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FAT POLYMORPHISM AND CRYSTAL SEEDING EFFECTS ON FAT BLOOM STABILITY OF DARK CHOCOLATE

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Abstract

The effects of seeding with fine crystal powders on the physical properties of dark chocolate are reviewed in terms of the polymorphism and crystallization behavior of cocoa butter (CB) and of its major fat constituents. The polymorphic structure of four symmetric mixed acids saturated-oleic-saturated (Sat-O-Sat) triacylglycerols (TAGs) [POP (1,3-dipalmitoyl-2-oleoyl-glycerol); SOS (1,3-distearoyl-2-oleoyl-glycerol); AOA (1,3-diarachidoyl-2-oleoyl-glycerol); and BOB (1,3-dibenhenoyl-2-oleoyl-glycerol)], and of tristearoyl-glycerol (SSS) are briefly explained. An attempt is made at replacing the currently used tempering method in the chocolate solidification process, by a simple cooling technique using fat seed crystals. CB (form VI), SOS ($\beta_1$), BOB (pseudo-$\beta$), BOB ($\beta_2$), and SSS ($\beta$) are examined as seed materials. The addition of all powders accelerated the crystallization of dark chocolate. Fat bloom stability is also improved by the seed crystals, except with SSS. The effect is highly dependent on the physical properties of the seed material employed. The most influencing factors are the similarities in the polymorphic behavior between the seed material and cocoa butter, especially, chain length structure. Thermal stability of the seed crystal is also very important. In view of all physical properties examined, the present review concludes that the $\beta_2$ form of BOB performs best as a seed material. In particular, it gives rise to an accelerated crystallization of form V of CB and moderates change in viscosity and anti-bloom effects after thermal incubation of dark chocolate below and above the melting point of CB.

Introduction

Chocolate consists of solid particles such as cocoa, sugar, and milk solids which are dispersed in a continuous fat phase. In the case of dark chocolate, the milk solids are absent. The properties of chocolate are influenced by the size and distribution of the above solid particles, and by the crystallographic properties of the fat phase. In particular, fats influence heat-resistance, snap, gloss, quick and sharp melting in the mouth and bloom-resistance. Fat structures in chocolate have been investigated from various points of view (Huyghebaert and Hendrickx, 1971; Johnstone, 1972; Lovegren et al., 1976; Timms, 1980; Manning and Dimick, 1981; and Chaiseri and Dimick, 1989).

The major fat in chocolate is cocoa butter (CB). About eighty percent of CB is composed of specific triacylglycerols (TAGs) of a Sat-O-Sat (saturated-oleic-saturated) type, such as POP (1,3-dipalmitoyl-2-oleoyl-glycerol), POS (2-oleoyl-palmitoyl-stearoyl-glycerol), and SOS (1,3-distearoyl-2-oleoyl-glycerol). CB, as a mixture of POP, POS and SOS, is polymorphic, revealing six forms (Forms I through VI), as identified by Wille and Lutton (1966). The polymorphic form of CB in the end products is Form V, since this form has the most desirable melting and solidification behavior compared to other polymorphs. Form V is not the most stable polymorph, form VI is; therefore Form V transforms to Form VI either through a solid-state or a melt-mediated transformation (Chapman, 1971). This transformation to Form VI gives rise to undesirable physical properties of the end products. Particularly, it causes fat bloom (Aronhime and Garti, 1988). Similarly, the less stable forms, such as Form III or Form IV crystallize more rapidly than form V (Wille and Lutton, 1966). The occurrence and transformation of less stable forms to Form V also result in undesirable effects, such as a non-temper type fat bloom. Therefore, control of polymorphic crystallization of CB on a manufacturing scale requires very careful thermal treatments.

In current practice, the chocolate industry uses...
two methods to control crystallization: tempering and seeding. In tempering, the completely melted (50-60°C) chocolate is first cooled to 27-28°C, then reheated to 30-32°C, where the chocolate is held so that all of the metastable forms of CB transform to Form V. Thereafter, chocolate is simply cooled to around 15°C for the final solidification. The seeding method is aimed at simplification of chocolate solidification with the aid of seed crystal powders.

In this review, we present: (1) a historical review of the seeding technique applied in the chocolate solidification process, (2) the physical properties of the polymorphism of CB and its constituents, as well as some of the improved properties of the final chocolate produced by the new seeding technique, particularly fat bloom stability.

Historical Survey of the Seeding Techniques

The seeding method has so far been employed in small scale production, for example by local small candy makers or in small scale manufacturing trials. Small pieces of chocolate cut or shaved by knife have been employed as seed materials. Several fundamental studies have been devoted to analyze the seeding mechanism. Duck (1958) and Campbell and Keeney (1968) added chocolate powders to molten chocolate and measured the viscosity changes in an attempt to estimate the amount of seed crystal formed during the tempering process. Hettich (1966) studied the relationship between the anti-bloom stability and the degree of tempering by adding the CB seed powders during the tempering process.

None of these efforts, however, have been used in industrial chocolate manufacturing. This may be due to a lack of understanding of the complicated polymorphism of CB and its constituents, as well as the difficulties in producing, on a large scale, fine powders usable as seeding materials.

Polymorphic Crystallization of Four Sat-O-Sat TAGs and Cocoa Butter

In this section we discuss the polymorphism and melt crystallization of POP, SOS, AOA (1,3-diarachidoyl-2-oleoyl-glycerol), BOB (1,3-dibehenoyl-2-oleoyl-glycerol), and CB as well as SSS (tristearoyl-glycerol). These Sat-O-Sat TAGs exhibit essentially common polymorphic behavior which is closely related to seeding effects as described later.

Polymorphism

Literature on the polymorphism of Sat-O-Sat TAGs contains serious contradictions (see Sato et al., 1989, and references therein). This is mainly attributed to the uncertain purity of the samples. Wang et al. (1987) identified five basic polymorphs: alpha (α), gamma (γ), and three forms of beta (pseudo-β', β', and β1) in POP, SOS, AOA and BOB with X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Using the same methods, Sato et al. (1989) confirmed the occurrence of the five basic polymorphs of POP and SOS in pure (99.9%) samples. In POP, however, the polymorphism was slightly modified, since there are two pseudo-β forms. Arishima and Sato (1989) grew crystals of β2 and β1 from acetonitrile solutions, clearly proving the occurrence of two β forms. The differentiation of the two β forms is directly related to Form V and VI of CB. Guth et al. (1989) confirmed the existence of the five polymorphs in SOS, examining the effects of addition of sorbitan monoesterate on the crystallization of the SOS polymorphs.

The XRD patterns of the six polymorphs of POP are shown in Fig. 1. The XRD patterns of forms α, γ, β2 and β1 of POP are nearly identical to those of SOS, AOA and BOB. The two pseudo-β' forms differ from those of the other three TAGs. Melting points, XRD long spacing, and chain length structure of the four Sat-O-Sat TAGs are summarized in Table 1. From these observations we reach four conclusions:

1) The chain length structure differs in different polymorphic forms. The least stable α forms have double chain length structure in all TAGs. The two pseudo-β' forms of POP are also double. The rest of the polymorphs are in the triple chain length structure. As depicted in Fig.2, the saturated and oleoyl acyl chains are packed in the same lamellar pattern in the double chain length, but they are separated in the triple chain length polymorphs.

2) Melting points increase with increasing thermodynamic stability of the different polymorphs,
Fat Bloom Stability of Dark Chocolate

Table 1: Physical properties of polymorphs of Sat-O-Sat TAGs

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>TAG</th>
<th>Melting point (°C)</th>
<th>Long spacing (nm)</th>
<th>Chain length structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)</td>
<td>POP</td>
<td>15.2</td>
<td>4.65</td>
<td>double</td>
</tr>
<tr>
<td></td>
<td>SOS</td>
<td>23.5</td>
<td>4.83</td>
<td>double</td>
</tr>
<tr>
<td></td>
<td>AOA</td>
<td>31.5</td>
<td>5.52</td>
<td>double</td>
</tr>
<tr>
<td></td>
<td>BOB</td>
<td>41.5</td>
<td>5.61</td>
<td>double</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>POP</td>
<td>27.0</td>
<td>6.54</td>
<td>triple</td>
</tr>
<tr>
<td></td>
<td>SOS</td>
<td>35.4</td>
<td>7.05</td>
<td>triple</td>
</tr>
<tr>
<td></td>
<td>AOA</td>
<td>45.5</td>
<td>8.04</td>
<td>triple</td>
</tr>
<tr>
<td></td>
<td>BOB</td>
<td>49.5</td>
<td>8.41</td>
<td>triple</td>
</tr>
<tr>
<td>(\beta_2)</td>
<td>POP ((\beta_2))</td>
<td>30.3</td>
<td>4.24</td>
<td>double</td>
</tr>
<tr>
<td></td>
<td>POP ((\beta_1))</td>
<td>33.6</td>
<td>4.24</td>
<td>double</td>
</tr>
<tr>
<td>pseudo-(\beta)</td>
<td>SOS</td>
<td>36.5</td>
<td>7.00</td>
<td>triple</td>
</tr>
<tr>
<td></td>
<td>AOA</td>
<td>46.5</td>
<td>7.60</td>
<td>triple</td>
</tr>
<tr>
<td></td>
<td>BOB</td>
<td>50.5</td>
<td>8.03</td>
<td>triple</td>
</tr>
<tr>
<td>(\beta_1)</td>
<td>POP</td>
<td>36.7</td>
<td>6.10</td>
<td>triple</td>
</tr>
<tr>
<td></td>
<td>SOS</td>
<td>43.0</td>
<td>6.50</td>
<td>triple</td>
</tr>
<tr>
<td></td>
<td>AOA</td>
<td>46.6</td>
<td>7.07</td>
<td>triple</td>
</tr>
<tr>
<td></td>
<td>BOB</td>
<td>53.0</td>
<td>7.36</td>
<td>triple</td>
</tr>
</tbody>
</table>

POP has two pseudo-\(\beta\) forms.

and with increasing chain length of the saturated part of the molecule.

(3) There are two \(\beta\) forms in each TAGs, which differ in melting point as well as in their XRD short spacing patterns (Fig. 1). Note that \(\beta_2\) and \(\beta_1\) were also found in a mixture system of POP/SOS/SOS having a weight ratio of 18.2/47.8/34.0 (Sagi et al., 1989).

(4) The basic polymorphism in Sat-O-Sat TAGs is more complicated than that of SSS which has three double chain length polymorphs, \(\alpha\), \(\beta\) and \(\beta\) (Hagemann, 1988).

Compared with CB (Sato, 1987; Aronhime and Garti, 1988), Forms II, V and VI correspond to \(\alpha\), \(\beta_2\) and \(\beta_1\) of Sat-O-Sat TAGs, respectively. As for Forms III and IV, they seem to be equivalent to two pseudo-\(\beta\) forms of POP, as far as the XRD short spacing and the double chain length structure are concerned.

Melt crystallization of POP and SOS

Before explaining the crystallization of dark chocolate, we describe the rate of melt crystallization of POP and SOS, since those data are closely related to the polymorphic crystallization of CB. Pure (> 99.9%) POP and SOS were examined with a polarizing optical microscope equipped with a CdS photo sensor (Koyano et al., 1989). The sample was placed on a thermostated glass growth cell with the temperature controlled at a crystallization temperature \(T_c\). Optically anisotropic crystals, shown in Fig. 3, were found. Fig. 4 shows a typical output of the photo sensor in the melt-cooling of POP measured at two \(T_c\) values. The polymorphic form of each crystallized sample was determined by XRD and DSC, in an attempt to clarify the polymorph-dependence of the crystallization rate. From Fig. 4, it is clear that the induction time \(r\) is shorter in the crystallization of \(\gamma\) at \(T_c = 23.2°C\) than in the crystallization of pseudo-\(\beta\) at \(T_c = 26.3°C\). The difference in the crystallization rate is also reflected in the time dependence of the photo sensor output.

Two methods of crystallization are applied, simple cooling and melt mediation. The latter involves the crystallization of the more stable forms, which were induced after the melting of the less stable forms by rapidly raising the temperature. The tempering process may involve the melt-mediated transformation. The occurrence domains of the polymorphs of POP and SOS are summarized in Table 2. Combining the accurate measurement of the crystallization rate of each polymorph (Koyano et al., 1989) and the results in Table 2, the following conclusions can be drawn:
Table 2. Occurrence domains of polymorphs of POP and SOS from melt (melt-cooling and melt-mediated).

<table>
<thead>
<tr>
<th>POP</th>
<th>Tc (°C)</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
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<tr>
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</tr>
<tr>
<td>point</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt-</td>
<td>α</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cooling</td>
<td>γ</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>α-Melt-</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mediated</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Melt-</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mediated</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SOS</th>
<th>Tc (°C)</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting</td>
<td>α</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>point</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt-</td>
<td>α</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cooling</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Melt-</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mediated</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Melt-</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mediated</td>
<td>γ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3. Optical system for induction time measurement of melt crystallization. (Koyano et al., 1989).

Figure 4. Output of photo sensor in case of simple cooling of POP at Tc = 23.2 and 26.3 °C (Koyano et al., 1989). The crystallization rates differ for the two polymorphs.
Fat Bloom Stability of Dark Chocolate

(1) The less stable forms crystallize more easily than the more stable forms by the two crystallization modes.
(2) The rate is always higher in melt-mediated crystallization, than in simple cooling.
(3) The rate of \( \beta_2 \) crystallization is extremely low in both POP and SOS.

From this, we assume that the first rapid cooling may cause the preferable crystallization of the less stable forms of CB in the tempering process of chocolate. These forms may transform to Form V through melt-mediated crystallization by the subsequent reheating process. This is proved by careful analysis as described below.

Cocoa Butter Crystallization in Tempering process

Some arguments have been presented to estimate the amount of CB crystals formed after the tempering procedure, assuming the optimal amount of seed crystals to be added in the seeding techniques. Hettich (1966) reported that 0.1% of CB is crystallized and that this quantity is most suitable for bloom resistance. On the other hand, Campbell and Keeney (1968) concluded that the amount is 0.5%. We used a rotational viscometer (Hachiya et al., 1988b) to measure the viscosity of the sample. Varying amounts of the CB seed crystals of Form VI were added, and the viscosity was recorded to make a calibration curve between the CB crystal concentration and the viscosity change. We concluded that the amount of the seed crystals crystallized in the tempering process was 0.2%.

Kinetics of seed Crystallization of Dark chocolate

We discuss here the crystallization behavior of dark chocolate seeded with five fat crystal powders: CB (Form VI), SOS (\( \beta_1 \)), BOB (\( \beta_2 \)), BOB (pseudo-\( \beta \)) and SSS (\( \beta \)). All of the measurement were made with a rotational viscometer (Hachiya et al., 1989b).

Figure 5 shows the torque value of dark chocolate which was crystallized at \( T_c = 30^\circ C \) by cooling the melt from 50°C. The seed powders of SOS (\( \beta_1 \)), with the concentration of 0.035 and 0.5%, are added at 30°C. It is clear that the rate of crystallization increases with increasing amount of the SOS (\( \beta_1 \)) seed powders. In order to numerically express the rates of the seed induced crystallization in comparison to that of the non-seeded crystallization, we define the crystallization time (\( t_c \)) as the period when the torque increase (mV) due to crystallization reaches 3 mV.

Figure 6 shows the crystallization rate of dark chocolate seeded with five fat powders. The relative crystallization time (\( t_i \)) is defined as: \( t_i = t_c \) (seeded) / \( t_c \) (non-seeded). The results show that the degree of acceleration goes in the following order: SOS (\( \beta_1 \)) = CB (Form VI) > BOB (\( \beta_2 \)) > BOB (pseudo-\( \beta \)) > SSS (\( \beta \)).

From this, it appears that two major factors,
Table 3. Demolding and fat bloom occurrence of seeded dark chocolate just after cooling at 15°C for 15 minutes.

<table>
<thead>
<tr>
<th>Amount of crystal Powder in percent*</th>
<th>Cocoa Butter (Form VI)</th>
<th>SOS (β₁)</th>
<th>BOB (β₂)</th>
<th>BOB (pseudo-β*)</th>
<th>SSS (β)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Demolding</td>
<td>Fat bloom</td>
<td>Demolding</td>
<td>Fat bloom</td>
<td>Demolding</td>
</tr>
<tr>
<td>0.001</td>
<td>good</td>
<td>slight</td>
<td>good</td>
<td>slight</td>
<td>bad</td>
</tr>
<tr>
<td>0.005</td>
<td>good</td>
<td>slight</td>
<td>good</td>
<td>slight</td>
<td>good</td>
</tr>
<tr>
<td>0.01</td>
<td>good</td>
<td>no</td>
<td>good</td>
<td>no</td>
<td>good</td>
</tr>
<tr>
<td>0.05</td>
<td>good</td>
<td>no</td>
<td>good</td>
<td>no</td>
<td>good</td>
</tr>
<tr>
<td>0.1</td>
<td>good</td>
<td>no</td>
<td>good</td>
<td>no</td>
<td>good</td>
</tr>
<tr>
<td>0.5</td>
<td>good</td>
<td>no</td>
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</tr>
<tr>
<td>1.0</td>
<td>good</td>
<td>no</td>
<td>good</td>
<td>no</td>
<td>good</td>
</tr>
<tr>
<td>2.5</td>
<td>good</td>
<td>no</td>
<td>good</td>
<td>no</td>
<td>good</td>
</tr>
<tr>
<td>5.0</td>
<td>good</td>
<td>no</td>
<td>good</td>
<td>no</td>
<td>good</td>
</tr>
</tbody>
</table>

*Amount with respect to fat content of dark chocolate.

Figure 6. Relationship between relative crystallization time of cocoa butter and concentration of seed materials at \( T_c = 30°C \): (●) cocoa butter (Form VI); (□) SOS (β₁); (▲) BOB (β₂); (▲) BOB (pseudo-β*); (□) SSS (β) (Hachiya et al., 1989a).

Concentration of Seed Crystal (%)

polymorphic structure and thermal stability, influence the crystallization acceleration in a combined manner (Hachiya et al., 1989a). As to the thermal stability it follows that the degree of acceleration increases with melting point. This factor becomes clear when one compares the two forms of BOB to each other, and SOS (β₁) with CB Form VI. However, this does not apply to SSS (β) whose melting point is highest, nor to SOS (β₁) and CB (Form VI) whose melting points are lower than those of the two forms of BOB. Hence the similarity in the polymorphic structure between the seed crystal and CB seems more determinative. No argument may be needed for SOS (β₁) and CB (Form VI). As to the two forms of BOB, their melting points (Table 1) are far below that of SSS (73°C; Hagemann, 1988). But the molecular structures, particularly the triple chain length structure, of both forms of BOB are similar to those of CB. The lower acceleration effect of BOB compared to SOS and CB may be due to a difference in the chain length of the saturated portion of the molecules. The importance of the chain length structure is seen in the extremely low acceleration effect of SSS which is of the double chain which quite differs from the triple chain length of Form V of CB.

Consequently, it was concluded that seed crystallization of dark chocolate is highly dependent on the polymorphic properties of the seed materials. The most preferable seed material, in view of the crystallization rates are CB (Form VI), SOS (β₁) and BOB (β₂).

Seeded Solidification Behavior of Dark Chocolate

Table 3 summarizes the degree of demolding and the occurrence of fat bloom of seed-solidified dark chocolate, examined just after the solidification. The dark chocolate seeded at 30°C is directly cooled at 15°C. The results are summarized as follows; CB (Form VI) and SOS (β₁) show easy demolding and no fat bloom at seed concentrations above 0.01%. By contrast, undesirable properties were observed for BOB (pseudo-β*) and SSS (β). From this observation,
we conclude that CB (Form VI) and SOS (β₁) are most suitable; to a lower extent BOB (β₂) also showed good results at the level of 0.01%.

**Anti-bloom Effects by Seeding**

The effects of the fat crystal seeding on blooming of dark chocolate were examined using the seeds of CB (Form VI), SOS (β₁) and BOB (β₂) (Hachiya et al., 1989b). Two thermo-cycle tests were applied. In the 32/20 test, one cycle involves incubation of the sample at 20°C and 32°C for 12 hours each. In the 38/20 test, the chocolate was kept at 38°C for 12 hours where the chocolate was completely melted, and 20°C for 12 hours.

The results are shown in Tables 4A and B. In all of the seed materials employed, bloom stability was confirmed at seed concentrations between 0.05% and 1%, being highly dependent on the seed materials. CB (Form VI) and SOS (β₁) show quite similar behavior, summarized as follows:

1. In the 32/20 test, fat bloom does not occur at seed concentrations of 0.05 through 1% below 4 cycles. However, fat bloom occurs at concentrations of 2.5 and 5%. The decrease is manifest at higher concentrations, in which the fat bloom occurs through one cycle.

2. In the case of the 38/20 cycle test, fat bloom occurs at all seed concentrations.

In contrast, seeding with BOB (β₂) gives rise to
significant stability against fat bloom through the 32/20 and 38/20 cycle tests, when the seed concentration is increased. In particular, the sample seeded at concentrations of 1, 2.5, and 5% does not produce fat bloom even through six cycles in the 32/20 test. In the case of the 38/20 test, the fat bloom is observed at low seed concentrations, but the seeding of 5% completely prevents fat bloom at one cycle (Fig. 7).

From these observations of the anti-bloom effects combined with the earlier results of crystallization kinetics, we conclude that the BOB (β₂) seeding shows two advantageous effects in the crystallization and transformation of the chocolate fats: the acceleration of the crystallization of Form V of CB, and the anti-bloom stability in temperature ranges below and above the melting point of CB.

Application of BOB Seeding Techniques in Factory-Scale Chocolate Production

In this section, we review several aspects related to the application of the BOB seeding technique on the factory scale.

**Solidification Process**

No tempering machine is required in the seeding technique. Instead, the molten chocolate is cooled to 15°C in two steps. First, it is cooled to 33°C where seed is added. When the seed is added below 33°C, “over seeding” occurs, causing too enhanced crystallization. Then the seeded chocolate is cooled to 15°C. By controlling the amount of seed crystal, one may handle the chocolate solidification by simpler temperature control compared to the traditional tempering method.

**Viscosity Change After Seeding**

Viscosity of the chocolate during the solidification process is critically important for workability, which is greatly influenced by crystallization.

The traditional tempering method involves first cooling of the melt around 27°C, followed by heating around 30°C, and then the second cooling at 15°C. The crystallization during the first cooling is influenced by spontaneous nucleation of cocoa butter crystals. The induction time for nucleation scatters a lot and the occurrence of specific polymorphic modification is a result of competition of the rates of nucleation of different polymorphs. This uncertainty is particularly revealed in Form V of CB. Hence, its crystallization is attained by the transformation from the less stable Forms III and IV which crystalized during the first cooling. Accordingly, one has to be very careful with the cooling-heating-cooling steps in the tempering process.

In the seeding technique, however, the crystallization process is fairly controllable. This is demonstrated in the viscosity of seed-crystallized chocolate. Figure 8 compares the viscosity changes of dark chocolate made by the normal tempering and by the BOB (β₂) seeding. Viscosity of the tempered chocolate begins to increase immediately after the completion of tempering. However, viscosity of the BOB (β₂) seeded chocolate gradually increase after an induction period of about 50 minutes. This is a clear advantage for the chocolate manufacturer because it permits easier plant operation.

**Solubility of BOB (β₂) Crystals in Cocoa Butter**

Solubilization of BOB (β₂) seed crystals in molten CB, being highly temperature dependent, diminishes the seeding effect. Figure 9 shows the solubility of BOB (β₂) and BOB (pseudo-β') crystals in molten CB (Mori, 1989). This shows that a portion of BOB (β₂), when added at 5%, remains undissolved at 38°C. This result helps explain the anti-bloom effect in the 38/20 test (Table 4B).

**Mouth Feel of Chocolate Seeded with BOB (β₂)**

There is no difference in the feel of the chocolate in the mouth when BOB (β₂) seed powders are used because, as shown in Fig. 10, their dimensions do not exceed 70 μm, almost same as that for the other solid particles (cocoa mass, sugar, milk solids) in chocolate as shown by Hachiya et al. (1988a).

**Production of BOB (β₂) Seed Powders**

BOB is presently produced from fatty acid esters containing behenic acid and high oleic oils by trans-esterification using an enzyme catalyst (Mori, 1989). The reactant is fractionated and concentrated. The enzyme esterified BOB is transformed to the polymorphic form β₂ by incubation. The fine powders of BOB (β₂) are produced with a cryo-mill (Fuji Powder: Atomizer EI-75) which can pulverize at -60°C~100°C using liquid nitrogen (Hachiya et al., 1989c). The particle sizes are 20 ~ 70 μm; no change in melting point was detected in powder samples.

The seeding method with BOB (β₂) fine powder (patented with US Patent 4,877,636 (1989); European Patent 87309981.6, and Japanese Patent 63-240745) has now been in use in chocolate production plants of Japan.

**Acknowledgements**

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**References**


Fat Bloom Stability of Dark Chocolate

Figure 7. Photograph showing (a) bloomed chocolate (normally tempered) at left; and (b) non-bloomed chocolate (BOB $\beta_2$ seeded) at right; after thermocycle test of 38/20 for 3 cycles.

Figure 8. Viscosity changes in normally tempered chocolate and BOB $\beta_2$ seeded chocolate at 30°C.

Figure 9. Solubility curve of BOB crystal in cocoa butter (●) BOB (pseudo-$\beta$); (○) BOB ($\beta_2$) (Mori, 1989).

Figure 10. Cryo-scanning electron micrograph, taken at -100°C~ -130°C of BOB $\beta_2$ powders pulverized at -60°C~ -100°C.


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Discussion with Reviewers

J. Chevalley: BOB is not legally allowed in Europe and is not permitted in chocolate under current U.S. standards. Please comment on the legal aspects of BOB.

Authors: Only Japan allows to add BOB seeds, all of the other countries do not. Meiji and Fuji Oil are now requesting the approval of the Food and Drug Administration in the United States and similar agencies in other countries. Fat bloom is fascinatingly improved with BOB seed, as Meiji has observed in the market.