

Effect of cocoa butter equivalent on cocoa butter crystallization behavior and on dark chocolate

ABSTRACT

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The aim of this work was to evaluate the crystallization behavior of commercial cocoa butter (CB) and cocoa butter equivalents (CBE) and their mixtures to assess the best proportions that do not compromise the crystallization process in chocolates. Blends were prepared using CBE concentrations of 5%, 10%, 15%, 20% and 37.5% and were evaluated by: fatty acids composition, triacylglycerols (TAG) composition, solid fat content, isothermal analysis, polarized light microscopy, thermal behavior, X-ray diffraction and consistency. The higher amount of CBE in a blend without compromising the CB crystallization were further applied in a dark chocolate. CBE presented a similar fatty acids composition as CB in the same proportions, but the TAGs of the CBE presented more TAG StOst, imparting fast crystallization, a higher SFC content and a higher hardness. Even with full compatibility between CB and CBE, the CBE proportion in ratios of CB/CBE must be restricted because higher concentrations of this fat are not allowed by the regulations of many countries and can lead to a final product with a waxy feel due to the higher melting point of CBE TAGs. The dark chocolate with CBE/CB (20/80) did not present any physical (snap, microstructure and polymorphism) difference from the regular chocolate pure in CB.

KEYWORDS: chocolate; cocoa butter; cocoa butter equivalent; crystallization.

INTRODUCTION

Cocoa butter is solid at room temperature (25 °C) and melts at body temperature (37 °C), with a melting range between 27 and 35 °C. The major fatty acids are palmitic (P), stearic (St), and oleic (O) acid, The physical and chemical properties of cocoa butter are dictated by triacylglycerols (TAG) composition, and the main TAGs are POP, POST and StOSt (SCHENK; PESCHAR, 2004; JAHURUL *et al.*, 2013). Monounsaturated TAG, with unsaturation at the sn-2 position, contributes to special characteristics, such as polymorphism, consistency and others sensorial attributes in chocolates (WANG *et al.*, 2006).

Chocolate produced exclusively by cocoa butter is a high value product, since the high cost of cocoa butter, and their limited production. The melting properties of this pure cocoa butter chocolates might be inadequate for some purposes and some climate conditions, as the found in tropical countries. For that reason the analogous to cocoa butter are also used in the production of chocolate, chocolate-like products, and cream products (SHUKLA, 2006; TORBICA; JOVANOVIC; PAJIN, 2006).

Some countries allow the use of vegetable fats compatible with cocoa butter in small amounts in chocolate products since these fats show a similar crystallization and sensorial profile. In 2000, the European Union announced EU Directive 2000/36/EC relating to cocoa and chocolate products intended for human consumption. This directive allowed vegetable fats for use in chocolate non-lauric products rich in symmetrical monounsaturated TAGs. These allowed fats must be miscible in any proportion with CB and compatible with its physical properties. The addition of these fats should not exceed 5% of the finished product (UNION, 2000). Most countries permit higher levels of CBEs in chocolate, but these products cannot be labeled "chocolate," and must be labeled "compound." (LONCHAMPT; HARTEL, 2004; DE CLERCQ *et al.*, 2017). In Brazil, there is no limit as long as the final chocolate contains at least 25% of cocoa solids (BRAZIL, 2005).

Cocoa Butter Equivalent (CBE) is a vegetable fat similar in composition and physical properties to cocoa butter. It can be used for technological or economic reasons (WANG *et al.*, 2006; MING, 2008), and it is usually produced by modifications and mixtures of others oils and fats such as palm oil and shea and Illipe butters (LONCHAMPT; HARTEL, 2004). The CBE fatty acid composition is very similar to CB; the main fatty acids are P, St and O, and they appear in very similar amounts. TAGs may vary, but the major fats are POP, POST and StOSt, and CBE present different amounts of each, depending on the raw material used (DE CLERCQ *et al.*, 2017).

From a functional standpoint, the replacement of cocoa butter with CBE requires the following characteristics: same melting range, similar fatty acids and TAG composition, same polymorphic form (β V), good flavor and good stability with no change in the processing line and shelf life of the product (TALBOT, 2011).

The use of alternative fats is increasing to meet the demand for chocolate and chocolate products in the market. Thus, the aim of this study was to evaluate the crystallization behavior of commercial CB, CBE and blends by evaluating macroscopic (consistency, solid fat content and melting point) and microscopic (polarized light microscopy, isothermal crystallization, melting profile and polymorphic form) characteristics to assess the best proportions for application in dark chocolate.

MATERIALS AND METHODS

EXPERIMENTAL DESIGN

Cocoa butter (CB) were kindly donated by Cargil (Ilhéus, Bahia, Brazil) and the Cocoa butter Equivalente (CBE) was obtained from Loders Croklaan (Wormerveer, Netherlands). For sample preparation, first the CB and CBE were completely melted, weighed, and blended in a hot plate with stirring at 150 rpm to ensure complete miscibility and interaction between the two fats. The blends concentrations were selected based on the fat content of a 50% dark chocolate (~32%). Usually, the chocolate are composed by 12% of added CB and 20% of CB from the cocoa liquor. Samples A–E contained 5%, 10%, 15%, 20%, and 37.5% CBE. The initial concentration of CBE was set at 5% because this concentration is commonly used in various products, and allowed in many countries. A sample containing 37.5% CBE simulated the replacement of all added pure CB (12% of the chocolate).

CHOCOLATE PROCESSING

The CB:CBE best proportion 80:20, was choose for application in dark chocolate. Two formulations of dark chocolate was produced, the standard pure CB with 47.5% of sugar, 40% cocoa liquor, 12% CB, 0.3% lecithin and 0.2% PGPR. The replaced chocolate (CBE), has 6.4% of CBE and 5.6% of CB. Two kilograms of each formulation was prepared, they were processed at Chocolab Ital (Campinas, Brazil). The following steps for chocolate production were used: mixing, refining, couching, tempering, molding, and cooling. Tempering was performed by hand on a marble table. The temper index before molding varied between 4.5 and 5.5 for the different chocolates. The samples were subsequently stored at 20 °C for 48 h and analyzed.

FATTY ACID COMPOSITION

The fatty acid composition of CB and CBE was determined using Gas Chromatography (GC) system (Santa Clara, CA, USA) in an Agilent 6850 Series equipped with a capillary column 60-m DB-23 Agilent capillary column (Santa Clara, CA, USA) (50% cyanopropyl methylpolysiloxane) with an internal diameter of 0.25 mm coated with a 0.25 µm film for separation. The esterification was performed according to the method of Hartman; Lago (1973). The fatty acid methyl esters were separated as described by AOCS Method Ce 2-66 (AOCS, 2009). The chromatograph was operated under the following conditions: analysis at 110°C for 5 min in the oven temperature program, followed by heating from 110 °C to 215 °C at 5°C/min and held at 215°C for 24 min, detector temperature: 280 °C, injector temperature: 250 °C; helium used as the carrier gas; a split ratio of 1:50; and a 1.0-µL injection volume. The qualitative composition was determined by comparing peak retention times to the respective standards for fatty acids. The qualitative composition was determined by area normalization and expressed as a mass percentage. Samples were analyzed in triplicate and the values reported are the means of three injections.

TRIACYLGLYCEROL COMPOSITION (TAGs)

TAGs composition was also performed in triplicate using a capillary GC CGC Agilent 6850 Series GC System (Santa Clara, CA, USA), with a DB-17 HT Agilent

capillary column (Santa Clara, CA, USA) (50%-phenyl-methylpolysiloxane, 15 m long and 0.25 mm internal diameter coated with a 0.15- μ m film). The operating conditions were as follows: 1:100 split injection ratio; initial column temperature of 250 °C, heated until 350 °C at 5 °C/min; helium as stripping gas at 1.0 mL/min; injector temperature of 360 °C; detector temperature of 375 °C; 1.0 μ L injection volume and sample concentration of 10 mg/mL in tetrahydrofuran. TAG were identified by comparing retention times to standard samples and quantified using relative peak area (FILHO; MENDES; LANÇAS, 1995).

SOLID FAT CONTENT, COMPATIBILITY AND MELTING POINT

Solid fat content profiles for CB, CBE and their blends were determined using Nuclear Magnetic Resonance (NMR) spectrometry (Bruker pc120 Minispec, Silberstreifen, Rheinstetten, Germany) and TCON 2000 high-precision dry baths (0–70 °C) (Duratech, Carmel, USA). The samples were first tempered using the followed crystallization condition: 100 °C for 15 min for completely melted, 0 °C for 90 min, 26 °C for 40 h and at 0 °C for 90 min. The samples were held at each measuring temperature (10, 15, 20, 25, 30, 35 and 40 °C) for 60 min prior to SFC measurements according to AOCS Cd 16b-93 (AOCS, 2009). The experiments were made in triplicate, and the results are the means of three measurements. The compatibility diagram was plotted with SFC results *versus* the CBE concentration in the mixture at each temperature (QUAST *et al.*, 2013). The melting point range was obtained from the plotted SFC curve and determined as the temperature range corresponding to an SFC of approximately 4% (KARABULUT; TURAN; ERGIN, 2004).

CRYSTALLIZATION ISOTHERMAL

The fat samples were melted (70 °C for 15 min) and maintained at 50 °C for 1 h in a high-precision dry bath (TCON 2000, Duratech, Carmel, IN, USA) before measurements. The increase in solid fat content due to crystallization time was monitored every minute at 17.5 °C (MARANGONI; MCGAULEY, 2003) automatically using a Nuclear Magnetic Resonance spectrometer (Bruker pc120 Minispec, Silberstreifen, Rheinstetten, Germany) for 180 min. The crystallization kinetics were calculated using the induction period (t_{SFC}) – relative to the onset of crystal formation, maximum solid fat content (SFC_{max}) and relative time to obtain 50% of the maximum content of solids ($t_{1/2}$) (CAMPOS, 2005). The results are the mean of three measurements. The original Avrami equation was used to model the crystallization process (Equation 1).

$$SFC = SFC_{max} (1 - e^{-kt^n}) \quad \text{(Equation 1)}$$

Where SFC (t) is the solid fat content (%) as a function of time, SFC (∞) is the asymptotic value of the solid fat content, k is the Avrami constant (min^{-n}), which considers both the nucleation and rate of crystal growth, and n is the Avrami exponent, which indicates the mechanism of crystal growth (CAMPOS, 2005). The equation was linearized to determine k and n. The $t_{1/2}$ expresses the values in accordance with Equation 2.

$$t_{1/2} = (0.693/k)^{1/n} \quad (\text{Equation 2})$$

THERMAL BEHAVIOR

Thermal analysis of CB, CBE and their blends were performed using differential scanning calorimetry (DSC) (model Q2000, TA Instruments, New Castle, DE, USA) according to AOCS Method Cj 1-94 (AOCS, 2009), with an adapted rate 2 °C/min for better discrimination of the crystallization step. Approximately 10 mg of melted sample was weighed, and an empty sealed aluminum pan was used as a reference. The equipment was previously calibrated using indium. The operating conditions for crystallization were as follows: initial temperature of 80 °C for 5 min, cooling to a temperature of -40 °C at a rate of 2°C/min, and constant -40 °C for 5 min. The melting process before measurement was similar to the tempering process described for stabilizing confectionary fats, the Solid Fat Content analysis, according to AOCS Cd 16b-93 (AOCS, 2009), and the conditions for melting were as follows: 25 °C for 5 min, melting to 60 °C at 5 °C/min, and constant 60 °C for 5 min. The following data were calculated for the crystallization (c) and melting processes (m): onset temperature (T_{ons}), peak temperature (T_p), enthalpy (ΔH) and final temperature (T_f) (BILIADERIS, 1983).

POLARIZED LIGHT MICROSCOPY

Crystal morphology of the fats were evaluated using polarized light microscopy (Olympus, model BX 51, San Jose, USA) coupled to a digital video camera (Media Cybernetics, Bethesda, USA). Samples were melted at 100 °C. Approximately 1 drop of each sample was placed on a pre-heated glass slide at the same temperature using a capillary tube and covered with a coverslip. The samples were prepared and analyzed according to the tempering method for special fats from SFC in the AOCS method Cd 16b-93 (AOCS, 2009).

CONSISTENCY

Consistency of the fats was determined using a texture analyzer (TA-XT Plus, Stable Micro Systems, Surrey, UK). Initially, samples were heated to 70 °C for complete melting of the fat crystals and then subjected to the tempering already described according to AOCS Cd 16b-93 (AOCS, 2009) to completely stabilize the blends; the test was performed at 25 °C. The operating conditions were as follows: a Plexiglas® probe with a cone non-truncated tip angle of 45° was used with a penetration depth of 10 mm and a probe velocity of 2 mm/s, time 5 s. The compression force was obtained in kilogram force (kgF) (RODRIGUE; GIOELLI; ANTON, 2003). Following Haighton (HAIGHTON, 1959), the compression force was converted to the yield value (YV) with the following equation (Equation 3).

$$YV = K * W / p^{1.6} \quad (\text{Equation 3})$$

Where YV is the yield value, in kgF/cm²; and K is a constant dependent on the cone angle—for a cone with 45°, the value was 4700—W is compression force, in

kgF; and p is penetration depth in units of 0.1 mm. The samples were analyzed in quadruplicate, and the results were expressed as the means of the replicates.

X-RAY DIFFRACTION

X-ray diffraction analyses of the fats and chocolate were performed according to AOCS method Cj 2-95 (AOCS, 2009) using a Philips PW 1710 diffractometer (PANalytical, Almelo, the Netherlands) with Bragg-Brentano ($\theta:2\theta$) geometry and $\text{CuK}\alpha$ radiation ($\lambda = 1.51418 \text{ \AA}$; tension, 40 kV; and current, 30 mA). For chocolate samples a preview preparation in order to remove the sugar influence on the diffractograms was made adapted from CEBULA; ZIEGLER (1993). The geometry used caused the X-ray diffraction by the sample through a graphite monochromator crystal located just before the detector. All measurements were obtained with short spacing at steps of 0.03° in 2θ and an acquisition time of 2 s, with scans from 15° to 30° (YAP *et al.*, 1989; SCHENK; PESCHAR, 2004). Samples were prepared for analysis using the tempering process for fat stabilization according to the AOCS method Cd 16b-93 (AOCS, 2009).

SCANNING ELECTRON MICROSCOPY

The chocolates microscopy was evaluated using a scanning electron microscopy (SEM) using a TM-3000 table-top microscope (Hitachi High Technologies America, Inc., Japan). Samples were cut into 20 mm \times 20 mm sections. The crystal network was observed on the chocolate surface using the Analy mode with 1000 \times magnification.

SNAP TEST

The snap test was performed with a texturometer TA-XT Plus (Stable Micro Systems, UK), com o probe HDP/3PB – Three point bend rig. The test conditions were: pretest speed as 3.0 mm/s, test speed as 1.7 mm/s and post-test speed as 10 mm/s. Eight bars of each sample were used for this test and the results are expressed as breaking strength (g) (REZENDE *et al.*, 2015).

STATISTICAL ANALYSIS

Statistical analyses were based on analysis of variance (ANOVA) and Tukey's Test to determine the significant differences in the means at a probability level of 5% ($p < 0.05$) using Statistica 8.0 (Statsoft, USA).

RESULTS AND DISCUSSION

CRYSTALLIZATION STUDY OF CB:CBE BLENDS: CHEMICAL COMPOSITION

The fatty acid composition of CB consists mainly of P, St and O acids at respective concentrations of 25.67%, 33.92% and 34.96% (total 94.55%). CBE has the same main components as CB, but with some differences in concentration. CBE consists of 22.95% P, 38.71% St and 32.32% O (total 93.98%). These values are in agreement with others

found in the literature for CB (SABARIAH; ALI; CHONG, 1998; LIPP *et al.*, 2001; QUAIST *et al.*, 2013; MASUCHI; GRIMALDI; KIECKBUSCH, 2014) and CBE (LIPP *et al.*, 2001; TORBICA *et al.*, 2015; DE CLERCQ *et al.*, 2017). The smaller differences between CB and CBE resulted in smaller differences in fatty acid blends, and all values had intermediate P, St and O contents between CB and CBE (Table 1).

Table 1. Fatty acids (FA) and triacylglycerols (TAG) composition of cocoa butter (CB), cocoa butter equivalent (CBE) and the blends (A, B, C, D e E).

FA	Fatty acids composition (%)						
	CB	CBE	A	B	C	D	E
C16:0	25.67	22.95	25.53	25.40	25.26	25.13	24.65
C18:0	33.92	38.71	34.16	34.40	34.64	34.88	35.72
C18:1	34.96	32.32	34.82	34.69	34.56	34.43	33.97
C18:2	3.40	3.82	3.43	3.45	3.47	3.49	3.56
C20:0	1.13	1.30	1.14	1.15	1.16	1.17	1.20
TAG	Triacylglycerols composition (%)						
PPP	0.33	1.10	0.37	0.41	0.45	0.48	0.62
PPSt	0.39	0.40	0.39	0.39	0.39	0.39	0.39
POP	16.45	24.96	16.88	17.30	17.73	18.15	19.64
PLP	2.16	3.31	2.22	2.28	2.33	2.39	2.59
PStSt	1.53	0.35	1.47	1.41	1.35	1.29	1.09
POSt	40.30	9.28	38.75	37.20	35.64	34.09	28.67
POO	3.62	2.68	3.57	3.53	3.48	3.43	3.27
PLO	0.92	1.24	0.94	0.95	0.97	0.98	1.04
StStSt	0.33	0.49	0.34	0.35	0.36	0.37	0.39
StOSt	23.66	43.59	24.66	25.66	26.65	27.65	31.14
StOO	5.28	2.98	5.17	5.05	4.94	4.82	4.42
OOO+StLSt	2.54	4.69	2.65	2.76	2.86	2.97	3.35
StOA	1.26	2.35	1.31	1.37	1.42	1.48	1.67
Groups							
SSS	2.58	3.10	2.61	2.63	2.66	2.68	2.78
SUS	83.84	84.68	83.88	83.92	83.96	84.01	84.15
SUU	11.04	7.53	10.86	10.69	10.51	10.33	9.72
UUU	2.54	4.69	2.65	2.75	2.86	2.97	3.35

NOTE: ^aSamples A (5% of CBE), B (10% of CBE), C (15% of CBE), D (20% of CBE) and E (37.5% of CBE).

Despite the similarity in fatty acids composition, TAG composition was very different. According to GUNSTONE *et al.* (2005), small differences in fatty acid composition significantly affect TAG composition and consequently the melting profile and fat crystallization.

Both CB and CBE are composed primarily of POP, POSt and StOSt, with respective concentrations for CB of 16.45%, 40.30% and 23.66% (total 80.41%) and for CBE of 25.04%, 9.29% and 43.47% (total 77.8%), with total values lower than the range found in the literature for CBE (79.6 to 85.7%) (BOOTELLO *et al.*, 2012) and for CB (87.7 to 91.7%) (RIBEIRO *et al.*, 2012; BUSCATO; GRIMALDI; KIECKBUSCH, 2017). The important characteristic of this CBE is the high amount of StOSt compared to other CBE studied before (DE CLERCQ *et al.*, 2017). StOSt content gives an indication of heat resistance, and fats

enriched in this fraction act as cocoa butter improvers and decrease the tempering time of chocolate (LIPP *et al.*, 2001).

Due to the composition of raw materials, the fat mixtures studied also showed significant and proportional variation in three major TAG with CBE addition; the range for each TAG was 16.88% to 19.64% for POP, 38.75 to 28.67% for POST and 24.66 to 31.14% for StOSt (Table 1). The change in TAG components found in the blends might be due to the dilution and solubilization of the fat blended (JAHURUL *et al.*, 2014). BIGALLI (1988) concluded that high-quality CBE contained a high proportion of StOSt and POST because CBEs rich in POP are excessively smooth and show eutectic effects at a minimal concentration in blends with CB. Analyzing the TAGs for all samples (CB, CBE and their blends) presented the TAG SUS as the majority, with approximately 84% of the total, followed by the TAG SUU at approximately 9%, and UUU and SSS, with 2.5% on average (Table 1).

CRYSTALLIZATION STUDY OF CB:CBE BLENDS: SOLID FAT CONTENT, COMPATIBILITY AND MELTING POINT

The equilibrium between solid and liquid masses in a fat on different temperatures are expressed by the solid fat content (SFC), this parameter affect the physical properties, consistency, as sensory properties of the fat and fat food products (QUAST *et al.*, 2013). CB and CBE have the similar SFC profiles, but CBE has higher SFC at all temperatures (Figure 1A). The SFC for CB and CBE was similar in the literature for Brazilian tempered CB (RIBEIRO *et al.*, 2012; MASUCHI; GRIMALDI; KIECKBUSCH, 2014) and tempered CBEs (DE CLERCQ *et al.*, 2017).

The mixtures showed small differences in SFC at different temperatures. Until 20% replacement, the SFC profile of the blends was similar, but at 37.5%, CBE showed a higher SFC between 30 and 35°C. The large similarity in these mixtures could be a result of the tempering process, which stabilized the polymorphism for all samples. In the literature, blends of CBE and CB between 5% and 30% of CBE showed no differences in SFC at any temperature (KANG *et al.*, 2013).

An important data point on the SFC curve for the CB industry is the SFC at 25 and 35 °C and the presence of more than 5% SFC at 35 °C; such an SFC concentration at 35 °C gives an undesirable waxy mouth feeling in confectionary products (TALBOT, 2011). All blends and the CB showed fast melting between 25-35 °C, with SFC below 5% at 35 °C, which are good characteristics for the confectionary industry, but these characteristics were not observed for pure CBE, which limits its use alone.

Figure 1B shows the compatibility between CB and CBE blends, and no incompatibility was observed for any proportion of CBE at any temperature. Previous studies showed fully compatibility between various CBEs and CB on different ratios (SHUKLA, 2006; SONWAI; KAPHUEAKNGAM; FLOOD, 2014), resulting on desirable physical properties as higher melting point and seeding. The eutectic behavior between these two fats was only observed when the CBE contains higher amounts of TAGs as PPP, PPO, POO, and POP (SHUKLA, 2006).

CRYSTALLIZATION STUDY OF CB:CBE BLENDS: ISOTHERMAL CRYSTALLIZATION

The isothermal crystallization of CB, CBE and their blends is presented in Figure 2. All samples are characterized by crystallization in two steps. In accordance with MARANGONI;

MCGAULEY (2003), the crystallization in two steps depends on the isothermal temperature and composition of each fat, and this crystallization is developed as follows: first, the total of solid fat rises without an considerable induction time, and the value remains more or less constant for a while. Finally, the amount of solid fat levels off to a second plateau. Plateau formation in an isothermal crystallization, results from a polymorphic transition in the sample from less stable to more stable polymorphs. Pure CBE achieves the second plateau faster than pure CB, which demonstrates the faster polymorphic transition to more stable polymorphs of CBE. This faster transition of CBE was a positive influence of the blends because as more CBE is added faster, the sample achieves the second plateau.

In Figure 2, the numerical data for the isothermal conditions are shown in Table 2. The first parameter was induction time (t_{sfc}), i.e., the necessary time to form stable nuclei. There is a significant difference between CB and CBE in t_{sfc} : CBE needs only 8 min to form the first nuclei while CB needs 16 min. In the blends, t_{sfc} decreases as the proportion of CBE in the blends increases. The maximum Solid Fat Content (SFC_{max}) is very similar between the two fats and their blends.

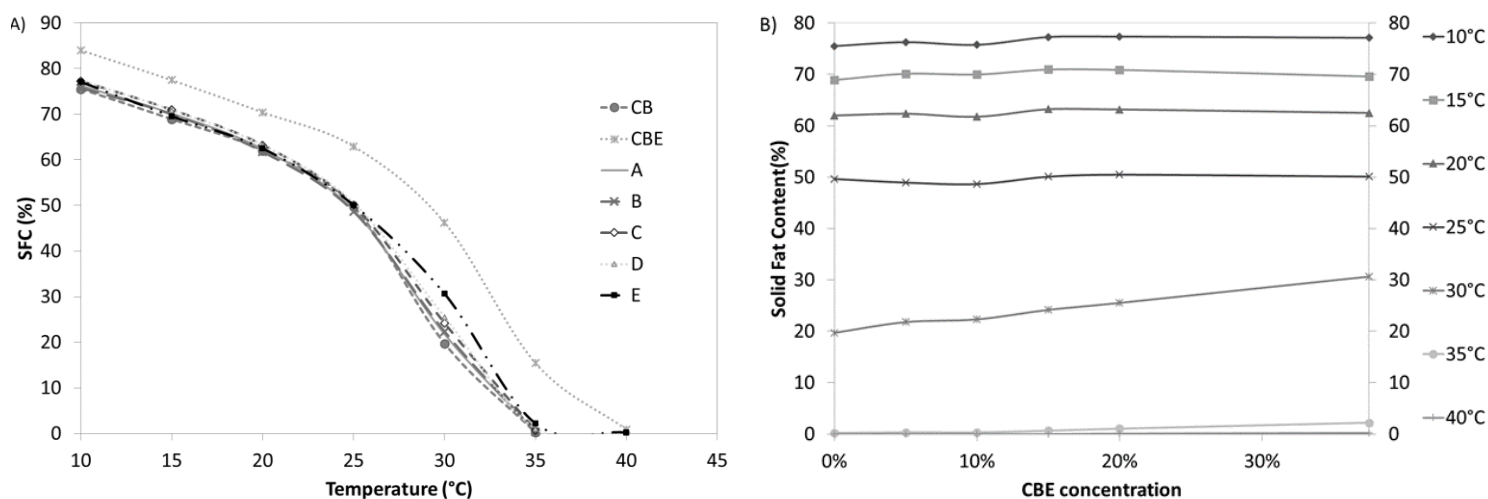


Figure 1. (A) Solid Fat Content and (B) compatibility diagram of cocoa butter (CB) and cocoa butter equivalent (CBE) and their blends. For sample A, B, C, D and E, please see Table 1.

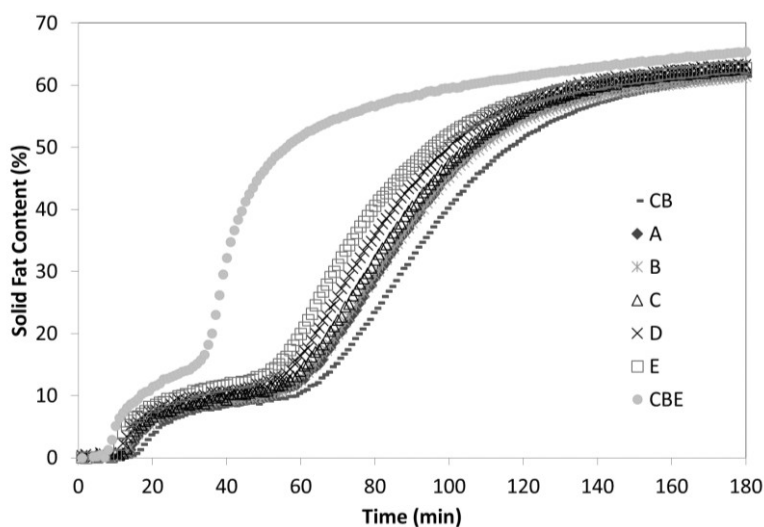


Figure 2. Isothermal crystallization curves at 17.5 °C of pure cocoa butter (CB) and cocoa butter equivalent (CBE) and their blends. For samples A, B, C, D and E, see Table 1.

Table 2. Isothermal crystallization parameters of cocoa butter (CB), cocoa butter equivalent (CBE), and their blends (A, B, C, D and E)

Samples	Avrami Parameters					
	t_{sfc} (min)	SFC _{max} (%)	k (min ⁻¹)	n	$t_{1/2}$	R ²
CB	16±0.47 ^a	63.50±0.15 ^a	0.00000514 ^a	2.63±0.08 ^a	88.30±1.16 ^a	0.9927
CBE	8±0.47 ^d	65.43±0.31 ^d	0.000671 ^c	2.03±0.11 ^c	40.14±0.50 ^e	0.9845
A	14±0.47 ^b	61.82±0.37 ^b	0.00000270 ^a	2.83±0.03 ^a	81.72±1.37 ^b	0.9921
B	14±0.47 ^b	61.41±0.57 ^b	0.00000336 ^a	2.78±0.04 ^a	81.00±0.83 ^b	0.9919
C	13±0.47 ^b	62.77±0.04 ^{ac}	0.00000541 ^a	2.69±0.09 ^a	78.95±1.66 ^{bc}	0.9917
D	12±0.47 ^c	63.41±0.49 ^a	0.00000537 ^a	2.72±0.21 ^a	75.33±2.48 ^c	0.9922
E	11±0.47 ^c	62.98±0.14 ^{ac}	0.00003009 ^b	2.37±0.04 ^b	69.64±0.49 ^d	0.9898

NOTE: ^a Values are shown as mean ± standard deviation of three replication. Means represented by different small letters in all columns indicate that the samples are statistically different (P < 0.05) by Tukey's test. ^b For samples, A, B, C, D e E, nomenclature please see Table 1.

To confirm the shown by the Avrami parameters, we calculated the crystallization half-time ($t_{1/2}$) of the samples, this parameter is expressed in minutes and reproduce the magnitude of the parameters k and n. The $t_{1/2}$ characterizes the time at which half the sample crystallizes. This parameter is important when one the proposes is to apply the fat since it shows not only the beginning of the crystallization or SFC_{max} at the end but also how the sample works in all crystallization process (DA SILVA et al., 2017). CBE showed a smaller $t_{1/2}$ than crystallization of CB, which could be represented by a faster polymorphic transition for this fat, and consequently, their blends presented faster $t_{1/2}$ as the concentration of CBE in the blend increased.

The constant k is the crystallization velocity, which considers nucleation and crystal growing rate, and depends largely on crystallization temperature. The k is very quick for pure CBE, approximately 130-fold higher, which confirms the faster crystallization of CBE. CBE and CB are present at the end the same profile, but CBE achieves this stable profile faster, with is very positive in industry because the same product will be completely crystallized for commercialization in a shorter time. The blends significantly differ in k for 37.5% CBE addition, which indicates that CBE can influence the rate of crystallization in higher amounts.

The Avrami exponent (n) gives information about nucleation and crystal growth processes, and conditions in which n is not a whole number indicate a combination of different nucleation mechanisms. CBE, CB and their blends showed an n value of approximately 2, which indicates disk type growth with instantaneous nuclei or needle-shaped type growth with sporadic nuclei (CAMPOS, 2005).

CRYSTALLIZATION STUDY OF CB:CBE BLENDS: THERMAL BEHAVIOR

In Figure 3A, the crystallization profile of CB, CBE and their blends in DSC are shown. CB and CBE, and their blends, show only one peak in the crystallization process. This peak presented a sub-division in a first sub-peak due to the trisaturated TAGs (SSS) PPP, PPSt, PStSt and StStSt; even in their smaller concentrations, this peak was well defined in CBE due to the higher amounts (~1% more) of TAGS SSS in these fats, and consequently increased in the blends as CBE concentration increased. The

second sub-peak is represented by disaturated (SUS) and monosaturated (SUU) TAGs. The main difference between the fats is the fast beginning of crystallization in CBE compared to CB (same result obtained by isothermal crystallization), but the blends did not show an expressive change in DSC parameters. CB required higher heat for complete crystallization than CBE, and this value for blends was similar to CB values, as observed for the size of the crystallization peaks.

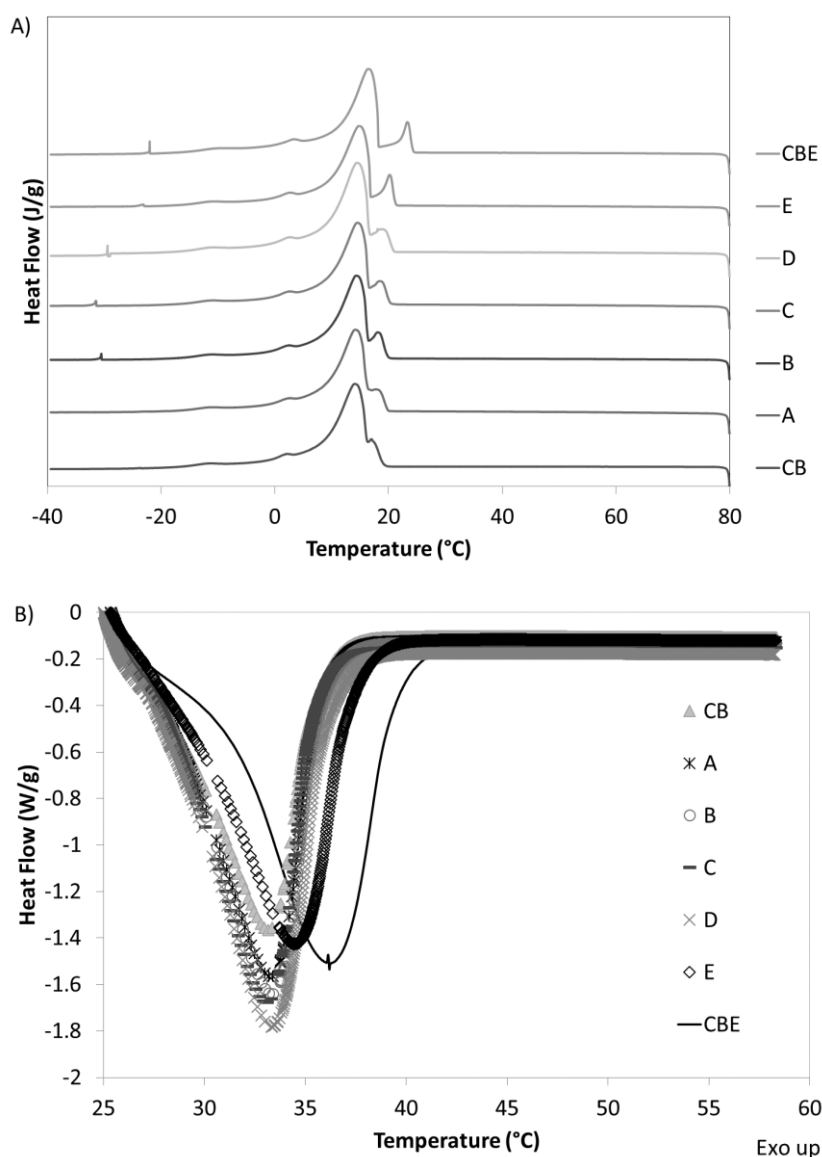


Figure 3. DSC crystallization (A) and melting profiles (B) of cocoa butter (CB), cocoa butter equivalent (CBE) and their blends. For samples concentration A, B, C, D and E, please see Table 1.

The melting profile in DSC is presented in Figure 3B. In this result, CB and CBE showed a different profile, where CBE showed a melting peak shift compared to CB, and thus all temperature parameters (T_{onset} , T_{pm} and T_{em}) were higher for CBE and higher heat was required for complete the melting (ΔH_m), which could be associated with a higher melting point and high amounts of StOst. This characteristic profile from CBE was

observed only in blends with higher amounts of CBE (D and E). The melting parameters in DSC for CBEs found in the literature are very variable (KANG *et al.*, 2013). This results from different crystallization and melting rates and the high sensitivity of DSC and different conditions on sample preparation.

CRYSTALLIZATION STUDY OF CB:CBE BLENDS: MICROSTRUTURE

TAGs are organic molecules; these molecules lead to connect on basis of standard structural organic chemistry and form crystals. However, predict the interaction and crystal structure formed is non-trivial, since they have different ways of packing which can form different polymorphic forms (NARINE; MARANGONI, 1999).

The microstructure of CB, CBE and their blends are shown in Figure 4. Both CB and CBE are characterized by clusters: CB showed higher clusters with no crystal formation between them; CB clusters were formed by higher nuclei formed by small crystals surrounded by medium needles, forming a structure similar to a flower. CBE (Figure 4) showed smaller clusters and a homogeneous crystallized area between clusters with small crystalline nuclei; CBE clusters formed the same flower structure of CB, but in this case, the nuclei are very small surrounded by the same needle form. The blends did not present different microstructure forms but resembled CB microstructure, and the CBE amount increased the microstructure of the blend's similarity with CBE characteristics. The increase in crystal density with increased CBE concentration could relate to the high amount of the TAG SSS in CBE or the higher amount of the TAG StOst (BOOTELLO *et al.*, 2012; JAHURUL *et al.*, 2014).

According to the Avrami parameter n , all samples studied presented crystals as needle-shaped growth from sporadic nuclei or disk-shaped growth from instantaneous nuclei, and this mechanism was the same for all samples analyzed. In Figure, 4 we can confirm that the needle-shaped crystal was predominate for all samples.

CRYSTALLIZATION STUDY OF CB:CBE BLENDS: CONSISTENCY

Consistency is an important sensory parameter for select special fats for food application. Changes in food consistency could drastically affect consumer preference (MASUCHI; GRIMALDI; KIECKBUSCH, 2014). Figure 5 show the Yield Value (YV) of CB, CBE and their blends. CB showed a YV of 20 kgf/cm², but CBE had a high value. Higher hardness CBEs are characterizing as high-quality CBE (BILIADERIS, 1983). The difference between CB and CBE is due the microstructural difference observed. These because, the consistency analysis is made with cone penetration. The cone penetration, allows samples with more homogeneity in terms of spatial distribution of the crystals more resistance to penetration than samples with lower crystal density. In the latter case, when the cone penetrates the samples, there is more space for microstructures to rearrange in CB, allowing higher penetration depths, even when they are in a more stable polymorphic form (CAMPOS *et al.*, 2002).

In addition to the difference between CB and CBE, the blends presented values very similar to pure CB (Figure 5); this is expected when fats that are very similar chemically are blended. According to HAIGHTON (1959), a fat is considered "very hard" when its YV is above 1.5 kgf/cm². At 25°C, all samples and blends showed a higher value, which is a natural characteristic found for Brazilian CB (RIBEIRO *et al.*, 2012). Hence, higher CBE proportions improved CB melting, and higher SFC and StOSt of CBE could be used to

increase the hardness of CB, which may be advantageous for use in chocolates in warm climates (SHUKLA, 2006; JAHURUL *et al.*, 2014). Based on that results, a chocolate made with either of these two fat blends should exhibit good characteristics with proper melting behavior, solid at room temperature and melting quickly in the mouth (SONWAI; KAPHUEAKNGAM; FLOOD, 2014).

CRYSTALLIZATION STUDY OF CB:CBE BLENDS: X-RAY DIFFRACTION

X-ray diffraction is a more direct and informative technique to study polymorphism (JIN *et al.*, 2008). Figure 6 shows the short-spacing for the samples studied. The D-spacing calculated for CB was 5.44, 4.61, 4.00, 3.88, 3.77 and 3.68. The polymorphic form βV is characterized by a strong peak at 4.6 followed by four smaller peaks between 3.9 and 3.6 D-spacing values (HIMAWAN; STAROV; STAPLEY, 2006). The CBE presented the following values of D-spacing: 5.46, 4.61, 4.26, 4.01, 3.91 and 3.7. The D-spacing obtained was very similar for CB, but as seen in Figure 6, a strong tendency in merging of the last two peaks in the diffractogram is observed, suggesting the natural presence of the βVI form (VAN LANGEVELDE *et al.*, 2001). In this way, we can conclude that the CB in this study is pure in the βV form and that CBE presents a mix of predominately βV with a small amount of βVI . The blends between CB and CBE (Figure 6) presented the βV form with the same peaks as in pure CB, and the same result was observed for blends between CB and CBE studied by BOOTELLO *et al.* (2012).

The βV polymorphic form shows the crystallization of symmetric TAGs (SUS) (D'SOUZA *et al.*, 1990). As CB and CBE and their blends are primarily formed by SUS TAGs, we expected this polymorphic form for all samples. Almost all TAGs are symmetric and are the same TAGs, which also favors co-crystallization and compatibility between the two fats (HIMAWAN; STAROV; STAPLEY, 2006). The crystallization and formation of the βV form was speculated, and the βV form is influenced by the first, fast crystallization of StOSt, after which StOSt rearranged and co-crystallized with POP, POST, and other minor triglycerides to maintain the first polymorphic form (MARANGONI; MCGAULEY, 2003). The higher amounts of StOSt in the CBE could explain the formation of small amounts of the βVI polymorph.

CB:CBE BLENDS IN CHOCOLATE

Sample 20% was the highest CBE concentration that did not change any parameter in the blend compared to a pure CB. This blend presented same hardness, melting peak temperature, SFC and polymorphic form than pure CB, and for this reason it was used in for application in a dark chocolate.

Observing the data in Figure 7, as similar to the CB in the blends study, we can observe that the replacement of 20% of the CB by CBE in dark chocolate does not change the microstructure, hardness or polymorphism of the chocolate compared to the pure CB chocolates either. The addition of 20% of CBE in a dark chocolate did not change visually or the white index in a previous work either (DA SILVA; GRIMALDI; GONÇALVES, 2017).

These results confirm that when there are no differences in the fat blends physical properties the replacement of a CB for CBE on those amounts do not interfere in the chocolate quality either. Besides that the use of CBE is advantage due the presence of higher amounts of StOSt triacylglycerols that can strengthen the development of β crystals in the tempering process—desirable in the chocolate production and also inhibit the

formation of fat bloom during chocolate storage (BUSCATO; GRIMALDI; KIECKBUSCH, 2017). As found in a previous work for the same chocolate composition after temperature cycling 20/33 °C (DA SILVA; GRIMALDI; GONÇALVES, 2017).

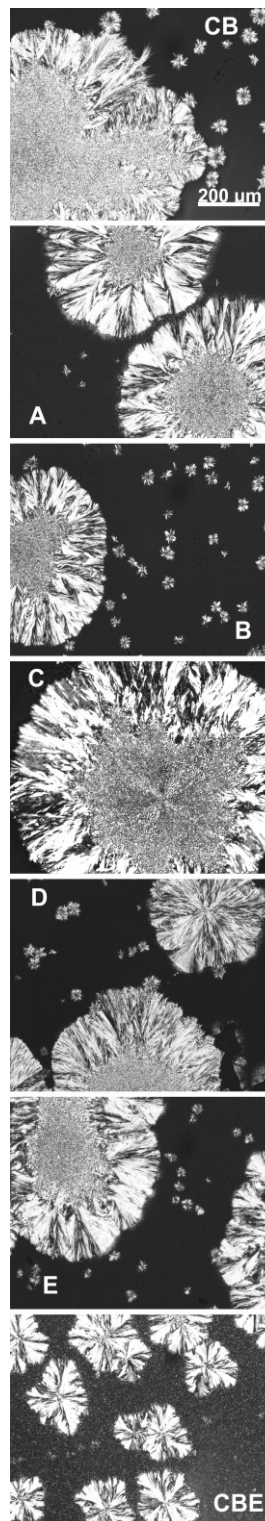


Figure 4. Polarized light microscopy pictures of crystals obtained cocoa butter (CB), cocoa butter equivalent (CBE) and their blends. For samples concentration A, B, C, D and E, please see Table 1

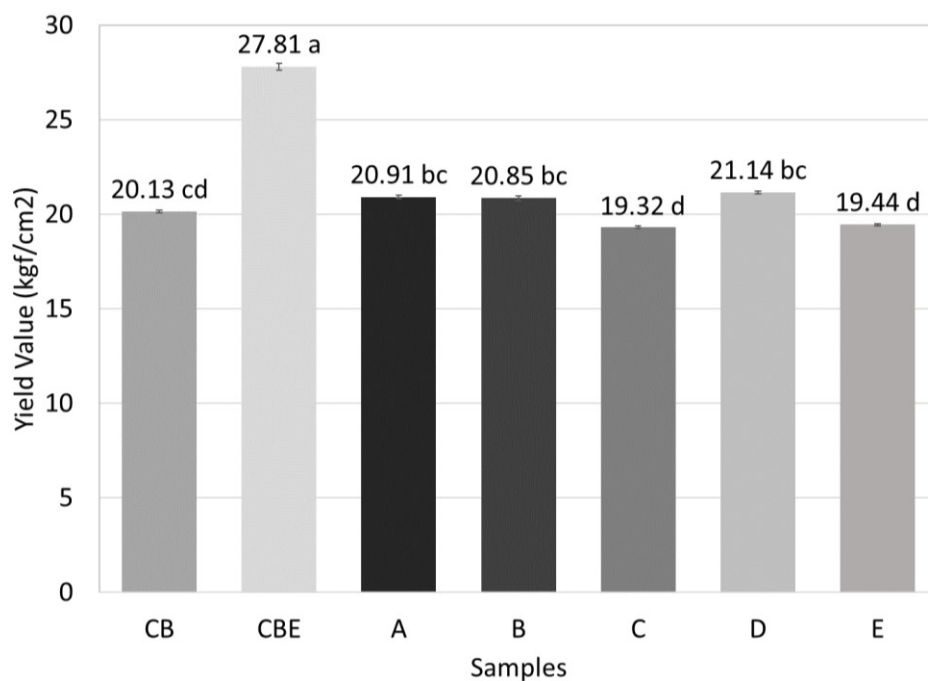


Figure 5. Yield Value of cocoa butter (CB), cocoa butter equivalent (CBE) and their blends. For sample concentration A, B, C, D and E, please see Table 1.

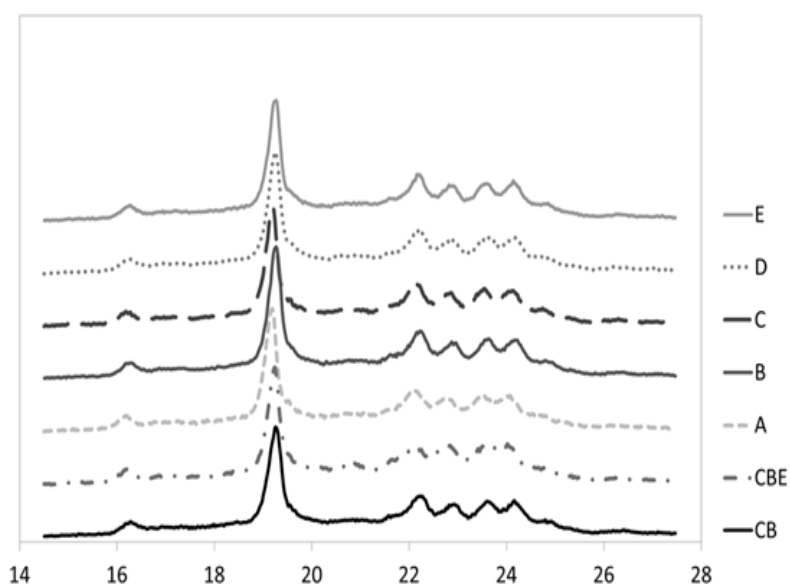


Figure 6. X-ray diffraction patterns of cocoa butter (CB), cocoa butter equivalent (CBE), and their blends. For samples concentration A, B, C, D and E, please see Table 1

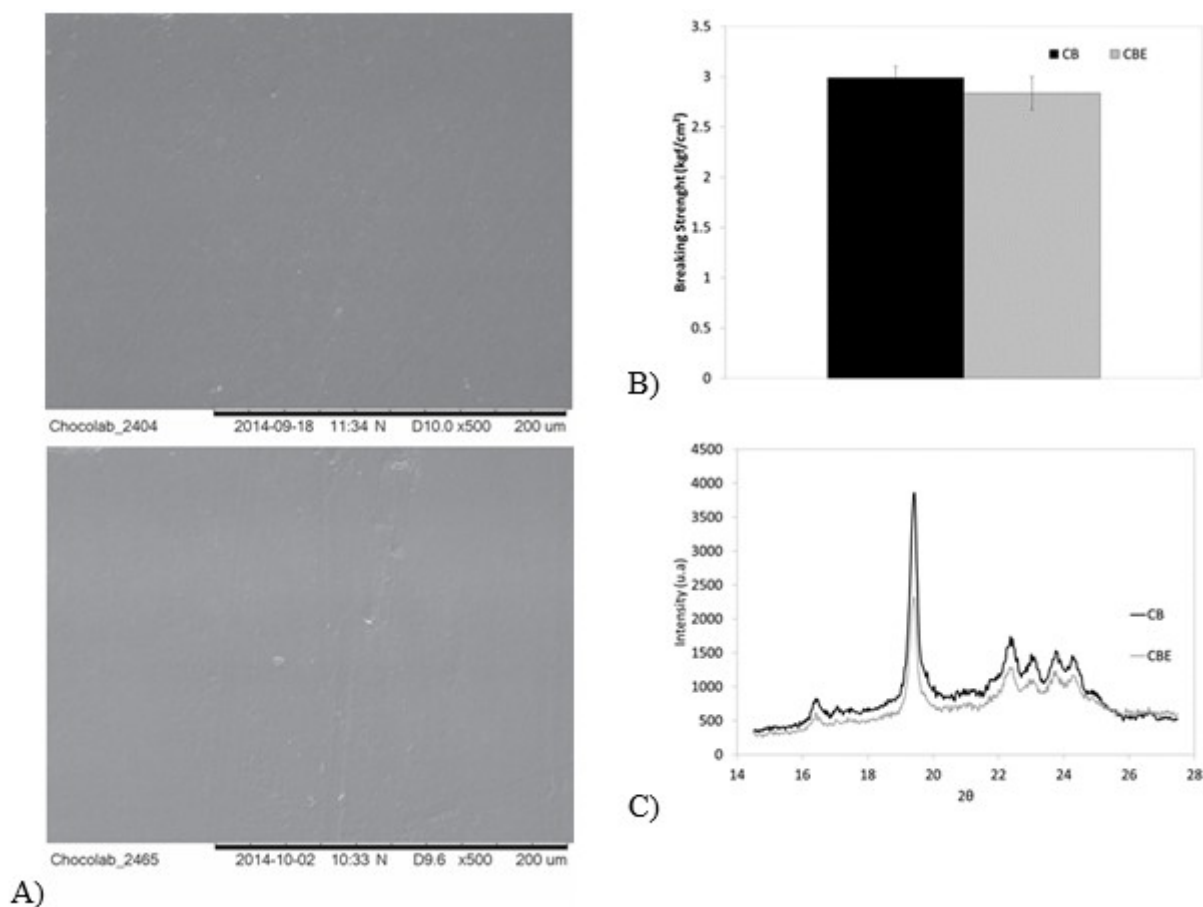


Figure 7. Cocoa butter (CB) and cocoa butter equivalent (CBE) chocolate characteristics (A) scanning electron microstructure (B) breaking strength and (C) polymorphism.

CONCLUSIONS

This study highlights the crystallization behavior of CB and how it can be replaced by CBE without significant changes in the crystallization process. CBE have natural chemical and physical similarities with CB, which is required for the fat to be called a CBE. However, even with the similarities, some important differences must be highlighted, including the proportion of the major TAGs (POP, POST and StOST), SFC at 35 °C, fast crystallization and high hardness. This study contributes to knowledge about the phenomena important for different laws for the use of CBE to replace CB, ruling out full replacement, but encouraging its use in blends with CB in chocolate products. The use of CB/CBE blends in the production of chocolates reduces production cost, improves the milk fat tolerance of CB, increases the resistance to storage at high temperatures and increases fat bloom control. The CBE proportion in the blends is recommended at 20%, because this concentration does not change the physical properties of the final chocolate as snap, microstructure and polymorphism.

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Efeito do equivalente de manteiga de cacau no comportamento de cristalização da manteiga de cacau e no chocolate amargo

RESUMO

O objetivo deste trabalho foi avaliar o comportamento de cristalização de manteiga de cacau comercial (CB) e equivalentes de manteiga de cacau (CBE) e suas misturas para avaliar as melhores proporções que não comprometam o processo de cristalização em chocolates. As misturas foram preparadas utilizando concentrações de CBE de 5%, 10%, 15%, 20% e 37,5% e avaliadas por: composição de ácidos graxos, composição de triacilgliceróis (TAG), teor de gordura sólida, análise isotérmica, microscopia de luz polarizada, comportamento térmico, Difração de raios-X e consistência. A maior quantidade de CBE em uma mistura sem comprometer a cristalização do CB foi aplicada posteriormente em um chocolate escuro. O CBE apresentou uma composição semelhante de ácidos graxos que o CB nas mesmas proporções, mas os TAGs do CBE apresentaram mais TAG StOSt, proporcionando rápida cristalização, maior conteúdo de SFC e maior dureza. Mesmo com total compatibilidade entre CB e CBE, a proporção de CBE em proporções de CB/CBE deve ser restrita porque concentrações mais altas dessa gordura não são permitidas pelos regulamentos de muitos países e podem levar a um produto final com uma sensação de cera devido à maior ponto de fusão dos CBE TAGs. O chocolate escuro com CBE/CB (20/80) não apresentou diferença física (snap, microestrutura e polimorfismo) em relação ao chocolate normal puro em CB.

PALAVRAS-CHAVE: chocolate; manteiga de cacau; equivalente de manteiga de cacau; cristalização.

REFERENCES

AOCS (2009) American Oil Chemists' Society. Official Methods and Recommended Practices of the American Oil Chemists' Society, 5ed edn.

BIGALLI, G.L. Practical aspects of the eutectic effect on confectionery fats and their mixtures. **The Manufacturing Confectioner**, v. 53, p. 65–80, 1988.

BILIADERIS, C. Differential scanning calorimetry in food research—A review. **Food Chemistry**, v. 10, p. 239–265, 1983.

BOOTELLO, M.A.; HARTEL, R.W.; GARCÉS, R.; MARTÍNEZ-FORCE, E.; SALAS, J.J. (2012) Evaluation of high oleic-high stearic sunflower hard stearins for cocoa butter equivalent formulation. **Food Chemistry**, v.134, p.1409–1417, 2012.

BRAZIL (2005) ANVISA – Agência Nacional de Vigilância Sanitária. Resolução RDC nº 264, de 22 de setembro de 2005.

BUSCATO, M.H.M.; GRIMALDI, R.; KIECKBUSCH, T.G. Cocoa butter symmetrical monounsaturated triacylglycerols: separation by solvent fractionation and application as crystallization modifier. **Journal of Food Science and Technology**, v.54, p. 3260–3267, 2017.

CAMPOS. R. Experimental methodology. In: Marangoni AG (ed) **Fat crystal network**, Marcel Dek. New York, p. 267–349, 2005.

CAMPOS. R.; NARINE, S.S.; MARANGONI, A.G. Effect of cooling rate on the structure and mechanical properties of milk fat and lard. **Food Research International**, v. 35, p. 971–981, 2002.

CEBULA, D.J.; ZIEGLER, G. Studies of Bloom Formation Using X-Ray-Diffraction from Chocolates after Long-term Storage. **Fett Wissenschaft Technologie-Fat Science Technology**, v. 195, p. 340–343, 1993.

DA SILVA, T.L.T.; DOMINGUES, M.A.F.; CHIU. M.C.; GONCALVES, L.A.G. Templating effects of dipalmitin on soft palm mid fraction crystals. **International Journal of Food Properties**, 2017.

DA SILVA, T.L.T.; GRIMALDI, R.; GONÇALVES, L.A.G. Temperature, time and fat composition effect on fat bloom formation in dark chocolate. **Food Structure**, v. 14, p. 68–75, 2017.

D`SOUZA, V.; DEMAN, J.M.; DEMAN, L. Short spacings and polymorphic forms of natural and commercial solid fats: A review. **Journal of the American Oil Chemists' Society**, v. 67, p. 835–843, 1990.

DE CLERCQ, N., KADIVAR, S.; VAN DE WALLE, D., DE PELSMAEKER, S.; GHJELLYNCK, X.; DEWETTINCK, K. Functionality of cocoa butter equivalents in chocolate products. **European Food Research Technology**, v. 243, p. 309–321, 2017.

FILHO, N.R.A.; MENDES, O.L.; LANÇAS, F.M. Computer prediction of triacylglycerol composition of vegetable oils by HRGC. **Chromatographia**, v. 40, p. 557–562, 1995.

GUNSTONE, F.D. **Vegetable Oils**. In: Shahidi F (ed) Bailey's Industrial Oil and Fat Products, 6th edn. Copyright# 2005 John Wiley & Sons, Inc, pp 213–267, 2005.

HAIGHTON, A.J. The measurement of the hardness of margarine and fats with cone penetrometers. **Journal of the American Oil Chemists' Society**, v. 36, p. 345–348, 1959.

HARTMAN, L.; LAGO, R.C.A. Rapid preparation of fatty acid methyl esters from lipids. **Laboratory Practices**, v. 22, p. 475–476, 1973.

HIMAWAN, C.; STAROV, V.M.; STAPLEY, A.G.F. Thermodynamic and kinetic aspects of fat crystallization. **Advances in Colloid and Interface Science**, v. 122, p. 3–33, 2006.

JAHURUL, M.H.A.; ZAIDUL, I.S.M.; NORULAINI, N.A.n.; SAHENA, F.; ABEDIN, M. Z.; MOHAMED, A.; MOHD OMAR, A. K. Hard cocoa butter replacers from mango seed fat and palm stearin. **Food Chemistry**, v.154, p. 323–329, 2014.

JAHURUL, M.H.A.; ZAIDUL, I.S.M.; NORULAINI, N.A.N.; SAHENA, F.; JINAP, S.; AZMIR, J.; SHARIF, K.M.; MOHD OMAR, A.K. Cocoa butter fats and possibilities of substitution in food products concerning cocoa varieties, alternative sources, extraction methods, composition, and characteristics. **Journal of Food Engineering**, v. 117, p. 467–476, 2013.

JIN, Q.; ZHANG, T.; SHAN, L.; LIU, Y.; WANG, X. Melting and Solidification Properties of Palm Kernel Oil, Tallow, and Palm Olein Blends in the Preparation of Shortening. **Journal of the American Oil Chemists' Society**, v. 85, p. 23–28, 2008.

KANG, K.K.; JEON, H.; KIM, I.H.; KIM, B.H. Cocoa butter equivalents prepared by blending fractionated palm stearin and shea stearin. **Food Science and Biotechnology**, v. 22, p. 347–352, 2013.

KARABULUT, I.; TURAN, S.; ERGIN, G. Effects of chemical interesterification on solid fat content and slip melting point of fat/oil blends. **European Food Research Technology**, v. 218, p. 224–229, 2004.

LIPP, M.; SIMONEAU, C.; ULBERTH, F.; ANKLAM, E.; CREWS, C.; BRERETON, P.; DE GREYT, W.; SCHWACK, W.; WIEDMAIER, C. Composition of Genuine Cocoa Butter and Cocoa Butter Equivalents. **Journal of Food Composition and Analysis**, v. 14, p. 399–408, 2001.

LONCHAMPT, P.; HARTEL, R.W. Fat bloom in chocolate and compound coatings. **European Journal of Lipid Science and Technology**, v. 106, p. 241–274, 2004.

MARANGONI, A.G.; MCGAULEY, S.E. Relationship between Crystallization Behavior and Structure in Cocoa Butter. **Crystal Growth & Design**, v. 3, p. 95–108, 2003.

MASUCHI, M.H.; GRIMALDI, R.; KIECKBUSCH, T.G. Effects of Sorbitan Monostearate and Monooleate on the Crystallization and Consistency Behaviors of Cocoa Butter. **Journal of the American Oil Chemists' Society**, v. 91, p. 1111–1120, 2014.

MING, H.L.M. Specialty fats – How food manufacturers can get more out of them. **Lipid Technology**, v. 20, p. 35–39, 2008.

NARINE, S.S.; MARANGONI, A.G. Microscopic and rheological studies of fat crystal networks. **Journal of Crystal Growth**, v. 198–199, p. 1315–1319, 1999.

QUAST, L.B.; LUCCAS, V.; RIBEIRO, A.P.B.; CARDOSO, L. P.; KIECKBUSCH, T. G. Physical properties of tempered mixtures of cocoa butter, CBR and CBS fats. **International Journal of Food Science and Technology**, v. 48, p. 1579–1588, 2013.

REZENDE, V.; BENASSI, M.T.; VISSOTTO, F.Z.; AUGUSTO, P.P.C.; GROSSMANN, M.V.E. Original article Effects of fat replacement and fibre addition on the texture , sensory acceptance and structure of sucrose-free chocolate. **International Journal of Food Science and Technology**, 2015.

RIBEIRO, A.P.B.; SILVA, R.C.D.; GIOIELLI, L.A.; GONÇALVES, M.I.A.; GRIMALDI, R.

GONÇALVES, L.A.G.; KIECKBUSCH, T.G. Physico-chemical properties of Brazilian cocoa butter and industrial blends. Part I Chemical composition, solid fat content and consistency. **Grasas y Aceites**, v. 63, p. 79–88, 2012.

RODRIGUES, J.N.; GIOIELLI, L.A.; ANTON, C. Propriedades Físicas De Lipídios Estruturados Obtidos De Misturas De Gordura Do Leite E Óleo De Milho 1. **Ciência e Tecnologia de Alimentos**, v. 23, p. 226–233, 2003.

SABARIAH, S.; ALI, A.R.; CHONG, C.L. Chemical and Physical Characteristics of Cocoa Butter Substitutes , Milk Fat and Malaysian Cocoa Butter Blends. **Journal of the American Oil Chemists' Society**, v. 75, p. 905–910, 1998.

SCHENK, H.; PESCHAR, R. Understanding the structure of chocolate. **Radiation Physics and Chemistry**, v.71, p. 829–835. 2004.

SHUKLA, V.K.S. **Cocoa Butter Equivalent** , and **Cocoa Butter Substitutes**. p. 279–307, 2006.

SONWAI, S.; KAPHUEAKNGAM, P.; FLOOD, A. Blending of mango kernel fat and palm oil mid-fraction to obtain cocoa butter equivalent. **Journal of Food Science and Technology**, v. 51, p. 2357–2369, 2014.

TALBOT, G. Vegetable Fats. In: Beckett ST (ed) **Industrial chocolate manufacture and use**, 4th edn. John Wiley & Sons, Ltd, 2011.

TORBICA; A.; JAMBREC, D.; TOMIC, J.; PAJIN, B.; KRAVIĆ, S.; LONČAREVIĆ, I. Solid fat content, pre-crystallization conditions, and sensory quality of chocolate with addition of cocoa butter analogues. **International Journal of Food Properties**, v.19, p. 1029–1043, 2015.

TORBICA A.; JOVANOVIĆ, O.; PAJIN, B. The advantages of solid fat content determination in cocoa butter and cocoa butter equivalents by the Karlshamns method. **European Food Research Technology**, v. 222, p.385–391, 2006.

UNION E. Directive 2000/36/EC of the European Parliament and of the Council relating to cocoa and chocolate products intended for human consumption, 2000.

van LANGEVELDE, A.; VAN MALSSSEN, K.; PESCHAR, R.; SCHENK, H. Effect of temperature on recrystallization behavior of cocoa butter. **Journal of the American Oil Chemists' Society**, v. 78, p. 919–925, 2001.

WANG, H.X.; WU, H.; HO, C.T.; WENG, X.C. Cocoa butter equivalent from enzymatic interesterification of tea seed oil and fatty acid methyl esters. **Food Chemistry**, v. 97, p. 661–665, 2006.

YAP, P.; MAN, J.D.; MAN, L.D. Polymorphism of palm oil and palm oil products. **Journal of the American Oil Chemists' Society**, p. 693–697, 1989.

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