

Palm Based Mono-Diacylglyceride as an Emulsifier in Producing Chocolate with Cocoa Butter Substitute

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Abstract

Emulsifier used in the preparation of chocolate has the function to stabilize fat and water that can prevent the occurrence of blooming. Emulsifier generally used in the preparation of chocolate is lecithin. However as an alternative mono-diacylglycerol (MDAG) can be used. MDAG can be synthesized from vegetable oil such as palm oil and its fraction. This research was conducted to study the effect of palm MDAG and variation of its concentration on quality of chocolate. The palm MDAG used was palm kernel oil MDAG (MDAG PKO), palm olein MDAG (MDAG POL), palm stearin MDAG (MDAG PS) at the concentration between 0.3 to 0.9%. Results of the study showed that chocolate which used palm MDAG did not cause blooming. Increase of MDAG concentration tended to increase fat content but the reverse result was observed in the case of lecithin. The melting point of chocolate tended to increase with increasing concentration of MDAG POL and MDAG PS but the reverse result was observed in lecithin, meanwhile for MDAG PKO similar result was observed. The protein content of chocolate tended to decrease with increasing MDAG concentration but the reverse result was observed in lecithin. Viscosity of chocolate with lecithin, MDAG PKO and MDAG POL decreased in accordance with increasing concentration, meanwhile in MDAG PS at the concentration of 0.3% in the beginning viscosity decreased but later on increased with increasing concentration. The use of emulsifier at the concentration of 0.3–0.9% did not have significant effect on fat content, melting point of fat and protein content, but it had significant effect on viscosity. Results of organoleptic testing showed that the use of palm MDAG have not significant effect on texture, taste, and appearance of chocolate. Types and concentrations of palm MDAG which were highly accepted by the panelist there were MDAG PS and MDAG PKO with concentration 0.3% and 0.5%, respectively.

Keywords: chocolate, cocoa butter substitute, lecithin, palm oil, palm kernel oil

INTRODUCTION

Fraction of fat has an important role in the formulation of chocolate since it can determine the texture, appearance, and handling of process and storage of the product. Generally the fat fraction in chocolate is derived from chocolate fat and milk fat (Misnawi & Wahyudi, 2008). Recently

for varying chocolate products and reducing production cost, a part of cocoa fat or even all of the fat is substituted by other kinds of fat consisting of cocoa butter equivalent (CBE) or cocoa butter substitute (CBS) originated from vegetable oil such as palm oil and palm kernel oil. CBE has physicochemical characteristics similar with cocoa fat whereas in CBS only its physical characteristic which

is similar with cocoa fat (Basiron *et al.*, 2000; Wang *et al.*, 2010; Abdullah & Zamri, 2011).

The technology of CBS production from palm kernel oil (PKO) can be carried out by fractionation, hydrogenation and its combination. PKO fractionation produces two fractions, i.e. olein and stearin. Stearin fraction is solid with melting point between 30–34°C so that it can be applied as CBS. Beside fractionation, hydrogenation of PKO and its fraction can produce various type of CBS. Completely hydrogenated stearin fraction is CBS with physical characteristic similar to that of cocoa fat with melting point between 33.2–36.8°C (Calliauw *et al.*, 2005; Zaidul *et al.*, 2007; Hasibuan *et al.*, 2012; Hasibuan & Siahaan, 2013).

The obstacle found in the preparation of chocolate with cocoa fat and its mixture with CBE or CBS is the occurrence of blooming which is shown by existence of white spots on the surface of chocolate. The white spot is fat crystal or diffused sugar (Misnawi & Wahyudi, 2008; Mulato *et al.*, 2010). One of the efforts to reduce blooming is by adding emulsifier. The emulsifier has the function for reducing surface tension and improve mixing by stabilizing fat and water so that it can influence chocolate characteristic such as blooming, its stability in packing and oxidation (Svanberg *et al.*, 2011). Emulsifier can also make the chocolate more liquid so that it can minimize the use of fat and reduce the production cost (Schantz *et al.*, 2003).

Emulsifier usually used in chocolate product is lecithin originated from yellow egg or soybean (Hartomo & Widiatmoko, 1993; Pua *et al.*, 2007). Other types of emulsifier that may be used in the preparation of chocolate is polyglycerol polyricinoleate (PGPR), tri stearate, ammonium phosphatide and mono-diacylglyceride (MDAG) (Schantz

& Rohm, 2005; Tisoncik, 2010; Graef *et al.*, 2011; Peker *et al.*, 2013).

MDAG is mixture between monoglyceride and diglyceride, both of which have been used as synthetic emulsifier in food industry. Monoglyceride has two free hydroxyl groups, so that its surface activity is stronger than diacylglycerol (Kaewthong & Kittikun, 2005; Chetpattananondh & Tongurai, 2008; Hasenhuettl & Hartel, 2008). MDAG can be prepared from various kinds of oil and fat. Indonesian Oil Palm Research Institute (IOPRI) had prepared various kinds of MDAG using basic material from palm kernel oil, olein and stearine fractions of palm oil. In addition IOPRI had also prepared chocolate with CBS material and lecithin as emulsifier (Hasibuan & Siahaan, 2012). Therefore this research is conducted to study the use of palm MDAG as emulsifier in the preparation of chocolate with material of CBS that fit with tropical climate.

MATERIALS AND METHODS

Basic material used in this research were cocoa butter substitute (CBS) and palm mono-diacylglycerol (MDAG) obtained from Research Group of Post Harvest Processing and Quality of IOPRI. CBS was originated from stearin fraction of completely dehydrogenated palm kernel oil, and used as an alternative fat to substitute chocolate fat. CBS contained high lauric acid as much as 56%. Palm MDAG used was originated from palm kernel oil (PKO), palm olein (POL), and palm stearin (PS) with mono-glyceride content of 55–60% and 30–35% diglyceride. Cocoa powder was originated from Indonesian Coffee and Cocoa Research Institute (ICCRI) in Jember. Other formulation material was sugar, powder milk, lecithin and vaniline. All materials used were classified as food grade, obtained from a bakery shop in Medan, North Sumatera.

Chocolate was prepared using standard of IOPRI as presented in Table 1. The materials were mixed and ground in ball-mill refiner during 20 hours at the temperature of 50°C and then the dough was undergone conching during 10 hours at the temperature of 68°C (Sulistiyowati & Misnawi, 2008; Mulato *et al.*, 2010). Afterwards four kinds of emulsifier consisting of MDAG PKO, MDAG POL, MDAG PS and lecithin at concentration of 0.3; 0.5; 0.7 and 0.9% of chocolate weight were added to chocolate product. Addition of emulsifier was done 2 hours before conching finished. Each treatment was replicated twice. The dough was further cooled up to temperature of 35-38°C, then it was printed and cooled to temperature of 10–12°C. Chocolate from each treatment was printed in the form of candy with the size of 1 cm x 1 cm x 1 cm. Chocolate was characterized including blooming, fat content, melting point of fat, protein content, viscosity and organoleptic test on taste, texture and appearance of chocolate product. Blooming was determined by detecting the occurrence of white spot layer on the surface of chocolate after cooling and moulding (Bricknell & Hartel, 1998).

Fat content of chocolate product was determined by extraction using hexan solution in soxhlet apparatus during 8 hours at temperature of 60°C. Fat was separated from mixture of fat and solution by evaporation. The rest of solution was discarded by further evaporation

in the oven at the temperature of 100°C during 2 hours. The fat produced was further analyzed its melting point using capillar pipe and cooled at temperature of 0°C during 16 hours and determined using standard method (MPOB, 2004).

Composition of fatty acid was determined using gas chromatography apparatus (GC-2010, Shimadzu) by referring to standard method (MPOB, 2004). As much as 0.025 g sample was added with 1.4 mL NaOH methanolic 0.5 N. The mixture was then heated in water boiler at the temperature of 100°C during 5 minutes. The mixture was cooled and then 2 mL BF₃ methanol (14% b/v) was added and heated again at temperature of 100°C during 30 minutes. The mixture was cooled and then added with 1 mL isooctane and stirred during 1–2 minutes. The mixture was added with 5 mL saturated NaCl and stirred. Isooctane layer was removed and transferred to the vial, then 1 mL isooctane was injected to gas chromatography. The column used in the analysis of fatty acid composition was DB-23 J & W Scientific. Operation condition of gas chromatography was settled at detector and injector temperature of 260°C. Temperature of oven was programmed in the beginning condition at 70°C, then increased 20°C/minute up to 180°C, and afterwards it was increased 1°C/minute up to 182°C, then increased 10°C/minute up to 220°C and maintained during 2 minutes.

Table 1. Cocoa butter substitute based chocolate making recipe

Ingredient	%
Cocoa butter substitute	31.0
Cocoa powder	12.5
Fine sugar	38.5
Milk powder	18.0
Vanila	0.02
Lecithin	In accordance with treatment

Protein content of chocolate was determined by Kjeldahl method. Viscosity of chocolate was determined with digital viscosimeter (Brookfield Engineering) using spindle 4 measured at revolving speed of 6 rpm and temperature of 40°C (Schumacher *et al.*, 2009).

Organoleptic test was conducted by 25 panelists on chocolate candy based on acceptance test. Panelist was asked to evaluate based on level of preference consisted of taste, texture and appearance. Evaluation of preference used hedonic scale. Score of hedonic scale used for taste, texture and appearance was 5 (very pleased), 4 (pleased), 3 (quite pleased), 2 (less pleased), and 1 (dislike). The data collected was statistically analyzed and followed by Duncan multiple range test for detecting significant difference between treatments.

RESULTS AND DISCUSSION

Chocolate made in this research used cocoa butter substitute (CBS) as ingredient. CBS had monomorphic stable crystal form (b and b') so that the chocolate product resulted did not require tempering process (Wang *et al.*, 2010). Chocolate dough in this research used cocoa powder containing cocoa fat as much as 20.2%. Cocoa fat was fat which had polymorphic unstable crystal form (Basiron *et al.*, 2000; Sri-Mulato *et al.*, 2010).

Beside containing fat the dough also had moisture content for CBS (0.03%), sugar (1.12%), milk (6.78%), cocoa powder (3.92%), lecithin (0.2%) and vanilla (20.8%). However, moisture in the dough seemed to evaporate during conching process (temperature 68°C). Moisture content in the last product after processing was 0.42%. This value has followed qualification of moisture content in chocolate product, i.e. between 0.4–0.6%. According to Schumacher *et al.* (2009), the high moisture content in chocolate product caused migration of dough material to the surface of chocolate and resulted in blooming. Meanwhile, chocolate with low moisture content would produce lump that caused the chocolate difficult to melt when it was heated (Afoakwa *et al.*, 2007).

In this research chocolate without addition of emulsifier that did not experience tempering showed white spots on the surface of chocolate with blooming (Table 2). It happened because the fat diffused from the dough and the white spot was CBS fat which was proved by lauric acid content of 55.2%. CBS fat was separated from the dough and did not completely cover cocoa powder particle, sugar, and milk since CBS could not mix perfectly with cocoa fat due to incompatibility between the fat mixed. Basiron *et al.* (2000) showed that CBS could not perfectly mixed with cocoa powder with a high fat content. Incompatibility between cocoa fat and CBS stimulated the occurrence

Table 2. Effect of emulsifier types and concentration on blooming

Emulsifier	Emulsifier concentration				
	0	0.3%	0.5%	0.7%	0.9%
Lecithin	blooming	tb	tb	tb	tb
MDAG PKO	blooming	tb	tb	tb	tb
MDAG POL	blooming	tb	tb	tb	tb
MDAG PS	blooming	tb	tb	tb	tb

Notes: tb = no blooming; MDAG PKO = mono-diacylglyceride made of palm kernel oil; MDAG POL = mono-diacylglyceride made of palm olein; MDAG PS = mono-diacylglyceride made of palm stearin.

of fat migration (Ghosh *et al.* 2005; Sabariah *et al. cit.* Misnawi & Wahyudi, 2008). According to Bigalli (1988), if two different fat substances were mixed the mixture solidified and melted at lower temperature than the two materials mixed. The use of emulsifier was expected to be able to reduce the surface tension and improved mixing between fat (Misnawi & Wahyudi, 2008).

Table 2 showed that addition of emulsifier either lecithin or palm MDAG from 0.3 to 0.9% did not produce white spot without having tempering process. It meant that addition of emulsifier could prevent blooming. Table 2 also showed that addition of emulsifier either lecithin or palm MDAG at 0.3% could increase compatibility between CBS fat and cocoa fat. Higher concentration of emulsifier caused the surface of chocolate more glossy.

Fat Content

Determination of fat content was important because it could influence the quality of chocolate produced (Prawira & Bariinger, 2008). Results of observation of fat content

in chocolate product by addition of emulsifier was presented in Table 3. Fat content of chocolate added with palm MDAG tended to increase in accordance with increasing concentration, but the reverse result was observed on lecithin. However increasing concentration of emulsifier did not have significant effect ($p>0.05$) on fat content because concentration of emulsifier was between 0.3–0.9%.

Fat content of chocolate product increased with increasing concentration of palm MDAG because MDAG was monoglyceride and diglyceride containing fatty acid. Monoglyceride was fat molecule containing a fatty acid and two hydroxyl whereas diglyceride has two kinds of fatty acid and one hydroxyl fastened on glycerol (Kaewthong & Kittikun, 2008; Chetpattananondh & Tongurai, 2008; Chen *et al.*, 2009). Decrease of fat content with increasing lecithin concentration was caused by low content of phospholipide in lecithin. According to Beuschelberger (2004), Ketaren (2005) and Cabezas *et al.* (2009), lecithin contained phospholipide, protein, triglyceride, glycolipide, phytosterol, tocopherol, fatty acid and water.

Table 3. Effect of emulsifier types and concentration on chocolate fat content (%)

Emulsifier	Concentration				
	0	0.3%	0.5%	0.7%	0.9%
Lecithin	38.3 ^a ±0.13	38.1 ^a ±0.15	37.9 ^a ±0.12	37.6 ^a ±0.23	36.9 ^a ±0.24
MDAG PKO	38.3 ^a ±0.15	38.5 ^a ±0.19	38.6 ^a ±0.28	38.7 ^a ±0.03	39.2 ^a ±0.08
MDAG POL	38.3 ^a ±0.20	38.6 ^a ±0.21	39.1 ^a ±0.09	39.6 ^a ±0.15	40.0 ^a ±0.12
MDAG PS	38.3 ^a ±0.17	38.4 ^a ±0.20	38.5 ^a ±0.29	38.7 ^a ±0.17	39.5 ^a ±0.11

Notes: see Table 1 for abbreviation; no significantly different among treatments, $p>0.05$.

Table 4. Effect of emulsifier types and concentration on chocolate fat melting point (°C)

Emulsifier	Concentration				
	0	0.3%	0.5%	0.7%	0.9%
Lecithin	35.0 ^a ± 0.05	34.8 ^a ± 0.07	34.8 ^a ± 0.06	34.6 ^a ± 0.04	34.6 ^a ± 0.06
MDAG PKO	35.0 ^a ± 0.07	35.0 ^a ± 0.08	35.0 ^a ± 0.05	35.0 ^a ± 0.03	35.0 ^a ± 0.07
MDAG POL	35.0 ^a ± 0.04	35.0 ^a ± 0.10	35.2 ^a ± 0.05	35.2 ^a ± 0.03	36.0 ^a ± 0.06
MDAG PS	35.0 ^a ± 0.03	35.4 ^a ± 0.06	36.0 ^a ± 0.05	36.3 ^a ± 0.05	36.6 ^a ± 0.07

Notes: see Table 1 for abbreviation; no significantly different among treatments, $p>0.05$.

Fat Melting Point

Misnawi & Wahyudi (2008) demonstrated that melting point of fat was one of the main factors determining texture and hardness of chocolate candy. The good chocolate did not easily melt at ambient temperature but in the mouth it was melted. Results of measurement of melting point showed that kinds and concentration of emulsifier did not significantly influence ($p>0.05$) on melting point of cocoa fat. Table 4 showed that melting point of cocoa fat increased in accordance with increasing concentration of MDAG POL and MDAG PS, but in MDAG PKO it was relatively the same. Meanwhile melting point of chocolate fat tended to decrease with increasing concentration of lecithin.

Melting point of fat was much influenced by composition of its fatty acid. According to Hasibuan & Siahaan (2013), CBS from perfectly hydrogenated stearin fraction of palm kernel oil had main component of fatty acid consisted of lauric acid (56.4–61.4%), miristate (18.6–22.4%), and palmitate (7.0–8.6%). Meanwhile, Hasibuan *et al.* (2012) reported that PKO had composition of main fatty acid lauric acid as much as 48–54%. Therefore the use of MDAG PKO did not change melting point of cocoa fat with CBS material because its characteristic was nearly the same. Results of testing the fatty acid composition showed that MDAG PKO contained fatty acid component especially lauric acid (47.2%), miristate (16.1%), and palmitate (9.7%). MDAG POL had fatty acid component dominated by oleic acid (42.8%) whereas

MDAG PS was dominated by palmitate acid (60.5%).

Protein Content

Protein content of chocolate added with palm MDAG and lecithin at concentration of 0.3–0.9% varied between 6.2% and 6.9% (Table 5). The higher the palm MDAG concentration the protein content tended to decrease, but the reverse result was observed in the case of lecithin. However increase concentration of emulsifier did not have significant effect ($p>0.05$) on protein content. Palm MDAG was fat which did not contain protein while lecithin had high protein content which could be used as protein source.

Viscosity

Viscosity of chocolate added with palm MDAG and lecithin was presented in Figure 1. Type and concentration of palm MDAG and lecithin had significant effect ($p>0.05$) on viscosity of chocolate. In general, emulsifier used in this research reduced the viscosity of chocolate. Nebesny & Zyzelewicz (2004) also stated that viscosity of chocolate tended to decrease in accordance with increased amount of emulsifier added. Lecithin could reduce viscosity of chocolate two times higher than that of palm MDAG. The same case had also been mentioned by Schantz *et al.* (2003), that the use of MDAG was not as good as lecithin because the chocolate produced had higher viscosity and hardness.

Table 5. Effect of emulsifier types and concentration on chocolate protein content (%)

Emulsifier	Concentration				
	0	0.3%	0.5%	0.7%	0.9%
Lecithin	6.8 ^a ± 0.24	6.9 ^a ± 0.14	6.9 ^a ± 0.21	7.0 ^a ± 0.04	7.1 ^a ± 0.14
MDAG PKO	6.8 ^a ± 0.26	6.8 ^a ± 0.24	6.8 ^a ± 0.25	6.5 ^a ± 0.14	6.4 ^a ± 0.03
MDAG POL	6.8 ^a ± 0.34	6.7 ^a ± 0.16	6.6 ^a ± 0.14	6.6 ^a ± 0.20	6.4 ^a ± 0.05
MDAG PS	6.8 ^a ± 0.14	6.8 ^a ± 0.22	6.6 ^a ± 0.16	6.4 ^a ± 0.19	6.2 ^a ± 0.18

Notes: see Table 1 for abbreviation; no significantly different among treatments, $p>0.05$.

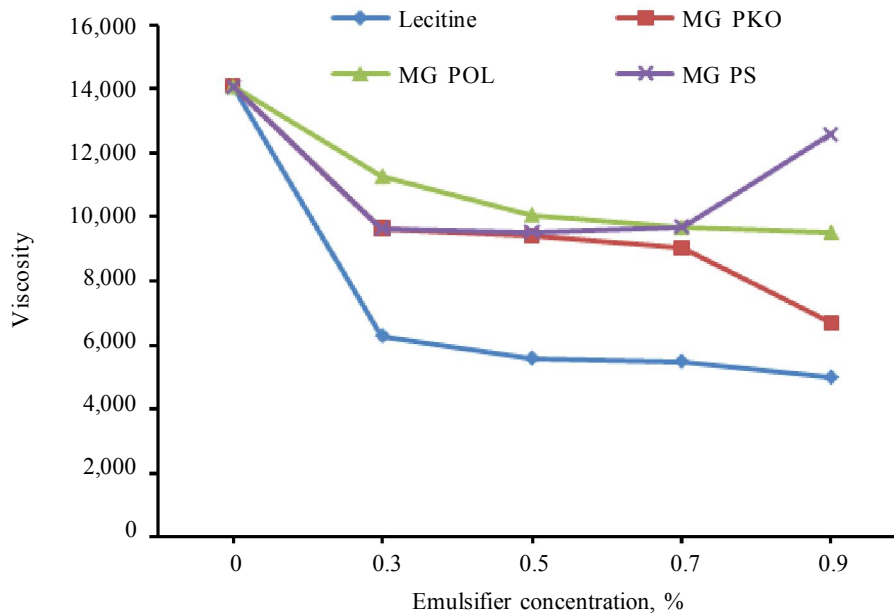


Figure 1. Effect of emulsifier types and concentration on chocolate viscosity

Notes: see Table 1 for abbreviation; no significantly different among treatments, $p > 0.05$.

Lecithin, MDAG PKO and MDAG POL tended to reduce viscosity of chocolate. MDAG PS at concentration of 0.3% in the beginning reduced viscosity of chocolate but with increasing concentration it tended to increase the viscosity of chocolate. This case was caused by different characteristic of each MDAG emulsifier. In ambient temperature MDAG PKO was fluid whereas MDAG PS was solid. The main material of MDAG had also different shape at ambient temperature. PKO and POL was liquid while PS was solid (Hasibuan & Siahaan, 2013). Lecithin was also fluid and contained phospholipide and triglyceride with a high oleic acid component of 55–63% (van Niewenhuysen & Tomas, 2008).

Organoleptic Test

Results of organoleptic test of chocolate candy produced by addition of lecithin emulsifier, MDAG PKO, MDAG POL and MDAG PS on taste, texture and appearance

was presented in Table 6. Average value of acceptance level varied between 3.42–3.83 which mean that the panelist was *nearly like to like*. The use of lecithin, MDAG PKO and MDAG POL at the concentration of 0.5% had relative high level of acceptance, while for MDAG PS was low. Chocolate treated with relative high addition of MDAG PS cause the chocolate become more viscous that it could influence its flavour. According to Hartomo (1993) viscosity of chocolate was one of the important factors and chocolate with high viscosity might become clot when it was consumed. Besides this texture was much influenced by softness of the chocolate product, and according to panelist which used palm MDAG and lecithin it was enough soft. According to Sokmen & Gunes (2006) particle size above 35 μm was felt rough in mouth, but its interval of acceptance was different for each consumer.

Level of acceptance of panelist to chocolate taste was in the position of accepted

Table 6. Effect of emulsifier types and concentration on preference of chocolate product

Emulsifier	Texture	Taste	Appearance
No emulsifier	3.58 ^a ± 0.67	2.92 ^a ± 0.79	2.42 ^a ± 0.79
Lecithin 0.3%	3.50 ^a ± 0.58	3.33 ^a ± 1.19	3.05 ^a ± 0.94
Lecithin 0.5%	3.83 ^a ± 0.79	3.33 ^a ± 1.16	3.33 ^a ± 0.87
MDAG PKO 0.3%	3.58 ^a ± 0.72	3.25 ^a ± 0.80	3.02 ^a ± 0.67
MDAG PKO 0.5%	3.83 ^a ± 0.90	3.42 ^a ± 1.04	3.25 ^a ± 0.90
MDAG POI 0.3%	3.83 ^a ± 0.67	2.83 ^a ± 0.78	3.17 ^a ± 0.75
MDAG POI 0.5%	3.58 ^a ± 0.39	3.08 ^a ± 0.65	3.25 ^a ± 0.65
MDAG PS 0.3%	3.83 ^a ± 0.51	3.50 ^a ± 0.62	3.50 ^a ± 0.79
MDAG PS 0.5%	3.42 ^a ± 0.58	3.00 ^a ± 0.90	3.08 ^a ± 0.87

Notes: see Table 1 for abbreviation; no significantly different among treatments, $p > 0.05$ (\pm standard deviation of mean).

except in the case of addition of MDAG POL at 0.3% and without addition of emulsifier. It was caused by too high viscosity of chocolate without addition of emulsifier and MDAG POL 0.3% compared to that of other treatments. Panelist acceptance to appearance of chocolate candy was at the level of *like* except in chocolate without addition of emulsifier. It was proved that without addition of emulsifier the surface of chocolate was not glossy.

Table 6 showed that panelist acceptance to texture, taste, and appearance of chocolate added with lecithin (as a control) was lower than that of palm MDAG. However analysis of variance for texture, taste and appearance of chocolate added with several emulsifier showed not significant difference. This meant that panelist could not differentiate between taste of chocolate which used palm MDAG and that of lecithin.

CONCLUSION

Palm mono-diacylglyceride (MDAG) could be used as an alternative emulsifier for substituting lecithin in the preparation of chocolate. The use of MDAG did not cause the occurrence of blooming in chocolate product. Kinds and concentration of palm MDAG in the range of 0.3–0.9% did not have significant effect on parameters tested con-

sisting of fat content, melting point of fat, protein content, and organoleptic characteristic of chocolate product except viscosity. Decrease viscosity of chocolate added with MDAG was not as good as that of lecithin. Lecithin could decrease viscosity of chocolate by two times higher compared to that of palm MDAG. From the results of organoleptic test it appeared that kinds and concentration of palm MDAG that could be applied in the preparation of chocolate were MDAG PKO and PS at concentration of 0.5% and 0.3%, respectively.

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