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OBSERVATION OF SEEDING EFFECTS ON FAT BLOOM OF DARK CHOCOLATE

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Abstract

Surface microstructures and polymorphism of seeded dark chocolate were observed with cryo-SEM, to clarify the effects of seeding on fat bloom stability of dark chocolate. Two thermal tests, cycling between 32 and 20 C (32/20) and 38 and 20 C (38/20), were applied to examine the fat bloom stability of the chocolate. We used three crystalline powders: Form VI of cocoa butter; the most stable β_1 form of SOS (1,3-distearoyl-2-oleoylglycerol); and the second stable β_2 form of BOB (1,3-dibehenoyl-2-oleoylglycerol) as seed materials. Seeding with cocoa butter (Form VI) and SOS (β_1) at concentrations of 0.5 ∿ 1 wt.% showed good fat bloom stability in the 32/20 test. In the case of the 38/20 test, however, fat bloom was not prevented. Seeding with BOB (β_2) gave the best fat bloom stability in both thermo-cycles; in particular, 5 wt.% BOB (β_2) completely prevented fat bloom after the 38/20 test.

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KEY WORDS: Cryo-scanning electron microscopy, seeding effect, fat bloom, dark chocolate, polymorphism, cocoa butter, surface microstructure, 1,3-dibehenoyl,2-oleoyl-glycerol.

Introduction

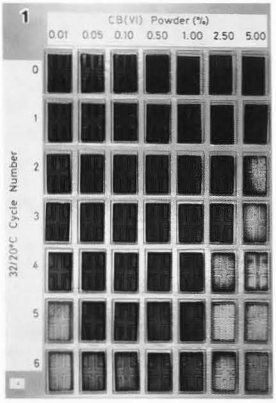
In chocolate production, pre-crystallization influences viscosity, demolding, and qualities of the final product such as gloss, snap, heat resistance, fat bloom resistance and so on (5,6,14,16). The tempering process, necessary to stabilize the cocoa butter crystals, involves well-controlled cooling/heating/cooling (5,18). In comparison with tempering, seeding is simpler and more convenient since cocoa butter crystallization is caused by adding seed crystal powders while simply cooling the molten chocolate. The seeding method, however, has not been used for two major reasons. First, crystals having small dimensions were difficult to produce on the factory scale. Second, details of the seeding conditions have not been examined, although some attempts have been made to clarify the solidification kinetics of tempering (1,3,7-9,13)

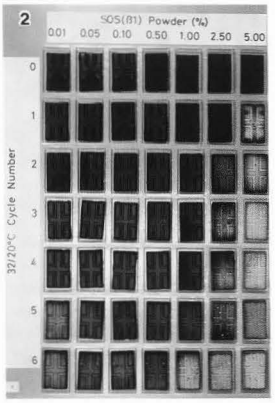
We have recently studied seeding effects on the solidification of cocoa butter and dark chocolate, aiming to use the seeding technique in factory-scale chocolate production. In previous reports, we developed a method to mass produce seed crystals of small dimensions using a cryo-mill at -50 ∿ 100 C with liquid nitrogen (10). The crystallization kinetics of cocoa butter were measured in relation to the concentration and polymorphism of various seed crystals (12). We related the physical properties of seeded dark chocolate to demolding and anti-bloom phenomena, showing that seed materials of thermodynamically stable polymorphs of St-O-St type triacylglycerols (St=saturated acyl chain) have the most favorable physical properties.

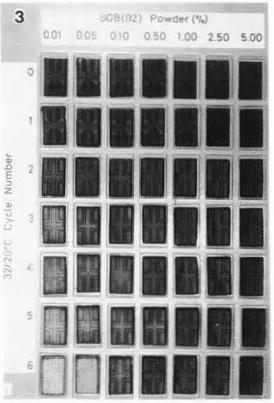
In this paper, we carefully observed the effects of seeding on the fat bloom stability of dark chocolate. We used three seed materials, cocoa butter (Form VI), SOS(β_1) and BOB (β_2) in which S, O and B stand for stearoyl, oleoyl abd behenoyl acyl chains, respectively, since these three accelerated the crystallization of cocoa butter most effectively.

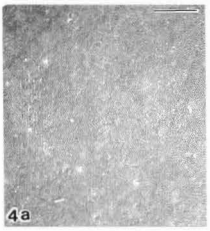
Materials and Methods

The three types of crystal were pulverized with a cryo-mill at -50 ∿ -100 C using liquid nitrogen. The dimensions ranged from 20 to 70 μm as measured with cryo-scanning electron microscopy (cryo-SEM) at -100 ∿ -130 C. The desired polymorphic forms of the above fat


1
CB(VI) Powder (%)
0.01 0.05 0.10 0.50 1.00 2.50 5.00
32/20°C Cycle Number
0
1
2
3
4
5
6


2
SOS(β1) Powder (%)
0.01 0.05 0.10 0.50 1.00 2.50 5.00
32/20°C Cycle Number
0
1
2
3
4
5
6


3
BOB(β2) Powder (%)
0.01 0.05 0.10 0.50 1.00 2.50 5.00
32/20°C Cycle Number
0
1
2
3
4
5
6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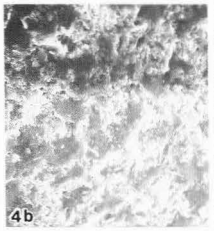
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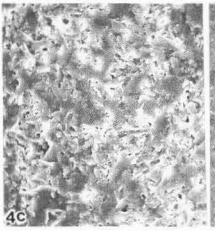
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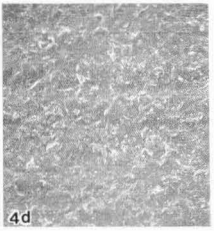
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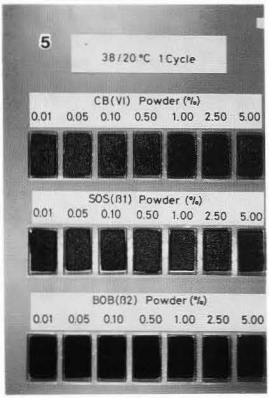
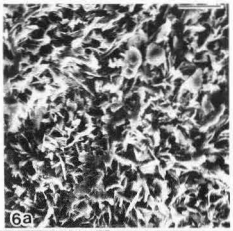

5
38/20 °C 1Cycle
CB(VI) Powder (%)
0.01 0.05 0.10 0.50 1.00 2.50 5.00
SOS(β1) Powder (%)
0.01 0.05 0.10 0.50 1.00 2.50 5.00
BOB(β2) Powder (%)
0.01 0.05 0.10 0.50 1.00 2.50 5.00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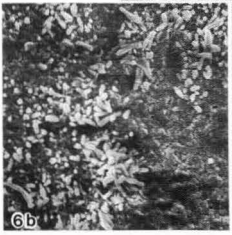
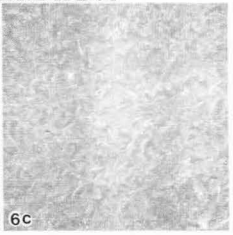

6b


6c

materials were prepared by the method of Wang et al. (23). The polymorphism of the fats was determined by DSC at a scanning rate of 10 C/min, and X-ray diffraction (XRD). The purity of the fat materials were analyzed with high-performance liquid chromatography (HPLC). Major triacylglycerols invovled in cocoa butter employed were POP (15.8 %), POS (32.7 %), in which P stands for palmitoyl acyl chain, and SOS (22.5 %). The purity of the seed crystals was 78.7 % (SOS) and 72.5 % (BOB). SOS and BOB were of industrial purity. The melting points of the seed crystal powders, defined as temperatures at the peak of DSC melting, were cocoa butter (Form VI) 34.0 C, SOS (β_1) 42.0 C and BOB (β_2) 51.4 C. Dark chocolate was manufactured by the following formulation: chocolate liquor 33.00 wt.%, sugar 41.65 wt.%, cocoa butter 24.85 wt.% and soya lecithin 0.50 wt.%.

We examined the fat bloom stability of seed-solidified dark chocolate by the following methods. the molten dark chocolate, 60 C, 250 g weight, was cooled to 30 C within 10 minutes with agitation (194 rpm) in a rotational viscometer (11). Seed crystals were added at different concentrations with respect to the cocoa butter content of dark chocolate (43 wt.%), at the time when the temperature of dark chocolate reached 30 C. Seed concentration ranged from 0.01 to 5 wt.%. After seeding, the dark chocolate was agitated for 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 x 20 mm x 3.5 mm) made of ethylene chloride resin (thickness of 0.5 mm). The dark chocolate in the mold was immediately cooled to 15 C and solidified for 15 minutes in a cooling box. After cooling, the molded samples were aged by storing at 20 C for one week.

After aging, thermo-cycle tests were carried out using a thermostated chamber. The cycle involves heating at 32 or 38 C for 12 hours and cooling at 20 C for 12 hours, referred to us 32/20 or 38/20, respectively. During the thermo-cycle test, we observed changes in the appearance of the samples, both on the surface and interior, using an optical microscope and cryo-SEM (-100 ∿ -130 C). Polymorphic modification of the seed-solidified chocolate was measured with XRD and DSC at a scanning rate of 5 C/min, during the thermo-cycle test. Prior to the XRD study, sugar in the sample was dissolved by the method of Giddey and Clerc (9): the sample was sliced with a knife into powder below 8 mesh size, and put in 120 ml of water (7 ∿ 10 C) to dissolve the sugar.

Results and Discussion

32/20 Thermo-cycle test

Figures 1,2,3 show the surface appearance of the seeded dark chocolate after the 32/20 test, in which the fat bloom is revealed in white-color areas. Cocoa butter (Form VI), Fig.1, and SOS (β_1), Fig.2, showed similar trends with increasing number of cycles and seed concentration; fat bloom was prevented in the range of the seed concentration from 0.05 to 1 wt.% and below 4 cycles. At 0.01 wt.%, fat bloom stability decreased slightly. Similarly, the high-concentration seeding of 2.5 and 5 wt.% lowered stability against fat bloom. In the case of the 5 wt.% seeding, fat bloom occurred after one cycle. In contrast, seeding with BOB (β_2), Fig.3, improved fat bloom stability with increasing seed concentration. No fat bloom was observed after 6 cycles, when the seed concentration exceeded 1 wt.%.

Figure 4 shows cryo-SEM photographs of the surface microstructure of a non-bloomed sample with 0.5 wt.% of SOS (β_1) seed taken prior to the thermo-cycle test (normal sample), bloomed sample seeded with 5 wt.% of cocoa butter (Form VI) and SOS (β_1) after 6 cycles, and a non-bloomed sample seeded with 5 wt.% BOB (β_2) after 6 cycles. The normal sample showed a very smooth surface even at high magnification (Fig.4a). The bloomed samples, however, showed rough surfaces (Fig.4b and c). In the case of the non-bloomed sample seeded with 5 wt.% BOB (β_2), Fig.4d. a smooth surface was observed, although it was slightly rougher than the normal untreated sample (Fig.4a).

The polymorphic conversion from Form V to Form VI was observed during this 32/20 cycle test. The polymorphs of the sample seeded with cocoa butter (Form VI) and SOS (β_1) were both Form VI, whereas Forms V and VI at similar concentrations were confirmed in the chocolate seeded with 5 wt.% BOB (β_2).

Legends for figures on the next page.

Fig.1 Photographs showing dark chocolate, seeded with powder crystals of cocoa butter (Form VI) at seven concentrations, during the 32/20 thermo-cycle tests up to 6 times (see text).

Fig.2 Photographs showing dark chocolate, seeded with powder crystals of SOS (β_1) at seven concentrations, during the 32/20 thermo-cycle tests up to 6 times.

Fig.3 Photographs showing dark chocolate, seeded with powder crystals of BOB (β_2) at seven concentrations, during the 32/20 thermo-cycle tests up to 6 times.

Fig.4 Cryo-SEM photo-micrographs showing the surface microstructures of dark chocolate after 6 cycles of the 32/20 test:(a) non-treated sample; (b) bloomed sample seeded with 5 wt.% cocoa butter (Form VI); (c) bloomed sample seeded with 5 wt.% SOS (β_1); and (d) bloomed sample seeded with 5 wt.% BOB (β_2)(Scale bar=20 μm).

Fig.5 Photographs showing dark chocolate, seeded with cocoa butter (Form VI), SOS (β_1) and BOB (β_2), after one cycle of the 38/20 test.

Fig.6 Cryo-SEM photo-micrographs showing the surface microstructures of dark chocolate after one cycle of 38/20 test: (a) bloomed sample seeded with 5.wt.% cocoa butter (Form VI); (b) bloomed sample seeded with 5 wt.% SOS (β_1); and (c) bloomed sample seeded with 5 wt.% BOB (β_2) (Scale bar=20 μm).

38/20 Thermo-Cycle Test

Figure 5 shows photographs of seeded dark chocolate after the 38/20 test. Significant fat bloom occurred in all samples seeded with cocoa butter (Form VI) and SOS (β_1) after one cycle. In the seeding of BOB (β_2), however, high seed concentration improved fat bloom stability. In particular, a seed concentration of 5 wt.% BOB (β_2) completely prevented fat bloom after one cycle.

As to the 38/20 test, a white network was formed on the bloomed rough surface. The interior of the bloomed dark chocolate changed into a very rough structure look like closely packed small spheres, whose sizes ranged from 0.3 to 1.5 mm. Figure 6 shows cryo-SEM photographs of the surface microstructures of bloomed samples seeded with 5 wt.% of cocoa butter (Form VI) and SOS (β_1), and a non-bloomed sample seeded with 5 wt.% BOB (β_2), after one cycle. Numerous needle-like crystals were formed on the surface of the bloomed samples (Fig.6a and b). In contrast, the non-bloomed sample in Fig.6c, seeded with BOB (β_2), reveals a smooth surface which is almost the same as that of the non-bloomed surface in Fig.4d. As to polymorphism, all bloomed and non-bloomed samples were Form V.

Mechanism of Fat Bloom

In Table 1, we summarize the features of fat bloom formation through the above two thermal treatments. It appears that the mechanisms of fat bloom formation differ between 32/20 and 38/20 tests. The difference may be related to whether or not the thermal cycle goes above the melting point of cocoa butter 34 (C). However, the growth of large crystals of cocoa butter which scatter light, resulting in a white appearance on the chocolate surface, may occur in both cases as the basic mechanism (16,17).

Table 1 Fat Bloom Formation in Dark Chocolate

	Thermal test*	
	32/20	38/20
Rate	slow	rapid
Appearance	white	white color network
Internal structure	no significant change	small particle aggregation
Polymorphism	VI >> V	V

*) 32 or 38 C for 12 hours, and 20 C for 12 hours.

In the case of the 32/20 test, the bloom-causing grain growth may be initiated by Form VI crystals of cocoa butter which are formed either through solid-state transformation or by the seed crystals themselves. The large grains of Form VI, which was converted from Form V through thermal treatment, grew at the expense of small grains of Form VI via Ostwald ripening (15). This process may provide the solute molecules of cocoa butter which are incorporated in the growing Form VI crystals. The increasing concentration of the two seed crystals, cocoa butter (Form VI) and SOS (β_1), may not interrupt the stable grain growth of Form VI. Hence, the excess seed crystals accelerated the growth of the large grains of Form VI. This may be justified by the fact that Form VI of cocoa butter and β_1 of SOS are same with respect to chain length structure and subcell packing (19, 21, 23).

In the case of the 38/20 test, fat bloom may form by the same mechanism as that in non-tempered chocolate (16). There is the possibility that thermal unstable seed crystals completely melt or dissolve in the molten chocolate, due to high temperature (38 C) and long treatment (12 hours); this might occur in the seed crystals of SOS (β_1) and cocoa butter (Form VI). When the completely molten dark chocolate was subsequently cooled to 20 C, it solidified in the same manner as non-seeded crystallization, which readily causes bloom-related growth of Form V by transformation from the first crystallized, metastable forms of cocoa butter, presumably Form III and IV (2,4,22,24). There is a trend that, with increasing rate of crystallization, less stable forms of triacylglycerols crystallized more readily than more stable forms (20). This is the reason why only Form V was detected in the bloomed samples after the 38/20 test. As to BOB (β_2), the seed crystals do not melt at 38 C for 12 hours, since the melting point is reasonably high. Hence, the remaining BOB (β_2) crystals induce stable crystallization of Form V without causing the formation of other metastable forms.

Concluding Remarks

BOB (β_2) seed crystal exhibited the most favorable solidification behavior, with no fat bloom even after the 38/20 thermal treatment. We assume that BOB (β_2) is the most suitable seed crystal for chocolate production, since it also accelerates the crystallization rate of dark chocolate. Studies to determine optimal conditions will be needed to apply the seeding method to industrial chocolate production.

Acknowledgment

Fuji Oil Co. kindly provided the fat samples.

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Discussion with Reviewers

G.Ziegleder: Cocoa butter (CB) Form VI crystals are more heat-resistant than cocoa butter Form V, arising during the industrial pre-crystallization process. Therefore, chocolate seeded with CB Form VI is rather stable at a 32/20 cycle test. Is the chocolate seeded with CB Form VI more bloom-resistant in comparison to industrial chocolate at milder temperature below 30 C ?
Authors: It is highly possible, as you indicate, to observe that seeding of CB Form VI may reveal better fat bloom stability than CB Form V after thermal test below 30 C. However, we did not examine this phenomenon in the present study.

G.Ziegleder: There may be different origins of fat bloom: the polymorphic transition (as you describe) or some fractionation effects in mixtures of CB with non-compatible fats. Could BOB retard fat bloom of the second type, too ?
Authors: In a separate experiment, we examined fat bloom stability of a blended dark chocolate involving CB and non-lauric cocoa butter replacer (CBR) having concentration ratios of CB/CBR=95 ∿ 80/5 ∿ 20 both by usual tempering and seeding. The results showed remarkable fat bloom stability by using BOB (β_2).

J.Shlichter-Aronhime: The BOB gave excellent fat bloom stability which is not surprising if crystal structure compatibility of the impurity with the fat host is considered as a possible mechanism for this action. The authors could examine their findings in view of the proposed mechanism of the "button syndrome". What do you think about that ?
Authors: We agree with your idea of "button syndrome" in the present case of seeding of BOB (β_2), in a sense that the affinity in the molecular structure between host molecules (CB) and guest molecules (BOB) plays decisive roles.

J.de Man: Apparently, the seeding of chocolate with BOB was effective because of the high melting point of BOB (53 C). This would probably impart sandiness to the chocolate when added at a level of 5 %.
Authors: The BOB β_2 crystal powders did not impart sandy mouth feel at all when their dimensions did not exceed ca. 70 μm as we have examined in the present study, since the dimensions of cocoa mass particles dispersed in chocolate are of the same order of magnitude.

J.de Man: The BOB seeding does not appear to be of any practical value, because this compound would no doubt not be a permitted additive.
Authors: In Japan, an approval for the use of lipase-catalyzed interesterified fats in food products like BOB has been given. So, chocolate seeded with BOB crystals has already been placed on the market in Japan.

Editor: How may be a reader obtain ref.6, 14 and 17 ?
Authors: These Proceedings of the Pennsylvania Manufacturing Confectioners Association Production Conferences are available from: P.M.C.A., P.O Box 68, Route 29, Perkiomenville, PA 18074, USA.