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Mixture experiment on rheological properties of dark chocolate as influenced by cocoa butter substitution with xanthan gum/corn starch/ glycerin blends

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

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

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Abstract

The impacts on both rheological parameters; Casson yield stress and Casson viscosity were determined. The interactions among blend's components; xanthan gum (XG), corn starch (CS), glycerin (GL) and their relationship with both flow parameters were also investigated by using D-Optimal mixture design. Three levels of cocoa butter substitution assigned in chocolate production were at 5%, 10% and 15% level with random proportions of each component generated by Design Expert software. An appropriate mathematical model was applied to evaluate each response as a function of the proportions of the components enabling in prediction of future response by using any blend of components. As the incorporation of the blends (XG/CS/GL) in chocolate production was elevated from 5% to 15%, both parameters; viscosity and yield stress of chocolate were gradually increased, as in range 7.819 to 10.529 Pa, and 2.372 to 3.727 Pa.s, respectively. Neither binary nor ternary component-component interaction exhibited synergistic effect. Nevertheless, strongest antagonistic effect on both rheological parameters of substituted chocolate at 5% level and 10% level were respectively observed at ternary interaction region for the former, and at binary interaction area of CS:GL, closer to CS corner as for the latter. This study somehow provides ideas on how component-component interactions influence experimented response.

Introduction

In chocolate production, cocoa butter is a vital ingredient acting as continuous phase in chocolate system as how it is responsible in providing desirable flow properties (Beckett, 2008). Casson model was applied in characterizing the flow properties of the molten chocolate. This model has often been successfully exercised to analyze the rheological properties of chocolates as in the study by Keogh *et al.* (2003), Briggs and Wang (2004) and Lee (2009). Casson model stated that plots of the square root of shear rate vs square root of shear stress will result in straight line. Linear equation; y = mx+c, where m is gradient and c is y-intercept. By referring to Casson model, Casson viscosity and Casson yield stress can be obtained from the gradient and y-intercept of such a plot, respectively.

The Casson yield stress is the force required to initiate the chocolate to flow and represent the low shear-rate properties of chocolate. Meanwhile, the Casson viscosity is related to the energy needed to keep chocolate shifting once it has started to flow (Beckett, 2008). Squeeze flow rheometer is an instrumentation to evaluate highly viscous material such as polymer melts, food pastes and polymer composites. In such analysis, the material is placed between rigid parallel plates, which are then driven together at constant speed, load and strain rate. The development of pressure distribution within the tested material could be observed as deformation proceeds. The factors influencing the distribution are characterized by material properties and prevailing wall boundary conditions (Gibson and Toll, 1999; Engmann *et al*., 2005). The force to squeeze a sample between parallel plates depends on the material rheology as well as friction characteristics of the material-plate interface (Laun *et al*., 1999).

However, the high cost, strong fluctuation in supply and demand has broadened interest in finding replacement for cocoa butter in chocolate and other confectionery applications. Pinyaphong and Phutrakul (2009) revealed that cocoa butter equivalent (CBE) with a triacylglycerol's composition similar to cocoa butter is used as an alternative source as reflected of the increased cost, severe changes in supply and market demand.

By reviewing numbers of published journals and previous studies, the idea of using xanthan gum, corn starch and glycerin in cocoa butter replacement is potentially considered to be further investigated. The method of producing (heat resistant chocolate) HRC by Ogunwolu and Jayeola (2006) elucidates that the addition of corn starch at levels of 2.5, 5.0, 7.5, or

*Corresponding author.
Email: *shaphic06@gmail.com*

10% to other chocolate ingredients at the grinding and mixing stage of conventional manufacture resulted in an increase of melting point of chocolate. At any suitable level, humectants such a, glycerin could be incorporated into chocolate (O'Rourke, 1959, Stortz and Marangoni, 2011). The increasing amount of humectants in the chocolate resulted in increment of moisture absorption which is the ultimate determinant of an increase in heat resistance. Moreover, the viscosity of the mix was found to increase jointly with the increment of time and/or temperature together with the increasing amount of polyols used (Stortz and Marangoni, 2011). Mandralis and Weitzenecker (2001) discloses a heat-resistant chocolate which comprises mixing of a polyol gel in particulate form with a flowable chocolate or a flowable mixture of ingredients for preparing chocolate and chocolate-like compositions. The polyol gel is produced by the use of gelling agents such as xanthan gum.

Idea would be earned from this study as a discovery of a new source in replacing cocoa butter in chocolate production which is originated from non-fat derivatives that behaves better or precisely like genuine cocoa butter to some extent. This discovery would be great as it is more economical and released from supply and demand impediments. To certain extent, consumer able to filter out the chocolate product made without any additional of foreign fat source such as vegetable oil, milk fat, or other cocoa butter substitutes. Lower calorie (less fat) and healthier products (high in fiber) would be created, ultimately.

In another hand, dealing with mixture experiment is not as simple. Each factor (component) of a mixture gives different effects on particular response. Nevertheless, the impediments and difficulties of dealing with mixture would be paid off as this study provides ideas in employing component-component interactions to yield desirable responses. Three dimensional view and contour plot of each response make ease to the experimenter indicates which interaction yield particular effect (high or low) on the response. Eventually, once the understanding on mixture experiment is achieved, the ideas could be applied to other applications as long as it is a work of mixture. Hence, this research is intended to develop XG/CS/GL blend as a new alternative in replacing cocoa butter in chocolate production as well as to investigate their effects on rheological responses.

Table 1. Proportion of substitutes used in cocoa butter substitution

Assay	Substitution at 5% level			Substitution at 10% level			Substitution at 15% level		
	XG	CS	GL	XG	CS	GL	XG	CS	GL
1	0.50	3.50	1.00	0.67	8.50	0.83	2.00	11.00	2.00
2	0.00	4.00	1.00	1.00	8.00	1.00	1.50	11.50	2.00
3	0.83	3.83	0.33	0.75	8.25	1.00	1.33	12.00	1.67
4	0.50	3.50	1.00	1.00	8.25	0.75	1.50	11.50	2.00
5	0.50	4.00	0.50	0.83	8.33	0.83	1.67	11.67	1.67
6	1.00	3.50	0.50	1.00	8.25	0.75	1.00	12.00	2.00
7	1.00	3.50	0.50	1.00	8.00	1.00	2.00	12.00	1.00
8	0.33	4.00	0.67	0.50	8.50	1.00	1.50	11.50	2.00
9	0.67	3.67	0.67	0.83	8.50	0.67	2.00	11.50	1.50
10	1.00	3.50	0.50	1.00	8.50	0.50	1.50	12.00	1.50
11	0.50	4.00	0.50	0.75	8.50	0.75	2.00	11.00	2.00
12	0.33	3.67	1.00	0.75	8.25	1.00	1.83	11.33	1.83
13	0.67	3.33	1.00	0.75	8.50	0.75	1.50	12.00	1.50
14	1.00	4.00	0.00	1.00	8.33	0.67	2.00	11.67	1.33
15	1.00	3.00	1.00	0.75	8.25	1.00	2.00	11.50	1.50
16	1.00	4.00	0.00	0.92	8.17	0.92	1.67	12.00	1.33

Notes: XG = Xanthan gum, CS = Corn starch, GL = Glycerin

Materials and Methods

Materials

All raw materials were food graded and purchased from a local source. All materials such as pure Favor Rich Prime Pressed (natural) Cocoa Butter (Ghana), 100% Ghana Favor Rich Cocoa Liquor, glycerin, soy lecithin and vanillin powder were obtained from cocoa distributor in Johor, named Welltop Food Ingredients Sdn Bhd. Meanwhile, xanthan gum and corn starch were obtained from Bagus Bakery in Shah Alam, Selangor, Malaysia.

Production of chocolate

Batches of 100 g chocolate samples were produced with accurately weighed ingredients: 42.45 g of cocoa liquor, 45 g of 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 of the ingredients were blended well in a concher (CAPCO Triple Roll Mill). The conching process lasted for about 6 hours, at the temperature of 65-90^{o}C. Tempering was conducted to achieve 27oC before reheating back to achieve 32^{o}C prior to moulding and lastly chilling at 5-12^{o}C. Demoulding of products were done about an hour later and stored in individual container according to formulations.

Out of 15% cocoa butter used, its substitution was achieved at 5%, 10% and 15% (no cocoa butter used) by using blends of xanthan gum (XG), corn starch (CS) and glycerin (GL). Generation of formulation batches were constructed by using Design Expert® software. Table 1 has briefly described the proportions of substitution in percentage, with regard to the upper and lower limits of each component used.

Rheological analysis

Flow properties of chocolate are important as in two major ways; firstly, chocolate with incorrect viscosity would be assumed as poor quality product. Another importance of chocolate viscosity is related with the sensory perception at which the flavor of chocolate in the mouth is affected by its flow properties (Beckett, 2009).

In this study, flow properties were investigated on a Thermo Haake RS600 rheometer. The methods were adapted from Lee Suyong *et al.* (2009). Tests were performed at 400C using parallel plate geometry, with 40 mm diameter. Samples were pre-sheared at 5 s^{-1} for 5 minutes and their steady shear viscosities measured as a function of shear rates (1-100 s^{-1}). The rheological data was analyzed by using the Casson model, which is given below; where σ is shear stress, ý is shear rate, a is Casson yield stress, and b is Casson viscosity.

$$\sqrt{\sigma} = \sqrt{a} + \sqrt{b}\sqrt{\gamma'} \quad \text{(Equation 1)}$$

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. ANOVA is used to prove that the null hypothesis (i.e., there is no difference between the data sets), is not valid. 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.

Moreover, means ± standard deviations calculated from all 5 replicated analysis of different responses were also transported into the Design-Expert® 6.0.10 (Software for Design of Experiments, Stat-Ease, Inc., Minneapolis, MN, USA) under the category of D-Optimal in constrained mixture design. A linear design model was applied to examine the interaction of ingredients within the designated mixture designs. This model was calculated based on the modified lease square regression. To examine the reaction of ingredients in each component mix, a graphical depiction was used.

The optimal ingredient-mixing ratio was designated, and the experimental points predicted, was done by using the numerical optimization in Design-Expert® 6.0.10. The goal area of each response of the model coefficients were selected in respect to different variable.

Results and Discussion

Rheological response

As an aside note, the trend of rheological response was constructed after gathering all data from all level of cocoa butter substitution. The values of each bar in Figure 1 were the midpoint taken in between the highest and the lowest data of each

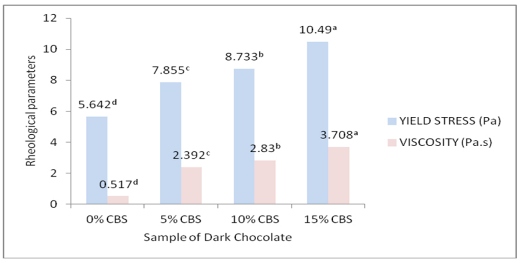

Figure 1. Trends of Casson yield stress and Casson viscosity of dark chocolate as across level of cocoa butter substitution.

Notes: Mean bearing with different superscript (a-d) is significantly different at α = 0.05. Standard deviation = 0.00. CBS = Cocoa butter substitution.

response. This procedure was carried out in order to explain in brief the behavior of flowing response across level of cocoa butter substitution. In order to signify the significance of difference among the level of cocoa butter substitution, the value of each bar was purposely triplicated with the same value (with standard deviation equal to zero) to be brought for further statistical analysis.

As shown in Figure 1, both rheological parameters were went uphill as across the level of cocoa butter replacement from 5% to 15%. Since both parameters are proportionally interrelated to each other, it should be noted that they both experienced the same trend. As suggested by Servais *et al.* (2004), Casson yield stress is influenced by several factors; inter particles contact, the amount and specific surface area of the particles, surfactant (emulsifier) and moisture content. The augmentation of XG/CS/GL addition from 5% to 15% was greatly affected the rheological properties of chocolate, in particular, Casson yield stress. The addition of XG/CS/GL is one of the mean of increasing solid particles which in contact with cocoa butter itself. Along with the gradual slash down of cocoa butter, solid particles were dominantly interacted with each other (and cocoa butter left) and yielded a great collisions, frictions and resistance which required to be broken down to make chocolate begin to flow (Servais *et al*., 2004).

The great water-capturing ability of xanthan gum and glycerin also assisted in the increase of yield stress. With such ability, the trapped moisture (bound water) act as sticking agent and agglomerates sugar particles to form gritty clods and moisture attached on sugar particles (surface) directly increase the friction and apparent viscosity (Afoakwa *et al.*, 2007) and Chevalley (1999) once suggested, moisture (at 3-4%) increases viscosity and yield value of the chocolate.

The application of thickening agent really gives influence on rheological properties of fluid (William and Phillips, 2003). Ciullo and Andersson (2000) in their published article mentioned that xanthan gum forms a gel structure which is shear thinning and

Table 2. Estimated regression coefficients (in pseudo value) and adjusted coefficient of determination (R^2) of model fits for rheological responses (yield stress and viscosity)

Term	Fitted with linear model		Fitted with cubic model			Fitted with special cubic model
	Yield Stress (15)	Viscosity (15%)	Yield Stress (10%)	Viscosity (5%)	Viscosity (10%)	Yield Stress (5%)
X_1	10.53	3.73	8.78	2.40	2.85	7.89
X_2	10.46	3.69	8.64	2.37	2.78	7.82
X_3	10.50	3.71	8.72	2.38	2.82	7.83
X_1X_2	-	-	-	-0.039	-*	-0.094
X_1X_3	-	-	-	-	-	-
X_2X_3	-	-	-0.085	-	-0.045	-
$X_1X_2X_3$	-	-	4.62	-0.15	2.41	-0.30
$X_1X_2(X_1-X_2)$	-	-	-	-	0.30	-
$X_1X_3(X_1-X_3)$	-	-	-	0.072	-	-
$X_2X_3(X_2-X_3)$	-	-	-2.73	-	-1.34	-
Adjusted R^2	0.9467	0.9511	0.9920	0.9826	0.9910	0.9573

Notes: X_1 = Xanthan gum, X_2 = Corn starch, X_3 = Glycerin. Percentages in bracket (5%, 10%, 15%) are levels of substitution

is often used in combination with other rheology modifiers, particularly glycerin as the combination of two to give great effects. Higher yield stress and viscosity of solution resulted from xanthan gum-glycerin affinity was also reported in their article. The Casson yield stresses of dark chocolate announced by other studies were in a range of 4 to 32 Pa (Aeschlimann and Beckett, 2000).

In this study, Casson viscosity of chocolate increased exponentially, ranging from 0.517 to 3.708 Pa.s. Servais *et al.* (2002) suggested that chocolate viscosity should be attributed to several factors; fat content, shape of particles and particle size distribution. Fat (cocoa butter) is the only continuous phase in chocolate makes it responsible for the dispersion of all other constituents and also for the physical properties of chocolate (Lipp and Anklam, 1998). The reduction of fat (cocoa butter) from 5% to 15% led to the augmentation in viscosity of chocolate. Cocoa butter play a role in transporting other constituents flow past each other (Beckett, 2008). Insufficient quantity of this continuous phase along with the addition of solid particles (XG and CS) gives a great effect on flow behavior of chocolate. Augmentation in Casson yield stress and viscosity caused by the diminution of fat content has also been reported by Lee (2009), Liang and Hartel (2004) and Nebesny (2005). Aeschlimann and Beckett (2000) in their trials to determine the factors affecting the measurement of chocolate viscosity had revealed that the Casson viscosity of dark chocolate were in the range 2.1 to 3.9 Pa.s.

Fitted regression model and three-dimensional plot

The percentage of cocoa butter used was a factor in manipulating the rheological response in which the blends of XG/CS/GL might react differently at different level of cocoa butter. This implies that particular responses would not

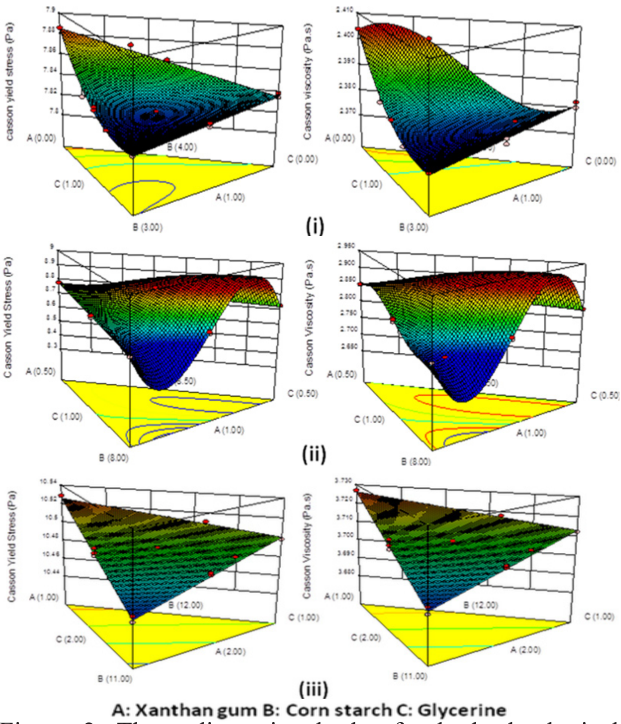

Figure 2. Three dimensional plot for both rheological parameters; Casson yield stress (left side) and Casson viscosity (right side). Romani numerals indicate the level of cocoa butter substitution where (i) is at 5% level, (ii) is at 10% level and (iii) is at 15% level.

necessarily fit into similar model at different level of cocoa butter substitution. As supported by Hemat (2003), hydrocolloids may interact with other food components to provide specific functions and the mixture of different type hydrocolloids may, for example; act synergistically to increase the viscosity or antagonistically to reduce it.

Certain models were reduced from its original model as either several individual terms are not significant or the Lack of Fit is significant. Rheological parameters at 15% level of cocoa butter replacement were fitted by linear model as they demonstrated too many insignificant interaction terms (Table 2). Different model was fitted to the both response at 5% level of cocoa butter replacement. In spite of the different model fitted, R^2 or respective models were significantly high. In addition, both models presented identical pattern of contour and three-dimensional plot.

As Casson yield stress and Casson viscosity are such interrelated, both rheological parameters would be discussed together. Different model were found to be fitted by different data with respect to each level of cocoa butter replacement. At 5% level, Casson yield stress and Casson viscosity has fitted special cubic model and cubic model, respectively. Meanwhile, both parameters were observed to fit cubic and linear model at 10% and 15% level, respectively.

As portrayed by the three-dimensional plot (Figure 2), neither binary nor ternary component-component interaction exhibited synergistic effect. Nonetheless, strongest antagonistic effect on both rheological parameters were observed at ternary interaction region at 5% level, and at 10% level by binary interaction area of CS:GL, closer to CS corner.

The equations below were provided in order to verify which term is the factor of the effects, either synergistic or antagonistic. Since both yield stress and viscosity are interrelated, seemingly similar pattern of contour and three-dimensional plot could be observed for both responses at respective level of cocoa butter replacement.

$$\text{Yield stress (5\%)} = 7.89X1 + 7.82X2 + 7.83X3 - 0.092X1X2 - 0.30X1X2X3$$

(Equation 2)

$$\text{Viscosity (5\%)} = 2.40X1 + 2.37X2 + 2.38X3 - 0.039X1X2 - 0.15X1X2X3 + 0.072X1X3(X1 - X3)$$

(Equation 3)

$$\text{Yield stress (10\%)} = 8.78X1 + 8.64X2 + 8.72X3 - 0.085X2X3 + 4.62X1X2X3 - 2.73X2X3(X2 - X3)$$

(Equation 4)

$$\text{Viscosity (10\%)} = 2.85X1 + 2.78X2 + 2.82X3 - 0.045X2X3 + 2.41X1X2X3 + 0.30X1X2(X1 - X2) - 1.34X2X3(X2 - X3)$$

(Equation 5)

$$\text{Yield stress (15\%)} = 10.53X1 + 10.46X2 + 10.50X3$$

(Equation 6)

$$\text{Viscosity (15\%)} = 3.73X1 + 3.69X2 + 3.71X3$$

(Equation 7)

As discussed earlier, strongest antagonistic effect for Casson yield stress and Casson viscosity were contributed by ternary interactions (XG:CS:GL) evaluated as valley region. By referring to the Equation 2 and Equation 3, the value of coefficient for X1X2X3 were the lowest (in respective equation) indicates that ternary interaction yielded strongest antagonistic effect.

Neither synergistic nor antagonistic effect could be observed from both parameters at 15% level of cocoa butter replacement as the model resulted in a linear equation where there were no such interactions (binary or ternary). In addition, at this level of replacement, single component of the blend, XG was observed to yield the greatest effect for both rheological parameters.

Conclusion

Both rheological parameters experienced similar trend as across the level of substitution since they are inter-related to each other. As the level of substitution raised, both parameters were also increased from 7.819 to 10.529 Pa (for yield stress), and 2.372 to 3.727 Pa.s (for viscosity). In spite of acknowledging the indispensability of genuine cocoa butter in providing such superior qualities of chocolate, the use of XG/CS/GL presents the opportunity to develop chocolate with reduced fat and calories also with dietary fibers. The application of mixture design is really a good instrument in creating such formulations for experimentation

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