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Study of the crystallization and polymorphic structures formed in oleogels from avocado oil



Estudio de la cristalización y de las estructuras polimórficas formadas en oleogeles de aceite de aguacate

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ABSTRACT

Key words:

Calorimetry
Monodiglycerides
Cooling rate
Thermal behavior

The effect of the concentration of monodiglycerides, beeswax and sorbitan monostearate (SMS) on the thermal behavior of oleogels prepared from avocado oil, as well as the effect of the cooling rate on the onset temperature (T_{onset}) and the crystallization temperature (T_c), were evaluated by DSC and X-ray diffraction. The results showed that the structuring agents have a significant effect ($P < 0.05$) on the T_c and T_{onset} , which demonstrated their ability to form solid lipids. Moreover, it was found that the presence of SMS decreased the T_c and T_{onset} , possibly due to their cocrystallization process. It was found only in the presence of the polymorphic form β' in the oleogels prepared. The T_c varied between 1.6 and 51.4 °C and T_{onset} between 3.9 and 53.8 °C.

RESUMEN

Palabras claves:

Calorimetría
Monodiglicérido
Rapidez de enfriamiento
Comportamiento térmico

Se evaluó el efecto de la concentración de los monodiglicéridos, la cera de abejas y monoestearato de sorbitán (SMS) sobre el comportamiento térmico de los oleogeles de aceite de aguacate, así como el efecto de la velocidad de enfriamiento sobre el inicio (T_{onset}) y temperatura de cristalización (T_c), usando DSC y difracción por rayos x. Los agentes estructurantes mostraron tener efecto significativo ($P < 0.05$) sobre la T_{onset} y la T_c del aceite de aguacate, lo que indica su capacidad de formar estructura. La presencia de Span 60 disminuyó la T_{onset} y la T_c , posiblemente debido su proceso de cocrystalización. Se evidenció únicamente la presencia de la forma polimórfica β' en los oleogeles preparados. La T_c y la T_{onset} varió en el rango entre 1,6-51,4 °C y 3,9-53,8 °C respectivamente.

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In the industry sector there is a clear trend towards the development of new and healthier food products. New ways for reducing the risk of diseases related to trans fats, has been motivation for the development of solid lipids from edible oils containing structuring agents, but that do not contain trans fats (Da Pieve *et al.*, 2011). These solid lipids are produced from commercial grade additives and are called oleogels. The Oleogels are defined as an organic liquid confined in a thermoreversible three-dimensional network created by an organogelator. Typically, these structures are formed from very low concentrations of organogelator and their ability to form structures is dependent on the nature and symmetry of the molecule, its molecular weight, and the difference in solubility to the solvent (Omonov *et al.*, 2010; Raut *et al.*, 2011; Permetti *et al.*, 2007; Dassanayake *et al.*, 2011). In the food industry oleogels have been produced from a variety of compounds, such as vegetable waxes, monodiglycerides, alcohols or esters of fatty acids, phospholipids and sterols. There is a close relationship between the structure of the organogelator agent and the composition of the edible oils used, which influences the microstructural and physical chemical characteristics of the oleogel (Toro-Vazquez *et al.*, 2010; Murdan *et al.*, 1999b; Bot *et al.*, 2011). The chain fatty acids in triacylglycerols (TAGs) are forced into alignment, grouping and leading to the formation of several polymorphic structures. Vegetable fats and oils contain basically three polymorphic forms: α , β' , and β , the first is the least stable structure, and the thermodynamically more stable is the β -form (Marangoni, 2002; Sato and Ueno, 2011; Himawan *et al.*, 2006; Ortiz-Moreno *et al.*, 2003). The aim of the present study was to evaluate by DSC technique and X-ray diffraction the effect of the concentration of the organogelators such as monoglycerides, beeswax, sorbitan monostearate and cooling rate on the onset temperature (T_{onset}) and crystallization temperature (T_c) in the avocado oil oleogels.

MATERIALS AND METHODS

Extraction of avocado oil

This process was carried out using the methodology proposed by Betancur (2011) with some modifications. The ripe avocado (*Persea americana* Mill. cv. Hass) was purchased from a local market; it was washed, peeled and pulped. The pulp was liquefied with water to prepare a solution of avocado to 15%, the oil was then extracted using a centrifuge (Hettich, Universal

320 R) at 3500 rpm for 15 min, thereby separating the lipid fraction from the soluble fraction, unlike Betancur who used a cream separator at 8070 rpm at 50 °C. The extracted oil was stored at 5 °C and subsequently used to prepare oleogels.

Preparation of oleogels

The methodology of oleogel preparation was developed based on previous works (Lupi *et al.*, 2012; Morales-Rueda *et al.*, 2009) with modifications. The oleogels (100 g) were prepared with different concentrations of organogelators (commercial grade): monoglyceride (monoester 99%), beeswax and sorbitan monostearate (SMS). Avocado oil was preheated to 75 °C on a hot plate. The amounts of organogelator, according to the experimental design given in table 1, were weighed. They were then mixed with the avocado oil for 10 min to ensure that the solid components reached their melting points and that the proper homogenization of the blend was achieved. The oleogels were allowed to stand at a temperature of 5 °C for 24 h to achieve the thermal characterization. Two replicate experiments were conducted for each test.

Thermal characterization: Differential Scanning Calorimetry (DSC)

The thermal characterization of the oleogels was conducted by analyzing the thermogram obtained in a DSC TA Q2000 (TA Instruments, New Castle, Delaware). The equipment was calibrated with indium before analysis. Nitrogen was used as a purge gas for the system $5 \times 10^{-5} \text{ m}^3 \text{ min}^{-1}$. For the analysis, 12-15 mg of oleogel was weighed in aluminum pans. An empty aluminium pan was used as reference. To eliminate any memory structure, the samples were heated and kept at 75 °C for 10 min, then cooled at 3 or 5 °C min^{-1} to -20 °C (Table 1). The results of thermal analysis were processed using TA Universal Analysis 2000 software (TA Instruments, New Castle, Delaware). Each sample was performed in duplicate.

X-ray diffraction

An isothermal crystallization was performed before analyses. Samples were heated and kept at 75 °C for 10 min, subsequently cooled at 10 °C for 1 min and kept at 19 °C to achieve crystallization. The X-ray diffraction was carried out with an Empyrean diffractometer (Panalytical Almelo, The Netherlands), The diffractometer was equipped with a sealed Cu-X-ray tube, 0.04 rad primary and secondary

Table 1. Experimental design for formulation of oleogels prepared from avocado oil.

Test	Monoglycerides (%)	Beeswax (%)	SMS (%)	Avocado oil (%)	Cooling rate (°C min ⁻¹)	T _c (°C)	T _{onset} (°C)
1	0	1	0	99	3	33.3	36.8
2	0	1	2	97	3	30.2	33.2
3	5	0.5	1	93.5	5	45.4	46.5
4	6.3	0.64	0	93.06	3	49.7	48.6
5	7.3	0.34	2	90.37	5	49.1	50.6
6	10	0	0	90	3	46.3	49.8
7	5	0.5	1	93.5	5	46.3	48.0
8	10	1	0.99	88.01	3	51.4	52.8
9	10	0	1.24	88.76	5	50.4	52.4
10	0	1	0.79	98.21	5	27.6	29.1
11	5.73	0	2	92.27	3	45.7	52.1
12	0	0	0	99.04	3	29.4	33.4
13	10	0.42	2	87.58	3	51.3	53.8
14	6.25	0.13	0	93.62	5	44.3	46.7
15	10	1	2	87	3	45.4	48.1
16	10	0.42	2	87.58	3	46.0	48.2
17	5	0.5	1	93.50	5	45.2	47.9
18	0	0	0.96	99.04	3	29.3	32.5
19	6.25	0.93	2	90.83	3	50.2	51.1
20	10	1	0	89	5	46.5	52.4
21	0	0	2	98	5	35.5	36.3
22	1	0.63	1.99	96.39	5	36.1	37.4
23	0	0	0	100	5	3.1-8.4	12.2
24	6.3	0.64	0	93.06	3	41.4	50.4

Soller slits and a Ni-filter, with radiation Cu-K α ($k=1.541$ Å, voltage 45 kV, current 40 mA, $\lambda = 1.540$). The sample was scanned from 1 to 40° in 2 θ , with a step size of 0.026°. The oleogel samples were crystallized at 19 °C and placed on a rectangular sample holder to carry out the analysis. Each sample was performed in duplicate.

Experimental design and statistical analyses

Determination of the effects of each of the factors on onset temperature (T_{onset}) and crystallization temperature (T_c) was performed with response surface methodology using d-optimal design with three numerical factors: destilied monoglycerides (0 and 10%), beeswax concentrate (0 and 1%) and sorbitan monostearate (0 and 2%). Also, the categorical factor defined as the cooling rate of 3 and 5 °C for 1 min was considered. The experimental design consisted of 14 points for the model, five to determine unadjusted factors and 5 replicates. Analysis of variance (ANOVA) were carried out to evaluate the influence of the response variables of interest, considering a significance

level of 5%. The results were analyzed and processed using Desing Expert Software 8.0.5.

RESULTS AND DISCUSSION

The Analysis of Variance (Table 2), shows that the organogelator has a significant effect ($P<0.05$) on the T_c and T_{onset} of avocado oil and therefore on the oleogel prepared, affecting the crystallization in the temperature range studied. Interactions among the factors of monoglyceride and SMS, as well as beeswax and SMS, also have a significant effect on the T_c and T_{onset}. On the other hand, there is no significant interaction among the factors of beeswax and cooling rate nor among SMS and cooling rate on the T_c and T_{onset}.

Effect of monoglycerides and beeswax on the crystallisation

Figure 1 shows the thermal behavior of the oleogel prepared by monoglycerides 10% (Test 6), monoglycerides 6.3%-beeswax 0.64% (Test 24), as well as the thermal

Table 2. Analyses of variance for the statistical design.

Factors	T_c	T_{onset}
	(p-value)	
Monoglycerides (A)	<0.0001	<0.0001
Beeswax (B)	0.141*	0.274*
SMS (C)	0.003	0.011
Cooling rate (D)	0.021	0.025
AB	0.117*	0.225*
AC	0.004	0.018
AD	0.192*	0.114*
BC	0.004	0.007
BD	0.902*	0.982*
CD	0.145*	0.184*
A ²	0.002	0.005
B ²	0.781*	0.980*
C ²	0.177*	0.200*

* not statistically significant ($\alpha \leq 0.05$)

behavior of avocado oil. The formation of two structures crystallizing between 14 °C, and 47 °C can be observed. These temperatures are close to the crystallization temperatures shown by monoglycerides commercial grade, but with a smaller peak crystallization. The crystallization observed at elevated temperatures was related to the content of the saturated fatty acids in the monoglycerides and in the beeswax, and the crystallization located at a lower temperature was due to the presence of the unsaturated fatty acids.

It may also be observed that the T_{onset} and T_c (Table 2) are affected by the concentration of monoglycerides ($P < 0.05$), probably due to the interaction between them and the TAGs from avocado oil. When the solid concentration is low (Test 24), the T_c and T_{onset} are moved to a lower temperature region, while crystallization enthalpy (ΔH_c) decreases. Results similar to the above have been found in the crystallization study of milk fat, in fat blends having low and high melting points, in oleogels of palm with diacylglycerol and in oleogels from candelilla wax (Toro-Vazquez *et al.*, 2009; Martini *et al.*, 2008; Higaki *et al.*, 2004; Tan and Che Man, 2002; Saberi *et al.*, 2011; Foubert *et al.*, 2004). The unsaturated fatty

acids of avocado oil as oleic, linolenic and linoleic acid can affect the crystallization temperature, shifting the T_c and T_{onset} of the oleogel to a region of lower temperature. This phenomenon can be attributed to the steric effect of double bonds present in the TAGs of oil, which prevents the accommodation of monoglycerides chains, forming a less compact structure and a lower T_c and T_{onset} .

Given the high unsaturation of most TAGs present, the thermal behavior for avocado oil (Figure 1) showed a T_{onset} around 12.2 °C and a T_c at 8.4 and 3.1 °C, this result agrees with those found in studies of the crystallization of the oleogels of candelilla wax using safflower oil high in triolein (Toro-Vazquez *et al.*, 2009). It was verified that the organogelators employed are capable of increasing the crystallization temperature of the avocado oil: the three organogels shift the crystallization to a zone of higher temperature, and this was dependent on the concentration of each one ($P < 0.05$). This result agrees with those found in studies of the crystallization of the oleogels of candelilla wax, in the crystallization of milk fat and oleogels prepared with sorbitan monostearate (Toro-Vazquez *et al.*, 2009; Martini *et al.*, 2008; Murdan *et al.*, 1999a; Hwang *et al.*, 2011).

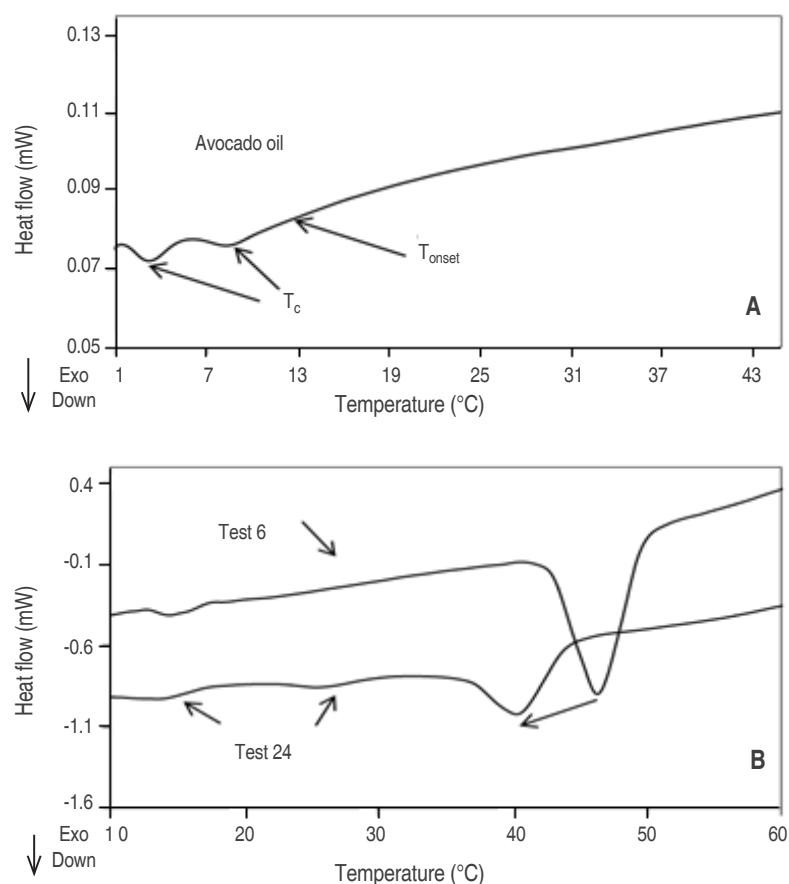


Figure 1. DSC thermogram of avocado oil (A) and oleogels Test 6 and Test 24 (B). This shows the measurement of heat flow on cooling.

Effect of cooling rate, beeswax and SMS on the crystallisation

The increase of the T_c of avocado oil can be observed in figure 2. Oleogel (Test 2, 3 °C min⁻¹) with SMS 2%-beeswax 1% has one crystallization peak at 30.2 °C. The crystallization occurred at a lower temperature than in the oleogel with beeswax 1% (Test 1, 3 °C min⁻¹). The presence of SMS adversely affects the appearance of the T_c , this phenomenon was associated with the heterogenous nucleation of beeswax induced by the crystallization of SMS. When the cooling rate was increased in the Test 2 to 5 °C min⁻¹, a decrease of its T_c and an increase in its enthalpy was observed, yielding values of 27.4 °C (Figure 2). In all of the oleogels a similar trend to reduce the T_c was observed when the cooling rate was performed at 5 °C min⁻¹. A similar result was reported by Bouzidi and Narine (2012) in the crystallization of tristearoilglycerol and 1-palmitoyl-2,3-stearoyl glycerol.

Effect of cooling rate monodiglycerides on the crystallisation

The oleogel shown in figure 3 revealed the presence of three exothermic peaks, probably caused by the crystallisation processes of α , β' , β -forms. The first one is in the high temperature range between 40-54 °C and ΔH_c 2.09 J·g⁻¹ (Test 20.5 °C min⁻¹), this peak can be caused by the presence of the β polymorph, attributed to the presence of a high concentration of trisaturated TAG. Another peak appears at 30 °C, which may be caused by the presence of the β' polymorph. The latter exothermic crystallisation peaks at 14.9 °C can be caused by the presence of the α polymorph, which crystallised at low temperatures, it can be probably due to the presence of unsaturated fatty acids. Likewise, there is a tendency to reduce the T_c when the cooling rate increases. This result agrees with that found in the oleogels of soybean oil and esters of waxes, and

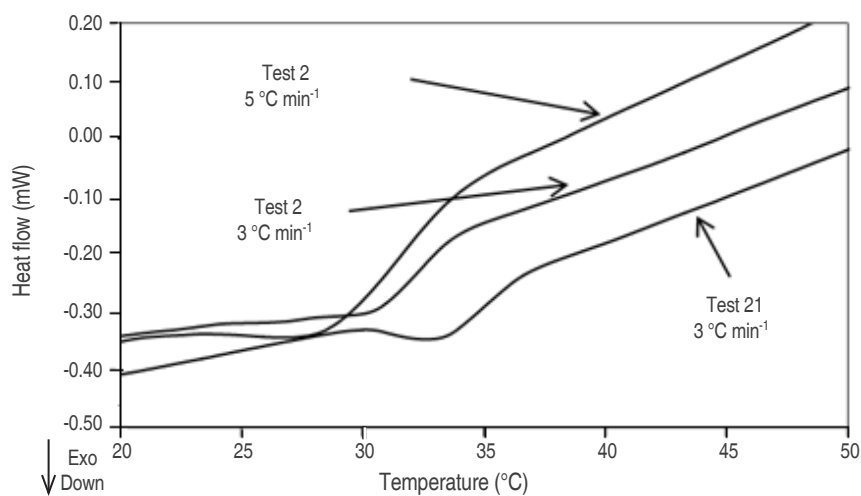


Figure 2. DSC thermogram of oleogels from avocado oil Test 2 (3 and 5 °C min⁻¹) and Test 21. This shows the measurement of heat flow on cooling.

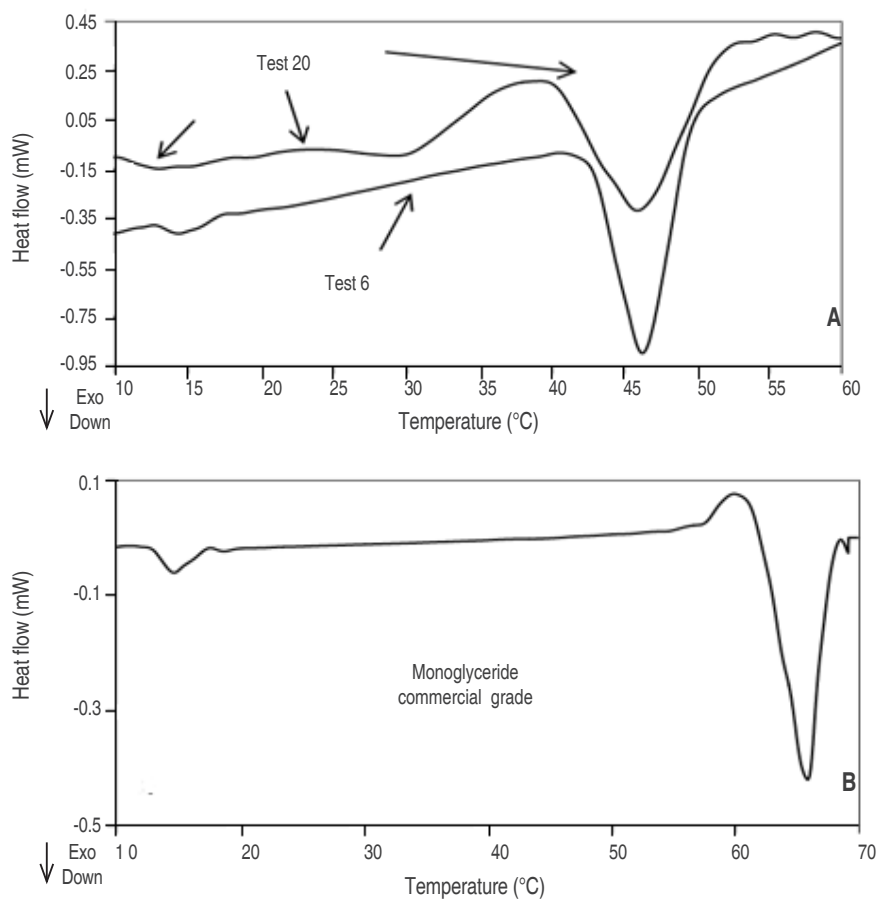


Figure 3. DSC thermogram of oleogels from avocado oil Test 6 and Test 20 (A) and monoglyceride commercial grade (B). This shows the measurement of heat flow on cooling.

candelilla wax and tripalmitin preparations (Hwang *et al.*, 2011; Toro-Vazquez *et al.*, 2009). At a lower cooling rate, it is likely that the crystals tend to join more slowly and create smaller structures, which require less energy (enthalpy of crystallization) to crystallize. The opposite occurs with a high cooling rate, which forms larger crystals that require more energy to crystallize. This behavior was reported in the crystallization of palm oil and tripalmitin monoacylglycerols (Basso *et al.*, 2010).

According to figure 3, the oleogel prepared with monoglycerides 10% (Test 6) shows two crystallization peaks. The first peak occurs at 47.3 °C with an enthalpy of 7.08 J·g⁻¹. The T_c is lower compared to the one presented by monoglycerides (commercial grade). Another peak appears at 14.5 °C with an enthalpy of 0.22 J·g⁻¹, which is close to that exhibited by the unsaturated components from monoglycerides (commercial grade). These exothermic crystallisation peaks can be caused by the presence of the β and α polymorphs respectively,

similar results were found by Basso *et al.* (2010) in the study of crystallization of palm oil with tripalmitin and monoacylglycerols, it is shown that the addition of monoacylglycerols accelerated the crystallisation of palm oil by increasing the number of crystallisation seeds, reducing the size of the crystals formed and favouring the formation of β -crystals. The higher percentages of diglyceride promoted the crystallisation of the stable β polymorph (Saber *et al.*, 2011).

Effect of beeswax and SMS on the crystallisation

The combination of the organogelators of monodiglycerides 10% w/w-beeswax 1% w/w (Test 20) has three peaks of crystallization (Figure 4). The first one is in the high temperature range. It can be verified that in this zone, the increased concentration of beeswax from 0.64% w/w and monodiglycerides 6.3% (Test 4) to monodiglyceride 10%-beeswax 1% (Test 20) increases the solids content, thus increasing the T_c ; this affects the shape and size of the peak. The bimodal melting profile is probably due

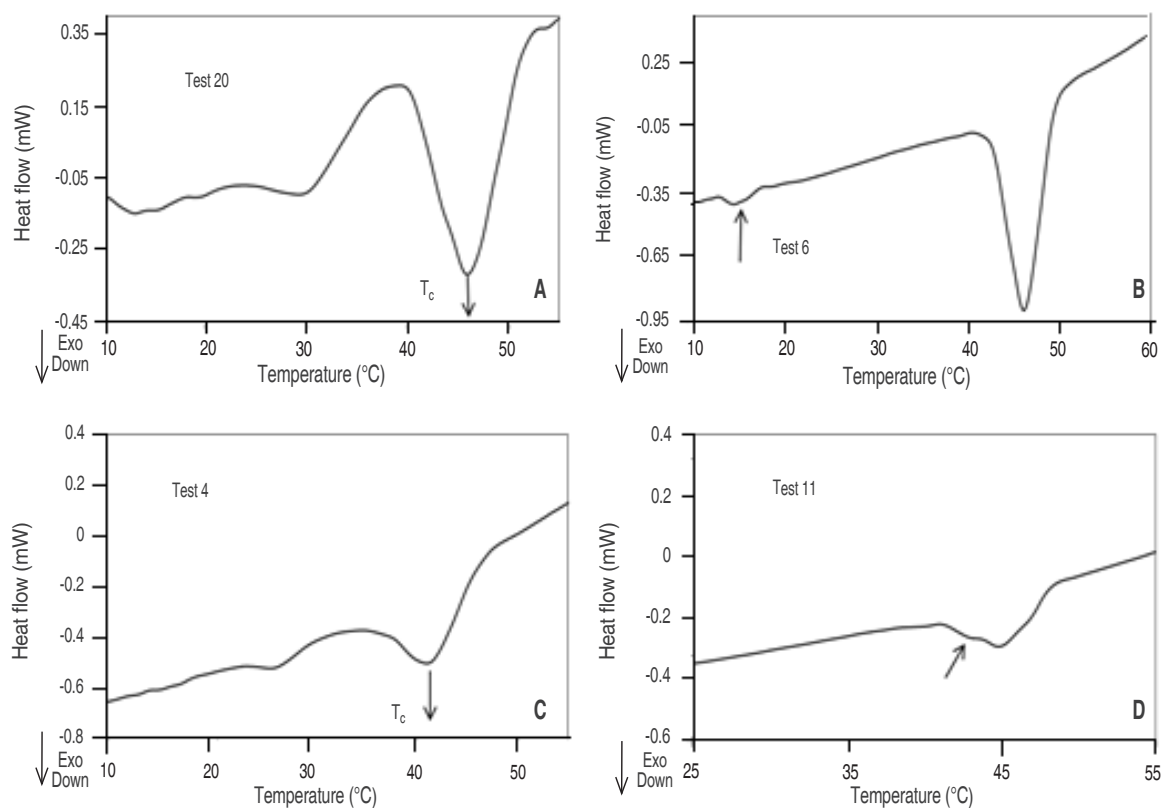


Figure 4. DSC thermogram of oleogels from avocado oil Test 20 (A), and Test 6 (B), Test 4 (C) and Test 11 (D). This shows the measurement of heat flow on cooling.

to the formation of a recrystallized polymorphic form at that temperature. Similar results were found in oleogels of fully hydrogenated canola oil (Omonov *et al.*, 2010). The mixture of SMS 2%-monodiglycerides 5.73% (Test 11), leads to the crystallization of avocado oil at about 46 °C with an enthalpy of 0.9 J·g⁻¹. SMS affects the crystallization of the unsaturated components present in the oleogel, causing them to avoid crystallization in the region close to 14 °C, an area in which they normally crystallize, as shown in the thermogram of monodiglycerides 10% (Test 6). Sorbitan mono and tristearate have been shown to retard polymorphic transitions of saturated monoacid triglycerides into the more stable form (Jacome *et al.*, 1989; Elisabetini *et al.*, 1995). A near shoulder can also be observed at 42 °C (Test 11), probably due to the formation of structures formed by parallel chains saturated monodiglycerides and recrystallized SMS in this area. Generally, the presence of SMS affects the appearance of crystallization when mixed with monodiglycerides. Thus, in the high temperature zone, a tendency to decrease the T_c was observed. However, this can also be attributed to a lower concentration of monodiglycerides: the sample contains

5.73% monodiglycerides-2% SMS (Test 11) compared to 10% of the oleogel containing only monodiglycerides (Test 6).

X-ray diffraction Analysis

Figure 5 A,B shows the XRD patterns for oleogels produced (crystallized at 19 °C) from the combination of the three structuring agents (Tests 20, 8, 6 and 4). They are characterized by the absence of a strong signal at 4.2 Å (20.5° 2 θ) that indicates the absence of a polymorphic form in alpha (α) configuration. Two peaks with medium intensity patterns 3.7 and 3.9 Å (22-23° 2 θ), characteristic of the polymorphic form β' were found, although these patterns in Test 8 were not clear. On the other hand, signal around 4.6 Å indicates the transformation of the polymorphic forms β' to β , but it was not found, this indicates that the oleogels made from avocado oil (Tests 20, 6, 8 and 4) contain the β' form and that oleogel experienced no change in its structure under these conditions. The polymorphic form β' can be due to the presence of diglycerides in the mixture. A similar result was found by Saberi *et al.* (2011). In the study by X-ray diffraction of palm oil in

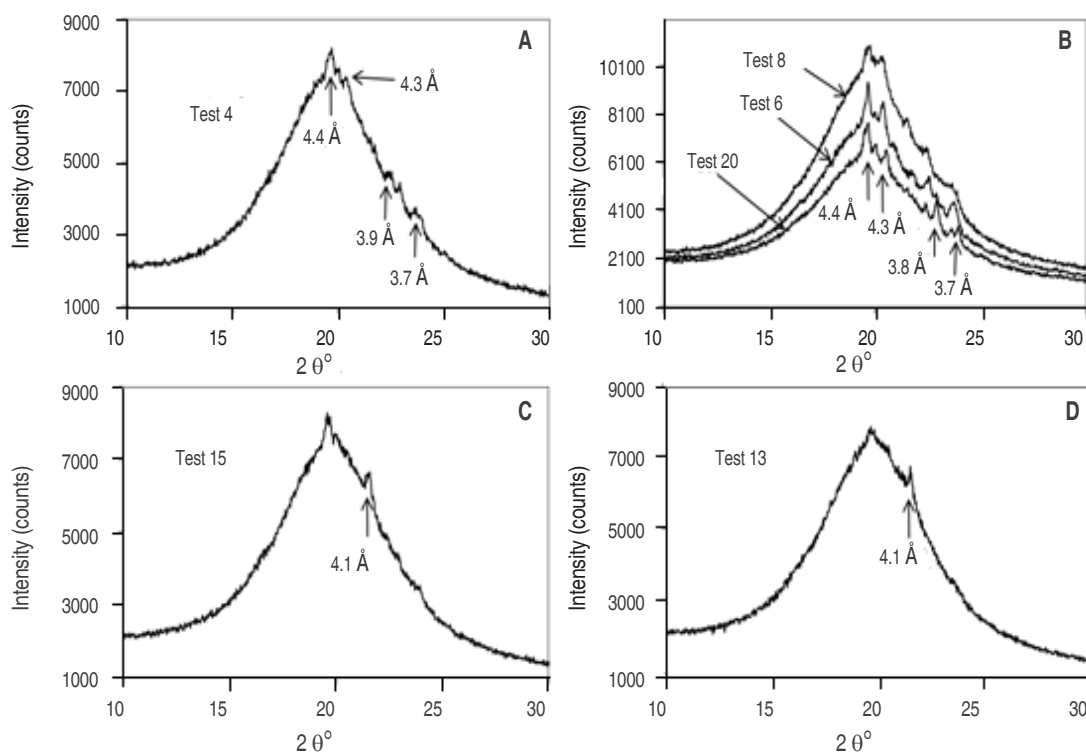


Figure 5. XRD patterns for oleogels from avocado oil Crystallized at 19 °C.

blends with palm based diacylglycerol, it is shown that the polymorphic form β' exists at room temperature. This is the product of stearic acid content, which increases its stability. Avocado oil has 78% of unsaturated fatty acids, which necessarily affects the symmetry of the molecules of TAGs, forcing the folding of the chains and generating asymmetric structures. According to Timms (1984) these are responsible for the formation of polymorphic structures in the β' state. However, in several studies it has been established that the monoglycerides induce the formation of structures in the β state (Saber *et al.*, 2011; Szydłowskaczerniak *et al.*, 2005; Ghotra *et al.*, 2002; Ribeiro *et al.*, 2009; Basso *et al.*, 2010).

Figure 5 C,D shows the XRD patterns for oleogels (crystallized at 19 °C) with SMS (Tests 13 and 15). One diffraction peak at 4.1 Å characteristic of the polymorphic form α were found. Similar results were found by Perneti *et al.* (2007) in the study of crystallization of sunflower oil with lecithin and sorbitan tri-stearate, in comparison to other Tests (20, 6, 8 and 4) when the concentration of SMS was increased to 2% in the Test 13 and 15, a β' -destabilizing effect on oleogels from avocado oil was observed.

CONCLUSIONS

Beeswax, monodiglycerides and SMS, or combinations thereof, have the ability to increase the T_c and T_{onset} of avocado oil. The three organogelators shift the crystallization to a zone of higher temperature, and this is dependent on the concentration of each one. In all of the oleogels the tendency to decrease the T_c was observed when the crystallization process is performed at 5 °C min⁻¹. At a higher cooling rate, the T_c is lower, and the crystallization enthalpy is higher. The XRD patterns for the oleogels produced from the three organogelators and crystallized isothermally at 19 °C, are characterized by the absence of the polymorphic form beta β . When the concentration of SMS was increased to 2 % a β' -destabilizing effect on oleogels made from avocado oil was observed.

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