

EFFECTS OF DIFFERENT EMULSIFIERS AND REFINING TIME ON RHEOLOGICAL AND TEXTURAL CHARACTERISTICS OF COMPOUND CHOCOLATE

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ABSTRACT

The purpose of this study was to investigate the possibility of producing reduced fat dark compound chocolate in the ball mill refiner and using some selected emulsifiers. The effects of selected emulsifiers including lecithin, Polyglycerol polyricinoleate (PGPR) and citrem in two levels and two refining times on the characteristics such as moisture, particle size, hardness and rheological properties of the samples was examined. Data analysis revealed that the Casson model was appropriate to describe the rheological behavior of the samples containing lecithin and citrem; however, Power law model was appropriate for the samples containing PGPR. The results showed that citrem is the most effective emulsifier to reduce hardness and rheological parameters such as apparent viscosity; casson viscosity and casson yield value and using citrem as a part of formulation in the production of reduced fat dark compound chocolate can solve many technological problems.

Keywords: citric acid ester, Casson model, Power law, PGPR, lecithin, reduced fat compound chocolate

1. INTRODUCTION

Production of chocolate and chocolate products in ball mill refiner is currently spreading worldwide due to lower costs and easier operational systems. The increase of diseases caused by dietary misbehaviors in industrialized countries, leads to larger knowledge for nutritional requirements by the consumer and, therefore, by food industry (DIAS *et al.* 2015). As a result, the possibility of developing a formulation for chocolate models by reducing its fat content while maintaining its richness and flavor will give the consumer a new and healthy food option to enjoy. Chocolate is a fat-based suspension with about 30%wt fat. Reducing fat content causes an increase in hardness and molten chocolate viscosity that leads to difficulties in the process and a loss of eating quality in the final product. There are, however, some technical issues that must be scrutinized to achieve successful ball mill processing. Generally, several methods are introduced to reduce the fat content of chocolate with acceptable viscosity and hardness such as increasing the emulsifier levels and/or using emulsifier blends (KAISER *et al.*, 1998), using fat replacers (BECKETT, 2009), and substituting fat phase with a water-in-oil emulsion (HUGELSHOFER, 2000). Optimizing the particle size distribution is another method of decreasing the fat content (MONGIA and ZIEGLER, 2000; DO *et al.*, 2007). The optimization of the particle size distribution (PSD) method has a significant effect on the rheological and textural properties of chocolate samples such as reduction of the apparent viscosity, decrease of hardness and an increase of melting rate in the mouth (MONGIA and ZIEGLER, 2000). The non-Newtonian flow behavior of molten chocolate is generally studied by some well-known models for shear thinning fluids such as power law, Bingham, Herschel-Bulkley and Casson (SOKMEN and GUNES, 2006). In terms of utilization of the latter model, comparing the rheological methods proposed by International Confectionary Association (ICA, 2000) and Chocolate Manufacturers Association (CMA, 1997) revealed a high correlation between: I) Casson plastic viscosity and apparent viscosity; II) between Casson yield value and yield stress; III) Casson plastic viscosity and Casson yield value and IV) yield stress and apparent viscosity (AFOAKWA *et al.*, 2009). In order to have a quality product, investigating the changes which occur in the product matrix at every manufacturing stage could be very useful (GLICERINA *et al.* 2013). Structurally, chocolate is made from fat phase (cocoa butter and emulsifier), in which solid material (crystal sugar, milk powder and cocoa powder) are spread (BECKETT, 2000). The composition of chocolates in terms of fat and nonfat cocoa solids, and sugar content affect their rheological characteristics (FERNANDES *et al.*, 2013). In addition to cocoa butter, emulsifier also forms one of the constituents of chocolate fat phase. In the chocolate matrix, emulsifiers cover sugar particles to develop the flow in cocoa butter. This assists in the equal distribution of particles in emulsion and prevents agglomeration. Some emulsifiers decrease viscosity and yield stress significantly, so they will be very useful additives in production of chocolates with reduced fat. Lecithin and PGPR are emulsifiers usually used in chocolate (SCHANTZ and RHOM, 2005). Both lecithin and PGPR work synergistically with other emulsifiers, such as ammonium phosphatide and citric acid esters (STIER, 2009). Citric acid ester has the attributes of the lecithin and PGPR combination (BECKETT, 2009). Emulsifiers have ability of changing viscosity in certain foods (WALTER and CORNILLON, 2001). This feature is extremely important in producing chocolate, for example in chocolate coating, pumping and molding, etc. (RECTOR, 2000). Emulsifiers have been used in chocolate to modify and improve the flow characteristics of chocolate since chocolate was first processed. However, the most important of emulsifier applications in chocolate industry is improving flow parameters and minimizing consumption of cocoa butter and its costs of production (SCHANTZ and RHOM, 2005). Achieving desirable functional properties is not only

related to providing a basic level of knowledge about ingredients, but also understanding each ingredient's effect in the combinational form will help the manufacturers to satisfy the consumers expectations (MANZOCCO *et al.*, 2014). The purpose of this study was to investigate the possibility of producing reduced fat compound chocolate in ball mill refiner and using some selected emulsifiers in the manufacturing process including lecithin, polyglycerol polyricinoleate and citrem (citric acid ester).

2. MATERIAL AND METHODS

2.1. Materials

Cocoa powder (Guan Chong cocoa manufacture Sdn Bhd, Malaysia), refined sugar, cocoa butter substitute (CBS) (Cargill, Malaysia), Lecithin, Polyglycerol polyricinoleate (PGPR) and citrem (Palsgard, Juelsminde, Denmark).

2.1.1 Preparation of compound chocolate samples

The basic formulation of the dark compound chocolate contained 46.5% cocoa powder, 30% sugar, 23% CBS, and 0.5% lecithin. The method for producing compound chocolate was as follows: first, all raw materials, including cocoa powder, refined sugar, palm kernel oil and lecithin, were weighed and poured into semi-industrial Ball mill device (Sepehr machine company, Tehran, Iran). Eventually, fourteen formulas were produced (twelve formula in addition to two basic formula with 60 and 90 refining times as the control samples). Mixing, refining (in two groups, one for 60 and the other one for 90 minutes) and conching were done simultaneously in this device for 30 min at 60 °C and speed of 100 rpm. Each sample was then divided into seven portions. Afterward, emulsifiers were added to the samples (Lecithin and citrem at two levels of 0.5 and 1 % and PGPR at two levels of 0.25 and 0.5%). The conching process was performed (Heidolph mixer) at a speed of 60 rpm for 30 minutes. Next, the mixture was refrigerated at 4°C for 30 min in silicon containers. Finally the samples were kept in aluminum foils and stored at room temperature for analysis.

2.1.2 Moisture content measurements

The moisture content of chocolate samples was determined using oven method (IOCCC, 1952).

2.1.3 Particle size distribution measurements

Particle size distribution was determined through laser diffraction method by particle analysis machine (SHIMADZU SALD-2101), according to MCFARLANE (1999). Before analysis, the compound chocolate samples dissolved in acetone solvent and stirred vigorously under ultrasonic waves of 50 Hz, 200 W for 5 minutes. Low-intensity ultrasound produced optimal component emission. After the initial preparation, samples were transferred to the laser chamber. Results obtained from the laser chamber of the parameters of the largest particle size (D90), the mean particle volume (D50) and the smallest particle size (D10) in micrometer scale were determined (ALAMPRESE *et al.*, 2007) with three replicates.

2.1.4 Hardness measurements

Hardness of samples was measured using a texture analyzer (TA-XT plus, stable micro systems Ltd, Surrey, UK), connected to the computer with the software Texture Expert 1.05. The flow bottom steel probe with 2 mm diameter was utilized for measurements. The maximum force of penetration to samples (45×20×10 mm) was determined with a depth of 5 mm at a speed of 1 mm/s at room temperature. Loading force was set to 0.05 N direction of the sample, and kept constant for all samples. Hardness was taken as the maximum peak force in Newton. Results for hardness are expressed as the mean value of three replicates conducted on each sample.

2.1.5 Rheological measurements

Samples were prepared according to the proposed methods of the International Confectionery Association (ICA, 2000); the compound chocolate sample was and melted in an incubator at a temperature of 50°C for 75 minutes and then, transferred to the rheometer cub. After a pre-shear period of 15 min at 5/s, shear rate was applied from 5 to 50 (ramp up) within 120 s and then shear rate was reduced from 50 to 5 (ramp down), and in each ramp 50 measurements were taken. The temperature was kept constant at 40°C. An Anton Paar rheometer (RheolabQC SN80677512, Austria) was used for all rheological measurements and the data were collected by use of the Rheoplus/32 service V3.10 software. The apparent viscosity of the samples was measured at 40/s and results are reported as the mean value of two replicates. SERVAIS *et al.* (2003) reported that the apparent viscosity can be measured at 30, 40 or 50/s depending on the type of product, but recommended the measurement at 40/s for the chocolate regarding to its repeatability. In this study, a locally designed model for analysis of flow time independent characteristics was utilized to analyze the flow properties of compound chocolate. Due to the decrease in viscosity by increasing the shear rate for all rheological behavior applied and non-Newtonian actions of compound chocolate samples, 4 non-Newtonian models (dependent on shear rate) were fitted on the test data (shear stress – shear rate). These four models include (should be in the sequence that is in the Table 2):

Power law ($\tau = k(\dot{\gamma})^n$), Bingham ($\tau - \tau_0 = \eta_{pl}\dot{\gamma}$), Herschel-Bulkley ($\tau - \tau_0 = \eta_{pl}(\dot{\gamma})^n$) and Casson ($\tau^{0.5} = \tau_0 + (\eta_{pl})^{0.5} \cdot (\dot{\gamma})^{0.5}$);

Where,

τ is shear stress, τ_0 is yield stress, η_{pl} is plastic viscosity, $\dot{\gamma}$ is shear rate, n is flow behavior index and K is consistency index. Molten chocolate is a non-Newtonian fluid with a yield stress, which can be characterized using a number of mathematical models, including the Bingham, Herschel-Bulkley and Casson models (ICA, 2000; SERVAIS *et al.*, 2003; KONAR, 2013). To select the best model for describing time-independent rheological behavior of compound chocolate samples, three statistical parameters of correlation coefficient (R), Root Mean Square Error (RMSE) and Standard Error (SE), were utilized.

2.1.6 Statistical analysis

The SPSS version 21, Curve expert softwares and analysis of variance (ANOVA) were used for statistical analysis of experimental data. Due to unequal levels of used emulsifiers in the formulae, the significance of difference among samples was examined By Nested following Duncan's multiple range tests for mean comparisons.

3. RESULTS AND DISCUSSIONS

3.1. Moisture content

Moisture content of all samples ranged from 0.39 to 0.52. Moisture contents of all samples were within an acceptable range for chocolate (below 1.5 percent). AFOAKWA *et al.* (2007) reported that a moisture content of the chocolate samples over 1.5 percent would have a negative impact on the rheological properties.

3.2. Particle size distribution

Results for the D90, D50 and D10 of the samples are shown in Table 1. Since increase in emulsifier level and conching did not lead in change of particle size, only base formula was studied. The mean particle size in the D90, D50, and D10 was 10%, 50% and 90%; the particles were finer than this size, respectively. In this study, as expected, by increasing the refining time, all parameters in the particle size distribution were reduced. Observations in this study determined the particle size of both samples to be below 30 μm . BECKETT (2009) reported that the size of the largest particle is a key parameter for chocolate production and plays a critical role in the hardness, sensory properties, and other properties of chocolates. The largest particle size (D_{90}) plays an important role in the creation of grittiness and mouth feel, however smaller particles affect the flow properties (BECKETT, 2000; MONGIA and ZIEGLER, 2000). Particle size in chocolate roughly ranges between 1 and 50 μm , whereby particles larger than 30 μm cause a gritty perception in the mouth. KRUGER (1999) reported that minimum D90 size for optimal rheological properties was 6 μm . However, in this study, the minimum size of D90 in both of samples was greater than 6 μm . Particle size and flow properties of chocolate are very important factors in determining the viscosity and also texture of final product (MINIFIE, 2012).

Table 1. D_{90} , D_{50} , and D_{10} values in control and basic formulae.

Sample	D_{50} (μm)	D_{90} (μm)	D_{10} (μm)
CH ₁	26.87±0.59	7.67±0.04	1.71±0.04
CH ₂	22.21±0.34	6.91±0.05	1.59±0.03

(CH₁: basic formula, 1: refining time in 60 min, 2: refining time in 90 min).

3.3. Hardness

Hardness of samples ranged from 32.09 to 53.25 N. As expected, hardness decreased by increasing the levels of emulsifiers in the samples (Fig. 1). Hardness showed inverse relationships with PS, fat and lecithin contents specially in low fat (25%) chocolate samples (AFOAKWA, 2009). At both 60 and 90 minutes of refining time, citrem 1% was the softest and the PGPR 0.25% was the hardest sample (Fig. 1). There was no significant difference between samples containing 0.25% PGPR at 60 min refining time and 0.5% PGPR and citrem at 90 min refining time ($p < 0.05$) and also the results showed that, there was no significant differences between samples containing 0.5% PGPR, 0.5% and 1% lecithin at the first refining time ($p < 0.05$). Previously, TISONCIK (2010) claimed that increasing concentrations of lecithin and PGPR led in decrease of hardness characteristics of dark chocolate. By increasing the refining time from 60 to 90 minutes and reducing the particle

size from 26.87 μm to 22.211 μm , the hardness of the samples containing lecithin, PGPR and citrem increased due to the interaction between the particles of the compound chocolate. Reducing the particle size leads to increase in resistance of chocolates to break and gives a harder texture (AFOAKWA *et al.*, 2009). In similar results, AFOAKWA *et al.* (2008) reported that by reducing the particle size from 50 microns to 18 microns, the hardness of chocolate samples increased. Do *et al.* (2007) concluded that by selecting a specific range of particle sizes, hardness of chocolate samples could be reduced and controlled. BECKETT (2009) reported different factors like formulation, production method, tempering, polymorphism and cooling temperatures determine the hardness of the chocolate samples. In this study no tempering was required since CBS had been used. In addition, the cooling temperature and production method of all samples were the same. So it can be concluded that desired hardness was achieved by changing the emulsifier or by combination of emulsifiers. There is direct correlation between sensory properties during consumption and hardness; therefore, measuring the hardness parameter is an important indicator for assessing qualitative changes of chocolates with different formulations.

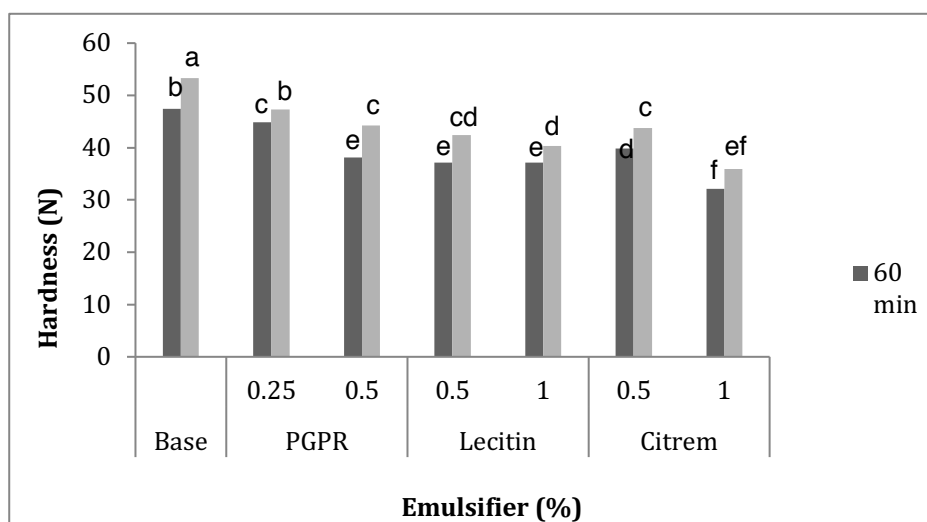


Figure 1. Hardness of the all samples with different emulsifiers at two refining times. Different letters indicate statistically significant differences ($p < 0.05$).

3.4. Rheological parameters

3.4.1 Evaluation of fitted models

Table 2 illustrates the results of the three statistical parameters of R, RMSE and SE. By fitting the data of the shear rate - shear stress on the four rheological models of Power Law, Bingham, Herschel-Bulkley and Casson, the Casson model showed the highest R, low RMSE and the lowest SE. Therefore it was the best model to analyze the samples containing lecithin and citrem. The ICA (2000) has proposed Casson model as an appropriate model to analyze the rheological properties of chocolates. In the samples containing PGPR, due to a low yield stress and close to zero, a negative intercept was obtained in the Casson, Bingham and Herschel-Bulkley models. Therefore, the Casson model could not be used for analysis, while the power law model was successful in analyzing the samples containing PGPR.

Table 2. The measured values of the three statistical parameters of R, RMSE and SE.

	Model	R	RMSE	SE
CH _{bn}	Power law	0.996	4.263	18.11
	Bingham	0.989	4.206	30.57
	Herschel-Bulkley	0.998	3.602	12.97
	Casson	0.993	3.575	0.48
CH _{bn}	Power law	0.999	3.627	10.49
	Bingham	0.995	2.854	25.37
	Herschel-Bulkley	0.998	3.754	14.63
	Casson	0.998	2.105	0.29
CH _{bn}	Power law	0.999	3.672	2.53
	Bingham	0.998	1.706	14.03
	Herschel-Bulkley	0.999	2.961	4.24
	Casson	0.999	0.894	0.13
CH _{bn}	Power law	0.999	2.333	8.66
	Bingham	0.993	3.216	11.46
	Herschel-Bulkley	0.999	2.143	7.93
	Casson	0.999	2.274	0.27
CH _{bn}	Power law	0.999	1.575	4.28
	Bingham	0.999	2.057	11.13
	Herschel-Bulkley	0.999	0.998	8.60
	Casson	0.999	1.072	0.19
CH _{bn}	Power law	0.999	3.015	3.60
	Bingham	0.994	2.706	5.66
	Herschel-Bulkley	0.999	0.589	3.43
	Casson	0.998	1.421	0.23
CH _{pn}	Power law	0.999	3.787	1.96
	Bingham	-	-	-
	Herschel-Bulkley	-	-	-
	Casson	-	-	-
CH _{pn}	Power law	0.999	1.673	7.63
	Bingham	-	-	-
	Herschel-Bulkley	-	-	-
	Casson	-	-	-
CH _{pn}	Power law	0.999	3.212	6.54
	Bingham	-	-	-
	Herschel-Bulkley	-	-	-
	Casson	-	-	-
CH _{pn}	Power law	0.999	2.229	9.18
	Bingham	-	-	-
	Herschel-Bulkley	-	-	-
	Casson	-	-	-
	Casson	0.999	1.050	0.11
CH _{cn}	Power law	0.999	1.469	5.72
	Bingham	0.999	0.464	2.83
	Herschel-Bulkley	0.999	0.712	1.29

CH _{1c}	Casson	0.999	0.420	0.06
	Power law	0.995	2.370	14.70
	Bingham	0.985	4.451	27.60
	Herschel-Bulkley	0.997	3.303	12.68
CH _{2c}	Casson	0.993	3.497	0.40
	Power law	0.999	0.812	3.33
	Bingham	0.999	1.169	6.03
	Herschel-Bulkley	0.999	1.004	1.53
CH _{3c}	Casson	0.999	0.410	0.04
	Power law	0.999	2.194	5.36
	Bingham	0.999	0.875	5.02
	Herschel-Bulkley	0.999	2.830	0.95
CH _{4c}	Casson	0.999	0.395	0.03
	Power law	0.999	2.194	5.36
	Bingham	0.999	0.875	5.02
	Herschel-Bulkley	0.999	2.830	0.95

(CH₁: The sample containing base formulation, CH₂: The sample containing lecithin, CH₃: The sample containing PGPR, CH₄: The sample containing citrem; the first number: Refining time (1: 60 min, 2: 90 min), the second number: Emulsifier level (1: 0.5% or 0.25% (the sample containing PGPR), 2: 1% or 0.5% (the sample containing PGPR)).

3.4.2 Apparent viscosity

The apparent viscosities of the samples are shown in Table 3.

In this study, no significant differences between samples containing lecithin and basic formula in second refining time ($p < 0.05$) were found. A general trend regardless to fat content was seen as consistent decreases in apparent viscosity while increasing particle size (AFOAKWA 2009); increase in particle size from 18 to 50 μm caused noticeable decrease in apparent viscosity- which was similar with Casson plastic viscosity- specially at low fat (25%). in addition, it was reported that by increasing lecithin from 0.3 to 0.5%, the apparent viscosity decreased regardless to particle size and fat content. This study proves that different refining times have no effect on the specified levels of samples containing citrem, whereas, amount of citrem is effective on apparent viscosity.

Table 3. The measured values of Casson viscosity, Casson yield, and apparent viscosity for different formula.

Sample	Casson viscosity (Pa.s)	Casson yield value (Pa)	Apparent viscosity (Pa.s)
CH _{1a}	18.74 ^b	16.92 ^d	24.7 ^b
CH _{2a}	22.56 ^c	22.18 ^c	30.4 ^a
CH _{1b}	21.25 ^b	18.66 ^d	28 ^b
CH _{2b}	14.89 ^c	29.37 ^b	22.1 ^c
CH _{1c}	20.94 ^c	31.92 ^b	28.9 ^a
CH _{2c}	17.22 ^b	66.09 ^a	29.6 ^b
CH _{1d}	15.13 ^c	10.23 ^c	21.7 ^c
CH _{2d}	13.46 ^c	11.15 ^c	18.6 ^d
CH _{1e}	14.97 ^c	21.23 ^c	20.9 ^c
CH _{2e}	14.59 ^c	15.88 ^d	19.3 ^d

(CH₁: The sample containing lecithin, CH₂: The sample containing citrem; the first number: Refining time (1: 60 min, 2: 90 min), the second number: Emulsifier level (1: 0.5%, 2: 1%). Different letters indicate statistically significant differences ($p < 0.05$).

Casson model

Casson Viscosity

Values for Casson viscosity and Casson yield value were determined through the Casson model fit on the data (shear stress - shear rate). Casson viscosity values ranged between 13.46 and 22.56 Pa.s (Table 3). In this study, there were no significant differences between samples containing citrem at both refining times and different levels ($p < 0.05$). The results showed that different refining time have no effect on samples containing 0.5% lecithin, whereas, in the samples containing 1% lecithin, by increasing refining time, Casson viscosity increased and also by increasing lecithin, Casson viscosity decreased at both refining time. AFOAKWA (2009) reported increase in Casson viscosity while increasing refining time and reducing particle size. Moreover, it was seen that, especially at lower fat and lecithin levels, Casson plastic viscosity, Casson yield value, yield stress and apparent viscosity decreased in higher particle sizes. Fat reduction up to 30% has little effect on the Casson parameters; however, in chocolates with a fat content of less than 30%, by reducing the fat content, the Casson parameters, particularly the Casson viscosity, will increase (BECKETT, 2000).

Casson yield value

The Casson yield values are shown in Table 3. The yield stress or yield value relates to shape retention, pattern holding, feet and tails, inclined surface coating and presence of air bubbles (SEGUINE, 1988). The Casson yield values ranged 10.23 to 66.09. The sample having citrem in the initial refining time and level of 0.5% had the least yield value and lecithin in second refining time and level of 1% had the highest yield stress. In all samples, by increasing refining time and reducing particle size, the Casson yield stress increased. Evaluation of rheological characteristics revealed that increasing particle size, fat percentage (more specifically in low fat samples (25%)) and lecithin concentration play as a reduction agent for Casson yield values (AFOAKWA, 2009). It was observed that Casson yield value of the samples containing lecithin was more than samples with base formulations. The reason is that if the amount of lecithin rises above 0.3%, Casson yield stress increases (FINCKE, 2013). The samples containing citrem at initial refining time was the most effective in reducing Casson yield value ($p < 0.05$). Yield value is affected largely by interparticle contacts and consequently shows a linear dependence on the mean particle size, or more accurately, on the specific surface area (MONGIA, 1997; MONGIA and ZIEGLER, 2000). By decreasing the particle size there are more particles for intermolecular contact, thus the Casson yield value increases. PRENTICE (1984) reported that when particle size decreases, interactions and subsequent friction constants between the particles increase, thus the Casson yield stress increases.

Power law model

As described before, power law model was chosen as an appropriate flow model for PGPR containing samples (Table 4). The shear stress-shear rate tests (in the mentioned range) showed a consistency coefficient range of 17.49 to 26.05 for the four formulations. However, the estimated flow behavior indices showed to be close to $n=1$ for all formulae. It can be concluded that adding PGPR emulsifier to the compound chocolate caused change in consistency index but it did not affect the flow behavior index. It is also worthy to note that, in samples containing 0.25% PGPR, increasing refining time was affective and

led to increased consistency index, whereas, there was no significant difference between samples having 0.5% PGPR ($p < 0.05$).

Table 4. The values of consistency index, flow behavior index, and apparent viscosity for the samples containing PGPR.

Sample	Consistency index (Pa.s)	Flow behavior index	Apparent viscosity (Pa.s)
CH _{1p1}	17.49 ^c	0.99 ^a	19.5 ^c
CH _{1p2}	19.72 ^b	0.99 ^a	22.6 ^b
CH _{2p1}	26.05 ^a	0.99 ^a	25.5 ^a
CH _{2p2}	20.40 ^b	0.99 ^a	22.4 ^b

(CH: The sample containing PGPR, the first number: Refining time (1: 60 min, 2: 90 min), the second number: Emulsifier level (1: 0.25%, 2: 0.5%). Different letters indicate statistically significant differences ($p < 0.05$).

4. CONCLUSIONS

To conclude, the refining time as a main factor affecting particle size distribution, emulsifier types and their levels are two important factors in optimization of compound chocolate with reduced fat content. Reduction of particle size increased the Casson yield value, although the rheological properties were related to type of emulsifiers and refining times, too. In addition, the hardness of the samples decreased by increasing emulsifier content and decreasing refining time. The Casson model was selected as an appropriate rheological model to illustrate the rheological parameters of the samples containing the citrem and lecithin as emulsifiers. Nevertheless, chocolate models with reduced fat content containing the PGPR were not in a good agreement with the Casson model. On the contrary, the power law model showed the highest correlation to their flow behavior. Finally, reduction of fat content leads to an increase in the molten compound chocolate viscosity and hardness, therefore, using citrem emulsifier because of significant reduction in the hardness and rheological parameters such as apparent viscosity, Casson viscosity and Casson yield value can be effective and useful for production of reduced fat dark compound chocolate.

REFERENCES

- Afoakwa E.O., Paterson A. and Fowler M. 2008. Effects of particle size distribution and composition on rheological properties of dark chocolate. *Eur. Food Res. Technol.* 226:1259-1268.
- Afoakwa E.O., Paterson A. and Fowler M. 2007. Factors influencing rheological and textural qualities in chocolate – a review. *Trends Food Sci. Technol* 18:290-298.
- Afoakwa E. O, Paterson A., Fowler M. and Vieira J. 2009. Microstructure and mechanical properties related to particle size distribution and composition in dark chocolate. *Int. J. Food Sci. Technol.* 44:111-119.
- Alamprese C., Datei L. and Semeraro Q. 2007. Optimization of processing parameters of a ball mill refiner for chocolate. *J Food Eng.* 83:629-636.
- Beckett S.T. 2009. "Industrial chocolate manufacture and use". 4th ed. West Sussex: Wiley-Blackwell.
- Beckett S.T. 2000. "The Science of Chocolate". 2nd ed. London: Royal Society of Chemistry Paperbacks.
- CMA. 1997. "Chocolate Manufacturers Association". Nutrient database for three selected major ingredients used in the NCA/CMA recipe modeling database: chocolate liquor, cocoa powder, and cocoa butter.

- Dias J., Alvarenga N. and Sousa I. 2015. Effect of hydrocolloids on low-fat chocolate fillings. *J. Food Sci. Technol.* 1;52(11):7209-7217.
- Do T.A.L., Hargreaves J.M., Wolf B., Hort J. and Mitchell J.R. 2007. Impact of particle size distribution on rheological and textural properties of chocolate models with reduced fat content. *J. Food Sci.* 72:E541-E552.
- Fernandes V. A., Müller A.J. and Sandoval A.J. 2013. Thermal, structural and rheological characteristics of dark chocolate with different compositions. *J. Food Eng.* 116:97-108.
- Fincke H. 2013. "Handbuch der Kakaoerzeugnisse". Springer-Verlag.
- Glicerina V., Balestra F., Rosa M.D. and Romani S. 2013. Rheological, textural and calorimetric modifications of dark chocolate during process. *J. Food Eng.* 119:173-179.
- Hugelshofer D. 2000. Structural and rheological properties of concentrated suspensions mixed with an emulsion. Thesis. Technische Wissenschaften ETH Zürich, Nr. 13776, 2001.
- ICA. 2000. "International Confectionery Association". Viscosity of cocoa and chocolate products. Analytical Method 46. B-1000 Bruxelles, Belgium: CAOBISCO, rue Defacqz 1.
- IOCCC. 1952. "Methods of Analysis". Determination of Moisture (oven Method). International Office of Cocoa, Chocolate and Sugar Confectionery.
- Kaiser J.M., Gestel A.V. and Vercauteren J. 1998. Reduced-fat confectioneries comprising emulsifying agent combinations, and preparation thereof. US Patent WO 99/45790.
- Konar N. 2013. Influence of conching temperature and some bulk sweeteners on physical and rheological properties of prebiotic milk chocolate containing inulin. *Eur. Food Res. Technol.* 236(1):135-143.
- Kruger C. 1999. "Sugar and bulk sweetener". In: Beckett, S.T. (Eds.), *Industrial Chocolate Manufacture and Use*, pp. 36-56, Oxford: Blackwell Science.
- Manzocco L., Calligaris S., Camerin M., Pizzale L. and Nicoli M.C. 2014. Prediction of firmness and physical stability of low-fat chocolate spreads. *J. Food Eng.* 126:120-125.
- McFarlane I. 1999. Instrumentation. In: Beckett S.T. (Eds.), "Industrial Chocolate Manufacture and Use", pp. 347-376, New York: Chapman and Hall.
- Minifie B. 2012. "Chocolate, cocoa and confectionery: science and technology". Springer Science & Business Media.
- Mongia G. 1997. Particle Size Distribution Affects the Rheology and Sensory Attributes of Milk Chocolate. Ph.D. Thesis. University Park. PA: The Pennsylvania State University.
- Mongia G. and Ziegler G.R. 2000. Role of particle size distribution of suspended solids in defining flow properties of milk chocolate. *Int J Food Prop*, 3,137-147.
- Prentice J.H. 1984. "Measurements in the rheology of foodstuffs". Elsevier Applied Science Publishers Ltd.
- Rector D. 2000. Chocolate-controlling the flow. Benefits of polyglycerol polyricinoleic acid. *Manuf Confect*, 80, 63-70.
- Schantz B. and Rhom H. 2005. Influence of lecithin-PGPR blends on the rheological properties of chocolate. *Lebensm Wiss Technology*, 38, 41-45.
- Seguine E. S. 1988. Factors influencing the taste, selection and specification of chocolate, 42nd PMCA Conference. pp, 56-61.
- Servais C., Ranc H. and Roberts I. D. 2003. Determination of chocolate viscosity. *J. Texture Stud* 34(5-6):467-497.
- Sokmen A. and Gunes G. 2006. Influence of some bulk sweeteners on rheological properties of chocolate. *LWT-Food Sci. Technol.*, 39(10), 1053-1058.
- Stier R. 2009. Fats, from nutritional nuances to physical functionality. R&D Applications Seminar, p 50-56.
- Tisoncik M.A. 2010. Impact of emulsifiers on physical, sensory, and microstructural properties in formulated dark chocolate with an innovative educational approach. Ph.D. Thesis, University of Illinois at Urbana-Champaign.
- Walter P. and Cornillon P. 2001. Influence of thermal conditions and presence of additives on fat bloom in chocolate. *J. Am. Oil Chem. Soc.*, 78:927-93.

Paper Received January 25, 2017 Accepted September 8, 2017