TECHNICAL

Seeding Effects on Solidification Behavior of Cocoa Butter and Dark Chocolate. I. Kinetics of Solidification

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Effects of seeding of fat crystals on the crystallization kinetics of cocoa butter and dark chocolate were examined with a rotational viscometer. The seed crystals employed were cocoa butter, 1,3-distearoyl-2-oleoylglycerol (SOS), 1,3-dibehenoyl-2-oleoylglycerol (BOB) and 1,2,3-tristearoylglycerol (SSS). The seed powders were prepared by pulverization below −50°C, the dimensions being in a range from 20–70 μm. Particular attention was paid to the influence of polymorphism of the seed crystal. We found that all of the above seed materials accelerated the crystallization, the degree of acceleration being in a following order; SOS (β_1) > cocoa butter (Form V) > SOS (a mixture of pseudo-β' and β_2) > BOB (β_2) > BOB (pseudo-β') ≫ SSS (β). Precise measurements of the crystallization kinetics showed that the most influential factors in the seeding effects are the physical properties of the seed materials—above all, thermodynamic stability, and similarity in the crystal structure to cocoa butter are the most determinative.

In chocolate manufacturing, careful control of the solidification processes is quite important because it significantly influences both rheological properties of chocolate which determine the workability in the production processes, and physical properties of end products such as gloss, snap, texture, heat resistance, fat bloom stability, etc. (1–8). The physical properties are related to polymorphism of cocoa butter, which comprises the major solid fat in chocolate. Six polymorphs of cocoa butter have been identified (9–12); Forms I, II, III, IV, V and VI.

Currently two-stage crystallization processes are applied in factory-scale production of chocolate; pre-crystallization and bulk crystallization (6–8). The pre-crystallization is carried out by cooling/reheating process, the molten chocolate was first cooled at 26∼27°C, then heated again at 30∼31°C. Thereafter, the bulk crystallization is processed for molding at about 8∼15°C to produce the end products. The pre-crystallization is related to the polymorphic control of the first-crystallized cocoa butter. The initial cooling at 26∼27°C crystallizes both metastable and stable polymorphs of cocoa butter (7,13). The metastable forms, which may cause undesirable solidification behavior, are transformed to the more stable forms during the subsequent reheating at 30∼31°C. In the bulk crystallization process, the crystals present after the pre-crystallization induce the solidification of cocoa butter in Form V (3,10,14). The pre-crystallization is processed with a tempering machine equipped with a sophisticated temperature control system. The tempering machine enables the occurrence of preferable polymorphic forms, having most optimal dimensions and concentrations of the crystals which may serve as seed crystals during the subsequent bulk crystallization. Despite of this importance, the tempering process has some disadvantages on a production scale—difficulty in controlling the tempering conditions and the high cost of energy and space.

The effect of seeding of fat crystals on the chocolate crystallization has been elucidated with two purposes; (a) to analyze the crystallization mechanism in the above tempering process (15–20), and (b) to replace the tempering procedure by simpler seeding techniques. In the seeding procedure related to the second purpose, the fat crystals having melting temperatures above 34°C (melting point of cocoa butter) are added to the molten chocolate. After the seeding, the molten chocolate is directly cooled at the production temperature, 8∼15°C, without the pre-crystallization procedure. However, because of two major difficulties this method has not been utilized in the industry so far. These difficulties are: (a) Production of seed powder crystals of small dimensions on a factory scale, and (b) selection of the seed materials. Recently we succeeded in producing the crystal powders of cocoa butter of dimensions of 20∼70 μm using a cryo-mill at − 50∼−100°C (21). The second difficulty is related to seed material and its polymorphic behavior, the dimension and concentration of the seed crystals, optimal temperature for seeding, rheological changes of molten chocolate due to the seeding, influences on the crystallization kinetics and physical properties involving fat blooming. In this regard, solving these problems may be promoted by referring to recent progress in researches for the physical properties of the solid fats: re-examination of the polymorphism of cocoa butter (22) and triacylglycerol components (23) of the bulk crystals produced in the crystallization of cocoa butter, the high shearing effects on the chocolate crystallization (24) and polymorphism of POP, SOS, AOA and BOB (25–28).

We have recently studied the seeding effects on the solidifcation behavior of cocoa butter. We analyzed the concentration and polymorphic forms of the cocoa butter crystals produced in the tempering procedure (21). The cocoa butter crystallized in Forms V and VI after a simple cooling. By contrast, only Form V was crystallized by cooling/reheating process. Then, we constructed a rotational viscometer to measure the crystallization rate of cocoa butter and chocolate (29). We confirmed that the torque value of the rotational viscometer was proportional to viscosity measured with a Brookfield-type viscometer. Using this viscometer, we measured the crystallization rates of cocoa butter using the seed powders of Forms III, V and VI of cocoa butter (30). The crystallization was accelerated by the three seed crystals, among which the Form VI seed powders were most effective. This suggested the critical importance of the polymorphism of the seed materials.

This paper (Paper I) describes the effects of seeding on the crystallization behavior of cocoa butter and dark chocolate in order to investigate a wider possibility of usage of the seed materials besides cocoa butter. We examined SOS, BOB, and SSS (S:stearoyl, O:oleoyl, B:behenoyl). In the second paper (Paper II) we discuss several physical properties of seed-solidified dark chocolate in relation to the polymorphism of the seed materials employed.

MATERIALS AND METHODS

Seed materials preparation. The purity of the sample was on the level of industrial usage (Table 1). As for SOS and BOB, we prepared the polymorphic forms of β_1, and a mixture of pseudo-β' and β_2 of SOS, pseudo-β' and β_2 of BOB, according to the method of Wang *et al.* (25). The β form was employed for SSS. Pulverized powder samples were produced at −50–100°C with a cryomill (Fuji Power Ltd., Tokyo; Atomizer EIIW-type), which requires >500 g sample. The temperature was lowered with liquid N_2, and the running time was 1.5 minutes for the 500 g sample. As a reference, cocoa butter powders of Forms V and VI were examined. The powder sizes were distributed from 20 to 70 μm, as observed with a cryo-SEM (Hitachi Ltd., Tokyo; S-570) below −100°C. In case of SSS, the cryo-mill was not applied due to lack of 500 g-level sample. Therefore, the SSS powder was formed by a simple grinding, the powder size being 20∿150 μm.

Major triacylglycerol components of the seed materials were analyzed with HPLC (31): pump (Shimadzu, Kyoto; LC-6A), ODS column (Merck, Darmstadt, FRG; Lichrosorb RP-18, 5 μm, 4.6 mm × 250 mm), differential refractometer (Shimadzu Co., Kyoto; RID6A), mobile phase (acetonitrile-acetone 27:73 [v/v], 1.0 ml/min). The data are shown in Table 1.

Polymorphic structures of the seed crystals were determined with X-ray diffractometry (XRD) (Rigaku Ltd., Tokyo; 2027 type, Cu-Kα) and DSC (Seiko Ltd., Tokyo; SSC 580 type, scanning rate, 10°C/min).

Chocolate manufacturing. Dark chocolate was formed by the following procedure: Chocolate liquor, 33.00 wt%; sugar, 41.65 wt%; cocoa butter, 24.85 wt%; and soya lecithin, 0.5 wt%, all of which were refined and conched before the solidification process. Chocolate liquor was produced from cocoa bean (Ghana) roasted in our laboratory. The particle sizes of ingredients were reduced with a refining roll (Buhler Ltd., Uzwil/Swiss; 30SD) to about 25 μm.

Viscosity measurement. We employed the rotational viscometer (29), a steel beaker with a water jacket connected to two water baths, a thermister, agitating blades, a motor load detector, a computer with Multiplexer and Digital multimeter.

350 g molten cocoa butter or 400 g dark chocolate were first melted at 60°C in the steel beaker, agitated at

TABLE 1

Major Triacylglycerol Components of Cocoa Butter, SOS, BOB and SSS Analyzed with HPLC (wt%)

Cocoa butter	POP: 15.8 POS: 32.7, SOS: 22.5
SOS	SOS: 78.7, POS and SLS: 13.3
BOB[a]	BOB: 79.2, BOS: 9.1 BOB: 72.5, BOS: 7.9
SSS	SSS:82.3

[a] Pseudo-β' of BOB employed 79.2 wt%, but β_2 of BOB 72.5 wt%.

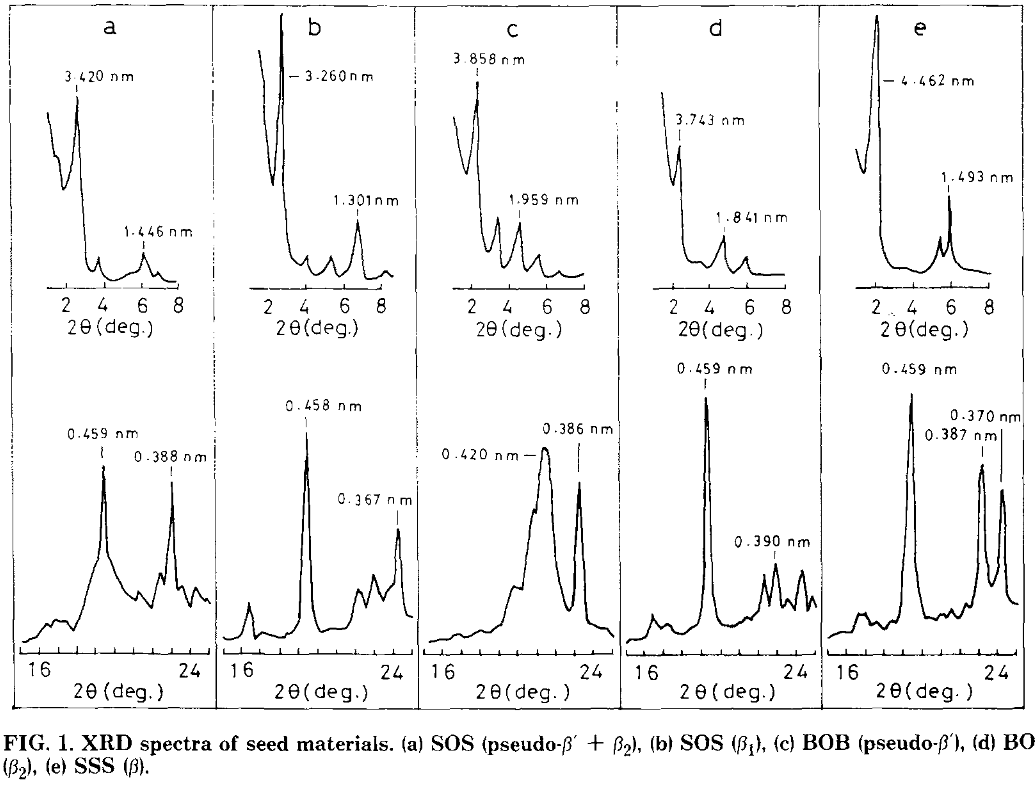

FIG. 1. XRD spectra of seed materials. (a) SOS (pseudo-β' + β_2), (b) SOS (β_1), (c) BOB (pseudo-β'), (d) BOB (β_2), (e) SSS (β).

126 rpm, and cooled to crystallization temperature (T_C). We defined crystallization time (t_C) in a manner similar to Kleinert (32), $t_C = t_S - t_0$, in which t_0 is the time when the temperature of the sample reached T_C. t_S is the time when the increase in the output voltage of the torque value reached 3.00 mV. In case of the seeded crystallization, the seed crystals were added at $t = t_0$, the amount being in a range from 0.01 to 0.50 wt%, with respect to the total fat content in case of dark chocolate. To compare t_C of the seeded crystallization with that of the non-seeded crystallization, a relative crystallization time, t_r, was calculated as $t_r = t_C$ (seeded)/t_C (non-seeded).

RESULTS

Physical data of seed crystals. Figure 1 shows long and short spacing spectra of XRD of the seed crystals of SOS, BOB and SSS. DSC peaks of these seed crystals are shown in Figure 2.

SOS in Figure 1a is the mixture of pseudo-β' and β_2 because it has a strong short spacing 0.388 nm (pseudo-β') and 0.459 nm (β_2), and a long spacing value (6.80~7.00 nm) of pseudo-β'. DSC melting peaks (Fig. 2a), proved the existence of the two polymorphs of SOS. Figure 1b shows typical XRD patterns of β_1 of SOS, which are characterized by a very strong peak of 0.458 nm and a medium peak of 0.367 nm in the short spacing, and also by the long spacing of 6.54 nm. This form has a single endothermic peak at 42.0 C in DSC (Fig. 2b). BOB in Figure 1c is pseudo-β'; a strong peak of 0.420 nm and a medium peak of 0.386 nm in short spacing, and long spacing of 7.80 nm. The BOB sample in Figure 1d corresponds to β_2 with short spacings of a very strong 0.459 nm and a medium 0.390 nm peaks, and 7.41 nm of long spacing. As to the DSC data of pseudo-β' and β_2 of BOB in Figures 2c and 2d, the melting point of pseudo-β' is a bit higher than that of β_2. This contrasts with the fact that β_2 is more stable than pseudo-β' (28). This contradiction appeared occasionally, since we employed the BOB sample of β_2, whose purity was lower than for pseudo-β' (Table 1). The β form of SSS showed the typical XRD and DSC patterns (Fig. 1e and Fig. 2e).

Viscosity change and crystallization kinetics. Figure 3 shows two torque curves of dark chocolate with an addition of 0.035 wt% and 0.5 wt% of SOS (β_1) at $T_C = 30°C$ under 126 rpm agitation. In both cases, the torque value was raised due to the increase in viscosity when the temperatures decreased from 60°C to T_C. Just after T_C was reached, the seed crystals were added at $t = t_0$ (Fig. 3). An initial increase of the torque value is detectable after the seeding due to a solid mass of the seed materials. Obviously, the initial increase is larger in the 0.5 wt% seeding than in the 0.035 wt% seeding. The torque value kept the same level, after the seeding, at 0.68 mV (0.035 wt%) and at 0.76 mV (0.5 wt%) over a short duration. Then, the viscosity increased in a semi-exponential manner with increasing time, being accompanied with a slight raise of the temperature of sample due to the heat of crystallization. The time, t_S, when the increase in the torque value reached 3.00 mV, was 69.3 min (0.035 wt%) and 38.0 min (0.5 wt%). Therefore, the crystallization time, t_C, equals 59.0 min (0.035 wt%) and 27.4 min (0.5 wt%).

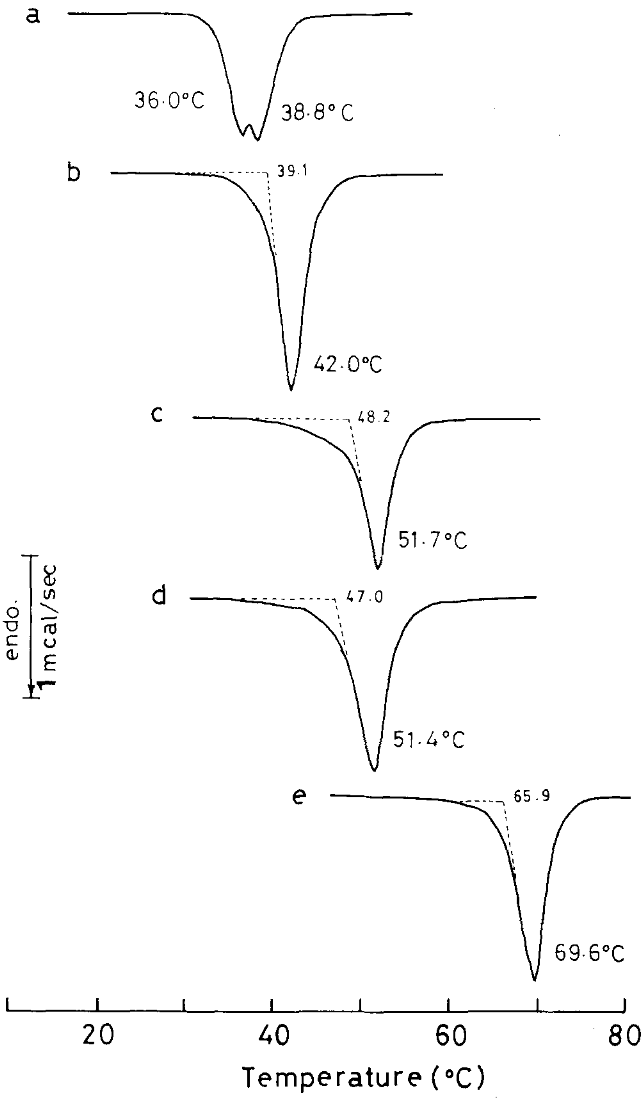

FIG. 2. DSC peaks of seed materials. (a) SOS (pseudo-β' + β_2), (b) SOS (β_1), (c) BOB (pseudo-β'), (d) BOB (β_2), (e) SSS (β).

As a reference, the values of t_C of non-seeded crystallization at $T_C = 30°C$ were 661.6 and 291.1 min for cocoa butter and dark chocolate, respectively. Hence, the relative crystallization time (t_r) became 0.203 (0.035 wt%) and 0.094 (0.5 wt%).

Figure 4 shows the t_r values of cocoa butter at various concentrations of the seeding crystals of SOS, BOB and SSS. For comparison, the t_r values of the seeding of cocoa butter (Forms V and VI) (30) are reproduced in Figure 4. Figure 5 shows t_r of dark chocolate. Both results indicate two similar tendencies with respect to the seed concentration and the physical properties of the seed materials. In the first, t_r decreased with increasing concentration of the seed crystals. The relationship can be expressed by the following experimental equation:

$$t_r = -K \ln C_0 + K_0$$

in which C_0 is the concentration of the seed crystal (wt%), K(>0) and K_0 are experimental parameters. For example, in case of dark chocolate seeded with SOS (β_1),

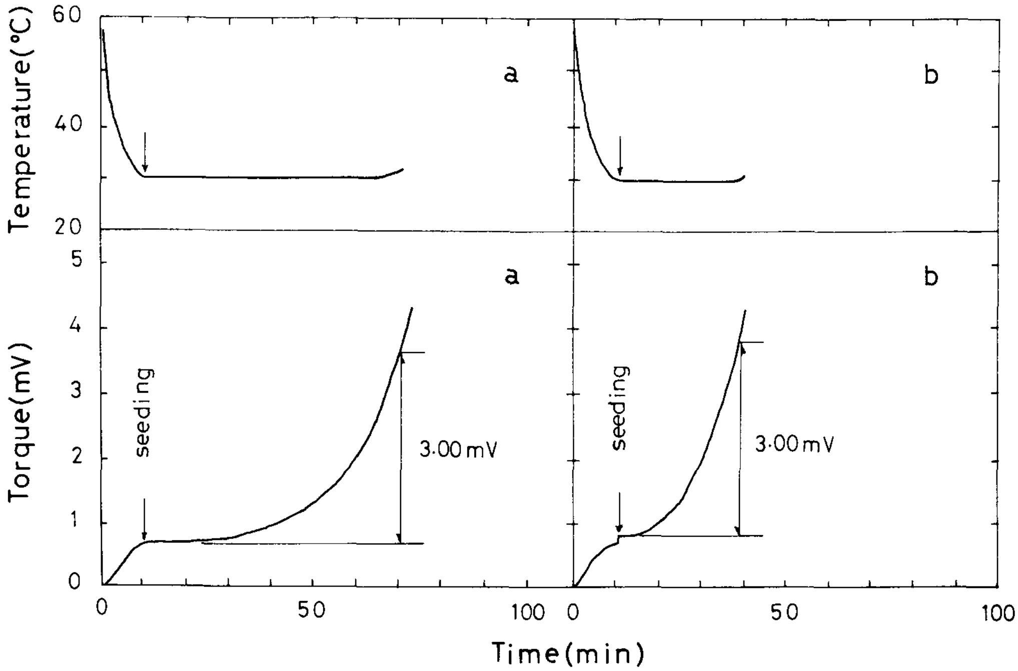

FIG. 3. Changes of torque and temperature of dark chocolate seeded with SOS (β_1) at T_c = 30°C: (a) 0.035 wt%, (b) 0.5 wt%.

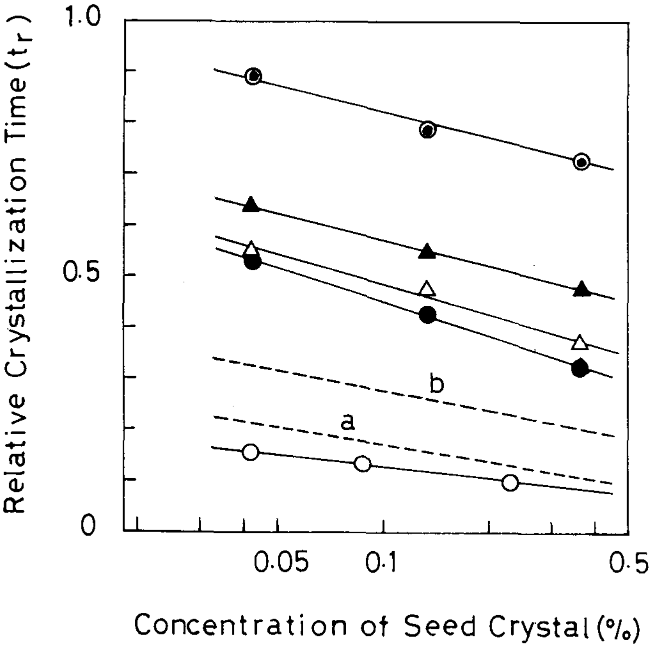

FIG. 4. Relationship between relative crystallization time (t_r) of cocoa butter at T_c = 30°C and the concentration of seed materials: (a) Cocoa Butter (Form VI), (b) Cocoa Butter (Form V), (○) SOS (β_1), (●) SOS (pseudo-β' + β_2), (△) BOB (β_2), (▲) BOB (pseudo-β'), (◉) SSS (β).

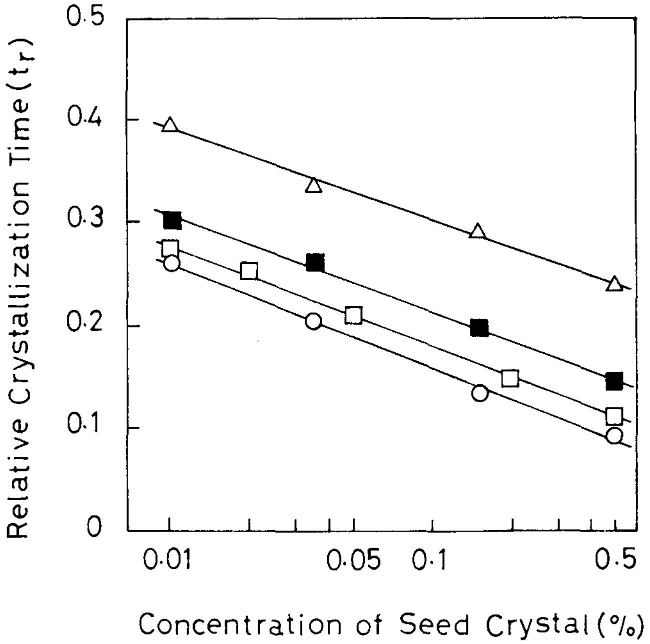

FIG. 5. Relationship between relative crystallization time (t_r) of dark chocolate at T_c = 30°C and the concentration of seed materials which was based on fat content of dark chocolate: (○) SOS (β_1), (□) Cocoa butter (Form VI), (■) Cocoa Butter (Form V), (△) BOB (β_2).

K is 0.044 and K_0 is 0.056. Secondly, it is evident that, for the same material, the more stable polymorph shortened the crystallization time more remarkably both in cocoa butter and dark chocolate. It seems surprising to conclude that SSS (β) did not accelerate the crystallization remarkably, despite the fact that its melting point is highest. Obviously, SOS (β_1) most accelerated the seeded crystallization.

DISCUSSION

All of the seed crystals remarkably enhanced the crystallization rate of cocoa butter and dark chocolate.

TABLE 2

Polymorphic Behavior of Forms II, III, IV, V, and VI of Cocoa Butter, Pseudo-β', β_2 and β_1 of SOS, Pseudo-β' and β_2 of BOB, and β of SSS

	Cocoa butter[a]					SOS[b]			BOB[c]		SSS[d]
	II	III	IV	V	VI	Pseudo-β'	β_2	β_1	Pseudo-β'	β_2	β
Long spacing (nm)	4.9	4.9	4.5	6.3	6.3	7.0	6.5	6.5	8.0	7.4	4.5
Chain length structure[e]	d	d	d	t	t	t	t	t	t	t	d
Subcell structure[f,g]	ni	ni	ni	$(\mathrm{T}_{/\!/})$	$(\mathrm{T}_{/\!/})$	$(\mathrm{T}_{/\!/},0_{\perp})$	$(\mathrm{T}_{/\!/})$	$(\mathrm{T}_{/\!/})$	$(\mathrm{T}_{/\!/},0_{\perp})$	$(\mathrm{T}_{/\!/})$	$\mathrm{T}_{/\!/}$
Melting point (°C)	23.3	25.5	27.3	33.8	36.3	36.5	41.0	43.0	50.5	53.0	73[h]

[a] Wille and Lutton (9).

[b] Sato *et al.* (28); the data based on 99.9% purity of SOS.

[c] Wang *et al.* (25); the data based on 71.5% purity of BOB.

[d] Small (36).

[e] d = Double chain length structure, t = triple chain length structure.

[f] ni = Not identified.

[g] In the triple chain length structure, the subcell structure of saturated and oleoyl lamella can be different. The existence of $\mathrm{T}_{/\!/}$ or $0_{\perp}$ examined by spectoscopic and XRD studies are indicated by a parenthesis (25,28).

[h] Hagemann (39).

The acceleration mechanism of crystallization by the seeding is essentially the same between cocoa butter and dark chocolate, because the major fat in dark chocolate is cocoa butter. The basic mechanism of the semi-exponential increase of the crystallization rate is ascribed to secondary nucleation (30). The secondary nuclei are the seed crystals added and many small crystal pieces which may be formed due to collision of crystal-crystal, crystal-agitation blades or due to shearing stress of the crystal-melt suspension caused by the agitation (33). The rate of secondary nucleation depends on the size, concentration and thermal stability of the secondary nuclei (34). The thermal stability is evaluated by solubility of the seed crystal in molten chocolate; the higher the solubility, the lower the stability of the nuclei, since the actual number of the crystal nuclei is reduced due to solubilization. In addition, the influences of polymorphism is also important. The interfacial steric hindrance at growing crystal surface may give rise to less effective influence in enhancing the rate of secondary nucleation, if the polymorphic structures between the seed and host molecules are largely different.

The results of Figures 4 and 5 show that the degree of acceleration of crystallization is in the following order, SOS (β_1) $\approx$ cocoa butter (Form VI) $\approx$ cocoa butter (Form V) $>$ SOS (pseudo-β' + β_2) $\approx$ BOB (β_2) $\approx$ BOB (pseudo-β') $\gg$ SSS (β). This order does not straightforwardly equal an order of melting points of the seed crystals, SSS (β) > BOB (β_2) > BOB (pseudo-β') > SOS (β_1) > SOS (pseudo-β' + β_2) > cocoa butter (Form VI) > cocoa butter (Form V). This clearly means that the melting point is not the most influential factor. Instead, the polymorphic relationship between the seed material and cocoa butter is the most influential.

The polymorphic structure and thermal stability of triacylglycerol is characterized by carbon number of the acyl chain, chain length structure, lateral chain packing and the melting point (35). All of these characteristics are summarized in Table 2. The seed materials of SOS and BOB are in the triple chain length structure in which the saturated acyl chain and oleoyl chain are packed in different layers due to a chain segregation. By contrast, β of SSS is of the double chain length (36). The lateral packing of β of SSS is triclinic parallel (36). In the case of pseudo-β', β_2 and β_1 in SOS and BOB, the packing structures are complicated due to the chain segregation. The XRD and Raman data indicate that the saturated acyl layers of pseudo-β' of BOB and SOS may be in orthorhombic perpendicular packing, whereas triclinic parallel packing may be revealed in β_2 and β_1 (25–28). In turn, the long spacing data of cocoa butter (9) showed that Forms V and VI are triple chain length. As to the lateral packing, we assume that the molecular structures of Forms V and VI correspond to β_2 and β_1 of SOS, respectively, since the XRD short spacing spectra and DSC melting behavior exhibited entire similarity (25–28). Furthermore, we assume that, according to the polymorphism of a mixture of POP/POS/SOS (38), Forms II, III and IV may correspond to γ and pseudo-β'.

The seed materials may be divided into three groups with respect to the degree of acceleration of the seeded crystallization (Fig. 4 and 5). The first group involves SOS (β_1), cocoa butter (Form V) and cocoa butter (Form VI). The second group involves SOS (pseudo-β' and β_2), BOB (β_2) and BOB (pseudo-β'); and the third group, SSS (β). This classification is reasonably justified in relation to the polymorphic structures.

SSS (β) is of double chain length structure involving no oleoyl lamella. This causes significant steric hindrance with the major triacylglycerol components of cocoa butter; POP, SOS and POS, and the acceleration effect is reduced. As to the second group, the two forms of BOB are packed in the triple chain length like cocoa butter, but they differ in the length of the saturated acyl chains by four or six. The difference in the acyl chain length over four carbons causes the instability of the interlamellar packing (39). This factor may reduce the acceleration effect of the two forms of BOB. In case of the mixture of pseudo-β' and β_2 of SOS, their molecular structures are similar to cocoa butter. However, the two forms are thermodynamically less stable than β_1 of SOS, being more soluble in the molten cocoa butter. It is worthy to note that the pseudo-β' forms both of SOS and BOB involve orthorhombic perpendicular packing in the saturated lamella (25,28). This packing may reduce the acceleration effects two-fold; it reduces thermodynamic stability in comparison to β_2 and β_1, and causes steric hindrance with regard to the lateral molecular packing between cocoa butter's Forms V and VI, which assume triclinic parallel packing in the saturated lamella. Finally, Forms V and VI of cocoa butter most accelerated the crystallization of cocoa butter itself as well as dark chocolate, since there is no structural dissimilarity. The fact that SOS (β_1) affected more than Forms V and VI may be attributed to the thermal stability.

To conclude, the crystallization kinetics of cocoa butter and dark chocolate was remarkably accelerated by the seeding of SOS, BOB and cocoa butter, the degree being highly dependent on the molecular and thermodynamic properties of the seed materials. To further elucidate, it is necessary to examine the seeding effect on physical properties of the end products, particularly on the fat bloom (Paper II describes this experiment). If both the crystallization rate and the fat blooming are simultaneously improved by the seeding procedure, the possibility of the utilization of the seeding technique will be actually raised in the factory scale production.

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