Preparation of Sharp-Melting Hard Palm Midfraction and Its Use as Hard Butter in Chocolate

Satsuki Hashimoto, Toru Nezu, Hiroshi Arakawa, Tomonori Ito, and Shoji Maruzeni*

Fats & Oils Research Department, Food Development Laboratory, Foods Division,
Asahi Denka Kogyo K. K., Tokyo, 116-8553, Japan

ABSTRACT: Preparation of hard palm midfractions (PMF) and its use as a cocoa butter equivalent ingredient were studied. Hard PMF is obtained by multistep fractionation of palm oil involving dry fractionation (DF) and/or solvent fractionation (SF), usually using hexane or acetone. From our experience, in acetone, a polar solvent, symmetrical 1,3-disaturated triacylglycerols tend to selectively crystallize more than nonsymmetrical 1,2- or 2,3-disaturated triacylglycerols, making it suitable for obtaining the solid midfraction. Unfortunately, triacylglycerols are very soluble in hexane, and temperatures at least 15 degrees lower than those required for acetone must be used for equivalent crystal yields. On the other hand, DF is a less expensive and safer process. Thus, multistep fractionation combining DF and SF using acetone was developed to achieve sufficient removal of high-melting components, and further enrichment of 1,3-dipalmitoyl-2-oleoylglycerol and the hard PMF was obtained by triple-step fractionation of palm olein or double-step fractionation of soft PMF. Compared to conventional hard PMF, this hard PMF had a steeper melting curve and better snapping and sharp-melting qualities when used in chocolate. Heat resistance of the hard PMF chocolate was similar to the conventional hard PMF chocolate, and its bloom resistance could be improved by adding polyglycerol fatty acid esters.

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KEY WORDS: Chocolate, cocoa butter equivalent (CBE), 1,3-dipalmitoyl-2-oleoylglycerol (POP), dry fractionation, hard palm midfraction, multistep fractionation, solvent fractionation, trisaturated triacylglycerols (SSS).

Hard palm midfractions (PMF) used as an ingredient of cocoa butter equivalents (CBE) are obtained by multistep fractionation of palm oil (1). Palm oil is abundant, inexpensive, and a good source of CBE. For example, palm oil [iodine value (IV) = 51–53] can be fractionated into palm stearin (IV = 32–40) and palm olein (PO; IV = 56–58), and the PO can then be fractionated into soft PMF (sPMF; IV = 44–50) and palm super-olein (IV = 63–65). A hard PMF (IV = 34–36) can finally be obtained by fractionation of the sPMF by separation from the PO fraction (IV = 64–70) (all IV values depend on fractionating conditions).

Hard PMF is rich in 1,3-dipalmitoyl-2-oleoylglycerol (POP) and is characterized by its hardness at room temperature and sharp melting property at around 30–35°C, like cocoa butter. However, the content of a few percent of higher-melting trisaturated triacylglycerols (SSS) and of diacylglycerols (DG) in hard PMF has an adverse effect on these properties, and is best removed completely to achieve more rapid and complete melting in the mouth.

From our experience, acetone, a polar solvent, is suitable for obtaining the solid midfraction, because symmetrical 1,3-disaturated triacylglycerols (SUS) in acetone tend to selectively crystallize more than nonsymmetrical 1,2- or 2,3-disaturated triacylglycerols (SSU), while in nonpolar hexane, both symmetrical and nonsymmetrical disaturated triacylglycerols (S_2U) tend to be nonselectively crystallized. Triacylglycerols are very soluble in hexane, but this means that temperatures at least 15°C lower than those required for acetone must be used for equivalent crystal yields, and, therefore, the process requires a cooling facility of larger capacity.

On the other hand, dry fractionation (DF) is a less expensive and safer process because there is no use of solvents. Timms (2) showed that hexane is suitable for obtaining a liquid fraction because high-melting DG are less soluble in hexane than triacylglycerols. Acetone is the preferred solvent for obtaining an SUS-rich midfraction as DG is removed as a liquid fraction (2). However, the use of more than one solvent to achieve the desired triacylglycerol composition in multistep fractionation would make the whole process more complicated and expensive. Thus, multistep fractionation combining DF and solvent fractionation (SF) using acetone was assumed to be the most efficient and suitable method. This method was chosen in order to achieve sufficient removal of high-melting components and further enrichment of POP in hard PMF. The use of the hard PMF as a CBE ingredient will be discussed.

EXPERIMENTAL PROCEDURES

Materials. PO (IV = 55.9) and sPMF (IV = 47.1), obtained from Soctek Edible Oils Sdn. Bhd. (Pasir Gudang, Malaysia), were used as starting materials. Theiracyl triglycerol compositions are shown in Table 1. Acetone with less than 0.2% moisture was used for solvent fractionation. Cocoa butter and conventional hard PMF were used as reference samples. The cocoa butter was obtained from Daitocacao Co., Ltd. (Tokyo, Japan), and the conventional hard PMF was obtained from our plant (Asahi Denka Kogyo, Kashima-gun, Ibaragi, Japan).

*To whom correspondence should be addressed at Fats & Oils Research Department, Food Development Laboratory, Foods Division, Asahi Denka Kogyo K. K., 7-2-35, Higashi-ogu, Arakawa-ku, Tokyo, 116-8553, Japan. E-mail: sho-maruzn@adk.co.jp

TABLE 1
Triacylglyceride Composition of Palm Olein (PO) and Soft PMF (sPMF)

	PO	sPMF
Iodine value	55.9	47.1
(wt%)		
P_2L[a]	10.3	9.7
P_2O	29.3	45.7
POSt	5.1	7.7
St_2O	0.7	1.0
P_2M	0.3	0.0
PPP	0.3	1.3
P_2St	0.0	0.3
PSt_2	0.0	0.1
(wt%)		
DG[b]	6.9	4.5
SSS	0.3	2.1
S_2U	45.4	64.2
SU_2 + UUU	47.4	26.7
P_2L/P_2O	0.35	0.21

[a]Abbreviations used for acylchains in the triacylglycerols: P, palmitic acid; St, stearic acid; O, oleic acid; L, linoleic acid; S, saturated fatty acid; U, unsaturated fatty acid; PMF, palm midfraction.
[b]Diacylglycerol.

DF. In a 2-L concentric, cylindrical glass crystallizer where water, a coolant, flowed through the gap between the inner and outer concentric cylinders, starting oil was completely melted at 60°C for 1 h and cooled at a rate of −11°C/h while being agitated with a pitched-blade impeller at a rate of 40 rpm. As the temperature reached the seeding temperature, seeds (prepared by solidifying PO at −20°C and agitating the PO solid until it became pastelike) of up to 1% of the mass of starting oil were added. The mixture was further cooled to crystallizing temperature at a reduced rate of −2°C/h; held at the crystallizing temperature until desired triacylglycerol composition, by high-performance liquid chromatography (HPLC), was obtained; and then filtered with a plate and frame filter press at the crystallizing temperature under a pressure of 10^3 kPa.

Fractions and types of fractionation in each step were abbreviated as follows; O, olein fraction or liquid-oil fraction; S, stearin fraction or solid-fat fraction (3); d, fractionated by DF; s, fractionated by SF. For example, sPMF-OdSs means the stearin fraction of sPMF-Od obtained by solvent fractionation. Here, the sPMF-Od is the olein fraction of sPMF (soft PMF) obtained by dry fractionation.

SF. Acetone and starting oil were added into the same 2-L concentric, cylindrical glass crystallizer used for DF, and the mixture was heated at 45°C for 30 min to eliminate any crystal memory and cooled at a rate of −12°C/h while being agitated at a rate of 70 rpm. When the temperature reached the seeding temperature, seeds (prepared by crystallizing the starting mixture at −20°C) of up to 1% of the mass of the starting mixture were added. The cooling continued until the crystallizing temperature was reached, and then the mixture was held at the crystallizing temperature for a few hours. The mixture was then separated with a membrane-filter funnel under vacuum. The crystal was washed with acetone, which was cooled to the corresponding temperature.

Fractionation starting from PO. In the first fractionation step (step 1), removal of hard S from PO was done by DF as follows: mass of starting PO, 1 kg; seeding, 24°C, 0.2%; crystallization, 20°C for 2 h; and fraction collected, olein (PO-Od). In step 2, removal of low-melting triacylglycerols from PO-Od was done by either SF or DF. Step 2 by SF was done as follows: oil/acetone ratio, 1:4, w/w; seeding, 12°C, 1%; crystallization, 0°C for 1 h; and fraction collected, stearin (PO-OdSs). Step 2 by DF was done as follows: mass of starting oil, 500 g; seeding, 17°C, 0.05%; crystallization, at 17°C for 45 h; and fraction collected, stearin (PO-OdSd). In step 3, removal of low-melting triacylglycerols from PO-OdSs or PO-OdSd was done by SF as follows: oil/acetone ratio, 1:4, w/w; seeding, 16°C, 1%; crystallization, 0 or 10°C for 1 h; and fraction collected, stearin (PO-OdSsSs or PO-OdSdSs).

Fractionation starting from sPMF. In step 1, removal of hard stearin from sPMF was done by either DF or SF. Step 1 by DF was carried out as follows: crystallization temperature, 25°C for 13 h; and fraction collected, olein (sPMF-Od). Step 1 by SF was done as follows: oil/acetone ratio, 1:0.5, w/w; seeding, 0–2°C higher than the crystallization temperature, 0–0.2%; crystallization temperature, 17–18°C; acetone used for washing of stearin, kept at a temperature 2°C lower than the crystallizing temperature to avoid any loss from dissolving of crystals; and fraction collected, olein and the olein fraction in the acetone used for washing added together (sPMF-Os). In step 2, removal of low-melting triacylglycerols from sPMF-Od or sPMF-Os was done by SF as follows: oil/acetone ratio, 1:4, w/w; seeding, 15°C, 0.2%; crystallization temperature, 8°C for 2 h or 12°C for 4 h; and fraction collected, stearin (sPMF-OdSs or sPMF-OsSs).

Fractionation process for conventional hard PMF. The conventional hard PMF used in this study was obtained by double-step SF of PO. In step 1, removal of low-melting triacylglycerols from PO was done by SF as follows: oil/acetone ratio, 1:3, w/w; seeding, 12°C, 0.2%; and crystallizing temperature, 0°C for 1 h (PO-Ss yield, 50%). In step 2, removal of low-melting triacylglycerols from PO-Ss was done by SF as follows: oil/acetone ratio, 1:4, w/w; seeding, 12°C, 0.1%; and crystallization temperature, −2°C for 1 h (PO-SsSs yield, 75%).

Analysis. Glyceride composition was measured in a JASCO (Tokyo, Japan) HPLC system using an RI-71 refractive index detector (Showa Denko Co., Ltd., Tokyo, Japan). The solvent system was acetone/acetonitrile (7:3, vol/vol) at a flow rate of 1.0 mL/min. The sample was injected in dichloromethane. A JASCO L-column ODS of 150 mm length and 4.6 mm i.d. was used at a column oven temperature of 37°C. Sampling during fractionation was done with a 2-mL syringe and Advantec (Tokyo, Japan) disposable syringe filter units (0.45 µm, hydrophilic).

The concentration of POP in the di-palmitoyl-mono-oleoyl-glycerol (P_2O) triacylglycerols was measured by obtaining the P_2O fraction by preparative HPLC and measuring its *sn*-2 fatty acid composition. Firstly, 3 mL of sample solution (10% in ace-

tone, wt/vol) was injected into the solvent (acetone/acetonitrile, 7:3; flow rate, 18 mL/min) and passed through an ODS column (20 mm diameter × 250 mm). As soon as the P_2O fraction was detected, the fraction was collected. Secondly, after 50 mg of the P_2O fraction was added to a mixture of 7 mL 0.1M-tris-aminomethane-HCL buffer solution (pH = 8.0) and 0.5 mL 1 M $CaCl_2$, 2 mL of 1,3-position specific lipase, *Rhizopus delemar* (Tanabe Seiyaku Co., Ltd., Osaka, Japan), in the previously mentioned buffer solution (10%, wt/vol) was added for hydrolysis at 40°C. Lipids were extracted by ethylether and were then fractionated by preparative thin-layer chromatography (TLC) with solvent (ethylether/hexane/formic acids, 70:30:0.7). The fractionated monoacylglycerol obtained was extracted with hexane and the fatty acid composition was measured by gas–liquid chromatography (GLC) according to AOCS Official Method Ce 1c-89 (6).

Solid fat content (SFC) was determined by pulsed nuclear magnetic resonance (NMR) (model SFC-900; Praxis, San Antonio, TX). The sample was melted completely at 60°C for 1 h, chilled at 0°C for 30 min, kept at 20°C for 2 h, and tempered in a programmable incubator in which the temperature was 30°C for 1 h and then 20°C for 2 h per cycle for a total of seven 3-h cycles. After the accelerated tempering procedure (ADK method, generally used in our laboratory), the tempered sample was chilled again at 0°C for 30 min and kept at the desired temperatures for 30 min prior to SFC measurements.

Deodorization. The hard PMF was deodorized by steam distillation at 220 or 240°C for 1 h.

Chocolate-making test. Chocolates using the hard PMF (sPMF-OsSs), obtained by double-step fractionation of sPMF in this study, and a typical conventional hard PMF were made according to the chocolate composition shown in Table 2. Both hard PMF represented 100% of the hard PMF used and their properties were compared.

With constant and thorough stirring, 400 g of the melted chocolate at 60°C was cooled to 25°C, held at 25°C for 5 min, heated to 27°C, and held at 27°C for 2 min. The chocolate was then molded (in a plastic mold of 70 × 30 × 10 mm × 20 units, kept at 27°C) and chilled at 5°C for 30 min. During the chilling, the percentages of chocolate units in a mold that were well detached were measured at 10-min intervals. The solidified chocolates were then kept at 20°C for 1 wk and used for measurements of their physical properties.

TABLE 2
Composition of Chocolate

Component	Content (%)	Fat content (%)[a]
Cocoa mass	15	8
Hard PMF	22	22
Whole milk powder	17	4
Sugar	46	
Lecithin	0.4	
Vanillin	0.03	

[a]Fat contents of cocoa mass and whole milk powder were 55 and 25%, respectively.For abbreviation see Table 1.

Sensory tests of the chocolates stored at 20°C for 2 wk were performed with 10 panelists, in a room air-conditioned at 20°C.

The rheology of the chocolates was measured with a Fudoh (Tokyo, Japan) rheometer at a table lifting rate of 2 cm/min, using a tooth-shaped adapter for snapping quality and a needle-shaped adapter for hardness.

Heat resistance of the chocolates was measured by keeping them at test temperatures for 1 h prior to measurements and pushing the surface lightly with an index finger to observe any changes left by the finger on the surface.

Bloom resistance was measured as follows: the chocolates were kept in a programmable incubator, where the temperature shifted repeatedly from 20°C for 12 h to 28, 29, or 30°C for 12 h per day, and observed daily for any formation of bloom (whitening) on the surface. The effect of polyglycerol fatty acid ester, hexaglycerol octastearate (Taiyo Kagaku Kogyo K.K., Yokkaichi, Japan) (1% the mass of hard PMF) on bloom resistance was also tested by adding it to the chocolates.

RESULTS AND DISCUSSION

The triacylglycerol compositions of the hard PMF obtained in this study are shown in Table 3. All their P_2O concentrations were enriched to more than 72% and concentrations

TABLE 3
Solid Fat Content (SFC; %) and Triacylglycerol Composition (wt%) of Hard PMF

Process no.[a]	—	1		2	3	4
		PO-OdSsSs		PO-OdSdSs	sPMF-OdSs	sPMF-OsSs
Ctf[b]	Conventional hard PMF	0°C	10°C	10°C	8°C	12°C
SFC						
20°C	81.6	86.3	89.6	86.9	87.2	88.8
25°C	69.8	80.5	85.6	82.5	83.0	83.6
30°C	38.1	26.0	42.2	46.2	38.9	50.1
33°C	6.6	0.0	0.0	8.5	0.0	9.3
35°C	1.7	0.0	0.0	0.0	0.0	0.0
37°C	0.1	0.0	0.0	0.0	0.0	0.0
P_2L[c]	9.5	9.2	6.1	5.9	5.4	4.7
P_2O	63.5	72.1	73.6	72.9	73.4	74.4
POSt	12.3	14.0	15.4	14.7	14.5	13.7
St_2O	2.8	1.8	2.0	1.7	2.2	1.5
DG[d]	1.6	0.1	0.1	0.4	0.4	0.5
$SU_2 + U_3$	6.6	2.1	2.3	3.2	2.9	3.5
S_2U	88.7	97.1	97.1	95.2	95.8	94.4
SSS	3.1	0.7	0.5	1.3	0.7	1.4
P_2L/P_2O	0.15	0.13	0.08	0.08	0.07	0.06

[a]Fractions and types of fractionation in each step of these processes are abbreviated as follows: O, olein fraction or liquid-oil fraction; S, stearin fraction or solid-fat fraction (3); d, fractionated by dry fractionation (DF); s, fractionated by solvent fractionation (SF).
[b]Crystallization temperature of the final step for removal of low-melting triacylglycerides.
[c]See Table 1 for abbreviations used for acyl chains in the triacylglycerols.
[d]Diacylglycerol.

of DG and SSS were lower compared to conventional hard PMF.

Process 1: PO → PO-Od → PO-OdSs → PO-OdSsSs. In step 1, dry fractionation of PO resulted in sufficient removal of SSS to 0.0% with an olein yield of 94.5%. In step 2, concentration of P_2O was enriched to 63.2% with a stearin yield of 38.7%. The glyceride compositions of the PO-OdSsSs obtained in step 3 by crystallization at 0 and 10°C (Table 3) were almost the same except the P_2L/P_2O ratio of the latter was smaller. The stearin yields were 79.5 and 62.3%, respectively.

Process 2: PO → PO-Od → PO-OdSd → PO-OdSdSs. The method followed and the results of step 1 were the same as step 1 of process 1. In step 2, PO-OdSd (stearin yield, 43.2%) with a composition similar to sPMF (P_2O, 49.4%) but with a lower SSS concentration of 0.5% was obtained. In step 3, the PO-OdSdSs (stearin yield, 40.2%) obtained was similar to PO-OdSsSs of process 1 with a slightly higher SSS concentration.

Process 3: sPMF → sPMF-Od → sPMF-OdSs. In step 1, SSS could be removed to 0.1% (olein yield, 93.5%). The sPMF-OdSs obtained (stearin yield, 44.5%) in step 2 had a glyceride composition similar to PO-OdSsSs (of which the crystallization temperature was 10°C in step 3) of process 1.

Process 4: sPMF → sPMF-Os → sPMF-OsSs. In step 1, SSS could be removed down to 0.4%, but this SF step was not as effective as the corresponding step by DF (olein yield, 96.5%). Thus, the SSS concentration in the final sPMF-OsSs was greater than that of sPMF-OdSs obtained in process 3, and the overall composition was similar to PO-OdSdSs of process 2 (stearin yield, 43.9%).

Stereospecific triacylglycerol composition. The concentrations of oleic acid in the *sn*-2 fatty acids of the P_2O obtained from sPMF-OdSs and conventional hard PMF by preparative HPLC were 96.0 and 88.5%, respectively, corresponding to the approximate concentrations of stereospecifically symmetrical POP in the P_2O. In addition, the concentration of POP in the P_2O fraction of palm oil was reported to be approximately 87% (4). Therefore, not only P_2O but, most importantly, POP was concentrated in the sPMF-OdSs compared with the conventional hard PMF.

SFC. SFC of hard PMF obtained in this study and an example of a typical conventional hard PMF are also shown in Table 3.

The hard PMF obtained in this study, PO-OdSsSs, PO-OdSdSs, sPMF-OdSs, and sPMF-OsSs, had higher SFC at lower temperatures and sharper melting properties at higher temperatures and were expected to be even more ideal for chocolates with these properties than the conventional hard PMF. In addition, hard PMF with their SSS removed to a concentration below 1% melted completely at 33°C, while those with their SSS slightly higher, above 1%, did not, and the former hard PMF were expected to be better in giving the chocolate a rapid and complete melting feel in the mouth.

The PO-OdSsSs with a lower P_2L/P_2O ratio had a higher SFC at 30°C and was likely to be a better hard PMF with good snapping property and sharper melting at temperatures above 30°C than the PO-OdSsSs with a higher P_2L/P_2O ratio.

Therefore, hard PMF that were likely to be ideal for chocolates that are hard at room temperature and melt rapidly in the mouth could be obtained by removing as much SSS as possible, preferably by DF, and lowering the P_2L/P_2O ratio by performing the final fractionation step at a fairly high crystallization temperature of around 8°C or above.

From our experience (Maruzeni, S., unpublished data), acetone, the polar solvent, is the solvent in which symmetrical POP crystallizes more selectively than PPO. This is in contrast to hexane, in which both symmetrical POP and nonsymmetrical PPO triacylglycerols crystallize nonselectively. Although hexane was not used in this study, the great enrichment of POP in the hard PMF obtained in this study could probably be explained by this selective characteristic of acetone. If hexane had been used for the preparation of hard PMF with the same IV and stearin yield, an equivalent sharp-melting property probably would not have been achieved.

For the fractionation starting from sPMF, the hard PMF obtained by DF removal of high-melting SSS had a higher rapid-melting characteristic than that obtained by SF, as SSS were removed more effectively *via* DF. Moreover, because DG are more soluble in acetone, the enrichment of POP in acetone also resulted in removal of DG that stayed in the liquid fraction. In addition, when the crystallization temperature of the final step for removal of low-melting triacylglycerols was considerably high, the ratio of P_2L concentration to P_2O concentration decreased, enabling further enrichment of P_2O. As a result, multistep fractionation made up of DF for the removal of SSS and SF using acetone for the enrichment of POP seems to be an excellent combination. Taking the costs into consideration, double-step fractionation starting from sPMF by removing the high-melting glycerols by DF seemed to be the best out of the four processes tested and it is more cost efficient if the starting sPMF is obtained by DF. DF has become a general technique, and multistep fractionation combining more DF steps will continue to be the preferred technique for production of specialty fats in the future.

Deodorization. The sPMF-OsSs was deodorized to be used for the following chocolate tests. By deodorization of sPMF-OsSs at 240°C, the concentration of S_2U decreased and the concentration of SSS increased, presumably due to randomization *via* interesterification of glycerols, and this led to a slight but obvious decrease in the hard and sharp-melting characteristic of the fat shown by the SFC in Figure 1. Lowering the deodorization temperature 20°C to 220°C succeeded in reducing the change in the glyceride composition and retained the melting characteristic with a sufficient decrease in the acid value to 0.03.

Chocolate-making test. The viscosity of chocolate made of typical hard PMF felt by the hand during the tempering process was higher than that of the chocolate made of sPMF-OsSs, making the tempering process more difficult. This was probably due to the higher concentrations of hard SSS and DG in the

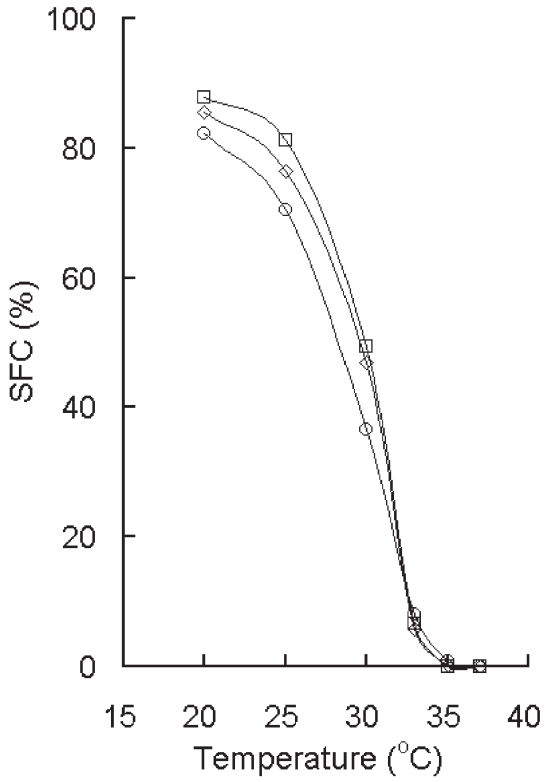

FIG. 1. Effect of deodorization temperature on solid fat content (SFC) of hard palm midfraction (PMF). ◇, sPMF-OsSs (240); □, sPMF-OsSs (220); ○, conventional (= conventional hard PMF). Numbers in parentheses indicate the deodorization temperature.

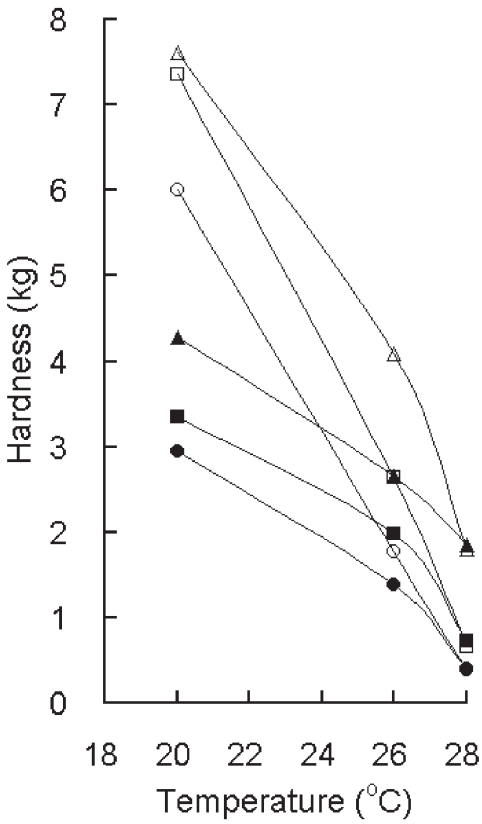

FIG. 2. Rheology of chocolates. □, sPMF-OsSs snapping; ■, sPMF-OsSs hardness; ○, conventional snapping; ●, conventional hardness; △, cocoa butter snapping; ▲, cocoa butter hardness. Abbreviations: snapping, hardness measured with a tooth-shaped adaptor; hardness, hardness measured with a needle-shaped adaptor; see Figure 1 for other abbreviations.

typical hard PMF that crystallized at a higher temperature during tempering, increasing the viscosity.

If chocolate is tempered properly by adequate and even cooling, the chocolate is well-demolded due to good contraction (5). The sPMF-OsSs chocolate could be well-tempered without any blooming and well-demolded as 10, 70, and 90% of the units in the mold were demolded when cooled at 5°C for 10, 20, and 30 min, respectively. In contrast, the conventional hard-PMF chocolate was stuck to the mold; no sign of detachment was observed after 10 and 20 min, and only 20% of the units in the mold were demolded even after 30 min. The conventional hard PMF forcibly demolded after the 30-min chilling had a duller surface than the sPMF-OsSs chocolate.

The overall comments made by the panel members are summarized as follows: the first bite of the sPMF-OsSs chocolate felt harder with a better snapping property and melted more sharply with a cooling and complete melting mouth-feel than the conventional hard-PMF chocolate. These results coincided with the expectations based on the SFC data.

In Figure 2, snapping quality and hardness (measured with a rheometer) of the sPMF-OsSs chocolate and the conventional hard-PMF chocolate were compared with chocolate made of cocoa butter. Both snapping quality and hardness of the sPMF-OsSs chocolate were greater than those of the conventional hard-PMF chocolate. The snapping quality of the sPMF-OsSs chocolate at 20°C was just as good as the cocoa-butter chocolate, while at 26 and 28°C it became lower and closer to the conventional hard-PMF chocolate. The sPMF-OsSs chocolate measured with a needle-shaped adaptor was not as hard as the cocoa-butter chocolate. Again, differences in these results of the sPMF-OsSs chocolate and the conventional hard-PMF chocolate were in line with the sensory-test results.

When the surfaces of the sPMF-OsSs and the conventional hard PMF chocolates were pushed with a finger at 28°C, there were no apparent changes on the surface. When the temperature was raised to 29°C, the chocolate made of conventional hard PMF felt softer than the chocolate made of sPMF-OsSs, and the changes appeared more obviously as there was a sunken-in spot on the former and a fingerprint mark on the latter. At 30°C, the surface of the sPMF-OsSs chocolate became as soft as the conventional hard-PMF chocolate, leaving a sunken-in spot from the finger. The overall heat resistance of the sPMF-OsSs chocolate was slightly better than the conventional hard-PMF chocolate despite its sharp melting characteristic.

The bloom resistance of the chocolates is shown in Table 4. When the chocolates were placed in a programmable incubator shifting repeatedly from 20°C for 12 h to 30°C for 12 h per day, the first sign of bloom started to appear on both of the hard PMF chocolates after 1 d, and the addition of

TABLE 4
Bloom Resistance[a] of the Chocolates

Temperature setting[b]	Time (d)	sPMF-OsSs	sPMF-OsSs +PG[c]	Conventional hard PMF	Conventional hard PMF +PG	Cocoa butter
20°C/30°C	1	+ –	+ –	+ –	+ –	–
	2	+	+ –	+ –	+ –	–
	5	+ +	+	+	+ –	–
	6	+ +	+ +	+	+ –	–
	8	+ +	+ +	+ +	+	–
	12	+ +	+ +	+ +	++	+ –
20°C/29°C	7	+ –	–	–	–	–
	8	+ –	+ –	+ –	+ –	–
	14	+	+ –	+ –	+ –	–
20°C/28°C	7	+ –	–	–	–	–
	25	+ –	–	+ –	–	–
	26	+ –	–	+ –	+ –	–
	30	+	+ –	+ –	+ –	–

[a]Shown by symbols as follows: –, no change; + –, slight bloom; +, obvious bloom; + +, covered in white.
[b]Kept in an incubator with temperature settings shifting repeatedly from 20°C (12 h) to 30°C, 29°C or 28°C (12 h) per day.
[c]Hexaglycerol octastearate (PG) (1% the mass of hard PMF) added. For abbreviations see Tables 1 and 3.

hexaglycerol octastearate (1% the mass of hard PMF) did not seem to improve their bloom resistance significantly. On the other hand, the cocoa butter chocolate remained bloom-resistant for more than 10 d at this 20°C/30°C cycle.

When the chocolates were kept at a milder condition of temperatures shifting repeatedly from 20°C for 12 h to 29°C for 12 h per day, they remained bloom-resistant for a longer period of time than at the 20°C/30°C cycle, as expected, and the first sign of bloom started to appear on the sPMF-OsSs chocolate 1 d earlier than the conventional hard-PMF chocolate. By the addition of hexaglycerol octastearate (1% the mass of hard PMF), bloom resistance of the sPMF-OsSs chocolate was improved by 1 d while that of the conventional hard PMF chocolate did not change. The cocoa butter chocolate remained bloom-resistant during the 14-d test period.

With an even milder condition of temperatures shifting repeatedly from 20°C for 12 h to 28°C for 12 h per day, the bloom resistance of the sPMF-OsSs chocolate stayed the same; the first sign of bloom appeared 18 d earlier than in the conventional hard-PMF chocolate. Through the addition of hexaglycerol octastearate, the bloom resistance of the sPMF-OsSs chocolate improved by 23 d, while that of the conventional hard-PMF chocolate improved by only 1 d. As expected, the cocoa butter chocolate remained bloom-resistant during the 26-d test period. The effect of hexaglycerol octastearate was more obvious in the sPMF-OsSs chocolate especially if the temperature settings were between 20 and 28°C.

The bloom resistance of the chocolate made of the new hard PMF was improved by adding the polyglycerol fatty acid ester at 20°C/28°C to a degree that was even greater than that of the cocoa butter chocolate at 20°C/30°C. Moreover, the content of hard PMF in the chocolate composition tested was 22%, which might be seen as an extreme example, especially with the new chocolate directive in Europe allowing only 5% of selected vegetable fats (including palm oil) other than cocoa butter in chocolate. Therefore, even with this extreme chocolate composition, the bloom resistance or shelf life of the chocolates made of the new hard PMF, with the aid of emulsifiers as antibloom agents, was expected to be sufficient for commercial use if the temperature is well-controlled and under 28°C for transport and storage of the chocolates. This could be easily realized in the winter season or in most developed countries where a huge network of properly air-conditioned convenience stores and transport systems are available.

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