Melting and Textural Characteristics of Dark Chocolate Formulated with Carrageenan-based Hydrogel Sweetened with Sucrose

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ABSTRACT
Chocolate has some unique characteristics that solid at room temperature, brittle when broken and completely melts at body temperature. In the tropics, a specific approach in formulating chocolate is needed due to its high average temperature. This research aimed to develop formulation of heat-resistant chocolate with the addition of carrageenan-based hydrogel (CG). Experimental variables used were four concentrations of hydrogel namely 0%, 3%, 5%, and 7%. Four parameters including moisture content, particle size, melting profile and hardness were evaluated at 0, 4, 8, and 12 days. The result manifested that the addition of carrageenan-based hydrogel influenced chocolate parameter. As the concentration of hydrogel increased, moisture content, melting point, hardness and particle size also increased.

Keywords: *dark chocolate, carrageenan, hydrogel, melting point, textural characteristics.*

1. INTRODUCTION

Chocolate is unique and there are so many things to explore about it. Chocolate does not only have good taste, but also have some benefit for blood circulation, high antioxidant content and can reduce the risk of heart disease [1]. Chocolate is solid at room temperature but brittle and completely melts in your mouth at body temperature.

The characteristic of chocolate that easily melts corresponds to the constituent fat consisting of triglycerides (stearate, oleic acid and palmitic acid [2] that melt at 32-34ºC [3]. In the tropics with high average temperature, chocolate melting point becomes an issue that has to be overcome. Innovation on producing heat resistant chocolate (HRC) has been conducted for decades. HRC is a chocolate which has comparatively a higher melting point and can conserve its properties and structure [4,5,6]

There are several methods to produce HRC such as substituting the cocoa butter with high melting point fat, fat phase interesterification, the addition polymer which binds fat, develop network microstructure and indirect incorporation of water [4]. The latter can be done by adding hybrid hydrogel which has ability to bind good amount of water thus retard the melting of cocoa butter [7].

Several studies about hydrogel addition into chocolate has been conducted. The use of polysaccharides to formulate the hydrogel for chocolate addition were varied. Pectin-based hydrogel has been used as fat mimetic to produce HRC [7]. The previous studies to formulate HRC using Xanthan Gum-based hydrogel [8] and Konjac glucomannan [9] were also conducted. Carrageenan is a type of polysaccharides that is potential to be used for hydrogel production.

The purpose of this study was to investigate the use of Carrageenan-based hydrogel to produce HRC. Hydrogel was made by different concentration of carrageenan. The maturation duration was used as variable to determine the correlation between crystal formation and the change in chocolate parameter during storage time.

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2. MATERIALS AND METHODS

The study was conducted from November 2021 to June 2022 at the Laboratory of Food and Postharvest Engineering and the Laboratory of Biophysics, Faculty of Agricultural Technology, Universitas Gadjah Mada.

2.1. Materials

The materials used in the study were cocoa paste and cocoa powder. These ingredients were purchased from Indonesian Coffee and Cocoa Research Institute (Jember, East Java), while the cocoa butter was bought from UGM Cocoa Teaching and Learning Industry (Batang, Central Java). Sugar was bought at PT Sugar Group Companies and food grade Carrageenan powder was purchased from Alfa Kimia Biomedikatama (Yogyakarta). The characteristics of the ingredients can be seen in Table 1.

Table 1. Characterization of Ingredients

Ingredients	Moisture content (%)	Fat content (%)	Fineness Modulus
Cocoa powder	3.78	27.76	0.33
Cocoa butter	0.07	100	-
Cocoa mass	1.66	52.42	-
Carrageenan	17.33	-	1.99
Sucrose	0.10	-	-

2.2. Sample preparations

Reference chocolate (CG0) containing 36% fat was made of 26% cocoa powder, 10.9% cocoa paste, 23.1% cocoa butter and 40% sugar. Chocolate samples used in this study (36% of fat content) were dark chocolates formulated Carrageenan-based hydrogel (CG) with three different level of hydrocolloid namely 3%, 5% and 7%. After tempering process, chocolates were stored in thermostat cabinet at 10ºC for maturation. The analyses were conducted at day 0, 4, 8, and 12 (D). There were 16 samples in this study (Table 2).

Table 2. Name of Chocolate

Name of the Sample				
Hydrocolloid Content	Maturation (Day-)			
	0	4	8	12
0%	CG0D0	CG0D4	CG0D8	CG0D12
3%	CG3D0	CG3D4	CG3D8	CG3D12
5%	CG5D0	CG5D4	CG5D8	CG5D12
7%	CG7D0	CG7D4	CG7D8	CG7D12

2.3. Hydrogel preparations

Hydrogel was prepared by mixing distilled water and Carrageenan with magnetic stirrer with 750 rpm at temperature of 80-90ºC for 5 minutes. Carrageenan proportions used in hydrogel formulation were 0%, 3%, 5% and 7%.

2.4. Chocolate processing

Dark chocolate was produced in two stages of using small scale processing system. The first stage consists of mixing all the main ingredients (cocoa powder, cocoa mass, cocoa butter and sucrose), refining and conching-like process for 10 hours using Santha Grinder. The second stage was conducted in a Premier Wonder Grinder. In this process, chocolate was added with 2% Carrageenan-based hydrogel and then mixed for 5 hours. The chocolate was heated at 60ºC with heat gun for 5 minutes in every 30 minutes of interval. After this process, chocolate was tempered manually following a method developed by Kurniasari et al., [10]. Afterwards, chocolate was molded and vibrated to remove the air bubble. Chocolate was then stored in a thermostat cabinet at 10ºC and tested at day-0, 4, 8 and 12.

2.5. Analytical Methods

2.5.1 Melting point

A 250 ml beaker glass was placed inside a water bath. Water was poured into glass and water bath and conditioned to the same height. The initial temperature of water inside the beaker glass and water bath was set to be 27ºC, measured using a thermocouple. Afterwards, 1 cm x 1 cm x 1 cm chocolate was put in a concave spoon and placed inside beaker glass, submerge into the water. The sample was slowly stirred and temperature of water bath was increased by 1ºC in 1 minute of interval. The chocolate melting point was indicated by the change of chocolate formation inside the spoon that become softer and melts easily.

2.5.2Moisture content

Chocolate samples were heated in the oven at a temperature of 105ºC for 24 hours. The sample was further cooled and put in a desiccator for ± 15 minutes. Chocolate moisture content was determined using thermogravimetric methods (Equation 1)

$$MC\ (wb, \%) = \frac{M0 - M1}{M0} x\ 100\% \quad (1)$$

Where:

Wb = wet basis moisture content, the ratio of the weight of water to the total weight of initial mass

M_1 = Final mass (g)

M_0 = Initial mass (g)

Table 3. Two Way ANOVA

Parameter	Hardness	Melting Point	Particle Size	Lightness	Redness	Yellowness	Hue	Chroma
Sample (S)	*	*	*	*	*	*	-	*
Maturation (M)	*	*	*	*	*	*	-	*
S x M	*	*	*	*	*	*	*	*

*) Significantly different at $p < 0.05$

2.5.3 Particle Size

The measurement of chocolate particle size was conducted according to Fadilah et al., 2022 [8] with slight modification. Approximately 0.5 g of chocolate was melted in the oven at 55°C for an hour and dissolved in 10 ml of vegetable oil. Sample was homogenized by vortex mixing for 1 minute. After mixing, the solution was drip into prep glass and the particle size was measured. Chocolate particles were measured using optical microscope Olympus CX23 equipped with LED lighting system and Optilab camera to capture the chocolate microparticle. The sample was then measured using Image Raster 3 software.

2.5.4 Hardness

Chocolate hardness was measured using Brookfield texture analyzer with probe no. 39 with diameter of 2 mm. The measurement was conducted using compression test with 3 mm target value. The measurement was recorded as load value in gram, then converted to tension in N/mm^2. The conversion is formulated using equation 2.

$$\sigma = \frac{load\ x\ a}{\pi r^2} \quad (2)$$

2.5.5 Color measurement

The chocolate color was tested using a chromameter according to Bangun et al., [9]. The setting used was L*, a*, b*. Color testing was done by placing the chromameter just above the sample and then pressing the measurement button. The L*, a*, b* value can be seen on the screen when the chromameter emit light simultaneously with button pressing. From the a* and b* value, the hue and chroma value can be calculated using equation 3 and 4.

$$\text{hue}^{o} = \tan^{-1}\left(\frac{b^*}{a^*}\right) \text{ x } \frac{360^{\circ}}{(2 \text{ x } \pi)} \quad (3)$$

$$\text{Chroma} = \sqrt{(a^{*2}) + (b^{*2})} \quad (4)$$

2.6. Data analysis

Data was analyzed using IBM SPSS version 25.0 software consist of Analysis of Variance. Prior to the one-way ANOVA test, the homogeneity of the sample was tested using the Levene's test. Tukey test was chosen to determine the differences in sample variations.

3. RESULT AND DISCUSSION

The addition of Carrageenan-based hydrogel influenced some physical characteristics of chocolate. The type of sample and the maturation duration were significantly influenced chocolate hardness, melting point, particle size, lightness, yellowness and chroma. There was strong interaction between sample and maturation duration in chocolate characteristics (Table 3).

3.1. Melting point

Melting point is one crucial parameter that indicates chocolate quality. The polymorphic formation of fat during tempering process affects the stability of final chocolate product [2] [11]. Chocolate characteristics are also significantly influenced by its moisture content. High moisture content in chocolate forms sugar network which can maintain chocolate structure thus resulted in a higher melting point. Chocolate with the addition of Carrageenan-based hydrogel showed a higher melting point. In can be observed from Figure 1. the higher the proportion of the Carrageenan-based hydrogel, the higher the melting point of chocolate.

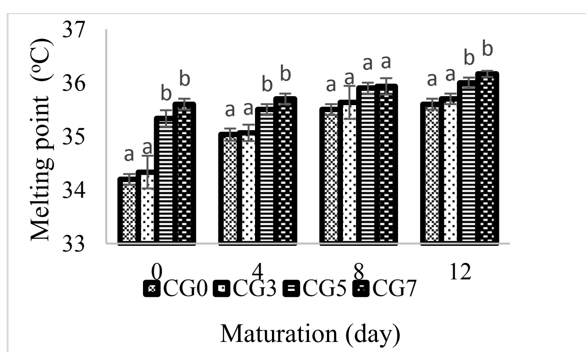

Figure 1. Melting point of chocolate formulated with Carrageenan-based Hydrogel

Overall, chocolates melting temperature were above 34°C. According to Stortz & Marangoni [4] chocolate melting point that higher that 33,8°C can be categorized as heat resistant chocolate. The duration of maturation also influenced the increase of melting point. Chocolate crystal formation reached a stable state after approximately 7 days storage. To produce a good quality of heat resistant chocolate, this melting point result, however should be conformable to the other chocolate properties.

3.2. Moisture content

Moisture content is a parameter that have direct correlation with chocolate melting point, hardness, flowability and appearance. A good chocolate should be lower than 2% in moisture content [12]. Carrageenan-based hydrogel contains high moisture content. High moisture content in chocolate can cause agglomeration that influences chocolate microscopy and change the final chocolate product [13]. In this study, all chocolates contained moisture content lower than 2%.

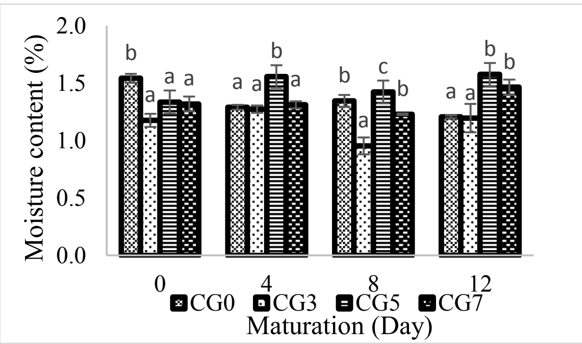

Figure 2 Moisture content of chocolates formulated with Carrageenan-based Hydrogel

3.3. Hardness

Chocolate hardness is influenced by fat content, moisture content, particle size and tempering process [14]. The result of this study showed that the higher the carrageenan content in hydrogel, the harder the chocolate texture. Chocolate hardness has positive correlation with chocolate moisture content. The addition of hydrogel into chocolate created structure chain that binds particle thus result in higher hardness and viscosity [4].

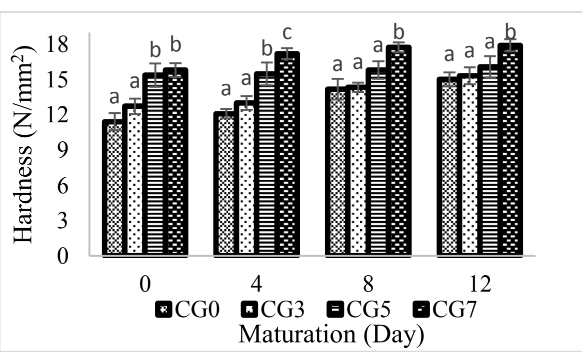

Figure 3 Hardness of chocolate with Carrageenan-based Hydrogel

3.4. Particle size

Chocolate particle size is important to determine the quality of chocolate. Particle size can be directly perceived when chocolate is consumed. Fine chocolate has small particle size and the refining process influences it [15, 16, 17]. The particle size of chocolate with Carrageenan-based hydrogel was bigger than 30 µm. This might be due to the addition of hydrogel that contained water that form sticky patches and agglomerated particle size [3, 18]

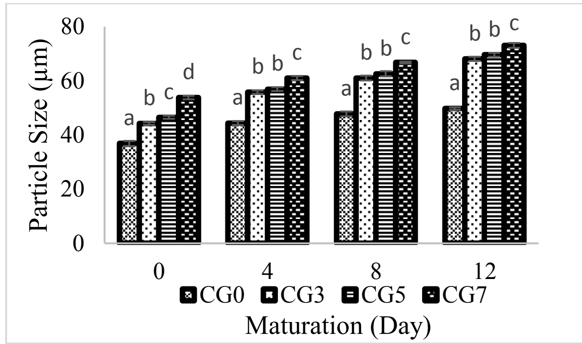

Figure 4 Particle size of chocolate with Carrageenan-based Hydrogel

3.4. Color

Color represents chocolate appearance. Several factors that influence chocolate color are materials, production method, tempering process [19] and storage duration [20]. Good chocolate has an even color and glossy. Chocolate with higher carrageenan content in hydrogel showed a tendency to be higher in lightness value. The redness, yellowness, hue and chroma of chocolate were fluctuated.

4. CONCLUSION

Chocolate formulated with Carrageenan-based hydrogel exhibited higher melting point, moisture content and hardness. The chocolate particle was categorized as gritty particle. The formulation has potential to be developed as HRC, however further research to optimize the chocolate characteristics should be done.

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REFERENCES

[1] K. Gunners, 7 Proven Health Benefits of Dark Chocolate, 2018, https://www.healthline.com, accessed on 9 June 2022

[2] M. Lipp, and Anklam, Review of Chocolate Butter and Alternative Fats for Use in Chocolate Part A, Compositional Data, Journal of Food Chemistry, 1998, 73-97.

[3] S.T. Beckett, The Science of Chocolate, RSC Publishing, Cambridge, UK Vol 26, 2008.

[4] T.A. Stortz, and Marangoni, A.G, Heat resistant chocolate, Trends Food Sci. Technol., vol. 22, 2011, pp. 201-204

[5] Lillah, A. Asghar, I.Pasha, G. Murtaza, M. Ali, Improving heat stability along with quality of compound dark chocolate by adding optimized cocoa butter substitute (hydrogenation palm kernel stearin) emulsion, LWT-Food Science and Technology 80, 2017, pp. 531-536.

[6] R.Nafingah, J. Kurniasari, A. Cahyani, E. Hermayani, A.D. Saputro, Investigating the impact of Palm Sap Sugar proportion and fat content on heat stability of Milk Chocolate, The 3rd International Symposium on Agricultural and Biosystem Engineering, IOP Conf. Series: Earth and Environmental Science 355, 2019, 012043. doi:10.1088/1755-1315/355/1/012043

[7] F.P. Francis, R. Chidambaram, Hybrid hydrogel dispersed low fat and heat resistant chocolate, Journal of Food Engineering, vol. 256, 2019, pp. 9-17

[8] M.A.N. Fadilah, A.D. Saputro, S.K. Bangun, S. Rahayoe, Y.D. Prasetyatama, A.D. Setiowati, Increasing the Melting Temperature of Chocolate by Adding Xanthan Gum-Based Hydrogel: A Preliminary Study, 2nd International Conference on Smart and Innovative Agriculture. Atlantis Press, 2022, Pp. 174-179.

[9] S.K. Bangun, A.D. Saputro, M.A.N. Fadilah, S. Rahayoe, Y.D. Prasetyatama, A.D. Setiowati, A Preliminary study: the addition of konjac glucomannan-based hydrogel into chocolate increases the melting point of chocolate, IOP Conference Series: Earth and Environmental Science Vol. 1038 (1), 2022, 012073

[10] J. Kurniasari, A. Cahyani, R. Nafingah, S. Rahayoe, E. Hermayan, A.D. Saputro, The use of oven as a device to temper molten Dark Chocolate. The 3rd International Symposium on Agricultural and Biosystem Engineering, IOP Conf. Series: Earth and Environmental Science 355, 2019, 012042 doi:10.1088/1755-1315/355/1/012042

[11] E. Ostrowska-Ligeza, A. Marzec, A. Gorska, M. Wirkowska-Wojdyla, J. Brys,A. Rejch, K. Czarkowska, A comparative study of thermal and textural properties of milk, white and dark chocolates, Thermochimica Acta 671, 2019, pp. 60-69.

[12] S.T. Beckett. Chocolate flow properties. Industrial chocolate manufacture and use (4th ed.) (2009) 224-246

[13] A.D. Saputro, D.V. Walle, B.A. Caiquo, M. Hinneh, M. Kluczykoff, and K. Dewettinck, Rheological behaviour and microstructural properties of dark chocolate produced by combination of a ball mill and a liquefier device as small scale chocolate production system, LWT-Food Science and Technology vol. 100, 2019, pp. 10–9

[14] E. O. Afoakwa, Chocolate Science and Technology, A John Wiley & Sons, Ltd., Publication, York UK, 2010.

[15] A.D. Saputro, D.V. Walle, S. Kadivar, M.D. Sintang, P.V. Meeren, & K. Dewettinck, Investigating the rheological, microstructural and textural properties of chocolates sweetened with palm sap-based sugar by partial replacement, Eur Food Res Technol, 2017, pp. 1729–1738.

[16] A. Cahyani, J. Kurniasari, R. Nafingah, S. Rahayoe, E. Harmayani, A.D. Saputro, Determining casson yield value, casson viscosity and thixotropy of molten chocolate using viscometer, The 3rd International Symposium on Agricultural and Biosystem Engineering. IOP Conf. Series: Earth and Environmental Science 355, 2019, 012041 doi:10.1088/1755-1315/355/1/012041

[17] V. Prosapio, I.T. Norton, Development of fat reduced chocolate by using water-in-cocoa butter emulsions. Journal of Food Engineering, 261, 2019, pp. 165-170 10.1016/j.jfoodeng.2019.06.018

[18] A.D. Saputro, D.V. Walle, R.P. Aidoo, M.A. Mensah, C. Delbaere, N. De Clercq, J. Van Durme and K. Dewettinck, Quality attributes of dark chocolates formulated with palm sap-based sugar as nutritious and natural alternative sweetener, Eur. Food Res. Technol. 243, 2016, pp. 177–91

[19] A.D. Saputro, D.V. Walle, S. Kadivar, M.D. Sintang, P.V. Meeren, and K. Dewettinck Investigating the rheological, microstructural and textural properties of chocolates sweetened with palm sap-based sugar by partial replacement, Eur Food Res Technol, 2017, pp. 1729–1738.

[20] J.V. Popov-Raljiü and J.G. Laliþiü-Petronijeviü, Sensory Properties and Color Measurements of Dietary Chocolates with Different Compositions During Storage for Up to 360 Days. Sensors vol. 9 (3), 2009.