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Original article

Physical properties of tempered mixtures of cocoa butter, CBR and CBS fats

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Summary Physical characteristics of precrystallised binary mixtures of cocoa butter (CB) and 5, 10, 15, 20, 25 and 30% (w/w) cocoa butter replacer (CBR) or cocoa butter substitute (CBS) were determined. The lipid composition was obtained by chromatography and the solid fat content (SFC) by nuclear magnetic resonance. Tempering was carried out using a lab-scale agitated jacket vessel reactor. Bars made with tempered samples were submitted to X-ray diffraction and rupture tests. Snap values of crystallised mixtures decrease with an increase in the amount of alternative fat. X-ray diffraction patterns confirmed the predominant formation of the beta polymorph habit for CB and beta prime form for CBR and CBS. Mixtures of CB and CBR exhibit chemical compatibility. The knowledge of the snap values and of the variation of SFC with temperature proved to suffice to adequately anticipate the influence of the addition of alternative fats on chocolates physical attributes.

Keywords Cocoa butter replacer, cocoa butter substitute, cocoa butter, solid fat content, X-ray diffraction.

Introduction

Cocoa butter, milk fat and alternative fats constitute the continuous phase in chocolate products and are therefore responsible for the dispersion of the other ingredients. Cocoa butter structuration is responsible for the functional attributes of chocolate products, such as hardness at room temperature and a pleasant mouth feeling during melting at body temperature. Cocoa butter contains three main fatty acids: palmitic (P), stearic (S) and oleic (O) acids. Practically, all oleic (unsaturated) acid is esterified at the sn-2 position of the glycerol molecule so that more than 75% of the total triacylglycerols (TAGs) are 1,3-dipalmitoyl-2-oleoylglycerol (POP), 1-palmitoyl-2-oleoyl-3-stearoyl-glycerol (POS) and 1,3-distearoyl-2-oleoylglycerol (SOS) (Minifie, 1989).

Cocoa butter exhibits polymorphic behaviour, that is, it can solidify into different crystalline forms depending on the temperature, melt shearing actions and the melt cooling rate. Polymorphism of cocoa butter has been reported in studies by Wille & Lutton (1966); Keller *et al.* (1996); Loisel *et al.* (1998); Sato (2001); MacMillan *et al.* (2002); Marangoni & McGauley (2003); Mazzanti *et al.* (2003); Schenk & Peschar (2004); Vazquez *et al.* (2004). Therefore, in chocolate manufacturing, cocoa butter should be precrystallised or tempered before the moulding or coating stages. Adequate precrystallisation will induce the formation of the beta-type crystal nuclei with higher thermodynamic stability. Tempering procedures for chocolate and/or cocoa butter have been established by Talbot (1994); Loisel *et al.* (1997); Stapley *et al.* (1999); Briggs & Wang (2004); Dhonsi & Stapley (2005); Foubert *et al.* (2004). Briefly, the tempering step starts with the complete melting of the lipid phase at 40 °C, followed by a controlled cooling under agitation to induce TAG crystallisation. The cooling rate should be close to 2.0 °C min^{-1}. During this stage, a small amount of undesirable crystals such as the alpha and beta prime form is also generated. These crystals have lower melting temperatures and are eliminated by heating the mass to 30–32 °C. In the manufacture of chocolates, crystallisation continues during the air cooling stage of the bars, which should proceed under controlled temperature to favour the entanglement of a stable crystal network.

Cocoa butter alternative fats, also known as CBA, are tailor-made through physical and/or chemical modifications of fats and oils and therefore maintain their distinguished normalised characteristics, thus allowing the manufacturers to standardise the quality of their products. The choice of the most adequate fat alternative depends on a cost vs. benefit relation and on the properties required in the final product (Beckett, 2008). Depending on the raw material used, some fats do not need to be submitted to the precrystallisation process because they crystallise directly to the

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beta prime form. These fats can be classified into two types: cocoa butter replacers (CBRs) and cocoa butter substitutes (CBSs).

Cocoa butter replacers (CBRs) are nonlauric fats routinely obtained through hydrogenation and fractionation of vegetable oils rich in palmitic (C 16:0), oleic (C18:1) and linoleic (C 18:2) acids and can be derived from soy, cotton, palm and canola oils. These oils contain long-chain fatty acids with molecular mass distribution similar to that of cocoa butter, but with a different triacylglycerol composition. CBRs show good physicochemical interaction tolerance to milk fat and mix well with cocoa butter (Minifie, 1989; Beckett, 2008).

Cocoa butter substitutes (CBSs) are fats derived from palm kernel, coconut or babassu oils. They have a high lauric acid (C12:0) content, resulting in short-chain triacylglycerols. The physical properties of CBSs are similar to those of cocoa butter, but due to the chemical incompatibility between the triacylglycerols of these fats, their mixture can develop eutectic effects (Lipp & Anklam, 1998; Koyano & Sato, 2002).

The physical-chemical characterisation of these alternative fats and the polymorphic form predominant in the mixtures after the crystallisation process serve as scientific basis for establishing the percentage of CBR and CBS that can be added to cocoa butter without significantly altering their physical properties and quality attributes. The objective of this study was to evaluate physical properties of precrystallised cocoa butter bars containing up to 30% of CBR or CBS to be able to establish limits and limitations of cocoa butter substitution, aiming the manufacture of chocolates. The approach of this work, with emphasis on the evaluation of precrystallised bars moulded only with the continuous fat phase in chocolate, is unprecedented in the literature.

Materials and methods

Raw material

Deodorised cocoa butter (blend of Brazilian and Indonesian cocoa butter) supplied by Barry Callebaut Brasil S/A, Bahia, Brazil. Cocoa butter replacer (CBR) low trans fat based on palm oil (Fuji Vegetable Oil Inc., Gent, Belgium) and cocoa butter substitute (CBS) based on palm kernel oil, supplied by Bunge S/A, (Brazil), were used for the preparation of the samples evaluated in this study. The CBR and the CBS were produced by chemical interesterification. All samples were kept in plastic bottles and stored under controlled temperature (23 ± 0.5 °C) until the time of use. The experiments were conducted using eight different proportions (0%, 5%, 10%, 15%, 20%, 25%, 30% and 100%) of CBR or CBS and cocoa butter. The mixtures of cocoa butter and alternative fats (w/w) are represented by: 95CB/5CBR (CBR5); 90CB/10CBR (CBR10); 85CB/15CBR (CBR15); 80CB/20CBR (CBR20); 75CB/25CBR (CBR25); 70CB/30CBR (CBR30); 0CB/100CBR (CBR100); 95CB/5CBS (CBS5); 90CB/10CBS (CBS10); 85CB/15CBS (CBS15); 80CB/20CBS (CBS20); 75CB/25CBS (CBS25); 70CB/30CBS (CBS30); 0CB/100CBS (CBS100). Pure cocoa butter was denoted as CB100.

Physical-chemical characterisation of raw materials and mixtures

Samples of cocoa butter, CBS and CBR were characterised according to the fatty acid and triacylglycerol composition. Solid profiles were determined for pure cocoa butter, CBS, CBR and for the different mixtures evaluated.

Precrystallisation of pure cocoa butter and of the mixtures

All fats were completely melted in an oven at 40 °C, and the mixture was then homogenised manually. Precrystallisation was conducted in a lab-scale glass jacketed vessel reactor (700 mL) coupled to a stirring system, made up of a 9 cm anchor-type paddle, a diameter corresponding to 95% of the internal vessel diameter, suitable for mixing viscous substances. The fat mixture temperature was controlled using two circulating water baths. One bath was used to control the initial cooling rate and also the final reheating of the mass. The second bath was set to maintain the mass at the precrystallisation temperature. The mixture previously heated to 40 °C was stirred at 96 rpm and then cooled at an average rate of 2.0 °C min^{-1} until the predetermined crystallisation condition was reached (Quast *et al.*, 2011). The cooling rate was defined as the temperature difference (initial temperature and tempering temperature) divided by the cooling time.

The samples with less than 20% CBR or CBS were cooled down and precrystallised at a temperature of 24 °C during 8 min. Mixtures with 20, 25 and 30% of CBR or CBS had to be cooled down and crystallised at a temperature of 23 °C and kept at this temperature for 10–16 min to avoid demoulding problems and low consistency of the mass, an indication of inadequate tempering (Quast *et al.*, 2011).

At the end of the tempering step, the samples were reheated to 31 °C to dissolve the unstable crystal nuclei. In a well-tempered sample, the amount of the stable crystals is situated between 1 and 5% of the total lipid phase (Jovanovic *et al.*, 1995; Loisel *et al.*, 1997).

Pure CBR and CBS fats were not submitted to a precrystallisation process because they present crystallisation characteristics that are different from that of

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cocoa butter, that is, they crystallise directly to the beta prime form.

After precrystallisation, the melt of fat mixture was poured into moulds (8.2 × 2.5 × 0.7 cm) and cooled down to 12 °C in an 8 m long tunnel using convective forced air. The residence time of the product in the tunnel was 23 min. After cooling, the samples were demoulded, wrapped manually with aluminium foil and transferred to a 24 ± 0.5 °C controlled temperature chamber, and kept for a period of 15 days to promote crystal network stabilisation. After this period, the bar samples were submitted to rupture tension and X-ray diffraction determinations.

Analytical procedures

Fatty acid composition

The fatty acid methyl esters (FAMES) were separated according to the AOCS Ce 2-66 method (AOCS, 2004). Methylation reaction was performed using NH_4Cl in methanol solution. In FAMES separation, saturated salt solution and petroleum ether were used according to the methodology proposed by Hartman & Lago (1973). FAMES in petroleum ether were transferred into vials and analyses were done in duplicate. Individual components were identified by comparison with commercial FAMES standards. The fatty acid composition was determined by an CGC Agilent 6850 Series GC System (Santa Clara, CA, USA) capillary gas chromatograph, with a 60 m long, 0.25 mm ID column packed with DB 23 (50% cyanopropyl-methylpolysiloxane). The chromatograph was operated under the following conditions: column flow rate of 1.00 mL min^{-1}, detector temperature 280 °C and injector temperature 250 °C. The oven temperature was programmed as follows: initial temperature 110 °C held for 5 min, then raised to 215 °C at a rate of 5 °C min^{-1} and held at 215 °C for 24 min. Helium was used as carrier gas. Qualitative composition was determined by comparing peak retention times with the respective standards for fatty acids. Quantitative composition was performed by area normalisation, expressed as mass percentage.

Triacylglycerol composition

Triacylglycerol composition was determined using an CGC Agilent 6850 Series GC System gas chromatograph, based on AOCS CE 5-86 methodology (AOCS, 2004). A 150 m length, 0.25 mm internal diameter DB 17 (50% phenyl-methylpolysiloxane) column was used with the following column temperature programme: initial temperature 250 °C, raised to a final temperature of 350 °C at a rate of 5.0 °C min^{-1} and held at 350 °C for 20 min. The detector temperature was 375 °C and the injector temperature was 360 °C. The carrier gas was helium and sample concentration was 20 mg mL^{-1} diluted in tetrahydrofurane, with at least two repetitions for each mixture. Triacylglycerol groups were identified by comparing retention times, following the procedures of Antoniosi Filho *et al.* (1995).

Solid fat content

Solid fat content (SFC) was determined by following the method AOCS Cd16b-93 (AOCS. 2004), using a Nuclear Magnetic Resonance Spectrometer (NMR) Bruker pc120 Minispec (Silberstreifen, Rheinstetten, Germany). The fat samples were previously submitted to the following sequential heating and cooling treatment using high precision dry baths (TCON 2000, Duratech, Carmel, CA, USA): heating to 100 °C and maintained at 100 °C for 15 min; cooling down to 60 °C and maintained at 60 °C for 5 min; cooling down to 0 °C and maintained at 0 °C for 90 ± 5 min; heating to 26 °C and maintained at 26 °C for 40 ± 0.5 h and cooling down to 0 °C and maintained at 0 °C for 90 ± 5 min. Solid fat content was measured at the following temperatures: 10, 20, 21.1, 25, 26.7, 30.0, 33.3 and 35 °C. Before each measurement, the sample was stabilised at the test temperature for 60 min.

X-ray diffraction

X-ray diffraction analyses of the samples were made in a Philips PW 1710 diffractometer (PANalytical, Almelo, the Netherlands), using the Bragg-Brentano (θ:2θ) geometry with Cuk α radiation, 40 kV tension and 30 mA current. In the geometry used, the beam of X-ray diffracted by the sample passes through a graphite monochromator crystal located just before the detector. All measurements were obtained at steps of 0.02 °C in 2θ and acquisition time of 2 s (Schenk & Peschar, 2004). The determinations were performed on fat samples in their crystallised solid form at an average controlled temperature of 22 °C. X-ray diffraction pattern curves were obtained for samples of cocoa butter, CBR, CBS and select mixtures with 10, 20 and 30% of CBR or CBS.

Rupture tension

A Universal TA-XT2i texturometer (Stable Micro Systems, Surrey, UK) with a three-point bend rig probe (HDP/3PB) was used to perform the snap tests on the bars. The determinations followed the methodology described by Jorge *et al.* (1999). The conditions used were as follows: distance between bar supports: 6 cm; pretest velocity: 3 mm s^{-1}; test velocity: 1.7 mm s^{-1}; posttest velocity: 10 mm s^{-1}. The rupture force applied at the centre of the bars, expressed in kg_f, was obtained from force vs. deformation graphs. Measurements were performed in a 20 ± 0.5 °C temperature-controlled room. To avoid the influence of

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variations in the thickness of the bars, the values of the force obtained in each test were divided by the cross-section area of each bar, and the rupture tension was expressed in $kg_f\ cm^{-2}$.

Statistical analysis

Precrystallisation tests were performed in duplicate. The process conditions had been optimised by means of a statistical experimental design published by Quast *et al*. (2007). X-ray diffraction assays were performed with one repetition after preliminary tests with cocoa butter indicating repeatability and reproducibility of the results. Fatty acid composition, triacylglycerol and solid fat content were made in duplicate, and the results were analysed using the Microsoft Excel software. Rupture tension was made with ten repetitions and results analysed statistically using Tukey's test ($P < 0.05$) at Statistic 5.5 (Statsoft), Tulsa, OH, USA.

Results and discussion

Chemical composition

Interrelationships among chemical composition and physical properties of cocoa butter and alternative fats exert a great influence on the quality and acceptance of chocolate and confectionery products. Sensorial attributes, shelf life and stability during storage are directly depending on chemical composition of the fat phase (Lonchampt & Hartel, 2004).

The composition in fatty acids of cocoa butter, CBR and CBS is presented in Table 1.

The values indicate that in the cocoa butter blend used, 61.26% of the total fatty acids are palmitic and stearic acids, and that oleic acid is the main monounsaturated fatty acid (33.96%). These results are in agreement with the range of values presented by Lipp *et al*. (2001), who analysed samples of forty two different countries.

The CBR sample showed a high palmitic acid content (52.87%), followed by oleic acid (32.3%), values that are characteristic of palm-based lipids (O'Brien, 2009). The total *trans* fatty acids content in the sample was 4.46%, a value that might demand precise label information concerning nutritional issues (Ribeiro *et al*., 2007; Dhaka *et al*., 2011).

As expected, the CBS contained the largest amount of short-chain fatty acids with lauric and myristic acids, representing 53.66% of the total. In addition, the CBS sample has a high content of saturated fatty acids (99.42%), which indicates that it has lower reactivity to oxidation and a higher melting point. Although CBS and cocoa butter show some similarities in their physical properties, the high lauric acid content (40.06%) has a tendency to promote chemical incompatibilities (Lipp *et al*., 2001). As a consequence, some blend compositions have lower melting points than expected from the linear interpolation between the melting temperatures of the pure component, characterising an eutectic situation (Timms, 1980). Table 2 presents the triacylglycerol composition of cocoa butter, CBR and CBS samples.

The triacylglycerols found in the cocoa butter sample have carbon number between 50 and 54. The values in Table 2 indicate that the main triacylglycerols found in cocoa butter were POS, SOS and POP, making up to 78.2% of the total, in accordance with literature information, which indicates a range of 75–85% for these compounds (Norberg, 2006). These triacylglycerol species are symmetrical in terms of saturated/unsaturated fatty acid substitutions and are responsible for the well-defined crystallisation patterns of cocoa butter. Foubert *et al*. (2004) evaluated the

Table 1 Fatty acid composition (%) of cocoa butter, CBR and CBS samples

Fatty acid (%)	Designation	Cocoa butter	CBR	CBS
Caprylic and capric	C8:0 and C10:0	–	–	5.79 ± 0.06
Lauric	C12:0	–	0.63 ± 0.007	40.06 ± 0.21
Myristic	C14:0	0.08 ± 0.00	1.09 ± 0.007	13.60 ± 0.035
Palmitic	C16:0	25.90 ± 0.042	52.87 ± 0.084	13.00 ± 0.084
Stearic	C18:0	35.36 ± 0.042	6.26 ± 0.007	26.68 ± 0.083
Oleic	C18:1 *trans*	–	4.22 ± 0.007	–
Oleic	C18:1	33.96 ± 0.014	32.30 ± 0.098	0.44 ± 0.162
Linoleic	C18:2 *trans*	–	0.24 ± 0.014	–
Linoleic and linolenic	C18:2 and C18:3	3.15 ± 0.008	1.30 ± 0.0035	0.14 ± 0.06
Arachidic	C20:0	1.23 ± 0.00	0.52 ± 0.00	0.29 ± 0
Behenic and lignoceric	C22:0 and C24:0	0.32 ± 0.001	0.57 ± 0.007	–
Σ Saturated		62.89	61.94	99.42
Σ Monounsaturated		33.96	36.52	0.44
Σ Polyunsaturated		3.15	1.54	0.14

–, not detected.

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Table 2 Triacylglycerol (TAG) composition of cocoa butter, CBS and CBR samples

Number of carbons	TAG	Cocoa butter	CBS	CBR
C30	CyCLa	–	0.54 ± 0.049	–
C32	CyLaLa	–	4.07 ± 0.233	–
C34	CLaLa	–	4.78 ± 0.141	–
C36	LaLaLa	–	14.2 ± 0.353	–
C38	LaLaM	–	5.51 ± 1.046	–
	CyOLa	–	8.33 ± 0.912	–
C40	LaLaP	–	14.1 ± 0.466	–
C42	LaMP	–	20.4 ± 0.707	–
C44	LaMS	–	11.48 ± 0.388	–
	LaOP		8.15 ± 0.353	–
C46	MPP	–	–	0.84 ± 0.007
	LaSS	–	6.98 ± 0.035	–
C48	PPP	–	–	3.3 ± 0.021
	MPO	–	–	1.8 ± 0.08
	MSS	–	1.53 ± 0.106	–
C50	POP	15.8 ± 0.155	–	–
	PLiP	4.63 ± 0.304	–	–
	PPS	–	–	75.0 ± 2.28
	PPO + PPL	–	–	1.11 ± 0.07
C52	POS	40.1 ± 0.445	–	–
	POO	8.61 ± 1.435	–	–
	PSS	–	–	9.13 ± 2.163
	PSO + POL	–	–	6.44 ± 0.403
C54	SOS	22.3 ± 0.700	–	–
	SOO	8.54 ± 0.438	–	–
	POA + SOO + OOO	–	–	2.36 ± 0.141

Cy, caprylic acid; C, capric acid; La, lauric acid; M, myristic acid; P, palmitic acid; S, stearic acid; O, oleic acid; L, linoleic acid; Li, linolenic acid; –, not detected.

triacylglycerol composition of cocoa butter samples of twenty-three different origin and found that the product from Brazil had the lowest amount of POS, which was 38.7%. This same trend was reported by Lipp & Anklam (1998), who obtained a value of 34.6% for POS in cocoa butter from Bahia. The value found in the present study is higher (40.1% of POS) due to the blend with the harder Indonesian butter (Ribeiro *et al*., 2012). The main asymmetrical triacylglycerols were the POO and SOO species. The levels of triacylglycerols disaturated-monounsaturated and monounsaturated-diunsaturated found in the cocoa butter blend summed up to 82.83 and 17.15%, respectively. There were no triacylglycerols trisaturated and triunsaturated in this raw material.

The values in Table 2 confirm that the triacylglycerols in CBS have a shorter carbon chain than those of the triacylglycerols in cocoa butter and in CBR sample. Each of the C36, C38 and C40 species in the CBS sample presented similar values, around 14%, and represent 42% of the total triacylglycerols. According to Lipp & Anklam (1998), CBS-type fats contain mainly triacylglycerols of the type LaLaLa, LaLaM and LaMM. In the present study, the triacylglycerols in higher percentage in the CBS sample were LaMP, LaLaLa and LaLaP. The results show that in the CBS and CBR samples, the trisaturated triacylglycerol was the predominant class, accounting for 83.61 and 88.27% of the total composition, respectively. PPS content was the highest, 75%, indicating, in this case, a large amount of palmitic acid, originated from palm oil. The CBR sample contained triacylglycerols with carbon number between 46 and 54, indicating a strong similarity with the chemical composition of cocoa butter.

Precrystallisation behaviour

Figure 1a, and 1b presents the temperature variation measured during the precrystallisation of the mixtures of cocoa butter with CBR and with CBS, respectively. For the purpose of comparison, a precrystallisation curve of pure cocoa butter is also shown in each figure.

The first 10 °C decay in temperature is faster, because until a temperature around 30–32 °C, no fat unstable nuclei crystal is formed and only the removal of sensible heat occurs. The final rate of approach to the tempering temperature is reduced because the viscosity of the system increases and in addition to the

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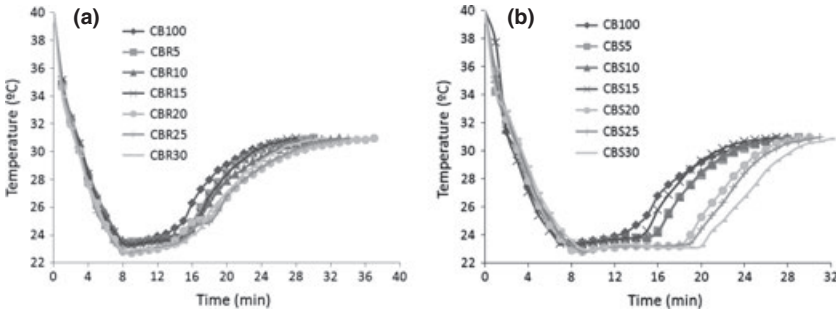

Figure 1 Temperature variation during tempering of cocoa butter (CB100) and the mixtures: (a) with cocoa butter replacer (CBR) and (b) with cocoa butter substitute (CBS).

sensible heat, the heat of crystallisation has also to be removed.

The behaviour of cocoa butter during the precrystallisation remained virtually unchanged with the incorporation of CBR, at the evaluated addition levels. In the reheating stage of the mixtures containing CBS, mainly in the proportions of 20, 25 and 30%, a deviation from the precrystallisation behaviour of pure cocoa butter can be observed. This effect can be directly associated with the chain size of the predominant triacylglycerols in the samples, which have great influence on the crystallisation kinetics of lipid systems. In general, the rate of molecular packing and solidification in a fat mixture increases with the similarity in size of the acyl groups in triacylglycerol molecules (Himawan *et al.*, 2006). The CBR fat used in this study showed a predominance of triacylglycerol species with 50 carbons (Table 2) close to the composition of cocoa butter, in which the predominant triacylglycerols were POS and SOS, with numbers of carbon, equal to respectively, 52 and 54. On the other end, for CBS fat, the number of carbons of the main triacylglycerol molecules was between 36 and 44, featuring triacylglycerol species of lower melting point (Ghotra *et al.*, 2002). The CBR and CBS fats presented mostly trisaturated triacylglycerols, with very similar concentrations. Therefore, one can conclude that the different behaviour of the mixtures with CBS regarding the precrystallisation requirements results mainly from the interference of the chain size of the triacylglycerols demanding more effective crystallisation conditions accordingly to the increase in the proportion of this alternative fat.

Solid fat content

Solid fat content (SFC) is a parameter that expresses the solid/liquid mass relation of a fat at different temperatures, affecting physical properties like consistency and stability and also important sensorial attributes. The solid fat content curve provides indications on technological performance of cocoa butter and its mixtures with alternative fats. SFC between 20 and 25 °C qualifies the cocoa butter hardness. The temperature range in which an expressive decline in SFC is evident represents the heating resistance, while the fast melting between 32 and 35 °C is responsible for cooling and creaminess sensation during tasting. One of the more important and practical parameter used in the industry for evaluating cocoa butter quality is the difference between the SFC at 25 and 35 °C (named ΔS). The presence of solid fat at temperatures above 35 °C is recognised as a waxy feeling and is easily detected during tasting. So, in order for the mixtures to be used in chocolate manufacturing, they should be hard and brittle at room temperature (SFC higher than 50% at 25 °C) and present adequate melting properties at mouth temperature (high ΔS value) and no waxy residual (no SFC above 35 °C) (Ribeiro *et al.*, 2012).

Figure 2a presents the solid fat content (SFC) of cocoa butter, CBR and their mixtures, and Fig. 2b shows the solid fat content of cocoa butter, CBS and their mixtures.

The SFC of the cocoa butter sample is 81.90% at 10 °C, with complete melting at 35 °C, a characteristic behaviour of this material. The curve for CBR100, with solid fat detected at temperatures above 35 °C, represents a typical profile of CBR fats, often with high levels of trisaturated triacylglycerols (Beckett, 2008).

The curves in Fig. 2a indicate that for mixtures containing CBR, the curves of solids are very close to the solids curve of pure cocoa butter in the temperature range of 10–27 °C. At 30 °C, however, the samples with 25 and 30% of CBR are totally melted. The other mixtures with CBR had a similar behaviour and are also completely melted at 35 °C.

Considering the melting behaviour requirements for chocolates, the results suggest no unpleasant fat residual sensation in the mouth if up to 30% CBR were used in the formulation of chocolates. At 25 °C, SFC values of the mixtures with CBR ranged between 57.90

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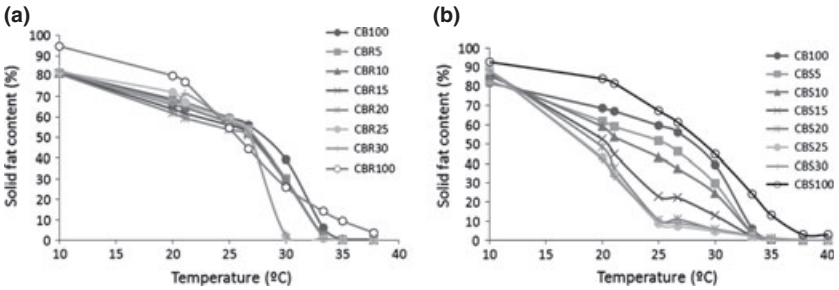

Figure 2 Solid fat content of pure cocoa butter (CB100) and: (a) pure cocoa butter replacer (CBR) (CBR100) and mixtures; (b) pure cocoa butter substitute (CBS) (CBS100) and mixtures.

and 59.20%, while for pure cocoa butter the SFC was 59.70%.

The mixtures with CBS revealed a different behaviour. Although the SFC curve of the pure CBS sample lies above that of cocoa butter at all evaluated temperatures, the addition of a percentage as low as 5% of CBS to cocoa butter resulted in a marked reduction in the solids content. As the amount of CBS increases, the reduction of solids content becomes more evident. At 25 °C, SFC values of the mixtures with CBS ranged between 10.50 and 51.80%, inconsistent, therefore, with the characteristics of hardness required for the application of these mixtures in chocolate. This confirms the existence of chemical incompatibilities between the components of the CBS fat and of cocoa butter, leading to the formation of eutectic effects, which shift the phase change region and cause the mixtures to become softer (Norberg, 2006).

The eutectic behaviour between cocoa butter and CBS can be more clearly observed when the curves are redrawn, as in Fig. 3, where the solid fat content is plotted against the percentage of CBS in the mixture at different temperatures.

Lines of constant temperature with a negative slope correspond to the formation of an eutectic system, which results in liquefaction of the mixture at specific compositions, anticipating problems in the application of these fats when the consistency and solid fat content are important (Himawan *et al.*, 2006). According to Liang *et al.* (2003), under certain circumstances, groups of triacylglycerols with short and medium chains, with smaller molecular volume and carbon numbers between 28 and 48, can behave as isolated entities, acting as solvent for solid phases composed of triacylglycerols with higher carbon numbers. This effect is directly associated with the decrease in the SFC values of cocoa butter as a result of incorporation of CBS, as shown in Fig. 2b.

Hassan & Megahed (1998) studied the behaviour of mixtures of cocoa butter with three different fats (5, 10 and 15%): two of lauric origin (Cebes and Nchox) and one nonlauric fat (lilexao). The authors also observed

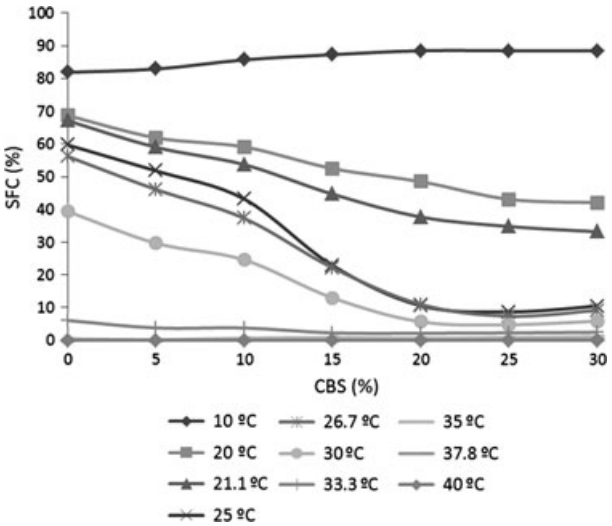

Figure 3 Binary diagram of mixtures of cocoa butter with cocoa butter substitute (CBS).

that in the case of the lauric fats, an addition of just 5% to cocoa butter promoted a significant reduction of the solids content at 25 °C. The lilexao fat showed a profile more similar to the solids curve of cocoa butter and was recommended to partially replace cocoa butter in the manufacture of chocolates for warmer climates.

X-ray diffraction

Polymorphism can be defined as the ability of a substance to exist as two or more crystalline phases that have different melting points. For cocoa butter, six polymorphic forms are verified as result of its fairly homogeneous triacylglycerol composition, known as γ (or I), α (or II), β′III, β′IV, βV and βVI, in accordance with current nomenclature (McGauley & Marangoni, 2002). Forms I and II are obtained by fast cooling to low temperatures, while forms β′III and β′IV are produced at moderate temperatures. Form βV

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is associated with the desirable stable crystalline habit in chocolate. The crystalline modifications in cocoa butter, with exception of form βVI, can be obtained directly from the liquid state, under proper cooling conditions. The transition V → VI is mediated only by solid-solid transformation and proceeds during the storage of chocolates (Loisel *et al*., 1998; Schenk & Peschar, 2004; Shi *et al*., 2005).

The X-ray patterns obtained for the cocoa butter and some selected mixtures with CBR and CBS fats are shown in Fig. 4. Table 3 presents the calculated *short spacings* and corresponding polymorphic forms for these samples.

Pure cocoa butter and samples CBR10, CBR20, CBR30, CBS10, CBS20 and CBS30 were presented as form V, whose characteristic *short spacings* are 3.65, 3.73, 3.87, 3.98, 4.22, 4.58, 5.13 and 5.38 Å (McGauley & Marangoni, 2002). The set of these diffraction lines is known as fingerprint region, being specific for each polymorph (Schenk & Peschar, 2004). This indicates that the conditions of tempering used were adequate for the formation of this required type of crystal habit. Keller *et al*. (1996) and Marangoni & Narine (2002) also identified the βV crystalline form by means of X-ray diffraction. Marangoni & Narine (2002) analysed cocoa butter that was crystallised at 22 °C and stored for a period of 20 days.

The CBR fat sample presented two peaks of strong intensity at 4.2 and 3.8 Å, which correspond to the occurrence of the β′ polymorph, as well as a low-intensity peak at 4.6 Å, which is associated with the presence of the β polymorph, as a result of its low diversity of fatty acid composition and relatively homogeneous triacylglycerol composition. However, due to the low magnitude of the peak 4.6 Å, this fat can be classified exclusively by the polymorphic habit β′, which corresponds to the crystalline form of its predominant triacylglycerol PPS (75%) (Ghotra *et al*., 2002). The CBS fat, in turn, was characterised only by the polymorph β′. The results obtained by X-ray

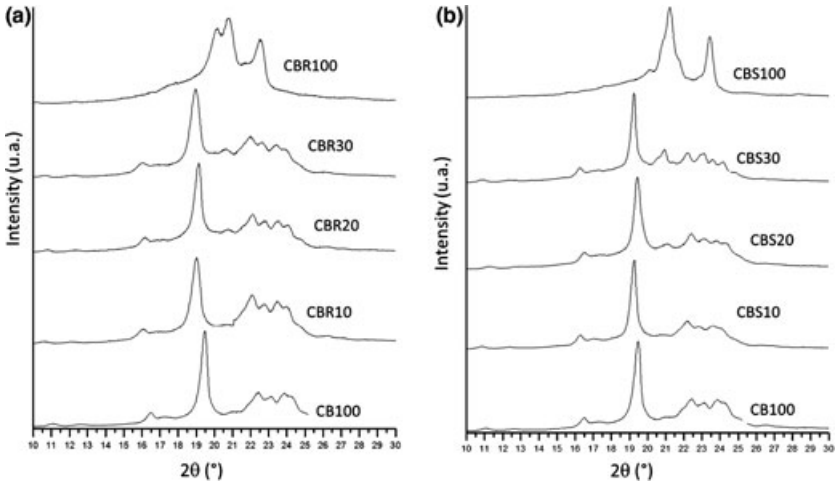

Figure 4 X-ray diffraction curves of cocoa butter (CB100) and: (a) Cocoa butter replacer (CBR) and their mixtures; (b) Cocoa butter substitute (CBS) and their mixtures.

Table 3 Polymorphic forms and short spacings of cocoa butter and mixtures with CBR and CBS

Sample	Short Spacings* (Å)								Polymorphic habit
	5.4	5.1	4.6	4.2	4.0	3.8	3.7	3.6	
CB100	5.42 (m)	5.13 (vw)	4.62 (vs)	4.24 (w)	4.01 (s)	3.87 (s)	3.78 (s)	3.67 (s)	βV
CBR10	5.44 (m)	5.13 (vw)	4.60 (vs)	4.21 (w)	4.00 (s)	3.80 (s)	3.77 (s)	3.66 (s)	βV
CBR20	5.42 (m)	5.12 (vw)	4.65 (vs)	4.22 (w)	4.00 (s)	3.86 (s)	3.78 (s)	3.65 (s)	βV
CBR30	5.42 (m)	5.11 (vw)	4.63 (vs)	4.22 (w)	4.05 (s)	3.84 (s)	3.78 (s)	3.66 (s)	βV
CBR100			4.61 (m)	4.20 (s)		3.81 (vs)			β′ ≫ β
CBS10	5.44 (m)	5.13 (vw)	4.63 (vs)	4.24 (w)	4.00 (s)	3.87 (s)	3.78 (s)	3.65 (s)	βV
CBS20	5.43 (m)	5.11 (vw)	4.62 (vs)	4.22 (w)	4.03 (s)	3.82 (s)	3.77 (s)	3.66 (s)	βV
CBS30	5.40 (m)	5.13 (vw)	4.62 (vs)	4.20 (w)	4.05 (s)	3.84 (s)	3.78 (s)	3.66 (s)	βV
CBS100				4.22 (vs)		3.83 (vs)			β′

*Intensities: v, very; w, weak; m, medium; s, strong.

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Table 4 Rupture tension ($kg_f\ cm^{-2}$) and breaking force (N) of bars

Sample	Snap ($kg_f\ cm^{-2}$)	Snap (N)	Sample	Snap ($kg_f\ cm^{-2}$)	Snap (N)
CB 100	2.48^{ab}	50.28	CB 100	2.48^{a}	50.28
CBR 5	2.60^{a}	53.44	CBS 5	2.14^{b}	44.97
CBR 10	2.33^{abc}	39.41	CBS 10	1.75^{c}	35.86
CBR 15	2.23^{bc}	42.77	CBS 15	1.43^{d}	29.01
CBR 20	2.06^{cd}	31.68	CBS 20	0.79^{e}	16.28
CBR 25	2.00^{cd}	39.81	CBS 25	0.52^{f}	11.56
CBR 30	1.81^{d}	38.02	CBS 30	0.39^{f}	8.45

Means followed by the same letter within a column indicate no significant difference ($P < 0.05$) by Tukey's test.

diffraction for CBR and CBS fats confirm, therefore, that these fats crystallise in β′ polymorphic form and do not require the tempering process.

The mixture of CBR and CBS with cocoa butter, in the proportion used in this study, did not influence its polymorphic habit, obtained as a result of the precrystallisation process. Although the pure CBR and CBS samples are characterised by the polymorph β′, which is inadequate for stable chocolates, these alternative fats showed no influence on the crystal structuration of cocoa butter. This result also demonstrates the effectiveness of the precrystallisation process used to obtain the actual polymorphic habit of interest in the production of chocolates.

Mechanical resistance

Table 4 shows the rupture tension and breaking force of bars of bars made with mixtures of cocoa butter and CBR and CBS. The results were analysed statistically using the Tukey's test at 95% confidence. Different letters show significant statistically difference.

The average rupture tension of 100% cocoa butter samples bars was 2.48 $kg_f\ cm^{-2}$. Although the composition of fatty acids and triacylglycerols of cocoa butter and CBR show differences, a proper compatibility between these fats after the tempering process can be observed, because the addition of up to 15% CBR did not significantly interfered in the values of rupture tension when compared with 100% cocoa butter. Addition of 20, 25 and 30% CBR to cocoa butter showed decreasing snap values. Table 4 shows that the addition of CBS in cocoa butter causes a significant lowering of the snap value. With 10% of CBS, the snap value (1.75 $kg_f\ cm^{-2}$) is already lower than that of the mixture with 30% CBR (1.81 $kg_f\ cm^{-2}$). As already pointed out during SFC results, the decrease in rupture tension of the mixtures with CBS can be attributed to the chemical incompatibility between the triacylglycerols of the fats, especially due to the high lauric fatty acid content in CBS, a component with high structural dissimilarities with the fatty acids of cocoa butter (Himawan *et al.*, 2006). In studies reported by Quast *et al.* (2011), the authors observed that the mixtures of cocoa butter with cupuassu fat showed snap values that are similar to those obtained in this study, for mixtures with CBR fat.

Conclusions

Mixtures of cocoa butter (Bahia + Indonesian blend) with CBR fat showed chemical compatibility. The solid fat content at 25 °C and the near zero SFC value at 35 °C together with the results of other determinations reassure that mixtures with up to 20% CBR fat and up to 5% CBS can be used in formulations of chocolates without significantly changing the physical properties of the final product. X-ray diffraction indicates that the tempering procedures used for crystallisation induce the formation of the desirable βV crystalline form in pure cocoa butter and their mixtures with the alternative fats. Snap values, solid fat content and X-ray diffraction determinations of the fat phase of chocolates proved to be a simple and rapid tool for the screening of valid formulations for chocolate production.

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