# Melting Behavior of Blends of Milk Fat with Hydrogenated Coconut and Cottonseed Oils

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**ABSTRACT:** The melting behavior of milk fat, hydrogenated coconut and cottonseed oils, and blends of these oils was examined by nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC). Solid fat profiles showed that the solid fat contents (SFC) of all blends were close to the weighted averages of the oil components at temperatures below 15°C. However, from 15 to 25°C, blends of milk fat with hydrogenated coconut oils exhibited SFC lower than those of the weighted averages of the oil components by up to 10% less solid fat. Also from 25 to 35°C, in blends of milk fat with hydrogenated cottonseed oils, the SFC were lower than the weighted averages of the original fats. DSC measurements gave higher SFC values than those by NMR. DSC analysis showed that the temperatures of crystallization peaks were lower than those of melting peaks for milk fat, hydrogenated coconut oil, and their blends, indicating that there was considerable hysteresis between the melting and cooling curves. The absence of strong eutectic effects in these blends suggested that blends of milk fat with these hydrogenated vegetable oils had compatible polymorphs in their solid phases. This allowed prediction of melting behavior of milk-fat blends with the above oils by simple arithmetic when the SFC of the individual oils and their interaction effects were considered.

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**KEY WORDS:** DSC, hydrogenated coconut oil, hydrogenated cottonseed oil, milk fat, NMR, solid fat content.

The performance of fats in food products depends on melting behavior. Thus, the solid fat content (SFC) of fats as a function of temperature is an important property to be determined to evaluate the matching of fats with suitable applications. The blending of milk fat with vegetable oils has been used to increase the buttery flavor of vegetable fats and change the physical properties of milk fat. For example, milk fat alone does not have the appropriate plasticity and hardness for use in pastries (1), but blending of milk fat with vegetable oils and fats results in a significant alteration of the physical properties of milk fat. Of particular interest to milk-fat producers is the development of milk-fat blends with vegetable oils and fats for confectionery, pastry, baking and other applications.

There have been many reports on the melting behavior of fat blends. However, the properties of blends cannot be readily predicted from their component oils (2). When two fats are mixed, the SFC of the blends may be lower than the weighted average of the component fats. Sometimes, the SFC can be lower than that of either fat. Timms (2), Mulder and Walstra (3), and Rossell (4) have reviewed the interactions between fat components.

Blends of natural coconut oil with hydrogenated palm oil are used in margarine and shortening production. Hardened cottonseed oils are used in pastry fat substitutes (5,6). Aini *et al*. (7) found that blends of milk fat with palm oil gave shortenings with softer consistency but better creaming ability than palm oil. A number of milk-fat–cocoa-butter blends have been investigated for use in confectionery applications. Generally, it has been found that these blends have strong eutectic interactions (8–11) which are reflected in disproportionate softening of chocolate when these blends are used in place of cocoa butter.

There is general interest in gaining knowledge about the melting behavior of blends of anhydrous milk fat (AMF) with hydrogenated coconut oil (HCO) or hydrogenated cottonseed oils (HCSO). The properties of these blends have not yet been investigated and reported in detail. This study was undertaken to explore the chemical and physical properties of these milk fat–hydrogenated vegetable oil blends, and to determine if a simple method could be developed for predicting the properties of binary blends made from different production batches.

## MATERIALS AND METHODS

*Materials.* Commercial samples of butter manufactured from Eastern Victorian milks of late spring 1997 (AMF1) and early Spring 1997 (AMF2) were obtained from Bonlac Foods Ltd. (Dandenong, Victoria, Australia). Subsequently, AMF3, manufactured from Eastern Victorian milk of middle spring 1998, was also obtained from the same supplier. AMF from the butter samples were prepared in the laboratory by heating the butter to 70°C for 45 min and centrifuging the melted butter at 70°C at 2,500 rpm for 15 min in BTL Bench Centrifuge [Baird and Tatlock (London) Ltd., Chadwell Heath Essex, United Kingdom]. The clear upper layer obtained on centrifugation was used.

Hydrogenated vegetable oils with different melting points were obtained from Meadow Lea Foods Ltd. (Footscray, Victoria, Australia) in 1997 (labeled as HCO1 and 2 and HCSO1 and 2) and in 1998 (labeled as HCO3).

An AMF standard [CRM 164 with a certified fatty acid composition by gas–liquid chromatography (GLC) analysis] was obtained from the Commission of the European Communities (Brussels, Belgium) (12). The AMF triglyceride standard was kindly supplied by Dr. Precht, Institute of Chemistry and Physics, Kiel, Germany, with his reference value.

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*Preparation of blends*. AMF prepared from either butter or commercial AMF and hydrogenated vegetable oils were melted at 70°C and blended at concentrations of 10, 20, 30, 40, 50, 60, and 80% hydrogenated vegetable oil in milk fat (w/w).

*Dropping point (D.P.)*. The D.P. was measured using the Mettler FP80HT Central Processor and the Mettler FP83 Dropping Point Cell (13). The D.P. of the oils and fats used were as follows: AMF1—33.5°C, AMF2—33.9°C, AMF3—32.1°C, HCO1—36.7°C; HCO2—41.5°C, HCO3—38.8°C, HCSO1—31.4°C and HCSO2—44.5°C.

*Fatty acid composition*. The fatty acid compositions were determined by GLC on a Shimadzu GC 17A (Shimadzu Corporation, Kyoto, Japan) equipped with a flame-ionization detector operated at 280°C. Fatty acid methyl esters (FAME) were made by transesterification of oils with 2 M potassium hydroxide in methanol. FAME were injected at 240°C on a BPX70 (SGE, Australia) capillary column (25 m × 0.25 mm i.d.). The temperature program for the column was as follows: 2 min at 50°C, followed by heating at 10°C/min to 160°C, 1°C/min to 175°C and 20°C/min to a final temperature of 240°C at which it was held for 2 min. Peak area percentages were corrected with response factors determined from the reference milk fat—CRM164.

*Triglyceride composition*. Triglyceride compositions of the fats were also determined by GLC using a Varian 3400 (Varian Instrument Group, Sunnyvale, CA) equipped with a flame-ionization detector operated at 420°C. The fat was melted at 65°C for 45 min and then dispersed in nonane (0.2% vol/vol). The solution was separated on an HT-SimDist WCOT Ultimetal column 5 m × 0.53 mm (Chrompack, Middelburg, The Netherlands). The temperature program for the column was as follows: 1 min at 200°C, followed by heating at 10°C/min to 300°C and 16°C/min to a final temperature of 380°C. Injector temperature was programmed from 80 to 380 at 250°C/min. Triglyceride peak area percentages were corrected by response factors determined from the triglyceride milk-fat standard. This method separates triglycerides on the basis of the total number of carbon atoms in the constituent fatty acid chains.

*SFC*. SFC of the fat was measured by pulsed NMR using the Bruker Minispec PC120 (Karlsruhe, Germany) (14). The fats in NMR tubes were melted at 70°C for 45 min and tempered at 60°C for 30 min and then at 0°C for 90 min. The relative proportions of solid and liquid fat were measured in 5°C increments between 0 to 40°C, after holding the sample at each temperature for 30 min.

The weighted average of the SFC of the original oils was calculated as:

$$\text{SFC} = X \cdot \text{SFC of AMF} + Y \cdot \text{SFC of HVO} \qquad [1]$$

where HVO represents hydrogenated vegetable oil and $X$ and $Y$ are the percentages of AMF and HVO in the blends.

*Differential scanning calorimetry (DSC)*. Thermal analyses of fats were determined by DSC using a 1020 series DSC 7 Thermal Analysis System (Perkin Elmer, Wellesley, MA) calibrated with indium (99.99%). Fats for DSC analysis were melted at 70°C for a half hour before sampling. About 5 mg of fat sample was weighed into aluminum sample pans (precisely to 0.1 mg) and hermetically sealed, and an empty sealed aluminum pan was used as a reference. Samples were heated at 65°C for 2 min, cooled at 5°C/min to –40°C, held at that temperature for 2 min, and then heated at 5°C/min to 65°C. The enthalpy change of fats and blends during melting or crystallization was measured. From the DSC melting thermograms, the SFC was calculated from the percentage integrated partial area in the temperature intervals as a fraction of the total melting area. All analyses were carried out in duplicate, and average values are reported.

## RESULTS AND DISCUSSION

*Fatty acid compositions*. Table 1 shows the compositions for major fatty acid of the fats used in this work. HCSO had high

**TABLE 1**
**Literature and Present Analysis Values for Major Fatty Acid Compositions (wt%) of Milk Fats and Hydrogenated Vegetable Oils Used**

| | Milk fat (AMF) | | | | | Hydrogenated coconut oil (HCO) | | | | Hydrogenated cottonseed oil (HCSO) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Fatty acid | AMF[a] | AMF1 | AMF2 | AMF3 | Coconut oil[b] | HCO1 | HCO2 | HCO3 | Cottonseed oil[b] | HCSO1 | HCSO2 |
| C4:0 | 4.4 | 4.2 | 3.9 | 4.2 | ND | ND | ND | ND | <0.1 | ND | ND |
| C6:0 | 2.4 | 2.4 | 2.2 | 2.5 | 0.4–0.6 | 0.8 | 0.8 | 0.6 | <0.1 | ND | ND |
| C8:0 | 1.4 | 1.4 | 1.2 | 1.5 | 6.9–9.4 | 8.7 | 8.7 | 7.1 | <0.1 | ND | ND |
| C10:0 | 2.9 | 3 | 2.6 | 3.3 | 6.2–7.8 | 6.3 | 6.6 | 5.7 | <0.1 | ND | ND |
| C12:0 | 3.2 | 3.5 | 3.1 | 3.7 | 45.9–50.3 | 44.8 | 44.8 | 45.3 | <0.1 | 0.2 | 0.2 |
| C14:0 | 10.4 | 11.2 | 10.5 | 10.6 | 16.8–19.2 | 16.3 | 14.7 | 17 | 0.5–2.5 | 0.8 | 0.8 |
| C16:0 | 28.1 | 28.7 | 31.9 | 24.9 | 7.7–9.7 | 9.1 | 11 | 9.9 | 17–29 | 23.2 | 23.7 |
| C16:1n- 7 | 1.5 | 1.4 | 2 | 1.3 | ND | 0 | 0 | 0 | 0.5–1.5 | 0.5 | 0.2 |
| C18:0 | 11.6 | 11.6 | 10 | 11.9 | 2.3–3.2 | 11.1 | 11.6 | 13 | 1.0–4.0 | 3.2 | 14.5 |
| C18:1 | 23.6 | 21.5 | 21.5 | 24.4 | 5.4–7.4 | 0.5 | 0.6 | 1.3 | 13–44 | 47.2 | 55.4 |
| C18:2n-6 | 1.5 | 1.2 | 1.4 | 1.5 | 1.3–2.1 | 0 | 0.5 | 0.1 | 33–58 | 16.9 | 0.2 |
| C18:3n-3 | 0.7 | 0.6 | 0.5 | 0.8 | ND | ND | ND | ND | 0.1–2.1 | ND | ND |

[a] Reference 15.
[b] Reference 5. ND, not detected.

levels of unsaturated fatty acids (about 65 and 56% for HCSO1 and HCSO2, respectively). HCO had unsaturated fatty acid contents of only about 1.1, 0.5, and 1.4% for HCO1, HCO2 and HCO3, respectively. As expected, hydrogenation had reduced the level of unsaturation of the oils compared with the natural oils reported in the literature (Table 1). In comparison to the hydrogenated vegetable oils, AMF had a broad range of short-chain fatty acids (Table 1). There were only small differences in fatty acid profiles among the AMF, except for C16:0 and C18:1 where the differences were somewhat larger, but fell well within the range reported for Australian milk fat survey (15). The fatty acid compositions of all blends were analyzed to check that the appropriate blending composition had been achieved. It was confirmed from these fatty acid compositions that all blends had been prepared correctly (results not shown).

*Triglyceride compositions.* The triglyceride compositions of the fats used in this work are given in Table 2. It should be noted that the triglyceride analysis used cannot distinguish between fats differing only in their degree of saturation. Thus these triglyceride compositions of cottonseed oils with different extents of hydrogenation were similar despite differences in melting properties and fatty acid profiles. Mares and Rezanka (16) only reported triglycerides of C48 and higher carbon number in natural cottonseed oil, whereas in HCSO1 and HCSO2 used in this study, small amounts of triglycerides with carbon number ≤46 were found. The most abundant triglyceride in the HCO was C36. This may be attributed to the high levels of C12:0 fatty acids in these oils. There were only slight differences in triglyceride compositions among the AMF; however, they still fall well within the range reported for Australian milk fat survey (17).

*SFC by NMR of pure oils and fats.* The SFC of AMF1, HCO1, HCSO1, and HCSO2 are shown in Figure 1. The other two HCO (HCO2 and HCO3) had almost identical melting features to HCO1 over the temperature interval from 0 to 25°C, but above this temperature there were some slight differences that accounted for the observed differences in their D.P. (Table 3). There were marked differences, up to 60% in SFC between the two HCSO. The SFC of the milk fats (AMF1 and AMF2) obtained from the same year of manufacture were similar. The commercial AMF3 obtained the following year had a consistently lower SFC than the other milk fats over the whole-temperature interval measured, which amounted up to 9% of SFC at 15°C. These melting profiles were typical and fall well within the range for Australian milk fat (18). The most notable difference among the oils and fats used was the significantly higher SFC of HCSO2, compared with the other individual oils and fats, at temperatures higher than 15°C. The large variations of SFC for these oils and fats can be mainly explained by differences in their fatty acid compositions (Table 1).

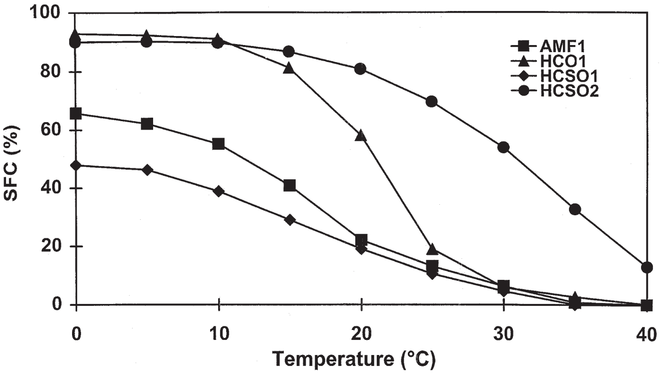

**FIG. 1.** Solid fat content (SFC) (%) of anhydrous milk fat (AMF)1, hydrogenated coconut oil (HCO)1, hydrogenated cottonseed oil (HCSO)1, and HCSO2 used in this study.

*Relationships between SFC, fatty acids, and triglycerides of pure oils and fats.* The high SFC of the HCO from 5 to

**TABLE 2**
**Literature and Present Analysis Values for Major Triglyceride Compositions (wt%) of the Milk Fats and Hydrogenated Vegetable Oils Used**

| | Milk fat | | | | | Hydrogenated coconut oil | | | | Hydrogenated cottonseed oil | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Triglyceride | AMF[a] | AMF1 | AMF2 | AMF3 | Coconut oil[b] | HCO1 | HCO2 | HCO3 | Cottonseed oil[c] | HCSO1 | HCSO2 |
| C:28 | 0.5 | 0.6 | 0.4 | 0.6 | 0.7–1.0 | 0.9 | 0.8 | 0.9 | 0 | ND | ND |
| C:30 | 1.0 | 1.3 | 1 | 1.2 | 2.8–4.1 | 3 | 3.2 | 2.9 | 0 | ND | ND |
| C:32 | 2.4 | 2.7 | 2.3 | 2.4 | 11.5–14.4 | 11.9 | 12.8 | 11.3 | 0 | 0 | 0 |
| C:34 | 5.4 | 6.3 | 6.1 | 5.8 | 15.6–17.6 | 15.6 | 16.2 | 16.5 | 0 | 0.2 | 0.1 |
| C:36 | 10.5 | 11.4 | 11.4 | 9.6 | 18.3–19.8 | 18.4 | 18.5 | 16.9 | 0 | 1.4 | 1.1 |
| C:38 | 12.8 | 12.8 | 12.6 | 12.3 | 15.1–17.7 | 16.6 | 15.5 | 16.3 | 0 | 1.7 | 1.4 |
| C:40 | 10.4 | 10.2 | 9.3 | 10.8 | 9.2–11.1 | 10.5 | 9.2 | 10.2 | 0 | 0.1 | 0.1 |
| C:42 | 7.1 | 7.3 | 6.9 | 7.3 | 6.5–8.0 | 7.7 | 6.4 | 7.4 | 0 | 0.1 | 0.6 |
| C:44 | 6.5 | 6.8 | 6.7 | 6.6 | 3.6–4.6 | 4.5 | 3.5 | 4.4 | 0 | 0.1 | 0.1 |
| C:46 | 7.2 | 7.4 | 7.7 | 7.2 | 2.1–3.0 | 2.7 | 2.1 | 2.8 | 0 | 0.3 | 0.3 |
| C:48 | 9.0 | 8.7 | 9.5 | 8.6 | 1.6–2.6 | 2.4 | 3 | 2.5 | 2.8 | 1.4 | 1.3 |
| C:50 | 11.3 | 10.4 | 11.4 | 10.9 | 0.8–2.0 | 2 | 3.5 | 2.5 | 16.3 | 15.1 | 15.1 |
| C:52 | 10.2 | 8.5 | 9.1 | 10 | 0.4–2.0 | 1.7 | 3 | 2.8 | 38.4 | 40.6 | 40.7 |
| C:54 | 5.1 | 4.3 | 3.9 | 6.1 | 0.1–1.5 | 1.2 | 1.8 | 1.8 | 42.5 | 35.3 | 35.1 |

[a] Reference 17.
[b] Reference 5.
[c] Reference 16. For abbreviations see Table 1.

**TABLE 3**
**Dropping Point (°C) of Milk Fats, Hydrogenated Vegetable Oils (HVO), and Their Blends Used in This Work[a]**

| Type of AMF and HVO | 100% AMF | 90%AMF: 10% HVO | 80%AMF: 20% HVO | 70%AMF: 30% HVO | 60%AMF: 40% HVO | 50%AMF: 50%HVO | 40%AMF: 60% HVO | 20%AMF: 80% HVO | 100% HVO |
|---|---|---|---|---|---|---|---|---|---|
| AMF1–HCO1 | 33.6 | 33.8 | 34.0 | 34.5 | 35.0 | 35.4 | 35.6 | 35.9 | 36.5 |
| AMF1–HCO2 | 33.4 | 34.3 | 35.3 | 36.7 | 37.5 | 38.5 | 39.3 | 40.2 | 41.4 |
| AMF3–HCO3 | 32.1 | 32.7 | 33.6 | 34.4 | 34.5 | 35.9 | 36.4 | 37.7 | 38.8 |
| AMF1–HCSO1 | 33.3 | 33.0 | 32.4 | 32.2 | 31.7 | 31.4 | 31.2 | 30.7 | 31.5 |
| AMF1–HCSO2 | 33.3 | 34.3 | 35.6 | 36.8 | 38.2 | 39.6 | 40.8 | 42.9 | 44.6 |

[a]See Table 1 for other abbreviations.

15°C and the rapid reduction in SFC from 15 to 25°C were related to the high percentage of short- and intermediate-chain (≤C12 and C14) saturated fatty acids in these oils. The large amount of C18:1 fatty acid in both of the HCSO cannot be identified as either oleic acid (*cis*) or elaidic (*trans*) with the fatty acid analysis method used in this study. However, the large difference between the SFC of the two HCSO over the whole-temperature interval suggests that apart from substantial differences of C18:2 between the two oils there were some differences in the proportions of *trans* isomer present. *Trans*-isomers have a higher SFC than the *cis*-isomers (5).

*SFC of milk-fat blends by NMR*. The melting properties and compositions of blends of AMF1-HCO1 were reasonably quite similar to those of blends AMF1-HCO2 and AMF3-HCO3. Therefore only SFC values of blends of AMF1 and HCO1 are shown (Fig. 2A). The SFC profiles of blends AMF1-HCSO1 and AMF1-HCSO2 are given in Figures 2B and 2C. In all cases, the SFC of the blends at 5°C were very close to the SFC-weighted averages of the original oils (Figs. 2A–C) and as well as at all temperatures for the blends of AMF1 with HCSO1 (Fig. 2B). However, at 15 and 20°C, there were obvious reduced SFC of the blends compared to the weighted averages of the AMF1 and HCO1 (Fig. 2A). At 25 and 30°C, the SFC of these blends were close to the weighted averages of the individual fats. From 20 to 35°C, the SFC of AMF1 and HSCO2 blends were consistently lower than the weighted averages of the individual fats (Fig. 2C). The reduced levels of SFC were generally more pronounced in the blends of AMF1 and HCO1 at 15 and 20°C than in blends with HSCO2 at 25 to 35°C.

*Interactions in blends of milk fat and hydrogenated vegetable oils*. Milk fat, the HCO, and HCSO are mainly composed of β′ polymorphs in the solid phase (2). This may explain the absence of strong eutectic interactions in the blends. It appeared that the solid phases from the blended fats were compatible in all blending ratios. However, there were differences in several of the curvatures of the SFC data of blends AMF1 with HCO1 and HCSO2 (Figs. 2A and 2C) which warrant discussion. To a large extent, these differences may be attributed to differing extents of dissolution of solid fat from one ingredient by liquid fat from the other ingredient (3). That is, the further the observed SFC were below the weighted average of the SFC of the ingredients, the greater the extent of dissolution of solid from one ingredient in liquid from the other.

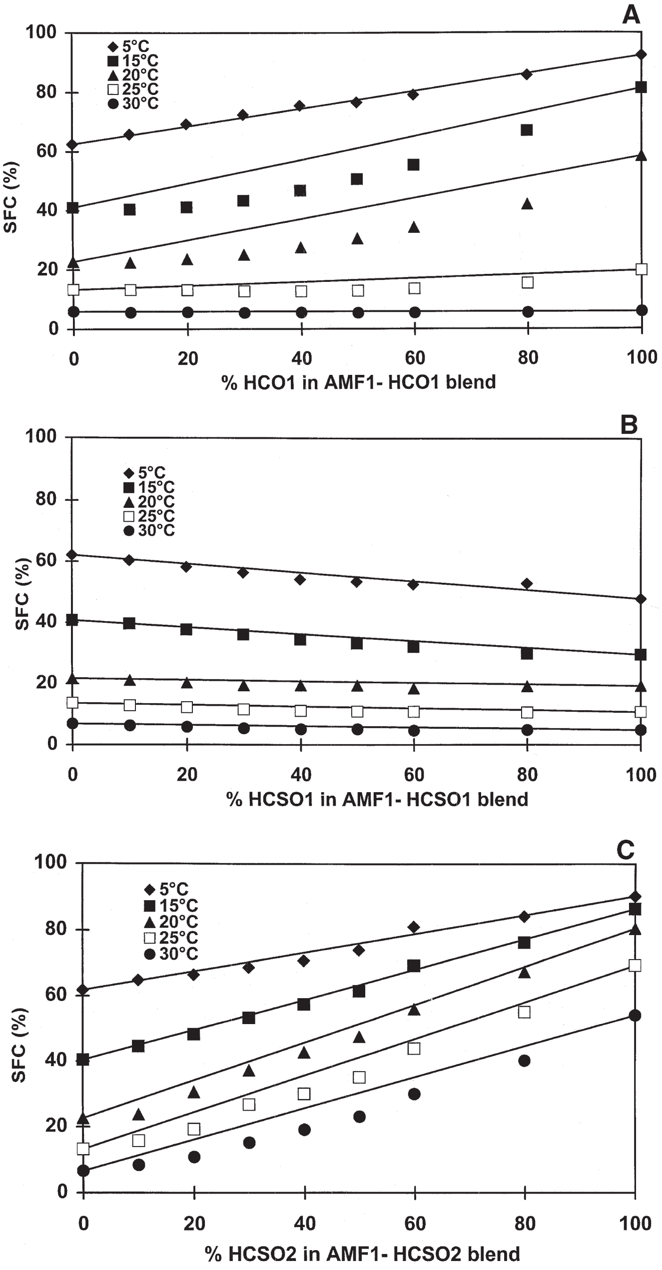

**FIG. 2.** (A) SFC (%) of AMF1, HCO1, and their blends (symbol, measured data; straight line, weighted average). (B) SFC (%) of AMF1, HCSO1, and their blends (symbol, measured data; straight line, weighted average). (C) SFC (%) of AMF1, HCSO2, and their blends (symbol, measured data; straight line, weighted average). See Figure 1 for abbreviations.

The curvatures were not observed at 5°C, where the individual fats had between 60 and 90% SFC (Figs. 2A,C). It may be that there was insufficient liquid fat available for substantial dissolution of solid fat, hence the SFC data lay close to the weighted average line. At most other temperatures there was notable downward curvature relative to the weighted average line (Figs. 2A,C). Apparently, slight differences of interactions in the solid phases can affect the curvature of the SFC data. Nevertheless, the interactions in the solid phases in this study were neither so unfavorable as to produce eutectic minima, nor so favorable as to produce maxima, i.e., compound formation.

Interestingly for AMF1 and HCSO1, where the SFC of the individual fat were similar to each other at all temperatures (Fig. 2B), SFC data of the blends lay also close to the weighted average line at all temperatures. This observation may be explained by a combination of effects. It can be hypothesized that although the solids from each ingredient still had potential to dissolve in liquid fat from the other ingredient, the solid phases were compatible and formed a solid solution, just as the liquid phases from the two ingredient fats, were completely miscible. Both the solid and liquid phases were equally stabilized by the mutual solubility of the ingredient fats and there was no decrease in SFC resulting from the blending. At temperatures higher than 25°C for milk-fat blends with HCO1, SFC values were so low that no clear trend could be observed.

*D.P.* The D.P. of blends of milk fats and hydrogenated vegetable oils are shown in Table 3. The D.P. of blends were generally close to the weighted average of the individual fats within about 0.5°C variation. The exceptions were blends with HCO2, where some D.P. were more than 1°C higher than the weighted average, and blends with HCSO1, where some D.P. were more than 1°C lower than the weighted average. The above behavioral differences were confined to the final stages of melting of the fats. At 30°C, all blends except those with HCSO2 had SFC less than 10% (Figs. 2A,B). From the similar SFC at 30°C (Figs. 2A,B) for all fats and blends of AMF1 with HCO1 and HCSO1 (Figs. 2A,B) and also AMF1 with HCO2 and AMF3 with HCO3 (NMR results not shown), and the different D.P. ranging from 31.2 to 41.4°C (Table 3), it can be seen that fats and blends differing widely in D.P. nevertheless had similar very low SFC at 30°C. Although often used for fats in product specification, the D.P. alone is not a good indicator of the whole softening and melting process in these fats and blends.

*Melting thermograms by DSC.* Melting thermograms of AMF3, HCO3, and corresponding blends of these fats are given in Figure 3. For AMF3, there was a major endothermic peak with a maximum at about 12°C, with two smaller shoulder peaks at *ca.* 3 and 7°C, as well as a plateau between 15 and 34°C. The major features of the melting thermogram were somewhat similar to those reported for milk fat previously (10,19), except that Timms (10) showed that the temperatures for the three endothermic peak maxima were at about 13, 24, and 29–40°C, respectively. Ten Grotenhuis *et al.* (19) found that the low, middle, and high endothermic peak maxima were at about 5, 15, and 20–35°C, respectively. These differences in the different studies may be partially explained by differences in milk-fat composition as well as the different tempering history and conditions used for DSC measurements, which affect the crystallization history of milk fat. The melting thermogram of the HCO3 had one major endothermic peak with a maximum at about 22°C from this study.

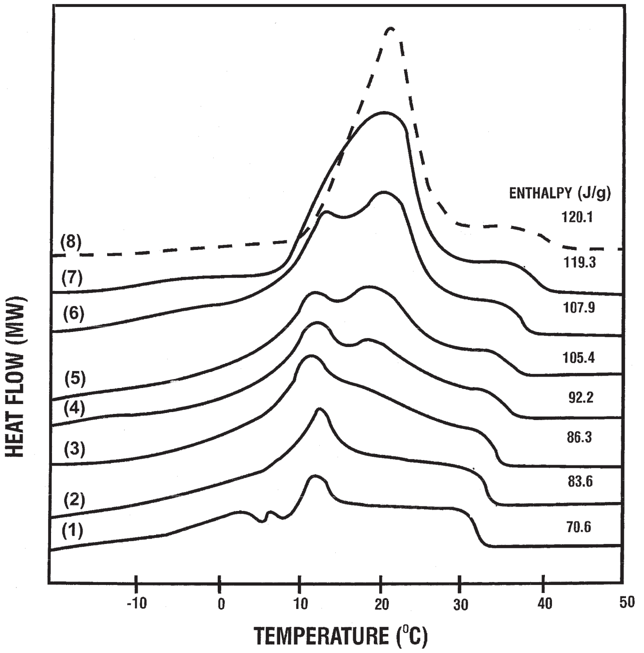

**FIG. 3.** Melting thermograms of differential scanning calorimetry (DSC) for AMF3, HCO3, and their blends. Melting curves (1), (2), (3), (4), (5), (6), (7), and (8) represent fat blends containing 0, 10, 20, 30, 40, 50, 80, and 100% of HCO3, respectively. See Figure 1 for other abbreviations.

The total enthalpy associated with fusion equalled 71 and 120 J/g for AMF3 and HCO3, respectively. The value for AMF3 was similar to the value of 72.8 and 69.8 J/g for milk fat that previously had been reported (11,21,22), but differed more from the values of 81.6 and 91.0 J/g reported by Lambelet (21) and Kankare and Antila (22). The melting enthalpy of fully hardened coconut oil (melting point not given) reported by Timms (23) was 130 J/g, which was reasonably close to values measured in this work. The total melting enthalpy of blends increased with increasing amounts of HCO3, although the increase was not linear.

The two peaks at 3 and 7°C, which were characteristic of the low-melting components of milk fat, disappeared in all blends. The most pronounced melting peak (12°C) of middle melting fraction of AMF remained distinct in blends containing up to 50% of HCO3. The plateau between 15 and 34°C of the high melting fraction of AMF became steeper after HCO3 was added until the major melting peak, characteristic of HCO3, appeared in blends containing ≥30% HCO3, but it shifted from 19 to 22°C with increasing levels of HCO3. In the blends containing 30–50% of HCO3, the two most pronounced melting peaks for AMF3 and HCO3 existed together in the melting thermograms. In the blends having 80% of HCO3, the major melting peak from HCO3 became dominant.

The disappearance of the peaks of the low melting fraction of milk fat from all blends might suggest that many of the triglycerides in the low melting fraction at 3 and 7°C have been incorporated into the higher melting crystal morphologies existing in HCO3 (Fig. 3). The middle melting peak of milk fat (at 12°C) remained distinct in blends containing up to 50% of HCO3, indicating that this solid phase had a greater tendency to persist in the presence of HCO3 solid phase. The major melting peak characteristic of HCO3 appeared after 30% HCO3 was added, but the maximum was shifted down in temperature relative to pure HCO3. The temperature shift probably resulted from the incorporation into this solid phase of some components from the milk fat.

*Crystallization thermograms of DSC.* The DSC crystallization curves of the individual fats and blends of AMF3 and HCO3 are shown in Figure 4. The crystallization curve for AMF3 was similar to that previously reported for milk fat (19,24). However the two major exothermic peaks were at about 4 and 11°C in this work, whereas at about 6 and 12°C were reported by Ten Grotenhuis *et al.* (19) and at 7.5 and 14.5°C by Coni *et al.* (24). The crystallization thermogram of HCO3 has a major exothermic peak with a minimum at about 2°C and a smaller one at 18°C.

The total crystallization enthalpies were 61 and 107 J/g for AMF3 and HCO3, respectively, over a temperature range from 25 to 40°C. The total crystallization enthalpy of blends having 10 and 20% of HCO3 was similar to that of AMF3, and at a higher level of HCO3 the enthalpy increased.

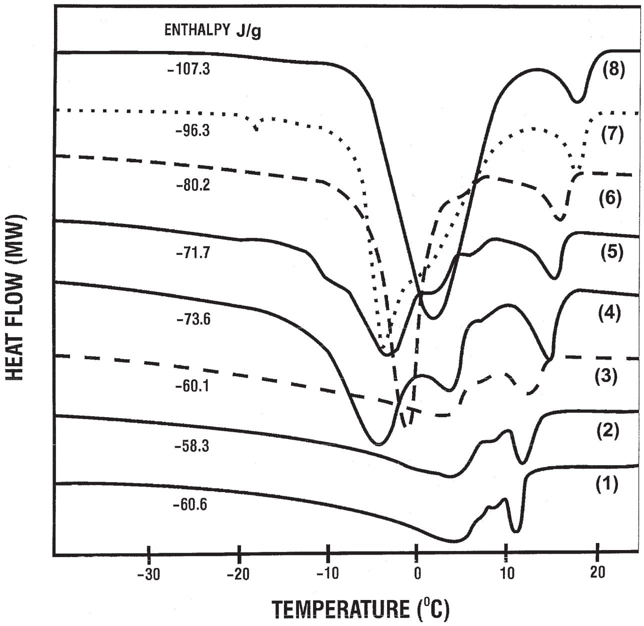

**FIG. 4.** Crystallization thermograms of DSC for AMF3, HCO3, and their blends. Crystallization curves (1), (2), (3), (4), (5), (6), (7), and (8) represent fat blends containing 0, 10, 20, 30, 40, 50, 80, and 100% of HCO3, respectively. See Figures 1 and 3 for abbreviations.

The minima at 4 and 11°C in pure AMF3 remained evident in blends having 10–30% of HCO3, but there were progressive changes in the temperature of the latter minimum as the proportion of HCO3 increased. The AMF3 minimum at 11°C shifted progressively through all blends to 18°C, at which there was a secondary minimum in pure HCO3. The primary minimum in pure HCO3 was at 2°C. As the proportion of AMF3 in HCO3 increased, the temperature of that minimum shifted first to −3 °C, then up to −0.7°C for the blend having 50% of HCO3, and then down again to −4°C for the blend having 30% of HCO3. At lower levels of HCO3, this minimum was absent.

A comparison of the melting curves with the crystallization curves showed that most crystallization occurred at lower temperatures than the corresponding temperatures of melting, referred to as hysteresis (3). This hysteresis was evident in AMF3, HCO3, and their blends and indicates that nucleation and crystal growth were slow, resulting in supercooling of the liquid phase. The greatest heat flow in the crystallization thermograms for milk fat and HCO was at about 4 and 2°C, respectively. However, for blends with >20% and <100% HCO3, the greatest heat flow occurred below 0°C. The lowest temperature of maximum heat flow was −4.3°C for the 30% HCO blends, indicating a high degree of supercooling. It seems that nucleation and crystal growth in the blends are more retarded relative to the unblended fats. This could be a result of the increased complexity of the mix of triglycerides in the blends. It is likely that postcrystallization, i.e., delayed crystallization or polymorphic transformations, will occur in these blends after the cooling is completed. There could be practical implications in the factory when crystallizing these blends in scraped surface heat exchangers. Postcrystallization is likely to occur after production during storage.

DSC thermal analysis can be a relatively simple "fingerprint" of milk fat. Incorporation of 10% of HCO in blends resulted in a melting thermogram that was quite different from that of pure milk fat. The ability of DSC measurements to be used to discriminate between pure fats and blends has also been previously observed (21,24).

*Comparison of SFC measured by DSC and NMR.* Generally, the values of SFC measured by DSC were higher than measured by NMR (Table 4), especially at lower temperatures. This agreed very well with findings by Norris and Taylor (25) and Lambelet (21,26). At the same temperature, the difference was much smaller for HCO than for milk fat. According to Md. Ali and Dimick (11) and Lambelet (21), SFC measured by DSC can be related to SFC measured by NMR if the former values are multiplied by a correction factor, allowing for differences in the heats of fusion of different triglycerides. Another factor impacting on the difference between the two techniques could be the rate of temperature change. In this study, the average rate of temperature change in the NMR procedure was about 30 times slower than for the DSC method. Since different crystal polymorphs show different heats of fusion and interconvert quite slowly, especially at low temperatures, the rate of temperature change could be im-

**TABLE 4**
**Comparison of SFC (%) measured by NMR and DSC of AMF3, HCO3, and Their Blends**[a]

| Temperature (°C) | Measure method | 100% AMF3 | 90%AMF3: 10% HCO3 | 80%AMF3: 20% HCO3 | 70%AMF3: 30% HCO3 | 60%AMF3: 40% HCO3 | 50%AMF3: 50% HCO3 | 20%AMF3: 80% HCO3 | 100% HCO3 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | DSC | 83.8 | 87.7 | 91.7 | 91.1 | 91.8 | 90.5 | 95.2 | 98.2 |
| | NMR | 61.2 | 64.3 | 67.8 | 71.3 | 74.9 | 77.6 | 87.6 | 93.0 |
| 5 | DSC | 73.0 | 79.0 | 83.2 | 84.1 | 85.2 | 84.7 | 92.1 | 96.5 |
| | NMR | 57.5 | 61.4 | 65.1 | 68.7 | 72.6 | 75.2 | 86.4 | 92.5 |
| 15 | DSC | 43.3 | 44.1 | 47.7 | 51.2 | 54.1 | 67.4 | 72.2 | 85.2 |
| | NMR | 34.2 | 34.0 | 35.7 | 39.1 | 43.6 | 48.5 | 67.0 | 81.1 |
| 20 | DSC | 29.7 | 29.5 | 30.6 | 33.2 | 34.4 | 37.1 | 46.2 | 57.2 |
| | NMR | 19.7 | 20.7 | 22.0 | 23.9 | 27.3 | 30.4 | 44.2 | 59.3 |
| 25 | DSC | 17.2 | 17.3 | 17.3 | 18.1 | 17.8 | 17.6 | 19.5 | NA |
| | NMR | 11.9 | 12.1 | 12.3 | 12.1 | 13.2 | 13.6 | 17.5 | 21.6 |
| 30 | DSC | 5.2 | 6.7 | 7.3 | 8.6 | 9.1 | 9.7 | 10.2 | 10.0 |
| | NMR | 5.9 | 5.7 | 6.0 | 6.0 | 6.7 | 7.0 | 7.9 | 8.6 |
| 35 | DSC | 0.8 | 1.1 | 1.1 | 1.9 | 2.7 | 3.2 | 4.8 | 5.1 |
| | NMR | 1.3 | 1.5 | 1.7 | 2.3 | 3.0 | 3.6 | 4.5 | 5.0 |

[a]NA, not available; DSC, differential scanning calorimetry; NMR, nuclear magnetic resonance; SFC, solid fat content. See Table 1 for other abbreviations.

portant. Milk fat usually needs to be completely solidified below −40°C (3); therefore at −20°C, the SFC of AMF3 was less than the 100% at which all milk fat was assumed solid for the DSC integration method used in this study. The SFC for milk fat determined by the two techniques showed greater discrepancy than observed in the SFC of the HCO.

*Prediction of SFC of blends of AMF and HCO.* AMF3 had from 4.8 to 6.8% less SFC than AMF1 between 0 and 15°C, with the difference increasing with temperature in that range. At 20 and 25°C, AMF3 had 3.0 and 1.5%, respectively, lower SFC than AMF1. The D.P. of the AMF3 was 2°C lower. HCO1 and HCO3 had almost identical SFC from 0 to 20°C but started to differ above 20°C with higher SFC for HCO3 having a 2°C higher D.P.

Examination of the SFC curves in this study revealed that each could be represented as the sum of a straight line joining the SFC of the ingredient fats and a deviation effect characteristic of the interactions between the fats. The straight line component can be expressed as: $n\%\cdot$SFC of $A$ + $(100 - n)\%\cdot$SFC of $B$, where $A$ and $B$ are the two ingredient fats. Adding the deviation term produces Equation 2:

$$\text{SFC (at } n\% \text{ of } A) = n\%\cdot\text{SFC of } A + (100 - n)\%\cdot\text{SFC of } B + \text{deviation of SFC (at } n\% \text{ of } A) \quad [2]$$

where the deviation (at $n\%$ of $A$) can be calculated from the difference between the measured SFC and the weighted average at $n\%$ of $A$. Comparing SFC curves for the blends of AMF1 and HCO1 (produced in 1997, Fig. 2A) and the blends of AMF3 and HCO3 (produced in 1998, measured values in Fig. 5), it appeared that the general shapes of the curves were preserved and that the deviation effects were similar for batches produced in different years.

Therefore, the following method for prediction of SFC of milk-fat blends was examined. The deviation effect, which was characteristic of the interactions of fat types including the extent of dissolution of the solids from one ingredient in liquid from the other, was assumed to be constant across different production batches of the same type of fats (AMF and HCO). All differences between SFC curves from different blend batches were assumed to result from changes in the SFC values of the ingredients. Hence, with this approach, the SFC curve for a blend of new production batches of similar type of fats could be calculated from the SFC of the new batches of ingredients (e.g., AMF3 and HCO3), together with the expected deviation effect as observed in blends of the previous production batches (AMF1 and HCO1).

Figure 5 shows graphically the close agreement of two sets of SFC curves of milk fat (AMF3) blends with HCO (HCO3) generated, respectively, by real measurements and predictive calculations using the above assumption from the previous production batches of AMF1 and HCO1. This prediction method can reduce the requirement for SFC measurements of milk-fat blends and would be a great convenience for industry use. Without the need for actual blending studies, measurements of SFC of the ingredient fats enable selection of blending ratios to give desired melting properties. However,

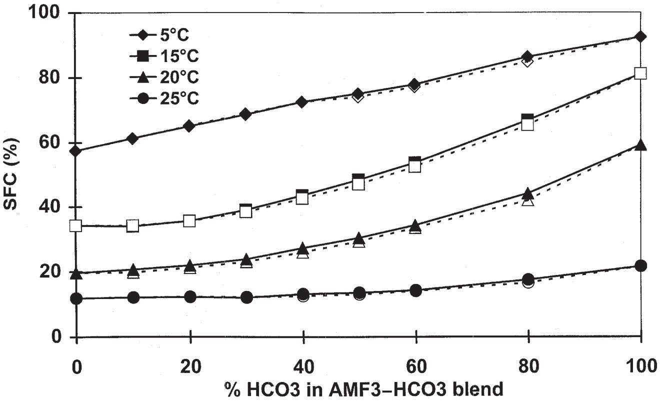

**FIG. 5.** Comparison of SFC value predicted (unfilled symbol and dotted line) with the measured (filled symbol and solid line). See Figure 1 for abbreviation.

more validation work is recommended before this method is generally adopted.

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