The Effects of Storage and Process Conditions on Fat Bloom Formation in Chocolate

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Assist. Prof. Dr. A. Coşkun DALGIÇ

by
Sami GÜLBAY
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T. C.
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NATURAL AND APPLIED SCIENCES
FOOD ENGINEERING DEPARTMENT

Name of the thesis: **The Effects of Storage and Process Conditions on Fat Bloom Formation in Chocolate**

Name of the student: **Sami GÜLBAY**
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Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Sadettin ÖZYAZICI
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science

Prof. Dr. Sami EREN
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science

Assist. Prof. Dr. A. Coşkun DALGIÇ
Supervisor

Examining Committee Members

Title and Name-surname	Signature
Prof. Dr. Ali Rıza TEKİN	_____
Prof. Dr. Ahmet KAYA	_____
Assist. Prof Dr. Bülent BELİBAĞLI	_____
Assist. Prof Dr. Metin BEDİR	_____
Assist. Prof Dr. A. Coşkun DALGIÇ	_____

ABSTRACT

THE EFFECTS OF STORAGE AND PROCESS CONDITIONS ON FAT BLOOM FORMATION IN CHOCOLATE

GÜLBAY, SAMİ
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Effects of processing conditions and storage temperature on fat bloom formation in chocolate were investigated in this study. Samples, chocolate coated cream filled with crispy rice, were produced due to different temper indexes, (TI 5, 6, 7), shell thickness' (1.5, 2.5, 3.5 mm), moulding rates (9, 12, 15, 18 mould/min) and storage temperatures (18 and 28 °C). Samples were analysed along for 40 weeks due to acidity % as oleic acid, peroxide value as meq O_2/kg and crystal structure peaks at differential scanning calorimetry (DSC) twice a month. Next; solid fat contents at nuclear magnetic resonance (NMR) and fatty acid compositions as % at gas chromatography/mass spectroscopy (GC/MS) in order to compare initial and final results to achieve verification with other periodic analysis. Finally; shelf life of samples was determined.

Storage conditions were effective for delaying bloom formation on chocolate surface. Storing chocolate samples at 28 °C instead of 18 °C caused a decrease in their shelf life from 8 months to 5 months due to bloom formation. *Slowly cooled chocolates* in chocolate production were more resistant to fat migration compared to fast cool-ones. The shelf life of products with a cooling rate of 9 mould/min was observed to be 4 months higher than the chocolates with 18 mould/min. *Shell thickness in chocolates* coated products was observed to be effective in delaying bloom formation. It was easier to migrate cream oil from inner to outer surface for thin shell (1.5 mm) products, whereas thicker one (3.5 mm) reached later to chocolate surface.

Key Words: Shelf life of chocolate, fat bloom, Cocoa Butter, Temper Index

ÖZET

DEPOLAMA VE PROSES ŞARTLARININ ÇİKOLATADA YAĞ KUSMASINA ETKİSİ

GÜLBAY, SAMİ
Yüksek Lisans. Gıda Mühendisliği
Danışman: Yrd. Doç. Dr. A. Coşkun DALGIÇ
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Bu tezde; proses şartlarının ve depolama sıcaklığının çikolatada yağ kusmasına etkisi araştırıldı. Krema dolgulu pirinç patlaklı çikolata numuneleri farklı temper indekslerinde, (TI 5, 6, 7), kabuk kalınlıklarında, (1.5, 2.5, 3.5 mm) ve kalıp hızlarında, (9,12,15,18 kalıp/dakika) üretilip farklı sıcaklıklarda (18 ve 28 °C) depolandı. İki haftada bir olmak üzere numunelerin asitliği % oleik asit olarak, peroksit değeri meq O_2/kg cinsinden ve kristallendiği sıcaklık DSC cihazında 40 hafta boyunca analiz edildi. Bu sure sonundaki ve yeni üretilen çikolatadaki % katı yağ miktarı NMR cihazında ve % yağ asidi kompozisyonları GC/MS cihazında analiz edilerek rutin yapılan diğer analizlerle kıyaslandı ve numunelerin raf ömürleri hesaplandı.

Depolama şartlarının çikolatanın yüzeyinde oluşan yağ kusmasını engellemede önemli bir parametre olduğu gözlendi. Numuneleri 18 °C yerine 28 °C'de saklamak, ürünün yağ kusmasına bağlı raf ömrünü 8 aydan 5 aya düşürdü. Çikolata üretim esnasında *yavaş soğutulan numunelerin* hızlı soğutulanlara oranla yağ migrasyonuna karşı daha dayanıklı olduğu gözlendi. 9 kalıp/dakika hızıyla üretilen numunenin yağ kusmasına bağlı raf ömrü 18 kalıp/dakika hızıyla üretilene göre 4 ay daha uzun oldu. Çikolatada *kabuk kalınlığının* yağ migrasyonuna geciktirmede önemli bir etkisi olduğu anlaşıldı. Dolgulu çikolatada krema yağının kabuk yüzeyine migrasyonuna ince kabuklu (1.5 mm) numunede daha kolay olduğu, kalın kabuklu (3.5 mm) numunede çikolata yüzeyine daha geç ulaştığı gözlendi.

Anahtar Kelimeler: Çikolatada raf ömrü, yağ kusması, kakao yağı, temper indeks.

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LIST OF ABREVIATIONS

A……	Arachidate
AMF……..	Anhydrous Milk Fat.
APCI……..	Atmospheric Pressure Chemical Ionization
CB……	Cocoa Butter
CBE…….....	Cocoa Butter Equivalent
CBR…….....	Cocoa Butter Replacer
CBS……...	Cocoa Butter Substitute
DSC……...	Differential Scanning Calorimetry
FFA……...	Free Fatty Acids
GC/MS……..	Gas Chromatography/Mass Spectroscopy
HPLC……	High Performance Liquid Chromatography
Li……...	Linoleate
LOO……..	1-Linolo diolein
LLO……...	1,2-Dilinolo olein
M……...	Myristate
MS…….	Mass Spectroscopy
NMR……..	Nuclear Magnetic Resonance
O……	Oleate
OOO……..	Triolein
OH…….	Hidroksil
P……	Palmitate
PC……..	Phosphatidylcholine
PE……..	Phosphatidylethanolamine
PI……...	Phosphatidylinositol
PV……..	Peroxide Value
PKO……..	Palm Kernel Oil
POS……...	1-Palmito–2-oleo–3-stearine
POP……...	1,3 di palmito olein
POO…….....	1-Palmito diolein
PGPR…….....	Poligliserol polirisineolat
PE…….....	Phosphatidylethanolamine
S……	Stearate
SFC……	Solid Fat Content
SOS……...	1,3-Distearo-olein
SOO……...	1-Stearo-diolein
TI…….....	Temper Index
TAG……..	Triacylglycerol
TUBITAK…….	Türkiye Bilim ve Teknik Araştırma Kurumu
USDA…….....	United States Department of Agriculture

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CHAPTER I

INTRODUCTION

Chocolate is a common confectionery material throughout the world that has seen generally increasing production trends over the last 10 years. Making chocolate requires an understanding of how the consumer perceives it. The preferred type of chocolate varies from country to country; for example, common U.S. and U.K. chocolate tastes are mutually incomprehensible, while the rest of Europe hates both of them! The different tastes and uses for chocolate reflect the histories of the industry in different places. The taste of chocolate is partially determined by the chemistry of the product; typical formulations of chocolate are shown in Table 1. Whatever type or taste of chocolate, however, the taste experienced by the consumer also depends critically on the micrometer-scale structure of the chocolate, which can consist of crystals and particles ranging from 10 μm to 120 μm in diameter, depending on the product. Taste depends on the release of flavor compounds to the mouth and nose, while perceived texture is a function of the way in which the material melts and breaks up in the mouth. This is a materials-science problem; making chocolate involves solving problems that are familiar in other areas of science (Freyer *et al.*, 2000).

Industrial chocolate processing is well developed and includes several complex operations for the development of flavor and texture. Chocolate is first mixed and ground to give a mixture of the correctly sized particles. The process of "conching" then involves the mixing and shear of the chocolate under controlled conditions and results in the removal of volatile components and adjustments in moisture content and viscosity. This process results in chocolate with the correct flavor profile. The production and structuring of the solid material prior to molding involve a further complex step, that of tempering, in which the chocolate is heated and sheared prior to its final solidification. The complexity of chocolate arises from the polymorphic nature of its constituent fats. Cocoa butter is chemically a multi-component mixture of triglycerides and trace compounds. Approximately 85% of the composition consists of just three triglycerides: 1,3 di palmito olein, POP (20%), 1-Palmito–2-oleo–3-stearine, POS (40%), and 1,3-Distearo-olein, SOS (25%), where palmitic (P), oleic (O), and stearic (S) acids are the fatty acids attached to the glycerol base. The exact composition depends on factors such as growing conditions and therefore can vary

between batches, especially from different geographic regions. Milk fats typically consist of one long chain and two short chains. Milk fat is one of the few fats that are compatible with cocoa butter, with which it builds a continuous phase. Addition of milk fats gives "milk chocolate," which is sweeter and cheaper than dark chocolate (Freyer *et al.*, 2000).

Table 1 Typical chocolate formulation (Jackson, 1999)

Component	Milk Chocolate %	Dark Chocolate %	Bitter-sweet chocolate %
Cocoa Mass (Cocoa solid & Cocoa Butter)	11.8	39.6	60.7
Added Cocoa Butter	20.0	11.8	2.6
Sugar	48.7	48.1	36.3
Lecithin	0.4	0.4	0.3
Flavoring Compounds (e.g. salt, vanilin)	0.1	0.1	0.2
Whole Milk Powders	19.1	-	-
TOTAL FAT	31.5	36.4	35.4

1.1 Chocolate Manufacturing

The main ingredients used in chocolate are cocoa mass, cocoa butter, sugar and milk. The major components of milk chocolate are sugar, cocoa mass, cocoa butter and dry matter from milk (whole milk powder, skim milk powder).Dark chocolate is made without matter from milk and white chocolate is made from sugar, cocoa butter and solid milks (Hodge *et al.*, 2002).

1.1.1 Fermentation of the Beans

Fermentation of the pulp surrounding the cocoa beans is carried out at the cocoa plantation and generally involves stacking the beans or placing them in boxes which allows air to penetrate. Apart from the simple products of fermentation, which include alcohol, acetic acid and finally carbon dioxide the fermentation produces a number of chemicals which are essential in producing the flavours and colours in chocolate. These chemicals diffuse from the fermenting pulp into the beans.

The process also modifies bitter polyphenols reducing the bitterness and astringency of the beans. Cocoa beans go through a number of different stages during fermentation (http://beerandwine.hobart.tased.edu.au).

Table 2 Fermentation of Beans (http://beerandwine.hobart.tased.edu.au)

Time after start	Main agent	Presence of air	Temp	Process	Other changes
24-36 hours	Yeasts	Anaerobic	~20°C	Sugar → alcohol	Proteins start to break down into peptides and amino acids. Proteins also react with bitter polyphenols.
48-96 hours	Lactic acid bacteria	Anaerobic	~45°C	Sugar → Lactic acid	Lactic acid is important in later reactions
4-7 days	Acetic acid bacteria	Aerobic	Much heat evolved ~50°C	Alcohol → Acetic acid → CO2	The protein-polyphenol compounds are oxidised, reducing the bitterness of the chocolate.

1.1.2 Drying

After fermentation the farmers will dry the beans at the plantation. The techniques used depend on the weather and on the circumstances at the plantation and can vary from simply spreading the beans out in the sun to using sophisticated commercial drying machinery. The beans are then packed, usually in hessian sacks, and sent to the cocoa processor.The chemical changes that take place during drying include:

- Removal of water (from about 65% to about 7%) helps prevent mould growth in the beans.
- Volatile (and unpleasantly flavoured) acids such as acetic acid are removed.
- Polyphenols become oxidised to produce brown compounds giving chocolate its colour (http://beerandwine.hobart.tased.edu.au).

1.1.3 Roasting

Roasting the beans develops the familiar chocolate colours and flavours through a variety of chemical reactions. The cocoa processor either roasts whole beans, followed by shell removes the shells and roasts the nibs. If the second option is chosen the

beans are usually dried at 70 – 90^{o}C for about 1 hour to facilitate the removal of the shells by "winnowing". During the actual roasting process the beans are heated to temperatures of 110-160°C over 15 minutes to 1 hour.

The main function of roasting is to convert the beans' flavor precursors into the compounds that give chocolate its distinctive flavour and aroma. More specifically, chemical changes that take place during roasting include:

*Maillard Reactions***:** These are very complex reactions between sugars and amino acids giving rise to compounds called mellanoidins which are responsible for much of the colour and flavour of the final chocolate. Maillard reactions are otherwise known as 'browning reactions' and are common in food processing.Astringent polyphenols are broken down, making the chocolate a lot more palatable.Many other flavouring compounds are produced including aldehydes, esters and other compounds.Many volatile compounds such as acetic acid and lower mass aldehydes, ketones, alcohols and esters have very unpleasant flavours and are removed during roasting (http://beerandwine.hobart.tased.edu.au).

1.1.4 Grinding (Milling)

The roasted nibs are ground between rollers to release the fat and produce a thick, creamy liquid. Cocoa mass is the first product produced by grinding the nib. It contains both solid materials and fats. When cocoa mass is heated (40°C) it liquefies to cocoa liquor (mass).Liquor is liquid when first produced as the heat generated in grinding the nibs causes the fat (cocoa butter) to liquefy. Cocoa liquor is an important ingredient in dairy milk and dark chocolates.If cocoa liquor is pressed in powerful hydraulic presses it is separated into cocoa butter (the fats) and press cake (the solids). When ground into a powder, the press cake is called cocoa powder. Cocoa butter is the main ingredient in high quality chocolate while cocoa powder is used in drinks and in compound chocolate (http://beerandwine.hobart.tased.edu.au).

1.1.5 Dutching the liquor

Adding alkali (potassium carbonate) to liquor in a process called 'Dutching' reduces the bitterness of the liquor and intensifies the dark colour that is due to the tannins in

chocolate.Phenols contain an OH group and undergo an equilibrium reaction with alkali:

<Rest of phenol>-OH + OH^- $\leftrightarrow$ <rest of phenol>-O^- + H_2O

Compounds with the $–O^-$ functional group are known as phenoxides which are the main colouring agent in solutions of polyphenols so that adding an alkali to a phenol and so driving the equilibrium to the right will enhance the brown colouring of the phenols in the chocolate. The harsh tannin polyphenols in the chocolate are also more soluble in alkaline solution and will dissolve away reducing any unpleasant bitterness in the chocolate (http://beerandwine.hobart.tased.edu.au).

1.1.6 Mixing and Refining

Milk chocolate results from the mixing cocoa mass, milk powder, sugar, cocoa butter and sometimes other products generally called *cocoa butter equivalent CBE* which may be used to improve flow characteristics and to reduce costs (cocoa butter is very expensive). If chocolate is made from crumb (milk solids, sugar and cocoa mass) then the crumb is mixed with cocoa butter. Milk powder is the main commercial alternative to crumb, but this does not have the same rich flavours as crumb (http://beerandwine.hobart.tased.edu.au).

1.1.7 Chocolate Crumb

Chocolate crumb is made from concentrated milk, sugar and cocoa liquor. Chocolate crumb is manufactured by first mixing sweetened condensed milk with sucrose and water and heating the mixture to 74 °C. Cocoa mass is added and mixed until completely blended. The mixture is continuously fed into an evaporator where is it held for 3 to 4 minutes at 125°C. The important Maillard reaction takes place at this stage. The crumb is then dried to a moisture content of about 1%. This can then be stored and used to minimise the impact of seasonal variation in milk supply.

Chemical reactions that take place during the crumbing process include:

- Milk protein and lactose undergo Maillard reactions that produce caramel flavours.This is an important consideration in the use of ‘crumb’ in chocolate production because the crumb flavours are richer than the flavours that are obtained with other starting ingredients.

- The breakdown of milk fats by enzyme action produces small amounts of free fatty acids that can impart a buttery and cheesy flavour (http://beerandwine.hobart.tased.edu.au).

1.1.8 Conching

Conching gives chocolate its 'velvety smooth' texture and also smoother, more mellow flavours. Conching is the mechanical working (stirring and shearing) of the refined chocolate flake at a temperature of about 45 – 70 °C, depending on the type of machine and the duration of conching.Depending on the process and desired product characteristics conching can last from several hours to 4 days and in general the longer the period of conching the smoother is the final chocolate.

Chemical reactions that take place during conching can be listed as;

1 *Reduction in moisture content*

  Water content is reduced from about 1.6% to about 0.6 – 0.8%

2 *Removal of unwanted flavour components.*

  Partial removal of low-boiling aldehydes and acetic acid, assisted by the removal of moisture

3 *Flavour development*

  - Removal of unwanted volatiles.
  - Additional Maillard reaction between free amino acids and reducing sugars Reaction is slow at conche temperatures but is assisted by the shearing force of the conche, which allows interaction particles are forced together.
  - Some of the astringent polyphenols in the chocolate may be removed by combining with proteins. This would give the chocolate a less astringent, more-mellow flavour.

4 *Homogenising*

  - Agglomerates of particles are broken down by shearing force
  - Particles of chocolate mass (which are astringent) and sugar (which on its own is unpleasantly sweet) are coated cocoa butter. The effect of this is to give softer and smoother flavours as well as a smoother texture.
  - The chocolate is worked until it is a uniformly liquid product that has the required flow characteristics.The chocolate may be made less viscous by addition of an emulsifier, lecithin (http://beerandwine.hobart.tased.edu.au).

1.1.9 Tempering

Before chocolate will change its state from liquid to solid, it has to be tempered i.e. cooled until the fat content in the chocolate starts to build crystals. This situation is called pre-crystallization (Jana *et al.*, 1993).

Tempering is the process of converting the liquid into solid chocolate by changing the crystal structure of the fats in the chocolate and is carried out by very carefully heating and cooling the chocolate.The time taken to temper chocolate varies considerably, depending on whether the chocolate is to be uses to make solid bars of chocolate or is used to make coated products (Kleiner, 1970).

Within the various tempering experiences, there are qualities differences. For good gloss, long shelf life and clean snap of the finished product, it is important that the tempering machine forms crystals in the high melting point crystal form, which these crystal agglomerates are present in small size and homogenously distributed throughout the chocolate (Sollich ,1996).

The temper or pre-crystallisation degree (i.e; quantity of fat which has been crystallised) should be correctly established before production begins. With too small a quantity (under-tempered) the result is too long a setting time during the cooling proses with the consequences of poor gloss and limited shelf life.Too high a proportion of crystallised fat (over-tempered) and you have an increased viscosity of chocolate in the enrober or the moulding plant and the consequences can be too little contraction during the final cooling and poor gloss (Sollich, 1996).

Using the tempermeter,you can establish what degree of temper you have through a simple measurement system within 10 minutes.To acvhieve this measurement,you need only a small sample of tempered chocolate in the sample beaker.The sample amount then is cooled under consistent cooling coditions resulting in a print-out of the cooling curve.The equipment automatically works out the deviation of the cooling curve at the point where the sample sets and the latent heat of crystallisation is given off which is the significant measurement for the degree of temper.The degree of temper is printed out with the term '*Temper Index'* as a numbered value.The

temperature ,at which the sample in the sample beaker sets (the temperature of the point of deviation)is printed out as '*Crystallisation °C*' This gives the indication of the type of crystals which have been formed(i.e. high or low melting point crystals) and thereby can give you a qualitative judgement of the temper characteristics (Sollich,1996).

If, during the measurement of degree of temper, there is a deviation from the ideal temper curve, it is easy thruogh a correction of the tempering or process machine,to re-establish the ideal temper degree.Thus it is possible during the whole the production time to operate with an almost constant degree of temper which is constant amount to say a constant viscosity (Sollich,1996).

Same viscosity means same enrobing thickness, same product weight, same cooling time, same shell thickness etc. By monitoring the degree of temper means, in addition to improving the concistency of optimum appearence of the product, you should be able to minimize give-away and thereby save chocolate by being able to achieve closer tolerances (Sollich, 1996).

Cocoa butter consists of a mixture of glycerides with different melting points,thus the melting curve of chocolate has no starting specific point,rather it has a melting range.During the cooling of chocolate,a further characteristics of cocoa butter becomes clear.Cocoa butter is very sluggish in its formation of initial crystal and in fact needs to be seriously over-cooled before solidification begins.Even though the melting range of Beta crystals form occurs around the 34 °C mark,those crystals will happily remain melted.i.e.not pre-crystallised when,without any agitation,the temperature is brought as low as 20°C. It is only at this temeperature that crystallisation begins.Crystallisation of this chocolate follows very slowly (Reade, 1980).

Pre-crystallised chocolate solidifies at a higher temperature and within a significantly shorter time.The total amount of latent heat is thus given off.Thus the cooling curve deviates remarkbly.During the solidification phase,it is possible that the chocolate will spontaneously re-heat.Following solidification the temperature starts to fall again (Reade,1980).

The chemistry of tempering: The triglyceride molecules in fats have three long 'arms' consisting of the fatty acid chains. In the liquid form, these three arms are free to move about at random. As the chocolate is cooled, the arms can pack together in a number of different ways to produce different types of solid crystals. Rapid cooling will produce 'untidy' structures in which the molecules are loosely packed. These crystalline forms tend to change over time, making the solid unstable. Carefully controlled cooling over a longer time allows the molecules to pack together in the most efficient way, so that the final crystalline solid is dense, stable and has a relatively high melting point. When liquids cool and crystallise, they tend to crystallise around 'seed' crystals so that an important part of tempering is to ensure that at some point in the process, the mixture contains only liquid chocolate and some solid 'seed' crystals of correct type (http://beerandwine.hobart.tased.edu.au).

The process of tempering: Tempering chocolate involves keeping the chocolate at a range of carefully controlled temperatures for the correct amount of time.

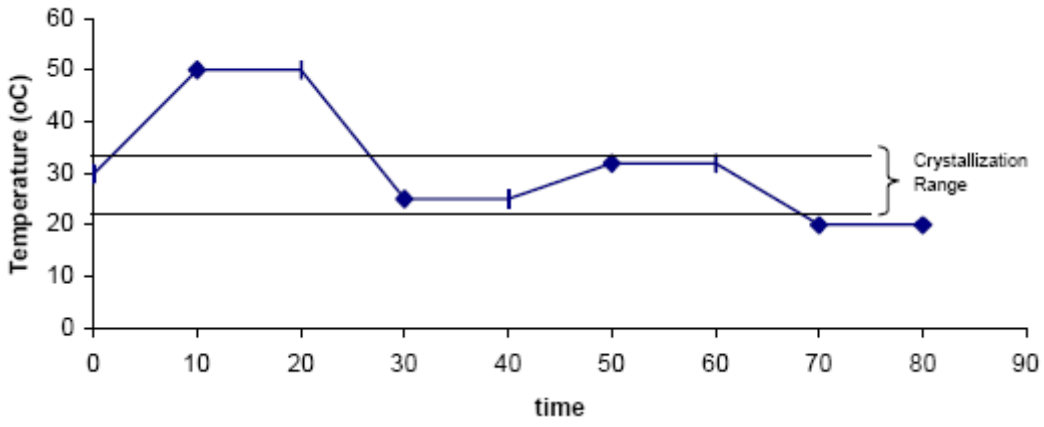

Figure 1 Tempering Process of chocolate (Parker, 2000)

The steps are:

- heating the chocolate to 50°C (dark chocolate) or 45°C (milk chocolate) to melt all fat crystals;
- cooling of the chocolate to point of crystallisation (about 30°C);
- allowing the temperature to fall to about 27°C so that the chocolate can begin to crystallise (solidify). A mixture of fat crystals will form, both stable and some unstable.

- The temperature is now carefully raised to about 30 - 32°C to melt out only the unstable crystal forms.
- At this stage, the only crystals left in the chocolate will be the 'good' crystals which give the chocolate its familiar texture. As the chocolate cools, these act as 'seeds' so that the remainder of the liquid chocolate will crystallise around these seeds into the correct form (http://beerandwine.hobart.tased.edu.au).

Interpretation of the Temper Curves: Temper curve of a well tempered chocolate mass always looks the same.During the first minute the curve describes a gentle fall.This changes to a steeper angle and 2-3 minutes thereafter returns again to the original slope.The reason for these changes in angle is the solidification process of the chocolate in the sample beaker, during which crystallisation heat is given off. According to the degree of pre-crystallisation, more or less crystallisation heat is given off whereby the sample, in spite of being subject to futher cooling for a specific period of time:

-stays at the same temperature (ideally tempered or pre-crystallised)

-heats up slighly (under-tempered or not sufficiently pre-crystallised)

-slowly dropping in temperature (well over-tempered or strongly pre-crystallised) (Sollich, 1996).

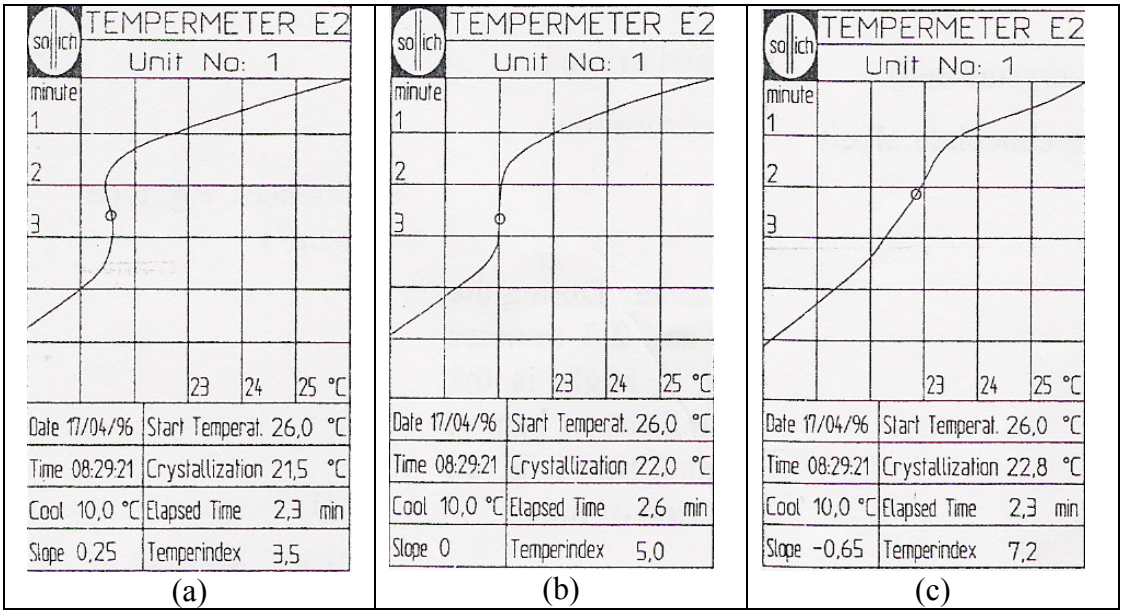

Figure 2 Same chocolate albeit with different degrees of temper (Sollich, 1996)

Under-tempered case: Figure 2.a represents the too little pre-crystallisation.If chocolate is too weakly pre-crystallised, i.e under-tempered.The storage of seed crystals means that the temperature of the chocolate falls further before crystallisation begins.Since with under-tempered chocolate, there is a relatively larger amount of fat in the liquid phase, at the point of solidification of the chocolate, relativeley larger amount of crystallisation heat will be given off which results in a spontaneous heating of chocolate (Sollich, 1996).

Well-tempered case: Figure 2.b represents ideally pre-crystallisation.An ideally pre-crystallised chocolate result in this typical temper curve with the vertical part of the curve of the curve being produced during the solidification phase.Thus the amount of solidification heat given off is equal to coolth being generated by the cooling unit (Sollich, 1996).

Over-tempered: Figure 2.c represents too strongly pre-crystallisation.Chocolate is heavily disributed with seed crystals.The result of this is that the solidification starts early, i.e. with a relative higher temperature.As a result of the larger proportion of fat crystals present, there is a relatively smaller amount of the fat content which is left to crystallise and, therefore, the amount of crystallisation heat given off with this chocolate is relatively small.Characteristic of this is the shallower slope of the cooling curve during the solidification range (Sollich,1996).
The degree of temper will be indicated numerically under the table 3.The numbers have the following meaning:

Table 3 Temper Index & Meaning (Sollich, 1996)

Temper type	Temper Index	Meaning
Under-tempered	1	very severely under-tempered
	2	severely under-tempered
	3	under-tempered
Well-tempered	4	slightly under-tempered
	5	ideally tempered
	6	slightly over-tempered
Over-tempered	7	over-tempered
	8	severely over-tempered
	9	very severely over-tempered

The deviation point of the temper curve is given a numerical value in °C with the description ‘Crystallisation’. This value will change even with the same chocolate sample according to the degree of temper.With different types of chocolate, however,this value would change even with same degree of temper.It will be lower with milk chocolates (dependent upon the content of milk fat and cocoa butter).In case of known choclate type and specific degrees of temper,this value,however,can act as an indication to the quality of tempering(the higher the value,the better the quality),and this is because high melting point crystals are present in the tempered chocolate (Sollich,1996).

A slightly over-tempered condition can be required if, for instance, There is a limited cooling tunnel lenght and It is needed to create quicker solidification of the chocolate in the cooling tunnel. A slightly under-tempered condition might be necessary if It is needed a thinner chocolate in an enrobing machine to achieve better coating result (Sollich, 1996).

1.2 Raw Materials and Properties

1.2.1 Sugars Used in Chocolate

Sugar is the sweetening agent in chocolate. Different types of sweeteners are used when making chocolate with special characteristics, e.g. chocolate for diabetics (Jackson, 1998).

Sucrose is commonly used in chocolate making. It is a disaccharide that can be obtained from sugar beet or sugar cane. To obtain the required purity (~99.8% sucrose) other mineral and organic material is removed by the addition of excess lime to precipitate them out of solution.The excess calcium hydroxide in solution is then removed by bubbling carbon dioxide through the solution, forming calcium carbonate.Filtration and then evaporation then give the crystalline sugar (Laustsen, 1991).

Lactose is also known as milk sugar as it is about 4.5% of dairy milk. Lactose has very little sweetening power compared to sucrose.Lactose is a disaccharide (Laustsen, 1991).

Glucose (also known as dextrose) and fructose are monosaccharides. They are found in many fruits and are often called fruit sugars. They can be obtained from the decomposition of sucrose by either addition of acids or by the action of enzymes. Produced in this way the mixture will contain equal parts of glucose and fructose and is known as *invert sugar*. Invert sugar is syrup which is usually used in things like cream centres rather than in chocolate itself (Laustsen, 1991).

1.2.2 Cocoa Solids

They correspond to the nonfat part of the cocoa beans. It can be used as powder (cocoa powder contains not less than 20% cocoa butter or it is label as fat reduced cocoa powder) or more often as chocolate liquor. Chocolate liquor corresponds to the roasted, hulled; ground substance obtained from fermented, dried cocoa beans.The difference between chocolate and compound coatings is based on the cocoa solids. Chocolate must contain not less than 32% total dry cocoa solids, including not less than 18% cocoa butter and not less than 14% of dry nonfat cocoa solids (Sato *et al.*, 2001).

Compound coating corresponds to product that doesn't match this definition. In most cases, the use of fats other than Cocoa Butter, CB, leads to the name compound coating on a product. Other vegetable fats can be used in order to obtain new flavors, to enhance the physico chemical properties of the product or to reduce production price (Sato *et al.*, 2001).

The fats in cocoa, like most fats, are triglycerides. These consist of a tri-ester of glycerol and three straight chain organic acids. Oleic acid, stearic acid, and palmitic acid account for more than 95% of the fatty acids in cocoa butter. The concentration of fat in the liquor is too high for making cocoa powder and too low for making eating chocolate. This is why eating chocolate is generally made from a mixture of the cocoa

liquor and some of the cocoa butter, while the presscake used to make cocoa powder has very little fat (Martin, 1987).

1.2.3 Cocoa butter

Cocoa butter is the main fat used for chocolate. It has a relatively simple triacylglycerol (TAG) composition that is responsible for a very specific yet complex polymorphism. The TAG composition of a fat is one of the most important parameters since it governs the physical properties as well as the polymorphic behavior of the fat (Chaiseri *et al.*, 1987).

Composition of Cocoa Butter

Chocolate is a mixture of fine particles of cocoa and sugar cemented together with cocoa butter. Cocoa butter is a fat which is extracted from the roasted bean from the cocoa plant (Parker, 2000).

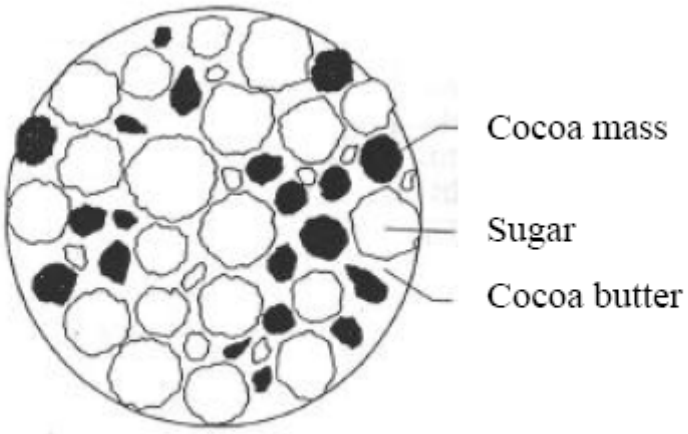

Figure 3 Composition of Dark Chocolate (Seguine, 1991)

The triacylglycerol (TAG) composition of a fat is one of the most important parameters since it governs the physical properties as well as the polymorphic behavior of the fat. Polymorphism is defined as the ability of a TAG molecule to crystallize in different molecular packing arrangements (polymorph or polymorphic form) corresponding to different unit cell structures, typically characterized by X-ray Diffraction Spectroscopy (Seguine, 1991).

Cocoa butter can vary greatly (depending on the type of bean used) in composition. It contains a variety of lipids including (usually more than 80%) triglycerides (also known as triacylglycerols, TAGs), diglycerides, monoglycerides, polar lipids, sterols and other volatile components. The TAGs are tri-esters of glycerol involving three long chain fatty acids such as arachidate (A), linoleate (Li), myristate (M), oleate (O), palmitate (P) and stearate (S).The three main TAGs present are POP, POS and SOS and much of the research done to date has investigated the properties of these pure components (Arishima et al., 1991).

Polymorphic Forms of Cocoa Butter

In addition to a range of different triglycerides, cocoa butter also exhibits polymorphism, which means that any species can solidify into many different crystalline forms, each having its own physical properties such as melting point and morphology. These polymorphs are not all stable and many have a tendency to transform into higher melting point forms. Only the highest form is stable (monotropic) but this form does not readily form from direct crystallisation methods. The second highest form is metastable at room temperature and can take months before it is fully transformed (Sato, 1999).

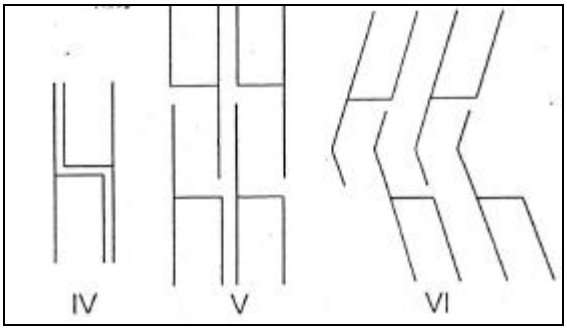

Figure 4 Polymorphic Crystal Structures Found in Cocoa Butter (Seguine, 1994)

The kinetics of these transformations has not yet been studied in any depth. However, many researchers have tried to identify the different polymorphs by Differential Scanning Calorimetry or by X-Ray Diffraction. The studies do not agree with one another and there has resulted much confusion about the number and identification of different crystal forms. The naming of these crystal types has also varied greatly with combinations of Greek letters and Roman numerals being used. However, the basis of

polymorph identification should be the melting temperature or crystal x-ray structure and in this there is general agreement. Table 4 shows researched results and melting temperatures and illustrates the confusion which has developed through inconsistent naming of the polymorphs (Parker, 2000).

Table 4 Nomenclature and Melting Temperatures (°C) of Cocoa Butter Polymorphs (Wille & Lutton, 1966)

Forms	Melting Points °C	Melting Points °F	Systematic Nomenclature
I	17,3	53,1	γ
II	23,3	73,9	α
III	25,5	77,9	β'2
IV	27,3	81,5	β'1
V	33,8	92,8	β2
VI	36,3	97,2	β1

Polymorph V is the form which is desired for final product chocolate because it is solid below room temperature and melts around 34- 36°C which is low enough to melt in the mouth (human body temperature, 37°C),whereas all other transitions occur in the liquid state except Form VI (Parker, 2000).

Polymorphism is defined as the ability of a TAG molecule to crystallize in different molecular packing arrangements (polymorph or polymorphic form) corresponding to different unit cell structures, typically characterized by X-ray diffraction spectroscopy. Fat polymorphs have been delineated in 3 main forms α, β, β', and variations within these main types (Chapman, 1971).Fats used in coatings can be classified according to their compatibility with CB, under three major family names (Wainwright, 1986).

– Fats that are totally compatible with CB are called, cocoa butter equivalent, CBE.

– Fats that are partially compatible with CB correspond to cocoa butter replacers, CBR.

– Fats that are incompatible with CB correspond to cocoa butter substitutes, CBS.

Cocoa butter equivalent (CBE) fats should be totally compatible with cocoa butter. Compatibility in this context corresponds to the ability of the TAG of two distinct fats to crystallize together without forming an eutectic, although some CBE do not show

total compatibility with Cocoa Butter. CBE are usually issued from some exotic fats (from the equatorial, tropical and sub-tropical countries) such as illipee, borneo allow, shea fraction or fractionated salfat. They can also correspond to synthesized oils, like coberine (Traitler *et al.*, 1985).

Cocoa butter replacers (CBR) fats may be called cocoa butter extenders, or hydrogenated domestic butter, because they do not replace the full amount of cocoa butter. Their compatibility with CB is lower than for CBE but higher than for CBS. Two main sources of CBR are available: either from hydrogenated or/and fractionated palm oil, or from hydrogenated domestic vegetable oil (soybean, cotton seed, etc.). CBR are usually issued from palm oil, so the main fatty acid is palmitic acid.

Cocoa butter substitutes (CBS), or lauric hard butter, contains trilaurin (C12) as the main TAG (Young, 1983).CBS fats come usually from coconut or palm kernel oils. Coconut and palm kernel oil (PKO) are usually hydrogenated or fractionated to increase their hardness and to improve their melting profile. The olein (or liquid) fraction can also be used directly for ice cream coatings, or after a partial hydrogenation. The stearin (or solid) fraction is used in its native form or after full hydrogenation (Wainwright, 2000). CBS replaces the totality of CB in a coating, except for the CB that is present in cocoa powder. Effectively, the compatibility of CBS with CB is very low (below 5%) due to the significant differences in TAG composition. The hydrogenated fractions of CBS do not need to be tempered, because of the direct crystallization in to the stable β' crystal.However, they need proper cooling. Rapid cooling to 10–12 °C initiate's crystallization, and removes the latent heat of fusion (Rossell, 1985).

1.2.4 Milk Fat

Milk fat is usually present in large amount in milk chocolate, but can also be used at lower extent in dark chocolate (usually under 5%)**.**The TAG composition of milk fat is very complex as it contains more than 100 different TAG with a very broad chain length (Kaylegian, 1998). It is also very variable and depends on the cow species, the feed and often on the season of production. Milk fat can be considered as an association of three largely independent melting fractions, corresponding to the high,

middle and low-melting point fractions (Timms, 1984). Milk fat can be used in different forms, either in its whole form or after fractionation but it may also be hydrogenated or interesterified (Campbell, 1984).

1.2.5 Emulsifiers

Emulsifiers are primarily used to improve the interactions between sugar and fat and thereby reduce the amount of fat needed for a given viscosity. Emulsifiers may also act as bloom inhibitors. They are authorized in chocolate at a level below 1.5% of the total mass; however, a maximal concentration exists for each individual emulsifier. Soybean lecithin is one of the most common emulsifiers used in chocolates and coatings. However, there are different kinds of emulsifier.Lecithin is a complex mixture of compounds, containing primarily phosphatidylcholine (PC), phosphatidylethanolamine (PE), and phosphatidylinositol (PI). Free fatty acids (FFA) also represent a major component (usually more than 30%) in lecithin. It is the most common emulsifier in chocolates and is used for its effects on rheology and fat bloom (Lonchampt et al., 2004). Poligliserol polirisineolat, PGPR**,** not only used as emulsifier but also used for adjusting viscosity of chocolate.

1.3 Chocolate Processing

Although chocolate composition varies slightly depending on the chocolate type, average levels of fat, cocoa solids and sugar are around 30, 20 and 50%, respectively. Flavor and emulsifiers are added at a level below 1 % (Beckett, 1994).

Processing Steps: It is better to divide raw materials into two categories as fatty and non-fatty group.Magnetic siever is used for non-fatty raw materials in order to control any metallic impurities coming from raw materials.There are mainly five major steps in chocolate processing:

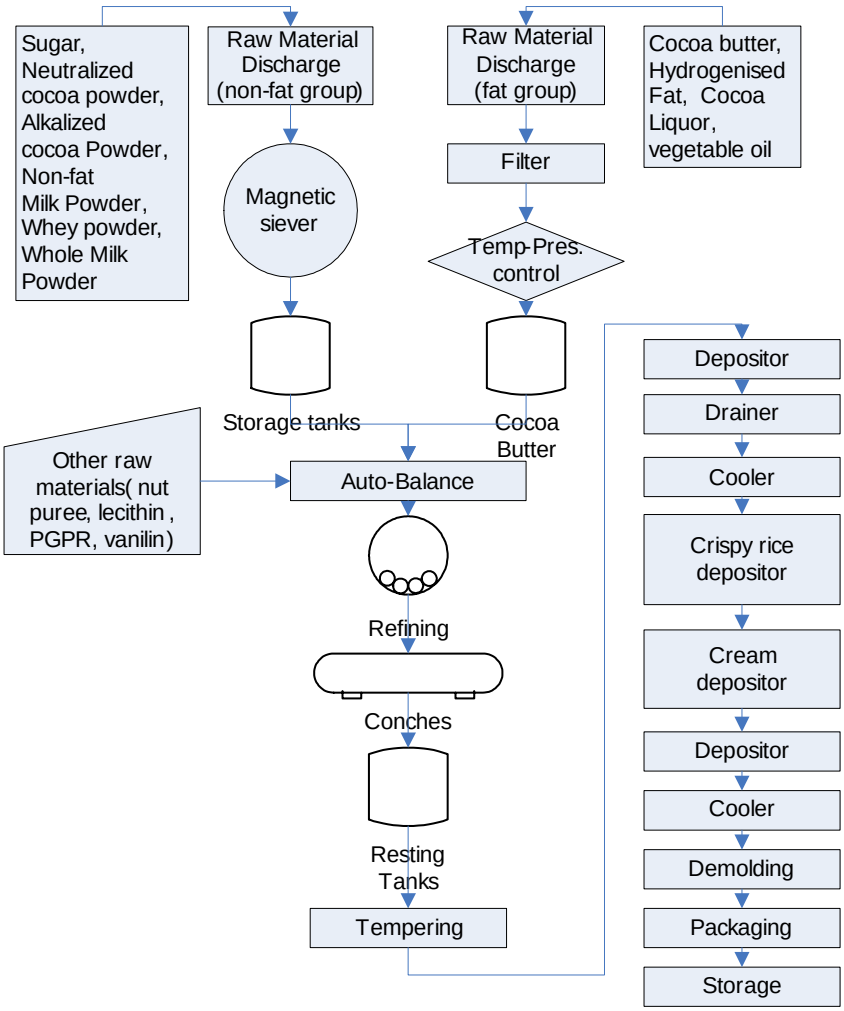

Figure 5 Processing flow chart for cream filled with crispy rice chocolate

a) Bulk ingredient mixing: Non-fatty groups containing sugar, skimmed and whole milk powders and cocoa powder are mixed with fatty-group raw materials after passing through magnetic siever.Vegatable oil in fatty-group used for cream filling recipes.Temperature control of oil is an important parameter in order to take a homogenous oil mixture.Finally small ingredients, lecithin and PGPR as emulsifiers and viscocity controllers, vanilin as flavouring compounds and nut puree are added into chocolate tank.

b) Refining: The size of sugar crystals and cocoa solid particles is reduced to obtain the smooth texture of the final product. The chocolate mass is passed through several rollers separated by gaps of decreasing size (Gerhard, 1979).

c) Conching: Flavor development, moisture decrease and release of volatiles occur during the conching. The paste is continuously agitated to coat the solid particles by the fat phase.Emulsifiers are added to improve the blend and extra fat is added towards the end of the conching step to obtain the desired viscosity (Johnson, 1987).

d) Tempering: Chocolate must be tempered to control the polymorphism of cocoa butter. The melted chocolate undergoes a temperature cycle to induce the formation of nuclei in β-V form (and also to destroy the other unstable forms). The addition of seed is also used to induce the crystallization step. New tempering method used β-VI cocoa butter seed. It facilitated greatly this step that is less sensitive to temperature fluctuation, quicker and gives even better final quality (Zeng et al., 2002). The seed crystals formed during tempering permit the surrounding liquid TAG to crystallize quickly in the right polymorphic form (Kleinert, 1970). Effectively, it is more favorable for TAG to attach to a growing crystal face than to find sufficient energy to create new nuclei. When the seed crystal concentration is sufficiently high (0.5 to 2% of total mass), the chocolate can be used for the production of molded or coated products (Seguine, 1991).

e) Cooling step: The product is cooled before storage to ensure complete solidification of cocoa butter. Proper temperature control during cooling is critical to growth of seed crystals in tempered chocolate (Lonchapt et al., 2004).

1.4 A Common Problem in Chocolate Industry: Fat Bloom

Fat bloom is a common problem in the confectionery industry. The problem can cause very significant product losses. This is not because there is a contamination or specific quality issue. It is mainly because the visual characteristics become unacceptable, due either to loss of gloss or to the appearance of a white "frosting" at the surface of the product. The white frosting (Figure 6) is sometimes mistaken for mould growth but quite definitely is not. It is a surface re-crystallization of fat caused generally by migration (Hammond et al., 2005).

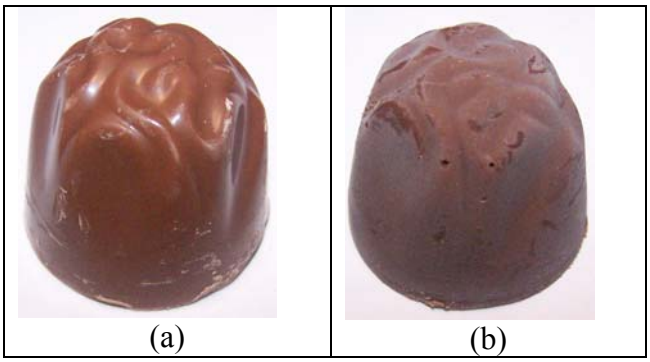

Figure 6 White "beta-form" bloom comparision on the chocolate:
(a) new processed product (b) After 10 months

Fat bloom is a situation that results when the chocolate has been stored at a high temperature for a period of time. During this time the temperature will cause the cocoa butter to separate from the rest of the crystallized chocolate mixture and rise to the surface. At the surface the cocoa butter re-crystallizes forming the white discoloration. Fat bloom can be distinguished as it will feel slightly oily and will melt upon contact with your hand. It also tends to be accompanied by small cracks that cause the chocolate to look relatively dull in appearance (Hammond et al., 2005).

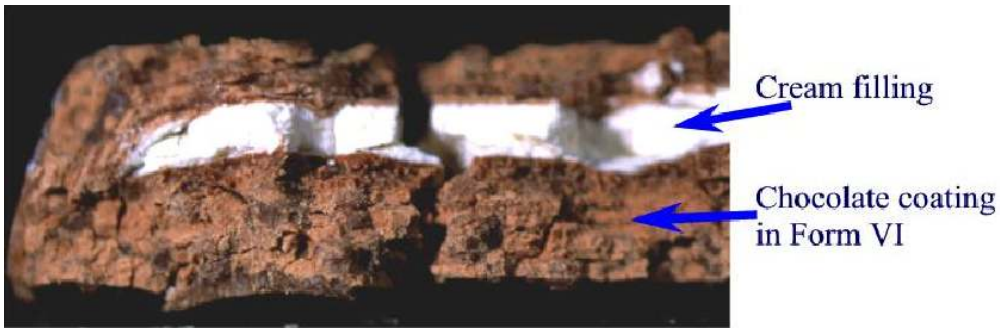

Figure 7 Form VI bloom in chocolate causes major structural change (Hammond et al., 2005)

The bloom that is a characteristic of chocolate (Figures 6 and 7) may be termed Form VI bloom. The bloom on the surface of chocolate can also appear on the surface of biscuits and even in semi-solid fats such as butter and fat spreads. This type is caused by a re-crystallization of fat and is often accompanied by a change in crystal morphology. This type may be loosely called "beta-form" bloom (Hammond et al., 2005).

Fat Crystallisation: All natural fats are mixtures of TAG. Each pure individual TAG will have a different crystallization temperature. However, when mixed this causes the fat to have a wide range of temperature over which crystallization occurs. Thus it is obtained the phenomenon of solid/liquid ratios in fat mixtures. These ratios can be determined using pulsed nuclear magnetic resonance (pNMR).If a product is made using one or more of the fat mixtures and then displayed for sale, the temperature of the display area will affect the state of the fat in the product. Thus as temperature cycles, so does the liquid/solid fat ratio. More importantly, the ratio will often be different in each fat phase at the given temperature, creating imbalances across the different food matrixes, e.g. biscuit dough, cream filling and chocolate coating in a biscuit snack (Ziegleder, 1997).

Crystallizing fat gives up heat energy (its heat of crystallization). As the process progresses to more stable forms a certain amount of heat energy might be required to begin the process. Thus if a fat has reached β' and is then stored at, say, less than 20 °C, it is unlikely to progress to β form, unless it is heated to above 25°C. This point brings us back to two issues mentioned above: cycled temperature storage and palletized storage (Ziegleder, 1997).

Cycled temperature storage applies significant energy stress to a product. This often results in a change of crystal form. In addition, during cycling temperatures, the crystalline fat can begin to separate from the liquid phase and undergo individual changes. For palletized storage of poorly cooled product, the crystallizing fat yields heat that cannot escape due to the insulating nature of palletized boxed products. This excess heat can raise the internal temperature by 2-3°C. This can be sufficient to cause fat/chocolate melting and re-crystallisation (Ziegleder, 1997).

Liquid Crystallisation: A pure chemical usually has a clearly defined melting temperature. Crystallisation occurs when the liquid is cooled below this melting temperature (sub-cooled). Crystallization will not occur, however, until crystal nuclei are present. Primary nucleation occurs in the absence of other particles at high concentration and the rate of production of crystals is dependent on the sub-cooled temperature. Seed crystals which experience shear and mixing can produce smaller crystal nuclei which then begin to grow. This is secondary nucleation and is more controllable than primary nucleation. Crystal growth occurs at the surface of the

crystal and increases the linear dimensions of the crystal at a constant rate when held at constant conditions. This rate is believed to increase with sub-cooling; the amount the temperature is below the melting temperature (Hewitt & Howlett, 1999).

1.4.1 Reasons of Fat Bloom

There are two main reasons those cause fat bloom in chocolate. First one is Re-crystallization of cocoa butter in chocolate, the other one is fat migration from cream filling to surface which cause breaking of cocoa butter crystals and so re-crystallization (Hartel, 1999).

1.4.1.1 Re-crystallization of Cocoa Butter

a) Polymorphism

Cocoa butter has an ability to crystallize at different forms. However; they always want to stay at form VI that is the most stable crystal form of cocoa butter during tempering and cooling. Beta V form is established that is the second fixed form of cocoa butter and so re-crystallization is limited. If Cocoa butter is used without tempering in chocolate; during the formation of Unstable α and β'crystals increase their ratio to ability re-crystallize. Hence; huge fat crystals perform which increase risk of fat bloom; because re-crystallization results from presence of liquid phase in chocolate (Hartel, 1999).

b) Post crystallization

Stable Beta V crystals formation should be provided during cooling. Chocolate is not completely crystallized if cooling tunnel is not so long because of presence of liquid phase of fat in chocolate during cooling. This liquid phase can re-crystallize in store period and cause fat bloom (Talbot, 1994).

c) Fractionation

Cocoa butter is composed of a mixture of triglycerides. This mixture has an unstable structure and can diverge to *solid phase* which contain more amount of high melted

triglycerides. This solid phase contain different symmetric triglyceride such as POP and SOS and has a tendency to crystallize (Talbot, 1994).

Palm oil contains; 2-oleoyl 1,3-dipalmitin (POP), 2-oleoyl 1,3-distearine (SOS), derived mainly from shea butter. These can be separated by solvent fractionation, which is used to make hard butters for chocolate production. The ratio of SOS to POP determines; the characteristics of the chocolate, such as *stability* against melting and organoleptic properties. Both SOS and POP are major component triglycerides of cocoa butter and have a tendency to polymorphism; As a result; they can be used in any ratio with cocoa butter (Talbot, 1994).

Triglyceride structure and composition of cocoa butter was determined by high performance liquid chromatography (HPLC) in tandem with atmospheric pressure chemical ionization (APCI) mass spectrometry (Talbot, 1994). The analytical results show that; coca butter in bloomed chocolate contains;

*POP, SOS and POS with high fractions,

*POO and SOO with low fractions

d) Size of crystal

In all crystal phases, coarse crystals are composed of accumulation of tiny particles. Accumulation of tiny particles is inhibited by tempering in chocolate production. High number-small sized crystals are desired to avoid fat bloom. Fat melts and liquid fat is drawn to the surface. This then cools quiescently and forms large crystal clumps that appear as bloom. This bloom is usually permanent. Such effects are caused, for example, by the hot plate, pack, end sealers overheating the packaging (Wennermark et al, 1999).

e) Composition effects

Two main composition problems tend to induce bloom. The first is when two "incompatible" fats are used in a chocolate or coating. The second composition problem occurs in filled chocolates, where the center is usually rich in oil content (Lonchampt *et al*., 2004).

Use of "incompatible" fats: It is important to differentiate incompatibility of fats due to dilution effects from problems due to eutectic mixing behavior. When two fats are compatible but have different melting points; a dilution effect is observed where the decrease in solid fat content is proportional to the amount of low-melting component added. In contrast, when truly incompatible fats are mixed together, they tend to separate from each other and the solid fat content decreases below that of either individual fat. The concentration at which the two fats separate determines the limits of solubility. Below this concentration, the fats are compatible, but above this concentration they are incompatible and tend to separate. To observe a true incompatibility, both fats must have a certain solid fat content (at the studied temperature). Two such blends can contribute to bloom formation in chocolates and coatings (Bigalli, 1988).

CB with CBS or CBR: Coatings made with hard lauric butter are very sensitive to the presence of cocoa butter (Noorden, 1982). A eutectic is formed at very low addition levels of CB to CBS. In addition to softening of the mixture, the blend of these two fats promotes bloom formation. A cocoa butter concentration above 4% can result in a bloomed product in a few months and that time drops to less than a week when the concentration is around 10% (Laustsen, 1991).If the proportion of CB in CBS is very high, bloom could appear in less than two days (Seguine, 2001).

Fractionated hydrogenated soy and fractionated hydrogenated soy/cotton oils are more tolerant to CB than the lauric hard butter. A eutectic is observed above 15–20% of CB. Moreover, the hydrogenated domestic hard butter was less bloom resistant in comparison to the fractionated hydrogenated domestic hard butter (Laustsen, 1991).

CBS and CBR with milk fat: Milk fat and its fractions enhanced the bloom formation when they were added with lauric hard butter products (Hartel, 1996). In this case, harder milk fat fractions led to quicker bloom appearance in coatings made with CBS.This behavior was opposite of that found in chocolate where harder milk fat fractions are known to prevent bloom. In a general sense, it appears that the shape of the isosolid phase diagram is not sufficient to predict bloom behavior of a fat mixture. The depression of isosolids lines of CB with addition of milk fat is not associated with

bloom, whereas a similar depression of isosolids lines when milk fat is added to CBR leads to bloom formation (Schmelzer et al., 2001).

f) Process effects

Two steps in processing, if done incorrectly, may lead to bloom formation, tempering and cooling.

Tempering

In the case of chocolate made with cocoa butter, tempering has long been recognized as one of the most crucial and essential steps in order to achieve a good and stable final product.Since compound coatings made with CBS crystallize directly in the most stable form (β'), they do not need to be tempered prior to cooling.

Under-tempering: Chocolate is considered to be under-tempered when the concentration of nuclei is not large enough to ensure a good crystallization of chocolate mass upon cooling. In this case, the crystallization time increases drastically since nucleation must occur rather than crystal growth. Furthermore, if new seeds are spontaneously generated during cooling, they form in an unstable polymorph, and re-crystallization problems can occur. In such cases, bloom occurs relatively quickly, often in less than two days, and causes a drastic modification of the surface, which appears as large white spots and/or white rings surrounding a black and glossy center (Hettich, 1966).

Over-tempering: The term over-tempered is used when the seed concentration in the melted chocolate mass is too high. The seed concentration may increase due to excessive tempering time. In this case, the extent of crystallization in the mold is not sufficient to produce the desired mass contraction. The molded surface is not bright and the unmolded surface turns a gray dull very quickly (Hettich, 1966).

Cooling rate

For chocolate, the cooling rate is also an important issue in preventing bloom formation.Cooling too fast may induce crystallization of unstable crystal polymorphs as well as formation of hair cracks and pores on the surface. Both effects could

promote further bloom. Homogenous heat release, which occurs through the inside as well from the outerlayer, is the best way to avoid any tension on the chocolate surface and consequently, reduce subsequent bloom (Kleinert, 1962).

For coatings, the cooling rate must be quick enough to insure complete crystallization (Seguine, 2001). Cooling requirements for the crystallization of coatings made (reviewed by Wennermark and Carlsson) with CBR (non-lauric) and CBS (lauric). Parameters like temperature profile, type of cooling tunnel and cooling time must be taken into account. The lower the temperature and the shorter the cooling time, the better the bloom resistance (Wennermark et al., 1994).

In filled chocolate, the temperature of the center is also very important. The center must be slightly warm before enrobing). Improper temperature during cooling, either too hot or too cold, may cause melting of the chocolate, enhance crack formation, or result in the deposition of moisture and so leading to sugar bloom (Kleinert, 1962).

g) Storage conditions

Even if all the conditions required during processing to avoid bloom are met, fat bloom can still appear at any time and any temperature. Both temperature and temperature fluctuations affect bloom during storage (Cebula et al., 1993).

Low temperature (<18 °C): Storage below 18 °C inhibited storage bloom in chocolate for over one year. The storage of chocolate at low temperature generally minimizes bloom formation; however, even if the storage temperature is low, bloom can occur after more than one year as the chocolate develops a gray dull appearance. In general, the lower the temperature, the lower the bloom risks (Cebula et al, 1993).

Medium temperature (18 < T > 30°C): In this range of temperature, which is below the melting point of βV crystals, bloom occurs more quickly with an increase in temperature (Cebula et al., 1993).

High temperature (>32 °C): When temperature goes sufficiently high, the cocoa butter is partially melted. Upon subsequent cooling, the cocoa butter crystallizes

uncontrolled, in unstable polymorphic forms. This is a similar cause for bloom as in under- or untempered chocolate: low seed concentration and unstable polymorph. Thus, bloom will occur very quickly after crystallization and the chocolate will exhibit large white spots (Cebula et al., 1993).

Temperature Fluctuations: Temperature fluctuations decrease the bloom induction time and increase bloom rate. In chocolate, even small temperature variations increase the rate of bloom formation. Hettich (1966) observed a difference in the bloom stability between chocolate stored at 24 °C and 24 ±1 °C. However, it is difficult to know which is the prevalent factor inducing bloom, the temperature or its fluctuation. Either way, the chocolate develops a more or less intense gray dull appearance. Researchers often use temperature cycling to accelerate the rate of bloom formation. The chocolate is submitted to high and low temperature plateaus over a variable time. The time-temperature parameters vary for different researchers. Low temperatures have varied from 15 to 21 °C and high temperatures from 25 to 32–38 °C. The residence times at these temperatures varied between 6 and 24 h. They can be equal for the high and low temperature, or they can differ (Tietz et al., 2000). The time-temperature parameters are generally determined empirically except for the highest temperature. In general, the high temperatures must be under 32 °C to avoid misinterpretation of results due to melting effects. No published research has attempted to define the effects of each parameter and thus, chocolate bloom tests are still not standardized.

h) Effect of Milk Fat

Milk fat has long been known to have anti-bloom effect when blended with CB in chocolates.

Hydrogenated milk fat: Bloom was inhibited by addition of milk fat and this effect was improved by using the high-melting point TAG of milk fat (Guice, 1959). The effects of hydrogenated milk fat were investigated (Campbell et al., 1969). Dark chocolate made with addition of 2.5% hydrogenated milk fat was four times more bloom resistant than chocolate made with non-hydrogenated milk fat. Furthermore, fully hydrogenated fat was more effective than partially-hydrogenated fat. However,

the amount of fully-hydrogenated fat was lower in order to avoid incompatible fat problems (Hendrickx et al., 1971).

Milk fat fractions: Jebson (1974) showed that incorporation of 3% hard milk fat fraction protected chocolate against bloom two times more than addition of unmodified milk fat. Lohman and Hartel (1994) compared 6 different milk fat fractions with whole milk fat. The higher the melting point, the longer the bloom delays. Furthermore, the two lowest melting milk fat fractions, obtained by solvent crystallization at 0 and 5°C, enhanced bloom in comparison to regular chocolate. Dimick et al. (1996) also reported the effect of different milk fat fractions on milk chocolate and confirmed previous results. The percentage of substitution, either 12.2 or 40% of total fat, was higher than with dark chocolate. Chocolate made with the hard milk fat fraction had the highest bloom stability and the higher the percentage of milk fat added, the more stable the chocolate.

Physical characteristics of chocolate: The effect of milk fat on the solid fat content (SFC) of chocolate may vary greatly with fraction type and added amount. When 6.4% (wt/wt) of milk fat fractions having melting points of 51.5, 50.4, and 45.4 °C were added to CB, the mixture had a higher SFC than CB alone. However, SFC of the mixture decreased when the melting point of the milk fat fraction was below 41.0 °C. The hardness of chocolate with 2% addition of the same milk fat fractions had similar variations as the SFC behavior. Chocolate was harder when made with the fractions having a melting point above 41.0 °C and was softer with milk fat fraction below 41.0 °C melting point (Lohmann, 1994). Timms and Parekh (1980) reviewed the different properties of chocolate, particularly SFC, after the addition of different amounts of milk fat products, including whole milk fat, hydrogenated, fractionated or interesterificated milk fat. The effect of milk fat fraction was dependent on temperature of the chocolate. Below 32 °C, SFC decreased when high-melting point milk fat fraction was added and the decrease of SFC was proportional to the amount added. However, the differences in SFC were quite small between the low-melting point milk fat fractions. Above 32 °C, the SFC of chocolate with added high-melting milk fat fraction increased as compared to pure chocolate.

In summary, the addition of a large amount (.10%) of milk fat decreased the hardness of chocolate, but even with a softened texture, this chocolate was more bloom resistant than “normal” chocolate (Dimick et al.,1996)

1.4.1.2 Fat Migration

In a crystallized fat, the liquid fat component is dispersed in and around the solid crystal clumps. The mobility of this liquid will to some extent depends upon the three-dimensional structure of the solid crystal network. At a given temperature, the liquid component will have a certain composition. As the temperature rises the amount of liquid fat will increase and its TAG composition will change (Bigalli, 1988).

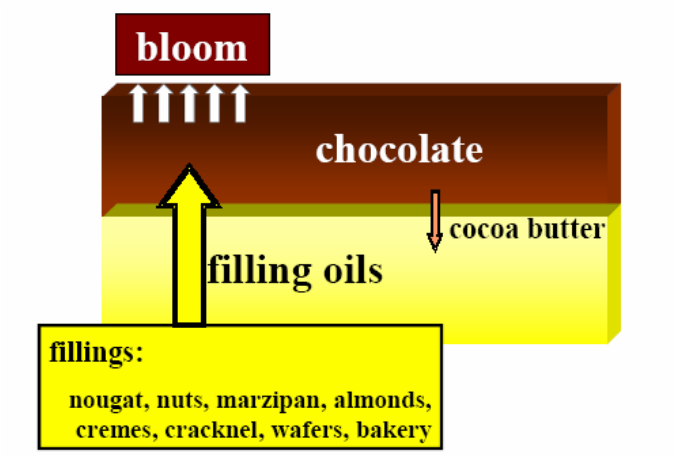

Figure 8 Fat migration in filled chocolate (Ziegleder, 1997)

In a single-matrix system, the consequence of this change may be nothing. Alternatively, it may trigger certain TAGs to separate or fractionate from the main bulk of the fat. This will lead to the growth of larger crystals over time that may be in the □ form (Bigalli, 1988).

In a system with more than one matrix, each containing a different fat, the picture becomes complex. There are different liquid/solid ratios, may be different total fat contents and different TAG compositions. All these points apply their own thermodynamic pressure for the liquid fat components to move or migrate between the matrixes (Bigalli, 1988).

As the liquid fats move between matrixes they mix with other liquid fat phases and thus change their composition. This may cause a change in the solid fat solution, i.e. more solid fat might dissolve at a given temperature, causing softening. In addition, the balance of the solution composition might change sufficiently to make other TAGs less soluble, causing them to crystallize out (Bigalli, 1988).

Mechanism of Fat Migration

In filled products two fat phases are in direct contact with each other. The triglycerides (TGs) in fillings, which often contain hazelnut or almond oils, are predominately liquid such as triolein (OOO) and other TGs from linoleic and oleic acids (LOO, LLO, POO, SOO). The fat phase in milk chocolate consists of cocoa butter and milk fat and contains high levels of the mostly crystalline triglycerides POS, POP and SOS (Ziegleder, 1997).

The migration rate of each triglyceride depends on its specific mobility and the concentration gradient. Liquid triglycerides are more mobile than crystalline triglycerides (Figure 9)

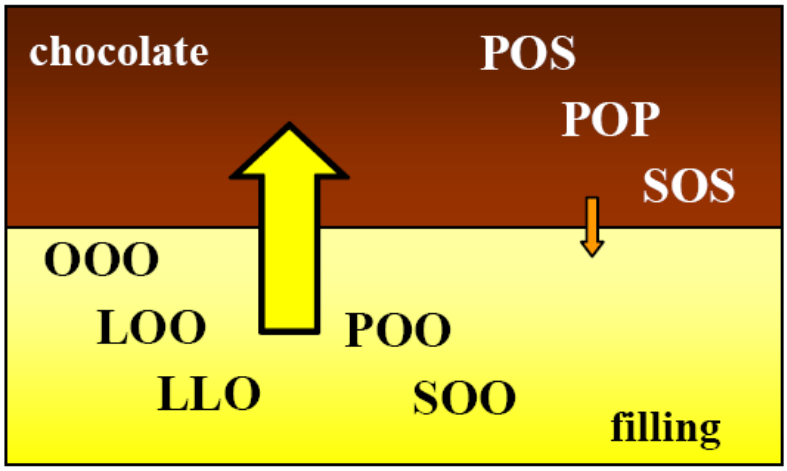

Figure 9 Diffusion of some triglycerides in chocolate and filling (Ziegleder,1997)

1.5 Aim of Study

The aim of this thesis was to estimate shelf life of chocolate coated product and to obtain definite data to create possible solutions for occurred problems along with expiration date. The effects of processing parameters on fat bloom formation were also objected.

In this investigation; a pilot product, cream filled with crispy rice and chocolate coated sample, was selected to study about a common problem such as fat blooming, in chocolate industry.

CHAPTER II

MATERIALS and METHODS

2.1 Materials and Used Chemicals

Chocolate coated cream filled with crispy rice sample was obtained from a chocolate factory, ŞÖLEN™, in Gaziantep, Turkey.

NMR Analyzer mq 20 (Bruker, Germany) to determine SFC values, GC/MS QP 2010 (Shimadzu, Japan) to evaluate fatty acid compositions of fat in chocolate, NF 800 R Centrifuge (Nüve, Germany) for extracting fat presence in chocolate, DSC (Mettler Toledo, Switzerland) to determine which type of crystals formed were used in this study.

Necessary chemicals were supplied from (Merck, Germany). These were; ethanol, petroleum ether, metilante solution (750 ml methyl alcohol, 250 ml benzene & 10 ml pure H_2SO_4 mixture), sodium sulphate, helium, sulphuric acid, potassium chromate, diethyl ether, phenolepytalyn, NaOH with 0.1 N, acetic acid-chloroform mixture (3+2 v/v), potassium iodide, starch solution (%1), sodium tio-suplhate (% 0.002).

2.2 Methods

2.2.1 Experimental Design

In this study; three types of tempered chocolate (Temper 5, 6 and 7) were selected and stored in two different storage temperatures (18°C and 28°C). In addition; there were also selected products up to different moulding velocities during cooling of chocolate coated product (9-12-15-18 mould/min respectively) with different shell thickness' (1.5-2.5-3.5 mm) to see the effects on fat bloom samples. Table 5 represents the operational parameters. Shell thickness of sample was adjusted by machines as minimum deviation, ±0.2 mm. Confirmation of this deviation was also controlled by measuring scale of thickness using calipers with 10 replications for each sample.

Table 5 Experimental Parameters for Shelf life study with processing conditions

Run No	Temper Index	Moulding Rate (mould/min)	Shell Thickness (mm)	Storage Temperature (^{o}C)
1	5	12	2.5±0.2	18
2	5	12	2.5±0.2	28
3	6	9	1.5±0.2	18
4	6	9	2.5±0.2	18
5	6	9	3.5±0.2	18
6	6	12	2.5±0.2	18
7	6	15	1.5±0.2	18
8	6	15	2.5±0.2	18
9	6	15	3.5±0.2	18
10	6	18	1.5±0.2	18
11	6	18	2.5±0.2	18
12	6	18	3.5±0.2	18
13	7	12	2.5±0.2	18
14	7	12	2.5±0.2	28

2.2.2 Production of Chocolate

Chocolate products were produced in a commercial chocolate line, (OPM, Italy). Firstly; shell of product (containing cocoa butter) was poured into moulds (T_{mould} 28 °C, L_{mould} 21 cm) from depositor at 38°C. After entrance of drainer with 35°C inside degree and 7 m long, de-moulding was followed to remove excess chocolate. Next step was cooling of shell of product in 7 m long cooling tunnel and 1°C inside temperature.

After cooling of shell; products moved along 18 m long conveyor gear system. Next; cream filling was poured at 32 °C onto moulds just after crispy rice had been added. The following step was vibration to supply homogenous dispersion of crispy in cream filling. After that; the bottom shell of product was made by pouring chocolate containing cocoa butter. Next; the surface of mould was brushed to remove excess chocolate and passed to cooling tunnel.

There were 4 steps in final cooling section of product. The cooling tunnel temperatures were 10 °C, 5°C, 8°C, and 13°C for Tunnel 1, 2, 3 and 4 respectively. The final process was de-moulding of product onto conveyor belts for the packaging machines.

Nutrition facts of sample were calculated theoretically by United States Department of Agriculture, USDA, data (www.usda.gov). Composition of every raw material for 100 g was listed as % protein, fat, carbohydrate, fiber etc. The total amount of nutritional facts was determined by multiplying percentage of raw material in the recipe with theoretical USDA data.

Table 6 Nutrition Facts of sample for 100 g chocolate

Energy (kcal)	536,7
Total fat (g)	34,8
Saturated fat (g)	26,2
Trans fat (g)	0,7
Cholesterol (mg)	9,7
Sodium (mg)	173,2
Total Carbohydrate (g)	56,2
Sugar (g)	47,8
Dietary fiber (g)	1,8
Protein (g)	5,6
Calories from fat (kcal)	313

2.2.3 Chemical Analysis

2.2.3.1 Fatty Acids Analysis

The main idea is to determine the qualitative and quantitative analysis of fatty acids generated from fats. Fatty acids are transformed into methyl esters and injected into GC/MS machines. Finally results are discussed.

Calibration of GC/MS was done twice a month. There were special calibration solutions containing pure stearic acid, oleic acid that was present in high amount in cocoa butter and special mixtures of cocoa butter fatty acids. These solutions were used to correlate GC/MS analysis results. Moreover; analyzed samples were also sent to other laboratories, like TUBITAK, for the verification of results to each other.

First of all; fat sample was homogenously melted in Oven at 105 °C. In order to prevent mistakes coming from impurities all necessary equipments used in experiment were washed with washing acid solution (containing sulfuric acid and potassium

chromate as 10 %), then, water, finally with acetone that dissolved water and oil. Approximately 50-100 mg of homogenized fat sample was boiled with 25 mL metilante solution (containing 750 mL methyl alcohol + 250 mL benzene and 10 mL pure Sulphuric Acid as catalyser) under back cooler (to increase reaction velocity and to supply continuity) and put in reaction for 30 minutes. In order to prevent explosion of balloon tubes a few boiling stones were added. By this way homogenous heating dispersion could be achieved. After reaction, 25 mL distilled water occupied to supply reaction becoming irreversible by increasing OH groups. Because during reaction; COOH groups were given up OH groups and instead of it, methyl groups bonded. This composed solution was extracted with petroleum ether twice and ester-ether solution was removed from mother liquid by separator funnel because of density and solubility differences and so completed in volumetric flask up to 50 mL. Small amount of Sodium Sulphate was put into solution to hold ambient water. Before injection of prepared solution; *tuning*, that supplied a stabilization of MS detector for impurities or gas particles coming from air, was applied. 1 μL was injected to GC/MS and results were recorded.

Identification fixing (Qualitative) was done by MS detector or standard injection. Quantity determination was calculated by correlation graphics that composed of standard injections with different concentrations (Hışıl, 1994).

$$\% K(x) = \frac{(a.A+C)}{50}$$

Where;

K (x): The amount of x fatty acid in sample (%)

a: The slope of correlation graphic line

C: The deviation line of correlation graph

A: The region of x fatty acid in sample

2.2.3.2 Acidity Determination

This determination indicates acidity value for sample in both semi-product and final-product. Mainly the principle is the neutralization of fat containing sample that dissolved with the presence of ethyl alcohol-diethyl ether with phenolphytalyn indicator.

Firstly shell of chocolate coated sample was separated and accumulated in centrifuge tubes. After measuring equal amount of shell of sample, equal amount of petroleum ether was put to dissolve oil in chocolate. More ether in tubes mean, faster dissolving but long time to removing. After that sample tubes were put in centrifuge machine, (Nüve NF 800 R). After 10 minutes with 9000 rpm, separated oil-ether solution was removed from tubes to Erlenmeyer and put in Oven at 105 °C. When all petroleum ether was completely vaporized, Erlenmeyer was put out. Next; it was weighted directly into Erlenmeyer flask about 10 g. Next; 15 mL ethyl alcohol and 15 mL di-ethyl ether was put into sample. It was heated slowly up to all oil disperses. Next, 1-2 drops of phenolphytalyn indicator was dropped. Finally; it was titrated with 0.1 M NaOH solutions and consumed NaOH solution was recorded (TSE; TS 1605 TS 3076, TS 894, TS 2383).

$$\% \text{ Acidity (as Oleic Acid)} = \frac{Vx2.82x100}{M}$$

Where;

V: Consumed NaOH (mL)

M: Amount of oil (g)

2.2.3.3 Peroxide Value Determination

This determination demonstrates formed peroxide amount for raw materials, semi-products and final products. Peroxide that can be present in sample is dissolved in acid-chloroform mixture. Free peroxides oxidize iodide anion molecules into iodine. This molecular iodine titrated with thio-sulphate and so determined.

Firstly shell of chocolate coated sample was separated and transferred to centrifuge tubes. After measuring equal amount of shell of sample, equal amount of petroleum ether was put to dissolve oil in chocolate. More ether in tubes mean, faster dissolving but long time to removing. After that sample tubes were put in centrifuge machine, (Nüve NF 800 R). After 10 minutes with 9000 rpm, separated oil-ether solution was removed from tubes to Erlenmeyer and put in Oven at 105 °C. When all petroleum ether was completely vaporized, Erlenmeyer was put out. Next; 25 g of sample weighted directly into Erlenmeyer flask. Next; 25 mL Acetic Acid-Chloroform mixture and 0.5 mL Potassium Iodide (KI) were put into sample. Mixture was stirred

for 1 min. its mount was covered with aluminum foil and kept in dark room for 10 minutes. After that, 30 mL distilled water was added and 1-2 mL starch was added. Finally; it was titrated with 0.002 N $Na_2S_2O_3.5H_2O$ solutions up to blue colour off. Consumed solution was recorded (Turkish Standards Institutes, TS 4964 TS 342).

$$\text{Peroxide (mg/kg)} = \frac{Vx2xF}{M}$$

Where;

V: Consumed Sodium Tio-sulphate (mL)

M: Amount of sample (oil in gram)

F: 0.002 N $Na_2S_2O_3.5H_2O$ factor

2.2.4 Physical Analysis

2.2.4.1 Solid Fat Content Analysis

The basic idea is the determination of solid fat content (SFC) of sample at a definite temperature. Every fat has a different crystalline temperature because of different oil compounds. For the quality of product, it is absolutely necessary to know the solid and liquid ratio of fat at a certain temperature. Oils or fats absorb radio frequencies in magnetic region. It takes time to give up this absorbed energy for fats. This necessary time called as *stagnation time* that is very different from each other for oils and fats. By this time difference SFC content can be determined.

Calibration of NMR Analyzer mq 20 was done twice a month with special calibration solutions containing 0 %, 31%, 71.7% SFC values with a definite temperature.

Fat sample was completely melted at 50-60 °C homogenously. Next; samples were put in NMR tubes up to a certain level. After that tubes were conditioned with different temperatures to respond in a certain way: 60 °C for 1 hour, 0 °C for 1.5 hours, then, 26 °C for 40 hours and finally 0 °C for 1.5 hours.

Next; tubes containing samples were kept at certain temperatures (at temperatures those were calculated SFC ratio) for one hour and measured very quickly. The result was directly read from NMR machine and recorded.

2.2.4.2 Crystal Structure Analysis (DSC)

This analysis is done for the determination of melting and freezing points of fats and oils, crystal structure of cocoa butter in which it gives peaks to have an idea about the crystal form of cocoa butter (β forms).

Calibration of DSC Mettler Toledo was done twice a month by zinc sample that melts at 157 °C actually.

First of all; nitrogen gases valve was allowed to move in cooling section of machine that supplied to cool sample. By this way pressure in the system was also adjusted. 'Actual Form Method' was used, which had a principle to cool sample up to 4 °C and reheat sample up to 46 °C by 2.00 °C/min heating rate and 0,71 mW heat flow with nitrogen gases (20.0 mL/min). 10-50 mg of sample was taken from product where it contained cocoa butter and put in an aluminum capsule. Next; it was put in the sample holder of the machine where an empty aluminum capsule was also put near to sample as reference. After starting measurement, graph was pictured by machine automatically by min-°C versus heat flow rate.

Peaks were interpreted due to originated temperature, size, and sharpness. The data also compared with the Cocoa butter forms reference Table (Wille & Lutton, 1966).

CHAPTER III

RESULTS AND DISCUSSION

3.1 The Effects of Storage Condition on Fat Bloom Formation

During storage of samples, the changes in appearance, acidity, PV and DSC results were observed. There is no standard maximum limit of acidity, peroxide values for chocolate samples to determine shelf life of product. However, in literature there is a limit for cocoa butter which is main fat used in chocolate manufacturing (acidity: 1.75 %, PV: 3.0 meq O_2/kg from TSE; TS 1605, TS 342). For DSC results due to Wille & Lutton (1966) gives optimum β-V and β-VI values, 33.8 °C and 36.3 °C respectively. These values give an idea about product to decide how far the sample from optimum value (β-V) and how near to bloomed form (β-VI). Hence; in this study, above values were used as an upper limit to end the shelf life of chocolate.

3.1.1 Effects of Temper Index (TI)

In order to compare TI values versus bloom time of chocolate, there were 3 different TI values; 5, 6, 7. Below values than TI 5 also tried but couldn't be de-moulding in large-scale production because of large amount of fat in the liquid phase.

There was a distance clearly from reference sample as appearance (present in Figure 5). Appearance of TI 7 was slightly different than TI 5 and TI 6. It was whiter than the other, i.e. more bloomed.

DSC results did not give a linear graph on Figure 10. There was a fluctuation. There were no sharp differences among samples with different temper index. Due to results; TI 6 was slightly more resistant to fat bloom than TI 5 and TI 7. After 32^{nd} weeks a sharp increase was seen in DSC values for TI 6.Similar increase also was seen for TI 5 and TI 7 after 31 and 29^{th} weeks respectively.

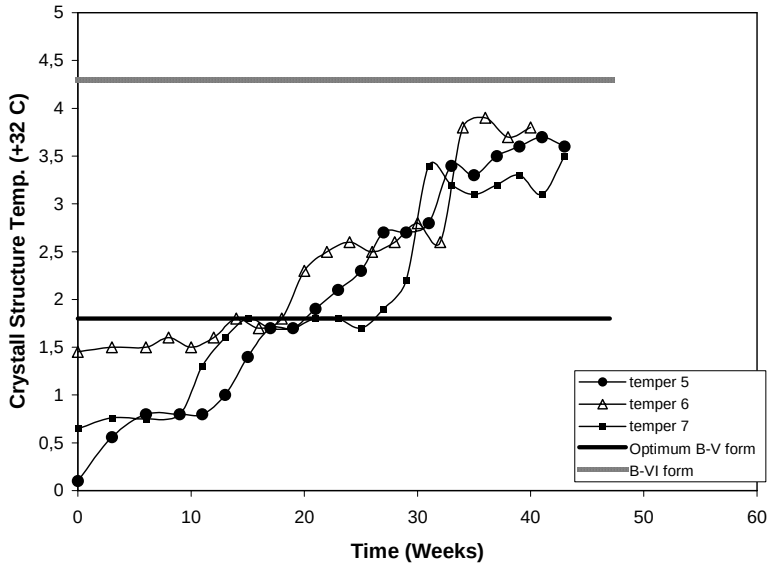

Figure 10 Crystal Structure of Samples of Temper Index 5, 6 and 7 stored at 18 °C

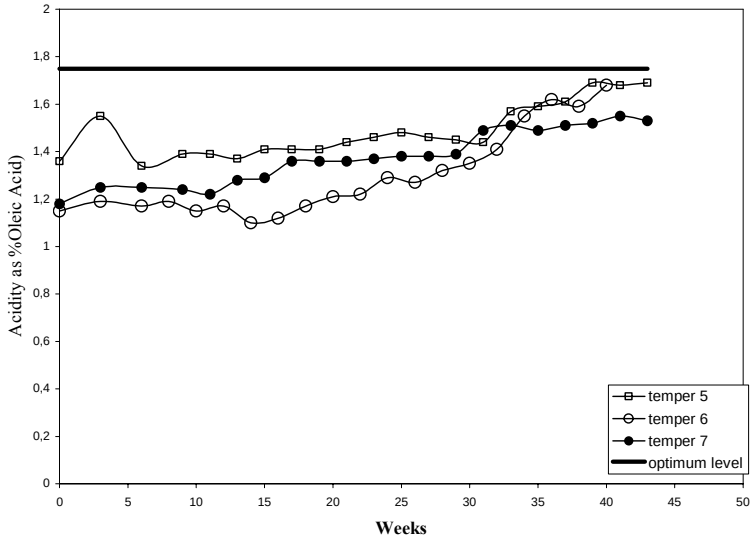

Figure 11 Acidity of Samples of Temper Index: 5, 6 and 7 stored at 18 °C

Acidity values (Figure 11) didn't reach the limit value (1.75) for all sample TI index 5, 6 and 7. There may have been an inhibiting factor coming from other ingredients such as crispy rice or cream filling.

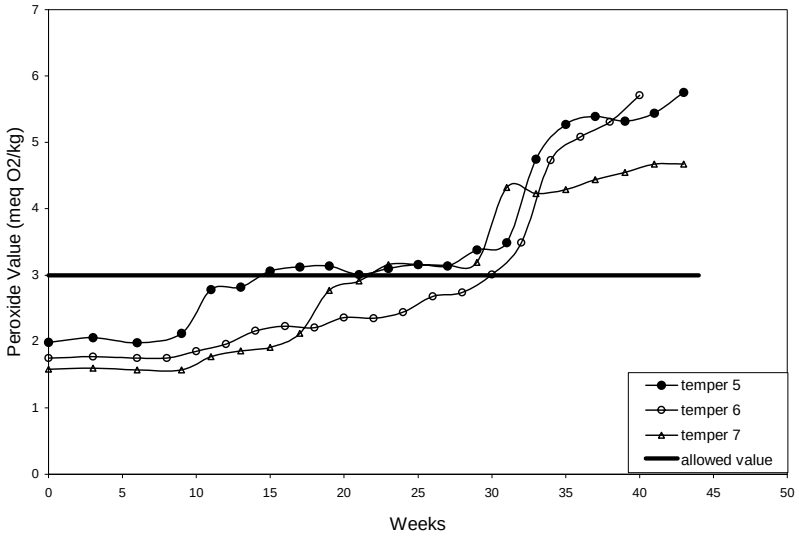

Figure 12 PV of Samples of Temper Index: 5, 6 and 7 stored at 18 °C

Difference in PV on Figure 12 gave an idea about the resistivity of product on fat bloom. Slight difference in endurance of bloom for TI 6 was recovered similar to DSC results.

3.1.2 Effects of Storage Temperature

Two different storage temperatures, 18 °C and 28 °C were accomplished. In order to test correspondence of results of analysis, two different TI values were selected, TI: 5 and TI 7.The photo of samples (Figure 13); PV, acidity and DSC results are shown in Figures 14-16.

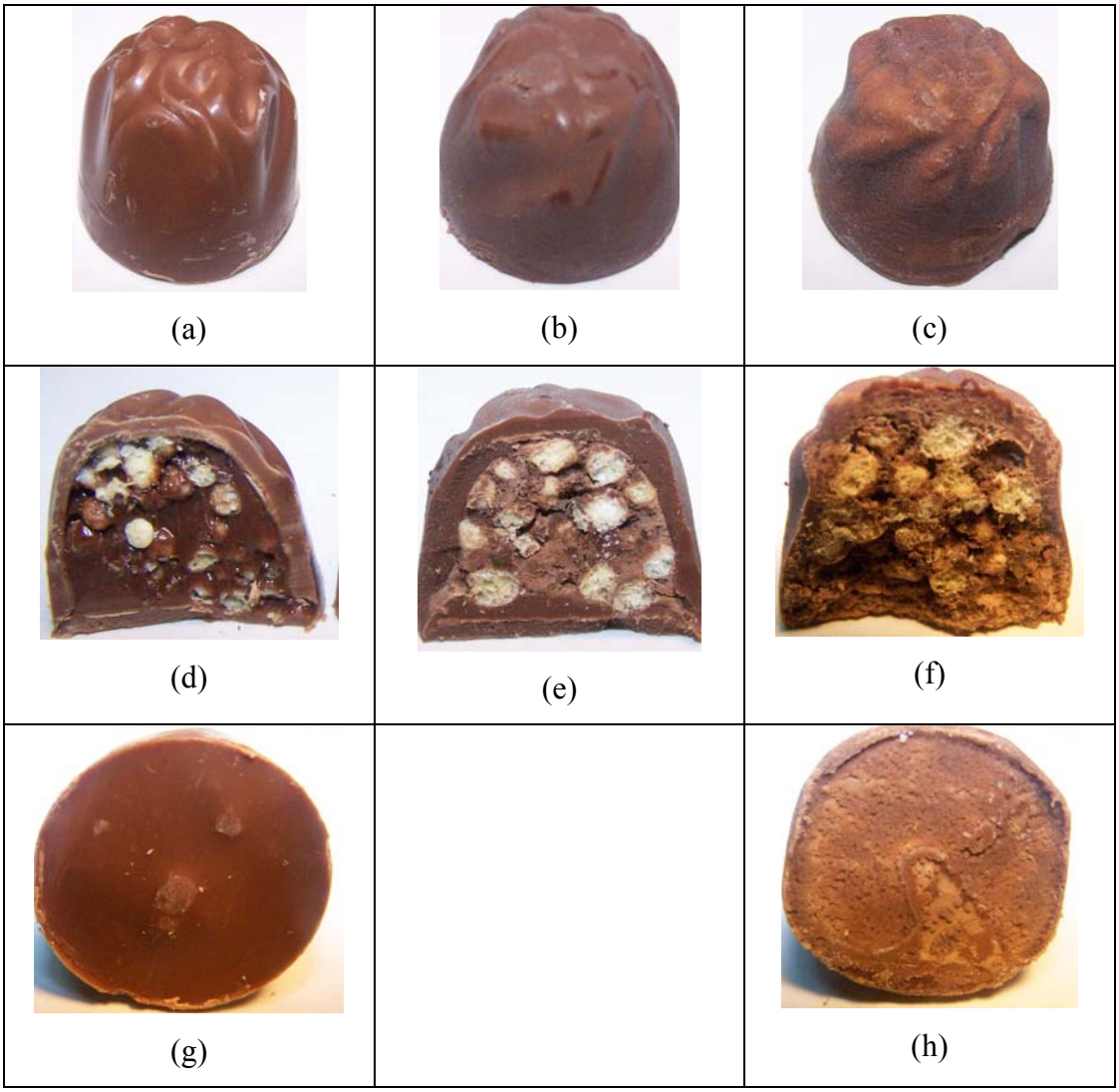

Figure 13 Photos of Samples: (a, d, g) TI 5 New Production, (b, e) TI 5 stored at 18°C, (c, f, h) TI 5 stored at 28°C

Effects of storage temperature on chocolate products could easily be seen even by naked eyes at Figure 13. Surface of product 'b' was whiter (more bloomed) than product 'a'. However product 'c' was further decomposed and products have been lost its specific color. Bottom of product 'c' contains little sized crystals, but would have had no crystals like original product 'a'. There was an absolute fat migration from inner to outer surface of product. Creamy structure had lost its viscous property and passed to drier phase. This migrated oil accumulated on the surface of chocolate and also changed the color of product from dark to light brownie. This change was appeared because of oxidizing of oil on the surface after migration. Moreover; crispy rice was also changed structurally.

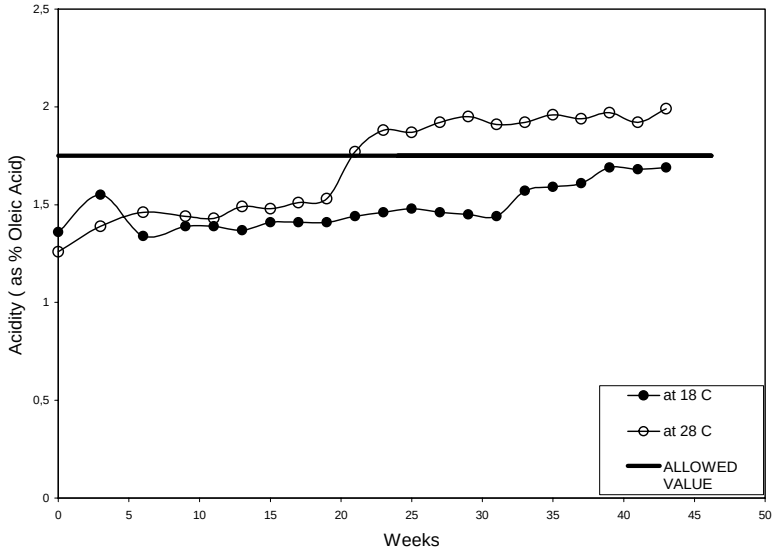

Figure 14 Acidity of Samples of Temper Index: 5 stored at 18 °C and 28 °C

Clear differences in acidity values of samples stored at 18 °C and 28 °C were also shown in Figure 14 in which there was an over-limit of allowed value for 28 °C after 21 weeks. On the contrary; other line (belongs to 18 °C) didn't pass to limited line (1.75) although increased slowly by weeks.

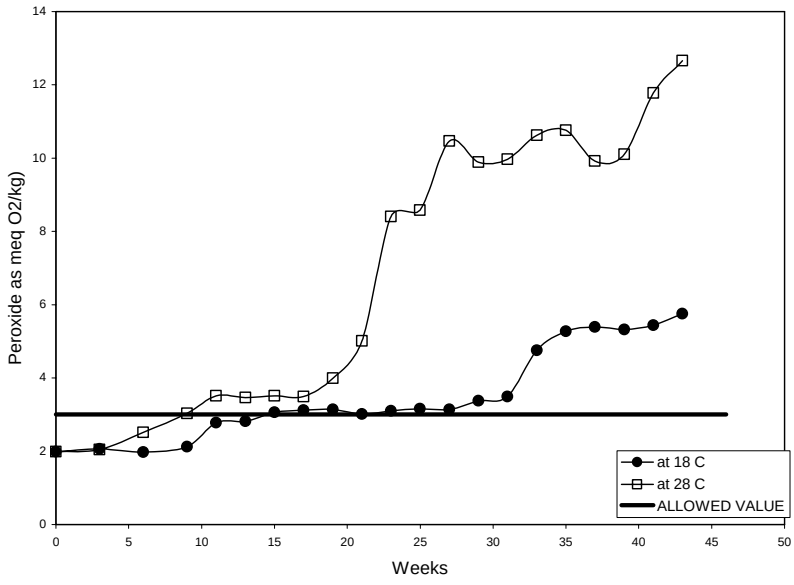

Figure 15 PV of Samples of Temper Index: 5 stored at 18 °C and 28 °C

After 19th weeks a sharp increase was attracted attention for sample stored at 28 °C in Figure 15. The line was continuously increased up to 12 meq O_2/kg along to storage

time. However; there was no sharp increase along to 31 weeks for line belonged to sample stored at 18 °C.

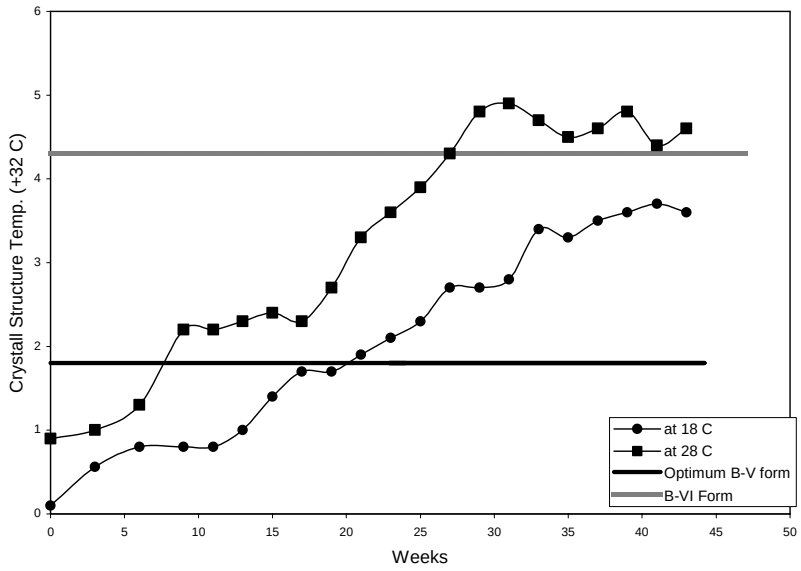

Figure 16 DSC Structure of Samples of Temper Index: 5 stored at 18 °C and 28 °C

There were two limits DSC Structure in order to decide whether shelf life of sample end or not. As discussed before; β-V form of cocoa butter in chocolate was optimum quality in appearance as gloss, shiny and more attractive to customers. β-VI form of cocoa butter meaned that; it was completely stable form as structure, lost its characteristic properties, had oily taste and not recommended to consume. Due to Figure 16; it can be obviously said that; storage chocolate products in high temperature places cause a sharp decrease in shelf life; because fat migration from inner to outer surface is alerted by heat.

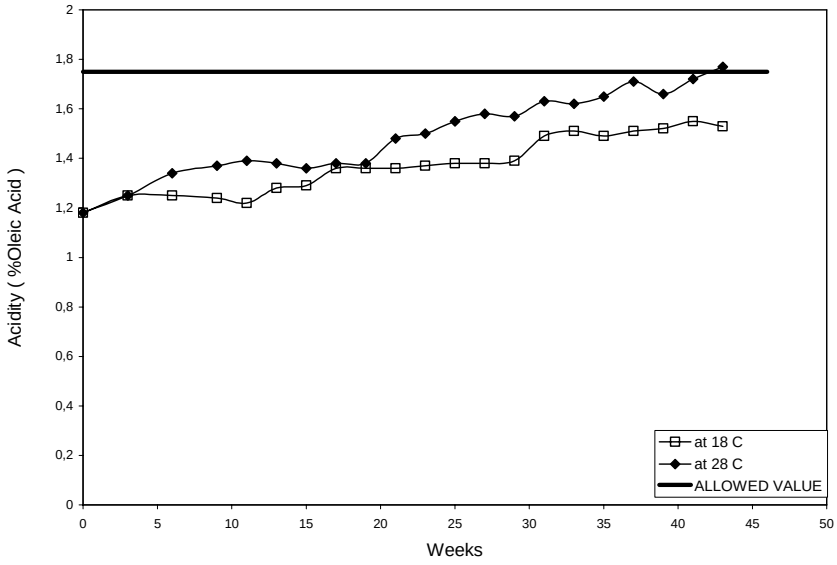

Figure 17 Acidity of Samples of Temper Index 7 stored at 18 °C and 28 °C

Similar to Acidity of TI 5 figures stored at 18 °C and 28 °C is easily differentiated from each other by lines.

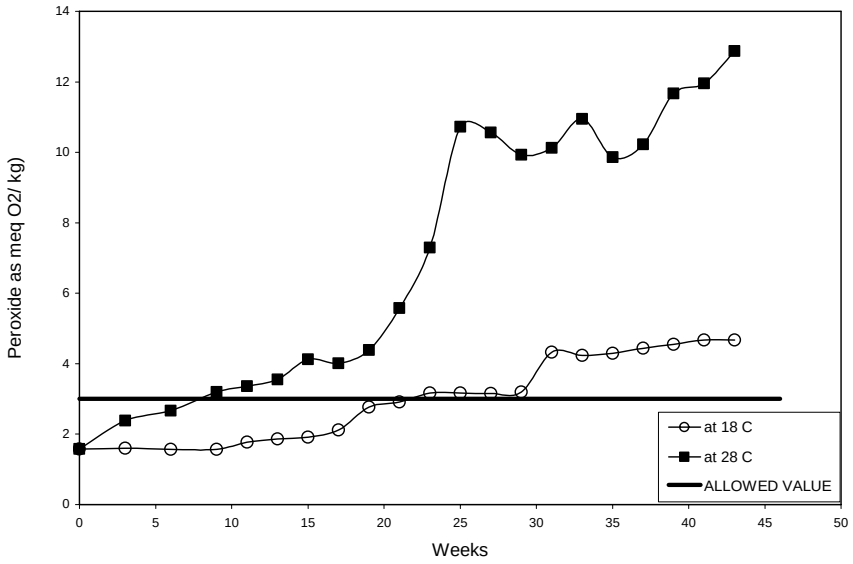

Figure 18 PV of Samples of Temper Index 7 stored at 18 °C and 28 °C

Figure 18 shows that; storing product at 28 °C was decreased shelf life about 11 weeks more than the 18 °C stored one; because after 17th weeks, an increase in slope of line could be seen.

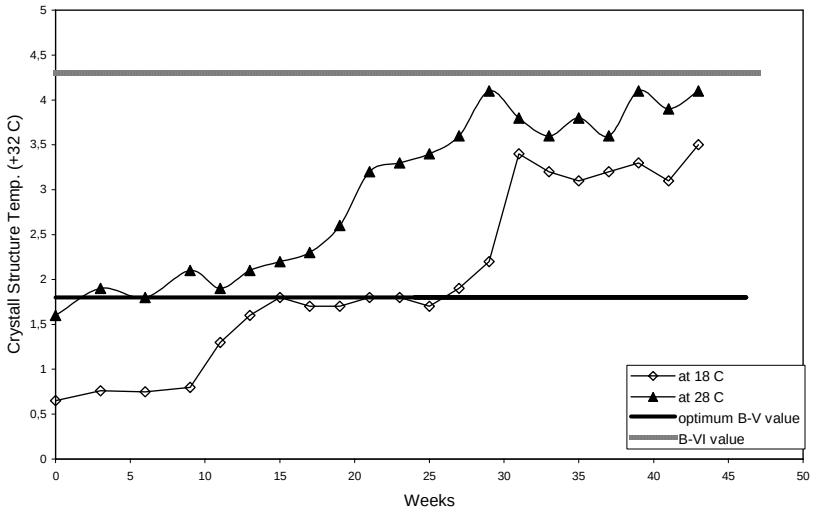

Figure 19 DSC Structure of Samples of Temper Index: 7 stored at 18°C and 28°C

There was a fluctuation in line for product stored at 28°C after 30th weeks. This mounted on irregular crystallization behavior.

3.2 Effects of Moulding Rate during Cooling and Shell Thickness on Fat Bloom Formation

3.2.1 Moulding Rate

Cooling velocity of product could be calculated by dividing cooling tunnel length (Section 2.2.2, *page:* 34) into mould length for each cooling tunnel sections. Production line speed, i.e. moulding velocity, in cooling section had a direct relationship on fat bloom formation in chocolate. Low moulding rate (low line speed) means slowly cooled product, contrary high moulding rate means fast cooled one (high line speed in cooling). In order to see effects of cooling velocity, moulding rate (velocity) was termed by unit, mould/min, as parameter.

There was a slight increase in appearance from 9 mould/min to 18 mould/min samples step by step. Fast cooling during manufacture was like a catalyzer for fat bloom.

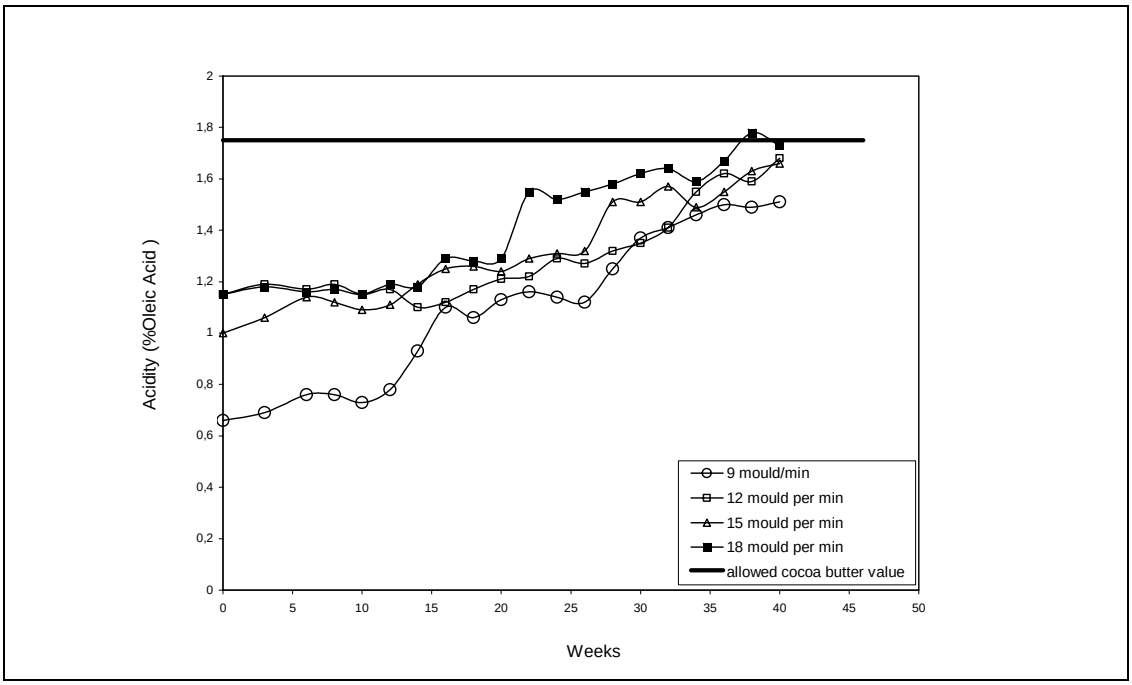

Figure 20 Acidity of Samples with different moulding velocities as normal thickness shell and stored at 18 °C

An increase in acidity from 9 mould/min to 18 mould/min was understood from Figure 20. Least acidity was reported in slow cooling, i.e. low moulding rate (9 mould/ min). On the contrary; most acidity was recorded in fast cooling, i.e. high moulding rate (18 mould/min).

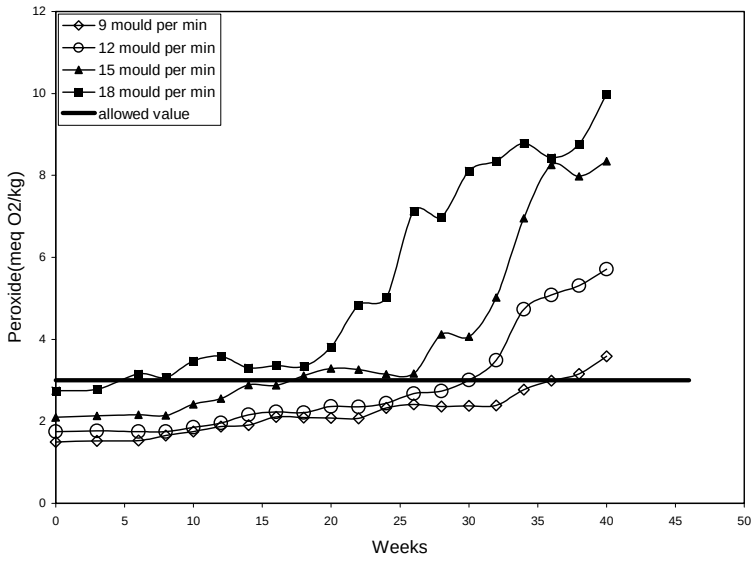

Figure 21 PV of Samples with different moulding velocities as normal thickness shell and stored at 18 °C

Differences in production speed lines with different moulding velocities were best shown in Figure 21. Due to results; 9 mould/min produced sample was highly resistant to bloom formation. Its PV value was watching under PV limit of cocoa butter allowed up to 38th weeks. However; for 18 mould/min produced sample was passed 3 meq 0_2/kg after 10 weeks and increased in line before reaching to 20th weeks. A similar small decrease was regarded, during entrance from 12 mould/min to 15 mould/min moulding velocities.

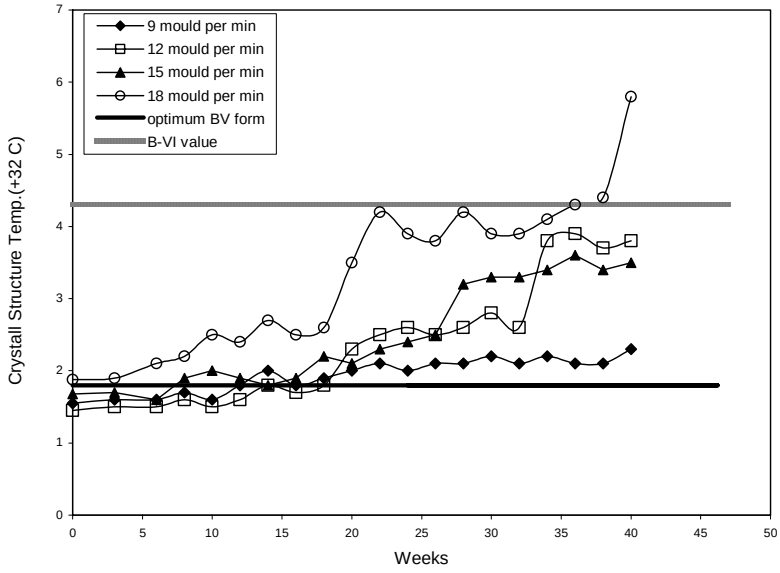

Figure 22 Crystal Structure of Samples with different moulding velocities as normal thickness shell and stored at 18 °C

An additional confirmation was seen on Figure 22 as crystal structure of samples for different moulding rates. Low moulding velocity (9 mould /min) caused optimum β-V crystal formation and kept this form longest time compared to other moulding velocities. On the contrary; high moulding velocity (18 mould /min) had fluctuations as line because of irregular and heterogeneous crystal formation. Moreover; high moulding velocities also caused regular β-VI form crystals, which was irreversible. In between values of moulding velocities (12 and 15 moulds/min) were also verified.

3.2.2 Shell Thickness

Thin shell sample was exposed to more bloom formation confronted with thick shell one for all moulding velocities except 18 mould/min production. Logically; after a certain time from production, due to processing and storage conditions, liquid oils in cream filling of sample began to migrate from inner to outer surface up to have same viscosities unless there was no barrier between two phases; chocolate and cream. This migration occurred easier for thinner shell samples and so accumulated on surface of chocolate. As a result; this collection on surface changes color of surface from brownie (dark or light depending on chocolate types) to white surfaced brownie, called bloomed.

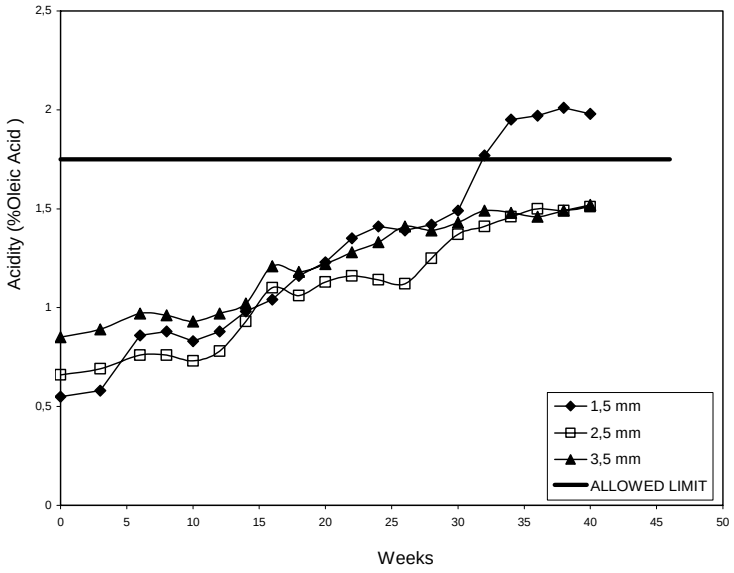

Figure 23 Acidity of Samples with different thickness shell that produced as 9 mould/min moulding velocity and stored at 18 °C

Thin shell was slightly different in acidity from normal and thick shell at high moulding velocity due to Figure 23. An over-limit for acidity was only present at thin shell, after 32nd weeks. It was difficult to say a difference between normal and thick shell samples at these moulding velocities.

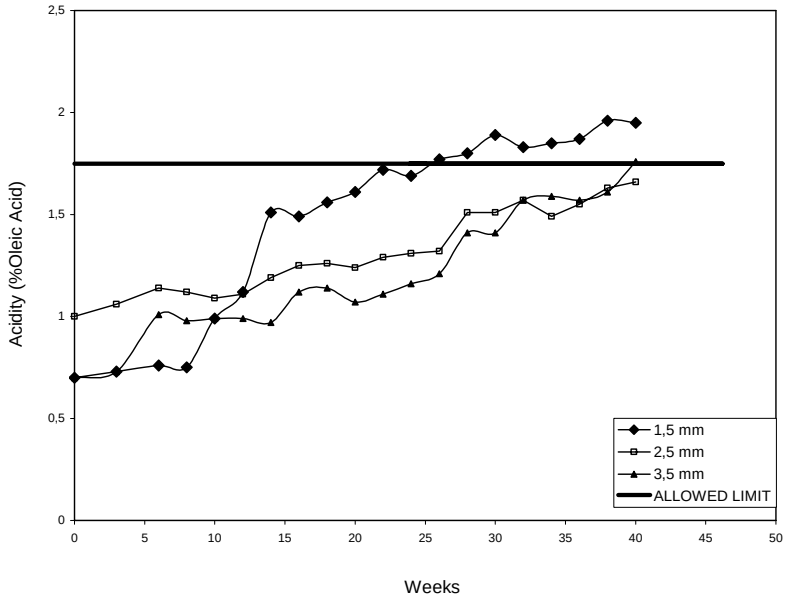

Figure 24 Acidity of Samples with different thickness shell that produced as 15 mould/min moulding velocity and stored at 18 °C

For this case; differences of acidity as % oleic acid between samples of thin, normal and thick shell were easily distinguishable (see Figure 24). A sharper over-limit was seen after 26th weeks for thin shell sample. Least acidity was occurred at thickest one (3.5mm).

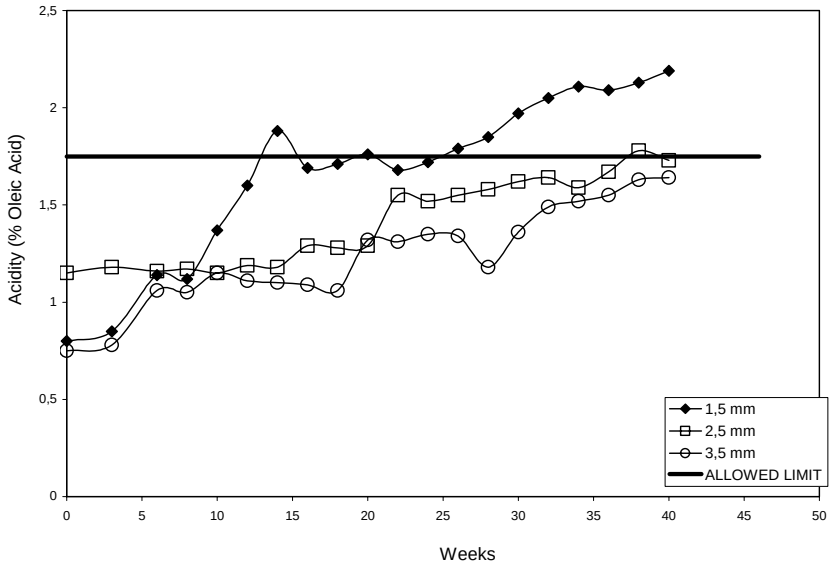

Figure 25 Acidity of Samples with different thickness shell that produced as 18 mould/min moulding velocity and stored at 18 °C

Thinner shell was slightly differentiated from normal one for fast cooled product during manufacturing. At 14th weeks there was a peak at line for thinner product. However; in between 14-24 weeks, fluctuation was seen. There may have been a measurable mistake at 14th week; because acidic formation was not a reversible phenomenon. Titration during measuring acidity of sample was not carried out at 14th week, consumed volume of solvent might have been higher than required amount, i.e. end point was over.

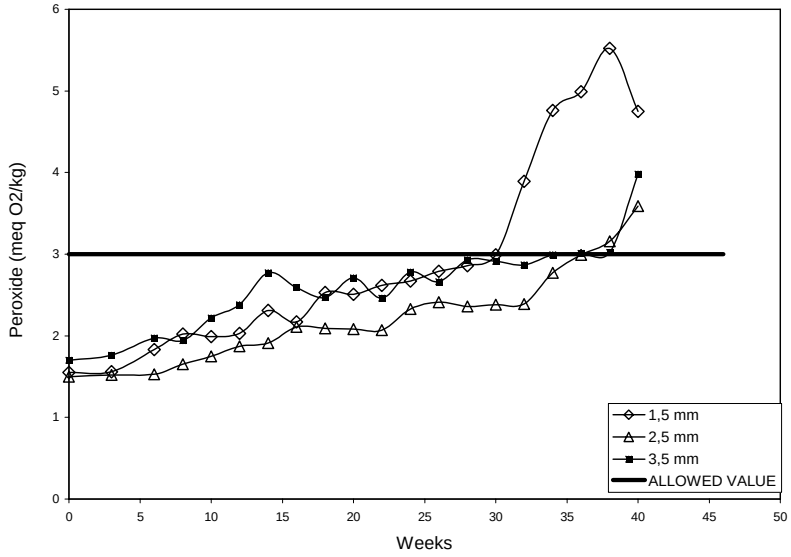

Figure 26 PV of Samples with different thickness shell that produced as 9 mould/min moulding velocity and stored at 18 °C

A difference for thin shell sample was seen after 30th weeks where a sharp increase was present. There was no noteworthy distinction between normal and thicker shell sample

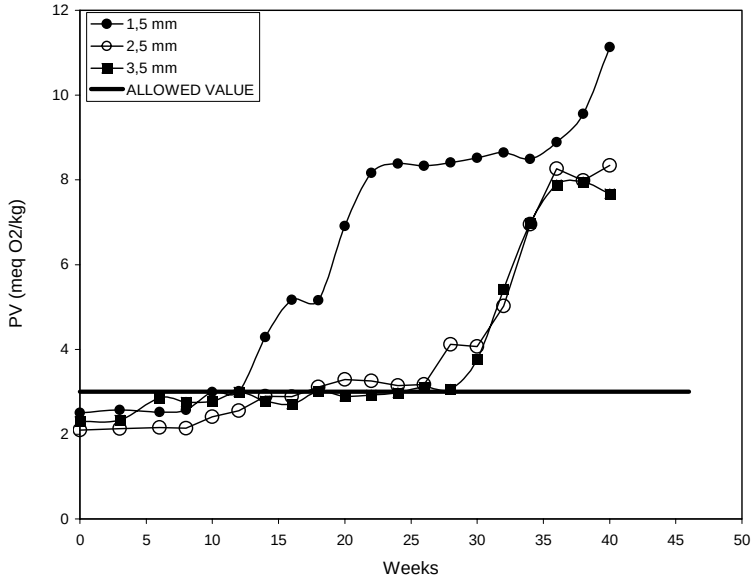

Figure 27 PV of Samples with different thickness shell that produced as 15 mould/min moulding velocity and stored at 18 °C

Frankly; a discrepancy in PV value of thin shell sample was observed from others. After 12th weeks, there was an incredible growing in line compared to normal and thick ones. At the end of shelf life, it passed to 10 meq O_2/kg.On the contrary; normal and thicker shell samples kept their qualities up to 26th and 30th weeks respectively.

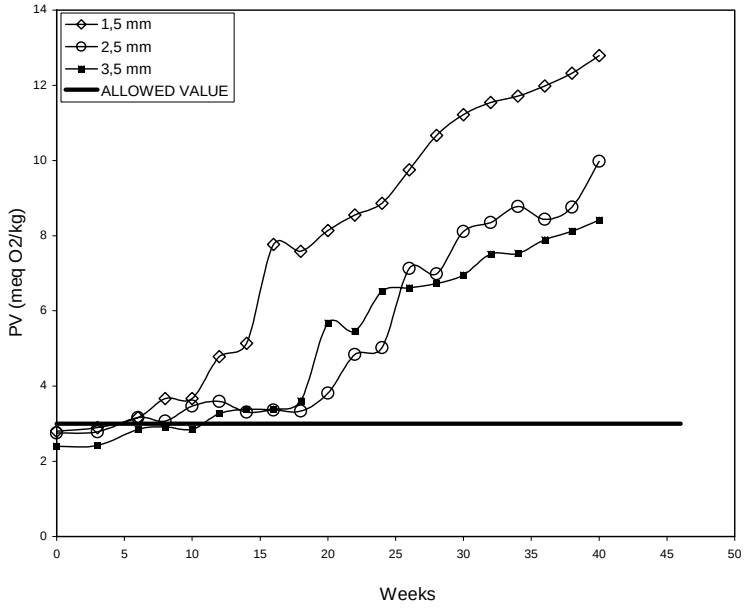

Figure 28 PV of Samples with different thickness shell that produced as 18 mould/min moulding velocity and stored at 18 °C

Resembling to Figure 28, first over-limit was seen on thin shell product after 10 weeks. Normal and thicker shell samples were watching together as values along to 18 weeks; but after 25th weeks an open difference was followed out for the normal shell sample resistively to bloom formation.

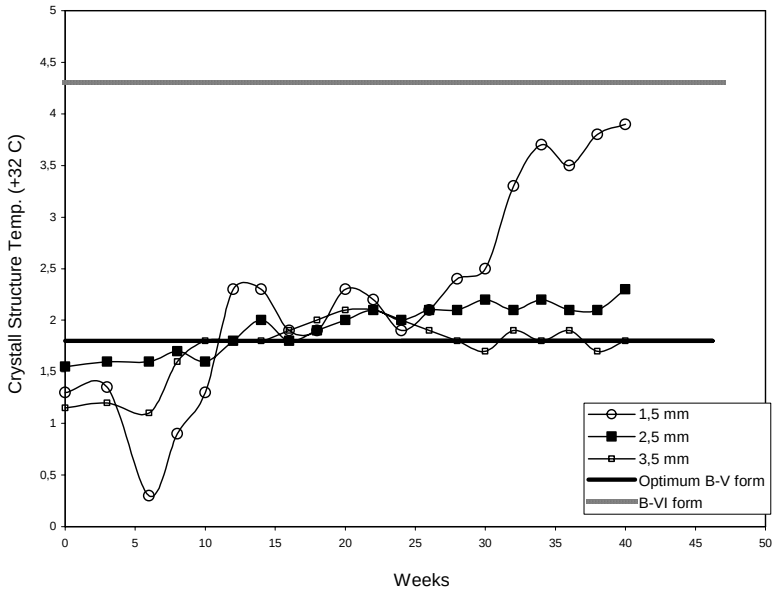

Figure 29 DSC values of Samples with different thickness shell that produced as 9 mould/min moulding velocity and stored at 18 °C

Most irregular crystallization of cocoa butter was present in chocolate produced as thin shell. The line depending on 1.5 mm thickness had more fluctuation and after 30th weeks increased sharply in order to reach stable β-VI form structure. Other shell samples had negligible differences up to 38th week. At the end of shelf life only thicker one was not bloomed and had almost β-V form structure.

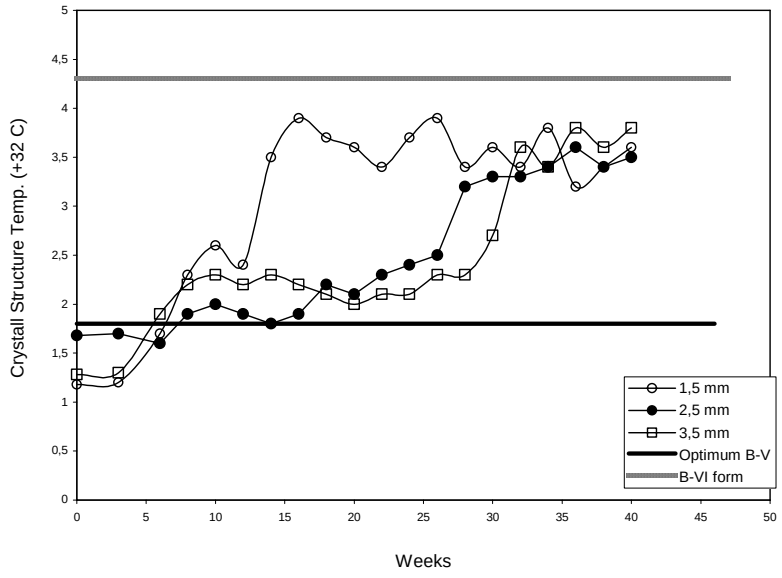

Figure 30 DSC values of Samples with different thickness shell that produced as 15 mould/min moulding velocity and stored at 18 °C

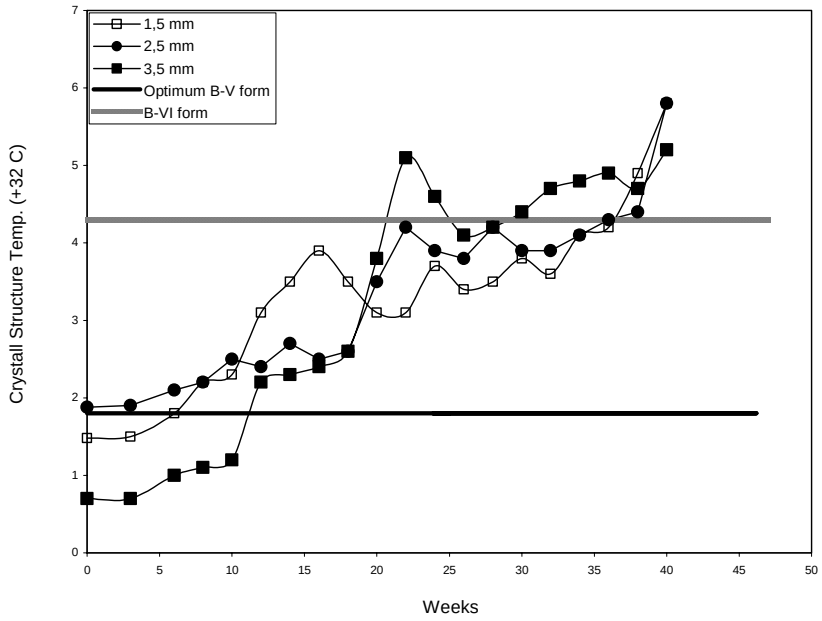

Figure 31 DSC values of Samples with different thickness shell that produced as 18 mould/min moulding velocity and stored at 18 °C

Fluctuations in lines demonstrated irregular crystallization of cocoa butter during cooling just after tempering. Figure 31 proved the importance of cooling step on processing of chocolate once more. Lines for all thickness were looking like same after 26th week.

3.3 Changes of Initial-Final Values of SFC & FA Compositions of samples

3.3.1 Fatty Acid Changes

Qualitative and quantitative analysis of fatty acids generated from fats were determined by transforming fatty acids into methyl esters using GC/MS and changes were observed. In order to minimize possible mistakes coming from guide and experiment; all necessary equipments used in experiment were washed with washing acid solution (containing sulfuric acid and potassium chromate as 10 %), then, water, finally acetone that dissolved water and oil.

At the beginning of this study; it was planned to analyze fatty acid changes in samples as once a month. However GC/MS machine wasn't provide from supplier at predicted time. Next; education time of user for guidance of machine and trial-error periods in order to apply optimum method for analysis and so on caused to miss chance to make periodical analysis. Hence; initial and final fatty acid values were comparing in order to verify all other results coming from analysis.

Main fatty acids present in cocoa butter were mentioned in Tables 7-10 as initial value as percent. There were no lauric and myristic acids in cocoa butter. Cocoa butter had about 39% stearic acid; but cream oil approximately 5%. Moreover; linoleic acid was present in cream oil in high amount (Approx. 30%), on the contrary in cocoa butter very low percent, about 2 %. These differences gave an idea about migration of oil at the end of shelf life. More migration means, more possibility of fat bloom formation.

Table 7 Initial and Final Fatty Acid Compositions of Samples for different Temper Index: 5, 6 and 7 and stored at 18 °C

Fatty Acid Compositions % at 18 °C				
Fatty Acid Name	Initial	After 10 Months		
		Temper 5	Temper 6	Temper 7
	%	%	%	%
Lauric Acid	-	1,18	1,29	1,49
Myristic Acid	-	1,11	0,93	0,76
Palmitic Acid	27,78	33,11	31,15	30,07
Stearic Acid	40,47	28,62	28,09	27,98
Oleic Acid	29,97	30,91	30,57	30,04
Linoleic Acid	1,78	5,09	7,97	9,66

Table 7 demonstrated fatty acid compositions of samples for different TI values. Least and most lauric acid percentages were in temper 5 and 7 respectively. Highest linoleic acid (occasionally coming from cream oils) portion was belonged to TI 7. There was also a decrease in stearic acid percent compared to original cocoa butter percentage; but no clear difference in Stearic acid % was occupied between different TI values. Hence; migration easily were seen due to table 7, classified as: most migration for TI 7 and least one for TI 5, i.e. more bloomed TI 7, least bloomed TI 5 samples.

Tables 8-10 indicated initial and final fatty acid compositions of samples for different shell thickness with different moulding velocities. There may have been some experimental mistakes during removing shell of chocolate from product. If cream filling mixed with chocolate, there could be a deviation from origin. In this case; it might have been calculated as migrated oil and so final proportions of fatty acid may be different.

Table 8 Initial and Final Fatty Acid Compositions of Samples for different shell thickness with 9 mould/min moulding velocity and stored at 18 °C

Fatty Acid Compositions at 9 mould/min				
Fatty Acid Name	Initial	After 10 months		
		1,5mm	2,5 mm	3,5 mm
	%	%	%	%
Lauric Acid	-	2,56	3,06	2,75
Myristic Acid	-	1,22	1,42	1,41
Palmitic Acid	27,78	27,69	27,14	27,29
Stearic Acid	40,47	29,64	29,79	32,31
Oleic Acid	29,97	29,86	30,49	29,69
Linoleic Acid	1,78	9,03	8,11	6,57

Table 9 Initial and Final Fatty Acid Compositions of Samples for different shell thickness with 15 mould/min moulding velocity and stored at 18 °C

Fatty Acid Compositions at 15 mould/min				
Fatty Acid Name	Initial	After 10 months		
		1,5 mm	2,5 mm	3,5 mm
	%	%	%	%
Lauric Acid	-	3,19	4,49	3,53
Myristic Acid	-	1,49	1,79	1,48
Palmitic Acid	27,78	27,61	27,77	28,42
Stearic Acid	40,47	31,2	26,05	30,82
Oleic Acid	29,97	29,24	29,48	28,19
Linoleic Acid	1,78	7,27	10,42	7,56

There were lauric and myristic acid percentages after 10 months for each sample (in Table 8), which mean that, an absolute migration was possibly taken place. More linoleic acid percentages in 1.5 mm thickness sample signified more cream oil migration (initially: 1.78% and finally 9.03 %). Similar verification for 3.5 mm thickness (thickest one) could also be done (Final 6.57 %).

Considerable decrease in stearic acid percentages of 15 mould/min produced sample with different thickness told that; a clear oil migration was taken place to outer surface. Comparisionaly; initially there were no lauric and myristic acids present; whereas after 10 months, more than 3 % lauric and 1% myristic acid were observed. There should be a clear mistake during removing of shell from product for normal

thickness (2.5 mm) sample in which lauric acid was in highest portion (4.49) compared to 1.5 and 3.5 mm thickness shell samples, 3.19 and 3.53 respectively. In addition; linoleic acid percentages also were confirmed to miss-measuring, 7.27, 10.42 and 7.56 % for 1.5, 2.5 and 3.5 mm thickness samples respectively. Probably; this fault was coming from mixing of inner cream oil with outer cocoa butter during removing shell chocolate from sample.

Table 10 Initial and Final Fatty Acid Compositions of Samples for different shell thickness with 18 mould/min moulding velocity and stored at 18 °C

Fatty Acid Compositions at 18 mould/min				
Fatty Acid Name	Initial	After 10 months		
		1,5 mm	2,5 mm	3,5 mm
	%	%	%	%
Lauric Acid	-	5,27	3,18	2,78
Myristic Acid	-	2,11	1,46	1,51
Palmitic Acid	27,78	31,68	27,35	27,96
Stearic Acid	40,47	23,11	29,94	32,59
Oleic Acid	29,97	27,39	30,13	28,81
Linoleic Acid	1,78	10,42	7,94	6,36

Results of production with highest moulding velocity (18 mould/min) with different shell thickness were shown in Table 10. Values were clearly supported to oil migration; because absolute percentages of lauric (% 5.27) and myristic (% 2.11) acids were present in thinner shell. Thin shell sample had most linoleic acid (10.42 %) compared to thicker one (6.35 %). A clear difference in stearic acid portion also could be seen on table by lowest portion (23,13 %) for thin sample. On the contrary; highest portion of stearic acid (32.59 %) and lowest percentage of linoleic acid (6.35 %) also occupied in thicker sample and so on.

3.3.2 SFC Changes

The basic idea is the determination of solid fat content (SFC) of sample at a definite temperature. Every fat has a different crystalline temperature because of different oil compositions. For the quality of product, it is absolutely necessary to know the solid and liquid ratio of fat at a certain temperature. Oils or fats absorb radio frequencies in

magnetic region. It takes time to give up this absorbed energy for fats. This necessary time called as *stagnation time* that is very different from each other for oils and fats. By this time difference SFC content can be determined.

At the beginning of this study; it was planned to analyze SFC changes in samples once a month. However NMR machine wasn't procure from supplier at promised time. Next; training time of user for guidance of machine and trial-error periods in order to find and test optimum method for SFC analysis caused to miss chance to make periodical analysis. Hence; initial and final SFC values were compared in order to verify all other results coming from analysis.

Four temperatures, 20°C, 25°C, 30°C and 35 °C, were selected in order to discuss migration of oil from inner to outer surface of chocolate. Melting temperature ranges of cocoa butter and cream oil were 32-34 °C and 23-26 °C respectively. Selected temperatures were upper and below values for both of two types fat used in product. Cream oil SFC values for 20°C, 25°C, 30°C and 35 °C were 3.5, 0.84, 0.17 and 0 as % respectively. Migration rate was achieved by comparison of SFC values for samples in between at different temperatures. Low SFC values mean more oil migration to surface of shell. The best comparisions of SFC % could be done at 30 °C at which temperature cream oil was completely in liquid phase.

Table 11 Initial and Final SFC values of samples for different Temper Index: 5, 6 and 7 and stored at 18 °C

SFC % for different Temper Index values at 18 °C				
Temperature	Initial	After 10 months		
		Temper 5	Temper 6	Temper 7
	%	%	%	%
20 °C	72,15	36,44	37,02	37,78
25 °C	62,61	21,41	21,53	21,63
30 °C	37,97	6,03	6,67	7,01
35 °C	0,72	0,45	0,46	0,44

Initial and final values of solid fat content were determined in chocolate shell for different TI values (Table 11). Data present on this table shown that; there was an absolute fat migration to outer surface as cream oil, when compared to initial SFC of

cocoa butter which was single fat used in chocolate shell. Because initial SFC of cocoa butter at 20 °C is 72.15 %; but final SFC % of different TI values were around 36-37 %. Similar sharp differences were also obtained in other selected temperatures. However; SFC values of Temper Indexes 5, 6 and 7 were not clearly differentiated from each other. Results of them were very close to each other; i.e. negligible differences.

Table 12 Initial and Final SFC values of samples for different shell thickness with 9 mould/min moulding velocity and stored at 18 °C

SFC % for 9 mould/min				
Temperature	Initial	After 10 months		
		1,5 mm	2,5 mm	3,5 mm
	%	%	%	%
20 °C	72,15	32,41	41,05	44,06
25 °C	62,61	16,65	22,52	28,33
30 °C	37,97	5,64	8,09	12,14
35 °C	0,72	0,61	0,97	1,26

Comparision of initial and final SFC %'s of samples shown in Table 12 with different shell thickness. It could be easily decided that there was a migration in augmented amount from thinner to thicker shell for all selected amounts. Absolute difference was seen at 30 °C where no solid cream oil. Present SFC % is 5.64 at thin shell (1.5 mm thickness); but 12.14 % at thick shell (3.5 mm thickness). Data for 35 °C had experimental errors. Because initially; SFC value on cocoa butter was 0.72 % at this temperature. After 10 months it was increased to 0.97 and 1.26 % for normal and thicker shell respectively. It was impossible to see a similar rise as SFC. Therefore; faults were done during putting test tubes into NMR machine holder where SFC analysis was done. Waiting time had biggest portion of this mistaken pie. Temperature of laboratory, (20°C), where analyses were done was lower than selected analysis temperature, 35°C. Duration time to move test tubes from water bath to NMR eyes has taken more seconds than ignored time. Probably there was a heat exchange between room and test tubes during a few seconds. Finally; it caused to solidify small portion of oil in tubes.

Table 13 Initial and Final SFC values of samples for different shell thickness with 15 mould/min moulding velocity and stored at 18 °C

SFC % for 15 mould/min				
Temperature	Initial	After 10 months		
		1.5 mm	2.5 mm	3,5 mm
	%	%	%	%
20 °C	72,15	36,17	39,34	40,04
25 °C	62,61	19,47	22,62	21,38
30 °C	37,97	6,86	7,58	8,11
35 °C	0,72	0,69	0,71	1,12

Table 14 Initial and Final SFC values of samples for different shell thickness with 18 mould/min moulding velocity and stored at 18 °C

SFC % for 18 mould/min				
Temperature	Initial	After 10 months		
		1,5 mm	2,5 mm	3,5 mm
	%	%	%	%
20 °C	72,15	35,46	40,31	44,46
25 °C	62,61	17,98	22,34	27,12
30 °C	37,97	6,12	8,02	11,21
35 °C	0,72	0,35	0,57	0,93

Tables 13 and 14 confirmed cream oil migration to outer surface of chocolate, and so bloom formation. Verification was also clearly understood from these tables for shell thickness & oil migration relation. Thinner shell samples had least and thicker ones had most SFC percentages for every selected temperature. An over-limit duration time to move test tubes from water baths at 35 °C to NMR sample eyes was understood because of data at 35 °C. Because thicker shell samples at Tables 13-14 had higher SFC %'s from initial value of cocoa butter SFC percentage.

3.4 Shelf Life Study of Analyzed Samples

Shelf life of samples were listed in Table 15 by comparision and correlation of acidity, peroxide value and crystal structure results from DSC at same graph due to time vs. property, present in Appendix. Increase in slope of line for associated point was selected in order to determine shelf life of sample.

Table 15 Shelf life of studied products

Run No	Temper Index	Moulding Velocity (mould/min)	Shell Thickness (mm)	Storage Temperature (^{o}C)	Shelf Life (week)
1	5	12	2.5±0.2	18	31
2	5	12	2.5±0.2	28	19
3	6	9	1.5±0.2	18	30
4	6	9	2.5±0.2	18	38
5	6	9	3.5±0.2	18	40
6	6	12	2.5±0.2	18	32
7	6	15	1.5±0.2	18	12
8	6	15	2.5±0.2	18	26
9	6	15	3.5±0.2	18	28
10	6	18	1.5±0.2	18	10
11	6	18	2.5±0.2	18	20
12	6	18	3.5±0.2	18	18
13	7	12	2.5±0.2	18	29
14	7	12	2.5±0.2	28	18

CHAPTER IV

CONCLUSION

• Three different temper indexes, (TI 5, 6, 7), three different shell thickness (1.5, 2.5, 3.5 mm ±0.2), four different moulding velocities (9, 12, 15, 18 mould/min) and two different storage conditions (18 and 28 °C) were analysed along 40 weeks for acidity, peroxide value and crystal structure twice a month. SFC values at NMR and fatty acid analysis at GC/MS were done as % in order to compare initial and final results to achieve verification with other periodic analysis.

• Samples of temper indexes 5, 6 and 7 produced in condition of 12 moulds/min and stored at 18 °C have had very close shelf lives; 31, 32 and 29 weeks respectively. Results showed that; TI 6 was most resistant to fat bloom formation on chocolate.

• TI 5 and TI 7 samples were stored at two different temperatures, 18 and 28 °C in order to see how changes shelf life, fat bloom formation rate, with temperature. Results have given a considerable idea about recommended storage conditions. Keeping product at 28 °C instead of 18 °C has decreased shelf life about 3 months, up to 19 and 18 weeks for TI 5 and 7 respectively.

• Different shell thicknesses indicated that; there was a direct relationship between oil migration and thickness. Thinner shell definitely had more migration. Thicker shell attacked as a barrier fat migration, i.e. delayed oil reaching to surface.

• Due to results of analysis; moulding velocity of products during cooling was another important parameter for keeping eating and structural quality of products for a long time. Slowly cooled sample (9 mould/ min) kept its edible property up to 38^{th} weeks, whereas fast cooled sample (18 mould/ min) began to decompose after 20^{th} weeks. Middle moulding velocities (12 and 15 mould/min) have confirmed this result, had 32 and 26 week shelf life respectively.

Suggestions for Plant Process

• Products should be stored at a temperature lower than at a temperature, 18 °C was inhibited storage bloom in chocolate for over 8 months. In contrast; storing chocolate at 28°C was decreased shelf life to 5 months. The lower the temperature, the lower the bloom risks.

• Optimum cooling velocity should be selected or degree of cooling temperature should be decreased. Because; the lower the temperature and the shorter the cooling time, the better the bloom resistance.

• Optimum shell thickness should be selected without affecting eating quality.

• TI 5 & TI 6 values recommended in tempering process during manufacturing of chocolate.

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http:// beerandwine.hobart.tased.edu.au/chocolate folder/chocolate flowchart.doc

APPENDIX

SHELF LIFE DETERMINATION FIGURES

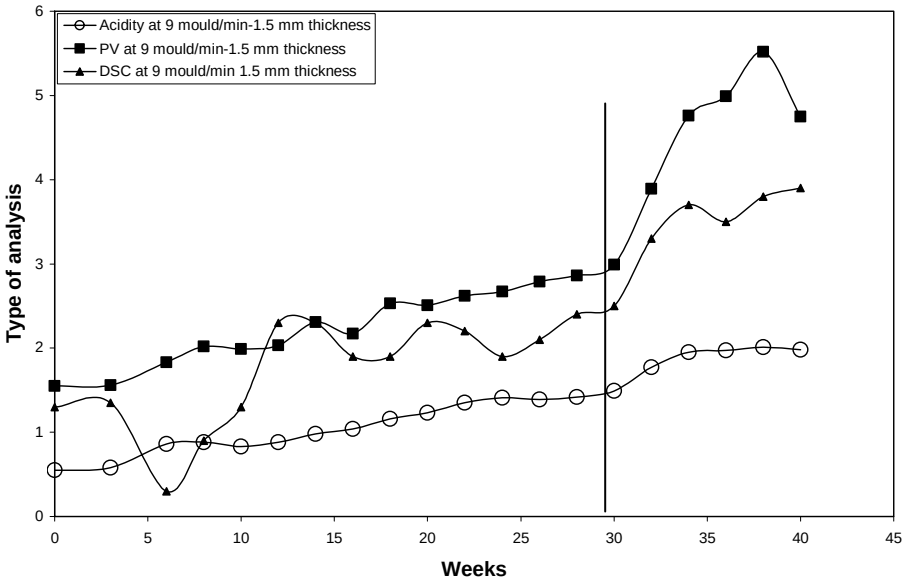

Figure A.1 Shelf life of sample produced at 9 mould/min with 1.5 mm shell thickness stored at 18 °C

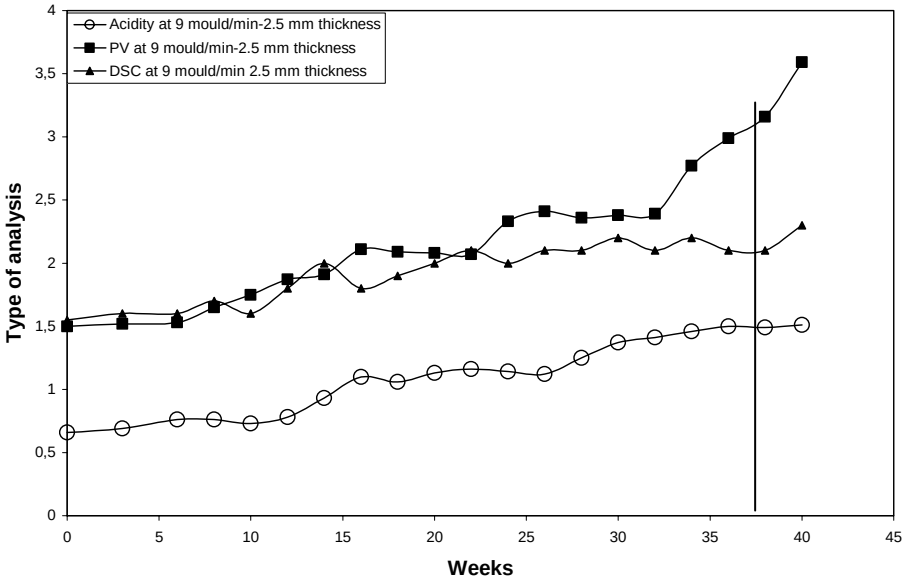

Figure A.2 Shelf life of sample produced at 9 mould/ min with 2.5 mm shell thickness stored at 18 °C

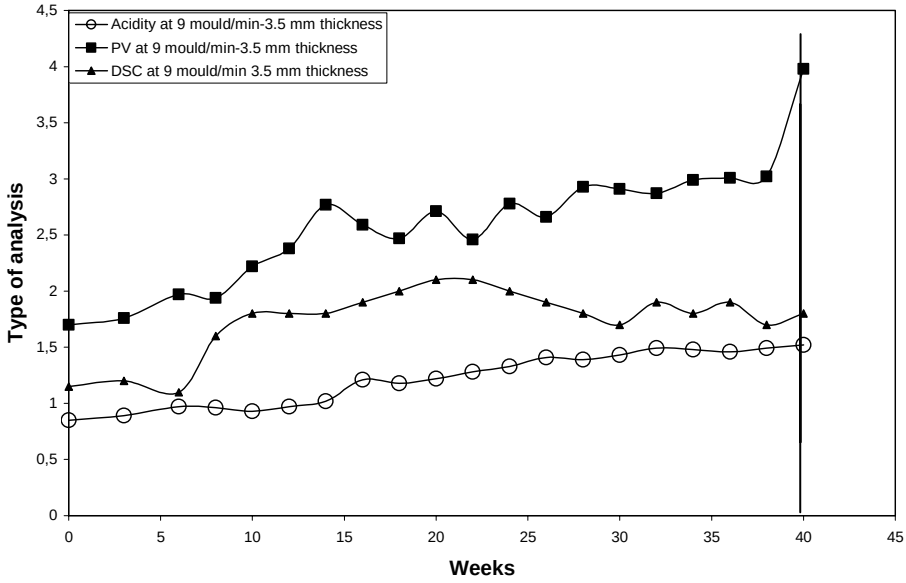

Figure A.3 Shelf life of sample produced at 9 mould/ min with 3.5 mm shell thickness stored at 18 °C

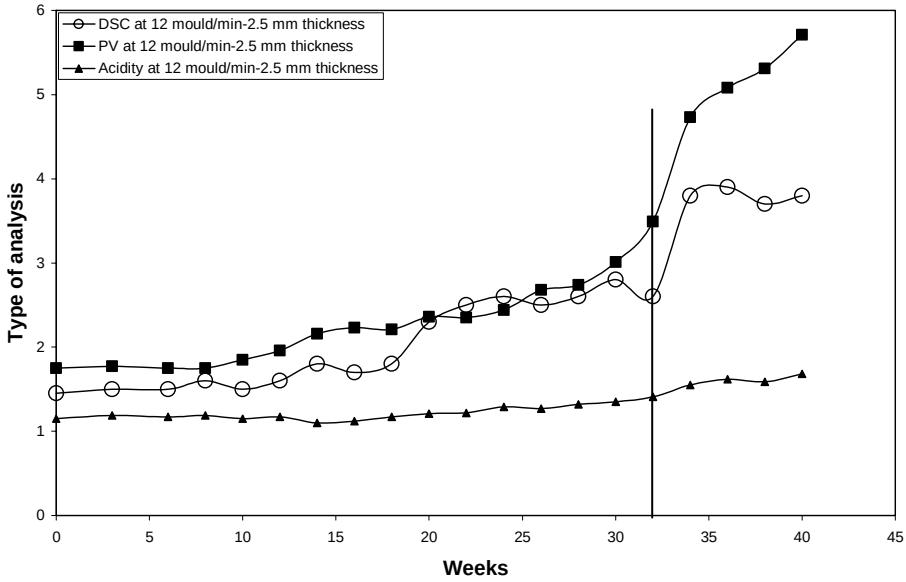

Figure A.4 Shelf life of sample produced at 12 mould/ min with 2.5 mm shell thickness stored at 18 °C

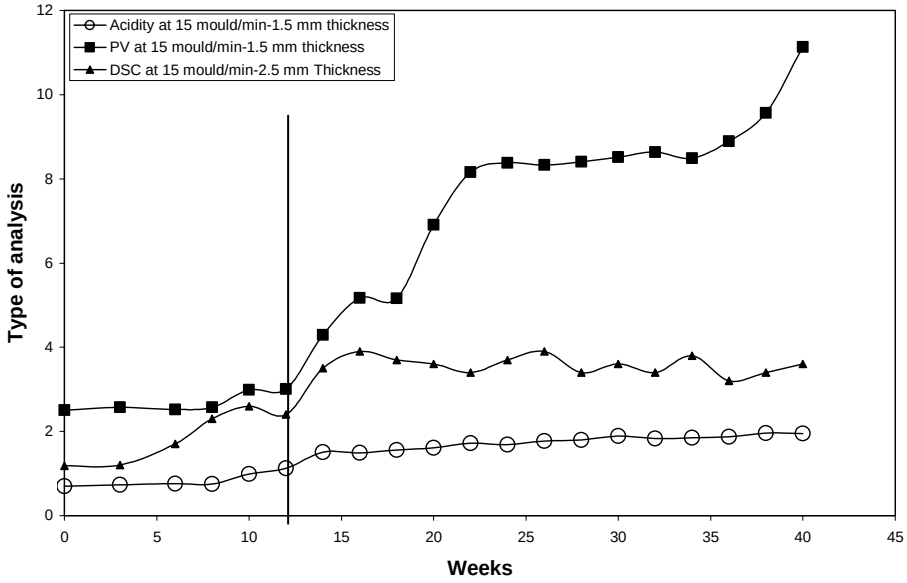

Figure.A.5 Shelf life of sample produced at 15 mould/ min with 1.5 mm shell thickness stored at 18 °C

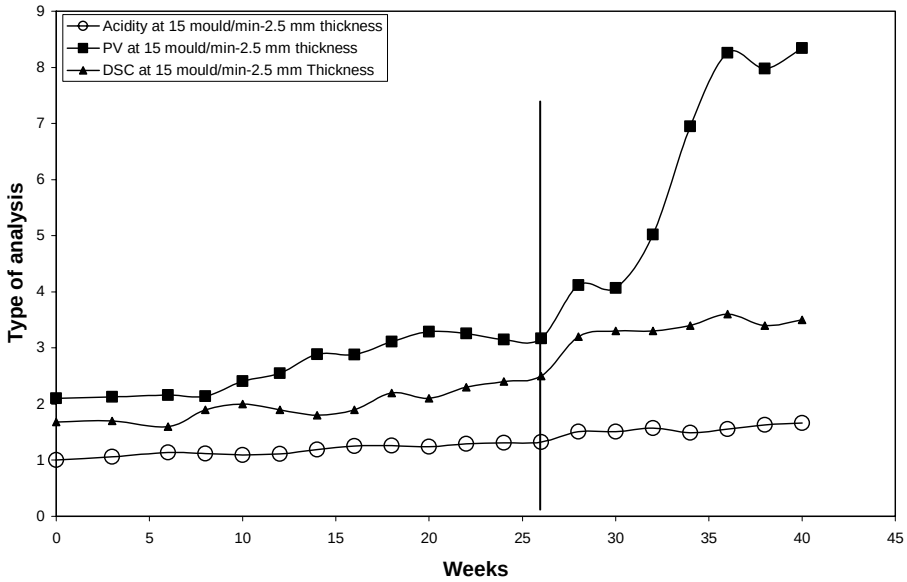

Figure A.6 Shelf life of sample produced at 15 mould/ min with 2.5 mm shell thickness stored at 18 °C

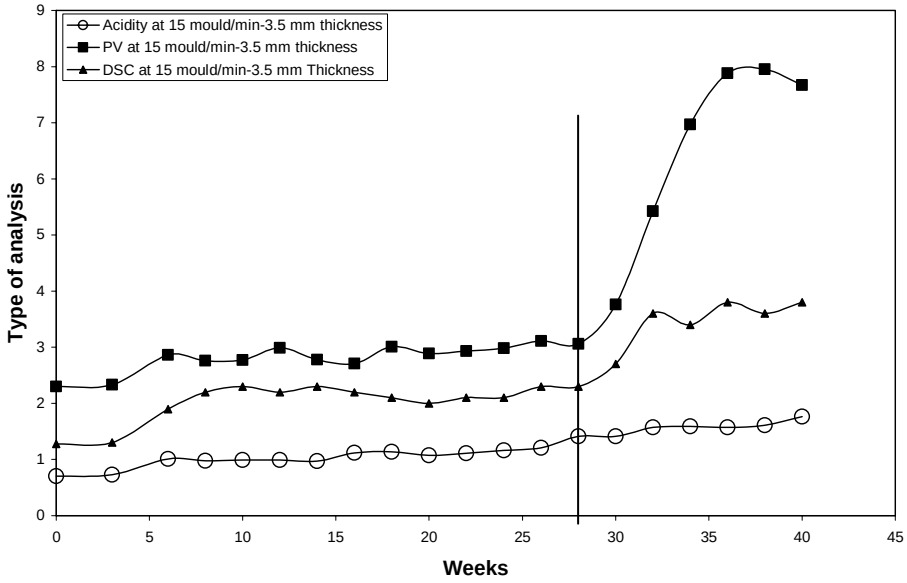

Figure A.7 Shelf life of sample produced at 15 mould/min with 3.5 mm shell thickness stored at 18 °C

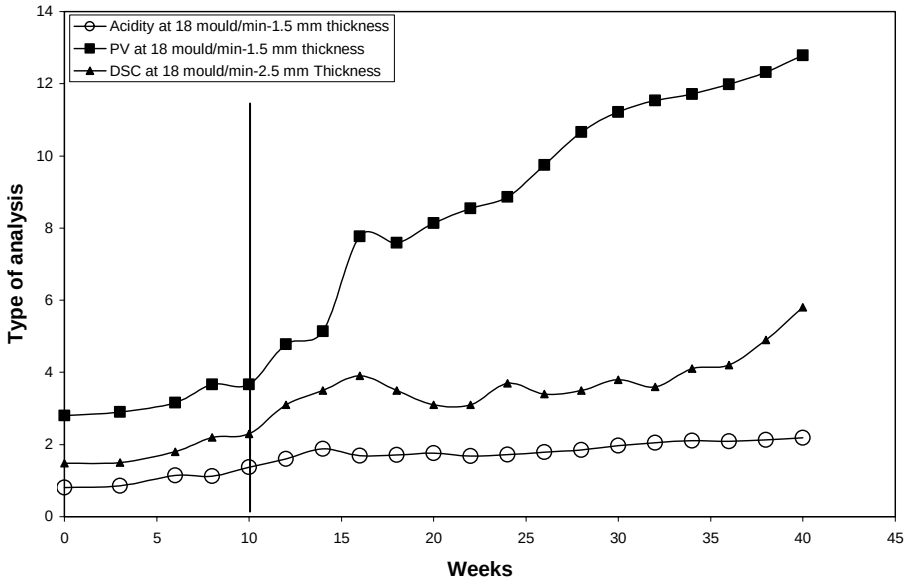

Figure A.8 Shelf life of sample produced at 18 mould/min with 1.5 mm shell thickness stored at 18 °C

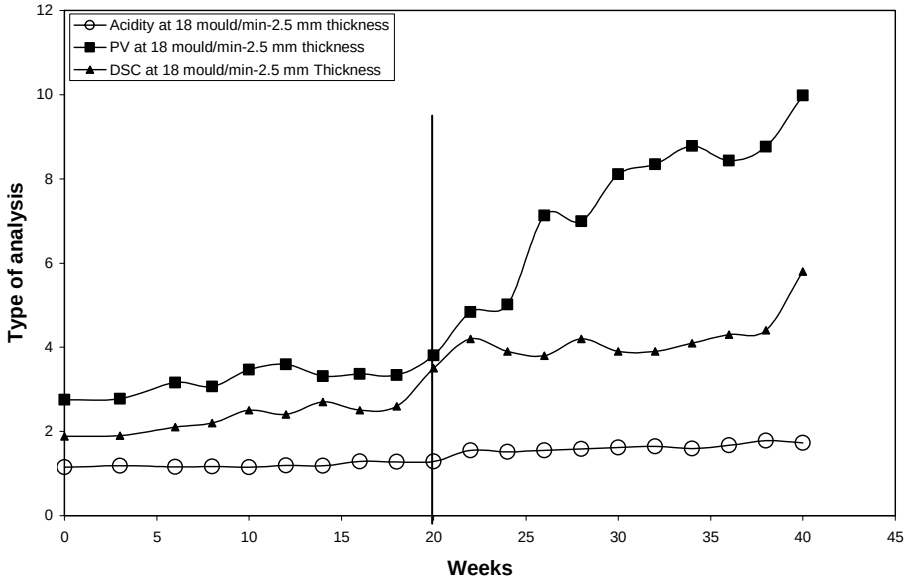

Figure A.9 Shelf life of sample produced at 18 mould/min with 2.5 mm shell thickness stored at 18 °C

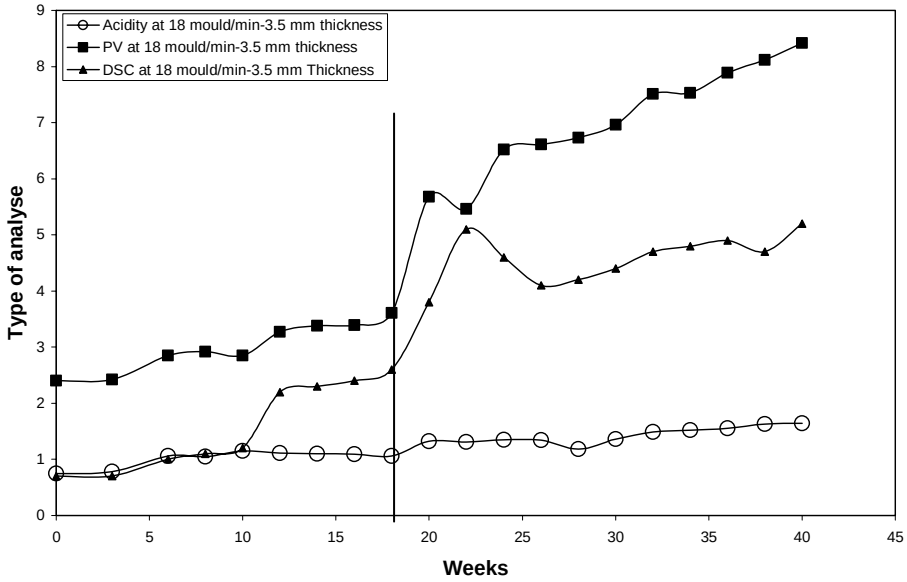

Figure A.10 Shelf life of sample produced at 18mould/min with 3.5 mm shell thickness stored at 18 °C

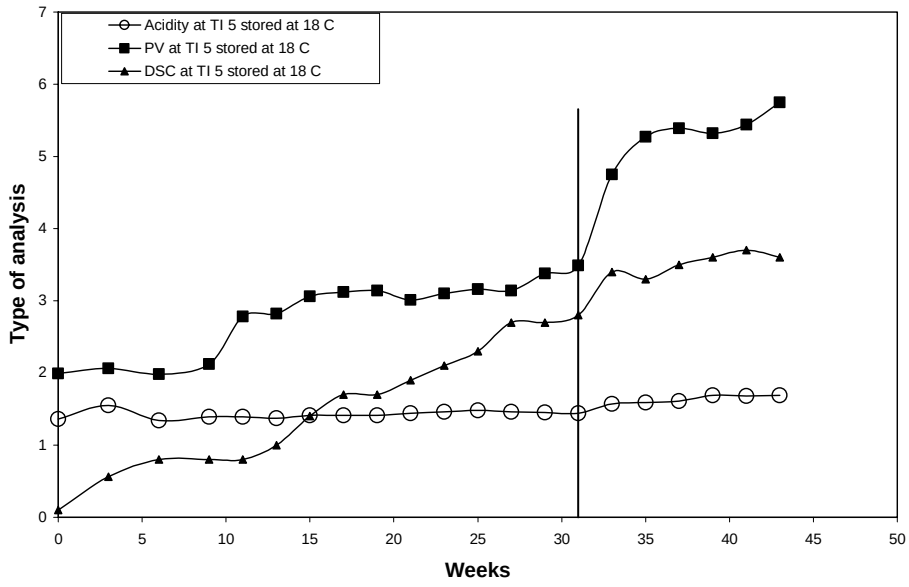

Figure A.11 Shelf life of sample produced at TI 5 with 12 mould/min and 2.5 mm shell thickness stored at 18 °C

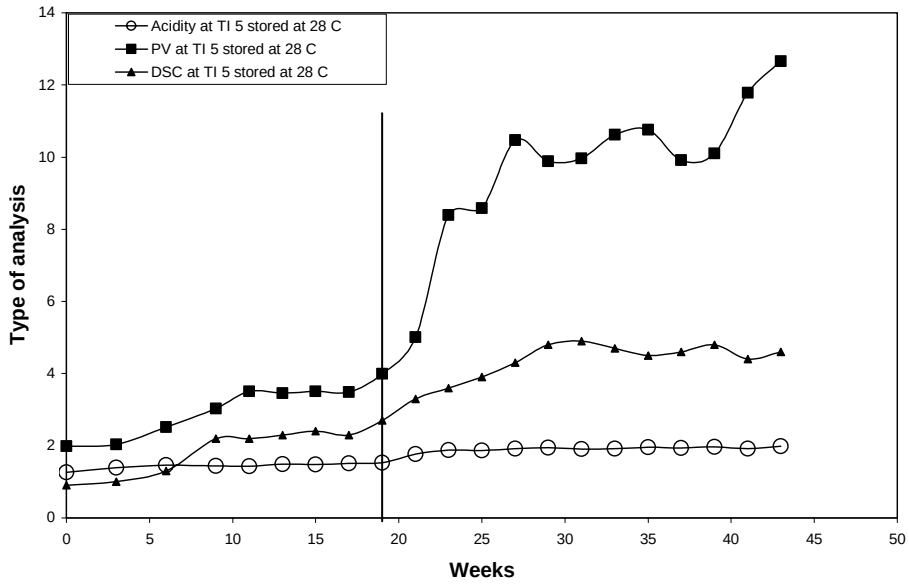

Figure A.12 Shelf life of sample produced at TI 5 with 12 mould/min and 2.5 mm shell thickness stored at 28 °C

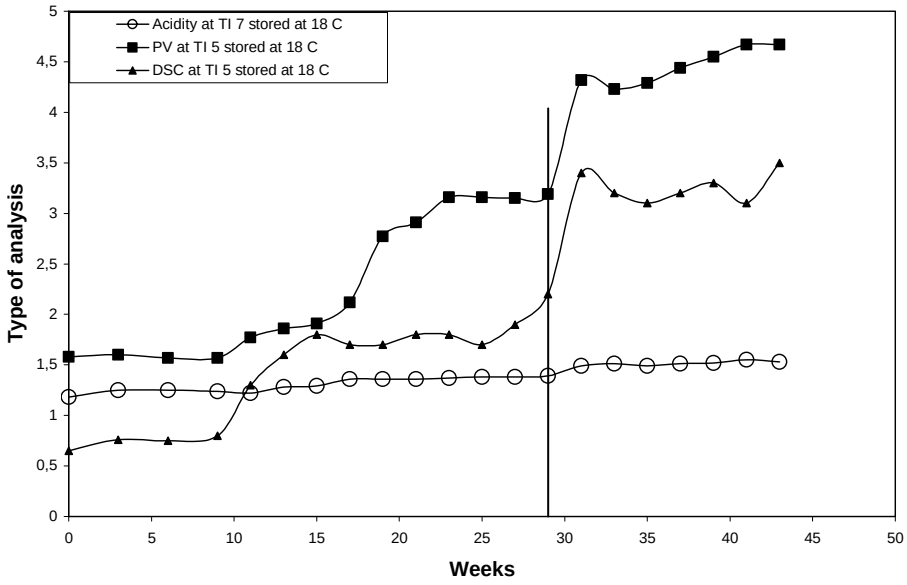

Figure A.13 Shelf life of sample produced at TI 7 with 12 mould/min and 2.5 mm shell thickness stored at 18 °C

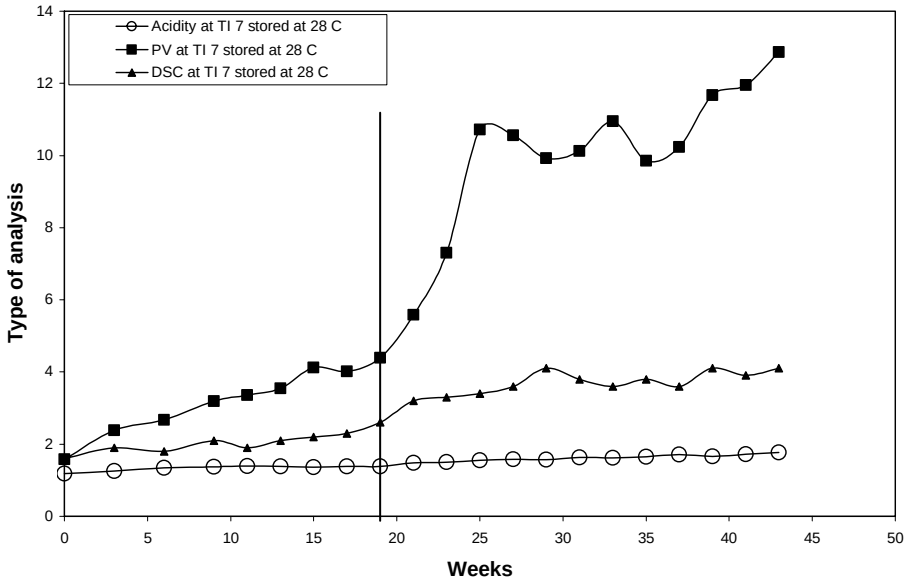

Figure A.14 Shelf life of sample produced at TI 7 with 12 mould/min and 2.5 mm shell thickness stored at 28 °C