Thermal Analysis of Palm Mid-Fraction, Cocoa Butter and Milk Fat Blends by Differential Scanning Calorimetry

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Commercial samples of anhydrous milk fat (AMF), Ivory Coast cocoa butter (CB) and palm mid-fraction (PMF) were blended in a ternary system. The melting characteristics of the blends were studied by differential scanning calorimetry (DSC). Results suggest that in the studies of interaction involving more than two fats, partial area (A_i) under the melting peak should be converted to partial enthalpy (ΔH_i) rather than to solid fat index. The ΔH values of the blends decreased as the amount of AMF was increased and increased as the amount of CB was increased. In general, the effect of PMF was less pronounced compared to the effect of the other two fats. Eutectic effects within the ternary system could be detected by measuring the deviation of melting enthalpy by DSC, and from the corresponding values that were calculated for the thermodynamically ideal blends. The deviation reached a maximum when the amount of AMF was about 33%. On the binary line of CB/PMF, the eutectic effect was maximum at about 50–75% PMF. The interaction effect in the system was more noticeable at 30 and 20°C than at lower temperatures. Evaluation at 30°C was preferred because both the effect of AMF in the ternary system and the effect of PMF on the binary line were more readily observed.

KEY WORDS: Anhydrous milk fat, cocoa butter, confectionery fats, differential scanning calorimetry, palm mid-fraction, ternary system.

Differential scanning calorimetry (DSC) melting thermograms of fats give valuable information on how they melt in the mouth during mastication. It is generally accepted that the partial area (A_i) under the melting peak (endotherm) is equivalent to the percentage of solid fat remaining at the selected temperature. Lambelet and Raemy (1) described computer programs to control sampling of data from the DSC and to plot iso-solid diagrams of fat blends in binary fat systems. Lambelet (2) pointed out, however, that DSC analyses would yield consistently higher solid fat index (SFI) values than nuclear magnetic resonance (NMR). He also noted that the relationship between the SFI values determined by NMR and DSC was linear for cocoa butter (CB), but not for CB and milk fat mixtures. Buning-Pfaue and Bartsch (3) suggested that the measurement of differences in crystallization enthalpy between those measured by DSC, and those calculated for the thermodynamically ideal blends would indicate the effect of blending on crystallization. By using the calculation method, they clearly noted the compatibility of lauric fat with milk fat and the noncompatibility of lauric fat with CB in binary system. This method also allows the analysis to be completed in a short time because no tempering treatment is required. Nevertheless, it is well understood that the measurement should be done on the melting enthalpy when fats that possess complex polymorphic behavior, such as CB or its equivalent fat, are present. The objective of the present work was

to investigate the interaction that occurs in a ternary system involving anhydrous milk fat (AMF), CB and palm mid-fraction (PMF) by means of DSC.

EXPERIMENTAL PROCEDURES

Commercial AMF and Nigerian CB were used in this study. PMF was obtained from the Palm Oil Research Institute of Malaysia (PORIM). Fatty acid composition of each fat was determined as fatty acid methyl esters (FAME) by gas–liquid chromatography (Hewlett Packard 5880; Hewlett-Packard, Palo Alto, CA). FAMEs were injected at 249°C on a Supelco (Bellefonte, PA) Omegawax 320 capillary column (30 m × 0.25 mm i.d.), under the following conditions: 2 min isothermal at 100°C for AMF, and at 150°C for PMF and CB; programmed heating at 4°C/min to a final temperature of 180°C; and 30 min holding time at the final temperature. Detection was with a flame-ionization detector at 280°C.

The fats were blended in various ratios, shown later in Tables 2 and 3. Each blend was prepared in duplicate. The solidification and melting characteristics were studied by using a Perkin-Elmer DSC Model 4, equipped with a Perkin-Elmer 3600 data station (Norwalk, CT). Calibration was done with a gallium standard (m.p. 29.78°C, ΔH_f 19.4 cal/g) (4). About 3 mg of a precisely weighed (±0.0005 mg) fat sample in the DSC pan was melted at 60°C for 30 min before cooling to 0°C and then was held for 90 min. The pan, with the samples, was then transferred to a 26°C incubator and held for 40 ± 0.5 h or 7 d for stabilization. The stabilized samples were again cooled at 0°C and held for 90 min before being held at −25°C for 5 min on the DSC head prior to measurement. DSC melting curves were recorded at a heating rate of 0.5°C/min from −25°C (T_o) to a maximum temperature of 50°C (T_i). SFI values, at measured temperatures (T), were calculated with a Perkin-Elmer DSC-4 "Partial Area software program" by sequentially integrating the DSC melting curves and normalizing the values obtained (A_i) by the total surface englobed by the DSC curves (A) (1). Partial enthalpies were calculated by using the same method, except the A_i to A ratios were multiplied by the total melting enthalpy of the samples.

$$SFI = \frac{A_i}{A} \times 100 \qquad [1]$$

$$\Delta H_i = \frac{A_i}{A} \times \Delta H \qquad [2]$$

Partial melting enthalpy (ΔH_i) for the thermodynamically ideal blends were calculated based on the reported method (3), which can be summarized as:

$$\Delta H_{iPMF/CB/AMF\ (x/y/z)} = x \cdot \Delta H_{PMF} + y \cdot \Delta H_{CB} + z \cdot \Delta H_{AMF} \qquad [3]$$

where x, y and z are the partial amounts of PMF, CB and AMF, respectively, present in the blends. Data obtained

from the measurements were analyzed by using the SAS package (SAS, Cary, NC) on an IBM mainframe, as reported previously (5).

RESULTS AND DISCUSSION

Table 1 shows the fatty acid compositions of AMF, CB and PMF used in this study. CB was characterized by the high palmitic (27%), oleic (33%) and stearic (36%) acid content. PMF had higher palmitic acid content (56%) than CB at the expense of lower stearic acid content, while AMF was characterized by the presence of short-chain fatty acids.

CB showed the highest melting enthalpy (35.4 cal/g), followed by PMF (29.5 cal/g) and AMF (17.4 cal/g) (Fig. 1). Thus, different conversion factors would be required when converting ΔH_i value to SFI for fats of different types (Fig. 2). In addition, each blend may have specific interactive effects. For example, the CB/AMF (1:1) blend showed a closer relationship to AMF, whereas CB/PMF (1:1) blend was closer to CB. Results suggest that, in the studies of interaction between fats, it would be more appropriate to convert the partial area (A_i) into partial enthalpy $\Delta(H_i)$, rather than into SFI. Because DSC measures energy, this would eliminate the calculated conversion error. This is especially important when more than two fats are present in a system and different interactions occur simultaneously.

Figure 3 shows the iso-line diagram of partial melting enthalpy $(\Delta H_{30°C})$, required to bring the ternary fat blends from 30°C to a complete melt, after 40-h stabilization at 26°C. Detailed data on partial melting enthalpy of the blends are presented in Table 2. Results demonstrated that as the AMF content of the blends was increased from point G to point A, the $\Delta H_{30°C}$ value decreased from 20.4 to 2.4 cal/g. The increase of CB content increased the $\Delta H_{30°C}$ value, as can be seen from point

TABLE 1

Fatty Acid Compositions (wt%)[a] of the Commercial Samples

FAME	Cocoa butter	Palm mid-fraction	Anhydrous milk fat
C6:0	—	—	2.2
C8:0	—	—	1.4
C10:0	—	0.2	3.2
C12:0	—	0.1	3.7
C14:0	0.1	0.8	11.5
C16:0	27.1	55.7	29.8
C18:0	36.1	6.0	12.0
C18:1	32.8	32.4	24.9
C18:2	2.6	3.7	3.1
C18:3	—	—	0.1
C20:0	0.9	0.4	—

[a]Average values determined in duplicate. FAME, fatty acid methyl esters.
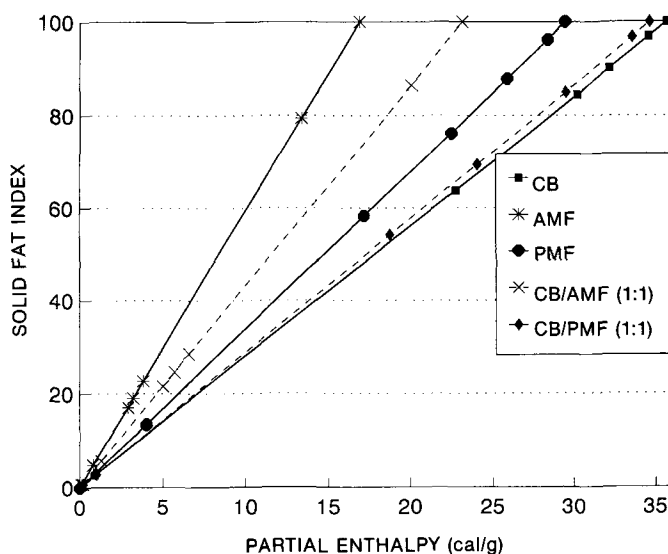
FIG. 2. Relation between partial melting enthalpy and solid fat content of CB, AMF, PMF and blends. Abbreviations as in Figure 1.
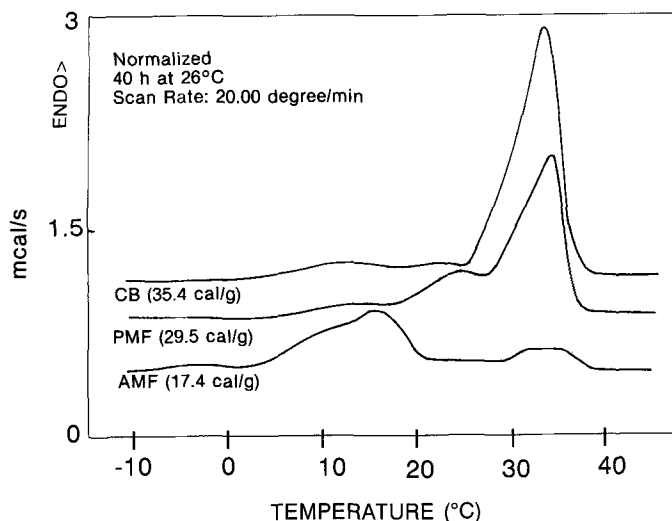
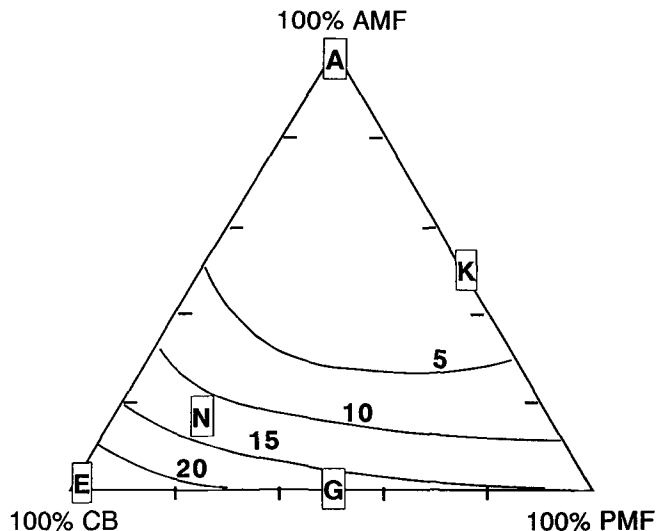FIG. 1. Melting thermogram of anhydrous milkfat (AMF), cocoa butter (CB) and palm mid-fraction (PMF).

FIG. 3. Iso-line diagram of partial melting enthalpy required to bring the blends from 30°C to a complete melt $(\Delta H_{30°C})$ after 40-h stabilization at 26°C. Abbreviations as in Figure 1.

TABLE 2

Melting Enthalpy[a] of CB, AMF and PMF Blends as Measured by DSC, and Calculated Deviation Values for the Thermodynamically Ideal Blends (after 40-h stabilization at 26°C)[b]

Blending		Melting enthalpy (ΔH) Partial value at				Deviation value (ΔH) at			
Code	AMF/CB/PMF ratio	$-15°C$	$10°C$	$20°C$	$30°C$	$-15°C$	$10°C$	$20°C$	$30°C$
A	1:0:0	17.4	12.1	3.8	2.4	0.0	0.0	0.0	0.0
B	3:1:0	21.0	17.0	3.4	2.4	−0.9	−0.7	−7.4	−5.1
C	1:1:0	23.2	19.5	6.6	5.0	−3.2	−3.1	−11.3	−7.7
D	1:3:0	30.7	28.1	21.1	13.5	−0.2	−0.7	−3.8	−4.3
E	0:1:0	35.4	34.3	31.9	22.9	0.0	0.0	0.0	0.0
F	0:3:1	35.4	34.0	30.6	21.6	1.5	1.2	0.3	0.1
G	0:1:1	34.7	33.6	27.1	20.4	2.3	2.4	1.7	0.4
H	0:1:3	32.8	31.5	26.5	13.7	1.8	1.8	−0.7	−4.9
I	0:0:1	29.5	28.2	25.6	17.2	0.0	0.0	0.0	0.0
J	1:0:3	26.3	23.5	7.7	3.5	−0.2	−0.7	−12.5	−10.0
K	1:0:1	23.2	19.7	4.2	3.5	−0.3	−0.5	−10.5	−6.3
L	3:0:1	21.3	16.7	3.9	2.5	0.9	0.6	−5.4	−3.6
M	4:1:1	16.9	15.1	3.1	2.4	−3.9	−3.4	−9.0	−5.9
N	1:4:1	28.2	27.0	20.5	16.4	−3.2	−2.6	−5.7	−2.1
P	1:1:4	25.8	24.0	14.2	4.7	−2.7	−2.6	−8.8	−11.0
Q	1:1:1	24.1	20.0	5.0	2.9	−3.3	−4.9	−15.4	−11.3

[a]Average values determined in duplicate.
[b]CB, cocoa butter; AMF, anhydrous milk fat; PMF, palm mid-fraction; DSC, differential scanning calorimetry.

K (3.5 cal/g), to N (16.4 cal/g) and to E (22.9 cal/g). The increase of PMF content reduced the $\Delta H_{30°C}$ value. However, as shown by the contour lines (Fig. 3), the effect of PMF was less pronounced compared to the effect of AMF and CB. Similar patterns of iso-partial enthalpy lines were found at other measured temperatures (−15, 10 and 20°C; figures not given) during the melting. A similar pattern was also found after the prolonged stabilization of the fat samples up to 7 d (Fig. 4), but with some increases of ΔH_i values. The increases were most noticeable at about point Q. As shown in Tables 2 and 3, the partial melting enthalpies at 30°C of blend Q after

100% AMF

100% CB

100% PMF

FIG. 4. Iso-line diagram of partial melting enthalpy required to bring the blends from 30°C to a complete melt ($\Delta H_{30°C}$) after 7-d stabilization at 26°C. Abbreviations as in Figure 1.

40 h and after 7-d stabilization were 2.9 and 8.8 cal/g, respectively.

Figures 3 and 4 do not clearly show the inflection of contour lines that occur because of the eutectic interaction between fats. However, with the Buning-Pfaue and Bartsch (3) method, the eutectic effect can readily be seen (Fig. 5). This is evident, based on the significant deviation of its measured melting enthalpy at 30°C from the values calculated for their respective thermodynamically ideal blends. Data in Table 2 show that, after 40-h stabilization, the deviations reached their maximum when the amount of AMF was about 33% (point Q; −11.3 cal/g), yielding curves close to the binary line of AMF/PMF (Fig. 5). Data also show mild eutectic interaction along the binary line of CB/PMF, as indicated by the deviation value at point H (−4.9 cal/g).

Prolonged stabilization (Fig. 6) reduced the eutectic effect in the CB/PMF binary system, as indicated by the decrease of the deviation value at point J from 10.0 cal/g (after 40-h stabilization) (Table 2) to 5.1 cal/g (after 7-d stabilization) (Table 3). This, however, made the eutectic effect within the CB/AMF binary system more prominent, as shown by the higher deviation values at point B (increased to −6.6 cal/g), point C (increased to −8.6 cal/g) and point D (increased to −7.2 cal/g). The present results are in agreement with those reported by Hogenbirk (6), which showed a decrease in solid fat content at 30°C for a blend of CB and PMF; and by Kheiri (7), which showed the limited compatibility between CB and milk fat.

Data in Tables 2 and 3 show that, in general, the interaction (deviation values, ΔH) was more noticeable (higher negative values) at 30 and 20°C than at lower temperatures. Evaluation at 30°C was generally preferred because more interactions were noticeable. For example, the incompatibility between PMF and CB (blend H after 46-h stabilization; blend F, G, H after 7-d stabilization) could only be readily observed at 30°C.
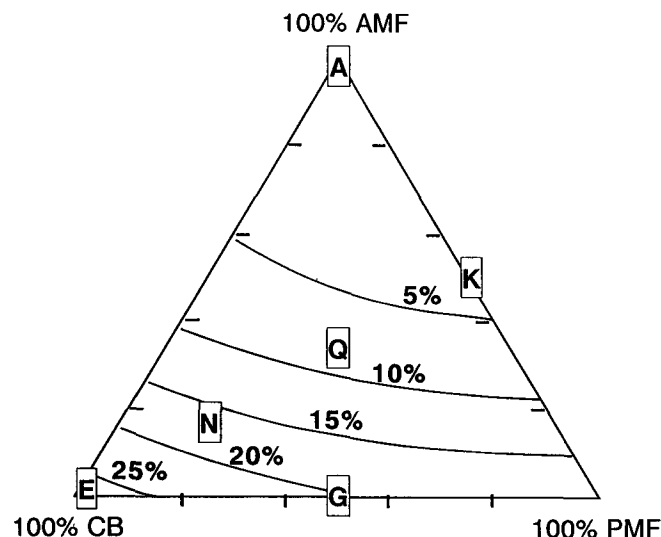
TABLE 3

Melting Enthalpy[a] of CB, AMF and PMF Blends as Measured by DSC, and Calculated Deviation Values for the Thermodynamically Ideal Blends (after 7-d stabilization at 26°C)[b]

	Blending	Melting enthalpy (ΔH); partial value at				Deviation value (ΔH) at			
Code	AMF/CB/PMF ratio	−15°C	10°C	20°C	30°C	−15°C	10°C	20°C	30°C
A	1:0:0	17.3	13.3	3.9	3.0	0.0	0.0	0.0	0.0
B	3:1:0	20.2	14.9	3.5	2.6	−1.6	−3.7	−7.6	−6.6
C	1:1:0	25.2	21.4	9.2	6.8	−1.3	−2.6	−9.1	−8.6
D	1:3:0	30.4	27.6	21.9	14.4	−0.6	−1.7	−3.6	−7.2
E	0:1:0	35.5	34.6	32.7	27.8	0.0	0.0	0.0	0.0
F	0:3:1	35.5	34.5	31.3	22.2	1.0	1.4	0.4	−3.1
G	0:1:1	35.0	32.9	29.2	18.8	1.4	1.3	0.0	−4.1
H	0:1:3	33.1	32.4	28.2	15.9	0.6	2.2	0.8	−4.5
I	0:0:1	31.6	28.7	25.7	17.9	0.0	0.0	0.0	0.0
J	1:0:3	28.6	26.3	15.4	9.1	0.6	1.5	−4.9	−5.1
K	1:0:1	19.2	14.8	5.4	3.7	−5.3	−6.2	−9.4	−6.8
L	3:0:1	21.4	15.7	3.9	2.6	0.5	−1.5	−5.5	−4.1
M	4:1:1	18.4	13.5	3.3	2.4	−4.4	−5.9	−9.0	−7.2
N	1:4:1	30.9	28.7	23.9	16.7	−0.9	−1.4	−2.8	−5.3
P	1:1:4	29.9	28.4	19.8	8.7	0.1	1.3	−3.4	−8.4
Q	1:1:1	26.7	24.2	12.6	8.8	−1.4	−1.3	−8.2	−7.4

[a]Average values determined in duplicate.
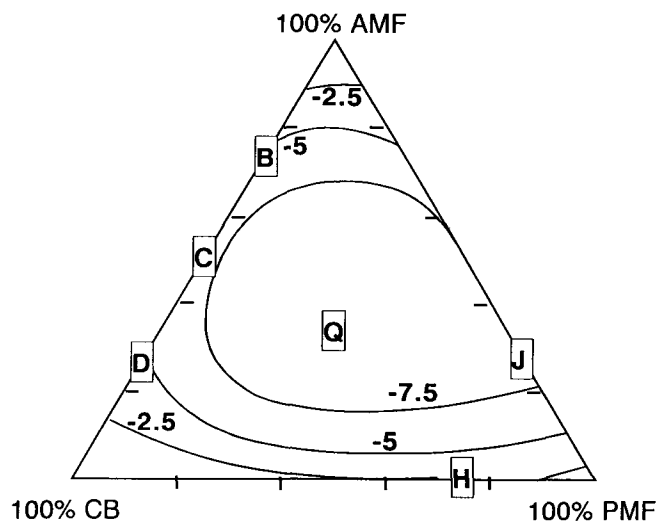[b]Abbreviations as in Table 2.

FIG. 5. Iso-line diagram of the calculated enthalpy deviation at 30°C, after 40-h stabilization at 26°C. Abbreviations as in Figure 1.
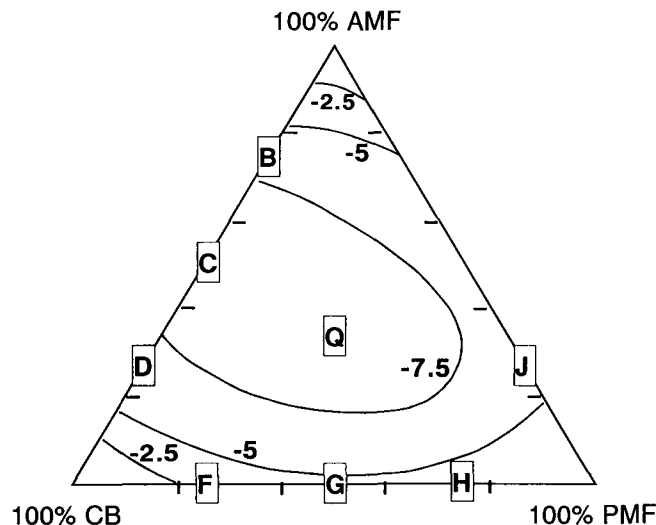

FIG. 6. Iso-line diagram of the calculated enthalpy deviation at 30°C, after 7-d stabilization at 26°C. Abbreviations as in Figure 1.

The above results demonstrated that the physical interaction of PMF, CB and AMF in ternary blends can be monitored well by DSC from the changes in thermal characteristics, such as melting and partial melting enthalpy.

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