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M.Sc. in Food Engineering

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**REPUBLIC OF TURKEY
GAZİANTEP UNIVERSITY
GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES**

**EFFECTS OF DRIED BERGAMOT PEEL POWDER ON THE
STRUCTURAL PROPERTIES OF DARK CHOCOLATE**

**M.Sc. THESIS
IN
FOOD ENGINEERING**

**BY
HAZAL SARIGÜL
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M.Sc. Thesis

in

**Food Engineering
Gaziantep University**

Supervisor

Prof. Dr. Ali Rıza TEKİN

by

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May 2019



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GAZİANTEP UNIVERSITY
GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES
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Hazal SARIGÜL

ABSTRACT

EFFECTS OF DRIED BERGAMOT PEEL POWDER ON THE STRUCTURAL PROPERTIES OF DARK CHOCOLATE

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M.Sc. in Food Engineering

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Functional chocolate is a new trend that the food-grade ingredients are used in and is preferred by consumers due to flavour or other beneficial nutritive constituents. The aim of this study is to examine the effect of dried bergamot peel powder on the structural properties of dark chocolate such as the solid fat content, melting point and textural and sensory properties of chocolate. Bergamot peel powder has been added to dark chocolate with the percentages of 0.75%, 1.00%, and 1.25%. The melting points of the three samples did not change significantly on DSC plots and were around 32°C which was the same melting temperature of the standard dark chocolate. At the 0th, 15th, 30th and 365th days, melting points were in the range of 31.3°C – 32.5°C. SFC analysis results of bergamot dark chocolate samples showed that % solid fat content were not significantly different at different temperatures. Hardness of the chocolate samples were analyzed by Texture Analyzer and the analysis showed that the bergamot dark chocolate samples were harder than the standard dark chocolate. The reason for this is thought to be the reduction in the percentage of cocoa mass added to chocolate recipe and the fibrous nature of bergamot peel. The samples were evaluated by trained panellists. In this sensory analysis, a difference in flavour was clearly perceptible between the standard sample and bergamot chocolate samples. All the panellists noted that the bergamot flavour was felt dominantly on all three samples. Consequently, use of bergamot peel powder at minimal ratios didn't affect the melting point and solid fat content of chocolate, but it increased the hardness and strengthened the flavour on a severe level.

Key Words: Bergamot, Chocolate, Dark Chocolate, Cocoa, Sensory Analysis

ÖZET

KURUTULMUŞ BERGAMOT KABUĞU TOZUNUN BİTTER ÇİKOLATANIN YAPISAL ÖZELLİKLERİ ÜZERİNE ETKİLERİ

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62 sayfa

Fonksiyonel çikolata, içinde gıdaya uygun girdiler kullanılan, aroması ya da diğer yararlı besleyici bileşenleri sebebi ile tüketiciler tarafından tercih edilen yeni bir trenddir. Bu çalışmanın amacı, kurutulmuş bergamot kabuğu tozunun bitter çikolatanın katı yağ içeriği, erime noktası, dokusal ve duyuşal özellikleri gibi yapısal özellikleri üzerine etkisini incelemektir. Bergamot kabuğu tozu bitter çikolataya %0.75, %1.00 ve %1.25 oranlarında eklenmiştir. DSC grafiklerinde çikolata örneklerinin erime noktalarının önemli derecede değişmediği, standart bitter çikolata ile erime noktalarının benzer ve 32°C civarında olduğu görülmüştür. Çikolataların 0., 15., 30. ve 365. günlerde DSC analizleri yapılmış ve erime noktalarının 31.3°C – 32.5°C aralığında olduğu görülmüştür. Bergamotlu bitter çikolata örneklerinin SFC analizleri, % katı yağ içeriğinin farklı sıcaklıklarda önemli düzeyde farklı olmadığını göstermiştir. Standart ve bergamotlu bitter çikolataların tekstür analizi, bergamotlu bitter çikolataların standart örnekten daha sert olduğunu göstermiştir ve sebebinin ise reçeteye eklenen % kakao kitlesindeki azalmadan ve bergamot kabuğunun lifli yapısından kaynaklanabileceği düşünülmüştür. Bergamotlu çikolata örnekleri eğitimli panelistler tarafından duyuşal panel ile değerlendirilmiş ve tattaki farklılık, standart numune ve bergamotlu çikolata örnekleri arasında net şekilde algılanmıştır. Tüm panelistler, bergamot tadının üç numunede de baskın şekilde hissedildiğini belirtmiştir. Sonuç olarak, bergamot kabuğu tozunun düşük yüzdeli oranlarda kullanılması; çikolatanın erime noktası ve katı yağ içeriğini etkilememiş, diğer yandan sertliğini arttırmış ve lezzetin şiddetli düzeyde güçlenmesini sağlamıştır.

Anahtar Kelimeler: Bergamot, Çikolata, Bitter Çikolata, Kakao, Duyusal Analiz



to my dear uncle Erdoğan BAYDIK...

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
DSC	Differential Scanning Calorimetry
NMR	Nuclear Magnetic Resonance
PGPR	Polyglycerol Polyricinoleate
SFC	Solid Fat Content
TPA	Texture Profile Analysis

CHAPTER I

INTRODUCTION

1.1 General Objective

Chocolate is one of the most popular confectionery products in the world. There are a lot of well-known chocolate varieties such as nut chocolate, flavoured or filled chocolate and wafer chocolate etc. However, mainly there are three types of chocolate which are milk chocolate, bitter (dark) chocolate and white chocolate. This diversity originates from the usage of different ingredients in chocolate. Chocolate is a very sensitive product due to the cocoa butter, cocoa mass and sugar content. It is possible to produce new chocolate types by changing the ingredients and this helps develop the confectionery industry.

Confectionery industry is developing day by day. This allows consumers to see many new products on the market shelves. The increase in the number of product types serves as a refreshment in the markets. However; the point here is that, these products should have something unique in order to be preferred and purchased by customers. There are a lot of factors that buyers usually consider in the process of choosing a product which are appearance, first experience, good taste etc. However, people are more interested in the ingredients of the food products nowadays. This situation shows that consumers are now more conscious and want to know what they are eating. Therefore the purchased food products must be healthy and produced with food-grade ingredients. Unnatural ingredients, artificial or synthetic aromas are not preferred by consumers. Food-grade aromas make people feel healthier and fruit can be evaluated as one of the healthiest aroma enhancers.

According to the information mentioned above bergamot peel powder was chosen as a food-grade aroma for dark chocolate. Bergamot is a fragrant fruit and its peel has a pungent odour.

This thesis researches the effect of dried bergamot peel powder on the structural properties of dark chocolate. Raw materials of the dark chocolate are cocoa mass,

cocoa butter, sugar, alkalized cocoa, vanillin, soy lecithin, PGPR (Polyglycerol polyricinoleate) and bergamot peel powder. Milk powder is not used in dark chocolate.

Chocolate has a long and onerous process to fulfill the consumers' expectations and to make them happy. In this study, bergamot peel powder has been added to the chocolate with three different percentages. The aim of this research was to determine how the addition of bergamot peel powder affects the solid fat content (SFC), differential scanning calorimetry (DSC), textural and sensory properties of chocolate.



CHAPTER II

LITERATURE SUMMARY

2.1 Dark Chocolate

The production process of dark chocolate is the same with milk chocolate. However, dark chocolate does not contain milk powder. This is the main difference between them. Dark chocolate can be produced with three different percentages of cocoa mass. The bitter taste of chocolate increases proportionally when the cocoa mass amount increases in chocolate. Dark chocolate contains min. 18% cocoa mass, min. 14% cocoa butter and minimum 35% cocoa solids totally, the other ingredients are; sugar, alkalized cocoa, vanillin, soy lecithin, PGPR (Polyglycerol polyricinoleate).

2.2 History of Chocolate

According to Caobisco, “chocolate is a long and passionate history”.¹

In the UK in 1847, cocoa butter was used as an ingredient by Joseph Fry who was the first to produce a plain dark chocolate bar (Beckett, 2000). In 1828 by Van Houten, after the increasing of demand for cocoa, chocolate processing became mechanised with development of cocoa pressing to produce cocoa butter and cocoa powder. Henri Nestlé had the idea of adding milk powder as an invention. After these developments the invention of the conching machine was inevitable, in 1880 Rudolphe Lindt invented it. Thus, which is now associated with good-quality chocolate the chocolate came to take on the fine taste and creamy texture. Chocolate was still very much an exclusive product until 1900, then it became accessible to the middle class by dropping considerably the price of chocolate’s two main ingredients, cocoa and sugar (Beckett, 1994; Afoakwa, 2010).

2.3 World Production and Consumption of Cocoa and Chocolate Products

Producing chocolate is a complex process and it requires numerous technological operations. Understanding the technological processes and the science of chocolate

¹ www.caobisco.com (29.10.2017)

production that can lead to the expected product quality is paramount. Also, adding pre-specified ranges of ingredients into the products give them suitable physical and chemical attributes, taste parameters and appearance which are other quality paramounds. In addition, chocolate processing differs due to historical development within producing companies and geographical locations in which products are sold. Therefore it requires the necessary expertise to achieve the required quality attributes, rheological characteristics, flavour development and thus sensory perception that are needed to satisfy a specified consuming population (Afoakwa, 2010). Consuming preference changes from person to person. Some people like milky taste while the others like bitter taste.

2007 International Confectionery Association results on per capita consumption of chocolate by country are given in Figure 2.1. For our country, the consumption percentage is at fairly low levels although there are a lot of chocolate factories in Turkey. The brands manufacture a lot of kinds of chocolate which are special for children and adults. Except the daily consumption, chocolate is indispensable for the food festivals, celebrations and especially for religious holidays in Turkey.

Dark chocolate demand is increasing and currently accounts for 8–10% of global chocolate tablet sales. It was reported in 2006 that 33% of chocolate products launched were dark chocolate confectionery. Dark chocolate consumption in the US increased at about 9% per annum over the period 2001–2005. Dark chocolate popularity is also related to research findings on positive effects of cocoa and chocolate on cardiovascular health (Afoakwa, 2010)

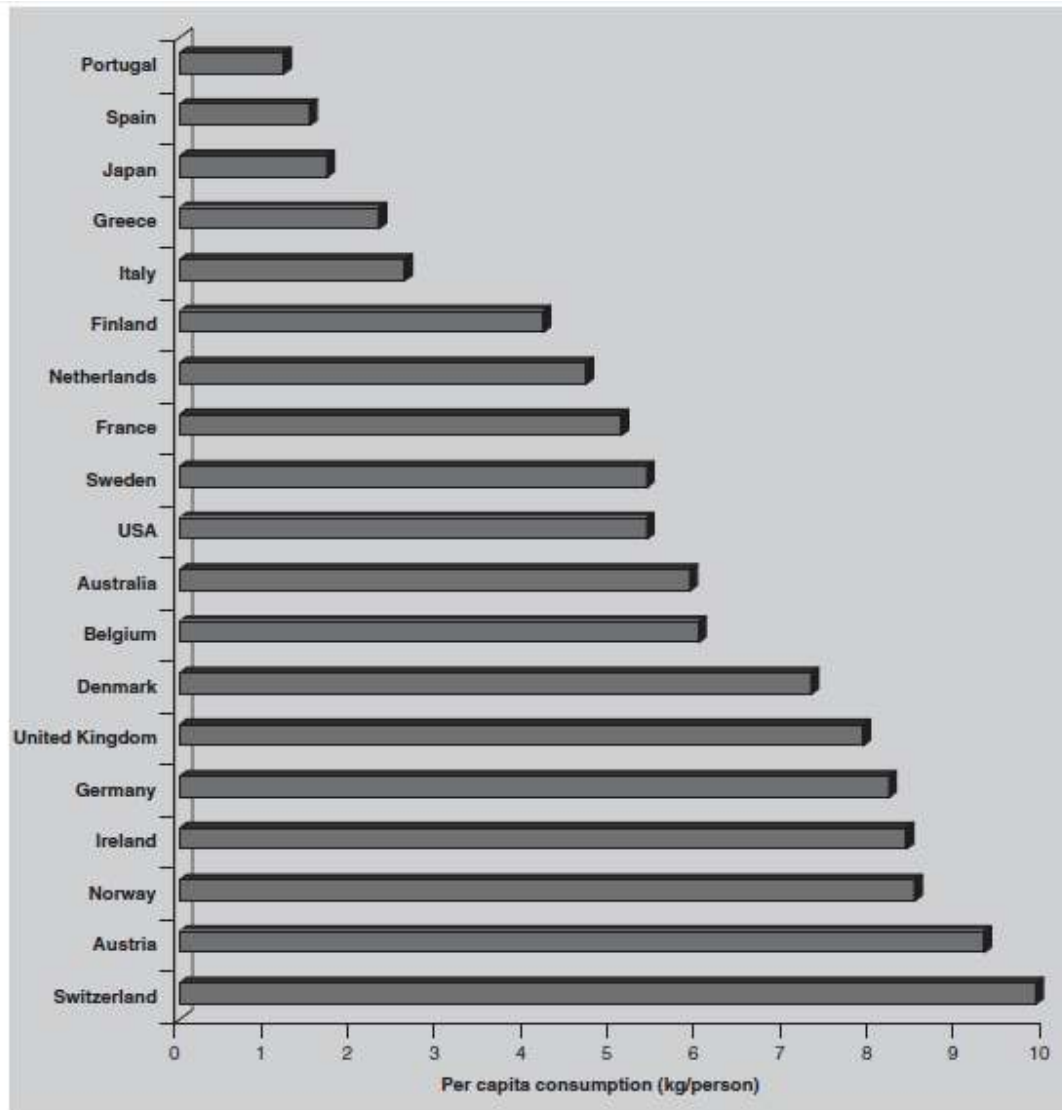


Figure 2.1 Per capita consumption of chocolate by country (International Confectionery Association, 2007)

2.4 Raw Materials of Dark Chocolate with Bergamot Peel Powder

The raw materials of dark chocolate are cocoa mass, cocoa butter, sugar, vanillin, soy lecithin, PGPR and bergamot peel powder. There are a lot of kinds of dark chocolate, the difference can come from the usage of different percentages of cocoa mass. When cocoa mass amount increases, feeling of bitter taste in chocolate increases too. However, dark chocolate can be produced with food-grade additives like nuts, dried fruit particles (orange, raspberry, strawberry etc.) or powder and their peel powder. In this study, bergamot peel powder has been used as an additive for dark chocolate.

2.4.1 Cocoa Liquor (Cocoa Mass)

Cocoa liquor is one of the main ingredients of chocolate. Cocoa liquor is produced from aromatic cocoa beans. The cocoa beans are firstly fermented. The fermentation process is important for the development of colour and flavour. After fermentation, the beans are cleaned, winnowed and ground between plates; after this process, cocoa liquor and cocoa press products are obtained (Lees and Jackson, 1973).

Dark chocolate is desired to have a stronger cocoa aroma than other types of chocolate. At this point, quality of cocoa beans and the amount of cocoa liquor are considered as the most important factors for the creation of the bitter sense (Lees and Jackson, 1973).

2.4.2 Cocoa Butter

Cocoa butter is produced by hydraulic pressing of the cocoa liquor. Cocoa liquor contains about 55% cocoa butter. As in other oil / fat production processes, cocoa butter is deodorized too. Deodorization process affects the final chocolate by controlling flavour and free fatty acids (AAK Academy, 2016).

The role of cocoa butter is to surround the non-fat components, which is the continuous lipid phase in chocolate (Smith, 2001). Cocoa butter affects chocolate properties, such as appearance, snap, gloss, mouth feel, flavour, fastness and completion of the melting in the mouth and hardness at room temperature. Furthermore, it also affects processing conditions, such as tempering and cooling, depend on characteristics of cocoa butter (Bootello et al., 2012).

Cocoa butter crystallizes in six different polymorphic forms of which βV and βVI are the most stable. In chocolate production, the crystal form βV is the desirable form preferred by consumers, not only for its melting characteristics, but also its hardness (Wille and Lutton, 1966).

2.4.3 Sugar

Granulated sugar is not used directly in chocolate. If the sugar has previously been milled, a better quality chocolate will be produced. Milling of sugar is important for the texture of chocolate and it impacts the particle size and melting quality. If the sugar content is increased, the fat content should be decreased to maintain the desired viscosity of chocolate. (Lees and Jackson, 1973)

2.4.4 Vanillin

Vanillin is one of the numerous compounds of vanilla extract. It can be made synthetically from eugenol and ligninsulfon acid and it is widely used in confectionery products. Vanillin and ethyl vanillin can be used in fillings at concentrations up to 0.05%. It is used to strengthen the flavour of chocolate (Talbot, 2009).

2.4.5 Soy Lecithin

Soy lecithin is produced from soybean. Lecithin is used as an emulsifier to reduce the viscosity of chocolate. A little amount of lecithin is enough instead of adding more cocoa butter. It is a highly recognized fact that it is preferred by chocolate manufacturers because of the high cost of cocoa butter (Lees and Jackson, 1973).

2.4.6 PGPR (Polyglycerol polyricinoleate)

PGPR contains polymerized ricinoleic acid that is a derivation of castor oil with polymerized glycerol. PGPR usage can be considered as an advantage for chocolate, because it minimally affects plastic viscosity while it reduces yield stress. Therefore, flowing and filling of chocolate gets easier. If it is used with lecithin, it reduces the need for cocoa butter in chocolate and supplies lower fat content. Also, it provides lower energy consumption on processing (Hartel et al., 2018).

2.4.7 Bergamot Peel

Bergamot fruit belongs to a tree of the Genus Citrus, class Polyadelphia, order Icosandria, it is named by Linneus in his system Citrus aurantium. According to Tree Hughes, bergamot is originated from the Barbados highlands. The origin of this tree is not known. It is generally used to extract the essential oil from the fruit. (Calabrò Anzalone, 1804).

Linalool and linalyl acetate, which are the major components of bergamot oils, have important flavor characteristics (Arctander 1969). Both of these compounds contribute fresh, floral, fruity, woody notes and also exhibit lavender attributes. Linalool has a creamy, floral taste. Linalyl acetate has a fruity, sweet, pear-like taste (Dugo and Bonaccorsi. 2014).

Some recipes for cakes and cookies call for bergamot peel, but the peel is difficult to obtain, so the bergamot oil is used as a substitute for the peel (Dugo and Bonaccorsi. 2014). In this study, bergamot peel was directly used as an ingredient for dark chocolate.



CHAPTER III

MATERIALS AND METHODS

3.1 Materials

Most of the incomes, which can be listed as cocoa mass, cocoa butter, sugar, vanillin, lecithin and pgpr, were supplied from Şölen Çikolata, which is a chocolate factory in Gaziantep. Fresh bergamot was purchased from a local market in Antalya. The bergamots were firstly peeled into small pieces, the peels were dried in a laboratory at room temperature and then ground. There are 3 recipes of dark chocolate with bergamot peel powder. Amount of the bergamot peel powder added into the chocolate was kept low while determining the percentage of it. The reason why it was done so, was because the aroma of bergamot peel is very strong.

Four dark chocolate recipes are formulated on Table 3.1, Table 3.2, Table 3.3 and Table 3.4.

Table 3.1 Formulation of standard dark chocolate without bergamot peel powder

Ingredients	% (w/w)
Cocoa mass	38.00
Cocoa butter	21.50
Sugar	39.88
Vanillin	0.10
Lecithin	0.30
PGPR	0.22
Bergamot	0.00

Table 3.2 Formulation of dark chocolate with 0.75% bergamot peel powder

Ingredients	% (w/w)
Cocoa mass	37.25
Cocoa butter	21.50
Sugar	39.88
Vanillin	0.10
Lecithin	0.30
PGPR	0.22
Bergamot	0.75

Table 3.3 Formulation of dark chocolate with 1.00% bergamot peel powder

Ingredients	% (w/w)
Cocoa mass	37.00
Cocoa butter	21.50
Sugar	39.88
Vanillin	0.10
Lecithin	0.30
PGPR	0.22
Bergamot	1.00

Table 3.4 Formulation of dark chocolate with 1.25% bergamot peel powder

Ingredients	% (w/w)
Cocoa mass	36.75
Cocoa butter	21.50
Sugar	39.88
Vanillin	0.10
Lecithin	0.30
PGPR	0.22
Bergamot	1.25

3.2 Methods

Chocolate manufacturing is a hard and long process. Cocoa and chocolate production flow charts are shown step by step in Figure 3.1.

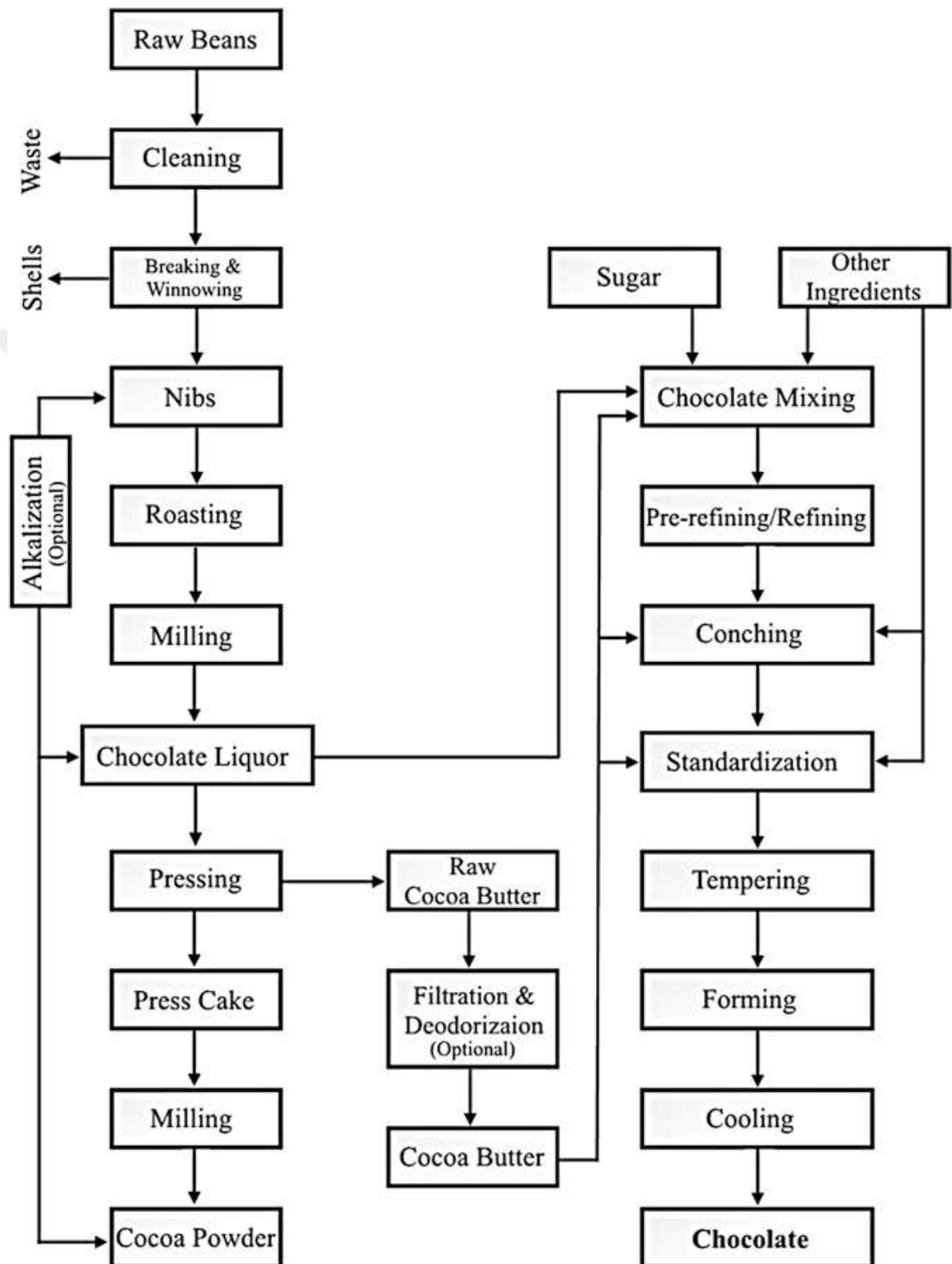


Figure 3.1 Processing steps for cocoa and chocolate manufacture (Hartel et al., 2018)

3.2.1 Mixing, Refining and Particle Size

Ingredients are mixed and then added to refiner. Refining process is important for smooth texture of chocolate. For refining process two-roll and five-roll refiners are used. Two-roll refiner is the first step of refining, and it is also named as pre-finer.

The chocolate mixture is refined to particle size of less than 30 μm normally. Rheological and sensory properties of chocolate are significantly influenced with final particle size (Afoakwa, 2010).

Moulding and enrobing processes need a good flow behaviour of chocolate, the particle size distribution affect the flow behaviour. For end product, when the particle size becomes smaller, the appearance of chocolate becomes lighter (Beckett, 1999).

In summary, particle size affects melting, taste, texture, viscosity and glossiness of chocolate. The mixtures of standard dark chocolate and bergamot dark chocolate were refined to a particular size of about 18 – 22 μm by Bühler SDY 200 refiner.

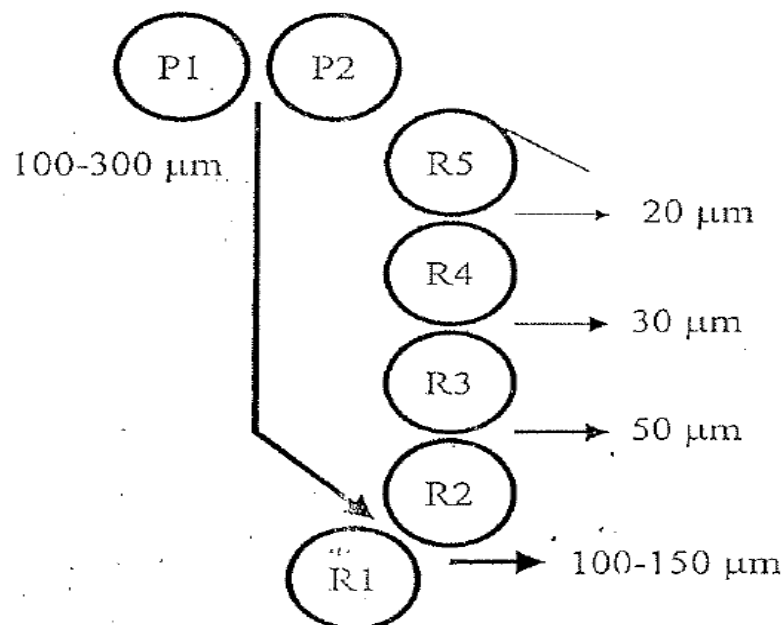


Figure 3.2 Schematic diagram of a five roll refiner, P1 and P2 show the previous two-roll refiner (Beckett, 1999)

3.2.2 Conching Process of Dark Chocolate with Bergamot Peel Powder

Conching aims at removing the undesired volatiles such as butyric and propionic acids, reduction of moisture, splitting agglomerates, covering solid particles with fat and improving the flowability and also giving to final product a softer, more pleasant taste. (ZDS practice course in Chocolate Confectionery, 2009)

Refined chocolate flaky (chocolate mix) was received to 5 kg-capacity laboratory-scale conching machine which is ELK single-shaft conche, Bühler, AG, Switzerland. The temperature and rotation speed was set to the machine.

There are 3 steps of conching process which are shown in Figure 3.3. On the first step, which is dry conching, the flaky was rotated for 1 hour at a temperature of 45°C and the rotation speed was 1200 rpm. By the starting of the second step that is pasty phase (or plasticizing), the temperature and rotation speed increased fractionally. The pasty phase realized at 70-80°C range for 4 hours and the rotation speed was in the range of 1300-1900 rpm. On the third step which is liquid conching, the rotation speed was firstly increased up to 2000 rpm, but at the same time the temperature was decreased. Then, the rotation speed decreased to 750 rpm whereas the temperature was decreasing to 45°C. This last step (liquid conching) took 45 minutes.

Conching process affects the final product at different points.

Conche-open and low temperature (~ 65°C) produce a milky flavor, but conche-closed and high temperature (~ 80°C) process produces caramel taste in chocolate. (ZDS practice course in Chocolate Confectionery, 2009)

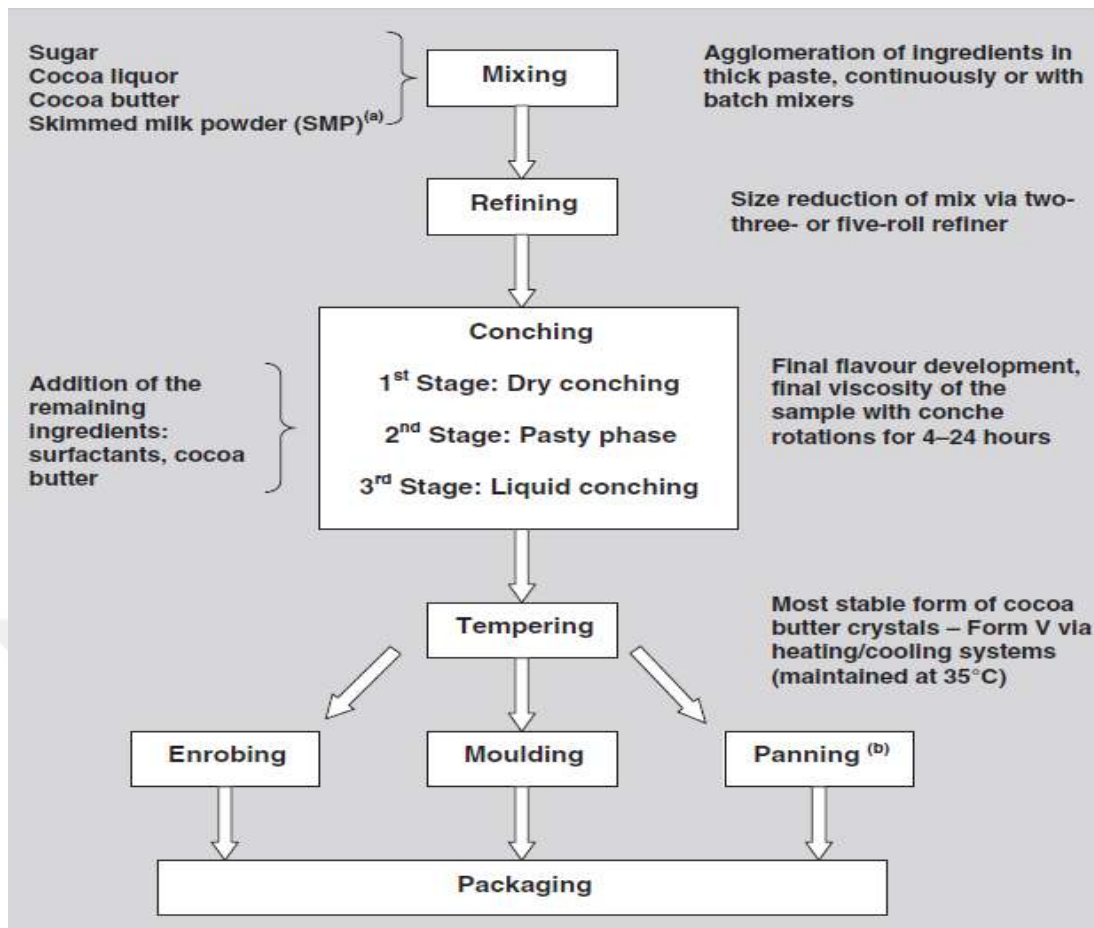


Figure 3.3 Process flow for chocolate manufacture with the details of the production steps (Afoakwa et al, 2007a)

3.2.3 Tempering Process

Tempering process is necessary to ensure a long shelf-life for chocolate. This is a method of inducing cocoa butter to crystallize in a stable form in the fluid chocolate mass. If the chocolate is tempered incorrectly, it has inadequate stability, poor gloss and a short shelf-life. Insufficiently tempering process causes blooming problem. The first one is fat blooming; unstable fat crystals develop on the surface of the chocolate. The second one is sugar blooming which arises from crystallization on the surface of the chocolate. A successful tempering process depends on these factors: viscosity, composition of chocolate, temperature, state of temper and the composition of center (if it is enrobed). State of temper simply means the stable crystal amount in melted chocolate (Lees and Jackson, 1973).

Untempered chocolate also causes demoulding problems (Talbot, 2009).

The melting characteristic of dark chocolate is very important in order to evaluate the effects of cocoa butter polymorphism. Well-tempered chocolate has a glossy appearance, good snap, contraction and resistance to bloom (Beckett, 2000).

There are six complex polymorphic forms which are named as Roman numerals I through VI of cocoa butter (Wille and Lutton, 1966) and are given in Table 3.5. For a well-tempered chocolate, β polymorph form V is the most desirable one. In cocoa butter Forms V and VI are the most stable forms. Form VI has the highest melting point (36°C) and its crystals are large and gritty on the tongue. The unstable Form I melts at 17°C and is rapidly converts into Form II that transforms more slowly into III and IV. During the production process, tempering is usually conducted at set temperature and time regime to get the desirable β V crystal form with melting temperature of 32°C - 34°C which is preferred in chocolate to impart the desired good snap, glossy appearance and sensory mouth-feel (Talbot, 2009).

Table 3.5 Melting points and chain packing of the polymorphic forms of cocoa butter (Talbot, 1999 and Afoakwa et al., 2007a)

Polymorphic forms of cocoa butter		Melting point (°C)	Chain packing
Form I	β'_2	16–18	Double
Form II	α	21–22	Double
Form III	Mixed	25.5	Double
Form IV	β_1	27–29	Double
Form V	β_2	32–34	Triple
Form VI	β'_1	34–36	Triple

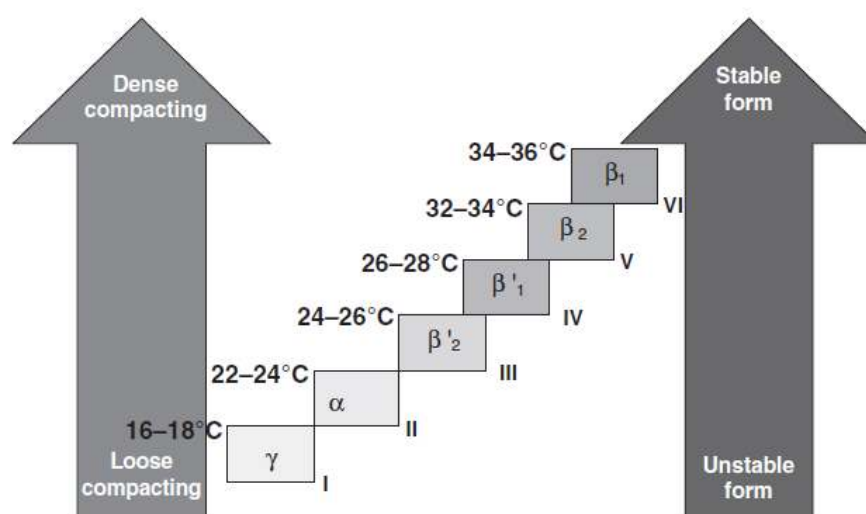


Figure 3.4 Temperature regimes and degree of stability in six polymorphic forms of cocoa butter (Beckett, 2008)

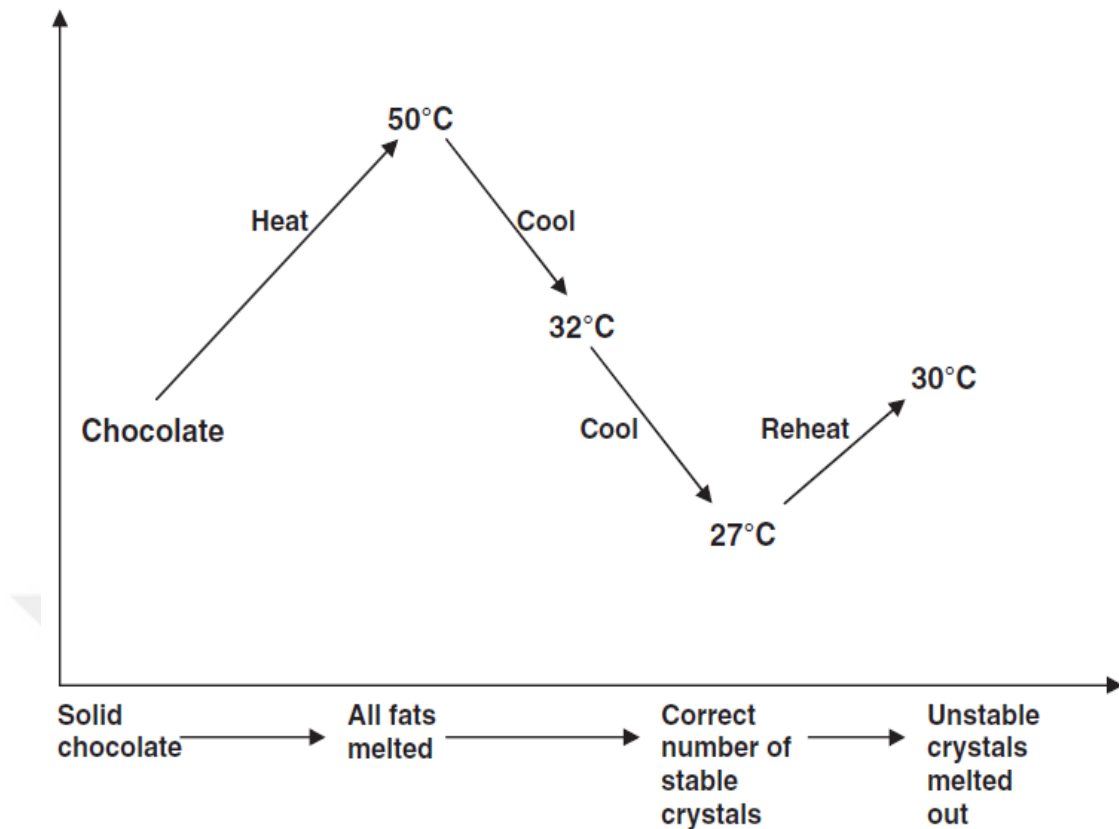


Figure 3.5 Tempering sequence during lipid crystallization in chocolates (Afoakwa, 2010)

In laboratory conditions, GAMI s.r.l. t240 temper machine was used to temper the chocolate samples. Standard dark chocolate and the other 3 bergamot dark chocolate samples were tempered at a temperature of 28-32°C. After tempering process, temper indexes of all the samples were measured by Bühler Multitherm TC tempermeter. The tempermeter curves showed that the temper indexes of all the samples were in the range of 5.1 – 5.3. The desirable temper index is 4-6 in general in chocolate sector, but it can differ from type to type, and it is also related to how a final product is desired.

3.2.4 Moulding Process

Moulding is a synchronous process with tempering. Tempered chocolate is deposited to moulds in determined amounts. Then it is shaped and hardened by cooling. Moulds are used to give shape to liquid chocolate. Chocolate moulds can be made of rubber, plastic or special polycarbonate materials.

For moulding process, the cycle starts with heating of the moulds to a temperature which approaches to temperature of the tempered chocolate. Then, the moulds receive the chocolate from depositors and subjected to violent vibration. The purpose of vibration process is to remove air bubbles from the bottom of the mould because, after demoulding, the bottom side will be the face of chocolate, and if the air bubbles are not removed, the chocolate would have an uneven appearance (Minifie, 1989).

Bergamot dark chocolate samples were moulded and vibrated by hand in laboratory conditions. Moulded chocolates were cooled at about 9-12°C for 15-20 minutes.

Moulds with chocolate or water (caused of washing) remnants, insufficient cooling or tempering and incorrect cooling temperatures cause an undesirable appearance of chocolate. For chocolate sector; besides the taste of chocolate, appearance and glossiness are the most important factors that affect the system to attract the customers.

3.2.5 Differential Scanning Calorimetry (DSC) Analysis

Differential Scanning Calorimetry (DSC) is a well-established measuring method and it is used in different areas of quality inspection, testing, research and development. DSC ensures to identify thermal characteristics and the relevant temperature also the characteristic calorie values can be determined using substance quantities in the milligram range. DSC curves work to identify substances. The DSC curve is a plot of heat flow against temperature (Rehbein and Oehlenschläger, 2009).

Differential Scanning Calorimetry is a thermal analytical technique which is used to determine the thermal characteristics. It also looks at the heat capacity changes (C_p) of a material by temperature.

Mass sample is heated or cooled during this analysis, the changes in the heat capacity of the sample are tracked as changes in the heat flow. Thus, curing, phase changes, melts etc. transitions are detected by the analysis.

In this study for DSC analysis, Mettler Toledo DSC822e differential scanner calorimeter was used. Approximately 10 mg chocolate sample was placed to 40 μ l aluminium pan. Start temperature was -3°C, end temperature was 50°C and the heating rate was 4°C/min. Nitrogen (N_2) gas was used as the segment gas.

3.2.6 Solid Fat Content (SFC) Analysis

Solid Fat Content analysis is a method to determine the percentage of solids in fat at specified temperatures. Fat-based products or blended masses with solid fat can be characterized according to their melting profiles.

In chocolate industry “melting in mouth” factor is important for producers and consumers. However, the cocoa butter is the main ingredient of chocolate and its triglyceride composition has specific fatty acid contents. There are three predominant fatty acids which are palmitic acid (C 16:0, P), stearic acid (C 18:0, St) and oleic acid (C 18:1, O) in cocoa butter. By combining these fatty acids three dominant symmetrical triglycerides are obtained, namely 2-oleodipalmitin (POP), 2-oleopalmitostearine (POSt) and 2-oleodistearine (StOSt), which highly resemble each other and constitute almost 80% of cocoa butter, determining its specific crystallization attributes (Torbica et al., 2005). At this point, crystallization and melting of cocoa butter have a big role.

In this study, Bruker mq20 NMR analyser was used. Solid fat content analysis results were aimed to show whether the added bergamot peel has any solid fat content, or not. Firstly, cocoa butter was separated from the chocolate samples by cold centrifuging method. Approximately 10 mg of cocoa butter which could contain a little amount of bergamot peel oil samples were transferred into tubes. Firstly, the tubes were conditioned in 60°C water bath for 1 hour. Then, the tubes were taken to 0°C water bath and conditioned for 1.5 hours. After this step all the tubes were transferred to 26°C water bath and the samples were kept here for 40 hours. All the samples were again transferred to 0°C water bath and conditioned here for 1.5 hours. Lastly, the tubes were transferred to different water baths which are at temperatures between the ranges from 10°C to 40°C. For water bath, Lauda RE104 branded equipments were used.

3.2.7 Texture Profile Analysis (TPA)

According to Brookfield Engineering, “Texture analysis is primarily concerned with the evaluation of mechanical characteristics where a material is subjected to a controlled force from which a deformation curve of its response is generated. These mechanical characteristics in food can be further sub-divided into primary and

secondary sensory characteristics which have proven to be correlated to sensory perception.”²

There are numerous deformation testing methods for food products, they aim to simulate the events of chewing or biting.

Hardness of the chocolate samples was measured using TA-XT plus Texture Analyser (Stable Micro Systems Ltd, Godalming, Surrey, UK) with the Texture Exponent 32 programme. This analysis gives a force versus time graph. The peak shows the force peak resulting from each breaking cycle. The hardness of the product is determined according to the peak point in the graph. The product with high peak point is a harder product.

In this analysis, hardness of products was measured using TA-XT Plus Texture Analyzer with a penetration 2 mm probe (needle P/2) attached to an extension bar and a 5-kg load cell and a platform. Test speed was set to be 0,5 mm/sec, distance was 3 mm and Trigger force was 5 g. This analysis was repeated twice for each kind of 4 chocolate samples. 3 of these samples were bergamot dark chocolate which had different ratios of bergamot, 4th sample was the standard dark chocolate with the same recipe but without bergamot. The chocolate samples were stored in a room which was 18°C until analysing. Each sample was taken to the 22°C conditioned room and analysed without waiting.

3.2.8 Sensory Analysis

Sensory analysis is the scientific measurement, interpretation, analysis and the identification of the properties of a product and they are perceived through the five senses of smell, sight, taste, touch and hearing (Carpenter et al., 2000).

For consumers, while buying a food product, flavour, appearance, aroma, and texture are very important characteristics. In case of the consumers' acceptability for chocolate unique sensory properties are the most important. Especially, textural characteristics such as smoothness hardness and meltiness have a big role in the sensory assessment of chocolate (Viane and Januszewska, 1999). To investigate the effects of ingredients and processing variables on the final sensory quality of a food product, different sensory analysis methods can be used (Murray et al., 2001) For

² www.brookfieldengineering.com (12.09.2018)

sensory evaluation, descriptive techniques are frequently used as the most appropriate method. Descriptive sensory analysis helps identifying underlying ingredient and process variables and enables us to obtain complete sensory description of products. These techniques can provide complete sensory description of products, determine how ingredient or process changes affect product characteristics, and identify key sensory attributes that promote product acceptance (Phang and Chan, 2009).

Beside the descriptive analysis, a scoring method is also a useful procedure for the assessment of products' to define the quality level. There are a lot of comparison methods for sensory analysis. In this study, the 5-point hedonic scale method was used. The following points were taken into consideration when selecting the panellists: interest to chocolate manufacturing and development. Also the panellists had no chocolate craving, allergies or intolerance against dark chocolate.

The bergamot dark chocolate samples with 3 different formulations were encoded with random three-digit numbers. The samples were served with a white plate. Each plate was divided into 3 parts and numbers were written on these parts. Each chocolate sample had the same shape and appearance, was placed to the related number part in the plate. Sensory panel was set at room temperature (21-23°C).

Sample scoring form which is given in Figure 3.6 was prepared to record the scores given by the panellists to score the samples and write their opinions.

SENSORY EVALUATION PANEL FORM																	
PANEL NAME	 Panel Test																
Presentation	A sample chocolate product is given to you to evaluate in terms of taste and flavour.																
Question	Compare the dark chocolate samples given to you according to the following criteria and score them 1 to 5 points. Your comments are very important for us, do not forget to write your comments!																
		<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;">PANELIST NAME</td> <td style="width: 50%; padding: 5px;"></td> </tr> <tr> <td style="padding: 5px;">PANEL DATE</td> <td style="padding: 5px;"></td> </tr> </table>	PANELIST NAME		PANEL DATE		<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;">TYPE OF PANEL</td> <td style="width: 50%; padding: 5px;"></td> </tr> <tr> <td style="padding: 5px;">Single Product Test</td> <td style="padding: 5px;"></td> </tr> <tr> <td style="padding: 5px;">Triple Test</td> <td style="padding: 5px; text-align: center;">X</td> </tr> <tr> <td style="padding: 5px;">Triangle Test</td> <td style="padding: 5px;"></td> </tr> </table>	TYPE OF PANEL		Single Product Test		Triple Test	X	Triangle Test			
PANELIST NAME																	
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TYPE OF PANEL																	
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<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td colspan="2" style="padding: 5px;">Scoring</td> </tr> <tr> <td style="width: 30%; padding: 5px; text-align: center;">441</td> <td style="width: 70%; padding: 5px; text-align: center;">535 656</td> </tr> </table>		Scoring		441	535 656	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 10%; padding: 5px; text-align: center;">1</td> <td style="width: 90%; padding: 5px;">I didn't like it at all</td> </tr> <tr> <td style="padding: 5px; text-align: center;">2</td> <td style="padding: 5px;">I didn't like it.</td> </tr> <tr> <td style="padding: 5px; text-align: center;">3</td> <td style="padding: 5px;">I neither liked nor disliked it</td> </tr> <tr> <td style="padding: 5px; text-align: center;">4</td> <td style="padding: 5px;">I liked it.</td> </tr> <tr> <td style="padding: 5px; text-align: center;">5</td> <td style="padding: 5px;">I liked it a lot.</td> </tr> </table>		1	I didn't like it at all	2	I didn't like it.	3	I neither liked nor disliked it	4	I liked it.	5	I liked it a lot.
Scoring																	
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1	I didn't like it at all																
2	I didn't like it.																
3	I neither liked nor disliked it																
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<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px; text-align: center;">Taste of the Product</td> <td style="width: 50%; padding: 5px;"></td> </tr> <tr> <td style="padding: 5px; text-align: center;">General Taste</td> <td style="padding: 5px;"></td> </tr> </table>	Taste of the Product		General Taste														
Taste of the Product																	
General Taste																	
PANEL RULES 1. In comparative product panel tests, product samples will be evaluated both within themselves and against each other. 2. Tasting of the samples should be done immediately after their presentation to you in panel room. Tastes should not be done immediately after eating or after smoking. Please rinse your mouth with water between tastes of different samples.																	

Figure 3.6 Sensory analysis scoring form for panellists

3.2.9 Statistical Analysis

The statistical software package, Statistica version 8.0 (StatSoft, Inc., Tulsa, OK USA) was used for regression analysis of the experimental data. One-way ANOVA (analysis of variance) test was carried out to estimate the statistical parameters. By the analysis, p-values were checked to see the difference between bergamot dark chocolate samples. One-way ANOVA test was carried out for differential scanning calorimetry peak point results, solid fat content analysis results and sensory analysis results.

For texture profile analysis, average results of trials were calculated to see the needed force and brittleness of bergamot dark chocolate samples.

Spider plot was created to see the given scores of panellists for each bergamot dark chocolate sample.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Differential Scanning Calorimetry (DSC) Analysis

Differential scanning calorimetry analysis was performed on standard dark chocolate and the 3 bergamot dark chocolate samples. Standard dark chocolate was analysed with others, because it was considered as a reference to comment on other plots. The analysis was made on 0th day and then repeated on 15th, 30th and 365th days of chocolate samples. The plots were presented between Figure 4.1 and Figure 4.16.

DSC plots are time vs. temperature graphs. The peak point shows the starting of chocolate's melting point. All the values were compared in Table 4.1.

The melting points of the three chocolate samples did not change significantly on DSC plots and were around 32°C which was the same melting temperature of the standard dark chocolate. On the 0th, 15th, 30th and 365th days, melting points were in the range of 31.3°C – 32.5°C and all other plots were notably alike.

The results showed that the minimal change of raw materials do not affect the melting point of chocolate because its cocoa butter composition decreased at a minimal level and also the bergamot oil did not affect the chocolate fat composition.

Table 4.1 DSC analysis results comparison chart of the chocolate samples at 0th, 15th, 30th, 365th days

SAMPLE NAME and %	time	onset	peak	endset	left limit	right limit
STANDARD DARK CHOCOLATE SAMPLE	0th day	30.46	31.78	33.90	24.72	35.02
	15th day	31.50	32.22	33.44	26.51	34.34
	30th day	31.41	32.20	33.62	26.24	34.42
	365th day	31.17	32.02	34.53	24.99	35.48
0.75% BERGAMOT DARK CHOCOLATE SAMPLE	0th day	29.69	31.37	33.89	24.64	34.90
	15th day	30.81	32.04	33.73	25.83	34.68
	30th day	31.40	32.26	34.10	26.64	35.02
	365th day	31.60	32.42	34.54	24.75	35.61
1.00% BERGAMOT DARK CHOCOLATE SAMPLE	0th day	31.02	31.67	34.21	24.70	34.96
	15th day	30.27	31.68	33.82	26.66	34.90
	30th day	31.48	32.49	34.30	26.43	35.34
	365th day	29.56	31.72	33.52	23.73	34.65
1.25% BERGAMOT DARK CHOCOLATE SAMPLE	0th day	30.88	31.90	34.13	24.53	34.85
	15th day	29.64	32.22	33.52	25.95	34.57
	30th day	30.55	32.19	34.40	26.59	35.51
	365th day	30.79	32.37	34.59	24.22	35.78

In addition to the information given above an One-Way ANOVA test was carried out to prove the H_0 .

H_0 : There is no significant difference among the differential scanning calorimetry analysis peak point results of dark chocolate samples with bergamot content on the 0th, 15th, 30th and 365th days.

H_1 : There is a significant difference among the differential scanning calorimetry analysis peak point results of dark chocolate samples with bergamot content on the 0th, 15th, 30th and 365th days.

Table 4.2 One-Way ANOVA Test for the Differential Scanning Calorimetry
Analysis Peak Point Results

Effect	SS	Degree of Freedom	MS	F	p
Intercept	16,419.22	1	16,419.22	144,580.45	0.00
Sample	0.16	3	0.05	0.47	0.71
Error	1.36	12	0.11		

According to the results observed in Table 4.2, there is no significant difference among the differential scanning calorimetry analysis peak point results of dark chocolate samples with bergamot content on the 0th, 15th, 30th and 365th days ($p=0,71 > 0,05$). In this case, H_1 is rejected whereas H_0 accepted.

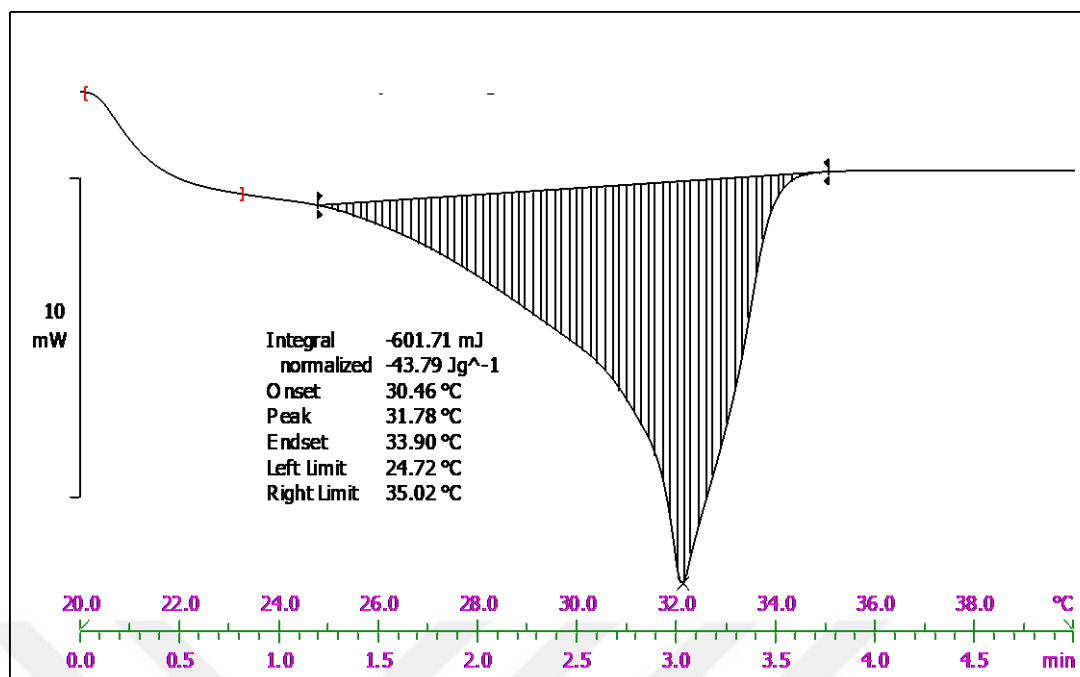


Figure 4.1 DSC results of 0th day standard dark chocolate without bergamot

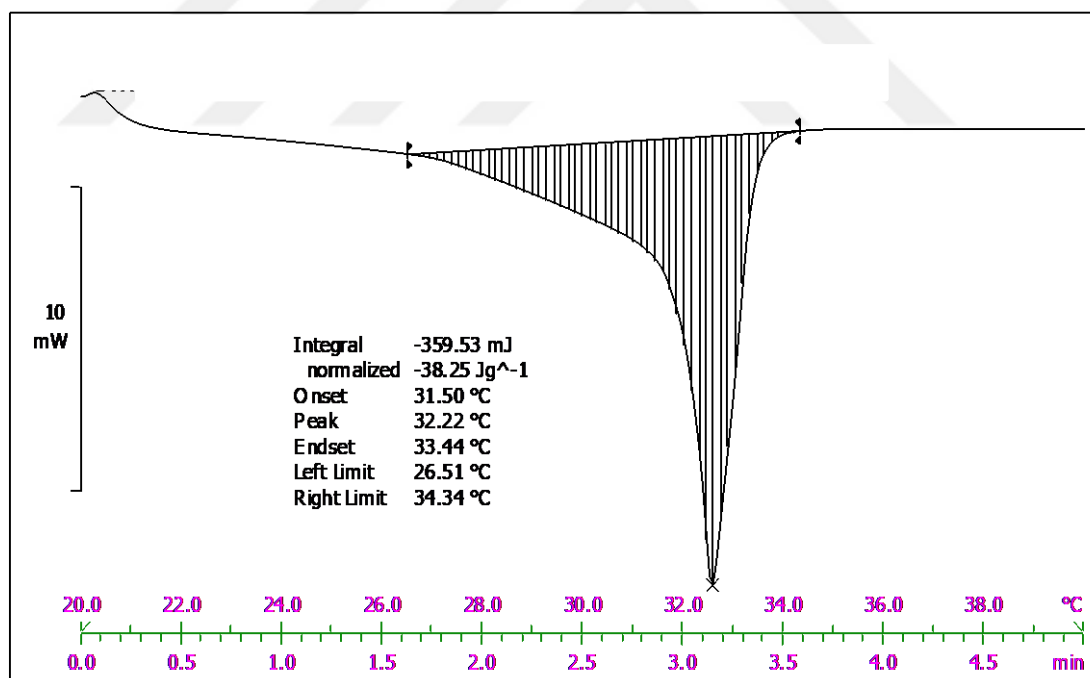


Figure 4.2 DSC results of 15th day standard dark chocolate without bergamot

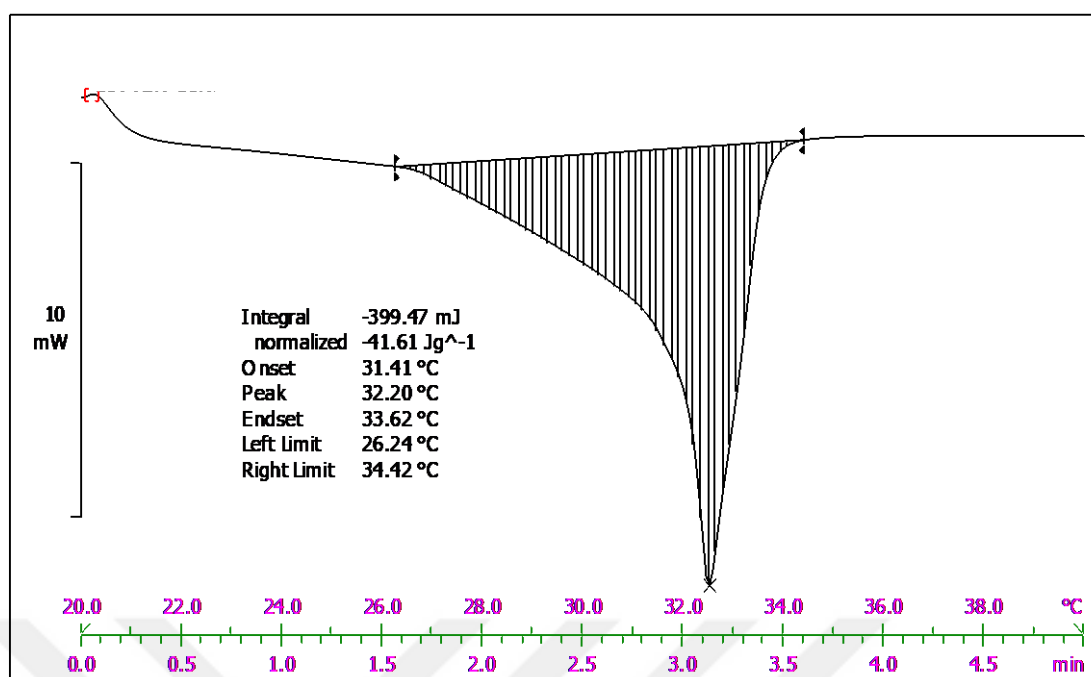


Figure 4.3 DSC results of 30th day standard dark chocolate without bergamot

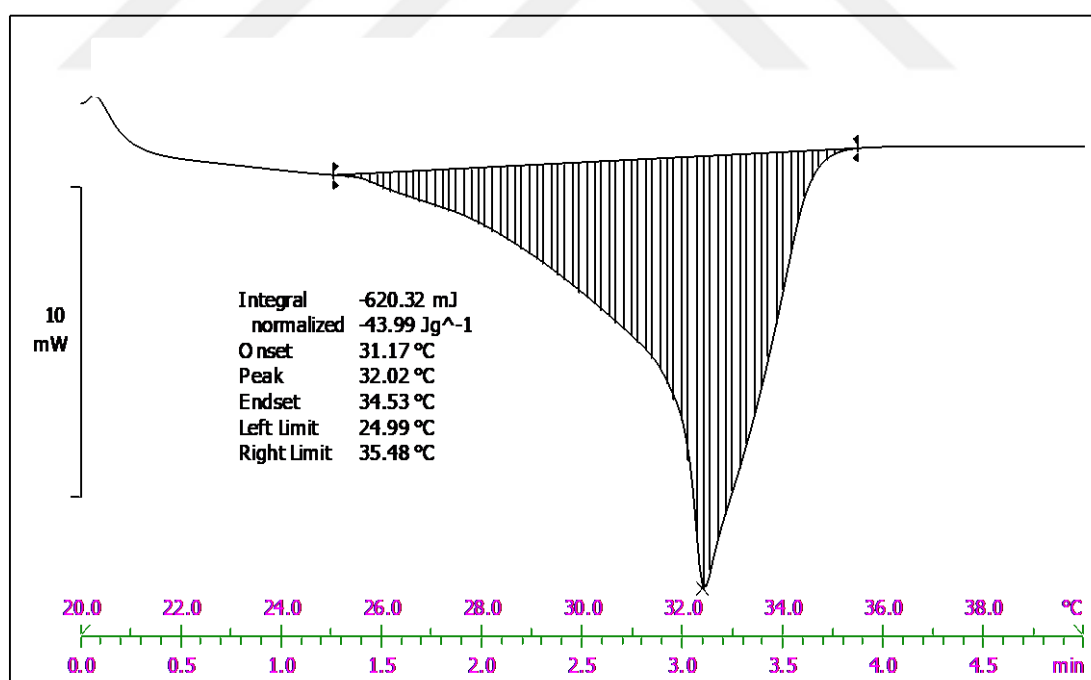


Figure 4.4 DSC results of 365th day standard dark chocolate without bergamot

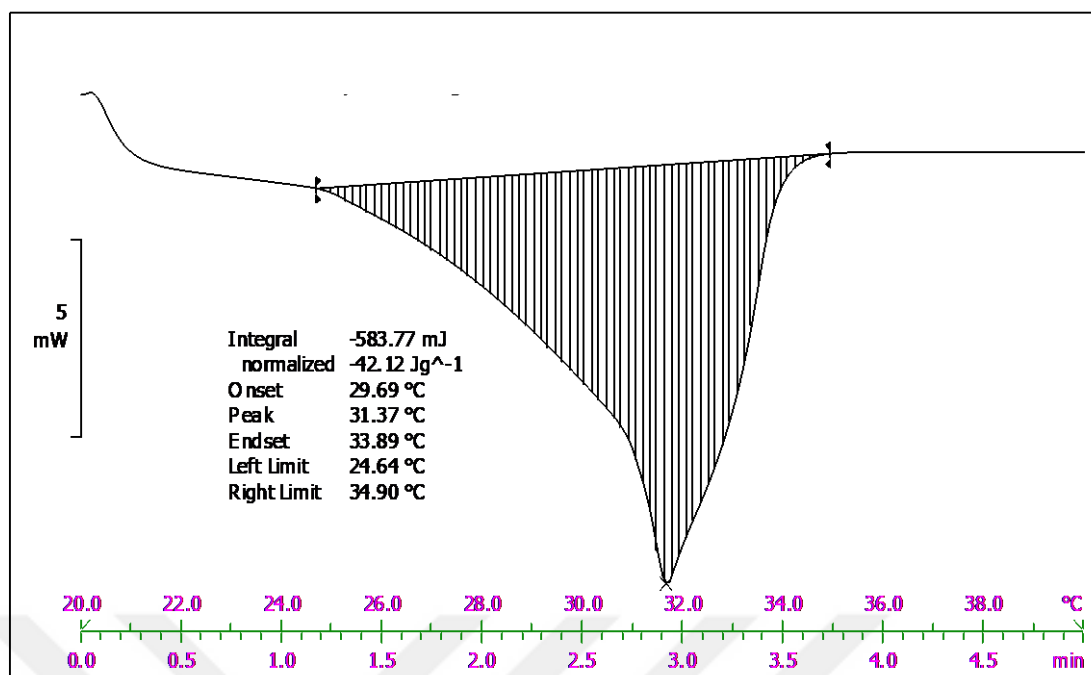


Figure 4.5 DSC results of 0th day 0.75% bergamot dark chocolate

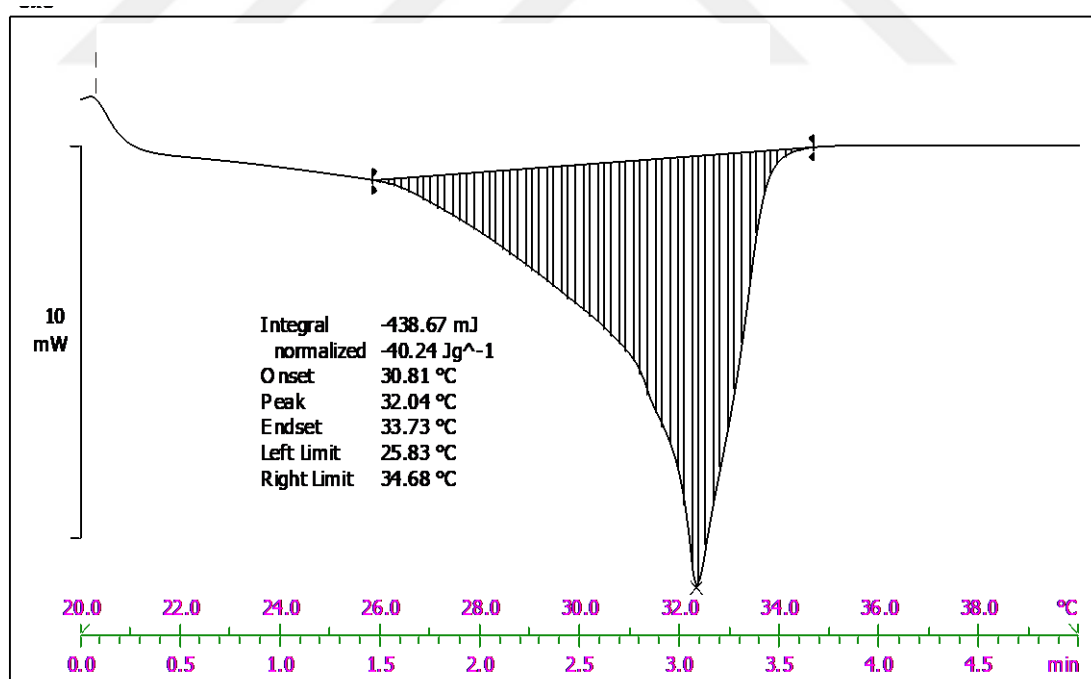


Figure 4.6 DSC results of 15th day 0.75% bergamot dark chocolate

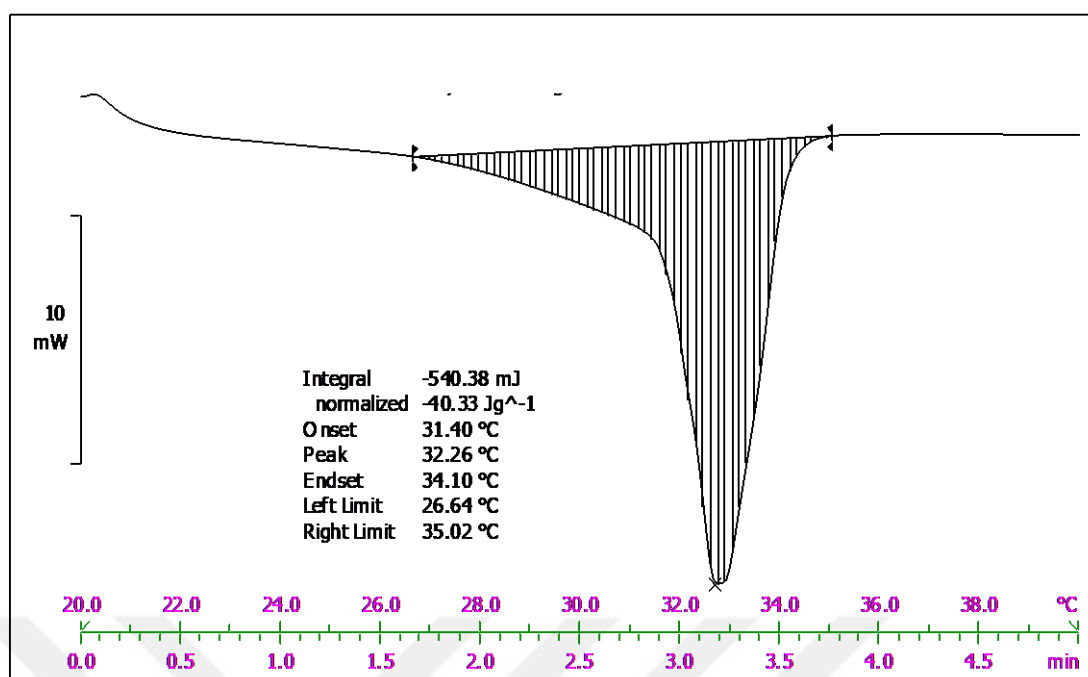


Figure 4.7 DSC results of 30th day 0.75% bergamot dark chocolate

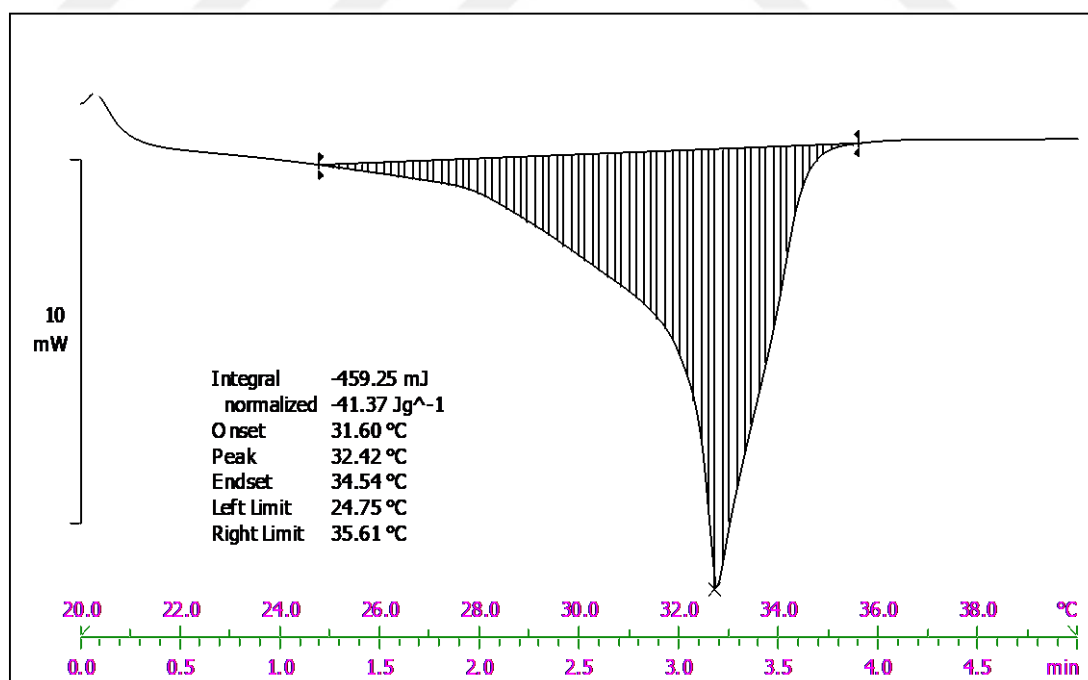


Figure 4.8 DSC results of 365th day 0.75% bergamot dark chocolate

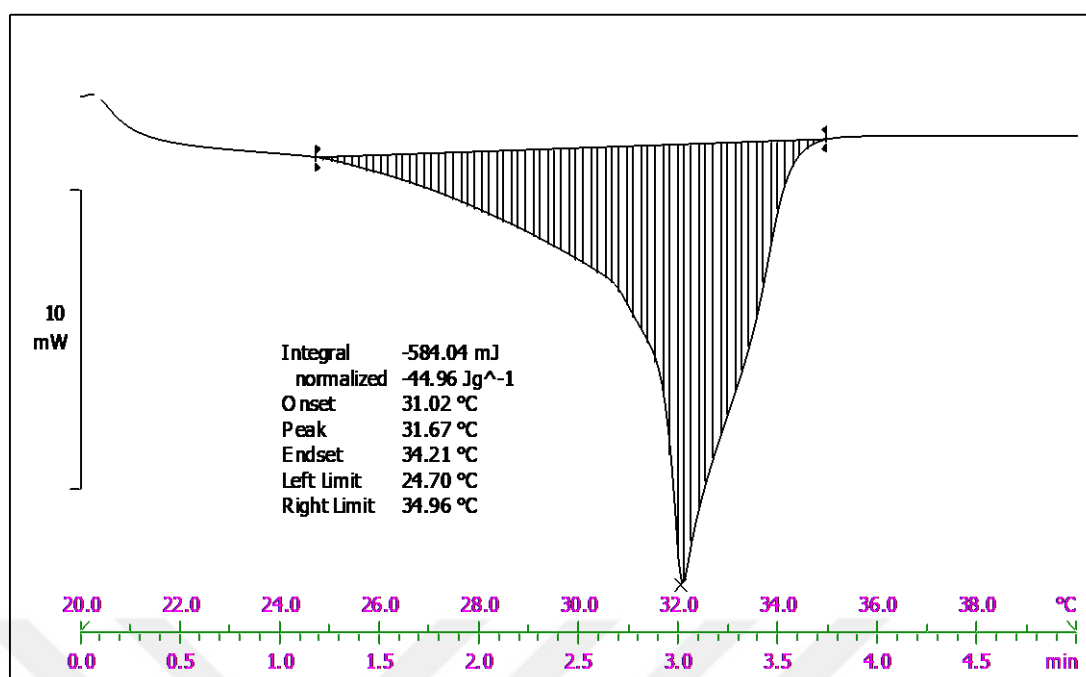


Figure 4.9 DSC results of 0th day 1.00% bergamot dark chocolate

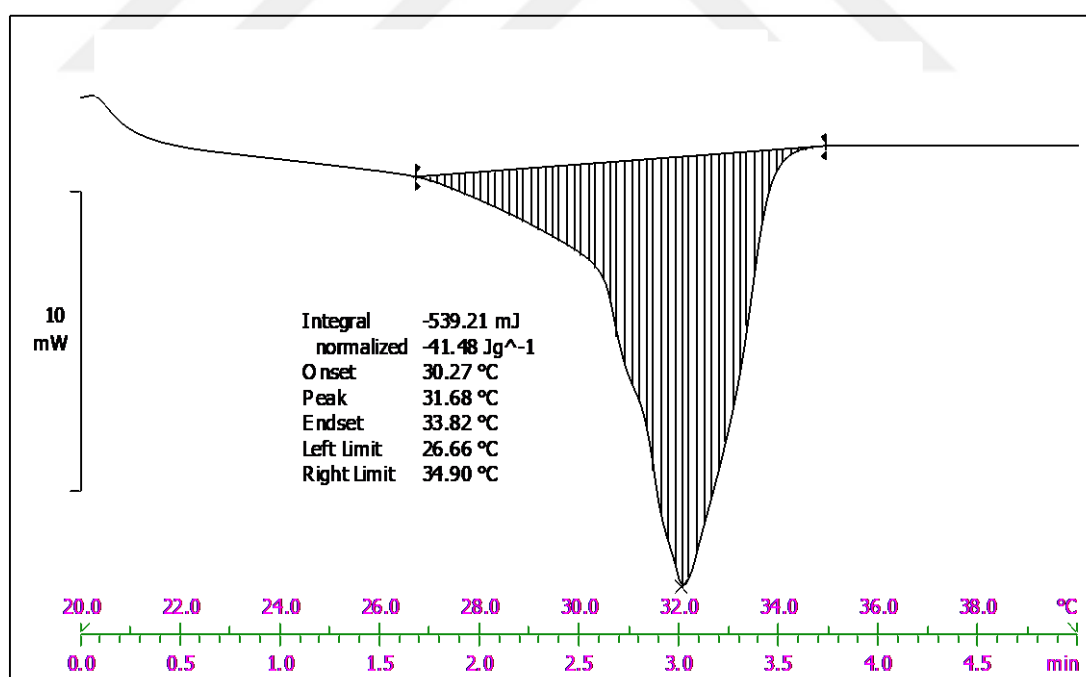


Figure 4.10 DSC results of 15th day 1.00% bergamot dark chocolate

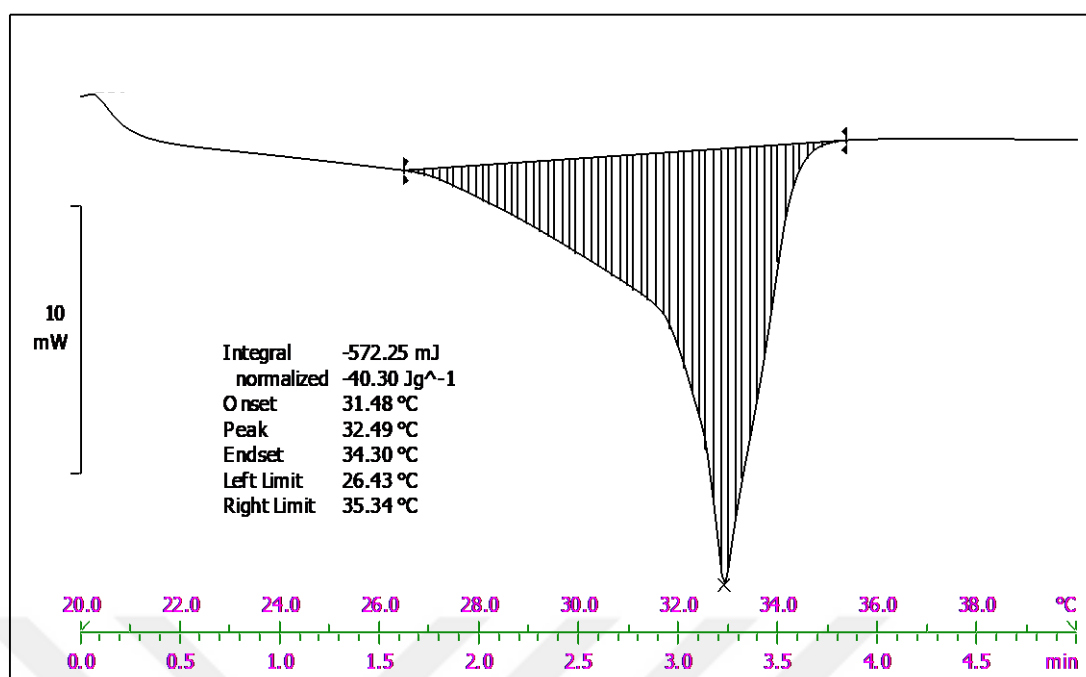


Figure 4.11 DSC results of 30th day 1.00% bergamot dark chocolate

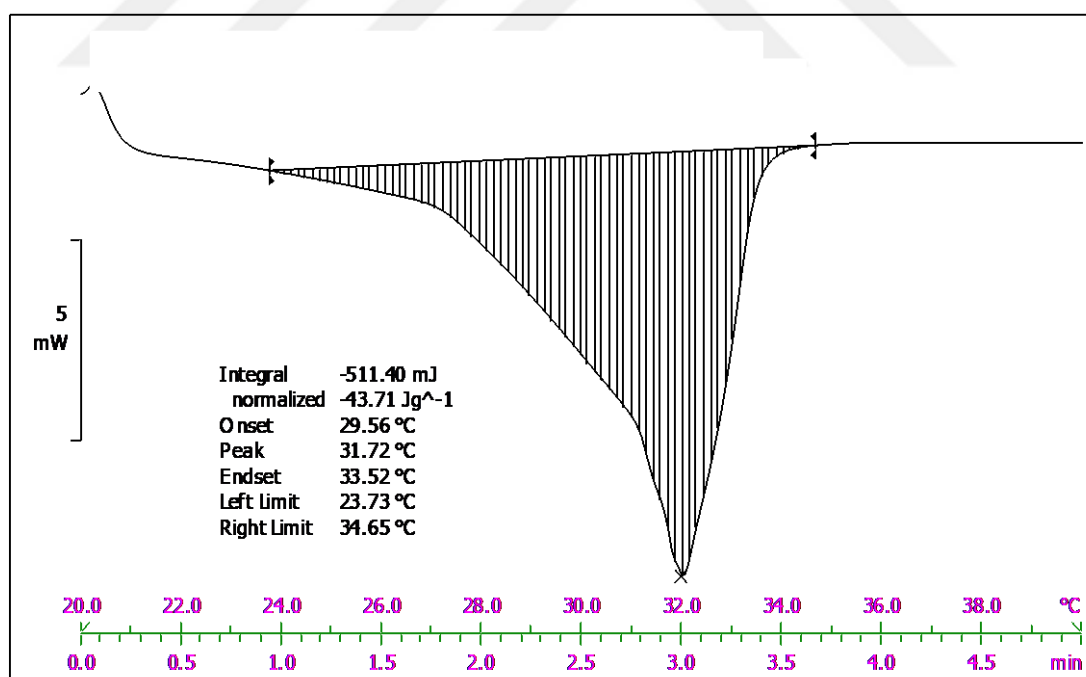


Figure 4.12 DSC results of 365th day 1.00% bergamot dark chocolate

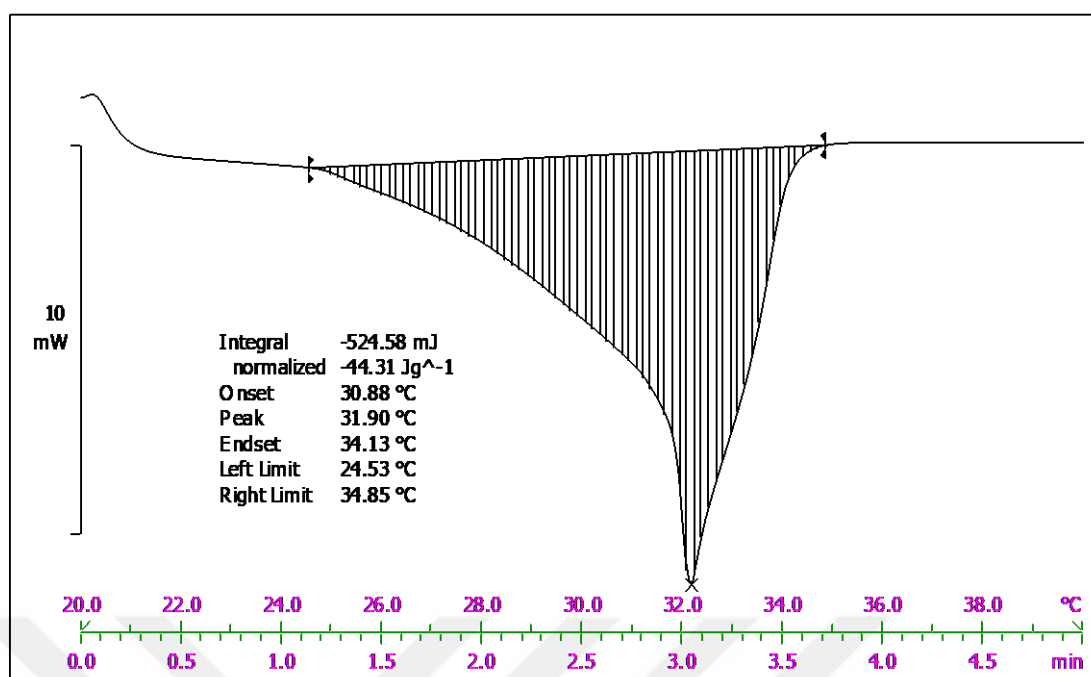


Figure 4.13 DSC results of 0th day 1.25% bergamot dark chocolate

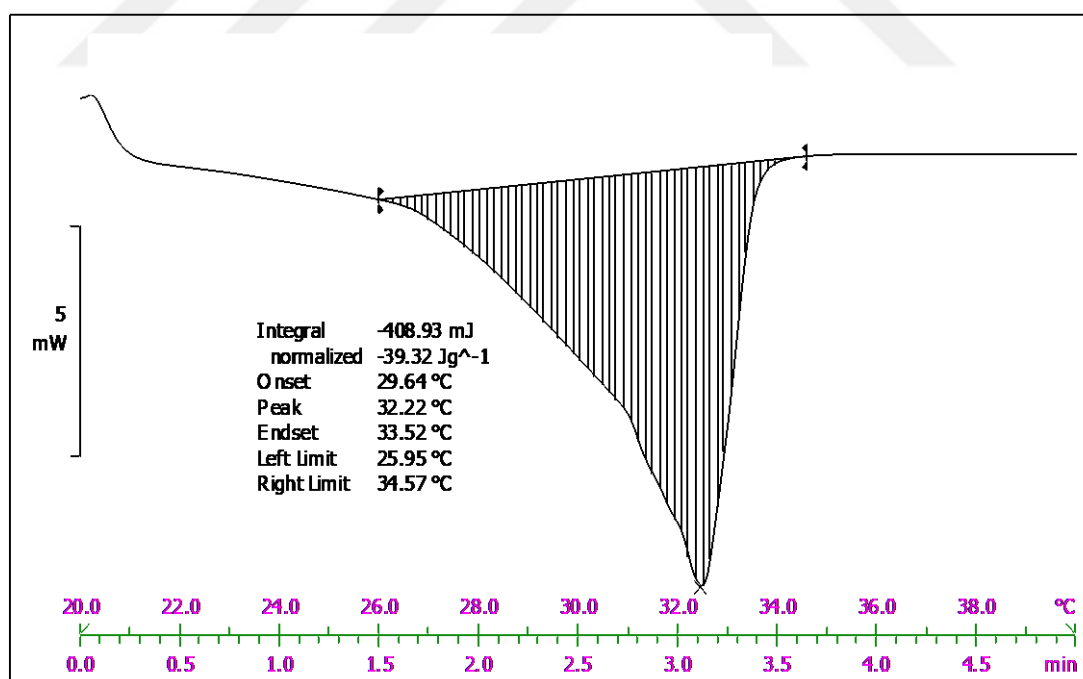


Figure 4.14 DSC results of 15th day 1.25% bergamot dark chocolate

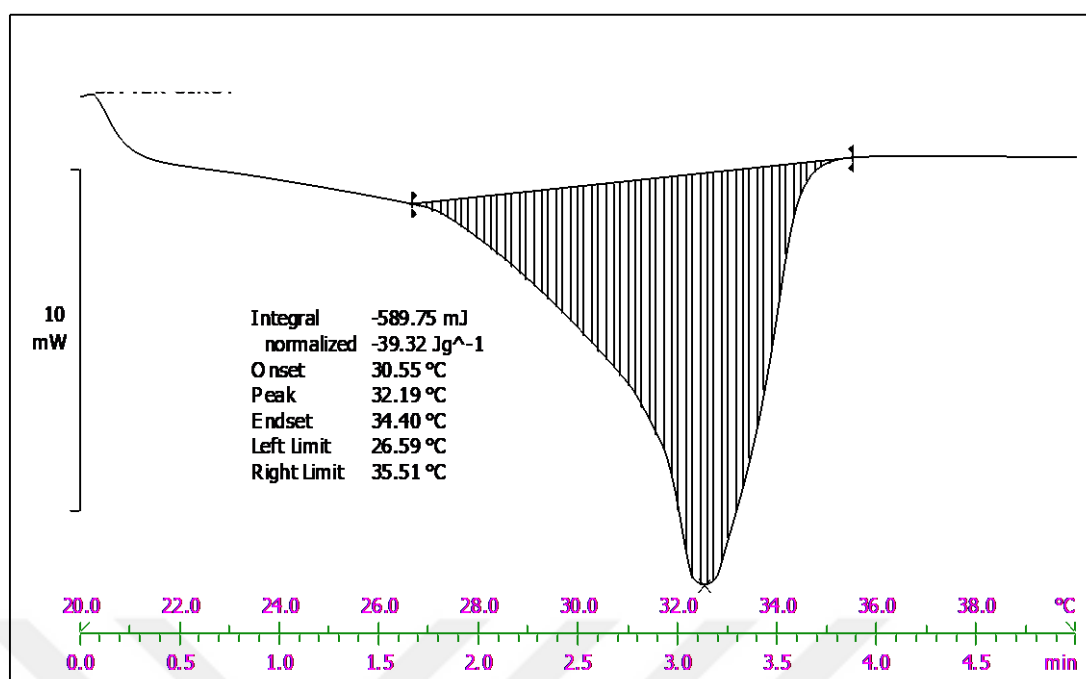


Figure 4.15 DSC results of 30th day 1.25% bergamot dark chocolate

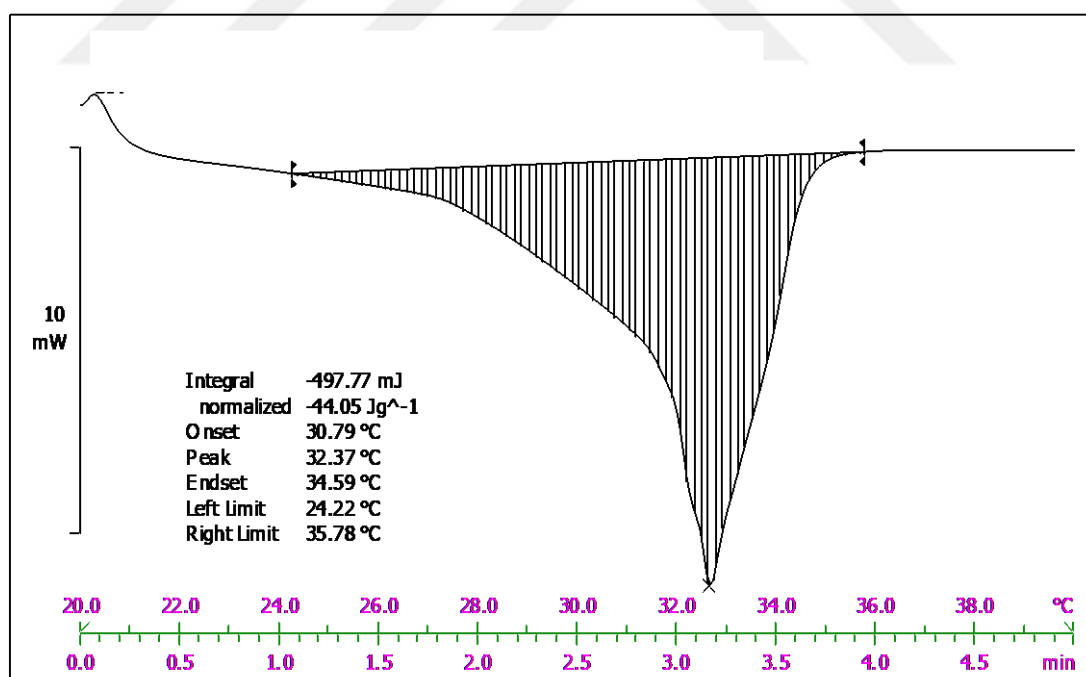


Figure 4.16 DSC results of 365th day 1.25% bergamot dark chocolate

4.2 Solid Fat Content (SFC) Analysis

Solid fat content analysis was performed to the cocoa butter samples which were separated from all the chocolate samples to see the % quantity of them. From 10°C to 25°C the samples lost approximately 33.3% of their solid fat content. The results in Table 4.3 showed that as the temperature increased, the fat content of the chocolate samples decreased. The solid fat content percentages were not significantly different at different temperatures, at 40°C none of the samples had solid content.

The bergamot content in the low percentages added to the chocolate did not affect the melting profile and did not cause any major changes in the fat content of the samples. It was thought that this was due to the low amount of bergamot peel powder and its low fat content.

Table 4.3 SFC analysis comparison chart of the chocolate samples

Temperature (°C)	Standard Dark Chocolate	0.75 % Bergamot Dark Chocolate	1.0 % Bergamot Dark Chocolate	1.25 % Bergamot Dark Chocolate
	SFC (%)			
10°C	83.53	84.17	82.6	80.15
20°C	73.12	74.13	74.00	69.70
25°C	67.53	68.51	66.00	59.58
30°C	47.77	47.73	50.45	43.71
35°C	0.55	0.81	0.94	0.62
40°C	0.00	0.00	0.00	0.00

In addition to the information given above an One-Way ANOVA test was carried out to see the difference in Solid Fat Content Analysis results.

H₀: There is no significant difference among the solid fat content analysis results of dark chocolate samples with bergamot content at different temperatures.

H₁: There is a significant difference among the solid fat content analysis results of dark chocolate samples with bergamot content at different temperatures.

Table 4.4 One-Way ANOVA Test for the Solid Fat Content Analysis Results

Effect	SS	Degree of Freedom	MS	F	p
Intercept	50,035.14	1	50,035.14	36.90	0.00
Sample	0.68	3	0.23	0.00	1
Error	27,084.52	20	1,354.23		

According to the results observed in Table 4.4, there is no significant difference among the solid fat content analysis results of dark chocolate samples with bergamot content at different temperatures ($p=1,00 > 0,05$). In this case, H₁ is rejected whereas H₀ accepted.

4.3 Texture Profile Analysis (TPA)

Texture profile analysis (TPA) was carried out for 5 chocolate samples to measure the hardness. Any kind of dark chocolate was analysed to see the difference between standard recipe of dark chocolate in this study.

The peak force shows the hardness in plots. Each sample was analyzed duplicate to compare peak force points.

Texture analysis results are given in Table 4.5. As the bergamot percentage increased, the force point increased in direct proportion with it. The peak force points are close to each other, because the bergamot peel powder percentages were also close.

In Figure 4.18 which is the second TPA plot of standard dark chocolate, the view of plot is different from the first TPA plot of standard dark chocolate. It is thought to be the probe touched a particle in chocolate sample and the difference in plot views was sourced from the particle on chocolate sample, and 2 peak points were occurred.

Also the same situation is the case for Figure 4.19 which is the first plot of 0.75% bergamot dark chocolate. In Figure 4.19, this is thought to be that the probe touched a particle of bergamot peel powder, and 2 peak points were occurred.

According to the plots and the average results given in Table 4.5, chocolate with high bergamot peel powder content needs more force than others to be broken.

The results showed that the bergamot dark chocolate samples were harder than the standard dark chocolate. The reason for this is thought to be the fibrous nature of bergamot peel and also because of the decreasing percentage of the cocoa mass in the recipe.

To produce harder chocolate, bergamot peel powder can be used. However, even minimal content of bergamot peel powder is considerably felt, the higher percentage usage of it can reduce the quality of eating.

Table 4.5 Comparison of texture analysis results of chocolate samples

Sample Name	Force (g)		
	1st trial	2nd trial	Average
Any kind of Dark Chocolate	1446.00	1438.20	1442.10
Standard Dark Chocolate	2183.70	1883.40	2033.55
0.75 % Bergamot Dark Chocolate	2233.50	2260.60	2247.05
1.00 % Bergamot Dark Chocolate	2362.60	2341.50	2352.05
1.25 % Bergamot Dark Chocolate	2573.00	2369.20	2471.10

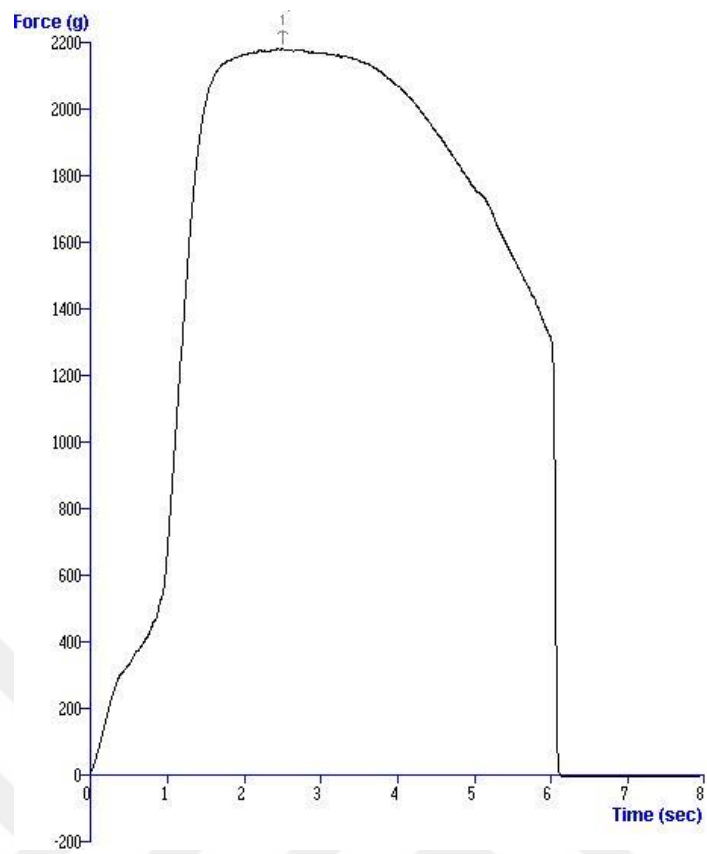


Figure 4.17 TPA 1st plot of standard dark chocolate

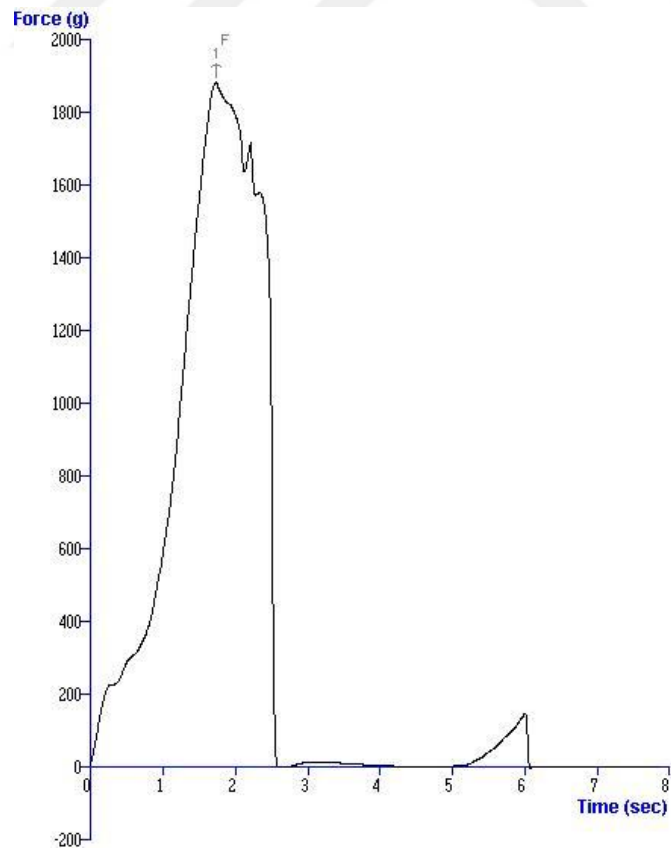


Figure 4.18 TPA 2nd plot of standard dark chocolate

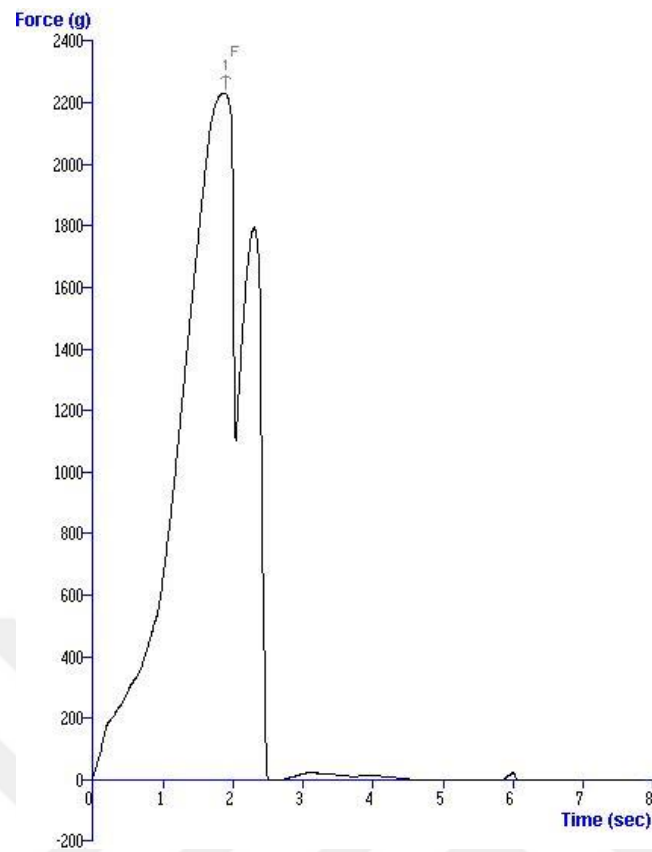


Figure 4.19 TPA 1st plot of 0.75% bergamot dark chocolate

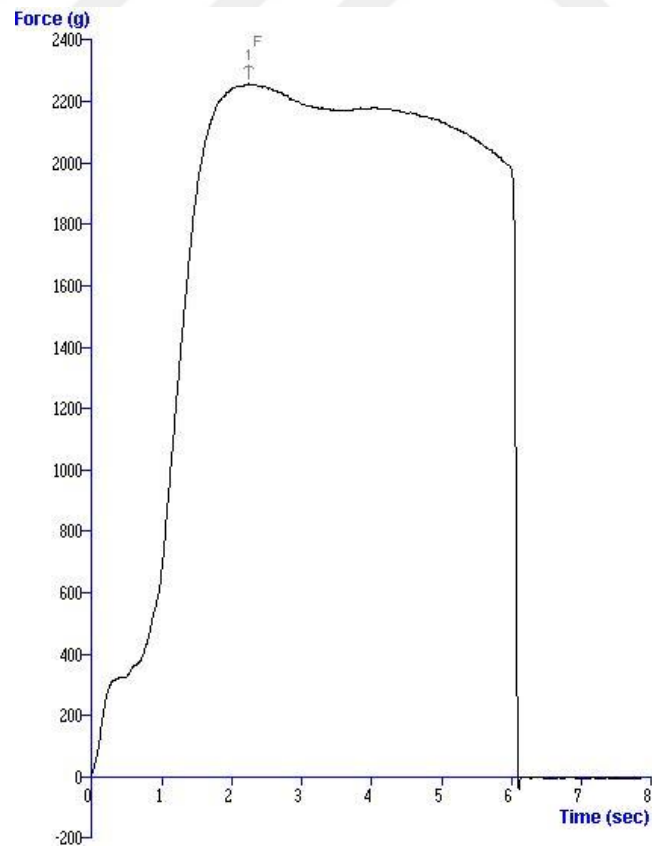


Figure 4.20 TPA 2nd plot of 0.75% bergamot dark chocolate

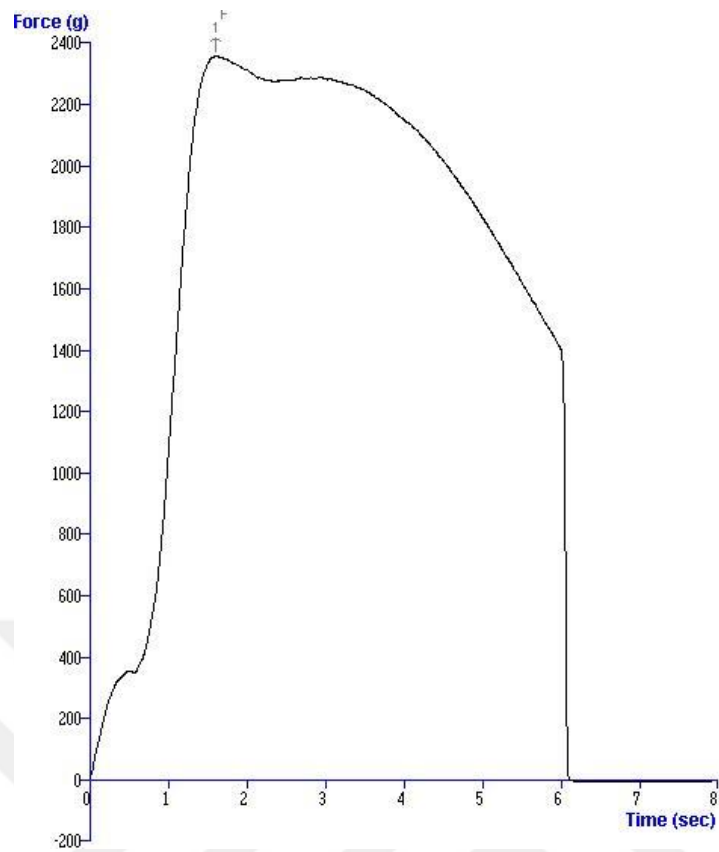


Figure 4.21 TPA 1st plot of 1.00% bergamot dark chocolate

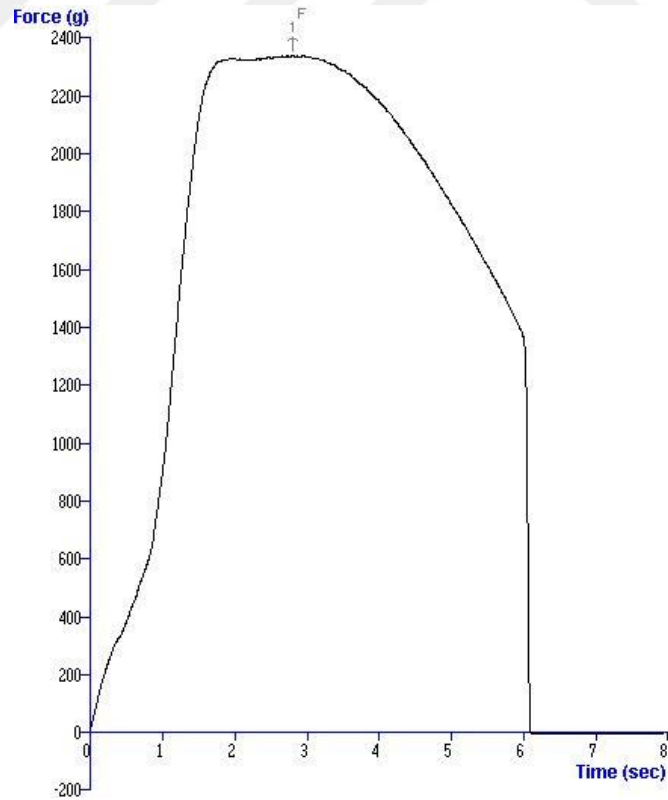


Figure 4.22 TPA 2nd plot of 1.00% bergamot dark chocolate

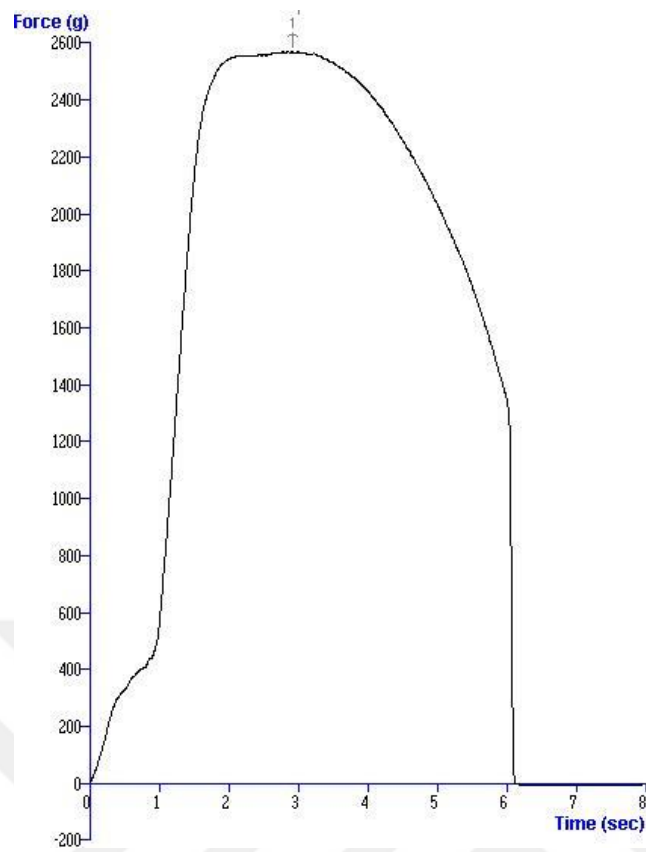


Figure 4.23 TPA 1st plot of 1.25% bergamot dark chocolate

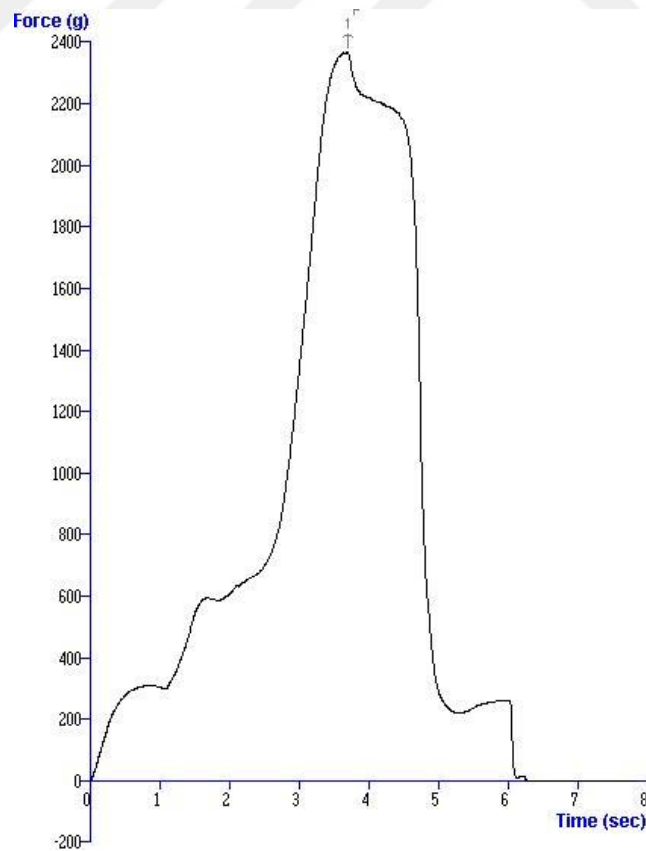


Figure 4.24 TPA 2nd plot of 1.25% bergamot dark chocolate

4.4 Sensory Analysis

Three chocolate samples were presented to 20 trained panellists to choose the best taste and flavour and to grade them in a scale from 1, being the worst to 5, being the best. Sample numbering against percentage is given in Table 4.6 and degree of preference values is given in Table 4.7.

In this panel, bergamot flavour was not liked by some panellists while some of them liked it. Three panellists disliked the sample 535 which has 1.25% bergamot peel powder. However, 5 panellists graded the same sample with 5 score. It is thought that the bergamot flavour has a sharp line when it comes to the issue of preferring or not preferring.

Average results were calculated for 20 different preferences on the results evaluated on the panel final report. The spider plot of the sensory analysis scores was indicated in Figure 4.25.

Table 4.6 Sensory Analysis Sample Numbering chart

Number	Sample
441	1.00% bergamot dark chocolate
535	1.25% bergamot dark chocolate
656	0.75% bergamot dark chocolate

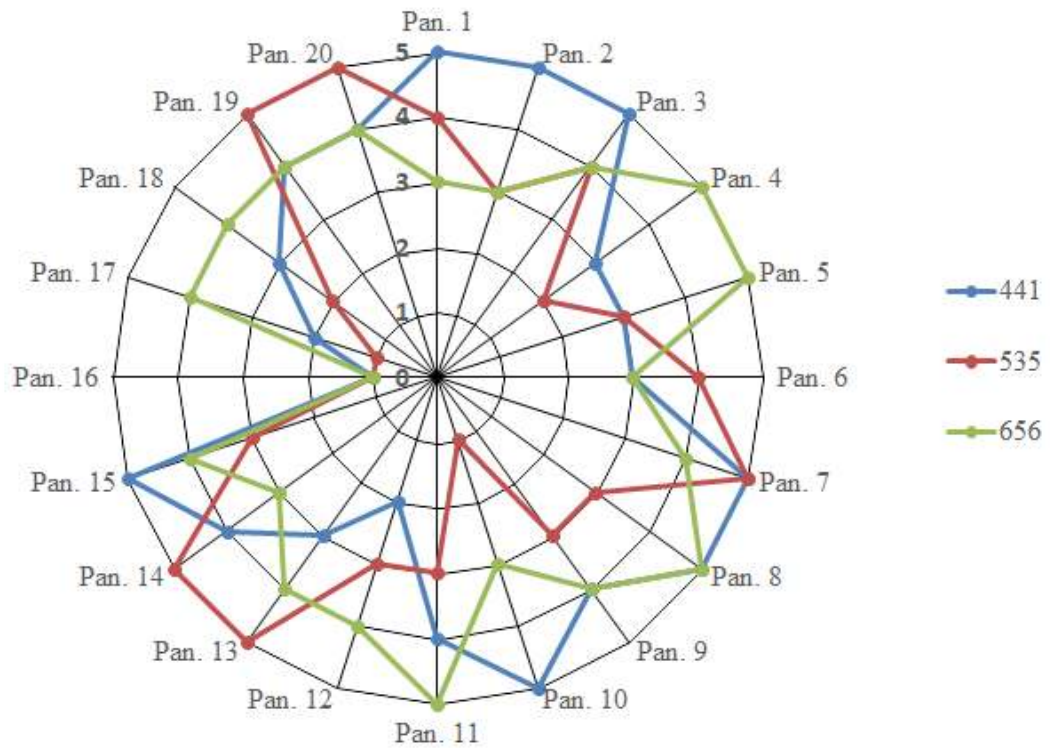


Figure 4.25 Spider plot of sensory analysis scores

The preference ratios were nearly the same between the samples of 0.75% and 1.00%. All the panellists noted that the bergamot flavour was felt dominantly on all 3 samples.

According to the calculation results, the dark chocolate which has the minimum bergamot peel powder content that is numbered 656, was preferred with the highest average score.

All the sensory analysis results say that more bergamot peel powder flavour can cause undesired taste in chocolate. It is thought that the reason why the low-content bergamot dark chocolate got the highest preference rate can be due to the fact that the flavour of bergamot is quite unconventional in Turkey. The bergamot flavour is customary for tea in Turkey, not for chocolate.

Table 4.7 Degree of preference chart of bergamot dark chocolate samples

Taste of Samples		
Bergamot %	Sample number for Panel	Rate of Preference
0.75	656	3.80
1.00	441	3.75
1.25	535	3.25

In addition to the information given above an One-Way ANOVA test was carried out to see the difference in Sensory Analysis results.

H₀: There is no significant difference among the sensory analysis results of dark chocolate samples with bergamot content.

H₁: There is a significant difference among the sensory analysis results of dark chocolate samples with bergamot content.

Table 4.8 One-Way ANOVA Test for the Sensory Analysis Results

Effect	SS	Degree of Freedom	MS	F	p
Intercept	777.60	1	777.60	549.23	0.00
Sample	3.70	2	1.85	1.31	0.28
Error	80.70	57	1.42		

According to the results observed in Table 4.8, there is no significant difference among the sensory analysis results of dark chocolate samples with bergamot content ($p=0.28 > 0.05$). In this case, H_1 is rejected whereas H_0 accepted. Because of the acceptance of H_0 hypothesis the Post-hoc analysis were not needed to carry out for the results.

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

Dark chocolate was studied with the addition of bergamot peel powder to see the changing of melting point, solid fat content, texture and also sensorial profile development. The following results have been reached:

1. Bergamot peel powder didn't affect the fat content of chocolate. Addition of bergamot peel powder at minimal ratios neither increased nor decreased the melting point of dark chocolate. This was an expected result.
2. Solid fat content of dark chocolate didn't change at different temperatures. There was no solid fat content difference between the standard dark chocolate and the bergamot dark chocolate samples.
3. Bergamot peel powder hardened the dark chocolate. As the bergamot ratio increased, brittleness of dark chocolate also increased. This resultant brittleness made the chocolate feel more high-quality and also affected the biting-feel positively. The resultant brittle structure made the chocolate better quality, and also created a positive biting-feel. Thus, this hardness contributed a positive impact on chocolate texture.
4. Sensory profile and flavour of dark chocolate were strictly changed by addition of bergamot peel powder. The dark chocolate gained a new taste and flavour with bergamot peel powder. 14 panellists have scored the chocolate samples with 3, 4, 5 scores. The results show that the chocolate samples were liked by 70% of panellists and bergamot flavour is an acceptable taste.

According to the results, the study contributed the chocolate sector by presenting a new kind of chocolate. A new chocolate form can be produced by changing the ingredients with little touches, as in this study.

Bergamot peel powder can also be used in other confectionery and bakery products like cream, candies, jellies and cakes. It can appeal to a new audience who like bergamot taste and odour.

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APPENDIX



Figure A.1 Whole bergamot fruit



Figure A.2 Dried bergamot peel



Figure A.3 Dried and ground bergamot peel

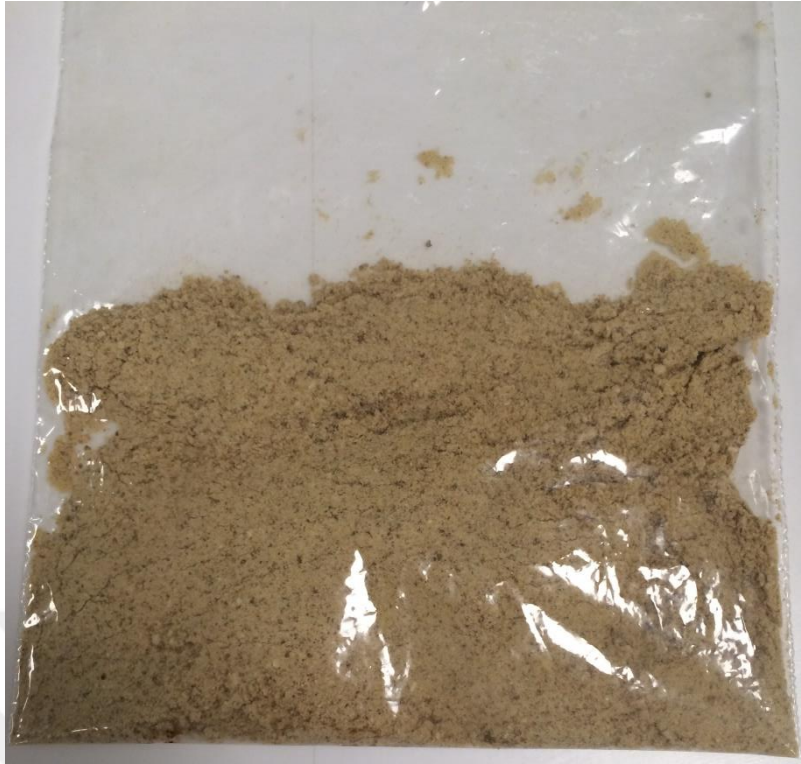


Figure A.4 Bergamot peel powder



Figure A.5 (Liquid (melted) cocoa mass

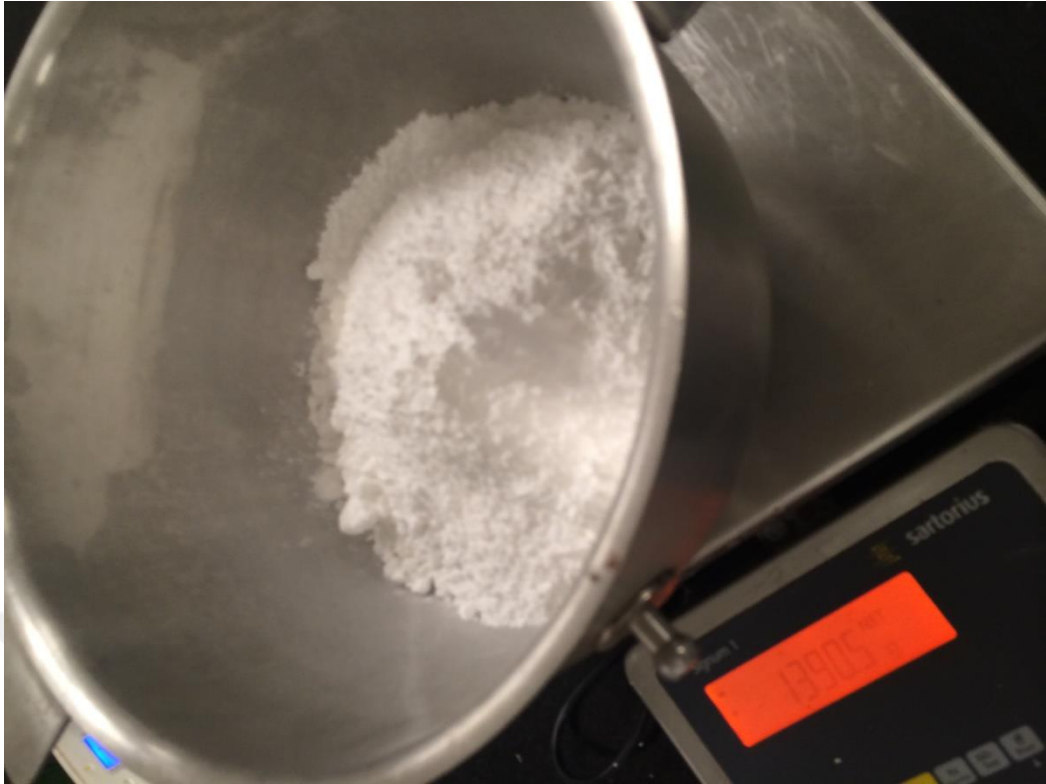


Figure A.6 Powdered sugar



Figure A.7 Adding of bergamot peel powder to chocolate mix



Figure A.8 Adding of melted cocoa mass to chocolate mix



Figure A.9 Adding of melted cocoa butter to chocolate mix



Figure A.10 Mixing step of the chocolate ingredients



Figure A.11 Refining of chocolate production



Figure A.12 Conching step of chocolate production



Figure A.13 Tempering step of chocolate production



Figure A.14 Sampling of chocolate to measure temper index

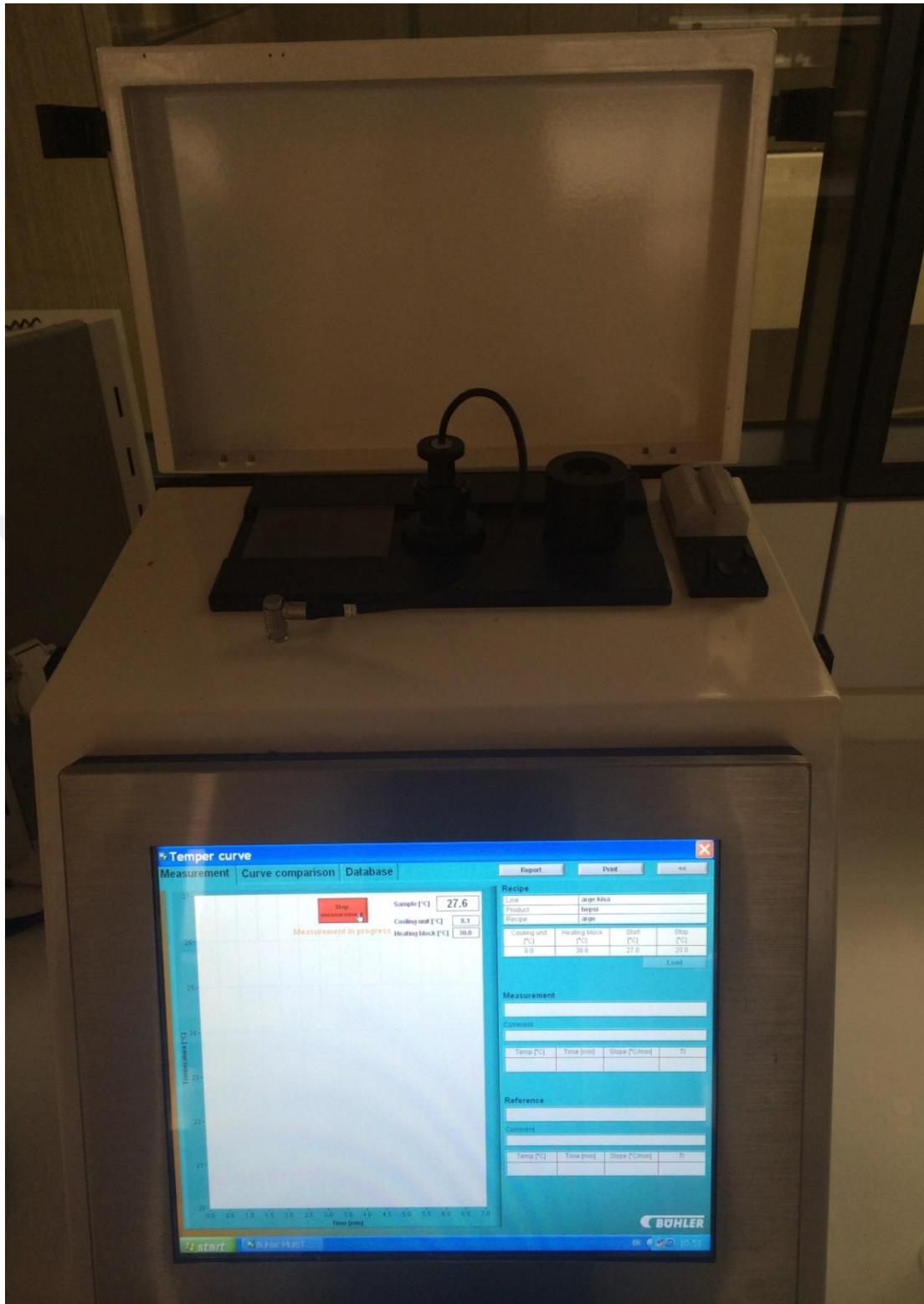


Figure A.15 Bühler Multitherm TC thermometer

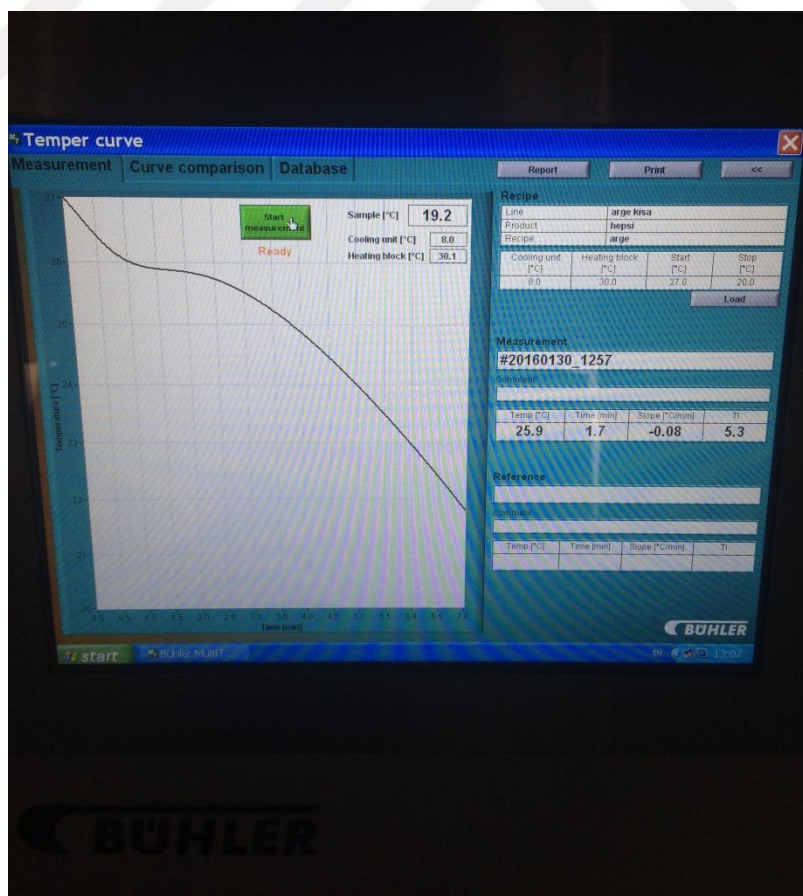
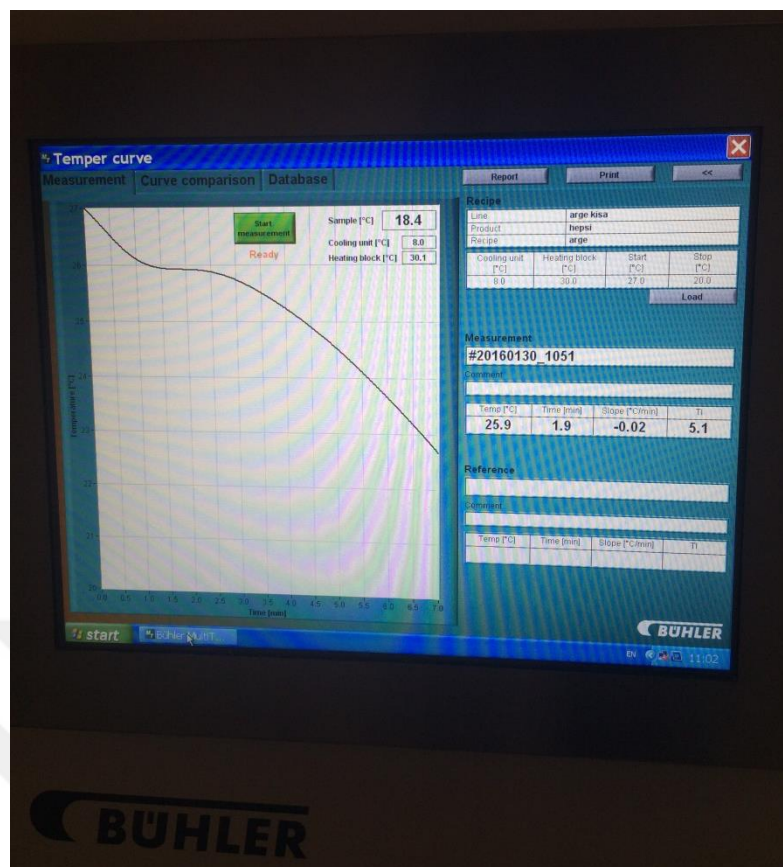


Figure A.16 Temper curves of chocolate samples



Figure A.17 Moulding of chocolate

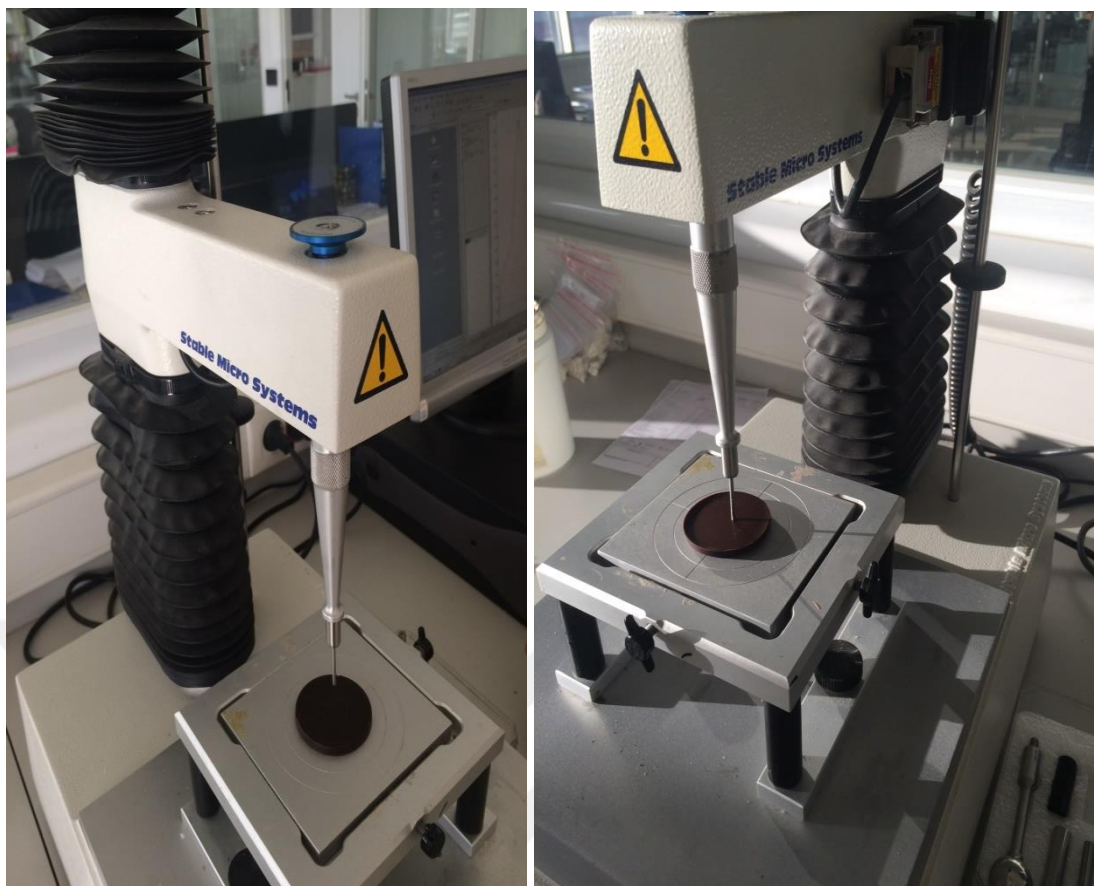


Figure A.18 TA-XT plus Texture Analyser



Figure A.19 Sensory panel presentation of bergamot dark chocolate samples