Food Chemistry 214 (2017) 497–506

Contents lists available at ScienceDirect

Food Chemistry

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

Crystallization kinetics of cocoa butter in the presence of sorbitan esters

Sopark Sonwai [a], Pawitchaya Podchong [a], Dérick Rousseau [b,*]

[a] Department of Food Technology, Faculty of Engineering and Industrial Technology, Silpakorn University, Thailand
[b] Department of Chemistry and Biology, Ryerson University, Toronto, Canada

ARTICLE INFO

Article history:
Received 10 March 2016
Received in revised form 3 June 2016
Accepted 12 July 2016
Available online 13 July 2016

Keywords:
Cocoa butter
Crystallization
Sorbitan esters
Microstructure
Polymorphism

ABSTRACT

Cocoa butter crystallization in the presence of sorbitan mono- and triesters or canola oil was investigated. Solid-state surfactant esters accelerated early-stage cocoa butter solidification while suppressing later growth. Sorbitan tristearate showed the strongest effect, followed by sorbitan monostearate and sorbitan monopalmitate. Liquid-state surfactants suppressed cocoa butter crystallization at all time points, with sorbitan trioleate showing a stronger effect than sorbitan monooleate, which behaved in a similar fashion to canola oil. Via DSC, the palmitic and stearic-based surfactants only associated with cocoa butter's high-melting fraction, with the oleic acid-based surfactants and canola oil showing little influence. All sorbitan esters had little effect on polymorphism, whereas canola oil accelerated the form II-to-III-to-IV transition. The palmitic and stearic-based surfactants greatly reduced cocoa butter crystal size whereas the oleic acid-based surfactants and canola showed no notable effect. Overall, sorbitan esters impacted cocoa butter crystallization kinetics, though this depended on surfactant structure and concentration.

1. Introduction

Most research efforts on cocoa butter (CB) crystallization have focused on optimizing the structure and presence of the form V polymorph, given its importance in ensuring desirable chocolate characteristics such as gloss, snap and bloom resistance. Comparatively little research has been performed on early-stage CB solidification (*i.e.*, the first 1–3 h), and even less in the presence of commonly-used surfactants. Yet, many crystallization phenomena (*e.g.*, seeding effects, promotion/suppression of polymorphic transitions, *etc.*) often dictate the long-term stability, quality and texture of chocolate.

Over 80% of CB triacylglycerols (TAGs) consist of 1,3-dipalmitoyl-2-oleoyl-glycerol (POP), 1,3-distearoyl-2-oleoyl-glycerol (StOSt) and *rac*-palmitoyl-stearoyl-2-oleoyl-glycerol (POSt) (Dimick, 1991; Mudge & Mazzanti, 2009). Fundamentally, solid-state TAGs exist in one of three key polymorphs, largely defined by the lateral packing of their fatty acid chains [the hexagonal (H) (α-form), orthorhombic (O⊥) (β′-form) and triclinic (T//) (β-form) sub-cells], with at least six forms and sub-forms (I through VI) identified in CB (Chapman, Akehurst, & Wright, 1971; Schlichter Aronhime, Sarig, & Garti, 1988; Schlichter, Sarig, & Garti, 1985; Wille & Lutton, 1966).

CB isothermal melt crystallization is a two-stage process, typically starting with the nucleation and growth of higher-melting TAGs that then act as a template to promote the crystallization of the dominant CB TAGs (Davis & Dimick, 1989a; Loisel, Lecq, Keller, & Ollivon, 1998). In this regard, surfactants may significantly impact CB nucleation, crystal growth, or both, depending on their composition, added amount and mechanism of action (Smith, Bhaggan, Talbot, & van Malssen, 2011).

Sorbitan esters (SEs) are lipophilic, non-ionic surfactants produced by the esterification of sorbitol and a fatty acid, usually stearic, oleic, palmitic or lauric acid. Given this variety, when combined with various degrees of esterification, SEs with significantly different effects on TAG crystallization can be generated. Sorbitan tristearate may block the form V → VI transformation in CB (Garti, Schlichter, & Sarig, 2006), whereas sorbitan monostearate has been shown effective in retarding the β′ → β transition in margarines (Smith et al., 2011). Krog (1977) mentioned that sorbitan esters of stearic and palmitic acids stabilized the intermediate β′-form of fats, thus preventing formation of the β-form. Garbolino, Bartoccini, and Flöter (2005) showed that sorbitan fatty acid esters (mono laurate, monopalmitate, monostearate and tristearate) had an effect on the crystal morphology as well as the textural properties of a fat blend containing palm oil, palm kernel oil and sunflower oil. Cebula and Smith (1992) found that increasing the amount of native diacylglycerols in a CB equivalent increased its early-stage crystallization and nucleation temperature. Wahnelt, Meusel, and Tulsner (1991) found that adding

* Corresponding author at: Department of Chemistry and Biology, Ryerson University, 350 Victoria St, Toronto, Ontario, Canada.
E-mail addresses: ssonwai@gmail.com (S. Sonwai), p.podchong@gmail.com (P. Podchong), rousseau@ryerson.ca (D. Rousseau).

http://dx.doi.org/10.1016/j.foodchem.2016.07.092
0308-8146/

1,2-dipalmitoylglycerol, 1,3-dipalmitoylglycerol, 1,2-dioleoylglycerol or 1,3-dioleoylglycerol did not influence CB nucleation. Sorbitan mono- and tristearate have been found to retard the $\alpha \rightarrow \beta$ transformation in tristearin (Garti, Wellner, & Sarig, 1982) and palm oil (Kawamura, 1980). More recently, Masuchi, Grimaldi, and Kieckbusch (2014) found that sorbitan monostearate and monooleate altered CB crystallization, with the latter showing a larger effect, notably a sharp increase in crystallization onset temperature. Finally, it has been shown to sorbitan monolaurate may delay crystallization onset and lower SFC of soy-based fats (Ming & Gonçalves, 2015).

Though surfactants are a mainstay of the fats and oil industry, there remains a dearth of information on their structure-function relationship and the mechanisms by which they influence TAG nucleation and growth. In this study, the crystallization kinetics, microstructure and polymorphism of CB in the presence of five sorbitan esters or canola oil were investigated, with a particular focus on the link between surfactant molecular structure and its effects on CB crystallization parameters, crystal morphology and polymorphic behaviour. The results from this study show that the solid-state surfactants accelerated early-stage CB solidification while suppressing later growth, whereas the liquid-state surfactants suppressed its crystallization at all time points. All surfactants had little effect on polymorphism.

2. Materials and methods

2.1. Materials

CB (acid value <1.5) was purchased from Sino-Pacific Trading (Thailand) Co., Ltd. Canola oil was purchased from a local supermarket in Toronto, ON, Canada (acid value <0.2) (AOCS, 1998a). The following SEs were obtained from Sigma-Aldrich (Oakville, ON, Canada) and used without further purification: sorbitan monopalmitate (SMP), sorbitan monostearate (SMS), sorbitan tristearate (STS), sorbitan monooleate (SMO) and sorbitan trioleate (STO). The former three were defined as solid-state surfactants given their solid appearance at room temperature, whereas the latter two were considered liquid-state surfactants given that they are liquid at room temperature. Blends were prepared by adding 0.1–5 wt% SE to CB after which the mixture was melted at 80 °C and thoroughly mixed to ensure homogeneous surfactant distribution throughout the fat.

2.2. Isothermal crystallization

The solid fat content (SFC) of the CB-SE blends vs. time during crystallization at 22.5 °C was determined using a pulsed nuclear magnetic resonance (p-NMR) spectrometer (Minispec-mq20, Bruker, Karlsruhe, Germany). Samples were pipetted into 10 mm O.D. p-NMR tubes to a height of ~4 cm, tempered at 80 °C for 10 min in a waterbath to remove crystal history and then transferred to a cooling bath set to 21 °C. Once the sample temperature reached 23 °C, the tube was removed from the cooling bath, wiped dry and rapidly put into the p-NMR sample port set at 22.5 °C. SFCs were then continuously recorded for 8 h. SFC data were fitted to the Avrami model as follows:

$$SFC_t = SFC_{eq}\left(1 - e^{-K(t-T_{lag})^n}\right) \quad (1)$$

where SFC_t and SFC_{eq} represent the SFC at time t and at equilibrium. T_{lag} corresponds to the induction time prior to crystallization onset. The value of n, the Avrami exponent, gives an indication of the dimensionality of crystal growth and is sensitive to the time dependence of nucleation. The parameter K, the Avrami constant, is an indicator of crystal growth and nucleation rate. A program was written in Microsoft Excel v.14 (Redmond, WA, USA) that allowed rapid determination of relevant parameters for stage 1 and 2 crystallization (n, SFC_{eq}, K and T_{lag}) of all samples.

2.3. Crystallization and melting profiles

The crystallization and melting profiles of the fat samples were determined with a Perkin-Elmer differential scanning calorimeter (DSC) (model DSC 8000, PerkinElmer Co., Norwalk, CT, USA) following AOCS method Cj 1–94 (AOCS, 1998b). The instrument was calibrated with indium (mp 156.6 °C) as a reference standard. A fat sample of 3–5 mg was placed in an aluminum pan (20 μL capacity) and hermetically sealed with a sample press. An empty pan served as reference and was used to obtain baseline settings. Samples were heated from room temperature to 80 °C and held for 10 min to ensure homogeneity and to remove any crystal memory. The sample was then cooled at 5 °C/min to −60 °C and held for 30 min followed by heating at 5 °C/min to 80 °C. The crystallization onset/peak temperatures and enthalpy were determined with the built-in DSC software. Multiple peak deconvolution of CB's DSC thermal profile was performed using Igor Pro v6.2.2 (Wavemetrics, Lake Oswego, Oregon, USA). Three peaks between 0 and 40 °C were fitted to a Gaussian distribution with a cubic background.

2.4. X-ray diffraction

Temperature/time-dependent small and wide-angle X-ray diffraction (SAXD and WAXD) of the CB and CB + SE samples was investigated using a Hecus S3-MICRO high flux system (Hecus, Graz, Austria). The unit uses a 50 W, high brilliance GeniX microfocus source and customized FOX-3D multi-layer point focusing optics (Xenocs SA, Grenoble, France), with a $100 \times 250\ \mu m^2$ FWHM (vertical × horizontal) at focus. The X-ray beam was generated by a 50 kV, 1 mA Cu K_α anode. The sample-detector distance was ~280 mm (SAXD) and ~300 mm (WAXD). Spectra were captured with dedicated Hecus 1-D position-sensitive detectors (model PSD-50 M). X-ray ranges were 2000 Å > d > 11 Å and 4.9 > d > 3.3 Å for the SAXD and WAXD regions. For sample preparation, ~20 μL of melted sample were placed in 1.5 mm O.D. quartz capillaries (Charles Supper Company, Inc., Natick, MA, USA), using a long needle and syringe. The sample was then transferred to the unit's sample port and kept at 80 °C for 10 min (to erase any memory) and then cooled from 80 to 50 °C at 5 °C/min, followed by cooling from 50 to 10 °C at 1 °C/min. The sample was held at 10 °C for 3 h. Calibration was performed using silver behenate for the SAXD region with bromobenzoic acid and β-tripalmitin used for the WAXD region. Based on the spectra obtained, characteristic polymorphic forms and lamellar arrangements were assigned to all CB and CB + SE mixed samples.

2.5. Crystal morphology

The crystal morphology of CB and CB + SE samples crystallized under static conditions at 22.5 °C was observed by polarized light microscopy (PLM) (Olympus BX51, Olympus Optical Co., Ltd., Tokyo, Japan), with images captured with a digital camera (Olympus C-7070, Olympus Optical Co., Ltd., Tokyo, Japan). Each 20 μl sample was melted at 80 °C for 10 min then placed on a glass slide pre-heated to 80 °C and covered with a pre-heated glass cover slip. Crystal growth was evaluated at set times (0.5, 1, 3 and 48 h) at 22.5 °C. Samples were observed under polarized light at magnifications of 100× and 400×. Four slides per sample were examined and at least three images per slide were captured.