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Investigation of the rheological, thermal, sensory properties, and particle size distribution of sesame paste white compound chocolate as influenced by the soy flour and emulsifier levels

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Abstract: The impacts of replacing various levels of skim milk powder with soy flour (0%, 7%, and 14.5% w/w), as well as the quantity of emulsifier (mono-glyceride, 0 and 1.5% w/w) on particle size distribution, rheological, textural, thermal, and sensory properties of sesame paste white compound chocolate were studied. Enhancing the percentage of soy flour along with concurrent decrease of milk powder, increased particle size distribution parameters, as D_{90} increased from 9.33 to 16.6 (μm). The outcomes indicated that different contents of soy flour affected the hardness along with having greater impact on the samples containing emulsifier. Adding mono-glyceride to chocolate resulted in an excessive reduction in the hardness and also in particle size distribution parameters. Values of Casson plastic viscosity ranged from 2.46 to 5.8 (Pa.s), the Casson yield values and apparent viscosity varied between 9.95 and 111.72 (Pa), and 6.3 and 12.1(Pa.s), respectively. Moreover, analyzing the data demonstrated that soy flour had notable impact on the sensory properties of the samples. Also, soy flour and emulsifier could be manipulated for achieving the desirable rheological properties of sesame paste white compound chocolate.

Keyword: particle size distribution; rheological properties; sensory properties; sesame paste chocolate; thermal properties.

1 Introduction

The growing reputation of the chocolate throughout the world is due to its unique texture, flavor and eating pleasure [1]. In chocolate production, milk powder is an important ingredient due to its functional and sensory effects on the product, but there are several lactose intolerant individuals who will benefit from replacement of milk powder. In addition, the milk powder required for chocolate production is imported in some countries. Therefore, it significantly increases the cost of the production [2]. The most common approach to overcome these problems is to use less expensive and meanwhile nutritional alternative to milk powder. Soy flour has great capacity to replace the milk powder in chocolate due to its high protein content [3]. Refined soy flour, as a natural antioxidant, was added to confectionary to prevent spoilage [4]. Soy protein isolates (SPI) was incorporated in chocolate formulation to develop high protein chocolates and reduce the amount of full cream milk formulation [5]. Moreover, the effects of soya milk on nutritive as well as rheological properties of chocolate produced in a ball mill were investigated [6, 7]. Also, soy flour is easily available in abundance and at a reasonable cost. This will reduce the production cost of chocolate, thereby making it more affordable, popular and nutritional. Soy protein provides many health benefits such as promoting the heart health by reducing the risk of cardiovascular disease and providing the anticarcinogenic effects to hormone-related diseases [8]. Due to the good health beneficial effects of sesame paste, there has been great interest for using it as an ingredient for chocolate products. A comprehensive review of the health benefits of sesame and it's by products can be found in Nagendra et al. [9]. Replacement of milk powder by soy flour in sesame paste chocolate combines the two types

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of vegetable protein to achieve a reasonable balance to the plant protein. Actually, applying emulsifiers to modify the chocolate masses flow tvjmline=properties is considered as a frequent attempt [10]. Also, mono-glycerides that are widely applied in confectionary can be considered as effective edible emulsifiers. Mono-glycerides received the nomenclature E471 in food industry [11]. Although different studies have been carried out on formulation of conventional chocolate, to our knowledge, this is the first study on the presence of the sesame paste in chocolate formulation. This research aimed at developing a nutritious compound chocolate by a) incorporation of sesame paste in chocolate formulation, b) using different levels of soy flour as replacement of milk powder, c) applying different concentrations of emulsifier (mono-glyceride), and analyzing the rheological, textural, thermal, sensory properties and particle size distribution (PSD) of sesame paste white compound chocolate.

2 Materials and methods

2.1 Materials

The materials including sugar (Iran sugar Co., Tehran, Iran), whole soybean flour containing 22.08% oil and 39.28% protein (Toos Soyan, Mashhad, Iran), skim milk powder containing 39.28% protein and 3.5% moisture (Golshad, Mashhad, Iran), lauric Cocoa Butter Substitute (composed of hydrogenated palm kernel oil, Mettler Dropping Point: 36–42 °C/97–108 °F, supplied from Indonesia, Fuji oil Inc. sesame paste (fat 50.64%, protein 21.87%, Simorgh Company, Mashhad, Iran), Mono-glyceride (Danisco Company, Iran) constituted the components for the production of sesame paste white compound chocolates.

2.2 Experimental Design

This study was conducted as a two-factor experiment which included:

(1) The concentration of Emulsifier (mono-glyceride) in the sesame paste white compound chocolates: 0 and 1.5% (w/w). Other chocolate components including sesame paste, and Cocoa Butter Substitute (CBS) were held constant.

(2) The replacement of skim milk powder by soy flour at levels of: 0, 7, and 14.5% (w/w).

Table 1 shows the formulations of the produced samples.

2.3 Formulation of sesame paste white chocolate

Batches of 500 g chocolate samples were produced with accurately weighed ingredients. Soy flour was combined according to the substitution levels of respectively 0, 7, and 14.5% w/w at the weight of 0 g, 37.5 g, and 72.5 g. All of the ingredients were mixed well in a mixer, and were added to the ball mill (made by Iranian company, Sepehr Machine, Tehran, Iran) containing 9.1 mm diameter stainless steel balls. Mono-glyceride was added 15 min before the end time for some formulation. Refining was performed at 60 °C at an agitator shaft speed of 100 rpm. The refined and conched chocolate was discharged into molds shaken gently to remove the air bubbles and then placed in the refrigerator which was set at 10 °C for 15 min. After cooling and demolding, the samples were wrapped in an aluminum foil, packed, and stored at ambient temperature until the corresponding analysis [6, 10]. Table 1 shows the proportions of chocolate components and replacing levels of milk powder with soy flour in percentage, considering the upper and lower amount of emulsifier.

Table 1: The formulation of the produced samples.

Sample ID	Ingredient (%)					
	CBS	Sugar	Sesame paste	Milk powder	Soy flour	Emulsifier (E471)
ME	30	38.5	15.5	14.5	0	1.5
M	30	40	15.5	14.5	0	0
MSE	30	38.5	15.5	7.5	7	1.5
MS	30	40	15.5	7.5	7	0
SE	30	38.5	15.5	0	14.5	1.5
S	30	40	15.5	0	14.5	0

ME: sample containing milk powder and emulsifier. M: sample containing milk powder.
MSE: sample containing milk powder, soy flour, and emulsifier.
MS: sample containing milk powder and soy flour. SE: sample containing soy flour and emulsifier S: sample containing soy flour.

2.4 Determining the particle size distribution

Particle size distribution (PSD) was measured by the laser light-scattering method, using a particle size analyzer Shimadzu 2600 (Shimadzu, Sald 2101, Japan). Before the analysis, each chocolate sample was diluted and dispersed with acetone at ambient temperature and ultrasonic dispersion (Branson Ultrasonic Corporation, Danbury, CT, USA) was maintained by stirring the samples to ensure that the particles were independently dispersed. PSD parameters obtained included specific surface area, largest particle size (D_{90}), mean particle volume (D_{50}), and the smallest particle size (D_{10}). The measurement was repeated three times and results are expressed in micrometers [12].

2.5 Texture analysis

A three point bend test was performed on a texture analyzer (Stable micro system, TA.XTplus, England), equipped with a 5 kg load cell and a plastic cutting probe. The fracturability is the maximum load [N] necessary to fracture a bar (25 × 35 × 5 mm) of the sesame paste chocolate. Hereby, the measurements start at a trigger of 0.2 N. The probe descended at 5 mm/s until the chocolate bar was broken. For every chocolate, three bars were subjected to the three-point bend test [13].

2.6 Melting profile

Differential scanning calorimeter (SPICO, DSC-100, Iran & China) was used to monitor the melting behavior of sesame paste chocolate. About 17–20 mg of the molten samples were transferred to the standard DSC aluminum pans and then hermetically sealed. An empty hermetically sealed DSC aluminum pan was used as a reference. The temperature was scanned from 0 to 80 °C at a heating rate of 5 °C per minute. Thermal Analysis Software used to calculate the onset temperature (T_{onset}), maximum temperature (Tm), and enthalpy of melting (ΔH_{melt}). Each sample was analyzed in triplicate and mean values and standard deviations reported [14].

2.7 Rheological properties

Rheological properties of sesame paste chocolate were measured with a Bohlin Visco 88 viscometer (Bohlin instrument, UK) equipped with a bob and cup geometry (bob length: 60 mm; bob diameter: 14 mm; gap width: 1 mm) and a heating circulator (Julabo, Model F12-MC, Julabo Labortechnik, Germany). Chocolate Samples were prepared and tested according to the International Confectionery Association (ICA) guidelines as follows: to melt the compound chocolate samples they were incubated at 50 °C for 75 min, and then the appropriate volume of the sample was transferred into the cup [15]. The viscometer was set at a fixed temperature of 40 °C and each sample was kept at this temperature for 8 min to obtain the temperature equilibrium considering the fact that the viscometer is equipped with computer software and the operating condition of the device is controllable, for all tests. The time-dependent rheological properties were examined by shearing samples at the constant shear rates (50 s^{-1}) for a period of 5 min. This procedure is a standard method, which was found to remove the time dependency initially observed on our samples, recommended for conventional chocolates by the ICA [15]. Then the time dependency properties of samples were measured by fitting the experimental data to two models:

(1) Weltman model:

$$\tau = A + B\,\mathrm{Ln}(t)$$

(2) First order stress decay model, with a non-zero equilibrium stress value:

$$\tau - \tau_{eq} = (\tau_0 - \tau_{eq})e^{-kt}$$

where, τ is the shear stress (Pa), t is the shearing time, τ_0 is the initial shear stress value, τ_{eq} is the equilibrium shear stress, k is the breakdown rate constant (1/s), A and B, respectively, are the initial shear stress and time dependent feature of behavior (Extent of breakdown). Initial tests proved that the 5 min is enough to obtain the equilibrium condition. After this period, rheological behavior is independent from the time of shearing. According to available sources and previous research, chocolate has a non-Newtonian behavior. Effect of shear rate on the rheological behavior of the samples was examined by increasing the shear rate from 15 s^{-1} to 300 s^{-1}. Collected data (shear rate-shear stress) were fitted with the following model:

(3) Herschel-Bulkley:

$$\pi = \pi_{0H} + k(\gamma^o)^n$$

(4) Bingham:

$$\pi = \pi_{0B} + n_B\gamma^o$$

(5) Pawer law:

$$\pi = k\gamma^{o\,n}$$

(6) Casson:

$$\sqrt{\tau} = \sqrt{\tau_{0c}} + \sqrt{\eta_c}\cdot\sqrt{\gamma^o}$$

where, τ is the shear stress (Pa), γ^o is the shear rate (s^{-1}), τ_0 the Casson yield or yield stress (Pa), ηc standing for viscosity (Pa.s), k is the consistency coefficient $(Pa.s)^n$, and n is a flow behavior index (dimensionless) [16].

2.8 Sensory test

Sensory assessment of sesame paste white compound chocolate was carried out on non- emulsifier samples (M, MS, and S). The chocolate samples were investigated for preference test, acceptance test and descriptive test. The samples were encoded by English letters, and were kept in plastic containers. Participants were asked to take a small bite of crackers and then drink taste-free water to rinse their palate after tasting each chocolate [17].

2.8.1 Preference tests: In this type of test, the panelist is asked to choose one sample between the presented samples based on the preference. The binary preference test is the simplest type of preference test, in which two samples are encoded and presented to the evaluators in order to select a sample as their preferred sample. The evaluators (15 females and 15 males, aged 23–29) were asked to only select one sample, even if two samples seemed the same [18]. The orders of provided samples were MS, S; M, S; M, MS.

2.8.2 Acceptance test: Acceptance test was done based on 9-point hedonic scale, ranging from 1 (dislike extremely) to 9 (like extremely). Panelists evaluated overall acceptability of different types of sesame paste white compound chocolate. Samples were encoded and provided to the evaluators to rank them according to the acceptance rate [19].

2.8.3 Descriptive test: In the descriptive test, trained evaluators present a comprehensive sensory description of the sample including the features of appearance, smell, texture, and taste. To conduct the descriptive test, it is necessary to give early trainings to evaluators in order to identify the concepts and definitions of features. The main features of chocolate were evaluated according to the Table 2. The 10 selected panelists (5 females and five males, aged 23–29) were further trained and descriptive test was carried out using a 9 cm unstructured line scale with anchor of 1 (the weakest attribute) to 9 (the strongest attribute) [20]. Table 2 shows definitions used in sensory-descriptive test.

3 Statistical analysis

Minitab 16 (Statistical and Process Management Software, Minitab Inc., Pennsylvania, USA) was used to examine the effects of the soy flour and emulsifier levels on the rheological, textural, thermal properties, and particle size for

Table 2: Definitions used in sensory-descriptive test.

Studied feature	Concept	Reference sample
Creamy color	Its color varies between white and creamy	Weak: milk powder Strong: soya flour
Sweetness	Refer to sucrose in aqueous solution	Weak: - Strong: diluted sugar powder
Astringent flavour	It refers to used sesame paste in sample	Weak: - Strong: sesame paste without additive
Hardness	The first force used in the process of squeezing the sample under tooth	Soft: produced cheese in Pilot Tough: Sohan
Oiliness	Feeling a greasy mouth	Soya cream produced in Pilot

distribution of sesame paste white chocolate. A confidence level of 95% ($p = 0.05$) was used to compare the mean value of data obtained between the formulations as well as between the levels of substitution. It was specified that the samples with different letters (as seen in tables) have statistically significant differences of their means. All experiments were performed in triplicate; however, rheological experiments were done once.

4 Result and discussion

4.1 Particle size distribution

Table 3 shows the results of the PSD of sesame paste white chocolate samples. Increasing the replacement of the soy flour with milk powder in all samples (M, MS, and S) increased the $D_{(90)}$, $D_{(50)}$, and $D_{(10)}$ and decreased the specific surface area. Other researchers reported similar results. $D_{(90)}$ is directly related to $D_{(50)}$, $D_{(10)}$ and it is reversely related to the specific surface area [21]. The process of size reduction in the ball mill is performed by applying the fracture force and shear force. These forces lead the particles to be crushed. During milling process, the oil existing in the soy flour was slowly released and acted as a lubricant causing particles to easily slip over each other and preventing particles to be crushed excessively. In lesser oil content, particles scratched highly over each other and crushed more to the pieces. In the similar results obtained by Afakowa et al. [21] the increase of fat from 25 to 35% in the dark chocolate formulation significantly decreased the specific surface area and increased other PSD parameters. Some researchers [22] explained that higher levels of fat (26%) during the grinding process would cause to produce coarser particles and less small particles. The presence or absence of mono-and diglyceride emulsifier in the chocolate formulation depending on the formulation had different effect on PSD parameters. In samples containing milk powder and no soy flour (ME and M) also in samples containing soy flour and no milk powder (SE and S) adding the emulsifier reduced all parameters of PSD. The presence of emulsifier increased the PSD parameters when nearly equal proportions of milk powder and soy flour were used to formulate the chocolate (MSE and MS samples).

4.2 Thermal properties

Table 4 shows the results of the melting properties of the samples. As it can be observed, the T_{onset} is in the range of 28.5–30.9 °C. T_m is in the range of 33.2 and 33.9 °C, the enthalpy value is in the range of 5.2–18.3 J/g. In samples M, MS, and S increasing the soy flour replacement decreased the T_{onset} but it was not significant ($p > 0.05$). In the combination of vegetable oils, this result is expectable due to the eutectic effect of the oils. In this study, the onset temperature was also affected by the presence of the emulsifier. Although in a sample without soy flour (M and ME) and a sample containing 7% soy flour (MS and MSE) the presence of emulsifier decreased the T_{onset}, in the sample containing 14.5% soy flour (SE and S) the presence of emulsifier increased the T_{onset}. While in non-emulsifier samples (M, MS, and S) increasing the replacement of the soy flour increased the enthalpy, in samples containing emulsifier (ME, MSE, and SE) the enthalpy value decreased. The enthalpy value depends on the particle accumulation and the relative strength of the joints between the particles in different products [23]. Adding the soy flour and emulsifier to the composition of chocolate led to less solid density and decreased the connections between the solid particles therefore reduced the enthalpy. Afoakwa et al. [21] stated that the increase in lecithin concentration affects the dimensions of fat crystals and the melting properties. In non-emulsifier samples (M, MS, and S), increasing the replacement of the soy flour increased the T_m. Therefore, the soy flour in the formulation of sesame paste white chocolate induced formation of more stable crystals with higher melting temperatures. There was no significant effect on T_m by adding the emulsifier to sesame paste white chocolate composition.

Table 3: The particle size distribution of the sesame paste white chocolates.

Samples ID	**Particle size distribution**			
	$D_{(90)}$ **(µm)**	$D_{(50)}$ **µm)**	$D_{(10)}$ **(µm)**	**Surface (cm^2)**
ME	9.33 ± 0.22^{a}	2.97 ± 0.11^{b}	$1 \pm .0.02^{a}$	2.94 ± 0.09^{f}
M	13.55 ± 0.34^{a}	4.64 ± 0.13^{cb}	1.21 ± 0.04^{a}	2.23 ± 0.15^{f}
MSE	14.94 ± 0.25^{a}	5.9 ± 0.15^{cb}	1.34 ± 0.05^{a}	1.96 ± 0.08^{f}
MS	14.3 ± 0.23^{a}	5.38 ± 0.12^{cb}	$1.25.03^{a}$	2.1 ± 0.11^{f}
SE	15.15 ± 0.32^{a}	5.56 ± 0.17^{cb}	1.36 ± 0.07^{a}	1.99 ± 0.17^{f}
S	16.6 ± 0.28^{a}	6.52 ± 0.14^{c}	1.41 ± 0.03^{a}	1.88 ± 0.14^{f}

Means ± standard deviation from triplicate analysis.
Means values followed by the same letter in each column are not significantly different ($p > 0.05$).
$D_{(0.1)}$, $D_{(0.5)}$, and $D_{(0.9)}$, respectively, represet 10, 50, and 90% of all particles finer than this size.

Table 4: The effect of replacement levels of soy flour and emulsifier levels on melting and textural properties.

Sample	**Melting properties**			**Texture properties**
	T_{onset} **(°C)**	**Tm (°C)**	ΔH_{melt} **(J/g)**	**Hardness (N)**
ME	28.7 ± 0.3^{a}	33.9 ± 0.3^{b}	18.3 ± 0.4^{d}	29.95 ± 0.47^{ab}
M	30.9 ± 0.2^{a}	33.2 ± 0.2^{b}	9.1 ± 0.4^{c}	27.85 ± 1.49^{bc}
MSE	29.5 ± 0.5^{a}	33.9 ± 0.2^{b}	16.3 ± 0.5^{d}	19.14 ± 1.46^{e}
MS	30.6 ± 0.4^{a}	33.7 ± 0.4^{b}	10.3 ± 0.2^{ef}	33.3 ± 0.74^{a}
SE	30.7 ± 0.3^{a}	33.5 ± 0.3^{b}	5.2 ± 0.3^{g}	22.59 ± 1.71^{d}
S	28.5 ± 0.4^{a}	33.6 ± 0.5^{b}	12.6 ± 0.2^{e}	26.81 ± 2.5^{c}

Means ± standard deviation from triplicate analysis.
Means values followed by th e same letter in each column are not significantly different ($p > 0.05$).
T_{onset} (°C): Onset temperature determined by the intersection of the baseline with the absolute highest tangent of the melting curve.
T_m (°C): Maximum temperature is the temperature at which the melting curve reaches its peak maximum.
ΔH_{melt} (J/g): Enthalpy of melting is the heat taken up by the sample during melting, this was calculated by integrating the area of the melting peak.
Hardness (N): In the tree-point bend test, force at the breaking point is considered as Hardness.

4.3 Textural properties

Hardness is one of the most important features of chocolate that is measured while breaking. This feature can be measured by three-point bend test. Force – distance curve observed in this test can be related to the hardness. The chocolate curve with desirable hardness of texture is sloped and is broken down quickly during the test. But chocolate with undesirable hardness of texture has lower slope due to its tendency to bend. In the three-point bend test, force at the breakpoint is considered as hardness [24]. According to Table 4, in non-emulsifier samples (M, MS, and S), 7% replacement of soy flour increased the hardness from 27.85 (N) to 33.3 (N) which was 19% increase comparing to the initial state. This can be attributed to the predominance role of a gel network derived from soy protein leading to hardness increase. When milk powder was completely replaced by soy flour, the hardness of chocolate was decreased from 27.85 (N) to 26.81 (N) which was 3.7% reduction compared to the initial state. This reduction was expectable, because some soybean oil was added to the chocolate composition and reduced the hardness. Other scientists reported similar results about adding the varieties of oils to the chocolate. Pandy & Sing [3] stated that adding the soybean oil in chocolate formulation decreased the hardness, which may be due to low melting point or low levels of saturated fatty acids in soybean oil compared to the cocoa butter. As it can be seen in Table 4, in all samples except M and ME, the presence of emulsifiers reduced the hardness.

4.4 Rheological Properties

Two models were used to fit the shear stress-time data: Weltman model and the first order stress decay model with a non-zero equilibrium stress value. According to the statistical parameters including coefficient of determination (R^2) and root mean square error (RMSE) presented in Tables 5 and 6 both models were found adequate to describe the time-dependent flow properties of samples containing emulsifier (ME, SME, and SE), but they were not suitable models to evaluate the data of samples without emulsifiers (M, MS, and S) [25]. Therefore, the samples containing emulsifier were more time dependent than non-emulsifier samples which is clearly showed up in Figure 1. The results of this research showed that the shear stress decreased with increasing time of shearing, which means that sesame paste white chocolate exhibits a thixotropic behavior [26]. Table 5 shows the parameters of Weltman model and Table 6 shows the parameters of the first-order stress decay with a non-zero equilibrium stress value, evaluated at different soy flour replacement levels. The thixotropy amount is exemplified by the extent of B [26] and increased from 30.62 to 103.23 Pa with increasing soy flour replacement levels. The adverse effect of shearing on the molecular structure of sesame paste white chocolate manifests itself via a larger magnitude of B [26]. It can be said that the greater values of B can result in the larger departure from thixotropy behavior [27]. So, the samples containing higher level of soy flour were more thixotropic than non-soy flour sample. The K is the decay rate constant, which is an indication of how fast the sesame paste white chocolate reaches the equilibrium stress value, under the shearing action, beyond which the apparent viscosity remains constant; hence no further irreversible breakdown of the molecular structure [26]. Replacement of 7% soy flour in the sesame paste white chocolate increased the value of the breakdown rate constant (K) from 0.046 to 0.81 s^{-1}. Then, it was decreased significantly by substitution of 14% soy flour and reached at 0.029 s^{-1}. In the sesame paste white chocolate, replacement of soy flour resulted in higher values of initial shear stress (A and τ_0) at all levels of soy flour. Consequently, the soy flour existence in the composition of sesame paste white chocolate could lead to greater viscosity at the time-dependent test beginning, compared to the sample without soy flour. The findings of this study are consistent with the outcomes of the study by Abu-Judayil et al. [26], who investigated the dependency of time to sesame paste using three models as follows: Weltman, first-order stress decay with a zero value of equilibrium stress value, and also first-order stress decay with a non-zero equilibrium stress value. In conclusion, these models could effectively explain the obtained investigational information at high time of shearing. In Figure 2 the flow curves of sesame paste white chocolate samples are reported. Values of these products viscosity reduced along with the increase of the shear rate, which emphasize on the existence of a shear thinning behavior. Also, the structural breakdown of the molecules can explain this behavior, in accordance with the produced hydrodynamic forces, and also due to the enhanced alignment of the constituent molecules [28]. As illustrated by Figure 2, sample M showed the highest values of viscosity with an initial value of around 18.37 Pa.s, followed by sample SE with initial viscosity values of around 12.66 Pa.s. Samples ME, MSE, and MS had initial values of around 12, 12, and 11 Pa.s, respectively. The lowest initial viscosity values belonged to sample S. Moreover, the shear stress versus shear rate data were best fit by the Casson model, with coefficient of determination (R^2) values greater than 0.90. Obtained Casson parameters are reported in Table 7. In non-emulsifier samples (M, MS, and S), 7% replacement of soy flour increased the Casson viscosity from 3.27 to 5.8 Pa.s, and decreased the apparent viscosity from 12.1 to 8.4 Pa.s and the yield stress from 111.72 to 9.95 Pa. Viscosity is heavily affected by a low percentage increase of solids in high solid compounds suspensions [29]. Higher plastic viscosity with soy flour may be attributed to the lower soy flour density compared to the milk powder, since milk powder was replaced on weight basis with soy flour. Thus, addition of the soy flour in the chocolate composition increased the proportion of solid components and the possibility of the particles friction together. Lower yield stress with soy flour may be associated with the forces acting between the particles which was subordinating of the shape and size of the particles. Milk powder was obtained by the spray dryer being smoother and spherical while the soy flour was produced by the roller mill having larger particles and foliaceous shape; therefore, the specific surface area of soy flour particles was lower. Increasing the volumetric proportion of soy flour caused lower contact of the particles and reducing yield stress. Reduction of apparent viscosity with soy flour was apparently related with its oil content. Presence of soybean oil in the chocolate composition could facilitate the movement of particles thus it reflected the effect of soy flour on rheological properties more accurately. Free fat contributes to the particle passing through each other easily due to the lubricant role and reduces the viscosity [30]. The effect of fat on viscosity is more obvious than the yield stress [31]. Because the fat which is added to

Table 5: Rheological parameters of sesame paste white chocolate samples obtained by Weltman model.

Samples ID	The parameters of Weltman model			
	A (Pa)	**−B (Pa)**	**R^2**	**RMSE%**
ME	519.08 ± 5.9^a	30.62 ± 1.2^h	0.81	3.31
M	750.58 ± 9.9^b	25.37 ± 0.02^i	0.51	3.29
MSE	689.89 ± 4.8^c	67.48 ± 0.92^j	0.97	2.74
MS	616.7 ± 5.73^d	20.3 ± 1.17^k	0.67	2.3
SE	952.97 ± 13^e	103.23 ± 2.8^l	0.90	6.34
S	309.32 ± 1.8^f	6.87 ± 0.37^m	0.69	1.36

Means ± standard deviation from triplicate analysis.
Means values followed by the same letter in each column are not significantly different ($p > 0.05$).
A (Pa) and B (Pa) parameters were obtained by fitting experimental data to Weltman model ($\tau = A + B \ln t$).
R^2: coefficient of determination, RMSE: Root Mean Square Error.

Table 6: The parameters of the First-order stress decay model, with a non-zero equilibrium stress value for sesame paste white compound chocolate.

Sample	The parameters of First-order stress decay model, with a non-zero equilibrium stress value model					
	τ_0 (Pa)	k (s^{-1})	τ_{eq} (Pa)	$\frac{\tau_0-\tau_{eq}}{\tau_{eq}}$	R^2	% RMSE
ME	560.76 ± 8.63^a	0.046 ± 0.0023^v	360.28 ± 0.81^j	0.55^m	0.91	2.25
M	676.75 ± 3.6^b	0.001 ± 0.0003	293.79 ± 2995.52	1.3	0.79	2.12
MSE	583.9 ± 5.42^c	0.081 ± 0.0006^r	322.59 ± 1.53^k	0.81^m	0.96	2.9
MS	553.64 ± 2.38^d	0.046 ± 0.0009	60.31 ± 58.33	8	0.82	1.69
SE	911.03 ± 14.17^e	0.029 ± 0.001^s	407.44 ± 2.23^l	1.23^m	0.95	4.43
S	293.47 ± 1.2^f	0.008 ± 0.001	267.38 ± 1.33	0.09	0.78	1.19

Means ± standard deviation from triplicate analysis.
Means values followed by the same letter in each column are not significantly different ($p > 0.05$).
τ_0 (Pa), k (s^{-1}) and τ_{eq} (Pa) parameters were obtained by fitting experimental data to First-order stress decay model, with a non-zero equilibruim stress value: $\tau - \tau_{eq} = (\tau_0 - \tau_{eq})e^{-Kt}$.
R^2: coefficient of determination, RMSE: Root Mean Square Error.

chocolate in the form of free fat and stays only in the free space between the particles and makes the particles move easily beside each other. Complete replacement of soy flour with milk powder (14.5%) decreased the Casson viscosity respectively from 3.27 to 2.46 Pa.s and yield stress from 111.72 to 35.76 Pa and apparent viscosity from 12.102 to 6.3 Pa.s. The reduction of Casson viscosity, the yield stress and apparent viscosity in this case can be attributed to the size of particles. According to Table 3, the replacement of the soy flour with milk powder increased the particle size and decreased the specific surface area. This makes it easy to cover the particle surface with fat and the friction between the particles and the continuous phase decreased and resulted in reduction of the viscosity. Covering the particles surface increased the particles distance from each other and reduced the forces acting between the particles. Therefore, it reduced the yield stress. In all samples, the presence of emulsifiers significantly reduced the Casson viscosity and increased the yield stress. In similar results, Afakowa et al. [31] stated that the viscosity decreased in lecithin concentration of higher than 0.5%, but the yield stress increased continuously. An increase in the yield stress may be due to the formation of micelles in the continuous phase which enveloped the layered structure around the sugar particles and prevented the easy flow of chocolate particles. In

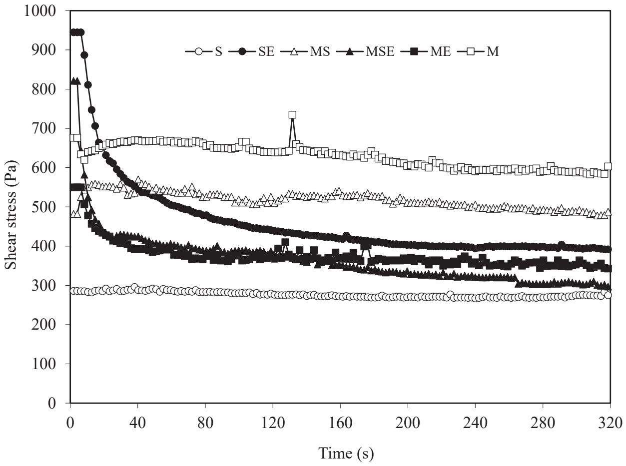

Figure 1: Shear stress of sesame paste white compound chocolate as a function of shearing time: sample containing milk powder (M); sample containing milk powder and emulsifier (ME); sample containing milk powder and soy flour (MS); sample containing milk powder, soy flour, and emulsifier(MSE); sample containing soy flour and emulsifier(SE); sample containing soy flour (S).

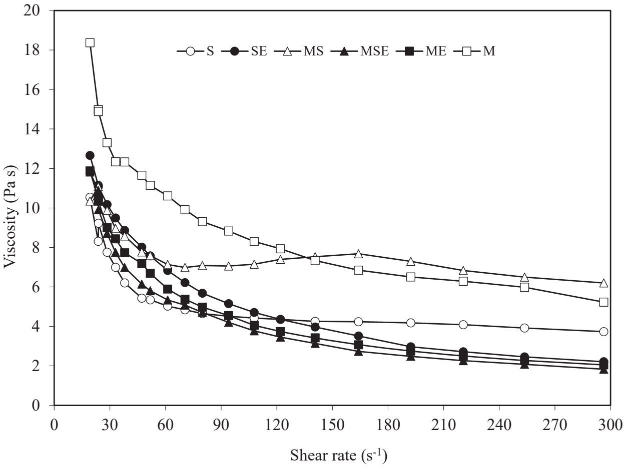

Figure 2: Apparent viscosity as a function of shear rate for sesame paste white compound chocolate at different soy four substitution levels and emulsifier content: sample containing milk powder (M); sample containing milk powder and emulsifier (ME); sample containing milk powder and soy flour (MS); sample containing milk powder, soy flour, and emulsifier (MSE); sample containing soy flour and emulsifier (SE); sample containing soy flour (S).

Table 7: The effects of replacement levels and emulsifier levels on Casson visosity, Casson yield value and apparent viscosity.

Sample	The parameters of casson model				
	Casson plastic viscosity (Pa.s)	Casson yield (Pa)	Apparent viscosity (Pa.s)	R^2	RMSE%
ME	0.55 ± 0.035^c	161.03 ± 0.32^f	7.54^n	0.96	0.56
M	3.27 ± 0.39^b	111.72 ± 0.36^g	12.1^m	0.99	0.53
MSE	0.44 ± 0.032^c	159.26 ± 0.3^f	7.06^n	0.98	0.89
MS	5.8 ± 0.063^a	9.95 ± 0.58^i	8.4^n	0.96	0.5
SE	0.59 ± 0.056^c	184.41 ± 0.52^e	8.46^n	0.92	0.88
S	2.46 ± 0.039^{cb}	35.76 ± 0.4^h	6.3^n	0.98	0.68

Means ± standard deviation from triplicate analysis.
Means values followed by the same letter in each column are not significantly different ($p > 0.05$).
η_c Casson plastic viscosity (Pa.s), τ_0 Casson yield (Pa), and Apparent viscosity parameters were obtained by fitting experimental data to Casson model: $\sqrt{\tau} = \sqrt{\tau_{0c}} + \sqrt{\eta_c} \cdot \sqrt{\gamma^o}$.
R^2: coefficient of determination, RMSE: Root Mean Square Error.

Table 8: Results of the preferential test for the samples.

Samples	MS, S	M, S	M, MS
No. of panelists	30	30	30
No. number of correct responses	20^{ns}	23^{**}	19^{ns}

"ns" is non-significant and "**" is significant. The significance level was obtained by comparing the correct responses with the statistical tables.

Table 9: Results of the acceptance test performed on the samples.

Sample code	Replacement level of soy flour and powdered milk	Overall acceptability
M	0	8.05 ± 0.11^a
MS	7	8.45 ± 0.19^a
S	14.5	5.15 ± 0.29^b

Means ± standard deviation from triplicate analysis.
Means values followed by the same letter in each column are not significantly different ($p > 0.05$).

the process of chocolate production, the main aim of using emulsifier is reducing the viscosity and the yield stress. Therefore, because of increasing of yield stress by mono-and diglyceride, it is not a good emulsifier to produce the sesame paste white chocolate. It should be used in combination with other emulsifiers to obtain a balanced yield stress and viscosity. Chocolate manufacturers now use a combination of lecithin and PGPR emulsifiers. Adding lecithin decreases significantly the viscosity, and adding PGPR decreases the yield stress. In samples containing 0 and 7% soy flour (MSE and ME), the emulsifier reduced the apparent viscosity, and in the sample containing 14.5% soy flour (SE), the emulsifier increased the apparent viscosity. An increase in the apparent viscosity in the presence of an emulsifier may be due to the fact that the efficiency of the emulsifier can be reduced as a result of emulsifiers-protein bind in the presence of soybean protein. Acar et al. [30] reported the similar results that, an increase in Casson viscosity in the presence of citrem emulsifier and milk proteins could be attributed to creation of the hydrogenic and electrostatic bond between the citrem and the milk protein, which reduced the citrem surface activity and its efficacy.

4.5 Sensory evaluation

4.5.1 Preferential Test

The results of the preferential test are shown in Table 8. Panelists only found a significant difference between the sample containing soy flour without milk powder (Sample S) and the sample containing the milk powder without soy flour (sample M) ($p < 0.05$), attributing to the flavor of the soy flour dominating the flavor of the chocolate. This helped the panelists to easily distinguish between the sample containing the soy flour and the free-soy flour sample. Therefore, it can be said that replacing 14.5% of the soy flour with the powdered milk had significant effect on the sensory properties of sesame paste chocolate. Whereas,

Table 10: The results of descriptive sensory test.

Samples			
Attributes	M	MS	S
Sweetness	7.65 ± 0.45^a	6.85 ± 0.32^a	6.52 ± 0.42^a
Creamy color	4.31 ± 0.89^c	8.75 ± 0.82^{cd}	9.95 ± 0.96^d
Astringentflavour	6.6 ± 0.45^e	5.52 ± 0.34^e	4.45 ± 0.65^e
Hardness	$8.82 \pm .063^f$	7.96 ± 0.32^f	8.65 ± 0.21^f
Oiliness	6.55 ± 0.5^h	7.62 ± 0.42^h	7.89 ± 0.21^h

Means ± standard deviation from triplicate analysis.
Means values followed by the same letter in each row (a–h) are not significantly different ($p > 0.05$).

panelists did not find a significant difference between other samples containing a combination of soy flour and powdered milk.

4.5.2 Acceptance Test

The results of the overall acceptability test performed on the samples are shown in Table 9.

According to the results of 9-point hedonic rating of overall acceptability of different sesame paste white chocolate samples, the sample containing 7% of soybean flour and 7.5% of powdered milk (MS) has the highest acceptability among the consumers, followed by samples containing 14.5% of powdered milk (M) and samples containing 14.5% of soybean flour (S). While there was no significant difference in terms of acceptability between M and MS samples, a significant difference was found between MS and S samples and between M and S samples ($p > 0.05$).

4.5.3 Descriptive sensory test

The results of descriptive sensory test are shown in Table 10. Sweetness of the samples decreased by increasing the replacement level of soy flour with powdered milk, associated with the dominant flavor of soy flour, i. e., although the amount of sugar is equal in all samples, less sweetness was felt by the panelists with the presence of soy flour, so the soy flour seems to cover the sweetness of the chocolate. The astringent flavor of the sesame paste was felt more severely in the presence of the powdered milk. The results of the sensory analysis showed that, the astringent flavor of the sesame paste reduced by increasing the soy flour in the formulation. Decrease in the hardness of the samples was expected by increasing the soy flour in the formulation and consequent soy oil. However, the results of the sensory analysis were contrary to the expectations, resulting from the inability of the panelist in appropriately detecting the hardness of the chocolate samples. Oiliness of the samples was well predictable in the sensory test because, the sesame paste white chocolate contains sesame oil, which is liquid at room temperature. So, the oiliness was felt by touching at the body temperature. As the content of soy flour increased, an increase was found in the oiliness of the samples, attributing to the combination of soy oil and sesame oil producing more severe oily feeling. Results showed that creamy color of the samples changed in different concentration of soy flour. The highest mean score related to S sample, which could be due to the maximum amount of soy flour in chocolate composition.

5 Conclusion

The aim of this study was to develop an acceptable and nutritious soy fortified sesame paste chocolate. The results indicated that replacement level of soy flour and emulsifier directly affected the rheological, textural, thermal properties and PSD of sesame paste white chocolate. PSD parameters were increased at all replacement levels of soy flour, but the addition of emulsifier from 0 to 1.5 % moderately reduced the PSD parameters of products. Although changes in the emulsifier content and replacement level of soy flour affected the T_m and T_{onset} insignificantly ($p > 0.05$), there were significant ($p < 0.05$) differences in melting enthalpy. Partial replacement of soy flour with milk powder up to 7% in non-emulsifier samples increased the chocolate hardness. In samples containing 7 and 14% soy flour, the effect of emulsifier decreased the hardness. The non-emulsifier samples showed a weak time-dependent behavior. Casson yield of sesame paste white chocolate significantly increased by adding the mono- and diglecyride emulsifier. This problem could probably be solved using the combination of two different emulsifiers. The use of soy flour as a replacement for milk powder provides the opportunity to formulate a healthy sesame paste chocolate with nutritional and functional properties. The results from this study suggested that application of 7% soy flour in sesame paste white compound chocolate as milk powder replacer produced acceptable product and mono-glyceride should be used in combination with other emulsifiers to obtain desirable rheological properties.

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References

1. Aidoo RP, Depypere F, Afoakwa EO, Dewettinck K. Industrial manufacture of sugar-free chocolates – applicability of alternative

sweeteners and carbohydrate polymers as raw materials in product development. Trends Food Sci Technol 2013;32:84–96.

2. Aidoo H, Sakyi-Dawson E, Abbey L, Tano-Debrah K, Saalia FK. Optimisation of chocolate formulation using dehydrated peanut – cowpea milk to replace dairy milk. J Sci Food Agric 2012;92:224–31.
3. Pandey A, Singh G. Development and storage study of reduced sugar soy containing compound chocolate. J Food Sci Technol 2011;48:76–82.
4. Riedel HR. Applications of Nurupan in chocolates and sugar confections. Confect Prod 1990;56:722–3.
5. Norma H, Asiah MZ, Jinap S. Effect of soy protein isolates on quality of chocolates. ASEAN J Sci Technol Dev 1995;12:51–64.
6. Yeganehzad S, Mazaheri TM, Mohebbi M, Habibi NM, Baratian Z. Effects of replacing skim milk powder with soy flour and ball mill refining time on particle size and rheological properties of compound chocolate. J Agr Sci Tech 2013;15:125–35.
7. Zarić DB, Pajin BS, Rakin MB, Šereš ZI, Dokić LP, Tomić JM. Effect of soya milk on nutritive, antioxidative, reological and textural properties of chocolate produced in a ball mill. Hem Ind 2011;65: 563–73.
8. Childs JL, Yates MD, Drake MA. Sensory properties of meal replacement bars and beverages made from whey and soy proteins. J Food Sci 2007;72:S425–34.
9. Nagendra Prasad MN, Sanjay KR, Prasad DS, Vijay N, Kothari R, Nanjunda Swamy S. A review on nutritional and nutraceutical properties of sesame. J Nutr Food Sci 2012;2:2.
10. Ashkezary MR, Yeganehzad S, Vatankhah H, Todaro A, Maghsoudlou Y. Effects of different emulsifiers and refining time on rheological and textural characteristics of compound chocolate. Ital J Food Sci 2017;30. https://doi.org/10.14674/IJFS-759.
11. Al-Mahasneh M, Rababah T, Alu'Datt M. Effect of palm oil (PO) and distilled mono-glycerid (DMG) on oil separation and rheological properties of sesame paste. J Food Process Preserv 2017;41: e12896.
12. Alamprese C, Datei L, Semeraro Q. Optimization of processing parameters of a ball mill refiner for chocolate. J Food Eng 2007; 83:629–36.
13. De Clercq N, Moens K, Depypere F, Ayala JV, Calliauw G, De Greyt W, et al. Influence of cocoa butter refining on the quality of milk chocolate. J Food Eng 2012;111:412–9.
14. Clercq ND, Depypere F, Delbaere C, Nopens I, Bernaert H, Dewettinck K. Influence of cocoa butter diacylglycerols on migration induced fat bloom in filled chocolates. Eur J lipid Sci Technol 2014;116:1388–99.
15. International Office of Cocoa, Chocolate, and Sugar Confectionery. Viscosity of cocoa and chocolate products (analytical method 46). Brussels: CABISCO; 2000.
16. Karnjanolarn R, McCarthy KL. Rheology of different formulations of milk chocolate and the effect on coating thickness. Journal Texture Stud 2006;37:668–80.
17. Nightingale LM, Lee SY, Engeseth NJ. Impact of storage on dark chocolate: Texture and polymorphic changes. J Food Sci 2011;76: C142–53.
18. Watts BM, Ylimaki GL, Jeffery LE, Elias LG. Basic sensory methods for food evaluation. Ottawa, ON, CA: IDRC; 1989.
19. Kiumarsi M, Majchrzak D, Yeganehzad S, Jäger H, Shahbazi M. Comparative study of instrumental properties and sensory profiling of low-calorie chocolate containing hydrophobically modified inulin. Part 1: Rheological, thermal, structural and external preference mapping. Food Hydrocolloids 2020;104:105698.
20. De Melo LL, Bolini HM, Efraim P. Sensory profile, acceptability, and their relationship for diabetic/reduced calorie chocolates. Food Qual Prefer 2009;20:138–43.
21. Afoakwa EO, Paterson A, Fowler M. Effects of particle size distribution and composition on rheological properties of dark chocolate. Eur Food Res Technol 2008;226:1259–68.
22. Bolenz S, Manske A. Impact of fat content during grinding on particle size distribution and flow properties of milk chocolate. Eur Food Res Technol 2013;236:863–72.
23. Aidoo RP, Appah E, Van Dewalle D, Afoakwa EO, Dewettinck K. Functionality of inulin and polydextrose as sucrose replacers in sugar-free dark chocolate manufacture – effect of fat content and bulk mixture concentration on rheological, mechanical and melting properties. Int J Food Sci Technol 2017;52:282–90.
24. Beckett ST, Fowler M, Ziegler GR, editors. Beckett's industrial chocolate manufacture and use. Chichester, West Sussex: John Wiley & Sons; 2017 Feb 15.
25. Mohammadi TM, Razavi SMA, Malekzadegan F, Ardekani AS. Chemical composition and rheological characterization of pistachio green hull's marmalade. Journal Texture Stud 2009;40: 390–405.
26. Abu-Jdayil B, Al-Malah K, Asoud H. Rheological characterization of milled sesame (tehineh). Food Hydrocolloids 2002;16:55–61.
27. Razavi SM, Najafi MH, Alaee Z. Rheological characterization of low fat sesame paste blended with date syrup. Int J Food Prop 2008;11:92–101.
28. Izidoro DR, Scheer AP, Sierakowski MR, Haminiuk CW. Influence of green banana pulp on the rheological behaviour and chemical characteristics of emulsions (mayonnaises). LWT-Food Sci Technol 2008;41:1018–28.
29. Sokmen A, Gunes G. Influence of some bulk sweeteners on rheological properties of chocolate. LWT-Food Sci Technol 2006; 39:1053–8.
30. Ačkar Đ, Škrabal S, Šubarić D, Babić J, Miličević B, Jozinović A. Rheological Properties of milk chocolates as influenced by milk powder type, emulsifier, and cocoa butter equivalent additions. Int J Food Prop 2015;18:1568–74.
31. Afoakwa E, Paterson A, Fowler M. Factors influencing rheological and textural qualities in chocolate – a review. Trends Food Sci Technol 2007;18:290–8.