



Cocoa butter replacers from blends of mango seed fat extracted by supercritical carbon dioxide and palm stearin

M.H.A. Jahurul^{a,b}, I.S.M. Zaidul^{c,*}, N.A. Nik Norulaini^d, F. Sahena^a, B.Y. Kamaruzzaman^e, Kashif Ghafoor^f, A.K.M. Omar^{a,**}

^a School of Industrial Technology, Universiti Sains Malaysia, Minden, 11800 Penang, Malaysia

^b Department of Food Science and Nutrition, Faculty of Applied Sciences, UCSI University, 56000 Kuala Lumpur, Malaysia

^c Faculty of Pharmacy, International Islamic University, Kuantan Campus, 25200 Kuantan, Pahang D/M, Malaysia

^d School of Distance Education, Universiti Sains Malaysia, Minden, Penang 11800, Malaysia

^e Faculty of Science, International Islamic University, Kuantan Campus, 25200 Kuantan, Pahang D/M, Malaysia

^f Department of Food Science and Nutrition, King Saud University, Riyadh 11451, Saudi Arabia

ARTICLE INFO

Article history:

Received 28 February 2014

Received in revised form 22 June 2014

Accepted 28 June 2014

Available online 4 July 2014

Keywords:

Cocoa butter replacers

Mango by-products

Mango seed fat

Palm stearin

Physico-chemical properties

ABSTRACT

Mango seeds are waste agro-industrial by-products produced in large quantities in the tropical countries. Supercritical fluid extraction was used for the extraction of high quality mango seed fat from mango seed wastes. The supercritical fluid extracted mango seed fat (MSF) was blended with palm stearin (PS) at different ratios to obtain cocoa butter replacers (CBRs). A total of 10 blends were formulated and the fatty acid constituents and physico-chemical properties of these blends were analyzed. Four blends of MSF/PS (90/10, 85/15, 80/20 and 75/25) possessed fatty acid constituents, iodine value (41.8 to 42.4 g I₂/100 g fat), saponification value (195.7 to 195.9 mg KOH/g fat), acid value (2.4 to 2.9%) and slip melting point (37.7 to 39.9 °C) similar to those of commercial cocoa butter. Thus, these blends were considered recommendable as CBRs, due to their fatty acid constituents, iodine value, slip melting point, saponification value, and acid value consistent with cocoa butter.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Cocoa butter is a light yellow fat obtained from cocoa bean of the cocoa plant (*Theobroma cacao*). It is highly demanded by food, pharmaceuticals and cosmetic industries. Moreover, it is unique among vegetable fats due to its composition and crystallization behavior. The fatty acid composition of cocoa butter is one of the most important indicators of its chemical properties. Four major fatty acids that include palmitic acid (C_{16:0}, 24.4%), stearic acid (C_{18:0}, 33.6%), oleic acid (C_{18:1}, 37.0%) and linoleic acid (C_{18:2}, 3.4%) account for more than 98% of the total fatty acids in commercial cocoa butter (Shekarchizadeh, Kadiyar, Ghaziaskar, & Rezayat, 2009). Depending on the origin of the cocoa butter, the amounts of these fatty acids vary within narrow ranges. The properties of any kinds of fats, fat fractions or their mixtures are basically the properties of the triglyceride mixtures. Cocoa butter is the only commercially available natural fat which is rich in saturated and mono-unsaturated fatty acids that lead to symmetrical triglyceride mixtures containing 33.7–40.5% 1(3)-palmitoyl-3(1)-stearoyl-2-monoolein (POS); 23.8–31.2% 1,3-distearoyl-2-oleoylglycerol (SOS) and 13.6–

15.5% 1,3-dipalmitoyl-2-oleoyl-glycerol (POP) types (Shekarchizadeh & Kadiyar, 2012). These relatively simple triglyceride compositions of cocoa butter confers on it the melting profiles, being highly solid at 20 °C and melts between 30 and 35 °C which is appreciated by consumers as well as desirable in confectionery applications (Shukla, 1995). Moreover, the triglyceride compositions of cocoa butter are responsible for its various polymorphic crystallization forms, whereas liquid fat converts into a solid as a result of fatty acid compositions (Afoakwa, Paterson, & Fowler, 2007; Awua, 2002).

The price of cocoa butter is one of the highest among all commercial fats and oils due to low availability and high demand. Consequently, there is an intense effort by food companies to develop methods for producing cocoa butter replacers (CBRs) for emerging food markets. Mango seed fat (MSF) has the potential to provide a low-cost and high quality source of CBRs. Mango (*Mangifera indica* L.) fruit belongs to the family of *Anacardiaceae* which is grown commonly in tropical countries. Recently, it has occupied the second position as a tropical crop next only to banana in terms of production and acreage (Muchiri, Mahungu, & Gituanja, 2012). There is a good and increasing demand for mango fruit and its processed products in international market. In the industry, only the pulp of mango is used for the production of juices, fruit in syrups, jams, jellies and so on. Consequently, the huge amounts of mango seeds are discarded as agro-industrial by-product, creating both disposal and environmental problems. The mango seeds and

* Corresponding author. Tel.: +60 95704841; fax: +60 95716775.

** Corresponding author. Tel./fax: +60 46 585 435.

E-mail addresses: zaidul@ium.edu.my (I.S.M. Zaidul), akmomar@usm.my (A.K.M. Omar).

peels are major by-products of mango juice industries and represent around 60% of the total fruit. Mango seeds are considered as waste however they contain 7.3–15% fat (Dorta, González, Lobo, Sánchez-Moreno, & Ancos, 2014; Jahurul et al., 2014a; Jahurul et al., 2013). Mango seed fat is a rich source of stearic and oleic acids. This group of fats have received considerable attention due to their particular physical and chemical properties which make them very suitable for the manufacturing of confectionery products. Consequently, the lipid constituents of mango seed have drawn immense research interest due to their potential application in the confectionery industry as a source of CBRs (Ali, Gafur, Rahman, & Ahmed, 1985; Gaydou & Bouchet, 1984; Hemavathy, Prabhakar, & Sen, 1988; Lakshminarayana, Rao, & Ramalingaswamy, 1983; Rukmini & Vijayaraghavan, 1984).

According to the Malaysian Palm Oil Council (MPOC), palm stearin is obtained by fractionation of palm oil after crystallization at controlled temperatures. Consequently, palm stearin is cheaper than other palm oil products; making it a cost effective ingredient in various applications. The physical properties of palm stearin differ from those of any other palm oil product such as it has a wider range of melting points. Palm stearin is meant to be blended with softer MSF and it is the melting point of the blend that counts and not that of its components. Therefore, palm stearin was used as blending components in this study because they do not give any waxy tastes and contain no *trans* fatty acids. Moreover, these oils have low level of linoleic acid, hence not much prone to oxidation (Samsudin & Rahim, 1996). Meanwhile, the applications of palm stearin have been well reviewed by Kellens, Gibon, Hendrix, and Greyt (2007). They also reported that the palm stearin is suitable for CBRs or coating materials. The blending of MSF with palm stearin can lower the costs comparative to commercial cocoa butter, while having the desired taste of cocoa butter. Blending of solvent extracted fats from various sources has been used to obtain CBRs. However, the supercritical fluid extraction and direct blending processes may have additional advantage and can be consistent with the consumers' trend toward natural high quality products. The triglyceride compositions, thermal properties, solid fat content, and or crystal morphologies of MSF/PS blends were reported in our previous study (Jahurul et al., 2014b). In the present study, the physico-chemical properties such as fatty acids in terms of triglyceride compositions, iodine value, slip melting point, saponification value and acid value of the newly formulated (MSF/PS blends) CBRs were investigated.

2. Material and methods

2.1. Materials

Mango seed fat was extracted from waterlily mango variety using supercritical carbon dioxide (SC-CO₂) and its fatty acid constituents were described previously (Jahurul et al., 2014a). This MSF was used as a blending component along with palm stearin in this study. Palm stearin was obtained from Sime Darby Research Sdn Bhd, Malaysia. Commercial liquefied carbon dioxide (purity, 99.9%) was purchased from Malaysian Oxygen Ltd., Penang, Malaysia. The n-hexane, AR Grade (Merck, Germany), cyclohexane, glacial acetic acid, isopropanol, ethanol, potassium hydroxide, potassium iodide free from iodine or iodate AR Grade, Wijs solution for iodine number analysis (QREC, Asia Sdn Bhd), sodium thiosulfate, potassium dichromate (Bendosen, Laboratory chemicals), hydrochloric acid (HACH, Germany), starch (Bendosen, Laboratory chemicals), and phenolphthalein indicator (R & M Essen, UK) were purchased from local companies in Penang, Malaysia. The reference standard Supelco 37 component FAME mixtures (Sigma-Aldrich, Supelco, Bellefonte, Pa., U.S.A.) were used for GC analysis. The sodium methoxide used for preparing FAME was purchased from Sigma-Aldrich, USA. The BPX70 (70% cyanopropyl polysilphenylene-siloxane, 30 m in length, with a 0.25 µm film coating, 0.25 mm ID, SGE France) capillary column was used to determine the fatty acid constituents.

2.2. Supercritical fluid extraction

The soaking method of supercritical fluid extraction was carried out at a pressure of 42 MPa, at a temperature of 72 °C, and at CO₂ flow rate of 3.4 ml/min (2.926 g/min) to obtain total MSF. The CO₂ consumption was calculated according to Sahena et al. (2010). The density of CO₂ was calculated using the National Institute of Standards and Technology (NIST) according to Lemmon, McLinden, and Friend (2005). The total CO₂ consumption was 351.16 g for 2 h at 42 MPa and 72 °C. The yield of total MSF was 11.51%. Further, details of the experimental set-up of supercritical fluid extraction process were described in our previous report (Jahurul et al., 2014a).

2.3. Blending of fat

The SC-CO₂ extracted MSF was blended with palm stearin in various ratios of MSF/PS: 95/5 (blend 1), 90/10 (blend 2), 85/15 (blend 3), 80/20 (blend 4), 75/25 (blend 5), 70/30 (blend 6), 65/35 (blend 7), 60/40 (blend 8), 55/45 (blend 9), and 50/50 (blend 10) as listed in Table 1. Each blend was melted at 90 °C with the help of thermostatic water bath. The triglycerides in terms of fatty acid constituents and the physico-chemical properties of each blend were analyzed using different methods.

2.4. Analysis of fatty acid compositions of MSF/PS blends

The fatty acid profiles of the blends were quantitatively and qualitatively determined using a gas chromatography with a flame ionization detector (GC-2010 Plus + AOC-5000, Shimadzu, Osaka, Japan). The detailed procedure for fatty acid analysis is discussed in our previous report (Jahurul et al., 2014a).

2.5. Determination of physico-chemical properties

The determinations of iodine value, slip melting point (SMP), saponification value, and acid value were carried out according to methods describes by American Oil Chemists' Society (AOCS, 2003).

2.5.1. Determination of iodine value

Samples were melted at 90 °C; homogenized thoroughly and finally filtered using filter paper. Approximately 0.4 g of blend sample was taken in a 500 ml conical flask. Cyclohexane (20 ml) was added into the sample in a conical flask and then the flask was warmed slightly to dissolve the fat sample. Wijs solution (25 ml) was added to the sample solution; shaken gently; the flask was placed in the dark for 1 h to facilitate the reaction mechanism and then exactly 20 ml of potassium iodide solution and 100 ml of water were added. The resultant solution was titrated with sodium thiosulfate solution until the yellow color due to iodine has almost disappeared. The starch solution (1 to 2 ml) was added as an indicator and the titration continued until the blue color just disappeared. Three replications of the same sample were prepared

Table 1
Blending ratios (%) of SC-CO₂ extracted MSF and PS in 100 g (w/w).

Blend number	Ratios	
	MSF (%)	PS (%)
1	95	5
2	90	10
3	85	15
4	80	20
5	75	25
6	70	30
7	65	35
8	60	40
9	55	45
10	50	50

and blank tests were carried out simultaneously using the same conditions as described for the sample.

2.5.2. Determination of saponification value

The blend sample was melted (90 °C) and homogenized thoroughly and in order to remove any impurities, the homogenized sample was then filtered through filter paper. The test sample (0.005 g) was taken into a conical flask and 25 ml ethanolic potassium hydroxide solution was added. The flask was then connected to a reflux condenser and boiled for 60 min along with swirling the flask from time to time. The contents in flask were cooled and 1 ml of phenolphthalein solution was added to the sample solution as an indicator followed by titration against 0.5 N hydrochloric acid till the pink color just disappeared.

2.5.3. Determination of acid value

Determination of acid value of each blend was carried out according to AOCS (2003). Briefly, the blend sample was melted at 90 °C and weighed (5–10 g) in an Erlenmeyer flask. The neutralized solvent (ethyl alcohol, 50 ml) was added into the flask which was then placed on a hot plate. The temperature of the hot plate was regulated at 40 °C and the sample solution was titrated against sodium hydroxide, along with gentle shaking of the contents, to the first appearing permanent pink color.

2.5.4. Determination of slip melting point (SMP)

SMP was determined according to the AOCS (2003) method. Briefly, three clean capillary tubes were dipped into the test sample. The column of fat in the tubes was ca. 10 mm high and was chilled at once by holding and rolling the sample containing ends of the tubes pressed against a piece of ice, until the fat had solidified. The open ends of the fat containing tubes were not allowed to touch the ice and were wiped with the help of tissue paper immediately. The tubes were placed in a test-tube that was held in a water containing beaker and equilibrated at 10 ± 1 °C in a thermostatic water bath and held for 16 h. Capillary tubes were removed from the test tube and attached, as well as leveled, with a thermometer using a rubber band. The thermometer was immersed into a beaker containing boiled distilled water. The starting temperature of the bath was adjusted at 8–10 °C. The water bath was agitated and the temperature increased until the fat column rose in each tube at a heating rate of 1 °C per min. The temperature of the water bath was observed at which each column rises and the average for all tubes was calculated.

2.6. Statistical analysis

All the analyses in this study were carried out in triplicates. Analysis of variance (ANOVA) was used to test the differences between different

fatty acids in different blends. A $p < 0.05$ was considered to be statistically significant. The Minitab software (version 16) was used to perform the statistical analysis.

3. Results and discussion

3.1. Fatty acid compositions

Table 2 shows the fatty acid constituents of SC-CO₂ extracted mango seed fat, palm stearin and their blends, and commercial cocoa butter. Some of the gas chromatograms of recommended blends, for examples are shown in Fig. 1. The fatty acid constituents in the MSF/PS blends were significantly affected by the ratios of blends. The amounts of certain fatty acids were also significantly ($p < 0.05$) different among blends. Mango seed fat contains both saturated and unsaturated fatty acid constituents such as palmitic (7.7%), stearic (42.3%), oleic (41.4%), and linoleic acids (5.1%). On the other hand, palm stearin also has a high concentration of both saturated and unsaturated fatty acid constituents of palmitic acid, oleic acid, and linoleic acid at 58.3%, 29.4% and 5.9%, respectively. Blending of mango seed fat with palm stearin in ratios of 90:10 (MSF/PS, blend 2) and 70:30 (MSF/PS, blend 6) resulted in significant increases in the C_{16:0} contents from 16.7 to 26.6%, whereas the contents of C_{18:0} and C_{18:1} were diluted from 36.0 to 28.3% and 39.3 to 37.1%. On the other hand, C_{18:2} constituents increased from 5.1 to 5.3% within the same blends. The modifications of the fatty acid constituents observed in this study were due to the dilution and solubilization of the fatty acids in blends of two fats from different sources i.e. mango seed fat and palm stearin. Our findings are in line with the findings of Anwar, Hussain, Iqbal, and Bhanger (2007), Mariod, Matthaus, Eichner, and Hussain (2005), Ramadan and Wahdan (2012) and Zaidul, Norulaini, Omar, and Smith (2007), who also reported the modifications in fatty acid constituent concentration after blending fats from different sources.

In all blends prepared in this study, the amounts of shorter chain saturated fatty acids (C_{12:0} and C_{14:0}) decreased to a small extent with mango seed fat in the fat mixtures. On the other hand, the amounts of longer chain saturated fatty acids such as C_{20:0} and C_{22:0} increased slightly with mango seed fat. These changes in fatty acid composition are the results of different ratios of each constituent in the blends. Similar amounts of saturated shorter and longer chain fatty acids compared to the commercial cocoa butter were found in all blends. Simultaneously, the longer chain fatty acids such as C_{16:0}, C_{18:0}, and C_{18:1} were also found closer to those of commercial cocoa butter and this trend was observed in blends containing 65 to 90% MSF. The total amounts of these three fatty acids in blends containing 65 to 90% MSF ranged from 91.7 to 92.0% which was closed to the contents of these three fatty acids in commercial cocoa butter (95.6%). It can be clearly observed from data

Table 2

Fatty acid compositions (area %) of SC-CO₂ extracted MSF and PS blends at various ratios of 5 to 50% of PS, and commercial CB^b.

Blend number	Fatty acid composition								
	C ₁₂	C ₁₄	C ₁₆	C _{18:0}	C _{18:1}	C _{18:2}	C _{18:3}	C ₂₀	C ₂₂
1	Trace	0.13	11.35 ± 0.01	39.98 ± 0.01	40.61 ± 0.02	5.02 ± 0.02	0.53	1.73	0.36
2	0.05	0.28	16.72 ± 0.01	35.99 ± 0.01	39.27 ± 0.01	5.06 ± 0.01	0.50	1.53	0.31
3	0.05	0.32	18.34 ± 0.01	34.61 ± 0.01	39.02 ± 0.02	5.14 ± 0.01	0.48	1.49	0.30
4	0.05	0.38	21.03 ± 0.03	32.42 ± 0.03	38.24 ± 0.04	5.21 ± 0.01	0.44	1.45 ± 0.01	0.30
5	0.06	0.46 ± 0.01	23.45 ± 0.01	30.59 ± 0.02	37.89 ± 0.01	5.27 ± 0.01	0.42	1.36	0.27
6	0.07	0.53	26.56 ± 0.02	28.26 ± 0.01	37.14 ± 0.01	5.33 ± 0.01	0.41	1.25	0.24
7	0.08	0.60	29.13 ± 0.03	26.57 ± 0.02	36.22 ± 0.01	5.49 ± 0.01	0.36	1.16	0.22
8	0.08	0.62	31.84 ± 0.01	24.06 ± 0.01	36.09 ± 0.01	5.40 ± 0.01	0.36 ± 0.01	1.12	0.22
9	0.09	0.69	33.70 ± 0.01	22.78 ± 0.01	35.53 ± 0.06	5.45 ± 0.02	0.32	1.05 ± 0.01	0.22
10	0.10	0.75	36.33 ± 0.1	20.68 ± 0.01	34.99 ± 0.02	5.53 ± 0.01	0.30	0.96	0.19
MSF	0.01	0.05	7.71	42.27	41.41	5.09	0.62	1.78	0.38
PS	0.17	1.28	58.29	4.49	29.38	5.94	0.33	0.06	0.06
CB	Trace	0.7	25.2	35.2	35.2	3.2	0.2	1.2	0.2

^a Mean value ± standard deviation of three replications.

^b Kheiri (1982), Pease (1985), Lipp and Anklam (1998).

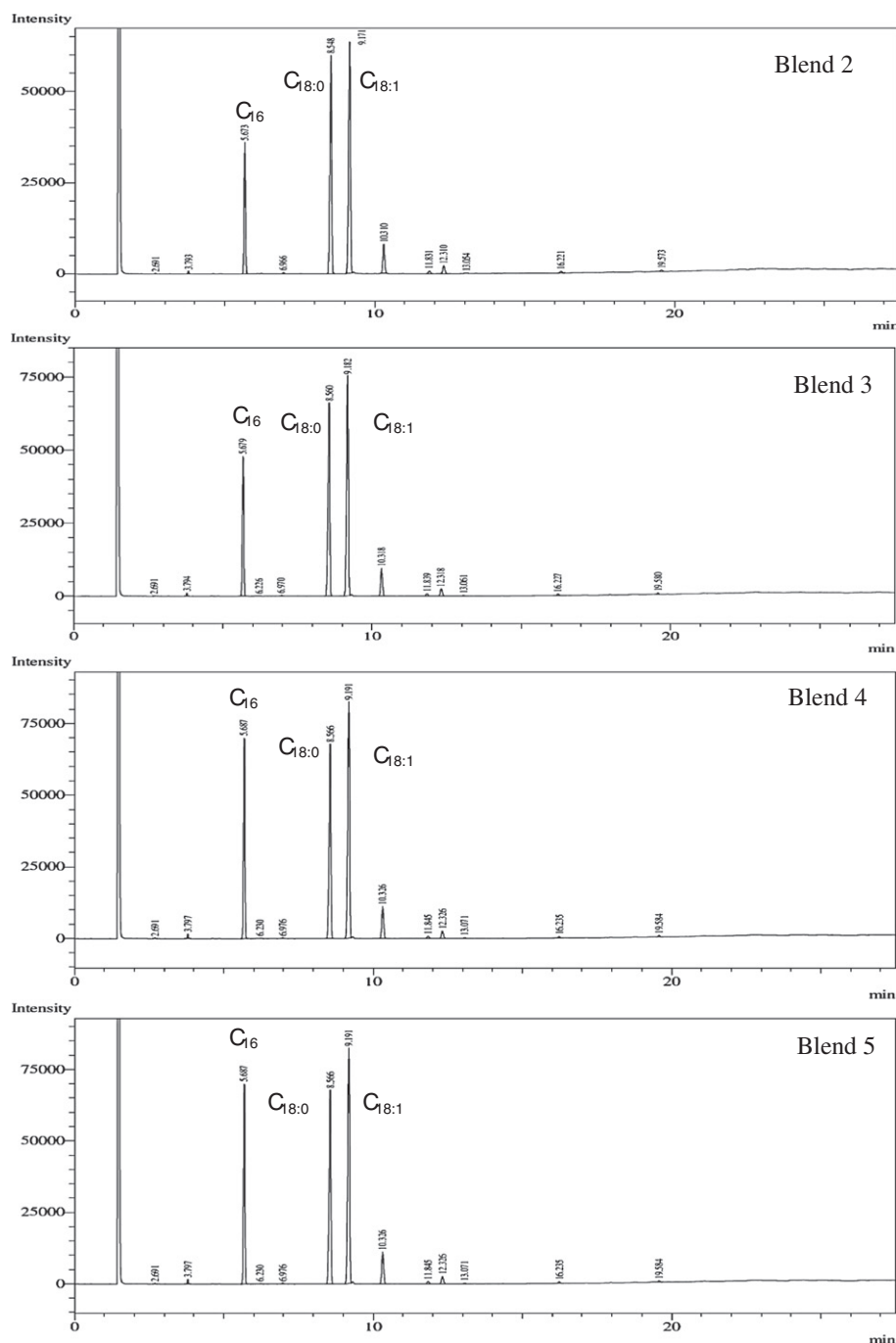


Fig. 1. GC chromatogram of fatty acid methyl esters of MSF and palm stearin blends (blends 2 to 5).

presented in Table 2 that the fatty acid compositions of blends 2 to 7 were more comparable in the contents of $C_{16:0}$, $C_{18:0}$ and $C_{18:1}$, with those of commercial cocoa butter. Moreover, the stearic and oleic acids were higher in the blends containing 90 to 95% of MSF. These blends can be defined as hard butter as they retained high level of stearic and oleic acids. The effects on triglyceride compositions, thermal properties, solid fat content, and crystal morphology of the same blends were studied and reported previously (Jahurul et al., 2014b) where it was observed that such blends can be utilized by chocolate manufacturers in tropical countries. Sonwai, Kaphueakngam, and Flood (2012) also investigated the fatty acids in different blends of MSF and palm oil mid-fraction (POMF) at various ratios to obtain cocoa butter equivalent (CBE) and reported that fatty acid profiles of certain blends were similar to those of commercial cocoa butter. The fatty acid constituents

obtained in blends 2 to 5 (Table 2) were more closer to commercial cocoa butter than those reported by Sonwai et al. (2012).

3.2. Physico-chemical properties

Table 3 shows the physico-chemical properties such as iodine value, SMP, saponification value and acid value of blends of MSF/PS and commercial cocoa butter.

3.2.1. Iodine value

Table 3 also shows the iodine value for all blends when mango seed fat and palm stearin were used as blending components. The values ranged from 40.3 to 42.7 g I_2 /100 g fat. The differences in iodine value among the blends were small; however, when compared with those

Table 3

Iodine value (Iv), slip melting point (SMP), saponification value (Spv), and acid value (Av) determined (referred to SC-CO₂ extracted MSF and PS as blending components according to the blending ratios in Table 1) for all blends and commercial CB.

Blend number	Iv (g I ₂ /100 g fat)	SMP (°C)	Spv (mg KOH/g fat)	Av (%)
1	42.7 ± 1.01	36.9 ± 0.45	195.6 ± 0.08	3.1 ± 0.19
2	42.4 ± 0.71	37.7 ± 0.22	195.7 ± 1.0	2.9 ± 0.09
3	42.2 ± 0.42	38.4 ± 0.45	195.7 ± 0.34	2.7 ± 0.23
4	41.9 ± 0.81	39.2 ± 0.32	195.8 ± 0.51	2.5 ± 0.07
5	41.8 ± 1.0	39.9 ± 0.09	195.9 ± 0.09	2.4 ± 0.21
6	41.5 ± 0.53	40.7 ± 0.16	195.9 ± 0.33	2.1 ± 0.11
7	41.1 ± 0.61	41.4 ± 0.29	196.0 ± 0.29	1.8 ± 0.08
8	40.8 ± 1.0	42.2 ± 0.41	196.0 ± 0.41	1.6 ± 0.15
9	40.5 ± 0.69	42.9 ± 0.33	196.1 ± 0.08	1.4 ± 0.26
10	40.3 ± 0.52	43.7 ± 0.08	196.2 ± 0.21	1.1 ± 0.05
MSF	42.9 ± 1.09	36.2 ± 0.11	195.5 ± 0.07	3.23 ± 0.10
PS	38.15 ± 1.03	51.2 ± 0.31	197.2 ± 0.27	0.04
CB	37.9 ^a	35.0 ^b	193.5–196.7 ^a	0.4–3.1 ^a

Mean value ± standard deviation of three replications.

^a Chaiseri and Dimick (1989).

^b Kheiri (1982).

of cocoa butter, iodine values for all blends were similar. The iodine value of blend 1 (MSF/PS, 95/5) was higher, while it was lower in blend 10 (MSF/PS, 50/50). The higher iodine value found in blend 1 containing 95% mango seed fat can be attributed to higher amounts of saturated fatty acids, particularly C_{18:0} constituent in blend 1. Depending on the unsaturation, mango seed fat exhibited the highest iodine value (42.9 g I₂/100 g fat), while the iodine value of palm stearin was the lowest with a small extent (38.1 g I₂/100 g fat). This indicates that the palm stearin is harder than mango seed fat. It is also understandable that the increasing palm stearin in fat mixtures can result in the gradual decrease of iodine value, the reason being lesser unsaturation of palm stearin than mango seed fat. Increase or decrease in the amounts of palm stearin and mango seed fat in fat mixtures affects the unsaturated fatty acids and thereby increased or decreased double bonds of the fats in the mixtures. The iodine value of mixtures became closer to that of commercial cocoa butter when the relative amount of MSF was decreased. The iodine value of blends containing 50 to 80% MSF was the closest to that of commercial cocoa butter. Although the iodine value for blends containing 85 to 95% MSF was slightly higher than that of commercial cocoa butter, they can still be regarded as acceptable.

Iodine values have a great impact on quality of fats and oils. It is useful for determining the degree of hardness of any kind of fats. The higher iodine values indicate higher contents of unsaturated fatty acids which contribute to the softness in cocoa butter. The iodine value ranged from 42.0 to 42.3 as reported by Sonwai et al. (2012), who blended mango kernel fat from Kaew mango variety with palm oil mid-fraction (POMF) to produce CBE. They claimed that the iodine values of certain blends were similar to those of commercial cocoa butter. Chaiseri and Dimick (1989) compared cocoa butter from various origins for hardness and found different iodine values ranging from 34.40 to 38.65 (g I₂/100 g fat). They reported significantly higher iodine values in Peruvian cocoa butter (37.94), followed by Brazilian cocoa butter (37.46) and Nigerian cocoa butter (37.33), respectively. In the same study, on the other hand, lower iodine values were also reported in Bolivian cocoa butter (36.01) followed by Mexican cocoa butter (35.79), Ivory Coastarian cocoa butter (35.54), and Malaysian cocoa butter (34.74). They also stated that cocoa butter with higher iodine value is softer than that one with lower iodine value. Results obtained in the present study were in good agreement with the results reported by Chaiseri and Dimick (1989), Zaidul et al. (2007) and Sonwai et al. (2012).

3.2.2. Slip/sharp melting point

The SMP for all blends, mango seed fat, palm stearin and commercial cocoa butter is shown in Table 3. In the case of all blends, it ranged from

36.9 to 43.7 °C which was closest to that of commercial cocoa butter. Variations of SMP to a small extent were observed among the blends which are due to the different blending ratios of the components that contain different unsaturations. Moreover, both unsaturated and short chain fatty acids were presumably the key factors for causing SMP variations in blends. The SMP of palm stearin (51.2 °C) exhibited higher than the SMP of pure mango seed fat (36.2 °C). On the other hand, the SMP of mango seed fat was almost similar to that of commercial cocoa butter (35.0 °C). A higher SMP (43.7 °C) was found in blend 10, and it was because of the higher amount of palm stearin (50%) used in blend 10. On the contrary, lower SMP found in blend 1 (36.9 °C) could be due to 5% palm stearin used in the blend being the lowest palm stearin amount among all blends. Table 3 also reveals that the SMP decreased with the decrease in palm stearin ratio in the blends. Although slightly lower and higher SMPs were obtained among the blends, they were almost closer to those of commercial cocoa butter. As shown in Table 3, blends no. 1 to 6 were found to be the best blends in terms of SMP when compared with commercial cocoa butter.

Blending of solvent extracted mango seed kernel fat with POMF was studied by Sonwai et al. (2012) and reported that SMP ranged from 29.3 to 33.2 °C. The authors claimed that the SMP for all blends resembled that of commercial cocoa butter. Our findings were consistent and closer than those reported by Sonwai et al. (2012) to those of commercial cocoa butter. At room temperature, cocoa butter is hard and brittle and its hardness is directly related to SMP. Thus, the SMP of good quality CBRs should be closer to the SMP of commercial cocoa butter. More than 80% commercial cocoa butter melts between 27 and 35 °C reflecting that commercial cocoa butter has a relatively short melting temperature range. These physical properties are unique to cocoa butter and are very desirable. Cocoa butter products and in particular chocolate products have all the mechanical properties such as snap, brittleness, hardness and stickiness and so on. Commercial cocoa butter melts sharply just below the body temperature leaving no greasy film or sensation on the palate at ambient temperature (Kheiri, 1982, 1985). Increasing PS in the blends can result in a gradual increase of SMP.

3.2.3. Saponification value

The results of saponification value obtained from all blends are shown in Table 3. The values ranged from as low as 195.6 mg KOH/g fat for blend 1 (MSF/PS, 95/5) to as high as 196.2 (mg KOH/g fat) for blend 10 (MSF/PS, 50/50). The results of all blends varied within a narrow range due to the fact that the saponification values of pure mango seed fat and palm stearin were quite close to each other. The saponification values of most of the blends were observed to be closer to those of commercial cocoa butter. The data in Table 3 reveals that values became more closer to those of commercial cocoa butter when palm stearin was increased in the blends. An increase in mango seed fat ratio in blends resulted in a small decrease in saponification values and similar pattern was observed for all MSF/PS blends.

Manifie (1999) reported that the saponification value of commercial cocoa butter ranged from 191 to 198 mg KOH/g fat. In another study, Chaiseri and Dimick (1989) also reported the saponification values (193.58–196.71 mg KOH/g fat) for commercial cocoa butter obtained from different countries. In their study, significantly higher saponification value was found in Panamanian cocoa butter (196.71 mg KOH/g fat) followed by Peruvian cocoa butter (195.92 mg KOH/g fat), Ecuadorian cocoa butter (195.85 mg KOH/g fat) and Colombian cocoa butter (195.75 mg KOH/g fat). On the other hand, significantly lower saponification values were also reported in Ivory Coastarian cocoa butter (193.58 mg KOH/g fat), Nigerian cocoa butter (193.62 mg KOH/g fat), Mexican cocoa butter (193.72 mg KOH/g fat) and Malaysian cocoa butter (194.36 mg KOH/g fat). The saponification values of all blends found in this study were considered as the closest to those of saponification values of commercial cocoa butter reported by Chaiseri and Dimick (1989), and Manifie (1999).

3.2.4. Acid value

The results obtained for acid values of all blends are presented in Table 3. Acid value ranged from 1.1 to 3.1% for different blends. The determined acid values were acceptable because commercial cocoa butter is reported to have acid values of 0.42 to 3.11% (Chaiseri & Dimick, 1989). The acid value (1.1%) of blend 10 (MSF/PS, 50/50) was significantly lower than the values for other blends. Blend 1 (MSF/PS, 95/5) showed an acid value of 3.1% which was significantly higher than the rest of blends. In addition, Table 3 also shows that the acid value significantly decreased with decreasing MSF in the blends. This phenomenon can be attributed as a result of higher acid value of pure MSF than that of palm stearin. A higher acid value was reported in Peruvian cocoa butter (3.11%) followed by Malaysian cocoa butter (2.02%), and Ecuadorian cocoa butter (1.94%) (Chaiseri & Dimick, 1989). On the other hand, a lower acid value was also reported in Nigerian cocoa butter (1.21%), Panamanian and Colombian cocoa butter (1.07%). These figures were in line with the figures obtained in the present study. Acid values for all blends were found to be close to those of commercial cocoa butter.

4. Conclusions

In order to obtain good quality CBRs, MSF was blended with palm stearin at different ratios and their physico-chemical properties were investigated. A total of 10 blends were studied and those containing 90:10 (blend 2), 85:15 (blend 3), 80:20 (blend 4) and 75:25 (blend 5) respective MSF and palm stearin ratios can be recommended as CBRs. This recommendation is based on the physico-chemical properties of these blends such as fatty acid profiles, iodine value, SMP, saponification value and acid value. Although C_{16:0} constituent was a little lower and C_{18:1} constituent was a little higher in these blends as compared to commercial cocoa butter however, these constituents do not affect other properties of MSF/PS blends. Moreover, other fatty acid constituents of these blends were observed to be closer to those of commercial cocoa butter. The SMP decreases linearly with mango seed fat in the blends. The blends containing 10 to 25% palm stearin had physico-chemical properties like fatty acid profiles, iodine value, SMP, saponification value and acid value close to those of commercial cocoa butter. The blending strategy proposed and studied here is recommendable as a feasible alternative of CBRs. This study also encourages the use of MSF (obtained using supercritical CO₂) and palm stearin in CBR formulation.

Acknowledgments

The authors wish to acknowledge the University Postgraduate Research Grant Scheme (PRGS, No. 1001/PTEKIND/845026) for the financial support and Universiti Sains Malaysia (PRGS, No. 1001/PTEKIND/845026) for the fellowship provided to M.J.H.A.

References

Afoakwa, E. O., Paterson, A., & Fowler, M. (2007). Factors influencing rheological and textural qualities in chocolate – A review. *Trends in Food Science and Technology*, 18, 290–298.

Ali, M.A., Gafur, M.A., Rahman, M. S., & Ahmed, G. M. (1985). Variations in fat content and lipid class composition in ten different mango varieties. *Journal of the American Oil Chemists' Society*, 62(3), 520–523.

Anwar, F., Hussain, A. I., Iqbal, S., & Bhanger, M. I. (2007). Enhancement of the oxidative stability of some vegetable oils by blending with *Moringa oleifera* oil. *Food Chemistry*, 103, 1181–1191.

AOCS (2003). *Official methods and recommended practices of the American Oil Chemists' Society* (5th ed.). Champaign, Illinois, USA: American Oil Chemists' Society (Part 1, A–C).

Awua, P. K. (2002). *Cocoa processing and chocolate manufacture in Ghana*. Essex, UK: David Jamieson and Associates Press Inc.

Chaiseri, S., & Dimick, P.S. (1989). Lipid and hardness characteristics of cocoa butters from different geographic regions. *Journal of the American Oil Chemists' Society*, 66(11), 1771–1775.

Dorta, E., González, M., Lobo, M. G., Sánchez-Moreno, C., & Ancos, B. (2014). Screening of phenolic compounds in by-product extracts from mangoes (*Mangifera indica* L.) by HPLC–ESI–QTOF–MS and multivariate analysis for use as a food ingredient. *Food Research International*, 57, 51–60.

Gaydou, E. M., & Bouchet, P. (1984). Sterols, methyl sterols, triterpene alcohols and fatty acids of the kernel fat of different Malagasy mango. *Journal of the American Oil Chemists' Society*, 61(10), 1589–1593.

Hemavathy, J., Prabhakar, J. V., & Sen, D. P. (1988). Drying and storage behaviour of mango (*Mangifera indica*) and composition of kernel fat. *Asian Food Journal*, 4, 59–63.

Jahurul, M. H. A., Zaidul, I. S. M., Norulaini, N. N. A., Sahena, F., Jaffri, J. M., & Omar, A. K. M. (2014a). Supercritical carbon dioxide (SC–CO₂) extraction and studies of mango seed kernel for cocoa butter analogy fats. *Cyta-Journal of Food*, 12(1), 97–103.

Jahurul, M. H. A., Zaidul, I. S. M., Nik Norulaini, N. A., Sahena, F., Abedin, M. Z., Mohamed, A., et al. (2014b). Hard cocoa butter replacers from mango seed fat and palm stearin. *Food Chemistry*, 154, 323–329.

Jahurul, M. H. A., Zaidul, I. S. M., Norulaini, N. N. A., Sahena, F., Jinap, S., Azmir, J., et al. (2013). Cocoa butter fats and possibilities of substitution in food products concerning cocoa varieties, alternative sources, extraction methods, composition, and characteristics. *Journal of Food Engineering*, 117, 467–476.

Kellens, M., Gibon, V., Hendrix, M., & Greyt, W. D. (2007). Palm oil fractionation—A review. *European Journal of Lipid Science and Technology*, 109, 336–349.

Kheiri, M. S. A. (1982). *Formulation, evaluation and marketing of cocoa butter replacers fat*. Kuala Lumpur: Palm Oil Research Institute of Malaysia (PORIM).

Kheiri, M. S. A. (1985). Palm oil products in cooking fats. *Journal of the American Oil Chemists' Society*, 62(2), 410–415.

Lakshminarayana, G., Rao, T. C., & Ramalingaswamy, P. A. (1983). Varietal variations in content, characteristics and composition of mango seeds and fat. *Journal of the American Oil Chemists' Society*, 60(1), 88–89.

Lemmon, E. W., McLinden, M.O., & Friend, D.G. (2005). Thermophysical properties of fluid systems in NIST chemistry webbook, NIST standard reference database number 69. In P. J. Linstrom, & W. G. Mallard (Eds.), Gaithersburg MD: National Institute of Standards and Technology (<http://webbook.nist.gov/chemistry/>).

Lipp, M., & Anklam, E. (1998). Review of cocoa butter and alternative fats for use in Chocolate. Part A. Compositional data. *Food Chemistry*, 62, 73–97.

Manifie, W. M. (1999). *Chocolate, cocoa, and confectionary science and technology* (3rd ed.). New York: Aspen Publishers Inc.

Mariod, A., Matthaus, B., Eichner, K., & Hussain, I. H. (2005). Improving the oxidative stability of sunflower oil by blending with *Sclerocarya birrea* oil and *Aspongopus viduatus* oils. *Journal of Food Lipids*, 12, 150–158.

Muchiri, D. R., Mahungu, S. M., & Gitunja, S. N. (2012). Studies on mango (*Mangifera indica*, L.) kernel fat of some Kenyan varieties in Meru. *Journal of the American Oil Chemists' Society*, 89, 1567–1575.

Pease, J. J. (1985). Confectionery fats from palm oil and lauric oil. *Journal of the American Oil Chemists' Society*, 62(2), 426–430.

Ramadan, M. F., & Wahdan, K. M. M. (2012). Blending of corn oil with black cumin (*Nigella sativa*) and coriander (*Coriandrum sativum*) seed oils: Impact on functionality, stability and radical scavenging activity. *Food Chemistry*, 132, 873–879.

Rukmini, C., & Vijayaraghavan, M. (1984). Nutritional and toxicological evaluation of mango kernel oil. *Journal of the American Oil Chemists' Society*, 61(4), 780–792.

Sahena, F., Zaidul, I. S. M., Jinap, S., Jahurul, M. H. A., Khatib, A., & Norulaini, N. A. N. (2010). Extraction of fish oil from the skin of Indian mackerel using supercritical fluids. *Journal of Food Engineering*, 99, 63–69.

Samsudin, S., & Rahim, M.A. A. (1996). Use of palm mid-fraction in white chocolate formulation. *Journal of the Science of Food and Agriculture*, 71, 483–490.

Shekarchizadeh, H., & Kadivar, M. (2012). A study on parameters of potential cocoa butter analogue synthesis from camel hump by lipase-catalysed interesterification in supercritical CO₂ using response surface methodology. *Food Chemistry*, 135, 155–160.

Shekarchizadeh, H., Kadivar, M., Ghaziaskar, H. S., & Rezaayat, M. (2009). Optimization of enzymatic synthesis of cocoa butter analog from camel hump fat in supercritical carbon dioxide by response surface method (RSM). *The Journal of Supercritical Fluids*, 49, 209–215.

Shukla, V. K. S. (1995). Cocoa butter properties and quality. *Lipid Technology*, 7, 54–57.

Sonwai, S., Kaphueakngam, P., & Flood, A. (2012). Blending of mango kernel fat and palm oil mid-fraction to obtain cocoa butter equivalent. *Journal of Food Science and Technology*. <http://dx.doi.org/10.1007/s13197-012-0808-7>.

Zaidul, I. S. M., Norulaini, N. A. N., Omar, A. K. M., & Smith, R. L., Jr. (2007). Blending of supercritical carbon dioxide (SC–CO₂) extracted palm kernel oil fractions and palm oil to obtain cocoa butter replacers. *Journal of Food Engineering*, 78, 1397–1409.