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In situ synchrotron radiation X-ray scattering study on the effect of a stearic sucrose ester on polymorphic behavior of a new sunflower oil variety

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ABSTRACT

The effect of the stearic sucrose ester (SE) S-170 on crystallization behavior and polymorphism of two stearins obtained from a new variety of high stearic high oleic sunflower oil was studied by pulsed nuclear magnetic resonance (p-NMR), small (SAXS) and wide (WAXS) angle X-ray scattering using synchrotron light and differential scanning calorimetry (DSC). p-NMR studies showed that there is always a crystallization temperature below which SE S-170 accelerated crystallization and above which SE S-170 delayed nucleation and growth. The effect of SE S-170 strongly depended on supercooling. It was efficient as a seed for high supercooling (low crystallization temperatures) but this efficiency diminished at low supercooling (temperatures close to the melting point) when few crystals were formed. SAXS and WAXS results demonstrated that depending on crystallization temperature SE S-170 promoted crystallization of α and β forms with more polymorphic similarity and inhibited occurrence of β' forms especially the β'_2 polymorph. However, in some conditions SE S-170 favored crystallization of β'_1 polymorph. DSC experiments showed that SE S-170 significantly diminished total melting enthalpies when the effect was a delay in crystallization. For other conditions no significant differences were found in melting temperatures or total melting enthalpies. When stearins were stored at 25 °C, crystallization in the β_2 form was promoted. Depending on crystallization temperature, polymorphic forms β'_1 and β_2 may be obtained as the main polymorphic forms. This is very relevant from the technological point of view. Depending on the application, SE S-170 may help obtain the required polymorphic form: β'_1 form for spreads and β_2 polymorph for chocolate production.

1. Introduction

Composition, tempering regime, the presence of other lipids or additives, and mechanical treatment (e.g., shear, agitation) influence how a lipid solidifies from the melt. In the food industry, these parameters are all used to direct polymorphic behavior and morphological development in fats. Polymorphism of fats is a fundamental property that determines food products appearance. For example, in margarine production, maintaining β'-crystallinity is imperative to preserve smooth texture and acceptable spreadability. In chocolate manufacturing, careful tempering is used to promote the crystallization of the metastable β-V form of cocoa butter, responsible for much of chocolate's organoleptic and shelf life properties (Braipson-Danthine & Deroanne, 2004; Loisel, Lecq, Keller, & Ollivon, 1998; Narine & Marangoni, 1999). Small angle X-ray scattering (SAXS) is a powerful tool to study polymorphism. A synchrotron source allows in situ characterization of phase formation in a sample holder and the competition between the different polymorphic species to be followed quantitatively (Loisel, Keller, Lecq, Bourgaux, & Ollivon, 1998; Lopez, Lavigne, Lesieur, Bourgaux, & Ollivon, 2001; Lopez, Lesieur, Bourgaux, Keller, & Ollivon, 2001; Lopez, Lesieur, Bourgaux, & Ollivon, 2005; Lopez et al., 2002; Mazzanti, Guthrie, Sirota, Marangoni, & Idziak, 2003; Peschar et al., 2004). In addition, as a pattern is taken in 10 s, the structural dynamics of sunflower stearins in the early stage of crystallization can be described. This early stage of crystallization is very important since it determines the later evolution of the system (Cisneros, Mazzanti, Campos, & Marangoni, 2006).

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FDA rule about reporting *trans* fats in food labels that was effective on January 1st, 2006 and *trans* fat rules issued in many other countries encouraged food manufacturers to reformulate their products. The modification of fatty acid composition through plant breeding was one of the strategies developed to replace *trans* fats (Kodali, 2005). A new high stearic high oleic (HSHO) sunflower oil variety was developed recently and although it does not contain enough solids at ambient temperature it may be fractionated resulting in hard fractions called stearins. HSHO sunflower oil-stearins' polymorphic behavior during isothermal crystallization was recently described (Rincón-Cardona, Martini, Candal, & Herrera, 2013). Five different polymorphic forms were characterized and the polymorphic transformations that occurred at different temperatures were quantified using small angle X-ray scattering with synchrotron radiation (Rincón-Cardona et al., 2013).

The growing interest on sugar ester surfactants is due to their enhanced performance and environmental compatibility in comparison with petrochemically derived products. Sugar ester surfactants may be obtained from renewable raw materials such as fatty acids and sucrose; they are readily biodegraded in an aqueous environment, and have the potential to be non-toxic and non-allergenic. Hence, they are used in the fields of cosmetics and food additives for a variety of functions, including emulsifying and foaming, in various products such as bread, ice cream, margarine, and fat substitutes (Garti, Aserin, & Fanum, 2000). The effect of some food emulsifiers on the crystal structure of fats crystallized from the melt has been known for many years. Several authors have used in situ X-ray techniques to follow the effects of sucrose esters (SE) and other emulsifiers on fats crystallization in bulk and in emulsion systems (Arima, Ueji, Ueno, Ogawa, & Sato, 2007; Arima, Ueno, Ogawa, & Sato, 2009; Awad & Sato, 2002; Huck-Iriart, Candal, & Herrera, 2009; Kalnin, Schafer, Amenitsch, & Ollivon, 2004; Sakamoto et al., 2004; Sonoda, Takata, Ueno, & Sato, 2006), to name a few. A detailed review of the submicron effects that these minor components have on nucleation, crystal growth, morphology, heat capacity and polymorphic stability have been reported by Smith, Bhaggan, Talbot, and van Malssen (2011). According to these authors, the majority of research on those effects is of an empirical and descriptive nature. In a limited number of studies, underlying mechanisms are proposed, but they are not always properly supported by the experimental results. The aim of the present work is to describe the effect of a stearic sucrose ester, S-170, on polymorphic and crystallization behaviors of HSHO sunflower oil stearins. Isothermal crystallization behavior changes were followed in real time by using SAXS and wide angle X-ray scattering (WAXS), employing a synchrotron source. Nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) were also used to document S-170 effects on crystallization.

2. Materials and methods

2.1. Starting materials

Two commercial HSHO sunflower oil stearins from Mar del Plata, Buenos Aires, Argentina were used in this study. Stearins were obtained as previously described (Rincón-Cardona et al., 2013). Briefly, a soft stearin (SS) was obtained through dry fractionation of the sunflower oil while a hard stearin (HS) was obtained using a solvent fractionation of the SS. The fatty acid and triacylglycerol compositions of both stearins were previously reported (Rincón-Cardona et al., 2013). The melting point of SS and HS were determined using AOCS Method Cc 1-25 (1993). SS and HS samples had melting points of 30.6 ± 0.1 and 35.7 ± 0.1 °C, respectively. Stearic sucrose ester, SE S-170, with HLB of 1 was a commercial blend of esters supplied by Mitsubishi-Kasei Food Corporation (Tokyo, Japan). It had a MDP of 59.5 °C. The monoester content of S-170 was 1 wt.%, with di-, tri-, and polyesters constituting 99 wt.%. S-170 was added at a concentration of 1 wt.%. The selected concentration was within the range commonly used in foods.

2.2. Crystallization procedure

Samples were melted at 60 °C in an oven and kept at this temperature for at least 30 min. Then, they were transferred to appropriate sample holders (NMR tubes for solid fat content [SFC] determination). For DSC, SAXS and WAXS studies, samples were melted at 60 °C in the sample holder and kept at that temperature for 2 min and then cooled to crystallization temperature (T_c) at 10 °C/min. Both stearins were crystallized isothermally at T_c. For HS selected temperatures were 10, 21, 22, 23, 24, and 25 °C. SAXS patterns were recorded as a function of time for 50, 70, 70, 80, 80 and 100 min, respectively. SS was crystallized to 5, 15, 16, 17, 18.5, and 19 °C for 50, 40, 40, 70, 120, and 115 min, respectively. Polymorphic transitions and solid fat content (SFC) of the samples were measured as a function of crystallization time, where zero time corresponds to the moment when the samples reached the crystallization temperature. By using this procedure it can be assumed that crystallization occurred mostly isothermally, since for samples without emulsifier (control samples) no signal indicating the presence of solid material appeared in the first X-ray pattern ($t = 0$) in all cases. Selection of temperatures was based on the melting points reported for the crystalline phases of pure TAG present in these samples. In all cases, X-ray analyses were performed long enough to crystallize at least 70% of the equilibrium solid fat material (SFC) at a defined temperature as measured by nuclear magnetic resonance (NMR). It was evident from patterns that intensities did not change significantly at those times. For NMR analyses crystallization was followed for 120 min. HS and SS were also stored for 48 h at T_c. The polymorphism of stearins was analyzed at this time.

2.3. SFC by NMR

The actual SFC of SS and HS was measured by using a Bruker mq20 minispec analyzer (Bruker, Rheinstetten, Germany) equipped with a cell with temperature control. SFC with time was determined at the same temperatures used for X-ray studies. Duplicate runs were performed on consecutive days for each set of samples and three tubes were measured in each run. SFC values were expressed as an average of six data and standard deviations were reported as well.

2.4. SAXS and WAXS studies

The synchrotron X-ray scattering measurements (small and wide angle, SAXS and WAXS, respectively) were made at the SAXS1 beamline of the Synchrotron National Laboratory (LNLS, Campinas, Brazil) with a 1.55 Å wavelength. The scattering intensity distributions as a function of scattering angle (2θ) were obtained in the 2θ range between 0.88° and 27.68°. One pattern per min was acquired in all experiments. One-dimensional curves were obtained by integration of the 2D data using the program FIT-2D. For SAXS experiments, 15 mg of fat samples was placed in a hermetical aluminum DSC pan with a transparent circle of 4 mm of diameter, in both base and lid. Then, the pan was placed in a DCS cell and the sample was crystallized as indicated in Section 2.2. Sample to detector distance was 235.28 mm. Assignment of the subcell packing (α, β′, or β polymorphs) was done on the basis of information from the literature (Cisneros et al., 2006; Lopez, Lavigne, et al., 2001; Lopez, Lesieur, et al., 2001; Mazzanti et al., 2003; Rincón-Cardona et al., 2013). In addition to short spacing signals, each polymorphic form showed characteristic long spacing signals. The area under the SAXS peak (usually called normalized integrated intensity) was integrated using commercial software (OriginPro 8 SR0 v 8.0724, Origin Lab Corporation, Northampton, USA). The diffraction profiles were fitted to a Gaussian equation and the normalized integrated intensity was plotted as a function of time. Induction times for crystallization were also measured from SAXS and WAXS patterns as the interval between the moment crystallization temperature (T_c) was reached and