Effects of fat polymorphic transformation and non-fat solid particles on surface changes of untempered chocolate

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Abstract

1. Introduction

Chocolate is primarily composed of cocoa butter and non-fat particles. Non-fat particles include sugar, cocoa particles, and for milk chocolates, milk powder. Bloom is a general term that relevant to various origins and mechanisms of formation [1]. Fat bloom or storage bloom often refers to the whitish appearance formed on chocolate products after a long period of storage. This type of bloom is due to the separation and deposition of needle-like, thin plate-like, or foliated fat crystals (≤5μm) on the surface of plain chocolate or filled chocolate confections [2]. Another type of bloom forms on the surface of untempered chocolate and originates from the redistribution of fat content. After processing, a phase separation occurs; the movement of fat leaves only non-fat particles at the surface of the chocolate [1].

Kinta and Hatta [2] describe the bloom on untempered chocolate in five steps: 1) the crystal history of cocoa butter is removed by increasing the temperature above the melting point; 2) during cooling or storage, relatively stable crystal nuclei are formed; 3) the surrounding liquid fat travels through the spaces between static non-fat solid particles and crystallizes around the crystal nuclei; 4) during step 3), more stable crystals form and the volume of the fat phase reduces; 5) finally, the low fat content areas are lighter in colour. The authors concluded that the driving force for this kind of bloom is crystal formation around more stable crystal nuclei.

Polymorphic transformations may occur in the fat phase during bloom formation. A roman numbering system (I to VI) is commonly used to represent the six cocoa butter polymorphic forms; type I is the least stable and type VI is the most stable. Type V is often found in commercial chocolates [3, 4]. Despite numerous studies on the polymorphic transformation of cocoa butter from type V to VI during long periods of storage [5, 6], there is little information available on the transformation process from type IV to V.

Lower relative humidity has been shown to promote bloom formation on untempered chocolate [1]. However, other factors which may influence the rate and extent of bloom development, such as the non-fat particulate network, have not yet been thoroughly investigated.

The objective of this study was to use a simple cocoa mass chocolate model to investigate the polymorphic transformation of cocoa butter from type IV to V. Furthermore, to relate this polymorphic transformation to the surface changes which occur during untempered chocolate bloom. In addition, the effects of non-fat particle amount and spatial distribution on bloom formation were studied. A deeper understanding of bloom formation on untempered chocolate will contribute to new chocolate product designs without tempering.

2. Materials and Methods

2.1 Materials

Seven chocolates were investigated in this study (nutritional information is presented in *Table 1*): four cocoa mass chocolates with differing particle size distributions and three commercial dark chocolates with differing cocoa content. The cocoa mass chocolates were prepared by grinding roasted cocoa nibs (Chocolate Brown, Warkworth, NZ) in a chocolate melanger (Spectra 11 stone melanger, Coimbatore, India) to produce the mass. For each of the four batches, 600g of cocoa nibs were pre-ground at 700rpm for 40 minutes. The four different particle size distributions were obtained by further grinding the liquor at 1200rpm for either 3, 5, 6, or 10 hours.

Three Lindt Excellence (LE) dark chocolates (70%, 85%, and 90% cocoa) were selected in a grocery store. The fat ratio (41.0, 46.0, and 53.4% wt, respectively), sugar ratio (29.0, 11.0 and 6.3% wt respectively), and the other non-fat solids (30.9, 43.0 and 40.3% wt, respectively) were taken into consideration.

2.2 Fat removal and particle size measurements

Direct hexane extraction is commonly used in the cocoa industry as an efficient method for cocoa butter extraction [7]. Hence, it was selected as the method for fat removal in nib chocolate samples. Approximately 5g of cocoa mass chocolate sample was dissolved in 20ml of n-hexane (>98.5%). Samples were left for 24 hours to allow the cocoa particles to settle on the bottom of the beaker. The upper hexane layer in which the cocoa butter was dissolved was carefully removed using a pipette. This procedure was repeated a total of three times using fresh n-hexane for each extraction. Then the cocoa particle layer was dried in a fume hood for 2 hours until all of the n-hexane had evaporated. To separate the particles, the cocoa powder layer was crashed in a grinding bowl.

The cocoa particles obtained were measured by a laser diffractometer Mastersizer 2000 (Malvern Instruments Ltd., Malvern, U.K.). Approximately 0.1g of powdered sample was dispersed in water

and ultrasound treated for 2 minute. The refractive index of the dispersant was set to 1.33 and a pump speed of 2000 rpm was used. Each sample was measured in triplicate. Particle size distribution curves and size parameters were obtained.

2.3 Sample preparation

Each of the cocoa mass and LE chocolates was re-melted in a 60ºC water bath (WB-11, WiseBath, South Korea). The molten chocolate was continuously agitated for 1 hour at 200 rpm using a mechanical stirrer (RW 20 digital, IKA-works Inc. NC, USA) to ensure all crystal histories were erased. The liquid was poured into cylindrical moulds (diameter = 4.5cm and depth = 1.2cm) and sealed in a container before cooling in a refrigerator (5 ± 0.5 ºC) for 1 hour. The containers were then removed from the refrigerator and stabilized at ambient temperature (20 ± 0.5 ºC) for 12 hours prior to demoulding. Afterwards, all samples were stored at ambient temperature with humidity never excessed 50%.

2.4 Measurements (microscopies, X-ray diffraction and surface whiteness)

During bloom formation, a differential interference contrast (DIC) optical microscope and an X-ray diffraction machine (Bruker, D2 Phaser) were used to examine the surface characteristics and cocoa butter polymorphs, respectively. Every 24 hours, the surfaces of the same samples were viewed using the DIC microscope as a non-destructive tool. For X-ray diffraction, a piece (with a flat surface) was cut from each sample using a scalpel. It was measured by the machine using Cu-Kα X-rays (a goniometer step size = 0.02°, a dwell time = 0.1s) and the diffraction pattern was recorded.

At the end of the bloom process, surface microstructures were imaged using a variable pressure scanning electron microscope (VP-SEM, Quanta 200 FEG SEM, FEI Company, Eindhoven, Holland) and an XL30S FEG SEM (cryo-SEM, Philips/FEI Company, Eindhoven, Holland). For VP-SEM, the sample was cooled to a temperature of -5°C on a peltier cooled stage to avoid thermal damage [8]. The sample surface was imaged in a nitrous oxide atmosphere at a pressure of 0.58 Torr. An accelerating voltage of 10 kV was used for imaging. For cryo-SEM, the XL30S was fitted with an Alto 2500 cryo-trans system (Gatan UK, Abingdon, UK). The sample was plunge frozen in liquid nitrogen slush and sputter coated with platinum before imaging.

The machine vision system was used to measure changes in surface Whiteness Index (WI) during bloom, and the “two images” method, which eliminates the influence of background colour, was employed [9, 10]. The images were analysed using LensEye software (Gainesville, FL, USA) and the Whiteness Index values were automatically displayed. The calculation of the Whiteness Index is based on L^*, a^* and b^* values by the software:

$$WI = 100 - \left[(100 - L^*)^2 + a^{*2} + b^{*2} \right]^{0.5}$$

3. Results and Discussion

3.1 Non-fat particle sizes in cocoa mass chocolates

The sizes of non-fat solid particles (cocoa particles) in the chocolates were represented by D_{90} values (90%<) and ranged from approximately 18 to 56μm. D_{90} values are commonly used in chocolate studies to indicate the proportion of the largest particles corresponding to mouthfeel [11, 12]. The particle sizes are presented in *Table 2.* A cocoa mass chocolate with a smaller D_{90} consists of a larger ratio of small particles and less large particles.

3.2 Evolution of surfaces

When freshly demoulded, the chocolate surface was brown and homogeneous. However, within several hours, small spots which were lighter in colour developed. The number and area of the spots increased during the first 2 days. As seen in *Fig. 1*, from day 3, a sandy periphery began to appear and surround the light small spots. At approximately 6 days of storage, the lighter peripheral areas had joined together making up the majority of the surface colour; the original brown colour had almost disappeared.

The bloom process was confirmed with the DIC microscope. From day 6, lighter coloured spots darkened (*Fig. 2, S1 to S3 to S6*) and sandy periphery areas (*Fig. 2, P1 to P3 to P6*) rapidly expanded into the surrounding areas that appeared to be tempered chocolate. Thereafter, changes in spot appearance were minimal but the areas surrounding the spots became whiter. At approximately 10 days of storage, the chocolate surface had a “honeycombed” appearance forming well-distributed sub-units.

The honeycomb-like structure was also found inside the samples as shown by images of internal fracture surfaces in *Fig. 3*. This indicates that the continuous structural changes occurred uniformly throughout the entire sample.

3.3 Polymorphic transformation

One issue that complicates the use of X-ray diffraction on chocolate is that sugar obscures cocoa butter diffraction peaks [13]. Two commonly used methods to overcome this issue are: (1) removal of sugar prior to X-ray diffraction using repeated cold water rinsing; or (2) subtraction of the molten chocolate diffraction pattern from that of the solid chocolate [13-15]. However, this is not an issue with the cocoa mass chocolates as they were formulated without sugar. The cocoa butter transformation from type IV to V was observed; all four cocoa mass chocolates showed a similar polymorphic transformation during storage. Representative diffraction patterns during bloom formation are shown in *Fig. 4.* The fresh samples had a diffraction pattern showing the presence of cocoa butter polymorph type IV with two strong peaks at around 4.15 and 4.34Å. These are in agreement with characteristic peak positions reported in literature [3, 16-18]. The less stable type IV

gradually transformed to type V. Type V has a very strong peak at 4.59Å, a distinctive weaker peak at around 3.99Å, and three other peaks at approximately 3.89, 3.77, and 3.67Å; these are similar to peak positions reported by the above authors. During the first 6 days of storage, the diffraction peaks of polymorph type IV disappeared, and characteristic type V peaks appeared. From day 6, the peak intensity of type V became stronger and the characteristic peaks sharpened as an indication of continuous growth of type V crystals.

This study indicates that significant changes in structure occur within 6 days of untempered chocolate demoulding. By day 6, important changes in the untempered chocolate surface and cocoa butter polymorphs were observed; spots which were light when they initially appeared became dark and the sandy periphery rapidly developed. In addition, most of type IV cocoa butter crystals transformed to type V.

3.4 Surface morphology of bloom

The surfaces of the bloomed samples were viewed using VP-SEM and Cryo-SEM after 25 days of storage. The surface morphology was similar for all four cocoa mass chocolates; *Fig. 5* shows typical images of the bloomed samples. Separated fat crystals were found in the dark spots by both imaging techniques (c, VP-SEM and d, Cryo-SEM). This confirms that the dark spots were fat-based. The sandy periphery (b, VP-SEM and e, Cryo-SEM), was mainly composed of static cocoa particles without fat. Empty voids were visible between cocoa particles (f, Cryo-SEM). The pre-existing fat could have been driven to surrounding or internal fat-rich spheres. The overall volume of fat phase decreased due to more stable fats being more dense [19]. Microscopic observations of fat-rich centres and periphery (bloom) lack of fats is in agreement with chemical analysis by Kinta [20] and a thermoanalytical method used by Lonchampt [1].

Superficial structure of fat crystals depositing on fat-rich spots of untempered chocolate showed similarities to storage bloom on well-tempered chocolates. However, the x-ray diffraction pattern of untempered chocolates at day 25 (*Fig. 4*) revealed that the cocoa butter was still in type V rather than the most stable type VI found in well-tempered chocolates with fat bloom [21]. In addition, the bloom on untempered chocolate is the particle area excluding fat, since it seems to contribute more in diffracting light and appear whiter.

Kinta *et al*. [2, 20] stated that the bloom formation in untempered chocolate could be considered as a redistribution of fat within the chocolate matrix and proposed the formation of more stable fats around the crystal nuclei as the main driving force. Afoakwa *et al.* [22] further defined the growth of more stable crystals as Ostwald ripening. Our microscopic observations are in agreement with these mechanisms, thus proving that bloom on untempered chocolate was due to withdrawal of fat to fat-rich spheres rather than a simple surface phenomenon. Initially, the light spots (*Fig. 2, S1*) appeared due to the formation of more stable nuclei crystals. The surrounding unstable cocoa butter or liquid

cocoa butter was driven and developed onto the centre, which ended up with large fat-rich spheres (*Fig. 2, S6*).

3.5 Effects of particle size

The four cocoa mass chocolates had similar initial absolute Whiteness Index (WI) values in *Fig. 6*. During the first 6 days of storage, WI increased exponentially as described by Lonchampt [1]. Although the 18μm and 25μm (34μm and 56μm) cocoa mass chocolates had similar WI changes, overall the samples with smaller D_{90} values appear to undergo larger increases in WI (h1>h2); e.g. the cocoa mass chocolates with a larger portion of small particles and less large particles appear whiter. This could be due to stronger light diffraction by smaller particles on the surface of the sample.

3.6 Effects of non-fat solid ratio

The three types of LE chocolates differed in non-fat solids ratio and the composition of non-fat solids. With increasing cocoa content (or decreasing non-fat solid ratio), the samples had decreasing initial and final WI values (as shown in *Fig. 7).* The WI of the 90% LE chocolate increased by a value of approximately 16 (h5), where the other two increased by approximately 22 (h3 and h4).

It has to be aware that factors other than the size and amount of non-fat particles also affect the surface whiteness. These factors include: (1) the surface properties of particles; (2) the degree of honeycomb-like structure formation (bloom area); and (3) the fat crystals formed on fat-rich areas. The 90% LE chocolate had the highest total fat ratio which was similar to the cocoa mass chocolates. The 70% Lindt chocolate, however, had the highest non-fat solid ratio and sugar content. It should be noted that 85% LE chocolate had lower sugar content than the 70% LE chocolate, but the highest ratio of non-fat solids apart from sugar. The results of this study indicate that the amount of particles could influence changes in WI changes if the effects of particle surface properties are not taken into consideration.

4. Conclusion:

5. References:

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