Low sat-structured fats enriched in α -linolenic acid: physicochemical properties and crystallization characteristics

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Abstract This work sought to obtain and evaluate zero trans-fat reduced in saturated fatty acids, with higher content of unsaturated fatty acids. Palm oil (PO) was used as the reference of zero trans lipid base. Different amounts of linseed oil (LO) were added to PO, obtaining the following blends: 100:0; 80:20; 60:40; 40:60; 20:80 and 0:100 of PO:LO (w/w%), respectively. These blends were added to fully hydrogenated soybean oil (FHSO) as the crystallization modifying agent, and to sorbitan monostearate (SMS) as the structuring element, both at a proportion of 3% to build the structured fractions. The control and the structured blends were evaluated for fatty acid composition, solid fat content, consistency, crystallization kinetics, thermal behavior, microstructure and polymorphism. With the addition of LO to the PO, an increase of up to 80% was observed in the content of alpha-linolenic acid and a reduction of saturated fatty acids to 47% in the blends. FHSO and SMS offered thermal resistance to the blends, with relevant changes in the crystallization kinetics and microstructure, affecting macroscopic characteristics with the increase in consistence. It was possible to obtain a lipid formulation with features of plasticity and enhanced nutritional quality, compatible with several food applications.

Keywords Linseed oil · Palm oil · Fully hydrogenated soybean oil · Sorbitan monostearate · Low saturated fat · Lipid crystals · Crystallization modifiers · Structuring oil

Introduction

Oils and fats are important elements of foods and their composition is directly linked to health aspects. The over consumption of trans fatty acids and saturated fatty acids indicates, based on evidences, higher risk for development of cardiovascular diseases. In contrast, several studies indicate that the replacement of trans and saturated fatty acids by polyunsaturated fatty acids in foods contributes to reduce heart disease risks (Watkins et al. 2005; Novello et al. 2010).

Food consumption in western countries present omega 6 fatty acids as one of the main dietary elements (particularly represented by linoleic acid (LA)), resulting from the elevated consumption of vegetal oils. In contrast, these places present a reduced ingestion of omega 3 fatty acids, including the alpha-linolenic (ALA), eicosapentaenoic (EPA) and docosahexaenoic (DHA) fatty acids (Garofolo and Petrilli 2006).

ALA is an essential fatty acids and is not synthesized by humans, therefore it must be included in the diet. In the organism, it is converted to EPA and DHA, both of which have indicated to provide health benefits. However, the contribution of this fatty acid in western diets is very small. Consumption of LA ranges from 8.3 to 19.0 g/day among men and 6.8 to 13.2 g/day in the diets of women, about ten times superior to the consumption of ALA (FAO/WHO 2010). This data creates a concern and a need to enrich foods with omega 3 fatty acids for a higher functional contribution, even if the conversion rate of ALA for the

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formation of these fatty acids is considered low (Watkins et al. 2005).

Modification processes of oils and fats aim to produce tailor-made lipid bases for specific application in formulated products, for example the zero trans fractions, with reduced saturated fatty acids content and higher quantities of polyunsaturated fatty acids, particularly omega 3 fatty acids (Rogers 2009; Siraj et al. 2015).

The use of palm oil (*Elaies guinensis*) in food, partially replacing hydrogenated fats showed to be highly feasible due to its features of oxidative stability, technological functionality and availability. However, in addition to the large amount of saturated fatty acids (approximately 50%), palm oil presents slow crystallization and is associated with the formation of crystalline groups that can cause technological problems, such as undesirable granulation after product formulation (Marangoni and Narine 2002; Mamat et al. 2005).

Due to nutritional issues, there is a greater interest in the addition of high-quality vegetable oils to conventional technical fat formulations to increase the quantity of polyunsaturated fatty acids and alter the lipid profile of fat fractions for use in foods. Linseed oil (*Linum usitatissimum*) presents 57–67% of linolenic acid, being considered rich in omega 3 fatty acids, in addition to presenting approximately 20% oleic acid. However, its consumption is considered low in many countries due to the lack of habit and information for consumers (Cordeiro et al. 2009; Madhusudhan 2009).

A technological approach of recent studies regarding the technology of oils and fats consists of the development of healthier lipid bases by the structuration of blends containing higher proportions of vegetal oils rich in polyunsaturated fatty acids (de Oliveira et al. 2015a; Siraj et al. 2015). The addition of structuring agents in triacylglycerol matrices allows for the formation of organic gels, materials which may demonstrate a technological functionality equivalent to plastic fats. Therefore it is possible to obtain structured systems with specific thermal properties and consistence. The structuring blends should be nutrition, low cost and safe for human consumption (Rogers 2009; Marangoni 2012).

Several additives have been employed as structuring agents for this purpose (Rogers 2009). Among those most utilized are monoacylglycerols (Ojijo et al. 2004), fatty acids, fatty alcohols, waxes and sorbitan alkylates (Daniel and Rajasekharan 2003), phytosterols, oryzanol and their mixtures (Bot et al. 2008).

Organic gels are composed of large quantities of liquid oil retained by a smaller content of solid material, forming a self-supported network. For the structuration of edible oils two paths are typically applied: (1) dispersion of the external phase by using solid crystals, separated drops or

dead particles which form crystals in the process of nucleation followed by their growth in the oily phase, and (2) self-assembly systems, in which there is self-organization at a molecular level in the oily phase (Dassanayake et al. 2011; Siraj et al. 2015).

Fully hydrogenated vegetable oils, technically referred to as hardfats, are low cost products which can be used as structuring agents in order to modify the crystallization properties of lipid bases. Hardfats present homogeneous composition, characterized by the presence of trisaturated triacylglycerols with high melting points. Particularly, fully hydrogenated soybean oil (FHSO) has stearic acid as its main fatty acid (approximately 87%), which presents neutral physiological effects on the body (Bonanome and Grundy 1988; Snook et al. 1999; Ribeiro et al. 2013).

Sorbitan esters have been recently evaluated as potential structuring agents in vegetable oils, since they can modulate the crystallization process in lipids systems. The presence of saturated long-chain hydrocarbons indicates the formation of solid esters including sorbitan monostearate (SMS), formed by stearic acid ester and sorbitol. The SMS has no smell or taste and is capable of forming semi-solid and thermic reversible oil gels, immobilizing the organic fluid represented by the vegetable oil (Smith et al. 2011).

Elements with similar molecular and chemical structures frequently exhibit positive interactions regarding the events of particle dispersion and self-assembly, as in the case of FHSO with SMS, since both are characterized by the predominance of stearic acid in their composition (de Oliveira et al. 2015c).

In this context, the objective of current study was to evaluate the structuring of blends containing PO and LO at different proportions for using the SMS and the FHSO as structuring agents via the general crystallization properties of the lipid systems. This allows the development of lipid blends with reduced saturated fatty acids content and higher content of ALA, which may present appropriate technological functionality in food applications.

Materials and methods

Material

Deodorized palm oil (PO), provided by Agropalma S.A., Belem, Brazil; linseed oil (LO), provided by Vital Atman, Uchoa, Sao Paulo, Brazil; fully hydrogenate soybean oil (FHSO), provided by Cargill Agricola S.A., sorbitan monostearate (SMS) produced by Sigma Aldrich (United Kingdom), with 50% purity were obtained. The raw materials were maintained in a dry location and protected from light until usage.

Blend preparation

The binary blends PO:LO were prepared at the proportions of 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100 (w/w), corresponding to the control samples. The structuring agents were incorporated to the control blends at the concentration of 3% (w/w) SMS and 3% (w/w) FHSO, characterizing the structuring blends (S). For total homogenization of the structuring agents, the blends were melted at 100 °C and stirred for 10 min.

Analytical methods

Palm oil (PO), linseed oil (LO), fully hydrogenated soybean oil (FHSO) and control and structuring blends were evaluated according to the following analytical and physical–chemical methods.

Fatty Acid Composition

The fatty acid composition was determined in triplicate by gas chromatography, using an Agilent series 6850 GC system chromatograph (Santa Clara, CA, USA), after esterification employing the method (Hartman and Lago 1973). The methyl esters of the fatty acids were methylated and separated according to the AOCS Ce 2-66 method (AOCS 2009); using the capillary column DB-23 AGILENT (50% cyanopropyl-methylpolysiloxane 60 m length, internal diameter of 0.25 mm and 0.25 µm film thickness) with the following analysis conditions: flow of 1.0 mL/min, linear speed of 24 cm/s, detector temperature of 280 °C, injector temperature of 250 °C, oven temperature: 110 °C for 5 min, 110–215 °C (5 °C/min), 215 °C for 24 min, carrier gas: helium, injected volume: 1.0 µL, split 1:50. The qualitative composition was determined by comparison of the peak retention times of the respective fatty acid standards, expressed in mass percentage.

Solid fat content–SFC

The structuring and control blends were melted and homogenized in a microwave at 80 °C or above, in order to guarantee complete destruction of the crystals. They were then maintained in a dry thermostatic bath with temperature control by the PeltierTcon 2000 system (Duratech, Garden Grove, EUA) and later submitted to tempering conditions according to the Method AOCS Cd 16b-93 direct method I. Measures were taken in series (AOCS 2009). The SFC measurements were performed twice at the temperatures of 10, 20, 25, 30, 35, 40 and 45 °C, with tempering for the non-established fats, in a Nuclear Magnetic Resonance (NMR) spectrometer of pulsed low

resolution, Bruker pc120 Minispec (Silberstreifen, Rheinstetten, Germany).

Isothermal crystallization

The control and structuring blends were melted and homogenized at a microwave oven at 80 °C or above, and afterwards they were maintained in a thermostatic dry bath with temperature controlled by the Peltier, system (DuratechTcon, USA) at 70 °C for 1 h for the complete destruction of its crystals. After this period, the blends were submitted to isothermal crystallization at 20 °C, with automatic solid content measurements every 60 s, in a pulsed, low resolution Nuclear Magnetic Resonance (NMR) spectrometer, Bruker pc120 Minispec (Silberstreifen, Rheinstetten, Germany). All analyses were performed in triplicate. Characterization of the crystallization kinetics was performed according to the induction period (tSFC), maximum solid fat content (SFCmax) and time required to obtain 50% of the maximum solid fat content (t_{1/2}SFCmax) (Campos 2005; Ribeiro et al. 2009b).

Consistency

Consistency of the control and structuring blends was determined by using a texture analyzer TA-XT Plus (Stable Micro Systems, Surrey, United Kingdom), controlled by a microcomputer. The samples were heated in a microwave oven to approximately 100 °C for complete melting of the crystals, and then processed in 50 mL beakers. Processing was performed in an incubator for 24 h at 5 °C for crystallization of the fat, and then for 24 h at the following measurement temperatures: 10, 15, 20, 25 and 30 °C (Rodrigues et al. 2003). In order to determine the consistency an acrylic cone with pointed tip and 45° angle was used. The tests were performed with the following conditions: penetration distance = 10 mm, speed = 1 mm/s, time = 5 s (Campos 2005). The maximum compression force (gf) was determined and the penetration data was converted to Yield Value, according to Haighton (1959):

$$YV = \frac{K \times W}{p^{1.6}}$$

where, YV = Yield Value, in gf/cm², K = constant of the cone's angle (equal to 4700 for a 45° cone); W = force at maximum compression (gf); p = depth of the penetration (mm/10). The samples were analyzed four times and the results correspond to the average. Yield values were statistically analyzed via a one-way analysis of variance (ANOVA) using the software *STATISTICA* Version 8 (StatSoft Inc., Tulsa, OK, USA). Tukey's post hoc test was applied for statistical comparisons of the means with a significance level of 5% ($P < 0.05$).

Thermal Behavior

The thermal behavior of the samples was assessed by differential scanning calorimetry (DSC), TA Instruments equipment, Q2000 V4.7A model, connected to a refrigeration system RCS90 TA Instruments (New Castle, USA), according to the modified AOCS Cj 1-94 method (AOCS 2009). Samples between 8 and 10 mg were weighted inside aluminum pans of approximately 53 mg. One aluminum pan, empty and hermetically sealed was used as a reference. The analysis conditions were: an isothermal stage at 80 °C for 10 min, then the samples were submitted to cooling with at a temperature rate of 10 °C/min until reaching −80 °C, and maintained at this temperature for 30 min. The software TA Universal Analysis 2000 V4.7A was used for obtaining the crystallization curves along with the following evaluation parameters: temperature of crystallization onset (T_{oc}), temperature of the crystallization peak (T_{pc}), enthalpy of crystallization (ΔH_c), and final temperature of crystallization (T_{fc}) and intensity of the crystallization peak (I). All the analyses were performed in duplicate.

Microstructure

Determination of the microstructure (morphology and crystalline dimensions) was performed by polarized light microscopy. The samples were melted at 70 °C in an incubator. With the aid of a capillary tube, a drop of each sample was placed over a glass slide pre-heated to the temperature of 70 °C, which was covered with a cover slip. The slides were maintained in an incubator for 3 h at 25 °C. Morphology of the crystals was evaluated using a biological microscope with infinity corrected optical system UIS, BX51 (San Jose, USA), connected to a color digital video camera Media Cybernetic, model Evolution Micro Publisher 5.0 Mpixel (Bethesda, USA). The slides were put on the base of the heating plate [FP82 Mettler Toledo (Columbus, USA)], maintained at the same crystallization temperature of 25 °C. The images were captured by the Image-Pro Plus software, version 7.01, Media Cybernetic (Bethesda, EUA), using polarized light and 40 times amplification. For each slide, four visual fields were focalized, from which only one was chosen in order to represent the observed crystals.

Polymorphism

The polymorphic form of the oil crystals was determined by X-ray diffraction (DRX), according to the AOCS Cj 2-95 method (AOCS 2009). Analyses were performed with a Philips PW 1710 diffractometer (PANalytical, Almelo, Holland), by using Bragg–Brentano geometry (θ : 2 θ) with

Cu α radiation ($\lambda = 1.54056 \text{ \AA}$, voltage of 40 kV and current of 30 mA). Measurements were taken at steps of 0.02° at 2 θ and acquisition time of 2 s, with scans from 5 to 40° (2 θ scale). Before analysis the samples were melted in a microwave oven at approximately 100 °C and crystallized at 20 °C during 24 h in an incubator. Identification of the polymorphic forms was performed from the short spacings of each crystal. The relative proportions of the different crystal types were estimated from the relative intensity of the short spacings (AOCS 2009).

Results

Fatty acid composition

Figure 1 shows the fatty acids composition of control and structured blends, according to the polyunsaturated, monounsaturated and saturated fatty acid content. In sample 100:0 the PO presented 47.38% saturated fatty acids and 52.50% unsaturated fatty acids, while in sample 0:100 the LO was characterized by 86.60% unsaturated fatty acids, of which 50.73% corresponded to linolenic acid. The FHSO presented all saturated fatty acids, with 87% stearic acid and 11% palmitic acid, in agreement with the previous studies of Ribeiro et al. (2009a, 2013).

With the addition of LO to PO, an obvious reduction in the quantity of saturated fatty acids was observed, particularly palmitic acid, and therefore there was also an increase in the content of unsaturated fatty acids, particularly polyunsaturated fatty acids (linoleic and linolenic acids). As an example, the proportion of linolenic acid (C18:3) was altered from 0.2% in 100:0 blend, corresponding to PO, to approximately 50% in 0:100 blend, corresponding to LO. Regarding the saturated fatty acids, composition of 100:0 and 0:100 blends were 47.38 and 13.07%, respectively. With the addition of FHSO and SMS to the control blends changes in the fatty acid composition were less than 2%, and therefore not relevant for modifying the content of saturated, unsaturated and polyunsaturated fatty acids.

Solid fat content–SFC

With increased addition of LO to the PO, a reduction in the amount of solid fat was noted, due to the increased concentration of unsaturated fatty acids in the blends, with a consequent reduction in the melting point of the samples. At 10 and 15 °C the 100:0 and 80:20 control blends did not show different results for the SFC values in relation to their respective 100:0 S and 80:20 S structured blends, possibly due to the high quantities of PO in the samples. Although the FHSO and SMS blends were characterized as

Fig. 1 Polyunsaturated, monounsaturated and saturated fatty acids (FA) (%) of the control blends of PO:LO (w/w) (100:0, 80:20, 60:40, 40:60, 20:80, 0:100) and the structuring blends of PO:LO (100:0 S,

80:20 S, 60:40 S, 40:60 S, 20:80 S, 0:100 S) with 3% of SMS and 3% of FHSO (w/w). Values are shown as mean of three replications

presenting higher thermal resistance, the solid profiles characteristic of the control samples were little influenced by incorporation of the structuring elements. This result suggests that the increase in thermal resistance promoted by crystallization modifiers is preferentially associated with formation of a more cohesive network than the solid fat content.

The SFC of the 60:40, 40:60, 20:80 and 0:100 control blends were below those observed for the respective structured blends at 10 °C. This same characteristic was observed in the 100:0 and 80:20 blends in relation to their structuring correspondents, at 20 °C. All control blends were liquid at 35 °C, with SFC below 4% (Ribeiro et al. 2009a). The 100:0 S, 80:20 S, 60:40 S blends showed, at this same temperature, 7.1, 5.7 and 4.7% solids, respectively. The structured blends presented higher plasticity characteristics compared to the control blends, with gradual decline in the SFC values with increase in temperature (O'Brien 2009).

Isothermal Crystallization

From the isothermal crystallization the parameters: crystallization induction time (t_{SFC}), half-life time ($t_{1/2SFCmax}$), which corresponds to the time for the sample to reach half of the total solids, and the maximum solids content can be obtained (SFC_{max}) (Campos 2005; Ribeiro et al. 2009c).

According Fig. 2, sample 60:40 presented a reduction in the t_{SFC} from 39 to 8 min with addition of the structuring

elements; for 40:60 sample this value was expressively reduced from 65 to 9 min. Samples 20:80 and 0:100 were completely melted at the analysis temperature. However, when structured they were characterized by nearly equal t_{SFC} values of 8 and 9 min, respectively, even with significant increase in the content of unsaturated fatty acids resulting from the incorporation of LO to the blends. Thus, all structured samples presented t_{SFC} between 8 and 9 min, which can be observed at Fig. 2, independent of the saturated fatty acids content.

The SFC_{max} (%) values at 20 °C ranged from 0 to 10.9% for the control blends; while the structured blends presented values between 4.7 and 14.4% for this parameter. The 60:40 blend reached 6% solids and the 40:60 blend showed no crystallization at the analysis temperature, while its structured correspondents presented SFC_{max} values of 9.1 and 7.0%, respectively. Control samples showed $t_{1/2SFCmax}$ ranging from 29 to 61 min; for the samples with more than 80% LO, it was not possible to obtain any measurable result at 20 °C. When incorporating the addition of the structuring agents, all samples, including 0:100, exhibited $t_{1/2SFCmax}$ values between 10 and 13 min.

Thermal behavior

A typical crystallization curve obtained by DSC is represented by exothermic peaks which indicate the energy released during the process (Campos 2005).

Fig. 2 tSFC (min) of the PO:LO control blends (w/w) (100:0, 80:20, 60:40, 40:60, 20:80, 0:100) and PO:LO structuring blends (100:0 S, 80:20 S, 60:40 S, 40:60 S, 20:80 S, 0:100 S) with 3% of SMS and 3% of FHSO (w/w), for isothermal crystallization measured at 20 °C

The thermal profile of FHSO crystallization, which has only trisaturated triacylglycerols, presented a single exothermic peak, with crystallization onset at 51.13 °C. SMS indicated the start of crystallization at 51.55 °C and was characterized by a larger peak followed by a non-defined thermal event. The 100:0 sample, correspondent to the PO, had a crystallization onset temperature (T_{oc}) equal to 19.80 °C. In this blend, addition of the structuring elements altered crystallization onset to 29.37 °C. This effect occurred in all structured blends and was stronger as the LO content incorporated to the PO was increased. The lowest onset crystallization temperature (T_{oc}) of the structured blends was 26.25 °C, corresponding to the 0:100 blend. The 40:60 S and 20:80 S samples showed crystallization onset temperatures (T_{oc}) of 27.29 and 26.82 °C, values above the crystallization onset temperature of PO. This effect highlights the efficiency of structuring elements to increase the thermal resistance in blends containing high-unsaturated fatty acid contents.

In most cases the crystallization process of the blends showed two peaks or crystallization events, as indicated in Fig. 3, where the first is related to the trisaturated (SSS) and disaturated-monounsaturated triacylglycerols (SSU), and the second is represented by the diunsaturated-monosaturated (SUU) and triunsaturated (UUU) triacylglycerols. PO presents approximately 6, 45, 38 and 7% of SSS, SSU, SUU and UUU triacylglycerol species, respectively, while LO has only SUU and UUU, in proportions close to 64 and 36%, respectively (O'Brien 2009).

In the control blends, addition of LO promoted a reduction in the exothermic energy of the first peak; in LO (0:100) this first peak was not detected due to absence of the SSS and SUS triacylglycerols. Furthermore, the

reduction in enthalpy of crystallization (ΔH_{c2}) is related to increase in the proportion of UUU triacylglycerols. Since there is a large amount of trilinolenin triacylglycerol (LnLnLn) in the LO, it is not possible to affirm that the analysis expressed this region due to its melting point (O'Brien 2009).

With the incorporation of SMS and FHSO to the blends, structured samples showed two crystallization peaks (T_{pc1} , T_{pc2}). The greatest alteration in response to the addition of structuring agents occurred in the crystallization peak temperature (T_{pc1}), without indication of segregation of structuring agents (Fig. 3). The crystallization peak temperature (T_{pc}) values were significantly modified due to structuration. For example, the 40:60 blend exhibited 9.09 °C for this parameter, while for its structured correspondent (40:60 S) the crystallization peak temperature (T_{pc1}) was 25.77 °C. Addition of the structuring elements did not influence crystallization peak temperature (T_{pc2}), since for this specific parameter the control and structured blends showed similar profiles.

Consistency

In the application study of lipid bases in foods, the consistency analysis is one of the most important test. Consistency of the blends is presented according to the Yield Value (YV) (gF/cm²) parameter (Haighton 1959), for the control and structured blends at 10, 15, 20, 25 and 30 °C (Table 1). The YV decreased with the increase of liquid oil and the rise of the measured temperature for all blends, due to melting of the high-melting point triacylglycerols.

Considering the typical YV ranges for different applications according to Haighton (1959), fat bases are

Fig. 3 Crystallization curves obtained by DSC, A) blends of PO:LO (w/w) (100:0, 80:20, 60:40, 40:60, 20:80, 0:100) and B) structured blends of PO:LO (100:0 S, 80:20 S, 60:40 S, 40:60 S, 20:80 S, 0:100 S) with 3% of SMS and 3% of FHSO (w/w)

Table 1 Yield value (gf/cm²) at mixture of PO:HOSO pure and structured (S)

Blends	Yield value (gf/cm ²)				
	Temperature (°C)				
	10	15	20	25	30
100:0	8662,3 ^b	3784,5 ^c	83,1 ^{f,g}	80,3 ^f	–
100:0 S	23272,2 ^a	13141,5 ^a	4516,9 ^a	964,3 ^a	211,8 ^c
80:20	3390,8 ^{c,d}	1410,0 ^c	48,8 ^g	26,4 ^{f,g}	–
80:20 S	11477,7 ^b	6102,6 ^b	1672,8 ^b	587,1 ^b	275,7 ^b
60:40	1015,7 ^{d,e}	334,3 ^g	45,7 ^g	–	–
60:40 S	5416,0 ^c	2103,8 ^d	851,1 ^c	400,1 ^c	236,0 ^a
40:60	144,6 ^e	46,8 ^g	–	–	–
40:60 S	1783,2 ^{d,e}	900,5 ^f	564,5 ^d	307,1 ^d	155,5 ^d
20:80	27,6 ^e	–	–	–	–
20:80 S	433,3 ^e	268,4 ^g	228,2 ^e	181,2 ^e	91,9 ^e
0:100	–	–	–	–	–
0:100 S	40,8 ^e	35,4 ^g	166,8 ^{e,f}	55,6 ^e	87,4 ^e

* Same letters to the same temperature indicate that there is no difference between the means evaluated by Tukey test ($P < 0.05$)

classified as following: YV below 50 gF/cm²: very soft and almost fluid; YV from 50 to 100 gF/cm²: very soft and non-spreadable; YV from 100 to 200 gF/cm²: soft, but spreadable; YV from 200 to 800 gF/cm²: plastic and spreadable; YV between 800 and 1000 gF/cm²: hard but satisfactory spreadability; YV from 1000 to 1500 gF/cm²: very hard with limited spreadability; YV above 1500 gF/cm²: very hard.

According to this classification, at 10 °C only the 60:40 and 20:80 S blends showed YV compatible for direct

application in formulations such as plastic and spreadable fats, with YV equal to 829.6 and 762.4 gF/cm², respectively. At 15 °C, the YV of these blends corresponded to 503.1 and 459.8 gF/cm², respectively, characterizing them as plastic. At this temperature the 40:60 S blend presented the same classification, with YV of 792.6 gF/cm². At 20 °C the blends 80:20, 60:40 S, 40:60 S and 20:80 S showed plasticity, with YV of 927.7, 839.8, 454.0 and 371.0 gF/cm², respectively; at 25 °C the blends 100:0 S and 80:20 S, with YV of 883.9 and 439.7 gF/cm², were classified as plastic and spreadable fats. At 30 °C, none of the control blends presented measurable results, since they were in a semi-liquid or liquid state. For the structured blends the YV were below 200 gF/cm², characterizing them as soft or very soft fats.

All samples supplemented with SMS and FHSO showed a relevant increase in consistency in relation to the corresponding control blends, with potentially expressive results for application in foods. For example, at 10 °C the 60:40 blend had a YV equal to 829.60 gF/cm²; while for the 60:40 S blend the YV was 4176.90 gF/cm².

Microstructure

The microstructure provides information about the state, quantity, shape, size, spatial relationship and interaction of the components of fat crystal network (Ribeiro et al. 2009c).

Figure 4 presents the images obtained by polarized light microscopy for the evaluated blends. The PO (blend 100:0) showed larger spherical crystals also observed by Tarabukina et al. (2009) and de Oliveira et al. (2015c). The addition of LO to PO promoted an increase in the proportion of low-melting point triacylglycerols, resulting in a

Fig. 4 Polarized light micrograph of fat crystals obtained under static isothermal crystallization at 25 °C, for 3 h, magnification of 40×. Blends of PO:LO (w/w) (100:0, 80:20, 60:40, 40:60, 20:80, 0:100) and structured blends (S) with 3% of SMS and 3% of FHSO (w/w)

larger quantity of liquid oil and crystalline networks of lower visual density. The higher the amount of LO incorporated to the blends, more evident was the dispersion of the crystalline elements, confirming the reduction in consistency due to the incorporation of LO in PO.

Addition of structuring agents to the control blends promoted formation of denser and more homogeneous crystalline networks, with noticeable visual changes. As a result, the structured blends presented greater crystal quantities per visual field, with smaller elements presenting undefined morphology.

The presence of PO in blends is important for the contribution of SSS and SSU triacylglycerols in crystal network formation. Adding FHSO to the blends provides higher-melting point triacylglycerols, changing the crystallization process and therefore promoting the formation of more crystals with reduced dimensions. The 100:0 blend showed the denser crystalline network, while the 80:20 S, 60:40 S, 40:60 S and 20:80 S blends presented more homogenous morphology than their respective control blends. Considering the analysis temperature of 25 °C, the visual microstructure results were compatible to those obtained in the evaluation of consistency. The 0:100 S blend was characterized by a lower density crystalline network due to the higher proportion of liquid oil, with unsatisfactory parameters regarding plastic lipid bases. The presence of greater quantities of small fat crystals and networks that are more cohesive may be associated to the higher consistency of these blends compared to the control blends.

Polymorphism

The triacylglycerol crystals are basically found in three polymorphic forms, α , β' and β , in order of increasing stability and melting point (Himawan et al. 2006). These crystalline forms are characterized by specific short spacing or distances between the fatty acids chains, which can be measured by X-ray diffraction. The characteristic short spacings correspond to 4.15 Å for α , 3.8 and 4.2 Å for β' and 4.6 Å for β forms, and are used to determine the proportion and type of polymorphs present in the specific blends. In fats for spreads and margarines, crystals should preferably be stabilized in the β' form; while for chocolates the β form is desirable for quality products Young and Wassell (2007, 2008). The qualitative relationship of the evaluated polymorphs is presented in Table 2.

The PO presented stable crystals in the β' form, due to its diverse fatty acid composition, and particularly the greater quantity of palmitic acid. The LO (0:100) also presented crystals in the β' form. As a result, all control blends presented preferential polymorphism in the β' form. With the incorporation of SMS and FHSO, structured

blends presented a combination of the β' and β polymorphic forms. Stabilized FHSO presents of β' and β polymorphs simultaneously; the β fraction is related to the low variability of fatty acids present in this hardfat (Ribeiro et al. 2013). Structured LO (0:100S) showed no crystalline phase at the analysis conditions.

Discussion

Similarity in the proportion of saturated and unsaturated fatty acids characterizes PO as a semi-solid fat at room temperature, justifying its broad use in the food industry (Garbolino et al. 2005). Additionally, its low content of polyunsaturated fatty acids provides high oxidative stability, maximizing its potential for application in processed products.

According to Kochhar (2011), LO must contain more than 50% in order to be identified as such. In comparison with vegetable oils of high nutritional and economic relevance, such as soybean and canola oils, LO presents the best $\omega 6:\omega 3$ ratio (approximately 0.3:1). For soybean and canola oils, this proportion corresponds to 7:1 and 2:1, respectively (Logan 2004; Morris 2007).

The behavior of an oil or fat at different temperatures is described by the solid profiles (SFC). According to its application particularities, this data qualifies and directs a certain lipid base for industrial use, because the amount of crystalline solids in oil is responsible for the general physical properties for food application (Karabulut et al. 2004; Ribeiro et al. 2013).

SFC values at low temperatures (10 °C, for instance) determine the spreadability of refrigerated products, and the lipid base for these should not exceed 32% solids. Temperatures between 20 and 22 °C determine the stability and exudation of liquid oils in fat products, where this effect is minimized when the fat fraction presents a minimum of 10% solids in this temperature range. Temperatures between 35 and 37 °C characterize the oral melting profile and the softness sensation, features which require solid contents below 4% (Wassell and Young 2007; Ribeiro et al. 2013).

In a study by Ribeiro et al. (2013), the incorporation of FHSO to cocoa butter, at the proportions of 1.3 and 5% (m/m) significantly increase the solid content of this raw material at all temperatures. Masuchi et al. (2014) evaluated the isolated effect of SMS in cocoa butter at the concentrations of 0.5, 1.0 and 1.5%(w/w). These incorporation levels were associated with the higher thermal resistance of cocoa butter for application in chocolates and confectionery products. In this study, the combined use of the structuring FHSO and SMS in the PO:LO blends promoted an increase in the solid fat content at different

Table 2 Short spacings and polymorphic forms of PO:LO control blends and structured blends (S), at 25 °C *

Blends	Short spacings							Polymorphic form
	4.6	4.5	4.4	4.3	4.2	3.8	3.7	
100:0				4.30 (s)	4.18 (vs)	3.81 (m)		β'
80:20				4.34 (m)	4.20 (ws)	3.81 (m)		β'
60:40					4.17 (s)	3.77 (w)		β'
40:60					4.19 (m)	3.79 (vw)		β'
20:80		4.45 (m)			4.19 (m)	3.76 (vw)		β'
0:100			4.42 (m)		4.17 (m)		3.71 (vw)	β'
100:0 S	4.55 (m)				4.19 (vs)	3.80 (m)		$\beta' + \beta$
80:20 S		4.53 (m)			4.16 (vs)	3.78 (m)		$\beta' + \beta$
60:40 S	4.56 (m)				4.17 (s)	3.78 (w)		$\beta' + \beta$
40:60 S		4.5 (m)			4.20 (s)	3.76 (w)		$\beta' + \beta$
20:80 S			4.43 (m)		4.20 (m)	3.76 (vw)		β'
0:100 S								Liquid

* Intensities: v. very; w. weak; m. medium; s. strong

temperatures, a result also observed by Oliveira et al. (2015c) in the structuration of PO with canola oil and these additives together.

Regarding the kinetic effects associated with the crystallization, the addition of LO to PO promoted an increase in the induction period (t_{SFC}) of the blends due to the presence of low-melting point unsaturated triacylglycerols. With the addition of FHSO and SMS, a combined effect relative to the decrease of the induction period (t_{SFC}) and increase of the maximum solids dose (SFC_{max}) was verified. Furthermore, a reduction of the $t_{1/2\text{SFCmax}}$ of crystallization confirms accelerated formation of the crystalline network at 25 °C.

When submitted to super-cooling at a controlled and established rate in DSC, oils and fats show fractionated crystallization of their triacylglycerol classes, represented by SSS, SSU, SUU and UUU classes, with consequent segregation according to the melting range of the triacylglycerol classes. In general, peaks situated in temperature range of 47 to 73.5 °C are characteristic of the SSS and SSU triacylglycerols; and at temperatures below 5 °C the UUU triacylglycerol peak is identified (Bockisch 1998; Peyronel and Marangoni 2014).

Increase of the crystallization onset temperature (T_{oc}) in all the structuring blends and the small change in enthalpy of crystallization (ΔH_{c1}) confirms co-crystallization of the structuring agents and their action as crystallization modifiers. This result may be associated with the large quantity of stearic acid in these additives, which influences the general crystallization behavior due to the size of its hydrocarbon chain, melting point and molecular stability (Cebula and Smith 1991; de Oliveira et al. 2015a). Minimum alterations in the values of crystallization temperature

(T_{pc2}) and enthalpy of crystallization (ΔH_{c2}) indicate that the additives did not change the crystallization events of the SUU and UUU triacylglycerols, which were influenced only by the incorporation of LO to PO.

With increasing temperature, fat crystals show progressive melting with the destruction of the crystalline network and reduction in the consistency of the blends. At low temperatures the crystalline network becomes more solid, due to crystallization of a higher proportion of triacylglycerols. In parallel, when the SMS molecules are submitted to cooling they present lower solubility in liquid oil, minimizing the mobility of the crystals and providing the crystalline network with greater resistance to deformation (Rogers 2009; Ribeiro et al. 2013; Masuchi et al. 2014).

Considering the SFC data, at 10 to 15 °C the 100:0 blend and its corresponding structured blend showed similar values regarding this parameter. When considering the consistency results at the same temperatures, a relevant increase in the YV is observed when the structuring agents are incorporated. For comparison, the 100:0 blend showed YV of 10514.3 and 3683.6 gF/cm² and the 100:0 S blend had YV equal to 16844.5 and 9224.6 gF/cm² at 10 and 15 °C, respectively. This fact indicates that consistency does not depend on the isolated contribution of the SFC, but instead other mechanisms are involved in the macrostructural properties, as for example the morphology and the crystal size (Santos et al. 2014; de Oliveira et al. 2015c).

According to Haighton (1959), lipid bases with plastic properties and satisfactory spreadability present YV ranging from 200 to 800 gF/cm². The samples that best fit in this classification were the structured blends, since they

were characterized by higher thermal resistance, an effect that was maintained at higher LO proportions.

The solids content, polymorphism and microstructure of the crystalline network affect the macroscopic characteristics of lipid systems (Shi et al. 2005). The PO has a well-known feature for the formation of spherical crystals, with defined dimensions and morphology. Adding FHSO to the blends caused the formation of a large numbers of small crystals, with formation of denser crystalline networks, besides affecting the consistency and some technological properties, including thermal resistance (de Oliveira et al. 2015b). The study of Ribeiro et al. (2013) highlights that tristearin, predominant in FHSO triacylglycerols, would act as a potential agent to harden the lipid bases. Furthermore, SMS demonstrates capacity for structuring the crystalline network, through the formation of typical tubular networks, promoting retention and immobilization of liquid oil fractions (Dassanayake et al. 2011; de Oliveira et al. 2015a).

The process of formation and stabilization of fat crystals is associated with the different polymorphic forms. The study of de Oliveira et al. (2015b) showed that stabilized FHSO presented a combination of the crystalline forms β' and β , predominantly the β form. It suggests that the formation of β crystals in the structured blends can be attributed to the incorporation of FHSO. According to Podmore (2011), triacylglycerols with fatty acids presenting the same chain length tend to form β form crystals. FHSO contains predominantly tristearin, with approximate content of 64% (Ribeiro et al. 2013). It is assumed that in the blends the polymorph β' is associated with the contributions of the PO and LO, and also the molecular restriction caused by addition of the SMS. SMS demonstrates co-crystallization capacity with triacylglycerol molecules, due to the appropriate chemical bonding, but as a result of its differentiated spatial structure it does not allow rotation and rearrangement of triacylglycerol molecules at 90°, delaying the transition of the polymorphic form β' to β (Guth et al. 1989; Young and Wassell 2008).

Considering these results, the combined use of SMS and FHSO significantly contributed to the structuration of the lipids systems composed of blends containing liquid or semi-liquid oils, as indicated in alterations related to the SFC profiles, crystallization kinetics, thermal behavior, consistency, microstructure and polymorphism of all the structured blends. All of these modifications were observed at the micro and macro-scales, with effects from the nucleation phase until stabilization of the crystallization process, featuring structured blends with properties of plastic fats, even with the large increase in proportion of unsaturated fatty acids.

In general, the FHSO promoted an increase in the SFC of the structured blends, due to its high-melting point triacylglycerols. Furthermore, FHSO was responsible for

changes in the induction time of crystallization, since its triacylglycerols act as preferable nuclei in the process of molecular organization in the lipid system, accelerating crystalline network formation (Cebula and Smith 1991; Ribeiro et al. 2013).

The SMS, through a self-assembly mechanism described in previous studies on organogels, would be responsible for the formation of long tubular structures, which in association originate a homogeneous tridimensional network, immobilizing liquid oil fractions. Therefore, the SMS would assist in stabilization of the fat crystalline network by developing a gel which, when cooled down, has an opaque, semi-solid appearance, with soft texture and properties of thermal-reversibility, which in addition to the presence of FHSO justifies the higher consistency values of the structured blends compared to the control blends (Murdan et al. 1999; Rogers 2009; Dassanayake et al. 2011).

Another presumable factor for the contribution of SMS as a structuring agent is the presence of stearic acid, predominant in its composition, associated with positive interactions among triacylglycerols from the lipid system, including FHSO triacylglycerols (Garbolino et al. 2005; Masuchi et al. 2014). This chemical similarity allows co-crystallization of SMS and FHSO through connection of this additive molecule to the surface of the FHSO triacylglycerols, thus limiting the growth of large crystals and consequent formation of agglomerates (Garbolino et al. 2005).

Organogels demonstrated high potential for the developing of fats formulations. In the present study, structuring of the PO:LO blends with simultaneous of SMS and FHSO incorporation allowed the development of lipid bases with high content of liquid oil, which can be applied for the substitution of technical fats with saturated fatty acids. This study indicated that it is possible to obtain lipid bases of proper nutritional quality, with appropriate technological characteristics for application in processed foods. The formulation of plastic lipid bases with reduced saturated fatty acids and high content of polyunsaturated fatty acids, particularly alpha-linolenic acid, was effective. In this context, some blends presented important parameters that should be evaluated in technical fats for direct use. At 25 °C, the structured blends 80:20 and 60:40 PO:LO presented consistency, plasticity and spreadability properties compatible with plastic fats. The blends 40:60 S and 20:80 S may be viable for applications which involve the use of very soft fats. Such blends were characterized by the increase of up to 80% in the proportion of alpha-linolenic acid and consequent reduction in the amount of saturated fatty acids up to 47%. Additionally, stearic acid which is the main species in FHSO does not increase the level of low-density lipoprotein (LDL) in the blood plasma,

presenting a neutral metabolic effect (Bonanome and Grundy 1988; Snook et al. 1999).

Conclusion

In this study, the efficiency of fully hydrogenated soybean oil and sorbitan monostearate in structuring blends of palm oil (PO) and linseed oil (LO) was assessed for different proportions of PO:LO. Both additives, at similar concentrations (3%w:w), demonstrate capacity for structuring of lipid systems with high content of unsaturated fatty acids, promoting modifications to the properties of solid fat content, crystallization kinetics, consistency, thermal behavior, microstructure and polymorphism. This strategy enables the development of lipid formulations with a better nutritional profile and characteristics of plasticity compatible to several food applications.

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