Chemical and Physical Characteristics of Cocoa Butter Substitutes, Milk Fat and Malaysian Cocoa Butter Blends

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ABSTRACT: Two ternary systems of confectionery fats were studied. In the first system, lauric cocoa butter substitutes (CBS), anhydrous milk fat (AMF), and Malaysian cocoa butter (MCB) were blended. In the second system, high-melting fraction of milk fat (HMF42) was used to replace AMF and also was blended with CBS and MCB. CBS contained high concentrations of lauric ($C_{12:0}$) and myristic ($C_{14:0}$) acids, whereas palmitic ($C_{16:0}$), stearic ($C_{18:0}$), and oleic ($C_{18:1}$) acid concentrations were higher in MCB. In addition, AMF and HMF42 contained appreciable amounts of short-chain fatty acids. CBS showed the highest melting enthalpy (143.1 J/g), followed by MCB (138.8 J/g), HMF42 (97.1 J/g), and AMF (72.9 J/g). The partial melting enthalpies at 20 and 30°C demonstrated formation of a eutectic along the binary blends of CBS/MCB, AMF/MCB, and HMF42/MCB. However, no eutectic effect was observed along the binary lines of AMF/CBS and HMF42/CBS. Characteristics of CBS included two strong spacings at 4.20 and 3.8 Å. MCB showed a strong spacing at 4.60 Å and a weak short-spacing at 4.20 Å. On the other hand, AMF exhibited a very weak short- spacing at 4.60 Å and two strong spacings at 4.20 and 3.8 Å, while HMF42 showed an intermediate short-spacing at 4.60 Å and also two strong short-spacings at 4.20 and 3.8 Å. Solid fat content (SFC) analyses at 20°C showed that CBS possessed the highest solid fat (91%), followed by MCB (82.4%), HMF42 (41.4%), and AMF (15.6%). However, at 30°C, MCB showed the highest SFC compared to the other fats. Results showed that a higher SFC in blends that contain HMF does not necessarily correlate with a stronger tendency to form the β polymorph.

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KEY WORDS: Binary and ternary system, CBS, FAC, MCB, melting characteristics, milk fat, polymorphism, SFC.

Milk chocolate is always formulated with cocoa butter (CB) and milk fat (MF). However, in compound chocolate formulated for coating, cocoa butter substitute (CBS) is the main fat added to reduce cost. The presence of many different types of fats used in the chocolate system could change chocolate's physical properties. For example, such changes will cause chocolate products to soften, bloom, lose gloss and color, snap, and contract.

The nature of interaction between CB and other vegetable fats, such as palm mid-fraction (PMF), Illipe (IP), Sal stearin (SLs), cottonseed oil and others, has been studied (1–6). Also, the study on mixtures of CB and MF has been described (7–10), and work on the interaction between CB, lauric and nonlauric oils has been carried out (11–13).

However, not much work has been conducted on ternary blends. The objective of the present study was to determine the melting properties, polymorphic stability, and solid fat content (SFC) changes in binary and ternary blends of CBS, MF, and CB with respect to their chemical properties.

EXPERIMENTAL PROCEDURES

CBS was obtained from Intercontinental Specialty Fats Limited (Port Klang, Malaysia); anhydrous milk fat (AMF) and the high-melting fraction of milk fat (HMF42) were obtained from Anchor Products Limited (Paerata, New Zealand). Malaysian CB was obtained from Malaysian Cocoa Manufacturing Limited (Seremban, Malaysia). Their chemical compositions are given in Table 1. The fats were blended in various ratios as shown in Tables 2 and 3.

The fatty acid composition of each fat was determined as fatty acid methyl esters (FAME) by gas chromatography on a glass column (1.8 m × 3 mm i.d.) packed with 10% SP 2330 on 100–120 Supelcoport (Supelco, Bellefonte, PA), at 200°C with the flow rate of N_2 at 40 cm^3 min^{-1}. FAME were prepared by dissolving 0.05 g of the sample in 0.95 mL hexane to which was added 0.05 mL of 1 M sodium methoxide. Data were processed with a Perkin-Elmer Sigma 10 integrator (Norwalk, CT).

The melting characteristics were studied with a Perkin-Elmer DSC 7, equipped with 1020 series Thermal Analysis System software. Calibration was performed with *n*-decane (m.p. –29.66°C, ΔH_f 202.09 J/g) and indium (m.p. 156.60°C, ΔH_f 28.45 J/g). About 2 to 2.5 mg of the fat sample in the differential scanning calorimetry (DSC) pan was melted in an oven at 60°C for 30 min before being stored at 0°C for 90 min. The samples were then stabilized at 26°C for 40 h. An empty covered sample pan was used as the reference. The sta-

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TABLE 1
Fatty Acid Composition (wt%)[a] of CBS, AMF, HMF42, and MCB

FAME	Cocoa butter substitutes (CBS)	Anhydrous milkfat (AMF)	High-melting fraction milkfat 42 (HMF42)	Malaysian cocoa butter (MCB)
$C_{6:0}$	—	1.6	1.6	—
$C_{8:0}$	2.3	1.2	1.2	—
$C_{10:0}$	2.9	2.6	2.8	—
$C_{12:0}$	54.6	3.3	3.8	—
$C_{14:0}$	20.7	11.5	13.4	0.1
$C_{16:0}$	9.2	31.2	36.6	25.3
$C_{18:0}$	8.7	11.4	12.9	37.6
$C_{18:1}$	—	19.9	13.9	32.1
$C_{18:2}$	—	1.1	0.4	2.9
$C_{18:3}$	—	1.0	0.4	0.2
$C_{20:0}$	—	0.7	0.2	1.2

[a]Average values determined in duplicate; FAME, fatty acid methyl esters.

bilized samples were again cooled at 0°C and held for 90 min before being transferred and held at −30°C for 5 min on the DSC head prior to measurement. DSC melting curves were recorded at a heating rate of 20°C/min from −30°C to a maximal temperature of 50°C. The partial melting enthalpies at 20 ($\Delta H_{20°C}$) and 30°C ($\Delta H_{30°C}$) were calculated by means of the Perkin-Elmer DSC-7 partial area software (14). Experiments were conducted in duplicate. Data obtained from the measurements were analyzed with the SAS package (15) on an IBM (White Plains, NY) personal computer.

The polymorphic form of the fat crystals in the samples was determined with the FT 592 Enraf-Nonius Diffractis X-ray generator (Delft, Holland) and an Enraf-Nonius Model FR 552 Guinier camera. The samples were tempered in the same way as for DSC analyses prior to measurement. The samples were measured at 20°C in a customized single-compartment cell, equipped with temperature control by means of an external-circulation thermostated bath. Kodak (Eastman Kodak Co., Rochester, NY) diagnostic film direct exposure (Cat. No. 155 8162) was used, and the spacings on the X-ray film were measured with an Enraf-Nonius Guinier viewer capable of reading to the nearest 0.001 nm under illuminated magnification.

SFC was measured with a Newport wide-line nuclear magnetic resonance (NMR) analyzer MK IIIA. The instrument was set at 1.5 G gatewidth, 45 μA R.F., 375 A.F. gain, and 32 s integration time. The weight of the sample was 1.5 g. Triolein was used as the standard. The samples in the NMR tube were first melted at 70°C for 30 min, cooled at 0°C for 90 min, stabilized at 26°C for 40 h, and held at measurement temperatures of 20 or 30°C for 30 min each prior to measurement (16). Data obtained were then analyzed with the SAS package (15).

RESULTS AND DISCUSSION

Results from gas–liquid chromatography analyses are shown in Table 1. The melting thermograms of the fats are presented in Figure 1. CBS showed the highest melting enthalpy (143.1 J/g), followed by MCB (138.8 J/g), HMF42 (97.1 J/g), and AMF (72.9 J/g). The higher melting enthalpy of HMF42, compared to AMF, is related to the higher content of saturated medium- and long-chain fatty acids, namely $C_{12:0}$, $C_{14:0}$, $C_{16:0}$ and $C_{18:0}$, and lower content of unsaturated long-chain fatty acids ($C_{18:1}$, $C_{18:2}$, and $C_{18:3}$).

The iso-line diagrams of $\Delta H_{20°C}$ of CBS/AMF/MCB and CBS/HMF42/MCB are depicted in Figure 2A and B. CBS showed the highest $\Delta H_{20°C}$ (133.4 J/g), followed by MCB (119.2 J/g), HMF42 (60.1 J/g), and AMF (20.3 J/g). The ternary diagram of CBS/AMF/MCB showed lower $\Delta H_{20°C}$, compared to CBS/HMF42/MCB. For example, the $\Delta H_{20°C}$ for blends coded Q and Q′, where all component fats were present in the ratio of 1:1:1 (w/w/w), were 40.1 and 49.2 J/g. Eutectic interactions, as indicated by the $\Delta H_{20°C}$ iso-lines, were observed along the binary lines of CBS/MCB, AMF/MCB, and HMF42/MCB. In addition, in ternary blends, minimal $\Delta H_{20°C}$

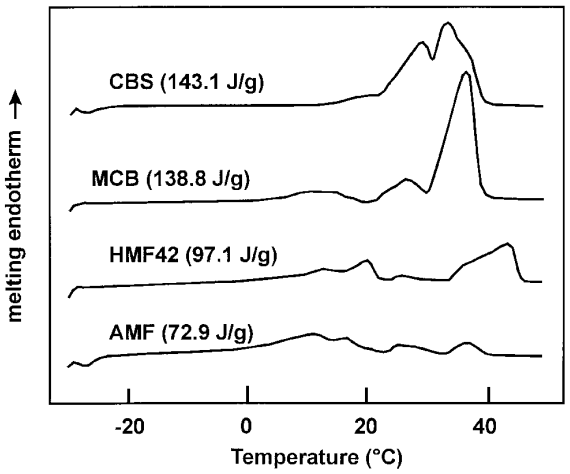

FIG. 1. Melting thermograms of cocoa butter substitute (CBS), anhydrous milk fat (AMF), high-melting fraction of milk fat (HMF42), and Malaysian cocoa butter (MCB).

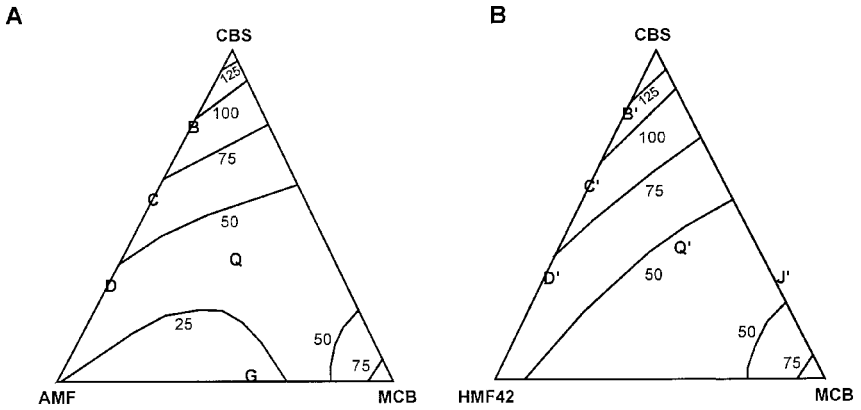

FIG. 2. Iso-line diagrams of partial melting enthalpy ($\Delta H_{20°C}$) for (A) CBS/AMF/MCB and (B) CBS/HMF42/MCB after 40 h stabilization at 26°C. See Figure 1 for abbreviations.

were observed toward point G (8.3 J/g) and J′ (26.1 J/g) in the blends of CBS/AMF/MCB and CBS/HMF42/MCB, respectively.

However, no eutectic effects were noted along the binary lines of AMF/CBS and HMF42/CBS at $\Delta H_{20°C}$. This was evident in the blends coded B,C,D for AMF/CBS in which $\Delta H_{20°C}$ is 98.5, 65.1, and 38.2, respectively. Similar trends also were observed in blends coded B′, C′, and D′ for HMF42/CBS at $\Delta H_{20°C}$. Md. Ali and Dimick (14) reported that, in general, enthalpy values of the blends decrease with an increase in concentration of milk fat in the system. Figure 3A and B shows the iso-line diagrams of $\Delta H_{30°C}$ for CBS/AMF/MCB and CBS/HMF42/MCB. Similar trends of the interaction also were observed in both $\Delta H_{30°C}$ systems.

Table 2 shows the X-ray diffraction patterns of CBS, AMF, and MCB blends. CBS characteristics were two strong peaks at 4.20 and 3.78 Å, and the type of polymorph was β′. Increasing the concentration of CBS into MCB increased the proportion of the β′ form in the mixture. However, addition of AMF to CBS at any ratio did not change the polymorphic form.

AMF exhibited a very weak short-spacing at 4.55 Å and a strong short-spacing at 4.22 Å. This results in the formation of a mixture of β′ and β polymorphs, with the β′ form being dominant. This is in accordance with the findings by Timms (17). Addition of AMF to MCB at the ratio of 3:1 (w/w) did not change the dominant polymorphic form β′ of AMF. However, at blend ratios of 1:1 and 1:3 (w/w) of AMF/MCB, a distinctive change in the polymorph form was observed, i.e., the β polymorphic form dominated. MCB shows a strong short-spacing at 4.55 Å and a very weak short- spacing at 4.16 Å. The β polymorph dominates, and the presence of a small amount of β′ crystals was attributable to the liquid component that was solidified at 0°C prior to measurement. The blend ratio 1:1:1 (w/w/w) of CBS/AMF/MCB results in greater formation of β than β′.

Table 3 shows the characteristics of X-ray diffraction patterns of CBS, HMF42, and MCB blends. Pure HMF42 shows that the β′ form still dominated over the β form, but the degree of domination was reduced. However, addition of HMF42 to CBS at any ratio showed only formation of β′ polymorph.

The iso-solid diagrams at 20°C for blends CBS/AMF/MCB and CBS/HMF42/MCB are shown in Figure 4A and B.

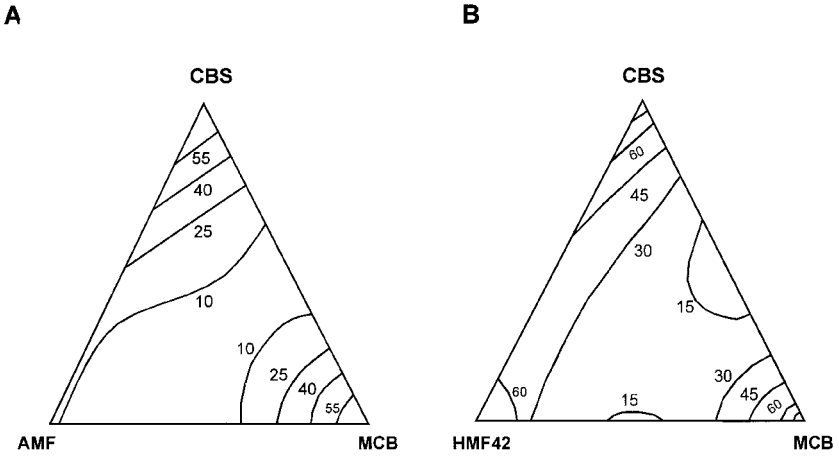

FIG. 3. Iso-line diagrams of partial melting enthalpy ($\Delta H_{30°C}$) for (A) CBS/AMF/MCB and (B) CBS/HMF42/MCB after 40 h stabilization at 26°C. See Figure 1 for abbreviations.

TABLE 2
X-Ray Diffraction Patterns of CBS, AMF, and MCB Blends Measured by X-ray Diffractometer After Stabilization (at 26°C for 40 h)

Code	Blends CBS/ AMF/ MCB	Short-spacing (Å)													Polymorphic form
		5.3	5.2	4.6	4.5	4.4	4.3	4.2	4.1	4.0	3.9	3.8	3.7	3.6	
A	1:0:0						4.38m[a]	4.20s			3.99w		3.78s		β′
B	3:1:0						4.38m	4.20s			3.99w		3.78s		β′
C	1:1:0				4.5vw		4.39w	4.25m	4.16s	4.05w	3.97vw	3.87vw	3.78s		β′
D	1:3:0					4.49vw	4.34w	4.21m		4.05vw			3.78s		β′
E	0:1:0				4.55vw		4.35m	4.22s		4.05m			3.78s		β′ >>> β
F	0:3:1				4.55vw		4.35m	4.22s		4.05m			3.78s		β′ >>> β
G	0:1:1	5.38w			4.55s				4.19w		3.95w		3.78m	3.62vw	β >> β′
H	0:1:3	5.38w	5.19vw		4.55s	4.46vw		4.24w	4.16vw	4.05vw	3.94m	3.83m	3.71m	3.62w	β >>> β′
I	0:0:1	5.38m	5.19w		4.55s	4.46w		4.24vw	4.16vw	4.05w	3.94m	3.83m	3.71m	3.62m	β >>> β′
J	1:0:3	5.38m	5.19vw		4.55s			4.24vw	4.16vw	4.05vw	3.94m	3.83m	3.71m	3.62m	β >>> β′
K	1:0:1	5.37w	5.20vw		4.55s		4.38w	4.26m	4.17s	4.08m	3.95w		3.78s	3.62w	β + β′
L	3:0:1						4.38m	4.20s			3.99w		3.78s		β′
M	4:1:1				4.50vw		4.39m	4.25m	4.16s	4.05w	3.97m	3.87vw	3.78s		β′
N	1:4:1						4.34w	4.21m		4.08vw			3.78s		β′
P	1:1:4	5.38m			4.55s			4.24w	4.16w	4.05vw	3.94m	3.83m	3.71m	3.62m	β >> β′
Q	1:1:1	5.38w			4.55m				4.19w		3.95vw		3.78s	3.62vw	β > β′

[a]Intensities estimated visually as : s, strong; m, medium; w, weak; vw, very weak. See Table 1 for other abbreviations.

Among the fats studied, CBS possessed the highest SFC at 20°C (91.1%), followed by MCB (82.4%), HMF42 (41.4%), and AMF (15.6%). The SFC results were similar to the melting analysis in the DSC where eutectic formation was observed along the binary lines of CBS/MCB, AMF/MCB, and HMF42/MCB. Paulicka (2) stated that CB has a lower solubility in CBS, mainly due to the smaller molecular size of the lauric-containing triacylglycerol. However, no eutectic formation was observed along the binary lines of AMF/CBS and HMF42/CBS.

According to Shukla (18), softer CB would contain about 63% solid fat at 20°C and 20% solid fat at 30°C. In this study, the criteria at 20°C for binary blends of CBS/AMF and CBS/HMF42 were fulfilled if the content of AMF or HMF42 was less than 25% (point w and w′ in Fig. 4A and B, respectively). Moreover, in the binary system that contained MCB, such criteria were met when the content of AMF or HMF42 was 10% or less (points x and x′ in Fig. 4A and B, respectively).

At 30°C, for the binary blend containing CBS, this criterion was fulfilled if the content of AMF was less than 25% (point y in Fig. 5A). Blends of CBS and HMF42 fulfilled the criteria at any blend ratio. In the binary blends containing MCB, the HMF42 or AMF should be limited to 30% or less. Timms (8) mentioned that the addition of about 30% milk fat to CB would result in eutectic interaction, thus contributing to the softness of CB/AMF mixtures, although the effect is

TABLE 3
X-Ray Diffraction Patterns of CBS, HMF42, and MCB Blends Measured by X-ray Diffractometer After Stabilization (at 26°C for 40 h)

Code	Blends CBS/ HMF42/ MCB	Short-spacing (Å)													Polymorphic form
		5.3	5.2	4.6	4.5	4.4	4.3	4.2	4.1	4.0	3.9	3.8	3.7	3.6	
A′	1:0:0						4.38m[a]	4.20s			3.99w		3.78s		β′
B′	3:1:0				4.50vw		4.39m	4.25s	4.16s	4.05vw	3.97w	3.87vw	3.78s		β′
C′	1:1:0				4.50vw		4.39w	4.25m	4.16m	4.05w	3.97vw	3.87vw	3.78s		β′
D′	1:3:0				4.51vw		4.35w	4.22s		4.05m			3.78s		β′
E′	0:1:0				4.57m	4.40m		4.26s	4.10m			3.81s	3.74vw		β′ > β
F′	0:3:1				4.57vw	4.40m		4.26s	4.10m	4.08w		3.81s			β′ >>> β
G′	0:1:1	5.36w			4.55s		4.37vw	4.23m			3.95w		3.79s	3.63vw	β > β′
H′	0:1:3	5.38m			4.55s	4.46vw		4.24m		4.05vw	3.94m	3.83m	3.71m	3.62w	β > β′
I′	0:0:1	5.38m			4.55s	4.46w		4.24vw	4.16vw	4.05w	3.94m	3.83m	3.71m	3.62m	β >>> β′
J′	1:0:3	5.38m			4.55s			4.24vw	4.16vw	4.05vw	3.94m	3.83m	3.71m	3.62m	β >>> β′
K′	1:0:1	5.37w	5.20vw		4.55s		4.38w	4.26m	4.17s	4.08m	3.95w	3.78s	3.70vw	3.62w	β + β′
L′	3:0:1						4.38m	4.20s			3.99w		3.78s		β′
M′	4:1:1				4.50vw		4.39m	4.25m	4.16s	4.05w	3.97w	3.87vw	3.78s		β′
N′	1:4:1				4.51vw		4.35m	4.22s		4.05m			3.78s		β′
P′	1:1:4	5.38m			4.55s			4.24vw	4.16vw	4.05vw	3.94m	3.83m	3.71w	3.62m	β >>> β′
Q′	1:1:1	5.38vw			4.55m				4.19m	4.07vw	3.95vw		3.78s	3.62vw	β + β′

[a]Intensities estimated visually as : s, strong; m, medium; w, weak; vw, very weak. See Table 1 for other abbreviations.

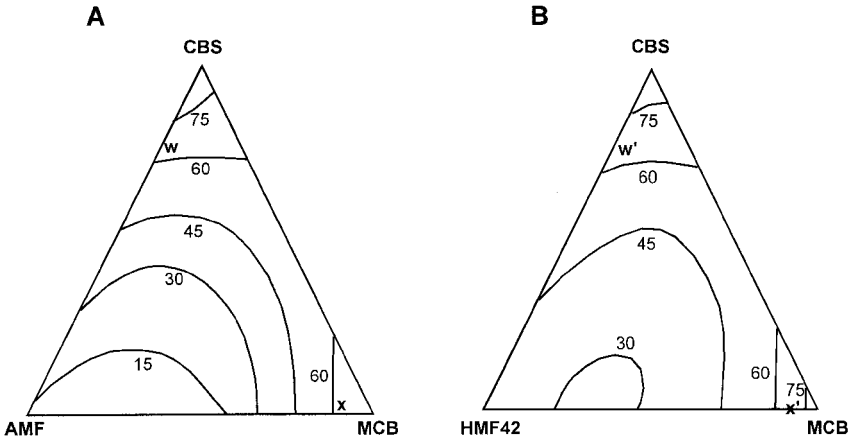

FIG. 4. Iso-solid diagrams of (A) CBS/AMF/MCB and (B) CBS/HMF42/MCB at 20°C after stabilization at 26°C for 40 h.

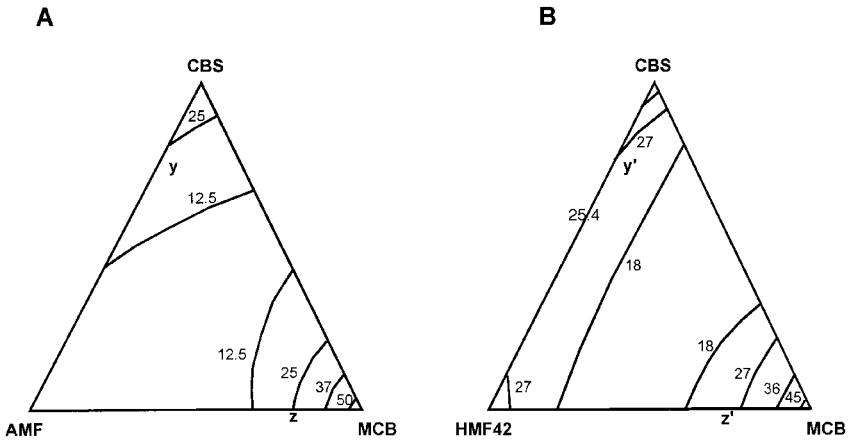

FIG. 5. Iso-solid diagrams of (A) CBS/AMF/MCB and (B) CBS/HMF42/MCB at 30°C after stabilization for 40 h. See Figure 1 for abbreviations.

relatively small. However, SFC data at 20 and 30°C indicate that the ternary blend of CBS/HMF42/MCB possesses higher solid fat than CBS/AMF/MCB. Thus, in general, the results show that, in making of chocolate confectionery that contains high proportions of milk fat, such as truffle filling, the extent of liquid migration from the center could be reduced by substituting AMF with HMF. However, higher SFC in the filling containing HMF does not necessarily facilitate the formation of β polymorphs.

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