Seeding Effects on Solidification Behavior of Cocoa Butter and Dark Chocolate. II. Physical Properties of Dark Chocolate

Iwao Hachiya[a], **Tetsuo Koyano**[a] and **Kiyotaka Sato**[b]
[a]Food Research & Development Laboratories, Meiji Seika Ltd., Chiyoda, Sakado, 350-02, Japan and [b]Faculty of Applied Biological Science, Hiroshima University, Higashi-Hiroshima, 724, Japan

Demolding property just after solidification, we examined the polymorphism of cocoa butter in seed-solidified dark chocolate and fat-bloom stability through two thermocycle tests between 38 and 20°C (38/20) and between 32 and 20°C (32/20). The seed crystals employed are Form VI of cocoa butter, β_1 of SOS (1,3-distearoyl-2-oleoylglycerol), pseudo-β' and β_2 of BOB (1,3-dibehenoyl-2-oleoylglycerol) and β of SSS (1,2,3-tristearoylglycerol). The influence of the seed concentration was also examined. The seeding of cocoa butter (Form VI) and SOS (β_1) caused the crystallization of Form V of cocoa butter and exhibited better demolding. As to the fat-bloom stability, the two seed crystals were effective through the 32/20 cycle test, but the fat-bloom occurred through the 38/20 test. The seeding of β_2 of BOB caused better demolding, crystallization of Form V of cocoa butter, and the most preferable fat-bloom stability; particularly, the seeding of 5 wt% concentration of β_2 of BOB completely prevented the fat-bloom after the 38/20 test, although the seeding of all of the other materials and conditions caused the fat-bloom by this thermo-cycle test. The seeding of pseudo-β' of BOB did not prevent the fat-bloom, although the demolding property was improved. In the case of the seed of β of SSS, both the demolding and fat-bloom stability were not improved. We concluded that the seeding of β_2 of BOB revealed the most desirable influences on the demolding and the fat-bloom stability of dark chocolate. This conclusion suggests the usage of β_2 of BOB as the most preferable seed material in the solidification of dark chocolate, since the crystallization rate was also enhanced by this material as described in Paper I.

In Paper I we observed the accelerating effects of some seed crystals on the crystallization kinetics of cocoa butter and dark chocolate (1). Knowledge of the actual use of the seeding method in the chocolate industry is needed to clarify the influences of the seeding on the physical properties of the end product—heat resistance, gloss, fat-bloom stability, viscosity and demolding. This paper describes that, among the seed crystals examined in our previous work (1), BOB (β_2) remarkably improved the fat-bloom stability, while revealing the better demolding behavior.

MATERIALS AND METHODS

Materials of seed crystals and dark chocolate. We employed cocoa butter (Form VI), SOS (β_1), BOB (pseudo-β' and β_2) and β of SSS as the seed materials. The physical properties of these materials were described in Paper I (1). Dark chocolate was prepared in the same way as described in Paper I (1).

Evaluation of demolding and fat-bloom stability. We first evaluated the degree of demolding just after the seeded solidification process. Then, the fat-bloom stability of solidified dark chocolate was examined through a thermo-cycle test by the following methods. The molten dark chocolate, 60°C of 250 g weight, was cooled to 30°C within 10 minutes with agitation (194 rpm) in a rotational viscometer whose design was described in a previous report (2). The seed crystals were added at different relative concentrations with respect to cocoa butter content of dark chocolate (43 wt%) at a time when the temperature of dark chocolate reached 30°C. The seed concentration ranged from 0.001 to 5 wt%. After the seeding, dark chocolate was agitated during 5 minutes at 30°C in order to homogeneously disperse the seed crystals in the molten chocolate. Thereafter, 4 g of the seeded dark chocolate was put in a mold (10 $mm^W \times 20$ $mm^L \times 3.5$ mm^D) made with ethylene chloride resin with a thickness of 0.5 mm. The dark chocolate in the mold was immediately cooled and solidified at 15°C for 15 minutes in a cooling box (Tabai Mfg. Ltd.; PR-1). After the cooling, two properties of the solidified sample were observed: a fractional percentage of the chocolate surface which was easily detached from the mold, and the occurrence of fat-bloom on the surface. Thereafter, the molded samples were stored at 20°C for one week (aging). After the aging, the thermocycle test (3–7) was examined using a thermostat chamber (Nagano Science Ltd.; LH-20): one cycle involves heating at 32° or 38°C for 12 hours and cooling at 20°C for 12 hours. The fat-bloom was observed visually and measured by changes in color of the sample surface with a color difference meter (Minolta Ltd.; CR-100). The degree of whiteness was determined by Hunter's method (8). We also observed the chocolate surface with a Cryo-Scanning Electron Microscope (Hitachi Ltd.; S-570) at −100∼−130°C.

Determination of polymorphism of dark chocolate. The polymorphic modification of the seed-solidified dark chocolate was determined with DSC at a scanning rate of 5°C/min after the three solidification processes: (a) just after the solidification at 15°C for 15 minutes, (b) after the aging of solidified samples at 20°C for one week and (c) after the thermo-cycle test. The melting point was defined as peak top temperature of the DSC melting peak. We measured the X-ray diffraction (XRD) short-spacing spectra of sugar-free dark chocolate which was prepared by a method of Giddey and Clerc (9): the sample was sliced with a knife into powder below 8 mesh size, and 2 g of this powder were put into filter paper, then it was rinsed with 120 ml of water (7∼10°C) to dissolve sugar.

RESULTS

Physical properties just after solidification. Figure 1 shows the DSC melting peaks of dark chocolate samples just after the solidification at 15°C for 15 minutes with and without seeding. Table 1 shows the degree of demolding and the occurrence of the fat-bloom of the seeded dark chocolate, examined just after the bulk crystallization at 15°C. The results are summarized as follows:

TABLE 1

Demolding and Fat-Bloom Occurrence of Seeded Dark Chocolate Just After Solidification at 15°C for 15 Minutes

Seed crystal concentration (wt%)[a]	Cocoa butter (Form VI)		SOS (β_1)		BOB (β_2)		BOB (pseudo-β')		SSS (β)	
	Demold*	Fat-bloom**	Demold*	Fat-bloom**	Demold*	Fat-bloom**	Demold*	Fat-bloom**	Demold*	Fat-bloom**
0.001	80	+	80	+	40	++				
0.005	80	+	80	+	80	+				
0.010	90	−	80	−	80	+				
0.050	90	−	90	−	90	−	0	++	0	++
0.100	80	−	90	−	90	−				
0.500	80	−	80	−	90	−	60	+		
1.000	80	−	80	−	80	−			0	++
2.500	80	−	80	−	80	−	90	+		
5.000	80	−	80	−	80	−	90	+	0	++

[a]Concentration with respect to fat content of dark chocolate.
*Detouched surface (%) estimated by visual evaluation.
**Fat-bloom occurrence evaluated by visual observation: (−); no fat-bloom, (+); very slight fat-bloom, (++) fat-bloom.

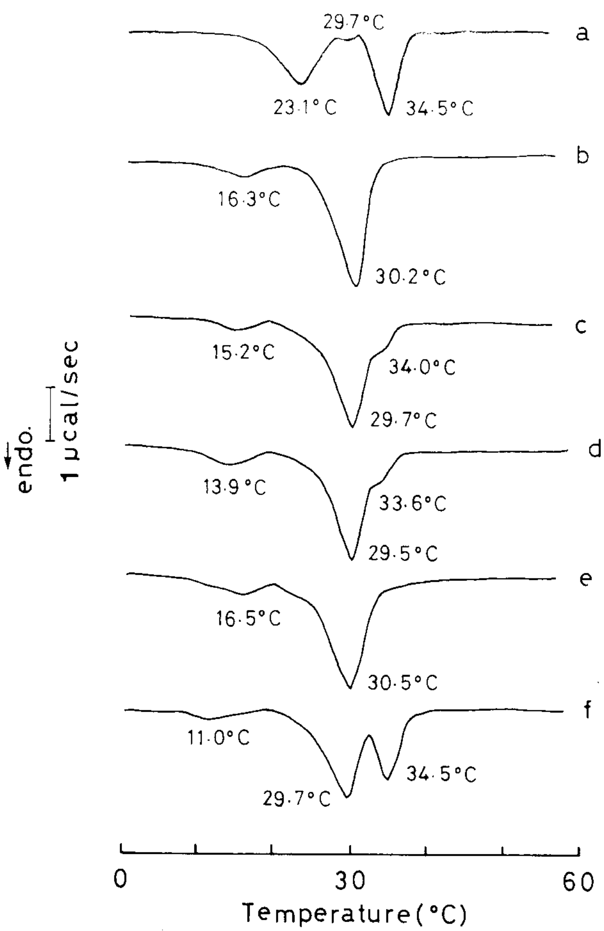

FIG. 1. DSC peaks of solidified dark chocolate at 15°C for 15 minutes after an addition of seed crystals: (a) nonseeded, (b) 0.1 wt% of Cocoa Butter (Form VI), (c) 5 wt% of Cocoa Butter (Form VI), (d) 5 wt% of SOS (β_1), (e) 5 wt% of BOB (β_2), (f) 0.05 wt% of BOB (pseudo-β').

cocoa butter (Form VI) and SOS (β_1) showed easy demolding and no fat-bloom at the seed concentration of more than 0.01 wt%. BOB (β_2) showed no fat-bloom at the seed concentration of more than 0.05 wt%, and better demolding of more than 0.005 wt%. By contrast, undesirable properties were observed for BOB (pseudo-β'), and no preferable result was observed for SSS (β). Although not displayed in Table 1, the nonseeded sample did not detach from the mold and caused the fat-bloom formation. This is shown in three DSC endothermic peaks at 23.1, 29.7 and 34.5°C in Fig. 1a. A peak at 23.1°C is the melting of a metastable form, Form III, of cocoa butter. A small peak at 29.7°C is the melting of Form V and the melting peak at 34.5°C is of Form VI (10). This melting behavior of the nonseeded sample, particularly Form III and Form VI, is quite different from the seeded samples which exhibited better demolding and no fat-bloom.

In the case of the seeding of cocoa butter (Form VI), SOS (β_1) and BOB (β_2), the solidified samples showed a large endothermic peak at 29.5~30.5°C which corresponds to the melting of Form V and small peaks at 13.9~16.5°C which correspond to unstable Form I and II (Fig. 1b~e). Two samples with an addition of 5 wt% of cocoa butter (Form VI) and SOS (β_1) showed an additional small melting peak of Form VI at 33.6~34.0°C. Hence, the better demolding just after the solidification in the seed-solidified samples using the above seed materials resulted in better demolding properties except the 0.001 wt% seeding of BOB (β_2) (Table 1). In Fig. 1f, the solidified sample with 0.05 wt% of BOB (pseudo-β') showed two peaks of Form V at 29.7°C and Form VI at 34.5°C, which were accompanied by a small peak at 11.0°C. In the case of SSS (β), four endothermic peaks were observed, corresponding to the melting of Forms II, III, V and VI.

From the DSC data, we conclude that the better demolding without the fat-bloom is related to the occurrence of Form V of cocoa butter.

Fat-bloom stability after thermo-cycle test. The sample which revealed the better demolding summarized in Table 1 did not show the fat-bloom after the aging of the solidified sample at 20°C for one week. The major change in the polymorphic structure during the aging is the disappearance of the metastable forms having the melting points below 20°C, as shown in Figure 2. The small melting peaks, however, of Form VI did not disappear during the aging in the seeded dark chocolate using 5 wt% cocoa butter (Form VI) and SOS (β_1).

Through the thermo-cycle tests, the fat-bloom formation was prevented in the samples using a particular group of the seed materials under limited seeding conditions. The results are shown for the seed materials of cocoa butter (Form VI) in Table 2, SOS (β_1) in Table 3 and BOB (β_2) in Table 4. In all of the seed materials, the seed concentrations less than 0.01 wt% did not show the fat-bloom stability. The seeding effect at the concentrations higher than 0.05 wt% was dependent on the seed materials. Quite similar behavior was observed for cocoa butter (Form VI) and SOS (β_1); first, in the case of the 32/20 test, the fat-bloom did not occur at the seed concentration of 0.05 through 1 wt% below 4 cycles. However, the fat-bloom stability was lowered at the concentration of 0.01, 2.5 and 5 wt%. The decrease was manifest at higher concentrations, in which the fat-bloom occurred through one cycle. In the case of the 38/20 cycle test, all of the samples caused the fat-bloom at all seed concentrations.

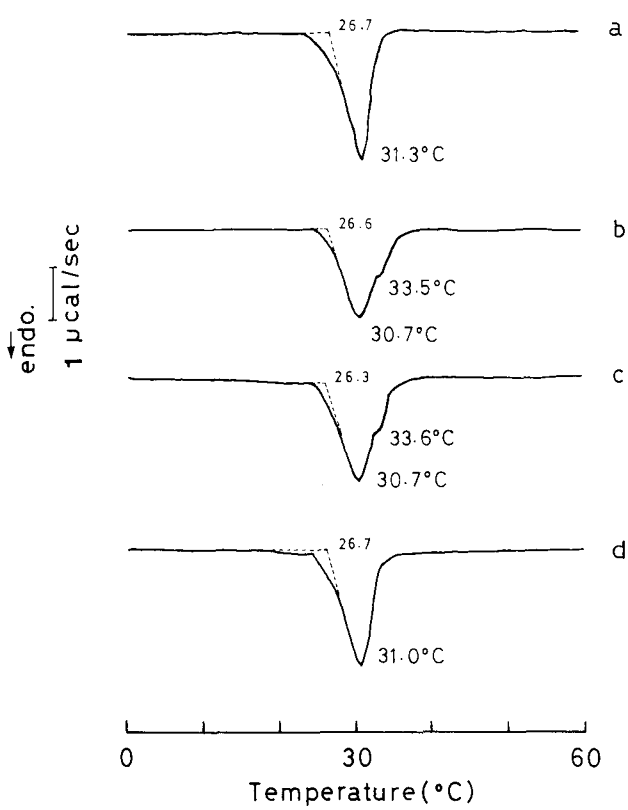

FIG. 2. DSC peaks of aged dark chocolate at 20°C for one week after the seeded solidification using (a) 0.1 wt% of Cocoa Butter (Form VI), (b) 5 wt% of Cocoa Butter (Form VI), (c) 5 wt% of SOS (β_1), (d) 5 wt% of BOB (β_2).

By contrast, the seeding of BOB (β_2) gave rise to the significant fat-bloom stability through the 32/20 and 38/20 cycle tests, when the seed concentration was increased. In particular, the samples seeded at 1, 2.5 and 5 wt% concentrations did not produce the fat-bloom even through the 6 cycle tests of 32/20. In the case of the 38/20 test, the fat-bloom was caused at low-seed concentrations, but the seeding of 5 wt% prevented the fat-bloom.

Polymorphism of bloomed dark chocolate. Figure 3 shows DSC melting peaks of samples seeded with 5 wt% of cocoa butter (Form VI), SOS (β_1) and BOB (β_2) after 6 cycle tests of 32/20, and also after one cycle test of 38/20. Figure 4 shows the XRD short-spacing spectra of the samples without sugar. After the 6 cycle tests of 32/20°C, bloomed samples using the seeds of cocoa butter (Form VI) and SOS (β_1) showed small melting peaks of Form V at 29.0∼29.6°C and a large peak of Form VI at 33.4∼33.6°C (Fig. 3a–b). Hence, the nonbloomed sample seeded with BOB (β_2) has two melting peaks of Form V (29.1°C) and Form VI (33.0°C) (Fig. 3c). In the XRD

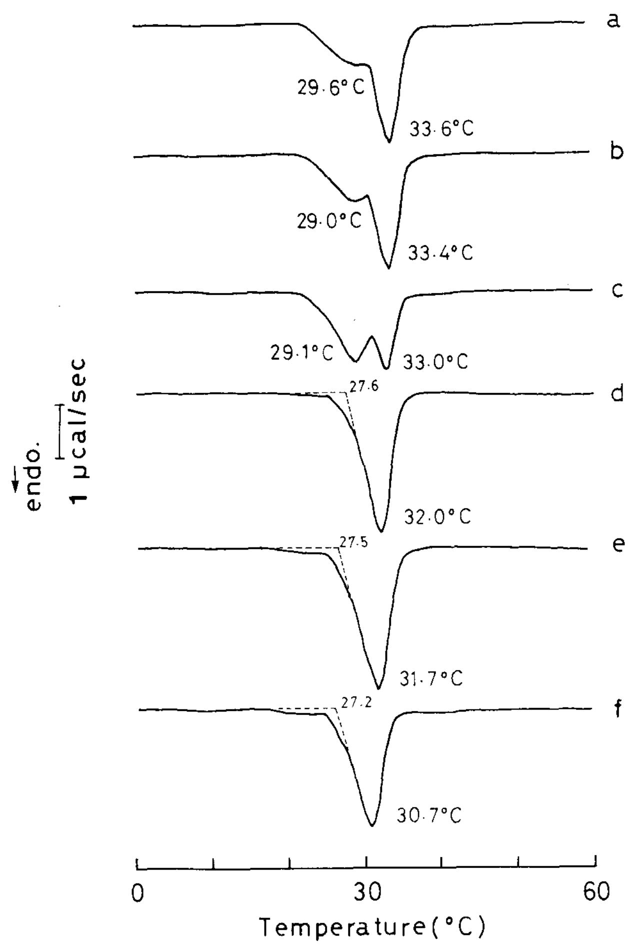

FIG. 3. DSC peaks of seed-solidified dark chocolate treated through thermo-cycle test: (a) bloomed sample; 5 wt% seeding of Cocoa Butter (Form VI) and 6 cycles of 32/20°C treatment, (b) bloomed sample; 5 wt% seeding of SOS (β_1) and 6 cycles of 32/20°C treatment, (c) nonbloomed sample; 5 wt% of BOB (β_2) and 6 cycles of 32/20°C treatment, (d) bloomed sample; 5 wt% of Cocoa Butter (Form VI) and one cycle of 38/20°C treatment, (e) bloomed sample; 5 wt% seeding of SOS (β_1) and one cycle of 38/20°C treatment, (f) nonbloomed sample; 5 wt% seeding of BOB (β_2) and one cycle of 38/20°C.

TABLE 2

Fat-Bloom Stability of Dark Chocolate Seeded With Cocoa Butter Powder (Form VI) and Aged for One Week at 20°C After Solidification (15°C, 15 min)

Cycle no.[a]	Cocoa butter powder (Form VI) concentration (wt%)[b]											
	0.05		0.10		0.50		1.00		2.50		5.00	
	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**
32/20												
0	−	29	−	30	−	31	−	30	−	30	−	31
1	−	30	−	31	−	31	−	30	−	31	++	33
2	−	31	−	31	−	31	−	31	+	31	+++	52
3	−	31	−	31	−	31	−	31	++	32	+++	61
4	−	31	−	32	−	31	−	32	+++	39	+++	63
5	+	32	+	32	+	32	+	32	+++	52	+++	64
6	+++	34	+++	35	+++	33	+++	34	++++	57	++++	65
38/10												
0	−	29	−	29	−	30	−	29	−	29	−	30
1	++++	31	++++	32	++++	31	++++	31	++++	30	++++	30

[a]One cycle is 32°C (12 hr) and 20°C (12 hr), and 38°C (12 hr) and 20°C (12 hr).
[b]Concentration with respect to fat content of dark chocolate.
*Fat-bloom occurrence evaluated by visual observation: (−); no-bloom, (+); weak bloom, (++); bloom, (+++); strong bloom, (++++); intensive bloom.
**Whiteness value measured with a color and color difference meter (6).

TABLE 3

Fat-Bloom Stability of Dark Chocolate Seeded With SOS Powder (β_1) and Aged for One Week at 20°C After Solidification (15°C, 15 min)

Cycle no.[a]	SOS powder (β_1) concentration (wt%)[b]											
	0.05		0.10		0.50		1.00		2.50		5.00	
	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**
32/20												
0	−	30	−	30	−	30	−	30	−	30	−	31
1	−	31	−	31	−	31	−	31	+	32	++++	60
2	−	31	−	31	−	31	−	32	+++	43	++++	63
3	−	30	−	31	−	30	−	31	++++	59	++++	62
4	−	32	−	32	−	32	−	32	++++	63	++++	64
5	+	32	+	32	+	32	+	34	++++	63	++++	64
6	+++	32	++	33	++	33	++++	51	++++	64	++++	64
38/20												
0	−	29	−	29	−	30	−	30	−	30	−	31
1	++++	30	++++	31	++++	32	++++	31	++++	32	++++	33

[a]One cycle is 32°C (12 hr) and 20°C (12 hr), and 38°C (12 hr) and 20°C (12 hr).
[b]Concentration with respect to fat content of dark chocolate.
*Fat-bloom occurrence evaluated by visual observation: (−); no-bloom, (+); weak bloom, (++); bloom, (+++); strong bloom, (++++); intensive bloom.
**Whiteness value measured with a color and color difference meter (6).

TABLE 4

Fat-Bloom Stability of Dark Chocolate Seeded With BOB Powder (β_2) and Aged for One Week at 20°C After Solidification (15°C, 15 min)

Cycle no.[a]	BOB powder (β_2) concentration (wt%)[b]											
	0.05		0.10		0.50		1.00		2.50		5.00	
	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**	Fat-bloom*	Whiteness**
32/20												
0	−	29	−	30	−	30	−	30	−	30	−	30
1	−	30	−	30	−	30	−	30	−	31	−	31
2	+	30	−	31	−	31	−	30	−	31	−	31
3	+		−		−		−		−		−	
4	+	31	+	32	−	32	−	31	−	31	−	31
5	++	32	+	32	+	31	−	31	−	31	−	32
6	++++	35	+	32	+	31	−	31	−	31	−	32
38/20												
0	−	29	−	29	−	29	−	29	−	29	−	30
1	++++	33	−−−−	32	++++	31	++++	31	+	31	−	31

[a]One cycle is 32°C (12 hr) and 20°C (12 hr), and 38°C (12 hr) and 20°C (12 hr).
[b]Concentration with respect to fat content of dark chocolate.
*Fat-bloom occurrence evaluated by visual observation: (−); no-bloom, (+); weak bloom, (++); bloom, (+++); strong bloom, (++++); intensive bloom.
**Whiteness value measured with a color and color difference meter (6).

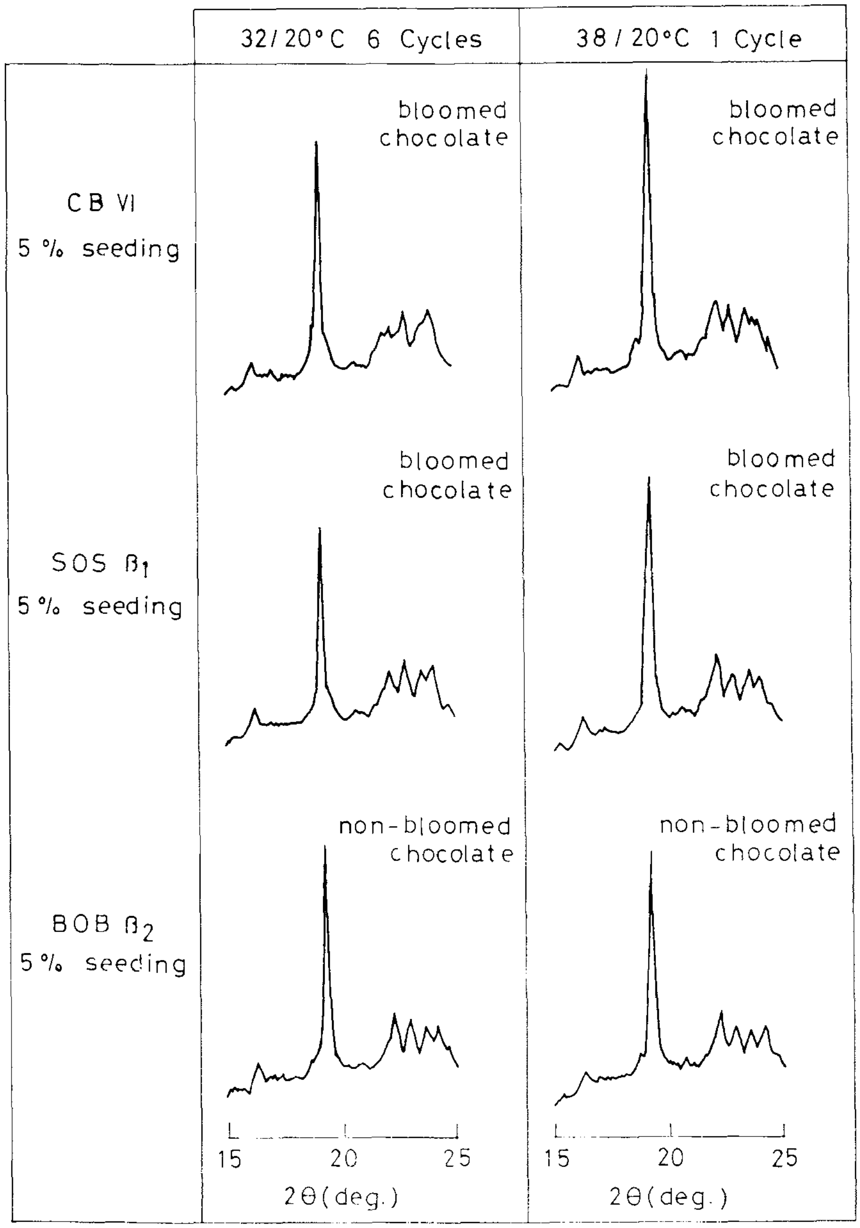

FIG. 4. XRD short spacing spectra of seeded dark chocolate treated through thermo-cycle test.

short-spacing spectra, bloomed samples using cocoa butter (Form VI) and SOS (β_1) showed Form VI-like patterns, but the nonbloomed sample using BOB (β_2) showed a Form V-like pattern (Fig. 4). On the other hand, in one cycle test of 38/20, both the bloomed samples using cocoa butter (Form VI) and SOS (β_1), and the nonbloomed sample using BOB (β_2) showed only one melting peak of Form V at 30.7~32.0°C (Fig. 3d~f). All of these samples revealed the XRD short-spacing spectra of Form V (Fig. 4).

Observation of bloomed surface. There were significant differences in the feature of the bloomed surfaces caused through the thermal-cycle tests between the temperatures below (32°C) and above (38°C), the melting point of dark chocolate. The bloomed surfaces using the seeds of cocoa butter (Form VI) and SOS (β_1) after the 6 cycle tests of 32/20 revealed homogeneous white color by increasing the number of the cycle test. However, in the case of one cycle test of 38/20, the bloomed surfaces using cocoa butter (Form VI) and SOS (β_1) lost smoothness and revealed many small "island-structures" surrounded by white areas having network patterns.

We show the results of microscopic observation of the nonbloomed and bloomed surfaces in Figure 5. Normal dark chocolate showed very smooth surfaces (Fig. 5a). Bloomed samples using cocoa butter (Form VI) and SOS (β_1) showed rough surfaces looking like a pavement of irregular slates when the samples were treated through the 6 cycle tests of 32/20. In the case of one cycle of 38/20, the bloomed samples using cocoa butter (Form VI) and SOS (β_1) showed three-dimensional crystal growth of island-like needle patterns (Fig. 5b). On the other hand,

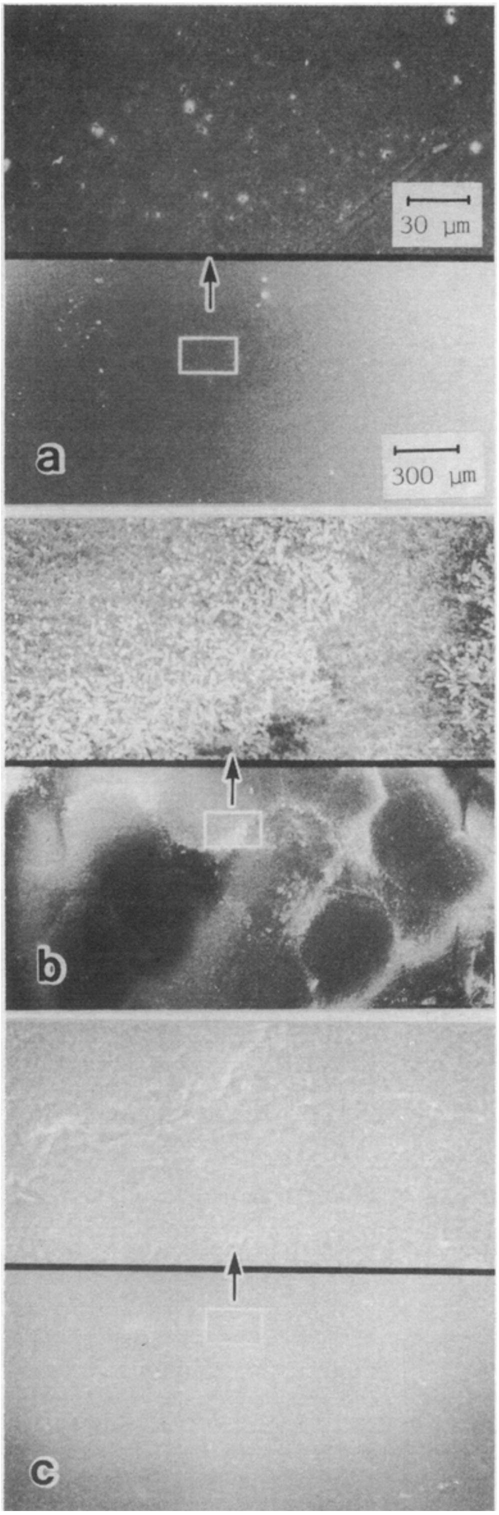

FIG. 5. Cryo-SEM micrographs of surfaces of seeded dark chocolate treated through thermo-cycle test: (a) untreated sample, (b) bloomed sample; 5 wt% seeding of SOS (β_1) and one cycle of 38/20°C treatment, (c) nonbloomed sample; 5 wt% seeding of BOB (β_2) and one cycle of 38/20°C. In each set of photos, the upper photo is an enlarged one of the portion denoted by a white line in the lower photo. Scale bars of the upper and lower photos are respectively common to the three sets.

the nonbloomed samples using BOB (β_2) through 6 cycle tests of 32/20 and one cycle of 38/20 showed smooth surfaces (Fig. 5c), although these surfaces were slightly rough in comparison to the normal sample. These differences in the feature of bloomed surfaces are consistent with the whiteness values caused by the above thermo-cycle tests.

DISCUSSION

We discuss two major experimental results: (a) the polymorphic relationship between the seed materials and cocoa butter solidified in dark chocolate, and (b) the effect of the seed material on the fat-bloom stability through the thermo-cycle test. The polymorphic structures of the fats examined in the experiments are discussed in terms of chain-length structure, subcell packing and melting point summarized in Table 2 of Paper I.

Polymorphism of solidified chocolate. Table 5 summarizes the polymorphic relationship between the seed material and the solidified dark chocolate at the seed concentrations of 0.2 and 5 wt%. All of the seed materials crystallized cocoa butter in Form V as the major polymorph. This makes a contrast to the fact that the nonseeded chocolate is crystallized in Forms VI and III as the major forms, and Form V as the minor form. We assume that the occurrence of Form VI in the nonseeded chocolate might be due to a V → VI transformation, not the direct crystallization (11), according to the very slow rate of the melt crystallization of cocoa butter without seeding (10).

The difference in the polymorphic occurrence of cocoa butter after the seeding is clearly seen at the seed concentration of 0.1 wt%. The seed crystals of cocoa butter (Form VI), SOS (β_1) and BOB (β_2) caused the crystallization of Form V, whereas other forms were solidified by the seeding of BOB (pseudo-β') and SSS (β). This comes from the effects of the chain-length structure and the subcell packing, both of which are similar among Forms V and VI of cocoa butter, β_1 of SOS and β_2 of BOB (12–15). This similarity gave rise to the preferable occurrence of Form V. Accordingly, the polymorphic transformation of V → VI might be reduced, because densely packed Form V crystals are formed. The occurrence of Form VI by the seeding of 5 wt% cocoa butter (Form VI) may be caused by the growth of Form VI of cocoa butter in dark chocolate during the agitation at 30°C before the molding. The growth of Form VI by an addition of SOS (β_1) is ascribed to the structural identity of two forms (13,15).

TABLE 5

Polymorphism of Total Fats of Seed-Solidified Dark Chocolate

	Seed material concentration	
Seed materials	0.1 wt%	5 wt %
No-seed	VI, III ≫ V	
Cocoa butter (Form VI)	V	V ≫ VI
SOS (β_1)	V	V ≫ VI
BOB (pseudo-β')	V > VI	V > III
BOB (β_2)	V	V
SSS (β)	III > II > V	V, III > II, VI

TABLE 6

Polymorphism of Total Fats of Dark Chocolate After Thermo-Cycle Tests Between 32 and 20°C (32/20), and Between 38 and 20°C (38/20) Using Seed Crystals of Cocoa Butter (Form VI), SOS (β_1) and BOB (β_2)

	Thermo-cycle condition	
Seed materials	32/20, 6 Cycles	38/20, 1 Cycle
SOS (β_1)	VI $\gg$ V	V
Cocoa butter (Form VI)	VI $\gg$ V	V
BOB (β_2)	V $\cong$ VI	V

The crystallization of Forms II, III and VI by the seeding of SSS (β) may be due to two reasons: the double chain-length structure of SSS (β) (16) preferred the double chain-length structures of Form II and III of cocoa butter (11). In turn, the triclinic parallel packing of SSS (β) (16) induces the might crystallization of Form VI. However, the crystallization was not accelerated by SSS (β) in comparison to SOS and BOB (1). This means the weakest interaction between SSS (β) and cocoa butter. Finally polymorphic forms having the melting points at 11~16°C might be formed by the crystallization of minor liquid fractions caused by the cooling process during the DSC scanning.

Fat-bloom stability. The principal mechanism of the fat-bloom in cocoa butter is growth of large crystals of more stable polymorphs at the expense of less stable forms: most typically the growth of Form VI (11,17,18), and in a particular case, the growth of Form V at the expense of Forms II, III, IV (7). In the present case of the seeded crystallization, the bloom-related grain growth may be induced by the seed crystals themselves, or the crystal newly transformed from the less stable forms. The molecules to be incorporated into the large growing crystals may be provided from two sources: less stable polymorphs of cocoa butter due to an oil-mediated transformation or small-size crystals due to Ostwald ripening (19). In both processes, the solute may migrate through the oil fraction having low-melting points. Based on this model of fat-bloom, we discuss the fat-bloom stability due to the seeding:

32/20 cycle test. (a) Cocoa butter (Form VI) and SOS (β_1): The fat-bloom was prevented at the seed concentrations of 0.05 wt% through 1.00 wt% by 4 cycles. On the other hand, the high-concentration seeding at 2.5 and 5 wt% remarkably reduced the fat-bloom stability. In the case of 5 wt% seeding, the fat-bloom occurred even after one cycle. (b) BOB (β_2): The fat-bloom occurred at the seed concentration lower than 0.5 wt% through the thermo-cycles over 2 or 5 tests. There was no fat-bloom when the seed concentration exceeded 1 wt% through 6 thermo-cycle tests.

Table 6 shows the polymorphs of the total fat after the thermo-cycle test. Form VI predominated Form V by the seeding of cocoa butter (Form VI) and SOS (β_1), whereas Forms V and VI have similar concentration in the case of BOB (β_2). The major polymorph was Form V before the thermal test, as shown in Table 5. This means that the polymorphic conversion from Form V to Form VI was manifest in the seeding of cocoa butter (Form VI) and SOS (β_1). Therefore, we assume that no fat-bloom by the seeding of cocoa butter (Form VI) and SOS (β_1) may be caused by the formation of small-grain crystals of Form V which prevented the crystals from converting to Form VI. The fat-bloom, however, occurred through 5~6 thermo-cycles in which the larger grains of Form VI eventually grew at the expense of small grains through Ostwald ripening. In turn, the higher concentration of the seed crystals of cocoa butter (Form VI) and SOS (β_1) interrupted the stable grain growth of Form VI, because the excess seed crystals present began to serve as the accelerator of the large grain growth:

38/20 cycle test. No fat-bloom stability was observed, except for a high concentration (5 wt%) of BOB (β_2). The total fat was crystallized in Form V in all cases. It is inferred that all of the seed materials, except 5 wt% BOB (β_2), would melt at 38°C for 12 hours. The subsequent cooling at 20°C caused the crystallization of unstable forms of cocoa butter, which transformed to Form V while growing the large-grain crystals. The seed materials of 5 wt% BOB (β_2) did not melt completely for 12 hours, serving as the seed materials to produce Form V during the subsequent cooling.

In view of the application of the seeding method to the industrial chocolate manufacturing, viscosity change due to the seeding during molding at 29~31°C is important. We confirmed that the seeding of 5 wt% BOB (β_2) resulted in a slight increase in viscosity at 30°C. However, the seeding of 5 wt% of cocoa butter (Form VI) and SOS (β_1) rapidly increased the viscosity just after the seeding.

To conclude, all of the present examinations proved that BOB (β_2) is the best seed material which prevents the fat-bloom formation and, at the same time, increases the solidification kinetics of dark chocolate. The seeding technique does not need the tempering machine. To apply this seeding technique in the factory-scale chocolate manufacture, we have to examine thermal and mechanical conditions for the seeding in a solidification process of molten chocolate: optimal seeding temperature, cooling rate, stirring conditions to distribute the seed materials, all of which are in progress.

ACKNOWLEDGMENT

M. Okada of Hiroshima University encouraged us throughout the present study. B. Petersson of Karlshamns AB gave us technical information about the preparation of water-rinsed chocolate for XRD measurements.

REFERENCES

1. Hachiya, I., T. Koyano and K. Sato, *J. Am. Oil Chem. Soc. 66*:1757 (1989).
2. Hachiya, I., T. Koyano and K. Sato, *J. Jpn. Oil Chem. Soc. 37*:613 (1988).
3. DuRoss, J.W., and W.H. Knighty, *Manufacturing Confectioner 45*:50 (1965).
4. Campbell, L.B., and P.G. Keeney, *Food Technology 22*:1150 (1968).
5. Hettick, A.K., *Manufacturing Confectioner 46*:29 (1966).
6. Cook, L.R., in *Chocolate Production and Use*, edited by L.R. Cook, Harcourt Brace Jovanovich Inc., New York, 1982, p. 408.
7. Aronhime, J.S., and N. Garti, in *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by N. Garti and K. Sato, Marcel Dekker Inc., New York, 1988, p. 376.
8. Hunter, R.S., *J. Opt. Soc. Amer. 50*:44 (1960).
9. Giddey, C., and E.T. Clerc, *Int. Choco. Rev. 16*:548 (1961).

10. Hachiya, I., T. Koyano and K. Sato, *Agric. Biol. Chem. 53*:327 (1989).
11. Wille, R.L., and E.S. Lutton, *J. Am. Oil Chem. Soc. 43*:491 (1966).
12. Wang, Z.H., K. Sato, N. Sagi, T. Izumi and H. Mori, *J. Jpn. Oil Chem. Soc. 36*:671 (1987).
13. Sato, K., *Food Microstructure 6*:151 (1987).
14. Koyano, T., I. Hachiya, T. Arishima, K. Sato and N. Sagi, *J. Am. Oil Chem. Soc. 66*:675 (1989).
15. Sato, K., T. Arishima, Z.H. Wang, K. Ojima and H. Mori, *J. Am. Oil Chem. Soc. 66*:664 (1989).
16. Small, M.D., in *Handbook of Lipid Research,* Vol. 4, edited by D.J. Hanahan, Plenum Press, New York, 1986, p. 347.
17. Jewell, G.G., 35th P.M.C.A. Production Conference, 1981, p. 63.
18. Chapman, G.M., E.E. Akehurst and W.B. Wright, *J. Am. Oil Chem. Soc. 48*:824 (1971).
19. Kahlweit, M., *Advance in Colloid and Interface Science 5*:1 (1975).

[Received March 8, 1989; accepted July 28, 1989]
[J5677]