



Characterization of crystallization and melting profiles of blends of mango seed fat and palm oil mid-fraction as cocoa butter replacers using differential scanning calorimetry and pulse nuclear magnetic resonance



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ARTICLE INFO

Article history:

Received 8 July 2013

Accepted 27 October 2013

Available online 5 November 2013

Keywords:

Mango seed fat

Palm oil mid-fraction

Triglyceride

Crystallization and melting characterization

Solid fat content

Cocoa butter replacer

ABSTRACT

Mango seed fat (MSF) and palm oil mid-fraction (POMF) blends were stabilized prior to investigate crystallization and melting behavior, solid fat content (SFC) and triglyceride compositions. Ten blends at various ratios of MSF/POMF, 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), 50/50 (blend 10) were used in this study. Results showed that the major triglyceride ranges in all blends were from 11 to 38.8% 1,3-dipalmitoyl-2-oleoyl-glycerol (POP), from 22.1 to 36.9% 1,3-distearoyl-2-oleoyl-glycerol (SOS), and from 15.4 to 16.2% 1-palmitoyl-3-stearoyl-2-oleoyl-glycerol (POS), respectively. The melting behavior indicated a single curve with only one maximum and one small shoulder for the blends of 3 to 6. The blends having 70, 75, 80, and 85% of MSF showed similar crystallization pattern with a single curve having one maximum peak heights at temperatures of 10.17, 10.58, 11.54, and 11.66 °C. The SFC of the blends no. 1 to 5 was found to be close to these SFC of commercial CB at 10 to 20 °C temperatures. A multiple regression equation was developed which showed strong correlations between triglycerides of blends 1 to 10 and their properties. The studies revealed that preparation of green quality cocoa butter replacers (CBRs) is possible using MSF and POMF.

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1. Introduction

Cocoa butter (CB) is a natural fat obtained from cocoa seeds, commonly used as an essential constituent of chocolate and different confectionary products. Palmitic (C₁₆), stearic (C_{18:0}), and oleic (C_{18:1}) acids are the major fatty acids present in CB. C₁₆ and C_{18:0} occupy *sn*-1 and *sn*-3 positions of the glycerol backbone respectively while C_{18:1} occupies the *sn*-2 central position. The composition and distribution of these fatty acids lead to a symmetrical triglyceride composition of CB rich in 1,3-dipalmitoyl-2-oleoyl-glycerol (POP), 1-palmitoyl-3-stearoyl-2-oleoyl-glycerol (POS) and 1,3-distearoyl-2-oleoyl-glycerol (SOS) (Bootello, Hartel, Garcés, Martínez-Force, & Salas, 2012). Usually, this triglyceride composition of CB is responsible for its several crystalline polymorphic forms whereas fatty acid compositions are responsible for fat solidification from its liquid state (Awua, 2002).

Mango (*Mangifera indica* L.) is an important annual tropical fruit. It has a single large seed covered with a shell. The kernel inside the seed represents 80% of the seed and around 20% of the whole fruit (Solís-Fuentes & Durán-de-Bazúa, 2011). Mango seed kernels contain about 7.1 to 15% crude fat on dry basis which is rich source of C₁₆, C_{18:0} and C_{18:1} acids (Abdalla, Darwish, Ayad, & El-Hamahmy, 2007; Ali, Gafur, Rahman, & Ahmed, 1985; Gunstone, 2011; Jahurul, Zaidul, Nik Norulaini, Sahena, Mohd Omar, in press). Like CB, mango seed fat (MSF) is a natural fat containing high saturated and monounsaturated fatty acids responsible for the symmetrical triglycerides such as POS (10 to 16%), SOS (25 to 59%) and POP (1 to 8.9%) (Gunjkar, 2005; Liddefelt, 2007). These relatively simple triglyceride compositions of MSF are desirable for confectionery applications, especially in chocolate processing.

The crystallization and melting behaviors of fats and oils are important properties in several prepared food products. The thermal properties of fats and oils, particularly fractionated fats, hydrogenated fats, and enzymatic interesterified fats from palm kernel oil (PKO), palm oil (PO), MSF, kokum butter, sal fat, shea butter, illipe fat and their blends, have received much attention owing to their valuable role in CB formulations and its widespread use in the confectionary (Calliauw et al.,

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2005; Jahurul, Norulaini, et al., 2013; Maheshwari & Reddy, 2005; Olajide, Ade-Omowaye, & Otunola, 2000; Reddy & Prabhakar, 1994; Zaidul, Norulaini, Omar, & Smith, 2007). The crystallization and melting profiles, heats of transition, phase diagrams, and solid fat content (SFC) of fat blends are determined by thermal-analytical techniques. Differential Scanning Calorimetry (DSC) is a thermal-analytical technique widely used in fats and oils (Santana, Fernández, Larrayoz, & Recasens, 2008). The SFC is affected by temperature and it is considered an important property of fats and oils. It is used to determine the matching of fats and oils, individually or their blends, with suitable applications. Meanwhile, much attention has been paid to the production of CBRs from various fats and oils via fractionation, enzymatic interesterification, and blending methods (Bootello et al., 2012; Liu, Cheng, Chang, & Shaw, 1997). However, blending methods resulting from supercritical carbon dioxide (SC-CO₂) extraction of CB analog fats from MSF and their blends are still unexplored area of research. The objective of this study was to determine the triglyceride composition of the blends of MSF and palm oil mid-fraction (POMF). We also determined the thermal behaviors and SFC of these blends using DSC and pNMR. Finally, the triglyceride compositions for various blends were correlated with their SFC.

2. Material and methods

2.1. Materials

The SC-CO₂ extracted MSF was blended with POMF into various ratios which were referred as blends 1 to 10. Total 10 blends with 5% increments of POMF were taken into account: MSF/POMF, 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). Standards of triglycerides, acetone, and acetonitrile (analytical grade) were purchased from Sigma, Merck, and Fisher (Malaysia).

2.2. Determination of triglyceride

A high performance liquid chromatography (HPLC) method established by American Oil Chemists' Society (AOCS, 2003) was used to analyze the triglyceride compositions in all blends. A 10% solution of each blend was prepared using acetone as solvent. The solution was then filtered through a TE 36 membrane filter (PTFE; 0.45 µm) (Millipore) before it was injected into the HPLC. Triglyceride content was determined using an Agilent HPLC instrument, Agilent HPLC Series 1200, Degasser Model G1322A, Quaternary Pump Model G1311A, RI Detector (Model G1362A), and a Lichrospher 100 RP-18e HPLC column (4 mm i.d. × 250 mm length) with a column temperature of 30–35 °C, column pressure of 5–6 MPa, acetone/acetonitrile 70:30 v/v as mobile phase, a mobile phase flow rate of 1 ml/min and an injection volume of 10 µl. The percentage of triglycerides was determined by calculating the peak area of the chromatogram. Analyses were conducted in triplicates.

2.3. Determination of solid fat content (SFC) by pulsed nuclear magnetic resonance (pNMR)

The SFC of fat blends as a function of temperature was determined by pNMR (Bruker minispec mq20 NMR analyzer) following the method developed by Fiebig and Lüttke (2003). Each blend was tempered at 80 °C for 30 min followed by chilling at 0 °C for 90 min, and kept at the desired temperatures for 30 min prior to measurements. The pre-equilibrated thermostat bath was used to carry out the melting, chilling and holding of the test samples. The temperature ranges used for determination of SFC were 10–80 °C. All analyses were conducted in triplicates.

2.4. Analysis of crystallization and melting characteristics by DSC

Differential Scanning Calorimetry (DSC Q200, TA Instrument) was used to monitor the melting and crystallization behavior of the blends of MSF and POMF. The DSC instrument was calibrated using indium. All the blends of MSF and POMF were melted at 80 °C. Approximately 3–5 mg of the molten samples was transferred to standard DSC aluminium pans using micropipette and then hermetically sealed. The pans were then placed in vials and melted at 80 °C for 30 min. For stabilization, the pans were placed in incubator at 26 °C for 7 days. After 7 days of incubation at 26 °C the pans were transferred to the DSC head. An empty hermetically sealed DSC aluminium pan was used as a reference. For the DSC experiments the following program was used: cooling to –60 °C and melting the samples at a rate of 30 °C/min to 80 °C for 20 min to ensure a completely liquid state, cooling at 10 °C/min to –60 °C, holding at –60 °C for 2 min, heating at 10 °C/min to 80 °C. During melting and cooling, the enthalpy change of fat blends was measured. All analyses were carried out in triplicates.

2.5. Crystal morphological study by polarized light microscopy (PLM)

Polarized light microscopy (Nikon, ECLIPSE E200, Tokyo, Japan) equipped with digital camera was used to monitor microstructure of crystal network of the blends of MSF and POMF. The method developed by Narine and Marangoni (1999) was used for crystallization of fat blends. All analyses were carried out in triplicates.

2.6. Statistical analysis

Analyses were carried out in triplicates in this study. A multiple linear regression equation was developed where a correlation between the triglycerides of blends 1 to 10 and their properties, and the coefficients of triglycerides were determined. The differences between the estimated and experimental values were determined, as they indicated the residual values. One-way analysis of variance (one-way ANOVA) was used to test the variations between the percent of different triglycerides in various blends. Statistical significance ($p < 0.05$) among them was considered controlling the experimental variables such as blending ratios and triglycerides. The Minitab software (version 16) and Microsoft office Excel 2007 were used to perform correlations analysis.

3. Results and discussion

3.1. Triglyceride compositions

The results of triglyceride compositions of MSF and POMF blends (1 to 10) are shown in Fig. 1. Similar to any other fats and oils, MSF and POMF blends are also complex mixtures of variety of fatty acid constituents in terms of triglyceride profiles. Thus, the results demonstrated that three main triglycerides, namely, POP, POS, and SOS existed in all blends. The SOS (22.1 to 36.9%) has been identified as the major triglyceride component followed by POP (11 to 38.8%) and POS (15.4 to 16.2%) in the blends. The major triglyceride profiles of all blends were significantly ($p < 0.05$) influenced by the addition of MSF in the blends. For this reason, a gradual decrease in POP contents in blends was observed due to the addition of MSF. The reverse trend was observed in SOS content where this component gradually increased with the addition of MSF. For instance, the percentage of POP decreased to a large extent from 26.3 to 16.9% with an increase in MSF from 70 to 85%. Contrary, the percentage of SOS increased from 28.7 to 33.7% as the amounts of MSF were increased from 70 to 85%. These observations could be explained by the fact that the amount of POP was lower and SOS was higher in pure MSF. In this work, the modifications of the triglyceride components observed in all blends could be due to the dilution and solubilisation of triglycerides in fat mixtures. Blending of natural fats and oils resulted in modification of the triglyceride compositions as

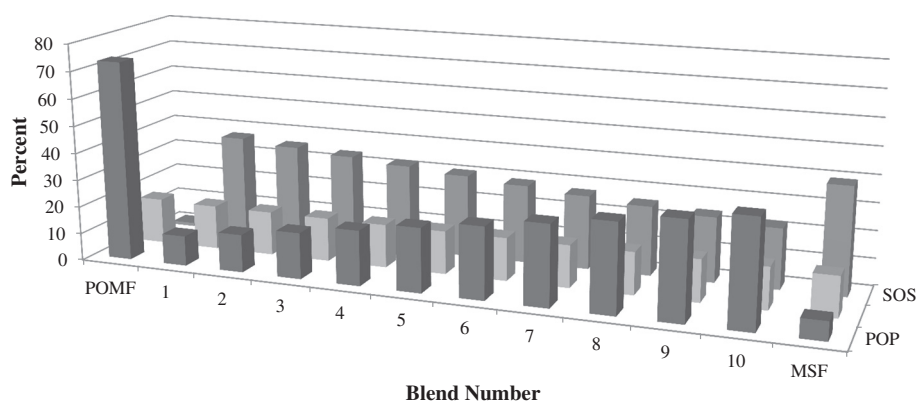


Fig. 1. Triglyceride compositions of blends of MSF and POMF (area %, mean of three replications, standard deviation (\pm) ranges from 0.46 to 1.20).

reported by many researchers (Jeyarani & Reddy, 1999, 2010; Maheshwari & Reddy, 2005; Rodrigues & Gioielli, 2003). In blends 3 to 6, amounts of major triglyceride components were found to be similar to that of commercial CB. Results of the present study were in good agreement with the results reported by Chaiseri and Dimick (1989) where POP, POS and SOS ranged between 17.5 to 22.6%, 35.8 to 41.4%, and 22.8 to 31.3% respectively, in different commercial CB. Blends 3 to 6 were observed to be the best blends in terms of triglyceride compositions and in comparison to the commercial CB.

3.2. Effect of blending on DSC melting thermograms

The DSC melting curves of the pure MSF, POMF and their blends (1 to 10) are shown in Figs. 2 and 3. It can be observed from melting curves that the pure MSF melts slowly, whereas POMF melts rapidly at higher temperatures (Table 1 and Fig. 2). The melting curve of MSF was found similar to that of previously reported by Solis-Fuentes and Duran-de-Bazua (2004), and Sonwai, Kaphueakngam, and Flood (2012) for MSF. A single melting peak with less open peak was started at -12.98 °C and ended at 36.07 °C in the present study, whereas -15.94 °C and 42.23 °C were reported by Solis-Fuentes and Duran-de-Bazua (2004), and 34.58 °C (start only) by Sonwai et al. (2012). Only small differences in peak temperatures were observed in the present study. These differences could be due to the variation of fatty acid constituents in MSF used in each study. Another possible explanation of these differences could be due to variable tempering history and conditions as well as the DSC calibration procedure used for DSC measurements in each study, which might affect the melting history of the MSF. The POMF, on the other hand, showed quite simple melting curve and

melted at 39.25 °C which was higher than the melting temperatures of MSF and commercial CB. This indicates that the high melting triglycerides (mainly constituted with saturated fatty acids) exist in POMF. Over a temperature range from -20.47 to 39.25 °C, the total melting enthalpy for pure MSF and POMF was found to be 67.68 and 76.97 J/g, respectively. The total enthalpy of MSF is comparable to that of commercial CB (Table 1).

As shown in Fig. 3, the melting profiles are relatively simple and correspond closely to the similarly simple triglyceride composition of certain blends. During melting period, certain blends showed two maxima corresponding to low and high melting temperatures of triglycerides between -16.74 and 37.46 °C. The first maxima indicated the low melting point fraction at 16.45 °C and the second maxima indicated the higher melting point fraction at 19.19 °C (Fig. 3). This finding is in accordance with Chaiseri and Dimick (1989) who studied melting thermogram of different commercial CB using DSC and reported the two maxima at 17 and 21 °C. In addition, a smaller melting peak was also observed between -16.33 and 4.36 °C which could possibly be due to the crystal structure I of the blends. Similarly, small peak was also reported between -17.16 and 5.32 °C in commercial CB (Solis-Fuentes & Duran-de-Bazua, 2004). In case of some blends, particularly 3 to 6, melting started at -14.10 °C and ended at 36.82 °C, whereas Solis-Fuentes and Duran-de-Bazua (2004) reported these points as -11.02 °C and 36.51 °C, respectively, for commercial CB. In melting thermogram, the peak temperatures increased gradually and shifted towards higher temperature with increase of POMF in the blends (Table 1 and Fig. 3). For example, in blend 3 the melting thermogram

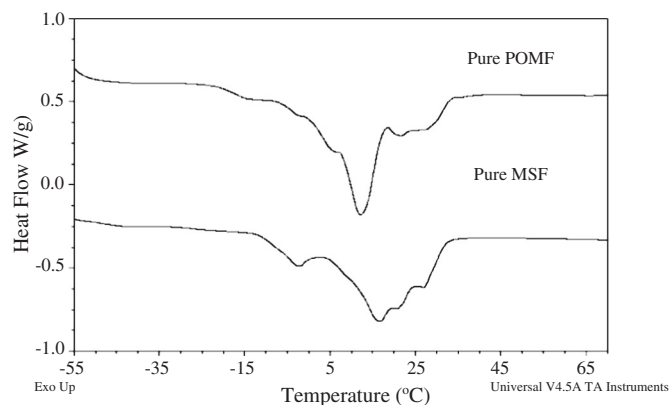


Fig. 2. DSC melting curves of pure MSF and POMF.

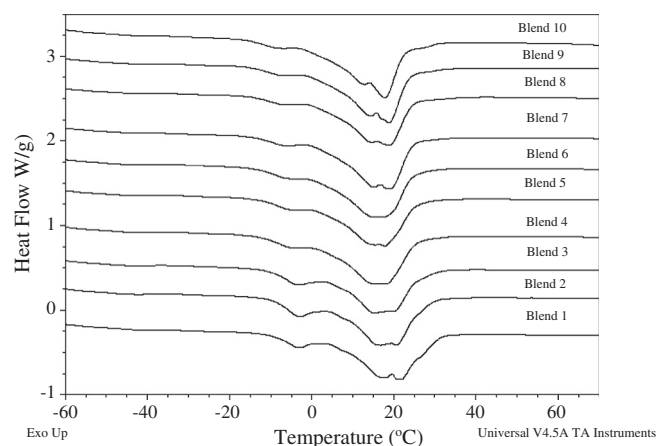


Fig. 3. DSC melting curves of blends of MSF and POMF. Melting curves of blends 1 to 10 represent fat blend containing 50 to 95% of MSF.

Table 1
Melting characteristics of pure MSF, POMF and their blends and commercial CB.

Blend no.	Peak		
	Onset temperature (°C)	Offset temperature (°C)	ΔH (J/g)
1	−13.35	36.10	67.14
2	−13.75	36.19	67.61
3	−14.10	36.35	68.07
4	−14.49	36.50	68.52
5	14.85	36.66	68.96
6	−15.23	36.82	69.39
7	−15.6	36.98	69.81
8	−15.98	37.14	70.22
9	−16.35	37.30	70.62
10	−16.74	37.46	71.01
MSF	−12.98	36.07	67.68
POMF	−20.47	39.25	76.97
MSF ^a	−15.94	42.23	70.12
CB ^b	−11.02	31.5–36.51	80.02–128.17

^a Solis-Fuentes and Duran-de-Bazua (2004).

^b Jeyarani and Reddy (1999), Solis-Fuentes and Durán-de-Bazúa (2011) and Maheshwari and Reddy (2005).

peak started at −14.10 °C and completed at 36.35 °C, whereas in blend 6 it started at −15.23 and ended at 36.82 °C. The melting enthalpies for blends 3 to 6 ranged from 68.07 to 69.39 J/g and gradually increased to a small extent with the addition of POMF. The values for blends 3 to 6 were similar to that of commercial CB (80.02 J/g) which was reported by Solis-Fuentes and Duran-de-Bazua (2004). The DSC melting curves of blends 3 to 6 were almost similar to that of commercial CB and melted at slightly higher temperature (Fig. 3).

3.3. Effect of blending on DSC crystallization thermograms

The DSC crystallization curves of the individual pure fats of MSF and POMF and their blends (1 to 10) are shown in Figs. 4 and 5. From the crystallization curves of pure MSF and POMF, it can be seen that the MSF crystallizes slowly, whereas POMF crystallizes rapidly at higher temperatures. The crystallization curve for MSF was similar to that previously reported for MSF by Solis-Fuentes and Duran-de-Bazua (2004) and Sonwai et al. (2012). A single crystallization peak started at 16.18 °C and ended at −24.32 °C in this study, whereas 14.64 °C and −24.27 °C were reported by Solis-Fuentes and Duran-de-Bazua (2004), and 18.98 °C (started only) was reported by Sonwai et al. (2012) (Table 2). The POMF, on the other hand, showed quite simple two crystallization curves and it was crystallized at higher temperature (17.03 °C). This indicates that the higher melting triglycerides were present in the POMF. Over a temperature range of 17.03 to −24.32 °C, the total crystallization enthalpies for pure MSF and POMF were found

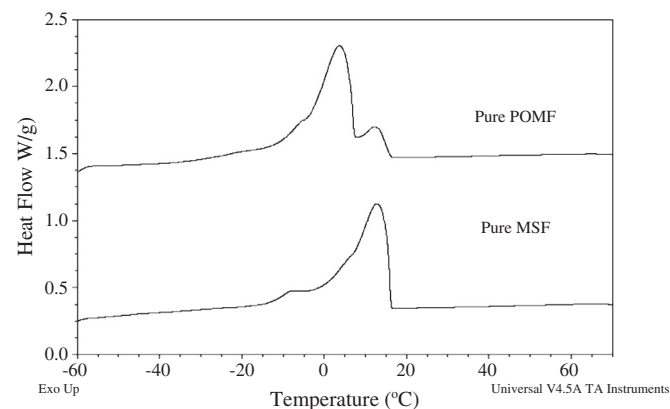


Fig. 4. DSC crystallization curves of pure MSF and POMF.

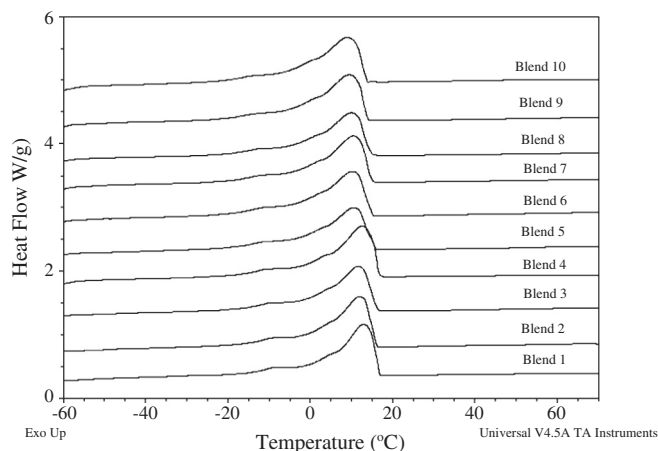


Fig. 5. DSC crystallization curves of blends of MSF and POMF. Crystallization curves of blends 1 to 10 represent fat blend containing 50 to 95% of MSF.

to be 56.23 and 65.61 J/g, respectively (Table 2). The total enthalpy of MSF is found to be comparable with that of commercial CB.

Fig. 5 shows a single crystallization curve for all blends with different onset and offset temperatures, similar to that of CB. For blends 3 to 6, the crystallization started at 14.71 °C and ended at −27.26 °C, whereas at 12.71 °C and −26.17 °C reported by Solis-Fuentes and Duran-de-Bazua (2004) for commercial CB. The crystallization onset increased gradually to a small extent with MSF in the blends. For example, blend 5 having 75% MSF showed crystallizing at 14.95 °C, while blend 3 having 85% MSF crystallized at 15.81 °C. The crystallization completion (end) on the other hand decreased with MSF in the mixtures. For instance, blend 6 showed crystallization completion at −27.26 °C, whereas blend 4 showed this completion at −27.56 °C. These increasing and decreasing phenomena of crystallization onset and offset temperatures in all blends observed in this study could be due to the presence of different triglyceride compositions as well as different fatty acid constituents in the blends. Other reasons could be the dilution and solubilisation of triglycerides in the blend mixtures.

In all blends, the total enthalpies ranged from 56.56 to 58.28 J/g. In case of blends 3 to 6, the total enthalpies were found to be 56.71, 56.92, 57.03, and 57.25 J/g, whereas enthalpies for the commercial CB ranged from 56.98 to 58.0 J/g (Jeyarani & Reddy, 1999; Solis-Fuentes & Duran-de-Bazua, 2004). The total enthalpies of blends having 70, 75, 80, and 85% of MSF were similar to that of CB, and at a lower level of

Table 2
Crystallization characteristics of pure MSF, POMF and their blends and commercial CB.

Blend no.	Peak		
	Onset temperature (°C)	End temperature (°C)	ΔH (J/g)
1	16.10	−28.35	56.56
2	15.91	−28.04	56.58
3	15.81	−27.74	56.71
4	15.62	−27.56	56.92
5	14.95	−27.40	57.03
6	14.71	−27.26	57.25
7	14.68	−27.13	57.49
8	14.14	−26.92	57.79
9	14.02	−26.71	58.07
10	13.59	−26.68	58.28
MSF	16.18	−24.32	56.23
POMF (first peak)	17.03	−28.53	65.61
MSF ^a	14.64	−24.27	56.06
CB ^b	12.71	−26.17	56.98–58

^a Solis-Fuentes and Duran-de-Bazua (2004).

^b Jeyarani and Reddy (1999) and Solis-Fuentes and Duran-de-Bazua (2004).

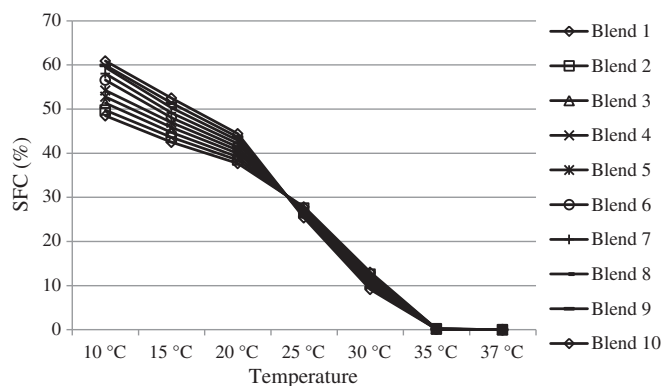


Fig. 6. Solid fat content (%; each blend represents the average of triplicates and standard deviation (\pm) ranges from 0.84 to 1.75) of blends 1 to 10 of MSF and POMF.

MSF the enthalpies increased. Thus, as the amounts of MSF in the blends were increased from 70 to 85%, the total enthalpy value decreased from 57.25 J/g to 56.71 J/g (Table 2). The total enthalpies for blends 3 to 6 in the present work were similar to the total enthalpy of commercial CB (58 J/g) reported by Jeyarani and Reddy (1999). Thus, the DSC cooling and melting curves of blends 3 to 6 were almost similar to that of commercial CB, melting slightly at higher temperature (Fig. 3), and the heats of cooling and melting (enthalpy) were also similar to those of commercial CB, respectively.

3.4. Solid fat content (SFC)

According to our previous report on blending ratios, the percentage of SFC of 1 to 10 blends of MSF and POMF measured by pNMR is shown in Fig. 6 where the SFC was found to be bit low in all blends. There was only a marginal difference among blends found in SFC at any temperature. This was further confirmed by the triglyceride profiles, which showed minor variations in the content of monounsaturated triglycerides among all blends of MSF and POMF (Fig. 1). In all blends, the SFC at 10 to 20 °C was found to be higher and gradually increased with the proportion of POMF in the blends and hence the hardness increased. Opposite trend was observed at temperature above 25 °C, where the SFC gradually decreased with the addition of POMF in the blends (Fig. 6). These observations are in line with Maheshwari and Reddy (2005), who reported gradual increase in SFC with the addition of hard kokum fat in CB. The SFC of all blends decreased significantly as the temperature increased.

The blends containing 70, 75, 80, and 85% MSF (blends no. 3 to 6) showed lowering of SFC at 10, 15, and 20 °C, unlike blends containing 50, 55, 60, and 65% of MSF (Fig. 6). It can be seen in Fig. 6 for blend 1 that there was 13% of SFC remained at 30 °C and dropped down to 0% at 37 °C. The SFC at 20 and 25 °C was found to be much lower in certain blends than that of commercial CB. The explanation of lower SFC found in blends could be due to lower amounts of POS present in the blends. In all blends, the SFC values at 35 °C were very close to the SFC of the commercial CB. With the addition of CB, the SFC of the formulated blends could even be lower than the original SFC. The results revealed

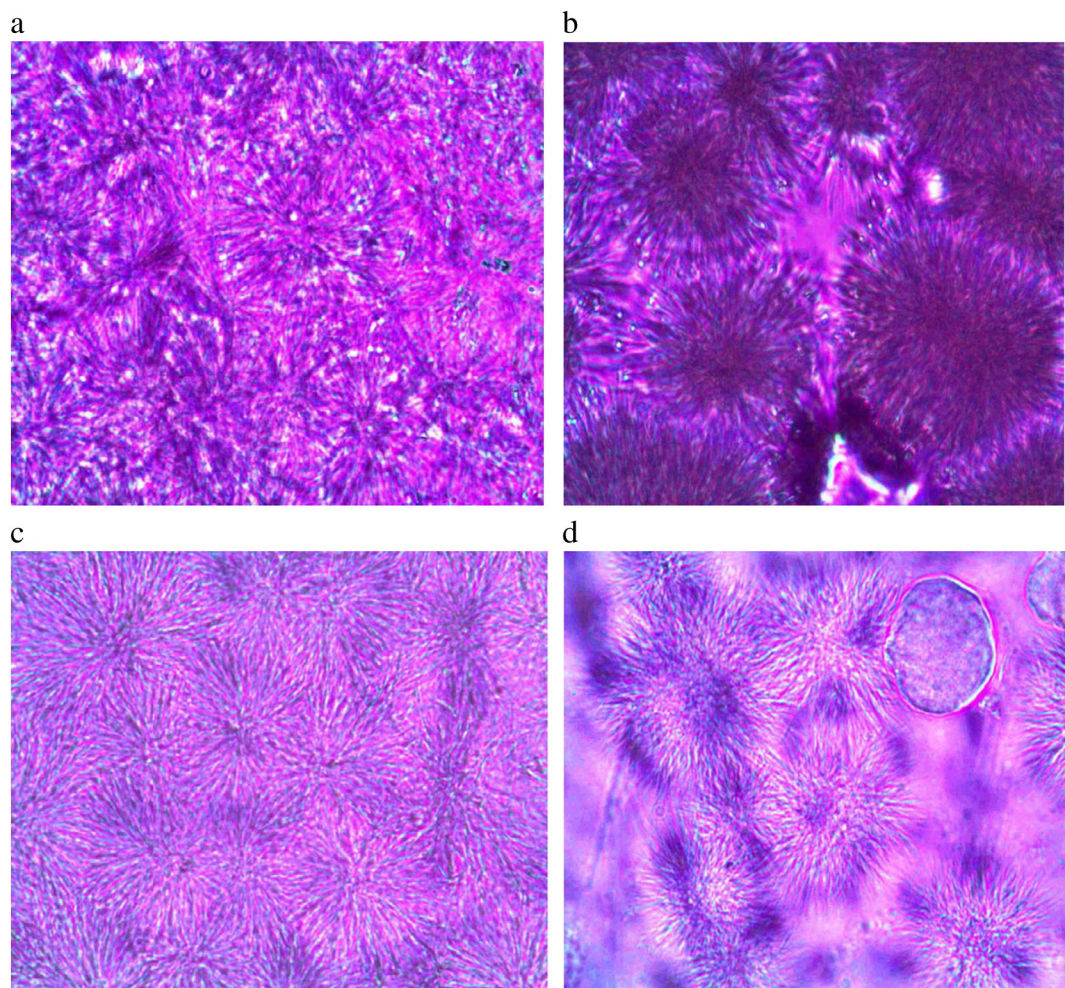


Fig. 7. Polarized light microphotographs (40 \times lens) of blends of MSF and POMF crystallized at 21–23 °C for 48 h. (a) 85% MSF, (b) 80% MSF, (c) 75% MSF, and (d) 70% MSF.

Table 3Multiple regression coefficients of triglyceride profiles of MSF: POMF blends, G is constant, and R^2 is coefficient determination.

SFC	A (POO)	B (POP)	C (SOO)	D (SLS)	E (POS)	F (SOS)	G (constant)	R^2
10 °C	−6.2046	0.2902	−594.591	573.404	−4.4838	156.3066	−277.489	0.9939
15 °C	−0.5282	0.0012	−2.2277	2.0046	−0.1257	−0.0738	66.9061	0.9999
20 °C	0.6768	−0.0060	−0.3744	0.4760	0.0558	−0.3794	50.6408	0.9999
25 °C	−0.5608	−0.0020	3.7325	−4.3485	−0.0933	−0.7601	27.6042	0.9999
30 °C	0.2265	0.0085	−1.9712	2.0170	0.0314	0.7876	1.0541	0.9999
35 °C	−4.0839	0.1087	−2.7549	2.8076	−0.0974	0.9667	2.3807	0.9332

that the blends containing 70 to 85% MSF are suitable for CBRs in terms of SFC, though they are slightly softer than that of commercial CB.

3.5. Relationships between SFC, fatty acids, and triglycerides of blends of MSF and POMF

The high SFC of all blends at 10 to 20 °C and rapid reduction in SFC from 20 to 30 °C was related to the high percentage of short and long chain (C_{12} , C_{16} and $C_{18:0}$) saturated fatty acids as well as triglycerides, particularly disaturated triglyceride (SOS) in the blends. These fatty acid constituents and SOS are responsible for increasing the hardness and SFC in the formulated blends. The differences among the SFC of all blends at any temperature interval could be due to the differences of C_{16} , $C_{18:0}$, $C_{18:1}$, and $C_{18:2}$ constituents present in the blends. These variations in the SFC among the blends suggest that apart from substantial differences of $C_{18:1}$ and $C_{18:2}$ constituents, there were some differences in the proportion of triglycerides in particular, POP, POS and SOS in the formulated blends.

3.6. Morphological study

The polarized light micrographs of blends 3 to 6 are shown in Fig. 7. The fat crystal network of all blends is composed of mainly tightly packed crystalline material. In particular, blends 3 to 6 had more closely and orderly packed crystalline materials like commercial CB. The microstructure of the crystals of blends 3 to 6 was spherulites consisting of needle like crystals radiating and branching outward from the central nuclei, similar to that of commercial CB. It can also be observed in Fig. 7 (blends 3 to 6), that the three-dimensional network was formed by the collection of microstructures through aggregation process. Similar observation has been reported by Marangoni and Narine (2002) who studied crystal network of commercial CB by PLM. Small differences in crystal network characteristics among all blends were observed (Fig. 7a–d). These differences could be due to the different triglyceride compositions and also the polymorphic behavior of the blends. Due to the presence of symmetrical triglycerides in all blends, packing into crystalline structure was observed. Moreover, the nature of triglyceride compositions of all blends resulted in the formation of packed network with structural elements. The results of present study are in line with those of PLM of commercial CB reported by Narine and Marangoni (1999).

Several factors are responsible for the hardness and the spreadability of commercial CB. In this connection, the fat crystal networks of CB and CB like fats have been studied by many other researchers (Narine et al., 2009; Marangoni & Narine, 2002; Narine & Marangoni, 1999; Rousseau, Forestiere, Hill, & Marangoni, 1996). The interest in fat crystal network study of CB or CB like fat produced by fractionation, enzymatically or blending of vegetable fats is increasing by the day. Moreover, investigation of fat crystal networks of chemically and enzymatically produced butter fats has received much interest owing to their valuable properties in food formulations and their widespread use in the food industries, in particular chocolate industries (Narine et al., 2009; Marangoni & Narine, 2002; Rousseau et al., 1996). Nevertheless, the analysis of fat crystal networks of CBRs obtained by the blending of MSF and POMF is still in its early stages.

3.7. Correlation between the triglycerides and SFC of the blends using multiple regression equation

It was useful to develop a statistical relation that could allow all blends to be studied for suitability as CBRs. In order to make a correlation between the triglycerides of all blends and their properties such as SFC at various temperatures, a multiple linear regression model was developed by Zaidul et al. (2007) and represented by the following equation.

$$Y = Ax_1 + Bx_2 + Cx_3 + Dx_4 + Ex_5 + Fx_6 + G \quad (1)$$

$$Y = \sum_{i=1}^n A_i x_i + G \quad (2)$$

where Y is the blend properties i.e. SFC and x_i is triglycerides of all blends of MSF and POMF, A_i is regression coefficient of x_i and G are constants. Ten blends were taken into account to study the relationship between the triglycerides and their SFC. The multiple regression coefficient results of triglycerides are shown in Table 3. The coefficients of some triglycerides are negative, showing monotectic relationship between MSF and POMF. However, the regression coefficients of triglyceride profiles at 10, 15, 20, 25, 30 and 35 °C indicated strong correlation among them, and R^2 varied from 0.9332 to 0.9999.

Fig. 8 shows the residual distribution of SFC of 1 to 10 blends at 10, 15, 20, 25, 30 and 35 °C. It can be clearly seen from Fig. 8 that the figures of residuals (differences between calculated and experimental values) of 1 to 10 blends were too small and distributed randomly within the regression line. The residuals ranged from −0.46 to 0.51 whereas R^2 from 0.9332 to 0.9999. These indicate that the model explained 93.32 to 99.99% original variability.

4. Conclusions

The thermal properties and SFC for the blends of MSF: POMF were characterized by DSC and pNMR. These blends were also analyzed to determine triglyceride compositions by HPLC. Thermal behavior and SFC are important factors because good quality CBRs should have thermal behavior and SFC closer to those of commercial CB. The triglycerides

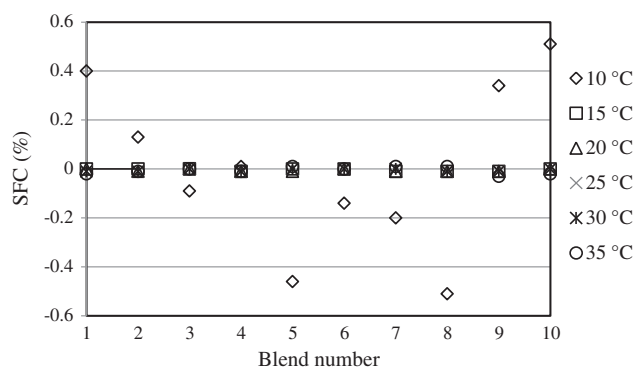


Fig. 8. Residual of experimental and calculated SFC (%) of blends versus blend number.

varied from 11 to 38.8% for POP, from 15.4 to 16.2% for POS and from 22.1 to 36.9% for SOS in the blends where SOS is the major component. Triglyceride compositions of blends 3 to 6 were relatively simple and similar to that of commercial CB. In these blends, the melting started at -14.10°C and ended at 36.82°C . The melting peak temperatures increased gradually and shifted towards relatively higher temperature with POMF. In the same blends, crystallization started at 14.71°C and ended at -27.26°C . The crystallization onset increased gradually to a small extent with MSF in the blends. Hence, blends 3 to 6 showed improved crystallization, melting characteristics, and SFC compared with any other blends formulated in this study and these properties were similar to those of commercial CB. The crystallization and melting curves demonstrated exotherms/endotherms representative of the high and low melting fractions of blends 3 to 6 which are similar to that of commercial CB. According to the results obtained in this study, blends 3 to 6 of MSF and POMF could be recommended as CBRs.

Nomenclature

Y	blend properties i.e., SFC
x_i	the triglycerides of all blends of MSF with POMF
A_i	regression coefficient of x_i
G	constant

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 for the fellowship provided to M.H.A. Jahurul.

References

- Abdalla, A. E. M., Darwish, S. M., Ayad, E. H. E., & El-Hamahmy, R. M. (2007). Egyptian mango by-product 1. Compositional quality of mango seed kernel. *Food Chemistry*, 103, 1134–1140.
- 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.
- AOCS (2003). Official methods and recommended practices of the American Oil Chemists' Society. (5th ed.) Champaign, Illinois, USA: American Oil Chemists' Society ((no. Ce 5b-89) Part 1, A–C).
- Awua, P. K. (2002). *Cocoa processing and chocolate manufacture in Ghana*. Essex, UK: David Jamieson and Associates Press Inc.
- Bootello, M.A., Hartel, R. W., Garcés, H. R., Martínez-Force, E., & Salas, J. J. (2012). Evaluation of high oleic-high stearic sunflower hard stearins for cocoa butter equivalent formulation. *Food Chemistry*, 134, 1409–1417.
- Calliauw, G., Foubert, I., De Grevt, W., Dijkmans, P., Kellens, M., & Dewettinck, K. (2005). Production of cocoa butter substitutes via two-stage fractionation of palm kernel oil. *Journal of the American Oil Chemists' Society*, 82, 783–789.
- 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.
- Fiebig, H. -J., & Lüttke, J. (2003). Solid fat content in fats and oils – Determination by pulsed nuclear magnetic resonance spectroscopy. *European Journal of Lipid Science and Technology*, 105, 377–380.
- Gunjikar, J. (2005). *Mango kernel fat – An exotic fat* International news on fats, oils and related materials : INFORM; ProQuest Central, 232.
- Gunstone, F. D. (2011). *Vegetable oils in food technology composition, properties and uses*. Wiley-Blackwell, CRC Press, 291–343.
- Jahurul, M. H. A., Norulaini, N. A. N., Zaidul, I. S. M., Jinap, S., Sahena, F., & Mohd Omar, A. K. (2013a). 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(4), 467–476.
- Jahurul, M. H. A., Zaidul, I. S. M., Nik Norulaini, N. A., Sahena, F., & Mohd Omar, A. K. (2013b). Supercritical carbon dioxide extraction and studies of mango seed kernel for cocoa butter analogy fats. *CyTA-Journal of Food*, <http://dx.doi.org/10.1080/19476337.2013.801038> (Article in press).
- Jeyarani, T., & Reddy, S. Y. (1999). Heat-resistant cocoa butter extenders from Mahua (*Madhuca latifolia*) and Kokum (*Garcinia indica*) fats. *Journal of the American Oil Chemists' Society*, 76(12), 1431–1436.
- Jeyarani, T., & Reddy, S. Y. (2010). Effect of enzymatic interesterification on physicochemical properties of mahua oil and kokum fat blend. *Food Chemistry*, 123, 249–253.
- Lidefelt, J. O. (2007). *Handbook of vegetable oils and fats* (2nd ed.) Karlshamn: AarhusKarlshamn.
- Liu, K. -J., Cheng, H. -M., Chang, R. -C., & Shaw, J. -F. (1997). Synthesis of cocoa butter equivalent by lipase-catalyzed interesterification in supercritical carbon dioxide. *Journal of the American Oil Chemists' Society*, 74, 1477–1482.
- Maheshwari, B., & Reddy, S. Y. (2005). Application of kokum (*Garcinia indica*) fat as cocoa butter improver in chocolate. *Journal of the Science of Food and Agriculture*, 85, 135–140.
- Marangoni, A. G., & Narine, S. S. (2002). Identifying key structural indicators of mechanical strength in networks of fat crystals. *Food Research International*, 35, 957–969.
- Narine, S. S., & Marangoni, A. G. (1999). The difference between cocoa butter and salatrim lies in the microstructure of the fat crystal network. *Journal of the American Oil Chemists' Society*, 76, 7–13.
- Olajide, J. O., Ade-Omowaye, B. I. O., & Ogunola, E. T. (2000). Some physical properties of shea kernel. *Journal of Agricultural Engineering Research*, 76, 419–421.
- Reddy, S. Y., & Prabhakar, J. V. (1994). Cocoa butter extenders from Kokum (*Garcinia indica*) and Phulwara (*Madhuca butyacea*) butter. *Journal of the American Oil Chemists' Society*, 71, 217–219.
- Rodrigues, J. N., & Gioielli, L. A. (2003). Chemical interesterification of milkfat and milkfat – Corn oil blends. *Food Research International*, 36, 149–159.
- Rousseau, D., Forestiere, K., Hill, A.R., & Marangoni, A. G. (1996). Restructuring butterfat through blending and chemical interesterification. 1. Melting behavior and triacylglycerol modifications. *Journal of the American Oil Chemists' Society*, 73, 963–972.
- Santana, A., Fernández, X., Larrayoz, M.A., & Recasens, F. (2008). Vegetable fat hydrogenation in supercritical-fluid solvents: Melting behavior analysis by DSC and NMR. *Journal of the Supercritical Fluids*, 46, 322–328.
- Solis-Fuentes, J. A., & Durán-de-Bazúa, M. C. (2004). Mango seed uses: Thermal behaviour of mango seed almond fat and its mixtures with cocoa butter. *Bioresource Technology*, 92, 71–78.
- Solis-Fuentes, J. A., & Durán-de-Bazúa, M. C. (2011). Mango (*Mangifera indica* L.) seed and its fats. In V. Preedy, R. R. Watson, & V. B. Patel (Eds.), *Nuts and seeds in health and disease prevention* (pp. 741–748). : Elsevier (Chapter 88).
- 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.
- Ziftçi, O. N., Fadiloğlu, S., & Göğüş, F. (2009). Conversion of olive pomace oil to cocoa butter – Like fat in a packed-bed enzyme reactor. *Bioresource Technology*, 100, 324–329.