s11746-008-1298-7

Campos, R. (2005). Experimental Methodology. In *Fat Crystal Networks* (Vol. 41, Issue 3, pp. 267–348). Marcel Dekker. https://doi.org/10.1590/S1516-93322005000300015

Chaves, K. F., Rocha, J. C. B., & Arellano, D. B. (2020). Simplified process to produce margarines with reduced saturated fatty acids using vegetable wax organogels. *Research, Society and Development*, *9*(4), 165943046. https://doi.org/10.33448/rsd-v9i4.3046

Daniel, J., & Rajasekharan, R. (2003). Organogelation of plant oils and hydrocarbons by long-chain saturated FA, fatty alcohols, wax esters, and dicarboxylic acids. *Journal of the American Oil Chemists' Society*, 80(5), 417–421. https://doi.org/10.1007/s11746-003-0714-0

Dassanayake, L. S. K., Kodali, D. R., Ueno, S., & Sato, K. (2009). Physical Properties of Rice Bran Wax in Bulk and Organogels. *Journal of the American Oil Chemists' Society*, 86(12), 1163–1173. https://doi.org/10.1007/s11746-009-1464-6

Dassanayake, L. S. K., Kodali, D. R., Ueno, S., & Sato, K. (2012). Crystallization kinetics of organogels prepared by rice bran wax and vegetable oils. *Journal of Oleo Science*, *61*(1), 1–9. http://www.ncbi.nlm.nih.gov/pubmed/22188800

Ema, Y., Ikeya, M., & Okamoto, M. (2006). Foam processing and cellular structure of polylactide-based nanocomposites. *Polymer*, *47*(15), 5350–5359. https://doi.org/10.1016/j.polymer.2006.05.050

Gandra, K. M. (2006). *Master Thesis - Production and characterization of sugarcane wax and its fractions*. Universidade Estadual de Campinas.

Himawan, C., Starov, V. M., & Stapley, a G. F. (2006). Thermodynamic and kinetic aspects of fat crystallization. *Advances in Colloid and Interface Science*, *122*(1–3), 3–33. https://doi.org/10.1016/j.cis.2006.06.016

Hughes, N. E., Marangoni, A. G., Wright, A. J., Rogers, M. a., & Rush, J. W. E. (2009).
Potential food applications of edible oil organogels. *Trends in Food Science & Technology*, 20(10), 470–480. https://doi.org/10.1016/j.tifs.2009.06.002

Hwang, H.-S., Kim, S., Evans, K. O., Koga, C., & Lee, Y. (2015). Morphology and networks of sunflower wax crystals in soybean oil organogel. *Food Structure*, *5*, 10–20. https://doi.org/10.1016/j.foostr.2015.04.002

Hwang, H.-S., Singh, M., Winkler-Moser, J. K., Bakota, E. L., & Liu, S. X. (2014). Preparation of Margarines from Organogels of Sunflower Wax and Vegetable Oils. *Journal of Food Science*, 79(10), C1926–C1932. https://doi.org/10.1111/1750-3841.12596

Jang, A., Bae, W., Hwang, H.-S., Lee, H. G., & Lee, S. (2015). Evaluation of canola oil oleogels with candelilla wax as an alternative to shortening in baked goods. *Food Chemistry*, *187*(4), 525–529. https://doi.org/10.1016/j.foodchem.2015.04.110

Lopes, J. D. (2010). *Master Thesis - Simplified process to production of concentrated long chain fatty acids from sugar cane wax (Saccharum officinarum L.)*. Universidade Estadual de Campinas.

Lupi, F.R., Gabriele, D., Facciolo, D., Baldino, N., Seta, L., & de Cindio, B. (2012). Effect of organogelator and fat source on rheological properties of olive oil-based organogels. *Food Research International*, *46*(1), 177–184. https://doi.org/10.1016/j.foodres.2011.11.029

Lupi, Francesca R., Gabriele, D., Seta, L., Baldino, N., & de Cindio, B. (2014). Rheological design of stabilized meat sauces for industrial uses. *European Journal of Lipid Science and Technology*, *116*(12), 1734–1744. https://doi.org/10.1002/ejlt.201400286

Mert, B., & Demirkesen, I. (2016). Evaluation of highly unsaturated oleogels as shortening replacer in a short dough product. *LWT - Food Science and Technology*, *68*, 477–484. https://doi.org/10.1016/j.lwt.2015.12.063

Miyazaki, Y., Yoshida, K., & Marangoni, A. G. (2011). Online Only Supplement - Lecture Abstracts of the 9th Euro Fed Lipid Congress, Rotterdam 18-21 September 2011. *European Journal of Lipid Science and Technology*, *113*(S1), 1–46. https://doi.org/10.1002/ejlt.201100363

Morales-Rueda, J. A., Dibildox-Alvarado, E., Charó-Alonso, M. A., & Toro-Vazquez, J. F. (2009). Rheological Properties of Candelilla Wax and Dotriacontane Organogels Measured with a True-Gap System. *Journal of the American Oil Chemists' Society*, 86(8), 765–772. https://doi.org/10.1007/s11746-009-1414-3

Morales-Rueda, J. A., Dibildox-Alvarado, E., Charó-Alonso, M. a., Weiss, R. G., & Toro-Vazquez, J. F. (2009). Thermo-mechanical properties of candelilla wax and dotriacontane organogels in safflower oil. *European Journal of Lipid Science and Technology*, *111*(2), 207– 215. https://doi.org/10.1002/ejlt.200810174

Parish, E. J., Boos, T. L., & Li, S. (2002). The Chemistry of Waxes and Sterols. In C. C. .
Akoh & D. B. . Min (Eds.), *Food Lipids - Chemistry, Nutrition, and Biotechnology* (p. 30).
CRC Press LLC. https://doi.org/10.1201/9780203908815.ch4

Patel, A. R., & Dewettinck, K. (2016). Edible oil structuring: an overview and recent updates. *Food Funct.*, 7(1), 20–29. https://doi.org/10.1039/C5FO01006C

Pereira, A.S. et al. (2018). Metodologia do trabalho científico. [e-Book]. Santa Maria. Ed. UAB / NTE / UFSM. Available at: https://repositorio.ufsm.br/bitstream/handle/1/15824/Lic_Computacao_Metodologia-Pesquisa-Cientifica.pdf?sequence=1. Accessed on: April 6th, 2020.

Pernetti, M., van Malssen, K. F., Flöter, E., & Bot, A. (2007). Structuring of edible oils by alternatives to crystalline fat. *Current Opinion in Colloid & Interface Science*, *12*(4–5), 221–231. https://doi.org/10.1016/j.cocis.2007.07.002

Pernetti, M., van Malssen, K., Kalnin, D., & Floter, E. (2007). Structuring edible oil with lecithin and sorbitan tri-stearate. *Food Hydrocolloids*, *21*(5–6), 855–861. https://doi.org/10.1016/j.foodhyd.2006.10.023

Rocha, J. C. B., Lopes, J. D., Mascarenhas, M. C. N., Arellano, D. B., Guerreiro, L. M. R., & da Cunha, R. L. (2013). Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil. *Food Research International*, *50*(1), 318–323. https://doi.org/10.1016/j.foodres.2012.10.043

Rogers, M. A. (2009). Novel structuring strategies for unsaturated fats – Meeting the zerotrans, zero-saturated fat challenge: A review. *Food Research International*, *42*(7), 747–753. https://doi.org/10.1016/j.foodres.2009.02.024

Rogers, M. A., Wright, A. J., & Marangoni, A. G. (2009a). Oil organogels: the fat of the future? *Soft Matter*, *5*(8), 1594. https://doi.org/10.1039/b822008p

Rogers, M. A., Wright, A. J., & Marangoni, A. G. (2009b). Nanostructuring fiber morphology and solvent inclusions in 12-hydroxystearic acid / canola oil organogels. *Current Opinion in Colloid & Interface Science*, *14*(1), 33–42. https://doi.org/10.1016/j.cocis.2008.02.004

Rogers, M. A., Wright, A., & Marangoni, A. G. (2008). Crystalline stability of self-assembled fibrillar networks of 12-hydroxystearic acid in edible oils. *Food Research International*, *41*(10), 1026–1034. https://doi.org/10.1016/j.foodres.2008.07.012

Severino, A. J. (1996). Metodologia do Trabalho Científico (20th ed.). São Paulo. Ed. Cortez.

Terech, P. (1992). 12-D-Hydroxyoctadecanoic acid organogels : a small angle neutron scattering study. *Journal de Physique II*, 2(12), 2181–2195. https://doi.org/10.1051/jp2:1992259

Toro-Vazquez, J. F., Morales-Rueda, J. A., Dibildox-Alvarado, E., Charó-Alonso, M., Alonzo-Macias, M., & González-Chávez, M. M. (2007). Thermal and Textural Properties of Organogels Developed by Candelilla Wax in Safflower Oil. *Journal of the American Oil Chemists' Society*, 84(11), 989–1000. https://doi.org/10.1007/s11746-007-1139-0

Vieira, T. M. F. de S. (2003). *Thesis - OBTENÇÃO DE CERA DE CANA-DE-AÇÚCAR A PARTIR DE SUBPRODUTO DA INDÚSTRIA SUCRO-ALCOOLEIRA : EXTRAÇÃO*, *PURIFICAÇÃO E CARACTERIZAÇÃO* [Universidade Estadual de Campinas]. http://www.bibliotecadigital.unicamp.br/document/?code=vtls000307074

Yılmaz, E., & Öğütcü, M. (2015). The texture, sensory properties and stability of cookies prepared with wax oleogels. *Food Funct.*, *6*(4), 1194–1204.

https://doi.org/10.1039/C5FO00019J

Zulim Botega, D. C., Marangoni, A. G., Smith, A. K., & Goff, H. D. (2013). The potential application of rice bran wax oleogel to replace solid fat and enhance unsaturated fat content in ice cream. *Journal of Food Science*, *78*(9), C1334-9. https://doi.org/10.1111/1750-3841.12175

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