STUDY ON THE INFLUENCE OF PROCESSED COCOA BUTTER TO THE PHYSICAL PROPERTIES OF CREAM FOR HEELS FORMULA USING MIXTURE DESIGN OF EXPERIMENT

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ABSTRACT – *Cocoa butter (CB) undergo several process stages and being categorized as pure prime pressed or deodorized before being used in chocolate manufacturing. The physical characteristics of the processed cocoa butter are slightly different to the fresh cocoa butter (FCB), especially melting point, pH and percentage of fatty acid composition. In this study, we used three types of cocoa butter, which are the pure prime pressed cocoa butter (PPPCB), deodorized cocoa butter (DCB) and fresh cocoa butter (FCB), to formulate the creams for heels. The physical properties (pH, viscosity and stability) of the formulated cream were measured in finding the influence of these cocoa butter. Although, the physical properties of these cocoa butter varied, the results showed that PPPCB, DCB and FCB have no influence to the physical properties of the formulated cream. Therefore, the cream for heels can be formulated with any types of cocoa butter as the properties of final products are similar to each other.*

***Key words**:* Cocoa butter, cream for heels, formulation, mixture design of experiment

INTRODUCTION

Cocoa butter was used as the main ingredients in formulation of cream for cracked heels made from cocoa butter. Previously, the formulation and performance of cream for treatment of cracked heels containing high content of cocoa butter had been reported (Karim, A.A. and Abdullah, N.A., 2012a; Karim, A.A. and Abdullah, N.A, 2012b; Karim, A.A and Abdullah, N.A, 2012c; Karim, A.A. and Abdullah, N.A, 2014). It was found out that presence of cocoa butter in the cream formula can enhanced the alleviation of cracked heels (Karim, A.A. and Abdullah, N.A, 2012a) and skin condition (Gasser, 2008).

Cocoa butter is solid at room temperature and melts rapidly at body temperature which makes the butter is very suitable to act as carrier for active ingredients mean to deliver onto the skin. The hardness can be characterized at temperature below 25^{o}C as in Figure 1. The heat resistant of cocoa butter can be observed at temperature of 25-30^{o}C. In the range of 27 to 33 °C, the intensive melting of cocoa butter occurs to bring the cooling sensation (Torbica, 2005). A high SFC value at temperatures above 35 °C causes a waxy taste (Torbica, 2005) or feeling on skin surface.

During formulation of the cream for heels, we come across two types of cocoa butter that are being used in the manufacturing, i.e. pure prime pressed cocoa butter and deodorized cocoa butter. Both are available commercially from the cocoa grinders. The PPPCB is cocoa butter that being expelled from the cocoa paste using hydraulic pressing machine. The cocoa paste is produced from the roasted cocoa beans that sometime undergo alkalization process. Meanwhile, the DCB is furthered treated pure prime pressed cocoa butter under high steam temperature (130-180^{o}C) in vacuum condition (1-5 mbar) for 15-30 min. The main purpose of deodorizing process is to remove the off-flavor. In overall, the physical properties of PPPCB and DCB remained the same although underwent the mentioned process, except for the 0.5% reduction of free fatty acid (Talbot, 2014). Additionally, we also used FCB, which was obtained directly from the unfermented cocoa bean using screw type mechanical expeller machine. The FCB was a by-product of polyphenols extraction process from unfermented cocoa beans of various clones. The FCB was usually produced in laboratory scale and not commercially available in the market.

In this short study, we want to determine whether different types of cocoa butter affect the physical properties of cocoa cream formulated for cracked heels. The result could be used as guidance to produce this cream in large scale.

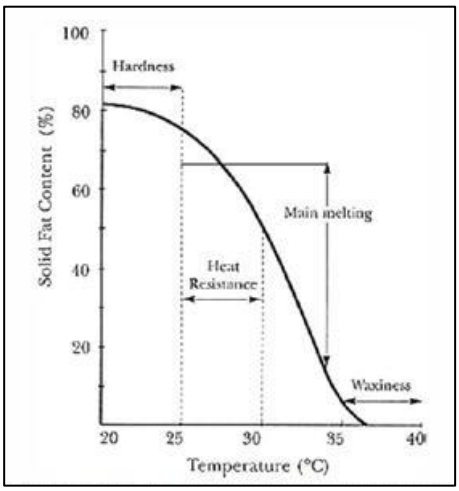

Figure 1: Cocoa butter SFC curve depending on Temperature (Torbica, 2005)

MATERIALS AND METHODS

Sample

Three types of cocoa butter were used for comparison. The PPPCB and DCB were purchased from the cocoa processing in Malaysia. The FCB was obtained from the laboratory using expeller machine. The samples were put in the container separately in room temperature until used.

Physical properties of cocoa butter

The following method was adapted from Analytical Service Laboratory (2010). The method was described in brief.

pH – The cocoa butter was melt in the oven at 50ºC. About 50 g of sample was weighed and added to equal amount of distilled water. The mixture was stirred in the water bath. Then, the water layer was separated and cool to 20ºC. The filtrate was measured with pH meter against calibration buffer.

Solid fat content – The measurement was carried out using pulsed nuclear magnetic resonance unit. The sample was melt at 50ºC in a glass container and shake vigorously until homogenous. Then, the sample was poured into measuring tube label for each of the measurement temperature (20ºC, 25 ºC, 30ºC, 35ºC, 37.5 ºC, and 40 ºC). All the labelled measuring tubes were immersed in the water bath and treated with the following temperature; 80ºC, 60ºC (5 min), 0ºC (90 min), 26ºC (40 h), 0ºC (90 min) and measuring temperature (60 min). The measurement was carried out immediately after the temperature and time was achieved.

Iodine value – About 0.4 g of cocoa butter was weighed in 250 mL bottle. The cocoa butter was dissolved in 15 mL of carbon tetrachloride. Then, 15 mL of Wij's reagent was added to the sample and placed in the dark for one hour. Prior to the titration with the sodium thiosulphate, 20 mL of potassium iodide and 150 of water were added to the mixture. The starch solution was added after the yellow color disappeared. The titration ended with the disappearing of blue color with vigorous shaking.

Melting temperature - The melting profile was obtained using Different Scanning Calorimeter (DSC, Pelkin Elmer 7). About 3-5 g of sample was weighed into DSC pan. Then, the DSC pan was treated with the following temperature: 60ºC for 30 min, 0ºC for 90 min, 26ºC for 40 h and 0ºC for 90 min. Finally, the DSC pan was transferred to DCS head (25ºC, 5 min). The measurement was carried out at the heating rate 20ºC/min from 25ºC to maximum of 50ºC.

Preparation of cream for heels

The formulation was adapted from Karim, A.A. and Abdullah, N.A (2012b). Cocoa butter comprised of at least 20% of the overall percentage of the formula. The PPCB, DCB and FCB were weighted according to the cocoa butter composition as in Table 3. Other ingredients (79 wt%) were water, ceteth-20, cetyl alcohol, glyceryl stearate, steareth-20, polyethylene glycol sorbitan monostearate, glycerin, sorbitol, alcohol (and) aqua (and) *Onopordum acanthium* flower/leaf/stem extract, aqua (and) *Fagus sylvatica* bud extract, acrylates/c10-30 alkyl acrylate cross polymer, fragrance and preservatives. To make the cream, the ingredients were divided into three phases, i.e. water, oil and active ingredients. The water and oil phases were heated up to 65ºC, in separate beaker, and then, were homogenized together until smooth. The cream was mixed with active ingredients with propeller until all the ingredients dissolved. Each cream was labelled according to the run order in Table 3.

Mixture Design of Experiment – MINITAB Software version 14.12 was used to design the experiment and find the interaction of the variables. In this study, we used extreme vertices design. The components of mixture are PPPCB, DCB and FCB (Table 3). The dependent variables measured were pH, viscosity (cPs) and demixing velocity (mm/day). Viscosity was

obtained using spindle No.7 (Brookfield Viscometer). Demixing velocity is a measurement of stability obtained using Lumifuge 116 (LUM GmbH, German). The method was described in detail in previous (Karim, A.A. and Abdullah, N.A., 2012b).

Statistical of Analysis **–** All experiments were performed in triplicates and data was tabulated by mean values. The ANOVA was carried out to determine the significances of physical properties data at p-value less than 0.05 ($p<0.05$).

RESULTS AND DISCUSSIONS

The physical properties of PPPCB, DCB and FCB were measured and summarized in Table 1. The pH of FCB was slightly lower than PPPCB and DCB. Although the FCB was more acidic compared to the other two cocoa butters, the pH was almost near to pH 5.5 which was recommended for topical product to maintain skin barrier (Schmid-Wendtner, M.-H. and Korting H.C., 2006).

Table 1: Selected Physical Properties of Cocoa Butter.

Physical Properties[1]	*Cocoa butter*			*Torbica (2006)*	*Talbot (2014)*[2]	*Standard specification MS1118:1988*[3]
	PPPCB	*DCB*	*FCB*			
pH	6.05	6.39	5.43	-	-	-
Solid fat content (%)						-
at 20°C	77.30±0.32[a]	76.67±0.09[b]	77.99±0.70[a]	67	min 76	81.9±1.63
at 25 °C	64.96±0.12[c]	66.98±0.17[b]	70.01±0.12[a]	56	-	76.6±6.01
[*]at 30°C	46.12±0.42[b]	44.36±0.07[c]	52.90±0.16[a]	38	min 42	61.5±6.65
at 35°C	1.08±0.39[abc]	1.62±0.19[a]	0.62±0.15[c]	0	min 1	0-0.2
at 37.5 °C	0.23±0.72	-0.41±0.41	-0.07±0.38			0
at 40 °C	0.16±0.36	-0.18±0.31	-0.00±0.48			-
Iodine value	34.98±0.05[a]	34.39±0.28[b]	33.96±0.21[b]	35	34-38	32-38
Melting temperature (°C)	36.07±0.47[abc]	35.40±0.47[c]	37.07±0.94[a]	33-37	-	32-35

[a b c] denotes different alphabets are significantly difference at $p<0.05$

[1] using standard protocols of Analytical Service Laboratory (Cocoa Innovation & Technology Centre, Malaysian Cocoa Board), [2] for deodorized cocoa butter, [3] on pure prime pressed cocoa butter; * main melting point

The FCB has similar percentage of solid fat content at 20°C with PPPCB (Figure 2), which was higher than the DCB, and revealed that FCB and PPPCB were harder compared to DCB. Hard form of cocoa butter is suggested for the good carrier of active ingredients of cream to retain the activity until being applied onto the skin (Kim, et al, 2020).

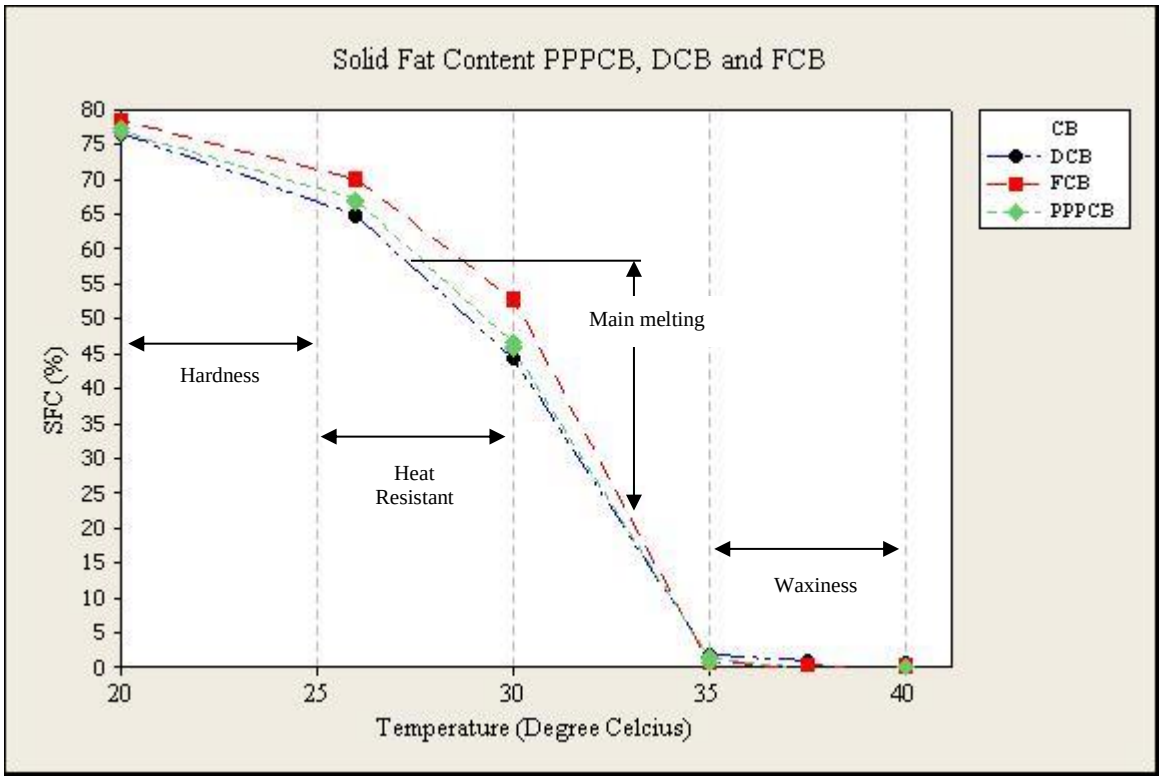

Figure 2: Solid Fat Content of PPPCB, DCB and FCB.

In comparison with PPPCB and DCB, the solid fat content profile of FCB at 25ºC to 30ºC was the highest. This result showed that FCB has the highest heat resistant properties. Theoretically, higher solid fat content indicated that the cocoa butter has extra content of long chain lipid (Torbica, 2005), where FCB has, as reported in Table 2. Cocoa butter with higher solid fat content is beneficial in cream formula, where the active ingredients are released slowly onto the skin, thus giving the skin an extra time to absorb the active ingredients (Kim, et al, 2020; Septiyanti et al, 2021). In addition, presence of oleic acid in cocoa butter enhanced the permeability of the epidermis (Lin, et al, 2018) for active ingredient to get absorb.

Table 2: Fatty Acid Composition of Cocoa Butter.

Fatty acid			*Concentration (%) in cocoa butter*			
Type of chain	*Lipid number*	*Common name*	*PPPCB*	*DCB*	*FCB*	*Frank, J. (2014)*
	C8	*caprylic acid*	0.004	-	-	
medium	C10	*capric acid*	0.004	-	-	
	C12	*lauric acid*	0.003	-	0.009	
	C14	*myristic acid*	0.091	0.098	0.055	
	C14:1	*myristoleic acid*	-	-	0.006	
	C15	*pentadecanoic acid*	0.026	0.035	0.028	
	C16	***palmitic acid***	25.529	25.354	28.802	26.0
long	C16:1	*palmioleic acid*	0.212	0.201	0.254	0.3
	C17	*heptadecanoic acid*	0.227	0.236	0.369	
	C17:1	*cis-10-heptadecanoic acid*	-	0.013	0.022	
	C18	***stearic acid***	37.205	37.614	38.108	34.5
	C18:1n9c	***oleic acid***	32.527	32.478	29.810	34.5

	C18:2n6c	*linoleic acid*	2.628	2.356	0.587	3.2
	C18:3n3A	*α-linoleic acid*	0.166	0.176	0.014	
	C20	*arachidic acid*	1.056	1.139	1.121	1.0
	C20:1n9	*cis-11-eicosenoic acid*	0.042	0.039	0.024	
	C20:3n6	*cis-8,11,14-eicosatrienoic acid*	-	-	0.012	
	C20:5n3	*cis-5,8,11,14,17-eicosapentaenoic acid*	0.281	0.262	0.259	
very long	C23	*tricosanoic acid*	-	-	0.328	
	C24:1n9	*nervonic acid*	-	-	0.193	

Bold fatty acids are major component in the cocoa butter forming the crystallization triglyceride fat structure (Torbica, 2005).

The cream for heels was formulated with about 20% of oil phase comprised of combination of the three types of cocoa butter as in Table 3. The results showed different types of cocoa butter give equally similar physical properties of the final product. The final pH of the products were insignificant different despite different type of cocoa butter used in the formula. Topical leave-on product was recommended to have slightly acidic to maintain the optimal pH of skin at pH4.7-5.75 (Lambers et al, 2006) in order to maintain skin hydration and protection from bacteria (Fiers, 1996). We were expecting that using FCB will produced low viscosity of the cream due to the presence of long chain of fatty acid, such as in Run Order 4, which however insignificantly different from other cocoa butter combination. Other combination such as equal amount of each types of cocoa butter can also produce lower viscosity cream such as in Run Order 3. Processed cocoa butter (PPPCB; Run Order 6 and DCB; Run Order 7) seem to increase the viscosity of the products compared to FCB alone, but the difference was insignificant. The viscosity and the stability of the products were not significantly affected by different types of cocoa butter used in the formula within these amount. Further experimental study is suggested to be carried out if other composition of cocoa butter to be used in the cream formula. This is due to the limitation of the experimental design (extreme vertices design) chosen, where it cover only small portion of the simplex within the selected composition (Minitab Support, 2022).

Table 3: Mixture Design of Experiment for Cocoa Butter Composition in Cream for Heels and its Effect on the pH, Viscosity and Stability of the Cream.

		Cocoa butter composition (g)			*Dependant variables*		
Run Order	*Point Type*	*PPPCB*	*DCB*	*FCB*	*pH*	*Viscosity*	*Demixing velocity (mm/day)*
1	-1	3.35	3.35	13.40	5.01	19730	2.376
2	-1	13.40	3.35	3.35	4.95	19680	1.737
3	0	6.70	6.70	6.70	4.83	18970	1.909
4	1	0	0	20.10	4.58	18940	0.968
5	-1	3.35	13.40	3.35	4.66	24100	2.074
6	1	20.1	0	0	4.86	23330	0.354
7	1	0	20.10	0	4.61	26590	1.590

Using Mixture Experimental of Design (Extreme Vertices Design);
Components: 3, Process variable: 0, Design points: 7, Design degree: 1, Mixture total: 20.10;
FCB is fresh cocoa butter, PPPCB is pure prime pressed cocoa butter, and DCB is deodorized cocoa butter.

CONCLUSIONS

In conclusion, various type of cocoa butter in this study, i.e. PPPCB, DCB and FCB has slightly physical characteristic differences, although, give similar properties of cream formulated within these specific range of cocoa butter composition.

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