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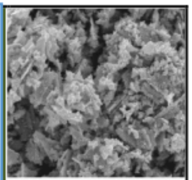

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Effect of Different Types of Emulsifiers on the Physical Characteristics and Fat Bloom Stability of Dark Chocolate with Cocoa Butter Alternatives

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ABSTRACT

An emulsifier is incorporated to delay the fat bloom formation and improve the overall quality of dark chocolate. This study aims to investigate the effects of different emulsifiers on the physical properties and stability of fat bloom in dark chocolate with cocoa butter alternatives (CBAs). Dark chocolate formulations were prepared containing different emulsifiers like lecithin, glycerol monostearate and a combination of both with CBAs like cocoa butter substitute (CBS) and cocoa butter replacer (CBR). Physical property analyses included hardness, snap texture, melting behaviour, pH, and water activity. The whiteness index was used to measure fat maturity. The results showed that the addition of lecithin, CBS, and CBR decreased the hardness value. Meanwhile, samples of chocolate formulation with the addition of glycerol monostearate (CB+GMS), and chocolate formulation with the addition of lecithin and glycerol monostearate (CB+2E), increased the hardness and snap texture. Besides, CBR increased the peak temperature, and emulsifiers increased the peak temperature in samples with CB and CBR while decreasing the melting enthalpy. Furthermore, the addition of CBA and emulsifiers improved the stability of the fat bloom. Therefore, mixed emulsifiers, which have favourable physical properties and higher fat bloom stability, are ideal for use in chocolate production. CBAs have the potential for practical application in chocolate production to improve fat bloom stability.

INTRODUCTION

Dark chocolate is a combination of cocoa powder and sugar dispersed in cocoa butter (CB). Cocoa butter alternatives (CBAs) such as cocoa butter substitute (CBS) and cocoa butter replacer (CBR) are used as lower-cost substitutions for CB. Formation of fat bloom is the primary concern in dark chocolate, which is associated with a white surface and loss of initial gloss of the surface. Polymorphic transition and phase separation theories are the most accepted mechanisms explaining fat bloom occurrence. The polymorphic transition mechanism explains the transition from a less stable βV to a more stable βVI form [1]. Phase separation theory explains that the high melting triacylglycerols tend to migrate to the surface of the chocolate and recrystallise on the chocolate surface [2].

As fat bloom inhibitors, emulsifiers such as lecithin, monoglyceride, and diglyceride are commonly added to chocolate production. However, there are fewer comprehensive studies investigating the effect of lecithin, glycerol monostearate and mixed emulsifiers on the properties of dark chocolate with different CBAs. This study aims to evaluate the effect of different

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types of emulsifiers on the fat bloom stability and physical characteristics of dark chocolate with cocoa butter alternatives (CBS and CBR).

MATERIALS AND METHODS

Cocoa butter was purchased from Take it Global Sdn. Bhd. (Penang, Malaysia). Cocoa butter substitutes and replacer were purchased from Baking Empire (Kelantan, Malaysia) and Lyn Happy Trade (Selangor, Malaysia). Cocoa powder and icing sugar were purchased from Bake with Yen (Selangor, Malaysia). Glycerol monostearate was purchased from Evahem (Selangor, Malaysia). Soy lecithin was provided by Lembaga Koko Malaysia Nilai (Negeri Sembilan, Malaysia). Dark chocolate samples were prepared in different formulations with different types of emulsifiers and CBAs based on **Table 1**. For this purpose, the melted cocoa butter and the other ingredients were continuously refined and conched in a chocolate melanger for 6 hours. The marbling tempering technique was then used to temper the liquid chocolate. The tempered chocolate was then moulded and stored at 13°C for an hour. The chocolate was then demoulded and stored at 25°C.

Table 1. The formulation of dark chocolate samples.

Ingredient	Ingredient (%)						
	Icing sugar	CB	CBS	CBR	Cocoa powder	Soy lecithin	GMS
Control	40.0	36.0	-	-	24.0	-	-
CB+L	39.4	36.0	-	-	24.0	0.6	-
CB+GMS	39.4	36.0	-	-	24.0	-	0.6
CB+2E	39.4	36.0	-	-	24.0	0.3	0.3
CBS	40.0	26.0	10.0	-	24.0	-	-
CBS+L	39.4	26.0	10.0	-	24.0	0.6	-
CBS+GMS	39.4	26.0	10.0	-	24.0	-	0.6
CBS+2E	39.4	26.0	10.0	-	24.0	0.3	0.3
CBR	40.0	26.0	-	10.0	24.0	-	-
CBR+L	39.4	26.0	-	10.0	24.0	0.6	-
CBR+GMS	39.4	26.0	-	10.0	24.0	-	0.6
CBR+2E	39.4	26.0	-	10.0	24.0	0.3	0.3

The hardness was measured using a texture analyser fitted with an HDP/BSK probe. While the snap texture was determined using a texture analyser with a three-point bend rig probe. Melting behaviour was measured using Differential Scanning Calorimetry (DSC). pH was determined using pH meter. Water activity was measured using a water analyser. Fat bloom assessment was conducted for 30 days under constant temperature and temperature cycling conditions between 25°C and 30°C. The whiteness index was used to determine the fat bloom formation with the following formula:

$$WI = 100 - [(100 - L*)^2 + a*^2 + b*^2]^{1/2}$$

L* = lightness value; a* = green-red colour value; b* = blue-yellow colour value.
One-way ANOVA and Turkey test were used to analyse the data with a significance level of 5%.

RESULT AND DISCUSSION

Water activity (a_w)

Table 2 shows no significant difference ($p>0.05$) between samples. The chocolate samples could be stable from bacteria due to the low free water availability ($a_w<0.6$) for biological reactions of spoilage microorganisms.

pH

Table 2 shows the control sample exhibited significant differences ($p<0.05$) from other formulations. The pH of chocolate significantly increased ($p<0.05$) with the addition of the emulsifiers, likely because of the apolar characteristic of emulsifiers [3]. The apolar characteristic enables emulsifiers to interact with the hydroxyl group of sucrose, hence decreasing the acidic behaviour of chocolate.

Table 2. Average water activity and pH of control, cocoa butter substitute (CBS), and butter replacer (CBR) with different types of emulsifiers.

Sample	Water Activity (a_w)	pH
Control	0.4917 ± 0.0160^{a}	7.64 ± 0.00^{f}
CB+L	0.4660 ± 0.0069^{a}	7.95 ± 0.02^{cde}
CB+GMS	0.4903 ± 0.0025^{a}	7.96 ± 0.05^{bcde}
CB+2E	0.4925 ± 0.0035^{a}	7.88 ± 0.06^{e}
CBS	0.4925 ± 0.0035^{a}	8.01 ± 0.03^{abcd}
CBS+L	0.5260 ± 0.0035^{a}	7.96 ± 0.01^{bcde}
CBS+GMS	0.5273 ± 0.0076^{a}	8.04 ± 0.07^{abc}
CBS+2E	0.5157 ± 0.0602^{a}	7.96 ± 0.02^{bcde}
CBR	0.4460 ± 0.0177^{a}	7.90 ± 0.04^{de}
CBR+L	0.5040 ± 0.0642^{a}	8.02 ± 0.04^{abc}
CBR+GMS	0.4520 ± 0.0122^{a}	8.11 ± 0.03^{a}
CBR+2E	0.4623 ± 0.0265^{a}	8.07 ± 0.02^{ab}

Mean ± standard deviation within a column with different superscripts indicates a significant difference ($p<0.05$).

Hardness and snap texture

Table 3 shows that the addition of GMS significantly increased ($p<0.05$) the hardness of sample CB and CBS due to it speeding up the crystal creation, promoting a denser network structure [4]. Conversely, chocolate with CBAs decreased the hardness of the chocolate due to the TAG content. When CBA and CB are combined, a eutectic state is created, which causes chocolate products to soften and the phases to separate [5]. The texture of chocolate with CBS becomes softer because it contains a higher proportion of unsaturated fat. In addition, the different solid fat content (SFC) also affects the changes in polymorphism [6]. Therefore, the lower SFC of CBR is an indicator of the lower hardness of the chocolate.

Table 3. The average hardness and rupture tension values of control are cocoa butter substitute (CBS) and butter replacer (CBR) with different emulsifiers.

Sample	Hardness (kg)	Rupture tension ($gf\ cm^{-2}$)
Control	17.52 ± 1.54^{b}	12.22 ± 3.24^{cde}
CB+L	9.18 ± 0.16^{de}	11.97 ± 1.94^{cde}
CB+GMS	22.36 ± 1.41^{a}	25.25± 4.32^{a}
CB+2E	20.92 ± 0.48^{a}	23.94 ± 5.19^{a}
CBS	8.45 ± 0.40^{e}	7.82 ± 0.09^{e}
CBS+L	7.99 ± 0.77^{e}	14.84 ± 1.09^{cd}
CBS+GMS	12.51 ± 0.16^{c}	8.48 ± 0.49^{de}
CBS+2E	8.35 ± 0.82^{e}	7.03 ± 0.90^{e}
CBR	10.87 ± 0.28^{cd}	23.42 ± 0.24^{ab}
CBR+L	20.50 ± 0.24^{a}	13.18 ± 0.42^{cde}
CBR+GMS	9.78 ± 1.02^{de}	17.22 ± 1.94^{bc}
CBR+2E	9.89 ± 0.29^{de}	15.91 ± 0.62^{c}

Mean ± standard deviation within a column with different superscripts indicates a significant difference (p<0.05).

Table 3 shows that adding GMS and 2E significantly increased the rupture tension. This is because GMS will accelerate the crystallisation, increasing hardness, and consequently contributing to the improvement in snap texture. The addition of CBS and CBR showed different effects on chocolate with different emulsifiers. This may be due to the eutectic behaviour of different fatty acid content in the blended [1].

Melting behaviour

Table 4 shows that the addition of CBR increased significantly the T_{peak}, consistent with Syafira et al. [9]. The control sample exhibited a higher peak temperature (T_{peak}), compared to the literature, ranging from 32°C to 33°C [7,8]. The addition of emulsifiers also significantly increased the T_{peak}. This is because lecithin can enhance the crystallisation kinetics and promote stable β polymorph [10]. While GMS, being a high melting point emulsifier and seeding agent, elevates the melting point and promotes the βV crystals formed [2].

Table 4. Overview of the melting profile of CB, CBR, CBR L, CBR GMS and CBR 2E.

ormulations	Temperature (°C)			Enthalpy, ΔH (J/g)
	T_{onset}	T_{peak} (°C)	T_{end}	
Control	29.660 ± 0.017^{a}	36.680 ± 0.017^{de}	44.047 ± 0.023^{abc}	47.954 ± 0.053^{a}
CB+L	32.890 ± 2.140^{a}	40.670 ± 1.456^{a}	45.737 ± 1.408^{a}	33.640 ± 5.390^{b}
CB+GMS	31.200 ± 0.132^{a}	39.853 ± 0.168^{abc}	45.440 ± 1.740^{a}	34.784 ± 0.537^{ab}
CB+2E	32.490 ± 2.280^{a}	39.970 ± 1.860^{abc}	45.830 ±1.820^{a}	27.690 ± 2.050^{bc}
CBS	31.300 ± 2.340^{a}	36.467 ± 0.180^{de}	41.067 ± 0.583^{cde}	17.350 ± 8.670^{cde}
CBS+L	30.727 ± 0.892^{a}	36.333 ± 0.577^{de}	40.713 ± 0.337^{cde}	14.820 ± 3.050^{cde}
CBS+GMS	30.637 ± 0.892^{a}	35.087 ± 0.150^{e}	39.327 ± 1.005^{de}	14.400 ± 4.590^{cde}
CBS+2E	30.930 ± 2.150^{a}	34.667 ± 0.665^{e}	44.987 ± 00.295^{e}	11.090 ± 8.240^{e}
CBR	31.643 ± 0.099^{a}	40.143 ± 0.170^{ab}	44.987 ± 0.295^{ab}	13.975 ± 1.135^{de}
CBR+L	32.610 ± 0.277^{a}	40.270 ± 0.292^{ab}	43.943 ± 0.283^{abc}	27.197 ± 0.580^{bcd}
CBR+GMS	30.963 ± 0.786^{a}	37.857 ± 0.472^{cd}	42.300 ± 1.420^{bcde}	16.220 ± 3.920^{cde}
CBR+2E	30.643 ± 0.046^{a}	38.173 ± 0.166^{bcd}	43.067 ± 0.767^{abcd}	18.050 ± 3.750^{cde}

Mean ± standard deviation within a column with different superscripts indicates a significant difference (p<0.05).

Whiteness index

Table 5 indicates no significant difference (p>0.05) in WI values for all dark chocolate samples stored at 25°C as 25°C is inadequate to induce the cocoa butter melting. **Table 6** shows the control sample exhibited the lowest stability with significant WI values increase on day 15, followed by CB+GMS on day 20, and CB+L and CB+2E on day 25. This indicates that emulsifiers enhance the fat bloom stability of dark chocolate due to it retarding the polymorphic transitions of βV to βVI crystal form [11]. Emulsifiers are amphiphilic and can adsorb on both fat and sugar, forming a three-dimensional network, trapping the crystals within it, and elevating the thermal resistance [8]. Meanwhile, the addition of CBAs also enhances fat bloom stability, likely due to the more complex crystalline structure in the CBR chocolate [6] and the Incompatibility between CBS and CB [12].

Table 5. The whiteness index of all dark chocolate samples stored under constant temperature for 30 days.

Day	Whiteness Index											
	control	CB+L	CB+GMS	CB+2E	CBS	CBS+L	CBS+GMS	CBS+2E	CBR	CBR+L	CBR+GMS	CBR+2E
0	24.60 ± 0.29^{a}	25.21 ± 0.19^{a}	24.98 ± 0.15^{a}	25.05 ± 0.19^{a}	25.74 ± 1.82^{a}	26.28 ± 1.58^{a}	26.89 ± 1.81^{a}	26.51 ± 1.81^{a}	27.80 ± 2.71^{a}	29.50 ± 0.32^{a}	29.07 ± 3.28^{a}	26.13 ± 0.33^{a}
5	25.59 ± 0.98^{a}	25.48 ± 0.36^{a}	25.96 ± 1.14^{a}	25.88 ± 0.18^{ad}	25.60 ± 1.52^{a}	26.45 ± 3.03^{a}	26.16 ± 1.45^{a}	26.13 ± 1.07^{a}	28.73 ± 2.29^{a}	29.93 ± 0.40^{a}	29.22 ± 1.46^{a}	26.89 ± 0.39^{a}
10	25.61 ± 0.78^{a}	25.79 ± 0.08^{a}	25.80 ± 0.67^{a}	25.47 ± 1.01^{a}	25.79 ± 1.44^{a}	26.52 ± 3.24^{a}	27.22 ± 2.59^{a}	26.86 ± 5.12^{a}	26.75 ± 2.01^{a}	29.59 ± 1.84^{a}	26.34 ± 1.42^{a}	24.16 ± 1.50^{a}
15	24.97 ± 0.62^{a}	25.58 ± 0.11^{a}	25.24 ± 0.47^{a}	25.38 ± 0.40^{a}	26.99 ± 2.47^{a}	26.56 ± 2.42^{a}	27.47 ± 2.09^{a}	27.18 ± 2.31^{a}	25.51 ± 1.30^{a}	28.92 ± 0.55^{a}	27.51 ± 1.98^{a}	24.86 ± 0.65^{a}
20	25.44 ± 0.97^{a}	25.45 ± 0.27^{a}	25.10 ± 0.64^{a}	25.47 ± 0.11^{a}	26.56 ± 1.93^{a}	27.10 ± 2.67^{a}	27.53 ± 2.60^{a}	28.22 ± 2.29^{a}	26.62 ± 2.60^{a}	29.62 ± 1.03^{a}	27.82 ± 3.19^{a}	24.39 ± 0.26^{a}
25	26.37 ± 0.24^{a}	25.41 ± 0.51^{a}	25.21 ± 0.52^{a}	25.41 ± 0.43^{a}	29.27 ± 1.35.^{a}	28.34 ± 3.04^{a}	28.32 ± 2.27^{a}	28.66 ± 2.75^{a}	28.55 ± 0.65^{a}	24.52 ± 0.31^{a}	23.82 ± 0.71^{a}	24.35 ± 0.14^{a}
30	26.19 ± 0.17^{a}	25.35 ± 0.22^{a}	25.36 ± 0.52^{a}	25.44 ± 0.25^{a}	29.39 ± 2.30^{a}	29.02 ± 3.10^{a}	29.24 ± 1.98^{a}	29.42 ± 4.27^{a}	25.48 ± 1.43^{a}	29.78 ± 1.09^{a}	27.90 ± 2.06^{a}	25.10 ± 0.23^{a}

Mean ± standard deviation within a column with different superscripts indicates a significant difference (p<0.05).

Table 6. The whiteness index of all dark chocolate samples stored under constant temperature for 30 days.

Day	Whiteness Index											
	control	CB+L	CB+GMS	CB+2E	CBS	CBS+L	CBS+GMS	CBS+2E	CBR	CBR+L	CBR+GMS	CBR+2E
0	24.69 ± 0.29^{a}	25.11 ± 0.14^{a}	24.29 ± 0.71^{a}	24.80 ± 0.72^{a}	25.74 ± 1.82^{a}	26.28 ± 1.58^{a}	26.89 ± 1.81^{a}	26.51 ± 1.81^{a}	27.80 ± 2.71^{a}	29.50 ± 0.32^{a}	29.07 ± 3.28^{a}	26.13 ± 0.33^{ab}
5	25.36 ± 2.54^{a}	25.22 ± 0.15^{a}	24.75 ± 0.10^{a}	24.99 ± 0.44^{a}	25.60 ± 1.52^{a}	26.45 ± 3.03^{a}	26.16 ± 1.45^{a}	26.13 ± 1.07^{a}	28.73 ± 2.29^{a}	29.93 ± 0.40^{a}	29.22 ± 1.46^{a}	$26.890.39^{a}$
10	$25.99 \pm 0.43^{a,b}$	25.24 ± 0.11^{a}	24.84 ± 0.17^{a}	24.52 ± 1.42^{a}	25.79 ± 1.44^{a}	26.52 ± 3.24^{a}	27.22 ± 2.59^{a}	26.86 ± 5.12^{a}	26.75 ± 2.01^{a}	29.59 ± 1.84^{a}	26.34 ± 1.42^{a}	24.16 ± 1.50^{c}
15	27.63 ± 0.06^{b}	25.22 ± 0.14^{a}	24.11 ± 0.31^{a}	24.09 ± 0.15^{a}	26.99 ± 2.47^{a}	26.56 ± 2.42^{a}	27.47 ± 2.09^{a}	27.18 ± 2.31^{a}	25.51 ± 1.30^{a}	28.91 ± 0.55^{a}	27.51 ± 1.98^{a}	24.86 ± 0.65^{bc}
20	27.72 ± 0.02^{b}	25.64 ± 0.36^{a}	25.59 ± 0.12^{b}	26.34 ± 1.07^{a}	26.56 ± 1.93^{a}	27.10 ± 2.67^{a}	27.53 ± 2.60^{a}	28.22 ± 2.29^{a}	26.62 ± 2.60^{a}	29.62 ± 1.03^{a}	27.82 ± 3.19^{a}	24.39 ± 0.26^{bc}
25	31.18 ± 0.98^{c}	27.37 ± 0.49^{b}	30.47 ± 0.35^{c}	29.83 ± 0.82^{b}	29.27 ± 1.35^{a}	28.34 ± 3.04^{a}	28.32 ± 2.27^{a}	28.66 ± 2.75^{a}	28.55 ± 0.65^{a}	24.52 ± 0.31^{a}	27.82 ± 0.71^{a}	24.35 ± 0.14^{bc}
30	37.34 ± 0.49^{d}	30.57 ± 0.72^{c}	31.07 ± 0.65^{d}	31.39 ± 0.45^{c}	29.39 ± 2.30^{a}	29.02 ± 3.10^{a}	29.24 ± 1.98^{a}	29.42 ± 4.27^{a}	25.48 ± 1.43^{a}	29.78 ± 1.09^{a}	27.90 ± 2.06^{a}	25.10 ± 0.23^{abc}

Mean ± standard deviation within a column with different superscripts indicates a significant difference ($p<0.05$).

CONCLUSION

In conclusion, the addition of mixed emulsifiers increased the hardness, snap texture, pH, and peak temperature of dark chocolate. Meanwhile, the addition of lecithin and mixed emulsifiers retard the formation of fat bloom better than GMS and control samples. Hence, mixed emulsifiers demonstrated their ability to be included in chocolate production as they improved the physical characteristics and enhanced the fat bloom stability of dark chocolate. Additionally, the dark chocolate samples with CBR and CBS demonstrated the highest fat bloom stability, as there was no significant increase in the whiteness index value throughout the storage period. Thereby, CBR and CBS showed their potential to replace cocoa butter for practical application due to their outstanding fat bloom stability.

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LIST OF ABBREVIATIONS

Cocoa butter (CB), Cocoa butter alternatives (CBAs), Cocoa butter substitute (CBS), Cocoa butter replacer (CBR), Glycerol monostearate (GMS), Chocolate formulation with the addition of lecithin (CB+L), Chocolate formulation with the addition of glycerol monostearate (CB+GMS), Chocolate formulation with the addition of lecithin and glycerol monostearate (CB+2E), Chocolate formulation with the addition of lecithin and CBS (CBS+L), Chocolate formulation with the addition of glycerol monostearate and CBS (CBS+GMS), Chocolate formulation with the addition of lecithin, glycerol monostearate and CBS (CBS+2E), Chocolate formulation with the addition of lecithin and CBR (CBR+L), Chocolate formulation with the addition of glycerol monostearate and CBR (CBR+GMS), Chocolate formulation with the addition of lecithin, glycerol monostearate and CBR (CBR+2E), Whiteness index (WI).

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