Surface bloom on improperly tempered chocolate

The surface composition, in terms of sugar and fat content, on untempered and over-tempered chocolates was estimated by carefully scraping the surface layer and analyzing fat and sugar melting enthalpies by differential scanning calorimetry. The dull surface of over-tempered chocolate had a fat and sugar composition similar to the initial chocolate mass, whereas the surface bloom formed on untempered chocolate was nearly depleted of fat, containing primarily sugar and cocoa solids. This was confirmed qualitatively by using polarized light microscopy, where no fat crystals could be observed in the bloom spots. Bloom on untempered chocolate corresponded to a phase separation between fat, sugar and cocoa solids. In contrast, the grey, dull aspect of the surface of over-tempered chocolate had essentially the same sugar-to-fat ratio as the intact chocolate and was due to a diffuse reflection of light on a rough surface, most likely induced by large cocoa butter crystals. Bloom on untempered chocolate developed regardless of the relative humidity of storage (between 0 and 75%). However, bloom developed more quickly and to a greater extent at lower relative humidity. Whiteness was directly related to the number, diameter and growth speed of the white bloom spots.

Keywords: Chocolate, bloom, over-tempered, untempered.

1 Introduction

Fat bloom, an undesired phenomenon for the chocolate industry, typically refers to the whitish haze that forms initially on a chocolate surface, which then may work its way through the bulk of the piece. The general term bloom, however, does not represent a single phenomenon corresponding to a single mechanism, since the origins and aspects of bloom are numerous [1, 2].

Bloom (or surface changes) can appear quickly after process problems or, more precisely, after poor tempering. Tempering induces crystallization of cocoa butter into a relatively stable polymorph that protects chocolate against bloom. During tempering, β'V seeds are formed at such a concentration that the chocolate mass crystallizes directly into the β'V polymorph during subsequent cooling [3–5]. Improper tempering can lead to rapid surface bloom (untempered) or dulling (over-tempered) due to the size or polymorphic form of cocoa butter crystals that are formed.

In well-tempered chocolate, fat bloom can occur due to four main reasons [6].

(a) Bloom can develop during storage depending on the temperature and fluctuations. High and fluctuating temperature leads to more rapid bloom.

(b) Bloom can also occur when the chocolate is exposed to a higher temperature than the melting point of cocoa butter.

(c) Liquid oil that migrates from a center to the chocolate can lead to bloom.

(d) Bloom due to composition problems is observed when two incompatible fats are blended together. Incompatible fats enhance bloom development, depending on the extent and amount of incompatible fat triacylglycerols [7].

Tempering is a directed pre-crystallization that consists of shearing the chocolate mass at controlled temperatures to promote proper cocoa butter crystallization [8, 9]. Although there are many ways to temper chocolate, the most common method utilizes temperature adjustment to promote formation of the desired number of seed crystals in the proper polymorphic form. In the first step, any crystalline memory is erased by holding the chocolate, with agitation, above 50 °C for a sufficient time to completely melt any crystals. The melted chocolate is then cooled to 26–28 °C to initiate seed formation. Nucleation of the fat crystals typically occurs into unstable polymorphs (α and β') because their energy of creation is lower than for more stable polymorphs. Once nucleation has been completed, the temperature is increased to just below the β'V polymorph melting point (typically 31–32 °C), where the unstable forms are melted or transformed into the desired β'V form. Specific temperatures are chosen to
accommodate crystallization behavior of different chocolates to control crystal formation and polymorph transformation.

Variations in the set temperatures, particularly the lower temperature, can induce variations in the concentration and polymeric habit of cocoa butter seed crystals. If the seed concentration is not high enough or if the seeds are not in the β'V polymorph, subsequent cooling of the chocolate causes crystallization into an unstable form, which will consequently bloom very quickly. Under-tempering means that the chocolate does not have sufficient βV seed content to completely crystallize the entire mass, and bloom occurs shortly after solidification. When chocolate mass has no seed before cooling, the chocolate is called untempered. In untempered chocolates, bloom also forms quickly. Chocolate is over-tempered when the mass has either too high a concentration of βV seed after tempering or the seeds are too large. In each case, the chocolates bloom or dull very quickly.

Bloom due to incompatible fats, oil migration and storage abuse have been investigated extensively, and mechanisms have been proposed for each of these types of bloom [2]. However, surface changes that occur in untempered and over-tempered chocolates have not been extensively studied. Whymper and Bradley [10] hypothesized that the powdery form of bloom on untempered chocolate was due to the development of small fat crystals on the surface of the chocolate. They concluded that bloom on untempered chocolate was the direct result of the separation and further crystallization of the high-melting fractions of cocoa butter. Vaeck [11] explained bloom on under-tempered chocolate as the recrystallization of the unstable β' form of cocoa butter into large β form crystals, thus inducing a sandy structure. This led to large crevices from which light was diffracted, creating the whitish appearance. This theory has been commonly accepted [7].

In this study, the primary goal was to characterize the changes in composition at the surface of improperly tempered chocolates and to investigate factors that affect their appearance.

2 Materials and methods

2.1 Preparation of chocolate samples

Three commercial chocolates were used: dark bittersweet couverture chocolate with high (64%) cocoa solid content (Guittard Chocolate, Burlingame, CA, USA), a regular dark bittersweet chocolate (Blommer Chocolate, Chicago, IL, USA) and milk chocolate (Hershey Foods, Hershey, PA, USA). The dark bittersweet couverture from Guittard contained approximately 63% cocoa mass (about 43% cocoa butter) and 37% sugar, in addition to a small amount of lecithin and vanilla flavoring. The other two chocolates contained approximately 45–50% sugar and 30–32% fat. Although the exact composition of these two chocolates is unknown, they represent typical commercial chocolates.

Untempered chocolate was obtained by melting the chocolate at 65 °C for 12 h. The mass was poured directly into disc-shaped plastic molds of 5 cm diameter and 7 mm thickness. These chocolates were allowed to cool at room temperature (about 20–22 °C) with only gentle air flow.

A three-stage tempering protocol was used to obtain over-tempered chocolate [9]. Chocolate was melted in a 1-L jacketed tempering beaker (Cole-Palmer, Chicago, IL, USA). A coated paddle stirrer (Cole-Palmer) was used to mix the samples, and a Master Servodyne motor head and controller (Cole-Palmer) governed stirrer speed and monitored viscosity. Melted chocolate at 70 °C was cooled to 26 °C in the tempering beaker and held there until viscosity approached a constant value. Temperature was raised to 32 °C until a viscous paste was obtained. The chocolate was poured into the disc-shaped plastic molds and cooled at room temperature (22–24 °C) with gentle air flow. Although the degree of temper was not characterized, all chocolates processed in this way, including the milk chocolate, exhibited the classic characteristics of over-tempering. They were excessively viscous, became dull very quickly and were not easily removed from the molds (inadequate contraction).

For comparison, well-tempered chocolates were also produced in a similar manner. A cooling-and-heating method was used (as for over-tempered chocolate), but with temperatures chosen to give chocolates with a glossy surface that were easily released from the molds.

2.2 Melting enthalpies (ΔH) of sugar and fat

Samples of the chocolate surfaces (bloomed for untempered and dull for over-tempered) were collected by carefully scraping the whitish or dull surface of the chocolate. Contamination by the interior chocolate was avoided as much as possible – samples were discarded in case of doubt. Samples (2–7 mg) of bloom scrapings were sealed in an aluminum pan, and melting enthalpies of sugar and fat were measured using a Perkin Elmer (Norwalk, CT, USA), Pyris 1, differential scanning calorimeter (DSC) monitored with Pyris software. To ensure complete standardization of the fat phase, each sample was melted at 50 °C for 5 min and then cooled to −20 °C.
To support the whiteness index measurement, the number and the diameter of white spots on each disk were determined visually starting from within the first few hours of molding the chocolate. A growth rate of spot diameter (in cm/day) was estimated as \( \Delta \) (spot diameter)/(time). At least four spots were used that were not affected by adjacent spots over the duration of the experiment.

Although only semi-quantitative, a nucleation rate on each disk was estimated based on the number of spots that appeared on the surface per day. This rate was calculated as \( \Delta \) (spot number)/(time).

### 2.5 Sorption isotherm

Three replicates (3–4 g) of each sample (sugar crystals and cocoa powder both initially and after coating with lecithin) were placed in desiccators containing saturated salt slurries with the following \( a_r \) values at 20 °C: LiCl, 0.11; KC\(_2\)H\(_3\)O\(_2\), 0.23; MgCl\(_2\), 0.31; K\(_2\)CO\(_3\), 0.43; MgNO\(_3\), 0.54; and NaCl, 0.75. Moisture uptake of samples was calculated (in percent) based on the gain in weight of sample per 100 g dry weight of sample.

To study the sorption behavior of chocolate components, sucrose crystals and cocoa powder were sieved to obtain a fraction between 45 and 105 \( \mu \)m particle size. This fraction was used either directly as sieved or coated with emulsifier. To prepare the coated samples, 150 g of each powder was mixed for 12 h in 500 mL chloroform with a soy lecithin concentration of 37.5 mM, after which it was filtered and dried under nitrogen. These lecithin-coated samples were used immediately for the determination of the sorption isotherm, as described above.

### 2.6 Moisture content of chocolate

The moisture content of chocolate was determined by Karl Fisher titration at the end of the sorption term (40 days of storage). Chocolate was finely ground and dissolved in anhydrous methanol at 60 °C for 6 h. Thereafter, 2 mL (in average) of this solution was used to determine the moisture content of chocolate. At least triplicate determinations were made for each sample.

### 3 Results and discussion

#### 3.1 Appearance of the chocolate surface

Typical examples of improperly tempered (both untempered and over-tempered) and well-tempered chocolate are shown in Fig. 1. Untempered chocolate is characterized by a whitish brown sandy color. The bloom grew...
either in spots or like a corona surrounding a dark chocolate center. Bloom on untempered chocolate appeared usually several hours after initial chocolate solidification and continued to develop for over 30 days.

Over-tempered chocolate showed a uniform thin, dull gray surface. The surface changes occurred during solidification and, once it formed, did not seem to vary or varied only slightly as a function of time.

### 3.2 Ratio of sugar to fat

The ratios of sugar to fat in the intact chocolates and associated surface structures after 1 week at room temperature were determined by DSC analysis. The results for the ratio \( \Delta H_{\text{Sugar}}/\Delta H_{\text{Fat}} \) are summarized in Tab. 1. The ratio of fat and sugar enthalpies depended on the chocolate type, which was dependent on its original composition. The couverture chocolate had lower values of fat and sugar melting enthalpies compared to the other chocolates, which were very similar to each other. The couverture chocolate had a sugar/fat enthalpy ratio of about 2, whereas the dark and milk chocolates had a ratio around 1.25.

The scraped surface (whitish or dull) of each chocolate was analyzed 1 week (at room temperature) after chocolate production. For the over-tempered chocolates, the fat enthalpy of the surface layer was about the same as for the well-tempered chocolates, whereas sugar enthalpy was slightly greater. Consequently, the fat content remained similar at the surface of over-tempered chocolate to the interior of the chocolate. That is, no phase separation between fat and either sugar or cocoa solids was evident at the surface of over-tempered chocolate. Consequently, dulling of the surface of these chocolates must be due to a rearrangement of the fat crystals without a separation of solids.

The situation was quite different for untempered chocolates. The melting peak of fat was almost nonexistent; \( \Delta H_{\text{Fat}} \) was tenfold smaller than that obtained for well-tempered chocolate. It was almost impossible to quantify any fat peak in the bloom scraped from dark chocolate. In contrast, no statistical differences were observed between the sugar peaks (\( \Delta H_{\text{Sugar}} \)) of bloom on the untempered chocolate and the well-tempered control. Greater variability in the results was observed with bloom on untempered chocolate than for the other samples, perhaps related to the heterogeneity of bloom. Each spot

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**Tab. 1.** Fat and sugar melting enthalpies (\( \Delta H \), J/g), as determined by DSC, of chocolates and their associated surfaces, after 1 week at room temperature. Mean and standard deviation of three replicates.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H_{\text{Fat}} )</th>
<th>( \Delta H_{\text{Sugar}} )</th>
<th>( \Delta H_{\text{Sugar}}/\Delta H_{\text{Fat}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark, bittersweet</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>couverture chocolate</td>
<td>Well-tempered</td>
<td>19.7 ± 2.6</td>
<td>39.9 ± 3.7</td>
</tr>
<tr>
<td></td>
<td>Untempered bloom</td>
<td>1.5 ± 0.65*</td>
<td>57.1 ± 17.2*</td>
</tr>
<tr>
<td></td>
<td>Over-tempered surface</td>
<td>16.5 ± 3.2</td>
<td>48.0 ± 1.8</td>
</tr>
<tr>
<td>Dark chocolate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Well-tempered</td>
<td>34.7 ± 4.0</td>
<td>44.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Untempered bloom</td>
<td>≈0*</td>
<td>45.0 ± 4.2</td>
</tr>
<tr>
<td></td>
<td>Over-tempered surface</td>
<td>33.2 ± 4.7</td>
<td>49.1 ± 2.5</td>
</tr>
<tr>
<td>Milk chocolate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Well-tempered</td>
<td>34.5 ± 4.0</td>
<td>43.4 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>Untempered bloom</td>
<td>3.5 ± 3.1*</td>
<td>35.0 ± 9.5</td>
</tr>
<tr>
<td></td>
<td>Over-tempered surface</td>
<td>NA*</td>
<td>NA</td>
</tr>
</tbody>
</table>

\( \Delta H_{\text{Fat}} \) was determined by DSC analysis.

\( \Delta H_{\text{Sugar}} \) was determined by DSC analysis.

\( \Delta H_{\text{Sugar}}/\Delta H_{\text{Fat}} \) was determined by DSC analysis.

* Significantly different (\( p < 0.05 \))

§ Bloom on over-tempered milk chocolate was not analyzed.

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might have had small composition differences caused by heterogeneity of the bloom taken on the surface. However, the apparent decrease in fat content of bloom on untempered chocolate was clearly evident in all three samples.

The decrease in fat enthalpy, as measured by DSC melting scan, documented the disappearance of fat in the bloom of untempered chocolate. Sugar and cocoa powder (which is not observable by DSC) were the primary substances found in this form of bloom. Thus, the previous conjecture that bloom on untempered chocolate is cocoa butter that has recrystallized into a more stable form must be incorrect (although this bloom is still likely to be caused by that polymorphic recrystallization).

3.3 Polarized light microscopy

The different chocolates and scraped surface samples were observed under a polarized light microscope (PLM) to verify the DSC results. Under the PLM, sugar and fat crystals exhibit polarization, whereas cocoa solids (amorphous) do not. Although not a quantitative measurement, the relative amount of polarizing matter observed for each sample was used to corroborate the DSC results.

Micrographs of well-tempered couverture chocolate, the white spots that appeared on untempered chocolate, and the surface of over-tempered chocolate are presented in Fig. 2 (a–c). Each sample exhibited polarization corresponding to the bright white spots on the micrographs. The sample opacity and high proportion of crystals did not allow determination of whether polarization came from sugar or fat. Moreover, differences of polarization intensity observed between samples were not quantitative since thickness and weight of the samples undoubtedly influenced the appearance.

To determine the origin of polarization, sugar was removed from the samples by addition of water to dissolve the sugar crystals. After washing to dissolve sugar crystals, the remaining polarization was due only to fat crystals. Images of the different samples after water treatment are also shown in Fig. 2 (a'–c'). Well-tempered couverture chocolate (Fig. 2a') and the surface scraped from over-tempered chocolate (Fig. 2b') both exhibited small polarization spots due to fat crystals that were dispersed homogeneously throughout the sample. However, bloom scraped from untempered chocolate (Fig. 2c') was totally dark; it did not exhibit any polarization. That is, this sample did not have any fat crystals. Only cocoa powder was observed after washing the sugar crystals. Similar results were obtained with dark and milk chocolates (images not shown). The microscope observations confirmed the results obtained by DSC. The surface of over-tempered chocolate exhibited a slight increase in sugar content, but the average composition was similar to well-tempered chocolate. However, bloom scraped from untempered chocolate was essentially devoid of fat, as documented by both DSC analysis and polarized light microscopy.

3.4 Nucleation rate of white spots

Development of white spots on the surface of untempered chocolate began at some time after solidification. On the untempered chocolates in this study, sometimes bloom spots generally appeared within a day or so, at which time the small black spots appeared, followed by a thin white corona around the spot. These spots then developed over time into the large sandy, white spots apparent on untempered chocolate. Fig. 3 shows the effect of RH on the number of white spots that developed on disks (at least triplicate disks were analyzed) of 5 cm diameter. An approximately linear trend was observed between the number of white spots and time for the first 20 days of storage. Thereafter, it was no longer possible to count individual spots due to overlap.

Fig. 2. Micrographs of couverture chocolate (a), the scraped surface of over-tempered chocolate (b), and bloom on untempered chocolate (c). The same samples after sugar dissolution by washing with water (a', b', c').
In general, the number of white spots that appeared on the chocolate disks increased as RH decreased. That is, higher RH led to slower development of bloom and to a lesser extent. A nucleation rate was calculated from the slope of each line, as given in Tab. 2. The nucleation rate of bloom spots on chocolate stored below 50% RH was almost twice the rate for those stored above 50% RH.

Tab. 2. Effect of RH of storage on nucleation rate of white spots on bloomed surface of untempered chocolate.

<table>
<thead>
<tr>
<th>RH [%]</th>
<th>Nucleation rate $^\dagger$</th>
<th>$R^2$ $^\sharp$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.9</td>
<td>0.93</td>
</tr>
<tr>
<td>11</td>
<td>11.6</td>
<td>0.94</td>
</tr>
<tr>
<td>23</td>
<td>7.5</td>
<td>0.89</td>
</tr>
<tr>
<td>31</td>
<td>7.1</td>
<td>0.94</td>
</tr>
<tr>
<td>43</td>
<td>4.2</td>
<td>0.86</td>
</tr>
<tr>
<td>54</td>
<td>3.6</td>
<td>0.87</td>
</tr>
<tr>
<td>65</td>
<td>3.8</td>
<td>0.86</td>
</tr>
<tr>
<td>75</td>
<td>4.1</td>
<td>0.86</td>
</tr>
</tbody>
</table>

$^\dagger$ Changes in number of white spots with time.  
$^\sharp$ Linear regression correlation coefficient.

3.5 Growth rate of white spots

Fig. 4 shows the effects of storage RH on the growth rate of the white spots on disks of untempered chocolate. In general agreement with the nucleation rate data, the growth rate was fastest at 0% RH and the rate generally decreased as RH increased. Between 10 and 43% RH, the growth rate was intermediate and essentially invariant. Growth rate decreased above 50% RH. Higher RH of storage significantly ($p < 0.05$) reduced the growth rate of white spots.

3.6 Whiteness index

Whiteness index based on colorimeter measurement was monitored for more than 1 month on untempered chocolates stored at different controlled RH (Fig. 5). Interestingly, the whiteness index did not change significantly until about 1 week of storage, despite visual detection of numerous white spots on the disks of chocolate within a day of solidification. Comparing the data in Fig. 3, there were between 15 and 75 white spots visible on the chocolate disks before the whiteness index began to increase at day 7. Apparently, the whiteness index method of characterizing bloom in untempered chocolates is not as sensitive a method as visual determination. Despite this limitation of the whiteness index data, the general trend of bloom increasing as RH of storage decreased is still evident in Fig. 5.

Each chocolate bloomed, regardless of the RH, with a trend in whiteness that had a common shape consisting of three parts. At the beginning, an induction phase was characterized by a constant whiteness value. There were either no white spots on the surface or the number was not sufficient to affect the measured whiteness index. As noted before, visual counting of white spots indicated that the colorimeter was not very sensitive when the number of spots was too low (less than 50–75 spots). Once there was a sufficient number of spots to affect the whiteness index, there was an exponential increase of whiteness. The number and diameter of white spots increased.
The chocolates stored between 0 and 43% RH all generally showed identical behavior, with a short induction time and high final whiteness index. However, above 50% RH, the induction time increased to about twice the induction time at lower RH and the maximal whiteness was also lower. This decrease was greater as the RH increased.

To be sure that the RH itself did not affect the perception or intensity of bloom, the whiteness variations of a sugar/cocoa powder blend (with a composition of 40 : 60 wt/wt, similar to bloom) was monitored as a function of RH of storage (data not shown). Whiteness remained constant for more than 6 weeks, except for the sample stored at 75% RH, where whiteness decreased slightly (three points) at the 6-week point. Thus, the simple effect of moisture on whiteness perception was not sufficient to explain the difference in whiteness observed between chocolates stored at the highest and lowest RH (Fig. 5).

3.7 Sorption isotherms

The sorption isotherm of untempered chocolate is presented in Fig. 6. Moisture content was below 1% until RH exceeded 45%, at which point it then increased quickly to 2.2% at RH above 60%. The result was similar to values obtained previously with well-tempered chocolate [13, 14]. Thus, the moisture uptake was not affected by the chocolate structure or type; the disorganized structure of untempered chocolate or the tight structure of well-tempered chocolate apparently have similar sorption behavior. Thus, a coating of fat on sugar and cocoa particles, which should prevent the sorption of water, was not a limiting factor for the moisture uptake of chocolate.

Hypothetically, the moisture mediator in chocolate could be cocoa butter, emulsifier, cocoa solids or sugar. In a general sense, fat is a good moisture barrier, with fats composed of saturated and longer fatty acids being more impervious to moisture. Landmann et al. [15] found a moisture permeability constant of 0 for paraffin, $1 \times 10^{-12}$ for hydrogenated cottonseed oil and $36 \times 10^{-12}$ for cocoa butter in its most stable form. Thus, cocoa butter is not totally impervious to moisture; it has a very low permeability due to a certain liquid fat content and the presence of minor compounds with emulsifying properties. Emulsi-
Emulsifiers are well known to interact with moisture. The lecithin in chocolate (0.3% of the total mass in average) adsorbs primarily on sugar particles, as confirmed by Johansson and Bergenstahl [16], who compared the adsorption of emulsifiers on fat or sugar crystals [17]. Emulsifiers adsorbed in multilayers on sugar crystals, whereas they adsorbed as mono- or bilayers on fat crystals. Moisture sorption in chocolate is almost certainly mediated by emulsifiers. However, Ogunmoyela et al. [18] showed that higher content of lecithin had only a slight effect on the moisture content of chocolate. In our results, no difference in moisture sorption was observed until RH was above 50% and the differences were very small even at 75% RH.

To develop a better understanding of moisture behavior in chocolate, the sorption isotherms of sugar and cocoa powder, either bare or coated with emulsifiers, were determined. Coating of particles with emulsifier was accomplished by soaking sugar and cocoa powder in a 37.5 mM soy lecithin solution (in chloroform as solvent). The extent of lecithin adsorption was quantified by an indirect method, corresponding to the difference of phospholipid concentration in the soaking solution before and after adsorption. It was found that 8.6% of the initial phospholipids were adsorbed on sugar, with phosphatidylcholine (61%), phosphatidylinositol (35%) and phosphatidylglycerol (3.5%) as the main adsorbants. A rough calculation of phospholipid adsorption based on an average sugar crystal size of 75 μm and coverage of 1.5 μmol/m² for a phospholipid monolayer [16] gave four phospholipid layers adsorbed on each sugar particle. With cocoa powder, it was not possible to quantify the phospholipid variations after coating. In fact, the concentrations of phosphatidylcholine and phosphatidylinositol in solution increased by 50% after the adsorption step compared to the initial soaking solution. Apparently, phospholipids were desorbed from cocoa powder.

The moisture sorption isotherms of sugar crystal and cocoa powder, coated with emulsifier or not, are presented in Fig. 7. The sugar crystal and cocoa powder moisture sorption isotherms were quite different. Cocoa powder had 4% moisture content when stored at 10% RH and that increased to 12% at 75% RH. The differences between bare and coated sample were very small. This is certainly due to the initial presence of phospholipids on the cocoa solids. In contrast, sugar crystals had a very low hygroscopicity. Bare sugar had a moisture content below 0.05% even when stored at high RH. Coating with emulsifier increased the extent of moisture uptake when RH >60%. In this case, moisture uptake increased substantially; however, moisture content was always very low, below 1%. Thus, moisture content in chocolate seemed to be mainly due to the moisture uptake of cocoa powder.

3.8 Correlation between chocolate moisture and bloom development

The final moisture content of chocolate after 40 days of storage at different RH was compared to the different parameters associated with bloom development. Moisture content of chocolate showed a good linear correlation with the whiteness value (y = −8.12x + 52.5, r² = 0.93) as well as with the growth rate of the white spots (y = 0.009x + 0.038, r² = 0.76) (Fig. 8a, c). The higher the moisture content, the lower the final whiteness of the chocolate as well as the slower the growth rate of the white spots. The effect of chocolate moisture content on nucleation rate seemed to be less directly related (Fig. 8b). It appeared that nucleation rate was greatly affected by RH for values lower than 40% RH, but above 40% RH, the nucleation rate was low and not affected by further increases in RH.

4 Conclusions

The surface characteristics of poorly tempered chocolates were characterized. Un tempered chocolate quickly forms a surface bloom, within a few hours to a few days,

Surface bloom

Fig. 8. Correlation between moisture content of chocolate (after 40 days of storage at different RH) and final whiteness index of untempered chocolate (a), nucleation rate of white spots (b), and growth rate of white spots (c).

that appears as numerous white spots surrounded by dark chocolate. These white spots consist of sugar crystals and cocoa solids, and are essentially devoid of fat. Recrystallization, and subsequent contraction, of the cocoa butter into more stable polymorphic forms is thought to be responsible for this type of bloom formation.

In contrast, the surface of over-tempered chocolate quickly, within minutes to hours, becomes dull, even during solidification, but this dull surface has essentially the same composition of fat as the original (and well-tempered) chocolate. Thus, surface dulling of over-tempered chocolate is apparently due to growth of cocoa butter crystals at the surface that influence light reflection and give the dull appearance, as suggested by Musser [19].

The rate and extent of bloom formation on untempered chocolate was found to be dependent on the RH of storage, with bloom occurring more readily at very low RH. We speculate that the mechanism of this type of bloom formation is related to the volume contraction that occurs during the polymorphic transformation from unstable β’ crystals to the more stable βIV and βVI polymorphs. As the cocoa butter molecules rearrange into more compact crystals, the gaps between crystals are regions where cocoa solids and sugar crystals become entrapped. At lower RH, formation of these white spots is enhanced compared to storage at higher RH. This suggests that either the particulate matter is less able to move when moisture content is higher or the transition of cocoa butter from less stable to more stable polymorphic forms is inhibited.

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References


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