Investigation of seedpowder technology for pre-crystallization processing of dark chocolate

- Effect on fat crystal structure and storage stability

Master of Science Thesis in the Master Degree Program Biotechnology

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CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2014

THESIS FOR THE DEGREE OF MASTER OF SCIENCE

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This thesis was performed at SIK – The Swedish Institute for Food and Biotechnology

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Cover picture: Melted dark chocolate.

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ABSTRACT

The biggest cause of loss in the chocolate industry is the development of fat bloom in chocolate products. Resistance to fat bloom and deterioration is highly linked to the crystal structure of the cocoa fat in chocolate. A chocolate with a stable crystal structure gets properties such as increased resistance to heat and fat bloom, good moulding, a glossy surface and a good snap. In order to achieve a structure with these properties the chocolate must undergo a pre-crystallization process. The most common pre-crystallization process today is the conventional tempering but a novel and simpler process is the use of seedpowder.

The aim of this Master of science thesis was to investigate the potential and usage of three different seedpowders (cocoa butter β_{VI}, cocoa butter β_V and chocolate β_V) for optimal pre-crystallization of chocolate. Evaluation of the powders was done with respect to reproducibility and robustness of the process, generated crystal structure of the chocolate as well as fat bloom development and fat migration during storage.

The results showed that all seedpowders can be used for pre-crystallization of chocolate and depending on the production and what the chocolate will be used for different seedpowder is preferred. The cocoa butter β_{VI} offer a less temperature sensitive production resulting in less powder needed and easier moulding. The cocoa butter β_V showed slightly better resistance to fat migration, which is a desired property in chocolate pralines. The chocolate β_V powder on the other hand does not change the composition of the chocolate.

Keywords: *Pre-crystallization, seedpowder, temper degree, crystal structure, fat migration and fat bloom*

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1. Introduction

The global market of chocolate was 83.2 billion dollars in 2010 with an estimated increase to 98.3 billion dollars in 2016 (MarketsandMarkets, 2011). Chocolate represents 55% of the global confectionary sales. These numbers illustrate how big the chocolate industry is worldwide and what possible improvements in the production chain could lead to. The biggest cause of loss in the chocolate industry is the development of fat bloom, meaning the formation of an unpleasant greyish haze on the chocolate surface and quality loss (Nightingale, Cadwallader, & Engeseth, 2012).

The resistance to fat bloom and deterioration is highly linked to the structure of the fat crystal network of cocoa butter in the chocolate. The cocoa butter can exist in different polymorphic forms where the β_V structure is preferred in chocolate. The β_V polymorphic form not only give better resistance to fat bloom but also other properties associated with good quality chocolate such as a glossy surface, good snap, colour, increased resistance to heat and good moulding properties. In order to achieve the desired β_V polymorphic form, the chocolate must undergo a pre-crystallization process during manufacturing. The majority of the chocolate industry today uses conventional tempering, which is a shear-temperature based pre-crystallization process, to induce fat crystallization in the β_V polymorphic form. The tempering is a complex process and the tempering conditions are difficult to control in large scale production. It is also a costly process because of great energy consumption due to the many steps of heating and cooling and the large spaces required.

A novel and simpler pre-crystallization process is the use of seedpowder that has great potential as a substitute to the conventional tempering. By using seeds of cocoa butter or chocolate in the β_V or β_{VI} polymorphic form, the pre-crystallization process could be shortened since the seeding process only has two cooling steps. Compared to the conventional tempering that involves several cooling and heating steps the seeding process could be both faster and have economic benefits. At SIK – the Swedish Institute for Food and Biotechnology research on the seeding process has been done previously (Svanberg, 2012).

In this work, a thorough investigation of the pre-crystallization process using three different types of seedpowders (cocoa butter β_{VI}, cocoa butter β_V and chocolate β_V) was performed and evaluated. No previous studies comparing and evaluating the pre-crystallization processing using the three seedpowders was found in the literature. Neither was any study comparing the storage stability of chocolate pre-crystallized by the different seedpowders found.

1.1. Aim

The objective of this Master of Science thesis is to evaluate and compare the potential and usage of three different seedpowders (cocoa butter β_{VI}, cocoa butter β_V and chocolate β_V) for optimal pre-crystallization of chocolate. The evaluation was done with respect to reproducibility and robustness of the process, generated crystal structure of the chocolate and fat bloom development and fat migration during storage.

2. Background

The following chapter will give a brief introduction to chocolate content and the chemical structure and polymorphism of cocoa butter. It will also cover crystallization and pre-crystallization of chocolate. Methods for analysing tempering degree, crystal structure, fat migration and fat bloom in chocolate will also be described.

2.1. Chocolate

Chocolate consists of sugar and cocoa particles surrounded by a continuous phase of crystalline and liquid cocoa butter (Nightingale, Cadwallader, & Engeseth, 2012). A common composition of dark chocolate is 47.5 wt% sugar, 30 wt% cocoa butter, 22 wt% cocoa particles and 0.5 wt% emulsifier (Svanberg L. , 2012). Cocoa butter is an important ingredient and the properties of the fat highly affect the characteristics and quality of the chocolate (Chaiseri & Dimick, 1995).

2.1.1. Cocoa butter

Chemical structure

Cocoa butter consists of three fatty acids linked to a glycerol backbone and together they form a triacylglycerol (TAG), see Figure 1. (Rogers, Tang, Ahmadi, & Marangoni, 2008). The fatty acids on the glycerol backbone can vary but there are three main fatty acids in cocoa butter; oleic acid (C18:1), stearic acid (C18:0) and palmitic acid (C16:0). Cocoa butter contains about 35 % of oleic acid and it is the most abundant fatty acid. The amounts of stearic acid and palmitic acid are about 34% and 26%, respectively (Beckett, 2000). Cocoa butter can also contain small amounts of linoleic acid and arachidic acid but compared to other fats with a greater number of fatty acids the composition of cocoa butter is very homogeneous (Dimick & Manning, 1987).

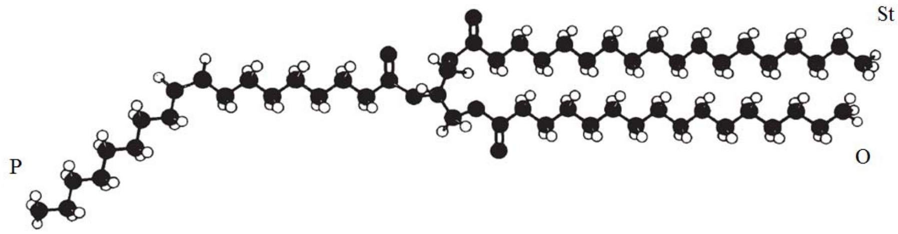

Figure 1. TAG molecule with the most common fatty acids in cocoa butter; stearic (St), palmitic (P) and oleic (O) linked to the glycerol backbone (Beckett S. T., 1994).

The region and the climate where the cocoa beans grow affect the composition of the fatty acid in cocoa butter. Depending on the composition the characteristics and melting points of the fat can differ (Lechter, 2009). Regions that are closer to the equator generally give softer cocoa butter. Depending on the use of the final chocolate product cocoa beans from different regions can be preferred. For example is the Brazilian cocoa butter softer and is preferred in frozen product compared to Malaysian that is harder and preferred in hot countries (Beckett, 2000).

Approximately 80% of the TAGs in cocoa butter have oleic acid on the second position and saturated fatty acids (stearic and palmitic acids) on position one and three which is often referred to as a Saturated-Oleic-Saturated (SOS) TAG. Because of the saturated fatty acids the SOS TAGs are solid at room temperature. 5-20% of the TAGs in cocoa butter are SOO and are liquid in room temperature because of the two unsaturated oleic acids. A small proportion, 1-2%, of the TAGs is SSS and has saturated fatty acids on all positions and they have the highest melting points. Because of the different compositions of fatty acids cocoa butter has both solid and liquid parts at room temperature. The composition of the TAGs affects both the texture and the chocolate products resistance to fat bloom (Beckett, 2000). Cocoa butter with high levels of unsaturated fatty acids are more soft and melt easier but fat with saturated fatty acids set faster and is harder (Lechter, 2009)

The packing of the TAGs also affect the melting points of the fat. They can either be ordered in a chair or in a tuning fork configuration. In cocoa butter the chair conformation is favoured because of its asymmetrical TAGs. When the TAGs solidify and forms crystals they pack the fatty acid chains parallel to each other and perpendicular to the glycerol backbone (Coultate, 2009). In this way they can be packed differently and overlap in two different ways, double chain and triple chains (Figure 2 a) and b)).

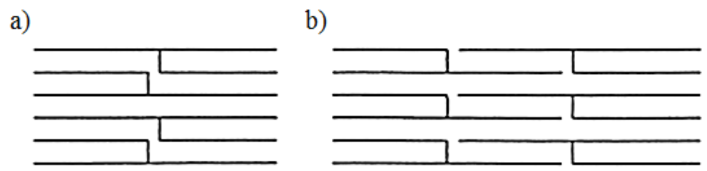

Figure 2. a) TAGs in chair configuration packed in a double chain packing. b) Triple chain packing of TAGs in chair configuration (Beckett, 2000).

Polymorphism

A common property among fats, including cocoa butter, is polymorphism. It is the ability of the TAGs to crystallize in several different forms. There are three basic crystal arrangements in polymorphic fats; α (including sub-α), β' and β (including β_V and β_{VI}) (Lawler & Dimick, 2008). When liquid fat is cooled relatively fast it crystallizes in the more unstable α- and β'-form. Depending on the temperature the α-crystals can transform into β'-crystals that in turn transform into the most stable β-crystals (Timms, 1984). The phase transitions can either be solid-solid phase transition where crystals rearrange without melting or by melt-mediated phase transition where the crystals melt and solidify in another phase (Rogers, Tang, Ahmadi, & Marangoni, 2008). The phase transitions are irreversible and can be seen in Figure 3.

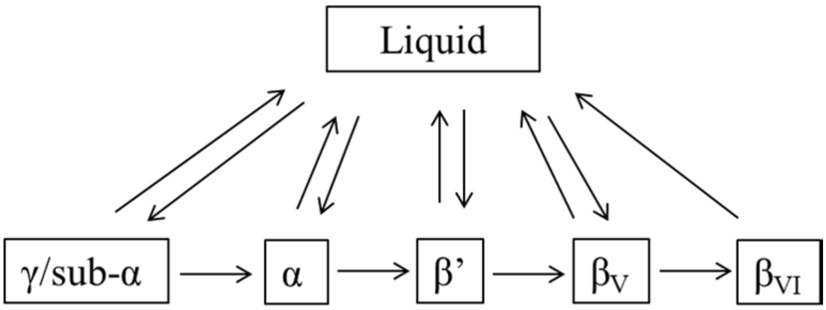

Figure 3. Schematic view of solid-solid phase transitions and melt-mediated phase transitions in cocoa butter. Adapted from (Lechter, 2009).

At fixed conditions there will be one polymorph with the lowest free energy and it is the most stable one for that particular condition. The other polymorphs can be quite stable over time but are considered metastable compared to the one with lowest free energy. The metastable polymorphs can transform into more stable crystals either by melting, dissolution followed by recrystallization, so called melt-mediated phase transition or by rearrangement without melting, so called solid state phase transition (Rogers, Tang, Ahmadi, & Marangoni, 2008).

The phase behaviour of cocoa butter has been studied extensively and there are several definitions of the polymorphs. Using x-ray diffraction six different phases have been identified and designated I-VI but some of them are sub-phases. Differential scanning calorimetry can also be used to distinguish the phases by their melting points but they are quite close and the different forms can be difficult to separate (Svanberg L. , 2012). The melting points of the different polymorphic phases have been reported differently in the literature. Table 1 shows the nomenclatures and corresponding melting points from different articles.

Table 1. Melting points and nomenclature of polymorphic forms reported in the literature.

Phase	Polymorph	(Wille & Lutton, 1966)	(Timms, 1984)	(Coultate, 2009)	(Lechter, 2009)
I	γ	17.3	17.3	~-5	17.3
II	α	23.3	23.3	~5	23.3
III	β'	25.5	25.5	25.5	25.5
IV	β'	27.5	27.5	27.5	27.3
V	β	33.8	33.8	33.8	33.8
VI	β	36.3	36.2	36.3	36.3

The least stable phase in cocoa butter is the γ-form, which is a sub-α form (Lawler & Dimick, 2008). It is also the least densely packed form and it is so unstable that it only forms at very low temperatures and quickly transforms into the more stable α-form. Because it is so unstable the melting point is difficult to determine but it has been approximated to be -8 to 5˚C (Van Malssen, van Langevelde, Pesc, & Schenk, 1999).

The α-form can either be formed via transition from the γ-form or directly when liquid cocoa butter is cooled. The α-form is more stable than the γ-form but it is still an unstable polymorphic form. At temperatures higher than 6˚C the α-form transforms to the β'-form within an hour (Van Malssen, van Langevelde, Pesc, & Schenk, 1999). The TAGs in the α-form are arranged in a hexagonal pattern, see Figure 4 a), and the zig-zag chains of fatty acids are randomly ordered (Rogers, Tang, Ahmadi, & Marangoni, 2008). The fatty acid chains are not so tightly packed but can oscillate (Timms, 1984).

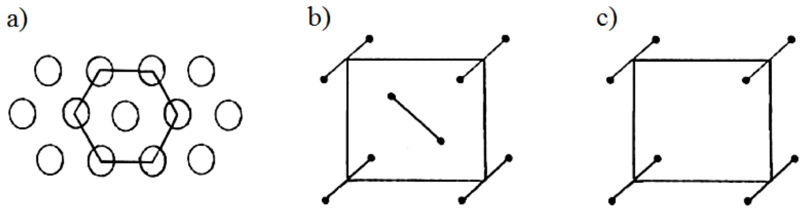

Figure 4. Arrangement of TAGs in different polymorphs viewed from the ends of the chains. a) Hexagonal arrangement in α-polymorphs b) Orthorhombic arrangement in β'-polymorphs c) Triclinic arrangement in β-polymorphs (Beckett, 2000).

In the β'-polymorph the TAG chains are ordered in an orthorhombic form (Figure 4 b)). The zig-zag planes of the fatty acids are arranged in alternating straight and perpendicular and the chains are tilted 50-70˚ (Rogers, Tang, Ahmadi, & Marangoni, 2008). Depending on the angle that the chains are tilted the fat get slightly different properties and melting point. Because of this there are several forms of β'-crystals (Lawler & Dimick, 2008). The packing in the β'-form is denser compared to the α-form and this makes the fat to contract more when it crystallize in this form (Lechter, 2009). Several melting characteristics of the β'-form have been reported and it is difficult to distinguish separate phases and the β'-phase is probably best described as a range of melting temperatures (Van Malssen, van Langevelde, Pesc, & Schenk, 1999).

The most stable polymorphic form is the β-form where the TAG chains are ordered in a triclinic arrangement (Figure 4 c)). The fatty acid chains have parallel arrangement in the same plane (Timms, 1984). The angle that the TAGs are tilted are the same as for β'-form, 50-70˚. The β polymorphic form is the form with the most densely packed crystals and it shows the greatest contraction, which is one of the desired properties in chocolate making (Lechter, 2009). The β polymorph is formed via solid-solid transition from the β'polymorphic form (Rogers, Tang, Ahmadi, & Marangoni, 2008).

Crystallization

When the temperature of a liquid fat is decreased to a few degrees below its maximum melting point the fat reaches its metastable region and a phase transition from liquid to solid starts. This supersaturation is called undercooling. The phase transition from liquid to solid is thermodynamically driven by the undercooling. In the metastable region TAGs start to aggregate and dissociate but forces between the TAGs are not strong enough to overcome the Brownian effects and the clusters does not get big enough to form nuclei. When the undercooling increases to a certain level the primary nucleation starts and clusters of TAGs start to form. It is followed by a secondary nucleation where the crystals grow layer by layer and when the clusters get big enough they become nuclei. The nuclei can induce crystallization in the liquid fat by acting as building blocks for the TAGs. The TAGs in the liquid diffuse to the surface of the nuclei and the crystal structure grows (Rogers, Tang, Ahmadi, & Marangoni, 2008).

2.1.2. Pre-crystallization

In chocolate processing the formation of nuclei is called pre-crystallization and it is an important step in the manufacturing (Zeng, Braun, & Windhab, 2002). It is the process where the crystal structure of the chocolate is determined and it is crucial for the quality of the final product. A well-tempered chocolate has characteristics such as glossy surface, good snap, colour and moulding properties. It is also more heat resistant and it has longer shelf-life and the melting properties are better compared to a chocolate that is not well-tempered (Afoakwa, Paterson, & Fowler, 2007) (Hachiya, Koyano, & Sato, 1989).

The pre-crystallization process aims to induce crystallization of small crystals in the β_V form. This crystal form is the most desired one in chocolate and it makes the chocolate feel smooth in the mouth and it melts fast releasing the solid compounds quickly giving it a nice flavour and taste. If the crystals get too big they can feel gritty in the mouth. Crystals that are in the β_{VI} form are very stable with melting point >34°C which can cause the chocolate to feel waxy in the mouth because they may not melt at the temperature of the mouth (Lechter, 2009). The improved moulding properties of chocolate in the β_V crystal form are caused by the contraction of the fat when it is cooled. Liquid cocoa fat is the least tightly packed and when it is put in a mould and is cooled the chocolate contract making it easy to get it out of the mould (Lechter, 2009).

Tempering

The most common pre-crystallization method used in the chocolate industry today is the conventional tempering. Figure 5 shows a schematic view of the different steps in the process. The first step is to heat the chocolate to~50˚C so that all fat is molten. The pre-crystallization process starts by subjecting the chocolate to shear and cooling it to~31˚C and then by further cooling to~28˚C. In these steps both unstable and stable polymorphs start to crystallize from the melt. The chocolate is then reheated to~31˚C in order to melt the unstable crystals and the stable crystals remain due to their higher melting point and act as seeds. The unstable crystals would cause the chocolate to crystallize in undesirable polymorphic forms (α and β') and because of this the increase in temperature is an important step in the conventional tempering. The chocolate is then cooled to 12˚C and the remaining stable seeds induce crystallization of the right polymorphic form in the chocolate. The time required to temper the chocolate depends on the origin of the chocolate and the desired quality of the final chocolate product (Svanberg L. , 2012) (Hachiya, Koyano, & Sato, 1989).

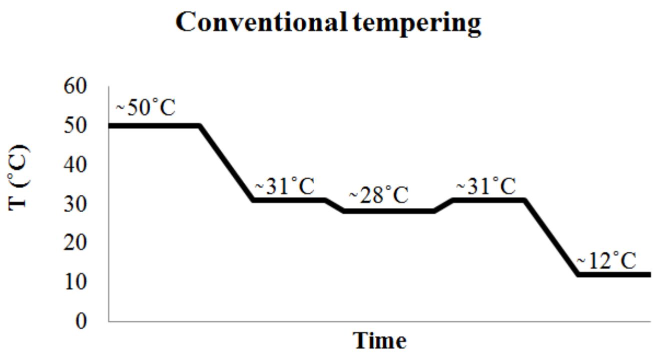

Figure 5. Schematic view of the conventional tempering process. The first step is the melting of the chocolate to~50˚C. The pre-crystallization process starts by cooling the chocolate to~31˚C and then by further cooling to~28˚C. Unstable and stable crystals are formed and in the next step the chocolate is reheated to~31˚C in order to melt the unstable crystals. The stable crystals remain and act as seeds when the chocolate is cooled to~12˚C.

Before the final cooling step to ~12°C, about 1-3 wt% of the cocoa butter is believed to be in solid state. If more than 3 wt% of the cocoa butter is in solid state the chocolate becomes over-tempered. This means that a too large fraction of the chocolate is solid prior to moulding which makes the de-moulding very difficult, as the chocolate does not contract sufficiently. An over-tempered chocolate is also associated with more fat bloom development during storage (Svanberg et al., 2012). If less than 1 wt% of the cocoa butter is in solid state the chocolate becomes under-tempered (Lechter, 2009). This means that not enough seeds generating β_V are present in the chocolate, which allow a "wild-crystallization" into less stable crystals (α and β') to take place. An under-tempered chocolate easily develops fat bloom during storage as part of its crystal structure is in less stable forms.

Pre-crystallization is a complex process and the tempering conditions are important but are difficult to control in large scale productions. The conventional tempering is also costly because of great energy consumption and large space required. A novel pre-crystallization technique called seeding is simpler and it uses cocoa butter seeds or chocolate seeds in order to get well-tempered chocolate (Hachiya, Koyano, & Sato, 1989).

Seeding

Seeding is a pre-crystallization technique where fat crystals in the β_V or β_{VI} form are used to crystallize the chocolate in the preferred crystal structure. A schematic view of the seeding process can be seen in Figure 6. It starts as the conventional tempering by heating of the chocolate to~50˚C. It is then cooled to the seeding temperature, the temperature of which the seedpowder is added. The temperature differs depending on the seedpowder but is about 32˚C. Approximately 0.2-2 wt% of the seedpowder is then mixed in the molten chocolate. The seeds act as nuclei and when the chocolate is cooled to about 12˚C in the last step they induce crystallization in the β_V form. As the formation of β_{VI} crystals is a solid-solid transition (Figure 3), both seeds in the β_V and β_{VI} polymorphic form induce crystallization in the preferred β_V form. The polymorphic form of the seeds has been shown to be the most important in the rate of the crystallization (Hachiya, Koyano, & Sato, 1989). The process time depend on the seedpowder but compared to the conventional tempering the seeding is a faster process. (Svanberg L. , 2012).

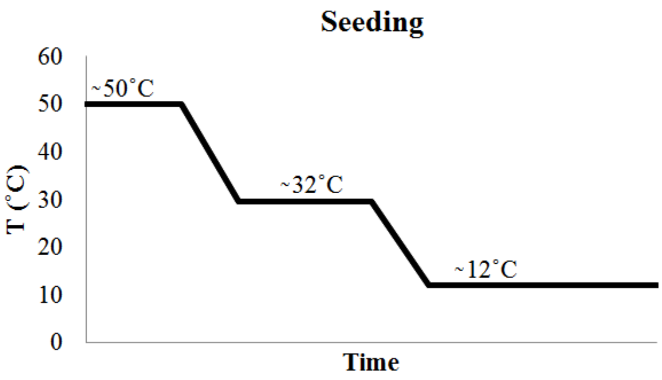

Figure 6. Schematic view of the seeding process. The first step is the melting of the chocolate to~50˚C. It is then cooled to the seeding temperature (~32˚C) where the seeds are added. When the chocolate is cooled to~12˚C the seeds induce crystallization.

2.2. Temper degree

The temper degree of chocolate can be measured by a tempermeter. It is done by cooling the chocolate in a controlled way while the temperature is measured by a temperature probe inside the chocolate. When the fat in the chocolate is cooled it crystallizes and then it releases heat. The heat released warms the chocolate and the temperature curve is affected and a change in the curve can be observed. Depending on the temper degree the changes of the curve are different. The cooling rate of the tempermeter is designed to give the temperature curve of the cooled chocolate a plateau when crystals in a well-tempered chocolate are formed, see Figure 7 b). If the fat is under-tempered the chocolate will crystallize in unstable crystals, see Figure 7 a). When the unstable crystals form; more under-cooling is required followed by an intense and simultaneous "wild-crystallization" where relatively much heat is released at the same time. This cause the temperature of the chocolate to rise because the cooling rate of the tempermeter is smaller in comparison. If the chocolate instead is over-tempered the crystallization begins at higher temperatures. Less amount of crystals are formed in the range of the plateau which cause the cooling to be greater than the heat released during crystallization. Because of this the temper-curve of over-tempered chocolate does not have a rise in temperature as can be seen in Figure 7 c) (Beckett S. T., 1994).

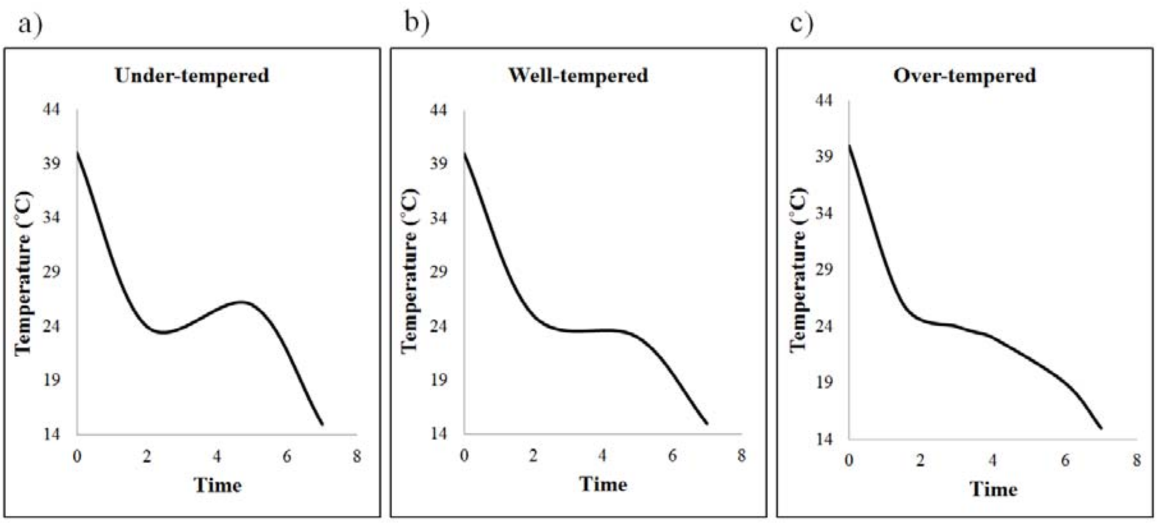

Figure 7. Schematic view of the different temper-curves a) Under-tempered chocolate b) Well-tempered chocolate with a plateau at ~24˚C c) Over-tempered chocolate.

2.3. Crystal structure characterisation

Differential scanning calorimetry (DSC) is an analytical technique that can be used to estimate the relative amount of each crystal form present in a sample (Beckett, 2000). DSC equipment measures the latent heat, the energy needed in order to melt a substance or energy released when a substance solidifies. When the sample is placed in the DSC it is exposed to a well-controlled temperature change that is predetermined. A typical temperature rise can be about 5˚C per minute. When the sample is heated to a temperature where crystals starts to melt more energy is needed in order to melt the crystals. The energy is used to melt the crystals and in order to maintain the even temperature rise more energy has to be added. To estimate the additional energy needed to melt the crystals the energy requirement is compared with the energy needed to heat a control sample, for example an empty container. The DSC will then show energy peaks at the temperature where each crystal phase melt. The range and shape of the peaks can then give information about what crystal forms that are present in the sample. At the peak maximum the rate of the melting is the greatest and the most crystals melt at that temperature (McFarlane, 1994) (Beckett, 2000). In Figure 8 an example of a DSC melting curve of dark chocolate is shown.

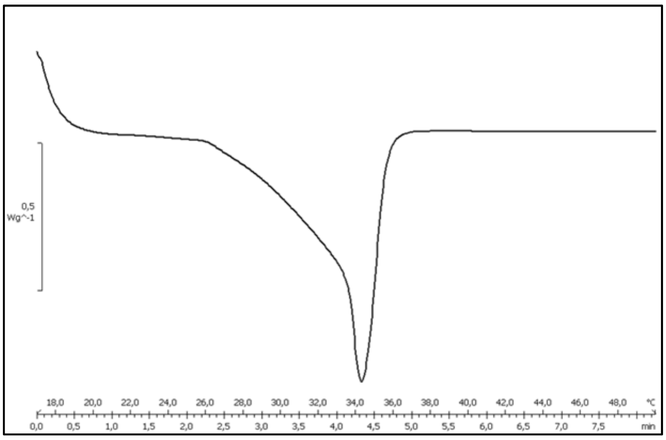

Figure 8. DSC melting curve of dark chocolate when heating from 17˚C to 50˚C at a rate of 4˚C per minute.

Liquid samples can also be studied by DSC but are cooled and start to crystallize. Crystallization is the opposite of melting and energy is released during the cooling of the sample. The energy released causes a need of increased cooling compared to the control sample. Depending on what crystals that are formed the sample release energy at different temperatures that correspond to the crystals formed. After crystallization the sample can be melted to get the melting curves (Beckett, 2000).

2.4. Fat bloom

Fat bloom is the appearance of white spots or coatings on chocolate products during storage. It is the biggest cause of product deterioration in the chocolate industry and causes both visual and textural quality loss. The fat bloom in chocolate is due to migration of liquid TAGs through the fat crystal network. Formation of fat bloom is strongly dependent on temperature and time but also the crystal structure achieved during production of the chocolate. Depending on this, fat bloom can be formed quickly or take up to some years to form. When the liquid TAGs reach the surface of the chocolate they re-crystallize and form the white coating. The cause of fat bloom is debated and not fully understood but there are some phenomena known to cause it (Afoakwa E. O., Paterson, Fowler, & Vieira, 2009) (Sahari, Zarringhlami, Barzegar, & Hamidi-Esfehani, 2013) (Svanberg L. , 2012).

There are several phenomena that can lead to fat bloom (Svanberg L. , 2012) (Beckett, 2000):

- Over time the fat in chocolate is thermodynamically driven to transform into more stable crystals and because of this the chocolate in β_V phase transform via solid state phase transition into β_{VI} crystals. The β_{VI} is a more compact structure than β_V and the chocolate contract during the transformation. The contraction forces liquid fat to migrate through the chocolate matrix to the surface where it re-crystallizes and form the white coating.

- Fat bloom can also appear if the pre-crystallization of the chocolate is insufficient. In that case the chocolate has a β_{IV} structure but transforms into a β_V structure within a few days. Since the β_V structure is more dense than the β_{IV} the chocolate contract causing the same mechanism as for chocolate transforming from β_V to β_{VI}.

- The migrating fat can dissolve some of the crystals in the network decreasing the solid fat content which in turn lower the melting point of the chocolate. This affects the sensory attributes of the chocolate that becomes softer.

The temperature is important in the prevention of fat bloom and temperature variations during storage can speed up the formation. Small variations in temperature (± 2-3˚C) can cause unstable crystals to melt and start migrating to the surface and develop fat bloom. If chocolate is melted the crystal structure is destroyed and during re-crystallization unstable crystals form and the same mechanism as for chocolate that is insufficiently pre-crystallized causes fat bloom (Svanberg L. , 2012).

To quantify fat bloom formation in chocolate during storage the colour of the samples surfaces is analysed. This can be done by capturing high resolution images of the samples in controlled light conditions. Measurements of the L*, a and b (CIELAB definition) in the pictures from the captured chocolate surface can then be used to calculate the whiteness index (WI). Chocolate that has developed fat bloom show an increase in WI (Svanberg L. , 2012).

3. Materials and methods

In the following chapter the materials used in this Master´s thesis will be stated. The methods used for characterisation of seeding powders, process development and storage stability trials will also be presented.

3.1. Materials

Dark chocolate (51 wt%) was kindly provided by CARLA (Dvur Kralove nad Labem, Czech Republic). The cocoa butter β_V seeds (SEED 100) and the chocolate β_V seeds (SEED 200, 36.3 wt% fat) were both kindly provided by Uelzena (Uelzen, Germany). The cocoa butter β_{VI} seeds were kindly provided by ETH – Swiss Federal Institute of Technology (Zurich, Switzerland). The rapeseed oil used for fat migration was from Zeta (Italy) and the filter papers were from Munktell filter AB (Grycksbo, Sweden).

3.2. Characterisation of seeding powders

Table 2 shows the three types of seedpowders that were investigated and the sample names they were given in the work. The cocoa butter β_{VI} were two years old and the cocoa butter β_V and chocolate β_V were newly produced.

Table 2. Types of seedpowder used for pre-crystallization and the sample names they were given.

Sample name	Type of seeds used
CB β_{VI}	Cocoa butter in β_{VI} polymorphic form
CB β_V	Cocoa butter in β_V polymorphic form (SEED 100)
Choc β_V	Chocolate powder in β_V polymorphic form (SEED 200)

The seedpowders were characterized using differential scanning calorimetry (DSC). The DSC method for characterizing the seeds started at 17˚C with an increase of 4 ˚C per minute until it reached a temperature of 50˚C. All DSC curves were normalized according to amount of fat in the sample. To estimate the percentage of each seedpowder that would melt at a certain temperature the DSC curves for each powder were integrated. The interval for integration was 20-X˚C, where X was 29.5˚C respectively 33˚C. The whole peak was also integrated from 20-40˚C and the percentage of seedpowder that would melt at a temperature of 29.5˚C or 33˚C was calculated according to equation 1.

$$Melted\ seedpowder\ (\%) = \frac{Integration\ (20-X°C)}{Integration\ (20-40°C)} \cdot 100 \qquad (1)$$

3.3. Pre-crystallization

A β_{VI} seeding method from (Svanberg L. , 2012) was used and further developed and optimised for each of the three seedpowders. A standard procedure for the seeding is presented below.

1. The chocolate was heated to >50˚C and kept for at least a few hours or overnight in order to erase any memory effects.
2. The chocolate was then cooled either in room temperature or in a water bath during stirring until it reached the seeding temperature.
3. The chocolate was then put in a water bath at the same temperature as the seeding temperature. The seedpowder was added during continuously mixing in 90 seconds to get a homogenous distribution in the chocolate.
4. Samples for tempermeter and DSC were taken directly after seeding.

3.3.1. Process development

The seeding process was developed and optimized with respect to cooling speed, seeding temperature and amount of seeds for each of the three different powders. The reproducibility was also considered.

The cooling speed of the chocolate was varied by cooling it in air at room temperature (21-23˚C) or in a water bath at 25˚C. The range of the seeding temperature tested was 28-33˚C and the amounts of seedpowder tested ranged from 0.5 wt% to 3 wt%. Triplicates of each optimal process were done in order to test the reproducibility and the standard deviations were calculated from the results.

3.4. Process evaluation

The optimal method for each seedpowder found in the process optimization was used for the storage stability experiments. The chocolate was seeded according to the procedure above and was than moulded into cylinders of chocolate. The newly moulded chocolates were stored at 12˚C for 20 min to set before storage. The temper degree was tested using a tempermeter directly after seeding and a sample for DSC was also taken to make sure that the chocolate was well-tempered. The samples were stored up to 72 days in the storage condition that was ~21˚C and 50% RH.

3.4.1. Temper degree

The temper degree was measured with a MultiTherm tempermeter (Bühler Group, Uzwil, Switzerland) directly after seeding of the chocolate. A small metal cup for the chocolate sample was inserted in the tempermeter. The probe was placed in the centre of the chocolate and cooling of the sample started from the walls of the cup. The shape of the tempercurve achieved was used by the tempermeter to estimate a temper index (TI). The TI value of a well-tempered chocolate should be about 5±0.1 according to the built in algorithm (Buhler Group). By the same definitions, TI for under-tempered and over-tempered chocolate is approximately 3±0.1 respectively 6±0.1.

3.4.2. Crystal structure

Differential scanning calorimetry (Mettler Toledo, Zurich, Switzerland) was used to analyse the crystal structure of the chocolate samples. The samples were analysed after 2, 7, 28 and 42 days of storage. Approximately 10 mg of the sample was put in a sealed aluminium pan. The temperature method used for evaluation of crystal structure started at 17˚C with an increase of 4 ˚C per minute until it reached a temperature of 50˚C. For analysis all DSC curves were normalized to the sample size.

3.4.3. Fat migration

To study fat migration in the chocolate gravimetric measurements were performed on samples from each type of seeding. A filter paper was put in a Petri dish and soaked in 1 ml rapeseed oil. Three chocolate cylinders were then placed in each Petri dish and stored in 21˚C and 50 %RH. To determine the fat migration the samples were weight before put on the filter paper and again after storage on the oil soaked filter papers. The percentage of weight gain because of oil uptake was calculated, see equation 2. The scale used had an accuracy of 0.001g (Mettler Toledo, Zurich, Switzerland). Samples were weight after 2 and 7 days of storage and then every 7^{th} day for 49 days. All measurements were done in triplicates and the average percentage of oil uptake was calculated according to equation 2.

$$Weight\ gain\ (\%) = \frac{m_1 - m_0}{m_0} \cdot 100 \qquad (2)$$

3.4.4. Fat bloom

In order to analyse the development of fat bloom Digital Colour Imaging System (DigiEye) was used. 10 chocolate samples of CB β_V and Choc β_V and 8 chocolate samples for CB β_{VI} were photographed when they were newly produced to be used as a reference. The samples were then stored in the storage conditions and photographed after 2 and 7 days of storage and then every 7th days for 70 or 72 days. To quantify the fat bloom the L*, a and b values of the surface of each chocolate piece was collected using the DigiEye Software and the whiteness index (WI) which is a standard tool for quantifying fat bloom on chocolate surface (Briones & Aguilera, 2005) was calculated according to equation 3.

$$WI = 100 - \sqrt{(100 - L^*)^2 + (a^*)^2 + (b^*)^2} \qquad (3)$$

4. Results and discussion

In the following chapter the results from characterisation of seedpowders, process evaluation and the storage stability will be presented and discussed.

4.1. Characterisation of seeding powders

The three types of seedpowders used for seeding were characterised using DSC. Figure 9 shows DSC curves of the CB β_{VI}, CB β_V and Choc β_V powders that were used for optimization of the seeding processes and the storage stability test. The β_{VI} powder was two years old and the CB β_V and Choc β_V powder was newly produced. The CB β_V and the Choc β_V seedpowders have only one peak compared to the CB β_{VI} seedpowder that show two more distinct peaks. The two peaks observed in the CB β_{VI} powder in Figure 9 (one at 33°C and the next as a plateau at 35°C) illustrates that this seedpowder contains two distinct crystal phases, one in the range of β_V crystals and one in the range of β_{VI} crystals. Compared to the melting curves of the other two seedpowders, the CB β_{VI} powder has its β_V peak at slightly lower temperature.

The CB β_V powder has one peak but at higher temperature than the β_V peak of the CB β_{VI} powder. This indicates that the crystal structure consists of a mix of more or less compact β_V crystals and probably some crystals in the β_{VI} phase. The crystals in the β_{VI} phase are not as many and stable as the β_{VI} crystals in the CB β_{VI} powder and because of this the CB β_V powder do not show a separate peak for the β_{VI} polymorphic form. Because of the mix of β_V crystals and β_{VI} crystals in the CB β_V powder the peak have a higher melting point than the β_V crystals in the CB β_{VI} powder.

The DSC curve of the Choc β_V powder in Figure 9 shows one peak similar to the CB β_V powder but its melting point is slightly lower than for the CB β_V powder. The crystal structure of Choc β_V also exist as a homogeneous mix of β_V crystals and some β_{VI} crystals that cause one distinct peak at slightly higher melting point than for the CB β_{VI} powder. The lower amount of cocoa butter in the powder is compensated in the normalization of the peaks but the Choc β_V powder only comprises 36.3% fat and therefore also contain other components that also have effect on the melting characteristics. Among other components chocolate contain cocoa particles that in turn contain fat such as mono- and diacylglycerols (Afoakwa E. , Paterson, Fowler, & Vieira, 2008). The lower fat content of the Choc β_V powder can be the cause of the decrease in melting temperature and the broader peak compared to the CB β_V.

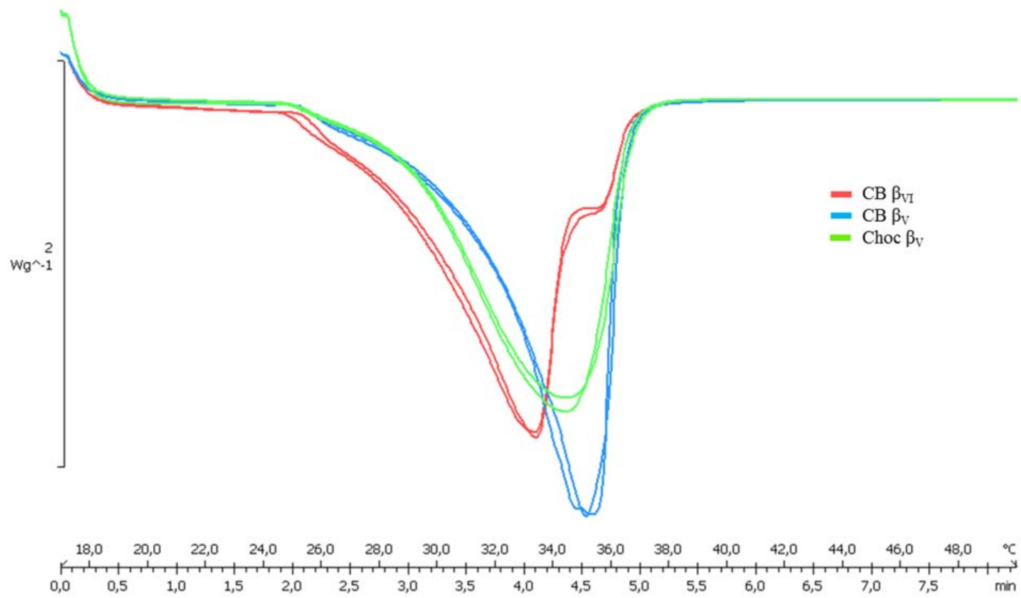

Figure 9. DSC curves of CB β_{VI}, CB β_V and Choc β_V seedpowder that were used in the process evaluation and storage stability trials.

Integration of DSC curves in Figure 9 can be used to approximate how much of each seedpowder that would melt at different seeding temperatures. Integrations between 20˚C and 29.5˚C respectively 33˚C for each seedpowder is shown in Table 3. As can be seen in the Table 3 a greater proportion of the CB β_{VI} powder melt at both 29.5˚C and 33˚C compare to the other seedpowders. As much as 65.68 wt% of the CB β_{VI} powder melts at 33˚C. The powder consists of β_V and β_{VI} crystals and the crystals that melt at 33˚C are mostly in the β_V phase. The remaining 34.32 wt% that does not melt consists of stable crystals that have great impact on the crystallization of the chocolate. At a temperature of 29.5˚C the CB β_V powder and Choc β_V powder show similar results and about 10 wt% of both seedpowders melt at that temperature. At a higher temperature of 33˚C the Choc β_V powder is more sensitive and a greater proportion melts compared to the CB β_V powder. This is an indication that the Choc β_V powder is not as stable as the CB β_V powder.

Table 3. Approximate wt% of the three seedpowders CB β_{VI}, CB β_V and Choc β_V that melt at 29.5˚C respectively at 33˚C. The values were calculated by integration of DSC curves for each powder.

	29.5˚C	**33˚C**
CB β_{VI}	18.27	65.68
CB β_V	10.28	37.28
Choc β_V	10.00	47.00

The changes in crystal structure of the seedpowders over time were also characterised by DSC. In Figure 10 DSC curves of CB β_V, Choc β_V and CB β_{VI} seedpowders that were both newly produced and two years old are shown. As can be seen in the graph all seedpowders tend to shift to higher melting point during storage. This is because the fat crystal network slowly undergoes solid-solid transition to more stable polymorphic form.

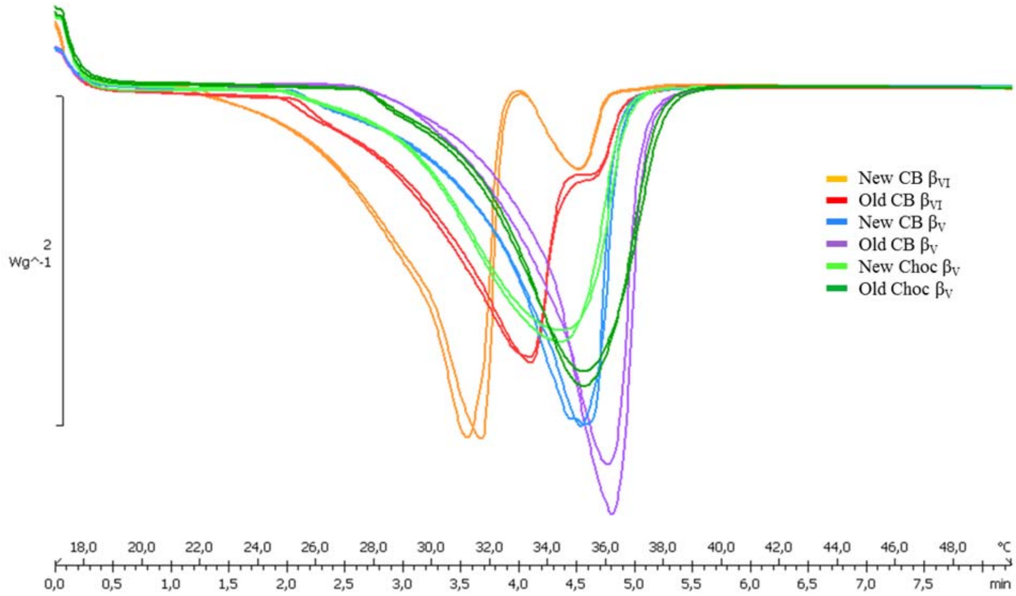

Figure 10. DSC curves of CB β_{VI}, CB β_V, and Choc β_V seedpowders for newly produced and two years old seeds.

Evaluation of the effect of the seedpowders particle size was not done in this work but differences between the powders were observed. By visual inspection, Choc β_V powder appeared to have the smallest seeds, CB β_{VI} the biggest seeds and the CB β_V seeds something in between. The CB β_{VI} powder had become a bit lumpy during the two years of storage. The CB β_V was newly produced and was not as lumpy as the CB β_{VI}. The CB β_V powder had some lumps but they were a bit smaller in size and not as many as in the CB β_{VI} powder. Samples of the same type of CB β_V seeds and Choc β_V seeds that was used in the trials but 2 years old showed the same tendency to form lumps as the 2 year old CB β_{VI}. The particle size of the seedpowder is believed to have an effect on the seeding. For example, bigger particles have a smaller surface area/volume ratio which is expected to influence the seeding effect and also dispersion and melting properties are affected by the particle size. Figure 11 show a picture of the three seedpowders.

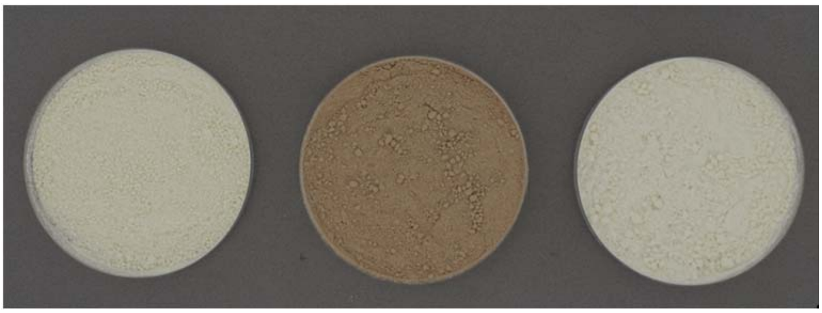

Figure 11. Picture of the three types of seedpowders from the left CB β_V, Choc β_V and CB β_{VI}. The Choc β_V powder had the smallest particles, the CB β_{VI} powder had the biggest particles and the size of the CB β_V powder is something in between.

4.2. Process development

In the following chapter the results from the development of seeding methods are presented. The methods were optimized for each type of seeds with respect to cooling time, temperature and amount of seeding powder. The reproducibility of the seeding method was also considered.

4.2.1. Seeding methods

Seeding with the CB β_{VI} powder was performed on chocolate that had been cooled in room temperature to a temperature of 33˚C. Different amounts of the seedpowder were tested to find the amount that gave well-tempered chocolate, a TI close to 5. In Table 4 the amounts of seedpowder tested for the CB β_{VI} seeding process and for the seeding processes of CB β_V and Choc β_V powders are shown. The results of the seeding processes with different amounts of CB β_{VI} powder are shown in Figure 12 a). The amount of powder that was found to give the best TI values was 0.52 wt%. Due to improved mixing effects at smaller sample sizes, the percentage of seedpowder needed is dependent on the amount of chocolate and because of this the amount is specific to the amount of chocolate used.

Table 4. The different wt% of seedpowder tested for each type of seeding process using CB β_{VI}, CB β_V respectively Choc β_V powder.

CB β_{VI}	0.40	0.50	0.52	0.60	0.61
CB β_V	1.45	1.55	1.65	1.75	1.85
Choc β_{VI}	2.00	2.50	3.00		

Characterisation of the seedpowders showed that about 37 wt% of the CB β_V powder (Table 3) would melt at a seeding temperature of 33˚C. Trials using a seeding temperature of 33˚C showed unsatisfactory results and the remaining 63 wt% of the CB β_V powder was not enough to achieve a well-tempered chocolate. To find optimal temperature for seeding screening trials were done. The temperature is an important factor in the industry and a high temperature of the chocolate makes it easier to handle because the pumping through pipes is facilitated. It is also an advantage in an economic perspective, a higher temperature makes the process cheaper because of reduced cooling of the chocolate. Trials with chocolate at a temperature of 30˚C did not show an increase in TI when the amount of seedpowder was increased (graph in appendix B). The highest temperature found to give good correlation between wt% seeds and TI was 29.5˚C. According to the DSC analysis of the pure powders, at 29.5˚C approximately 90 wt% of the seedpowder would remain after addition in the warm chocolate which was proven to be enough to get a good pre-crystallization.

The reproducibility was shown to be better when cooling of the chocolate was faster and controlled using a water bath at 25˚C instead of cooling it in room temperature. This indicates that the CB β_V powder was not as stable as the CB β_{VI} powder. A shorter cooling time decrease the "wild-crystallization" of the chocolate during the cooling step and it makes it is easier to control crystallization with the seedpowder. This step was shown to be necessary to get good reproducibility for the CB β_V powder. The optimal condition found was to add the seedpowder in chocolate cooled in a water bath (25˚C) to 29.5˚C. Different amounts of seedpowder (Table 4) were tested at this condition to find the optimal amount. In Figure 12 b) the results from the seeding trials with the amounts of CB β_V powder at the optimal conditions are shown. The optimal amount of seedpowder was found to be 1.75 wt%.

The DSC characterisation of the Choc β_V seedpowder showed that it had similar crystal structure to the CB β_V powder. Because of this the same process parameters for seeding temperature (29.5˚C) and water bath temperature (25˚C) was used for the Choc β_V seeding. The Choc β_V seedpowder only contain 36.3 wt% fat and because of this the amount of powder needed was greater than for the other powders that consisted of 100 wt% fat. The amounts of seedpowder tested in the Choc β_V process are shown in Table 4. The results of the different amounts of Choc β_V seedpowder used when the chocolate was cooled to 29.5˚C in a water bath are shown in Figure 12 c). The amount of Choc β_V powder that was found to give the best results regarding TI was 2.5 wt%.

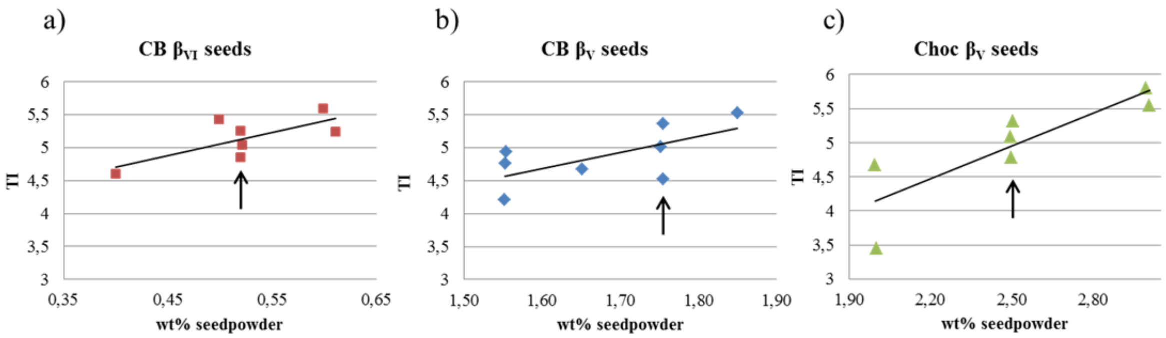

Figure 12. Temper index (TI) when seeding with different amounts of a) CB β_{VI} powder b) CB β_V powder and c) Choc β_V powder. A linear regression was calculated to find the amount of seedpowder needed to get a TI value of 5. Arrows show the wt% seedpowders that were found to give the best results. Note that the scale on the x-axis differs between all three graphs.

A linear regression was calculated for each seeding process and is shown in Figure 13 a). The coefficient of determination (R^2) for the CB β_{VI}, CB β_V and Choc β_V was 0.532, 0.423, and 0.723, respectively. In the Figure 13 a) the equation of the linear regressions are also shown. The steeper the linear regression the more impact does the powder have on the TI. The equation of the linear regression for CB β_{VI} shows that the slope is steeper than for CB β_V, 3.52 respectively 2.41. The difference in the slope shows that seeding with CB β_{VI} powder is more sensitive to the amount of powder used compared to the CB β_V powder since less powder is needed to get a change in the TI. The Choc β_V powder was the least sensitive with a slope of 1.61. Compared to the other powders more powder is needed to get an increase in TI.

The Choc β_V powder only contained 36.3 wt% fat and in Figure 13 b) this is taken into account and the results are normalized with respect to the fat content in the powders. The equations of the linear regressions are also shown in the Figure 13 b). When the fat content was taken into account the Choc β_V powder was shown to have the steepest slope with a value of 4.42. The Figure 13 b) also shows that the amount of fat needed to get well-tempered chocolate is less when using the Choc β_V powder compared to using the CB β_V powder. The lower amount of Choc β_V needed compared to CB β_V powder on the basis of the fat content may be a result of the cocoa particles and sugar in the powder. The cocoa particles contain di- and triacylglycerols that can be dissolved and act as nucleation sites. The surface of the sugar may induce heterogeneous nucleation where a foreign surface induces crystallization but research contradicts in this matter. Sugar and cocoa particles have been shown to promote crystals with lower melting points, hence the lower melting point of the seeding powder (Dhonsi & Stapley, 2005) (Svanberg, Ahrné, Lorén, & Windhab, 2011).

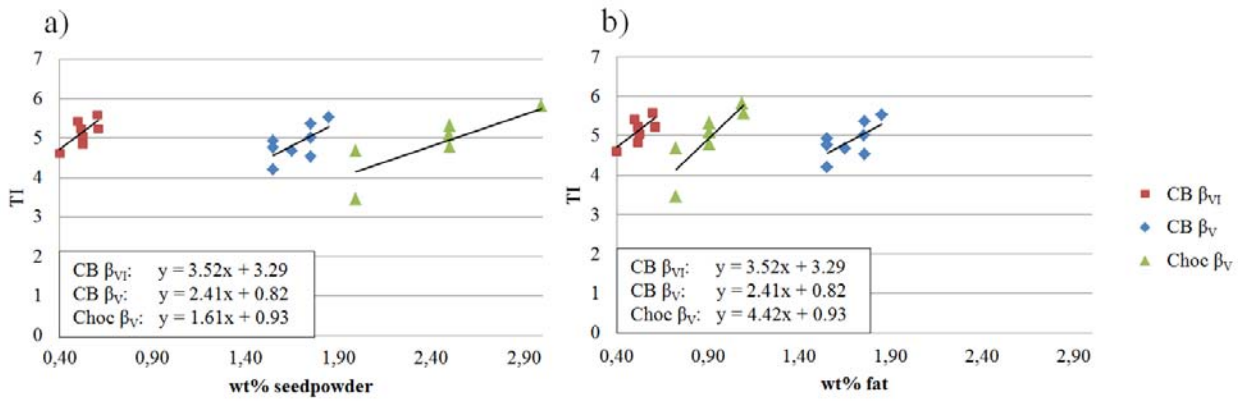

Figure 13. a) TI for all three types of seedpowder at different wt% powder with linear regression. The equation for each type of seedpowder is shown in the box. b) TI for all three types of seeds at different wt% fat with linear regression. The equation for each type of seedpowder is shown in the box.

4.2.2. Optimal process

The optimal process parameters were found to be slightly different for the three types of seedpowders. The final parameters for each type of seeds are shown in Table 5.

Table 5. Optimal process parameters for seeding with CB β_{VI}, CB β_V and Choc β_V seedpowder found in the process development.

	wt% seeds	T seeding (˚C)	T water bath (˚C)
CB β_{VI}	0.52	33.0	-
CB β_V	1.75	29.5	25.0
Choc β_V	2.50	29.5	25.0

Triplicates of the optimized seeding processes were done in order to test the reproducibility. The average TI and the standard deviation of the three triplicates for each type of seedpowder are shown in Figure 14. The seeding process of the CB β_{VI} powder showed a standard deviation of 0.2 which was the smallest of the three seedpowders. The CB β_V powder seeding had the greatest standard deviation of 0.42. The standard deviation of the seeding with Choc β_V powder was 0.27. The process of the Choc β_V powder required much more powder than the other processes and a small change in the amount of Choc β_V powder does not affect the TI value as the same increase in the other seeding processes. This makes the Choc β_V process less sensitive and this can be the reason for the smaller variation compared to CB β_V powder.

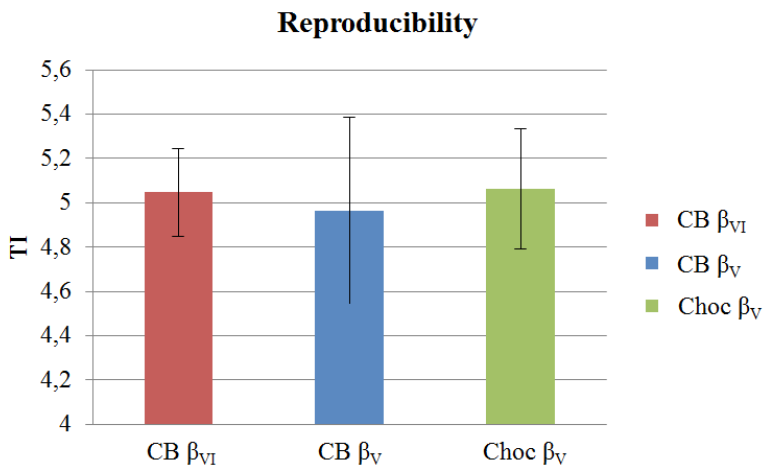

Figure 14. Reproducibility of the seeding processes was evaluated from the three replicates. Mean value of triplicates from seedings with each type of seedpowder with standard deviation are shown as error bars. CB β_{VI} showed best reproducibility, then Choc β_V and CB β_V had the greatest variation among the results.

4.3. Storage stability

In the following chapter the results from the storage stability tests of the seedpowders are presented. Storage stability was evaluated by analysis of fat migration, resistance to fat bloom and the crystal structure. The amount of seedpowder and TI of the chocolate samples used in the storage trials are shown in Table 6. Only one batch of chocolate seeded with the CB β_{VI} powder was produced due to lack of time. Tempercurves of the stored samples can be found in appendix C.

Table 6. Data for the seeded chocolate samples seeded according to the optimal processes found and used in the storage stability trials.

Stored samples	wt% seeds	TI
CB β_{VI}	0.52	5.39
CB β_V batch 1	1.75	5.23
CB β_V batch 2	1.75	5.24
Choc β_V batch 1	2.50	5.75
Choc β_V batch 2	2.50	5.74

4.3.1. Fat migration

Gravimetric measurements of fat migration in the chocolate samples were analysed after 2 and 7 days and then every 7th day for 49 days. The percentage of weight gain of the chocolate samples over time is shown in Figure 15. The results after 2 days were removed since it appeared as the chocolate samples had lost weight. The weight loss during the two first days was probably due to loss of moisture from the chocolate samples. After two days not much oil had been taken up and faulty results appear. Outliers caused by dissolution of chocolate into the filter paper or uneven distribution of oil on the filter paper during storage were also removed. As can be seen in the Figure 15 the differences between the seedpowders are quite small. This is because all of the samples was well-tempered and have a crystal structure that should resist fat migration to a higher extent than an under-tempered chocolate. An over-tempered chocolate have a denser crystal structure compared to well-tempered chocolate and should have great resistance to fat migration.

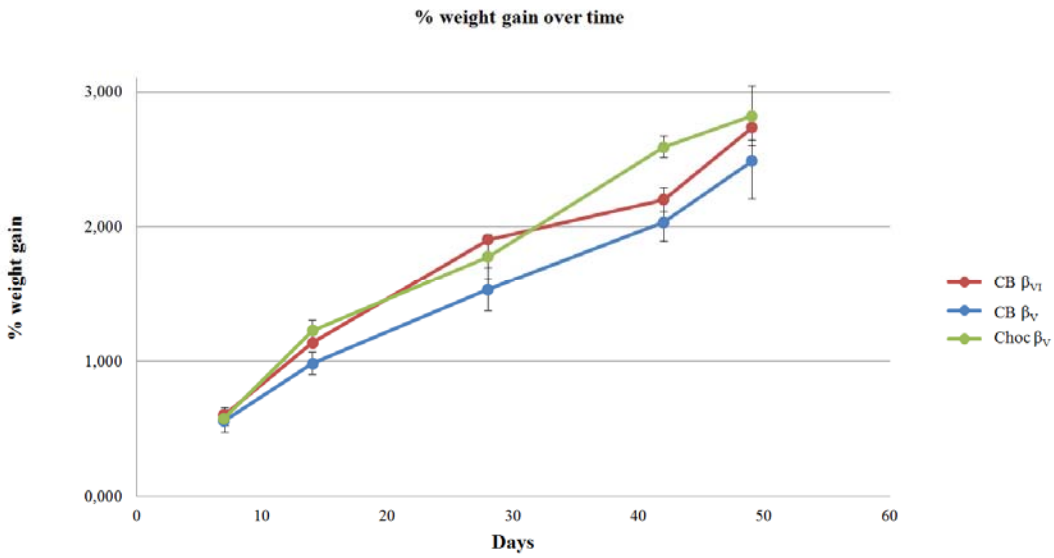

Figure 15. % weight gain due to fat migration into the chocolate samples over time.

The results from the fat migration showed that the chocolate samples seeded with Choc β_V powder had the highest uptake of oil. Both cocoa butter seedpowders showed better resistance to fat migration. The CB β_V samples had the lowest uptake of oil and were slightly better than the CB β_{VI} samples.

The reason that the Choc β_V had the greatest uptake could be explained by the crystal structure of the samples. They may take up more oil because the crystal structure appears to be more unstable (Figure 20) in the beginning of the storage and it gets more stable during storage (Nightingale, Lee, & Eng, 2011). The unstable crystals directly after seeding makes it easier for the fat to migrate into the crystals and thereby destroying the crystal network before it gets stable over time. In previous studies it has been suggested that the destruction of the crystal structure cause an increased fat uptake in the chocolate (Smith, Cain, & Talbot, 2007).

4.3.2. Fat bloom

This work also meant to study the seeded chocolate samples resistance to fat bloom. This analysis was performed using DigiEye but during the study technical problems with the equipment was discovered and the results could not be used for analysis. During the first six weeks the chocolates did not show any sign of fat bloom visible for the naked eye which indicates that all chocolate samples were well-tempered, which agree with the TI results from the tempermeter. An under- or over-tempered chocolate would not resist fat bloom to that extent in the storage conditions in the study. All pictures of the stored samples can be found in appendix C. In figure 16 five of the chocolate samples seeded with CB β_{VI} seedpowder are shown after 0 days of storage and 72 days of storage. Small differences can be observed and the surface of the samples is not as glossy as when they were newly produced. The loss of gloss is an early sign of fat bloom.

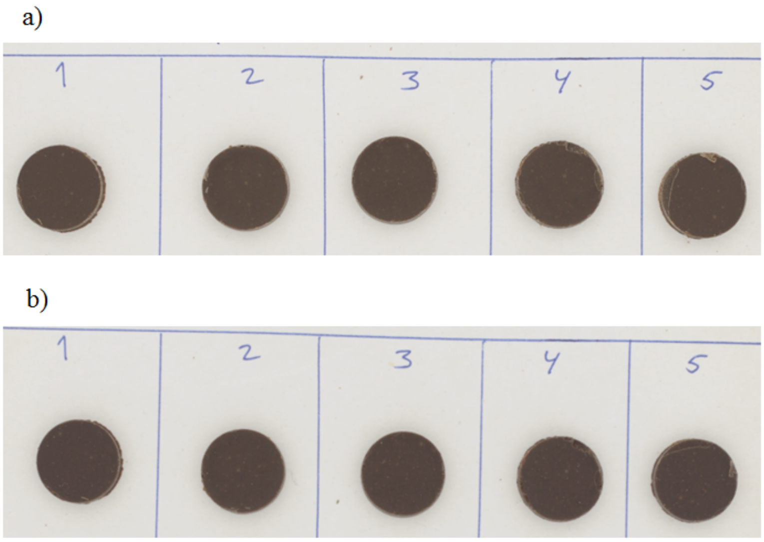

Figure 16. Five of the chocolate samples seeded with CB β_{VI} powder after a) 0 days of storage and b) 72 days of storage.

The Figure 17 shows five of the chocolate samples seeded with CB β_V seedpowder after 0 and 70 days of storage. Like the chocolate seeded with CB β_{VI} powder the chocolate samples of CB β_V show loss of gloss on the surface. On some of the samples a thin greyish haze appeared close to the edge of the samples.

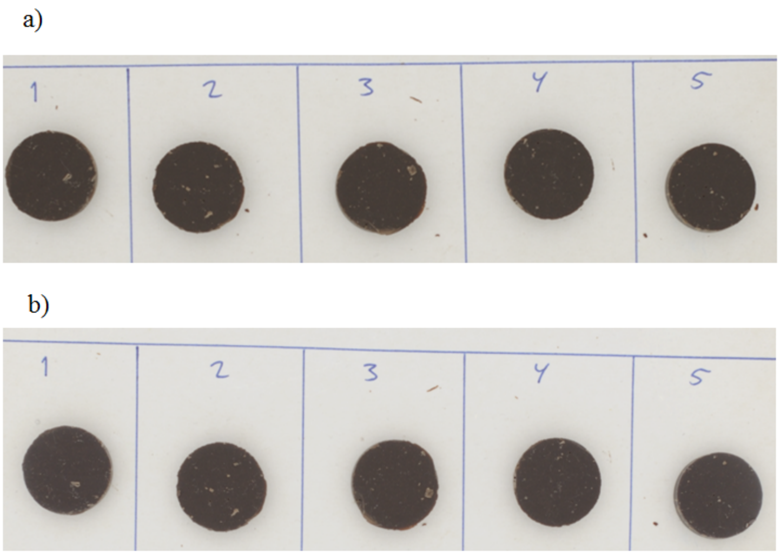

Figure 17. Five of the chocolate samples seeded with CB β_V powder after a) 0 days of storage and b) 70 days of storage.

The Figure 18 shows five of the chocolate samples seeded with Choc β_V seedpowder and stored 0 days and 70 days. The chocolate samples seeded with Choc β_V also showed a less glossy surface compared to day 0 and like some of the CB β_V chocolate samples some samples had a thin greyish haze close to the edge.

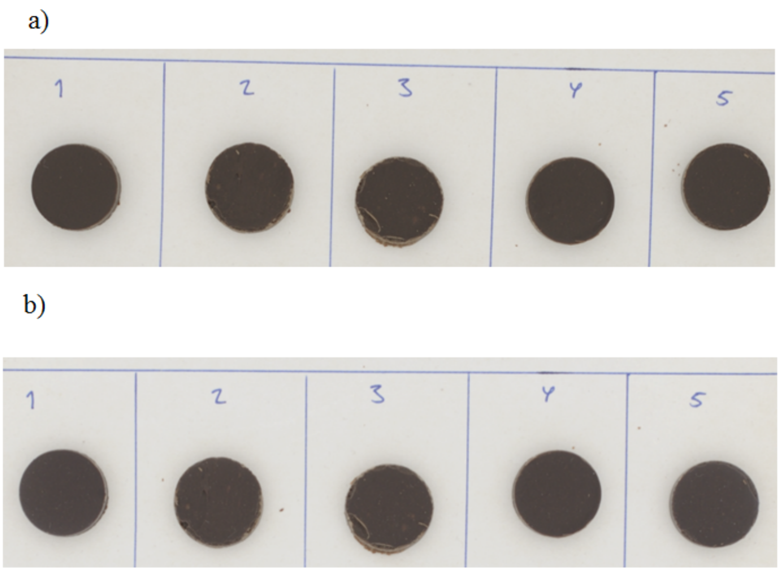

Figure 18. Five of the chocolate samples seeded with Choc β_V powder after a) 0 days of storage and b) 70 days of storage.

4.3.3. Crystal structure

The crystal structure of the stored chocolate samples were analysed with DSC. Figure 19 shows the DSC curves of chocolate seeded with the three different types of seedpowders CB β_V, Choc β_V and CB β_{VI} after two days of storage. All three samples have a peak maximum at about 32-33˚C and this indicates that all the chocolate samples were well-tempered and got the desired β_V polymorphic structure. A figure with DSC curves of chocolate samples stored for 7 days can be found in Appendix C.

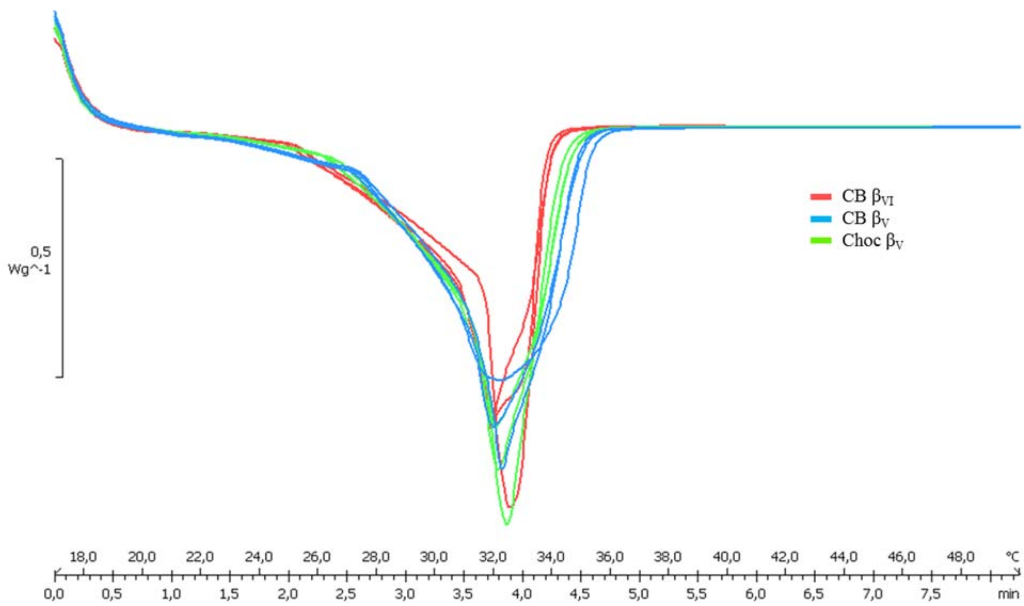

Figure 19. DSC curves of chocolate seeded with CB β_{VI}, CB β_V and Choc β_V powder after 2 days of storage.

In Figure 20 the DSC curves after 2 and 42 days of storage are shown for chocolate samples from each type of seedpowder. The curves for the CB β_{VI} chocolate samples in Figure 20 a) only show a small shift to more stable crystals. The crystal network contract and get more dense over time due to transformation to more stable crystals (Beckett S. T., 1994). After 42 days of storage there is tendency of a phase separation in the chocolate. A phase with melting point at 24-30˚C appear and it consists of so called lower melting crystals. The lipids with low melting points, such as short chain fatty acids and unsaturated fats, have been shown to be the most likely to migrate through chocolate (Ali, Selamat, Che Man, & Suria, 2001). The crystals with lower melting point that appear after 42 days may be polyunsaturated fats that are forced out of the tightly packed crystal network when it gets more dense during storage. The chocolate seeded with CB β_V powder shifted slightly more than the CB β_{VI} chocolate (Figure 20 b)). It had some unstable crystals with low melting points (20-27˚C) after 2 days of storage that had transformed into more stable crystals after 42 days of storage. The Choc β_V chocolates show the greatest shift (Figure 20 c)) and the peak maximum shifts from ~ 32˚C to ~ 33˚C. The observed shift of peak maximum of the Choc β_V chocolates indicates that more significant post-crystallization occurred during storage in these samples. This indicates that the structure in these samples were less resistant towards solid-solid transitions during storage.

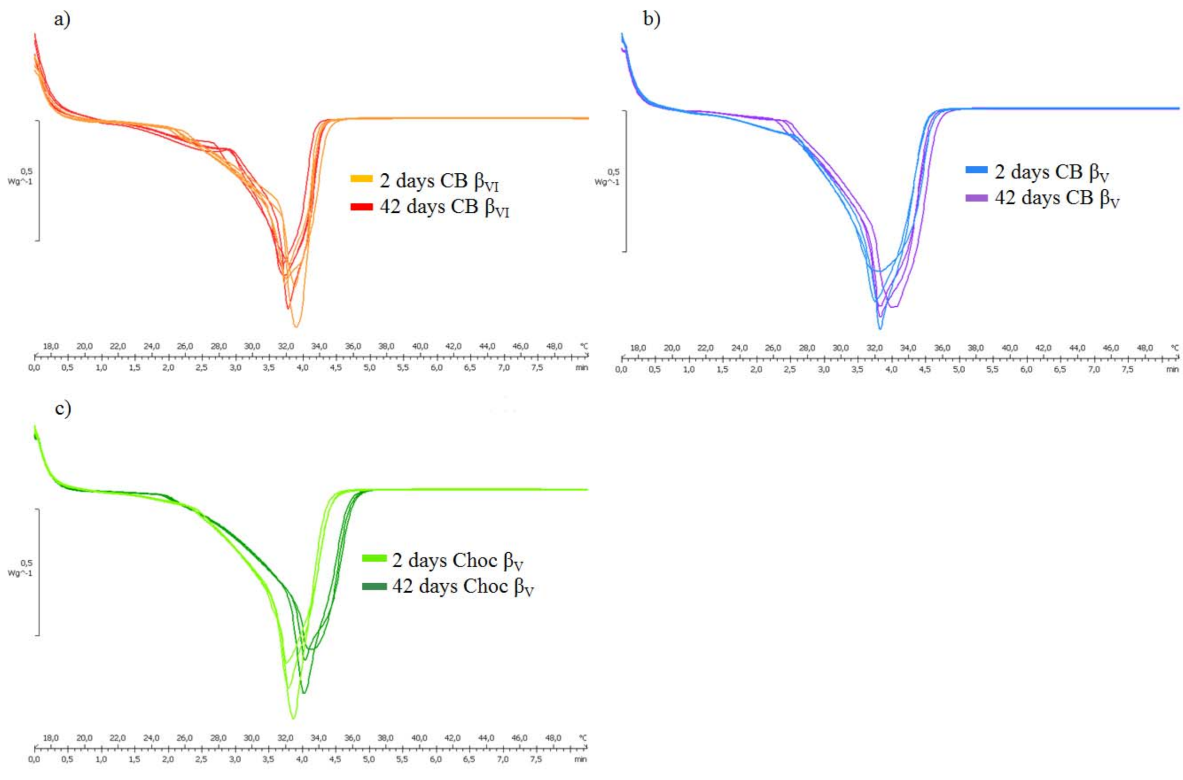

Figure 20. DSC curves for chocolate samples stored 2 days respectively 42 days. a) Chocolate samples seeded with CB β_{VI} seedpowder. b) Chocolate samples seeded with CB β_V seedpowder. c) Chocolate samples seeded with Choc β_V seedpowder.

After 42 days of storage (Figure 21) the peak maximum of the chocolate samples seeded with the three different seedpowders differ more than after 2 days. After the storage the chocolate samples from the CB β_{VI} seeding had an approximate peak maximum at 32˚C. The peak maximum was between 32-33˚C for the CB β_V chocolate and 33˚C for the Choc β_V chocolate. The melting properties are important for how smooth the chocolate is perceived in the mouth. It is also important for the rate of the melting that in turn determines the perception of both flavour and texture. A lower melting point makes the chocolate melt faster which is desirable because flavours from sugar and cocoa solids are released quickly in the mouth (Lechter, 2009). Even though the CB β_{VI} chocolate had the lowest melting point the crystals were still in the β_V polymorphic form which is very important for the quality. The CB β_V chocolates had slightly higher melting point and Choc β_V had the highest. If the melting point gets too high the chocolate might not melt in the temperature of the mouth and in such case the chocolate appears to have a gritty texture (Lechter, 2009).

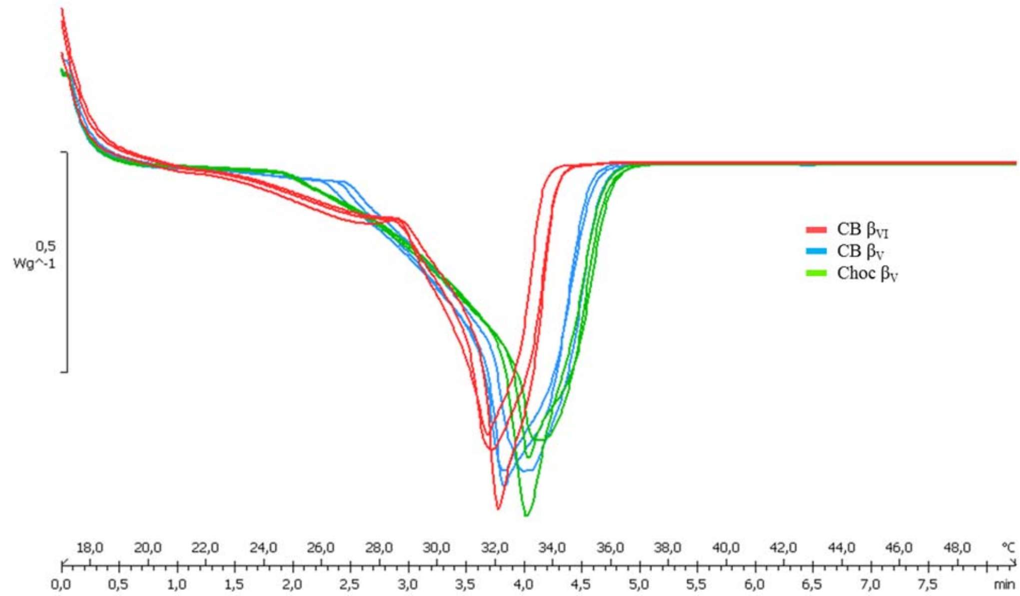

Figure 21. DSC curves of chocolate seeded with CB β_{VI}, CB β_V and Choc β_V seedpowder after 42 days of storage.

5. Conclusions

The characterisation of the seedpowders showed some differences in the crystal structure between the three powders. The CB β_{VI} powder appeared to have two distinct phases of β_V and β_{VI} crystals. The CB β_V and Choc β_V powder both showed results indicating that the crystal structure consists of a mix of more or less compact β_V crystals and probably some crystals in the β_{VI} phase.

In the process development of seeding methods for the three seedpowders the CB β_{VI} powder was found to have best reproducibility. It is probably due to the more stable crystals in the β_{VI} polymorphic form shown in the seedpowder characterisation. Compared to the other powders a higher seeding temperature could be used for the CB β_{VI} powder, 33˚C compared to 29.5˚C for CB β_V and Choc β_V powder. The CB β_V and Choc β_V powders required a faster and more controlled cooling and they were not stable enough to overcome the "wild-crystallization" of chocolate cooled more slowly in room temperature.

The amount of seedpowder needed in order to get a well-tempered chocolate was significantly lowest for CB β_{VI} powder, followed by CB β_V powder and the highest for Choc β_V powder. Since the Choc β_V seedpowder only contains 36.3 wt% fat a comparison of the amounts of fat needed it was shown to required less amount compared to CB β_V powder but still more than CB β_{VI} powder. Triplicates of the optimal processes showed that the variation of the results was smallest in the CB β_{VI} powder, slightly higher in the Choc β_V powder and the greatest in the CB β_V powder.

All pre-crystallization processes with respective seedpowder were shown to produce well-tempered chocolate. After 2 days of storage all samples had a β_V polymorphic structure with only a small difference between the powders. Analysis of the crystal structure after 42 days of storage showed that the chocolate samples seeded with CB β_{VI} had stable crystals that had only shifted to slightly higher melting points. This indicates that the pre-crystallization induce formation of a stable crystal structure that does not change much over time. The CB β_V chocolate samples also showed a small shift but the Choc β_V chocolate samples showed a much greater shift towards a higher melting temperature. The greater shift indicates that the pre-crystallization was not able to induce crystals stable enough to avoid shifts to higher melting points during storage.

The observed post-crystallization in the Choc β_V samples also reflected in the results from the other storage stability evaluations. Chocolate seeded with Choc β_V powder was found to have the highest oil uptake and did not resist fat migration as well as chocolate seeded with CB β_{VI} powder and CB β_V powder. The CB β_V samples were found to have the best resistance to fat migration. Evaluation of the fat bloom was only done visually and all samples showed loss of gloss on the surface which is the first sign of fat bloom. Some of the CB β_V and Choc β_V chocolate samples had slightly more fat bloom compared to CB β_{VI}. A few samples from both the CB β_V and the Choc β_V chocolate showed a thin greyish haze close to the edge after 70 days of storage. However, it should be noted that though Choc β_V had the least resistance to fat migration and fat bloom the differences between the samples were small and good resistance is to be expected since all samples were well-tempered.

In an industrial perspective there are some advantages and disadvantages with all seedpowders. The Choc β_V has the advantage of not changing the composition of the chocolate. In the industry this is an important aspect where an insufficiently pre-crystallized chocolate can be melted and go through the pre-crystallization step again. Using the other powders this cannot be done without recipe adaptations since they would have changed the composition of the chocolate in the first pre-crystallization. Another important aspect in the industry is the temperature. A high pre-crystallization temperature is preferred as it makes the moulding easier. Considering this the CB β_{VI} seedpowder is the preferred.

To summarise, all seedpowders can be used for seeding but there are some differences in the quality of the final product. Depending on the production and what the chocolate will be used for different powders are to prefer. According to the fat migration study the CB β_V would be preferred in chocolate pralines where fat migration is a big cause of deterioration. The CB β_{VI} powder offer a less temperature sensitive production resulting in smaller amounts of seedpowder and easier moulding while the Choc β_V powder does not change the composition of the chocolate.

6. Future work

Pre-crystallization using seedpowders have great potential in the chocolate industry and further studies can give additional knowledge to improve and possibly implement the process in the chocolate production. Characterisation of the seedpowders for example particle size of the powders and the effect on microstructure of the final chocolate product would be interesting and important for an industrial use.

In this Master's Thesis seeding with CB β_{VI} was never done on chocolate that was cooled fast and in a controlled way. By controlling the cooling the amounts of CB β_{VI} seedpowder needed may be even smaller and the reproducibility results may also get better. The CB β_{VI} seedpowder was shown to be more stable than the CB β_V and Choc β_V powder but it did not have the benefits of not changing the composition of the chocolate as the Choc β_V powder had. By combining the properties of CB β_{VI} and Choc β_V and produce a chocolate powder in the β_{VI} structure maybe the benefits from both could be achieved.

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Appendix

A. Characterisation of seedpowders

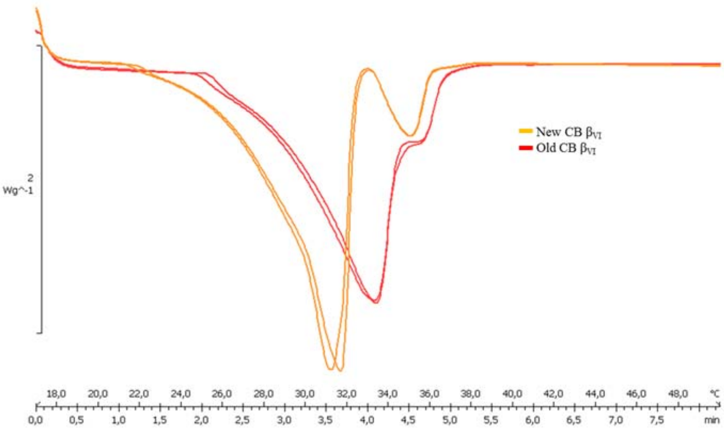

Figure 22. DSC curves of newly produced and 2 years old CB β_{VI} seedpowder.

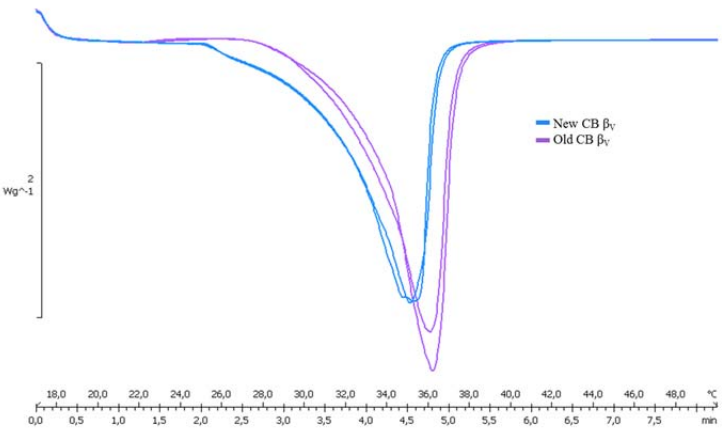

Figure 23. DSC curves of newly produced and 2 years old CB β_{V} seedpowder.

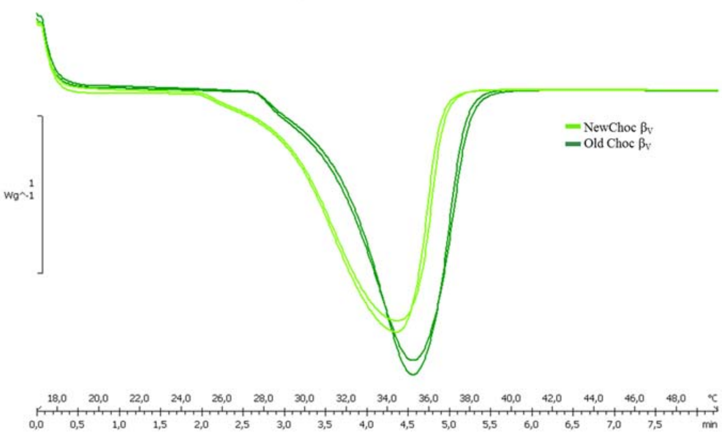

Figure 24. DSC curves of newly produced and 2 years old Choc β_{V} seedpowder.

B. Process development

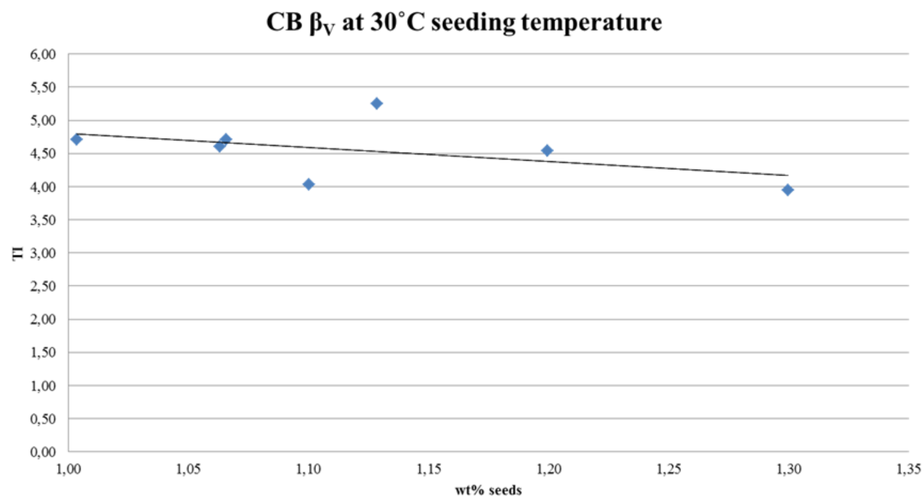

Figure 25. TI for different wt% CB β_V seedpowder when chocolate had been cooled in room temperature to 33˚C.

C. Storage stability

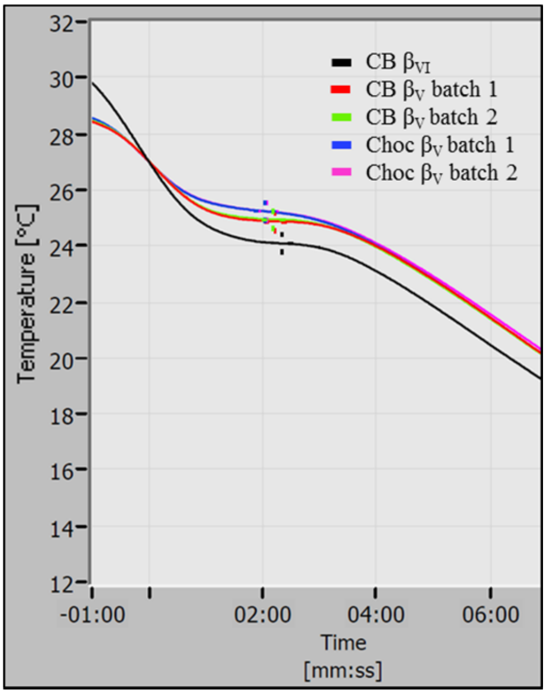

Figure 26. Tempercurves for stored chocolate samples seeded with one of the three seedpowders CB β_{VI}, CB β_V and Choc β_V.

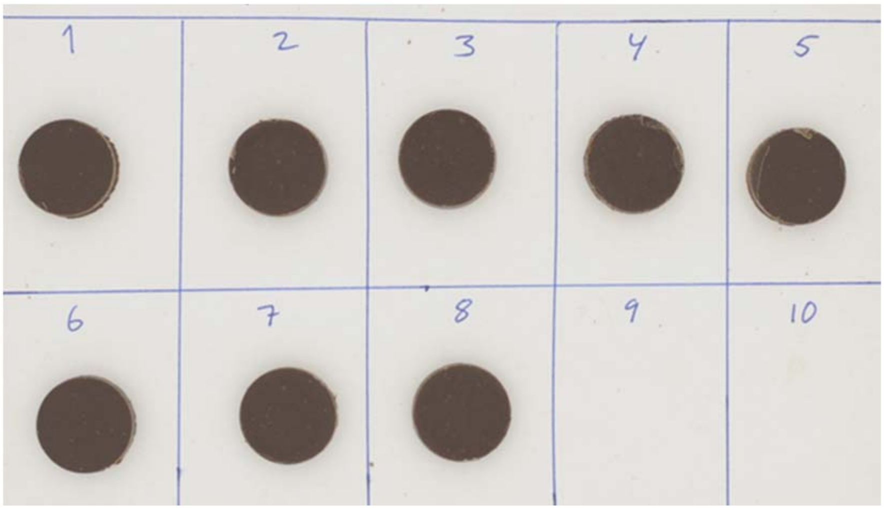

Figure 27. Chocolate samples seeded with the CB β_{VI} powder and stored 0 days.

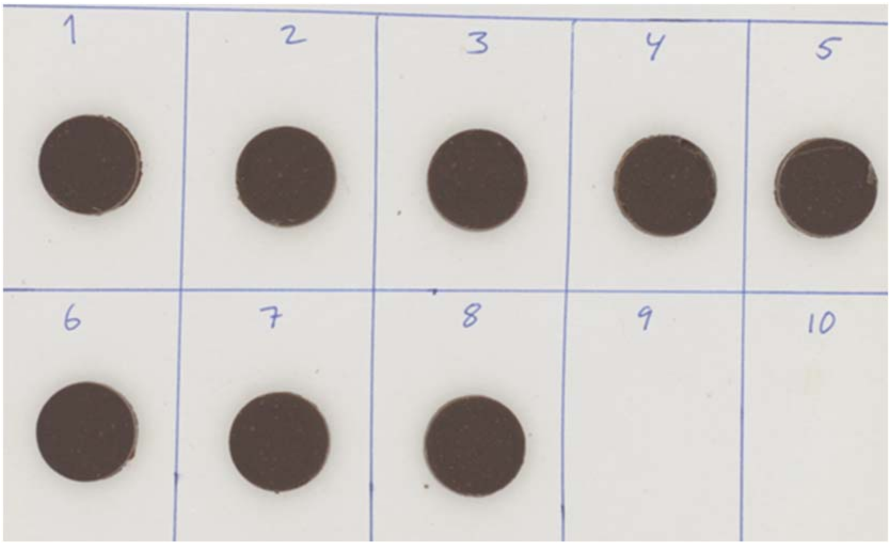

Figure 28. Chocolate samples seeded with the CB β_{VI} powder and stored 72 days.

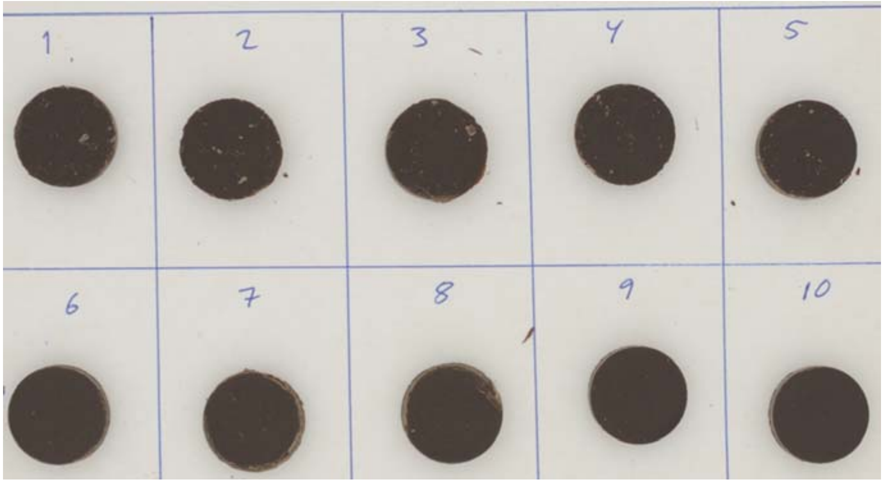

Figure 29. Chocolate samples seeded with the CB β_V powder and stored 0 days.

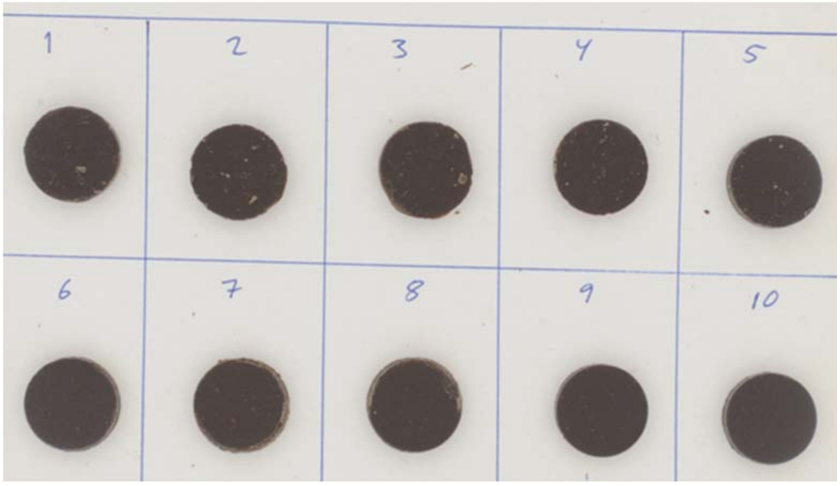

Figure 30. Chocolate samples seeded with the CB β_V powder and stored 70 days.

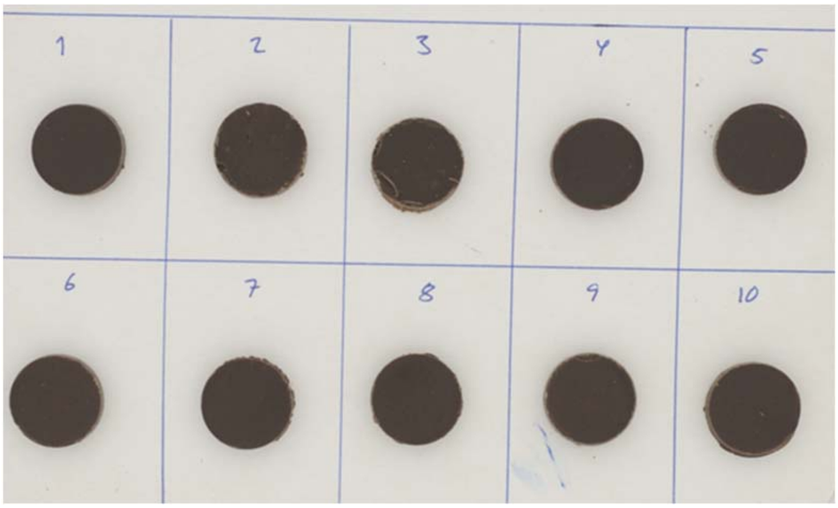

Figure 31. Chocolate samples seeded with the Choc β_V powder and stored 0 days.

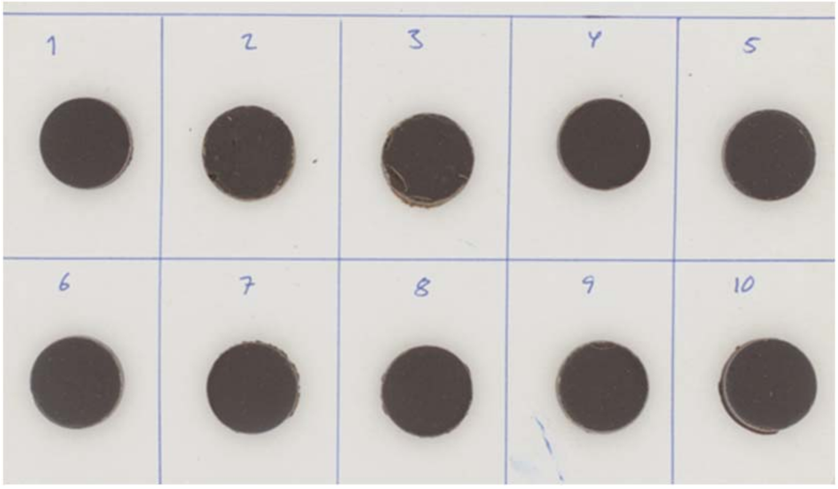

Figure 32. Chocolate samples seeded with the Choc β_V powder and stored 70 days.

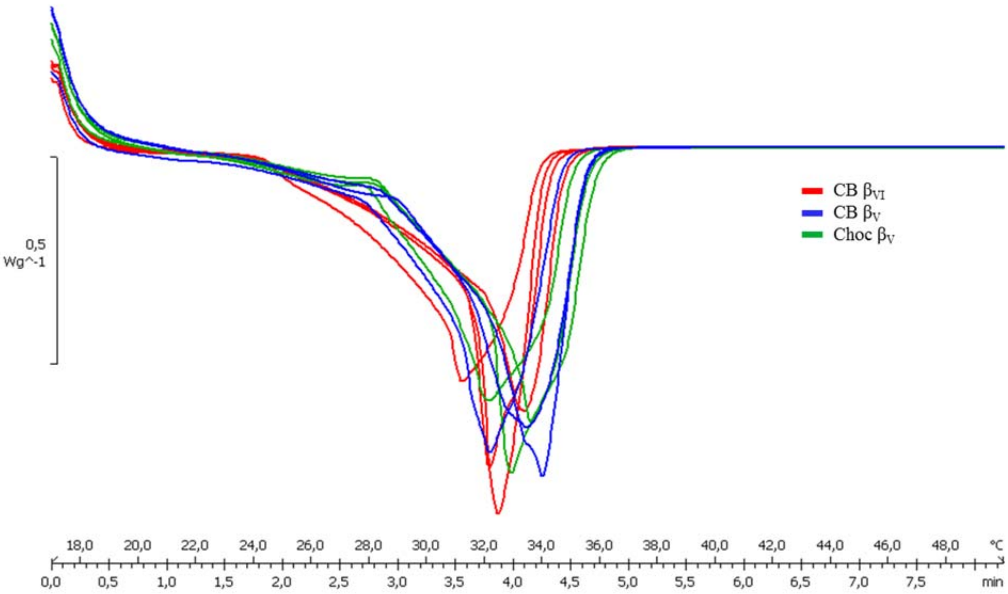

Figure 33. DSC curves for chocolate seeded with the three seedpowders and stored for 7 days.