LWT - Food Science and Technology 62 (2015) 122–130

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Sorbitan and sucrose esters as modifiers of the solidification properties of zero *trans* fats

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ARTICLE INFO

Article history:
Received 23 August 2014
Received in revised form
3 January 2015
Accepted 6 January 2015
Available online 14 January 2015

Keywords:
Sorbitan and sucrose esters
Zero *trans* fat
Crystallization process
Consistency
Scanning electron microscopy

ABSTRACT

Crystallization is the most important physical problem encountered in the industrial use of fats and oils. In this context, the objective of the present study was to analyze the action of sorbitan tristearate (STS) and sucrose stearate (SE) as potential modifiers of crystallization of the unsaturated triacylglycerols and to evaluate their effects on the physical properties of zero *trans* fat from soybean oil and fully hydrogenated soybean oil. The zero *trans* fat was obtained via chemical interesterification of a blend of soybean oil (70 g/100 g) and fully hydrogenated soybean oil (30 g/100 g). Samples containing 1 g/100 g, 3 g/100 g, and 5 g/100 g STS or SE were prepared and their crystallization properties were evaluated on the basis of the solid fat content (SFC), melting point, consistency, microstructure and visualization of the three-dimensional crystalline network. Both emulsifiers contributed to SFC adequacy, enhancing the consistency of the fat. As for compatibility, both emulsifiers were compatible with the interesterified fat. This was confirmed by the change in linearity of the curves at 15–20 °C. Samples with STS presented higher fractal dimension, indicating greater organization of the crystal lattice. Similarly, the visualization of three-dimensional crystalline network showed firmer structures for samples with STS compared with the samples SE.

1. Introduction

Oils and fats are important ingredients in a wide variety of foods, cosmetics, and pharmaceuticals. The fats available for industrial use have changed greatly over the years (Sato & Ueno, 2011). In the specific case of the food industry, an increasing concern for health has caused progressive amendments to food legislation, leading to the replacement of partially hydrogenated fatty bases (high in *trans* fatty acids) with interesterified, fractionated or blends bases. Interesterification has emerged as the main alternative for obtaining plastic fats with low levels of or without *trans* isomers (Ribeiro, Grimaldi, Gioielli, & Gonçalves, 2009).

However, the replacement of partially hydrogenated fats in food products, especially in shortenings and bakery products, is currently a challenge because it is difficult to achieve the appropriate texture and crystallization properties in the absence of *trans* fatty acids (Reyes-Hernández, Dibildox-Alvarado, Charó-Alonso, & Toro-Vazquez, 2007). In this context, the use of emulsifying agents as modifiers of the crystallization behavior of lipids has been a current focus in research in food technology. From numerous recent studies, it has been confirmed that emulsifiers affect the crystallization induction periods, composition of the seeds in the nucleation process, crystal growth rates, and polymorphic transitions (Smith, Bhaggan, Talbot, & van Malssen, 2011).

Sorbitan and sucrose esters are recognized as potential modifiers of the crystallization of fat bases. Sorbitan can be esterified with more than 1 mol of fatty acids as lauric, palmitic, oleic and stearic acid to form very lipophilic compounds such as sorbitan tristearate (also known as STS or Span 65). This molecules has three fatty acids extending from sorbitol, and exhibits a strong tendency to be adsorbed onto the fat surfaces from the lipid matrix during crystallization. STS is therefore a molecule with good potential for studies on fat crystallization. Sucrose esters are derived from esterification (fatty acids and sucrose) or transesterification (sucrose and fat) reactions. Because sucrose can be esterified with up to eight fatty acids, a wide variety of products can be obtained. The availability of sucrose esters of stearic, palmitic, oleic, and lauric acids has facilitated studies on the effect of these compounds on fat crystallization (Garti & Yano, 2001).

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http://dx.doi.org/10.1016/j.lwt.2015.01.008
0023-6438/

The selection criterion of these emulsifiers was based on their similarity to the acyl group composition (stearic acid) differing only in the hydrophilic portion (sorbitol; sucrose). Because of these considerations, the aim in this first study was to evaluate the behavior of sorbitan tristearate (STS) and sucrose stearate (SE) as modifiers of the solidification properties of soybean-based zero *trans* fat, verifying the effects on the solid fat content (SFC), consistency and crystalline structure.

2. Materials and methods

2.1. Materials

2.1.1. Raw materials

Soybean oil was acquired from the local trade and fully hydrogenated soybean oil was supplied by Triângulo Alimentos (Brazil). Sodium methoxide powder (Sigma–Aldrich) was used as a catalyst in the chemical interesterification. The emulsifiers, STS Grinsted-B-30 powder (hydrophilic-lipophilic balance (HLB) 2.1; melting point, 52 °C; DuPont, Brazil) and powdered S-370 (HLB 3; melting point, 66 °C; Mitsubishi-Kagaku Foods, Japan) were used in proportions of 1, 3, and 5 g/100 g.

2.1.2. Chemical interesterification

The blend was prepared using a ratio of 70 g/100 g soybean oil to 30 g/100 g fully hydrogenated soybean oil as described by Ribeiro et al. (2009) for obtaining the zero *trans* fat. The blend was melted at 100 °C and homogenized for 10 min to melt the crystals completely. Chemical interesterification was performed in a 4-L jacketed borosilicate glass reactor with a bottom drain port connected to a thermostated circulator bath, with a stirring system and pneumatic vacuum pump (Edwards, Model E2M18, Series 962053519). A two liter portion of the blend was placed into the reactor and dried for 20 min at 100 °C (in the reactor itself) under vacuum, using 0.4 g/100 g sodium methoxide as a catalyst. The reaction was carried out under constant stirring for 20 min and was terminated by addition of water and 5 g/100 g citric acid solution. The interesterified fat sample was thoroughly washed with distilled water (80 °C) to remove any soap that had formed, and then dried under vacuum at 110 °C for 30 min.

2.1.3. Sample preparation

The interesterified zero *trans* fat (IF) was heated until it was completely melted. The interesterified fat blends were then prepared with 1, 3, and 5 g/100 g sorbitan tristearate (STS), and 1, 3, and 5 g/100 g sucrose stearate (SE). Each blend was homogenized until the emulsifier was completely incorporated into the fat phase.

2.2. Methods

2.2.1. Fatty acid composition

The fatty acid composition was analyzed using the AOCS Ce 2-66 method (AOCS, 2009) by employing a capillary gas chromatograph CGC AGILENT 6850 Series GC System with an auto sampler and flame ionization detector. The fatty acid methyl esters were separated according to the method of Hartman and Lago (1973) using a capillary column (DB-23 AGILENT, 60 m long, 0.25 mm internal diameter, 0.25 μm film). The analysis conditions were as follows: oven temperature: 110 °C/5 min, 110–215 °C (5 °C/min), 215 °C/24 min; detector temperature: 280 °C; injector temperature: 250 °C; carrier gas: helium, split ratio 1:50; injection volume: 1 μL. The qualitative composition was determined by comparing the peak retention times with the respective standards for fatty acids. The iodine value was calculated based on the fatty acid composition, according to the AOCS official methods Cd 1c-85. The analysis was performed in triplicate.

2.2.2. Triacylglycerol composition

The triacylglycerol composition was analyzed according to the AOCS Ce 5-86 method (AOCS, 2009) using a gas chromatograph (GC CGC AGILENT 6850 Series GC) system and a capillary column (DB-17HT AGILENT, 15-m long, 0.25-mm internal diameter, 0.15-mm-thick film). The analysis conditions were: split ratio 1:100; column temperature: 250 °C, programmed up to 350 °C at a rate of 5 °C/min, carrier gas: helium at a flow rate of 1 mL/min; injector temperature: 360 °C; detector temperature: 375 °C; injection volume: 1 μL; sample concentration: 100 mg/5 mL of tetrahydrofuran. The triacylglycerol groups were identified by comparison of the retention times as described by Antoniosi Filho, Mendes, and Lanças (1995). The analysis was performed in triplicate.

2.2.3. Quantification of minority lipids

Samples were diluted in the proportion of 10 mg to 1 mL tetrahydrofuran and analyzed (20 μL) via liquid chromatography using a Rheodyne 7725i injector and a Waters 510 pump (Waters Corporation, Milford, MA, USA) with two columns (Ultrastyragel; 100 Å and 500 Å; Waters Corporation, Milford, MA, USA, 25 cm × 0.77 cm i.d.) packed with styrenedivinylbenzene copolymer (approximately 10 mm) connected in series with a refractive index detector (Hewlett Packard, California, USA). The analysis conditions were as follows: mobile phase: tetrahydrofuran (HPLC grade), flow rate: 1 mL/min; injected volume: 20 μL. The compound families were identified by comparing the elution times with the following standards: triacylglycerols (TAG), diacylglycerols (DAG), monoacylglycerols (MAG), and free fatty acids (FA) (Márquez-Ruiz, Jorge, Martín-Polvillo, & Dobarganes, 1996). The analysis was performed in triplicate.

2.2.4. Regiospecific distribution

The regiospecific distribution of the samples was determined by high resolution ^{13}C nuclear magnetic resonance (NMR) spectroscopic analysis of the TAG acyl chains. Analyses were performed on an NMR spectrometer (Silberstreifen, Rheinstetten, Germany; Bruker Avance DPX 300). ^{13}C spectra were acquired at a frequency of 75.8 MHz using a 5-mm multiple nuclear probe operating at 30 °C, according to the methodology described by Vlahov (1998, 2005). The results are presented as the composition of oleic and linoleic acids in the sn-2 and sn-1,3 positions of triacylglycerols. The analysis was performed in triplicate.

2.2.5. Solid fat content (SFC)

The solid fat content was determined using an NMR spectrometry (Bruker Minispec PC120) and a TCON 2000 high precision dry bath (0–70 °C) (Duratech, USA), according to the AOCS method Cd 16b-93. Sample readings were taken in series at 5 °C increments in the temperature range of 10–65 °C, with tempering for non-stabilized fats (AOCS, 2009). Compatibility diagrams were constructed by plotting the SFC versus emulsifier ratio for each temperature. The analysis was performed in triplicate.

2.2.6. Melting point

The melting point was calculated for the temperature corresponding to 4 g/100 g of solid content obtained from the SFC curve derived from NMR (Karabulut, Turan, & Ergin, 2004) by using polynomial functions fitted with the aid of Microsoft Excel.

2.2.7. Consistency

Consistency was determined by using a PC-controlled texture analyzer (TA-XT2i; Stable Micro Systems, Godalming, England). The