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EFFECTS OF DIFFERENT VEGETABLE FATS ON

CHOCOLATE PROPERTIES

M.Sc. THESIS

IN

FOOD ENGINEERING

BY

MESUT KAYIŞLI

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Effects of different vegetable fats on chocolate properties

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Supervisor

Prof. Dr. Zerrin Söylemez

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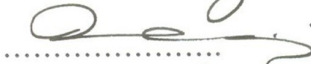Prof. Dr. Ahmet KAYA (Chairman)

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Mesut KAYIŞLI

ABSTRACT

EFFECTS OF DIFFERENT VEGETABLE FATS ON

CHOCOLATE PROPERTIES

KAYIŞLI, Mesut

M.Sc. Thesis in Food Engineering

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Viscosity, solid fat content (SFC), texture and melting profile have been studied by adding different vegetable fats, namely, hazelnut oil, palm kernel stearin and shea butter stearin to the dark chocolate formulation at a level of 5% (w/w) on product bases. Four different samples were tempered in a way to get a temper index 5 after conching with same steps. Then the samples were cooled at 12 ^{o}C for 2 hours after moulding in dimensions of 44 mm diameter and 4 mm height. The samples were stored at 18±3 ^{o}C up to the end of measurements. Viscosity and SFC measurements were done at the day of sample preparation. Melting profile and texture measurements were done after 0, 3, 15, 30, 45, 60 days storage.

Viscosity, SFC, melting profile and textural changes of the dark chocolate samples that were prepared with different vegetable fats were evaluated. Viscosity of standard sample (only with cocoa butter) and samples that were prepared with hazelnut oil, palm kernel stearin and shea butter stearin were found to be 13 000 cP, 19 875 cP, 28 625 cP ve 16 875 cP, respectively at 40 ^{o}C and 2 RPM.

When shea butter stearin mixed with cocoa butter, an increase in SFC of the mixture was observed, especially at 30 and 35 ^{o}C. But although palm kernel stearin has high SFC than cocoa butter, the mixture exhibited a significant decrease, especially at 20 ^{o}C, because of eutectic effect. SFC value of the hazelnut oil and cocoa butter mixture was decreased when compared with SFC of the cocoa butter.

It was founded that the melting profile of the sample that was prepared with shea butter stearin had higher melting point and harder structure from first day to the end of 60th day compared to standard sample. In addition, because of incompatible structure with cocoa butter, palm kernel stearin spoiled the melting profile of the chocolate, decreased melting point and hardness of chocolate despite the high SFC of palm kernel stearin. Due to low SFC, hazelnut oil decreased the melting point of the sample and gave a softening effect on chocolate.

Key Words: dark chocolate, cocoa butter, shea butter stearin, palm kernel stearin, hazelnut oil, melting profile, texture, solid fat content, viscosity

ÖZ

DEĞİŞİK BİTKİSEL YAĞLARIN ÇİKOLATANIN
ÖZELLİKLERİ ÜZERİNE ETKİSİ

KAYIŞLI, Mesut

Yüksek Lisans Tezi, Gıda Mühendisliği Bölümü

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Bitter çikolata formülasyonuna son üründe en fazla %5 olacak şekilde, değişik bitkisel yağlar, fındık yağı, palm çekirdeği stearin ve shea yağı stearin eklenerek, viskozitesi, katı yağ miktarı (KYM), tekstür ve erime profili çalışıldı. Dört farklı numune, aynı yolla konçlandıktan sonra temper indeksi 5 olacak şekilde temperleme işlemine tabi tutuldu. Daha sonra 44 mm çapında ve 4 mm yüksekliğinde ki kalıplara dökülerek 12 ^{o}C'da 2 saat soğutuldu. Numuneler ölçümler tamamlanıncaya kadar 18±3 ^{o}C'da saklandı. Viskozite ve KYM ölçümleri numunelerin hazırlandığı gün, erime profili ve tekstür ölçümleri ise 0, 3, 15, 30, 45 ve 60 gün saklama sonrası yapıldı.

Değişik bitkisel yağlarla hazırlanmış bitter çikolata numunelerinin viskozite, KYM, erime profili ve tekstür değişimleri değerlendirildi. Standart (Sadece kakao yağı) ve fındık yağı, palm çekirdeği stearin ve shea yağı stearin ile hazırlanan numunelerin 40 ^{o}C'da ve 2 RPM'deki viskoziteleri sırası ile 13 000 cP, 19 875 cP, 28 625 cP ve 16 875 cP olarak bulundu.

Shea yağı stearin kakao yağı ile karıştığında, özellikle 30 ve 35 ^{o}C'da, karışımın KYM'sini arttırdığı gözlendi. Fakat palm çekirdeği stearinin, özellikle 20 ^{o}C'da, KYM'si kakao yağından fazla olmasına rağmen, karışımda ötektik etki göstererek KYM'sini gözle görülür bir şekilde düşürdüğü gözlendi. Fındık yağının kakao yağı ile karışımında ise kakao yağına kıyasla KYM'si düştü.

Shea yağı stearin ile hazırlanmış numunenin, standart numuneye göre, ilk günden başlayarak 60. güne kadar daha yüksek bir erime noktasına ve tekstür olarak daha sert bir yapıya sahip olduğu bulundu. Bunun yanında, palm çekirdeği stearinin kakao yağından yüksek KYM'ye sahip olmasına rağmen, kakao yağı ile uyumsuz olduğundan dolayı çikolatanın erime profilini bozdu, erime noktasını düşürdü ve çikolatanın sertliğini azalttı. Fındık yağı ise, düşük KYM nedeni ile, çikolatanın erime sıcaklığını düşürdü ve tekstür olarak çikolataya yumuşatıcı etki yaptı.

Anahtar Kelimeler: bitter çikolata, kakao yağı, shea yağı stearin, palm çekirdeği stearin, fındık yağı, erime profili, tekstür, katı yağ içeriği, viskozite

TO MY PARENTS
FİLİZ-HAYRULLAH KAYIŞLI
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NOMENCLATURE

ΔH_{melt}	Enthalpy of crystallization
AOCS	American Oil Chemists' Society
CB	Cocoa Butter
CBAs	Cocoa Butter Alternatives
CBEs	Cocoa Butter Equivalents
CBEXs	Cocoa Butter Extenders
CBIs	Cocoa Butter Improvers
CBRs	Cocoa Butter Replacers
CBSs	Cocoa Butter Substitutes
cP	Centipoise
CTU	Chocolate tempering unit
DSC	Differential scanning calorimetry
HO	Hazelnut Oil
IUPAC	International Union of Pure and Applied Chemistry
M_{solid}	Solid mass of the lipid in Solid Fat Content calculations
M_{total}	Total mass of the lipid in Solid Fat Content calculations
NMR	Nuclear magnetic resonance
PGPR	Polyglycerol polyricinoleate
PKS	Palm Kernel Stearin
POO	1, palmitoyl-2,3-oleoylglycerol
POP	1,3-dipalmitoyl-2-oleoylglycerol
POS	1-palmitoyl-2-oleoyl-3-stearoylglycerol

SBS	Shea butter stearin
SFC	Solid fat content
SOS	1,3-distearoyl-2-oleoylglycero
StOO	1,stearoyl-2,3-oleoylglycerol
STS	Sorbitan tristearate
TAGs	Triacylglycerides
T_{peak}	Melting temperature of sample
YN	A synthetic phospholipid emulsifier

CHAPTER I

INTRODUCTION

1.1. Chocolate

Chocolate is a confectionery widely used all over the world and the production increases every year. Chocolate making is closely related with the consumer behaviour. The types of chocolate accepted best by the consumer change from one country to another; for example, chocolate common in U.S. and in U.K. does not accepted by Europian people. The use and taste of chocolate reflects the cultural differences of the countries and the industrial history in different places. The taste of chocolate is also dictated by the chemistry of the resultant product. The type of chocolate preferred and/or the taste of chocolate that are found acceptable by a society also determined by structural properties of the product, the size of crystals and particles generally in the range of 10 µm to 120 µm in diameter, depending on the product. The taste of chocolate depends on the release of flavour 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 (Gulbay, 2007).

Chocolate is a confection made from cocoa mass, cocoa butter and sugar. In fact, cocoa butter contributes 30 to 40% by weight to finished chocolates. Typical formulations of chocolate are shown in Table 1.1. The properties of the fat phase of chocolate dictate the properties of the final chocolate product. The desired quality of chocolate (hardness, snap, gloss and desirable melting properties) can be achieved by proper crystallization of cocoa butter (Metin, 1997).

Table 1.1 Typical Chocolate Formulations (Beckett, 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

1.1.1. Components of Chocolate

1.1.1.1. Cocoa Mass

Cocoa liquor is the ingredient responsible for the flavor, color and personality of a chocolate. Cocoa Liquor is perhaps the most widely used description around the world but other synonyms are in use including chocolate liquor, cocoa mass and cocoa paste. Use of the word "liquor" does not relate to any alcohol content (Anonymous, 2009). Cocoa mass is turned up with grinding of cocoa nibs that means perfectly roasted cocoa beans separated from their husks and broken into small bits. (Beckett, 1999).

Manufacturers produce two types of cocoa mass: one for making chocolate and another for pressing cocoa cake and cocoa butter. Cocoa mass for chocolate processing may be less fine than mass for pressing. After blending with sugar, milk powder etc., the final fineness is reached when this mixture is refined (Beckett, 1999).

In fact the term relates simply to cocoa mass flowable nature at temperatures about the melting point of cocoa butter. Cocoa mass influence on the flavor, color and quality of chocolate is dependent on four very distinct and equally important factors:

1. The origin, variety and quality of the cocoa bean.

2. The flavor precursor development in the bean during fermentation and drying.

3. The flavor formation during subsequent processing (i.e. roasting).

4. The amount of the cocoa liquor used in the formulation of a chocolate (Anonymous, 2009).

One of the desirable characteristics for cocoa the mass used in large modern chocolate and pressing plants is consistency of quality. This cannot easily be achieved when using one source of cocoa beans because of the large variability which exists. In stock, to have a lot of different types cocoa beans of known quality and to make the suitable blend can reduce these quality differences. About 30% of the world cocoa bean crop is converted into cocoa mass in the country where it is grown. A typical set of quality criteria for cocoa mass is given in Table 1.2 (Beckett, 1999).

Table 1.2 Typical Quality Criteria for Cocoa Mass

Fat Content (%)	50-58
Moisture Content (%)	Max. 2,5
pH	5,2-5,8
Shell Content	Max. 1,75
Total Plate Count (per g)	Max. 5000
Moulds (per g)	Max. 50
Yeasts (per g)	Max. 50
Enterobacteriaceae (per g)	Absent
E.coli (per g)	Absent
Salmonella (per g)	Absent

1.1.1.2. Nutritive Carbohydrate Sweeteners

Impart sweetness and taste appeal to the chocolate and provide energy (calories), usually as carbohydrates. Nutritive sweeteners include:

1. Monosaccharides (e.g. glucose, fructose)

2. Disaccharides (e.g. sucrose)

3. Some common nutritive carbohydrate sweeteners are: sucrose, glucose, fructose, maltose, lactose, corn syrup, honey, molasses, and brown sugar.

4. Sugar alcohols (polyols) are not approved as nutritive carbohydrate sweeteners in the Standards of Identity for chocolate (Anonymous, 2009).

Sucrose, is main nutritive carbohydrate sweetener that is used in chocolate, it is disaccharide which is derived almost exclusively from sugar cane or sugar beet. Naturally, it is formed as white crystals in its pure state, but it can also be purchased as liquid form, which is an aqueous solution. Impure sucrose, crystals with coatings of syrup which are dark in colour, are known as 'brown sugars'. Sucrose is a disaccharide and a non-reducing sugar (Manley, 2010). Sucrose has two monosaccharides—dextrose and fructose—linked together by an ether linkage. It is known with the results of splitting this molecule into its two component parts—the process known as inversion (Vink, 2001).

1.1.1.3. Fat Phase of Chocolate

Fat consists 35% of the chocolate content and this is important for chocolate quality. Fat characteristics have great effect on chocolate production process. Especially the tempering and cooling stages are affected. When perspective of consumer evaluated, the character of fat that is used in chocolate production has a significant importance for the final product quality, for example its consistency and masticatory melting behaviour (Torbica et al., 2006). For these reasons the cocoa butter (CB), one of the main ingredients of chocolate, is the natural fat present in the cocoa bean (Metin, 1997). Although an ideal fat for use in chocolate is not suitable for use in warmer or tropical climates, as CB and chocolate soften under these conditions (Maheshwari and Reddy, 2005). So, for this application, there are various suitable vegetable fats. On the other hand, to use vegetable fats contribute to significant savings on the cost of raw material for the manufacturer. This can be carried out without affecting the properties of the end product. Also these vegetable fats can be used to modify sensory characteristics of chocolate or even to improve the heat stability of chocolate. In most countries, the use of up to 5% vegetable fats in chocolate are allowed by legislation. (Alenden et al., 2007a).

1.1.2. Preparation of Chocolate

Chocolates are suspensions of sucrose and cocoa particles, coated in phospholipids in a continuous fat phase, generally cocoa butter, with total solid content of 65% to 75% (Afoakwa et al., 2008a).

All chocolate formulated from some or all of the following ingredients (Timms, 2003):

- Cocoa products-cocoa liqour, cocoa powder of various types;
- Milk products- skimmed milk powder, whole milk powder, whey powder, lactose powder;
- Added fat-cocoa butter, milk fat, non-cocoa vegetable fat;
- Sugar-usually sucrose, but may be lactose, fructose or a sugar alcohol such as lactitol, sorbitol or mannitol;
- Emulsifier- lecithin, polyglycerol polyricinoleate (PGPR), YN (a synthetic phospholipid emulsifier), lactic acid esters (Jovanovic and Pajin, 2004)
- Flavour-vanilin, fruits, flavours, etc.

Chocolate is prepared as a liquid product and then solidified to form the finished product. After raw materials are mixed, the steps followed are shown in Table 1.3.

Table 1.3 Chocolate Process Flow (Anonymous, 2009)

1. Chocolate Formulation	
2. Pre-Refining Paste	Sweetener, cocoa liquor (cocoa mass), milk powder, cocoa butter and dry flavors plus enough of the cocoa butter to achieve a paste consistency that is optimal for refining.
3. Roll Refining	Reduces the particle size of the ingredients to the specifications for the particular recipe which influences the mouth feel of the chocolate
4. Conching	Dynamic agitation of semi-dry ingredi-

	ents under high temperatures to volatilize objectionable acids/flavors notes, develop a desirable flavor profile (Maillard reaction), decrease moisture content, reduce viscosity, round particle edges, smooth agglomerates
5. *Liquefaction and Emulsification*	Cocoa butter, lecithin, and/or other emulsifiers are added to the conched paste to reduce the viscosity. In conjunction with the emulsifiers, continuous agitation will distribute the cocoa butter over the particles to maximize the reduction in viscosity and improve the rheological properties of the coating.
6. *Batch Adjustment*	The viscosity, total fat percentage and color are standardized to the specifications for a particular formulation. In addition, the flavor of the chocolate is compared to the control to assure its consistency over time.
7. *Standardized Chocolate*	Consists of several standardized batches which are homogeneously mixed prior to disposition.
8. *Tempering*	Creating cocoa butter crystals in the stable form, size and quantity for depositing into solid chocolate.

1.1.3. Cocoa Butter

1.1.3.1. Production of Cocoa Butter

Cocoa butter is extracted from the seeds of a small tree botanically known as *Theobroma cacao*. The tree is grown in all wet tropical forest regions, mostly within 20 degrees of latitude of the equator. The three main growing areas are West Africa, South East Asia and South America. World production of cocoa-beans in 1999/2000 was estimated at little over three million tonnes (Foubert, 2003).

Cocoa is usually classified into three types: Forastero, Criollo and Trinitario. About 95% of the world's cocoa is now derived from Forastero trees and this cocoa is termed bulk cocoa in trade. Criollo has white cotyledons and is the original cultivated type. The origin of the Trinitarios is usually stated as the result of hybridisation between Forastero and Criollo trees. The Trinitario and Criollo varieties produce mainly the 'fine' or 'flavour' cocoas (Foubert, 2003).

The different steps needed to produce cocoa butter from the cocoa pod are discussed in the following sections and summarized in Figure 1.1.
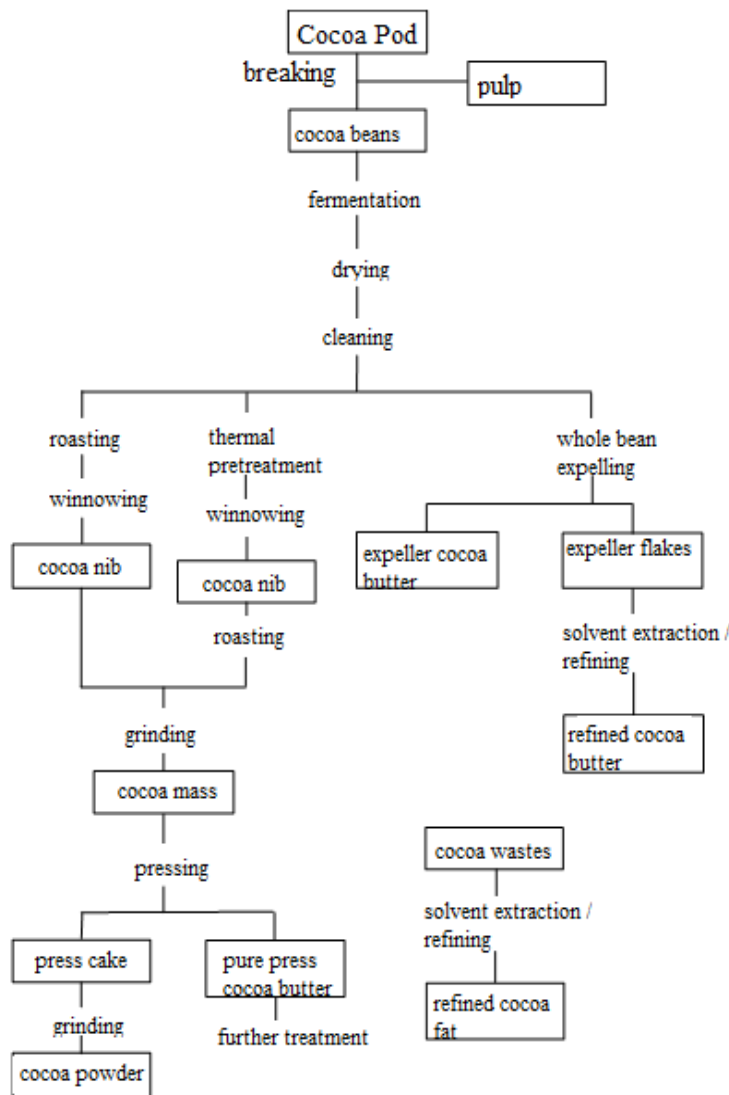
Figure 1.1 Overview of the steps in the production of cocoa butter (Foubert, 2003).

1.1.3.2. Chemical Properties of Cocoa Butter

The fat phase of the chocolate, cocoa butter, is described by specific physical proper-
ties. These properties are due to the triglyceride composition which is being formed
by specific fatty acids. Fatty acid content of cocoa butter, mainly composed of three
fatty acids, namely, palmitic acid (C 16:0, P), stearic acid (C 18:0, St) and oleic acid
(C 18:1, O) (Torbica et al., 2006). By combining these fatty acids are obtained pri-
marily triacylglycerides (TAGs) dominated by 1,3-disaturated-2-oleoylglycerol type:
1,3-dipalmitoyl-2-oleoylglycerol   (POP),   1-palmitoyl-2-oleoyl-3-stearoylglycerol
(POS) and 1,3-distearoyl-2-oleoylglycerol (SOS) and smaller quantities of mono-
and di-acylglycerides, polar lipids, free fatty acids and fat-soluble compounds

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(Afoakwa et al., 2008a). Although polyunsaturated triacylglycerides (TAGs) (StOO, 1,stearoyl-2,3-oleoylglycerol and POO, 1,palmitoyl-2,3-oleoylglycerol) are less than monounsaturated triacylglycerides (TAGs) also obtained (Loisel et al., 1998). Fatty acid and triglycerides composition of cocoa butter can be seen in Table 1.4.

Table 1.4 Composition of fatty acids and triglycerides of cocoa butter (Alenden et al., 2007b)

Fatty acids	
C16:0	23-25
C18:0	33-36
C18:1	33-37
C18:2	3-5
Triglycerides	
POP	15-18
POS	34-41
SOS	24-29
POO	2-5
SOO	4-8
Trisaturated TGs	2-3

1.1.3.3. Physical Properties of Cocoa Butter

Cocoa butter is a special fat because of its typical physical properties that are, of course, determined by its typical chemical composition. The most remarkable physical characteristic is the narrow melting range, between 32 and 35°C, i.e. just below body temperature. This property is determined by the relatively simple triacylglycerol composition when compared to other fats for example milk fat which has a much broader melting range caused by a much broader triacylglycerol distribution. Another special quality of cocoa butter is the quick meltdown in a narrow range of temperatures, which produces a cool sensation and is responsible for the pleasurable release of flavor (Foubert, 2003).

The other remarkable property is crystallization behavior. Cocoa butter can crystallize as a function of triglyceride composition into six polymorphic forms (I–VI), can

be seen in Figure 1.2. Although form V is the most desirable form, it is transformed to form VI which is the most stable form in storage. On the other hand, form I is the least stable form. Polymorphic triglyceride forms differ in distance between fatty acid chains, angle of tilt relative to plane of chain end methyl group and manner in which triglycerides pack in crystallization (Afoakwa et al., 2008a).

Nomenclatures[*]		Melting Points (^{o}C)	
γ	I	17	Highly unstable
α	II	23	
β`$_2$ -2	III	26	
β`$_1$ -2	IV	27	
β`$_2$ -3	V	34	
β`$_1$ -2	VI	36	The most stable form
*Both nomenclatures are used			

Figure 1.2 Crystal forms of cocoa butter (Alenden et al., 2007a)

The phenomenon of different molecular packing in such crystals is called polymorphism. Polymorphs differ in structure and also in other properties. They have different melting points, different melting enthalpies and different densities (Smith, 2006). They have also different stabilities as mentioned Figure 1.2. Crystal forms with low melting point are less stable and have a tendency to transform into more stable forms, with higher melting points. The speed with which polymorphic changes occur depends on relative stability of crystal forms and temperatures which they experience (Smith, 2006).

The form V is the most desirable form to obtain after chocolate has been produced. Form V has the suitable melting profile to melt quickly in the body temperature, obtaining maximum customer satisfaction. Chocolate needs tempering to have correct crystallisation status that is form V nuclei (Le Révérend et al., 2009).

1.1.3.4. Solid Fat Content

Many physical and sensory properties such as spreadability, firmness, mouthfeel, processing and stability are influenced by the solid fat content (SFC) of a lipid. (http://people.umass.edu).

The SFC expresses the percentage of the fat that is solid at various temperatures (Kniel, 2009). In other words;

SFC = 100 M_{solid}/M_{total}

M_{solid}: the mass of the solid lipid

M_{total}: is the total mass of the lipid in the food (http://people.umass.edu).

Figure 1.3. and Table 1.5. shows the cocoa butter SFC curve and %SFC values depending on the temperature.

Waxiness: If the SFC value at body temperature falls near to zero, the fat shows no or little waxiness. Significant levels of solids at 35 to 37°C means a waxy mouthfeel.

Melt: The graph shows a specific slope between 25 and 30°C. A sharp slope indicates a rapid melting of the fat and a fast release of the flavour. A shallow slope informs about an opposite tendency.

Hardness: Fats with high SFC values (> 50%) at room temperature are considered to have a hard texture.

Heat Resistance: Looking at the SFC level around 27°C can give an indication of the heat resistance of a fat (Kniel, 2009).

1.1.3.5. Tempering

Tempering is a directed pre-crystallization that consists of shearing chocolate mass at controlled temperatures to promote cocoa butter crystallization in a thermodynamically stable polymorphic form. During chocolate manufacture, tempering is used to obtain the stable form V of cocoa butter having a melting temperature of 32–34 °C, which gives the good snap, desired glossy appearance, residence to bloom, contraction and enhanced shelf life characteristics. The process involves pre-crystallization of a small proportion of triglycerides (TAGs), with crystals forming nuclei (1–3% total) for the remaining lipid to set in the correct form.
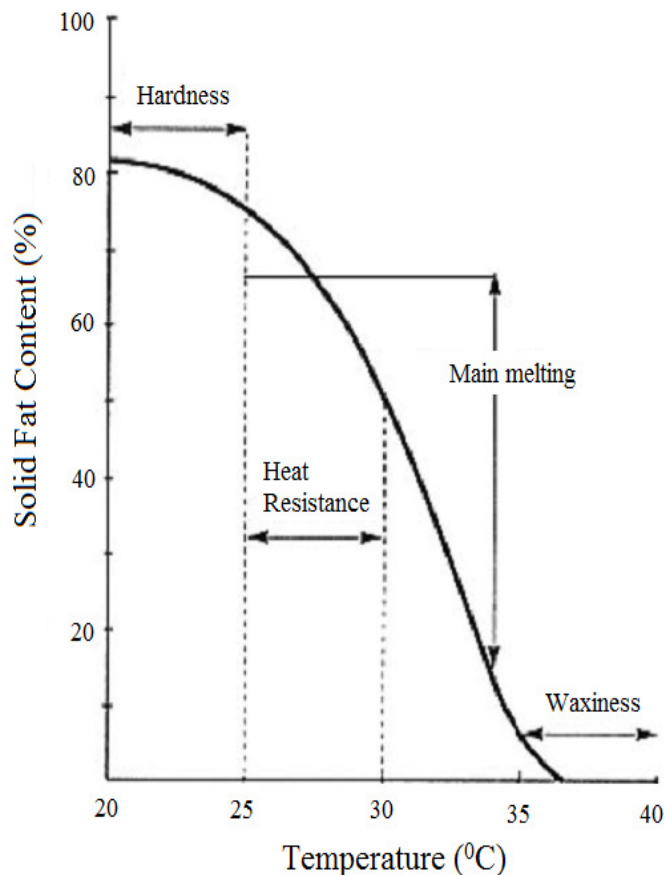
Figure 1.3 SFC curve of cocoa butter depending on the temperatures (Torbica et al., 2006)

Table 1.5 % SFC values of cocoa butter at various temperatures (Timms, 2003)

Temperatures	%SFC Value
At 20°C	75-80
At 25°C	66-75
At 30°C	40-50
At 35°C	0-3

moulds and cooled so that subsequent crystal growth occurs upon the existing seed crystals. Tempering has four key steps as like in Figure 1.4: melting to completion (at 50 °C), cooling to the point of crystallization (at 32 °C), crystallization (at 27 °C), and conversion of any unstable crystals (at 30–32 °C). Thereby, the tempering sequence is a function of recipe, equipment, and the final purpose (Afoakwa et al., 2008b).
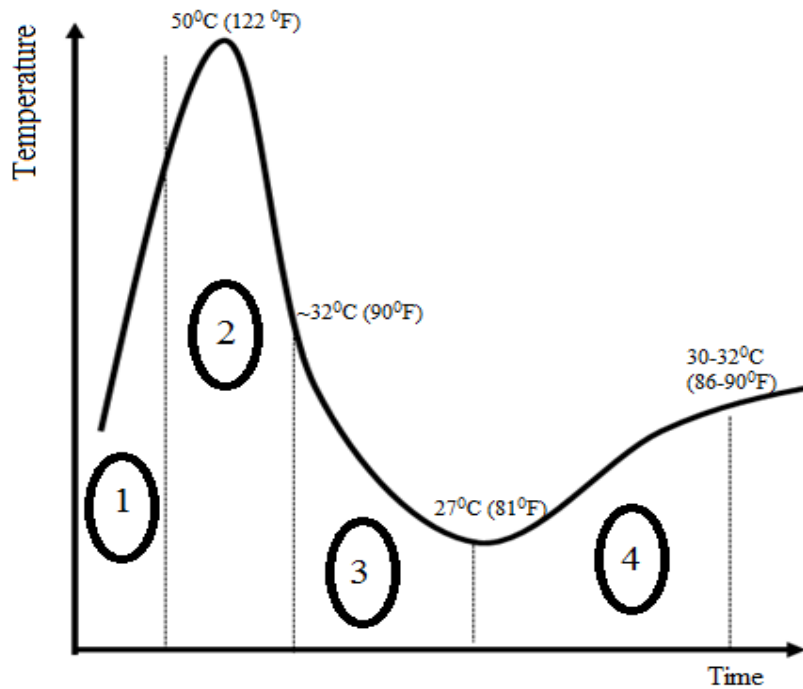
Figure 1.4 Chocolate tempering sequence (Beckett, 1999). 1, Melt out all of crystals; 2, Removal of "sensible" heat. No crystals formed; 3, Formation of both stable (βV) and unstable (βIV) crystals; 4, Melt out unstable (βIV) crystals leaving only stable (βV) crystals.

The degree of tempering, indicating the quantity of stable crystals that have been formed, can be measured by means of a tempermeter. With this method, a certain amount of liquid chocolate is cooled under specific conditions, and the temperature of the chocolate is registered with a temperature sensor (Anonymous, 2009).

Optimal tempering: When chocolate is tempered properly, its temperature will remain more or less constant for some time during cooling as is seen in Figure 1.5. The released crystallization heat is then balanced by an equal amount of cooling energy. Only when the liquid cocoa butter is transformed into solid crystals, the temperature of the chocolate drop further (Anonymous, 2009).
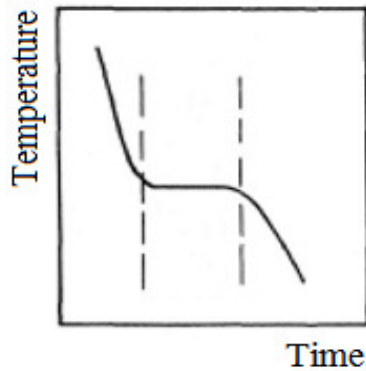
Figure 1.5 Optimal Tempering (Kniel, 2009)

Under tempering: If the chocolate is insufficiently tempered or not tempered at all, thus making fewer stable seeding crystals available, more crystallization heat will develop during cooling, as more liquid fat has to be transformed into the solid form. A significant increase can be seen in temperature at the beginning of crystallization. It will decline again after reaching a maximum (Figure 1.6.). This phenomenon is called under-tempered chocolate, and it often leads to demolding and fat bloom problems because insufficient stable crystals were present during the cooling of the end-product (Anonymous, 2009).

Over tempering: Chocolate can also contain too many stable seeding crystals. This will be perceptible in the rheology of the chocolate. Because a significant part of the liquid fat has been withdrawn from the continuous phase of the chocolate and is now transformed to the solid form, less liquid fat is available for pumping the product. This type of chocolate will release little crystallization heat during cooling, rendering
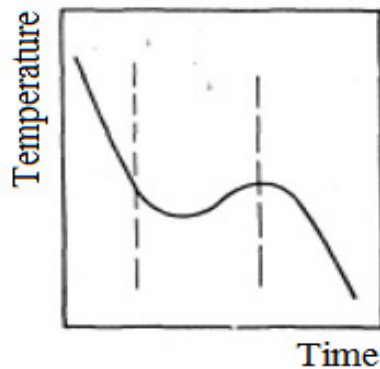
Figure 1.6 Undertempering (Kniel, 2009)

a rather flat cooling curve (Figure 1.7.). As a substantial part of the phase transition (from liquid to solid) has taken place before the chocolate reaches the mold, less contraction will occur in the mold, leading to demolding problems at the end of the process (Anonymous, 2009).
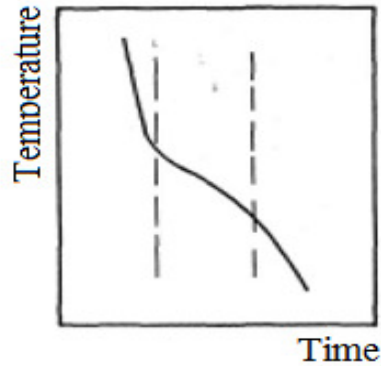
Figure 1.7 Over Tempering (Kniel, 2009)

1.1.3.6. Crystallization Behavior of Cocoa Butter

For the application of cocoa butter in chocolate, the crystallization behavior of cocoa butter is its most important functional property. The conversion from liquid into solid form is a critical step in the chocolate production process that not only determines the quality and the shelf life of the end-product but also requires capital investments in tempering and cooling equipment.

In the case of cocoa butter, at least six crystal forms (I-VI) can be distinguished as mentioned in Section 1.1.3.3. The most stable form is the one where the fat molecules are most densely packed and structured in such a way that the least space exists between them. This form requires the most heat to convert from the solid to the liquid form and is indicated for cocoa butter as forms V and VI. Between the forms I + II and V + VI lie the meta-stable forms III and IV (Anonymous, 2009).

All cocoa butters, regardless of origin, demonstrate this polymorphic behavior. To be able to make stable end-products, the cocoa butter must assume the crystalline form V. This can be achieved by a process called tempering that was defined before. The completely liquefied chocolate is cooled, usually by means of a scraped surface heat exchanger, so that part of the fat crystallizes into unstable crystals. Subsequently, the

temperature is raised, so that most of these crystals will liquefy again, but a part will re-crystallize into the stable form (Anonymous, 2009).

By maintaining the temperature below the melting point of the stable crystal form, the product (chocolate) is being seeded with stable crystals. These are the basis of the crystal structure that will be formed during subsequent cooling (Anonymous, 2009).

1.1.3.7. Texture

Texture is a combination of its surface and mechanical properties and the physical structure of the material. Chocolate's melting profile is unique in the mouth because cocoa butter has a melting point that is very close to body temperature. Part of the appeal of chocolate is smooth mouth-feel the texture is changed and a difference is perceived (Andrae-Nightingale, 2009).

Chocolate processing techniques that define texture of products and their relationships are important since chocolate consumers have well-informed opinions and expectations regarding appropriate texture and its melting characteristics. Successful new product development requires care regarding texture of products and their characteristic melting profiles, based on an understanding of factors such as ingredient composition, tempering, process conditions. Even though texture perception is a dynamic oral process before and during mastication, individuals also perceive texture through vision, touch, and hearing (Afoakwa et al., 2008c).

Researchers have completed various instrumental texture studies about chocolate. In these instrumental texture studies, a texture analyzer or texture probe is the most used method (Andrae-Nightingale, 2009).

1.1.4. Cocoa Butter Alternatives

Cocoa Butter is the only continuous phase in chocolate, thus responsible for the physical behaviour of chocolate. The properties such as its complete and quick melting at body temperature and its brittleness at room temperature are unique to cocoa butter. Because of economic and technological reasons, manufacturers made, and make efforts strongly to replace cocoa butter in part for chocolate production. Cocoa butter alternatives are called cocoa butter replacers (CBRs), cocoa butter equivalents (CBEs), cocoa butter substitutes (CBSs). These fats are produced from various vege-

table fats (often modified) as mixtures of as palm and palm kernel oil, ilipè fat, shea butter, sal fat and kokum butter. In addition, a large variety of other vegetable oils are used (Lipp and Anklam, 1998). Cocoa butter alternatives are shown in Figure 1.8.

1.1.4.1. Cocoa Butter Equivalents

They are non-lauric (not containing lauric acid) plant fats, which are similar in their pysical and chemical properties to cocoa butter and mixable with it in every amount without altering the properties of cocoa butter. CBEs can be divided into two groups;

Cocoa Butter Extenders (CBEXs) these fats are subgroup of CBEs that cannot mix with cocoa butter in every ratio,

Cocoa Butter Improvers (CBIs) thats are similar to CBEs, but with higher content in solid triglycerides; used for improving soft cocoa butters (Lipp and Anklam, 1998).
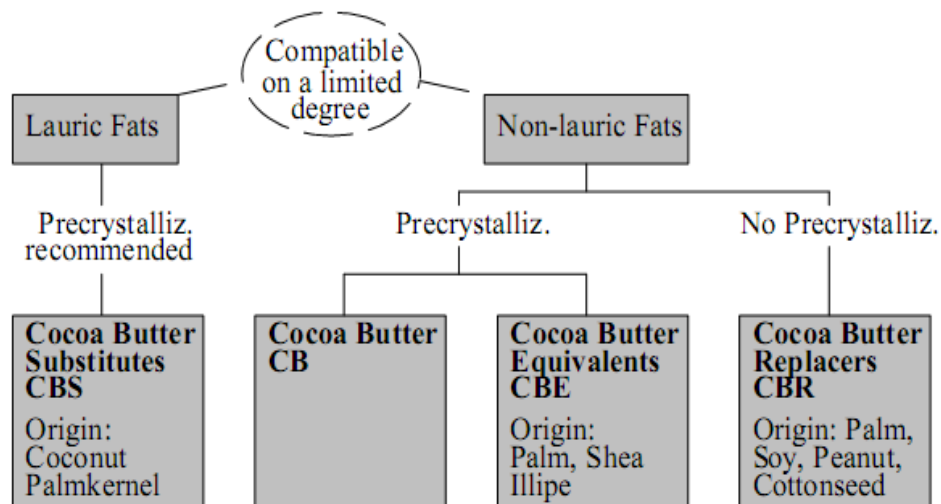
Figure 1.8 Cocoa butter alternatives (Kniel, 2009)

Generally, cocoa butter and CBEs show the same properties considering crystallisation, texture and eating properties in chocolate. The shelf life can be prolonged and the bloom stability improved with an addition of a good quality CBE to the chocolate formula. Using normal CBE does not need modification in the manufacturing process parameters but if softer or harder CBE is used slight adjustment of temperature may be needed during tempering process (Alenden et al., 2007a).

A good quality CBE and cocoa butter can be mixed in any proportion without changing the melting sequence, as is illustrated in Figure 1.9. And also CBE will give the

same reaction as cocoa butter when softening fats such as nut oils or milk fat are mixed in (Alenden et al., 2007a).

CBE must meet certain requirements:

- The melting profile of the CBE must reflect cocoa butter's.
- Fatty acid and triglyceride composition of the fat should be close to cocoa butter.
- Cocoa butter and the fat must be compatible with each other.
- The fat should allow processing of chocolate products in an identical manner to that of cocoa-butter-based products.
- When the fat crystallized, it must be the same polymorphic form as cocoa butter which is in the β form.
- The products with CBE should be at least as good as in terms of bloom-free shelf life and appearance products based on only cocoa butter.
- Flavor stability of the CBE should be good. (Beckett, 1999).
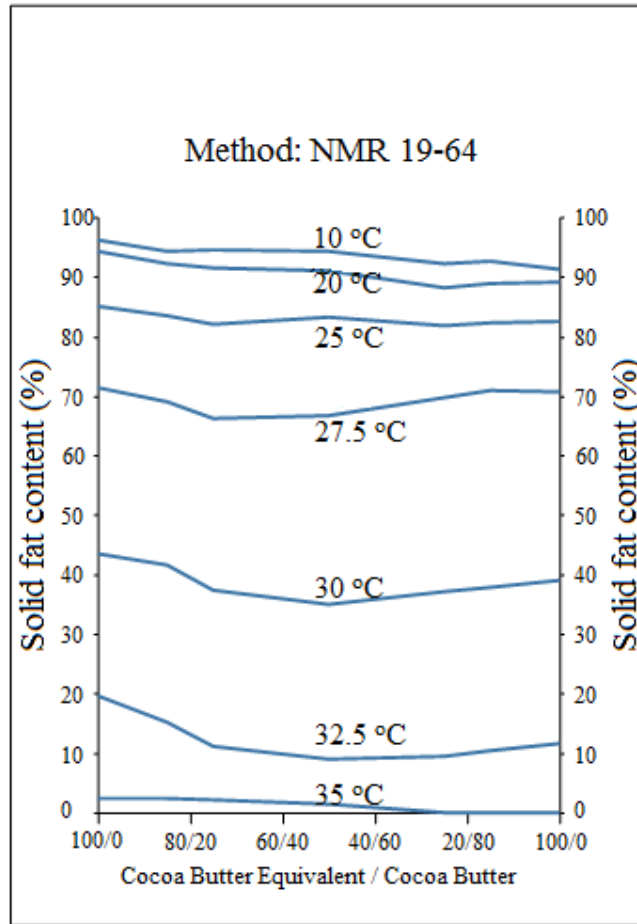
Figure 1.9 Solid Fat Content of CBE / CB mixtures (Alenden et al., 2007a).

Composition of CBEs: CBE are composed of the triglycerides POP, POS and SOS in order to mimic the properties of cocoa butter. POP is obtained from palm oil by fractionation and is then blended with fats rich in POS and SOS. A typical source of SOS is shea nut oil, hile illipe fat contains POS and SOS (Alenden et al., 2007a).

Other sources of oils and fats used in CBE are sal, mango and kokum. Today CBE products can also be manufactured through enzymatic interesterification of more abundant raw materials. However these products are not approved for use in chocolate in the European Union (Alenden et al., 2007a).

The melting points of the stable polymorphs of POP, POS and SOS are 37 °C, 37 °C and 43 °C respectively. This implies that the higher the SOS content of the fat the harder it will be, although an excessively high content may increase viscosity in the tempered chocolate mass. If POP is the main component, the fat will temper slowly

and be soft. Since POP is normally the cheapest component there must be an optimum cost/benefit depending on the application for the fat. There is also another dimension to fat quality: the pureness of the fractions or concentration of the required symmetric triglycerides that are used in the final CBE. This will also be reflected in the performance as well as the price of the fat (Alenden et al., 2007a).

1.1.4.2. Cocoa Butter Replacers

Although these fats, that are non-lauric fats, have similar fatty acid distribution with cocoa butter, have a different structure of the triglycerides. These fats are compatible with cocoa butter only in small ratios. (Lipp and Anklam, 1998).

Tempering is not necessary for compound chocolates and coatings that made with CBR because after cooling CBRs are crystallized in the stable form. (Alenden et al., 2007a).

CBRs are produced by hydrogenation and fractionation from raw materials that are non-lauric oils as palm oil and soybean oil. Although these CBRs contain palmitic, stearic and oleic acid, their arrangement within the triglycerides is more random and the structure differs considerably from cocoa butter. In addition, a high content of trans acid (elaidic acid) is present. Consequently cocoa butter and CBRs are incompatible on certain rates (Beckett, 1999).

There are two main reasons for using CBR instead of cocoa butter: the price is lower, and production is simplified since the tempering step can be omitted (Alenden et al., 2007a).

It is obvious that the triglycerides of cocoa butter are different from those of CBR. Since the fatty acids of both alternatives are C16 and C18, however, there is a certain degree of compatibility and up to 20 % cocoa butter (20 % of fat phase) can be tolerated before the eutectic effects get too severe for practical use. As is seen in Figure 1.10. blends of cocoa butter and CBR show a typical eutectic behaviour. Within limits this can be used to improve melting and sensory properties of CBR-based compounds (Alenden et al., 2007a).
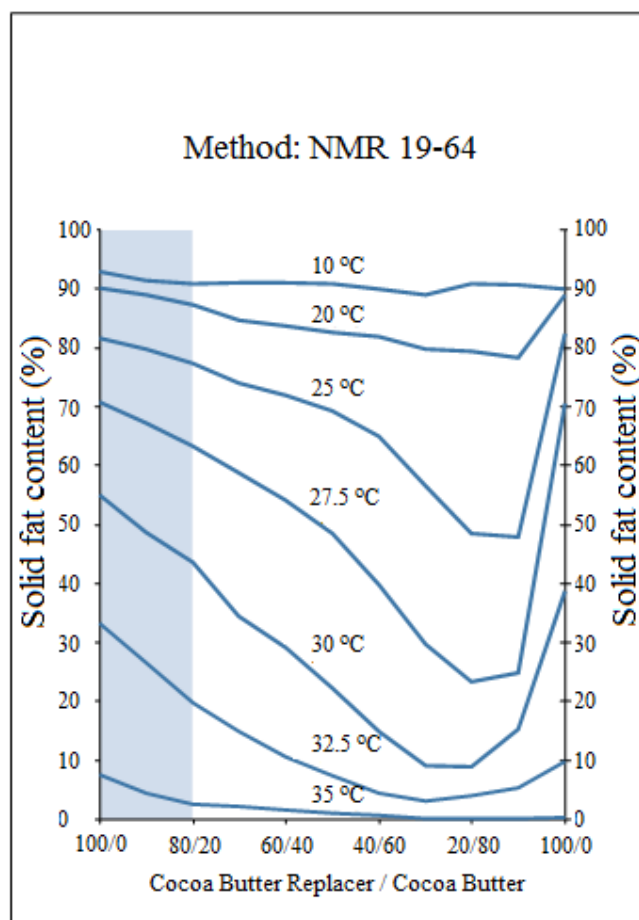
Figure 1.10 Solid Fat Content of CBR / CB mixtures (Alenden et al., 2007a).

In the 10-20 % range the addition of cocoa butter has a controlled softening effect that is more pronounced at higher temperatures. The use of higher levels of cocoa butter than 20 % is not commendable since the eutectic effects will be too severe (Alenden et al., 2007a).

Composition of CBRs: There are a lot of sources (raw materials) for CBR production such as soybean, rapeseed, palm, cottonseed and sunflower oil etc. To produce these kinds of fats from these raw materials, special hydrogenation and fractionation techniques are applied (Alenden et al., 2007a).

Main fatty acids are saturated palmitic and stearic together with monounsaturated oleic acid and its trans isomers. Thus, the fatty acid chain length is C16 and C18 (Alenden et al., 2007a).

CBR may contain small amounts of additives such as sorbitan tristearate (STS) that is a nonionic surfactant which is variously used as a dispersing agent, emulsifier, and stabilizer in food to help stabilize the crystallization form. This improves both the gloss retention and initial gloss of the compound coating (Alenden et al., 2007a).

1.1.4.3. Cocoa Butter Substitutes

These are lauric plant fats (containing lauric acid). Chemically totally different to cocoa butter, with some physical similarities; suitable only to substitute cocoa butter to %100 (Lipp and Anklam, 1998). This also means that there is a considerable degree of incompatibility between lauric CBRs and cocoa butter (Beckett, 1999).

To a large extent, the use of CBS in compounds is driven by the same motives as the use of CBR: lower costs and simplified production procedures. A CBS needs no tempering, and high crystallization rates allow a high throughput in the cooling tunnel (Alenden et al., 2007a).

CBS and cocoa butter have completely different fatty acid and triglyceride profiles. Hence, as is seen in Figure 1.11. eutectics are apparent already at low levels of cocoa butter in CBS. In contrast to CB/CBR blends the strongest effects are seen at intermediate temperatures, from 20 to 30 °C (Alenden et al., 2007a).

This means that cocoa liquor cannot be used in CBS-based compounds. Cocoa powders typically contain 10-12 % fat. A typical content of cocoa powder in compounds is 15 %, which gives a CBS/CB ratio of approximately 95/5. As may be seen in the diagram, going beyond this will result in excessive softening of the product (Alenden et al., 2007a).

Composition of CBSs: CBS are based on lauric fats, i.e. fats that contain a high percentage of lauric acid in their fatty acid composition as discussed above. The main raw materials in this group are coconut and palm kernel oil, with palm kernel
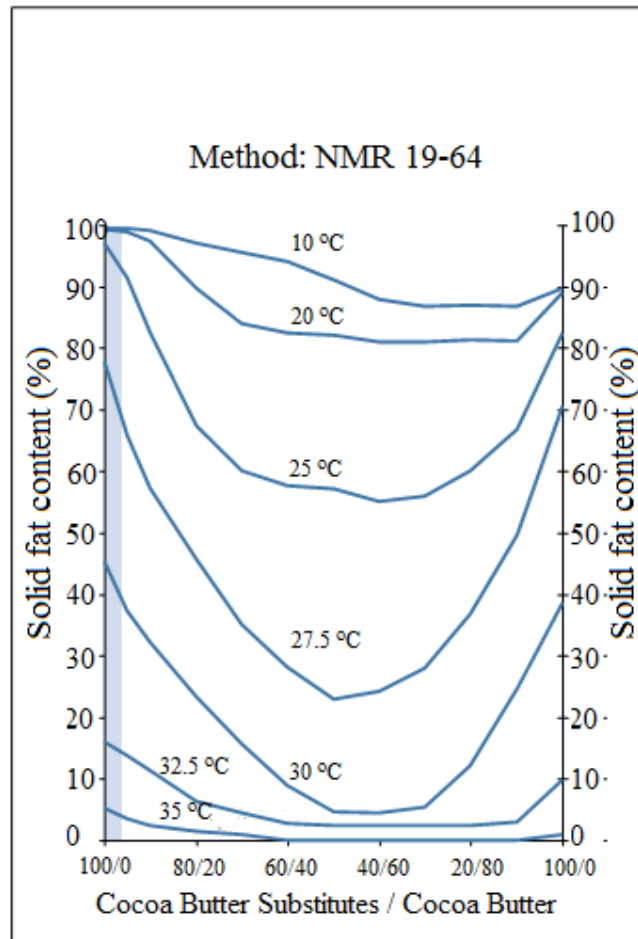
Figure 1.11 Solid Fat Content of CBS / CB mixtures (Alenden et al., 2007a).

being the preference for CBS manufacture. The production of CBS involves special hydrogenation and fractionation techniques. Lauric acid (C12) makes up approximately 50 % of the fatty acid composition, with myristic acid (C14) as the second most abundant. In addition, smaller amounts of the longer chain palmitic and stearic acids are present (Alenden et al., 2007a).

1.1.5. Measurement of Quality Parameters

1.1.5.1. Melting Behaviour of Chocolate

Melting behaviour of fats is often simply expressed as either clear, softening, dropping, slip or cloud points. These methods are well defined and standardized by AOCS (American Oil Chemist's Society). Although none of these methods gives information about "real" melting process, they provide auxiliary information to describe melting behaviour of fats. Nuclear Magnetic Resonance (NMR) is often used

to determine percent solid fat content (SFC) at selected temperature. NMR provides definitive data to describe solidification and melting profile of a fat according to a given tempering profile since SFC usually is dependent on temperature history for polymorphic fats. Thermal analysis methods can provide valuable information on melting and crystallization behavior as well as kinetics of crystallization. Differential Scanning Calorimetry (DSC) is the most common thermal analysis instrument for studying thermal behaviour of fats (Metin, 1997).

1.1.5.1.1. Solid Fat Content

Fats are mixtures largely comprising a range of structurally similar triacylglycerol molecules with differing fatty acid substituents. Because these compounds are to some extent mutually soluble, edible fats typically show a melting range rather than the clear melting point that is characteristic of a pure compound. The melting range of many food lipids occurs at the temperatures used in food preparation, storage, and use. Because the ratio of solid fat to liquid oil affects the texture, stability, and mouthfeel of foodstuffs, the melting range is a parameter of crucial interest to many food scientists involved in research and quality control. The ratio of solid to total fat is expressed as the solid fat content (SFC) (Coupland, 2001).

The melting profile is frequently further complicated by the presence of a number of types of metastable crystal habits and by the significant supercooling of liquid oils. A consequence of these factors is that it is impossible to accurately predict the solids content of a real food oil using only temperature and composition data; experimental investigations are therefore essential. Fortunately, many of the physical properties of solids and liquids are very different, and several appropriate techniques for measuring fats in both phases have been developed. The most widely used approach is pulsed nuclear magnetic resonance (NMR; Basic Protocol, direct method). The nuclei in solids have different resonance properties from those in liquids, and the two phases can be distinguished by NMR to provide their relative proportions easily and nondestructively (Coupland, 2001).

In NMR, the sample held in a uniform magnetic field, which causes the protons in it to become polarized and magnetisation to occur. A short radio frequency pulse, at a preselected frequency, causes a rotation of this magnetization vector around an axis

normal to the original magnetic field. After the pulse, the longitudinal and transverse components of the rotating magnetism return to equilibrium over different periods, known as relaxation times. Because of their greater mobility, the relaxation time for molecules in the liquid state is much longer than for those in the solid state. It is therefore possible to determine the relative proportions of these two states in sample (Beckett, 1999).

When the chocolate is being analysed account must be taken of the other solid components present, e.g. sugar, milk proteins, etc., that result in reduced sensitivity (Beckett, 1999).

Considering the facts that the quality of cocoa butter is not standard, and also cocoa butter is an expensive raw material. The melting properties of cocoa butter may be unsuitable to use for certain climate conditions and purposes, and that the chocolate manufactured using exclusively cocoa butter has limited gloss retention, fats analogous to cocoa butter are also used in the production of chocolate, chocolate-like products, and cream products. These fats are based on natural oils and fats and are produced applying various technological procedures. In these fats production various raw material with different origins are used according to the purpose of the manufacturer. The usage of these fats in combination with cocoa butter of optimal composition is the key factor in the manufacturing process of confectionery products, for it has a major influence on the quality of the final product (Torbica et al., 2006).

Mixed lipid system's phase behaviors are extensively under current research but it is not yet understood. Eutectic and diluent effects of fats in the mixtures have been studiied by using solid fat content (SFC) profiles by many investigators. From these profiles, compatibility of two fats can be readily determined. If two fats are perfectly compatible and exhibit similar melting behavior, the lines of constant SFC lie on straight horizontal lines that connect the melting temperatures of the individual fats. Two fats with different melting behavior can be compatible in phase behavior. In this way, lines of constant SFC are straight and connect points for the two pure fats, but decrease in temperature from the harder fat to the softer fat. In this case, diluent softening of the hard fat occurs by addition of the softer fat. For extreme incompatibility between fats, eutectic crystallization effects cause significant depressions in SFC for mixtures of two fats. On the isosolid diagram, this is seen as a compression of the

lines of constant SFC and melting temperatures below each of the individual fats. Thus, isosolid diagrams can be used to rapidly distinguish compatibility of two fats (Williams et al., 1997).

1.1.5.1.2. Thermal Behaviour

Differential Scanning Calorimeter (DSC) is the most common thermal analytical instrument for studying thermal properties of a fat. The basic principle of DSC is to measure the differential heat flow between sample and reference, which are maintained at nominally the same temperature, as temperature is changed. DSC needs to be calibrated to ensure accuracy in the temperature scale and calorimetric response. DSC analysis starts by placing sample and reference pans into their respective holders. As analysis begins, energy is supplied to or removed from each pan to maintain identical pan temperatures. As the temperature changes, increasing or decreasing at a certain rate, the sample takes in or gives off energy. The energy taken in or given off is offset by decrease or increase in energy supplied to the pan. The energy difference between sample and reference is recorded while maintaining the same temperature in both pans (Metin, 1997).

Two types of DSC systems can be distinguished depending on the method of measurement used: power-compensation DSC and heat-flux DSC. In power-compensation DSC, separate (identical) ovens control the reference and sample temperatures, the sample and reference temperatures independently. The temperature difference between the sample and the reference is maintained to zero by varying the energy input into the two ovens. This type of DSC thus directly measures the energy flow to and from the sample and therefore the heat absorbed or released by the sample as it is subjected to a specific time-temperature program (Foubert, 2003).

In heat-flux DSC the sample and the reference material are enclosed in the same oven together with a metallic block (constantan disc) with high thermal conductivity that ensures a good heat flow between sample and reference. Figure 1.12. shows a cross-sectional diagram of a DSC-cell of the heat-flux type. The reference material and the sample are put in pans sitting on raised platforms on the constantan disc. Heat is transferred through the disc and up into the sample and reference via the sample pans (Foubert, 2003).

dynamic sample chamber

reference pan   sample pan

gas purge inlet

lid

chromel disc

heating
block

thermocouple
junction

thermoelectric disc
(constantan)

alumel wire
chromel wire
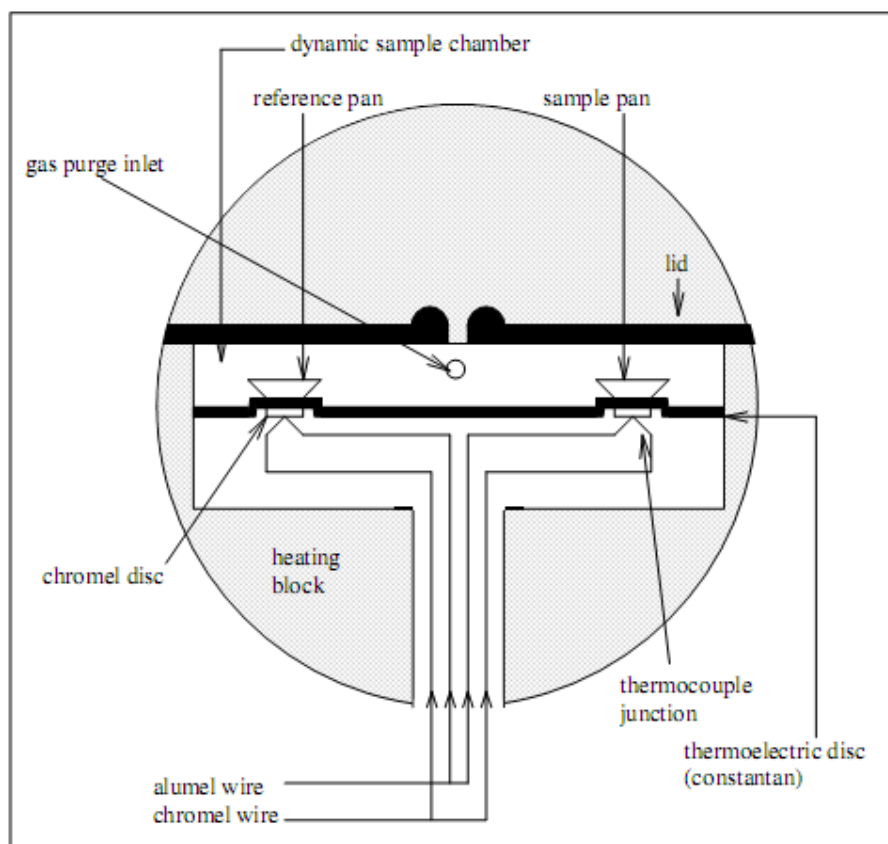
Figure 1.12 A DSC-cell of the heat-flux type

The most important factors influencing DSC curves are;

- The adjustment of the instrument, calorimetric sensitivity and scanning rate,
- The nature of the sample and its size,
- The reference material,
- The atmosphere, whether oxidizing or inert (Metin, 1997).

1.1.5.2. Texture of Chocolate

Chocolate is, actually, a suspension that cocoa mass and sugar suspended in fat phase (cocoa butter). Because of unique interactions between polymorphic lipid structures, cocoa butter has a discrete texture. Sugar bloom or fat bloom, which affect both textural and visual quality, can be formed with different storage conditions. (Andrae-Nightingale et al., 2009).

Texture is a combination of the physical structure of the material and its mechanical and surface properties. Chocolate has a unique mouthfeel because cocoa butter has a narrow melting point, very close to body temperature. Chocolate particle size is also extremely important to sample mouthfeel. Part of the appeal of chocolate is smooth mouth-feel; as bloom forms (both fat and sugar), the texture is changed and a difference is perceived (Andrae-Nightingale et al., 2009).

The mouth-feel of a product is determined by its texture, viscosity, and behavior during the (often short) period of residence time in the mouth. This can be described in such terms as hard, smooth, crunchy, watery, powdery, greasy, waxy or dry. The melting behavior of the fat phase can be of influence also. A product can be liquid, half liquid, paste, or solid, all forms in which cocoa-flavored products are available to the consumer (Anonymous, 2009).

1.2. The Aim of the Thesis

Chocolate can be defined as a mixture of cocoa butter, cocoa liquor and sugar, plus any milk fats added when manufacturing 'milk chocolate'. Cocoa butter is ideal fat for chocolate and it is responsible for physical behaviour of chocolate also which is unique with its quick and complete melting and brittleness at room temperature.

But there are strong considerations to replace cocoa butter in part for chocolate production for technological and economic reasons.

The general reasons of tending to industry cocoa butter alternatives (CBAs), partly in place of cocoa butter:

- Cocoa butter gets softer with the temperature. So it is not acceptale for warm climates.
- Cocoa butter is an expensive raw material.
- Cocoa butter is a natural raw material so it has no stable quality.
- Cocoa butter needs tempering.
- Cocoa butter has high production cost.

Therefore, efforts have been made to find an alternative to cocoa butter among vegetable oils and fats and to replace parts of the cocoa butter in chocolate. Since there is

no naturally occuring fat with the same physical properties as cocoa butter, possible alternatives are made by blending and/or modifying fats. Modifying the chemical composition of fats and oils to obtain the desired properties of the fat systems has been described in different studies a long period of time (Vereecken, et.al.,2009; Guice,V.et.al., 1958). Recently, Wang, et.al., (2010) have studied the effect of fat composition on both texture and bloom of lauric-based compound chocolates. A stearic acid-rich fat, kokum was used up to 5% by wt of the product to increase the heat-resistance property of chocolate so that it could be used in warm climates (Maheshwari and Reddy,2005).

The aims of this thesis were to study melting behavior and texture properties of dark chocolate samples which were prepared with different vegetable fats such as hazelnut oil, shea butter stearin and palm kernel stearin, in part in lab scale; and to compare physical properties of these samples with the standard sample prepared with only cocoa butter.

CHAPTER 2

MATERIAL AND METHODS

2.1. Materials

Materials used in this study were kindly provided by a chocolate factory, ŞÖLEN ÇİKOLATA A.Ş., in Gaziantep, Turkey (Table 2.1).

Table 2.1 Manufacturers of the raw materials

Raw Material	Manufacturers
Cocoa Butter (CB)	Altin Marka (Istanbul, Turkey)
Cocoa Mass	Altin Marka (Istanbul, Turkey)
Lecithin	Lasenor Emul, S.L. (Barcelona, Spain)
Vanillin	Eternal Pearl (Shanghai, China)
Hazelnut oil (HO)	DOK (Kahramanmaras, Turkey)
Shea Butter Stearin (SBS)	AarhusKarlshamn (Malmö, Sweden)
Palm Kernel Stearin (PKS)	Marsan (Adana, Turkey)

2.2. Methods

2.2.1. Preparation of Dark Chocolate Samples

All dark chocolate samples were prepared by using the formulation given in Table 2.2. For each dark chocolate sample except standard sample, cocoa butter was replaced at a level of 5% with different vegetable fats, hazelnut oil, HO, shea butter stearin, SBS, or palm kernel stearin, PKS by weight of the product. The standard sample was prepared with only CB, sample I with HO, sample II with SBS and sample III with PKS. Maheshwari and Reddy (2005) had been reported that some Europian countries permit the amount of 5% (w/w) vegetable fats on product bases. That is the acceptable limit in Turkey too.

All ingredients except lecithin, cocoa butter for standard sample and cocoa butter and other vegetable fats, HO, SBS or PKS, for sample I, II and III, respectively, were mixed by using a mixer (Welbilt, USA). Then the mixtures were passed through a three-roll refiner Buhler SDY 200 (Uzwil, Switzerland) keeping the temperature and pressure between rollers and pressure of the stripping knife constant for all samples. The resultant mass was conched (Buhler ELK-0005, Switzerland) for 5.5 hours at 70 °C by adding second porsion of the total fat (25 % w/w) and 12,5 % (w/w) of the total lecithin. At the end of conching, remaining cocoa butter, lecithin or vegetable fat (for samples I, II and III) were added and conched again for 5 min for mixing and liquefaction.

Table 2.2 Formulations of standard chocolate and chocolate with HO, SBS or PKS

Ingredient (%)	S	I	II	III
Sugar	41,86	41,86	41,86	41,86
Cocoa Butter	13,67	8,67	8,67	8,67
Cocoa Mass	44,00	44,00	44,00	44,00
HO	-	5,00	-	-
SBS	-	-	5,00	-
PKS	-	-	-	5,00
Lecithin	0,40	0,40	0,40	0,40
Vanillin	0,07	0,07	0,07	0,07
Total Fat Content	37,87	37,87	37,87	37,87

Each chocolate sample (5 kg batch for each formulation) was incubated at 50 °C for 4 h in order to melt the mass prior tempering (Afoakwa, 2008c). Later, tempering process was performed with cooling the chocolate at 30,7 °C by using a laboratory scale temperer (GAMI T240, Schio, Italy). As reported by Afaokwa (2008c), to ensure a temper index of 5.0 ± 1 CTU, pre-crystallization was measured using Tempermeter E4 (Sollich, Bad Salzuflen, Germany). Tempered chocolate samples were moulded using plastic moulds with dimensions of 44 mm diameter and 4 mm height. Moulds were allowed to cool in a Vötsch VC 0034 conditioning cabin (Balingen-Frommern, Germany) at 12 °C for 2 h (Afoakwa, 2008c). Then samples were de-moulded and conditioned in a storage room at 18 ± 3 °C to be used for further measurements. Temperature control was done with a temperature recorder TFA WS-9010

(Baden-Württemberg, Germany) which records temperature at every 4 h. Graph of temperature change in the storage room was given in Figure 2.1.
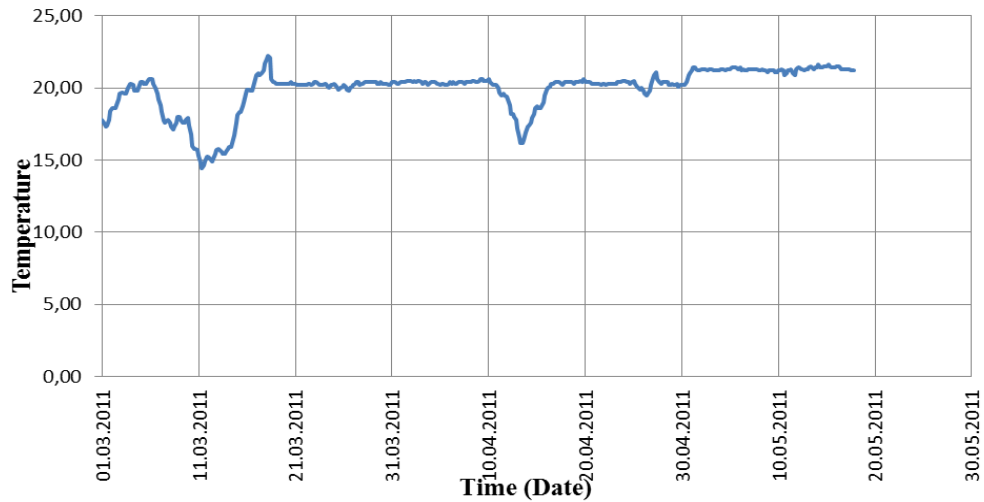

Figure 2.1 Temperature change of the storage room during analysis

2.2.2. Storage Prior Measurements

2.2.2.1. Determination of viscosity

The viscosity of the chocolates after conching was measured at 40 ^{o}C by using Brookfield DV III viscosimeter, with SC4-27 spindle and outer cylinder. Sample volume was ~10 cm^3 and different turning speeds such as 2-4-6-8-10-12-14-16 rpm were used. The temperature was maintained constant by using a water bath (Brookfield TC-602, USA). Shear stress, shear rate and viscosity were measured at each turning speed using Rheocalc V2.3 software. From these values Casson plastic viscosity and Casson yield stress (yield value) were also calculated using Rheocalc V2.3 software.

2.2.3. Measurements

2.2.3.1. Solid Fat Content

Preparation of samples: First of all, liquefied chocolate samples were transferred to centrifuge tubes and samples were mixed with equal amounts of petroleum ether in order is to dissolve oil in chocolate. Centrifugation was carried out for 10 min at 9000 rpm by a centrifuge machine (Nuve NF 800 R, Ankara, Turkey). Supernatant

consisting oil-ether solution of each tube was collected into erlenmeyers and all petroleum ether was completely vaporized in an oven at 105 °C. Thus fat samples were analyzed for solid fat content with Nuclear Magnetic Resonance (NMR) (Gulbay, 2007).

Solid fat content determination (SFC): SFC in the cocoa butter and cocoa butter-vegetable fat mixtures were determined by using Bruker mq20 minispec NMR (Ettlingen, Germany).

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

Every fat samples were filled into four NMR tubes up to 3 mL and SFC of fat and fat blends were determined at the following temperatures: 20°C, 25°C, 30°C, and 35°C.

NMR tubes were capped and tempered according to IUPAC method 2.150 as Wang et al. (2010) were studied and also according to ISO 8292-1. Samples were holded at 60°C for 30 min, at 0°C for 90 min, at 26°C for 40h, at 0°C for 90 min. Then all samples were kept at measuring temperatures which were 20°C, 25°C, 30°C, 35°C for 60 min. This tempering process was performed with Lauda Ecoline RE104 water baths (Lauda-Königshofen, Germany).

After tempering process, the results of four samples were directly taken from NMR machine and recorded.

2.2.3.2. Differential scanning calorimetry

A Mettler Toledo DSC 822 (Zurich, Switzerland) differential scanning calorimeter with a cooling system HAAKE EK90 (Canada) was used to obtain melting and crystallization characteristics of the samples.

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

Sample (10-20 mg) was loaded into the pans. Each pan was put into the sample holder of the machine where an empty aluminum capsule was also put near to sample as reference. As Afoakwa et al. (2008a) and (2008c) were studied, pans were heated at a

rate of 5 °C/min from 15 to 55 °C in a N_2 stream. At the end of each measurement, graph of heat flow rate versus time and temperature were plotted on the computer with software called STARe V8.10. Enthalpy of melting and melting point were estimated. Four samples were analyzed within 15-day intervals from 0 to 60 days.

2.2.3.3. Texture analysis

Textures of samples were analyzed with a TA-XT Plus Texture Analyzer (Stable Micro Systems, Surrey, UK) and a software called as Exponent Version 4.0.6.0. A aluminium & derlin 3 point bending rig (HDP/3PB) and heavy duty platform (HDP/90) were used for 3 point bending test according to Hartel and Deymonaz (2001) and Vincent et al. (2002).

3 point bending ring includes two kinds of unit. These are base with two adjustable supports and flexure unit. Test setting was done as follows: Pre-test speed of 1 mm/sec, test speed of 3 mm/sec, post-test speed of 10 mm/sec, distance of 5 mm, strain of 10%, trigger force 50g, trigger distance of 2 mm. Dimensions of chocolate samples were 44 mm diameter and 4 mm height. Distance between adjustable supports was 30 mm. Four samples were analyzed within 15-day intervals from 0 to 60th days. Every measurement was carried out as two trials.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Effects of fat type to the rheology

After conching process viscosity of the four samples (S, I, II, III) were evaluated. Viscosity of standard sample (only with cocoa butter) and samples that were prepared with hazelnut oil, palm kernel stearin and shea butter stearin were found to be 13 000 cP, 19 875 cP, 28 625 cP ve 16 875 cP, respectively at 40 oC and 2 RPM. As Maheshwari and Reddy (2005) reported, dark chocolate followed non-Newtonian flow. The viscosity is decreased with increasing shear rate. Rheology curves of dark chocolate with different fats are shown in Figure 3.1.
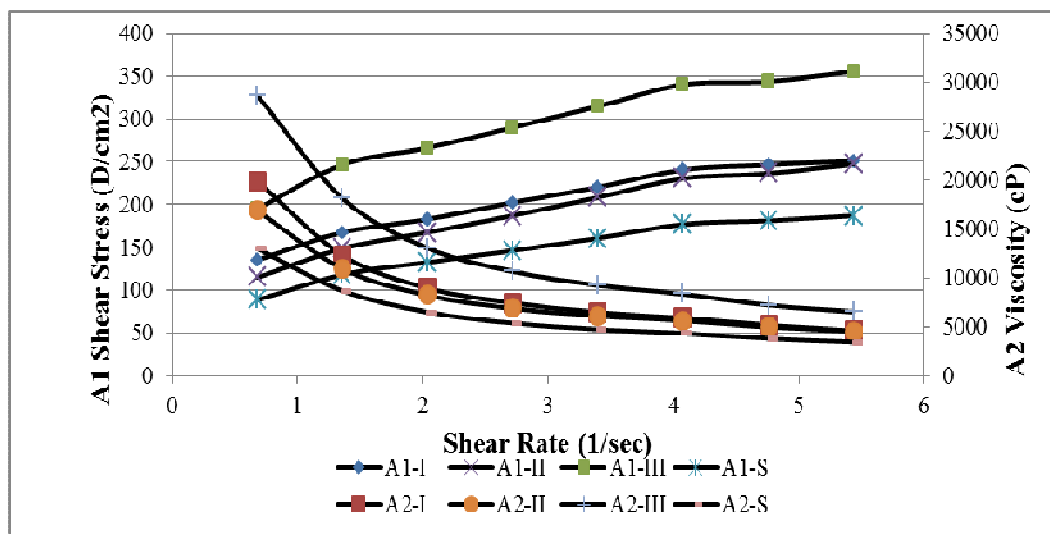

Figure 3.1 Effects of different fats on rheology of dark chocolate, S: Standart dark chocolate, I: Sample with HO, II: Sample with SBS, III: Sample with PKS

The Casson model is followed by the rheological behavior of samples that gives the best correlation coefficient for chocolate rheology according to Maheshwari and Reddy (2005) and Afoakwa et al. (2008c) (Table 3.1.).

Table 3.1 Casson plastic viscosity and Casson yield value of dark chocolate samples

Sample	Yield value (D/cm^2)	Plastic Viscosity (cP)	R^2
S	54,6	793,7	0,971
I	89,4	821,9	0,981
II	66,3	1124	0,981
III	136,3	1030	0,975

As Maheshwari and Reddy (2005) reported that shear stress is increased and the viscosity is decreased with increase in shear rate. Sample III had the highest shear stress and viscosity for every shear rate value. This was reflected in yield value and plastic viscosity as Maheshwari and Reddy (2005) mentioned. Only plastic viscosity of Sample II had a deviation. Sample III is showed a significant decrease in viscosity with increase in shear rate when compared other samples (S, I or II). In every shear rate there was no significant difference in viscosity and shear stress for all samples except Sample III. Sample S had the lowest viscosity, yield value and also plastic viscosity.

3.2. Effects of fat type to the solid fat content

As Torbica et al. (2006) studied, cocoa butter's solid fat content, values which was extracted from standart sample determined by IUPAC method 2.150 was shown in Figure 3.2.
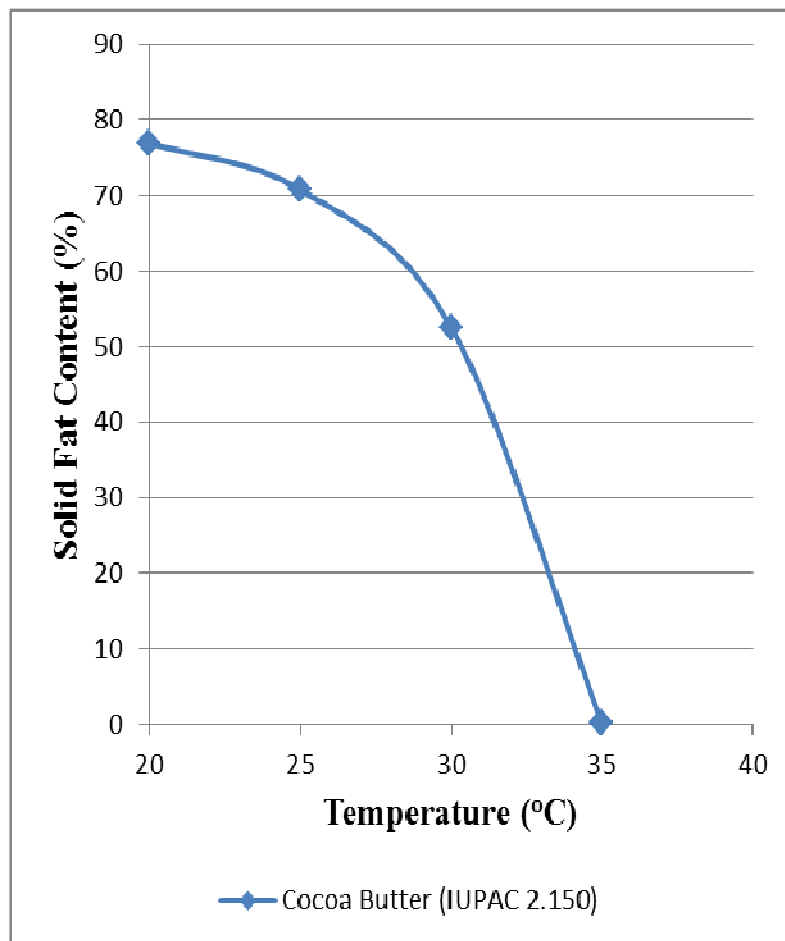
Figure 3.2 Cocoa butter SFC profile determined by the IUPAC 2.150

SFC values of cocoa butter and HO mixture (Mixture I) which was extracted from sample I were determined by IUPAC method 2.150 also. There was not a certain SFC value for pure HO in the literature. With respect to similarity to the olive oil in terms of chemical composition and liquidity at room temperature SFC value was assumed to be 0% from 20 ^{o}C to 35 ^{o}C (Alenden et al., 2007c) and (http://www.essentialoils.co.za/). Figure 3.3. shows the plots of the SFC curves of the CB, mixture I and pure HO.
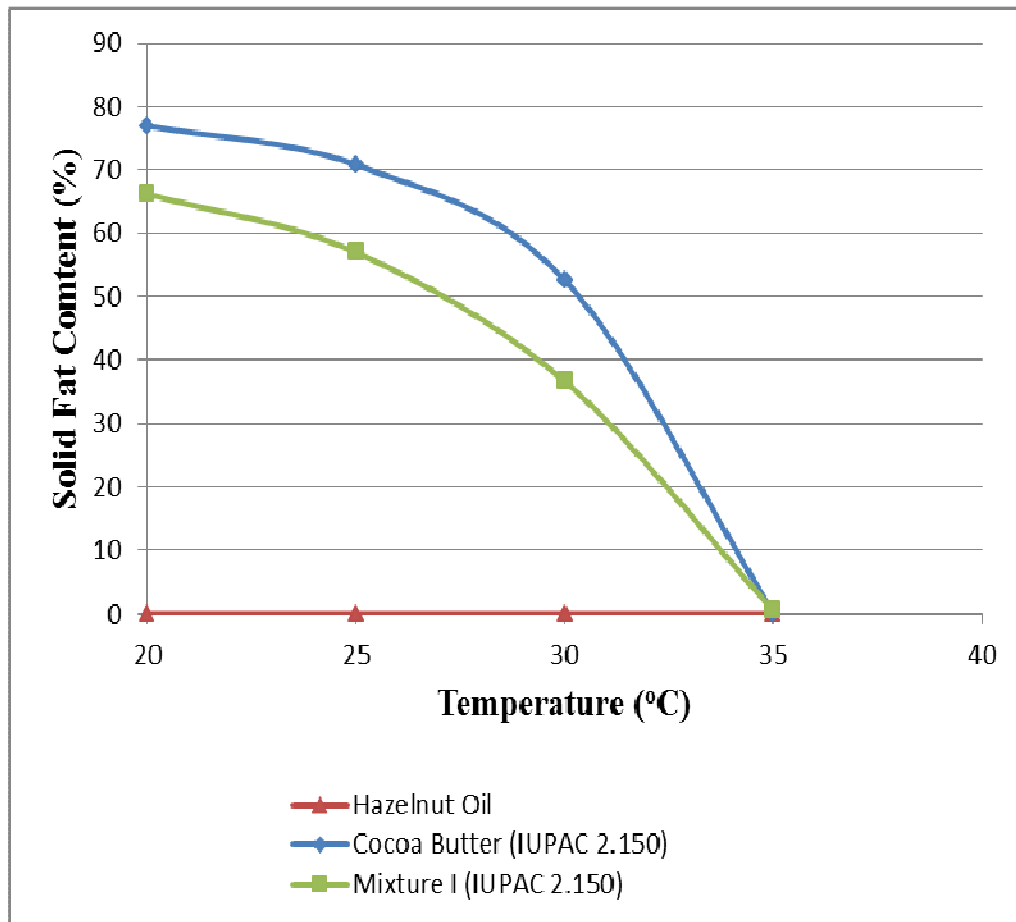
Figure 3.3 SFC profiles of the CB, HO and its mixtures

Solid fat contents were given in Table 3.2. The SFC of the HO is lower than the SFC in CB at all temperatures. The SFC of the HO was 0 % between 0°C and 35°C.

Table 3.2 SFC values of the CB, HO and its mixtures

Temperature (^{o}C)	Cocoa Butter (%)	Hazelnut Oil (%)	Mixture I (%) (13,2%/86,8%)
20	77	0	66,2
25	70,8	0	57
30	52,6	0	36,7
35	0,3	0	0,6

The resultant SFC profile of mixture I indicated that addition of HO had a softening effect on the cocoa butter.

SFC values of cocoa butter and SBS mixture (Mixture II) which was extracted from sample II were determined by IUPAC method 2.150 also. SFC values of pure SBS ensured from the product specification which was ensured from the supplier. Figure 3.4. shows the SFC profiles of the CB, mixture II and pure SBS.

Solid fat contents were given in Table 3.3. The SFC of the SBS was higher than the SFC of CB between the temperature interval of 20 and 35 $^{\circ}$C.

Table 3.3 SFC values of the CB, SBS and its mixtures

Temperature ($^{\circ}$C)	Cocoa Butter (%)	Shea Butter Stearin (%)	Mixture II (%) (13,2%/86,8%)
20	77	88	76,9
25	70,8	87	70,5
30	52,6	85	56,3
35	0,3	70	3,3

When calculating the SFC of the analyzed Mixture II by IUPAC 2.150, the resultant curves of Mixture II and CB were very close to each other. But SFC value of the Mixture II was a little bit higher between the temperature interval of 30 and 35 $^{\circ}$C. SBS showed an improvement in physical property of cocoa butter as to make it suitable for use as a cocoa butter improver (CBI).
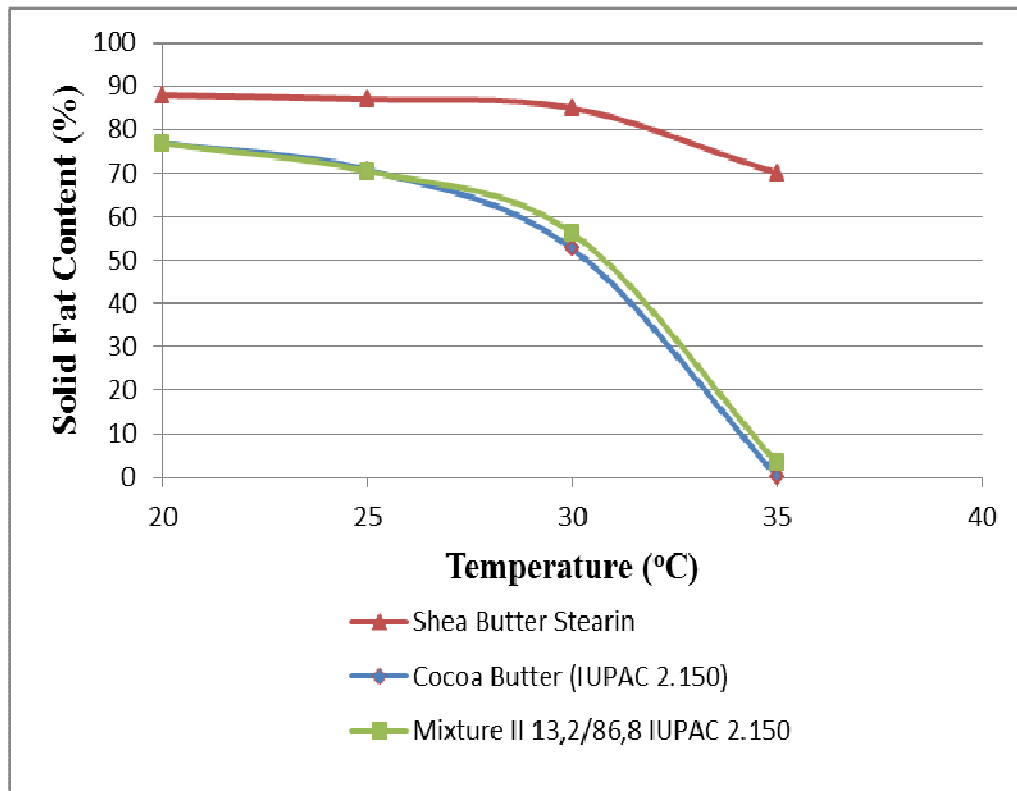
Figure 3.4 SFC profiles of the CB, SBS and its mixtures

SFC values of cocoa butter and PKS mixture (Mixture III) which was extracted from sample III determined by IUPAC method 2.150 also. SFC values of pure PKS ensured from Berger (2007) study. Figure 3.4. shows the SFC profiles of the CB, mixture III and pure PKS.

Solid fat contents were given in Table 3.4. The SFC of the PKS was higher than the SFC of CB between the temperature interval of 20 and 25 ^{o}C.

Table 3.4 SFC values of the CB, PKS and its mixtures

Temperature (^{o}C)	Cocoa Butter (%)	Palm Kernel Stearin (%)	Mixture III (%) (13,2%/86,8%)
20	77	82,8	68,9
25	70,8	68,2	52,5
30	52,6	34,6	31,3
35	0,3	3	0,4

As was seen in Figure 3.5., the significant decrease in Mixture III clearly showed the eutectic incompatibility of the CB and PKS, because of PKS' lauric fatty acid content. Despite PKS had harder SFC profile than CB at the beginning temperature; Mixture III had a softer SFC profile. This property of PKS makes it suitable for use as a cocoa butter substitute (CBS).
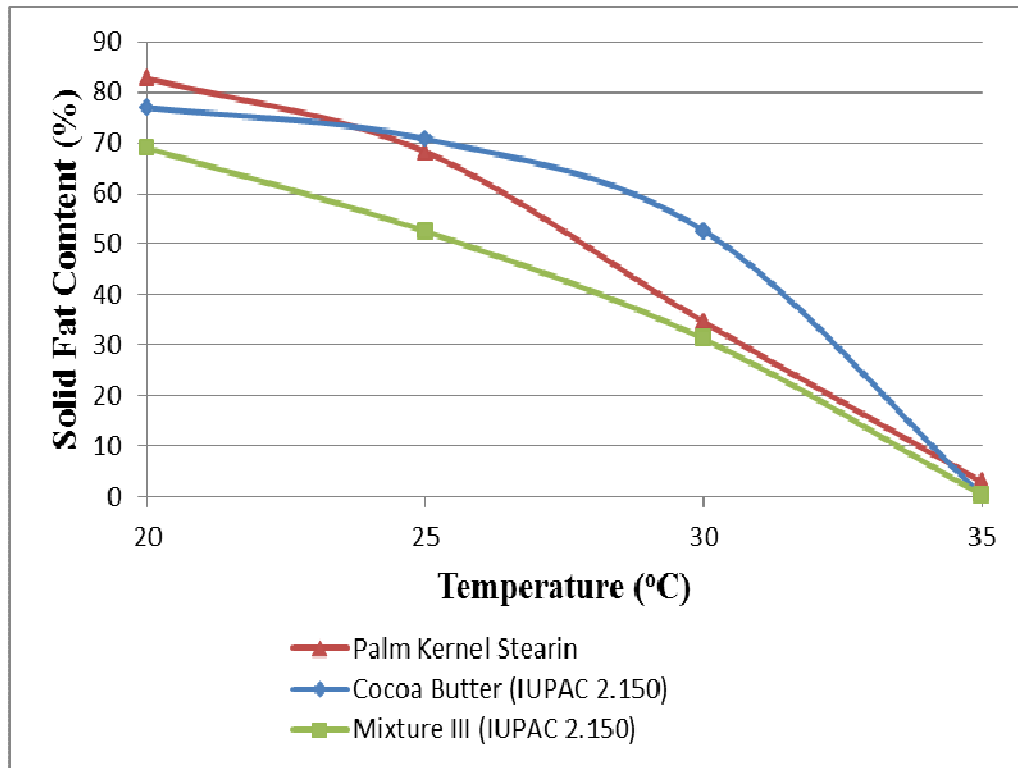

Figure 3.5 SFC profiles of the CB, PKS and its mixtures

3.3. Effect of fat addition on hardness (texture) of chocolate

The hardness of samples was measured at 20 ± 2 $^{\circ}$C to determine effects of different vegetable fats. Data from texture on hardness in relation to storage time was given in Table 3.5. Afoakwa (2009a) reported that storage of the samples are caused consistent and significant increase in hardness levels within the first 72 h. The hardness of sample S is increased nearly until 15th day. It had certain decrease till 30th day and became nearly firm after demoulding. The reasons of these differences could be the time period of measurements and thickness difference between samples that are analyzed 3rd, 15th and 30th days (Figure 3.6.).

Table 3.5 Changes in texture (hardness) during storage

Storage Time (Day)	Sample	Hardness (kg)
0	S	2,553±0,138
	I	3,279±0,008
	II	4,347±0,180
	III	3,822±0,153
3	S	3,485±0,000
	I	3,670±0,076
	II	4,754±0,127
	III	2,759±0,195
15	S	4,288±0,010
	I	2,460±0,139
	II	4,927±0,041
	III	2,444±0,107
30	S	3,461±0,028
	I	2,565±0,044
	II	4,726±0,207
	III	2,106±0,165
45	S	3,743±0,051
	I	2,606±0,051
	II	4,482±0,075
	III	2,488±0,060
60	S	3,460±0,064
	I	2,562±0,064
	II	4,235±0,057
	III	2,362±0,066

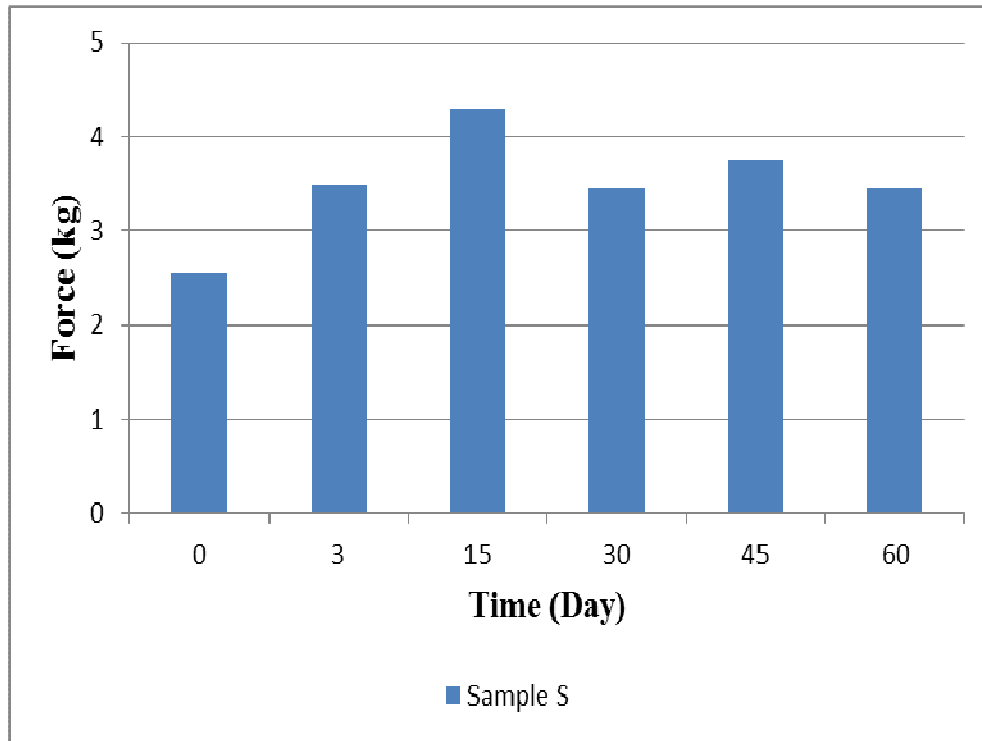Means ± standard deviation from duplicate analysis.

Figure 3.6 Changes in hardness of sample S during storage

The hardness of sample I was measured at 20 ± 2 ^{o}C also. As was shown in the Figure 3.7. at day 0 and 3rd day, hardness of sample I had small excess. This kind of differences could be derived from non-homogenous thickness of samples as was mentioned before. From the 15th day sample I had significant soft texture when compared with sample S. After the 15th day, sample I had nearly constant value for hardness until the 60th day. This softness was the result of low SFC of hazelnut oil in sample I.

The hardness of sample II was measured at 20 ± 2 ^{o}C too. As was shown in the Figure 3.8. at day 0 and 3rd day, hardness of sample II had significant increase when compared with sample S. Hardness of sample II was increased until 15th day similar to sample S. After 15th day as well decrease in hardness was observed until 60th day. But sample II still had high hardness than sample S. These results indicated that SBS fat that was used in sample II, increased the hardness of chocolate so that it can be used in warmer climates.
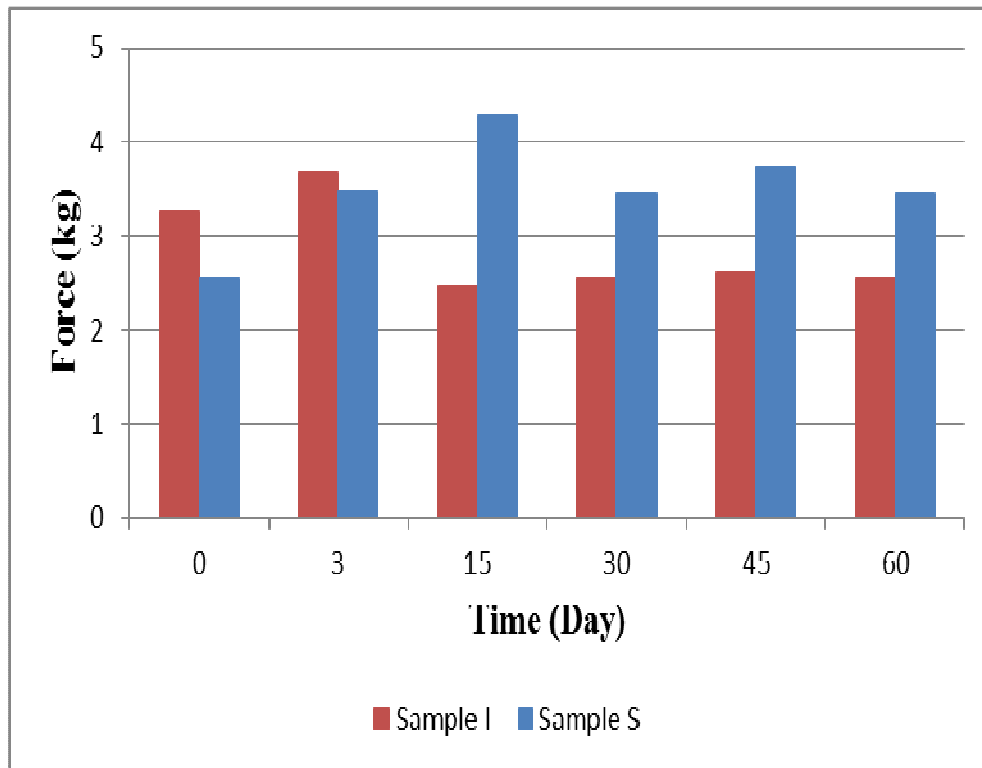
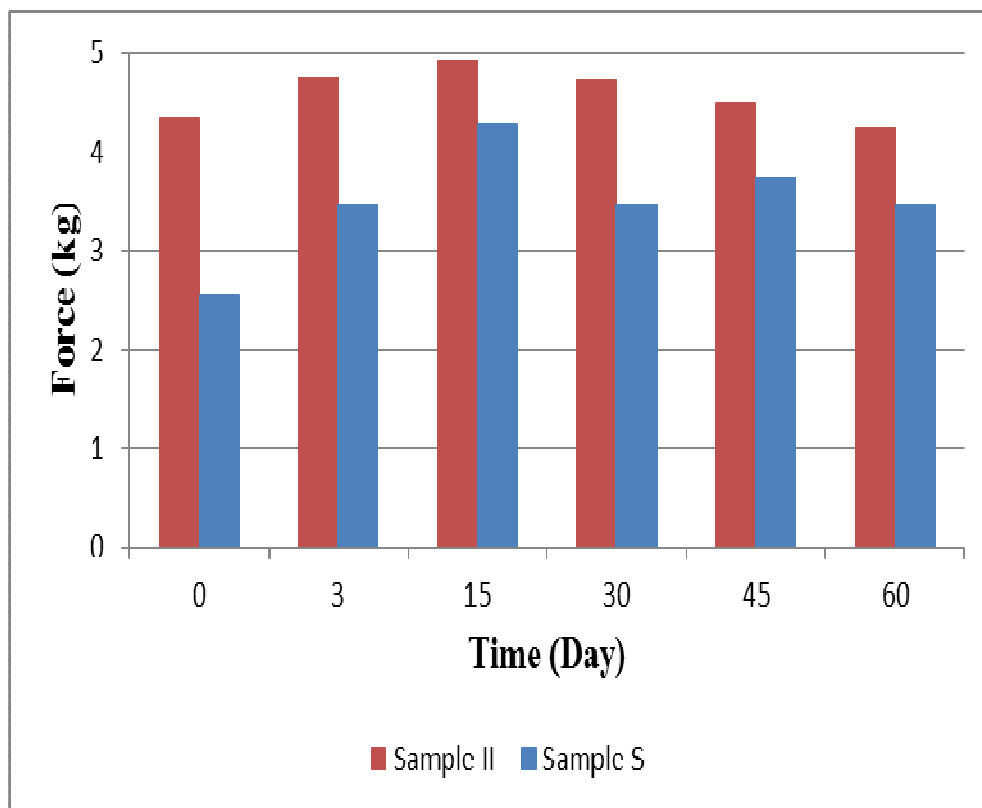Figure 3.7 Changes in hardness of sample I according to Sample S

Figure 3.8 Changes in hardness of sample II according to Sample S

The hardness of sample III was measured at 20 ± 2 ^{o}C similar to other samples. As was shown in Figure 3.9. starting from day 0, sample III was exhibited a serious decrease in hardness till 30th day, that might be called a softening effect. After the 30th day, sample III had an insignificant increase, assumed to be the result of sample thickness. This softening effect was related with the extremely eutectic effect happened in the PKS/CB mixtures in sample III as was reported by Wang et al. (2010).
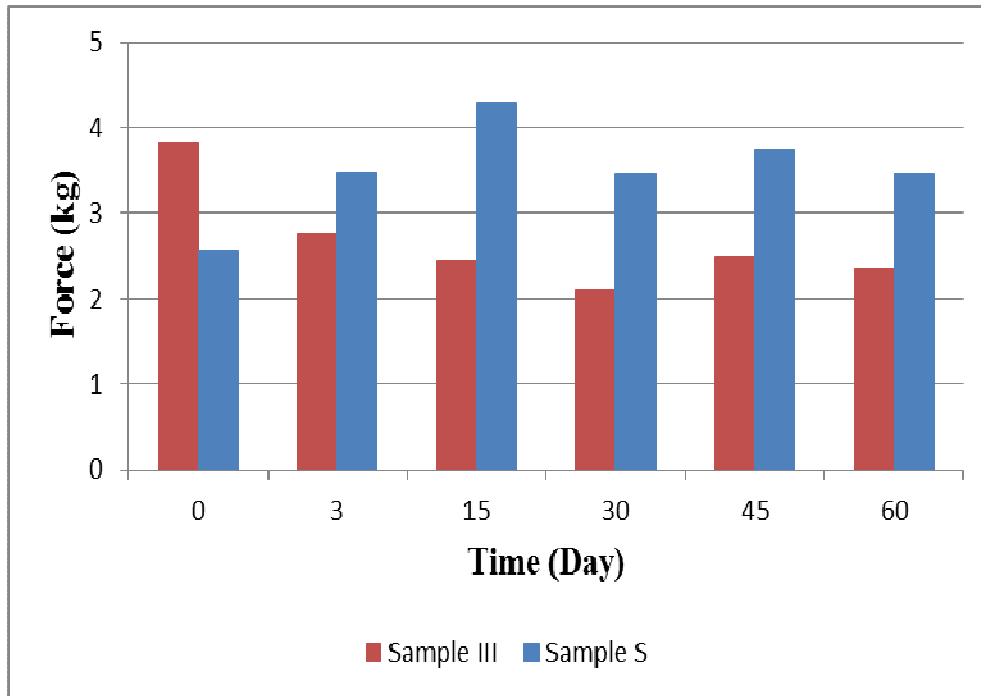

Figure 3.9 Changes in hardness of sample III according to Sample S

3.4. Effect of fat addition on melting properties of chocolate

Melting and crystallization profiles of the pure fats are shown in Figure 3.10 and 3.11.

DSC thermograms were obtained after 0, 3, 15, 30, 45 and 60 days storage and used for characterizing the melting properties of the samples prepared with different vegetable fats (Figures 3.10-3.15). All the samples exhibited similar distinct single endothermic transitions between 15 and 55 ^{o}C, the range was in good agreement for chocolate melting profiles by Afoakwa (2009b) reported. Data from the DSC on T_{peak} and ΔH_{melt} with respect to storage time and vegetable fat type was shown in Table 3.6.
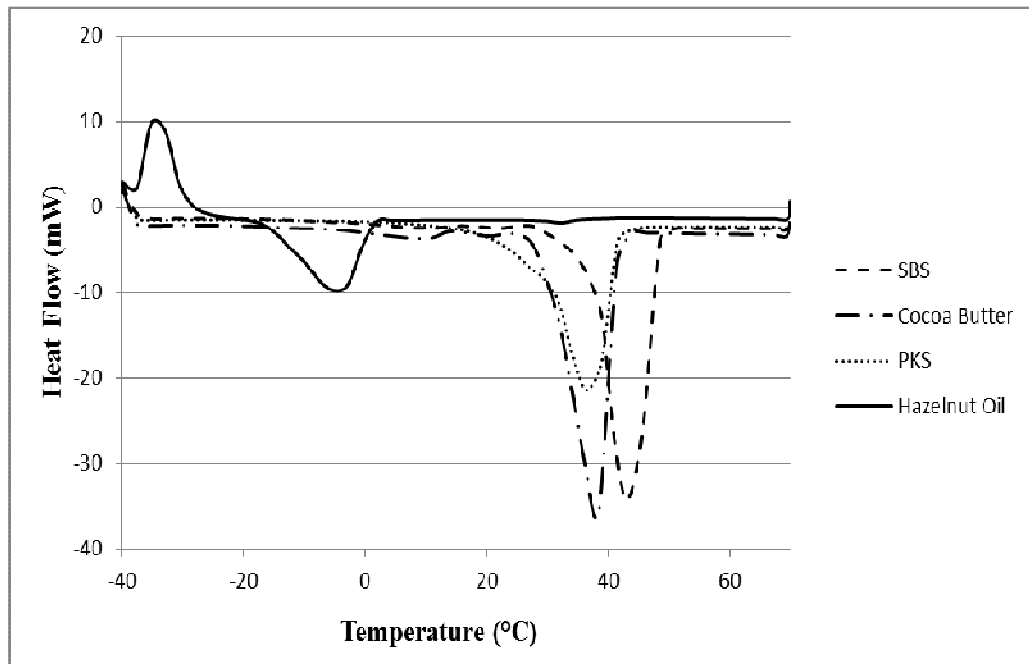
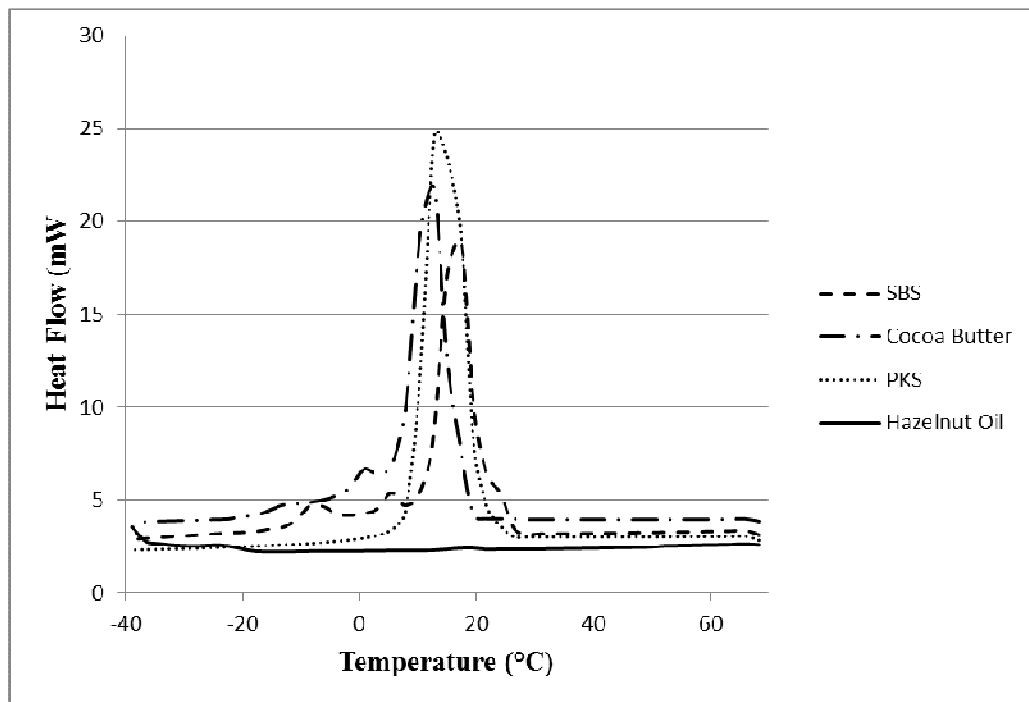Figure 3.10 Melting profiles of the pure fats

Figure 3.11 Crystallization profiles of the pure fats

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Table 3.6 Changes in melting properties during storage

Storage Time (Day)	Sample	Melting properties	
		T_{peak} (C^o)	ΔH (J/g)
0	S	32,8±0,2	34,09±0,77
	I	31,9±0,1	34,31±0,94
	II	34,7±0,9	34,62±1,71
	III	33,2±0,7	24,76±2,06
3	S	32,6±0,1	40,52±0,89
	I	32,1±0,0	30,41±0,91
	II	34,3±0,1	34,49±4,88
	III	31,8±0,5	27,73±3,04
15	S	33,2±0,6	27,88±2,83
	I	33,1±1,4	25,51±3,17
	II	33,4±0,1	36,46±0,11
	III	33,1±0,6	24,05±5,04
30	S	32,8±0,0	31,27±2,10
	I	31,6±0,2	30,23±0,31
	II	34,2±0,2	36,93±1,34
	III	31,3±0,4	28,39±0,72
45	S	32,2±0,4	37,44±0,64
	I	32,0±0,3	31,94±0,16
	II	34,0±0,2	33,80±2,55
	III	32,4±0,3	28,52±0,56
60	S	32,5±0,2	37,61±1,13
	I	32,8±0,2	23,48±3,14
	II	34,3±0,5	33,70±2,99
	III	31,5±0,5	30,55±0,05

Means ± standard deviation from duplicate analysis.

Data from DSC showed that changes in fat type and storage time caused changes in crystallinity and melting profiles, as observed differences in their peak widths.

When melting profiles compared with each other, sample I and sample III had greatest peak widths in their peak that means melting started earlier compared to sample S and sample II. Melting behavior of CB-PKS (sample III) mixture indicated that these fats are incompatible. CB-PKS mixture showed eutectic behavior as mentioned in part 3.3. Eutectic behavior is watched over as a constant SFC line, which is not a linear interpolation between pure fats at that SFC as was Williams et al. (1997) specified. HO decreased melting temperature for sample I because of HO's liquidity. On the other hand SBS that was used in sample II increased peak temperatures from the beginning to the end of storage that mean SBS could be used as a cocoa butter improver.

For Day 0, as was seen in Figure 3.10., sample II with SBS had maximum melting peak at 34,7 °C. Sample III had melting peak at 33,2 °C. But the start of melting temperature was lower because of eutectic effect compared to sample II. Sample I had the lowest melting peak at 31,9 °C which was lower than melting peak of sample S with 32,8 °C naturally due to the low SFC content of HO.
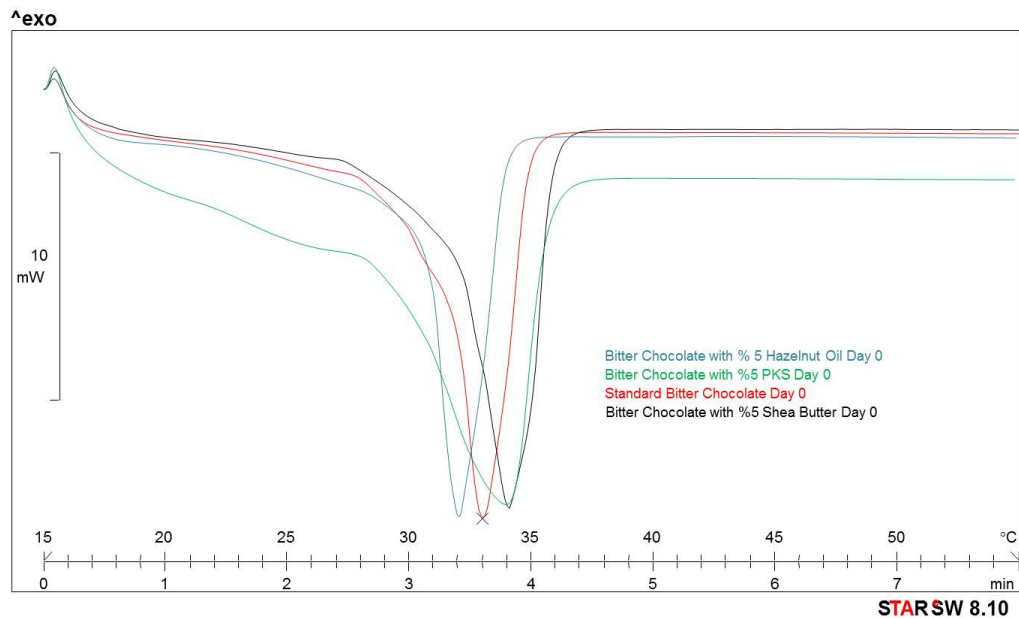

Figure 3.12 Melting profile of samples for day 0

For the 3rd day, as was seen in Figure 3.11., sample II had the maximum melting peak with 34,3 °C. Sample III had the melting peak at 31,8 °C. Sample I had a melting peak at 32,1 °C which was lower than sample S (32,6 °C). For sample I, the start of melting was earlier than the others.
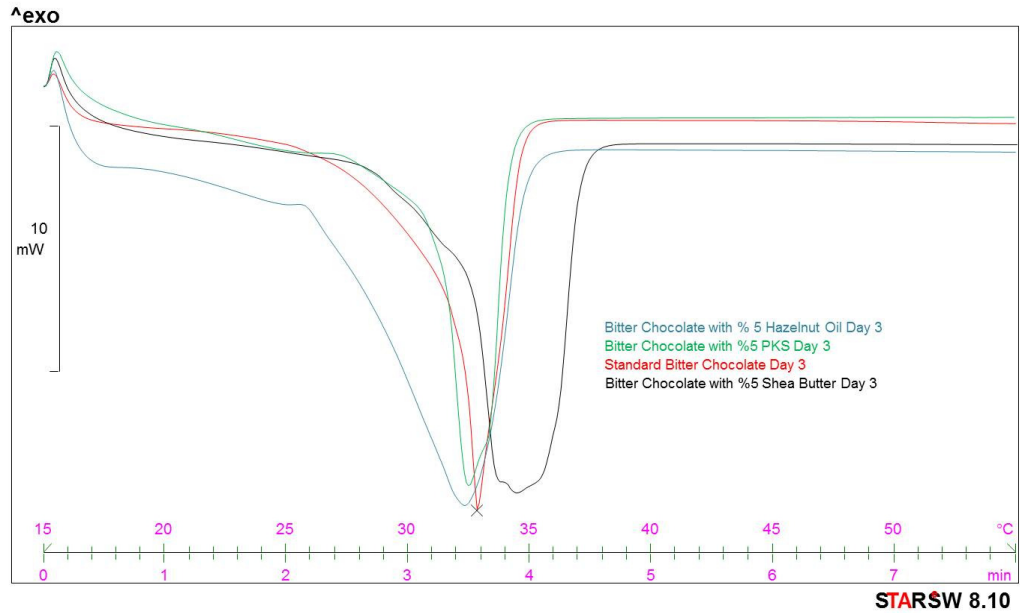
Figure 3.13 Melting profile of samples for the 3rd day

For the 15th day, as was seen in Figure 3.12., sample II with SBS had maximum melting peak at 33,4 ^{o}C. Sample III had melting peak with 33,1 ^{o}C. And start of melting was earlier than sample S and sample II also. Sample I had melting peak at 33,1 ^{o}C which was lower than sample S and sample II, melting peaks of sample S and sample II were 33,2 ^{o}C and 33,4 ^{o}C, respectively.
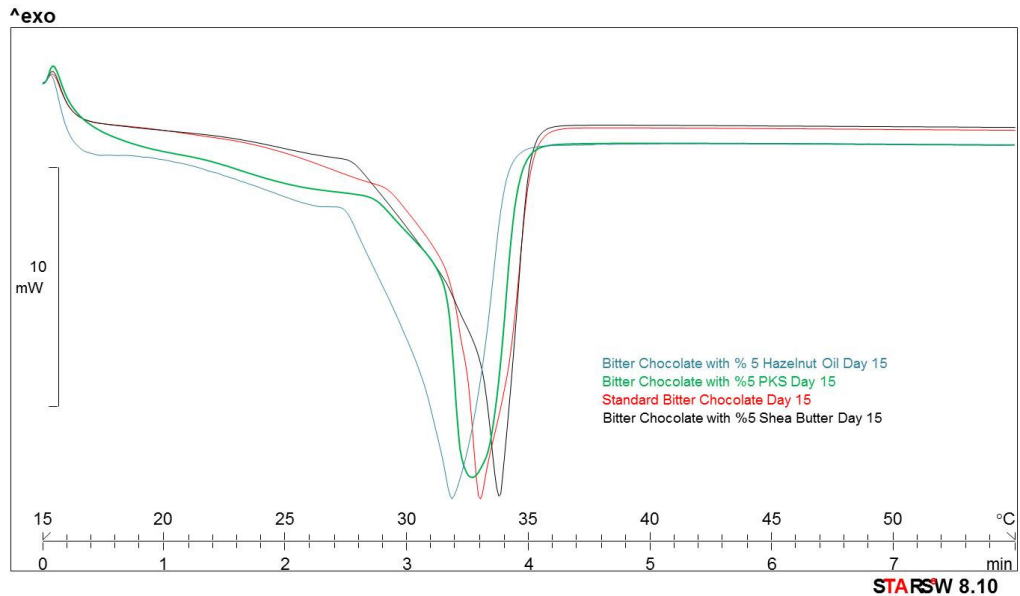

Figure 3.14 Melting profile of samples for the 15th day

For the 30th day, as was seen in Figure 3.13., sample II had the maximum melting peak at 34,2 °C. Sample III had the lowest melting peak at 31,6 °C and melting start temperature was very low. Sample I had a melting peak at 31,3 °C.
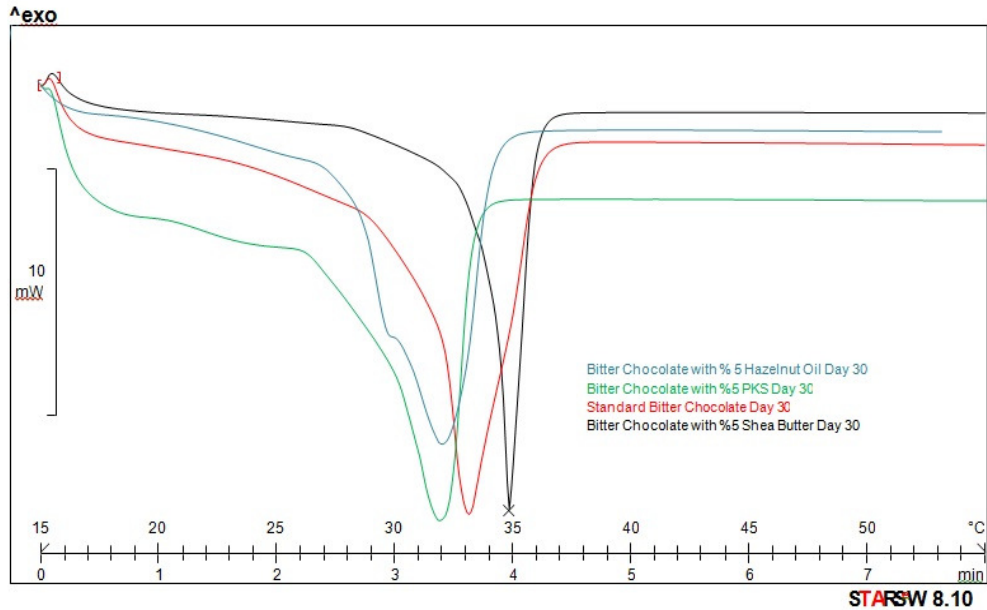

Figure 3.15 Melting profile of samples for the 30th day

For the 45th day, as was seen in Figure 3.14., sample II with SBS had maximum melting peak at 34,0 °C. Sample S had melting peak at 32,2. Sample III had melting peak at 32,4 °C but melting starting temperature was lower than sample S. Sample I had melting peak at 32,0 °C and lower melting start temperature than sample S.

For the 60th day, as was shown in Figure 3.15., sample II with SBS had a maximum melting peak at 34,3 °C as in all the measurement days. Sample III had the lowest melting peak at 31,5 °C and melting start temperature. Sample S had melting peak at 32,5 °C. Sample I had melting peak at 32,8 °C which was greater than sample S. But melting starting temperature was lower than sample S.
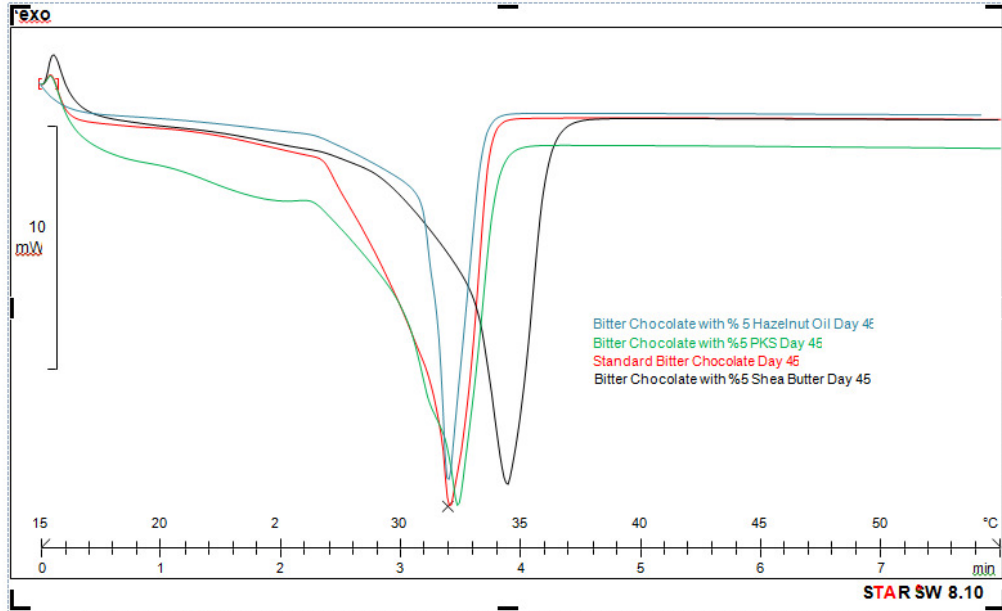
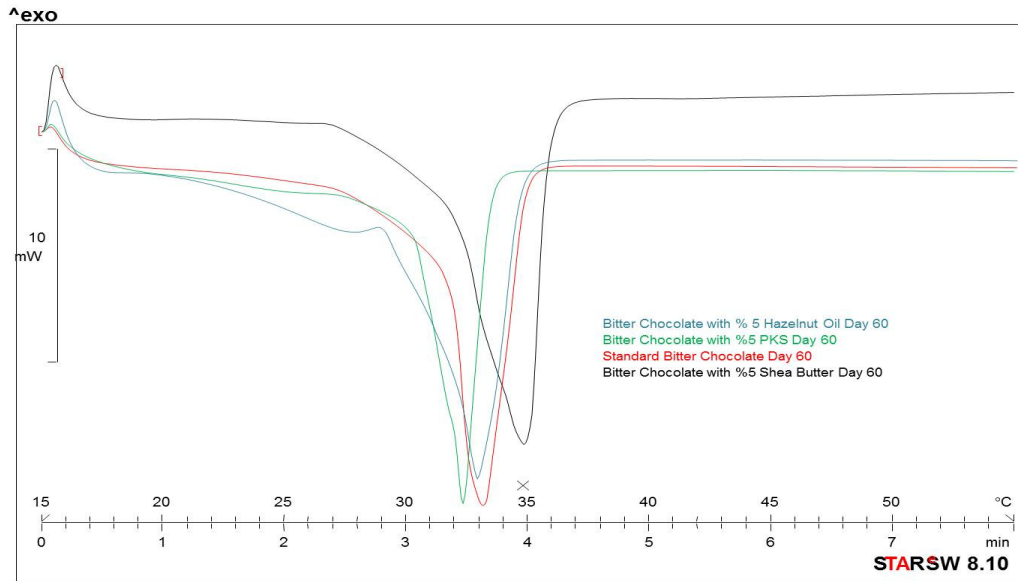Figure 3.16 Melting profile of samples for the 45[h] day

Figure 3.17 Melting profile of samples for the 60th day

CHAPTER 4

CONCLUSION

Dark chocolate samples were prepared with vegetable fats, HO, SBS and PKS at a level of 5% in combination with cocoa butter. The properties of these samples, texture, SFC and melting behaviour were compared with that of standard chocolate.

1. Dark chocolate samples were followed non-Newtonian flow. The viscosity decreased with increasing shear rate whereas shear stress increased. Sample III with PKS exhibited highest shear stress and sample II with SBS showed highest viscosity. Standard sample had the lowest viscosity and shear stress.

2. Solid fat content of sample I with HO was lower compared to standard sample at all temperatures studied. So the addition of HO has softening effect on the cocoa butter. SBS addition to the sample increased the heat stability of chocolate. SBS-CB mixture had higher SFC content at 30 to 35 ^{o}C.

3. Despite the high SFC content than cocoa butter between 20 ^{o}C to 25 ^{o}C, PKS could not be used as a CBI.

4. The hardness of standard sample has showed a significant increase during the first 15 days. Then, the hardness was nearly stationary up to 60 days with small fluctuations. Hardness of the sample with SBS increased during the first 15 days similar to standard sample. In addition, sample with SBS had highest hardness values when compared with standard sample. Despite the hardness of the sample with SBS decreased slightly, it had the higher hardness than standard sample at the end of 60 days. So, SBS could be used as a cocoa butter improver (CBI).

5. Sample with PKS had harder texture than standard sample during the first 3 days. The hardness of the sample had a sharp decrease.

6. The starting temperatures of melting with PKS and HO were lower and spoiled the melting profiles. On the other hand, sample with SBS exhibited an improved melting profile nearly for all measurement during 60 days. Stand-

ard sample and sample with SBS had sharp and flat melting profiles when compared with PKS and HO containing samples.

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