International Food Research Journal 20(4): 1991-1995 (2013)
Journal homepage: *http://www.ifrj.upm.edu.my*

D-Optimal mixture design on melting and textural properties of dark chocolate as affected by cocoa butter substitution with Xanthan gum/Guar gum blends

*Amir, I.Z., Sharon, W.X.R. and Syafiq, A.

Department of Food Science, Faculty of Agrotechnology and Food Science, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia

Article history

Received: 3 September 2012
Received in revised form: 29 January 2013
Accepted: 31 January 2013

Keywords

Mixture design
Hardness
Melting properties

Abstract

Impacts and relationships on physicochemical properties in dark chocolate produced from different substitution for cocoa butter by Xanthan gum (XG) and Guar gum (GG) blends were determined using D-optimal mixture design. This study involved three levels of substitution which are 5%, 10% and 15% with constrained cocoa butter content and random blend of gums. Linear design models were applied to analyze parameters including texture (hardness) measurement and melting profile of fat crystal. Products experienced undesirable raises of hardness jointly with the increment of gums incorporation across the level of cocoa butter replacement from 5% to 15%. Similar trend was also agreed with the melting behavior of products as their melting point increased with the gradual diminution of cocoa butter. After all, the replacement of cocoa butter using hydrocolloids was deemed possible as there were products whose melting point and hardness fell in the acceptable range.

Introduction

Across the world healthy eating is of increasing concern to consumers and regulators (Webber, 2009). Questions started to arise particularly on the benefits and drawbacks of chocolate as well. Chocolate confectionery industry is facing the challenge of producing lower fat, sodium and sugar content products with similar sensorial attributes. The industry is trying to introduce more products that are free from artificial flavouring or colouring besides low in calorie.

Traditionally, cocoa butter is the only source of fat used in chocolate production. However, due to high cost and strong fluctuations in the supply and demand of cocoa butter, cocoa butter equivalent (CBE) with a triacylglycerols' composition similar to cocoa butter is used as an alternative source (Pinyaphong and Phutrakul, 2009). Besides, cocoa butter has found to be not ideal for all applications and climates as well as possesses limited gloss retention that would eventually cause fat blooming; where fat bloom happens when a dull white film of fat crystals formed on the surface of the chocolate (Beckett, 1999). Yet the chocolate is still edible in spite the appearance of grayish white blotches and streak caused by unsuitable heat exposure during storage.

Nowadays, gums describe a wide range of polysaccharides that are widely used in food production industry functioning as thickener, gelling agent, stabilizer (for foams, emulsions, and dispersions), inhibitor for ice and sugar crystal formation, as well as controller in flavor release. The choice of gum for a particular food application is dictated by the functional characteristics required but is inevitably influenced by price and security of supply (Williams and Phillips, 2003). As in confectionery production, mainly gelatin, modified starch, gum Arabic, and pectin are used.

Hydrocolloid thickeners are ideal for controlling the consistency of liquids and foods and are an obvious choice for use in the management of dysphagia (Williams and Phillips, 2008). Modified starch (E 1442), Xanthan and Guar gum are the examples of most widely used thickeners but all possessing very diverse rheological profile. The choice of thickener usage depends largely on the palatability of the product.

This research investigates the effects of Xanthan gum and Guar gum on the physicochemical properties after substituting cocoa butter in dark chocolate. Aspects taken into the account of physicochemical properties of chocolate produced are melting properties as well as physical and textural properties. Besides that, proximate analyses particularly on ash, moisture, fat, protein and carbohydrate contents of the chocolate produced as well as the caloric or energy contribution can also be measured to determine

*Corresponding author.
Email: *amir@umt.edu.my*

the nutritional and health contributions. However, this research will be only discussing the effect of substitution on hardness and melting properties of chocolate produced.

Materials and Methods

Materials

All ingredients are roughly divided into two groups of cocoa derivative and non-cocoa derivatives. Cocoa derived ingredients such as cocoa butter and cocoa liquor will be obtained from a cocoa distributor in Johor. Xanthan gum, Guar gum, liquid sucrose, lecithin and vanillin were obtained from local supplier in Selangor.

Preparation of chocolate

A general formulation or recipe was decided: in overall, cocoa butter (15%), cocoa liquor (39.45%), liquid sucrose (45%), lecithin and vanillin made (0.5% and 0.05% respectively). All the ingredients are expressed in percentage (weight/weight) as well as gram per 100 gram. Batches of 100 g chocolate samples were produced with precisely weighed ingredients: 39.45 g of cocoa liquor, 45 g of liquid sucrose, 0.5 g of lecithin and 0.05 g of vanillin; whilst, cocoa butter was incorporated according to the substitution levels of 0% (acting as the control sample), 5%, 10% and 15% at the weight of 15 g, 10 g, 5 g and no incorporation respectively.

All the ingredients were accurately measured before mixing in an automatic concher. The conching process lasted for about 6 hours, at the temperature of between 65-90°C. Tempering was conducted to achieve 27°C before reheating back to achieve 32°C prior to molding and lastly chilling at 5-12°C. Demoulding of products were done about an hour later and stored in individual container according to formulations.

Substitution of cocoa butter was achieved through the replacement by Xanthan gum and Guar gum in 5%, 10% and 15%. D-Optimal mixture design (Design-Expert® software) which is applicable for highly constraint design was used to determine their proportions in the substitution. Table 1 shows the proportions of substitution in percentage including the control sample without any substitution for cocoa butter. The upper and lower limits of substitution for every interval used to generate the proportions of substitution is shown in Table 2.

Sample preparation

Samples produced were all molded in bars of 68 mm (height) X 45 mm (width) X 7 mm (depth) to produce a consistently flat, even surface required for texture analysis. However for the other analysis the chocolate samples were grated into fine particles by using a tower-like cheese grater. Electrical blender is avoided in the preparation as it generates undesirable heat due to the friction during the process which melts down chocolate sample.

Table 1. The proportion of cocoa butter alternatives used in different levels of replacement

LoS	0%		5%		10%		15%	
CBA	XG	GG	XG	GG	XG	GG	XG	GG
Proportions	-	-	4.00	1.00	8.00	2.00	8.00	7.00
	-	-	4.00	1.00	1.00	9.00	7.00	8.00
	-	-	3.00	2.00	8.00	2.00	7.50	7.50
	-	-	0.00	5.00	6.25	3.75	6.00	9.00
	-	-	4.00	1.00	1.00	9.00	7.00	8.00
	-	-	0.00	5.00	4.50	5.50	8.00	7.00
	-	-	1.00	4.00	2.75	7.25	8.00	7.00
	-	-	2.00	3.00	4.50	5.50	6.50	8.50
	-	-	2.00	3.00	8.00	2.00	6.00	9.00

LoS: Level of substitution, CBA: cocoa butter alternatives

Table 2. The upper and lower substitution limits of each cocoa butter alternatives

Level of	Xanthan Gum		Guar Gum	
Substitution	Lower Limit	Upper Limit	Lower Limit	Upper Limit
5%	0	4	1	5
10%	1	8	2	9
15%	6	8	7	9

Textural measurement

Penetration probing tests were conducted to investigate and compare the hardness of 4 batches sample of chocolates by using Ta-XT2 Texture Analyzer. Molded chocolates were penetrated by a flat stainless steel probe, 2 mm diameter at a constant speed of 1 mm s^{-1}. Maximum peak force was obtained from the force vs. time data. Five measurements were conducted on each sample, and three samples were tested from each chocolate formulation.

Melting properties measurement

Chocolate samples were melted down in an oven under controlled temperature of approximately 50°C. Sample was taken out and homogenized. 3-5 mg of samples were inserted into a 40 µl aluminium pan with pin and sealed with a 30 µl aluminium pan by using a sample press. Melting was carried out at 60°C for 30 minutes before cooled back down to 0oC and held for 90 minutes. Sample pan was then transferred to a 26°C incubator and held for 40 hours for crystal stabilization. Subsequently sample was cooled down to 0°C and held for 90 minutes. DSC was calibrated with indium and octadecane at a scan rate of 5°C/min using an empty aluminium pan as reference.

The sample was then transferred into the DSC

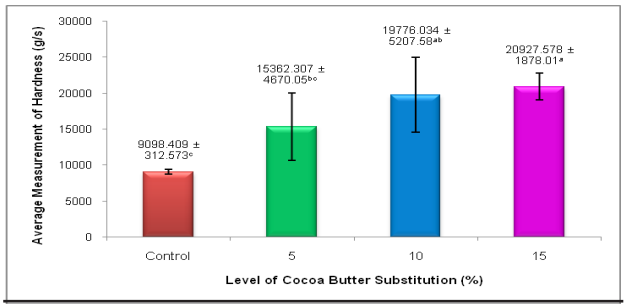

Figure 1. Graphical view of data collected in terms of mean ± standard deviation for the effect of different cocoa butter substitution levels on texture (hardness)

chamber and held at -50°C for 5 minutes. Another empty aluminium sample pan was used as the reference pan. Inert nitrogen stream was used at the flow rate of 30 cc/min. The melting profile of chocolate was measured at a heating rate of 10°C/min to a maximum temperature of 60°C. Analysis method and details employed were adapted and modified from Robinson & Sichina (2000).

Statistical analysis

Minitab 16 (Statistical and Process Management Software, Minitab Inc., Pennsylvania, USA) was employed to examine all data responding to the one-way analysis of variance (ANOVA) to determine the effects of factors and their interactions. A confidence level of 95% ($p = 0.05$) was utilized to compare means obtained in between formulations as well as in between levels of substitution by subjecting to the Tukey's Multiple Comparisons procedure for further comparison of significant differences. Mean value of data obtained from each level of substitution (3 means for each level) was used in order to explain the trends of each response in general.

Result and Discussion

Textural properties

Hardness is the main attribute in the texture of chocolate strongly manipulated by the content of cocoa butter or fat. The degree of 'snap' or hardness which is the most important property of chocolate that was determined by using the penetration probing test. Hardness is the force required to attain a given deformation to the food sample which could be determined by measuring the force required to compress a food between the molars. The maximum peak force is a measure of the hardness of the chocolates (Lee *et al.*, 2008). Figure 1 shows the hardness attribute of chocolate produced with different cocoa butter substitution levels.

The reduction of cocoa butter by 5% in each substitution levels engendered gradual and insignificant ($p > 0.05$) increase in texture of chocolate bars. Undeniably, cocoa butter decrement abates the 'snap' characteristic of chocolate where the hardness increases gradually instead.

Besides, the effect on hardness attributed by cocoa butter, incorporation of hydrocolloids actually denoted on the physical properties as well. Gums which was incorporated into the samples enhance the rheological properties of the lower fat products (Williams and Phillips, 2003). Incorporation of more than one type of gums might eventually leads to phase separation of the development of novel gel structure when one or more of the gums were able to form a gel. Lamkey (2011) reported that Xanthan gum is capable of synergistic interactions with other types of gums or rheology modifiers such as guar and taro. However shear thinning gel structure will be produced as the amount of guar gum is increased.

Furthermore, the presence of gum creates aggressive competition for water molecules which causes the rupture of peptide bonds in protein through hydrolysis. Increase in protein precipitation could be observed jointly with the increment of gum content. Precipitation or coagulation is commonly observed from the denaturation process of protein (Stoker, 2010). This partially denatured protein eventually built up a network of protein which eventually contributes in the augmentation of chocolate hardness through gel formation.

Lee *et al.* (2008) reported that chocolate hardness depends on the concentration of crystallized lipid phase (i.e., cocoa butter, milk fat) as well as the solid dispersed phase (i.e., sugar crystals, milk solids, cocoa solids). Besides, well-tempered chocolates have good snap, gloss, and stability against temperature and physical damage.

According to Afoakwa *et al*. (2008) and Beckett (1999), the final hardness of chocolate is affected by several factors including composition, manufacturing conditions and tempering and consequently fat crystal polymorphism. Likewise, Minifie (1989) suggested that hardness signifies well tempering or the degree to which a stable fat crystal network has been formed.

During manufacturing of chocolate, it was likely that the sample could have been poorly tempered since the viscosity and thickness of chocolate increases by the addition of Xanthan Gum and Guar Gum which is in this case act as thickening agent.

Melting properties

Thermal behavior or melting profile of fat and sugar components in samples produced from different substitution level for cocoa butter were analyzed by using differential scanning calorimetry

Table 3. Analysis of selected models and regression of equations for the physicochemical properties of dark chocolate (5%, 10% and 15% level of substitution)

Response	Model	F-Value	Prob>F	Equation in terms of actual component
5% LOS				
Texture (Hardness)	Linear	2.92	0.1311	2214.68968*XG+3758.67873*GG
Melting property	Linear	8.14	0.0246	7.0038*XG+ 6.81449*GG
10% LOS				
Texture (Hardness)	Linear	0.11	0.7453	2095.00823*XG+1865.30304*GG
Melting property	Linear	0.57	0.4752	3.42411*XG+3.37911*GG
15% LOS				
Texture (Hardness)	Linear	0.73	0.4214	1764.81202*XG+1061.97511*GG
Melting property	Linear	2.763	0.9595	2.25173*XG+2.27337*GG

LOS: Level of substitution

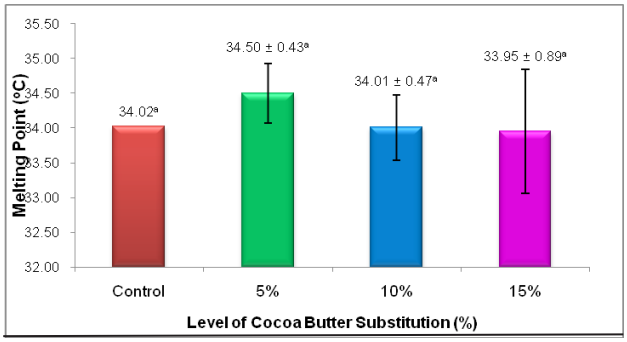

Figure 2. Graphical view of data collected in terms of mean ± standard deviation for the effect of different cocoa butter substitution levels on melting profile (T_{peak})

(DSC). Peak onset corresponds to the temperature at which a specific crystal form starts to melt; peak maximum, that at which melting rate is greatest; and end of melting, completion of liquefaction (Afoakwa *et al*., 2008). Heat capacity C_p gradually and consistently increased to onset temperature (T_{onset}) then progressively increased more rapidly until peak temperature (T_{peak}), after which it decreased to the end temperature (T_{end}) indicating the chocolate was completely melted. Figure 2 elucidates the effect of different cocoa butter substitution levels on melting profile generated by DSC.

Even though the trend of melting profile was irregular and fluctuating, ANOVA and multiple mean comparisons showed no significant difference ($p > 0.05$) among all samples, implying limited influence on melting profile. Increasing viscosity of a chocolate composition to create a non-flowable composition at temperatures well above the normal melting point of the cocoa butter or in the case of imitation chocolates, the melting point of vegetable fats and the like (Davila and Finkel, 2002). This explained the surge at 5% substitution.

On the other hand, substitutions at higher level of 10% and 15% increase the viscosity of chocolate mixture; the texture became like batter and for extremities of 15% substitution mixture was dry and brittle. Thus, tempering process is very hard or in specific shearing process. Shearing during the tempering process has generally been accepted as being of great importance to form the desired chocolate product (Koh, 2003). Study by Koh (2003) using quantified shear rate showed that increased shearing seem to increase the number of Form V crystals that form. Shear breaks up crystals and therefore increasing the number of seed crystals; which is known as secondary nucleation. Besides, shear aligns triglyceride molecules parallel to each other in the shear field, and then moves them past each other. This process increases the chance of nucleation. Lastly, shear improves the overall mixing. Inadequate tempering creates unstable crystals as there is insufficient development of seed crystals. These fat crystals melt at temperature as low as 5°C, for Form I crystals.

Varying fat content produce changes in crystallinity and melting properties observed in the differences in peak widths (Afoakwa *et al*., 2008). Afoakwa (2008) also suggested that chocolate of lower fat content melts at higher temperature. Likewise, increasing fat content caused consistent decrease in T_{index} of products, suggesting inverse relationship of Tindex with fat content. Lower fat chocolate requires longer time to melt than similar products with higher fat contents.

Viscosity is defined as the internal friction of the fluid which is represented by the strength measurement of bonds between particles (Leblanc *et al.*, 1999). Theoretically, it requires an amount of energy (heat) to break these bonds in order to make it more flowable and less viscous. In this study, the act of Xanthan Gum and Guar Gum which created a highly viscous chocolate mixture requires more energy (high temperature) to melt completely. It indicates that the chocolate with higher viscosity melts at higher temperature.

D-optimal design

Mixture design is an important methodology for an experiment in which factors are the proportions of the components of a blend and response variables vary as a function of these proportions. In order to effectively analyze the interaction effect on each chocolate mixture, modeling was necessary for each response. Though, the analysis of the selected models and regressions of the polynomial equations

are not done. But, instead, first-order linear modeling was selected for all variables.

Similar to usual handling method, the significance for the selected models was determined by the F-test. The interaction effects according to the component change were determined using graphical depictions. Each coefficient determined at the predicted linear Scheffé equation illustrated the effect of each component (i.e., cocoa butter, Xanthan gum and Guar gum) on each response as a numerical value, which indicated that the interaction effect of each component could be confirmed. This coefficient was fitted via regression. All of the generated relationships were summarized in Table 3 according to the levels of substitution.

A synergistic deflection off the linear blending slop on the response surface could be positive (i.e., synergistic for better performance) or negative (antagonistic), depending on the goal being maximization or minimization (Stat Ease, 2009). However, surface response graphical depictions were not discussed in detailed as they were analysed according to each response in each level of substitution.

Conclusion

Texture or hardness in particular, experienced significant augmentation jointly with the increasing additional of gums as the development of gel networks. Changes in the amount of cocoa butter had little and insignificant ($p > 0.05$) impact on melting profile determined through differential scanning calorimetry.

Acknowledgement

The authors are grateful for the financial support from Food Science Department, University Malaysia Terengganu.

References

Afoakwa, E. O., Paterson, A., Fowler, M. and Vieira, J. 2008. Characaterization of melting properties in dark chocolates from varying particle size distribution and composition using differential scanning calorimetry. Food Research International 41:751-757

Beckett, S. T. 1999. Industrial Chocolate Manufacture and Use, 3rd Edition. Oxford: Blackwell Science Publishers. 85-103

Davila, V. R. and Finkel G. 2002. Method of making heat-resistant chocolate and chocolate-like compositions with reduced apparent viscosity. United States Patent US006488979 B1.

Leblanc, G. E., Secco, R. A. and Kostic, M. 1999. Viscosity Measurement., p. 301-322. USA, CRC Press LLC.

Koh, A. B. C. 2003. Growth and identification of crystal phases in cocoa butter underdifferent storage conditions. Undergraduate thesis, Bachelor of Engineering (Chemical), Department of Chemical Engineering, The University of Queensland. Undergraduate Thesis.

Lee, S., Biresaw, G., Kinney, M. P. and Inglett, G. E. 2008. Effect of cocoa butter replacement with a β-glucan-rich hydrocolloid (C-Trim30) on the rheological and tribological properties of chocolates. Journal of the Science of Food and Agriculture 2009.(89): 163-167.

Pinyaphong, P. and Phutrakul, S. 2009. Modification of palm oil structure to cocoa butter equivalent by carica papaya lipase-catalyzed interesterification. World Academy of Science, Engineering and Technology. 54-55.

Robinson, P. and Sichina, B. 2000. Characterization of Chocolate Using Power Compensated DSC- In: Perkin Elmer Technical Note; PETech–43 1 (2000).

Lamkey, J. W. 2011. Hydrocolloids in muscle foods. In Hydrocolloids in food processing. Laaman, T. R. (Ed). Wiley Blackwell. IPT Press. 35-49

Stat Ease. 2009. Getting your toe into mixtures. Design Expert. p. 4-6.

Stoker, H. S. 2010. General, organic and biological chemistry. 5th Edition. Cengage Learning Inc. 684-685

William, P. A. and Phillips, G. O. 2003. Gums: properties of individual gums. In Caballero, B., Trugo, L. C. and Finglas, P. M. Encyclopedia of Food Sciences and Nutrition. 2nd ed. Vol. 3. United States: Elsevier Science Ltd.

William, P. A. and Phillips, G. O. 2008. Gums and stabilisers for the food industry 14. United Kingdom: The Royal Society of Chemistry (RSC) Publishing. p. 395.