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Review

Pre-crystallization process in chocolate: Mechanism, importance and novel aspects

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ABSTRACT

Pre-crystallization is an important step in the production of chocolate, which is defined as tempering of cocoa butter through primary and secondary nucleation. The goal of tempering is to obtain a sufficient amount of β_V polymorph of the right size. The pre-crystallization process has a great impact on the quality and production cost of final product. Development of chocolate technology requires the use of the most appropriate techniques and ingredients without negatively affecting the quality characteristics. Applications of novel technologies within the confectionery industry have allowed production of chocolate in sufficient quantities to meet the public needs. In order to provide and investigate the potential and usage of novel technologies, the present review focused on different pre-crystallization methods and factors affecting the processing conditions. Seeding and ultrasound-assisted pre-crystallization can be used as alternatives to conventional tempering process. However, in both methods, optimization of experimental conditions is required.

1. Introduction

Pre-crystallization process is an important stage in the manufacturing of chocolate, which influences its final quality (Dhonsi & Stapley, 2006; Glicerina, Balestra, Rosa, & Romani, 2013). Since cocoa butter displays polymorphic behavior, a pre-crystallization process is essential to obtain the stable polymorphic form (Afoakwa, Paterson, Fowler, & Vieira, 2008). Cocoa butter can crystallize into six various polymorphic phases named as form I ⟨alpha⟩, II ⟨alpha⟩, III ⟨beta-prime⟩, IV ⟨beta-prime⟩, V ⟨beta⟩, VI ⟨beta⟩ or as form sub-α, α, β'_2, β'_1, β_2, β_1, with respect to increasing stability and increasing melting points (Dahlenborg, Millqvist-Fureby, & Bergenstahl, 2015). The pre-crystallization process is carried out by a controlled melting and cooling of chocolate in order to attain the right crystalline structure of form V ⟨beta⟩ (Debaste, Kegelaers, Liegeois, Ben Amor, & Halloin, 2008).

In industrial chocolate manufacturing, crystallization of cocoa butter (alone or in chocolate) contains two steps: pre-crystallization by tempering to create seeds and secondary crystallization by cooling to allow the seeds to grow out. Producing the stable polymorphic form (β_V) requires complicated technology. For this reason, tempering of cocoa butter – a technique of controlled pre-crystallization – is applied to create a more thermodynamically stable polymorphic form of cocoa butter (Afoakwa, Paterson, Fowler, & Vieira, 2009a, 2009b; Mohos, 2010). If the correct tempering or pre-crystallization is applied, the proportion of the β_V crystal obtained by tempering is approximately 1–3% (Hartel, von Elbe, & Hofberger, 2018) and the proportion formed by cooling is about 45–60%. Crystallization is completed during storage, when the level of crystals of the β_V modification increases to 60–80% (Mohos, 2010).

Dramatic growth in emerging technologies, consumer's current satisfaction and future expectation, the global scale of industry and the advertisements all are the factors that have influenced chocolate market. Pre-crystallization is a sophisticated process and the tempering conditions are difficult to control in large scale productions. The conventional tempering is costly because of great energy consumption and also requires large space. In small manufacturing enterprises, the personnel professionality and experience of technician, determines the efficiency and validation of the pre-crystallization. However, under this strategy, standardized production might not be achieved. For this reason, inexpensive batch equipment exists in the market today.

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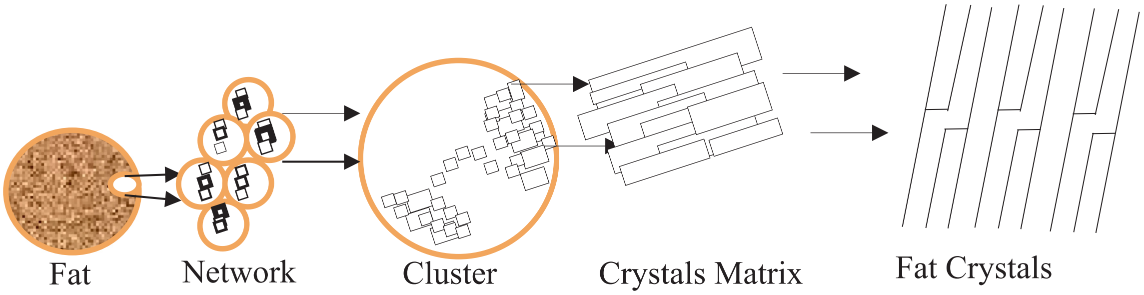

Fig. 1. The hierarchical structure of the crystals, cluster and network.

However, batch processes lead to processing inefficiencies, increase energy costs, and long processing times.

In addition, the effect of composition and novel ingredients such as alternative bulk sweeteners, alternative fats and emulsifiers or bioactive components on the tempering behavior of cocoa butter should be investigated, because, addition of sugar, cocoa particles, sorbitan monostearate and lecithin into chocolate have an impact on cocoa butter crystallization (Buscato et al., 2018; Dhonsi & Stapley, 2006; Miyasaki, Luccas, & Kieckbusc, 2015; Quast, Luccas, Ribeiro, Cardoso, & Kieckbusch, 2013; Svanberg, Ahrne, Loren, & Windhab, 2011). The addition of the sugar particles promoted the formation of polymorphs with lower melting points. It was suggested that the sugar acted as a heterogeneous nucleation agent, prolonging the nucleation and growth of cocoa butter crystals since foreign surfaces acted as nucleation sites for crystallization (Konar et al., 2017; Oba et al., 2017; Svanberg et al., 2011). In chocolate model systems, the addition of lecithin influenced the kinetics of cocoa butter crystallization. It somewhat retarded induction times in comparison to the cocoa butter/sugar mixture, which might be caused by lecithin covering the sugar crystals. This coating provides a weaker surface for heterogeneous nucleation to occur (Dhonsi & Stapley, 2006). For these reasons, new techniques as an alternative to conventional tempering process can be performed in order to induce the crystallization of the chocolate.

In the current review, the different pre-crystallization methods and influence of various techniques on final product quality have been studied extensively. The main contribution of this work is providing the industry with in-depth insights into how research and development experts can utilize different pre-crystallization methods in chocolate industry.

2. Cocoa butter and polymorphism

Cocoa butter is composed of three main fatty acids, palmitic, stearic and oleic, accounting for over 95% of the fatty acids in cocoa butter (Rogers, Tang, Ahmadi, & Marangoni, 2008). Fatty acids may exist in different positions on the glycerol molecule. The main cocoa butter fatty acids and their approximate proportions are: oleic acid (C 18:1, 29–38%), stearic acid (C 18:0, 29–38%) and palmitic acid (C 16:0, 20–26%) (Afoakwa, 2010; Beckett, 2000). The main triacylglycerols (TAG) in cocoa butter (80%) has a palmitic acid group in the sn-1 position, an oleic acid group in the sn-2 position and a stearic acid group in the sn-3 position. Each TAG will have a unique melting point and polymorphic structure related to that particular composition (Lipp & Anklam, 1998; Loren, Jonasson, Langton, & Hermansson, 2009; Minifie, 1989; Smit, 2011; Talbot, 1999).

A small proportion, 1–2% of cocoa butter TAGs, are all saturated (SSS, long chain tri-saturated triacylglcerols, where palmitic or stearic are the main saturated fats contributed on all positions) that melt at a much higher temperature than the other common types of TAGs. Based on composition, TAG may be either solid or liquid at room temperature; therefore, the composition of the TAGs is one of the main factors determining the chocolate's texture and also its resistance to fat bloom. The high amounts of unsaturated fatty acids in cocoa butter yields a softer product which melts easier, however cocoa butter with high levels of saturated fatty acids causes harder chocolate. In chocolates, long-chain tri-saturated triacylglycerols (SSS) will start to crystallize first from the molten mass. These triacylglycerols do not contribute to the temper of the final product. However, they will increase the viscosity of the tempered chocolate, because their crystallization reduces the amount of liquid fat in the chocolate. Afterwards, the SOS triacylglycerols (the StOSt, POSt and POP of the cocoa butter) will begin to crystallize. These triacylglycerols will give chocolate its temper which will seed the mass of the chocolate in a polymorphically stable form. In the second stage, the asymmetrical form of the SOS triacylglycerols, the SSO (saturated–saturated–oleic) group, can begin to crystallize. The SOS crystals determine the chocolate's texture and resistance to fat bloom (Beckett, 2008, 2009; Lindecrantz, 2014).

Fat crystal networks are formed of branched, interlinked particles that generate a three-dimensional network, and the voids are filled by liquid fat. These crystals aggregate to constitute clusters. Clusters further interact with each other to create flocs and finally form three dimensional networks. The resulting crystalline structure is responsible for different attributes of the product. For example, crystalline structure of cocoa butter not only influences gloss and stability of chocolate but is also responsible for the chocolate texture (Hartel et al., 2018). Fig. 1 illustrates the hierarchical structure of the concepts of crystallite, particle and cluster within the crystal network (Mohos, 2010).

There are two types of polymorphic behavior, namely monotropic and enantiotropic. Fundamental differences exist in their thermodynamic properties. In a monotropic manner, crystalline transition will only take place from less stable with lower melting forms to more stable with higher melting forms. However, in enantiotropic polymorphism, each crystal has a certain range of stability. Depending on the situation, crystalline modification can go in either direction to form stable crystalline form or vice versa. Cocoa butter exhibits polymorphism in a monotropic manner (Mohos, 2010).

A great number of studies have already been conducted in the field of polymorphism and phase transitions of cocoa butter. These studies approved the presence of five basic polymorphs in cocoa butter (Merken & Vaeck, 1980). However, in general the existence of six polymorphic forms of cocoa butter has been confirmed. They are: sub-α (β_I), α (β_{II}), β_2' (β_{III}), β_1' (β_{IV}), β_2 (β_V) and β_1 (β_{VI}) polymorphs. In unstable polymorphic forms (β_I and β_{II}) the fatty acid units have vertical oriented (zero tilt) structure and the molecules are packed randomly with hexagonal conformation. The fatty acids chains are vertical to the methyl end group. The mentioned polymorphs are the least stable crystals and have the lowest melting point, melting enthalpy and density. β'_{III} and β'_{IV} polymorphs are in an orthorhombic arrangement. In the crystal network, the chains are packed in a wavy arrangement with certain angles. For this reason, they have more stable crystals with higher melting points than hexagonal arrangement. The β_V and β_{VI} polymorphs have the fatty acid units packed parallel to each other in a triclinic form. The former polymorph is usually the most stable and possesses the highest melting point, melting enthalpy and density. In other words, the β′ forms are usually found in spherulites with needle arrangements, while β forms are more plate-like and may be stacked in multi-layers (Acevedo & Marangoni, 2015; Hartel et al., 2018). Thermodynamic properties are influenced by polymorphs due to molecular composition and chain packing of crystals. Melting points of the polymorphic forms of cocoa butter are: β_I: 16–18 °C, β_{II}: 21–22 °C, β_{III}: 25.5 °C, β_{IV}: 27–29 °C, β_V: 32–34 °C and β_{IV}: 34–36 °C.

The TAG chemical composition, amount of emulsifiers, the amount of milk fat and any other fat present have a major impact on the crystallization kinetics of a cocoa butter. This affects the formation of the crystal network, which in turn determines and consequently modifies the quality of chocolate. This is important in chocolate industry, which influences process control and final quality characteristics. Various factors affect the rate of polymorphic transition, including the processing conditions, composition of the fat, the genetic origin of cocoa butter, growth location, climatic and soil conditions (Afoakwa, 2010).

An example of monotropic polymorphism occurs in chocolate tempering. Least stable forms crystallize first and transform to more stable polymorphs over time. However, under the normal circumstances, all the polymorphs can be crystallized straightly from molten cocoa butter except for $\beta(_{VI})$. Fig. 2 illustrates the polymorphic phase transition (from melting to crystallization) scheme of cocoa butter under isothermal and nonisothermal conditions (Depoortere, 2011; Le Reverend, 2009). These transformations may either occur through two different mechanisms: i) melting and re-crystallization (melt-mediated) or ii) by molecular rearrangement (solid-mediated) (Hartel et al., 2018). Melt-mediated mode of polymorphic transformation occurs under commercial conditions in chocolate technology. During chocolate tempering a polymorphic transition from β′ to β takes place by mixing the chocolate mass. Fig. 3 indicates the transition $\beta'(_{IV}) \rightarrow \beta(_V)$ of the crystal modifications of cocoa butter.

The rate of polymorphic transition is influenced by several factors: in particular (i) the fat composition, (ii) components present in the matrix, and (iii) the processing conditions. In addition, temperature, shear/agitation and duration time may lead to phase transitions. Bulk sweeteners and emulsifiers used in chocolate formulation also affect the rate of polymorphic transformation (Konar et al., 2017; Oba et al., 2017).

3. Pre-crystallization and chocolate quality

Tempering is a critical phase in chocolate manufacture. βv polymorph (Form V ⟨beta⟩ or β_2) is the most preferred form, because it gives the desired sensory attributes (the proper melting point, glossy appearance, good snap and contraction) and provides the most resistance against liquid oil migration (enhance shelf life characteristics) (Afoakwa et al., 2008). The fat bloom and migration may be determined by the cocoa butter used (Depoortere, 2011) and process conditions especially pre-crystallization. Therefore, nucleation and growth of stable cocoa butter crystal polymorphs during tempering have a major effect on final quality.

Smith, Zand, and Talbot (2008) noted that the control of crystallization is crucial for color, texture, melting profile and other quality characteristics. Color is an important quality parameter of chocolate. The shiny or glossy appearance of chocolate is well appreciated by the consumer. Pre-crystallization process of chocolate has a major influence in obtaining desired appearance. In well-tempered chocolate the presence of very small cocoa butter crystals create a smooth layer at the surface of the chocolate. Thus a desirable shiny or glossy appearance is obtained. Tight crystalline cocoa butter matrix in well-tempered chocolate provides a glossy surface (Hartel et al., 2018). Strong crystal network exhibits high degree of snap and hardness.

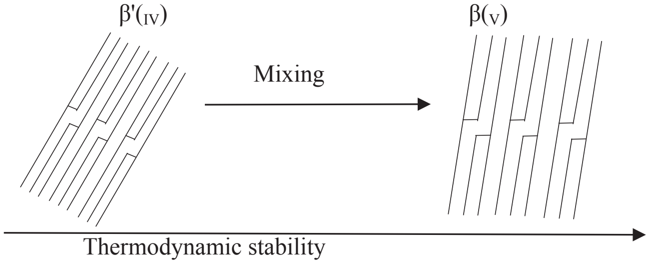

Fig. 2. Polymorphic transformation of cocoa butter polymorphs $\beta'(_{IV}) \rightarrow \beta(_V)$.

In over-tempered chocolate there will be large cocoa butter crystals and it is considerably more viscous than tempered chocolate. Over-tempered chocolate does not flow easily in enrobers or into molds, resulting in appearance defects such as air bubbles (Hartel et al., 2018). Under-tempered chocolates lead to the formation of unstable β_1' polymorph. Thermostability changes can be observed later as unstable β_1' polymorph with low-melting point transforms into more stable Form VI ⟨beta⟩ (β_1) polymorph. Therefore, this can cause undesirable fat bloom formation during storage (Altimiras, Pyle, & Bouchon, 2007).

The rate of crystallization is a critical factor in the handling of chocolate in tempering, enrobing, and molding. Nucleation and crystal growth also cause increase in chocolate density. Density not only affects transport of chocolate but also causes desired volume contraction, which facilitates the mold release (Lonchampt & Hartel, 2004; Minifie, 1989). If the degree of temper is acceptable, chocolate solidifies rapidly, contracts easily in molds and presents high degree of snap and hardness (Hartel et al., 2018). However, chocolate density depends also on the fat level and ingredients used in the chocolate composition.

4. The impact of novel ingredients on pre-crystallization

4.1. Alternative emulsifiers

Fat bloom formation is one of the key concerns related mainly with storage situations of chocolate. Fat crystallization transition is the main proof for this unpleasant phenomenon. Modifying chocolate composition is a solution to postpone fat bloom development. For example, replacement of lecithin by sorbitan tristearate, sorbitan monostearate or poly-oxyethylene sorbitan monostearate is considered to delay fat bloom formation by retarding the β_V to β_{VI} crystal transition (Lonchampt & Hartel, 2004). In the study of Masuchi, Grimaldi, and Kieckbusch (2014) adding 0.5% sorbitan monostearate to cocoa butter as crystallization modifier stimulated an increase in the onset of the crystallization temperature. The current behavior of sorbitan monostearate was related to its low solubility in organic medium and ability of self-assembling, creating a three-dimensional network able to entrap the lipid phase. Tran et al. (2015) assessed the addition of StOSt-rich stearins from non-cocoa butter fats to plain and to filled dark chocolates. They finalized that 70/30 combinations of cocoa butter with Vietnamese mango fat or with Indian mango fat stearin increased the fat bloom stability of dark chocolate, because it increased the amount of StOSt content.

Buscato et al. (2018) evaluated fat bloom development in dark chocolate by adding sorbitan monostearate or cocoa butter stearin. Results indicated that under oscillating storage situation, chocolates with cocoa butter stearin and sorbitan monostearate delayed the fat bloom formation by at least 45 and 15 days, respectively, compared to control chocolate. The addition of 6.0% of cocoa butter stearin increased the content of monounsaturated triacylglycerols (StOSt and POSt) in the chocolate formulation. The mentioned triacylglycerols – typically the StOSt – are the basic triacylglycerols responsible for the appropriate crystallization pattern of chocolate structure (Schenk & Peschar, 2004); thus, their existence in the cocoa butter stearin formulation led to the formation of a more stable β_V crystal network structure, increasing the thermal resistance of the dark chocolates, being able to delay fat bloom formation. The addition of 0.15% sorbitan

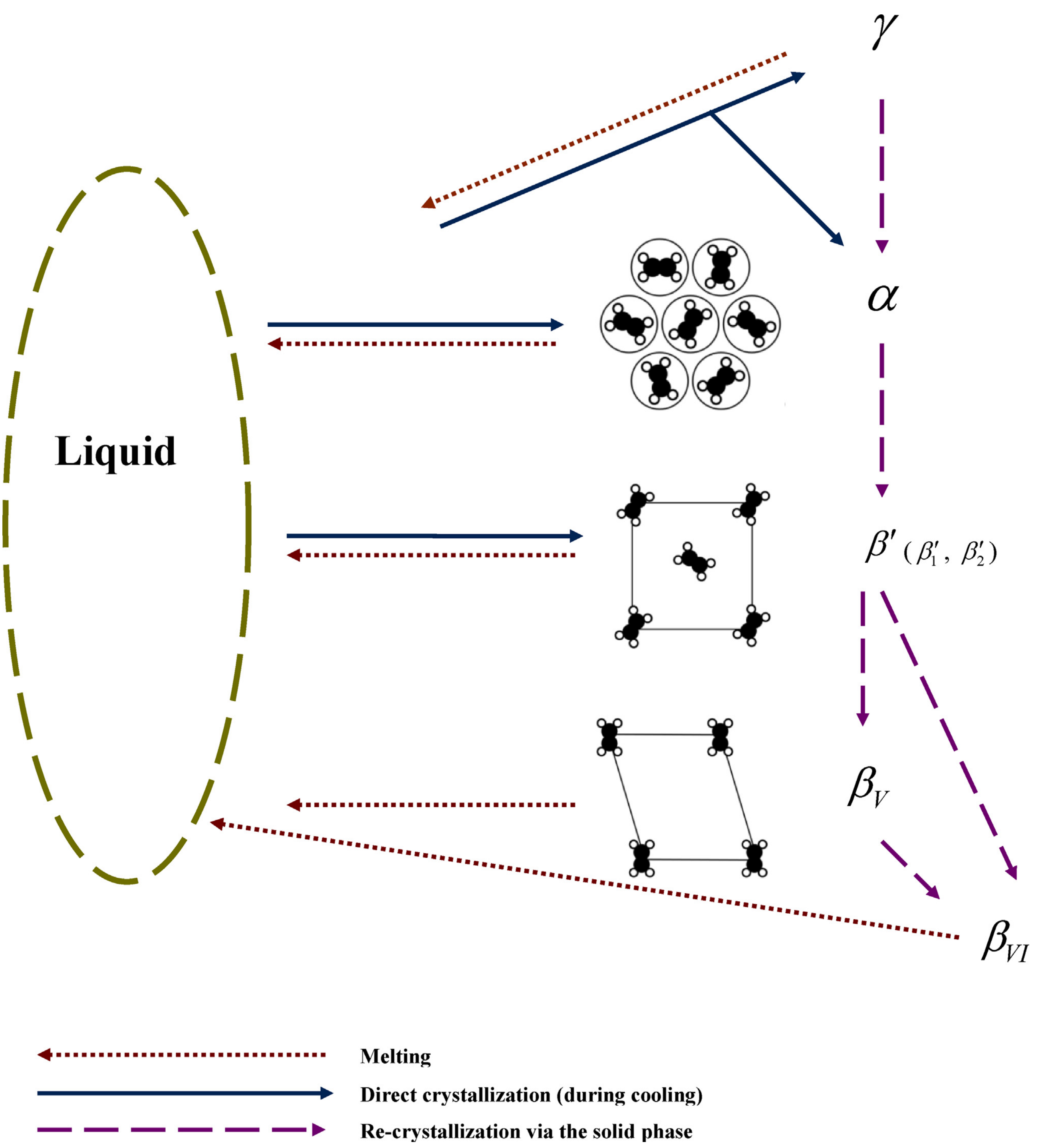

Fig. 3. Polymorph phase transition.

monostearate also retarded the fat bloom development in chocolates. This emulsifier was able to create a three-dimensional network and entrap lipid crystals in this frame, increasing the thermal resistance of the lipid phase and hampering the polymorphic transition (Masuchi et al., 2014).

Also modified soy lecithins could be used as alternatives to standard soybean lecithin. They can control polymorphism by acting as crystallization agent and anti-bloom agent. Miyasaki et al. (2015) determined the impact of modified lecithins (hydroxylated, enzymatically hydrolyzed, acetylated, and defatted lecithins – 0.2, 0.5, 0.8% w/w) on crystallization properties of cocoa butter. It was concluded that lecithins could act as co-crystallizers in cocoa butter crystallization. Thus, the increase in crystallization rate was contributed to presence of the high melting point phospholipids and also to solids present in lecithins.

4.2. Alternative fats

There are several fats that crystallize directly to the beta prime form, therefore do not require to be subjected to the pre-crystallization stage. These alternative fats are cocoa butter replacers (CBRs) and cocoa butter substitutes (CBSs). It seems that due to the physicochemical properties of the alternative fats and also their polymorphic form they can be used along with cocoa butter in chocolate production. Physical properties of pre-crystallized cocoa butter containing of CBR or

CBS fats (5–30% w/w) were evaluated by Quast et al. (2013). The results acknowledged the main formation of the beta polymorph form for cocoa butter and beta prime form for CBR and CBS. Mixtures of cocoa butter and CBR fat presented chemical compatibility. Mixtures with up to 20% CBR fat and up to 5% CBS was suggested for chocolate formulations without considerably altering the polymorphic habit. Also alternative fats had no impact on the crystal structuration of cocoa butter.

Hassan and Megahed (1998) assessed the behavior of mixtures of cocoa butter with three different fats: two with lauric origin and one nonlauric fat. In the case of the lauric fats, an addition of 5% to cocoa butter promoted a significant reduction of the solids content at 25 °C. The nonlauric fat exhibited a profile more similar to the solids curve of cocoa butter and was suggested to partially replace cocoa butter in the chocolate production.

5. Pre-crystallization methods

Two distinct steps exist in the crystallization process: (i) nucleation and (ii) growth. When a system has become supersaturated, nucleation can occur. In essence, an adequate number of molecules are required to form a molecular cluster of sufficient size to become a stable nucleus. Nucleation may be homogeneous or heterogeneous. Heterogeneous nucleation involves an external component during nucleus formation however homogeneous nucleation, occurs in the volume of the system and in the absence of any external surface (Chow, Blindt, Chivers, & Povey, 2005; Kurotani, Miyasaka, Ebihara, & Hirasawa, 2009). Heterogeneous is the nucleation on surfaces; not only on dust particles, but also on the container walls.

The industrial crystallization of chocolates consists of two steps: namely pre-crystallization (tempering) and cooling. Although conventional tempering involves different time-temperature processes for inducing nucleation of the cocoa butter, alternative methods are also developed to better manage the crystallization process. These new techniques have received attention because they either (i) avoid the nucleation phase in crystallization or they (ii) provide alternative methods to induce the crystallization of chocolate with appropriate and stable form of crystals.

Seeding technique is used as an alternative to conventional tempering process where nucleation of lipids is bypassed through addition of seed crystals; therefore, the seeds can initiate crystallization of the remaining cocoa butter. Ultrasonication as a mean of tempering has been applied to control lipid crystallization. In recent years, application of ultrasonic processing has been applied in chocolate manufacturing as a novel technique with positive impacts on lipid crystallization.

5.1. Conventional pre-crystallization – tempering

Tempering is typically a complex thermal process that generally involves mixing and cooling the liquid chocolate under controlled conditions to ensure that the cocoa butter phase can crystallize in its most desirable form, βv (Schenk & Peschar, 2004). The purpose of tempering is to produce an adequate number of seed crystals in liquid chocolate to enable solidification upon cooling with more stable and desired polymorphic form (βv).

During tempering, the amount of nuclei is critical, and in well-tempered chocolate the amount of 1.0–5.0% of stable cocoa butter crystals indicates completion of nucleation (Beckett, 2000), which also increases the viscosity of the liquid chocolate. In the first stage of tempering, chocolate should be heated to 45–50 °C to ensure complete melting of the crystals. Chocolate should not proceed to the next stage until all the chocolate is completely liquid. In the second stage, the melted chocolate is cooled (27–29 °C) and mixed to induce crystallization. The type of cocoa butter crystal formed at the wall is determined by the cooling wall temperature (Fig. 4). In the last stage, tempering is followed by a heating step above the melting point of the unstable α and β' crystals but below the melting point of the desired βv. The rise in temperature adjusts the chocolate viscosity for later molding or enrobing processes. The optimal temperature depends slightly on the nature of the fat phase in the chocolate (Richter, 2009; Smith et al., 2008). After tempering and forming, chocolate is gently cooled to promote crystal growth. Crystallization continues during cooling, forming a micro-homogeneous solid cocoa butter crystal network (Richter, 2009; Smith et al., 2008).

Time, temperature and agitation are the most important factors affecting tempering process (Hartel, 1991). The type of chocolate should also be taken into account when determining the crystallization temperature. This is because pre-crystallization kinetics are influenced by the presence of different fats in the composition. For instance, dark chocolate is cooled to 27–28 °C, while for milk chocolate this value is 26–27 °C. The reason is milk fat slows down cocoa butter crystallization; therefore the temperature is lowered to speed up the rate (Hartel et al., 2018). Heterogeneous nucleation is carried out at cooled walls in the cooling section of the tempering machine. At temperatures below 22 °C in the cooling section, least stable polymorphs (sub-α) are most likely to crystallize first based on differences in crystallization rate. This is explained with the lower energy barrier for crystal nucleation. However, between 22 °C and 27 °C in addition to unstable β_{III}/β_{IV} polymorphs, a small fraction of the stable β_V polymorph is formed. During mixing the chocolate mass, the unstable polymorphs are gently transformed into the β_V type due to the temperature increase in the subsequent reheating section. The increase in temperature melts the unstable forms, leaving behind some stable V ⟨beta⟩ crystals (Hartel, 1991; Richter, 2009; Smith et al., 2008).

In general, pre-crystallization requires time to produce stable nuclei in sufficient quantities to ensure a homogeneously tempered chocolate. The differences in crystallization time among cocoa butters are due to differences in cocoa butter origin, which influences fatty acid composition. Different chocolates will have different extents of seed crystal formation when tempered with the same temperature profile. According to Nelson (1988), when the chocolate is tempered over a longer period, the higher the concentration above the solubility and the more likelihood of metastable polymorph formation occurs. Hartel et al. (2018) stated that the rate of crystal nucleation influences crystal shape and size, which may have considerable impact on the physical characteristics of chocolate. However, the production capacity, energy efficiency and the costs should be taken into account in adjusting the tempering time. Furthermore, if tempered chocolate is held too long, it becomes over-tempered leading to difficulties in subsequent processes. Therefore, it is necessary to establish optimum pre-crystallization conditions to obtain sufficient amount of β_V polymorph.

Mixing efficiency, mass transfer rates and heat transfer rates are influenced by agitation or stirring rate applied in the pre-crystallization. However, it has been proven that the intense shearing in mixing negatively influences the polymorphic form by increasing temperature. For this reason, mixing speed needs to be optimized. Therefore, knowledge of the isothermal behavior of cocoa butter is important to optimize production processes (Foubert, Vanrolleghem, & Dewettinck, 2003).

In most chocolate industries, chocolate is tempered continuously by passing through a series of scraped surface heat exchangers that expose the melted chocolate to a controlled thermal profile. Appropriate temperature is applied to not cause temperature to go up (Hartel et al., 2018). Nowadays, industrial heat exchangers are generally provided with computer-aided control equipment. There are usually at least three heat exchangers. However, equipment with seven or more exchangers exist (Beckett, 2008).

As a general rule, the chocolate is cooled to 32 °C in the first heat exchanger. The product is cooled a little more in the intermediate exchangers. In this stage, crystallization occurs with mixture of polymorphs and ultimately in the last stage chocolate is reheated to transform the unstable polymorphs into the desired and stable β seed

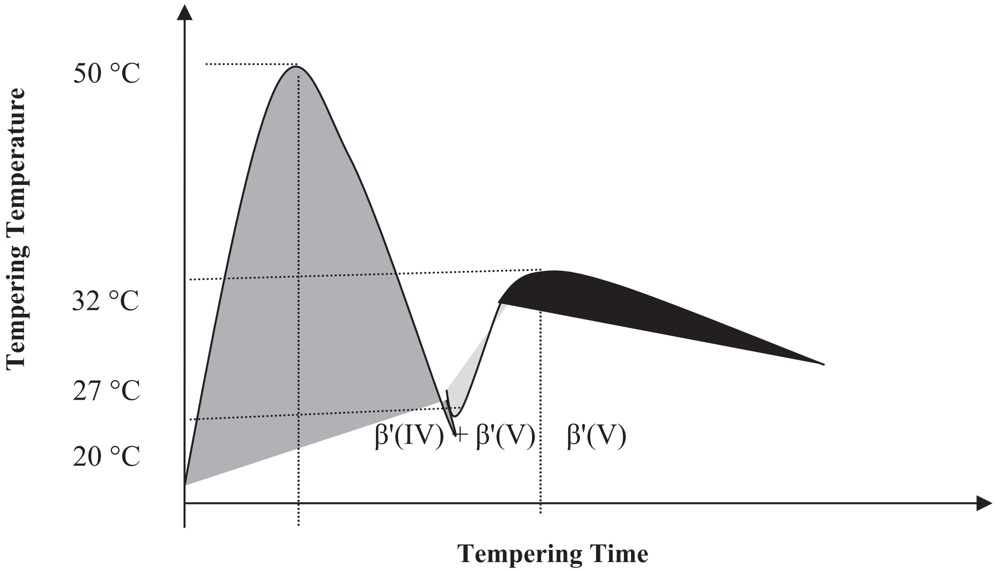

Fig. 4. Temperature-crystallization profile during tempering of chocolate.

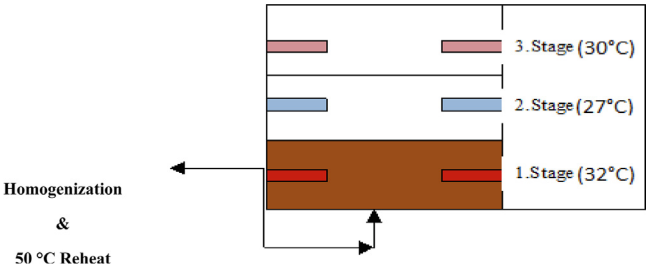

Fig. 5. Simplified image of a continuous tempering machine.

crystals. The process is shown in Fig. 5. During the final stage (zone 3), the temperature of the chocolate is raised to transform the unstable crystals to only stable, βv seed crystals (Cebula, Dilley, & Smith, 1991; Slettengren, 2010).

A wide range of heat exchangers for continuous tempering such as, screw-type tempering machines, horizontal, vertical, disc-type, scraped-surface and rotating-bowl tempering machines have been produced (Smit, 2011).

5.2. Seeding method

An alternative tempering process can be performed by inoculating solid chocolate (solid material with properties of nucleation agents) or cocoa butter consisting of forms V ⟨beta⟩ and/or VI ⟨beta⟩ nuclei (crystallization seeds) to melted chocolate to initiate the crystallization of chocolate with stable crystal forms. In this technique, nucleation of lipids is bypassed through addition of seed crystals (Konar et al., 2017). The nucleus arises spontaneously in the supersaturated system; the seed crystals are introduced purposely to facilitate crystallization. Importantly, the critical nucleus stands in labile equilibrium with the mother phase (i.e., the probabilities for its growth and dissolution are equal), while the seed crystals are much larger, thus ensuring crystal growth. Seeding was first introduced by Windhab (1999). This technique uses homogeneous mixing of 0.05–1.00% (w/w) cocoa-butter crystals in their most stable and desired form with pre-cooled chocolate (32–34 °C) which results in having a great number of small and well-defined crystal nuclei. Pre-crystallization with seeding has the potential to retard fat bloom (Kinta & Hartel, 2010; Lindecrantz, 2014; Svanberg, Ahrne, Loren, & Windhab, 2013) and fat migration in chocolate. Also it could work out the disadvantages including; inadequate tempering, heterogeneous nucleation during cooling, incomplete crystallization and crystalline instability (Ribeiro et al., 2015).

The seeding technology confers several advantages including improvement in shelf life (Svanberg et al., 2011), faster crystallization (Kinta & Hartel, 2010), lower energy consumption due to one stage of heat treatment and therefore less equipment and specialized personnel needs, (Lindecrantz, 2014) all resulting in cost reduction of the process. Furthermore, seeding has the ability to improve thermodynamic stability (Hachiya, Koyano, & Sato, 1989; Ribeiro, Basso, dos Santos, et al., 2013) and melting profile (Lindecrantz, 2014; Ribeiro, Basso, dos Santos, et al., 2013) as well as other quality properties associated with chocolate such as glossy surface and good molding properties (Lindecrantz, 2014). In the process of seeding, the temperature control is critical for the durability of stable crystalline seeds. Furthermore, the proportion of the mass of the solid material incorporated and the mass of the melted fat to be crystallized, inoculation temperature and cooling rate are the factors influencing this techniques efficiency (Debaste et al., 2008).

Various studies have related using the seeding technique during chocolate production and its influence on quality parameters. For example, Svanberg et al. (2011) studied the effect of sugar, cocoa particles and lecithin on cocoa butter crystallization prepared by both pre-crystallization methods, seeded and nonseeded. They reported that the addition of sugar prolonged the nucleation and growth of cocoa butter crystals compared to corresponding treatments with cocoa particles. The presence of sugar promoted the formation of lower melting polymorphs, because it seemed to act as a heterogeneous nucleation agent. Lecithin slightly retarded induction time compared to butter/sugar mixture. This effect is attributed by coating the sugar crystals by lecithin (Dhonsi & Stapley, 2006).

Other studies investigated the influence of β_V seeding technique as an alternative to conventional tempering process on milk (Konar et al., 2017) and dark (Oba et al., 2017) chocolates prepared by using different bulk sweeteners, i.e. maltitol and isomalt. Based on the obtained results, bulk sweeteners had a potential effect on pre-crystallization and influenced the quality characteristics of the chocolate.

Seed crystals can be formed from different sources although seed crystals must have the proper polymorphic form of cocoa butter or chocolate. The polymorphic form of the seeds and the chocolate origin are the most important factors affecting the pre-crystallization process. Saturated or unsaturated triacylglycerols are the active nucleation agents used in the seeding method. Symmetrical disaturated triacylglycerols are recommended to use for crystallization of cocoa butter due to its greater inclination to create the polymorph β_V. These crystallization agents also avoid the $\beta_V \rightarrow \beta_{VI}$ transition (Smith et al., 2008). In the study of Lindecrantz (2014), for optimal pre-crystallization of chocolate, three different seed powders (cocoa butter β_{VI}, cocoa butter β_V and chocolate β_V) were used. Chocolate seeded with cocoa butter β_V was found to have the best resistance to fat migration and fat bloom.

For polymorphic conformity, thermal stability and resemblance of aliphatic chain, particular molecular interactions between the crystallization agents and the fat should be carried out (Sato, 2001). The seed agents should contain the similar polymorphic form commonly β' or β. In terms of the resemblance of aliphatic chain it should have the similarity in chain length and also chemiscal structure of fatty acids (the degree of saturation). The differences in the number of carbon atoms between the crystallization agents and the fat should not be higher than 4 carbons (Takiguchi, Lida, Ueno, Yano, & Sato, 1998). The melting point of crystallization seeds should be higher than the melting point of the fat because in this way the seeding agent will not melt in the liquid phase at the inoculation temperature (Himavan, Starov, & Stapley, 2006).

Adequate agitation and time are needed to ensure complete dispersion of seed crystals into the chocolate mass (Hartel et al., 2018). Differences in agitation time among chocolates are due to differences in composition. The optimal Temper Index value (TI 4.0–6.0) was found to be slightly different for the two types of milk and dark chocolate produced with maltitol and isomalt. Using different bulk sweeteners significantly affected tempering attributes of the chocolate samples ($p < 0.05$) (Konar et al., 2017; Oba et al., 2017). The time between seed addition and cooling is a deterministic factor to ensure that the seed crystals grow enough to promote proper solidification (Hartel et al., 2018). Therefore, mixing time is one of the most important factors to be included in optimization studies when seeding is applied.

The amount of seed crystals needed in order to get a well-tempered chocolate is specific to the technique used. New seeding techniques use between 0.5% and 1.5% stable polymorphs seed crystals to obtain optimally-tempered chocolates. Compared to the conventional tempering, fewer amounts of crystals are needed and this may have economic benefits. The amounts of β_V polymorph targeted vary from 1 to 3% in the conventional process. This amount of seeds will ensure lower viscosity in the tempered chocolate. If higher amount of seeds are used, it will cause higher viscosity of chocolate, which could result in some difficulties in molding and enrobing processes. Therefore, optimization of ingredient amounts especially cocoa butter and emulsifier is a critical factor to be considered in seeding technique.

Furthermore, Padar, Jeelani, and Windhab (2008) and Zeng, Braun, and Windhab (2002) compared the crystal growth rate and fat bloom development in milk chocolates pre-crystallized with cocoa butter seed suspension and conventional method, respectively. Also, Svanberg et al. (2013) studied the effect of pre-crystallization process on storage stability of dark chocolate. It was argued that tempering by β_{VI}-seeding caused some advantages in terms of retarding fat bloom and fat migration. Svanberg et al. (2011) investigated the effect of sugar, cocoa particles and lecithin on cocoa butter crystallization in seeded and unseeded chocolate. The seeding technique had a pronounced effect on the crystallization kinetics resulting in homogenous microstructure and longer shelf life of chocolate. Ribeiro, Basso, dos Santos, et al. (2013) reported that the blends of cocoa butter/seed crystals proved to be effective additives to adjust the crystallization characteristics of cocoa butter in terms of crystallization kinetics and thermal behavior. Bloom formation in chocolate prepared with different levels of cocoa butter seed addition was investigated. The obtained results showed that the mechanism of bloom development in poorly tempered chocolate is due to formation of insufficient seeds. Higher amounts of added seed crystals lead to greater level of β crystal formation (Kinta & Hartel, 2010).

Hachiya et al. (1989) examined the effects of seeding of fat crystals on the crystallization kinetics of cocoa butter and dark chocolate. The findings indicated that the seeding process presents more advantages compared to conventional tempering. With this process, seed crystals containing β_{VI} polymorphs in addition to β_V polymorph were used. The remaining liquid cocoa butter solidifies around the seeds during cooling and grows in the preferred form of β_V. Regardless of which pre-crystallization method is applied, the amount of stable β_V crystal has a crucial impact on the shelf life of the chocolate product. In a conventional tempering, during the pre-crystallization stage, if insufficient amounts of stable crystal nuclei is formed, less stable polymorphs are generated, this result in a chocolate with a lower melting point. Such a chocolate will have shorter shelf life (Svanberg et al., 2013).

Crystallization seeds in form β_V, gained from spray freezing have been used in chocolate production and the results confirmed the brightness and well shelf-life stability of the samples (Van Malssen, Van Langevelde, Peschar, & Schenk, 2001). Moreover the different combinations of TAG were produced as crystallization seeds (Vereecken, Foubert, Smith, & Dewettinck, 2009). The optimum blends were reported as; blending crystals tripalmitin (PPP) and 1-palmitoyl-2-oleoyl-palmitin (POP) and tristearin (SSS) and 1-stearyl-2-oleoyl-stearin (SOS).

Hardfats or fully hydrogenated oils at low levels are suggested to be used as crystallization modifiers of fats and oils. de Oliveira, Ming, Ribeiro, and Kieckbusch (2011) showed that the addition of 1% hardfats (from cotton seed, palm, and soybean oils) into palm oil reduced the crystallization induction time. Ribeiro, Basso, and Kieckbusch (2013), reported that using hardfats offers efficient potential as modifiers of the physical properties of cocoa butter.

Different types of seeding techniques are available to obtain a controlled and stable number of polymorphs. For example, using micronization techniques in crystallization process is capable of generating very small and uniform particles of cocoa butter with different physical properties.

5.3. Ultrasound-assisted pre-crystallization – sonocrystallization

Ultrasound technology is described as sound waves with frequencies applied greater than the human hearing range. The hearing limited frequency in humans is generally 20 kHz–20,000 Hz. Several physical, chemical and biochemical effects are considered in a variety of applications however it depends on the frequency and also the amplitude of sound wave. Ultrasound waves are basically categorized into two groups according to their frequency and power. Ultrasound ranging above 1 MHz is specified as diagnostic ultrasound. Ultrasound ranging between 20 and 100 kHz is defined as power ultrasound, which is applied in food processing (Leonelli & Mason, 2010; Zheng & Sun, 2006), namely in drying, filtration and extraction (Higaki, Ueno, Koyano, & Sato, 2001; Rastogi, 2011). It has been illustrated that sonication affects crystallization in different lipid sources and can be applied to gain particular polymorphic forms. An important parameter that has a significant effect on fat nucleation is external energy input, whether by mixing or shearing rate from a stirrer or an external energy source for example, ultrasound (Hartel et al., 2018). Ultrasound assisted crystallization process is called “sono-crystallization”, a novel and effective technique in comparison with the conventional processes. The power ultrasound method that is used in super-cooled and supersaturated crystallization processes could enhance the nucleation rate, thus improving the crystal development and arrangement (Fig. 6). Therefore, sono-crystallization is a potential technology for application in cocoa butter crystallization and the utilizatiom of this technology could deliver commercially noteworthy advantages and consequences for the chocolate industry. Ultrasonic technology can propose a time/energy saving alternative to yield high quality chocolate without tempering. However, it is necessary to figure out the consequences of over-exposure and under-exposure of sonication in the chocolate mass; particularly its influences on polymorphic conformation and flavor effect.

Researchers have proved the impact of sonication technique on

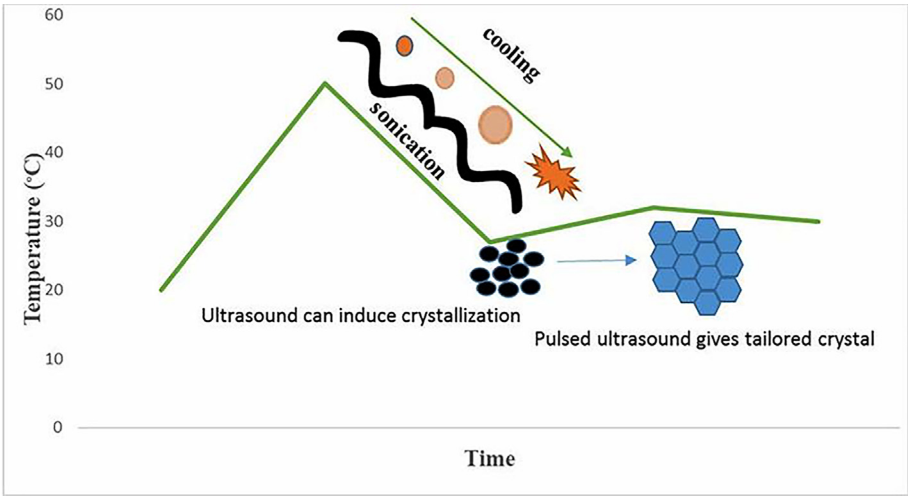

Fig. 6. Scheme of sono-crystallization.

cocoa butter crystallization (Higaki et al., 2001; Zhang, Sun, Zhiwei, & Cheng, 2015). In the case of crystallization processes, ultrasound is used for inducing nucleation and promoting the growth of crystals (Otero, Martino, Zaritzky, Solas, & Sanz, 2000), so the rate of crystallization could be enhanced (Chemat, Huma, & Khan, 2011). Under the ultrasound effect, the stochastic and spontaneous character of the crystallization could be adjusted (Delgado & Sun, 2001). Spontaneous polymorphic inter-conversion is energetically favorable. Therefore, even a speck of the lower energy polymorph could convert large stockpiles of unstable polymorphs.

The induction mechanism of primary and secondary nucleation by ultrasound may be via both acoustic energy and cavitations (Ruecroft, Hipkiss, Ly, Maxted, & Cains, 2005). The crystallization processes of different fats and oils including cocoa butter, trilaurin, tripalmitin, shortening, anhydrous milk fat, soybean oil and palm kernel oil have been extensively studied by the ultrasound technique (Higaki et al., 2001; Martini, Suzuki, & Hartel, 2008; Suzuki, Lee, Padilla, & Martini, 2010; Ueno, Ristic, Higaki, & Sato, 2003; Ye, Wagh, & Martini, 2011).

The results from the influence of ultrasound utilization on crystallization behavior of cocoa butter (Higaki et al., 2001) and the application of sonication method in dark chocolate tempering (Rosales, 2014) indicate that, ultrasound has the potential to give a stable and desired polymorphic form (β_V) yielding similar quality attributes to conventional tempered chocolate with enhanced storage stability. Furthermore, the findings obtained from Haupler, Peyronel, Neeson, Weiss, and Marangoni (2014) confirmed the related results to the ultrasound assisted crystallization of the cocoa butter. Ultrasonic crystallization enhances the characteristics of molecular shape, size and crystal arrangements as ultrasonication stimulates homogeneous interactions between lipid molecules by promoting their nucleation. In addition ultrasound increases the sample temperature, particularly at elevated crystallization temperatures. However, these applications need to be tested in various chocolate matrixes, because ingredients are considered to have a great impact on fat pre-crystallization (Konar et al., 2017).

Ultrasound-assisted crystallization requires further investigation to understand the nucleation behavior under different process conditions. Amplitude, frequency value, pulse width and time period are the main factors to be specified. Differences in temperature significantly influence the state and nature of pre-crystallization (formation of β_V polymorph); therefore, the temperature of chocolate mass should be kept constant. Raising the temperature is strongly dependent upon time of exposure. This illustrates that variation in chocolate mass temperature in using ultrasound method should be controlled to obtain the desired polymorphic form. A continuous system offers in-line ultrasound equipments based on the production capacity.

The application of ultrasonic as an alternative technique to conventional tempering has been extensively discussed by Rosales (2014). The supposition of the study was that sonocrystallization would assist formation of polymorph V ⟨beta⟩, resulting similar quality properties to conventional tempered chocolate. The influence of ultrasound (20 kHz) technique was explored in dark chocolate crystallization using instrumental and sensorial methods. Various kinds of ultrasound instruments were examined to bring ultrasound waves into the chocolate mass and achieve polymorphic transformation. Results showed that ultrasound method had a considerable effect on crystallization characteristics of dark chocolate and under optimal situations could be applied to attain a desirable polymorphic conformation (Form V ⟨beta⟩). Different sonication exposure times ended in different melting profiles and different polymorphs illustrating specified timing strategies were optimal (6 s and 9 s). Sensory results exhibited that sonication achieved a comparable sensory profile to traditional tempered sample. In over-sonication chocolate formulations, metallic attribute was stated. There was no remarkable changes in fatty acid composition as a result of over-sonication (20 s). Forty four odor-active components were recognized and no particular off-flavor was recorded. Overall, ultrasound-assisted crystallization was feasible to be used in chocolate production at industrial scale due to its high efficiency in providing stable polymorphs.

Higaki et al. (2001) evaluated the influences of ultrasonic power on the crystallization behavior of cocoa butter. The results indicated that sonication for a short time speeded up the crystallization of Form V ⟨beta⟩. Thus ultrasound technology concluded as efficient equipment for controlling polymorphic crystallization of cocoa butter. Baird and Su (2018) investigated the acoustic vibration effects in classical nucleation theory. The aim was to examine the influence of acoustic pressure on the rate of nucleation. The results indicated that acoustic pressure reduced both the size of the critical nucleus and also the work required to form it from monomers. The acoustic pressure increased the rate of nucleation.

The fundamental mechanisms underlying the polymorph-controlling sonocrystallization technique are not obvious (Higaki et al., 2001; Martini et al., 2008; Suzuki et al., 2010; Ueno et al., 2003; Ye et al., 2011). But, there is hypothesis that there may be some combined impacts intrinsic to sonocrystallization, most probably due to pressure-induced thermodynamic impacts and chain-chain interactions causing the establishment of stable molecular packing of triple chain length and subcells of polymorphic form V ⟨beta⟩. When sonicating liquids the sound waves that propound into the liquid media ends in alternating high-pressure and low-pressure cycles. The current mechanical stress acts on the attracting electrostatic forces including Van der Waals forces which are critical in crystallization (Hielscher Ultrasonics GmbH, 2014). Ueno et al. (2003) reported that sonication reduced induction times and increased nucleation rates because of high-pressure proximity of collapsing bubbles altering melting point and accordingly increasing supercooling, and also a significant decrease of the free-energy barrier for nucleation in comparison to non-sonicated samples.

As a whole it can be finilzaed that the sonication method impacts the nucleation processes via the following mechanisms: (a) intense collapse of cavitation bubbles could create active sites for nucleation, (b) boosted agitation may influence dynamism of crystallizing molecules, (c) cooling caused via evaporation from the surface of the cavity during the growth of a cavitation bubble could increase supercooling, (d) positional pressure could increase the melting point in the proximity of a disintegrating cavity, which means that the degree of supercooling is increased (Higaki et al., 2001).

6. Determination methods for pre-crystallization

6.1. Tempermeter method

Tempermeters quantify the crystal growth process during and/or after tempering for an identical product formulation in chocolate industry. For quality assessment, it is necessary to specify the temper degree. The functionality of tempermeter is to calculate some important characteristics of chocolate crystallization. Measuring chocolate temper includes the measuring the heat of crystallization of the chocolate as it cools and solidifies (Allen, 2017; Beckett, 2009).

By cooling the chocolate in a controlled manner, the temperature is measured by a temperature probe inside the chocolate. When the cocoa butter in the chocolate is cooled it crystallizes and releases its heat. By releasing the heat, chocolate warms, affecting the temperature curve, however, a change in the curve can be seen. Tempermeter consists of an ice bath, a probe for measuring temperature, and a recorder to store and plot the temperature. The temperature variation induced by the development of crystals are monitored and recorded by the temperature probe (Allen, 2017; Lindecrantz, 2014).

The Greer Assessment Curves are obtained with the fusion of heat loss and heat gain on a tape graph over time. For describing the curves properly, a method has been applied by scientists that created the primary temperature reduction and the most dominant temperature ascent slope due to heat of crystallization.

The Greer Temper Units or GTU was generated by diminishing an optional temperature amount from the temperature amount at the junction of the two tilt (Allen, 2017). The curves slope is used to determine the temper degree. The shape of the curve is used to define the tempering conditions. In novel tempermeters, the value of temper index is described in numerical and it is used to specify the quality of tempering. Well-tempered chocolate should display a TI value of 5 ± 0.1. TI for under-tempered and over-tempered chocolate is < 4.0 and > 6.0, respectively (Beckett, 2009). If the curve slope becomes 0, the chocolate is well-tempered, a negative slope indicates over-tempering. Under-tempered chocolate gives a positive slope in the tempermeter (Hartel et al., 2018).

In well-tempered chocolate the temperature drops quickly within cooling till reaching to thermodynamic equilibrium. The heat liberated due to crystallization is moderated by an adequate value of cooling energy.

During tempering procedure, over tempering can be observed when lower temperatures are liberated among multi-stage heat exchangers. This procedure leads very little crystallization heat released during product solidification thus affecting the product to be cooled slowly; as a result, further liquid cocoa butter is converted rapidly into solid nature. This causes a flat and slow cooling curve (Afoakwa et al., 2008).

6.2. NMR method

This technique nowadays is widely used in food industry and also it has been used for more than 30 years in chocolate confectionary (Ablett, 1992; Miquel & Hall, 1998). The presence of excessive amounts of resonance nuclei such as C, O, Na and P in the structure of food is frequently used in scientific and industrial studies conducted in food field of NMR (Miquel & Hall, 1998).

Two different NMR techniques are used to measure the melting and crystallization phenomena of the cocoa butter, namely, pulsed NMR and continuous scanning (Gunstone, 1999). NMR technique is used as a very effective method for determination of solid fat content (SFC) in the chocolate samples. Today for SFC measurements, pulsed NMR (pulsed = pNMR) or Fourier transform is applied (Foubert, 2003; Yetim & Çam, 2009).

In pulsed NMR, the sample is trapped in the electromagnetic field and then excited by radio frequency impulse, and magnetization occurs with protons and neutrons polarized. The pulsed NMR technique is widely expressed by the use of radio frequency, which activates the hydrogen proton when no neutrons are present. It is used as a standard laboratory application in determining the fat content of solids and liquid. The solid fat contents (SFC) of sample at different temperatures are calculated from their thermal profiles through comparison with the reference. Temperature adjustment of the NMR magnet and also setting defined sampling routine are necessary for gaining the sufficient precision at solid fractions (Beckett, 2009).

In the crystallization phase, reaching the appropriate crystal dimensions from the melted cocoa butter is dependent on the time-temperature conditions. In such situations, NMR technique is applied to optimize and control the crystallization by monitoring the development of the solid form. By comparing the measured values with the pulsed NMR gives information about the crystallization process, and at the same time, when the samples have the same temperature history, they have the greatest potential for reducing the differences between measurement methods. Though solid-state NMR is a powerful method for studying structural and dynamic characteristics of solids, adaptation of this technique for in-situ studies of chemical processes frequently encounters technical challenges (Harrison, Hughes, & Williams, 2015; Smith, Cain, & Talbot, 2007).

NMR is also a useful and rapid technique to obtain information about cocoa bean's geographical origin (Marseglia et al., 2016). The NMR technique has rapidly gained new features in the last 20 years by enabling the same NMR data to be spatially resolved in two or three dimensions. NMR has feasibility to be applied in chocolate industry and already has been used to evaluate the crystallization of cocoa butter and its different polymorphs. In addition, NMR can be used to follow the migration of fat, causing unwanted "fat bloom" of polymorphic cocoa butter in chocolate (Walter & Cornillon, 2002).

6.3. XRD method

Among the different methods developed, only X-ray diffraction supplies direct structural information about crystallization. In recent years, polymorphism behaviors of fats have been monitored by X-ray diffraction and radio-isotope fluorescence techniques (Yetim & Çam, 2009).

X-ray diffraction is usually used to determine the forms of fat crystals. In order to produce different X-ray patterns, there must be a significant difference in the structure of each crystal. Packing of the hydrocarbon chains leads to different crystallization characteristic. The nomenclature of the crystalline form of the butter is based on studies using X-ray diffraction (Baichoo, 2007; Carter & Malkın, 1939). These structures are separated by X-ray diffraction patterns based on the chain length of the crystals and the inter-chain distances (Baichoo, 2007).

When X-rays are impinged onto a single crystal or polycrystalline, the X-rays can also be reflected at very small angles of incidence from the solid surface and the X-rays scatter by parallel planes of atoms in the crystal. In a crystal, each of the atoms acts as a scattering center and emits a secondary wave. This is called diffraction. All of the secondary waves interfere with each other and the beam is diffracted into many specific directions. X-ray, neutron and electron diffraction are applied to determine crystal molecular structure, crystal purity, crystal phase transformations, the specific arrangements of atoms in crystal and crystal lattice planes (Aygün & Zengin, 1998; Cullity, 1996).

The ability to determine the relative amount and type of unstable and stable crystal forms found in chocolate using new techniques offers significant advantages for chocolate producers. Industrial applications and literature studies have limited results on crystal polymorphism of chocolate using XRD. The main difficulty with using XRD is that only a small part of the signal is obtained in the presence of sugar. XRD pattern of sugar signal displays strong peaks at 4.52 Å (overlapping with b crystals ≈ 4.58 Å) and the fat signal shows peak at 4.71 Å (Schenk & Peschar, 2004). In order to solve this difficulty, it is suggested glass can be removed or sugar can be removed by solid-liquid extraction techniques (Le Reverend, Fryer, Coles, & Bakalis, 2010).

6.4. DSC method

The DSC provides information about relative amounts of the different fat crystal types. However, it requires very accurate sample preparation and is expensive and complicated method for routine quality control (Beckett, 2008).

When a solidified fat melts, the elimination of heat from the environment indicates endothermic event. This endothermic heat flux is measured by the DSC, which presents the specific melting pattern. Also, when a liquid fat is cooled, it finally releases latent heat of fusion and crystallizes. This is detected as crystallization exo-therm (giving up heat) in the equipment.

In DSC measuring cell, a small sample (the sample weight, approx. 10–20 mg, should be measured with accuracy of ± 0.1 mg) is loaded in a metal container for solid fat. Then the sample is taken through a predetermined constant temperature range and the energy changes are monitored (Beckett, 2009). The amount of energy required to melt the crystal is compared with the energy required to uniformly heat a control sample (a metal such as an empty container, where no melting will occur). Peaks occur in the temperature ranges corresponding to the crystalline state. Various peaks can occur for the same fat sample demonstrating that more than one crystal type is present.

Onset temperature (T_{onset}), peak temperature (T_{peak}), end temperature (T_{end}) and energy required for complete melting of the samples (ΔH) are the thermal parameters determined by DSC. T_{onset} refers to the temperature that is associated with the beginning of the melting of a particular crystal. T_{peak} corresponds to the temperature at which melting rate is greatest. This information could be used to indicate the crystal type. T_{end} shows the completion of liquefaction. ΔH is the amount of energy necessary for overall melting of the fat. All the thermal parameters are related to the crystal type. The peak height, position and resolution are strongly dependent on the rate of temperature change (Cebula et al., 1991). The nature of the peaks is associated with the molecular composition and the polymorphic crystallization behavior.

Sometimes it is necessary to control the types of crystal present during the setting phase. For this purpose, the remaining liquid fat can be rapidly crystallized by immersing the sample into liquid nitrogen. This fat will be in the unstable and lower melting-point forms therefore it can be diagnosis from those crystals which have already set. For some products such as chocolate this technique can be used. When the chocolate sample is heated, peaks in the range of 28–32 °C show the presence of more stable forms (Beckett, 2009).

7. Conclusions

Optimization the process conditions leads to the improvements of quality attributes and the reduction of manufacturing costs. In order to carry out optimization studies, it is necessary to know and understand the changes in process stages and how these influence the mechanisms. In recent years, there has been growing interest in using sugar alternatives in chocolate confectionery. However, in an industrial-scale production with increased output of a product, the ways for reducing operating costs should also be taken into account. For this reason, identifying appropriate alternative production technologies can achieve the intended purpose. The current review aims to provide new perspectives on the pre-crystallization of chocolate. The seeding technique has a great potential in chocolate industry to by-pass tempering stage at small-scale production, however, optimization of seed quantity, mixing time and speed as well as the chocolate composition should be conducted. Under optimal conditions, ultrasound assissted pre-crystallization can be applied to achieve an appropriate and stable polymorphic conformation causing a time/energy savings in comparison to conventional tempering process.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Ablett, S. (1992). Overview of NMR in food science. *Trends in Food Science and Technology, 3*, 246–250. https://doi.org/10.1016/S0924-2244(10)80002-0.

Acevedo, N. C., & Marangoni, A. G. (2015). Nanostructured fat crystal systems. *Annual Review of Food Science and Technology, 6*, 71–96. https://doi.org/10.1146/annurev-food-030713-092400.

Afoakwa, E. O. (2010). *Chocolate science and technology.* UK: Wiley-Blackwell.

Afoakwa, E. O., Paterson, A., Fowler, M., & Vieira, J. (2008). Modelling tempering behavior of dark chocolates from varying particle size distribution and fat content using response surface methodology. *Innovative Food Science and Emerging Technology, 9*(4), 527–533. https://doi.org/10.1016/j.ifset.2008.02.002.

Afoakwa, E. O., Paterson, A., Fowler, M., & Vieira, J. (2009a). Influence of tempering and fat crystallization behaviours on microstructural and melting properties in dark chocolate systems. *Food Research International, 42*(1), 200–209. https://doi.org/10.1016/j.foodres.2008.10.007.

Afoakwa, E. O., Paterson, A., Fowler, M., & Vieira, J. (2009b). Microstructure and mechanical properties related to particle size distribution and composition in dark chocolate. *International Journal of Food Science and Technology, 44*(1), 111–119. https://doi.org/10.1111/j.1365-2621.2007.01677.x.

Allen, P. (2017). *Chocolate temper measurement.* Tricor Systems Inc.. [Accessed January 2017] https://www.tricor-systems.com/articles/chocolate-temper/.

Altimiras, P., Pyle, L., & Bouchon, P. (2007). Structure–fat migration relationships during storage of cocoa butter model bars: Bloom development and possible mechanisms. *Journal of Food Engineering, 80*(2), 600–610. https://doi.org/10.1016/j.jfoodeng.2006.06.022.

Aygün, E., & Zengin, M. (1998). *Atom ve molekül fiziği.* Ankara: Ankara Üniversitesi.

Baichoo, N. (2007). *The effect of rapid cooling on the fat phase of chocolate.* University of Nottingham.

Baird, J. K., & Su, C. H. (2018). Acoustic vibration effects in classical nucleation theory. *Journal of Crystal Growth, 487*, 65–71. https://doi.org/10.1016/j.jcrysgro.2018.02.008.

Beckett, S. T. (2000). *The science of chocolate.* London: Royal Society of Chemistry Paperbacks.

Beckett, S. T. (2008). *The science of chocolate* (2nd ed.). Cambridge: The Royal Society of Chemistry Publishing.

Beckett, S. T. (2009). *Industrial chocolate manufacture and use* (4th ed.). United Kingdom: Blackwell Publishing.

Buscato, M. H. M., Hara, L. M., Bonomi, E. C., Calligaris, G. D. A., Cardoso, L. P., Grimaldi, R., & Kieckbusch, T. G. (2018). Delaying fat bloom formation in dark chocolate by adding sorbitan monostearate or cocoa butter stearin. *Food Chemistry, 256*, 390–396. https://doi.org/10.1016/j.foodchem.2018.02.127.

Carter, M. G. R., & Malkın, T. (1939). An X-ray and thermal examination of the glycerides part VII. Unsymmetrical mixed triglycerides. *Journal of the Chemical Society, 1518–1521*. https://doi.org/10.1039/JR9390001518.

Cebula, D. J., Dilley, K. M., & Smith, K. W. (1991). Continuous tempering studies on model confectionery systems. *Manufacturing Confectioner,* 131–136.

Chemat, F., Huma, Z-e, & Khan, M. K. (2011). Applications of ultrasound in food technology: Processing, preservation and extraction. *Ultrasonics Sonochemistry, 18*(4), 813–835. https://doi.org/10.1016/j.ultsonch.2010.11.023.

Chow, R., Blindt, R., Chivers, R., & Povey, M. (2005). A study on the primary and secondary nucleation of ice by power ultrasound. *Ultrasonics, 43*(4), 227–230. https://doi.org/10.1016/j.ultras.2004.06.006.

Cullity, B. D. (1996). *X ışınlarının Difraksiyonu, (Çev.A.Sümer).* Yayınları, İstanbul: İstanbul Teknik Üniversitesi.

Dahlenborg, H., Millqvist-Fureby, A., & Bergenstahl, B. (2015). Effect of shell microstructure on oil migration and fat bloom development in model pralines. *Food Structure, 5*, 51–65. https://doi.org/10.1016/j.foostr.2015.06.002.

Debaste, F., Kegelaers, Y., Liegeois, S., Ben Amor, H., & Halloin, V. (2008). Contribution to the modeling of chocolate tempering process. *Journal of Food Engineering, 88*(4), 568–575. https://doi.org/10.1016/j.jfoodeng.2008.03.019.

Delgado, A. E., & Sun, D.-W. (2001). Heat and mass transfer models for predicting freezing processes – A review. *Journal of Food Engineering, 47*(3), 157–174. https://doi.org/10.1016/S0260-8774(00)00112-6.

de Oliveira, G. M., Ming, C. C., Ribeiro, A. P. B., & Kieckbusch, T. G. (2011). *Effect of the addition of hardfats on technological properties of palm oil: solid fat content, consistency and crystallization kinetics. International congress on engineering and food*. [Accessed 27 March 2014] http://www.icef11.org/content/papers/fms/FMS1048.pdf.

Depoortere, L. (2011). *The use and applicability of cocoa butter equivalents in chocolate products*[Master of Science Thesis]. Gent University.

Dhonsi, D., & Stapley, A. G. F. (2006). The effect of shear rate, temperature, sugar and emulsifier on the tempering of cocoa butter. *Journal of Food Engineering, 77*(4), 936–942. https://doi.org/10.1016/j.jfoodeng.2005.08.022.

Foubert, I. (2003). *Modellıng isothermal cocoa butter crystallızatıon: Influence of temperature and chemıcal composition*[Doctor of Biological Sciences. Chemistry Thesis]. Gent University.

Foubert, I., Vanrolleghem, P. A., & Dewettinck, K. (2003). A differential scanning calorimetry method to determine the isothermal cyrstallization kinetics of cocoa butter. *Thermochimica Acta, 400*(1–2), 131–142. https://doi.org/10.1016/S0040-6031(02)00484-7.

Glicerina, V., Balestra, F., Rosa, M. D., & Romani, S. (2013). Rheological, textural and calorimetric modifications of dark chocolate during process. *Journal of Food Engineering, 119*(1), 173–179. https://doi.org/10.1016/j.jfoodeng.2013.05.012.

Gunstone, F. D. (1999). Composition and properties of edible oils. In W. Hamm, & R. J. Hamilton (Eds.). *Edible oil processing* (pp. 1–33). UK: Sheffield Academic Pres.

Hachiya, I., Koyano, T., & Sato, K. (1989). Seeding effects on solidification behaviour of cocoa butter and dark chocolate. I. Kinetics of Solidification. *Journal of the American Oil Chemists Society, 66*(12), 1757–1762.

Harrison, K. D. M., Hughes, C. E., & Williams, P. A. (2015). Monitoring the evolution of crystallization processes by in-situ solid-state NMR spectroscopy. *Solid State Nuclear Magnetic Resonance, 65*, 107–113. https://doi.org/10.1016/j.ssnmr.2014.11.004.

Hassan, E. M., & Megahed, M. G. (1998). Studies on cocoa butter replacer mixtures suitable for the local chocolate production. *Grasas y Aceites, 49*, 446–449.

Hartel, R. W. (1991). Crystallization processes. *The Manufacturing Confectioner, 71*(8), 61–66.

Hartel, R. W., von Elbe, J. H., & Hofberger, R. (2018). *Confectionery science and technology.* Switzerland: Springer International Publishing AG.

Haupler, M., Peyronel, F., Neeson, I., Weiss, J., & Marangoni, A. G. (2014). In situ ultrasonic characterization of cocoa butter using a chirp. *Food and Bioprocess Technol, 7*(11), 3186–3196. https://doi.org/10.1007/s11947-014-1273-2.

Hielscher Ultrasonics GmbH (2014). *Ultrasound technology: Ultrasonic dispersing and deagglomeration.* Retrieved March 25, 2014, from http://www.hielscher.com/disperse.htm.

Higaki, K., Ueno, S., Koyano, T., & Sato, K. (2001). Effects of ultrasonic irradiation on crystallization behavior of tripalmitoylglycerol and cocoa butter. *Journal of the American Oil Chemists' Society, 78*(5), 513–518. https://doi.org/10.1007/s11746-001-0295-y.

Himavan, C., Starov, V. M., & Stapley, A. G. F. (2006). Thermodynamic and kinetic aspects of fat crystallization. *Advances in Colloid and Interface Science, 122*(1–3), 3–33. https://doi.org/10.1016/j.cis.2006.06.016.

Kinta, Y., & Hartel, R. W. (2010). Bloom formation on poorly-tempered chocolate and effects of seed addition. *Journal of the American Oil Chemists' Society, 87*(1), 19–27. https://doi.org/10.1007/s11746-009-1473-5.

Konar, N., Oba, S., Toker, O. S., Palabiyik, I., Goktas, H., Artik, N., & Sagdic, O. (2017). Rapid tempering of sucrose-free milk chocolates by βV seeding: Textural, rheological and melting properties. *European Food Research and Technology, 243*(10), 1849–1860. https://doi.org/10.1007/s00217-017-2891-5.

Kurotani, M., Miyasaka, E., Ebihara, S., & Hirasawa, I. (2009). Effect of ultrasonic irradiation on the behavior of primary nucleation of amino acids in supersaturated solutions. *Journal of Crystal Growth, 311*(9), 2714–2721. https://doi.org/10.1016/j.jcrysgro.2009.03.009.

Le Reverend, B. J. D. (2009). *Modelling of the phase change kinetics of cocoa butter in chocolate and application to confectionery manufacturing*[Chemical Engineering, Ph.D. Thesis]. The University of Birmingham.

Le Reverend, B. J. D., Fryer, P. D., Coles, S. J., & Bakalis, S. (2010). A method to qualify and quantify the crystalline state of cocoa butter in industrial chocolate. *Journal of American Oil Chemists' Society, 87*(3), 239–246. https://doi.org/10.1007/s11746-009-1498-9.

Leonelli, C., & Mason, T. J. (2010). Microwave and ultrasonic processing: Now a realistic option for industry. *Chemical Engineering Process, 49*(9), 885–900. https://doi.org/10.1016/j.cep.2010.05.006.

Lindecrantz, A. (2014). *Investigation of seedpowder technology for precrystallization processing of dark chocolate- Effect on fat crystal structure and storage stability.* Chalmers University of Technology: Department Of Chemical and Biological Engineering.

Lipp, M., & Anklam, E. (1998). Review of cocoa butter and alternative fats for use in chocolate-part A. Compositional data. *Food Chemistry, 62*(1), 73–97. https://doi.org/10.1016/S0308-8146(97)00160-X.

Lonchampt, P., & Hartel, R. W. (2004). Fat bloom in chocolate and compound coatings. *European Journal of Lipid Science & Technology, 106*(4), 241–274. https://doi.org/10.1002/ejlt.200400938.

Loren, N., Jonasson, J., Langton, M., & Hermansson, A. M. (2009). *Fat migration in chocolate and new methods to determine local diffusion in heterogeneous biomaterials. 5th International symposium on food rheology and structure*.

Marseglia, A., Acquotti, D., Consonni, R., Cagliani, L. R., Palla, G., & Caligiani, A. (2016). HR MAS ^{1}H NMR and chemometrics as useful tool to assess the geographical origin of cocoa beans – Comparison with HR ^{1}H NMR. *Food Research International, 85*, 273–281. https://doi.org/10.1016/j.foodres.2016.05.001.

Martini, S., Suzuki, A. H., & Hartel, R. W. (2008). Effect of high intensity ultrasound on crystallization behavior of anhydrous milk fat. *Journal of American Oil Chemists' Society, 85*(7), 621–628. https://doi.org/10.1007/s11746-008-1247-5.

Masuchi, M. H., Grimaldi, R., & Kieckbusch, T. G. (2014). Effects of sorbitan monostearate and monooleate on the crystallization and consistency behaviors of cocoa butter. *Journal of the American Oil Chemists' Society, 91*(7), 1111–1120. https://doi.org/10.1007/s11746-014-2469-3.

Merken, G. V., & Vaeck, S. V. (1980). Study of the polymorphism of cacao butter by means of DSC (differntial scanning) calorimetry. *LWT – Food Science and Technology, 13*, 314–317.

Minifie, B. W. (1989). *Chocolate, cocoa and confectionery.* London: Chapman & Hall.

Miquel, M. E., & Hall, L. D. (1998). A general survey of chocolate confectionery by magnetic resonance imaging. *LWT – Food Science and Technology, 31*(2), 93–99. https://doi.org/10.1006/fstl.1997.0329.

Miyasaki, E. K., Luccas, V., & Kieckbusc, T. G. (2015). Modified soybean lecithins as inducers of the acceleration of cocoa butter crystallization. *European Journal of Lipid Science and Technology, 118*(10), 1539–1549. https://doi.org/10.1002/ejlt.201500093.

Mohos, F. A. (2010). *Confectionery and chocolate engineering: Principles and applications.* UK: Willey Blackwell.

Nelson, R. B. (1988). Temperers, enrobers, moulding equipment and coolers. In S. T. Beckett (Ed.). *Industrial chocolate manufacture and use* (pp. 172–226). London: Blackie & Son, Glasgow.

Oba, S., Toker, O. S., Palabiyik, I., Konar, N., Goktas, H., Cukur, Y., ... Sagdic, O. (2017). Rheological and melting properties of sucrose-free dark chocolate. *International Journal of Food Properties, 20*(sub2), 2096–2106. https://doi.org/10.1080/10942912.2017.1362652.

Otero, L., Martino, M., Zaritzky, N., Solas, M., & Sanz, P. D. (2000). Preservation of microstructure in peach and mango during high-pressure-shift freezing. *Journal of Food Science, 65*(3), 466–470. https://doi.org/10.1111/j.1365-2621.2000.tb16029.x.

Padar, S., Jeelani, S. A. K., & Windhab, E. J. (2008). Crystallization kinetics of cocoa fat systems: Experiments and modeling. *Journal of the American Oil Chemists' Society, 85*(12), 1115–1126. https://doi.org/10.1007/s11746-008-1312-0.

Quast, L. B., Luccas, V., Ribeiro, A. P. B., Cardoso, L. P., & Kieckbusch, T. G. (2013). Physical properties of tempered mixtures of cocoa butter, CBR and CBS fats. *International Journal of Food Science and Technology, 48*, 1579–1588. https://doi.org/10.1111/ijfs.12127.

Rastogi, N. K. (2011). Opportunities and challenges in application of ultrasound in food processing. *Critical Reviews in Food Science and Nutrition, 51*(8), 705–722. https://doi.org/10.1080/10408391003770583.

Ribeiro, A. P. B., Basso, R. C., dos Santos, A. O., Andrade, G. C., Cardoso, L. P., & Kieckbusch, T. G. (2013a). Hard fats as crystallization modifiers of cocoa butter. *European Journal of Lipid Science and Technology, 115*(12), 1462–1473. https://doi.org/10.1002/ejlt.201300052.

Ribeiro, A. P. B., Basso, R. C., & Kieckbusch, T. G. (2013b). Effect of the addition of hardfats on the physical properties of cocoa butter. *European Journal of Lipid Science and Technology, 115*, 301–312. https://doi.org/10.1002/ejlt.201200170.

Ribeiro, A. P. B., Masuchi, M. H., Miyasaki, E. K., Domingues, M. A. F., Stroppa, V. L. Z., de Oliveira, G. M., & Kieckbusch, T. G. (2015). Crystallization modifiers in lipid systems. *Journal of Food Science Technology, 52*(7), 3925–3946. https://doi.org/10.1007/s13197-014-1587-0.

Richter, K. (2009). Tempering process technology. In G. Talbott (Ed.). *Science and technology of enrobed and filled chocolate, confectionery and bakery products* (pp. 344–361). New York: CRC Press.

Rogers, M. A., Tang, D., Ahmadi, L. F., & Marangoni, A. (2008). Crystal network. In J. M. Aguilera, & P. J. Lillford (Eds.). *Food material science – principles and practice* (pp. 369–414). New York: Springer.

Rosales, E. (2014). *Ultrasonic application as a potential alternative to tempering in dark chocolate manufacturing*[Doctor of Philosophy in Food Science and Human Nutrition, Doctor (Ph.D.) of Science Thesis]. Illinois, United States: University of Illinois.

Ruecroft, G., Hipkiss, D., Ly, T., Maxted, N., & Cains, P. W. (2005). Sonocrystallization: The use of ultrasound for improved industrial crystallization. *Organic Process Research and Development, 9*(6), 923–932. https://doi.org/10.1021/op050109x.

Sato, K. (2001). Crystallization behavior of fats and lipids: A review. *Chemical Engineering Science, 56*(7), 2255–2265. https://doi.org/10.1016/S0009-2509(00)00458-9.

Schenk, H., & Peschar, R. (2004). Understanding the structure of chocolate. *Radiation Physics and Chemistry, 71*(3–4), 829–835. https://doi.org/10.1016/j.radphyschem.2004.04.105.

Slettengren, K. (2010). *Crack formation in chocolate pralines*[Master of Science Thesis in the Master Degree Programme Biotechnology]. Chalmers University of Technology.

Smit, H. J. (2011). Theobromine and the pharmacology of cocoa. In B. B. Fredholm (Ed.). *Methylxanthines, handbook of experimental pharmacolog* (pp. 201–234). Berlin: Springer.

Smith, K. W., Cain, F. W., & Talbot, G. (2007). Effect of nut oil migration on polymorphic transformation in a model system. *Food Chemistry, 102*(3), 656–663. https://doi.org/10.1016/j.foodchem.2006.05.045.

Smith, K. W., Zand, I., & Talbot, G. (2008). Effect of antibloom fat migration from a nut oil filling on the polymorphic transformation of cocoa butter. *Journal of Agricultural and Food Chemistry, 56*(5), 1602–1605. https://doi.org/10.1021/jf072151s.

Suzuki, A. H., Lee, J., Padilla, S. G., & Martini, S. (2010). Altering functional properties of fats using power ultrasound. *Journal of Food Science, 75*(4), E208–E214. https://doi.org/10.1111/j.1750-3841.2010.01572.x.

Svanberg, L., Ahrne, L., Loren, N., & Windhab, E. (2011). Effect of sugar, cocoa particles and lecithin on cocoa butter crystallization in seeded and non-seeded chocolate model systems. *Journal of Food Engineering, 104*(1), 70–80. https://doi.org/10.1016/j.jfoodeng.2010.09.023.

Svanberg, L., Ahrne, L., Loren, N., & Windhab, E. (2013). Impact of pre-crystallization process on structure and product properties in dark chocolate. *Journal of Food Engineering, 114*(1), 90–98. https://doi.org/10.1016/j.jfoodeng.2012.06.016.

Takiguchi, A., Lida, K., Ueno, S., Yano, J., & Sato, K. (1998). Heterogeneous nucleation of n-alcohol crystals from solution assisted by vapor-deposited thin films of fatty acids. *Journal of Crystal Growth, 193*(4), 641–647. https://doi.org/10.1016/S0022-0248(98)00610-1.

Talbot, G. (1999). *Science and technology of enrobed and filled chocolate, confectionery and bakery products.* Oxford: CRC Press.

Tran, P. D., Van de Walle, D., Hinneh, M., Delbaere, C., De Clercq, N., Tran, D. N., & Dewettinck, K. (2015). Controlling the stability of chocolates through the incorporation of soft and hard StOSt-rich fats. *European Journal of Lipid Science and Technology, 117*(11), 1700–1713. https://doi.org/10.1002/ejlt.201400584.

Ueno, S., Ristic, R. I., Higaki, K., & Sato, K. (2003). In situ studies of ultrasound-stimulated fat crystallization using synchrotron radiation. *The Journal of Physical Chemistry B, 107*(21), 4927–4935. https://doi.org/10.1021/jp027840f.

Van Malssen, K. F., Van Langevelde, A. J., Peschar, R., & Schenk, H. (2001). Method for the manufacturing of chocolate. International patent application PCT/NL00/00525 (WO800148-Al), other numbers: ICT-WO0106863, EP1204330, NL1012691.

Vereecken, J., Foubert, I., Smith, K. W., & Dewettinck, K. (2009). Effect of SatSatSat and SatOSat on crystallization of model fat blends. *European Journal of Lipid Science and Technology, 111*(3), 243–258. https://doi.org/10.1002/ejlt.200800150.

Walter, P., & Cornillon, P. (2002). Lipid migration in two-phase chocolate systems investigated by NMR and DSC. *Food Research International, 35*(8), 761–767. https://doi.org/10.1016/S0963-9969(02)00072-8.

Windhab, E. J. (1999). New developments in crystallization processing. *Journal of Thermal Analysis and Calorimetry, 57*(1), 171–180. https://doi.org/10.1023/A:1010103105425.

Ye, Y., Wagh, A., & Martini, S. (2011). Using high intensity ultrasound as a tool to change the functional properties of interesterified soybean oil. *Journal of Agriculture and Food Chemistry, 59*(19), 10712–10722. https://doi.org/10.1021/jf202495b.

Yetim, H., & Çam, M. (2009). *Enstrümental Gıda Analizleri.* Erciyes Üniversitesi Yayınları No: 175149–151.

Zeng, Y., Braun, P., & Windhab, E. J. (2002). Tempering-continous pre-crystallization of chocolate with seed cocoa butter crystal suspension. *The Manufacturing Confectioner, 82*(4), 71–80.

Zhang, Z., Sun, D.-W., Zhiwei, Z., & Cheng, L. (2015). Enhancement of crystallization process by power ultrasound: Current state-of-the-art and research advances. *Comprehensive Reviews in Food Science and Food Safety, 14*(4), 303–316. https://doi.org/10.1111/1541-4337.12132.

Zheng, L., & Sun, D.-W. (2006). Innovative applications of power ultrasound during food freezing processes – A review. *Trends in Food Science and Technology, 17*(1), 16–23. https://doi.org/10.1016/j.tifs.2005.08.010.