

EFFECTS OF NON-TRADITIONAL INGREDIENTS ON THE STRUCTURE AND
TEXTURE OF CHOCOLATE

by

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(Under the Direction of Jake H. Mulligan)

ABSTRACT

Recent changes to the standards that define chocolate have made it possible to lower the cost to manufacture chocolate thereby increasing profitability for manufacturers. In this study, cocoa butter alternatives and polysaccharides were investigated for their affects on thermal behavior and final textural properties. The inclusion of these non-traditional ingredients may offer potential cost-savings to a chocolate producer that may improve profitability; however, the care must be taken in order to avoid detriment to product quality. Kinetics of crystallization are altered through the addition of alternatives to cocoa butter, leading to variations in crystalline state and final properties. The addition of polysaccharides to chocolate results in enhanced stability of fat in the chocolate, which will likely result in enhanced resistance to lipid oxidation and increased shelf stability.

INDEX WORDS: Chocolate, Cocoa Butter Alternatives, Polysaccharides, Differential Scanning Calorimeter, Raman Spectroscopy, Texture

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	iv
LIST OF TABLES	vi
CHAPTER	
1 INTRODUCTION.....	1
2 LITERATURE REVIEW.....	6
3 CONTROLLING THE TEXTURE AND STRUCTURE OF CHOCOLATE BY THE ADDITION OF COCOA BUTTER ALTERNATIVES.....	36
4 PROCESS-PROPERTY-STRUCTURE RELATIONSHIPS IN CHOCOLATE WITH THE ADDITION OF POLYSACCHARIDES	47
5 CONCLUSIONS.....	59

LIST OF TABLES

	Page
Table 2.1: Cocoa Butter Fatty Acid Composition.....	22
Table 2.2: Cocoa Butter’s Six Crystalline Polymorphic Forms	23
Table 3.1: Dark Chocolate Formulations Used in this Study Given as weigh percentages of each ingredient in relation to the final weight of the composition.....	44
Table 3.2: Average results from thermal analysis shown as glass transition, cold crystallization temperatures, and melting point for dark chocolate samples with and without addition of alternative fat.	45
Table 3.3: Average fracture force and strain measured by three-point bend for dark chocolate samples with and without added alternative fat.	46
Table 4.1: Dark chocolate formulations used in this study given as weigh percentages of each ingredient in relation to the final weight of the composition.....	56
Table 4.2: Average results from thermal analysis shown as glass transition, cold crystallization temperatures, melting temperatures, and area under the melting peak for dark chocolate samples with and without polysaccharide addition... .	57
Table 4.3: Average fracture force and strain measured by three-point bend for dark chocolate samples with and without added polysaccharide components... ..	58

CHAPTER 1

INTRODUCTION

Achieving desirable texture or 'snap' is one of the most difficult aspects in the production or manufacturing of chocolate items. Controlling the crystallization of cocoa butter during the tempering process has been quite an obstacle Chocolatiers have had to overcome in the past several decades. Although there has been much research showing how crystallization of cocoa butter occurs, little has been done on how to control it (Spigno *et al.*, 2001). The production of chocolate is a very delicate and time sensitive process, and there is considerable amount of monetary loss and waste produced if mishaps occur during chocolate production. Although vast improvements have been made recently on how to monitor this, there needs to be a way to control it (Svenstrup *et al.*, 2005).

Shelf life is another major problem associated with chocolate. Milk and dark chocolate have a shelf life of only about 18 months, while white chocolate's shelf life is reduced to 12 months. This is under the assumption the chocolate is stored in a cool dry environment in an air-tight container. Chocolate is very susceptible to temperature abuse, flavor and odor migration, and light. The most significant defect associated with shelf life is chocolate or storage bloom. This is due to phase separation of the triglycerides within the crystalline structure of the cocoa butter.

The addition of alternative ingredients may provide the answers for controlling texture during processing and extending the shelf life of chocolate products. However,

companies must be cautious that the addition of these ingredients does not alter the texture or flavor of the product in a negative way. Companies must continue to produce consistently good product without sacrificing quality or trait. Consumers have certain expectations when purchasing a product and if the addition alternative ingredients alter their perception negatively then these ingredients cannot be incorporated. As a result, it is important to solicit a sensory panel in research studies such as these. It allows companies to see if the product is deemed desirable or undesirable by the consumer. A company's overall goal is to try to meet or exceed those expectations to keep their customer happy, because they ultimately affect the bottom line. These factors, as well as new regulations which have been set by the EU (Agency, 2003), is what has led to this research. The goal is to incorporate non-traditional ingredients into chocolate products to attempt to control crystallization, increase shelf life and reduce cost.

The prices for the primary ingredients in chocolate (i.e. sugar, cocoa, and cocoa butter) are very costly and in recent months have been in high demand according to Bloomberg Businessweek (Campbell, 2010). Despite that fact, North and South America, as well as Europe and Asia, consume chocolate in considerable amounts. Thus, developing a product that will incorporate lower cost ingredients with no compromise in eating quality is highly desired. However, the major challenge for this work is that chocolate is one of the few foods where composition is controlled by the European Community (EC).

From 1973 to 2000, the standards were set by Directive 73/241/EEC. These standards restricted the inclusion of non-traditional ingredients in chocolate. In 2000,

standards were changed by Directive 2000/36/EC, which is far less rigid and allows possibility for new formulations in the chocolate industry. So far, research has focused on the possibilities of various fats other than cocoa butter in chocolate. This research has only focused on lipids as structural elements with little attention to improving the nutritional quality of the chocolate. According to the new EC Directive, vegetable oils other than cocoa butter may be used up to 5 percent. Additionally, the new directive has also simplified regulations regarding the usage of sugars, permitting different types of sugars and sugar replacers to be used at various levels.

In the first part of this research, three cocoa butter alternatives will be investigated. This study will be looking into how incorporating these cocoa butter alternatives in conjunction with cocoa butter can help control the crystallization process in chocolate production. By controlling the crystallization process, it will allow better control over textural qualities of the final product. These cocoa butter alternatives will give chocolatiers, bakers, and manufacturers the upper hand in controlling the tempering process, developing unique and custom textural characteristics, and cutting down on the amount of waste or product loss.

In the second part of this research, four polysaccharides will be added to chocolate in conjunction with sugar to enhance the consistency of the product on the manufacturing level. These polysaccharides include carrageenan, sodium alginate, xanthan gum, and guar gum. The polysaccharides will be used to improve the maintenance of quality during storage of chocolate and enhancing the crystallization of chocolate during the tempering process in manufacturing.

This particular research would be of interest to chocolate manufacturers and chocolatiers. It would help them to see how the texture and structure of chocolate behaves when other 'replacement' or non-traditional ingredients are added. In addition these alternative ingredients have shown to reduce cost, increase shelf-life, and improve aspects of the overall final product. If the addition of these alternative ingredients aid in controlling cocoa butter crystallization and increasing shelf life without affecting texture or flavor this would be a definite milestone in chocolate research.

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CHAPTER 2

LITERATURE REVIEW

A Brief Look into the History of Chocolate

Long before the conception of the first chocolate candy bar, mankind was enjoying the complex flavors from the pods of the *Theobroma cacao* tree. The first people to discover and utilize these cacao seeds were the Classic Period Mayans (250-900 A.D.), who lived in Mesoamerica. They would harvest, ferment, roast, and grind the seeds forming a thick paste (Hurst *et al.*, 2002). This mixture, along with other spices, would be added to water and whipped to a frothy consistency (Beckett, 1988) . The Aztecs called this drink 'Chocolat', which translates to warm liquid. It would be served during special occasions and was consumed often by royalty. Cacao beans became so highly valued it started to be used as an alternative currency.

During the early 16th century, the Aztec King, Montezuma, introduced the bitter chocolate drink to Cortez, who brought it back to Spain. The delicacy, however, was not an instant success, until sugar was introduced to the mixture to mask the bitter and astringent flavors. The newly reformed, luxurious drink spread rapidly among aristocracy and powerful families (Beckett, 2000a). Remarkably, the Spanish managed to keep this a secret from the rest of Europe for nearly a hundred years.

Territorial expansion of chocolate began in the 17th century when Spanish monks, who were traveling throughout Europe and France, began spreading the secret

of the chocolate beverage to their counterparts (Association, 2003). The beverage became a popular item and the Europeans thought of it as a 'health-giving' food (Beckett, 2000b).

Throughout the 17th and 18th centuries the chocolate drink became more mainstream and developed a following with the general public. Chocolate drinking houses started popping up all over Europe, especially in London, where young socialites and politicians would go after a long day. However, it was a common consensus among the consumers that the chocolate beverage was overly fatty (Beckett, 2000b).

In the beginning of the 19th century a Dutchman by the name of Van Houten developed the cocoa press which would extract the fat from the cocoa beans (Beckett, 2000a). This apparatus, which was manually operated, was able to separate the cocoa butter from the cocoa solids or powder. The cocoa powder used for beverages and cooking purposes, while the fatty cocoa butter made it possible to produce fluid chocolate that could be molded and hence conceiving the first chocolate bars (Minife, 1989b). Van Houten's invention was the beginning of modern day chocolate manufacturing.

Theobroma Cacao

The essential ingredients in chocolate derives from a unique species of tree which originated in South and Central America, known as *Theobroma cacao*, L. Cacao trees, of the family Sterculiaceae, thrive in tropical humid regions around the equator which receive heavy rainfall and hold deep, rich soil (Beckett, 2000a). Naturally, the

cacao tree flourishes in shaded regions under the canopy of banana or tapioca leaves, and at maturity only grows to about 12-15m in height. The lifespan of a cacao tree is about 100 years, however, they only bear fruit for about 60 years(Canizaro, 2002).

The fruit from these trees begin as tiny pink or white flower which grows from the trunk or larger branches of the cacao tree in the thousands. Out of thousands of tiny flowers which envelope the cacao tree only about 10% develop into mature fruit (Association, 2003). This mature fruit, or pods, are oval in shape, and contain the seeds that will later become cocoa beans. These pods are handpicked year round from the trunk or larger branches of the cacao tree once they have turned from a dark maroon color to a deep golden yellow color. On average each cacao tree yields about 20-30 pods per year, which equals approximately 1-5lbs of beans per year. At maturity these pods contain anywhere from 30-50 beans per pod, depending on the variety of tree and climate (Leal *et al.*, 2008).

The four principle varieties of cacao trees include: Criollo, Forastero, Nacional (also known as Arriba), and a hybrid cacao tree called Trinitario. Among other factors such as climate, rainfall, and the soil, the flavor of the cacao bean is largely dependent on the type of cacao tree. The bulk of the cacao beans on the market comes from the Forastero and Trinitario varieties (Schwan and Wheals, 2004). The Criollo and Nacional cacao trees produce very aromatic cocoa beans, but both are highly susceptible to disease and produce poor yield.

Presently, there are three major cocoa growing regions which include West Africa, South-East Asia, and South America. Nearly half of the world's supply of

commercial cacao comes from two countries located in East Africa. Cote D'Ivoire, also known as the Ivory Coast, is the primary exporter with 41%, and Ghana which exports about 13%. These two locations have seen a dramatic increase in production over the last several decades due to the exceptional quality. As a result these cocoa beans are being used in the finest quality chocolates and remain in high demand (Canizaro, 2002).

Nearly all of the world's cocoa supply is grown on small farms, with only 5% grown on large scale plantations. On these larger scale plantations, hundreds of cacao trees are planted together and subjected to full intense sunlight. This kind of farming stresses the cacao trees causing them to become more susceptible to pests and disease, and ultimately leading to a reduction in yield and unwanted product. In order to combat this problem the World Cocoa Foundation has set up a program which supports the sustainable cocoa growing in its mission to improve the standard of living for the cocoa farmers and their families. The WCF helps to educate farmers on efficient methods for producing quality cocoa in a sustainable environmentally friendly manner. This program has already shown great success in West Africa, Southeast Asia, and Latin America (Foundation, 2008).

Cocoa Bean: Postharvest

Year round cocoa bean farmers will hand pick fully developed, golden colored pods from the cacao tree biannually (Museum, 2007b). The process is usually done with a machete by experienced workers who carefully select the ripened pods. Because the growing season in the tropics is continuous, farmers are able to harvest the cacao pods year round. After the pods are selected, they are rudimentarily split open with a knife or

wooden club, and then about 30-50 seeds are scooped out along with a sugar gelatin like pulp (Tannenbaum, 2004).

Fermentation is then initiated when the cacao beans are heaped together in a pile or placed in boxes and covered, most often with banana leaves. Depending on the type of cacao bean and the region, the fermentation processes usually lasts from five to seven days (Tannenbaum, 2004). The actual fermentation occurs when the pulp surrounding the cacao bean is converted into alcohol by the yeasts which are naturally present in the atmosphere and from the heat generated by the pile or box. The beans are frequently mixed or turned in order to allow a limited amount of oxygen into the box or pile. This process transforms the alcohol to turn into lactic acid or acetic acid (Leal *et al.*, 2008).

The process of fermentation is essential in making good quality chocolate. During this time the beans undergo biochemical reactions, flavors begin to change from a primarily bitter to more, well rounded complex chocolate flavors. The color of the beans also changes from light yellow to a rich brown color (Association, 2003). In addition, this process also leads to the development of flavor precursors, which will fully emerge later in the process (Beckett, 2000a).

After the beans have undergone fermentation they can now be called cocoa beans. Before these beans are shipped, however, they have to undergo a drying procedure because of their high moisture content after the fermentation process. In this process, the cocoa beans are spread out on trays or drying mats and dried directly

under the sun or sheds (Museum, 2007b). This process usually takes about a week depending upon the climate and location of the plantation.

Once the percent moisture of the cocoa beans has reached 6-7%, the beans are then sorted according to their size, color, and type. The sorted cocoa beans are then bagged in burlap sacks and shipped to chocolate manufacturers all across the globe (Beckett, 2000a, Leal *et al.*, 2008).

Cocoa Bean Processing at the Manufacturer

There are three main stages of cocoa bean processing which are essential to creating all chocolate products (Afoakwa, Paterson *et al.* 2007). Stage 1 begins with the arrival of the cocoa beans at the chocolate manufacturer where they will endure a series of quality control checks. All raw materials are evaluated and tested before they enter the manufacturing facility to ensure that only quality ingredients are used to make the chocolate. At the Hershey's Chocolate manufacturing facility, small batches of cocoa beans are turned into chocolate liquor. This chocolate liquor is then evaluated based on flavor and aroma by experienced company taste tasters (Company, 1995). If the product passes all quality control checks, it then goes on to a rigorous cleaning and sorting process. The cocoa beans are sorted according to their country of origin, size, and type. Chocolate manufacturers then use blends of different cocoa beans to achieve their desired flavor in the final product. For finer, more expensive chocolates, manufacturers stick with a single blend of higher quality cocoa beans (Company, 1995).

After the beans are cleaned and sorted they proceed to the roasting process. Roasting is one of the most important steps in cocoa bean processing because it allows

the cocoa beans color and flavor to develop through a series of chemical reactions. In this process, cocoa beans are roasted in large revolving cylinder shaped roasters. Currents of air circulate inside the roasters, reaching temperatures of 250°F or higher, pass over the beans and lasts about 30 minutes to 2 hours depending on the size and type of the cocoa bean being roasted (Company, 1995).

From a chemical standpoint the roasting or controlled heating process causes the cocoa beans to undergo several important chemical reactions which contribute to aroma, color, and flavor. The chemical reactions in this process are suitably referred to as the “browning reactions”, which include carbonyl-amine reactions, non-enzymatic browning, or Maillard reactions. In these complex set of reactions the amines, usually from proteins or amino acids, and reducing sugars such as glucose, fructose, maltose, or lactose occur between one another in the presence of water (Tannenbaum, 2004).

After the roasting procedure the shells of the cocoa beans are quite brittle, so they are cooled for a short period of time before they are put through the winnowing machine. Inside this machine serrated cones do not crush, but rather crack open the thin shells to remove the contents inside. Giant fans then blow away these empty husks, leaving only the remaining broken bits, called nibs. These nibs then pass through a series of sieves, which strain and sort the nibs according to their size, in a process called winnowing. The composition of the cocoa nibs is approximately 53% cocoa butter and 47% pure cocoa solids (Beckett, 2000a).

Stage II begins when the roasted cocoa nibs proceed on to the grinding and refining process. In this process the cocoa nibs are milled or crushed between heavy

metal discs, this process generates enough friction and heat to liquefy the nibs into a thick paste called chocolate liquor. The chocolate liquor is then refined for several hours. The aim of this process is to get the particle size down to less than 30 microns, this allows for smooth texture in the final product (Beckett, 2000a).

The third and final stage involves extracting liquid cocoa butter from the chocolate solids. In this process, liquid cocoa butter is squeezed out due to tremendous amounts of force exerted by the hydraulic press. The cocoa butter is then drained through metallic screens and collected for further use. The cocoa butter can be added back to the chocolate liquor to make chocolate products, or used for a number of different applications(Beckett, 1988).

Once the cocoa butter has been extracted the remaining solid cocoa is pulverized into cocoa powder. Cocoa powder is what is left over from the mixture after the cocoa butter is pressed out. This product can be used to make final chocolate products or other confectionary treats. In order to get this product to the correct consistency the cocoa powder must go through an additional grinding, pulverizing, and refining process(Beckett, 1988).

Chocolate Manufacturing

Once the chocolate manufacturer has generated all of the necessary base ingredients, the lengthy and delicate process of chocolate making can commence. This process, which is usually proprietary from company to company, follows the same basic formula which is explained below. This process gives a general basic overview of how chocolate production would be produced in mass production in an industry setting.

Chocolate can also be made in smaller batches in laboratories, bakeries and confectionary shops, or at home using generally the same method.

The first step is a mixing procedure where certain ingredients, such as cocoa powder, cocoa butter, sugar, and milk components, are blended together and turned into a fine uniform paste. Depending upon the manufacturer and particulate product being produced, additional ingredients, such as cocoa butter or milk components, may be added (Beckett, 2000b). The paste is then fed into a roll milling machine where the mixture is constantly grinded and stirred between a series of steel or stone rollers. This process further reduces the particle size, giving the final product a more smooth texture and consistency. However, manufacturers must be careful with this process. If they do not refine or crush this mixture enough, the chocolate will be coarse and grainy; conversely, if manufacturers' over blend the mixture the chocolate will become pasty and gummy. Generally, the refining process depends largely upon the manufacturer and the preference of the consumer.

The refined chocolate is then transferred into large vats where the conching process begins. Conching agitates the paste for an allotted amount of time which could be anywhere from a few hours to several days. The time allotted for conching is dependent upon several factors which include: the amount of chocolate being processed, the standards set by the manufacturer, and the final product. The conching action smoothes out the sugar grains to give the chocolate a silky smooth texture. In addition, the process also allows air to become incorporated into the mixture which

allows the acids and moisture to evaporate. This creates a mellower, more well rounded flavor, but again, it all depends on the manufacturer.

According to Afoakwa et al.,2007, conching involves three stages: dry conching, pasty phase, and liquid conching respectively. Flavors are developed, and the desired viscosity of the chocolate is created during this step of the manufacturing process. In order to create the final viscosity, cocoa butter and lecithin may be mixed into the conching batch before tempering to this the chocolate (Afoakwa *et al.*, 2007).

The most common type of conching machine used by chocolate manufacturers' is the Rotary Conches. These conching machines contain jacketed chamber with mechanical stirring or mixing arms that continuously move and agitate the chocolate mixture in a rotating motion (Tilbrook, 1999) . Typically, these conching machines are time and temperature controlled to ensure consistent and optimal processing.

Tempering

The final and most critical procedure in producing good quality chocolate is the tempering process. In this process, temperature is used to help develop the texture of the final product. Chocolate that is tempered is more stable than chocolate that is not (Afoakwa *et al.*, 2007). Tempering requires the chocolate to be heated then cooled to specific temperatures that will cause a favorable formation of the crystal structure. Without proper tempering, the chocolate could form what is known in industry as 'bloom'. This quality defect is the result of lose fat solids migrating to the surface due to improper formation of the crystal structure. It causes a whitish grey appearance on the surface of the chocolate and thick mouth-feel type texture. If the chocolate is tempered

correctly, desirable attributes such as stability, glossiness, sheen, snap and heat-resistance occur.

Most chocolate manufacturers would agree that the amount of time, degree of temperature, and agitation of liquid chocolate is essential to the tempering process (Callebaut, 2008). This is a time-temperature sensitive process with four main temperatures points that must be reached in order to obtain good product. First, the solid chocolate is melted to 50°C, to melt all fats. The now molten chocolate is cooled to 32°C and crystallization begins to occur. The chocolate is then allowed to further cool and crystallize at 27°C, this step will allow the correct number of stable crystals to form. Finally, any large or unstable crystals are heated to 30°C and cooled once again in order to achieve the desired smooth texture and to ensure all unstable crystals have melted out.

Tempering chocolate has a huge impact on the mechanical properties of chocolate. The tempering process is extremely important in giving chocolate its smooth texture and structure. Tempering allows the chocolate's crystalline structure to form properly by evenly suspending and distributing the crystals throughout the final product. This time-temperature method of crystallization is important to develop not only a good texture but also good flavor. Crystals greatly affect mechanical and sensory properties of the chocolate product, which thereby affect the texture and release of flavors. In dealing with crystallinity the general rule is that the higher the crystallinity means stronger material, giving a better texture (Padar *et al.*, 2008).

Correctly tempered chocolate will yield a bright, crisp, and shiny chocolate, while incorrectly tempered chocolate will produce streaky and dull looking product(Windhab, 2006). Once the chocolate has completed the tempering process it is now ready for its final destination. This could include anything from chocolate kisses to coatings, depending on its intended purpose.

Storage Conditions

Chocolate is very susceptible to temperature damage, flavor and odor migration, light, and time spent in storage. The less time spent in storage, the better the quality chocolate. The shelf-life of chocolate is relatively short and must be stored under appropriate conditions. White chocolate can store up to 12 months, milk chocolate is optimal up to 18 months, and fondant can remain stable up to 24 months. With each of these chocolates, the first in/first out storage system is best for warehousing chocolate. The longer a chocolate product has been in storage, the sooner it will be distributed to stores (Callebaut, 2008).

As the temperature increases within storage, the chocolate experiences less gloss in its appearance and a softer texture. Generally, lower temperatures are best for chocolate storage. Uniform temperature storage is optimal to maintaining the appropriate texture and appearance of chocolate. Additionally, any strong or pungent odors must be stored separately or at a distance from any chocolate products. Chocolate has a strong tendency to absorb these scents which causes it to lose its characteristic smell (Callebaut, 2008). It is also important for the chocolate packaging to be free to such odors as well as not permit any foreign odors to penetrate through.

Other conditions, such as air and light, need to be controlled as well. Exposure to air and light affects the fat within the chocolate by oxidizing it. Oxidation leads to unfavorable changes in appearance, scent, and taste. Also, certain chocolates are more susceptible to the harmful effects of oxidation. White chocolate, because it does not contain any antioxidants, requires more protection due to its inability to fend off any oxidation (Callebaut, 2008).

Humidity is another factor to consider when storing chocolate. Walls and floors can easily collect moisture and because of this chocolate should not be stored in these places. The optimal relative humidity in the storage warehouse which contains chocolate or chocolate products should not exceed 70% (Callebaut, 2008).

Quality Defects Associated with Chocolate

There are many quality defects associated specifically with chocolate. The most common, as mentioned earlier, is known as chocolate 'bloom'. Chocolate bloom causes an unpleasant whitish grey film to form on the surface of chocolate. Most consumers believe this to be mold; however, that is not the case. Chocolate bloom can be caused by one of two things: fat bloom or sugar bloom (Kinta and Hatta, 2005).

Fat bloom, also known as fat migration, occurs because of rapid temperature changes, overly warm storage conditions, or just natural aging of the product. It is a result of the cocoa butter polymorphic transformations from the Form V into Form VI (Pajin and Jovanovic, 2005). When this phenomenon occurs, the fat crystals migrate to the surface of the product forming the white powdery surface (Kinta and Hatta, 2005). Form V is the most desirable form of chocolate to the consumer because it has a glossy

outward appearance and good snap upon breaking. However, Form VI is the most stable form and is often induced by fluctuation in temperature and aging of the product. Form VI often contains larger fat crystalline structures which begin to appear on the surface of the chocolate over time causing the appearance of bloom (Berger, 2008). It can also be caused by operational mishaps such as the pre-crystallization process not being properly performed (Pajin and Jovanovic, 2005).

Fat migration can also occur over time when lipid filler substances within chocolate products moves into the chocolate coating. Once the migration occurs, the chocolate coating softens while the inner filling hardens. If other fats that do not suitably mix with those in the chocolate, a negative effect occurs with the chocolate lipids causing bloom (Ali *et al.*, 2001).

To help prevent fat bloom, emulsifiers and other fats, such as milk fat, are often added to chocolate formulations to retard the process. According to Pajin et al., increasing the milk fat fraction content retards the chocolate tendency to form bloom. This decrease in bloom is due to the high amount of solid fat in the milk fat fraction which hinders the transformations of the polymorphic crystal forms, thus leading to chocolate bloom (Pajin and Jovanovic, 2005).

The other form of chocolate bloom is called sugar bloom. Sugar bloom is caused when moisture condenses on the surface of the chocolate, thus dissolving the sugar. As the water evaporates, the sugar remains forming unfavorable crystals. These large crystals give the chocolate an undesirable, dull appearance not suitable for quality control. Maintaining optimal temperature controls in the chocolate storage areas can

prevent sugar bloom from occurring. If chocolate is taken out of its cold storage, it must be placed in a warmer room for a while prior to packaging the chocolate so it condensation does not occur (Callebaut, 2008).

Defects can also be detected in the texture of chocolate, as discussed early, texture is very important with chocolate products, and achieving the correct texture is difficult balancing act. If molten chocolate is cooled too quickly after being tempered it might result in larger crystal formation which would cause a gritty and unpleasant texture in the final product. The reason is due to uneven melting and not allowing fats enough time to properly melt and crystallize. Another scenario would be if the product is kept at higher temperature for long periods of time. This would result in a product with smaller crystal formation which would have a gooey and more ductile texture. This due to the fats being melted at high temperatures for longer periods of time and not being properly cooled which would inhibit crystalline structure to form(Hoskin, 1994).

Chocolate Ingredients

Dark, milk, and white chocolate are the three main chocolate varieties produced ((Afoakwa *et al.*, 2007)). Each differ in amounts of cocoa powder and cocoa butter they contain, or do contain in the case of white chocolate which contains no cocoa powder at all. The primary ingredients in most chocolate varieties include cocoa powder, cocoa butter, and sugar. For each of these the ratio of each of these primary ingredients varies slightly. There are also other commonly used ingredients which are found in chocolate type products which include milk or milk powder(which can be found in milk chocolate) lecithin (which is an emulsifier) and added spices, most commonly found is vanilla,

however, other spices are known to add unique characteristics such as cinnamon or cayenne(Museum, 2007b).

Cocoa Butter

Cocoa butter serves as the continuous fat matrix in chocolate and is responsible for the dispersion and binding of all other components. The physical behavior of chocolate is due primarily to cocoa butters unique meltability and therefore is said to be the most important ingredient (Lipp and Anklam, 1998, Windhab, 2006). It has very little flavor itself, but it adds a considerable richness and depth to the flavor and texture of chocolate(Minife, 1989a). Cocoa butter is solid at room temperature and liquid between 30°C and 40°C, which allows for chocolates' unique characteristics of being fluid or molten when heated and crisp or solid when cooled. These characteristic traits are what allows chocolate to melt readily and smoothly at oral temperatures(Windhab, 2006).

Cocoa butter is an ivory colored fat which is pressed from the center of the nib of the cocoa bean. It constitutes about 50 to 54% of the roasted cocoa bean, and according to the National Confectioners Association, cocoa butter contains zero trans fats(Association, 2009).

Cocoa butter consists of a mixture of about 40-50 different triacylglycerols(TAG), with three dominant ones which include stearic, palmitic, and oleic(Schenk and Peschar, 2004). The TAG composition and different lengths of the hydrocarbon chain and unsaturation of their fatty acids, as well as their different melting points, are responsible for chocolate's complex thermal behavior. These characteristics are only common in a few types of fats which contain predominately stearic, palmitic, and oleic

(Spigno *et al.*, 2001). These fatty acids are in approximately equal ratios to one another as seen below in Table 1(Afoakwa *et al.*, 2007, Berger, 2008).

Table 2.1: Cocoa Butter Fatty Acid Composition

FA Symbol	Fatty Acid	CN:DB	% in Cocoa Butter
P	Palmitic	16:0	26.0%
St	Stearic	18:0	34.4%
O	Oleic	18:1	34.8%
L	Linoleic	18:2	3.0%
	Others		1.8%

Crystallization of Cocoa Butter

Cocoa butter has the ability to solidify into six different crystal forms, as seen below in detail in Table 2(Afoakwa *et al.*, 2007). The crystallization stability of cocoa butter is essential to the production of chocolate(Smith, 2003). The polymorphic fat undergoes crystallization producing up to six different types of crystals depending upon the processing conditions. Each crystal form has its own unique melting point and chain packing. Polymorphic Forms I through IV are associated with double chain packing while Forms V and VI are associated with triple chain packing(Afoakwa *et al.*, 2007).

Table 2.2: Cocoa Butter's Six Crystalline Polymorphic Forms

Roman Numeral	Crystals	Melting Point	Texture
I	Gamma (γ)	16-18°C	Soft and Crumbly
II	Alpha (α)	22-24°C	Soft and Crumbly
III	$\beta_{2'}(\beta_{2'})$	24-26°C	Firm with Poor Snap and Low melting temp
IV	$\beta_{1'}(\beta_{1'})$	26-28°C	Firm with Good Snap but Low melting temp
V	$\beta_2(\beta_2)$	32-34°C	Firm with good snap, gloss and melting temp
VI	$\beta_1(\beta_1)$	34-36°C	Hard and good melting temp

As discussed early, the most wanted form of crystal is Form V (β) due to its ability to produce a glossy piece of chocolate with desired snap and a resistance to bloom. However, when chocolate is not tempered appropriately, β Form IV crystals morph into Form V too quickly with the resulting chocolate appearing dull, feeling gritty, and containing an unstable structure due to the higher melting point and triple chain packing. Chocolate bloom is much more likely to occur when chocolate fat crystals are not tempered well(Afoakwa *et al.*, 2007). Avoiding fat bloom why tempering is such an important process in chocolate production, because, if not tempered properly it will not only melt at lower temperatures, but attribute to quality defects.

Chain packing, as stated previously, affects the structure and subsequent outcome of the chocolate product. The fat crystals either pack in double or triple-chain

form based upon the types and positions of the triglycerides. Form IV, a double-chain crystal, proves to not be as stable as Form V, a triple-chain crystal, because the structure of the chain in Form V allows for tighter packing and a higher melting point(Afoakwa *et al.*, 2007). Form V, has the most beneficial effects on texture and taste (Schenk and Peschar, 2004, Nesle *et al.*, 2007).

Rapid cooling of milk chocolate causes crystal polymorphs to transform into different crystalline structures. According to research done by Nesle and Tooh, milk chocolate was melted and re-hardened quickly showed changing polymorphs. Originally, the milk chocolate contained the cocoa butter polymorph of Form V. After the chocolate rapidly re-hardened, different polymorphs were observed in the chocolate mass, although the particular type of crystals could not be determined. Also, the texture and taste of the chocolate was jeopardized. Once re-hardened, the chocolate became brittle, felt gritty, and lacked the smooth taste characteristic of (Nesle *et al.*, 2007).

Due to the crystalline formation being such an essential part of the chocolate product, tempering, the process of fat crystallization within chocolate, is incredibly important. Tempering allows the manufacturer to create the most optimal texture, taste, and appearance of chocolate products(Afoakwa *et al.*, 2007).

Cocoa Powder

Cocoa powder is the other primary ingredients used in most chocolates, with the exception of white chocolate, which only contains cocoa butter, sugar, and milk powder. This means that white chocolate lacks the preserving qualities found in the antioxidants

contained within the cocoa powder(Beckett, 2000b, Beckett, 1988). These antioxidants help to sustain the shelf-life of chocolate products by restricting the breakdown of fats.

Cocoa powder is derived from the cocoa nib which is ground down to a very fine particle size. Ordinarily, cocoa powder used in chocolate manufacturing must be less than 30 microns in size in order to get proper mouthfeel. The fat content of the cocoa powder used is approximately 20-22%. Lower fat ranges are available; however, if the cocoa powder is free from any and all fat, it cannot legally be called cocoa powder (Beckett, 1988).

Sugars

Sugar is the other main component of chocolate products. There are numerous types of sugars which can be incorporated depending on the type product you wish to formulate. Sucrose is the most common sugar used in chocolate, followed by lactose, which is the milk sugar found in the milk chocolate products. Then there are other sugars which are used for diabetic friendly chocolates which include glucose, fructose, and sugar alcohols. These types of sugars are also being researched more heavily in order to develop lower calorie chocolate products. One particular research investigated the two monosaccharides (glucose and fructose) and one disaccharide (sacharose) which were added to separate batches of chocolate to investigate the effects the sugars had on the overall texture and melting procedure of the chocolate(Van Dujin and Gaspersz, 2008).

The glucose chocolate proved to create a semi-solid mass, while the fructose chocolate was solid, and the sacharose chocolate was mostly liquid. In terms of melting

procedure, the sacharose chocolate had a higher melting point than both glucose and fructose chocolate due to the sacharose structure. Sacharose, as stated earlier, is a disaccharide which means the bond between the two monomers is much more difficult to break, thus causing heat to take much longer to cleave the bonds. During the tempering process, these bonds remained intact, so the resulting sacharose chocolate stayed in liquid form (Van Dujin and Gaspersz, 2008).

In addition to these sugars, different types of sugars can replace the standard sucrose used in most chocolate products. Dextrose and lactose have already proved to be valuable contenders in taking the place of sucrose in low-caloric milk chocolates. Some sugar alcohols such as xylitol, mannitol, and lactitol are also used in low-caloric chocolate; however, they do not always produce chocolate of the same textural caliber as sucrose-added chocolate contains. Mannitol provided the closest fit to the desired glossiness, good snap, and smoothness of the chocolate (Afoakwa *et al.*, 2007). However, when formulating with sugar alcohols, one must be cautious of developing off flavors, more specifically bitter flavors which can be formed when used in high concentrations.

Secondary Chocolate Components

Commonly used in many chocolate products are milk powders or milk solids. When chocolate contains such ingredients, it is then most commonly referred to as milk chocolate. Milk chocolate products are very popular in most countries, out selling both white and dark chocolate products combined (Museum, 2007a). However, adding this component to chocolate formulations can be quite tricky because of the moisture

content of milk. Too much moisture will destroy the flow properties of liquid chocolate, so for this reason milk powder or milk solids are used (Minife, 1989a).

Lecithin, also known as a surface active agent, is commonly used in food products as an emulsifier or lubricant. Similarly, it is used in chocolate as an ingredient which helps keep the fat from separating out into the product by forming a barrier between the two non-mixable substances. Lecithin is a naturally occurring substance found most frequently in soya. It is most often used at levels between 0.1% and 0.3%. This is said to reduce the viscosity and allow the product to tolerate higher levels of moisture (Beckett, 2000b).

Other minor constituents which provide additional flavors to the product include various spices, such as vanilla, cinnamon, nutmeg, and for an extra kick cayenne pepper is often added (Museum, 2007a).

Substituting Ingredients

According to Berger, the cost of cocoa butter is much higher than other vegetable fats. Because of this expense, alternative fats are being studied as to if they alter the overall desired characteristics of chocolate (Berger, 2008). Certain vegetable fats may be added to chocolate without causing undesirable effects on the texture. These fats form different crystalline structures, but through the use of appropriate tempering procedures, the resulting chocolate still contains favorable traits (Afoakwa *et al.*, 2007).

These alternative fats are categorized into one of the following: cocoa butter equivalents (CBEs), cocoa butter replacers (CBRs), and cocoa butter substitutes (CBSs). CBEs are plant fats devoid of any lauric acid, and they have comparable

properties to that of cocoa butter which means they can mix well with cocoa butter. The three main fatty acids in CBEs are palmitic, steric oleic, and linoleic arachidic acids with the major triglycerides being POP, POS, and SOS(Lipp and Anklam, 1998). Palm oil, a CBE plant fat type, has similar properties as cocoa butter such as the solid fat content. Also, it contains two of the three major triglycerides found in cocoa butter: POP and POS(Berger, 2008).

CBRs are also non-lauric fats; however, they are structured much differently than cocoa butter triglycerides. This partial compatibility between CBRs and cocoa butter makes mixing the two materials more difficult. Elaidic, stearic, palmitic, and linoleic acids constitute the main fatty acids, while PEE and SEE are the main triglycerides(Lipp and Anklam, 1998). Finally, CBSs do contain lauric acid and are structurally different than cocoa butter; however, CBSs are most optimal if used for 100% substitution with cocoa butter. LLL, LLM, and LMM triglycerides create the lauric and myristic acids than make up the CBSs(Lipp and Anklam, 1998).

Whether CBEs, CBRs, or CBSs are used, the melting procedure of the fatty ingredients used must behave similarly to cocoa butter. This compatibility must occur to create the same texture, appearance, and taste found in cocoa butter chocolate. If a certain fat is found to alter the crystallization and melting procedure of the chocolate, it is deemed unsuitable for chocolate manufacturing(Lipp and Anklam, 1998).

Measuring the Heat Capabilities of Chocolate using a Differential Scanning Calorimeter

To measure the heat capacities of chocolate, a differential scanning calorimeter is commonly used. The DSC indicates the thermodynamics and thermal transitions

within a food system and provides information regarding melting, crystallization, and glass transition phases of foods like chocolate (Department of Polymer Science, 1997).

The DSC uses two calorimeters in which one heats a reference pan and the other heats the sample-containing pan. A computer system then changes the temperature of both pans on the same scale over time. In order for the sample-containing pan to remain at the same temperature as the reference pan, more heat is required. The temperature difference between the two calorimeters shows thermal transitions for the sample. Peaks are produced indicating the separation of the crystal stages with respects to heat flow change versus temperature change (Spigno *et al.*, 2001). The plot shows Glass Transition (T_g), Crystallization (T_c), and Melting (T_m).

There have been studies done using the DSC to look at the unique characteristics of cocoa butter. One study in particular was looking to identify a simple method the chocolate industry could use for knowing when cocoa butters polymorphic form was obtained during the final cooling process. The study proved that peaks could be identified to show when cocoa butter crystallization had completed (Spigno *et al.*, 2001). This could allow the chocolate industry to have consistently good product by knowing proper crystallization has occurred using the DSC. This would help cut down on the amount of waste and positively affect the company's bottom line.

Measuring Chocolate's Texture Using a Texture Analyzer

Texture analysis is the practice of testing physical properties of food products, usually by compression. Physical testing of food products can provide information about its tactile properties, such as firmness, fracturability, resilience, and more. Tactile

properties affect the consumer's sensory perception and acceptance of a food product, thus it remains important that texture analysis can be done to distinguish an acceptable from unacceptable product. The physical properties of food affect the design of processing equipment. Therefore, quantifying these physical properties is helping in selecting and adjusting equipment used in manufacturing and transporting(Brookfield, 2009).

For chocolate, snap and hardness are two of its most important textural characteristics. These are often measured as part of a chocolate companies quality control checks and are analyzed by using specific texture measuring instruments. Here probes or blades are driven down into a sample at a constant speed or force, while at the same time recording the resistive force or distance generated by a sample. The test commonly used for chocolate is the snapping test, and can be measured using the three-point bend test(Beckett, 2000b). A diagram of this can be seen below in Figure 4.

Measuring Chocolate's Structural Form Using Raman Spectroscopy

Raman spectroscopy is a very useful material characterization method. It is based on the Raman scattering effect, developed in the early 20th century by Sir C.V. Raman. The Raman scattering is a form of inelastic scattering. Photons enter into the material at one energy and emerge at slightly different energies or wavelengths due to inelastic scattering. These photons are changing their energy by exchanging some energy with the molecular vibrations of the material(Ferraro, 1994). The end result is a series of different size wavelengths which is transmitted to a computer which generates

a graph or diagram. The information provided by these diagrams can help provide both qualitative and quantitative information.

So far, little research has been done using this technology as a characterization tool for chocolate products. In fact, Raman spectroscopy is just beginning to enter into the world of food. Food processors are just recently recognizing Raman's value in applications such as food authentication, traceability and quality control. Because Raman is a non-destructive and simple to use, it has an advantage of infrared. Raman spectroscopy is currently being used in edible oil facilities for authentication of trans fats/oils, unsaturation, oxidation, free fatty acids and moisture(Li-Chan, 1996).

Some research work has been done using Raman spectroscopy to study cacao seeds and their extracts. In their research, Raman spectroscopy was successfully used to monitor the extraction stages of the processing of cacao seeds. This research proves that Raman spectroscopy could be used as a non-destructive and relatively rapid method of cacao seed process control and quality monitoring of the extracts(Edwards, 2005).

Sensory Analysis

Correlation of instrumental data with data provided by a sensory panel is extremely important when testing food products. Although obtaining data from a sensory panel can be difficult, expensive, and often time consuming, it is crucial that one understands what the customer considers to be desirable and undesirable(Andrae-Nightingale, 2009).

In a study conducted by Guinard et al., the sensory effects sugar and fat have on milk chocolate were observed. Higher sugar chocolates possessed desired traits such as smoothness and good snap. As the sugar content decreased, a bitter, gritty chocolate came about(Guinard and Mazzucchelli, 1999).

In regards to the fat content, increased levels of fat melted much quicker than lower levels of fat. When both the fat and the sugar amounts were lowered, a fattier, more oily and viscous chocolate was made. However, the study indicated that, due to other ingredient interference, the exact effects of sugar and fat were difficult to observe(Guinard and Mazzucchelli, 1999).

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CHAPTER 3

CONTROLLING THE TEXTURE AND STRUCTURE OF CHOCOLATE BY THE ADDITION OF COCOA BUTTER ALTERNATIVES

INTRODUCTION

Cocoa Butter Alternatives (CBAs) are becoming increasingly popular with the chocolate industry and confectionary researchers. Not only is the behavior of CBAs similar to cocoa butter, but they also provide the same flavor and texture. CBA's also provide a cheaper alternative to cocoa butters rising prices, which is another added benefit. So now that the EU has approved usage of CBAs at a 5% level, more research is coming out on CBAs useful functionalities (Timms, 2003).

Traditionally the only fat incorporated into chocolate was cocoa butter, which is a unique vegetable fat. Cocoa butter gives chocolate its texture, melting behavior, glossy appearance, and flavor release characteristics. Cocoa butter can often be incompatible with other fat systems and have a limited melting profile (Lechter, 2009). It can also be costly and, unlike Cocoa Butter Alternatives, it must be tempered. CBAs are lending flexibility and functionality to the chocolate products by allowing for higher melt coatings, higher bloom resistant product, or other specific functions for molding or enrobing purposes. Cocoa Butter Alternatives are broken down into three categories: Cocoa Butter Substitutes (CBSs), Cocoa Butter Replacers (CBRs), and Cocoa Butter Equivalent (CBEs).

Cocoa Butter Substitutes are generally incorporated with partially hydrogenated lauric fat compounds with very high melting profiles which results in a texture and mouth feel similar to cocoa butter(Lipp and Anklam, 1998). The raw materials for Cocoa Butter Substitutes usually consist of lauric products such as palm kernel and coconut oil. The advantages to using CBSs are that they melt down and give similar flavor release to that of cocoa butter. CBSs also crystallize rapidly, and product good gloss and bloom stability in the final product. However, the disadvantages to using CBSs are that they can only tolerate up to 5% max of any other fat, which includes milk fat. This means CBSs would do really well in dark chocolate products, but for would cause a lower melting point if used in milk chocolate products(Lipp and Anklam, 1998).

Cocoa Butter Replacers have very similar characteristics to Cocoa Butter Substitutes. CBRs have the added advantage of not needing to be tempered, which will help to simplify the production process. However, CBRs also have the disadvantage of not being able to tolerate added fat; with their tolerance being a little higher around 20%. The raw materials which make up CBRs consist generally of products such as soybean, cottonseed and palm oils(Lipp and Anklam, 1998).

Cocoa Butter Equivalentents are closest in behavior, fatty acid profile, and nutritional profile to cocoa butter. They must be tempered as cocoa butter is and have similar melting properties. However, when using CBEs there is not limitation to the amount of fat you can add. CBEs are usually a mixture of palm and shea oil(Lipp and Anklam, 1998).

Although none of the Cocoa Butter Alternatives discussed are going to completely replace real cocoa butter, they do bring other functionalities that are beneficial both cost effect and bring ease to processing. The objective of this study is to identify how each of these Cocoa Butter Alternatives can help better control the texture and extend the shelf life of chocolate products.

MATERIALS AND METHODS

Materials

The standard ingredients for making samples include the following: bitter sweet chocolate chips provided by Archer Daniels Midland Corporation (Milwaukee, WI), labeled Cocoa Liquor (Drops) 805000-5C; granular cocoa butter provided by Barry Callebaut (St. Albans, VT), code number 1804.0000; extra fine granulated (EFG) sugar was provided by Domino Foods (Williamsburg, NY); and granulated lecithin was purchased from Chocolate Alchemy (Yoncalla, OR). The granulated lecithin and cocoa butter samples were kept in refrigerated temperatures of 15°C.

The cocoa butter alternatives used in making the samples include the following: a refined/bleached/hydrogenated/deodorized/Palm Kernel 95' provide by Archer Daniels Midland (Decatur, IL), labeled Palm Kernel Oil 74-550-0; a Red Palm Oil purchased from Jungle Products Inc. (Healdsburg, CA); and Extra Virgin Coconut Oil purchased from Garden of Life – Living Foods (West Palm Beach, FL). All cocoa butter alternatives were kept at room temperature.

Sample Preparation

A Chocolate Melanger purchased from Chocolate Alchemy (Eugene, OR), was used to 'conch' each sample for three hours. The Chocovision Rev. 2 tempering machine, purchased from ChocoVision Corp. (Poughkeepsie, NY). When tempering the samples the Chocovision Rev. 2 would be set on the 'Dark Chocolate' program.

Table 3.1 shows the different formulations used with the three cocoa butter alternatives, as well as the control sample. Each sample took 4 h to complete from start to finish, and all finished samples were kept in a dry area at 18°C.

Procedure for Processing Chocolate Samples

Using an analytical balance, weigh out and combine the cocoa butter and one of the three cocoa butter alternatives and place over heating element. Heat the cocoa butter mixture to approximately 46°C, which usually takes about 5 min. Once the cocoa butter mixture has reached 46°C, add it to the Chocolate Melanger, along with the bittersweet chocolate chip and extra fine granulated sugar. The mixture will now be 'conched' in the Melanger for 3 h. During the last 30 min. of conching in the Melanger, add the appropriate amount of lecithin.

At this point in the process, the mixture is now a smooth chocolate liquid and can be transferred into the tempering machine. The Chocovision Rev. 2 tempering machine has several programs depending on the type of chocolate being formulated. For these samples, a 'Dark Chocolate' tempering program was chosen. While in the tempering machine, the liquid chocolate is heated and cooled several times for about 12-15 min. An audible beep signals the end the tempering process and the liquid chocolate is now transferred into molds. These molds are rectangular in shape, and create a sample

which is approximately 20 g in weight, 80mm in length, 45 mm in width, 4.5 mm in thickness. The samples usually take 30-35 min. to completely solidify at 20°C. Finished samples are placed into air-tight plastic zip-lock bags and stored in cool temperatures of 22°C. Each formulation would be made a total of three times.

Measuring Texture

A texture analyzer was used to perform a three-point bend test to measure and record the hardness and brittleness of each sample. The hardness of a sample is determined by the maximum force required to break a sample, while the brittleness of a sample is determined by the amount of distance the probe traveled to break the sample. The texture analyzer used was a Stable Microsystems TA-XT2 from Texture Technologies (Scarsdale, NY). For each sample the loading cell was set at 25 kg, the test speed set at 4 mm/s, distance set at 10 mm. Each 20 g sample could only be run through the texture analyzer once in order to achieve accurate measurements. Each sample was measured a total of six times.

Differential Scanning Calorimeter

A Differential Scanning Calorimeter (DSC), which is a thermoanalytical instrument, measures the temperatures and flow of heat associated with thermal transitions in a material. To obtain this data, very small amounts of sample are loaded into aluminum pans and then are subjected to extreme temperature ranges of -30-100°C. The temperature increases about 5°C/minute every minute, so samples usually take around 20-25 minutes from start to finish. The purpose of the using the DSC is to

obtain data on samples points of crystallization, melting, phase change, and glass transition. This instrument was manufactured by Mettler Toledo and is known as a DSC1. This procedure would be done a total of three times.

RESULTS AND DISCUSSION

Table 3.2 shows the thermal properties of the dark chocolate samples with and without added fat alternative. Glass transition behavior remains invariant with changing fat composition indicating that the overall miscibility within the system does not change with changing fat type. In the case of coconut oil and palm kernel oil, there is a low melting temperature fraction of the fat. This is likely due to imperfection in the crystal structure, leading to a low melting temperature component. Immediately following this melting, there is a significant cold crystallization peak. The likely cause of this is the low melting temperature fraction recrystallizing into a more stable structure during further heating. Full melting occurs at or below the melting temperature of the control in all cases except for coconut oil, which exhibits some type VI crystalline phase chocolate, unlike the other cases. Both red palm and palm kernel oil exhibit the weakest crystalline structure, both melting at 33°C, indicative of type IV crystalline phase which is unfavorable.

The mechanical texture analysis data shown in Table 3.3 is in general agreement with the thermal behavior shown in Table 3.2. The weaker crystalline structures exhibited by the presence of low melting temperature fraction lead to lower fracture forces and strains; however, this trend is not preserved in the case of palm kernel oil. This is likely due to the storage temperature. While most of the differential scanning

calorimetry data was measured within a few days after the chocolate was manufactured, the texture analysis was performed generally in excess of a week after this. The storage temperature and peak cold crystallization temperature were in near alignment, leading to continued loss of poorly crystallized fraction, while recrystallization took place under ideal conditions, thereby leading to a product with higher strength and more thermodynamic stability.

CONCLUSION

The inclusion of alternatives to cocoa butter may offer potential cost-savings to a chocolate producer that may improve profitability; however, the care must be taken in order to avoid detriment to product quality. Kinetics of crystallization are altered through the addition of alternatives to cocoa butter, leading to variations in crystalline state and final properties. Proper storage post-cooling indicates that an annealing step may be used in order to optimize crystalline structure and final product properties.

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Table 3.1: Dark chocolate formulations used in this study given as weigh percentages of each ingredient in relation to the final weight of the composition.

Treatment	Chocolate Liquor (%)	Cocoa Butter (%)	Sucrose (%)	Alternative Oil (%)	Lecithin (%)
Control	70	15	14.3	0	0.7
Coconut Oil	70	10	14.3	5	0.7
Red Palm Oil	70	10	14.3	5	0.7
Palm Kernel Oil	70	10	14.3	5	0.7

Table 3.2: Average results from thermal analysis shown as glass transition, cold crystallization temperatures, and melting point for dark chocolate samples with and without addition of alternative fat.

Treatment	Glass Transition (T _g)	Cold Crystallization (T _{cc})	Melting Point (T _m)
Control	1°C	14°C, 19°C	34°C, 35°C
Coconut Oil	1°C	20°C	12°C, 34°C, 37°C
Red Palm Oil	1°C	11°C, 17°C	33°C
Palm Kernel Oil	1°C	18°C	15°C, 33°C

Table 3.3: Average fracture force and strain measured by three-point bend for dark chocolate samples with and without added alternative fat.

Treatment	FRACTURE FORCE	STRAIN %
Control	9600	40
Coconut Oil	6800	33
Red Palm Oil	8000	33
Palm Kernel Oil	11000	37

CHAPTER 4

PROCESS-PROPERTY-STRUCTURE RELATIONSHIPS IN CHOCOLATE WITH THE ADDITION OF POLYSACCHARIDES

INTRODUCTION

Crystalline structure of the fat in chocolate is a critical factor in determining shelf stability, texture, and flavor release from chocolate. The fat phase is the only continuous phase in chocolate, and therefore responsible for its unique physical characteristics such as the melting behavior as well as the dispersion of all the other components (Lipp and Anklam, 1998).

Cocoa butter can exist in six different polymorphic forms, some of which are more favorable than others. The more favorable polymorphic forms include forms V and VI (Schenk and Peschar, 2004). To obtain these crystalline forms, tempering of the chocolate is necessary to allow for optimal chocolate crystallization. This process involves several stages of heating and cooling the chocolate to specific temperatures. Tempering involves pre-crystallization of a small proportion of triglycerides, with crystals forming nuclei for remaining lipids to set in the correct form (Akoakwa, 2007). This allows the fat crystals to align in the correct orientation and gives the final chocolate product the correct snap when cooled and a smooth, creamy texture at oral temperatures.

Tempering chocolate also decreases the chances of bloom formation occurring on the final product. This is due to the fat crystals closely packed formation, which decreases the chances of fat migration (Beckett, 2000). In addition, tempered chocolate, in the V or VI form, is able to withstand increased temperatures and therefore has a higher melting point.

Although there is extensive research on incorporating different types of sugars in to chocolate, no research has been conducted using polysaccharides in chocolate to control texture. The addition of a high molecular weight component may have multifold effects in controlling mechanical and physical properties. Depending on their interaction with the fat matrix, the polysaccharides may act to either stabilize the structure and reinforce the mechanical properties of the chocolate if there is a favorable interaction with the matrix, or if there is an unfavorable interaction with the matrix, the polysaccharide will weaken the chocolate. The high molecular weight component will also affect nucleation of crystals and the rate at which these crystals grow. Different polysaccharides will be used in a typical dark chocolate formulation to see how they affect the properties of chocolate. The justification behind this research is that chocolate crystallization affects chocolate texture, and therefore by altering the kinetics and crystal size, we can control the texture of chocolate. The overall objective of this research is to examine the effects of polysaccharides on the structural and textural characteristics of chocolate.

MATERIALS AND METHODS

Materials

The following includes a description of the ingredients and where they were obtained. Cocoa Liquor 805000-5C, this is a bittersweet chocolate chip obtained from Archer Daniels Midland Corporation (Milwaukee, WI). Cocoa Butter 1804.0000, was obtained from Barry Callebaut (St. Albans, VT) and kept at refrigerated temperatures. Extra Fine Granulated (EFG) Sugar was obtained from Domino Foods (Williamsburg, NY). Granulated Lecithin was purchased from Chocolate Alchemy (Yoncalla, OR), and kept in refrigerated temperatures.

The following include the four different types of Polysaccharides used, an item code, and where the samples obtained from. Xanthan Gum 6070774, Carrageenan 060617-C, and Sodium Alginate CM-61BF, were all obtained from Ingredient Solutions, Inc., (Waldo, ME). Guar Gum 14866, was obtained from TIC GUMS, (Belcamp, MD).

All ingredients were kept at room temperatures of 22°C unless otherwise specified.

Preparation of Chocolate Samples

To formulate each sample a Chocolate Melanger from Chocolate Alchemy (Eugene, OR) was used to 'conch' the sample for three hours. A Chocovision Rev. 2 Tempering Machine from ChocoVision Corp. (Poughkeepsie, NY) was used to temper the chocolate for 12-15 min.

Each half pound sample was formulated using the exact same procedure and ingredients with exception to the four different polysaccharides. A list of the ingredients

and amounts used are located in Table 4.1. Each sample took approximately 4 h to construct from beginning to end. Finished samples were then put into zip-lock bags and placed in a cool storage location with temperatures at 22°C.

Chocolate Processing

All ingredients were weighed out in appropriate amounts using an analytical balance. The cocoa butter was heated to 60°C in a mixing bowl over a heat source. The cocoa drops (chips), sugar, cocoa butter, and polysaccharide were all added to the Chocolate Melanger, where they would be conched and refined for approximately 3 h. The lecithin was added during the last 30 min. of conching. The mixture, which is now in the liquid form, would then be transferred to the Chocovision Rev. 2 Tempering Machine. In the tempering machine the mixture would be heated and cooled several times for about 12-15 min. After the mixture was finished tempering, the molten chocolate would be transferred into rectangular molds and then allowed to cool for approximately 30 min. After the chocolate had solidified, it was removed from the molds and placed into air-tight zip lock bags and placed into a cool dry place for storage. The final sample bar size was approximately 80mm in length, 45 mm in width, 4.5 mm thickness, and weighed approximately 20 g. Each formulation would make a total of 13 bars, and this procedure would be replicated three times.

Tempering Process

The Chocovision Rev. 2 Tempering Machine was set on the 'Dark Chocolate' program. The temperature of the molten chocolate going into the tempering machine was 38°C. The chocolate was then heated to 46°C and then cooled to 29°C. The

chocolate was again heated for a second time and reached a temperature of 32°C then cooled down to 30°C where it was transferred to molds.

Texture Analysis

The samples were measured using the Stable Microsystems TA-XT2 Texture Analyzer from Texture Technologies (Scarsdale, NY). A three point bend test was conducted to measure the mechanical characteristics of the sample. The conditions used were the following: test speed set at 4 mm/s, distance set at 10 mm, and loading cell 25 kg. The objective was to obtain information on the hardness and brittleness of the chocolate bar sample. Hardness was reported as the maximum force required to break the sample. Brittleness was measured as the distance on the force-distance curve where the sample broke. Each formulation had a total of six replications which would be performed.

Differential Scanning Calorimeter

The samples were then measured using a Mettler Toledo Differential Scanning Calorimetry (DSC1). This instrument is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. The samples were subjected to a temperature range of -30-100°C with an increase in temperature of 5°C/min. The data was then shown on a graph and analyzed. A total of three replications were performed for each formulation.

RESULTS AND DISCUSSION

Thermal behavior is shown in Table 4.2. The increasing glass transition temperature with added polysaccharide is a result of including higher molecular weight materials in the product. One significant factor that would lead to this is that the total number of molecules in the non-crystalline phase is significantly decreased with this addition, leading to fewer distinct ends of molecules and less free volume associated with free ends. Additionally, the large molecules themselves require more energy to move than small molecules, thereby increasing glass transition temperatures when they are present in a material. This would result in some embrittlement of the material, which can manifest in contributing to a lower fracture strain in the chocolate. There is one distinct glass transition for each sample which indicates that the samples are well mixed and phase separation is not occurring to a significant extent. Cold crystallization behavior is relatively unaffected in most samples containing polysaccharides; however, samples containing guar gum have a lower cold crystallization temperature. This would result in more structural changes during storage at room temperatures. Two crystalline phases can be seen as two separate melting temperatures in each sample (with the exception of samples containing xanthan gum). The crystalline phases shown are V and VI, with xanthan gum exhibiting only type V crystallization. In all cases with added polysaccharide, the melting temperatures increase, showing greater stability of the fat in the chocolate with added polysaccharide. The tendency for higher melting temperatures may also lead to embrittlement, resulting in lower fracture strain. Type V crystalline phase gives chocolate the best snap properties, and when xanthan gum is

added to the chocolate, the DSC thermograms show that the fat crystals are only of type V. This type of crystallization results in the increased fracture force and decreased fracture strain seen in the texture analysis. The development of more stable crystalline phases is likely due to two main effects of the polysaccharides as they act in the molten material. First, the high molecular weight fraction increases the viscosity of the melt. This facilitates transfer of stress through the melt, thereby increasing the number of crystal nuclei. These nuclei also grow more slowly, and due to their slower kinetics are able to form more thermodynamically stable crystallites.

Table 4.3 Shows the results from the TA.XT2 texture analysis, which are given in fracture force and strain percentage during three-point bend testing of chocolate samples. Fracture strain tends to be lower in samples containing polysaccharides, particularly in chocolate with included guar gum or sodium alginate. These two samples also had significantly lower fracture force than the control and chocolates containing either xanthan gum or carrageenan, with the chocolate containing carrageenan having the highest fracture force of all samples. The decreased fracture strain is an indication that the overall ductility of the chocolate has decreased with the addition of polysaccharide fraction. The major contributing factor to this would be the increase in glass transition temperature. However, this could be due to immiscibility between the fat and the polysaccharide. The fact that crystalline phase is more stable with inclusion of polysaccharides indicates that the fracture stress should increase; however, this is not always the case. In cases where fracture stress decreases, there is likely immiscibility between the fat and the polysaccharide that lead to the overall decrease in

material strength. In the majority of cases, when strength increases with polysaccharide addition, this is a likely result of increased stability of the crystalline phase.

CONCLUSION

The addition of polysaccharides to chocolate results in enhanced stability of fat in the chocolate, which will likely result in enhanced resistance to lipid oxidation and increased shelf stability. Phase separation does not occur when 1% w/w polysaccharide is included in a dark chocolate formulation, and polysaccharide type can be selected to control fracture properties of the chocolate at low concentration.

REFERENCES

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Table 4.1: Dark chocolate formulations used in this study given as weigh percentages of each ingredient in relation to the final weight of the composition.

Treatment	Chocolate Liquor (%)	Cocoa Butter (%)	Sucrose (%)	Polysaccharide (%)	Lecithin (%)
Control	70	15	14.3	0	0.7
Xanthan Gum	70	15	13.3	1	0.7
Carrageenan	70	15	13.3	1	0.7
Sodium Alginate	70	15	13.3	1	0.7
Guar Gum	70	15	13.3	1	0.7

Table 4.2: Average results from thermal analysis shown as glass transition, cold crystallization temperatures, melting temperatures, and area under the melting peak for dark chocolate samples with and without polysaccharide addition.

Treatment	Glass Transition (T_g)	Cold Crystallization (T_{cc})	Melting Point (T_m)	ΔA_{Peak}
Control	1.3°C	13.5°C, 18.5°C	33.5°C, 34.9°C	69.7
Xanthan Gum	3.3°C	13.6°C, 18.5°C	34.1°C	71.5
Carrageenan	1.8°C	13.9°C, 18.2°C	33.9°C, 35.0°C	70.7
Sodium Alginate	2.3°C	12.8°C, 18.0°C	33.8C, 35.6C	70.9
Guar Gum	0.6°C	12.2°C, 17.6°C, 22.2°C	33.7°C, 35.9°C	67.1

Table 4.3: Average fracture force and strain measured by three-point bend for dark chocolate samples with and without added polysaccharide components.

Treatment	FRACTURE FORCE	STRAIN %
Control	9600	40
Xanthan Gum	8400	37
Carrageenan	9800	36
Sodium Alginate	1300	33
Guar Gum	1200	30

CHAPTER 5

CONCLUSIONS

Controlling the crystallization of cocoa butter during the tempering process to achieving desirable texture or 'snap' is one of the most difficult aspects in the production and manufacturing of chocolate products. The production of chocolate is a very delicate and time sensitive process, and many manufacturing mishaps result in unsatisfactory products. Finding methods to control the crystallization process will greatly improve the way chocolate is manufactured. By incorporating non-traditional ingredients, such as cocoa butter alternatives and polysaccharides, chocolate manufacturers can improve the structure and texture of their chocolate products, while also increasing the shelf life.

A base composition of chocolate with and without added polysaccharides was studied. The control composition was 70% cocoa liquor, 15% cocoa butter, 14.3% sugar, and 0.7% lecithin. Xanthan gum, carrageenan, sodium alginate, and guar gum were added to chocolate formulations at a level of 1%, replacing part of the sugar fraction, as a means of moderating crystallization rate. The textural properties of the resulting chocolate samples were tested by fracture in three-point bend, and thermal properties (T_g , T_{cc} , and T_m) were measured by differential scanning calorimetry. Addition of polysaccharides results in lower fracture strain and tends to cause increased glass transition and melting temperatures. Samples containing xanthan gum tend to

contain only type VI crystalline fat, whereas all other samples, including the control exhibit type V and type VI crystalline fat.

The same procedure was used when formulating the chocolate samples with cocoa butter alternatives. The cocoa butter alternatives, which include red palm oil, palm kernel oil, and coconut oil, were added to the chocolate formulations at a level of 5%, replacing part of the cocoa butter fraction. Because cocoa butter alternatives are much cheaper than natural cocoa butter, potential cost-savings exist when chocolate manufacturers include them in their chocolate formulations. The disadvantage of incorporating cocoa butter alternative is their inability to perform as well as cocoa butter. The samples containing cocoa butter alternatives were much weaker in texture and strength, which will lead to faster formation of chocolate bloom. However, proper storage post-cooling shows that an annealing step may be used in order to optimize crystalline structure in final product properties.

This research has shown potential exists when non-traditional ingredients are incorporated into chocolate products. These ingredients allow for good quality chocolate to be produced on a consistent basis, at lower prices, and with increased shelf life.