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Crack formation in chocolate pralines

Master of Science Thesis in the Master Degree Programme Biotechnology

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Cover:
Chocolate pralines produced at SIK with model filling a_w 0.65 stored for 28 days.

Abstract

Chocolate pralines are complex food products that contain a soft filling surrounded by a chocolate shell. One problem with pralines is that the filling often starts to migrate through the shell which causes major structural changes that, for water or liquor based fillings, could result in cracking of the shell. Cracking is one of the major issues that lead to reduced shelf life in chocolate pralines. The main suggestions for crack formation are that cracks form due to moisture or ethanol migration through the chocolate shell, or due to an unbalanced distribution of moisture in the filling that causes some parts to shrink and other to expand.

In this work, two praline geometries and four different model fillings (with water activities (a_w) between 0.67 and 0.99) were analysed with respect to chocolate shell cracking during storage. The pralines were stored for 28 days, during which high resolution images of the pralines were collected and analysed by a digital colour imaging system. Furthermore, water activity measurements in the shell, combined with weight changes in the pralines gave information on migration properties during storage.

The results showed that pralines with a_w 0.99 in the model filling cracked first and to the highest percentage for both geometries. Pralines with model filling a_w 0.86 and a_w 0.78 had quite similar results to each other, and cracked to a considerably lower percentage than pralines with model filling a_w 0.99. For model filling a_w 0.67, square pralines did not crack at all while round pralines cracked at a low percentage. Round pralines started to crack first for all model fillings during the storage period.

The major conclusions that can be drawn from this work are that both water activity (a_w) in the model filling and praline geometry have an impact on crack formation in chocolate pralines.

Sammanfattning

Chokladpraliner är ett komplext livsmedel som består av en mjuk fyllning omsluten av ett chokladskal. Ett problem är att fyllningen ofta börjar migrera genom skalet, vilket orsakar stora strukturella förändringar. För vatten- eller likörbaserade fyllningar kan detta leda till sprickor i skalet. Sprickbildning är ett av de främsta problemen som leder till reducerad hållbarhet i chokladpraliner. De främsta förslagen till sprickbildning är att sprickor uppstår på grund av att vatten eller etanol migrerar genom skalet, eller på grund av en obalanserad fördelning av vätska i fyllningen som medför att vissa delar blir mindre medan andra blir större.

I det här arbetet har två pralingeometrier och fyra olika modellfyllningar (med vattenaktivitet (a_w) mellan 0,67 och 0,99) analyserats med avseende på tendens att spricka under lagring. Pralinerna lagrades i 28 dagar, under vilket högupplösta bilder av pralinerna togs och analyserades med ett digitalt bildanalyssystem. Vidare gav vattenaktivitetsmätningar i skalet, kombinerat med viktförändringar i pralinerna information om migrationsegenskaper under förvaringstiden.

Resultaten visade att för praliner med a_w 0,99 i modellfyllningen uppstod sprickbildning i skalet tidigt under lagringsförsöket för båda geometrierna. Praliner med modellfyllning a_w 0,86 och 0,78 gav relativt lika resultat och hade en procentuellt lägre andel med sprickbildning än praliner med modellfyllning a_w 0,99. För modellfyllningen med a_w 0,67 var fyrkantiga praliner intakta, medan endast några procent av de runda pralinerna fick sprickbildning. För samtliga modellfyllningar påverkades de runda pralinerna först.

De främsta slutsatserna som kan dras från det här arbetet är att både vattenaktivitet i fyllningen samt pralingeometri har en inverkan på sprickbildning i chokladpraliner.

Acknowledgement

1   Contents

1.   Introduction

Chocolate is generally considered as an affordable luxury product. The fact that it is solid at room temperature but melts in the mouth, giving a smooth delicate taste, makes it a unique product. From a more technical point of view, chocolate is a complex food consisting of solid particles of cocoa powder, sugar and milk powder in a continuous fat phase. The production of chocolate is a multi-step process where the tempering is one of the crucial steps. During this the temperature of the chocolate is varied to obtain the right crystalline form of the fat. Recently a novel technique has been developed where seeding materials are added to the chocolate for obtaining the right crystalline form instead of the more traditional tempering.

Chocolate pralines are an even more complex food product since they also contain a soft filling which can interact with the chocolate shell. The filling often starts to migrate through the shell which causes major structural changes that could result in cracking of the shell. Another effect that can be seen is a greyish haze on the praline surface, known as fat bloom, which can occur when liquid fat migrates through the shell and crystallize on the surface. Cracking and fat bloom are two major issues that lead to reduced shelf life in chocolate pralines. The main suggestions for crack formation are that cracks form due to moisture or ethanol migration through the chocolate shell, or due to an unbalanced distribution of moisture in the filling that causes some parts to shrink and other to expand.

In this work, two praline geometries and four different model fillings (with water activities (a_w) between 0.67 and 0.99) were analysed with respect to tendency to crack during storage. The pralines were stored for 28 days, during which high resolution images of the pralines were collected and analysed by a digital colour imaging system. Furthermore, water activity measurements in the shell, combined with weight changes in the pralines gave information on migration properties during storage.

This work was performed within the ProPraline project which is funded by the European Commission in the 7th framework programme.

2.   Objective

The aim of this project was to examine the impact of water based filling and different praline geometry on the crack formation in pralines. Water based fillings with four different water activities (a_w 0.67- 0.99) was tested together with two different geometries of the pralines.

3.   Theoretical background

In this chapter, a short literature review is presented on the composition and origin of chocolate, chocolate processing, crack formation in chocolate pralines and different analysing techniques.

3.1   Chocolate pralines – composition and origin

Production of chocolate is a several hundred year old processing technique. The final result is highly dependent on the initial quality of the cocoa beans and their processing, mixing and refining as well as the crystallization of the cocoa butter. Chocolate is defined as a mixture of cocoa butter, sugar, an emulsifier (e.g. lecithin or PGPR), and ground, roasted cocoa powder. The typical characteristic of chocolate is that it is solid in room temperature whereas it melts at body temperature, forming a smooth liquid in the mouth (Rousseau, 2007).

A praline is composed of a chocolate shell surrounding a soft filling (Figure 3.1), which can be fat, water or ethanol based (Becket, 2008). Fat based fillings often contain nuts, such as hazelnut, peanut or almond, while water and ethanol based fillings can be either fruit or alcohol based or a combination of the two (Ghosh, Ziegler, & Anantheswaran, 2002) (Benitez-Sanchez, Leon-Camacho, & Aparicio, 2003).
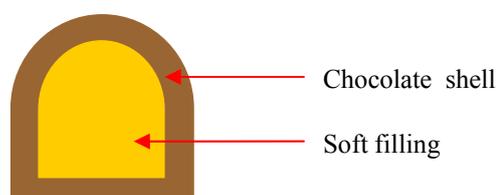
Figure 3.1: Image of a praline showing the two major components.

3.1.1   Chocolate shell composition

There are three main types of chocolate; dark, milk and white, which all have some notable differences in composition. Dark chocolate consists mainly of cocoa butter, cocoa powder and sugar, while milk chocolate also consists of added milk solids. White chocolate consists of cocoa butter, sugar and milk solids but no cocoa powder (Rousseau, 2007). In Table 3.1 typical formulations for milk, dark and white chocolate are presented.

Table 3.1: Typical composition (%) for milk, dark and white chocolate (Rousseau, 2007).

Ingredient (%)	Milk chocolate	Dark chocolate	White chocolate
Cocoa liquor (=cocoa particles suspended in cocoa butter)	12	40	-
Cocoa butter	19	12	23
Milk powder	20	-	30
Sugar	48.5	47.5	46.5
Lecithin	0.5	0.5	0.5

Traditionally chocolate contain about 50% sugars. The sugar in the chocolate is mostly in the form of sucrose, a disaccharide containing one glucose and one fructose monomer, which is shown in Figure 3.2 (Becket, 2008).
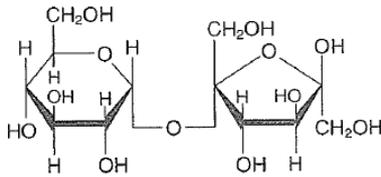
Figure 3.2: Sucrose, a disaccharide containing one glucose and one fructose monomer (Coultate, 2009).

The size and distribution of the particles in the chocolate matrix, together with the polymorphic form and morphology of the fat, strongly affect the sensory properties and quality of the chocolate (Rousseau, 2007). In Figure 3.3 a schematic image of the microstructure in milk chocolate is presented.
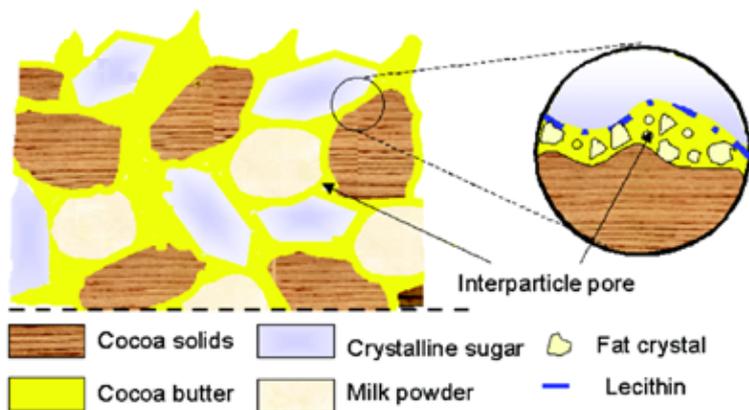
Figure 3.3: Schematic image of the microstructure in milk chocolate, where cocoa solids and crystalline sugar are surrounded by a continuous cocoa butter phase. The cocoa butter phase consists of both liquid and crystalline fat that are in contact with an emulsifier (enlarged to the right in the image). The size of the compounds is not correlated (Aguilera, Michel, & Mayor, 2004).

3.1.3 Composition and structure of cocoa butter

Cocoa butter consists of a mixture of about 40-50 different triacylglycerides (TAGs) (Schenk & Peschar, 2004). A triacylglyceride, also called triglyceride or triacylglycerol, consists of a glycerol backbone and three fatty acids of which the most common in chocolate are palmitic acid (P), oleic acid (O) and stearic acid (St) (Rousseau, 2007). These can be bound to the glycerol backbone in different orders and the TAG composition varies between cocoa beans from different growing areas (Becket, 2008). The three dominating TAG combinations in chocolate are POSt with 35%, StOSt with 23% and POP with 15% (Schenk & Peschar, 2004). The atomic structure of a POSt triacylglyceride is shown in Figure 3.4.

H–C–O–C–(CH$_2$)$_{14}$—CH$_3$

H—O–C—(CH$_2$)$_7$—CH=CH——(CH$_2$)$_7$—CH$_3$

H–C–O–C–(CH$_2$)$_{16}$——CH$_3$
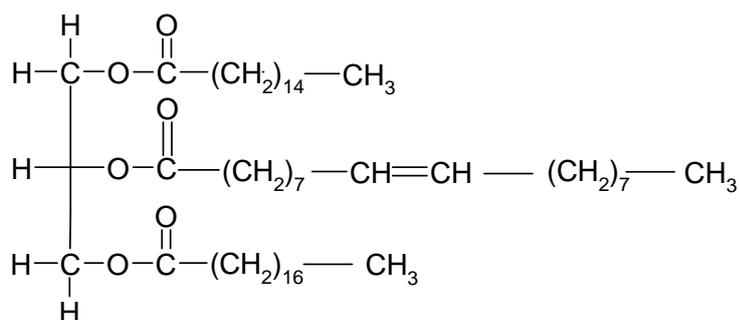
Figure 3.4: Atomic structure of a POSt triacylglyceride, where P stands for palmitic acid at the top, O for oleic acid in the middle, and St for stearic acid in the bottom.

Cocoa butter is polymorphic, which means that even if its fatty acid and TAG composition is constant, it can exist in different crystal forms, depending on the arrangement of TAGs within the solid fat matrix. Each crystal form has different thermodynamic stability. There are three primary polymorphic forms in food fat, α, β' and β, where α is the least and β the most stable. In cocoa butter there are six polymorphs, which can be noted with either Greek or Roman nomenclature. The desired form is the Form V polymorph, also called β$_V$, which gives a stable product with high resistance to fat bloom. Furthermore, it gives positive sensory attributes as its melting point is above room temperature and slightly below body temperature. In Table 3.2 the different polymorphic forms of cocoa butter and their melting points are shown (Rousseau, 2007).

Table 3.2: Melting points of the polymorphic forms of cocoa butter according to Duck (1964) and Wille and Lutton (1966). The more unstable and loosely packed forms are at the top, with an increasing stability and more dense packing for the forms down the table (Lonchampt & Hartel, 2004).

Polymorphic form (Wille and Lutton)	Melting point (°C)	Polymorphic form (Duck)	Melting point (°C)
I	17.3	γ	17.0
II	23.3	α	21-24
III	25.5	β''	28.0
IV	27.3	β'	33.0
V	33.8	β	34.4
VI	36.3		

Cocoa butter is a difficult fat to process and there are strong efforts to replace cocoa butter for chocolate production, either partly or wholly, both for technological and economic reasons. These cocoa butter alternatives (CBAs) are mostly mixtures of various vegetable fats, often modified, and can consist of palm and palm kernel oil, illipé fat, shea butter, sal fat and kokum butter. Such fats are referred to as cocoa butter equivalents (CBEs), cocoa butter substitutes (CBSs) and cocoa butter replacers (CBRs). In several countries within the EU other fats than cocoa butter is only allowed in chocolate up to 5% (Lipp & Anklam, 1998).

3.1.2 Filling properties

As mentioned earlier the filling can be fat, water or ethanol based (Becket, 2008). Fat based fillings often contain nuts, such as hazelnut, peanut or almond, while water and ethanol based fillings can be either fruit or alcohol based or a combination of the two. A distinct difference that can be observed between fat based and water/ethanol based fillings are that fat based fillings have a high liquid fat content in combination with a low water activity, while water and ethanol based fillings do not have any liquid fat content at all and a much higher water content (Ghosh, Ziegler, & Anantheswaran, 2002) (Benitez-Sanchez, Leon-Camacho, & Aparicio, 2003). A problem that can be seen in pralines with water or ethanol based fillings is cracking of the shell, while a more common problem in pralines with fat based filling is so called fat bloom (Ghosh, Ziegler, & Anantheswaran, 2002).

3.1.3 Model filling properties

Fillings are a complicated product to investigate. In order to reduce the different parameters that could affect the final results, a model filling can be used. To obtain a model filling with desired properties, different humectants can be used to vary the water activity, together with different thickeners to obtain good viscous properties.

3.1.3.1 *Humectants*

Water activity, a_w, gives good information about the stability of a food product since it accounts for the availability of water for degradation reactions. It is also of great importance for controlling microbial growth. Water activity is defined as the ratio of partial pressure of water vapour in the product, p, to the partial pressure of pure water, p_0 (Mathlouthi, 2001) (Coultate, 2009):

$$a_w = \frac{p}{p_0}$$

The water activity for some food products can be seen in Table 3.3. Below a_w 0.5 there are no bacterial growth (Coultate, 2009). As can be seen the water activity for pure chocolate is very low.

Table 3.3: Water activity for some different foods (Coultate, 2009) (Baylis, MacPhee, Robinson, Griffi, Lilley, & Betts, 1994).

Food	Typical water activity
Fresh meat	0.98
Cheese	0.97
Preserves	0.88
Salami	0.83
Dried fruit	0.76
Honey	0.75
Dried pasta	0.50
Milk chocolate	~ 0.40

The water activity can be lowered with water activity depressors, so called humectants, such as sugar, salt, citric acid and glycerol. Different substrates have a varying ability to depress

water activity, called humectancy. If sucrose is used as a reference standard with a humectancy of 1, the humectancy of different substrates can be compared. This can be seen in Table 3.4 (Mathlouthi, 2001).

Table 3.4: Comparison of humectancies of some substrates with sugar taken as reference standard (humectancy=1) (Mathlouthi, 2001).

Substrate	Humectancy
Sugar (sucrose)	1
Salt	11
Tartaric and citric acids	3
Glycerol	4

3.1.3.2 Thickeners

To stabilise fillings and other food products various thickening agents can be used. Examples of thickening agents are different polysaccharides, such as xanthan gum or carrageenan, or animalic extracts such as gelatin. Below follows a short description of the thickeners used in this project.

3.1.3.2.1 Xanthan gum

Xanthan gum is a natural polysaccharide produced by the bacterium *Xanthomonas campestris*. The xanthan polymer has a backbone of glucose units joined by β-1,4 linkages, such as for cellulose. Every fifth glucose unit carries a trisaccharide side-chain, including one or two charged carboxyl groups that give its high affinity for water (Figure 3.5). The distinctive feature for gums is their high affinity for water and the high viscosity of their aqueous solutions. They do not form gels, instead their solutions contain their plasticity even at relatively high concentrations. The essential structure for all gums is extensive branching, which do not leave any length of ordered backbone to form the characteristic junction zones of polysaccharide gels. The branches can still entrap a large amount of water and interactions between them gives a high viscosity even for dilute solutions. A special feature for xanthan gum is how easily the polymer chains associate together and are reversibly broken. When the gum is cool and stationary, the polymer chains form a zigzag shape of sufficient length for them to come together in junction zones and form a gel-like network, but just a small physical stress is enough to disrupt them (Coultate, 2009).
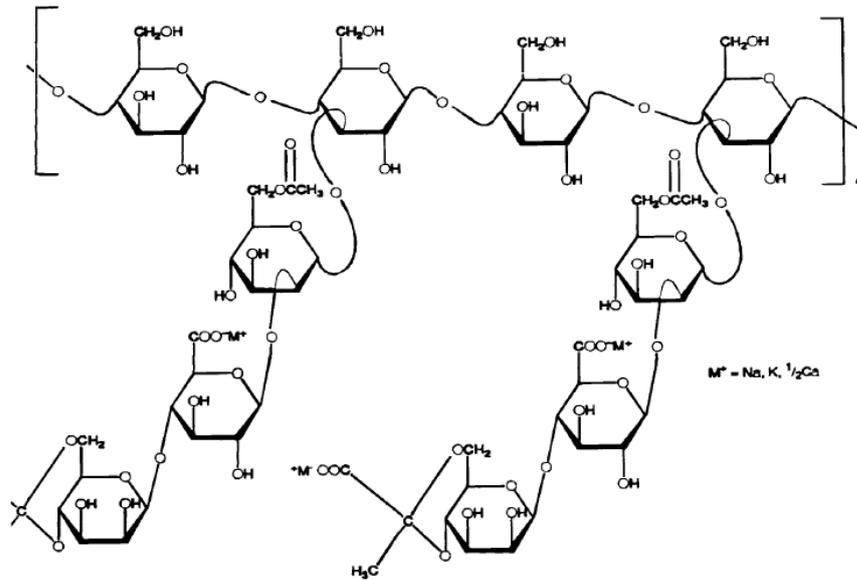
Figure 3.5: Xanthan gum, produced by *X. campestris* (García-Ochoaa, Santosa, Casasb, & Gómez, 2000).

Xanthan is approved as an emulsifier/stabilizer additive in Europe since 1980, as item E415. Due to its ability of emulsion stabilization, temperature stability, compatibility with food ingredients, and pseudo plastic rheological properties, xanthan has been used in a wide variety of foods. Xanthan gum is also used in pharmaceutical formulations, cosmetics, and agricultural products due to its properties in thickening aqueous solutions, as a dispersing agent, and stabilizer of emulsions and suspensions (García-Ochoaa, Santosa, Casasb, & Gómez, 2000).

3.1.3.2.2 Carrageenan

Carrageenan is the general name for a family of sulphated polysaccharides extracted from red sea weeds. Depending on the number and position of anionic sulphate groups, several types of carrageenans can be recognized. The three most commercially exploited are kappa-, iota-, and lambda-carrageenans (GAO, CHEN, XU, CHEN, & YAN, 2009). The repeating units of iota-carrageenan are shown in Figure 3.6. Different monosaccharides predominate in particular carrageenans, but the difference between different carrageenans in particular seaweeds is not always clear-out. Commercial carrageenans used as gelling or thickening agents in food are blends designed to have the right properties for a specific application (Coultate, 2009).
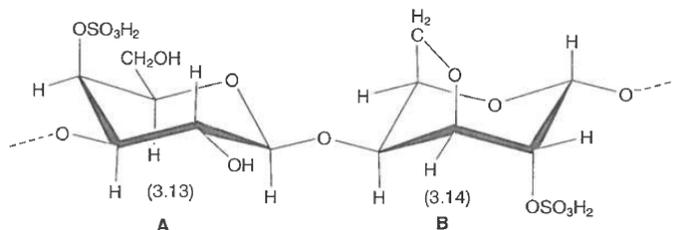
Figure 3.6: The repeating units of iota-carrageenan (Coultate, 2009).

Gelatination of carrageenan involves first the formation of double helices of galactan chains wound around each other. These chains are not sufficient to form gels by themselves, but

must first associate together and form so-called superjunctions, showed in Figure 3.7. To form these superjunctions neutralising cations are required, such as potassium (K^+) for kappa-carrageenan and calcium (Ca^{2+}) for iota-carrageenan (Coultate, 2009).
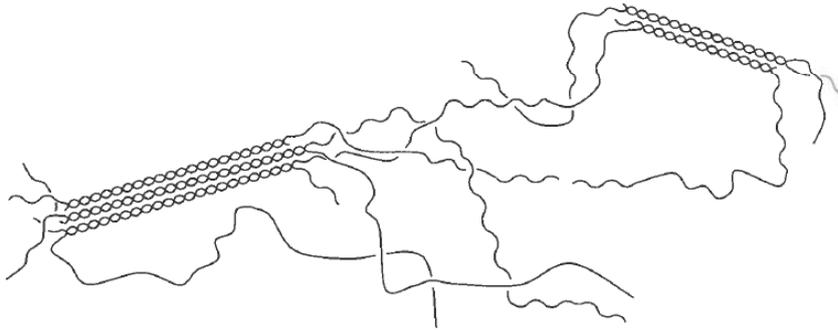
Figure 3.7: Carrageenan superjunctions (Coultate, 2009).

3.1.3.2.3   Gelatin

Gelatin is extracted from the protein collagen, which is the main constituent of connective tissues and bones (Eysturskarð, Haug, Ulset, & Draget, 2009). Gelatin is widely used as a gelling agent, especially in confectionary, desserts, and in meat products. Like gel forming polysaccharides, gelatin is insoluble in cold water but dissolves in hot water. When the solution cools the gelatin polymer revert from a disorganised "random coil" to a helical arrangement similar to that in original connective tissue. Like this, parts of the polymer chains associate together and form junction zones based on hydrogen bonding, as occurs in polysaccharide gels (Coultate, 2009).

3.2   Chocolate processing

Cocoa beans are collected from cacao trees, a small tree growing in tropical climate. The tree originates from South and Central America but now it is commercially grown around the equatorial line. The three major cocoa growing regions are West Africa, South-East Asia and South America (Becket, 2008). There are three main types of cocoa beans used in chocolates; *Criollo*, from the Caribbean and Central and South America, has beans with white cotyledons and a mild flavour, *Forastero*, dominating the West African cocoa crop, is more vigorous and *Trinitario*, representing a small fraction of the worldwide cocoa production, is a hybrid of the other two. There exist also a number of other varieties of beans, of which each bean will give a unique flavour and aroma to the chocolate (Rousseau, 2007).

Tiny flowers on the branches and the trunk of the trees grow into small pods called cherelles (Figure 3.8), which each contain about 30-45 cocoa beans. After the beans have been harvested they are fermented, which is essential to produce characteristic flavour compounds of the chocolate. After fermentation the beans must be dried before transportation to the manufacturing countries. The beans must be stored dry so that they do not take up water. They will become mouldy if the moisture level rises above 8% (Becket, 2008).

Figure 3.8: A cocoa tree with cocoa pods (Adhistory).

Before chocolate can be processed, the beans must be processed into cocoa mass, cocoa butter and cocoa powder. This process involves cleaning the beans, roasting, cocoa bean shell removing, also called winnowing, and cocoa butter extraction. The first step in chocolate manufacturing is then the blending of ingredients, especially sugar, cocoa powder, the emulsifier and cocoa butter, to a paste. After blending the paste is ground, while more cocoa butter is added. The particle size of the solid particles is not allowed to be larger than 30 µm to give chocolate its smooth texture. After grounding the blend is conched in a scraped-surface mixer (Rousseau, 2007). During conching the liquid chocolate is stirred continuously for several hours, which allow some undesirable off-flavour compounds to be driven off (Coultate, 2009). A flowchart of the chocolate manufacturing process is shown in Figure 3.9.
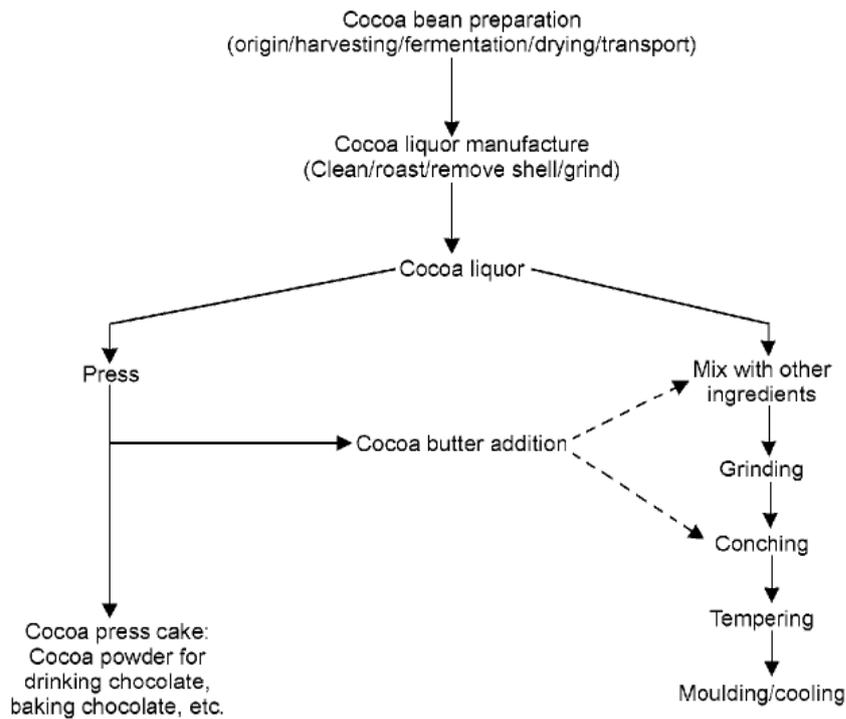
Figure 3.9: Flowchart of the chocolate manufacturing process (Rousseau, 2007).

3.2.1 Tempering

An important step in the production of chocolate is the tempering. By a well-defined temperature programme the crystallization of the cocoa butter is controlled to form the desired β_V form (Rousseau, 2007). A tempering sequence during lipid crystallization in chocolates is shown in Figure 3.10.
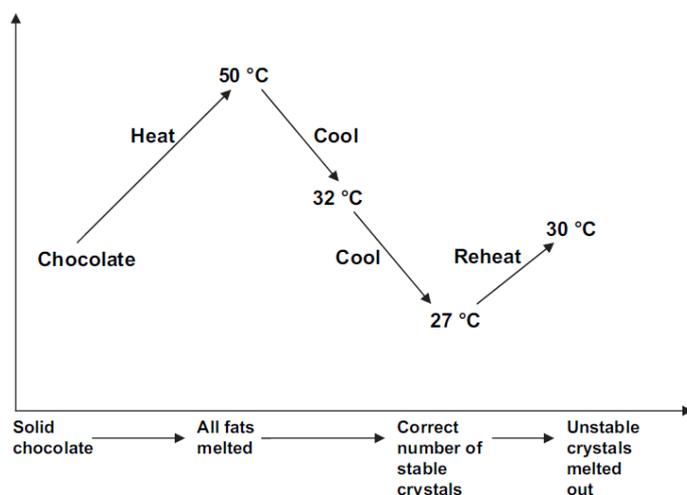
Figure 3.10: Tempering sequence during lipid crystallization in chocolates (Afoakwa, Paterson, & Fowler, 2007).

At the first stage of tempering the chocolate is maintained at 45-50°C to fully melt all fat crystals. In the second stage the chocolate is cooled to around 27°C under agitation, which promote formation of both stable and unstable forms of crystal nucleus, also called seeds,

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such as β'_{III}, β'_{IV} and β_V. The chocolate is then reheated to around 30°C to melt unstable polymorphs and ensure that only β_V crystal nucleus remains. Crystal growth is then promoted under agitation and shearing for the last stage (Rousseau, 2007).

Tempering of the chocolate is made in a tempering machine, which is basically a heat exchanger that heat and cool the chocolate as it passes through it. Since chocolate is a poor heat conductor it must be mixed well so that all of it comes in contact with the cold contact surface of the tempering machine. This is achieved with a rotating shaft on which is attached scrapers or discs that force the chocolate to flow alternatively to the wall and to the centre, instead of just passing through the machine. The faster the shaft rotates, the higher is the shear rate and further the crystallization rate. What limits the shear rate is the size of the motor and the heat formed by the mixing, which could start to melt the stable crystals as well. The temperature must be carefully controlled which is done within so called cooling zones. Figure 3.11 shows a simplified image of a tempering machine.
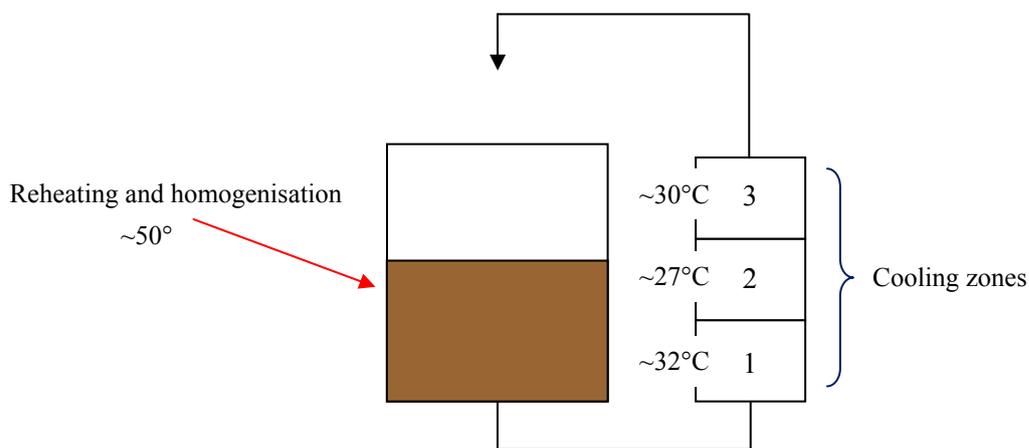
Figure 3.11: Simplified image of a tempering machine. The chocolate is heated to around 50°C to erase all crystal memory. In the cooling zones the chocolate is first cooled to a temperature where crystal nucleus can start to form (zone 1 and 2), varying for different types of chocolate, before its temperature is raised again to melt out unstable polymorphs (zone 3).

3.2.2   Seeding technique

Seeding is an alternative technique that can be used to obtain the right crystalline form of the cocoa butter. Instead of creating crystal nucleus by a temperature treatment, as in conventional tempering, it involves addition of cocoa butter in the β_{VI} form as seeds directly to the pre-melted chocolate. The chocolate is melted to about 48°C to erase all crystal memory. The temperature is then directly lowered to 32-33°C while mixing and 0.2-2 w% of cocoa butter crystal suspension, containing β_{VI} seeds, is added. The paste is mixed to ensure that the seeds dissolve evenly through the chocolate. When cooling, the β_{VI} seeds act as nucleus to form the desired β_V crystals. To summarize, the main difference between conventional tempering and seeding is that for tempering, seeds in form β_V and/or β_{VI} is produced by temperature treatment and for seeding, the β_{VI} seeds is added to the chocolate (Zeng, Braun, & Windhab, 2002).

3.2.3 Moulding of chocolate pralines

Moulding of chocolate pralines can mainly be done by three different moulding techniques; conventional, cold-stamp or one-shot. They all have their different benefits depending on the conditions and what type of product that is to be produced. In this work the pralines are produced by conventional moulding.

3.2.3.1 *Moulds used for chocolate production*

When moulding solid chocolate tablets, most moulds used today are made of plastic, compared to before when metal moulds were used. Plastics have the advantage of being lighter and making less noise, as well as being flexible, which can ease to remove the solid chocolate when sticking occurs. It is important that the moulds are preheated to within a few degrees of the temperature of the tempered chocolate before the moulding process begins. This is because if the tempered chocolate would come in contact with a too warm surface, the crystals within it would melt and there would no longer be enough seeds for the chocolate to crystallize properly. If the chocolate instead would come in contact with a cold surface, this could cause some of the fat to crystallize in the wrong form (Becket, 2008).

3.2.3.2 *Conventional moulding*

In conventional moulding, the chocolate can be fed into the mould either by hand or by equipment. The chocolate is then spread evenly in the mould and air bubbles are removed by vigorously vibrating it. This is due to that chocolate is a non-Newtonian liquid and it has a yield value, meaning that energy must be applied for it to start to move. This yield value will also stop air bubbles from rising through the chocolate. By vibrating it, the vibration decreases the viscosity of the chocolate, and thereby eases the removal of bubbles (Becket, 2008).

The mould is then turned upside down and vibrated, causing the liquid chocolate in the centre to pour out. There are several critical features for this step, such as to achieve a good viscosity of the chocolate. If the chocolate is not vibrated enough, it could lead to that no chocolate come out of the shell, while if it is vibrated to vigorously, too much chocolate could come out giving a too thin shell. Furthermore, the time that the mould is turned upside down and the chocolate is let to pour out is of importance. The mould is then turned again and the shell is let to cool before it is filled. It is important that the filling is not too hot so that it melts the chocolate. For fondants and fat based fillings this is quite easy to achieve, since they can be relatively fluid at about 30°C. This is more difficult for caramel, for which the viscosity changes rapidly with temperature (Becket, 2008).

Once the filling is in place a chocolate base is added to the shell. This is usually done by having a scraper blade pressing against the mould and having tempered chocolate poured into the mould in front of it. Like this any remaining indents or holes are filled while the scrape takes away any excess chocolate. Finally the mould is cooled in a cooling tunnel, to fully solidify the shell and base, before the praline is packed. Moulded pralines like these are usually much shinier than sweets produced using an enrobing process. This is because the fat at the outside of the shell crystallizes in contact with the mould surface, which gives a very

smooth and glossy praline surface (Becket, 2008). In Figure 3.12 a schematic diagram of a conventional moulding process is illustrated.
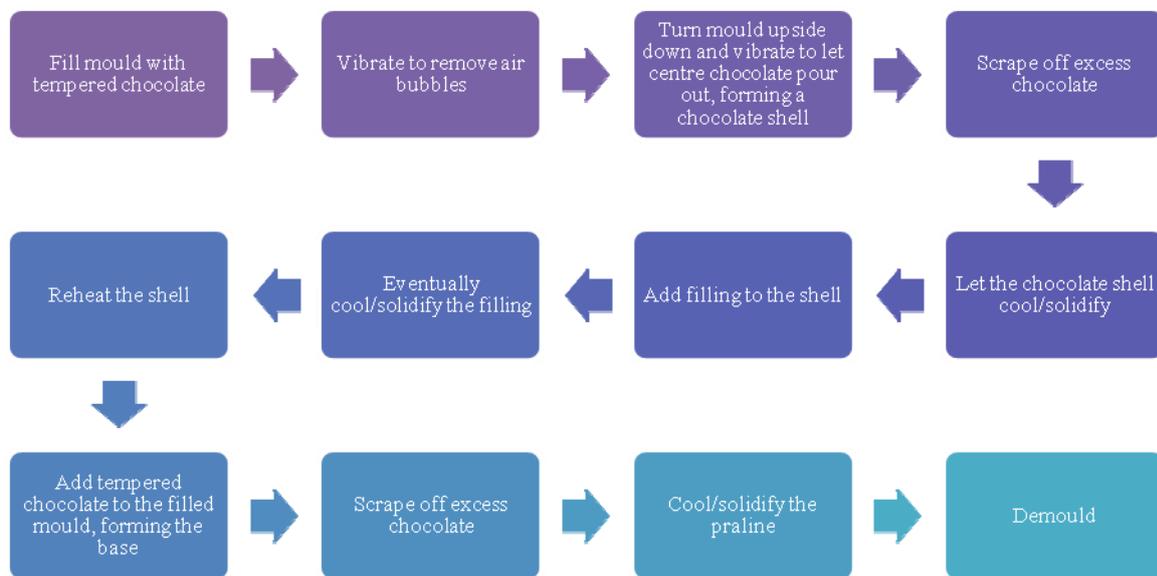
Figure 3.12: Schematic diagram of a conventional moulding process.

3.2.3.3 *Cold stamp process*

Cold stamp process, also called frozen cone moulding or cool core among other names, allows the production of thin and precise shells. Tempered chocolate is fed into a mould with a volume equivalent to the required shell size. A cooled stamp is lowered down into the moulds that presses out the chocolate and forms the shells. The cool surface induces the chocolate to partially solidify and when the shell is strong enough to not collapse the stamp is removed again. This only takes some seconds. The shell is then run through the usual cooling process and can be filled and covered with a base. Figure 3.13 shows a photo of a cold stamp process (Bühler Bindler) (Rossettini & Pellegrini, 2006).

Figure 3.13: Photo of a cold stamp process (Bühler Bindler).

3.2.5.3 *One shot technology*

With the one-shot technology the moulds are filled with both chocolate and filling at the same time. An inner nozzle shots out the filling while an outer nozzle shots out the chocolate that enrobes the filling. Figure 3.14 shows an image of a one-shot depositor. The technique has

been strongly refined in the last few years thanks to an improved electronic control of the dosing parameters. A recent development is one-shot products with double filling and with small inclusions mixed in the filling, which opens for new goals of this technology (Rossettini & Pellegrini, 2006).
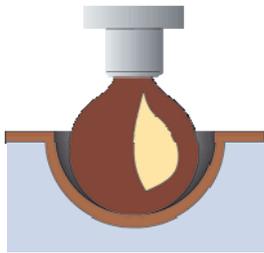
Figure 3.14: Image of a one-shot depositor (Bühler Bindler).

3.2.6   Cooling process and storage

After moulding most of the fat in the chocolate is still in a liquid state. To receive pralines that are hard enough to handle and package, most of the fat must solidify in the right crystalline form (Becket, 2008). This requires a cooling process where the temperature is strictly controlled, to not have unwanted polymorphic transformations (Rousseau, 2007). The cooling process is usually performed in a cooling tunnel, where cool air is blown over the pralines so that heat is removed by convection. The temperature of the surrounding tunnel should be maintained above the dew point, meaning the temperature at which moisture just starts to condense. If the temperature is too low the fat can set in the wrong form. Besides lowering the quality of the chocolate this can cause moulded chocolate to not contract properly so that they are difficult to remove from the moulds. A too low temperature can also cause the air to condense on cold surfaces and then drip onto the chocolate. This will dissolve some of the sugar within it, leaving a white powdery surface called sugar bloom on the chocolate when it is rewarmed and the water evaporates again (Becket, 2008).

Cooling tunnels are usually divided into different temperature zones. The initial cooling is quite gentle. This is followed by the coolest part of the process, of about 13°C. The temperature can be lower on condition that the air moves fast enough to not condensate. The time it takes for the chocolate to set depends on the amount of already existing crystals in the chocolate, as well of its type and amount. A large piece of chocolate naturally takes longer time to set than a small piece. Usually the cooling time vary between 10 and 20 minutes to obtain a high quality chocolate (Becket, 2008).

Since chocolate is very sensitive to temperature and humidity, storage should be maintained at a temperature of 15-17°C and a relative humidity (RH) below 50% (Rousseau, 2007).

3.3   Crack formation in chocolate pralines

Crack formation in chocolate is thought to be one of the major causes for shelf-life reduction in chocolate pralines. Cracking can be caused by different mechanisms, also depending of the type of filling. A reason for crack formation in pralines with water based fillings is migration of water from the filling into the chocolate shell. Similar observations have also been made with ethanol in liquor fillings.

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In cookie confectionary combinations a factor that causes cracking is redistribution of moisture within the cookie/wafer centre. This causes the centre to both contract and expand at the same time at different parts. Water vapour can also be absorbed through holes in the coating (Minson, 1990) (Barron, 1977).

Furthermore, cracking can occur during process. The fact that tempered chocolate shrinks upon cooling of the cocoa butter, which is essential for moulding, must be taken into account for enrobing. If the enrobed centre is allowed to cool too quickly it could result in that the shell cracks due to that it contracts more than the filling. On the other hand, could the chocolate be discoloured and soft if it cools too slowly (Man & Jones, 1994).

3.4　　Crack formation due to migration

As mentioned earlier, a suggested reason for crack formation in pralines with water based fillings is migration of water from the filling into the chocolate shell. In this chapter, that phenomenon is explained further.

3.4.5　　Effects of migration

Migration in chocolate can be divided into three main types; moisture, ethanol and fat, of which moisture and ethanol migration are quite similar and fat migration differ more significantly to the other two. Fat, in a fat based filling with e.g. nuts, will migrate into the coating mainly through the fat phase, while the non-fat particles are considered impermeable to the migrating fat. For moisture and ethanol migration, the non-fat particles are not impermeable, and water and ethanol molecules migrate both through and along the surfaces of these hydrophilic particles. Since the hydrophilic particles in chocolate are embedded in a continuous fat phase, migrating water and ethanol molecules must migrate through the fat phase to come in contact with the hydrophilic particles. However, migration of moisture will be slowed when increasing the fat content and fat migration will be slowed when increasing the hydrophilic part (Ghosh, Ziegler, & Anantheswaran, 2002).

3.4.5.3　　*Moisture migration*

Moisture that migrates through chocolate will get adsorbed by the hydrophilic particles within the chocolate. As a result this might cause swelling of the particles, which in turn might lead to crack formation and an acceleration of the moisture migration (Figure 3.15). Water adsorption could also lead to surface dissolution, accumulation of sugar and crystallization of amorphous milk powder, which could lead to sugar bloom (Ghosh, Ziegler, & Anantheswaran, 2002).
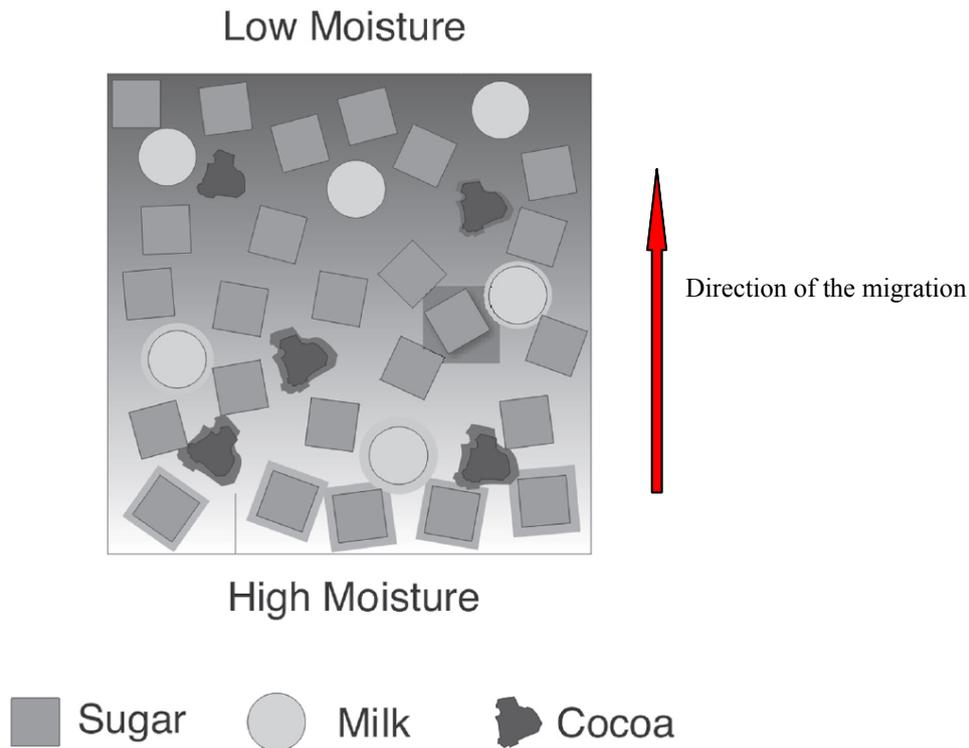
Figure 3.15: A model for the migration of moisture through chocolate. The moisture content is represented by the different background shading. The swelling of hydrophilic particles is marked as halos around the particles (Ghosh, Ziegler, & Anantheswaran, 2002).

Moisture migration occurs when regions with different moisture content are brought together, such as for a chocolate praline when a filling with high water content, e.g. fruit or liquor based, comes in contact with the chocolate shell. The migration does not necessarily take place from the region with the higher moisture concentration but from the region with the higher water activity (section 3.1.3.1) (Ghosh, Ziegler, & Anantheswaran, 2002).

Chocolate consists of hydrophilic particles that are embedded in a continuous fat phase. The amount of migrating moisture that will be absorbed by the hydrophilic particles in the chocolate can be obtained from a moisture sorption isotherm. A moisture sorption isotherm is a plot of the water content of a food, in mass of water per unit mass of dry material, towards the water activity at a given temperature. The amount of water that is adsorbed is less at a higher temperature for the same water activity, due to that molecular motion increases with temperature. In Figure 3.16, a moisture sorption isotherm for dark chocolate at different temperatures is shown (Ghosh, Ziegler, & Anantheswaran, 2002).
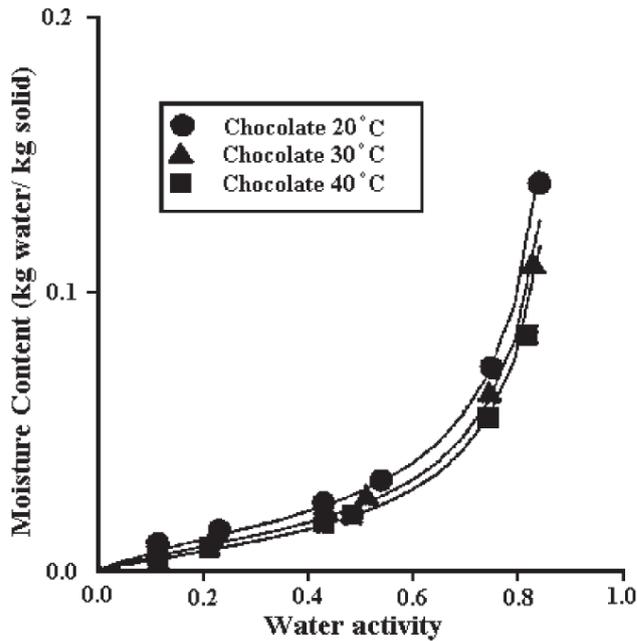
Figure 3.16: Moisture sorption isotherm for dark chocolate at different temperatures (Ghosh, Ziegler, & Anantheswaran, 2002).

Factors influencing moisture migration through chocolates are water activity or vapour pressure difference, storage temperature, composition and structure, thickness of the shell and solid fat content (Ghosh, Ziegler, & Anantheswaran, 2002). These factors are explained further below:

- *Shell thickness:* According to Fick's law, which relates the molar flux of a component to the concentration gradient, the water diffusion rate is suggested to decrease with increasing shell thickness (Ghosh, Ziegler, & Anantheswaran, 2002).

- *Structure of the cocoa butter:* There have not been done any systematic study on the effect of moisture migration through chocolate, but a close-packed fat crystal network could be expected to allow less moisture migration than a loose-packed one (Ghosh, Ziegler, & Anantheswaran, 2002). Each polymorph has a different morphology, where α-crystals, which are the least stable, also are the least densely packed compared to the β' and β forms. β-crystals, which have the highest melting point, also have a more dense crystal structure than the β'-form (Rousseau, 2007). A study by Landmann et al. showed that the permeability through a film of cocoa butter was much higher for cocoa butter with low melting polymorphs than for cocoa butter that had been properly tempered (Landmann, Lovegren, & Feuge, 1960).

- *Surrounding water activity (a_w):* An increased water vapour gradient or water activity increases the water vapour transmission rate and an increase of the relative humidity to 100% gives a large change in the permeability constant. The second can be explained by that e.g. sucrose and cocoa beans tend to absorb a significant amount of moisture at high humidity. This will swell the coating and change its structure, which will affect

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the permeability behaviour of the coating (Ghosh, Ziegler, & Anantheswaran, 2002) (Landmann, Lovegren, & Feuge, 1960).

- *Chocolate composition:* At low vapour pressures the presence of non-fat particles does not influence the migration rate or the permeability constant, but at high relative humidity it increases the migration rate drastically (Ghosh, Ziegler, & Anantheswaran, 2002) (Landmann, Lovegren, & Feuge, 1960).

- *Solid fat content:* Another important factor influencing water migration is the solid fat content. A fat with high solid fat content is a good moisture barrier since fat in solid state are more densely packed and allow less moisture to migrate (Ghosh, Ziegler, & Anantheswaran, 2002) (Landmann, Lovegren, & Feuge, 1960).

- *Temperature:* Temperature has a great influence on moisture migration. When changing the temperature it gives rise to phase and structural changes in the chocolate. An increase in temperature increases the diffusivity of the migrating molecule and decreases the solid fat content, which booth increases the migration rate. Also the thermal history of the chocolate is of great importance since it determines the structure of the coating (Ghosh, Ziegler, & Anantheswaran, 2002).

With these factors in mind, there are some methods to control moisture migration. By tempering the chocolate properly moisture migration can be reduced to a great extent, since it increases the amount of stable and more densely packed fat crystals, and further the solid fat content. Selection of proper emulsifiers and sweeteners are also aspects to consider. Since non-fat particles tend to adsorb a large amount of moisture and swell the chocolate, the selection of a sweetener that adsorbs less moisture could decrease the migration rate. Furthermore, shell thickness and storage conditions, such as temperature and relative humidity, are factors that can be controlled (Ghosh, Ziegler, & Anantheswaran, 2002) (Rousseau, 2007).

3.4.5.4 Ethanol migration

Chocolate pralines with ethanol based filling have the highest tendency of quality loss since they contain both ethanol and moisture, which are very mobile liquids. The changes start usually at the early stages of migration, where loss of liquid in the filling causes a decrease in volume of the centre. A continuous migration causes cracks in the chocolate surface, which accelerate the migration of ethanol and moisture even further, and eventually leads to a complete loss of liquid filling (Ghosh, Ziegler, & Anantheswaran, 2002).

The mechanism for migration of ethanol is believed to be quite similar to that of moisture. A difference is that ethanol is more soluble in the fat, why a faster migration of ethanol through the fat phase could be expected compared to that of moisture (Ghosh, Ziegler, & Anantheswaran, 2002).

3.4.5.5   *Fat migration*

Fat migration often occurs in chocolate when there is a compositional difference in the product, i.e. some parts contain more liquid fat than others. This can be seen in chocolate confectionary with nut-based centres, chocolate coated biscuits and cream filled chocolates, where the liquid oil from the filling or biscuit tend to migrate into the chocolate coating. The driving force for fat migration is the difference in TAG (triacylglycerol) concentration but since it is easier to measure the liquid fat content (LFC), fat migration is often modelled as a function of the difference in LFC (Ghosh, Ziegler, & Anantheswaran, 2002).

Migration of fat can result in softening of the coating and hardening of the filling, which both can decrease the perceived quality of the product. Softening of the coating depend on the compatibility of the fat in the filling and the fat in the coating. If they are incompatible they form a so called eutectic that contain a lower solid fat content than in either of the two fats separately (Ghosh, Ziegler, & Anantheswaran, 2002).

Fat migration occurs mostly through the liquid phase of the fat and the presence of non-fat particles can decrease the migration rate by increasing the tortuosity of the diffusion pathway. With tortuosity means the deviation from the linear migration path, which is illustrated in Figure 3.17. Migrating oil may also dissolve part of the solid fat in the coating, which increases the migration rate. This fat can re-crystallise on the surface of the coating and give rise to the whitish grey of so called fat bloom (Ghosh, Ziegler, & Anantheswaran, 2002) (Lee, McCarthy, & McCarthy, 2010) (Rousseau, 2007).
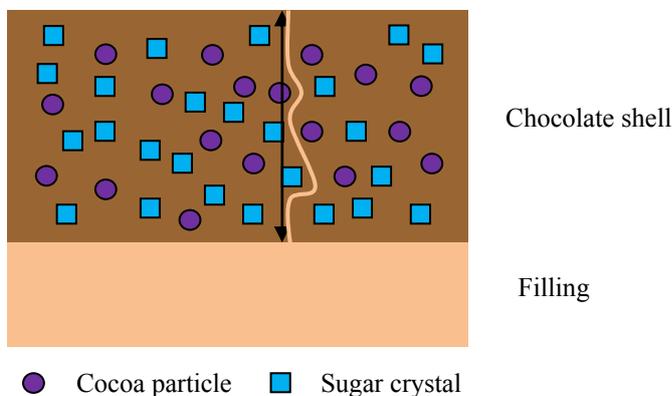
Figure 3.17: Illustration of what is called the tortuosity of chocolate. Diffusing fat from the filling cannot migrate in a straight path due to solid particles that force the fat to move around them.

3.4.6   **Suggested mechanisms for migration**

The mechanism for migration has been debated mainly between diffusion and capillary forces, which are explained further in the following section.

3.4.6.3   *Diffusion*

Diffusion is the process by which matter is transported from one part of a system to another by random molecular motion, and takes place when there is a concentrations gradient between two points in the system.   The molecules then migrate from the point with the higher concentration to the point with the lower concentration until the system reaches

thermodynamic equilibrium (Ghosh, Ziegler, & Anantheswaran, 2002). In chocolate pralines with e.g. water based filling there is a concentration gradient of moisture between the filling and the shell that makes moisture diffuse from the centre through the shell.

Mathematically diffusion can be expressed with Fick's first and second law. Fick's first law states that in a continuous medium and under the presence of a concentration gradient, the net migration of solute molecules due to random movement occurs from a region of high concentration to one of lower concentration (Aguilera, Michel, & Mayor, 2004).

For diffusion in only z direction, Fick's first law can be written (Welty, Wicks, Wilson, & Rorrer, 2001):

$$J_{A,z} = -D_{AB}\frac{dc_A}{dz}$$,   (Equation 1)

Where J_A is the molar flux of component A, D_{AB} is the diffusion coefficient for component A diffusing through component B, c is the concentration of component A and dc_A/dz is the concentration gradient in the z direction.

Furthermore, Fick's second law states that the rate at which this process proceeds at a point in space, where one solute is present in a large portion of solvent, is proportional to the variation of the slope of the concentration gradient (Aguilera, Michel, & Mayor, 2004). Unsteady-state diffusion according to Fick's second law can be written (Welty, Wicks, Wilson, & Rorrer, 2001):

$$\frac{\partial c_A}{\partial t} = D_{AB}\frac{\partial^2 c_A}{\partial z^2}$$,   (Equation 2)

Where $\partial c_A/\partial t$ is the change in concentration of component A with time, D_{AB} is the diffusion coefficient for component A diffusing through component B and $\partial^2 c_A/\partial z^2$ is the slope of the concentration gradient in the z direction.

3.4.6.4 *Capillary forces*

Since models based on the so-called Fickian diffusion fail to fully describe the migration of fat in chocolate, other mechanisms have been suggested, such as capillary pressure (Galdámez, Szlachetka, Duda, & Ziegler, 2009). Capillary flow is a spontaneous process driven by an interfacial pressure gradient. It occurs omnipresent in nature in fine pores and cracks. For instance capillary rise is what brings up water to the surface from the soil, allows dyeing and wetting of textile fabrics, and is the mechanism in wetting of cookies with hot coffee or tea that improves flavour release (Aguilera, Michel, & Mayor, 2004). An illustration of capillary flow is shown in Figure 3.18.
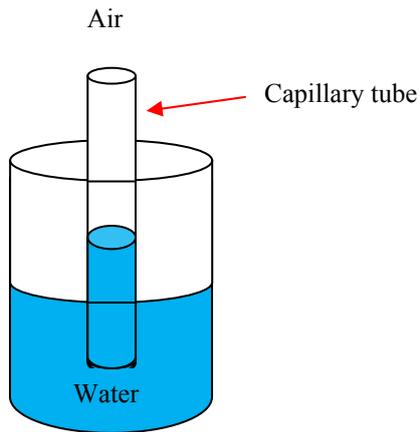
Figure 3.18: Capillary flow. Water is drawn into the tube due to a pressure gradient between the air and water.

The Lucas-Washburn equation is the most common expression for capillary rise and assumes that the capillary pressure in a cylindrical capillary in contact with an infinite liquid reservoir is compensated by viscous drag and gravity. The equation can be written:

$$\frac{2}{r}\gamma cos\theta = \frac{8}{r^2}\mu h\frac{dh}{dt} + \rho g h$$

(Equation 3)

Where h is the distance the fluid is drawn into the capillary, γ the surface tension of the fluid, θ the contact angle between the fluid and the capillary wall, r the radius of the capillary, ρ and μ the density respectively the viscosity of the liquid, and g the acceleration due to gravity (Aguilera, Michel, & Mayor, 2004).

An ideal model for capillary flow has cylindrical uniform pores, infinite liquid reservoir, and so on. The physical situation within a chocolate is quite different from that within an ideal model, but the Lucas-Washburn equation has proven to hold for several physical situations (Aguilera, Michel, & Mayor, 2004).

3.4.6.5   *Diffusion versus capillary forces*
Molecular diffusion has been a preferred mechanism to explain fat and moisture migration in chocolate. As mentioned earlier, diffusion of fat is thought to be due to a gradient in TAG concentration within the chocolate. In plain chocolate that has a homogeneous liquid phase of cocoa butter, this is less likely to occur (Aguilera, Michel, & Mayor, 2004).Whether the capillary rise theory is significant or not is debated. A study by *Afoakwa et al*. (2009) supports the capillary rise theory. They found that fat migration and bloom occurred faster in plain dark chocolate samples that had a greater particle size, 50 μm compared 18 μm, and hypothesized that larger particles give larger capillaries where fat can migrate faster (Afoakwa E. O., Paterson, Fowler, & Joselio, 2009). However, recent studies on oil migration through chocolate using magnetic resonance imaging have shown that diffusion is the dominating mechanism for fat migration. They conclude that if capillary pressure is involved it is a minor contributor (Galdámez, Szlachetka, Duda, & Ziegler, 2009).

3.5   The impact of praline geometries on the migration rate

According to Fick's law, the thickness of the chocolate layer influences the migration rate of moisture and fat. The higher amount of filling and the smaller amount of chocolate, the more intense will the migration be. Furthermore, the geometry of the product will influence the shell thickness. With a given chocolate content of 50% and a given weight, the coating in a half bowl shape would be thicker than in a cylindrical form, and a thick quadratic bar is advantageous compared to a flat, rectangular one (Ziegler, 1997).

3.6   Analysing techniques

Several techniques can be used to analyse chocolate pralines and other food products. In the following chapter follows a short description over the most important techniques used within this project.

3.6.1   Temper curves

To be sure that the chocolate have been well tempered and that there are enough of the β_V crystals in the chocolate, X-rays can be used to determine the exact type of the present crystals. This is a very expensive and slow technique, which works in the laboratory but not in industry. Instead the fact that heat is released when fat crystallizes is used. This effect is caused by that the energy required to melt the fat, the latent heat, is very much larger than the energy required to change its temperature by 1°C, the specific heat. This is also the case for chocolate when solidifying it, except that the latent heat is given out when the fat changes from a liquid to a solid. The latent heat for cocoa butter is 157 J/g, which can be compared to the specific heat of 2.0 J/g. By measuring a so called cooling or temper curve, it can be determined if the chocolate have the right amount of crystals present which is often correlated to the presence of desired β_V crystals (Becket, 2008).

A temper curve can be done with a tempermeter, which is made up of a metal tube with a cup in the top to hold the chocolate sample. The temperature is measured by a thermometer probe, which fits through a cap, which in turn fits tightly on to the cup. The temperature can be recorded on a chart recorder or on a computer database. The tube fits through a holder in a thermos flask, where the cup is held above the water in the flask. In the flask a mixture of water and ice is placed and then the tube is put in position. Tempered chocolate is poured into the cup and the thermometer cap is pushed on top. Finally a plot is made up of the temperature in the centre of the sample against time (Becket, 2008).

At first the temperature drops slowly and uniformly. If the chocolate is correctly tempered there is enough crystal nucleus distributed in the chocolate to make it crystallize quickly. During the crystallization latent heat is released that will compensate for the cooling and cause the temperature to remain constant for some time. This gives rise to a plateau in the temper curve that can be seen in Figure 3.19 (Becket, 2008).
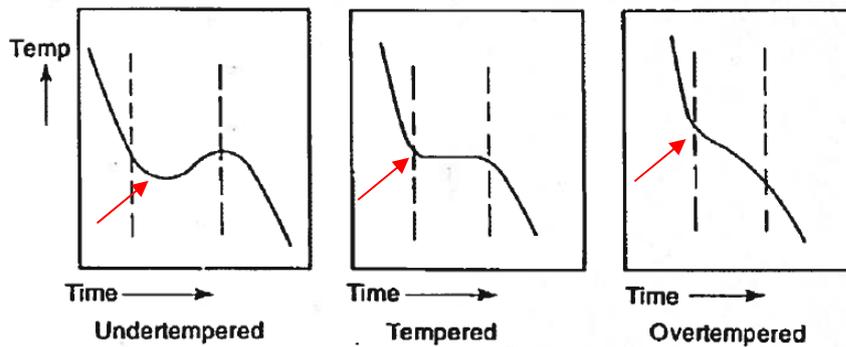
Figure 3.19: Temper curves for under tempered, correctly tempered and over tempered chocolate. The red arrows show the inflection point (Talbot).

If there are not enough crystal nucleuses in the chocolate, the chocolate is said to be under-tempered, and it will take longer time for the chocolate to crystallize. On the other hand, a smaller amount of crystal nucleus gives a larger amount of fat to crystallize during the cooling and further more latent heat to be released. However, due to the lack of crystal nucleus this will cause a longer initial drop in temperature, but when the fat starts to crystallize so much latent heat is released that it causes the temperature to rise again. When all latent heat has come out the temperature will continue to fall (Becket, 2008). During cooling new crystal nucleus can spontaneously be formed in an unstable polymorph, which can give rise to re-crystallization problems and a lower quality of the chocolate (Lonchampt & Hartel, 2004).

If almost none, or either far too many, crystal nucleus are present the chocolate is said to be over tempered and it will not crystallize correctly. With far too many crystal nucleus the latent heat will already have been removed and mainly specific heat will slowly be released (Becket, 2008). The presence of a high amount of seeds can be due to an excessive tempering time. With no or very few crystal nucleus present unstable polymorphs can form as with the case for under tempered chocolate (Lonchampt & Hartel, 2004).

At which temperature that the inflection of the curve occurs is also important since it indicates what polymorphic form the chocolate has. Higher temperature at the inflection point means that more stable crystals are present. The inflection point is shown with red arrows in Figure 3.19 (Becket, 2008).

3.6.2 Measurement of water activity

There are different techniques to measure water activity, of which one is by measuring the dew point by a so called chilled-mirror-technique. The sample is put in a chamber together with a closed air volume, where it is brought to moisture and temperature equilibrium. A mirror in the chamber is chilled to the dew point of the surrounding air. The temperature at which saturation of water is observed and the beginning of condensation, obtained by the chilled mirror, is related to vapour pressure and further to water activity. Photo detection of the condensation on the cooled mirror together with a precise measurement of the mirror temperature gives the relative humidity of the chamber where the food sample is disposed. In equilibrium the relative humidity of the air is equal to the water activity of the sample. This is

a rapid and precise method but that in reality only accounts for the water activity of the surface of the sample (Decagon Devices Inc., 2000) (Mathlouthi, 2001).

3.6.3   Digital colour imaging system

Digital colour imaging system is a computer controlled digital camera that can be used to measure colour and capture high quality repeatable images. The camera can obtain reflectance or colorimetric data from samples also with a very small area or a curved surface. Besides colour information it can capture the total appearance of an object including surface details, such as gloss, texture and surface characteristics. Captured images can for instance be coloured to specific standard shades to simulate final products, and can also be used for quality control etc. (DigiEye Plc., 2007). In this work it is used to analyse crack formation in the pralines.

The digital colour imaging system consists of an illumination cabinet that uniformly illuminates objects for capturing repeatable images, a digital camera that allows previewing and capturing of the image of the sample and enables targeting of selected areas, and a desktop personal computer running a software system with a colour monitor (DigiEye Plc., 2007).

Other methods for visual assessment exist. An advantage with the digital colour imaging system is that it is a non-destructive method to analyse visual quality characteristics of an object. It is cost-effective, quick, permits a permanent record for later examination and comparison, and the images are captured under controlled and reproducible conditions. The computer vision system was developed under the 1960's and became popular within the food industry during the 1990's. Earlier, it has for example been used in meat quality evaluation (Tan, 2004), to assess oriental noodles appearance and colour (Hatcher, Symons, & Manivannan, 2004), to determine bubble size distribution in beer (Heptworth, Hammond, & Varley, 2004), to inspect pizza topping percentage and distribution (Sun, 2000), and to evaluate fat bloom in chocolate (Chan Sui Ko, 2010).

4 Material and methods

In this chapter, is presented a description of the materials and methods used in the project.

4.1 Raw materials

In this section, is presented a description of the raw materials used in the project.

4.1.1 Chocolate

Dark chocolate was received from Aarhus/Karlshamn A/S. It was stored at 15 °C and 30% RH. Before usage it was heated in a heating oven (Heraeus – Kendro Laboratory Products) at 50 °C and poured into the tempering machine. The recipe for the chocolate is shown in Table 4.1.

Ingredients	Content (%)
Cocoa mass	40
Cocoa butter	10
Sugar	50

Table 4.1: Recipe of dark chocolate from Aarhus/Karlshamn A/S.

4.1.2 Filling thickeners

GENUGEL® carrageenan type CJ, KELTROL® TF Food grade xanthan gum from CP Kelco, and gelatin were stored at 20°C before they were used as thickeners in the model fillings.

4.1.3 Humectants

85% glycerol from Apoteket, 95% glycerol and 99.3 % glycerol from VWR, among with sugar from Danisco, calcium chloride hexa hydrate and citric acid were stored at 20°C before they were used as humectants in the model fillings.

4.1.4 Antimicrobial inhibitor

NATAMAX SF Natural Antimicrobial from Danisco was used in the model fillings to prevent mould growth in the pralines.

4.1.5 Ultrapure water

Ultrapure water that was used in the model fillings was produced with a NANOpure – ultrapure water system.

4.2 Methodology and equipment

In this section, is presented the methodology and equipments used during the project.

4.2.1 Preparation of model filling

Xanthan, carrageenan and gelatin were tested as thickeners in the filling to achieve a suitable viscosity, in combination with different humectants to lower the water activity. The humectants tested were glucose, citric acid, salt and glycerol (85%, 95% and 99.3%).

4.2.1.1   Model filling recipes

A model filling as thick as possible but that still was fluid enough to be pumped into the praline shells was desired, in combination with different water activities. Several combinations of thickeners and humectants were tested. An example of some combinations is presented in Table 4.2. All combinations are presented in Appendix 1.

Table 4.2: An example of tested amounts (w%) of thickeners with 30w% glycerol (85%).

Thickener	w%	Humectant	w%
Xanthan	5	Glycerol (85%)	30
Xanthan	6	Glycerol (85%)	30
Xanthan	7	Glycerol (85%)	30
Xanthan	10	Glycerol (85%)	30
Carrageenan	4	Glycerol (85%)	30
Carrageenan	3	Glycerol (85%)	30
Carrageenan	5	Glycerol (85%)	30
Carrageenan	3,5	Glycerol (85%)	30
Gelatin	3	Glycerol (85%)	30

4.2.1.2   Xanthan and carrageenan filling

The xanthan and carrageenan fillings were made according to the following scheme:

1. All the ingredients (humectant, thickener, ultrapure water) were measured in weight percent.
2. The humectant and the thickener were mixed together.
3. The mix was placed on a RCT basic IKA LABORTECHNIK (Tamro MED LAB) magnet stirrer and heated to 50°C.
4. Water was added during mixing.

4.2.1.3   Gelatin filling

The gelatin filling was prepared according to the following scheme:

1. All the ingredients (humectant, gelatin, Natamax and ultrapure water) were measured in weight percent.
2. The ingredients were mixed and the gelatin was let to swell for 10 min.
3. The mix was heated to 70°C in a water bath during stirring on a magnet stirrer of type RCT basic IKA LABORTECHNIK (Tamro MED LAB).
4. The mix was left to cool to 30°C in a second water bath on a magnet stirrer of type Heidolph MR 3003 control.

4.2.2   Praline production

4.2.2.1   Tempering of chocolate

The chocolate was tempered in a tempering machine of model AMK 10 (Aastedt Microverk A/S, Farum, Denmark) (Figure 4.1) and controlled with a MultiTherm Tempermeter (Bühler AG, Uzwil, Switzerland) (Figure 4.2).

Figure 4.1: Photo of the tempering machine of model AMK 10, with (a) a big holder for the chocolate, three cooling zones and a swinging arm where the chocolate pours out, (b) monitors showing the chocolate and water temperatures in the different cooling zones, and (c) a cooling system.

The cooling water temperatures were set to 26.0°C, 14.7°C and 33.0°C for zone 1, 2 and 3 respectively. The Bühler tempermeter measured the temper curve of the sample, which was controlled by the slope of the curve and the TI-value (Temperature Index). According to Bühler the chocolate was considered well tempered with a slope as close to zero as possible and a TI-value ~5. A lower TI-value indicated that the chocolate was under tempered and a higher TI value indicated that the chocolate was over tempered (Bühler group).
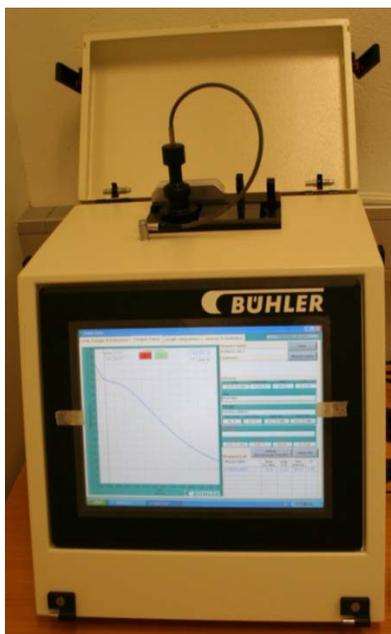
Figure 4.2: Photo of the MultiTherm Tempermeter, monitoring a temper curve. The slope of the temper curve should be as close to zero as possible and the TI-value should be ~5 for the chocolate to be well tempered (Bühler group).

4.2.2.2   Geometries

Pralines with two different geometries, squares and rounds (Figure 4.3), were produced and analysed at SIK.
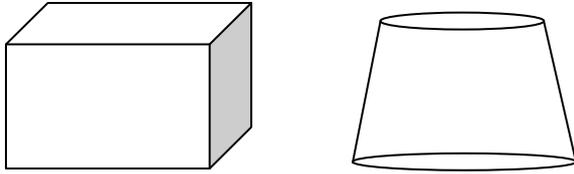
Figure 4.3: Illustration of the two praline geometries tested, square and round shaped.

4.2.2.3   Moulds

Plastic moulds with round and square shapes were kindly received from Aarhus/Karlshamn A/S and were used when moulding the pralines (Figure 4.4).

Figure 4.4: Photo of the round and square shaped plastic moulds from Aarhus/Karlshamn A/S.

4.2.2.4   Preparation of pralines

Pralines were manufactured manually at SIK according to the following scheme:

1. Tempered chocolate was filled into a plastic mould (Figure 4.5).
2. Excess chocolate was scraped off with a slick (Figure 4.5).
3. The filled mould was shaken on a Heidolph shaking table of type DSG302 for 30 seconds to reduce the air bubbles in the chocolate (Figure 4.5).
4. The filled mould was turned upside down and was slightly shaken for 1 minute and 20 seconds by hand to let chocolate pour out (Figure 4.6).
5. Excess chocolate were again scraped off with a slick (Figure 4.6).
6. The chocolate shells were let to cool next to a fan for 15 minutes according to the method developed by Martina Hellmansson (Figure 4.6).
7. Filling was pumped into each shell with a dispenser (3 ml in the round shaped and 5 ml in the square shaped pralines) (Figure 4.7).
    a. Xanthan and carrageenan fillings was spread out and let to cool/stabilize for 10 minutes next to the fan.
    b. Gelatin filling was left to cool for an hour in a refrigerator at 5-8°C (Figure 4.7).
8. The top of the shells were heated with a Bosch PHG600-2 CE thermo-electronic heating gun for 10 seconds each to have a better attachment of the base (Figure 4.7).
9. More chocolate was added to form the base of the praline (Figure 4.8).
10. Excess chocolate was scraped off with a slick (Figure 4.8).

11. The pralines were let to dry for 15 minutes next to the fan (Figure 4.8).
12. The pralines were carefully knocked out of the moulds (Figure 4.9).
13. The pralines were stored in a constant room with 20 °C and 50 % RH for five weeks (Figure 4.10).

Four different parameters were tested during production, which were:

- *Removal of air bubbles (shaking time)*: Different shaking times at the shaking table were tested to have a good removal of air bubbles (step 3).
- *Shell thickness (pouring time)*: Different pouring times were tested to achieve an optimal shell thickness (step 4).
- *Amount of filling*: Different amounts of filling were tested (step 7).
- *Heating time*: Different heating times with the thermo-electronic heating gun were tested to have a proper addition of the base (step 10).

Once the process had been optimized with respect to the four parameters listed above, 240 pralines were produced, with 40 pralines of each filling and geometry, and in addition ten empty shells of each geometry were produced as reference.

Figure 4.5: (1) Photo of chocolate being poured into a plastic mould, (2) a mould filled with chocolate where excess chocolate just have been scraped off, (3) and a chocolate filled mould being shaken on a shaking table to reduce the air bubbles in the chocolate.

Figure 4.6: (1) Photo of chocolate shells being formed by turning the chocolate filled mould upside down and letting the centre chocolate pour out, leaving only a thin layer on the sides of the mould. (2) Excess chocolate have been scraped off, (3) before the shells are left to cool in front of a table fan.

Figure 4.7: (1) Photo of the dispenser when filling the chocolate shells with model filling, (2) shells filled with model filling left to stabilise in a refrigerator, (3) and heating of the chocolate shells with a Bosch PHG600-2 CE thermo-electronic heating gun before adding the base.

Figure 4.7: (1) Photo of chocolate being added to the filled shells to form the base, (2) excess chocolate having been scraped off, (3) before letting the pralines cool in front of the fan.

Figure 4.8: Photo of ready produced pralines, square and round shaped.

4.2.3   Characterisation techniques during storage

The pralines were stored in a constant chamber with 20°C and 50 % RH for four weeks (Figure 4.10 and 4.11), during which physical appearance, weight, and water activity in the shell were analysed. All samples were analysed every 7th day with respect to weight changes and physical appearance. However, additional measuring occasions were added based on when the different samples were believed to crack, at which also water activity in the shell was measure. The pralines with model filling a_w 0.98 were analysed every day for five days, the pralines with model filling a_w 0.85 were analysed every second day for nine days, the

pralines with model filling a_w 0.75 were analysed every fourth day for sixteen days, pralines with model filling a_w 0.65 were analysed once a week for four weeks, and the empty shells used as reference were analysed every second week for four weeks, at only three measuring occasions. A full analysing scheme is shown in Table 4.3.

Table 4.3: Scheme of the analysing measuring occasions for all samples. D = Digital colour imaging (DigiEye), W = Weight, a_w = water activity.

a_w	0.99			0.86			0.78			0.67			ref		
Day	D	W	a_w	D	W	a_w	D	W	a_w	D	W	a_w	D	W	a_w
0	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
1	x	x	x												
2	x	x	x	x	x	x									
3	x	x	x												
4	x	x	x				x	x	x						
5				x	x	x									
6				x	x	x									
7	x	x		x	x		x	x		x	x	x	x	x	x
8				x	x	x	x	x	x						
9															
10															
11															
12							x	x	x						
13															
14	x	x		x	x		x	x		x	x	x	x	x	x
15							x	x	x						
16															
17															
18															
19															
20															
21	x	x		x	x		x	x		x	x	x	x	x	x
22															
23															
24															
25															
26															
27															
28	x	x		x	x		x	x		x	x	x	x	x	x
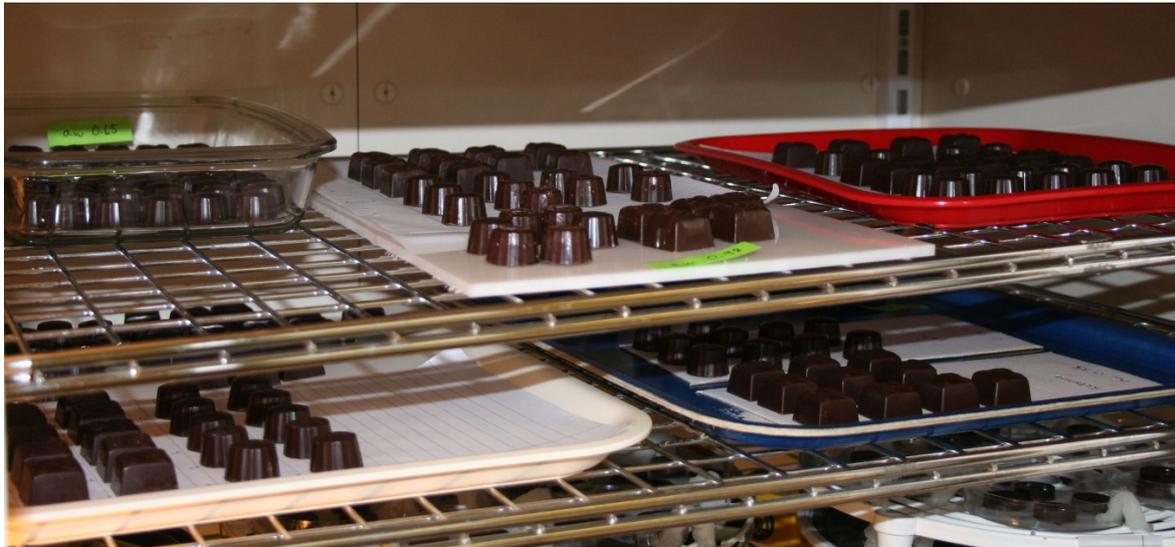
Figure 4.10: Photo of pralines being stored in a constant chamber at 20°C and 50 % RH.

Figure 4.11: Photo of the constant chamber with 20°C and 50 % RH where the pralines were stored.

4.2.3.1 Digital colour imaging

The pralines were photographed and analysed by a DigiEye camera of version 2.43 (Figure 4.12). For each filling and geometry the same 10 replicates as for weighing were photographed and analysed. For the reference samples the same four replicates from each geometry were photographed and analysed at each measuring occasion and every 7th day.
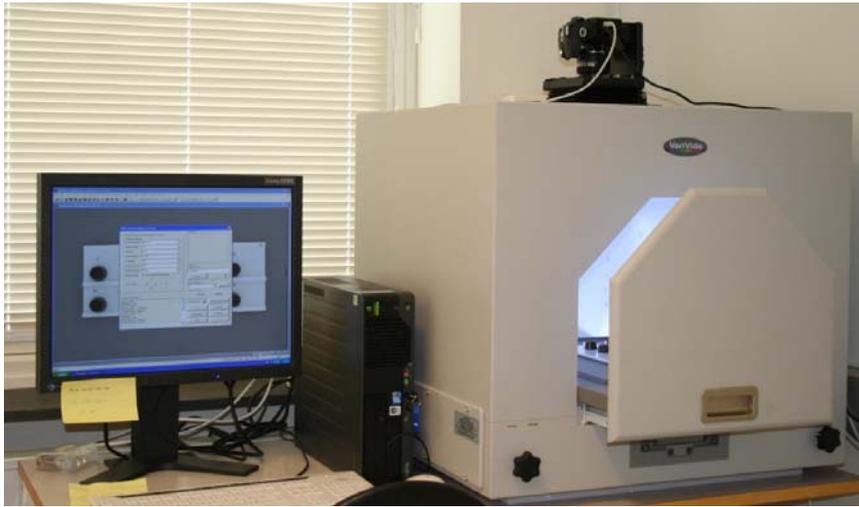
Figure 4.12: Photo of the DigiEye camera of version 2.43 when taking pictures of some praline samples.

4.2.3.1.1   Shell thickness

At the end of the storage period, after that all samples had been analysed, each praline was cut in two and photographed so that the shell thickness could be measured. The shell thickness was measured with Analysis Five program (Soft Imaging System GmbH) by measuring the shell thickness of the top, side and base of each praline (Figure 4.13). Four measurements were made on each side, giving in total 16 length measurements per praline.
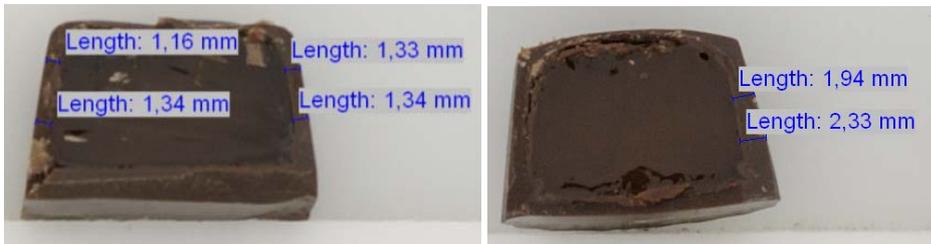
Figure 4.13: Intersection of a square and round praline where the shell thickness has been measured with Analysis Five program (Soft Imaging System GmbH).

4.2.3.2   Weighing of pralines

The pralines were weighed with a scale of type Mettler Toledo PR8002 (Figure 4.14). For each model filling and geometry the same 10 pralines were measured at five measuring occasions and every 7th day. For the reference samples four praline shells of each geometry were measured every 7th day.

Figure 4.14: Photo of the scale of type Mettler Toledo PR8002 measuring the weight of a praline.

4.2.3.3 *Water activity measurements*

Decagons AquaLab Series 3 (Figure 4.15) was used for water activity measurements. The water activity of the model fillings was measured before they were poured into the pralines and the water activity of the chocolate shell was measured during storage. To measure the water activity of the filling it was spread out in the sample cup so it covered the bottom. The chocolate shell was first shredded of the praline with a shredder before it was put in the sample cup (Figure 4.16). The sample was then measured by putting the cup in the chamber. For each filling and geometry five replicates were made for each measuring occasion. For the references of empty shells two replicates were made for each geometry at every measuring occasion.

Figure 4.15: Photo of Decagons AquaLab Series 3.

Figure 4.16: Photo of chocolate being shredded of a praline, filled in a sample cup and being measured in Decagons AquaLab Series 3.

5 Results

5.1 Filling thickeners

Desired properties for the model filling was for it to be as easy as possible to pour into the chocolate shells but at the same time stiff to being able to resist the pressure that was applied on it when adding the base.

Xanthan and carrageenan gave quite similar results but the problem with using them as thickeners was that it was difficult to achieve a stiff gel that was still fluid enough to easily being poured into the shells. This gave an uneven bottom, thicker on one side and thinner on the other, forming a sort of slope. This can be seen in Figure 5.1.

Figure 5.1: Intersection of a praline with carrageenan filling (3.5 w%). The filling is not rigid enough to withstand the pressure applied on it when adding the base why a chocolate "slope" is formed.

Gelatin turned out to be an outstanding thickener compared to xanthan and carrageenan. The benefit with gelatin was that it was liquid when heated so it could easily be pumped into the shells with the dispenser, and it gelatinised when cooled down and was then able to withstand the pressure performed on it when adding the base. The properties of gelatin were quite similar to that of a nougat filling. An intersection of a praline with a gelatin filling compared to nougat filling can be seen in Figure 5.2.

Figure 5.2: Intersection of a praline with gelatin filling (3 w%) to the left and nougat filling to the right. Since both gelatin and nougat are fluid when heated they are easy to pour into the shells, giving a smooth surface that becomes stiff enough when cooled to withstand the pressure performed on it when adding the base.

5.2 Humectants

Different humectants were tested to lower the water activity (a_w) of the model filling. Glycerol showed to be the absolute best humectant compared to sugar, salt and citric acid. Salt was very difficult to dissolve even in small amounts. Sugar was suitable for higher water activities but was difficult to dissolve in large amounts, thus it was not possible to reach lower water activities. Citric acid was tested in combination with sugar but did not improve the result why it was discarded.

5.3 Preparation of model filling

Glycerol (99.3%) turned out to be the best humectant and gelatin (3 w%) the best thickener for the model filling. Amount of glycerol, gelatin and Natamax used for the four fillings with different a_w are shown in Table 5.2. For each a_w 400 ml model filling was prepared.

Table 5.2: Amount (w%) of 99.3 % glycerol, gelatin and Natamax added in the final model fillings.

Water activity (aw)	Glycerol (w%)	Gelatin (w%)	Natamax (w%)
0.99	10	3	0.04
0.86	40	3	0.04
0.78	50	3	0.04
0.67	62	3	0.04

5.4 Preparation of pralines

During the praline preparation four parameters were tested, with the following result.

5.4.1 Removal of air bubbles (shaking time)

During the praline preparation different shaking times (step 3 in section 4.2.3.4) were tested to have a good removal of air bubbles. It was found that shaking time for 30 seconds gave an acceptable removal of air bubbles.

5.4.2 Shell thickness (pouring time)

The shell thickness varied depending on the time the chocolate was let to pour out from the filled moulds (step 4 in section 4.2.3.4). The amount of chocolate that poured out, and thus the shell thickness, varied also significantly with how vigorously the mould was shaken. When producing the pralines by hand this parameter was difficult to measure but special attention was paid to perform this in the same manner each time. The pouring time was measured and kept constant. The desired properties of the shell were to have it as thin and even as possible, and still being able to remove it from the mould and without the filling leaking out. A pouring time of 1 minute 20 seconds gave a good shell thickness for both square and round pralines.

5.4.3 Amount of filling

Different amounts of filling were tested in the pralines (step 7 in section 4.2.3.4). It was found that 5 ml and 3 ml were suitable amounts in the square and round shaped pralines respectively.

5.4.4 Heating time

Different heating times with the thermo-electronic heating gun (step 8 in section 4.2.3.4) were tested. It was found that 10 seconds was enough to get the base to attach well to the shell.

5.5 Results from characterisation of the pralines during storage

In this section, the results from characterisation of the pralines during storage are presented. The pralines were characterised by three methods; digital colour imaging system, weight measurements and water activity measurements. The results from these three methods are presented both with aspect to the different model fillings and to the two geometries.

Furthermore, the shell thickness of the pralines was measured to investigate its impact on the results.

5.5.1 Digital colour imaging

Crack formation in the pralines were registered and analysed with a digital colour imaging system. In this section, the results are presented according to the different model fillings followed by the two geometries. Furthermore, the results of a deeper analysis of from where the cracks originated are presented.

5.5.1.1 *Tendency to crack with different model filling*

A suggestion for crack formation in pralines is that water from the centre migrates through the chocolate shell due to a concentration difference. The pralines with higher a_w in the model filling is therefore expected to experience a higher level of migration due to a higher concentration difference and hence an increased tendency to crack.

In Figure 5.4 an example of cracks in a square and round praline is shown. As expected, the pralines with model filling a_w 0.99 cracked first and to the highest percent both for square and round pralines. The results for model filling a_w 0.86 and 0.78 were quite similar. Square pralines with model filling a_w 0.86 cracked a few days earlier than square pralines with model filling a_w 0.78. Round pralines with model filling a_w 0.86 cracked to a slightly higher percentage compared to round pralines with model filling a_w 0.78. Pralines with model filling a_w 0.67 had no (square) or very few (round) cracks and the reference of empty shells had no cracks at all. The results are presented in Figure 5.5 and 5.6.

Figure 5.4: Example of a cracked square and round praline with model filling a_w 0.99.
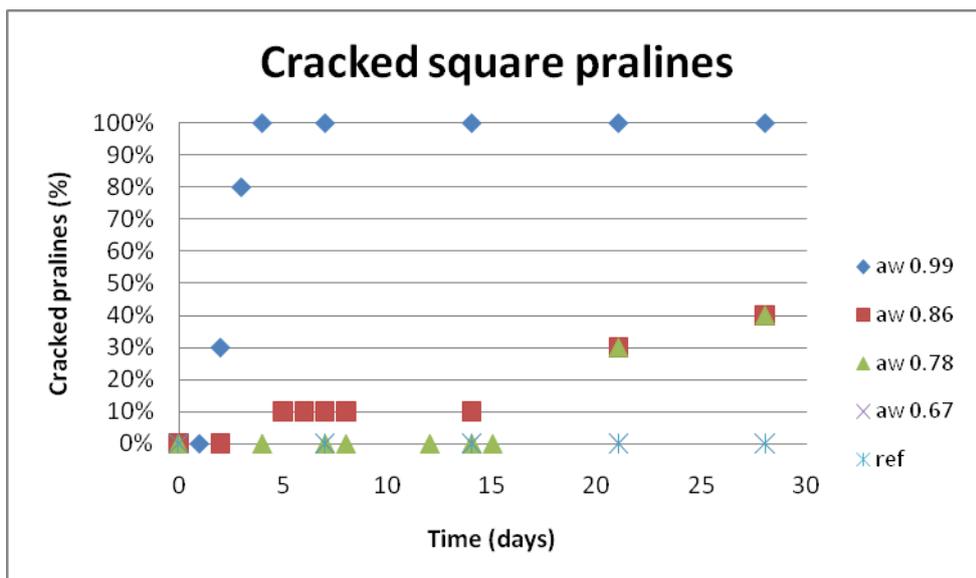
Figure 5.5: Total cracked square pralines (%) for each model filling and reference. Pralines with a_w 0.99 started to crack after 2 days and 100% had cracked after 4 days. Pralines with a_w 0.86 started to crack after 5 days and after 28 days 40% had cracked. Pralines with a_w 0.78 start to crack after 21 days and after 28 days 40% have cracked. The pralines with a_w 0.67 and the reference of empty shells had not cracked at all after 28 days.
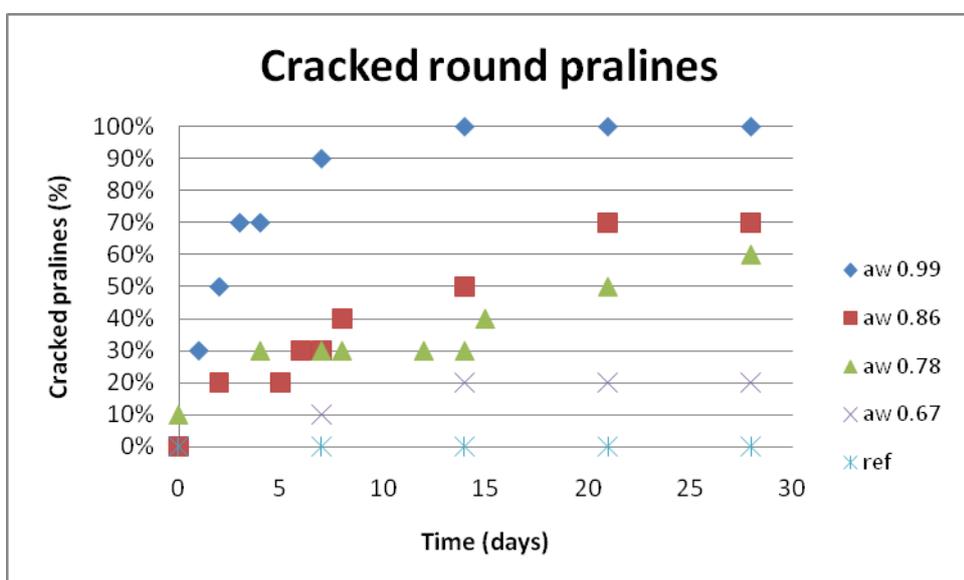
Figure 5.6: Total cracked round pralines (%) for each model filling and reference. Pralines with a_w 0.99 started to crack after 1 day and 100% of the pralines had cracked after 21 days. Pralines with a_w 0.86 started to crack after 2 days and after 28 days 70% had cracked. Pralines with a_w 0.78 had already cracked to 10% from day 0 due to inconsistency during production but had cracked further to 30% after 4 days and after 28 days 60% had cracked. The pralines with a_w 0.67 started to crack after 7 days and after 28 days 20% had cracked. The reference of empty shells had not cracked at all after 28 days.

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5.5.1.2 *Geometries*

Round pralines cracked first for all model fillings and to highest percent except for model filling a_w 0.99 where both geometries cracked to 100%. In Figure 5.7-10, the total percent of cracked pralines for the two geometries is presented.
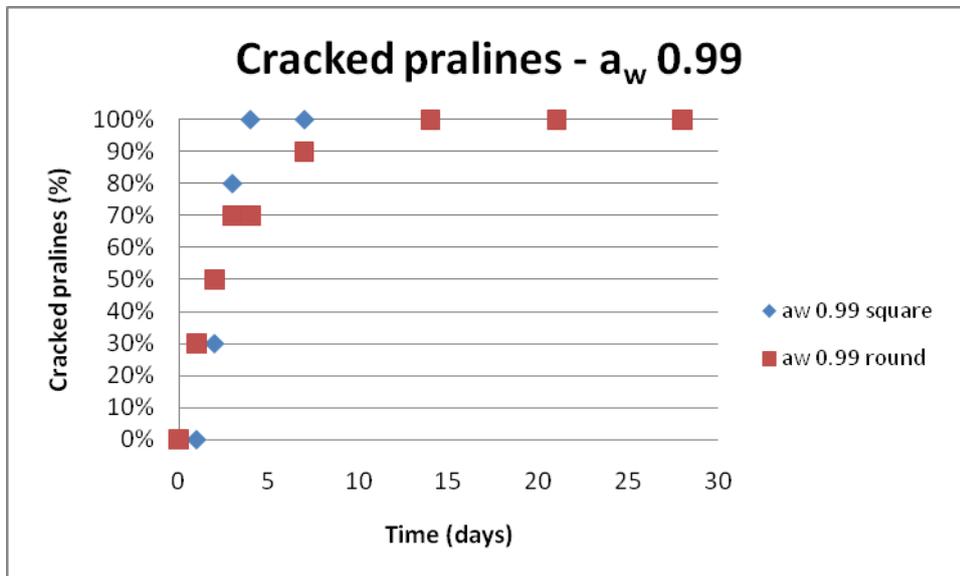
Figure 5.7: Total amount cracked pralines (%) for square and round pralines with model filling a_w 0.99. The square pralines started to crack after 2 days and had cracked to 100% after 4 days, while the round pralines started to crack after 1 day and had cracked to 100% after 14 days.
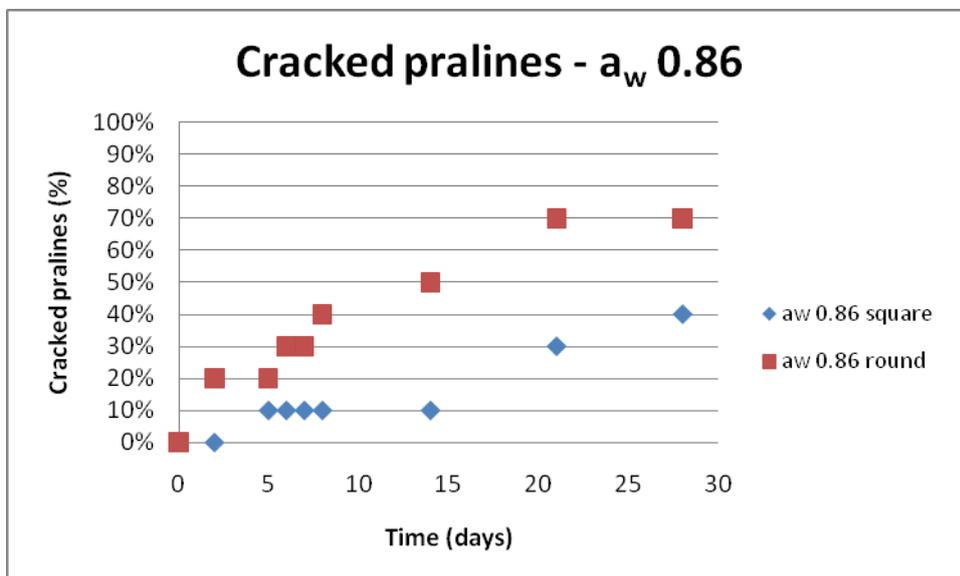
Figure 5.8: Total amount cracked pralines (%) for square and round pralines with model filling a_w 0.86. The square pralines started to crack after 5 days and had cracked to 40% after 28 days, while the round pralines started to crack after 2 days and had cracked to 70% after 28 days.
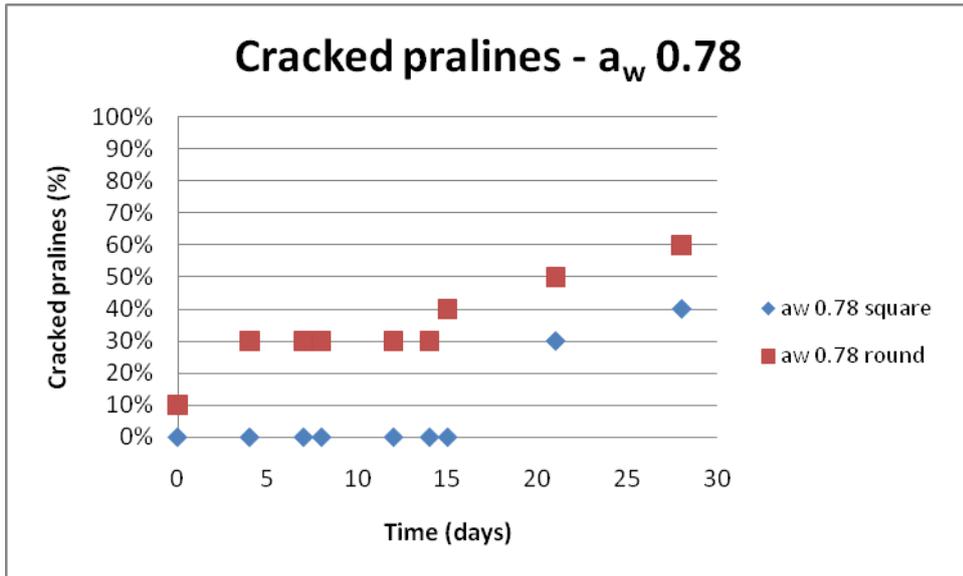
Figure 5.9: Total amount cracked pralines (%) for square and round pralines with model filling a_w 0.78. The square pralines started to crack after 21 days and had cracked to 40% after 28 days, while the round pralines started to crack after 4 days and had cracked to 60% after 28 days.
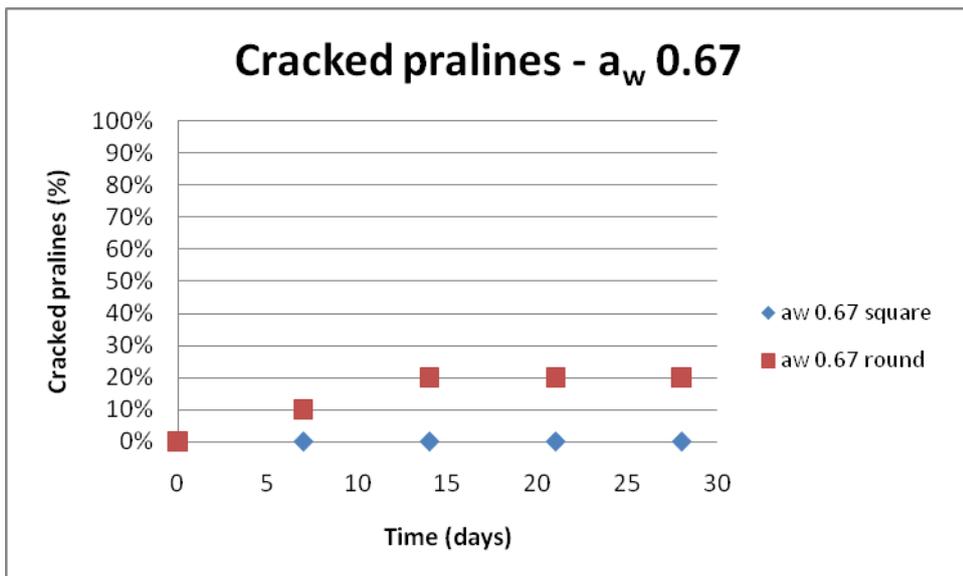
Figure 5.10: Total amount cracked pralines (%) for square and round pralines with model filling a_w 0.67. The square pralines did not crack at all, while the round pralines started to crack after 7 days and had cracked to 20% after 28 days.

In Figure 5.11 and 5.12, the crack formation in a square and round praline with model filling a_w 0.99 can be followed from day 0 to day 28. The square praline cracked after 2 days and the round praline after 1 day. The whitish on the square praline could be sugar from the chocolate or glycerol from the filling that have crystallised, which then is called sugar bloom. Alternatively it could be fat bloom if the chocolate was not optimally tempered. This was not studied further since it was not the aim with the project.
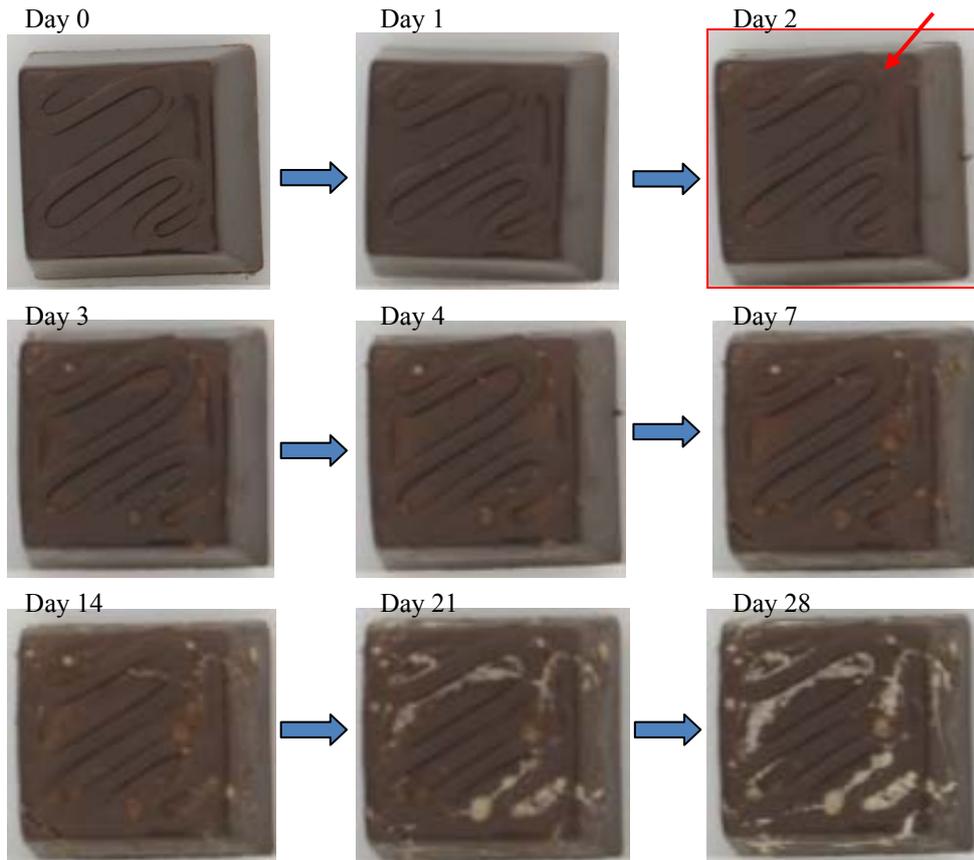
Figure 5.11: Square praline with model filling a_w 0.99 after 0 days, 1 day, 2, days, 3 days, 4 days, 7 days, 14 days, 21 days and 28 days. The praline cracked after 2 days (marked red) in the corner of the top (red arrow).
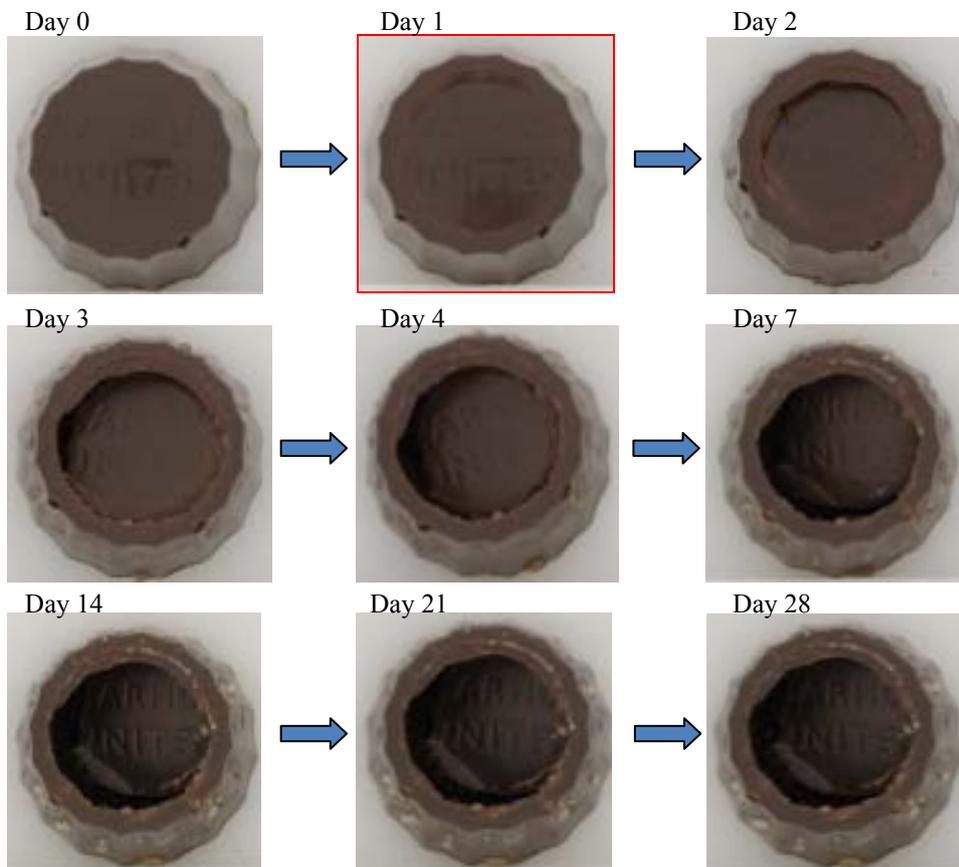
Figure 5.12: Round praline with model filling a_w 0.99 after 0 days, 1 day, 2, days, 3 days, 4 days, 7 days, 14 days, 21 days and 28 days. The praline cracked after 1 day (marked red) in the middle of the top by that the top imploded.

5.5.1.3   *Origin of the cracks*

To better understand the rise and reason for cracks, all pralines were analysed according to where the crack originated. The pralines were categorised in three zones; top, side and base, and further in corner/edge and middle (top), sealing, middle and corner (side) and sealing and middle (base) (Figure 5.13a and 5.14a).

Square pralines cracked mainly at the corners at the top/side of the praline and in the middle of the top. Round pralines cracked mainly at the top by that the top imploded and at the sealing between the shell and base. In Figure 5.13b and 5.14b, is presented the origins of cracks on square and round pralines with model filling a_w 0.99 that have been stored for 28 days. Figure 5.15 shows an illustration of where on the pralines most samples cracked.
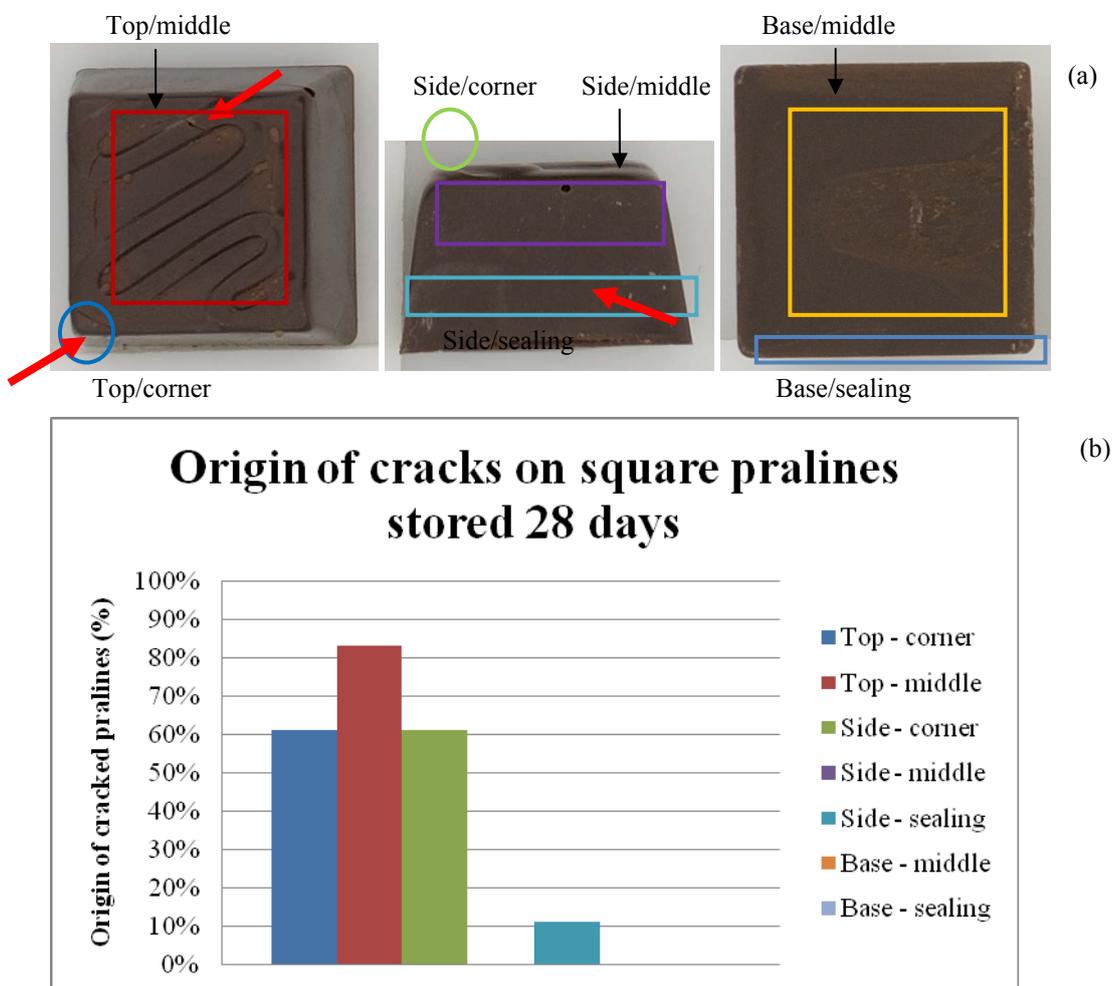
Figure 5.13: (a) From the left: top, side and base of a square praline. Coloured areas indicate the categorisation positions for cracks on the praline while red arrows point out examples of actual cracks. For square pralines the categorisation positions were corner and middle at the top; corner, middle and sealing at the side; middle and sealing at the base. (b) Origin of the cracks (%) on square pralines that have been stored for 28 days, out of a total number of 18 cracked pralines. Note that some pralines cracked on several places.
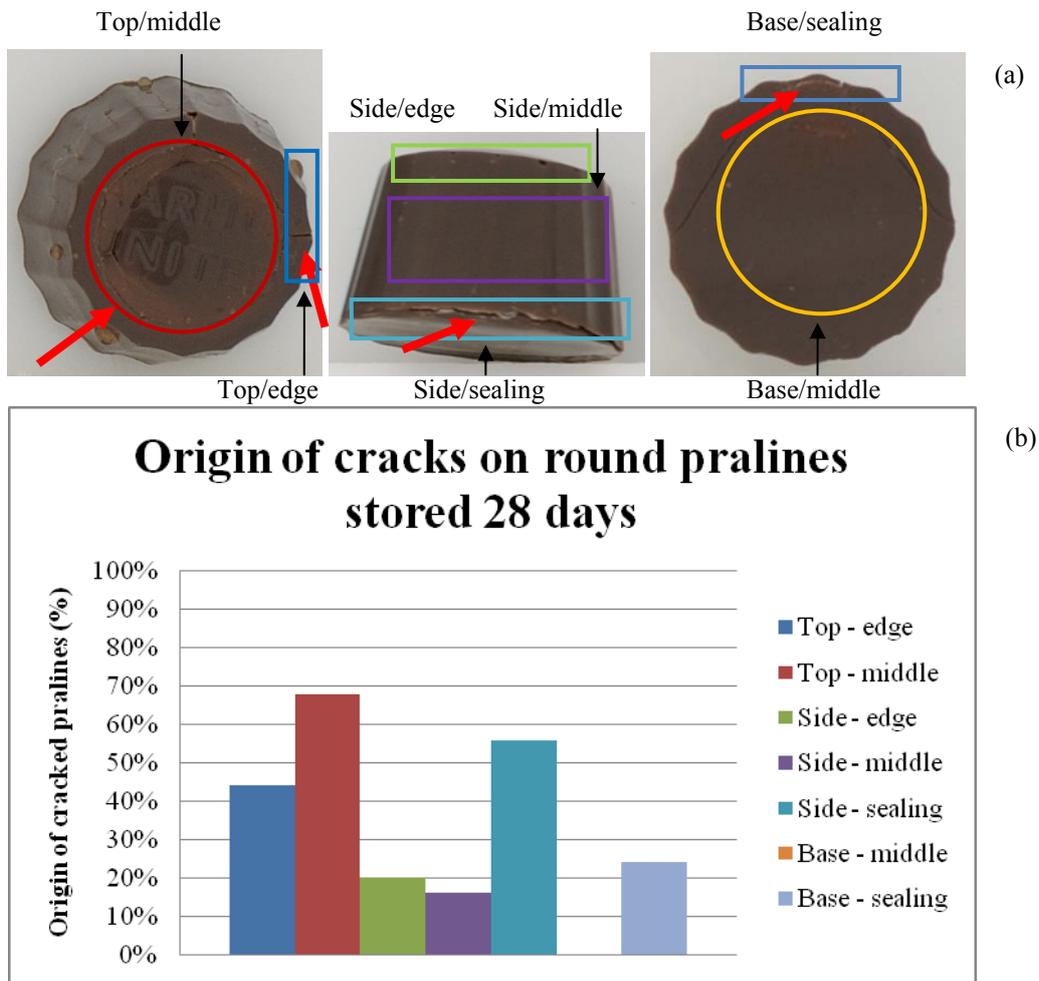
Figure 5.14: (a) From the left: top, side and base of a round praline. Coloured areas indicate the categorisation positions for cracks on the praline while red arrows point out examples of actual cracks. For round pralines the categorisation positions were edge and middle at the top; edge, middle and sealing at the side; middle and sealing at the base. (b) Origin of the cracks (%) on round pralines that have been stored for 28 days, out of a total number of 25 cracked pralines. Note that some pralines cracked on several places.
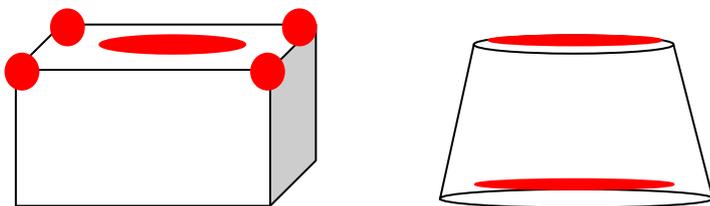
Figure 5.15: Illustration of a square and round praline. The red marks show where on the praline most of the pralines cracked. Square pralines cracked mainly at the middle of the top and at the corners on the top and sides. Round pralines cracked mainly in the middle and edge of the top and in the sealing between the shell and base.

5.5.1.4   *Shell thickness measurements*

It was difficult to achieve an even shell thickness all over the praline and for all samples. To investigate if the thickness of the shell had affected the results, the top, side and base was measured on each sample. The results showed that for square pralines, the base became much

thicker and had larger variation than the top and sides for pralines with all model fillings. The shell thickness for top and sides was otherwise quite similar between the square pralines. For the round pralines the shell thickness differed more between the pralines with different model fillings. The round pralines with model filling a_w 0.67 had much thicker top and sides, but thinner base, than the pralines with other model fillings. Mean shell thickness and standard deviation for all pralines are shown in Figure 5.17 and 5.18.
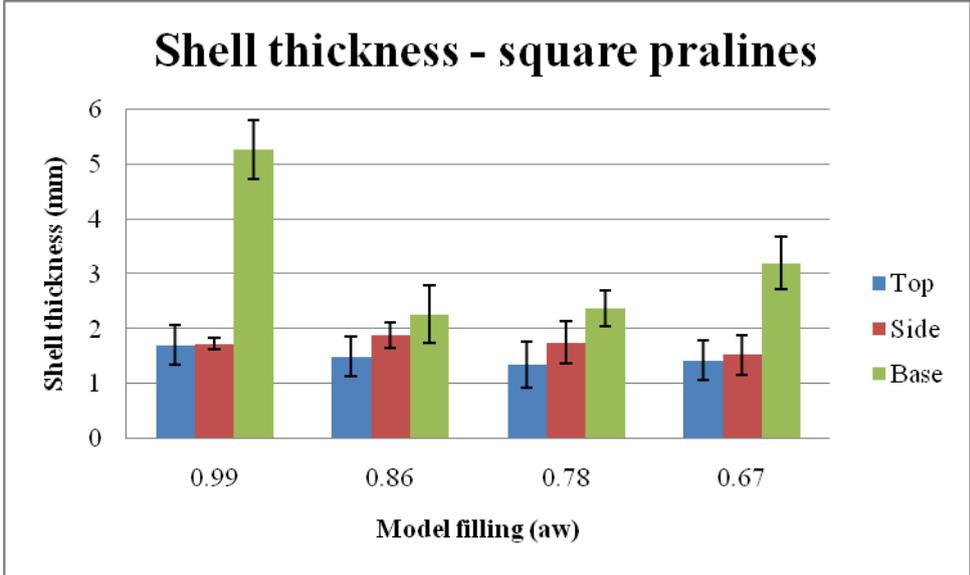
Figure 5.17: Mean shell thickness with standard deviation for square pralines with different model filling.
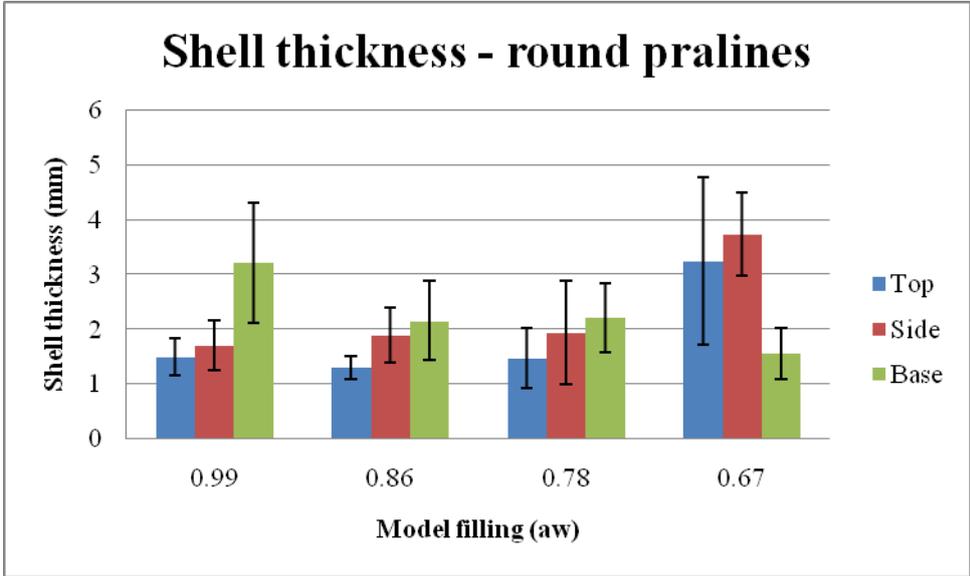
Figure 5.18: Mean shell thickness with standard deviation for round pralines with different model filling.

To further investigate the impact of shell thickness on crack formation, samples that differed from the other pralines, either by cracking first or resisting from cracks, was looked at individually. No clear correlation was seen between cracking and shell thickness. Neither did the pralines that cracked first have particularly thinner shell thickness, nor did the pralines that

did not crack have particularly thicker shell thickness. For example, for square pralines with a_w 0.99 sample 1, 5 and 6 cracked first (top and sides), but as can be seen in Figure 5.19 there is no large difference in shell thickness for the top and sides among the samples. The base is on the other hand significantly thicker for all samples.
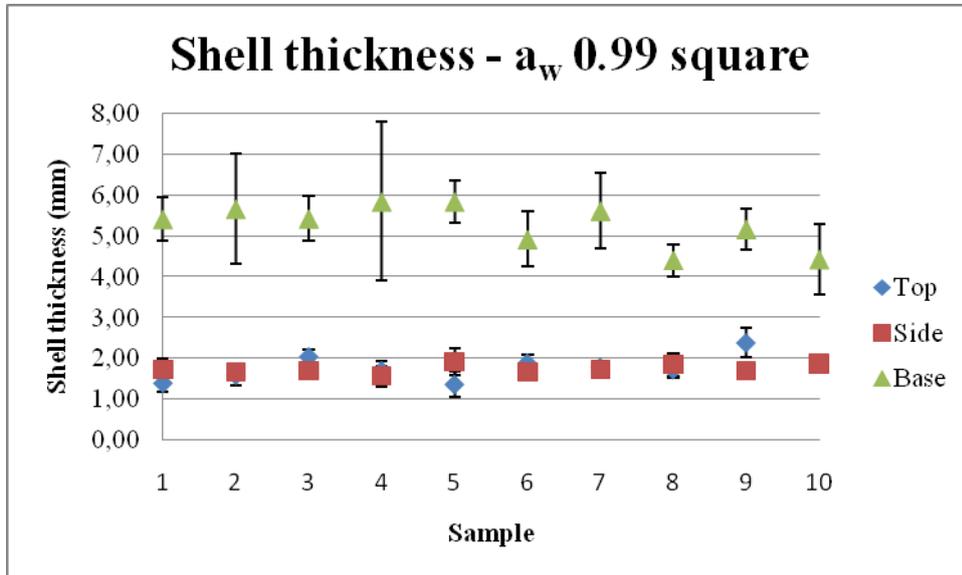
Figure 5.19: Shell thickness (mm) for square pralines with model filling a_w 0.99. All samples had cracked after 28 days. Sample 1, 5 and 6 cracked first.

Furthermore, for square pralines with a_w 0.86 samples 1, 4, 5 and 10 had cracked after 28 days, and sample 2, 3, 6, 7, 8 and 9 had not. As can be seen in Figure 5.20 there is no large difference in shell thickness for the top and sides where the pralines cracked. A slightly thicker base can be seen for all samples that cracked compared to the ones that did not, except for sample 7 that did not crack but still had a thicker base. All results are presented in Appendix 2.

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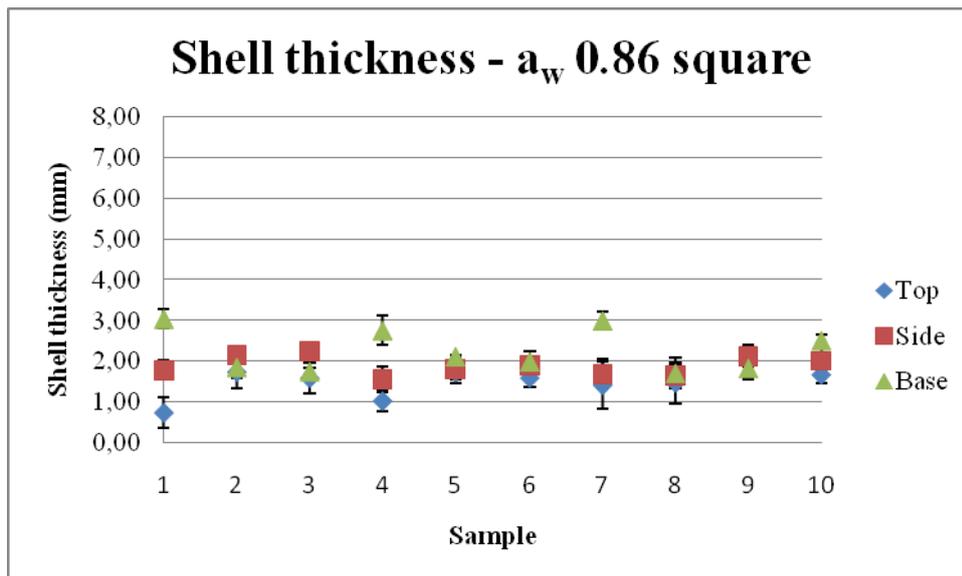
Figure 5.20: Shell thickness (mm) for square pralines with model filling a_w 0.99. After 28 days sample 1, 4, 5 and 10 had cracked, while sample 2, 3, 6, 7, 8 and 9 had not.

Besides shell thickness, some other parameters differed between the two geometries. The square pralines were somewhat larger than the round ones. This means that the square pralines both weighed more and had a higher filling content. Based on the shell thickness measurements, the mean chocolate volume could be calculated and showed that square pralines also had a larger chocolate volume. Furthermore, square pralines had a larger inner chocolate surface that comes in contact with the filling. What is interesting to look at is the ratio of contact surface to chocolate volume, and the amount of filling per amount of chocolate. Even though these ratios did not show any pronounced difference, both ratios were slightly larger for the round pralines. All parameters are presented in Table 5.3.

Table 5.3: Parameters that varied for square and round pralines. The numbers are mean values with standard deviation.

	Square pralines	Round pralines
Weight (g)	9.14 (±0.62)	6.40 (±0.22)
Filling volume (V_f) (mm^3)	3668 (±603)	2495 (±652)
Chocolate volume (V_c) (mm^3)	4938 (±603)	3193 (±652)
Contact surface (A_c) (mm^2)	1408 (±144)	1052 (±201)
A_c/V_c	0.29 (±0.07)	0.35 (±0.12)
V_f/V_c	0.77 (±0.22)	0.85 (±0.33)

5.5.2 Weight differences

In this section, results from the weight measurements are presented. Moisture in the filling was suggested to migrate from the centre through the shell, hence a weight decrease in the pralines was assumed to occur due to loss of moisture. A crack in the shell would lead to that the filling evaporated directly to the air and the migration can be assumed to decrease due to that the a_w difference decreases as the filling dries out. Moisture loss due to evaporation from a crack was further assumed to lead to a much faster weight loss than moisture loss due to migration through the shell.

5.5.2.1 Change in weight as a function of model filling

In Figure 5.21 and 5.22 the mean weight change for square and round pralines is presented with respect to each model filling. The weight change in percentage was calculated for each praline compared to its original weight and then the mean value and standard deviation was calculated for each model filling and praline geometry. Furthermore, the weight change for pralines that had not cracked was calculated to investigate the migration phenomenon. The graphs show measurements made after 0 days, 7 days, 14 days, 21 days and 28 days.
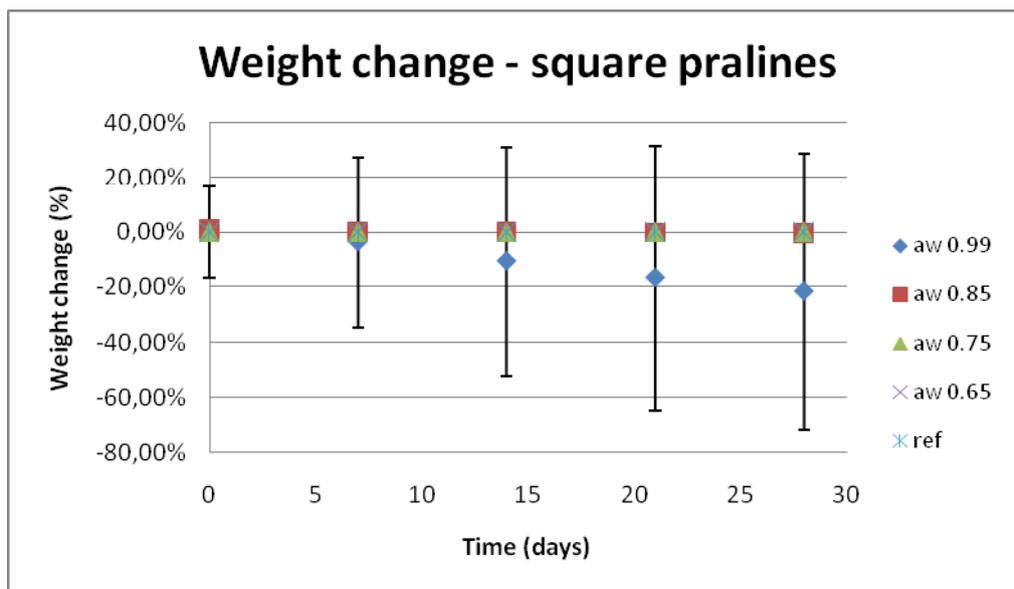
Figure 5.21: Weight change (%) for square pralines for each model filling and reference. The measurements are made after 0 days, 7 days, 14 days, 21 days and 28 days.
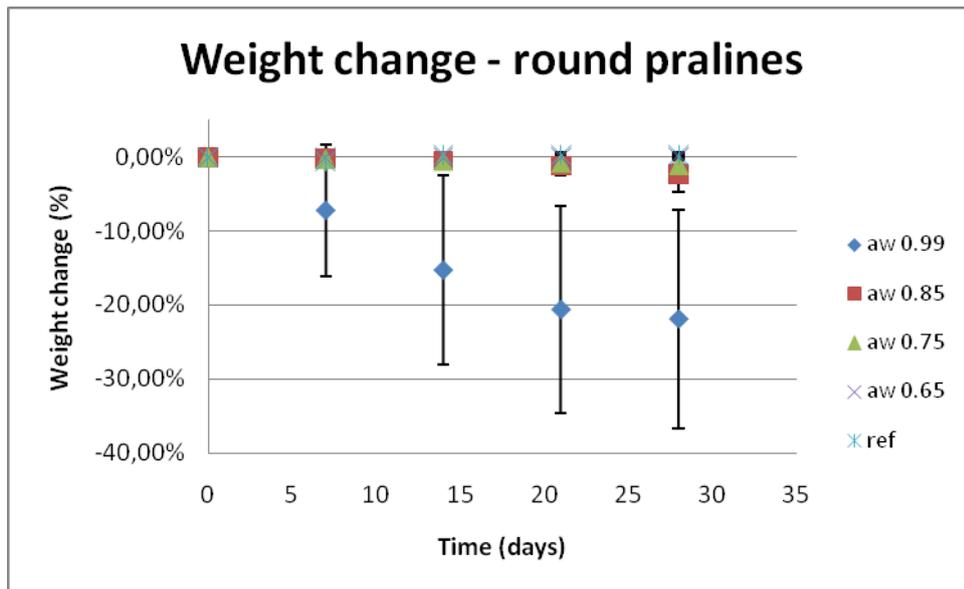
Figure 5.22: Weight change (%) for round pralines for each model filling and reference. The measurements are made after 0 days, 7 days, 14 days, 21 days and 28 days.

In both Figure 5.23 and 5.24 it can be seen that pralines with model filling a_w 0.99 have a major weight decrease compared to the pralines with model fillings with lower water activities. This correlates well to that pralines with model filling a_w 0.99 were the pralines that cracked first. A smaller weight change was seen for pralines with model filling a_w 0.86 and a_w0.78, which cracked somewhat later than model filling a_w 0.99 and not to the same extent. Pralines with model filling a_w 0.67 did not crack at all (square) or to a low extent (round) and have a very low weight difference. The same was true for the reference that did not contain any model filling.

It was expected that pralines that had not cracked should show a small weight decrease due to loss of moisture that had migrated from the centre through the shell and evaporated from the surface. Pralines with model filling a_w 0.86, which had the highest a_w of the pralines with samples that did not crack, were mainly expected to show this. However, neither square nor round pralines that had not cracked showed any major weight difference that confirms this. The weight change for square and round pralines with model filling a_w 0.86 that had not cracked is shown in Figure 5.23. Results for all model fillings are presented in Appendix 3.
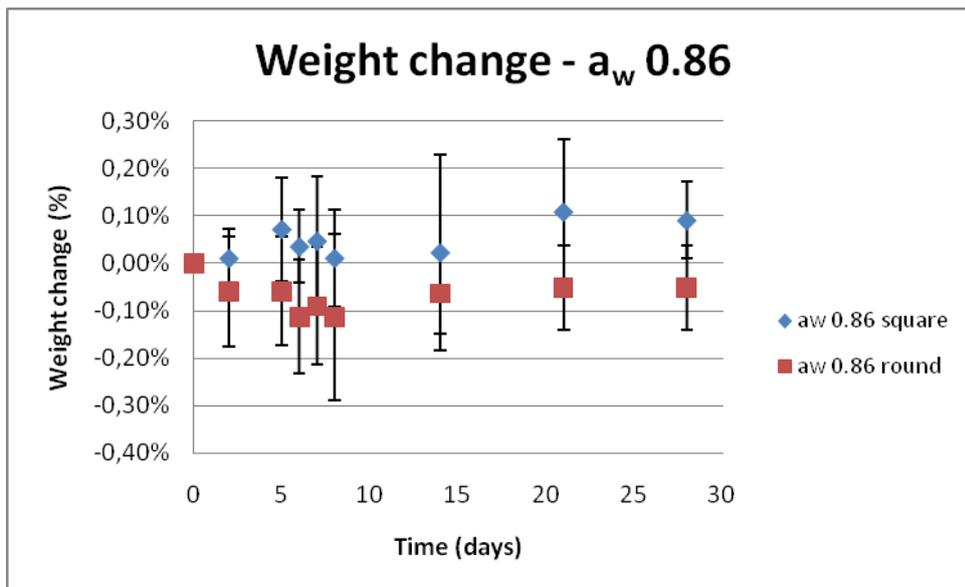
Figure 5.23: Weight change (%) for square and round pralines with model filling a_w 0.86 that had not cracked.

5.5.2.2   *Geometries*

Without adjustment for pralines that had cracked, round pralines had a slightly higher weight decrease, although not significant, compared to square pralines. That correlates to that the round pralines cracked first. Since no significant weight difference could be seen for pralines that had not cracked, no comparison between the geometries can be made concerning the migration phenomenon.

5.5.3   Water activity (a_w) measurements

The water activity (a_w) in the chocolate shell was measured at five different occasions (between day 0 and day 28) for the various model fillings depending on when they were assumed to crack. Moisture from the filling was assumed to migrate into the shell during storage, why the water activity in the shell was expected to increase with time. Since the water activity was measured at different storage times, the result for each model filling is presented separately.

The water activity did not increase with time as expected for any model filling. Instead it both increased and decreased during the storage period. The water activity for pralines with model filling a_w 0.78 is shown in Figure 5.24. The results for the other model fillings are quite similar and are presented in Appendix 4.
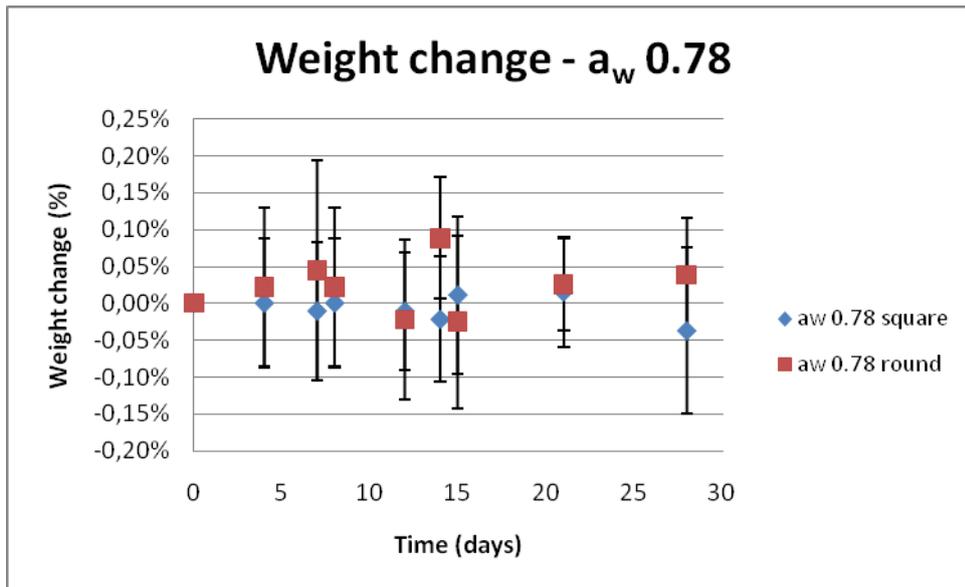
Figure 5.24: Mean water activity in the chocolate shell of pralines with model filling a_w 0.78 at various measuring occasions.

A reason for that the results was not as expected could be due to the methodology used to measure water activity. To exclude faults from the water activity measuring equipment it was controlled regularly during the measurements with specified salt solutions to see that it measured correctly. However, it was quite difficult to shred off chocolate from the pralines without breaking them. Therefore, the chocolate used for analysis was mainly chocolate from the outermost layer of the shell. During the storage time it is quite probable that the outermost layer was more affected by the relative humidity (RH) in the surrounding air than the filling. The chocolate pralines were stored in a constant chamber at 50% RH and 20°C, where the temperature and RH were controlled with a temperature and RH logger. Both temperature and RH were stable during the testing period, why the water activity then ought to have stayed constant. It is however possible that the shredding, which resulted in a larger surface area of the chocolate, enabled water to quickly evaporate into the surrounding before it could be placed in the Decagons AquaLab for a_w measurements.

6 Discussion

In this chapter the results from characterisation of the pralines during storage are discussed.

6.1 Visual characterization of cracking

6.1.1 The impact of model filling on cracking

The pralines with model filling with the highest a_w was expected to crack first since it contain more free water that can migrate into the shell, and a suggested mechanism for cracking is migration of moisture. This is confirmed by the results, which showed that pralines with model filling a_w 0.99 cracked first and to the highest percent for both square and round pralines. Since, there was almost no difference in cracking behaviour between the pralines with model filling a_w 0.86 or 0.78, although much lower than a_w 0.99, one could hypothesise that it should be possible to find a threshold value for water activity in the filling where cracking is significantly reduced. Further studies on model fillings with different a_w would be interesting to see if such a threshold value could be found.

6.1.2 The impact of praline geometry on cracking

When looking on the impact of praline geometry on cracking, it was found that the round pralines cracked first and to the highest percentage for all model fillings, besides for model filling a_w 0.99 where both geometries cracked to 100%. This is a very interesting result which can not solely be explained by shell thickness. One explanation could be that the round pralines showed a trend of a somewhat larger inner shell surface to chocolate volume ratio compared to the square pralines. This will expose the moisture in the filling to a larger surface area per amount of chocolate to initiate migration. Furthermore, the filling volume compared to the chocolate volume was slightly larger, although not pronounced, for round compared to square pralines. The higher amount of filling and the smaller amount of chocolate, the more intense will the migration be. Another reason could be due to production defects. The round pralines had a much higher percentage that cracked in the sealing between the shell and the base compared to the square pralines. This could be due to that the shell was not heated properly before adding the base or that some filling had come in between so that the base did not attach as it should. Worth to note though is that a high percent of the round pralines cracked at the top, which cannot be explained by production defects.

6.1.3 Origin of the cracks

On square pralines most of the cracks originated from the middle of the top or from the corners at the top and sides. Corners were expected to be a weak point due to forces induced by swelling of the shell in different directions. That such a high percentage cracked in the middle was more surprising. The measurements on the shell thickness did not show any large differences even though the mean thickness of the top is slightly thinner than the sides and base for all model fillings.

Round pralines mainly cracked in the middle of the top and in the sealing between the shell and base. At the top the shell cracked due to tensions the top caused by imploding towards the centre. That a high percentage of the pralines cracked in the sealing was expected since it was a critical step to properly attach the base to the shell. It was more surprising that only 10% of the square pralines cracked in the sealing. The sealing was assumed to be a weak point due to forces induced by swelling of the shell in different directions, similar as in the corners of the square pralines. The same reason can be used to explain that a relatively high percentage of the round pralines also cracked at the edge of the top.

6.1.4 The impact of shell thickness on cracking

The shell thickness varied somewhat between the samples, both between different model fillings and different geometries. Moisture was suggested to migrate through the shell in a shorter time in a thinner shell than through a thicker. Furthermore, pralines with thinner shells were assumed to crack first due to that the thinner the shell the less pressure it can withstand before it cracks. However, when examining the shell thickness on individual pralines no such correlation could be found.

The base on the shell was generally much thicker for all samples compared with the top and sides. Due to that the base is added separately to the shell after that the filling is added, it is not surprising that it had a variable thickness. The fact that the base was much thicker than the rest of the shell could have influenced that no praline cracked in the middle of the base. For the top and sides of the shell, where most of the cracks occurred, no major difference in shell thickness could be observed between square and round pralines.

6.2 Weight measurements

Weight was assumed to decrease with time due to loss of moisture, either by migration of moisture through the shell, or by evaporation of moisture through a crack. As expected, the weight measurements that included cracked pralines, showed a higher decrease in weight for the pralines with model filling a_w 0.99 than pralines with model fillings with lower a_w. This correlates well to the cracking ability of the pralines. Those with model filling a_w 0.99 cracked first and to the highest percentage, and hence had a higher evaporation of moisture from the filling. Furthermore, round pralines showed a somewhat, but not significant, higher weight loss than square pralines that correlates to that the round pralines cracked first.

For the pralines that had not cracked, there was no weight loss that indicated moisture migration through the shell. Pralines with model filling a_w 0.86 were most likely to show this due to the highest a_w of pralines that had not cracked. However, no significant weight change could be seen for any of the geometries or model filings. A reason could be that the storage period for the pralines in this project was too short or that the scale that was used only had a precision of 0.01 grams.

6.3 Water activity

The water activity in the chocolate shell was assumed to increase with time due to that moisture from the filling migrates into the shell. However, no such correlation was observed during the experiment. Instead the water activity both increased and decreased. A reason for

this could be due to the methodology that was used to measure water activity. To calibrate the equipment for a_w measurements it was controlled regularly during the chocolate sample measurements with specified salt solutions. However, it was quite difficult to shred off chocolate from the pralines without breaking them. Therefore the chocolate used for analysis was mainly chocolate from the outermost layer of the shell. During the storage time, it is quite probable that the outermost layer was more affected by the relative humidity (RH) in the surrounding air than the filling. The chocolate pralines were stored in a constant chamber at 50% RH and 20°C, where the temperature and RH were controlled with a temperature and RH logger. Both temperature and RH were stable during the testing period, why the water activity then ought to have stayed constant. A reason that the water activity still varied could be due to that the samples were left in room temperature for variable time periods before measurement. It is also possible that the shredding, which resulted in a larger surface area of the chocolate, enabled water to quickly evaporate into the surrounding before it could be placed in the Decagons AquaLab for a_w measurements. However, further development and verification of the methodology used to measure water activity in the shell is required in order to eliminate the possible sources of error mentioned above.

7   Conclusions

A major conclusion that can be drawn from this work is that the water activity in water based filling have a pronounced impact on crack formation in chocolate pralines. To produce pralines that do not crack, the water activity should therefore be held below 0.7. Square pralines mainly cracked at the middle of the top or at the corners at the top and sides, while round pralines mainly cracked in the middle of the top and in the sealing between the shell and base. For the model fillings with lower a_w, round pralines cracked to a higher percent than square pralines. This could be due to a somewhat larger inner shell surface to chocolate volume ratio, and hence a larger amount of filling per amount of chocolate, for round compared to square pralines, but further tests are required to confirm this. Another reason could be due to production defects. To conclude, this work shows that praline geometry is of importance for crack formation, but further studies on different praline geometries is needed to better understand its impact. Shell thickness could not be confirmed to have an impact on cracking in this work.

DigiEye was a good technique to visually analyse crack formation in pralines, even though the method could be developed further so that cracks could be measured after e.g. a standard. To measure moisture migration by weight changes, a more accurate scale is needed than the one used in this project. Furthermore, the method to measure a_w in the chocolate shell needs to be developed.

8   Further work

As one could hypothesise that it should be possible to find a threshold value for a_w in the filling where cracking is significantly reduced, further studies on model fillings with different a_w would be interesting to see if such a threshold value could be found. It would also be interesting to do more studies on different praline geometries to further investigate its impact on crack formation.

In this work the pralines were produced by conventional moulding and traditional tempering. It would be interesting to try different moulding techniques to see if the processes have an impact of the final quality of the chocolate pralines. Cold stamp process would be interesting to use to have a more precise shell thickness in the pralines, where also the shell thickness could be varied in a controlled way to investigate its influence on cracking. Furthermore, it would be interesting to compare the quality in chocolate that have been tempered with conventional tempering towards seeding.

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Appendix 1 – Filling recipes

In Appendix 1, the different combinations of thickeners and humectants that were tested are presented (Table A1.1-A1.3).

Table A1.1: Different combinations that was tested with xanthan as thickener.

Thickener	w%	Substrate	w%
Xanthan	1	Sucrose	10
Xanthan	3	Sucrose	15
Xanthan	2,5	Sucrose	20
Xanthan	0,5	Sucrose	65
Xanthan	1	Sucrose	70
Xanthan	0,4	Sucrose + Citric acid	80 / 0.4
Xanthan	1	Calcium chloride	3
Xanthan	3	Glycerol (95%)	1
Xanthan	3	Glycerol (95%)	5
Xanthan	2	Glycerol (95%)	5
Xanthan	3	Glycerol (95%)	6
Xanthan	2,5	Glycerol (95%)	10
Xanthan	2	Glycerol (95%)	30
Xanthan	2	Glycerol (95%)	40
Xanthan	2	Glycerol (95%)	45
Xanthan	2,5	Glycerol (95%)	50
Xanthan	2,5	Glycerol (95%)	55
Xanthan	2	Glycerol (95%)	60
Xanthan	0,4	Glycerol (95%)	60
Xanthan	2,5	Glycerol (85%)	10
Xanthan	3.5	Glycerol (85%)	30
Xanthan	5	Glycerol (85%)	30
Xanthan	6	Glycerol (85%)	30
Xanthan	7	Glycerol (85%)	30
Xanthan	10	Glycerol (85%)	30

Table A1.2: Different combinations that was tested with carrageenan as thickener.

Thickener	w%	Substrate	w%
Carrageenan	3	Glycerol (85%)	30
Carrageenan	3,5	Glycerol (85%)	30
Carrageenan	4	Glycerol (85%)	30
Carrageenan	5	Glycerol (85%)	30
Carrageenan	3,5	Glycerol (85%)	10
Carrageenan	3,5	Glycerol (85%)	20
Carrageenan	3,5	Glycerol (85%)	30
Carrageenan	3,5	Glycerol (85%)	40
Carrageenan	3,5	Glycerol (85%)	50
Carrageenan	3,5	Glycerol (85%)	60

Table A1.3: Different combinations that was tested with gelatin as thickener.

Thickener	w%	Substrate	w%
Gelatin	3	Glycerol (85%)	10
Gelatin	3	Glycerol (85%)	10
Gelatin	3	Glycerol (85%)	45
Gelatin	3	Glycerol (85%)	60
Gelatin	3	Glycerol (85%)	65
Gelatin	3	Glycerol (85%)	70
Gelatin	3	Glycerol (85%)	75
Gelatin	3	Glycerol (85%)	80
Gelatin	3	Glycerol (99,3%)	10
Gelatin	3	Glycerol (99,3%)	40
Gelatin	3	Glycerol (99,3%)	50
Gelatin	3	Glycerol (99,3%)	60
Gelatin	3	Glycerol (99,3%)	62
Gelatin	3	Glycerol (99,3%)	64
Gelatin	3	Glycerol (99,3%)	65
Gelatin	3	Glycerol (99,3%)	70

Appendix 2 - Shell thickness

In Appendix 2, the shell thickness for square pralines with model filling a_w 0.78 and a_w 0.67, and round pralines with model filling a_w 0.99, a_w 0.86, a_w 0.78 and a_w 0.67 is presented Figure A2.1-A2.6).
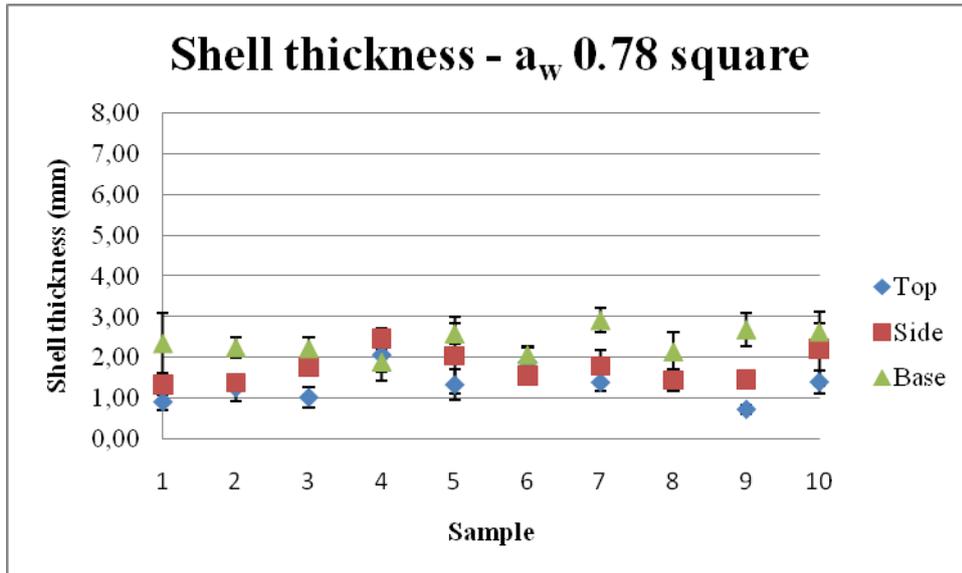
Figure A2.1: Shell thickness (mm) for square pralines with model filling a_w 0.78. Sample 2, 5, 6 and 7 had cracked after 28 days, while sample 1, 3, 4, 8, 9 and 10 had not.
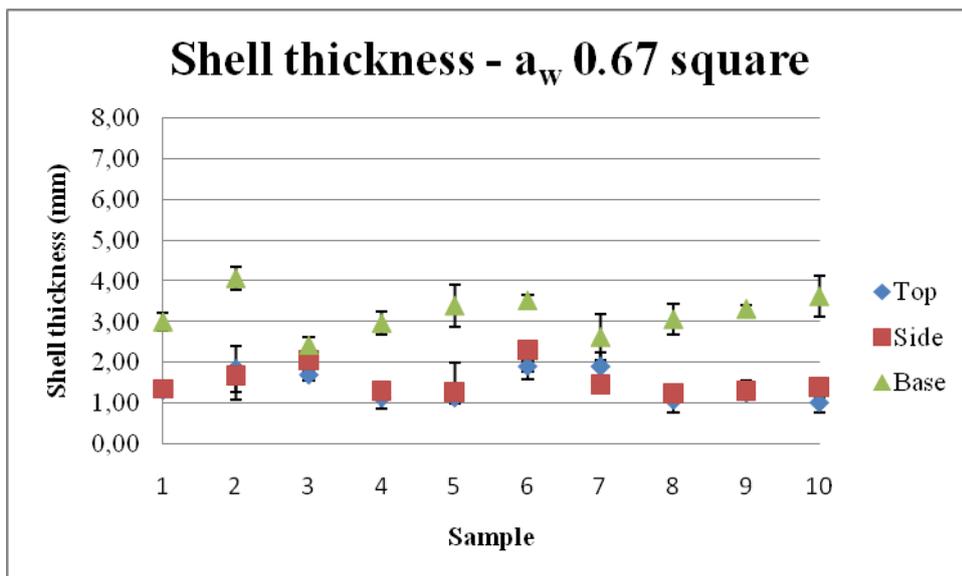
Figure A2.2: Shell thickness (mm) for square pralines with model filling a_w 0.67. No samples had cracked after 28 days.
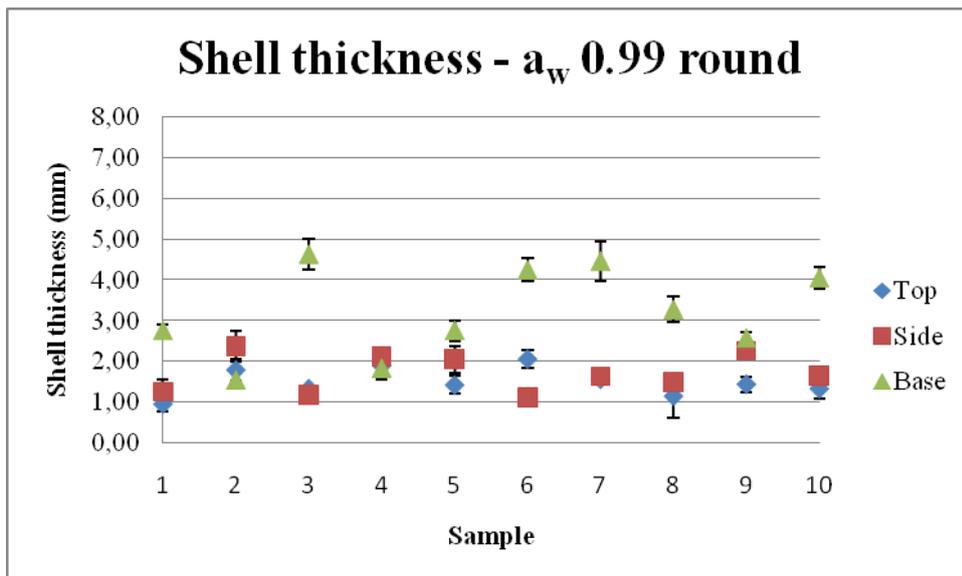
Figure A2.3: Shell thickness (mm) for round pralines with model filling a_w 0.99. All samples had cracked after 28 days. Sample 1, 3, and 8 cracked first.
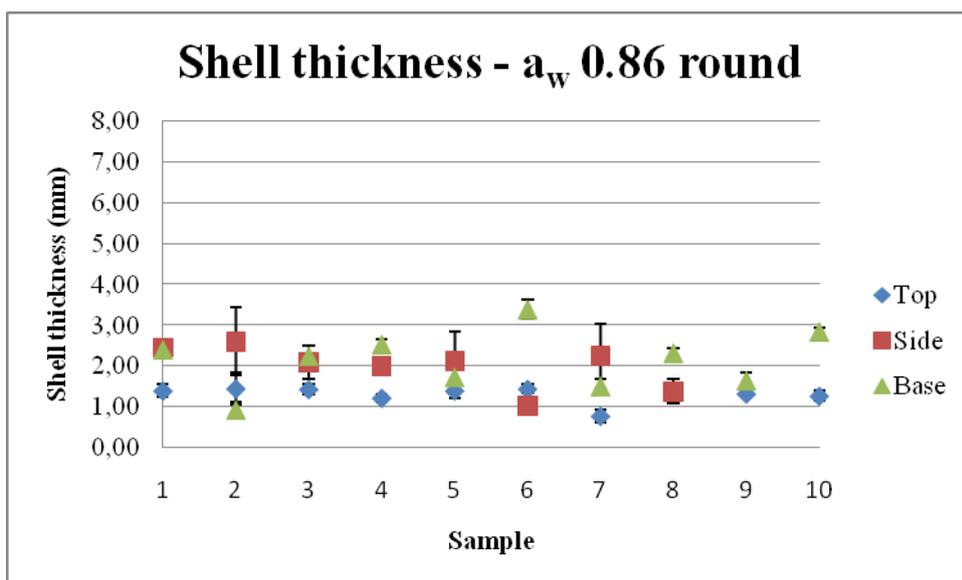
Figure A2.4: Shell thickness (mm) for round pralines with model filling a_w 0.86. Sample 3, 4, 6, 7, 8, 9 and 10 had cracked after 28 days, while sample1, 2 and 5 had not.
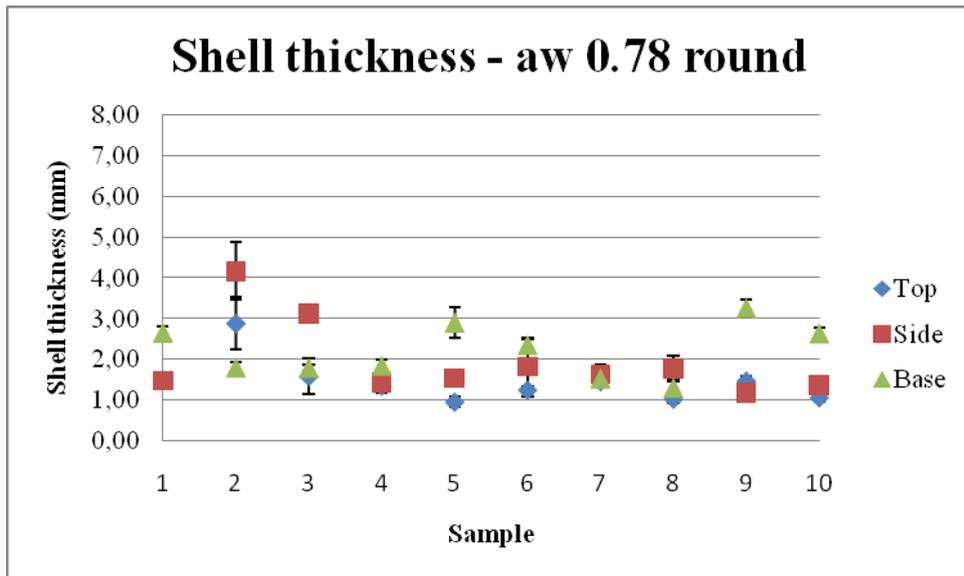
Figure A2.5: Shell thickness (mm) for round pralines with model filling a_w 0.78. Sample 2, 3, 5, 6, 7 and 9 had cracked after 28 days, while sample 1, 4, 8 and 10 had not.
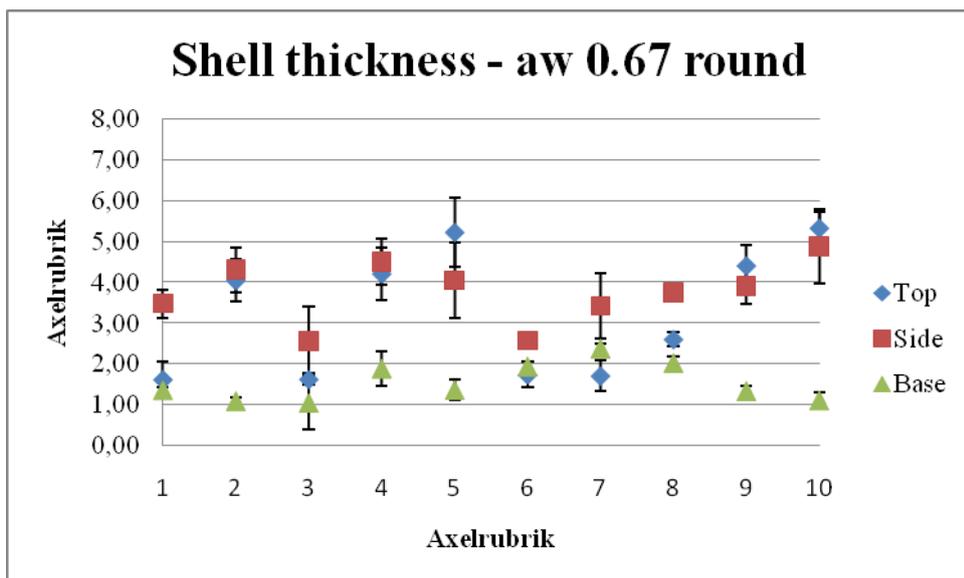
Figure A2.6: Shell thickness (mm) for round pralines with model filling a_w 0.67. Sample 6 and 7 had cracked after 28 days, while sample 1, 2, 3, 4, 5, 8, 9 and 10 had not.

Appendix 3 - Weight change

In Appendix 3, the weight change for pralines with model filling a_w 0.78 and 0.67 that had not cracked, and reference is presented (Figure A3.1-A3.3).
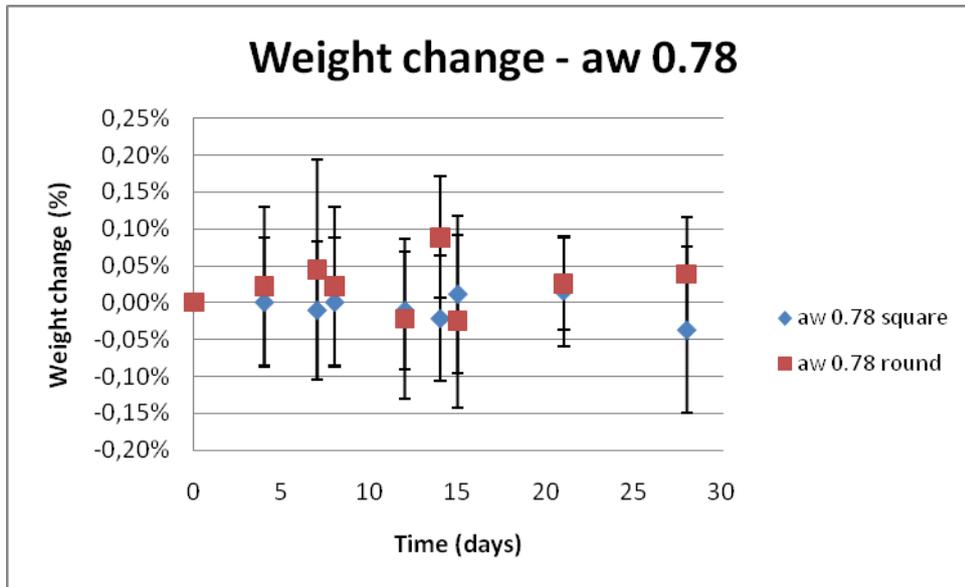
Figure A3.1: Weight change (%) for square and rounds pralines with model filling a_w 0.78 that did not crack.
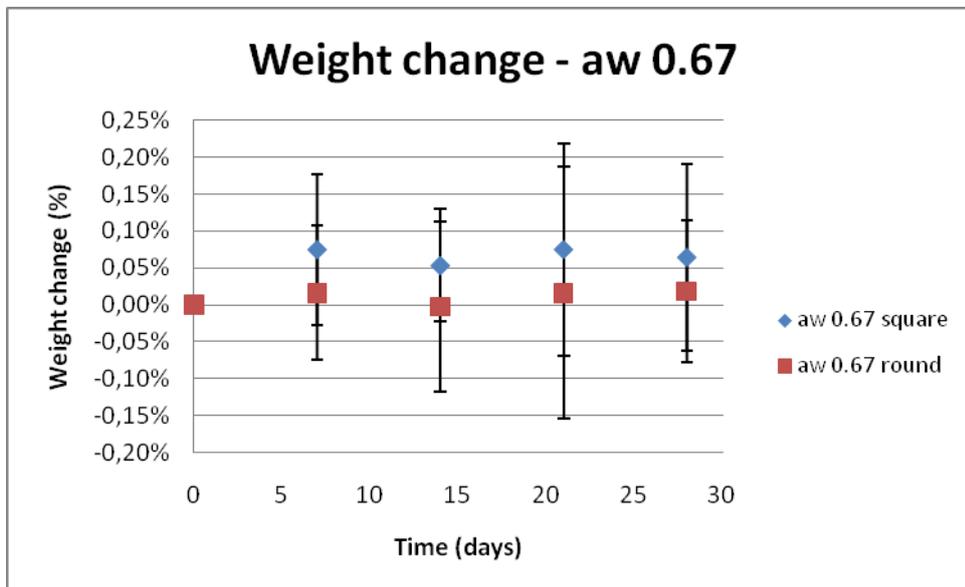
Figure A3.2: Weight change (%) for square and rounds pralines with model filling a_w 0.67 that did not crack.
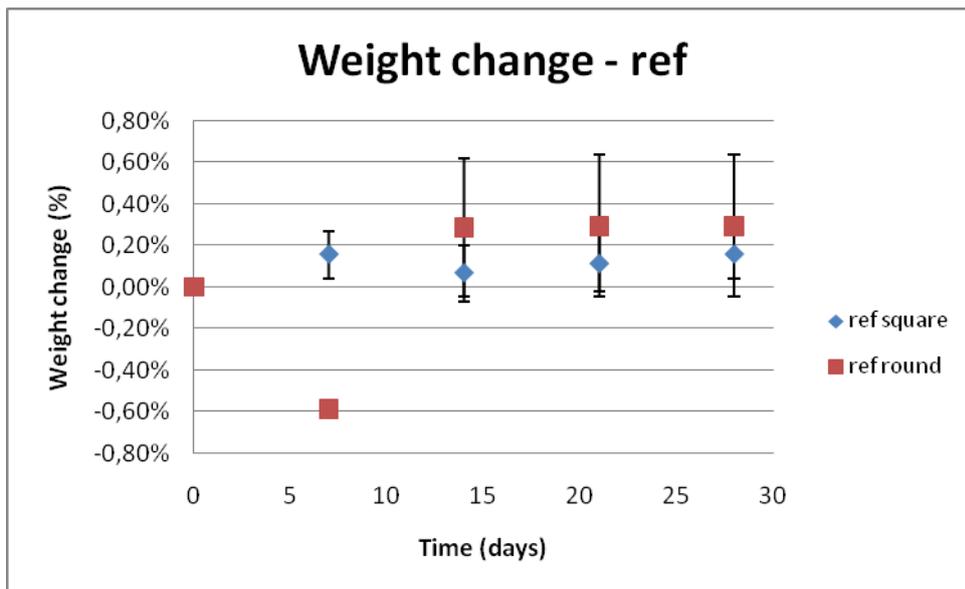
Figure A3.3: Weight change (%) for square and round reference pralines without model filling after different storage time.

Appendix 4 – Water activity

In Appendix 4, the water activity measurements for pralines with model filling a_w 0.99, 0.86, 0.67 and the reference of empty shells is presented (Figure A4.1-A4.4).
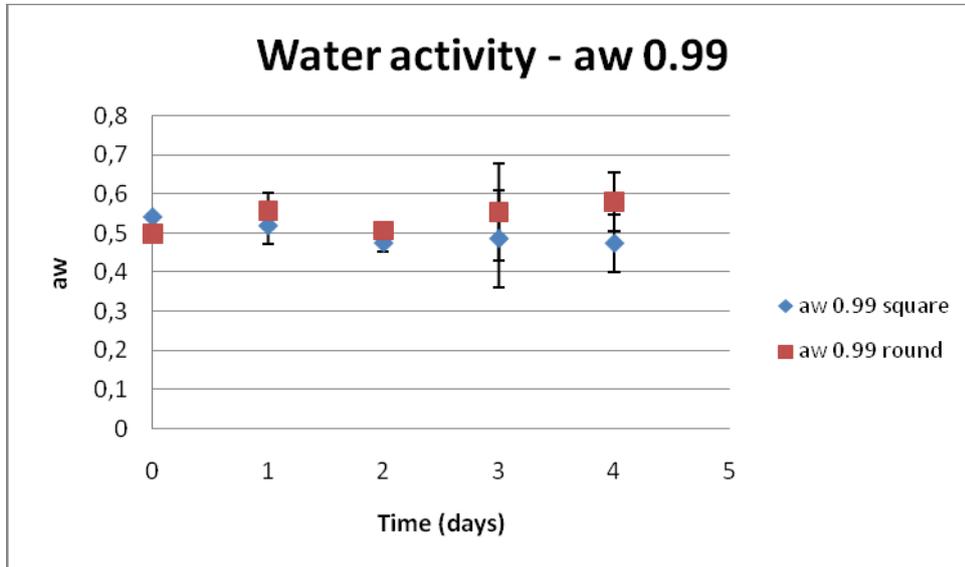
Figure A4.1: Mean water activity of the chocolate shell for pralines with model filling a_w 0.99 at various measuring occasions.
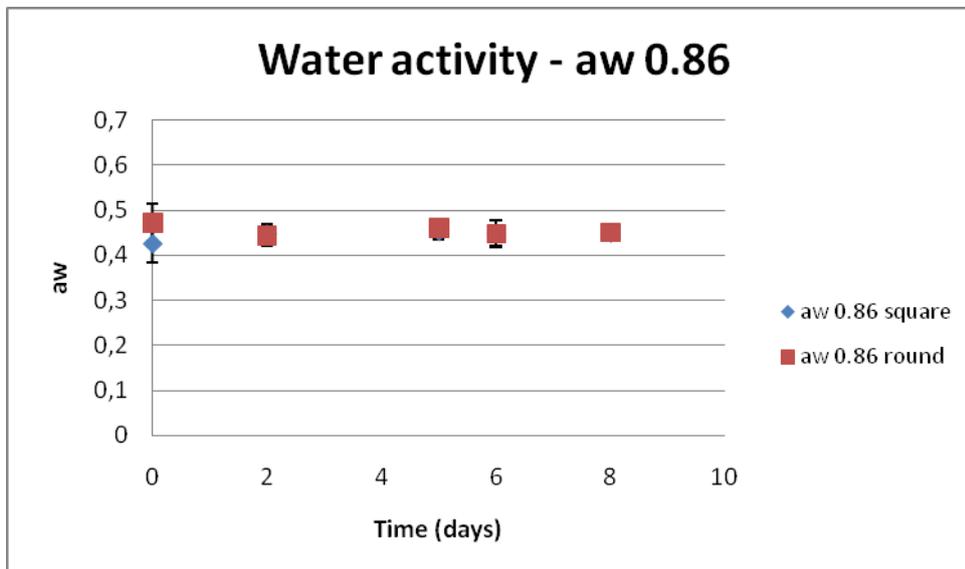
Figure A4.2: Mean water activity of the chocolate shell for pralines with model filling a_w 0.86 at various measuring occasions.
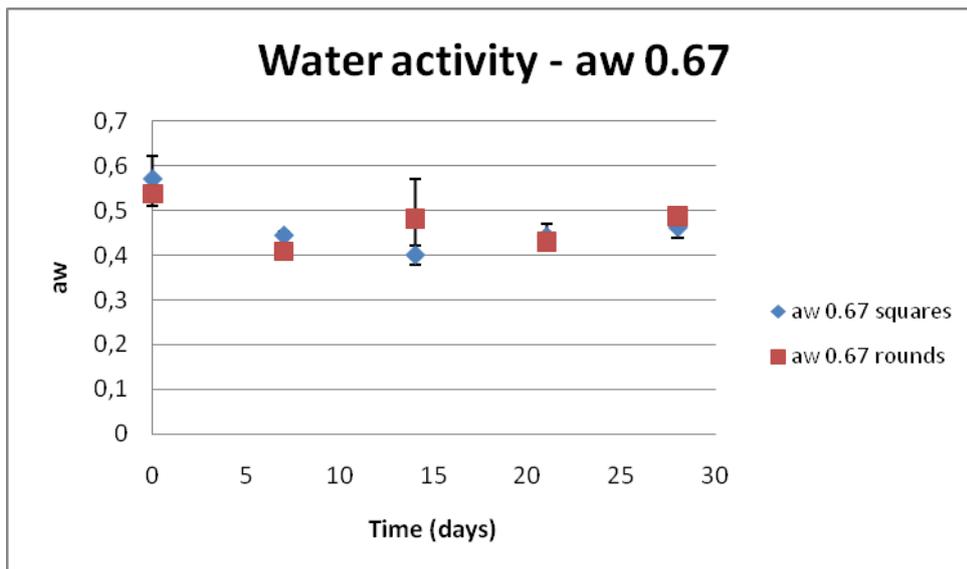
Figure A4.3: Mean water activity of the chocolate shell for pralines with model filling a_w 0.67 at various measuring occasions.
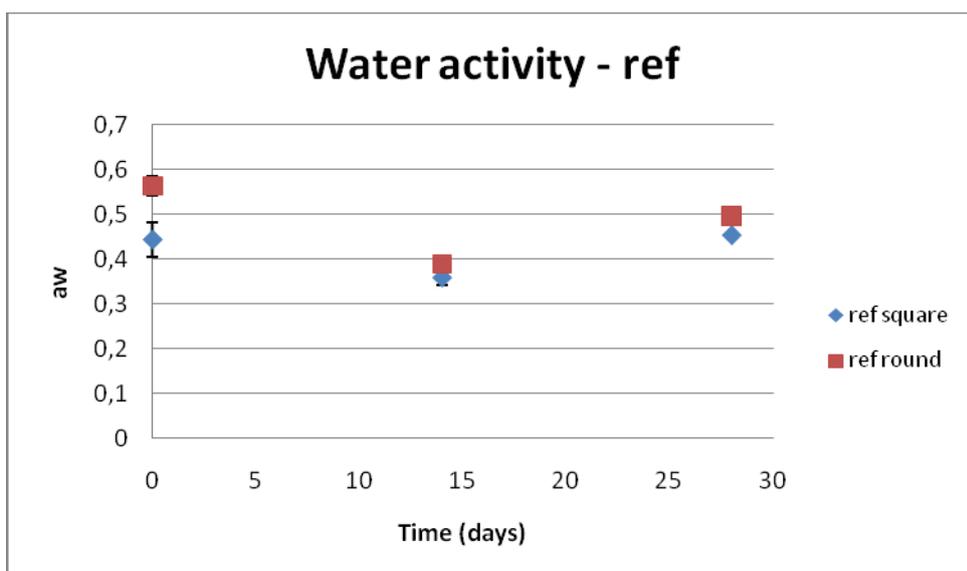
Figure A4.4: Mean water activity of the reference chocolate shells at various measuring occasions.