

Development of heat resistant chocolate



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PRALINE

The term 'cocoa' comes from the word 'cacao' that is taken directly from Mayan and Aztec languages. Chocolate has been derived from cocoa beans, present in the centre to the fruit of cocoa tree, *Theobroma cacao*, which originated from the South American region. (Afoakwa 2010)

Chocolate is one of the most popular products throughout the world. The fact that it is solid at room temperature but melts in the mouth, giving a smooth delicate taste, makes it one of the most yearned product. From a more technical point of view, chocolate is a complex food made of solid particles of cocoa powder, sugar and milk powder in a continuous fat phase. The production of chocolate consists of multiple steps among which tempering are one of the most important step. During this the temperature of the chocolate will be varied to get the right crystalline form of the fat.

Chocolate pralines are a lot more complex product since they also contain a soft filling which will interact with the chocolate shell. Migration can happen from the filling to the shell which can result in structural damages like cracking.

Another effect can be fat bloom which is a grayish haze on the praline surface.

This occurs due to the migration of the liquid fat through the shell to the surface and crystallizing.

Cracking and fat bloom are two major issues that lead to reduced shelf life in chocolate pralines. The main suggestions for crack formation are that cracks

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form due to moisture or ethanol migration through the chocolate shell, or due to an unbalanced distribution of moisture in the filling that causes some parts to shrink and other to expand. (SLETTENGREN 2010)

Most of the fat inside chocolate must be cocoa butter. Cocoa butter consists of different triacylglycerols (triglycerides), each of which will solidify at a different temperature and at a different speed in correlation with time. To make it more complicated there are six different ways the crystals can pack together.

If the fat is present is not right or if the chocolate has not been crystallized properly, then fat bloom occurs. All fats are made of mixtures of triglycerides i. e. they have three fatty acids attached to a glycerol backbone. In cocoa butter there are three main acids which account for over 95% of those present. Almost 35% is oleic acid (C18: 0) and almost 26% is palmitic acid (C16: 0). Since the cocoa butter has few main components that it melts rapidly over such a small range of temperature range i. e. between room and mouth temperatures.

POSt molecules are palmitic acid (P) in position 1, oleic acid (O) in position 2 and stearic acid in position 3. If the stearic and oleic acids are inverted then this would become PStO, which is quite atypical even though the constituents are similar.

The stearic and palmitic acids are saturated acids i. e. the hydrocarbon chain which makes up the fat does not have any double bonds.

In unsaturated fats this chain has one or more double bonds, as is the case for oleic acid. About 80% of the cocoa butter has oleic acid as the middle acid. 1% to 2% of cocoa butter has saturated long chain trisaturated triglycerides (SSS) where the saturated fat is mainly palmitic or stearic and the melting point is high.

From 5% to 20% on the other hand consists of two oleic acids and is mostly fluid at room temperature.

When the above two have been combined then fat of the cocoa butter will be partially fluid at room temperature. If the temperature is raised fat will melt according to the proportions of the different types of fat present.

The property of to crystallize every time differently is known as polymorphism. As the structure becomes denser and gets lowered in energy, it becomes more stable and harder to melt. Polymorphic forms are solid phases of the same chemical composition that differ among themselves in crystalline structure but yield identical liquid phases.

Because of their shape the fat molecules fit together with other molecules like stacking chairs which can be done in two ways i. e. via double chain packing and triple chain packing. There are basically 3 polymorphs (α , β , β') each with their own specific properties. The melting range and stability of the polymorphs are in the following range: $\alpha < \beta < \beta'$. The least stable polymorph will crystallize first and transform to a stable polymorph as a function of time.

Cocoa butter has six polymorphs. However the chocolate industry numbered them as I to VI. Forms V and VI are the most stable and are triple chain packing whereas the other forms are double. Form V is good for confectionary products as it is responsible for the hardness with a good snap, glossy appearance and the resistance to bloom. (SLETTENGREN 2010)

Mixing different fats (Fat eutectics)

It is important that after mixing two or more fats the final product should set at a suitable rate and has the correct texture and melting properties in the mouth. An unstable structure can form when other fats have been mixed with cocoa butter. Even though the fats are triglycerides it will be like fitting another size of chairs within the stacks. Disruption would be less if only a less amount of other fat is present. The actual hardness can be near to the expected one. When cocoa butter is mixed with vegetable or other fat in equal proportions then the softening effect is largest.

The original vegetable fat made by Unilever and many other that are now in the market are known as cocoa butter equivalents. These are like cocoa butters and can be put in any proportion without causing any major softening or hardening effect. Other fats can be used only if almost all the cocoa butter is replaced and these are known as cocoa butter replacers.

The vegetable fat should crystallise in the same way as cocoa butter (i. e. using the chair analogy, have the same size and shape chair) so that it can be added to the cocoa butter without causing eutectic effect. Cocoa butter contains palmitic (P), stearic (S) and oleic (O) on a glycerol backbone, with the majority of the molecules being POP, POSt, and StOSt.

From nuts or seeds of fruits generally two types of fractionation are used to obtain the easy melting and the hardest melting fraction. In dry fractionation the fat is kept at a more predefined temperature and then by pressing and filtering the liquid part is separated from solid. In solvent fractionation the fat is dissolved in acetone or hexane. After this the higher melting triglycerides are crystallized and filtered out. The StOSt and the increased amounts of POSt are hard to obtain.

By altering the proportions of StOSt it is possible to make the chocolate so that it will not melt until the temperature is several degrees higher than the normal cocoa butter, but cannot put behind the feeling of stickiness in the mouth. (SLETTENGREN 2010)

Legislation:

In June 2000, the European parliament agreed to permit the use of vegetable fat other than cocoa butter in chocolate. This directive came into force on August 2003 and for the first time, harmonised chocolate legislation across all the member states of Europe. A number of restrictions were placed on use of vegetable fat by the EU in terms of where oils should be sourced from, and what processing methods have to apply. To maintain miscibility and compatibility with cocoa butter (as is required by the EU Directive) it is necessary to use vegetable fats which contain a similarly high levels of these triglycerides. This means that a) these triglycerides would often need to be concentrated by fractionating the permitted base oils and b) the resulting fats would be needed to blend together to get an optimum mix of the three triglycerides. Even though the CBEs show equivalence with the cocoa butter

at all compositions but they have been restricted to a maximum level of 5% of the total composition in EU chocolate. (Geoff Talbot 2008)

Development of Heat Resistant Chocolate using high melting fat

Chocolate generally melts at 33.8°C when solid cocoa butter transitions to liquid and the crystals of cocoa butter are in stable form V. The development of heat resistant chocolate would allow it to be enjoyed in tropical and humid climates. Three main methods have been developed to make heat resistant chocolates: enhancement of the microstructure of the materials, addition of a polymer and increasing the melting point of the fat phase. The approach that is used for the development of heat resistant chocolates for this thesis is to incorporate fats with higher melting points. (Stortz and Marangoni 2011) (Stortz and Marangoni 2011)

One specific example of this was done by Jeyarani and Reddy (1999) and focused on using mahua (*Mahua Latifolia*) and kokum (*Garcinia indica*) fats to increase the melting point of cocoa butter blend. The kernels found in the fruits of mahua trees consist of semi-solid fat. Conversely, kokum kernels contain a hard, brittle fat with a melting point 39-43 C. The oils are fractionated and then blended. After that these fats were evaluated for their ability to increase the melting temperature of and replace the fat phase in chocolate products. Fractionation were used to separate the stearin fraction from kokum and mahua fats because it was reported that addition of fats rich in 2-oleodistearins to cocoa butter can increase the solid fat content (SFC) , increase the melting point and decrease the tempering time of chocolate.

The meted successfully produced a fat phase that achieved higher SFCs at elevated temperature than conventional chocolate. However, once the temperature reached 37.5 C the SFC of most of the blended fats was less than 20% indicating that the heat resistance of the chocolate would be lost at temperatures higher than this. Another attempt was done to improve the heat resistance via replacement of some cocoa butter with kokum fat. Kokum fat was refined but not fractionated. It was blended with cocoa butter at different levels. The chocolate had good sensorial properties. However, the heat resistance of the chocolate was not as desired considering the melting temperature is only 34.8C with 5% inclusion of kokum fat. Finally, the chocolate formulas exceeded some countries' legal limits for inclusion of NCVF. (Stortz and Marangoni 2011)

Gel Filling:

Hydrocolloids:

Hydrocolloids are a heterogeneous group of long chain polymers (polysaccharides and proteins) which are characterised by their property of forming viscous dispersions and/or gels when dispersed in water. Presence of large number of hydroxyl (-OH) groups increases their affinity for binding water molecules which results in hydrophilic compounds. Further, a dispersion is produced which is intermediate between a true solution and a suspension, and the properties exhibited are that of a colloid. Considering these two properties, they are aptly termed as hydrophilic colloids or hydrocolloids.

The important reason behind the ample use of hydrocolloids in foods is their ability to modify the rheology of food system. This includes the two basic properties of food system namely, flow behaviour (viscosity) and mechanical solid property (texture). The modification of texture and/or viscosity of food system modify its sensory properties, and thus, hydrocolloids are used as important food additives to perform specific purposes.

Hydrocolloids have a wide range of function. These include thickening, gelling, emulsifying, stabilisation, and controlling the crystal growth of ice and sugar through the basic properties for which hydrocolloids find extensive use as thickening and gelling. Hydrocolloids disperse in water to give a thickening or viscosity producing effect. This water thickening property is general for all hydrocolloids and is the primary reason for their overall use.

Gel formation is the phenomenon that involves the association or cross linking of the polymer chains to form a three dimensional network that traps or immobilises the water within to form a rigid structure that is resistant to flow. In other words, it becomes visco-elastic showing both the characteristics of a liquid and a solid. The textural properties (e. g. elastic or brittle, long or spreadable, chewy or creamy) of a gel vary widely with the type of hydrocolloid used. The other sensory properties such as opacity, mouth feel and taste also depend on the hydrocolloid employed. (Saha and Bhattacharya 2010)

Gels:

Gels may be defined as a form of matter intermediate between solid and liquid and show mechanical rigidity. They consist of polymer molecules cross

linked to form tangled and interconnected molecular network immersed in a liquid medium, which in food system is water. Food technologists use the word 'gel' for high moisture foods that are more or less retain their shape when released from their container. A gel is a visco elastic system with a storage modulus (G') larger than the loss modulus G'' . Hydrocolloids form gels by physical association of their polymer chains through hydrogen bonding, hydrophobic association and cat ion mediated cross-linking and differ from synthetic polymer gels, which normally consisted of covalently cross-linked polymer chains. Hence hydrocolloid gels are often referred as “physical gel”

The knowledge of the conditions required for gelling of particular hydrocolloid dispersion, the characteristics of the gel produced and the texture it confers are very important aspects to design a specific food formulation.

The formation of gel involves the association of randomly dispersed polymer segments in dispersion in such a way so as to form a three-dimensional network that contains solvent in the interstices. The associated regions known as junction zones are formed by two or more polymer chains. The gelation process is mainly the formation of these junction zones.

Hydrocolloid gelation can engage the hierarchy of structures, the most common of which is the aggregations of primary inter chain linkages into “junction zones”, which forms the basis for the three-dimensional network characteristics of a gel. The physical arrangement of these junction zones within the network can be affected by various parameters like temperature, presence of ions and inherent structure of hydrocolloid. For the gelation of

hydrocolloids, the three main mechanisms proposed are ionotropic gelation, cold-set gelation and heat-set gelation.

Ionotropic gelation occurs via cross-linking of hydrocolloid chain with ions, typically a cation mediated gelation process of negatively charged polysaccharides. Ionotropic gelation is carried out either by diffusion setting or internal gelation. In cold set gelation, hydrocolloid powders are dissolved in warm/boiling water to form a dispersion which on cooling results in enthalpically-stabilised inter-chain helix to form segments of individual chains leading to a three-dimensional network. Gelatine gel is formed by this mechanism.

Gelatin:

Gelatin is substantially pure protein food ingredient, obtained by the thermal denaturation of collagen, which are the structural mainstay and most common protein in the animal kingdom. Today gelatine is usually available in granular powder form. Ref: website

Gelatin forms a thermo-reversible gels with water, and the gel melting temperature ($<35^{\circ}\text{C}$) is below body temperature, which gives gelatine products distinctive organoleptic properties and flavour release. Gelatin melts at much lower temperature because of the junction zones are only bound by weak hydrogen bonds. It can be used as a gelling agent in jellied confectionary. Gelatin gels melt at relatively low temperatures and they are slow-setting; all these features make gelatin the preferred gelling agent in yoghurt products, low fat spreads and sugar confectionary.

Various factors affect the gel formation by hydrocolloids which include concentration of the gelling agent, pH of the medium, molar mass/ degree of polymerisation, temperature, ionic composition and solvent quality.

Rheological characteristics of gel involves characterizing a gel n the basis of various parameters like modulus of elasticity, yield stress, shear modulus, storage and loss modulus, complex viscosity , gel strength and compliance. These parameters are usually determined by conducting tests like compression test, dynamic oscillatory rheometry, creep and texture profile analysis, etc by employing instruments like universal texture measuring system, controlled shear rheometer.

Addition of sucrose results in an increase of true rupture stress in all these gals. The gel sweetness is related with mechanical properties of gel like gel strength, rupture stress, rupture strain and particularly with the amount of deformation required to break the network and its resistance to deformation. Besides co-solutes like sucrose, concentration of hydrocolloid, shear rate and temperature are also important variables that influence the rheological status of hydrocolloid gels. The blending of different polysaccharides offers an alternative route to the development of new textures. The major interest lies in the development of synergistic mixtures with improved or induced gelation.(Saha and Bhattacharya 2010)

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