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ORIGINAL PAPER

Bloom Formation on Poorly-Tempered Chocolate and Effects of Seed Addition

Yasuyoshi Kinta · Richard W. Hartel

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Abstract Bloom on chocolate with different levels of cocoa butter seed addition was investigated. When insufficient cocoa butter seed crystals were added to give proper temper, the chocolate developed bloom as dark brown spheres in lighter color areas, similar to that seen in bloom on untempered chocolate. These dark colored spheres overlapped and the lighter color areas disappeared with increasing seed amount added. The relationship between seed amount and lighter color area (bloom), as quantified by image analysis, showed that over 270 ppm seeds (fat basis) were needed to accomplish good tempering. The cocoa butter crystallization behavior with various amounts of seed was observed by light microscopy. Too few seeds caused sparse β crystallization and massive β' crystallization, which explains the appearance of poorly tempered chocolate bloom. As seed amount increased, β crystallization of cocoa butter took less time to reach the upper level of solid fat content and the size became smaller. In addition, DSC analysis was carried out to study crystallization and melting behavior of cocoa butter with different seed amounts. Higher levels of added seeds resulted in greater amounts of β crystal formation and the crystallization temperature increased, which meant crystallization occurred earlier. These results showed that the mechanism of bloom formation on poorly tempered chocolate (insufficient seeds) is due to sufficient time and space for phase (particles and fat) separation as the stable polymorphs grow.

Keywords Chocolate · Cocoa butter crystallization · Fat bloom · Tempering · Seeds · Microscopy · DSC

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Y. Kinta
Research Institute, Morinaga & Co., Ltd, 2-1-1 Shimosueyoshi, Tsurumi-ku, Yokohama, Kanagawa 230-8504, Japan

R. W. Hartel (✉)
University of Wisconsin, Madison, WI, USA
e-mail: rwhartel@wisc.edu; pokentoby@gmail.com

Introduction

Fat bloom formation on chocolate remains a continuing problem for the chocolate industry despite a number of detailed studies. Bloom can take numerous forms depending on the type of finished chocolate product, the processing conditions by which it is made and subsequent storage conditions [1–4]. For example, even well-tempered chocolate can bloom if there is migration of an incompatible oil within a coated piece or if the temperature of storage is elevated and cycled. This variety in causes and consequences leads to continued confusion regarding bloom phenomena.

Recently two new forms of visual fat bloom have been reported. One develops when the fat content is unevenly distributed, and the portions with a lower fat content become light colored, essentially composed of sugar and cocoa solids [5–7]. This type of bloom occurs when no seed crystals are formed; for example, when solidification occurs without a tempering process. The other form of bloom also shows similar light color but results from the roughness and/or porosity of the microstructure that is caused by the coarsened fat crystal network and of the liquid fat migration [8]. These two types of bloom contradict the common understanding that visual fat bloom is a consequence of separation of cocoa butter crystals at the surface of the chocolate [9–13]. With these recent observations, clearly much remains to be learned about fat bloom in chocolate.

The aim of this work was to investigate a type of visual fat bloom on poorly tempered chocolate. This type of bloom, seen in Fig. 1, is considered to be similar to the bloom without tempering but the two differ in that the former develops just after cooling, whereas the latter needs several days to develop. By using solid dark chocolate containing cocoa butter, differences in bloom formation and composition with various seed quantities were studied. In addition, cocoa butter crystallization behavior with different levels of seed addition was investigated using a polarized light microscope and differential scanning calorimeter to better understand the mechanism of bloom formation.

Experimental Procedures

Chocolate Preparation and Bloom Development

Chocolate containing 36.4% cocoa butter was prepared with refining by a roll refiner and conching from sugar (42%), cocoa mass (48%), cocoa butter (10%) and lecithin (0.5%). A solid chocolate sample was prepared with tempering using cocoa butter seeds on a marble slab. The tempering procedure with seeds was as follows: a bowl of chocolate melted at 60 °C was cooled to 30 °C, and cocoa butter seeds (Mycryo, Barry Callebaut, Belgium) were added into the bowl and mixed thoroughly using a silicone spatula. Based on DSC analysis, these seeds were primarily β V polymorph, with a small amount of β VI polymorph (results not shown). Cocoa butter seed quantities used were 2 ppm in chocolate (5.5 ppm in fat), 10 ppm (27), 100 ppm (270) and 500 ppm (1,370). For comparison purposes, chocolate was tempered on a marble slab as follows: a bowl of chocolate melted at 60 °C was cooled to about 40 °C, and two-thirds of this chocolate was turned over on a marble slab with a scraper until the chocolate was cooled to about 28 °C. The chocolate was added back into the bowl and mixed thoroughly using a silicone spatula. The final temperature of the well-tempered chocolate was then about 30 °C.

Fig. 1 Bloom formation on poorly tempered chocolate

For solidification, the liquid chocolates (untempered, tempered and with various levels of seed addition) at 30 °C were poured into polycarbonate molds and cooled to 10 °C for 30 min. The samples were removed from the molds after cooling and subjected to further analyses. Three different chocolate samples seeded at each addition level and tempered on the marble slab were prepared.

Bloom Quantification Using a Stereo Microscope

The molded surface of the chocolate sample was observed with a stereo microscope (Nikon SFZ.-10, Japan) and digital images taken with a Nikon camera (Digital Sight DS-SM, Japan) 3 days after preparation. Ten different digital stereomicroscope images taken randomly from three different chocolate samples were subjected to light color area calculation [14]. Image processing software (Optimas 6.0) was used to determine the light colored area (total area of a 4.7-mm square) of each chocolate. The means and standard deviations of ten replicates were calculated.

Analysis by Fourier-Transform Infrared Spectroscopy

To determine composition, dark- and light-brown parts of bloomed chocolate samples with 5.5 ppm seeds were carefully withdrawn using a needle and a stereo microscope. Each color part was smeared on a KBr thin plate for Fourier-Transform Infrared (FT-IR) Spectroscopy analysis. Transmittance spectra were acquired on an FT/IR-660Plus + IRT-30 (JASCO, Tokyo, Japan) spectrometer attached to a microscope, using the transmittance mode. The measurement area was 50 µm square for the dark- and light-brown parts of the bloomed chocolate sample. Scans were accumulated between 650 and 4,000 cm^{-1} with a 4 cm^{-1} resolution using a mercury cadmium telluride (MCT) detector. Three different samples of each color part were used for the measurement.

Observation of Cocoa Butter Crystallization Using a Polarized Light Microscope

To better understand the effects of seed crystals, cocoa butter crystallization was observed with different cocoa butter seed quantities and a single grain of cocoa butter seed using a polarized light microscope (Nikon LABOPHOT-2, Garden City, NY) equipped with a glass-made temperature control stage with thermostatted water. Cocoa butter (Mycryo, Barry Callebaut, Belgium) melted at 60 °C was cooled to 30 °C, and cocoa butter seeds (Mycryo, Barry Callebaut, Belgium) were added and mixed thoroughly. This slurry was spread on a glass slide set on a temperature control unit kept at 30 °C with circulating coolant. Cocoa butter crystallization was observed with cooling thermostatted water under two different conditions. The first condition involved cooling from 30 to 10 °C at 0.25 °C/min, and then heating to 40 °C at 0.55 °C/min in order to judge the crystal form. Cocoa butter seed quantities used were 0, 5.5, 270 and 1,370 ppm in fat. In addition, a single grain of cocoa butter was used as seed under this cooling condition. In this case, cocoa butter cooled to 30 °C was spread on a slide glass at 30 °C and a single grain of cocoa butter seed that was carefully withdrawn using a needle and a stereomicroscope was put onto it. The second condition involved cooling from 30 to 23 °C at 0.25 °C/min., and then holding isothermally at 23 °C. Cocoa butter seed quantities used were 5.5, 270 and 1,370 ppm in fat. In all cases, photographs were taken every minute in cooling and heating with a camera (Olympus Corp., Woodbury, NY) attached to the microscope.

Differential Scanning Calorimeter Analysis of Cocoa Butter Crystallization and Melting

Crystallization profile of cocoa butter with different cocoa butter seed quantities were measured using a Perkin Elmer (Norwalk, CT), Pyris 7, differential scanning calorimeter (DSC) monitored with Pyris software. The instrument was calibrated with indium and mercury to ensure accuracy of temperature readings and with indium to ensure accuracy of caloric data. Melted cocoa butter was cooled, and cocoa butter seeds were added and mixed thoroughly as described above. Cocoa butter seed quantities used were 0, 5.5, 270, 1,370 and 13,700 ppm in fat. About 5 mg of this slurry was put in an aluminum DSC pan. Dynamic crystallization was performed within the DSC from 30 to 10 °C at the rate of 0.25 °C/min, and then the measurement continued with heating at 5 °C/min in order to judge the crystal form from the melting profile. The measurement with each cocoa butter seed quantity was repeated at least three times and the means and standard deviations of crystallization and melting temperature were calculated.

Results

Bloom Progression

Figure 2 shows the appearance of poorly tempered chocolate bloom with different levels of seed addition. Dark brown circles surrounded by white spots were observed in the bloom with 5.5 ppm seeds. This appearance is similar to what develops on chocolate without tempering, where the white spots were found to be depleted in fat [5, 6]. Some circles can be also seen on the surface of chocolate made with 27 ppm seeds, suggesting that with increasing seed numbers, these circles overlapped each other and the light colored area was reduced. With even higher seed levels, the light-colored areas disappear to give a uniformly dark-colored chocolate surface, characteristics of well-tempered chocolate.

FT-IR analysis of dark- and light-brown parts of the bloomed chocolate sample (5.5 ppm seeds) verified that the fat content in the light-colored part was lower than that in the dark-brown part. This is seen in Fig. 3 as a decreased absorbance at 1,750 and 2,900 cm^{-1}, which correspond to a C and O double bond of an ester and a C and H single bond, respectively. It seems that the white spots observed on chocolates with too few seeds is the same bloom type as appears on chocolate without tempering. The light-colored, whitish spots are nearly depleted of fat while the dark brown spots contain the fat content expected of intact chocolate [5, 6].

The relationship between the quantity of seeds added and the quantitatively determined white surface area is shown in Fig. 4. The white surface area is a measure of bloom on these chocolates, with well-tempered chocolate (also seen in Fig. 4) essentially devoid of light-colored spots. The critical amount of seeds necessary to give a surface appearance equivalent to well-tempered chocolate is over 270 ppm. At 270 ppm, sufficient white area is still observed such that this chocolate is considered lightly bloomed (Fig. 2).

Cocoa Butter Crystallization by Polarized Light Microscopy

Cocoa butter crystallization during cooling of cocoa butter with various level of seed addition was studied by polarized light microscopy. In the first set, the cocoa butter was cooled from 30 to 10 °C at 0.25 °C/min with images taken periodically to document the progression of cocoa butter crystallization. Seed levels varied from 0 to 1,370 ppm. Crystallization around one large seed crystal was also studied.

Figure 5 shows a sequence of images when cocoa butter was cooled without seed addition. Nucleation occurred at about 23 °C with numerous small crystals forming and growing as temperature was reduced to 10 °C. When this sample was heated back to 30 °C, all of the crystals had melted, indicating that nucleation was completely in the β' polymorph (melting point <30 °C) [15, 16].

When a single large β seed crystal was added to the liquid cocoa butter at 30 °C and cooled, a similar behavior

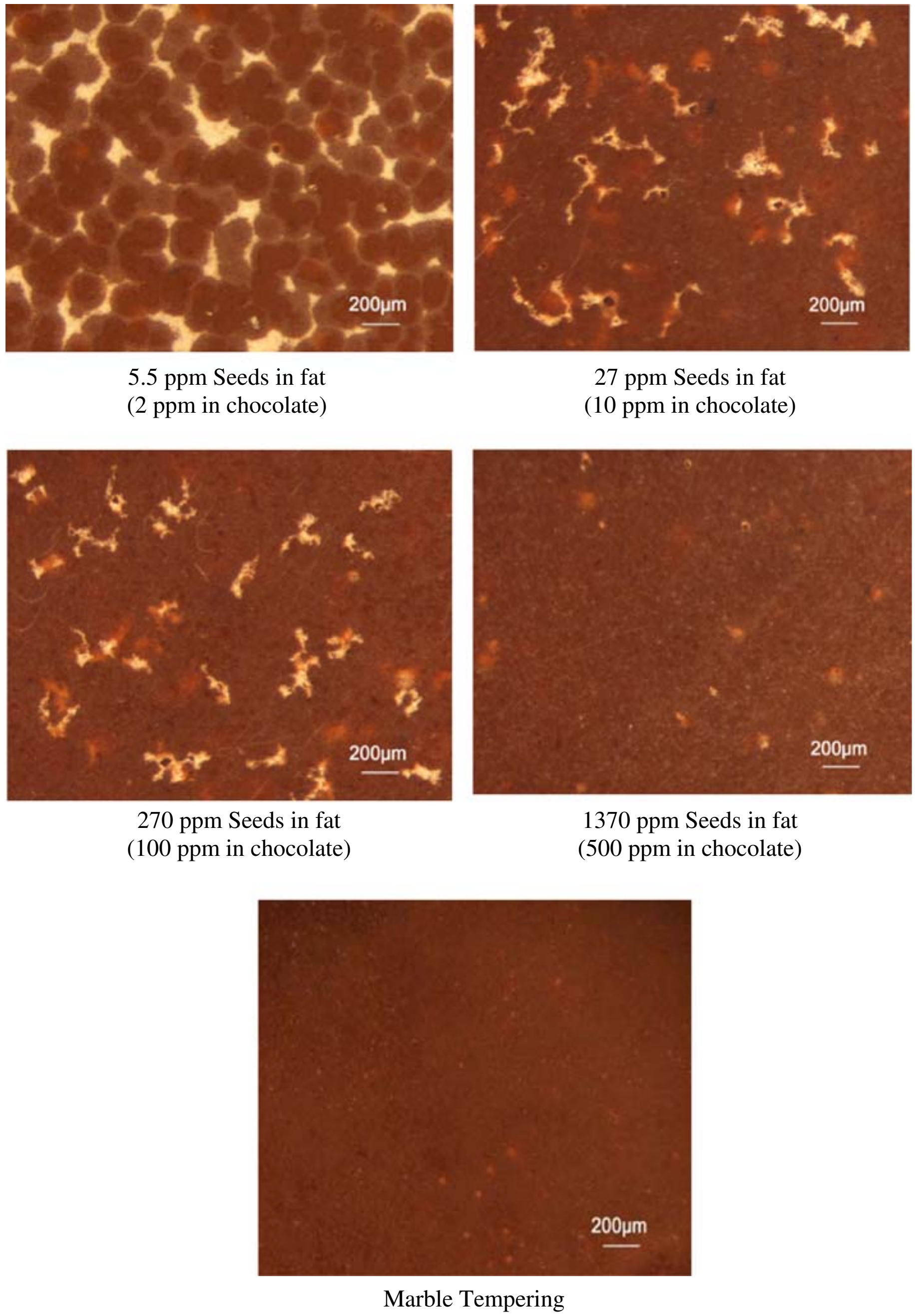

Fig. 2 Stereo microscopic images of the surface of chocolates made with different levels of seed addition, compared with well-tempered (marble) chocolate after 3 days of holding at room temperature

was observed (Fig. 6). As temperature was lowered, the β seed crystal grew, but at about 24 °C, the bulk of the cocoa butter nucleated in numerous small crystals. At 10 °C, the β seed crystal, with a central core and outer corona, had grown in size, but was surrounded by numerous small crystals. Upon heating, the small crystals surrounding the seed had disappeared by the time temperature had reached 30 °C. The nuclei that formed were once again the unstable β' polymorph; the β seed crystal had no effect on nucleation of the surrounding liquid cocoa butter upon cooling.

Cocoa butter crystallization with 5.5 ppm seed level addition is shown in Fig. 7. The large seed crystals were dispersed well so that no seeds were initially visible at 30 °C. When cooled, the liquid cocoa butter nucleated again at about 23–24 °C into the small crystals observed in the previous images. However, growth of larger crystals was also observed as cooling continued. At 10 °C, a mix of the smaller, lighter colored crystals and larger, browner crystals was observed. Upon melting, the small crystals were melted by 30 °C, whereas the larger crystals continued to grow after the smaller ones had melted. In this case, the seeds, which were stable β crystals, grew out as the smaller unstable β' crystals melted. Again in this case, the addition of the seed crystals had no apparent effect on

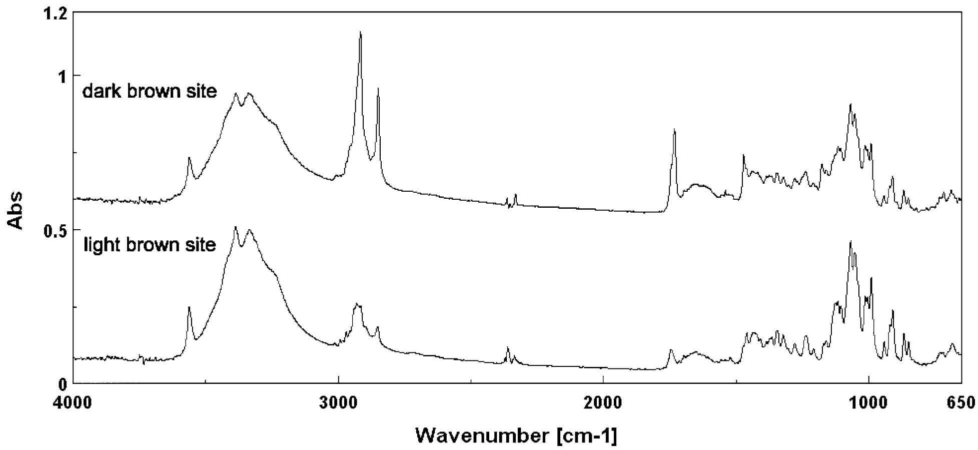

Fig. 3 Infrared spectral analysis of the different regions of a chocolate surface made with insufficient seeds

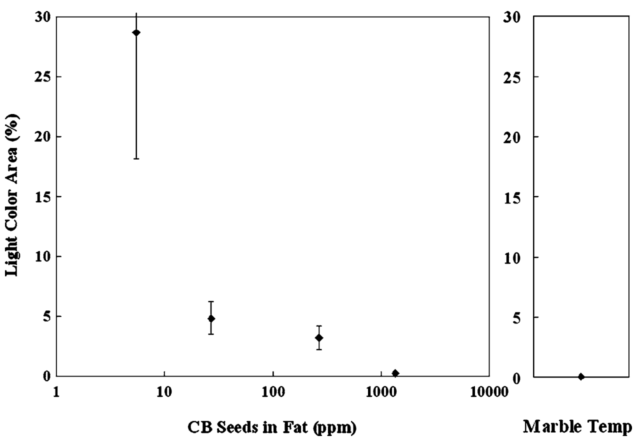

Fig. 4 Bloom on chocolates with different seed addition level as quantified by image analysis of white area

nucleation and growth of the unstable polymorphic crystals during cooling.

Not surprisingly, as the seed addition level increased to 270 ppm and 1,370 ppm, the relative ratio of cocoa butter mass in the β and β' forms changed with more stable polymorphs appearing with increasing seed addition level. At 1,370 ppm seed addition, a level that was seen to be nearly equivalent to well-tempered chocolate (Fig. 4), almost all of the cocoa butter had crystallized into the stable β polymorph. However, during cooling, formation of unstable β' polymorphs was still observed.

This effect was observed more clearly when the samples were cooled only to 23 °C and held for a period of time to follow crystallization. This condition allowed unstable β' crystallization to tkake place in addition to growth of the stable seed crystals. Figure 8 shows the

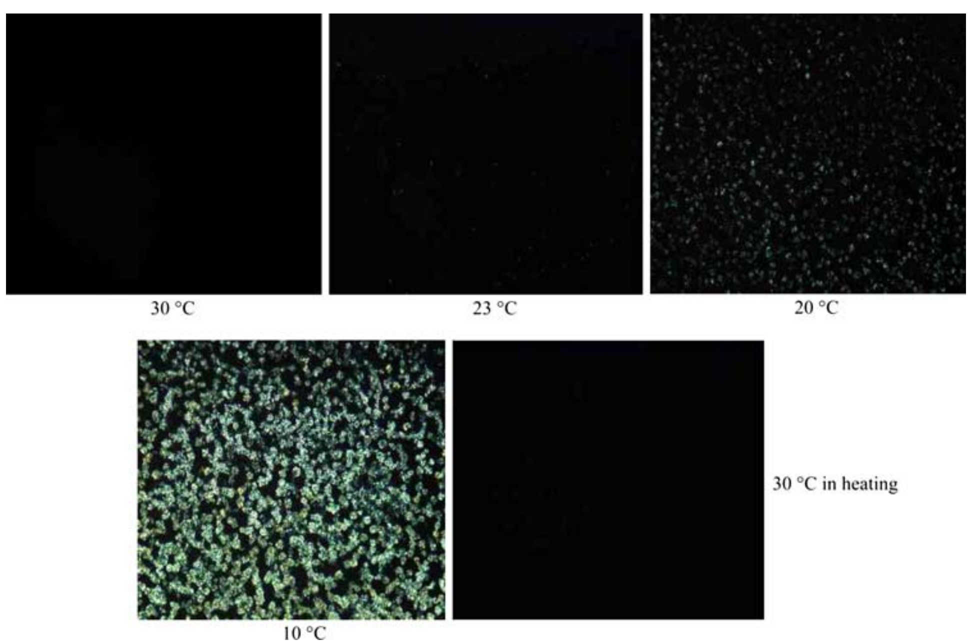

Fig. 5 Cocoa butter crystallization during cooling, without seed addition, from 30 to 10 °C on a polarized light microscope

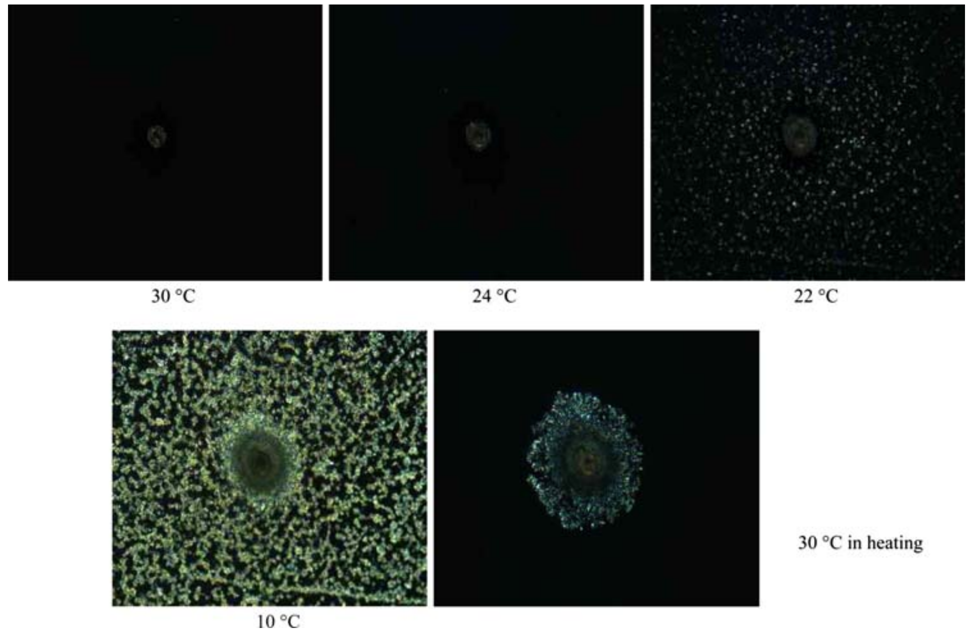

Fig. 6 Cocoa butter crystallization during cooling, with a single large β seed crystal, from 30 to 10 °C on a polarized light microscope

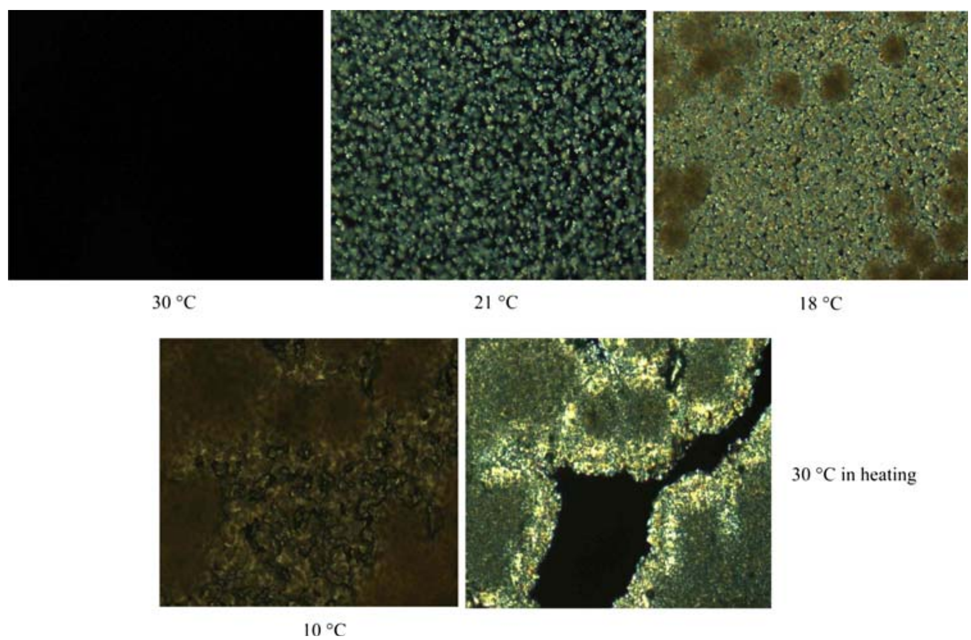

Fig. 7 Cocoa butter crystallization during cooling, with 5.5 ppm seed addition, from 30 to 10 °C on a polarized light microscope

effects of seed addition level on cocoa butter crystallization. In all cases, the appearance of unstable β' nuclei was observed at 23 °C, but the extent of stable β seed growth increased with increasing seed addition levels. As the seed level increased, the size of the stable β seed crystals decreased. Furthermore, the time required for development of the stable β seeds decreased with increasing seed level.

In Fig. 2, the size of the dark brown spots decreased with an increasing addition level of seed crystals, in much the same way as the size of the stable cocoa butter seeds decreased in size with increasing seed level in Fig. 8. This similarity is highly suggestive; perhaps the light brown spots of bloom in Fig. 2 are regions between where the cocoa butter seed crystals have grown out. When higher numbers of stable seed crystals are present in the initial chocolate, there is less space for phase separation between cocoa butter and chocolate particulates (sugar crystals and cocoa solids). An adequate number of seeds for tempered chocolate may then be defined as the number of seeds needed to completely fill in the chocolate mass when grown.

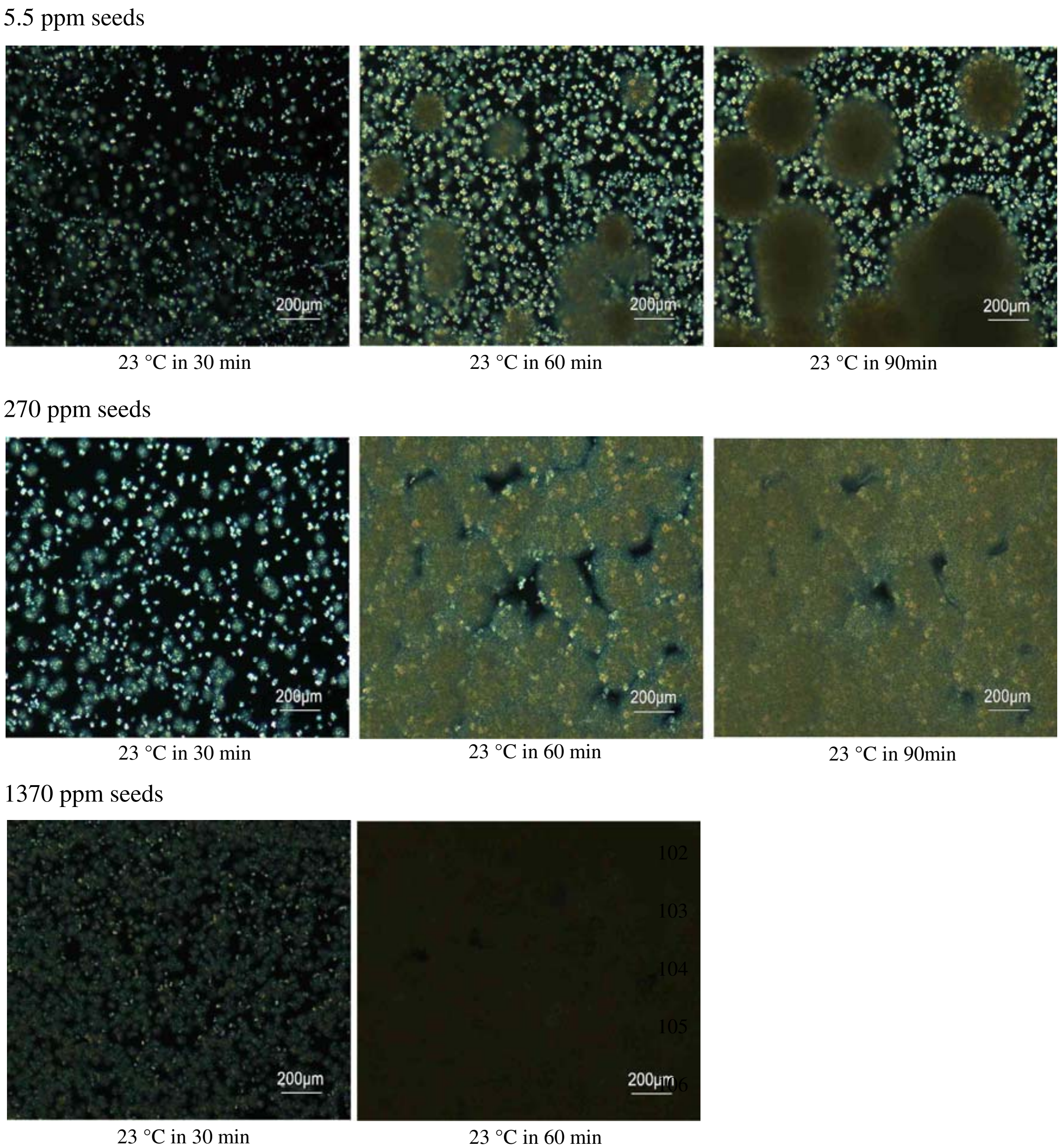

Fig. 8 Cocoa butter crystallization with varying seed level addition from 30 to 23 °C on a polarized light microscope

Calorimetry

To better elucidate the formation of stable and unstable crystals with different seeding levels, differential scanning calorimetry (DSC) was carried out on cocoa butter with different seed additions. Figure 9 shows characteristic DSC thermograms for cocoa butter crystallization with different seed addition levels, from 0 to 13,700 ppm. Without seed addition, only unstable β' crystallization was observed, in agreement with the results of polarized light microscopy. As the seed level increased, an increasing extent of crystallization occurred in the stable β polymorph, also in agreement with microscopy results. As seed level increased, the time required for stable β crystal growth decreased, meaning that less unstable nucleation occurred. The increased time for stable crystal formation when insufficient stable seeds were present is what leads to the phase separation and bloom formation in under-tempered chocolate. The change in peak temperatures, associated with the different polymorphs, with seed addition level is shown in Fig. 10. The small peaks detected around 35 °C in the heating profiles (Fig. 9) with 13,700 and 1,370 ppm seeds correspond to the small population of βVI polymorph in the seeds [15, 16].

Discussion

The mechanisms by which seed crystals in tempered chocolate promote crystallization of the rest of the cocoa butter into the stable polymorphic form has never been clearly stated. In this work, the effects of different levels of seed addition on cocoa butter crystallization were studied to better understand the solidification process and the onset of bloom in poorly-tempered chocolate.

Bloom on the surface of poorly-tempered chocolate appears as round spots of dark brown color amidst a background of whitish areas. Compositional analysis shows that the white areas are depleted in fat, as found in previous studies on untempered chocolate. With increasing seed addition, the number of dark brown circles increases, their size decreases and their overlap minimizes the white areas depleted in fat. When an adequate number of seeds is added to properly temper the chocolate, no white areas appear and the surface is completely brown.

Some interesting analogies to bloom appearance were observed when seeded cocoa butter was crystallized on a polarized light microscope. At low seed addition levels, equivalent to poorly-tempered chocolate, circular β crystals were observed to grow from the seeds as the system was cooled, although substantial nucleation of unstable β' crystals formed in the bulk of the cocoa butter. With an increase in the number of seeds added, the number of circular β crystals increased, their size decreased, and the time required for them to grow decreased. When the seed addition level was equivalent to that needed for well-tempered chocolate, the small circular cocoa butter crystals quickly overlapped to form a continuous surface of stable cocoa butter crystals, in much the same way as the surface of well-tempered chocolate.

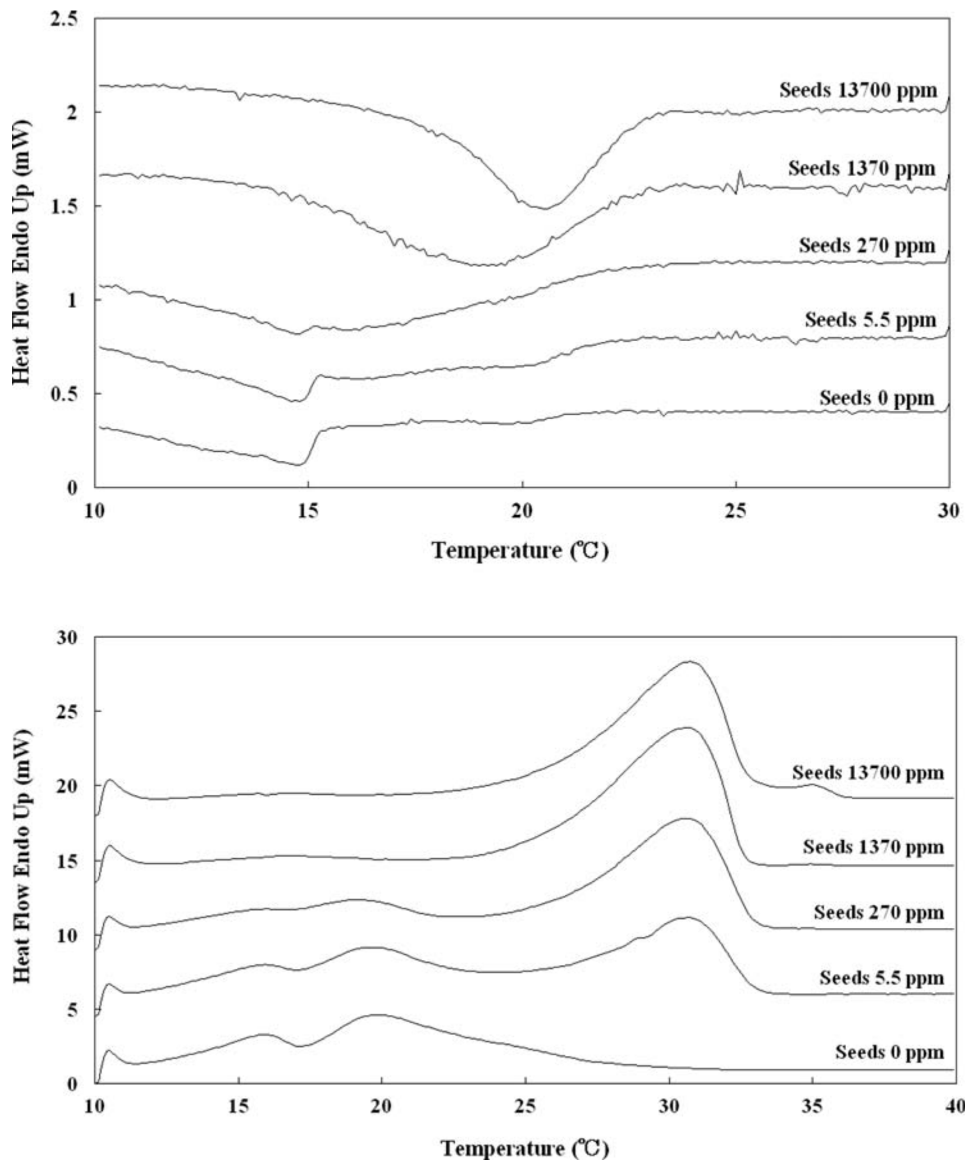

Fig. 9 Differential scanning calorimeter thermograms of cocoa butter with different seed addition levels (*top* cooling at 0.25 °C/min; *bottom* heating at 5 °C/min)

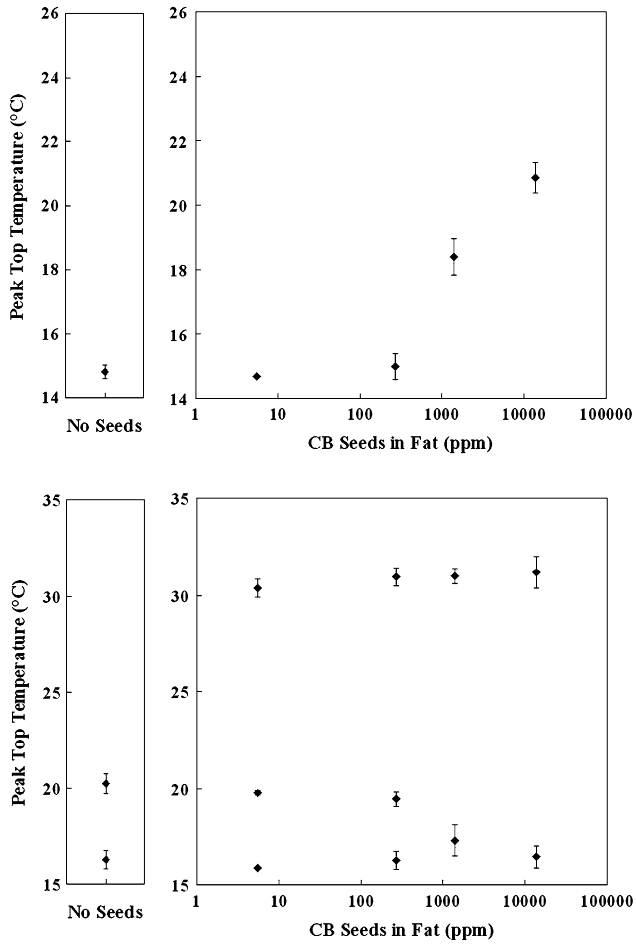

Fig. 10 Peak temperatures for DSC curves in cocoa butter crystallized with different seed addition levels (*top* cooling at 0.25 °C/min; *bottom* heating at 5 °C/min)

Although not conclusive, it is instructive to correlate the bloom results with the cocoa butter crystallization results. These results suggest that the small seed crystals in tempered chocolate grow quickly as chocolate is cooled, using up the available supersaturation in the liquid cocoa butter and thereby, reducing the extent of unstable β' polymorph nucleation.

When sufficient seed numbers are present to prevent bloom, β crystallization proceeds from many seeds simultaneously in cooling, and so takes less time to reach equilibrated solid fat content (SFC) at the temperature. In contrast, at low seed addition levels, β crystallization proceeds relatively slowly from only a few seeds and the equilibrium SFC is reached as the seeds grow to large size. Thus, in poorly-tempered chocolate, there is enough time and space for phase separation. Further, in poorly-tempered chocolate, certain triglycerides in cocoa butter, namely *sn*-1,3-saturated acyl *sn*-2-oleoyl glycerols (Sat-O-Sat), preferentially partition into the growing seed crystals, leaving powder materials (sugar crystals and cocoa solids) to accumulate. The light colored bloom then consists of the powder materials and less fat, which is depleted in Sat-O-Sat [6].

Bloom on poorly tempered chocolate is the same type of bloom as found on untempered chocolate, but the two differ in the time required for bloom to appear; the former develops just after cooling, whereas the latter needs several days to develop. The reason for this difference relates to the rate of stable polymorph formation. In the case of the bloom on untempered chocolate, β seeds need to be crystallized first, which takes time [16]. The β seeds that form statically are so sparse that phase separation occurs easily as the crystals grow. The presence of even a few stable seed crystals in poorly-tempered chocolate means that nucleation is not necessary, only growth of the existing seeds is required, and thus, the time for appearance of bloom is much shorter.

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