Melting and Solidification Characteristics of Confectionery Fats: Anhydrous Milk Fat, Cocoa Butter and Palm Kernel Stearin Blends

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Differential scanning calorimetry measurements of crystallization and melting characteristics of commercial samples of anhydrous milk fat (AMF), cocoa butter (CB) and hydrogenated palm kernel stearin (PKS) in ternary blends were studied. Results showed that stabilization at 26°C (either for 40 h or 7 d) did not greatly affect the melting thermogram trace of PKS. However, the effect of stabilization became prominent as CB was added into the system. Deviation of measured enthalpy from the corresponding values, calculated for thermodynamically ideal blends, showed clear interaction between all three fats. At 20°C, the strongest deviation occurred at about the AMF/CB/PKS (1:1:1) blend, whereas at 30°C the deviation moved toward the CB/MF (1:1) blend. The presence of 25% AMF in PKS had little effect on its solidification capability, but solidification was adversely affected with inclusion of CB.

KEY WORDS: Anhydrous milk fat, binary and ternary blends of cocoa butter, compatibility of confectionery fats, differential scanning calorimetry, hydrogenated palm kernel stearin.

From a practical point of view, cost has probably been the main incentive behind the use of lauric hard butters as cocoa butter substitutes (CBS) in confectionery coating formulations. The CBS fats are expected to have textural properties similar to cocoa butter (CB), i.e., they must be brittle at room temperature but must have a short melting range just below body temperature, which ensures a pleasant mouthfeel and may offer some technological advantages over CB. The tempering process for CBS confections may either be simplified or can be omitted for normal coating purposes. However, these fats have a low tolerance for CB addition (1). Nevertheless, lauric CBS has an acceptable hardness and rapid crystallization characteristics, even at high milk fat concentrations (2). The aim of the present research was to study the interaction between commercial lauric hard butter [palm kernel stearin (PKS)], CB and anhydrous milk fat (AMF) in ternary blends by measuring the deviation of the melting enthalpy by differential scanning calorimetry (DSC) as described previously by Md. Ali and Dimick (3).

EXPERIMENTAL PROCEDURES

Commercial AMF and Nigerian prime-pressed CB were used in this study. A completely hydrogenated PKS was obtained from Van Den Bergh Foods (Baltimore, MD). Fatty acid composition of each fat was determined as fatty acid methyl esters by gas-liquid chromatography with a Hewlett-Packard (Palo Alto, CA) 5880, as previously described (3).

A matrix of 16 samples was produced by blending the commercial fats in various ratios (presented later in Table 2). Each blend was prepared in duplicate. The solidification and melting characteristics were studied by using a Perkin-Elmer (Norwalk, CT) DSC Model-4, equipped with a Perkin-Elmer 3600 Data Station (3). About 3 mg of precisely weighted (±0.0005) fat sample in the DSC pan was melted at 60°C for 30 min before cooling to 0°C and held for 90 min. The pan 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 to 0°C and held for 90 min before being held at −25°C for 5 min on the DSC head prior to measurement. The nonstabilized samples were prepared by holding the melted sample at 0°C for 90 min and at −25°C for 5 min on the DSC head before measurement. DSC melting curves were recorded at a heating rate of 20°C/min from −25°C to a maximum temperature of 50°C. The crystallization patterns of the melted samples were scanned from 35 to −25°C at a cooling rate of 5°C/min. Partial melting enthalpies (ΔH_i) were calculated by the method reported earlier this year (3). Data obtained from the measurements were analyzed by using the SAS Package on an IBM mainframe (4). R^2 values, which indicate model fit of each of the constructed ternary diagrams (presented later in Figs. 3–5), were also determined and were found to be greater than 0.95.

RESULTS AND DISCUSSION

Data presented in Table 1 show the fatty acid composition of the CB, PKS and AMF. The CB was characterized by high concentrations of palmitic (27%), stearic (36%) and oleic (33%) acid content. Lauric (C12:0) and myristic (C14:0) concentrations in PKS were 56 and 21%, respectively, and the AMF contained appreciable amounts of short-chain fatty acids (C4:0–C12:0). Melting thermograms of the fats are presented in Figure 1. PKS showed the highest melting enthalpy (30.1 cal/g) for the nonstabilized samples, followed by CB(24.1 cal/g) and AMF (17.3 cal/g). Stabilization at 26°C for 40 h had little effect on the melting enthalpy of PKS (33.1 cal/g) and AMF (17.4

TABLE 1

Fatty Acid Composition (wt%)[a] of Commercial Samples of Cocoa Butter, Hydrogenated Palm Kernel Stearin and Anhydrous Milk Fat

FAME	Cocoa butter	Palm kernel stearin	Anhydrous milk fat
C6:0	—	—	2.2
C8:0	—	2.4	1.4
C10:0	—	3.2	3.2
C12:0	—	56.1	3.7
C14:0	0.1	20.6	11.5
C16:0	27.1	8.3	29.8
C18:0	36.1	8.7	12.0
C18:1	32.8	0.5	24.9
C18:2	2.6	—	3.1
C18:3	—	—	1.0
C20:0	0.9	—	—

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

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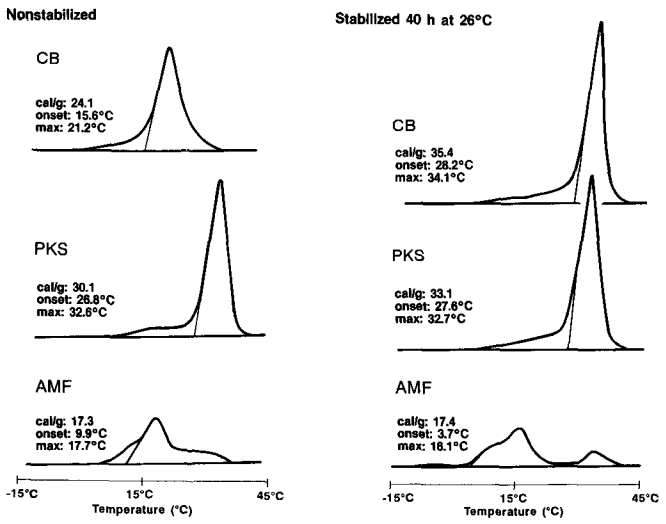

FIG. 1. Melting thermogram of nonstabilized and stabilized (for 40 h at 26°C) cocoa butter (CB), palm kernel stearin (PKS) and anhydrous milkfat (AMF).

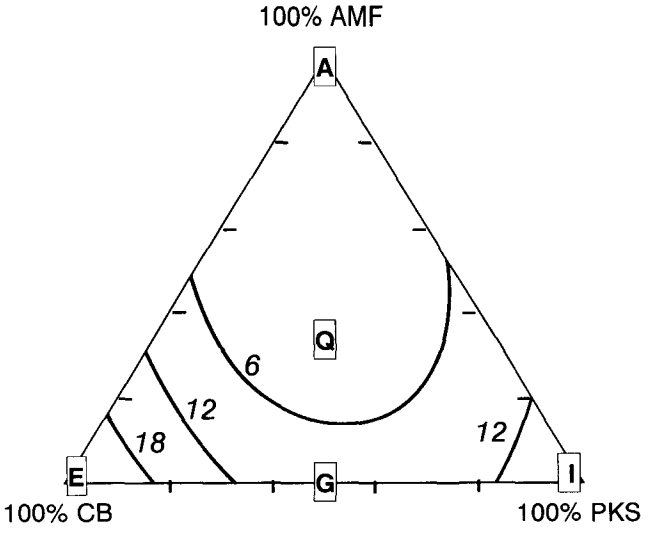

FIG. 2. Isoline diagram of partial melting enthalpies for AMF, CB and PKS blends required to bring the mixtures from 30°C to a complete melt ($\Delta H_{30°C}$) after 40 h stabilization at 26°C. Abbreviations as in Figure 1.

cal/g). However, a marked increase in the melting enthalpy of CB (from 24.1 cal/g to 35.4 cal/g) was evident. These results indicate the ease of PKS crystallization, which gives an advantage and flexibility in the confectionery coating or enrobing process as compared to CB, which requires tempering. Data presented in Table 2 indicate that crystal transformation was relatively complex in blends with high concentrations of CB. This was evident, for example, in blend codes C, G and N, in which the total melting enthalpies at 15°C without stabilization at 26°C (16.8, 22.1 and 22.8 cal/g, respectively) were much lower than the corresponding values after stabilization, either for 40 h (23.2, 32.0 and 30.4 cal/g, respectively) or 7 d (25.2, 34.2 and 31.5 cal/g, respectively).

The effect of blending ratios on the partial melting enthalpy, required to bring the AMF/CB/PKS blends from 30°C to a complete melt ($\Delta H_{30°C}$) after 40 h stabilization at 26°C, is depicted in Figure 2. This figure demonstrates a minimum point of $\Delta H_{30°C}$ at point G, and between point A to G (at point Q), where there is a 50:50 ratio between CB and PKS. It does not demonstrate any minimum point of $\Delta H_{30°C}$ along the binary lines of AMF/CB and AMF/PKS, but, in general, the enthalpy value decreases with an increase in concentration of AMF in the system. Similar interactions were found at other measured temperatures (ΔH_t, $\Delta H_{10°C}$ and $\Delta H_{20°C}$; data not given). Prolonged stabilization up to seven days increased the partial melting enthalpy slightly (Table 2). This, however, did not change the interaction patterns from those shown in Figure 2. These results are in accordance with previous

TABLE 2

Melting Enthalpy (ΔH; cal/g)[a] of AMF, CB and PKS Blends Measured by DSC, with and without stabilization at 26°C

Blend		Melting enthalpy (ΔH), partial value at (°C)											
		Without stabilization				Stabilized for 40 h				Stabilized for 7 d			
Code	AMF/CB/PKS ratio	−15	10	20	30	−15	10	20	30	−15	10	20	30
A	1:0:0	17.3	11.8	3.3	1.5	17.4	12.1	3.8	2.4	17.3	13.3	3.9	3.0
B	3:1:0	—	—	—	—	21.0	17.0	3.4	2.4	20.2	14.9	3.5	2.6
C	1:1:0	16.8	13.6	5.8	1.7	23.2	20.1	6.6	5.0	25.2	21.4	9.2	6.8
D	1:3:0	—	—	—	—	30.1	28.1	21.1	13.5	30.4	27.6	21.9	14.4
E	0:1:0	24.1	23.4	14.2	0.2	35.4	34.3	31.9	22.9	35.5	34.6	32.7	27.8
F	0:3:1	—	—	—	—	34.0	32.8	27.8	13.4	35.0	33.5	28.5	13.8
G	0:1:1	22.1	21.5	15.4	1.7	32.0	30.8	21.4	8.4	34.2	32.4	24.6	12.1
H	0:1:3	—	—	—	—	32.2	31.0	22.2	9.9	33.1	31.8	22.6	12.0
I	0:0:1	30.1	29.5	28.8	21.0	33.1	32.8	31.9	23.4	33.1	33.1	32.2	23.7
J	1:0:3	—	—	—	—	30.4	27.5	23.2	10.9	31.1	28.0	23.4	12.7
K	1:0:1	23.6	20.6	16.4	4.2	25.8	20.9	13.4	5.9	25.3	21.8	15.1	8.6
L	3:0:1	—	—	—	—	21.3	16.3	7.8	3.4	21.5	16.6	7.8	3.8
M	4:1:1	16.8	11.5	4.3	1.8	18.7	11.2	4.2	1.6	18.7	11.5	4.8	2.5
N	1:4:1	22.8	21.2	7.0	0.8	30.4	27.7	18.6	9.8	31.5	29.4	21.4	11.0
P	1:1:4	26.7	24.8	21.1	5.2	29.5	25.9	18.0	7.4	30.1	26.2	19.5	10.2
Q	1:1:1	24.4	20.0	9.8	1.6	24.9	20.2	8.0	3.1	26.9	22.9	8.9	4.9

[a]Means of duplicate samples. AMF, anhydrous milk fat; CB, cocoa butter; PKS, palm kernel stearin.

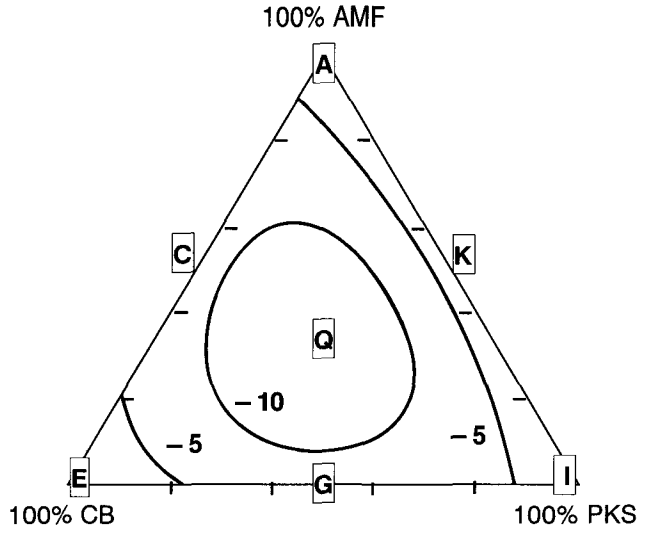

FIG. 3. Isoline diagram of the measured enthalpy deviation at 20°C after seven days stabilization at 26°C. Abbreviations as in Figure 1.

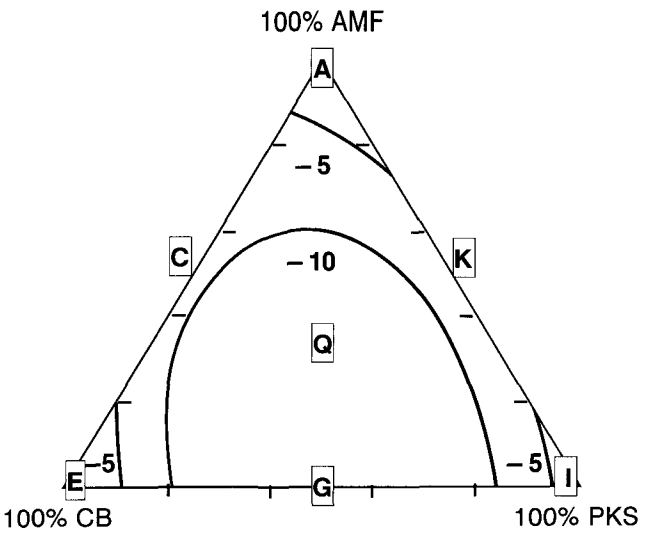

FIG. 4. Isoline diagram of the measured enthalpy deviation at 30°C after seven days stabilization at 26°C. Abbreviations as in Figure 1.

reports that demonstrated the incompatibility of CB with PKS (5) and the softening effect of AMF on CB and on PKS (6).

Figures 3 and 4 were constructed from the deviation values of calculated partial melting enthalpies to the corresponding values for a thermodynamically "ideal blend" (3) shown in Table 3. Data demonstrate the interaction between all the fats, either in binary or in ternary blends. At 20°C (Fig. 3), the strongest deviation occurred at about blend code Q (−14.0 cal/g), where the three fats are at equal ratio, whereas at 30°C (Fig. 4) it occurred at about blend code Q (−13.8 cal/g) to G (−13.7 cal/g). The deviation was generally highest in the CB/PKS system on the binary lines. The deviations also occurred in the AMF/PKS binary system, but they were less than that found in the AMF/CB system. For example, the deviation value of $\Delta H_{20°C}$ (Table 3 and Fig. 3) for blend code K (AMF/PKS, 1:1), was −2.9 cal/g, compared to −9.1 cal/g for blend code C (AMF/CB, 1:1). These data show that AMF is more compatible with PKS than with CB, as well as confirming previous research (6).

In Figure 5, the crystallization thermograms are shown for the individual fats and some of their blends: PKS/AMF (3:1), CB/AMF (3:1), CB/PKS (1:3) and PKS/CB/AMF (4:1:1). PKS had a short crystallization range with an onset transition temperature of 11.9°C. AMF and CB, which showed wider crystallization ranges, had onset transition temperatures of 15.5°C and 16.9°C, respectively. The higher tolerance of AMF with PKS can be seen in the PKS/AMF (3:1) thermogram, which indicates that the

TABLE 3

Deviation Values of the Measured Partial Melting Enthalpy (ΔH) of Matrix Samples from the Calculated Values for the Thermodynamically Ideal Blends After Seven Days Stabilization at 26°C[a]

Code	Blend AMF/CB/PKS ratio	Calculated partial enthalpy (cal/g) for ideal blends at: 20°C	30°C	Deviation value of the measured partial enthalpy (cal/g) at: 20°C	30°C
A	1:0:0	3.9	3.0	0.0	0.0
B	3:1:0	11.1	9.2	−7.6	−6.6
C	1:1:0	18.3	15.4	−9.1	−8.6
D	1:3:0	25.5	21.6	−3.6	−7.2
E	0:1:0	32.7	27.8	0.0	0.0
F	0:3:1	32.6	26.8	−4.1	−13.0
G	0:1:1	32.5	25.8	−7.9	−13.7
H	0:1:3	32.4	24.7	−9.8	−12.7
I	0:0:1	32.2	23.7	0.0	0.0
J	1:0:3	25.1	18.4	−1.7	−5.7
K	1:0:1	18.0	13.5	−2.9	−4.9
L	3:0:1	10.9	7.7	−3.1	−3.9
M	4:1:1	13.4	10.6	−8.6	−8.1
N	1:4:1	27.8	23.0	−6.4	−12.0
P	1:1:4	27.6	20.9	−8.1	−10.7
Q	1:1:1	22.9	18.7	−14.0	−13.8

[a]Abbreviations as in Table 2.

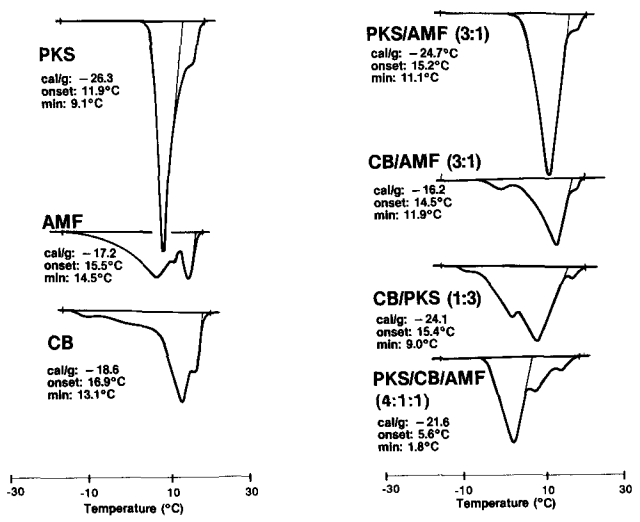

FIG. 5. Cooling exothermograms showing the effect of AMF on the solidification of PKS, CB and their blends. Abbreviations as in Figure 1.

presence of 25% AMF did not greatly widen the crystallization range when compared with PKS alone. Nevertheless, the presence of CB in blends containing PKS had adverse effects on the solidification performance, as noted by the broad solidification curves shown in the CB/PKS (1:3) and PKS/CB/AMF (4:1:1) thermogram.

Data obtained have shown that, to ensure a good processing and eating quality of lauric hard butter-based products, it is critically important to limit the amount of cocoa butter, and this applies whether milk fat is present or not in the formulation.

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