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Short communication



Melting Characteristics of Milk Chocolate with Different Sweetener Blends

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Abstract

Chocolate is a cocoa based product derived from cocoa beans the seed of *Theobroma cocoa* tree. Nowadays, the demand of natural sweetener for manufacturing of sugar-free chocolate has dramatically increased. However, their applicability in product formulation and how it affects the quality of chocolate still remain a big challenge. Despite providing sweet taste in chocolate, bioactive compounds present in stevia leaves, palm sugar and honey could enhance human health. The effects of Stevia leaves powder, palm sugar and honey on the melting characteristic and crystallization of the milk chocolate were measured using differential scanning calorimeter (DSC). The melting peak of all those sweeteners are in the range of 37-38 ℃ indicating the presence of form VI polymorphs. However, the presence of multiple peaks was also observed showing that there was a competition between the growth of low and high stability polymorphs. Besides, only the substitution of sugar with honey produced a significant change in the enthalpy value ($p<0.05$). From the results obtained, it can be concluded that stevia leaves powder, palm sugar and honey could be used for sugar free chocolate.

Keywords:*Stevia leaves; palm sugar; honey; chocolate;melting*

1. Introduction

Milk chocolate is a complex rheological system having solid particles (cocoa, milk powder and sugar) dispersed in cocoa butter which represents the fat phase [1]. The most important ingredients of milk chocolate is milk powder which affects the sensory characteristics of the final product, the processing behaviour and the rheological properties of the fluid chocolate mass in pregnant rats[2-3].

In chocolate processing, several factors may affect crystal formation either from the ingredients or the processing step in chocolate making. Cocoa butter can be crystallised in six different forms with different melting temperatures. However, only form V, which has the most stable form of crystal produces a good quality of chocolate. In order to obtain the right type of cocoa butter crystals, the chocolate needs to be tempered, and the chocolate should become crystallised at a temperature below 32 °C. Once seed crystals are formed, chocolate follows a heating and cooling phases steps, thus promotes the formation of the crystals in the form V rather than in the form VI [4].

Furthermore, the addition of sugar to cocoa butter in seeded samples proved to have an effect on the crystal growth rate compared to sample with pure cocoa butter [5]. Besides, Dhonsi & Stapley [6] reported that, a faster shear induced crystallization observed when sugar was added to cocoa butter as sugar particles provide sites for heterogeneous nucleation of cocoa butter crystallisation. Heterogeneous nucleation denotes the phenomenon where foreign surfaces acts as nucleation sites for crystallization [5].

According to Varsakas et al. [7], sweeteners are defined as food additives that are used or intended to be used either to give sweet taste to food or as tabletop sweetener. High intensity sweeteners, (also known as non-nutritive sweeteners) possess a sweet taste, but are non caloric, provide essentially no bulk to food, have greater sweetness than sugar and is used at very low levels.

Although sugar (sucrose) is the most common sweetener in food industry, it is not suitable for all applications. Due to that, most people especially diabetics and people looking to reduce calories are often looking for sugar substitutes. Thus, alternative sweeteners are needed to fullfill the sugar gap by controlling caloric, carbohydrate or sugar intake; managing weight problem; aiding in the management of diabetese; assisting in the control of dental caries and assist in other sweetening aspects such as sugar shortages and sweetening costs [7-8].

According to Ghanta et al. [9], *Stevia rebaudiana* Bertoni is a type of plant that is well-known for its high content of sweet diterpene (about 4-20%) in dry-leaf matter. It is the source of a number of sweet ent-kaurenediterpenoid glycosides [10] and stevia glycosides are the compound responsible for the sweet taste [11]. Stevioside, one of the stevia glycosides, is about 300 times sweeter than sucrose and this can be beneficial to those who suffer from obesity, diabetes mellitus, heart disease and dental caries [9]. Besides, it has relatively high melting points, can exist in various forms of polymorphic crystalline and can be isolated in amorphous forms [12].

Palm sugar known as ‘gulamelaka’ is one of the sugars that has been claimed to be a healthier alternative sweetener to sucrose because it contains minerals and vitamins, [13] and also exhibits low glycaemic index (GI 35-42) [14-15]. Hence, people with high blood sugar levels or diabetic can consume this type of sugar [16]. In addition, Ho et al. [17] reported that palm sap based sugars contain 2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one (DDMP). DDMP has caramel like flavour which is a Mailard reaction product that exhibits antioxidant activity [18].

According to Zhu et al. [19], honey is a naturally sweet and viscous product produced by honey bees and derived from the nectar

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of flowers. It is a supersaturated solution of sugars [20] composed of glucose and fructose containing also other important compounds such as minerals, proteins, enzymes, free amino acids, vitamin and many phenolic compounds [21] and also some organic acids and volatile substances [22-23].
Generally, in most milk chocolates, the amount of sugar is in the range of 53 to 57 g per 100 g of chocolate. However, the limit intake for daily consumption is 6.3 g relating to an energy intake of only 30 kcal/day [24]. Excessive consumption of processed sugar is widely recognized as a major cause of dental caries and contributes to heart disease, diabetes mellitus, insulin resistance, attention deficit-hyperactivity disorder and other conditions [25]. For that reason, there is a need to produce a product that contains no or less sugar, so that health problems among consumers can be reduced.
The *Stevia rebaudiana*, palm sugar and honey have been choosen to be the substitute for coarse sugar in chocolate processing due to the potential as sugar substitutes in food product especially in chocolate since it has quiet similar characteristics with coarse sugar. However, the substitution might affect the melting characteristic as well as the quality of the chocolate, Thus, this study aims to investigate the effect of sweetener blends on the melting characteristic of milk chocolate.

2. Materials and Methods

2.1. Materials

Cocoa butter, cocoa powder and whole milk powder were purchased from Sweet Berry Trading Bakery Supplies at Kota Bharu, Kelantan, Malaysia. Palm sugar and coarse sugar were purchased from PantaiTimur Supermarket, Jerteh, Terengganu, Malaysia while stevia leaves powder was purchased from Stevia Sugar Corporation (M) Sdn. Bhd. and honey was purchased from a local supplier.

2.2. Milk chocolate preparation

The formulations used for control milk chocolate, sample SP (stevia powder), SSP (sugar and stevia powder), PS (palm sugar), SPS (sugarandpalm sugar), H (honey), SH (sugarand honey), SPPS (stevia powder and palm sugar), SPH (stevia powder and honey) and PSH (palm sugar and honey) were based on the Table 1.

Table 1: Formulation of milk chocolate.

Ingredients	Amount (g)									
	Control	SP	SSP	S	PS	H	SH	SPPS	SPH	PSH
Cocoa butter	25	25	25	25	25	25	25	25	25	25
Whole milk powder	21	21	21	21	21	21	21	21	21	21
Cocoa powder	7	7	7	7	7	7	7	7	7	7
Sugar	47	-	23.5	-	23.5	-	23.5	-	-	47
Stevia leaves powder	-	10	5	-	-	-	-	5	5	-
Palm sugar	-	-	-	47	23.5	-	-	23.5	-	-
Honey	-	-	-	-	-	47	23.5	-	23.5	-

2.3. Differential scanning calorimeter (DSC) measurement

The DSC (Mettler Toledo) was used to measure the melting properties of solidified milk chocolate. Approximately 10 mg of solid chocolate was put into a 100 μL aluminium pan using a metal spatula. Then, it was sealed using a sample press and both the sample and empty (reference) pans were inserted into the DSC chamber using a tweezer. The pans were put on separate furnaces and ready to be scanned. The pans were then heated from 15 °C to 65 °C at heating rate of 5 °C/min. Peak temperature (T_{peak}) and enthalpy of melting (ΔH_{melt}) were calculated automatically by the software.

2.4. Statistical analysis

All the analyses was conducted in triplicate. The results obtained in this study were expressed as means ± standard deviation (SD). Analysis of variance (ANOVA) was conducted using SPSS 20 General Linear Model procedure (SPSS inc., USA). The calculated mean values were compared using Duncan's multiple range tests with significance level of $p<0.05$.

3. Results and discussion

Milk chocolate with different sweetener blends were produced. The melting temperature and enthalpy of milk chocolate were determined as shown in Table 2. It can be seen that the melting points of chocolate sweetened by stevia powder, palm sugar and honey were significantly different from the control. The melting point for control chocolate was 34.63 ± 2.25 °C which was closest to the range value of form V chocolate (32-34 °C). However, most of the chocolates have the melting points in the range of 36.15 °C to 38.00 °C which are near to the range value of form VI polymorphs (34-36 °C). This might be due to the product quality deterioration or bloom surface formation [26]. Previous study performed by Shah et al. [27] revealed that the replacement of sugar by incorporation of inulin in sugar-free chocolate increased the melting point.
In terms of enthalpy value, samples SP, SSP, PS and H did not produce a statistically significant change in enthalpy. It showed that the amount of crystals present in the chocolates were similar to the control. On the other hand, substitution of sugar with honey produced a significant different in the enthalpy value (samples SH, SPH and PSH). Honey used in this study was in the liquid form. Thus SH, SPH and PSH contain higher moisture contentcompared to other chocolates. Saputro et al. [16] reported that samples with high moisture and the presence of impurities will exhibit less crystalline part ofsugar, resulting in lower enthalpy value. This explains that the higher the enthalpy value, the higher the amount of crystals exist.

Table 2: Comparison of melting points and enthalpy values of chocolate samples.

Chocolate sample	Melting point (°C)	Enthalpy (kJ/mole)
Control	$34.63^{b} \pm 2.25$	$12.35^{bc} \pm 1.87$
SP	$37.05^{a} \pm 0.65$	$13.48^{bc} \pm 1.77$
SSP	$36.57^{ab} \pm 0.33$	$11.18^{bc} \pm 0.69$
PS	$38.00^{a} \pm 1.20$	$11.92^{bc} \pm 2.17$
SPS	$36.15^{ab} \pm 0.34$	$13.78^{b} \pm 2.24$
H	$37.77^{a} \pm 0.93$	$11.27^{bc} \pm 0.61$
SH	$36.82^{a} \pm 1.12$	$17.89^{a} \pm 0.53$
SPPS	$36.53^{ab} \pm 1.06$	$10.19^{cd} \pm 1.73$
SPH	$37.74^{a} \pm 0.22$	$8.25^{d} \pm 0.68$
PSH	$36.22^{ab} \pm 0.67$	$4.45^{e} \pm 0.30$

Presented data are mean value of triplicate ± standard deviation. Value in the same column with different alphabet are statistically significant from each other ($p<0.05$).

Fig. 1 shows the DSC heating curves for chocolates with 100% natural sweeteners. It can be observed that a single peak predominates for chocolates sweetened by white sugar. However, there are multiple peaks for chocolate SP, PS and H; small peaks are visible at about 27 ℃ and 32 ℃ and much larger peaksare visible at about 35 ℃ (SP), 39 ℃ (PS) and 36 ℃ (H). This suggests that there was a competition between the growth of low and high stability of polymorphs. According to Marangoni & McGauley [28], this split could be due to the presence of both solid phases or due to an artifactual heating, inducing transformation of the α to β phase during DSC run.

However, for PS chocolate, this finding is contradicting with the previous study by Saputro et al.[16], which stated that the melting point of chocolate formulated with palm-sap based sugar was slightly lower and exhibit similar peak to sugar.

Besides, fat migration and recrystallization during fat bloom generation (form VI) can be attributed to the insufficient formation of the stable polymorph (form V) in cocoa butter during tempering that causes the formation of large crystal on the surface chocolate [29-30].

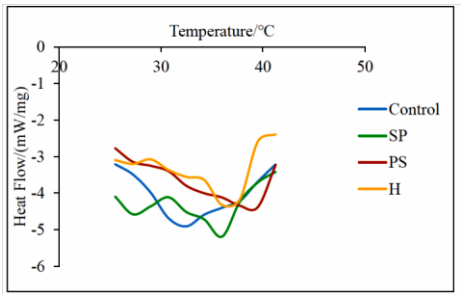
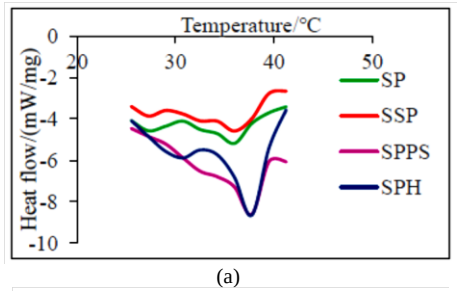
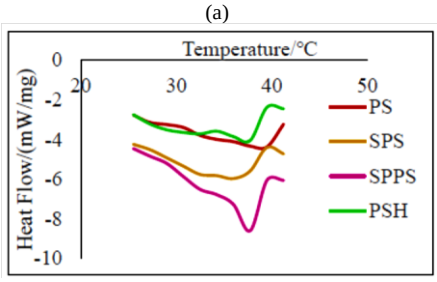


Figure 1: DSC heating curve for chocolate using 100% of each type of sweeteners.

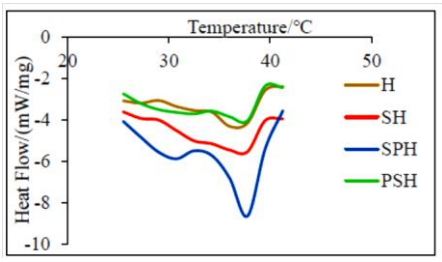
Based on Fig. 2 (a), the incorporation of stevia powder with sugar, palm sugar and honey did not produce type V polymorphs only. Three polymorphic forms were observed; one melting at 27.25 ℃, one melting at 32.5 ℃ (form V) and the other melting at 38 ℃ indicate the heterogeneous nucleation occurred. In Fig. 2 (b), wider peaks can be seen at temperature of 38 ℃ for SPS, SPPS and PSH samples. However the incorporation of palm sugar with sugar, stevia powder and honey has reduced the melting temperature of the chocolates. Heterogeneous nucleation was also observed in Fig. 2 (c). For all the chocolates which contain honey, a small peaks are visible at about 31 ℃ and much larger peaks are visible at about 37 ℃. Overall, the incorporation of the sweeteners used in this study produced chocolates with multiple polymorphic forms.



(a)



(b)



(c)

Fig. 2: DSC heating curves for a) SP; b) PS; c) H and its substitute.

4. Conclusion

The effect of incorporating Stevia leaves powder, palm sugar and honey on the milk chocolate quality was studied using sugar as control. When sugar is substituted by other sweeteners, multiple peaks present; small peaks visible at about 27 ℃ and 32 ℃ and much larger peak is visible at about 35 ℃ (SP), 39 ℃ (PS) and 36 ℃ (H) suggest that there was a competition between growth of lowand high stability polymorphs. Besides, the enthalpy value for H sample was lower indicating that there was less crystal part of sugar present.

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