Food Research International 106 (2018) 213–224

Contents lists available at ScienceDirect

Food Research International

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

Effects of cocoa butter triacylglycerides and minor compounds on oil migration

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ARTICLE INFO

Keywords:
Oil migration
Chemical composition
Cocoa butter
Diffusivity
Magnetic Resonance Imaging

ABSTRACT

In a multi-component chocolate product, oil migration, from high oil content filling into chocolate, is one of the major contributors to the product quality loss. Among various parameters influencing oil diffusivity, cocoa butter is studied intensively. Studies have shown that the rate of oil transportion in cocoa butter is affected by its composition, the way that it is crystallized, and also the storage conditions. To model and study effects of cocoa butter type and processing conditions on oil migration, five different cocoa butter samples were studied in this work. Samples' chemical compositions in addition to their structural properties were analyzed to understand and compare oil migrations in the networks. Crystallized cocoa butter samples were placed in contact with a cream as a source of liquid oil. Using Magnetic Resonance Imaging, the movement of liquid oil into samples was investigated. The effects of minor differences in the cocoa butter chemical compositions on oil migrations rate are shown clearly. The highest effective diffusion coefficient was observed in the sample with the higher unsaturated fatty acids and phospholipids content. Although shearing at 250 s^{-1} delayed oil migration in all the samples and a significantly lower diffusion coefficient was observed in the dynamic samples, the effects of chemical composition were still dominant. This study successfully highlighted that even minor differences in cocoa butter composition affect the network mass transfer phenomenon dramatically and that it is not easy to diminish these possessions by just crystallization processes.

1. Introduction

Oil migration is a major issue in confectionery products, which is often associated with degradation of food quality. For example, fat bloom, as a result of oil migration, leads to quality reduction and has negative impacts on sensory properties of the chocolate products. In order to study this phenomenon studies have investigated the effects of the various parameters on oil diffusivity. Among these factors, cocoa butter, as an important ingredient, was studied extensively. Cocoa butter is the continuous fat phase that provides texture and structure for chocolate products. Studies have shown that the rate of oil transportion in cocoa butter is affected by its composition, the way that it is crystallized and also the storage conditions (Maleky, Acevedo, & Marangoni, 2012; De Clercq, Depypere, Delbaere, et al., 2014). For example, processing conditions can influence oil diffusivity by varying the solid fat content and by causing structural alterations in that fat crystal network (Maleky, Acevedo, & Marangoni, 2012; Svanberg, Ahrné, Lorén, & Windhab, 2013). It is also shown that shearing associated with the formation of small and homogeneous particles can result in a lower oil migration rate in crystallized lipids (Maleky & Marangoni, 2011; Marty & Marangoni, 2009). Additionally, storage temperature now is thought to be an altering factor for oil migration rate in cocoa butter. The effects of temperature on both structural properties and fat bloom are documented in a number of publication (Depypere, De Clercq, Segers, et al., 2009; McCarthy & McCarthy, 2008). In these studies, oil migration is considered as a diffusive process; the movement of the oil molecules from a region of high chemical potential (high concentration) to that of low chemical potential (low concentration). This diffusive process can be described by Fick's second law. Many of these studies considered the triacylglycerols (TAGs) concentration gradient between different phases as the main reason of migration in fats and confections (Lee, McCarthy, & McCarthy, 2010; Rumsey & McCarthy, 2012). Although these considerations may provide important information for oil migration, a better understanding of the phenomenon would be provided if the effect of lipids TAGs and fatty acids concentration are also taken in to account. Hence, in this study, the effects of minor differences in cocoa butter's chemical composition and crystallization process on the kinetics of oil diffusivity in the crystallized cocoa butter samples are investigated. Considering the importance of the applied measurement techniques and the analysis on

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https://doi.org/10.1016/j.foodres.2017.12.057
Received 23 August 2017; Received in revised form 18 December 2017; Accepted 19 December 2017
Available online 27 December 2017
0963-9969/

oil migration quantification, Magnetic Resonance Imaging (MRI) was used. As a non-destructive technique, MRI provides us with an opportunity to accurately monitor the diffusing oil and its movement through the network in real time.

2. Materials

Five different cocoa butter samples (named as CB1–CB5) donated by ADM Cocoa (Milwaukee, WI, USA) and Mars Chocolate (Hackettstown, New Jersey, USA) were analyzed and used in this study. Interesterified hydrogenated palm oil (IHPO) was provided by Bunge Canada (Toronto, Canada). Peanut oil was purchased from a local retailer. A soft fat layer, as the source of liquid oil for oil migration experiment, was prepared by blending peanut oil and IHPO at the ratio of 60:40 w/w (Maleky, Mccarthy, et al., 2012).

2.1. Methods and results

2.1.1. Chemical composition analysis

Chemical compositions of the cocoa butter samples and the cream were analyzed using gas chromatograph (GC) and high-performance liquid chromatography (HPLC) techniques.

Using Agilent 6890-series Gas Chromatograph (Agilent Technologies, Inc., Wilmington, DE, USA) with 7683-series auto-sampler, samples' fatty acid methyl esters (FAME) were obtained according to a method described by Christie (1982). An amount of 20 mg of the fat (cocoa butter) was weighed, transferred into vials, and mixed with sodium-dried diethyl ether and methyl acetate until it was completely dissolved. After adding 1 M sodium methoxide in methanol, a saturated solution of oxalic acid in diethyl ether was added to the samples. Samples were centrifuged at about 1500 × *g* for 2 min and transferred to a 1.5 ml Agilent vial. Samples' FAME were analyzed using an Agilent 6890 GC (Agilent Technologies Inc., Santa Clara, CA) equipped with a split injection, a flame ionization detector (FID), an auto sampler (Agilent, model 7683), and a BPX70 column (60 m × 0.22 mm internal diameter with 0.25 μm film thickness (SGE Inc., Austin, TX, USA)). The oven temperature was programmed to increase from 110 to 230 °C at a rate of 4 °C/min and maintained at 230 °C for 18 min. The injector was operated at 20.2 psi flow of 17.7 ml/min at 250 °C. Helium was used as a carrier gas at an average velocity of 25 cm/s. The FAMEs were identified based on their retention times in comparison with fatty acid methyl ester standards purchased from Sigma-Aldrich, St. Louis, MO, USA.

The triacylglyceride composition of the cocoa butter samples was determined using a Waters Alliance model 2690 HPLC (Waters Millipore Co., Milford, MA) with a refractive index detector (Waters model 2410) and two Waters xbridge C18 columns (5 μm, 4.6 × 250 mm). 30 mg fat was first dissolved in 600 μl of chloroform, followed by 1.5 ml of 60/40 acetone/acetonitrile v/v. 10 μl of the sample was injected at once. The temperature for the sample chamber, column, and detector was set at 40 °C. Measurement was taken under isocratic flow rate at 1 ml/min with the mobile phase of acetone/acetonitrile (60/40 v/v). The assignment of TAG peaks and their concentrations in cocoa butter was determined by the retention time of TAG standards from Sigma (Sigma Chemical Co., St. Louis, MO). Both data collection and peak integration were performed with the Millennium software (Waters Corporation, Milford MA). Cocoa butter phosphorus content was determined by atomic absorption after wet digestion in sulfuric acid (McGauley & Marangoni, 2001). All the samples chemical compositions were reported in Table 1. Cocoa butter samples were named as CB1–CB5 in descending order of their saturated fat content. As reported in Table 1, CB5 sample has the lowest saturated fat content and the highest unsaturated fat content compared to the other samples. Moreover, the saturated fat content of the CB4 and the CB5 samples are significantly lower ($p < 0.05$) compared to that of CB1, CB2 and CB3. On further examination of the fatty acid profiles, CB2 samples are the highest in palmitic acid content and the lowest in stearic acid content compared to other samples. CB1 sample with a low content of palmitic acid contains the highest amount of stearic acid.

Due to the major effects of TAGs contents on cocoa butter structure properties and oil migration rate (OMR), the TAG content of the samples is reported in Table 1. The main TAGs groups in the samples, including tri-saturated SSS, symmetric di-saturated-mono-unsaturated SUS, mono-saturated-di-unsaturated UUS, and tri-unsaturated UUU are summarized in Table 2. As shown in Table 2, cocoa butter samples are mainly composed of symmetrical TAGs with oleic acid in the sn-2 position and the samples contain only a small amount of the unsymmetrical triglycerides (PPO, PStO, and StStO). However, the symmetrical TAGs compositions vary significantly among the samples. For example, while CB3 has the highest SSS and the lowest UUU content, the highest total tri-unsaturated UUU content is seen from CB5.

Moreover, the fatty acid and the TAG content of the cocoa butter samples, the effects on oil migration from phosphorus content of the samples is also considered. Studies have reported phospholipids as important minor components in cocoa butter that influence cocoa butter's crystalline network (Foubert, Vanrolleghem, Thas, & Dewettinck, 2004). Among the samples studied here, CB5 has significantly higher amount of phosphorus (75 ppm) compared to the other samples.

2.2. Crystallization process of the cocoa butter samples

All the cocoa butter samples were crystallized through two processing conditions named as static (ST) and dynamic (DY) crystallization. Irrespective of the processing, all samples (CB1–5) were heated to 65 °C and held at this temperature for 15 min to eliminate any crystal memory. For the static samples, the molten cocoa butter was transferred to a plastic mold with a dimension of 30 mm × 30 mm × 30 mm. Samples were cooled to 23 °C at 0.5 °C/min and stored at 23 °C for 24 h to complete the crystallization process. For the dynamic samples, the molten cocoa butter was sheared with a 3-bladed propeller (with a radius of 39 mm) at a shear rate of 250 s^{-1}. While shearing, an iso-temperature water bath was used to control the sample temperature. After 10 min of shearing with a 4.5 °C/min cooling rate, the samples were transferred to the plastic molds and stored at 23 °C for 24 h.

2.3. Structural properties analysis

2.3.1. Solid fat content

All the samples' solid fat contents (SFCs) were measured after 24 h of storage at 23 °C. Approximately 3 g of crystallized cocoa butter was cut into small pieces and placed into NMR glass tubes (10 mm diameter, 1 mm thickness, and 180 mm height). The solid fat content was measured by pulse nuclear magnetic resonance (p-NMR) using a Bruker Minispec spectrometer (Bruker Optics Ltd., ON, Canada) reported in Table 2. As shown in Table 2 this table, samples SFCs are in the range of 60%–78%. With no influence of processing conditions on the samples' solid fat content, the SFC values varied due to the samples composition. It has been observed that the CB1, CB2, and CB3 samples show significantly higher SFCs compared to the CB4 and CB5 samples. Both static CB5 and dynamic CB5 samples have the lowest SFC (60–61%) while the static CB3 sample has the highest SFC value among all the samples (78.82%). The higher content of tri-unsaturated TAGs (UUU) in the CB5 samples (5.10%) compared to others in the range of 0.50% (for CB3) to 1.90% (for CB2) could potentially explain the lower SFC of this sample (Table 2). Lipp and Anklam (1998) reported that a higher percentage of StOO softens the cocoa butter, which leads to an unfavorable crystallization characteristics. The CB5 sample has enormously high StOO (7%) compared to others which ranged from 1.8% (CB4) to 3.7% (CB3). The high content of these mono-saturated TAGs can interrupt the molecular packing of the symmetrical TAGs to influence cocoa butter