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Studies of isothermal crystallisation kinetics of sunflower hard stearin-based confectionery fats

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ABSTRACT

The crystallisation and polymorphic properties of three sunflower hard stearins (SHSs) and cocoa butter equivalents (CBEs) formulated by blending SHSs and palm mid fraction (PMF) were studied and compared with those from cocoa butter (CB), to explore their possibilities as confectionery fats. The isothermal crystallisation kinetics of these fats were examined by pNMR and DSC at three different temperatures. All samples studied displayed a two-step crystallisation profile that could be fitted to an exponential-Gompertz equation. Stop-and-return DSC studies showed that SHSs and CBEs exhibited different crystallisation mechanisms according to their triacylglycerol composition, with a quick formation of metastable crystals, followed by a polymorphic transition to the more stable β or β′ forms. X-ray diffraction (XRD) was used to investigate the polymorphic forms of tempered SHSs and CBEs in the long term. In all cases the resulting fats displayed short spacing patterns associated with β polymorphism. These formulations based on SHSs and PMF met all the requirements to be considered as CBEs; therefore they could be used as an alternative to traditional confectionery fats.

1. Introduction

Confectionery fats are the most important component of fat-based confectionery products. These fats can be produced from different sources, but all of them display similar physical properties. They should be a brittle solid at room temperature but must melt quickly at temperatures above 30–32 °C (Gunstone & Harwood, 2007). This behaviour yields a stable confectionery product that releases flavours in the mouth at body temperature without an undesirable waxy texture. The most common naturally-occurring confectionery fat is cocoa butter (CB), which has been traditionally used for the production of chocolates, coatings and candies. CB contains high levels of the saturated fatty acids stearic and palmitic, and the monounsaturated oleic (Shukla, 1995). These fatty acids are distributed on the glycerol backbone as disaturated triacylglycerols (TAG) with oleic acid primarily found at the sn-2 position. The main disaturated TAG species present in CB are 1,3-dipalmitoyl-2-oleoyl glycerol (POP), 1-palmitoyl-3-stearoyl-2-oleoyl glycerol (POSt) and 1,3-distearoyl-2-oleoyl glycerol (StOSt), which account for 82% of total TAGs. These TAGs dominate the crystallisation, polymorphism and phase transformations, providing chocolate with its characteristic textural and sensory properties (Afoakwa, 2010). Cocoa butter has a complex polymorphic behaviour and must be processed under controlled conditions (tempering) to obtain the stable polymorph (β_V), which gives the crystalline structure appropriate for confectionery uses (Gerhard, 1979; Jocanovic, Karlovic, & Jakovljevic, 1995; Talbot, 2009a).

Among the alternatives to CB for confectionery, cocoa butter substitutes (CBS) are formulations based on lauric fats, whereas cocoa butter replacers (CBR) are fats rich in *trans* fatty acids obtained by hydrogenation of vegetable oils (Okawachi & Sagi, 1985; Pease, 1985; Petersson, 1989). Both lauric and hydrogenated fats are not advisable within a healthy diet since they have been suggested to increase the level of LDH blood cholesterol (Stanley, 2009). The only healthy alternatives to CB are cocoa butter equivalents (CBEs). These fats are formulated with stearate-rich butter of tropical origin (shea, sal, kokum, illipe, mango kernel) and fractions from palm oil, displaying similar properties and polymorphism to CB (Yella Reddy & Prabhakar, 1989).

In recent times, oil seed biotechnology has been able to produce a variety of oil crops with modified fatty acid composition (Martínez-Force & Garcés, 1999). Among them, one with special interest for the production of new confectionery fats is the high oleic-high stearic (HOHS) sunflower oil, which is being commercialised under the brand *Nutrisun oil*. This oil contains fairly high levels of TAGs of the pattern 1,3-saturated-2-monounsaturated (SUS), which can be concentrated by fractionation to yield soft or hard

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stearins with potential for the formulation of both plastic and confectionery fats (Bootello, Garcés, Martínez-Force, & Salas, 2011; Salas, Bootello, Martínez-Force, & Garcés, 2009, 2011). In this regard, sunflower hard stearins (SHSs) prepared from HOHS sunflower oil can be blended with palm mid fractions (PMF) to yield fats compatible with CB and with a similar melting profile, with the advantage of being a healthy fat free of lauric and *trans* fatty acids and assuring a safe supply from a crop well established in temperate countries. In an earlier publication (Bootello, Hartel, Garcés, Martínez-Force, & Salas, 2012), the optimal compositions of CBEs formulated with these stearins were studied as a function of their melting profile and the compatibility of SHSs with PMF. However, no information has been published on the crystallisation behaviour and macroscopic properties of these stearins and their blends, which is a very important aspect when preparing food formulations with confectionery fats.

The main objective of this work was to investigate the pattern of crystallisation of several of these SHSs and CBEs formulated with them. Thus, crystallisation kinetic studies were fulfilled for three SHSs and two CBE formulations at different temperatures by the techniques of DSC and pNMR, applying the two-step Gompertz mathematical model. Moreover, a determination of the predominant polymorph after storage (1 month) was also studied by X-ray diffraction to make a comparison with CB.

2. Materials and methods

2.1. Oil material

The SHS fractions used in this work were produced by two stages involving dry and solvent fractionation of refined, bleached, deodorised and partially dewaxed HOHS sunflower oil provided by Nutrisun Business (Mar del Plata, Argentina). Dry fractionation of the initial oil was carried out on an industrial scale at the company Graydesa (Barcelona, Spain) using the conditions described by Bootello et al. (2011) for the optimal crystallisation of the oil. The resulting soft stearin (30% SUS, 25% stearic) was further fractionated in a mini-pilot plant at temperatures between 15 and 17 °C and oil/solvent ratios ranging from 1/2 to 1/4. The stearins resulting from solvent fractionation were filtered, washed with fresh acetone and dried by vacuum distillation. Three different SHS products were obtained in that system by using different fractionation conditions. The fractions contained 65%, 80% and 95% of SUS and were named SHS 65, SHS 80 and SHS 95, respectively. Palm mid fraction used in blends was provided by Lípidos Santiga (Barcelona, Spain). The blends, labelled as CBE1 and CBE 2, were obtained by mixing SHS 95 with 50% PMF (CBE1) and SHS 80 with 25%PMF (CBE2) as explained by Bootello et al. (2012). The sample of Ivory Coast cocoa butter (ICCB) was kindly supplied by ADM Cocoa (Milwaukee, WI, USA). These fats exhibited the following melting points: SHS 95 (41.5 °C), SHS 80 (40.2 °C), SHS 65 (36.5 °C), CBE1 (35.0 °C), CBE2 (36.5 °C) and ICCB (35.6 °C) as can be found in Bootello et al. (2012).

2.2. Chromatographic analysis of TAGs and fatty acids

The TAG composition of the different stearin fractions was determined by GC using an Agilent 6890 gas chromatograph (Santa Clara, CA) equipped with a Quadrex Aluminium-Clad 400-65HT (30 m length, 0.25 mm i.d., 0.1 μm film thickness (Woodbridge, CT, USA) and a flame ionisation detector. Hydrogen was used as the carrier gas at a linear rate of 50 cm/s and split ratio 1:80. The injector and detector temperatures were 360 and 370 °C respectively, the oven temperature was 335 °C, and a head pressure gradient from 100 to 180 kPa was applied. The relative response of the FID was corrected according to the method of Carelli and Cert (1993). For TAG determination 5 mg of fat were dissolved in 1.7 mL of heptane. Fatty acids were analysed as their methyl esters in a similar chromatograph but equipped with a Supelco SP-2380 fused silica capillary column (30 m length; 0.25 mm i.d.; 0.20 μm film thickness: Bellefonte, PA). The analysis conditions were carrier gas (hydrogen) flow at 28 cm s^{-1}, detector and injector temperature were 200 °C, whereas oven temperature was kept at 170 °C. Methylation of the TAG fatty acids was carried out at 80 °C for 1 h after adding a volume of 1.5 mL of methanol/toluene/sulfuric acid (88/10/2; v/v/v) to 5 mg of fat. For both TAG and fatty determinations the injection volume was 1 μL.

2.3. Isothermal crystallisation kinetics by p-NMR

Isothermal crystallisation kinetics were monitored by determining the SFC by pNMR using a Bruker Minispec unit, equipped with on-board software for data processing (Bruker, Milton, Ontario, Canada). NMR tubes with a 10-mm diameter were filled with approximately 2.0–2.5 g of completely melted fat and these were incubated at 65 °C for 1 h to eliminate any thermal history. Finally, the tubes were placed immediately in a water bath at crystallisation temperature. The isothermal period commenced 2 min after transfer to the water bath, to make sure the sample reached the chosen crystallisation temperature (18, 20 and 22 °C) for each experiment. This time interval was determined in preliminary trials prior to the crystallisation kinetics experiments. The SFC was measured at appropriate time intervals.

2.4. Kinetic data analysis

The data of SFC *versus* isothermal time obtained by p-NMR from SHSs, Ivory Coast cocoa butter and fat blends were fitted to a double sigmoid equation used to describe the two-step isothermal crystallisation (two-step Gompertz model).

$$F_c(t) = a_1\left\{1-\exp\left(\frac{2\mu_1 t}{a_1}\right)\right\} + a_2\left\{\exp\left(-\exp\left[\frac{\mu_2 e}{a_2}(\lambda_2 - t)+1\right]\right)\right\} \quad (1)$$

For the first step, a_1 is the maximum value for the fraction of crystals formed as SFC (%) measured by p-NMR and μ_1 corresponds to the maximum slope of this step (growth rate in %SFC·min^{-1}). For the second step, a_2 is the additional amount of crystals formed in the second stage (%), μ_2 corresponds to the maximum growth rate of this step (%SFC·min^{-1}) and λ_2 is the induction time (min).This equation is a combination of an exponential function and the reparameterised Gompertz equation as deduced by Zwietering, Jongenburger, Rombouts, and Van't Riet (1990), and Kloek (1998). This two-step model has also been used to describe isothermal crystallisation of milk fat (Foubert, Vanhoutte, & Dewettinck, 2004). Estimation of the parameters was performed by non-linear regression of the crystallisation model using OriginPro 8.0 software (OriginLab Corp., Northampton, MA).

2.5. Stop-and-return DSC method

Isothermal crystallisation and melting profiles of crystallised fats were obtained with a Q2000 V23.5 differential scanning calorimeter (DSC) (TA Instruments, New Castle, DE) with a refrigerated cooling system. The results were processed using the TA analysis software provided by the manufacturer. The instrument was calibrated prior to use with indium, azobenzene, and undecane purchased from Sigma–Aldrich (Madrid, Spain). Nitrogen was used to purge the system. About 6–8 mg of the melted fats were weighed using a Sartorius M2P electronic microbalance (Sartorius