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Impact of pre-crystallization process on structure and product properties in dark chocolate

L. Svanberg [a,b,*], L. Ahrné [a], N. Lorén [a], E. Windhab [b]

[a] SIK – The Swedish Institute for Food and Biotechnology, Box 5401, SE-402 29 Gothenburg, Sweden
[b] Swiss Federal Institute of Technology, Zurich, Institut für Lebensmittelwissenschaften, LFO E 12.1, ETH Zentrum, CH-8092 Zürich, Switzerland

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ABSTRACT

Dark chocolate microstructures with different structure densities, i.e., close-packing of the fat crystal lattice, and homogeneity i.e., evenness and connectivity of the fat crystal network, were created by β_{VI}-seeding or conventional pre-crystallization with various degrees of temper and were evaluated with respect to storage stability. The structure characterization was conducted by measuring the strength of the cocoa butter crystal network with traction tests combined with DSC melting curves. Subsequent storage stability was evaluated with DigiEye technique for fat bloom development and gravimetrical techniques for fat/moisture migration. The two pre-crystallization processes generated significantly different structures and storage stability. Well-tempered β_{VI}-seeding resulted in a dense and homogenous chocolate structure directly after solidification, which was optimal in order to retard fat bloom and fat migration. However, a too high structure density generated heterogeneous structures with reduced ability to withstand fat bloom. A lower structure density exhibited optimal resistance against moisture migration.

1. Introduction

Dark chocolate is a complex food product in which sugar crystals and cocoa particles are surrounded by a continuous phase of crystalline and liquid cocoa butter. Due to the hydrophilic nature of the sugar crystals a small portion of emulsifier, e.g., soy lecithin or polyglycerol polyricinoleate (PGPR), is often added to improve compatibility with the hydrophobic cocoa butter (Beckett, 2000). In comparison to the plain chocolate bar, filled confectionery products are more complicated as they contain a filling with fat or water components which have the potential of migrating into the surrounding chocolate shell causing structural and visual deterioration (Ghosh et al., 2002). Impairment or cracking of the shell, hardening of the filling, and development of a greyish haze on the product surface (fat bloom) has been associated with the migration of less stable TAGs or moisture from the filling (Ghosh et al., 2002; Hartel, 1999; Talbot, 1989; Ziegleder, 1997).

Cocoa butter can exist in six different crystalline or polymorphic forms (denoted by roman numerals I to VI and the Greek letters α, β and β′), each with a different thermodynamic stability and melting point (Timms, 1984; Wille and Lutton, 1966). The β_V form is the desired polymorph associated with good sensory attributes, stable microstructure, and retardation of fat migration (Dimick, 1991; Timms, 2002). The traditional pre-crystallization procedure during manufacturing for obtaining the stable β_V form involves subjecting the chocolate to a well-defined temperature program under the action of shear. This "conventional" pre-crystallization process induces the formation of a small proportion (i.e., 1–3% of volume) of seed crystals on which part of the remaining fat solidifies (Seguine, 1991; Stapley et al., 1999; Timms, 1984). An alternative "β_{VI}-seeding" pre-crystallization process was introduced in 1999 (Windhab, 1999). The β_{VI}-seeding uses homogeneous mixing of 0.05–1% (w/w) cocoa butter crystals in their most stable form (β_{VI}) with pre-cooled chocolate (32–34 °C) which results in a large number of small well-defined crystal nuclei. Although the seed crystal nuclei are in polymorphic form β_{VI}, the surrounding chocolate solidifies and grows in the preferred form β_V (Zeng, 2000; Zeng et al., 2002). Regardless of which pre-crystallization technique is applied, it is crucial for the shelf-life of the chocolate product that correct amounts of stable crystal nuclei for β_V-crystals are formed. Otherwise the chocolate is considered to be under- or over-tempered. If insufficient amounts of stable crystal nuclei have been produced during the pre-crystallization step, i.e., the chocolate is under-tempered, more under-cooling is required in order for crystallization to start and once it occurs, less stable polymorphic forms are generated, the crystallization rate is rapid and subsequent release of heat is high (Talbot, 2009). For over-tempered chocolate, high amounts of crystal nuclei are produced during pre-crystallization which induces crystallization already at high

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* Corresponding author at: SIK – The Swedish Institute for Food and Biotechnology, Box 5401, SE-402 29 Gothenburg, Sweden. Tel.: +46 10516 66 00; fax: +46 31833782.

E-mail address: lina.svanberg@sik.se (L. Svanberg).

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temperatures >30 °C. A frequently applied methodology to determine the state of temper is to plot the temperature–time relationship of the chocolate during cooling using a temper-meter device (Talbot, 2009).

The microstructure of under-, over- and well-tempered chocolate has previously been compared using mercury porosimetry, which established that well-tempered chocolate has a more dense structure (Loisel et al., 1997). Furthermore, recent work has shown that the contraction of chocolate during solidification differed depending on the degrees of temper which supports the idea that the decrease of volume causes a more dense structure, i.e., close-packing of the fat crystal lattice can be created (Galler 2011; Nestius Svensson 2011; Svanberg et al., 2011a). These results are coherent with migration studies where under-tempered chocolate proved to have higher saturation concentrations of hazelnut oil compared to well-tempered samples (Miquel et al., 2001) and also, the occurrence of fat bloom on samples with different temper degrees shows similar trends (Afoakwa et al., 2008; Loisel et al., 1997). Comparisons between conventional pre-crystallized and β_{VI}-seeded milk chocolate have previously been made with respect to solidification rate during cooling (Padar et al., 2008) as well as fat bloom development during storage (Zeng et al., 2002). However, no systematic study simultaneously comparing structure characteristics, fat/moisture migration and fat bloom during storage of under-, well- and over-tempered conventional and β_{VI}-seed pre-crystallized chocolate has been conducted.

The objective of this work was to gain a deeper understanding of the impact of the pre-crystallization process on storage stability in dark chocolate by characterizing physical and chemical properties that are related to the chocolate structure. Measurements were conducted both after solidification and during storage. Thus, chocolate microstructures with different structure density, i.e., close-packing of the fat crystal lattice, and homogeneity, i.e., evenness and connectivity of the fat crystal network, were created by β_{VI}-seeding or conventional pre-crystallization with different degrees of temper (over, well, under). The structure characterization after solidification and during storage was quantified by measuring the strength of the cocoa butter crystal network with traction tests combined with DSC melting curves to estimate the development stage of a homogeneous and dense fat crystal network. Subsequent storage stability was evaluated with the DigiEye technique for fat bloom development and gravimetrical techniques for fat and moisture migration.

2. Materials and methods

In this work an experimental approach to investigate the process–structure–property relationships in dark chocolate was developed. Estimates of the structure density were achieved by physical and chemical characterization of the dark chocolate using traction tests and DSC evaluation. An overview of the experimental set-up is presented in Fig. 1.

2.1. Sample preparation

Dark chocolate (39.6% cocoa mass, 10% cocoa butter, 50% sugar, 0.4% lecithin with a total fat content of 32%) kindly provided by Bühler Group AG (Uzwil, Switzerland) was pre-crystallized with conventional tempering or β_{VI}-seeding.

2.1.1. Conventional tempering

An Aasted Mikroverk laboratory three-stage tempering unit (Model AMK 10, Aasted Mikroverk A/S, Farum, Denmark) was used. First, the chocolate was heated to 50 °C for 2 h to erase previous crystal memory and thereafter the chocolate temperature in the three zones was adjusted to approximately 31 and 24 °C in zone 1 and 2 and varied between 29 and 31 °C in zone 3 to achieve under- and well-tempered chocolate.

2.1.2. β_{VI}-seeding

β_{VI}-seeds (seeds), were produced from a single stage shear crystallizer SeedMaster Cryst (Bühler AG, Uzwil, Switzerland). After production, the β_{VI}-cocoa butter crystal mass was allowed to solidify and stored at 15° until being used for pre-crystallization of dark chocolate. To establish that the solid cocoa butter/seed mix contained β_{VI}-seeds, DSC melting curves were collected before each pre-crystallization and displayed a distinct second peak at 34 °C (results not shown) corresponding to polymorphic form β_{VI}. The β_{VI}-seeding production was performed batchwise. For each production run, 2 kg chocolate was heated to 50 °C in a container for 2 h to erase previous crystal memory. The molten chocolate was thereafter poured into a water jacketed beaker connected to a wall-scraping mixer (BEAR Varimixer, A/S Wodschow, Brøndby, Denmark) and the temperature was quenched to 33 °C. Subsequently, the solid β_{VI}-seeds were grinded into a powder using a shredder and added to the pre-cooled chocolate. The mixture was left for 5 min while being stirred vigorously to allow dispersion of the crystal β_{VI}-nuclei. To obtain a different tempering degree, the amount of seeds added was adjusted and 0.2%, 0.7% and 2% of weight was used to achieve under-, well and over-tempered chocolate, respectively.

For both pre-crystallization processes the degree of tempering was verified with a MultiTherm Tempermeter TCTM (Bühler Group AG, Uzwil, Switzerland) and adjusted to give a temper index (TI) of 3 ± 0.1, 5 ± 0.1 or 6 ± 0.1 for under-, well- and over-tempered chocolate according to the built-in algorithm of the software. The given TI index values corresponds to under- (positive slope), well- (slope = 0) and over-tempered (negative slope) for the temperature vs cooling time plot as illustrated in Fig. 2. A summary of the different samples investigated is presented in Table 1. Each pre-crystallization process and subsequent sample production was repeated three times and 10 samples were collected from each production run for physical and chemical characterization and 25 samples for storage stability tests. This means that in total $5 \times 3 \times 35 = 525$ samples was produced for this study.

The pre-crystallized chocolate was poured into plastic molds, (cylindrically $h = 6$, $d = 22$ mm), except for the samples used for traction tests where the experimental set-up required a rectangular shape (5.5 × 7.7 × 55 mm), and allowed to solidify for 20 min in a temperature controlled cooling chamber at 11 °C.

2.2. Structure characterization by measurement of associated physical and chemical properties

The structure density, i.e., close-packing of the fat crystal lattice, and homogeneity, i.e., evenness and connectivity of the fat crystal network, was quantified by physical and chemical measurements. Physically, the strength of the fat crystal structure was measured with traction tests. Subsequently, assuming that the interaction between non-fat solids and cocoa butter was the same in all samples, an empirical relationship between the development stage of a connective fat crystal network and corresponding tensile strength could be established. The chemical analysis using DSC melting curves gave information on the polymorphic distribution in the structure as previously adapted by Afoakwa et al. (2009), Kinta and Hartel (2010) and Svanberg et al. (2011c).

2.2.1. Traction test

The tensile strength, i.e., tensile stress at the point of break, directly after solidification and during storage was measured by applying longitudinal forces to the samples by a traction test