JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Nature and Composition of Fat Bloom from Palm Kernel Stearin and Hydrogenated Palm Kernel Stearin Compound Chocolates

KEVIN W. SMITH,*,† FRED W. CAIN,§ AND GEOFF TALBOT#

Life Science, Unilever R&D Colworth, Sharnbrook, Bedfordshire MK44 1LQ, United Kingdom; Loders Croklaan BV, Postbus 4, 1520 AA Wormerveer, The Netherlands; and The Fat Consultant, Suite 250, St. Loyes House, 20 St. Loyes Street, Bedford, Bedfordshire MK40 1ZL, United Kingdom

Palm kernel stearin and hydrogenated palm kernel stearin can be used to prepare compound chocolate bars or coatings. The objective of this study was to characterize the chemical composition, polymorphism, and melting behavior of the bloom that develops on bars of compound chocolate prepared using these fats. Bars were stored for 1 year at 15, 20, or 25 °C. At 15 and 20 °C the bloom was enriched in cocoa butter triacylglycerols, with respect to the main fat phase, whereas at 25 °C the enrichment was with palm kernel triacylglycerols. The bloom consisted principally of solid fat and was sharper melting than was the fat in the chocolate. Polymorphic transitions from the initial β' phase to the β phase accompanied the formation of bloom at all temperatures.

KEYWORDS: Palm kernel stearin; hydrogenated palm kernel stearin; bloom; compound chocolate; polymorph

INTRODUCTION

Modified lauric fats are used extensively in the chocolate confectionery industry as cocoa butter substitutes. In this application they can be used in place of most of the cocoa butter (CB) that is present in normal chocolate. An important crude oil feedstock for such confectionery fats is palm kernel oil (PK). It can be modified by fractionation, hydrogenation, or a combination of the two to produce confectionery fats that have melting properties similar to those of CB.

Compound chocolates based on these fats have the advantage that, unlike normal CB-based chocolate, they do not require tempering. However, a limitation of their use is the fact that they cannot be used in recipes containing more than about 4 or 5% CB on the fat phase (*1*−*3*). This low level of CB can result in a poor chocolate flavor. However, if this limit is exceeded, the products become prone to phase separation and crystallization of fat at the surface of the compound chocolate. This is known as fat bloom and is very detrimental to the appearance of the product. Theories have been propounded for the mechanism of bloom formation (*2*, *4*), but it is fair to say that the details of the actual mechanism are still not fully understood, although a number of different factors may play a role. Lonchampt and Hartel make exactly this point in their recently published comprehensive review of bloom in chocolate and compound coatings (*5*), which is recommended as an excellent overview.

The objective of the present work was to undertake a systematic chemical and physical analysis of bloom from compound chocolate bars prepared from palm kernel stearin (PKS) or hydrogenated palm kernel stearin (HPKS), each containing CB at ∼10% of the fat phase, as a function of storage temperature.

MATERIALS AND METHODS

Materials. PKS, HPKS, and soy lecithin were supplied by Loders Croklaan BV. CB was supplied by Barry Callebaut. Icing sugar was supplied by Tate & Lyle and skimmed milk powder by Dairy Crest.

Chocolate Preparation. PKS and HPKS were formulated to a compound chocolate recipe, containing ∼10% CB in the fat phase, which is greater than the normal recommended maximum of 4−6% (*1*−*3*). The recipe was as follows: 15% cocoa powder (22−24% CB), 31% PKS or HPKS, 45% icing sugar, 8% skimmed milk powder, and 0.4% lecithin. All of the ingredients were combined in a Lloveras mill conch and processed for 5 h at 50−55 °C, after which the maximum particle size was <25 μm, as measured using a micrometer.

The compound chocolates were melted at 65 °C for 30 min, then cooled to 40 °C (taking ∼15 min), and held for a further 30 min in a stirred vessel. They were poured into tablet-form chocolate molds (50 g), held at 5 °C for 0.5 h, demolded, and stored at 15, 20, or 25 °C for 1 year. Note that, although the CB content was relatively high, no tempering procedure was used. The fat bloom that had developed on the surface of the compound chocolate after this period was scraped off carefully. To minimize contamination of the bloom with underlying chocolate, a scalpel and a magnifying lens were used to facilitate the removal of the bloom layer. However, some contamination with small amounts of the underlying compound chocolate was inevitable. The scalpel used had a thermally insulated handle to reduce the transfer of heat from the hand to the samples in order to prevent melting of the

* Author to whom correspondence should be addressed (telephone +44 1234 222786; fax +44 1234 222552; e-mail kevin.w.smith@unilever.com).
† Unilever R&D Colworth.
§ Loders Croklaan BV.
# The Fat Consultant.

10.1021/jf049401e CCC: $27.50
Published on Web 08/03/2004

Table 1. Summary of Differences between PKS, HPKS, and CB

fat[a]	HPLC[b]	TAG carbon no. GLC[c]	FAME GLC[d]	polymorph
PKS	mainly SatSatSat	mainly C36, C38, C40	C18:1, C12:0, C14:0	β'-2[e]
HPKS	mainly SatSatSat	mainly C36, C38, C40	C18:0, C12:0, C14:0	β'-2[e]
CB	mainly SatOSat	mainly C50, C52, C54	C16:0, C18:0, C18:1	β-3

[a] PKS, palm kernel stearin; HPKS, hydrogenated palm kernel stearin; CB, cocoa butter. [b] HPLC, high-pressure liquid chromatography; Sat, saturated fatty acid; O, oleic acid. [c] TAG, triacylglycerol; GLC, gas–liquid chromatography; C*nn*, TAG with a total of *nn* carbons in the acyl chains. [d] FAME, fatty acid methyl ester; C*n*:*m*, fatty acid with *n* carbons and *m* double bonds. [e] Note that, although PK fats tend to be β'-2 stable, trilaurin itself is β-2 stable.

bloom or chocolate. All of these operations were performed at 20 °C, in a temperature-controlled laboratory to reduce the risk of melting the bloom.

Argentation HPLC. This was performed on the bloom and the total fat phase from each compound chocolate following the method of Jeffrey (*6*). Separation of triacylglycerols (TAGs) is effected according to unsaturation, allowing separation between SatSatSat (Sat = saturated), SatOSat (O = oleic), SatOO, OOO, and others.

Gas−Liquid Chromatography (GLC). Triacylglycerol carbon number and fatty acid methyl ester (FAME) analyses were performed on the bloom and the total fat phase from each compound chocolate.

For FAME analysis, methyl esters were prepared by transesterification with potassium hydroxide catalysis in methanol/petroleum ether 1:4 according to the method of Thies (*7*). The esters were analyzed on a stainless steel column (2 m × 4 mm i.d.) packed with 10% silar 10C on 80/100 Gas Chrom Q in a Perkin-Elmer F30 gas chromatograph. Samples were injected as 2 μL aliquots of 0.5% solutions in iso-octane. Injection temperature was maintained at 250 °C and the flame ionization detector at 300 °C; the oven was programmed from 120 to 220 °C at 2 °C/min. Nitrogen carrier flow was 50 mL/min.

For TAG carbon no. analysis, a Perkin-Elmer Sigma 1 instrument was used. Samples were injected as 2 μL aliquots of 2.5% solutions in iso-octane. Columns were glass (0.5 m × 3 mm i.d.) packed with 3% ov-1 on 100/120 Gas Chrom Q. The injection port temperature was maintained at 365 ± 5 °C and the flame ionization detector at 375 ± 5 °C. The column temperature was programmed at 4 °C/min from 215 to 305 °C, with a nitrogen carrier at 55 mL/min.

Electronic integration was by a Perkin-Elmer Sigma 10 data processor for both FAME and TAG carbon no. analyses.

Visual Inspection. The onset of bloom was assessed by weekly visual inspection of the compound chocolate bars. The time at which bloom was first observed by eye was noted.

Differential Scanning Calorimetry (DSC). A Perkin-Elmer differential scanning calorimeter DSC-2 with a subambient temperature range accessory was used for studying the melting behavior of the fat bloom and compound chocolate samples. Solid carbon dioxide was used as the coolant.

Two samples were taken from each bar: (i) fat bloom and (ii) compound chocolate from the center of the bar. These were hermetically sealed into aluminum sample pans at 20 °C, in a temperature-controlled laboratory. Again, care was taken to avoid melting by using a microspatula with a thermally insulated handle for transferring the samples. Each loaded sample pan was rapidly cooled to −20 °C. An empty sample pan was used as a reference.

The melting behavior of the samples was studied from −20 to 60 °C, at a heating rate of 5 °C/min. Some solidification of fat that had been liquid at the loading temperature occurred on initial cooling to −20 °C. However, this method is preferable to that of heating directly from the storage temperature, where the starting transient (an artifact of the instrument, in part caused by differences in heat capacity between the sample and reference) could mask important endothermic transitions a few degrees above the storage temperature.

Temperatures were calibrated by reference to the melting points of ice and gallium (99.9999% pure), that is, 0 and 29 °C, respectively. Distilled, deionized water was used, which was forced into a flat film on the base of the DSC pan by dropping a small disk of aluminum cut from a second pan on top of the water.

X-ray Diffraction (XRD). Fat bloom samples were analyzed at 20 °C in an Anton-Paar TTK X-ray camera with Cu Kα radiation and a proportional counter detector. Intense diffraction peaks from the sugar made XRD analysis difficult; therefore, the compound chocolates were not studied.

Two slit arrangements were used during each scan, one for observation of the short spacings (divergence slit, 0.5°; receiving slit, 0.1 mm; scatter slit, 1°), the other for observation of the long spacings (divergence slit, 0.5°; receiving slit, 0.05 mm; scatter slit, 0.25°). This permitted observation of peaks with spacings up to 70 Å, at maximum intensity.

Table 2. TAG and FAME GLC Analysis of PKS, HPKS, and CB (Percent by Weight)

	PKS[a]	HPKS[a]	CB[a]
	TAG Carbon No. GLC[b]		
C32	3.6	3.5	
C34	6.5	6.6	
C36	26.3	25.7	
C38	23.9	23.2	
C40	14.3	14.2	
C42	9.1	9.0	
C44	5.2	5.2	
C46	3.4	3.3	
C48	2.7	2.8	0.4
C50	1.3	1.4	17.6
C52	1.1	1.4	45.8
C54	1.2	1.5	33.8
other	1.1	1.6	1.6
	FAME GLC[c]		
C10:0	2.6	2.5	
C12:0	59.7	59.0	
C14:0	20.2	19.7	0.1
C16:0	7.7	8.0	25.8
C18:0	2.2	8.7	34.2
C18:1	5.4	0.1	35.2
other	2.2	2.0	4.7

[a] PKS, palm kernel stearin; HPKS, hydrogenated palm kernel stearin; CB, cocoa butter. [b] TAG, triacylglycerol; GLC, gas–liquid chromatography; C*nn*, TAG with a total of *nn* carbons in the acyl chains. [c] FAME, fatty acid methyl ester; C*n*:*m*, fatty acid with *n* carbons and *m* double bonds.

RESULTS AND DISCUSSION

The principal TAGs in PK stearin fats are lauric-based trisaturated TAGs (SatSatSat), whereas in CB the principal TAGs are of the symmetrical monounsaturated type (SatOSat). In analytical terms this is a useful distinction. **Table 1** summarizes the principal differences between CB and PK stearin fats, whereas **Table 2** presents more detailed analysis applicable to the specific fats used here. The PK fats used here are relatively rich in C12:0, at almost 60%, but this might be typically nearer 50% (see ref *8*, for example).

Argentation HPLC (**Table 3**) showed that SatSatSat and SatOSat TAGs accounted for >93% of the total TAG material present in all of the samples. The level of SatOSat in the bloom at 15 and 20 °C was much higher than that of the corresponding compound chocolate. On the other hand, at 25 °C the bloom consisted almost exclusively of SatSatSat TAGs.

Table 3. Chemical Analysis of Compound Chocolate Fat and Bloom Removed Following Storage at 15, 20, or 25 °C (HPLC, Percent by Area; GLC, Percent by Weight)

	PKS/CB[a]				HPKS/CB[a]			
	chocolate	bloom at 15 °C	bloom at 20 °C	bloom at 25 °C	chocolate	bloom at 15 °C	bloom at 20 °C	bloom at 25 °C
				Argentation HPLC[b]				
SatSatSat	85.3	48.1	48.5	97.5	91.1	38.3	79.0	98.6
SatOSat	7.6	48.2	50.2	0.0	6.9	58.0	19.1	0.0
other	7.1	3.7	1.3	2.5	2.0	3.7	1.9	1.4
				FAME GLC[c]				
C12:0	48.9	30.5	41.3	54.3	49.6	30.1	52.3	67.4
C14:0	19.8	10.7	10.4	12.8	20.0	9.3	13.7	13.6
C16:0	11.1	15.9	10.2	9.9	10.6	25.1	7.9	6.1
C18:0	6.3	16.4	17.5	4.7	12.1	18.3	13.9	6.1
C18:1	10.0	18.2	13.6	7.8	4.2	11.3	5.8	2.2
other	2.5	5.2	4.7	3.8	2.3	4.4	5.2	3.6
				TAG Carbon No. GLC[d]				
C34	6.4	5.1	5.6	4.2	6.4	5.4	6.6	5.2
C36	23.4	17.9	23.7	37.8	24.5	16.5	29.4	43.8
C38	21.1	15.0	16.2	23.9	21.6	10.1	20.3	22.6
C40	12.7	8.6	7.3	13.3	12.7	4.5	9.2	10.0
C42	8.0	5.4	4.0	7.4	7.8	2.6	5.4	5.6
C44	4.5	3.2	2.1	3.0	4.4	1.4	3.0	2.1
C46	2.9	2.5	1.3	1.4	2.8	0.8	1.7	0.9
C48	2.4	2.3	1.2	1.0	2.3	0.8	1.5	0.7
C50	3.2	7.5	3.8	1.2	2.7	9.1	2.2	1.0
C52	5.6	16.7	13.2	2.2	5.1	26.2	7.4	2.4
C54	4.3	11.0	17.4	1.7	4.2	17.0	9.2	2.4
other	5.5	3.9	3.4	2.0	5.5	4.5	3.3	2.5

[a] PKS, palm kernel stearin; HPKS, hydrogenated palm kernel stearin; CB, cocoa butter. [b] HPLC, high-pressure liquid chromatography; Sat, saturated fatty acid; O, oleic acid. [c] FAME, fatty acid methyl ester; C*n*:*m*, fatty acid with *n* carbons and *m* double bonds. [d] TAG, triacylglycerol; GLC, gas–liquid chromatography; C*nn*, TAG with a total of *nn* carbons in the acyl chains.

The FAME analysis (**Table 3**) shows that the C12:0 content of the bloom increased with storage temperature, whereas the C18:1 content of the bloom decreased. The overall level of C18:1 was ~5−8% lower in the bloom from HPKS/CB than that from PKS/CB. This is not unexpected because PKS fat has a higher C18:1 content than HPKS fat. However, with respect to the original fat in the compound chocolate, the C12:0 is enriched at 25 °C but depleted at 15 °C. At 20 °C, the bloom from the PKS sample is slightly depleted, whereas that from the HPKS is slightly enriched.

Given et al. (*9*) state that the composition of bloom scraped from a PK-based coating was essentially the same as that of the parent fat system. However, their fatty acid data do show an increase in lauric acid, C12:0, in the bloom from about 36 to 45%, an increase that they state is not statistically significant. Their exact coating recipe and storage conditions are not supplied. Laustsen (*10*) similarly notes an increase in C12:0 levels in bloom relative to the initial fat phase, along with a reduction in C14:0, which we observe also.

The TAG carbon no. distribution of the bloom and compound chocolate fell into two main TAG groups: short-chain TAGs from the lauric fat, that is, PKS or HPKS, with a carbon number range from approximately C30 to C46, and long-chain TAGs predominantly from the CB, but with a small contribution from the lauric fat, in the range from C48 to C56 (**Table 3**).

The relative proportions of short-chain to long-chain TAGs in the bloom varied as a function of storage temperature. As a general trend, the proportion of long-chain material decreased with increased storage temperature. The main contribution to the long-chain TAGs was primarily from the CB.

The enrichment of each of the TAG groups in the bloom can be found by calculating an enrichment factor, C_b/C_c, where C_b = level of TAG group in bloom and C_c = level of TAG group in compound chocolate fat, with corresponding carbon number. Thus, an enrichment factor of 1 indicates that the particular TAG group concerned is present at equal levels in both bloom and chocolate fat. Enrichment factors are plotted in **Figure 1** for each TAG carbon no. group.

At 15 and 20 °C, the bloom is enriched, with respect to the chocolate fat, with TAGs originating from the CB. Traitler and Dieffenbacher (*11*) note a similar increase in SOS from the CB part when hydrogenated coconut oil, rather than PK, is used, although details of specific recipes and storage conditions are omitted. At 25 °C, the bloom is enriched with TAGs from the lauric fat, specifically C36 [cf. Kawada et al. (*12*, *13*)]. Coupled with the observation that C12:0 is similarly enriched, we can conclude that this is principally due to trilaurin. Although Laustsen (*10*) reaches the same conclusion, her samples were stored at 18−20 °C, at which temperature we find the bloom enriched in CB (C50, C52, C54) TAGs, not in PK (C36) TAGs.

Visual inspection of the compound chocolate bars detected the onset of bloom in the PKS products after 4 weeks at 15 °C and after 23 weeks at 20 and 25 °C. The HPKS products developed bloom after 10 weeks at 15 °C and after 23 weeks at 20 and 25 °C.

It is interesting to note that at 15 °C, the temperature at which the onset of bloom was the quickest, the enrichment factors for the CB TAGs were higher overall, whereas at 25 °C the principal enrichment tended to be of the lauric, C36, TAG.

DSC Analysis. The melting behavior of the bloom was clearly different from that of the compound chocolate (**Figure 2**). All of the samples of bloom had a single sharp peak in contrast to that of the compound chocolate samples, where up to five distinct peaks or shoulders could be observed for each sample.

The melting point, or peak onset (taken as the point where a tangent to the steepest leading edge of the peak intersects the extrapolated baseline), of the 20 and 25 °C bloom was 2−3 °C

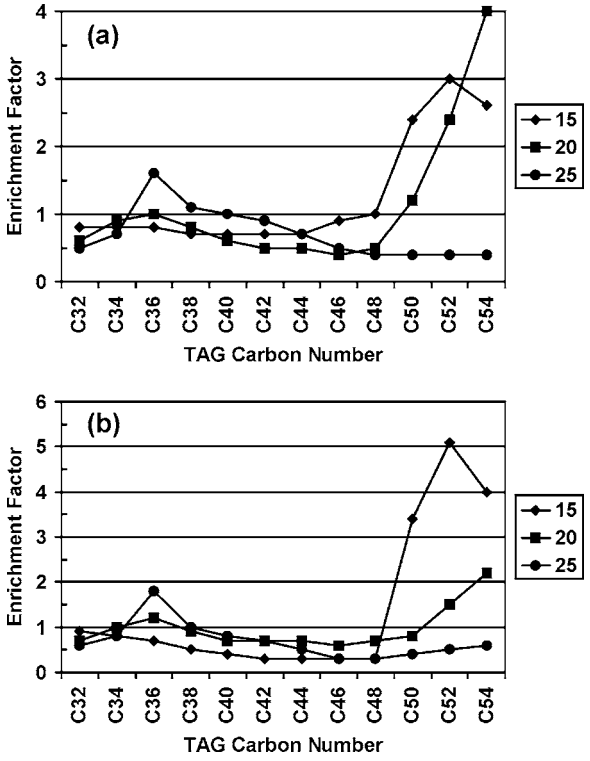

Figure 1. Calculated enrichment factors for TAGs in bloom on (**a**) PKS-based and (**b**) HPKS-based compound chocolates following storage at 15, 20, and 25 °C for 12 months. Carbon no. C32–C46 originate from the lauric fat and C50–C54 from the cocoa butter. C*nn*, TAG with a total of *nn* carbons in the acyl chains.

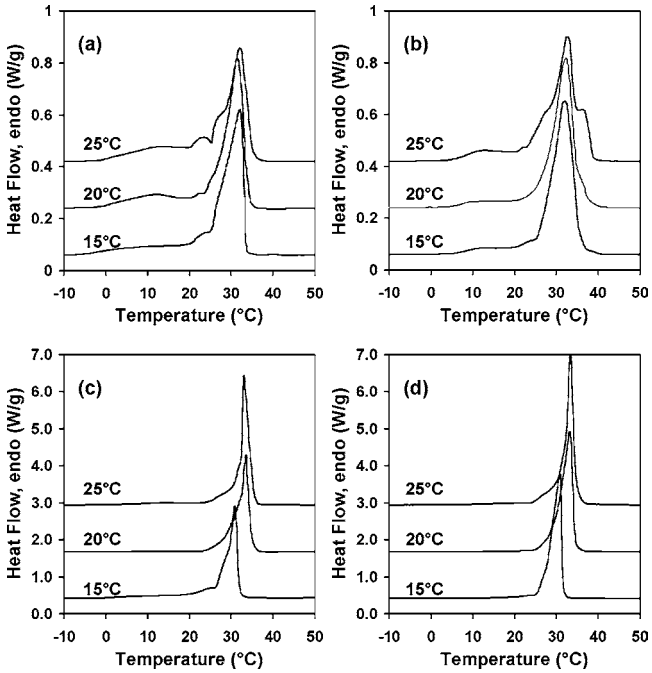

Figure 2. DSC melting thermograms of compound chocolates prepared from (**a**) PKS or (**b**) HPKS and the associated bloom, (**c**) PKS, or (**d**) HPKS, after storage at 15, 20, or 25 °C for 12 months.

higher than the temperature at which the bulk of the compound chocolate melted for both PKS and HPKS products. This is close to the 4 °C increase in melting point observed by Given et al. (*9*). Despite this, however, peak maxima occurred at similar temperatures. The bloom at 15 °C differed from that at 20 and 25 °C in that its melting point (onset) was similar to that of the

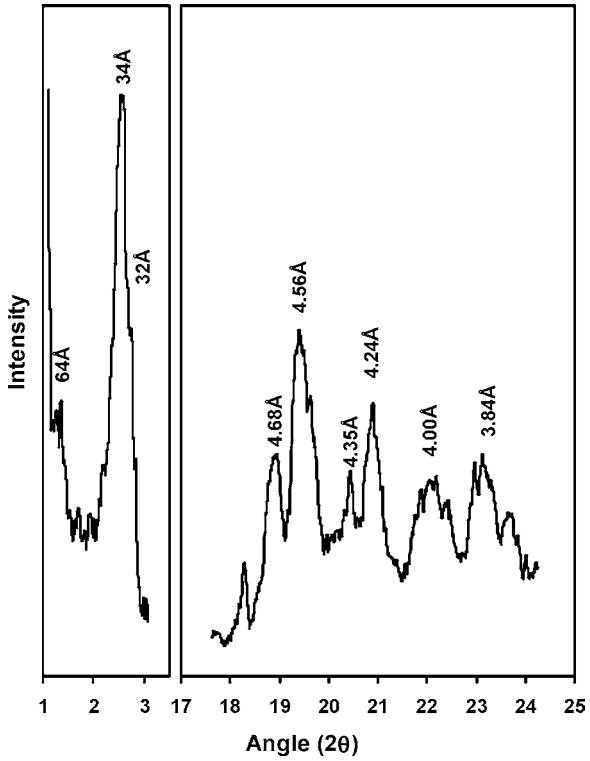

Figure 3. X-ray diffractogram of bloom removed from PKS compound chocolate following storage at 15 °C for 12 months.

compound chocolate, whereas its peak maximum was at a temperature lower than that of the chocolate.

The thermogram of the HPKS, but not the PKS, compound chocolate stored at 25 °C showed a high melting shoulder. There were indications of this in the thermogram of the chocolate at 20 °C also. This shoulder was higher melting than the bloom and suggests a fractionation of higher melting TAGs occurring within the chocolate, without transport of these to the surface.

As a consequence of the rapid cool to −20 °C, during the subsequent reheat peaks were observed at temperatures below the particular storage temperature. These occurred for some of the compound chocolate samples and were assumed to be due to material that was liquid at the storage temperature (see **Figure 2a**,**b**). Only small peaks, if any, were observed below the storage temperature for the samples of bloom at any of the storage temperatures studied (**Figure 2c**,**d**). This suggests that the bloom contained little liquid oil at the storage temperatures.

The interpretation of the short spacing X-ray diffractograms of bloom (**Figure 3**) is subjective due to the close proximity of the diffraction peaks of adventitious sugar to the diffraction peaks of the fat phase. However, the diffraction peak at ∼4.7 Å due to the sugar is reasonably well resolved from the intense diffraction peaks of the fats. Accepting that this peak is characteristic of the presence of sugar, only bloom at 15 and 20 °C from the PKS chocolate appeared to be contaminated to any extent by sugar and hence, presumably, by the underlying compound chocolate. The level of contamination, based on the intensity of the 4.7 Å sugar peak, was significant in the bloom from 15 °C. The enrichment factors for this sample may be somewhat distorted due to contamination from the fat phase of the compound chocolate.

The X-ray diffractograms all displayed strong peaks at ∼4.6 Å, which is indicative of the β polymorph. Peaks at about 3.8 and 3.7 Å are also probably associated with the β polymorph of the fat. The remaining small peaks at about 4.4, 4.2, and 4.0

Table 4. Polymorphic Form of Bloom Collected from Compound Chocolate Stored at 15, 20, or 25 °C, Indicating Basic Polymorph and Layer Spacing

PKS/CB[a]			HPKS/CB[a]		
bloom at 15 °C	bloom at 20 °C	bloom at 25 °C	bloom at 15 °C	bloom at 20 °C	bloom at 25 °C
$\beta' + \beta$, double and triple	$\beta' + \beta$, double and triple	$\beta' + \beta$, double	$\beta' + \beta$, double and triple	$\beta' + \beta$, double and triple	$\beta' + \beta$, double

[a] PKS, palm kernel stearin; HPKS, hydrogenated palm kernel stearin; CB, cocoa butter.

Å are from the β' polymorph (*14*). Compare these with the short spacings of β' PKS fat and β' HPKS fat: 4.44, 4.27, 4.07, and 3.83 Å.

The β' peak at ~3.85 Å is therefore likely to be masked by the β peak in the same position. Although both β' and β were present in the bloom, the β polymorph predominated (estimated to be >70% from peak heights).

The polymorphism of the fat phase of the compound chocolates was not determined due to the presence of sugar, so the fat phases (i.e., PKS/CB/lecithin 90:10:1 and HPKS/CB/lecithin 90:10:1) were formulated. These contained no sugar, no skimmed milk powder, and no cocoa solids. They were molded and cooled in exactly the same manner as was the compound chocolate used. They were then studied by X-ray diffraction after 24 h of storage at 20 °C. Both the PKS/CB/lecithin and the HPKS/CB/lecithin were observed in the β'-2 form after this simulated compound chocolate preparation. If the fat phase of the compound chocolate had crystallized in a similar fashion, then this would indicate that some of the fat had transformed from the β'-2 form to a mixed $\beta + \beta'$ in the bloom on storage. Noorden (*2*) also observed a β' to β transformation, after 5 months at 18−20 °C, accompanied by the formation of visible bloom. This transformation is confirmed by others, for example, Rossell (*15*) and Timms (*16*). Thus, the β' to β transition may be related to the mechanism of bloom formation. However, on the basis of the evidence here, we cannot state whether this polymorphic transition occurred before, during, or after the formation of bloom.

Because the β' polymorph was present at a low level in the bloom, it is possible that this is due to contamination with material from the fat phase of the compound chocolate, which had not undergone transformation.

The long spacings of the bloom samples (**Figure 3a**) were not masked by interference from the sugar because the latter has no peaks in the region of interest. Peaks were observed at about 64, 34, and 32 Å for the PKS/CB and HPKS/CB bloom at both 15 and 20 °C. At 25 °C, only one peak was observed at ~34 Å for both types of bloom.

The assignments of the peaks were as follows: 64 Å = 001 plane, triple-layer packing; 32 Å = 002 plane, triple-layer packing; 34 Å = 001 plane, double-layer packing.

The bloom at 15 and 20 °C exhibited both triple- and double-chain-length packing arrangements, whereas the bloom at 25 °C showed only a double-chain packing arrangement. The polymorphic forms of the bloom are summarized in **Table 4**.

This interpretation is consistent with the HPLC analysis because trisaturated TAGs, such as trilaurin, have a double-chain-length packing arrangement, and the most stable form of the SatOSat TAGs of cocoa butter (β) has a triple-chain-length packing arrangement. Thus, at 15 and 20 °C there were both triple- and double-packing arrangements due to the presence of trisaturated TAGs from the lauric fat and SatOSat TAGs from the cocoa butter, whereas at 25 °C, where the bloom contained trisaturated TAGs only, there was a double-chain-length packing arrangement.

From a knowledge of the TAG compositions of the PK fats and CB (**Table 1**) it is reasonable to assume that the C36, C50, C52, and C54 triacylglycerols of PK/CB systems are due principally to LLL, POP, POS, and SOS (L = lauric; P = palmitic; S = stearic), respectively. Thus, the high levels of these species in the bloom should provide insight into the mechanism of bloom formation. From the simulated compound chocolate preparation we saw that these TAGs crystallized into the β'-2 form initially, along with the other components of the fat phase. However, all four species are β stable (LLL is β-2 stable; POP, POS, and SOS are β-3 stable), and it is likely that they would have tended to convert to these polymorphs during storage. Thus, it would seem that the formation of bloom in these systems is accompanied by a polymorphic transition (β' to β) of fat phases rich in the β stable TAGs. However, it cannot be assumed that a polymorphic transition of the fat is always accompanied by bloom formation. Equally, it cannot be assumed that a polymorphic transition is a necessary prerequisite of bloom formation. Bloom can be defined as simply the development of a new (solid) phase in a chocolate fat, leading to surface roughening. In the present case we observed a separation of a new solid phase at the surface, with a concentration of SatOSat and/or LLL TAGs and accompanied by a polymorphic phase change.

The appearance of bloom at 20 and 25 °C was slower than that at 15 °C, and hence it is likely that the rate of polymorphic transition was slower (in absolute terms). This is consistent with published phase diagrams for unstabilized and stabilized HPKS/CB systems (*4*, *17*). As the temperature decreases, then so too does the composition region over which a single solid β'-2 phase is the stable state. Thus, for a given composition, a sample stored at a lower temperature (e.g., 15 °C) in the β'-2 form will be further from the "equilibrium" state (i.e., β-3 + β'-2 according to refs *4* and *17*) than will a sample stored at higher temperatures (e.g., 25 °C). Of course, this fact alone may not necessarily lead to a faster transition rate because temperature in its own right will influence the kinetics. It is not possible to interpret the present data exactly in terms of supposedly fully stabilized phase diagram; the solvus lines in the diagram are only approximate and also there is no mention of a β-2 phase, which this work clearly suggests is present.

It is important to understand more fully the kinetics of bloom formation because it is principally a shelf-life problem that is being considered. Thus, if bloom appearance could be sufficiently retarded, it would not be important whether the fat phase was metastable thermodynamically (although it would clearly be the most ideal situation if the thermodynamically stable form were present). Because the LLL itself undergoes a polymorphic transition (from β'-2 to β-2) and appears in the bloom, it seems unlikely that it would be possible to achieve a fully stable system. Indeed, Kawada et al. (*12*, *13*) found that bloom was promoted with the addition of LLL to the fat phase of a chocolate based on "rearranged hydrogenated palm kernel

oil" (no CB present), although he showed that other TAGs, for example, LML (M = myristic), LPL, and SSS, delayed the onset of bloom.

Conclusion. This study has demonstrated that bloom formation in PKS and HPKS compound chocolates is not due simply to trilaurin or CB separation (*10*). Instead, the composition of the bloom is temperature dependent, in line with the published phase diagrams. Whereas the TAGs are predominantly from the lauric fat, there is a considerable enrichment in CB TAGs at 15 and 20 °C. It is principally at 25 °C that we observe an enrichment in trilaurin. In all cases, bloom is almost fully solid and is sharper melting than the corresponding compound chocolate.

ABBREVIATIONS USED

TAG, triacylglycerol; DSC, differential scanning calorimetry; HPLC, high-performance liquid chomatography; GLC, gas−liquid chromatography; FAME, fatty acid methyl ester. XRD, X-ray diffraction; CB, cocoa butter; PK, palm kernel; PKS, palm kernel stearin; HPKS, hydrogenated palm kernel stearin; Sat, saturated; S, stearic; O, oleic; L, lauric; M, myristic; P, palmitic.

ACKNOWLEDGMENT

We thank B. S. Jeffrey, G. J. Sassano, and team for performing the GLC and HPLC analyses and P. Bishop and R. Andrews for DSC and X-ray diffraction measurements.

LITERATURE CITED

(1) Arishima, T.; McBrayer, T. Applications of Speciality Fats and Oils. *Manuf. Confect.* **2002**, *82*, 65−76.

(2) Noorden, A. C. Fat Bloom—Causes And Prevention When Using Lauric Hard Butters. *Susswaren Technik Wirtschaft* **1982**, *26*, 318−322.

(3) Hogenbirk, G. Compatibility of Specialty Fats with Cocoa Butter. *Manuf. Confect.* **1984**, *64*, 59−63.

(4) Timms, R. E. Interactions Between Fats, Bloom and Rancidity. *Confectionery Fats Handbook*; Timms, R. E., Ed.; The Oily Press: Bridgwater, U.K., 2003; pp 255−294.

(5) Lonchampt, P.; Hartel, R. W. Fat Bloom in Chocolate and Compound Coatings. *Eur. J. Lipid Sci. Technol.* **2004**, *106*, 241−274.

(6) Jeffrey, B. S. J. Silver-Complexation Liquid-Chromatography For Fast, High-Resolution Separations Of Triacylglycerols. *J. Am. Oil Chem. Soc.* **1991**, *65*, 289−293.

(7) Thies, W. Schnelle und einfache Analysen de Fettsäurezusammensetzung in einzelnen Raps-Kotyledonen. *Z. Pflanzenzuechtung* **1971**, *65*, 181−202.

(8) Williams, S. D.; Ransom-Painter, K. L.; Hartel, R. W. Mixtures of Palm Kernel Oil with Cocoa Butter and Milk Fat in Compound Coatings. *J. Am. Oil Chem. Soc.* **1997**, *74*, 357−366.

(9) Given, P.; Wheeler, E.; Noll, G.; Finley, J. Physical-Chemical Behavior Of Confectionery Fats. *J. Disper. Sci. Technol.* **1989**, *10*, 505−530.

(10) Laustsen, K. The Nature Of Fat Bloom In Molded Compound Coating. *Manuf. Confect.* **1991**, *72*, 137−144.

(11) Traitler, H.; Dieffenbacher, A. Palm Oil and Palm Kernel Oil in Food Products. *J. Am. Oil Chem. Soc.* **1985**, *62*, 417−421.

(12) Kawada, T.; Suzuki, S.; Kamata, F.; Matsui, N. The Study of Lauric Hard Butter. II. Fat Bloom. *J. Jpn. Oil Chem. Soc.: Yukagaku* **1971**, *20*, 332−335.

(13) Kawada, T.; Suzuki, S.; Kamata, F.; Matsui, N. Studies on the Lauric Hard Butter. III. Fat Bloom (2). *J. Jpn. Oil Chem. Soc.: Yukagaku* **1971**, *20*, 807−810.

(14) Lutton, E. S. Review of the Polymorphism of Saturated Even Glycerides. *J. Am. Oil Chem. Soc.*, **1950**, *27*, 276−281.

(15) Rossell, J. B. Fractionation of Lauric Oils. *J. Am. Oil Chem. Soc.* **1985**, *62*, 385−390.

(16) Timms, R. E. Physical properties of oils and mixtures of oils. *J. Am. Oil Chem. Soc.* **1985**, *62*, 241−248.

(17) Gordon, M. H.; Padley, F. B.; Timms, R. E. Factors Influencing the Use of Vegetable Fats in Chocolate. *Fette Seifen Anstrichm.* **1979**, *81*, 116−121.

Received for review April 14, 2004. Revised manuscript received June 21, 2004. Accepted June 27, 2004.

JF049401E