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Physico-Chemical Properties of Ternary Blends of Palm Mid Fraction, Virgin Coconut Oil and Canola Oil Blends

A.B. Aftar Mizan, M.K. Ayob, A.G. Ma'aruf, M. Mohamad Yusof and I. Izzreen

School of Chemical Science and Food Technology, Faculty of Science and Technology,
University Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

Abstract: A total of 14 ternary blends containing palm mid fraction (PMF), virgin coconut oil (VCO) and canola oil (CO) were prepared and analyzed for physico-chemical properties *i.e.* solid fat content (SFC), slip melting point (SMP), free fatty acid (FFA), iodine value (IV) and fatty acid composition (FAC). The results showed that the SFC for the ternary blends at 37.5°C were in the range of 0.00-2.44%, SMP for all blends were 24.8-31.3°C, FFA were 0.23-1.24%, IV were in the range of 33.49-55.99. FAC comprised of 31.4-50.6% palmitic acid, 3.8-5.2% stearic acid and 28.5-39.4% oleic acid. Based on the analyses, a ternary blend of PMF: VCO: CO (90: 5: 5%) the S3 or S10 with SFC at 25°C of 46.85°C or 46.40°C and SMP of 31.3°C was identified as closer to cocoa butter with SMP 31.1 °C.Hence, the blendcould be considered as a potential cocoa butter substitute (CBS).

Key words: Physicochemical Properties · Palm Mid Fraction · Virgin Coconut Oil · Canola Oil · Cocoa Butter Substitutes

INTRODUCTION

Malaysia is one of the main palm oil exporting countries in the world, second to Indonesia. Currently palm oil is one of the important vegetable oils used in the food industry. In order to diversify and expand its application in food and non-food industries, commonly the physico-chemical properties of the oils are modified via techniques such as fractioning, mixing, hydrogenation and esterification [4]. Among these processes, mixing is the cheapest technique, apart from its ability to retain original qualities of the mixed fats/oils such as flavor, vitamin content and antioxidant activity.

Palm mid fraction (PMF) is a product of oil palm produced in the second stage of fractionation. At room temperature, palm oil exists in half liquid phase and light yellow color. Usually, PMF is used as a starting material to produce a much cheaper cocoa butter substitute (CBS). Major triacylglycerols (TAGs) available in PMF are 1,3-dipalmitoyl-2-oleoyl-sn-glycerol (POP), 1-palmitoyl-2-oleoyl-3staeroyl-sn-glycerol (POSt) and 1,3-distearoyl-2-oleoyl-sn-glycerol (StOSt) [7]. On the other hand, virgin coconut oil (VCO) has many advantages, include as healthy functional foods, as nutriceuticals, pharmaceuticals and cosmoceuticals. VCO is widely known for its richness in medium chain fatty acid (MCFA) (50%), lauric acid, short chain fatty acid (SCFA) such as capric, caproic acid, caprylic acid and unsaturated fatty acids (8%) [2]. Canola oil (CO) is an important source of cooking oil and one of the healthiest edible oils available for consumers. Canola oil is unique among other vegetable oils because of its low saturated fatty acid content (6%) and low in cholesterol. The fatty acid content of canola oil is consistent with nutrition recommendations aimed at reducing the amount of saturated fat in the diet [6].

Since Malaysia is one of the major producers of palm oil, it is imperative that work to diversify its application in food industry, especially in producing value-added products. Among those value-added products is the CBS as a relatively cheaper alternative to cocoa butter (CB). Therefore, the objective of this study was to produce CBS from ternary blends containing PMF, VCO and CO.

MATERIALS AND METHODS

Materials: The palm mid fraction (PMF) used in this study was supplied by Alami Group Sdn. Bhd. PanglimaGarang, Klang; whereas the virgin coconut oil (VCO) and canola oil (CO) was purchased from a local supermarket.

Corresponding Author: M.K. Ayob, School of Chemical Science and Food Technology, Faculty of Science and Technology, University Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia.

Table 1: The ratio of Palm Mid Fraction (PMF),Virgin Coconut Oil (VCO) and Canola Oil (CO) determined via *Design Expert®* *version 6-(D-Optimal* Software).

Mixture Code	PMF (%)	VCO (%)	CO (%)
S1	82.50	12.50	5.00
S2	63.75	12.50	23.75
S3	90.00	5.00	5.00
S4	62.50	20.00	17.50
S5	75.00	20.00	5.00
S6	70.00	12.50	17.50
S7	50.00	20.00	30.00
S8	75.00	20.00	5.00
S9	50.00	20.00	30.00
S10	90.00	5.00	5.00
S11	65.00	5.00	30.00
S12	57.50	12.50	30.00
S13	65.00	5.00	30.00
S14	80.00	8.75	11.25

Sample Preparation: The palm mid fraction (PMF) was melted in an oven at 60°C for 1 hour. A total of 14 blends constituting PMF, VCO and CO at different ratios (Table 1) were prepared as generated by mixing procedure (D-Optimal) in *Design-Expert®version* 6 software. The blends were prepared by mixing the oil mixtures using a magnetic stirrer [9]. The blends were later subjected to physico-chemical characterization, *i.e.* solid fat content (SFC), slip melting point (SMP), free fatty acid (FFA), iodine value (IV) and fatty acid composition (FAC).

Solid Fat Content:Pulse nuclear magnetic resonance spectrometer (p-NMR) was used to determine the solid fat content (SFC) of each blend. Prior to analysis, the fat mixture were melted at 70°C for 30 minutes and subsequently placed into a 3cm tube and cooled to 0°C for 90 minutes. Then, the samples were placed into the tube at temperatures (0, 5, 10, 15, 20, 25, 30, 35 and 37.5°C) individually and the SFC was recorded for every 30 minutes [10].

Slip Melting Point: For slip melting point (SMP) determination, the fat samples were melted at 60°C for 30 min. Capillary tubes marked at 10 mm and 30 mm were dipped into the molten sample until the sample rose to reach the 10 mm mark. Then, the capillary tubes with the samples were cooled. This was carried out by holding the end of the tube and rotating I t through ice until the fat samples harden or turn into solids. Subsequently, the capillary tubes were warmed in a water bath at 10 ± 1 °C for 16 hours. After that, the capillary tubes were warmed in a water bath at the rate of 1°C per minute. The heating was continued until fat column started to rise. When the movement exceeded the 30 mm level, the temperature is recorded. This temperature was taken as the slip melting point for the sample [10].

Free Fatty Acid: Free fatty acid (FFA) content of the samples was determined based on [1]. Each sample (5.0 g) was weighed in a 100 mL conical flask and 25 mL diethyl ether:ethanol (1:1, v/v) was added and the flask was shaken gently until the sample was completely dissolved. The fatty acid content of the sample was determined via titration with 0.1 N NaOH, using phenolphthalein (1% in ethanol) as an indicator until the pink color was formed which ended for approximately 30 seconds.

Iodine Value: Iodine value (IV) of the samples was determined according to [10]. Samples (0.5 g each) were placed individually into 500 mL conical flasks. Then, 20 mL cyclohexane was added to dissolve the fat. If it did not dissolve, the conical flask was heated slowly till the fat is completely melted. Then, 25 mL Wij's solution was added and the flask was capped, shaken and stored in a dark place for an hour. After that, 20 mL saturated potassium iodide solution and 100 mL distilled water were added into the flask and the mixture was titrated with 0.1 N sodium thiosulphate until the color of the solution turned to pale yellow. Then, 2 mL starch indicator was added and the titration process was continued until the blue color disappeared. During the titration, the flask was shaken continuously. The steps above were repeated for blank test.

Fatty Acid Composition: Fatty acid composition (FAC) was determined as reported by [8]. It was carried out after the fatty acid has been converted into fatty acid methyl ester (FAME) through methylation steps. About 0.1 mL of each fat sample was dissolved in 1 mL n-hexane. Methylation was then proceeded by adding 1 mL 1M sodium methoxide. Subsequently, the mixtures were homogenized using a vortex mixer. After standing for 15 minutes, the clear supernatant was removed and 1 µL of it was injected into a silica capillary column SGE BPX 70, 60 cm x 0.32 µm which was purchased from Servco Services Sdn. Bhd., Klang Selangor. Fatty acid profile was analyzed using a gas chromatography, Shimadzu-17A, equipped with a flame ion detector (FID) and an integration apparatus (C-R6A Chromatopac).

RESULTS AND DISCUSSION

Solid Fat Content: Fig. 1 shows the solid fat content (SFC) of all ternary blends prepared. On the whole, SFC decreases as warming temperature increases.

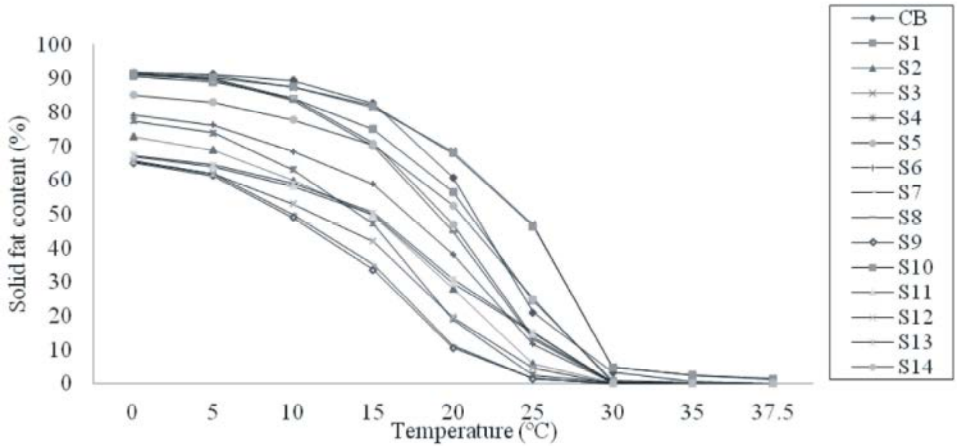

Fig. 1: Percent solid fat content (SFC) of palm mid fraction (PMF), virgin coconut oil (VCO) and canola oil (CO) mixtures according to different ratios of blending at different temperature.

Table 2: Slip melting point (SMP), free fatty acid (FFA) and iodine value (IV) of palm mid fraction (PMF), virgin coconut oil (VCO) and canola oil mixtures according to different ratios.

Mixture Code	Slip melting point (mean ± SD)°C	Free fatty acid (mean ± SD)%	Iodine value (mean ± SD)%
S1	27.2 ± 0.10[c]	0.85 ± 0.06[c]	36.06 ± 0.49[g]
S2	26.1 ± 0.10[g]	0.64 ± 0.03[d]	50.60 ± 0.39[c]
S3	31.3 ± 0.10[a]	0.81 ± 0.03[c]	37.83 ± 0.30[f]
S4	25.8 ± 0.06[h]	0.60 ± 0.03[de]	43.45 ± 0.49[e]
S5	26.9 ± 0.10[d]	1.24[b]	33.59 ± 0.54[i]
S6	26.4 ± 0.06[f]	0.23[g]	45.93 ± 0.69[d]
S7	25.0 ± 0.15[j]	0.54 ± 0.03[ef]	53.57 ± 0.66[b]
S8	26.7 ± 0.10[e]	1.24 ± 0.06[b]	33.49 ± 0.34[i]
S9	24.8 ± 0.15[k]	0.56 ± 0.06[e]	53.68 ± 0.46[b]
S10	31.3 ± 0.06[a]	0.81 ± 0.03[c]	37.54 ± 0.45[f]
S11	26.1 ± 0.06[g]	0.49 ± 0.03[f]	53.84 ± 0.54[b]
S12	25.3 ± 0.10[i]	0.55 ± 0.03[ef]	55.99 ± 0.39[a]
S13	26.1 ± 0.06[g]	0.49 ± 0.03[f]	53.82 ± 0.70[b]
S14	27.0 ± 0.06[d]	0.56 ± 0.06[e]	42.83 ± 0.88[e]
CB	31.1 ± 0.10[b]	1.41[a]	34.74 ± 0.86[h]

Note: The value are means for 3 sample replications.

[a-k] different alphabets on the same column showed the presence of significant difference ($p<0.05$)

Note: For the composition of blends, please refer to Table 1.

The SFC of individual blend differs even at the same temperature due to the difference in the ratio of PMF:VCO:CO. There was a decrease in SFC starting from 0 °C to 37.5 °C. For example in S1, the SFC decreased from 90.58-0.00%, S2 from 72.90-0.03%, S3 from 91.76-1.23%, S4 from 77.42-0.00%, S5 from 91.22-0.00%, S6 from 79.18-0.00%, S7 from 65.80-0.00%, S8 from 91.11-0.00%, S9 from 65.11-0.00%, S10 from 91.35-1.44%, S11 from 66.93-0.00%, S12 from 65.59-0.00%, S13 from 67.38-0.00% and S14 from 85.10-0.00%. These decreases were perhaps due to the narrow ratio in the warming temperature range and thus the fat became much softer [5].By comparing the SFC at 0°C, 25°C and 37.5°C to the one of CB, S3 or S10 was the best candidate for CBS. The SFC of S3 at 0°C, 25°C and 37.5°C were 91.76%, 46.85%, 1.23%, while the SFC of S10 at the corresponding temperatures were 91.35%, 46.40% and 1.44% respectively.

Slip Melting Point: The slip melting points (SMP) of 14 ternary blends are shown in Table 2. As expected, the mixture containing a higher percentage of PMF gave a high slip melting point, as demonstrated by S3 (31.3 ± 0.10°C) and S10 (31.3°C ± 0.06°C), while those containing a higher content of CO were lower in SMP as showed by S7 (25.0°C ± 0.15°C) and S9 (24.8 ± 0.15°C). Amongst the blends studied, S3 (31.3 ± 0.10°C) and S10 (31.3 ± 0.06°C) showed SMP closer to CB (31.1 ± 0.10°C), hence they may be considered as potential blends of CBS.

Free Fatty Acid: Free fatty acid percentages of ternary blends are shown in Table 2. On the whole, FFA in most ternary blends was in the range of 0.23-1.24%. As shown in Table 2, there was no significant difference ($p>0.05$) among the samples except S1-S3, S5-S8, S7-S12, S9-S14 and S11-S13 which show otherwise ($p<0.05$). However, all values were lower compared to free fatty acid value in CB (1.41 ± 0.00%). Higher FFA is normally associated with a poor quality of raw material [3] hence in this case, the quality of blends studied could be considered as good.

Table 3: Fatty acid composition (%) for mixtures of palm mid fraction (PMF), virgin coconut oil (VCO) and canola oil (CO) according to different ratios based on Design Expert® Version 6.0.

Fatty acid %	CB	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
C6-0	-	0.1	0.1	-	0.2	0.2	0.1	0.2	0.2	0.2	-	0.1	0.1	-	0.1
C8-0	-	1.1	1.1	0.4	2.1	1.8	1.2	1.8	1.8	1.8	0.4	0.5	1.1	0.5	0.8
C10-0	-	0.8	0.8	0.3	1.4	1.2	0.8	1.2	1.2	1.2	0.3	0.3	0.8	0.3	0.6
C11-0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C12-0	-	6.0	5.9	2.4	10.7	9.1	6.1	9.4	9.1	9.4	2.4	2.4	6.0	2.4	4.4
C13-0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C14-0	-	2.7	2.6	1.5	4.2	3.8	2.7	3.7	3.7	3.7	1.5	1.3	2.5	1.3	2.1
C15-0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C15-1	0.4	0.2	0.2	0.3	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
C16-0	26.9	47.3	37.6	50.6	36.0	44.4	40.8	31.4	44.4	31.4	50.6	37.5	34.3	37.5	45.5
C16-1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
C17-0	0.3	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
C17-1	-	-	-	-	-	-	-	-	-	-	-	0.1	0.1	0.1	-
C18-0	34.6	5.0	4.3	5.2	4.2	4.8	4.5	3.8	4.8	3.8	5.2	4.1	4.0	4.1	4.8
C18-1n9c	32.9	30.9	35.8	33.0	31.1	28.5	33.8	34.8	28.6	34.9	33.2	39.4	37.0	39.4	33.6
C18-2n6c	3.0	4.1	7.6	4.4	6.2	3.9	6.4	8.4	3.9	8.3	4.4	9.0	8.7	9.0	5.4
C18-3n6G	-	-	0.1	-	0.1	-	0.1	0.2	-	0.2	-	0.2	0.2	0.2	0.1
C18-3n3A	0.2	0.6	2.5	0.6	1.9	0.5	1.9	3.2	0.5	3.1	0.6	3.3	3.2	3.3	1.2
C20-0	0.9	0.4	0.4	0.4	0.3	0.3	0.4	0.4	0.3	0.4	0.4	0.4	0.4	-	0.4
C20-1n9	-	0.1	0.3	0.1	0.2	0.1	0.2	0.4	0.1	0.4	0.1	0.4	0.4	0.4	0.2
C20-2	-	-	-	-	-	-	-	-	0.1	-	-	-	-	-	-
C20-3n6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C20-5n3	-	-	0.2	-	-	-	-	-	-	-	-	-	0.2	-	-
C22-0	0.2	0.1	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	-	0.1	0.1
C22-1n9	-	-	0.1	-	0.1	-	0.1	0.2	-	0.2	-	0.2	0.2	0.2	0.1
C22-2	0.2	0.3	0.1	-	0.5	0.6	0.3	0.3	0.7	0.3	0.3	0.2	0.3	0.2	0.2
C23-0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C24-0	0.1	0.1	-	0.1	-	-	0.1	0.1	0.1	0.1	0.1	0.1	-	0.1	-
C22-6n3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C24-1n9	-	-	-	-	-	-	-	-	-	0.1	-	-	0.1	-	-

S8, S9, S10 and S13: replicates for S5, S7, S3 and S11, respectively.

Iodine Value: As shown in Table 2, iodine value for [S3] and [S10], [S5] and [S8], [S7] and [S9] and [S11] and [S13] were 37.83 ± 0.30 and 37.54 ± 0.45; 33.59 ± 0.54 and 33.49 ± 0.34; 53.57 ± 0.66 and 53.68 ± 0.46; 53.84 ± 0.54 and 53.82 ± 0.70 respectively. The range of iodine value for other blends ([S2], [S4], [S5] and [S6]) was 0.23-1.24. The higher content of CO as in S2, S7, S9, S11, S12 and S13, generally producing blends of higher iodine value. This is due to the fact that canola oil has low saturated fatty acid content. Likewise, the blends rich in PMF (S3 and S10) showed a lower iodine values. Iodine value is very crucial in determining the oxidative stability of fats and oils.

Fatty Acid Composition: Fatty acid composition of the ternary blends containing PMF:VCO:CO is shown in Table 3. The fatty acid composition will influence the nutrition value and physical properties of the fat or oil and its products. For example, the presence of polyunsaturated fatty acid such as linoleic acid and linolenic acid can give beneficial health effect. On the other hand, the high level of stearic acid can render the product becoming harder [4]. In this study it was found that the S3 and S10 contained the highest amount of palmitic acid (50.6%), while S1 had the highest stearic acid (5.0%) and linoleic acid (4.1%) contents respectively. The presence of TAG with high in palmitic acid in most palm oil product causes it to form stable β' crystals, thus making it suitable for cocoa butter substitute. Compared to CB, all blends were high in palmitic acid due to presence of PMF.

CONCLUSIONS

Since cocoa butter (CB) is a prime fat with a unique melting profile, there is a need to produce CBS from a cheaper and easily available raw material. In this study, the physico-chemical properties of ternary blends containing PMF, VCO and CO were analyzed and compared to CB. Among the blends studied, S3 or S10 (PMF:VCO:CO, 90:5:5) was closer to CB, especially with respect to SFC and SMP.

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