COMPOSITION AND THERMAL PROPERTIES OF QUATERNARY MIXTURES OF PALM OIL:PALM STEARIN:SOYBEAN OIL:COCOA BUTTER

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ABSTRACT:

Pam oil (PO) is a semi-solid substance with potential functional lipid characteristics. A study was carried out to evaluate the effect of addition of soybean oil (SBO), palm stearin (PS) and cocoa butter (CB) on the solidification behavior of PO to formulate a mixture to become similar to lard (LD). A total of three mixtures were prepared: PO:PS:SBO:CB (38:5:52:5), PO:PS:SBO:CB (36:5:54:5) PO:PS:SBO:CB (34:5:56:5) (w/w), and identified by the mass ratio of PO to PS, CB and SBO. The fat mixtures were compared with lard in terms of the fatty acid and triacylglycerol compositions using gas chromatography and high performance liquid chromatography, thermal properties using differential scanning calorimetry (DSC) and solid fat content (SFC) using p-nuclear magnetic resonance (p-NMR). Although there were considerable differences between lard and the fat mixtures with regard to fatty acid and triacylglycerol compositions, some similarities were seen on their DSC thermal properties and solid fat content profile. Of the fat mixtures, PO:PS:SBO:CB (38:5:52:5) displayed closer similarity to lard by having least difference to SFC profile throughout the temperature range and a common DSC thermal transition at around -3.59 °C.

Keywords: palm oil, DSC, lard substitute, cocoa butter, soybean oil, thermal analysis

1. Introduction

Animal fats have traditionally been used as medium of frying in many types of foods. They were used in food applications mainly due to economic reasons since voluminous amounts of animal fats are discarded by the industry. Flavor imparted on foods by animal fats is an important reason for animal fat use. For instance, in some food cultures, vegetable oils used for frying are blended with small amounts of lard to impart characteristic flavors. Although the use of animal fats such as lard, tallow, etc. is already popular, the bad effects of the consumption are also being studied since the consumer perception begins to be negative with regard to the use of animal fat. As a result, there has been a great deal of interest among researchers to investigate various plant-based substitutes as alternative for lard (MARIKKAR and NOORZIYANNA YANTY, 2018; HSU and YU, 2002). When exploring these plant-fats, comparing their composition and thermal properties with those of LD was an important aspect of the investigations. For example, FLOTER (2009) highlighted the importance of studying physical properties data in product development. Separately, GIVEN (1990) also emphasized the influence of fat and oil physicochemical properties on the expression of functionality in baked goods.

The special properties of LD is large due to its peculiar nature of TAG composition. As reported previously by SILVA *et al*. (2009), LPO, OPO and SPO were the predominating TAG molecular species of LD with oleic, palmitic and stearic acids occurring in higher proportions. Owing to this reason, LD alternative fats were formulated using plant fat mixtures having these TAG molecular species. Accordingly, a replacement for LD was investigated using binary fat mixtures of mee fat and palm stearin as well as binary fat mixtures composed of engkabang fat and canola oil (Yanty, 2016; NUR ILLIYIN *et al*, 2013). In a separate experiment, YANTY (2016) found that ternary blends of avocado (Avo) fat, PS and CB also satisfied this requirement. As a notable feature, these fat mixtures displayed solidification behavior closely similar to that of LD. For our knowledge, the compatibility of quaternary fat mixtures comprising palm oil (PO), PS, soybean (SBO) and cocoa butter (CB) has not been considered for the said purpose. According to previous studies, PO contained approximately 40% oleic, 10% linoleic, 45% palmitic and 5% stearic acids (TAN and CHE MAN, 2000). As solidification values of PO was always higher than that of LD throughout the temperature region, addition of liquid oils such as SBO would be necessary. SBO has very higher amount of oleic and lineic acids, and hence the blending would tend to affect the proportion of palmitic and stearic acid contents. Owing to this reason, inclusion of small amounts of PS and CB would be needed to maintain the required proportions of palmitic and stearic acids in the final mixture. In this study, three quaternary plant-based fat blends (PO, SBO, PS and CB) were formulated to make comparison to lard with respect to their composition, DSC thermal properties, and solidification profiles.

2. Materials and Methods

2.1 Materials

LD was extracted using three batches of adipose tissues of swine collected from local slaughter houses as described in previous reports. Samples of PO and PS were obtained as generous gift from Malaysian Palm Oil Board (MPOB). CB and SBO were purchased from Malaysian Cocoa Board and a local supermarket, respectively. All chemicals used in this experiment were of analytical or HPLC grade.

2.2 Preparation of quaternary mixtures

The fat samples were melted at 70°C for 1 h before mixing. A total of three fat mixtures were prepared: PO:PS:SBO:CB (38:5:52:5), PO:PS:SBO:CB (36:5:54:5) PO:PS:SBO:CB (34:5:56:5) (w/w), and identified by the mass ratio of PO to PS, CB and SBO. All samples were kept under frozen storage at –20°C. Prior to analyses, the fat mixtures were removed from frozen storage, and then left static at room temperature for 1 h before being warmed at 70° C until they became completely molten.

2.3 Determination of SMP and IV

SMP and IV of the fat samples were determined according to AOCS method Cc.3.25, and AOCS method Cd Id–92, respectively (AOCS, 1999).

2.4 Determination of FA composition

Fatty acid methyl esters were prepared by dissolving 50 mg portion of oil in 0.8 mL of hexane and adding 0.2 mL portion of 1 M solution of sodium methoxide (PORIM, 1995). The top hexane layer was injected on an Agilent 6890N gas chromatograph (Agillent Technologies, Singapore) equipped with a polar capillary column RTX-5 (0.32 mm internal diameter, 30 m length, and 0.25 μm film thickness; Restex Corp., Bellefonte, PA) and a flame ionization detector (FID). Split injection was conducted with a split ratio of 58:1, nitrogen was used as a carrier gas at a flow-rate of 1.00 mL/min. The temperature of the column was 50°C (for 1 min), and programmed to increase to 200°C at 8°C/min. The temperatures of the injector and detector were maintained at 200°C. The identification of the peaks of the samples was done with reference to a chromatographic profile containing a set of fatty acid methyl ester standards. The percentage of fatty acid was calculated as the ratio of the partial area to the total area (NUR ILLIYIN *et al*, 2013).

2.5 Determination of TAG composition

The TAG compositions of samples were determined according to the method described by YANTY (2016) using Waters Model 510 liquid chromatography equipped with a differential refractometer Model 410 as the detector (Waters Associates, Milford, MA). The analysis of TAG was performed on a Merck Lichrosphere RP-18 column (5 µm; 12.5 cm × 4 mm i.d.; Merck, Darmstadt, Germany) which was maintained at 30°. The mobile phase was a mixture of acetone:acetonitrile (63.5:36.5) and the flow rate was 1.5 mL/min. The injector volume was 10 µL of 5% (w/w) oil in chloroform. Each sample was chromatographed three times, and the data were reported as peak area percentages. The identification of the peaks of the samples was done using a set of TAG standards purchased from Sigma-Aldrich (Deisehofen, Germany) as well as the TAG profiles of lard (NUR ILLIYIN *et al*, 2013), PO (TAN and CHE MAN, 2000), PS (CHE MAN and TAN, 2000), CB (SEGALL *et al.*, 2005) and SBO (TAN and CHE MAN, 2000) reported previously.

2.6 Thermal analysis by DSC

Thermal analysis was carried out on a Mettler Toledo differential scanning calorimeter (DSC 823 Model) equipped with a thermal analysis data station (STARe software, Version 9.0x, Schwerzenbach, Switzerland). Nitrogen (99.999% purity) was used as the purge gas at a rate of ~20 mL/min. Approximately, 4–8 mg of melted sample was placed in a standard DSC aluminum pan and then hermetically sealed. An empty, hermetically sealed DSC aluminum pan was used as the reference. The oil/fat samples were subjected to the following temperature program: 70°C isotherm for 1 min, cooled at 5°C/min to –70°C. The samples were held at –70°C isotherm for 1 min, and heated at 5°C/min to reach 70°C (YANTY, 2016)

2.7 Determination of SFC

SFC was measured according to AOCS method Cd 16b-93 (AOCS, 1999) using a Bruker Minispec (Model Mq 20) pulse nuclear magnetic resonance (pNMR) spectrometer (Karlsruhe, Germany). The sample in the NMR tube was melted at 70°C for 15 min, followed by chilling at 0°C for 60 min, and then held at each measuring temperature for 30 min prior to measurement. Melting, chilling, and holding of the samples were carried out in pre-equilibrated thermostatic glycol containing baths, accurate to 0.1°C. SFC measurements were taken at 5°C intervals over the range of 0–70°C.

2.8 Statistical analysis

All analyses were carried out in triplicate and the results were expressed as mean value ± standard deviation. Data were statistically analyzed by one-way analysis of variance (ANOVA), by using Tukey's Test of MINITAB (version 15) statistical package at 0.05 probability level.

3. RESULTS AND DISCUSSION

3.1 FA composition, SMP, and IV

FA composition of PO, PS, SBO, CB, all three quaternary mixtures and LD were presented in Table 1. Values showed the great variability of the samples, which might influence melting point, iodine values and the shape of DSC thermal curves. According to Table 1, the most dominant FA of PO was palmitic (43.99%), followed by oleic (39.24%), and linoleic (10.25%) acids. PS, the hard stearin of PO contained palmitic (78.9%) as the most dominant fatty acid followed by oleic (10.6%), and stearic (6.32%) acids. In the meantime, CB was found to possess stearic (37.84%) as the predominant FA followed by oleic (32.83%) and palmitic (25.34%). SBO, on the other hand, contained linoleic acid (53.93%) as the most predominant FA, followed by oleic (23.87%), palmitic (11.33%) and linolenic (6.46%) acids. These values were found to be comparable to those reported previously by TAN and CHE MAN (2000). They found that SBO contained linoleic (53.3%) as the most predominant FA, followed by oleic (23.6%), palmitic (12.6%) and linolenic (6.3%) acids. In fact, additions of PS, SBO and CB into PO caused significant ($p<0.05$) increments in the proportions of stearic, linoleic, and linolenic acids with concurrent decreases in the amounts of palmitic and oleic acids. Among these FAs, linoleic acid was found to be increased considerably while palmitic and oleic acids were found to decreased. The increment in the proportion of linoleic acid (30.78 to 34.44) of the quaternary mixtures was due to the presence of higher proportion of linoleic acid in SBO. This was far higher than the proportion of linoleic in LD or any other animal fats. However, the proportions of palmitic and oleic in the three mixtures were somewhat lower than the corresponding amounts found in LD. When compared to LD, the palmitic and linoleic acid contents of the quaternary mixtures were significantly ($p<0.05$) higher while stearic and oleic acid contents were significantly ($p<0.05$) lower. With the decreasing amount of PO in the mixtures, the total SFA content was tended to decrease (from 36.76 to 34.40 %) while the total USFA content was found to increase (from 63.24 to 65.60 %). Among the mixture, total USFA (~63%) and SFA (~37%) contents of the PO:PS:SBO:CB (38:5:52:5) were found to be roughly similarly to the total USFA (~61%) and SFA (~39%) contents of LD.

According to Table 1, the SMP of PO, PS, CB and LD were 30.5, 59.5, 34.25 and 27.5°C, respectively. This measurement was not done for soybean oil because this method does not apply to this type of oil. Additions of PS and CB into PO were found to cause significant ($p<0.05$) increases in SMP values (from 38.0 to 41.25 °C) when

Table 1: Basic physico-chemical characteristics and fatty acid composition (%) of PO, PS, SBO, CB, quaternary mixtures of PO:PS:SBO:CB and LD

	PO	**PS**	**SBO**	**CB**	**PO:PS:SBO:CB (38:5:52:5)**	**PO:PS:SBO:CB (36:5:54:5)**	**PO:PS:SBO:CB (34:5:56:5)**	**LD**
SMP	30.50 ± 0.71^{e}	59.50 ± 0.71^{a}	nd	34.25 ± 0.35^{d}	41.25 ± 0.35^{b}	$39.25 \pm 0.35^{b,c}$	38.00 ± 0.71^{c}	27.50 ± 0.71^{f}
IV	54.00 ± 0.00^{f}	14.00 ± 0.01^{h}	136.85 ± 0.21^{a}	34.00 ± 1.41^{g}	92.26 ± 0.74^{d}	94.36 ± 0.08^{c}	96.95 ± 0.10^{b}	73.76 ± 0.34^{e}
FA								
C12:0	0.33 ± 0.01^{a}	$0.20 \pm 0.14^{a,b}$	n.d	n.d	0.11 ± 0.01^{b}	$0.10 \pm 0.01^{a,b}$	0.10 ± 0.01^{b}	0.09 ± 0.01^{b}
C14:0	1.10 ± 0.00^{c}	1.65 ± 0.07^{a}	n.d	n.d	0.54 ± 0.01^{d}	0.40 ± 0.01^{e}	0.27 ± 0.02^{f}	1.24 ± 0.01^{a}
C16:0	43.99 ± 0.20^{b}	78.90 ± 0.28^{a}	11.33 ± 0.13^{e}	25.34 ± 0.04^{c}	27.88 ± 0.01^{c}	26.69 ± 0.07^{c}	25.72 ± 0.03^{c}	22.68 ± 0.48^{d}
C16:1	0.18 ± 0.01^{b}	n.d	n.d	n.d	$0.11 \pm 0.00^{b,c}$	$0.08 \pm 0.01^{c,d}$	0.04 ± 0.01^{d}	1.42 ± 0.05^{a}
C18:0	4.36 ± 0.06^{e}	6.32 ± 0.17^{d}	4.42 ± 0.01^{e}	37.84 ± 0.14^{a}	7.83 ± 0.04^{c}	7.86 ± 0.02^{c}	7.87 ± 0.01^{c}	12.70 ± 0.28^{b}
C18:1	39.24 ± 0.20	10.90 ± 0.00	23.87 ± 0.00^{e}	32.83 ± 0.26	29.39 ± 0.01^{b}	28.45 ± 0.07^{c}	27.56 ± 0.01^{d}	38.24 ± 0.13^{a}
C18:2	10.25 ± 0.06	1.58 ± 0.60	53.93 ± 0.02^{a}	2.92 ± 0.06	30.78 ± 0.05^{d}	32.90 ± 0.10^{c}	34.44 ± 0.09^{b}	20.39 ± 0.04^{e}
C18:3	0.19 ± 0.01	n.d	6.46 ± 0.10^{a}	n.d	2.96 ± 0.02^{d}	3.28 ± 0.01^{b}	3.56 ± 0.02^{b}	0.98 ± 0.01^{e}
C20:0	0.36 ± 0.01^{c}	0.46 ± 0.08^{c}	n.d	1.07 ± 0.01^{a}	0.43 ± 0.00^{c}	0.47 ± 0.01^{c}	0.48 ± 0.01^{c}	0.67 ± 0.01^{b}
Others	n.d	n.d	n.d	n.d	n.d	n.d	n.d	1.59

Each value in the table represents the mean of three determinations. Means within each row bearing different superscripts are significantly ($p<0.05$) different.

Abbreviations: PO, palm oil: PS, palm stearin: SBO, soybean oil: CB, cocoa butter; LD, lard; FA, fatty acid; SMP, slip melting point; IV, iodine value; n.d, not detected compared to that of original PO. This could be due to the fact that CB and PD were crystalline solid fats and had comparably higher proportions of palmitic and stearic acids (Table 1). With regard to the degree of unsaturation, the IV of PO, PS, SBO and CB were 54, 14, 136.85 and 34, respectively. The IV of quaternary mixtures of PO:PS:SBO:CB were found to be in the range of 92.26 to 96.95. All fat mixtures of this study displayed significantly higher ($p<0.05$) IV than either PO (54.00) or LD (73.76). Based on these results, none of the quaternary mixtures of this study was found to have a SMP and IV closely similar to those of LD. The changes in SMP and IV of these mixtures as noted before (Table 1) could be mainly due to these changes in FA compositions.

3.3 TAG composition

The TAG compositions of PO, PS, SBO, CB, quaternary mixtures of PO:PS:SBO:CB were compared to that of LD as shown in Table 2. PO composed of PPO (31.61%), POO (24.76%), PPL (10.19%) and POL (9.96%) as dominant TAG molecules. These values were comparably similar to the ranges reported previously (MARIKKAR and GHAZALI, 2011). On the other hand, PS contained PPP (68.66%), PPO (15.23%), and StOP (11.07%) as major TAG molecules. The major TAG molecules of CB were SOP (40.78%), SOS (29.35%) and PPO (18.08%). SBO, on the other hand was found to possess LLL (23.56%), OLL (17.77%), PLL (15.82%) and POL (13.69%) as the major TAG molecules. After addition of PS, SBO and CB into PO, some of the TAG molecules were found to increase (e.g. PPL, OOL, POL, PPP and SOS) while others were tended to decrease (e.g. MMM, MPL, PPL, OOO, POO, PPO, SOO, SPO and PPS). The increments in the proportions of PLL, OOL and POL could be due to the presence of SBO in the mixture. There were significant increases in the proportions of PPP, and SOS as these were major TAG species of PS (NOR AINI and MISKANDAR, 2007) and CB (LIU *et al*., 2007; SEGALL *et al*., 2005), respectively. TAG molecular species namely, LLnLn, LLLn, OLnLn, LLL, PLLn, OLL, POLn and SSS were also found in the mixtures after addition of PS, SBO and CB into PO. Among the TAG molecular species, PPO (ranging from 13.48 to 12.09%) and POO (ranging from 10.87 to 9.70%) were found to reduce dramatically in the mixtures when compared to those of original PO (31.61 and 24.76%, respectively). In addition, UUU and StStSt TAG molecules were found to increase with respect to the original sample of PO. For instance, the UUU TAG was increased (34.89 to 37.14%) when compared to that of the original sample of PO (12.68%). The StStSt TAG molecules were also found to decrease slightly (24.86 to 22.47%). In the meantime, the amount of PPO in the mixtures was found to be somewhat similar to those of LD. When compared to LD, the amount of UUU and StStSt TAG of the PO:PS:SBO:CB mixtures were found to be higher with concurrent decreases of UUSt and UStSt TAG molecules. The increasing proportions of UUU TAGs in the fat mixtures could have led to the occurrence of greater amounts of oleic and linoleic acids as shown in the overall FA distribution

(Table 1). Among them, UStSt TAG content of PO:PS:SBO:CB (38:5:52:5) was found to be closely (24.86%) comparable to that of LD (26.60%).

3.4 Thermal characteristics

The cooling behaviors of PO, PS, SBO, CB, PO:PS:SBO:CB mixtures and LD were compared in Figure 1a. The cooling profile of LD (curve A) is characterized by two widely separated transitions: a high (a_1, a_2) and low (a_3) temperature regions. This was roughly similar to the findings reported previously (MARIKKAR and YANTY, 2014). According to Figure 1a, the cooling profile of PO (curve E) had four cooling transitions; one major sharp peak at 18.8 °C (e_1) and one broader peak at 5.0 °C (e_2), with a shoulder peak at -4.2 °C (e_3) which was in accordance with the previous findings (TAN and CHE MAN, 2000). In addition to these, a minor peak was also appeared in the lower-temperature region at around -42 °C (e_4). The cooling thermograms of PS (curve F) and CB (curve H) had one major sharp peak at around 42.8 (f_1) and 13.4 °C (h_2), respectively. In the case of CB, additional small peak (f_4) was also found at -30.7 °C. As SBO was a liquid oil, its DSC curve (curve G) had three cooling transition at low-temperature region (below 0 °C); the first peak was found at -9.2 °C (g_1), a broader peak at -37.7 °C (g_2) and a small peak at -64.5 °C (g_3). These agreed with the results reported in other studies (TAN and CHE MAN, 2000). Additions of PS, SBO and CB into PO brought considerable changes to cooling profiles of the three PO:PS:SBO:CB mixtures. Only two thermal transitions were displayed by the mixtures; a major sharp peak at around 21 °C and a minor peak at around -1 °C. With respect to original PO curve, the peak-maxima of the thermal transitions of quaternary mixtures were also found to have shifted slightly. These changes in the profiles of mixtures could be attributed to the changing SFA to USFA ratio as noted previously in Tables 1 and 2. This has been in accordance with the findings reported by others (NUR ILLYIN *et al*., 2013). On the other hand, the major and minor sharp peaks of LD were found at 10.3 and -18.0 °C, respectively. The high-melting cooling transitions of PO:PS:SBO:CB mixtures were found to be little higher (22.3 °C) when compared to that of LD (18 °C). These results suggested that none of the quaternary mixtures of PO:PS:SBO:CB had thermal transitions exactly matching with the cooling thermogram of LD. However, the peak corresponding to CB 13.4 °C (h_2) showed a closer similarity to the high melting transition of LD (10.3 °C).

Table 2: TAG composition of PO, PS, SBO, CB, quaternary mixtures of PO:PS:SBO:CB and LD

TAG	PO	PS	SBO	CB	PO:PS:SBO:CB (38:5:52:5)	PO:PS:SBO:CB (36:5:54:5)	PO:PS:SBO:CB (34:5:56:5)	LD
LLnLn	n.d	n.d	1.31±0.03^{a}	n.d	0.70±0.01^{b}	0.70±0.00^{b}	0.74±0.01^{b}	n.d
LLLn	n.d	n.d	7.66±0.01^{a}	n.d	3.93±0.01^{c}	4.10±0.01^{b,c}	4.29±0.01^{b}	1.54±0.21^{d}
OLnLn	n.d	n.d	0.02±0.00^{a}	n.d	0.01±0.00^{b}	0.01±0.00^{b}	0.01±0.00^{b}	n.d
LLL	n.d	n.d	23.56±0.03^{a}	n.d	12.23±0.00^{d}	12.72±0.01^{c}	13.15±0.01^{b}	0.68±0.21^{e}
PLLn	n.d	n.d	3.64±0.01^{a}	n.d	1.90±0.01^{d}	1.97±0.00^{c}	2.05±0.01^{b}	n.d
OLL	n.d	n.d	17.77±0.01^{a}	n.d	9.28±0.01^{d}	9.61±0.00^{c}	9.98±0.01^{b}	4.68±0.08^{e}
MMM	0.21±0.01^{a}	n.d	n.d	n.d	0.16±0.01^{b}	0.17±0.00^{b}	0.17±0.01^{b}	n.d
PLL	2.08±0.03^{f}	n.d	15.82±0.01^{a}	0.27±0.00^{g}	8.23±0.04^{d}	8.56±0.03^{c}	8.84±0.01^{b}	7.05±0.06^{e}
MPL	0.54±0.01^{a}	n.d	n.d	n.d	0.19±0.01^{b}	0.18±0.00^{b,c}	0.17±0.00^{c}	n.d
POLn	n.d	n.d	0.13±0.01^{a}	n.d	0.06±0.00^{b}	0.07±0.01^{b}	0.08±0.01^{b}	n.d
OOL	1.62±0.02^{d}	n.d	8.72±0.23^{a}	n.d	5.58±0.00^{c}	5.73±0.01^{c}	5.85±0.01^{c}	6.93±0.04^{b}
POL	9.96±0.01^{e}	0.32±0.03^{g}	13.69±0.02^{b}	0.85±0.01^{f}	11.31±0.02^{d}	11.86±0.01^{c}	12.15±0.11^{c}	20.00±0.27^{a}
PPL	10.19±0.01^{a}	1.03±0.10^{h}	2.25±0.01^{f}	1.55±0.00^{g}	5.02±0.01^{b}	4.73±0.01^{c}	4.52±0.01^{d}	2.62±0.04^{e}
OOO	3.97±0.02^{b}	0.13±0.01^{f}	2.02±0.13^{d}	0.69±0.01^{e}	3.14±0.00^{c}	3.13±0.01^{c}	3.12±0.01^{c}	4.33±0.21^{a}
POO	24.76±0.01^{a}	2.22±0.02^{g}	1.11±0.02^{e}	2.27±0.02^{f}	10.87±0.04^{c}	10.28±0.07^{d}	9.70±0.04^{e}	20.67±0.11^{b}
PPO	31.61±0.01^{a}	15.23±0.03^{c}	0.56±0.03^{h}	18.08±0.01^{b}	13.48±0.20^{d}	12.73±0.05^{e}	12.09±0.02^{f}	10.63±0.01^{g}
PPP	4.77±0.03^{c}	68.66±0.13^{a}	n.d	0.26±0.01^{f}	4.90±0.04^{b}	4.75±0.02^{c}	4.46±0.01^{d}	0.38±0.00^{e}
SOO	2.72±0.02^{c}	0.26±0.06^{g}	1.23±0.00^{f}	2.98±0.00^{b}	1.85±0.01^{e}	1.92±0.01^{e}	2.10±0.01^{d}	3.62±0.04^{a}
SPO	5.65±0.01^{d}	11.07±0.01^{c}	0.54±0.02^{g}	40.78±0.10^{a}	4.58±0.02^{e}	4.35±0.01^{f}	4.15±0.01^{f}	12.52±0.12^{b}
PPS	0.92±0.01^{a}	0.68±0.04^{c}	n.d	0.41±0.01^{d}	0.86±0.01^{a,b}	0.84±0.00^{a,b}	0.82±0.00^{b}	0.81±0.00^{b}
SOS	0.52±0.01^{e}	n.d	n.d	29.35±0.01^{a}	1.59±0.01^{b}	1.57±0.01^{b,c}	1.54±0.00^{c}	0.83±0.01^{d}
SSS	n.d	0.41±0.01^{a}	n.d	0.40±0.04^{a}	0.02±0.00^{c}	0.02±0.00^{c}	0.02±0.00^{c}	1.31±0.01^{b}
Others	0.48±0.01	n.d	n.d	2.11±0.14	n.d	n.d	n.d	1.41±0.33
UUU	12.68	0.13	61.06	0.69	34.89	36.00	37.14	18.16
UUSt	40.06	2.80	35.59	6.37	34.22	34.66	34.92	51.34
UStSt	47.97	27.33	3.35	89.76	24.86	23.56	22.47	26.60
StStSt	5.90	69.75	n.d	0.66	5.94	5.78	5.47	2.50

Each value in the table represents the mean of two determinations. Means within each row bearing different superscripts are significantly ($p<0.05$) different.

Abbreviations: TAG, triacglycerol; PO, palm oil; PS, palm stearin; SBO, soybean oil; CB, cocoa butter; LD, lard; O, oleic; P, palmitic; L, linoleic; Ln, linolenic; St, stearic; U, unsaturated; S, saturated; n.d, not determined

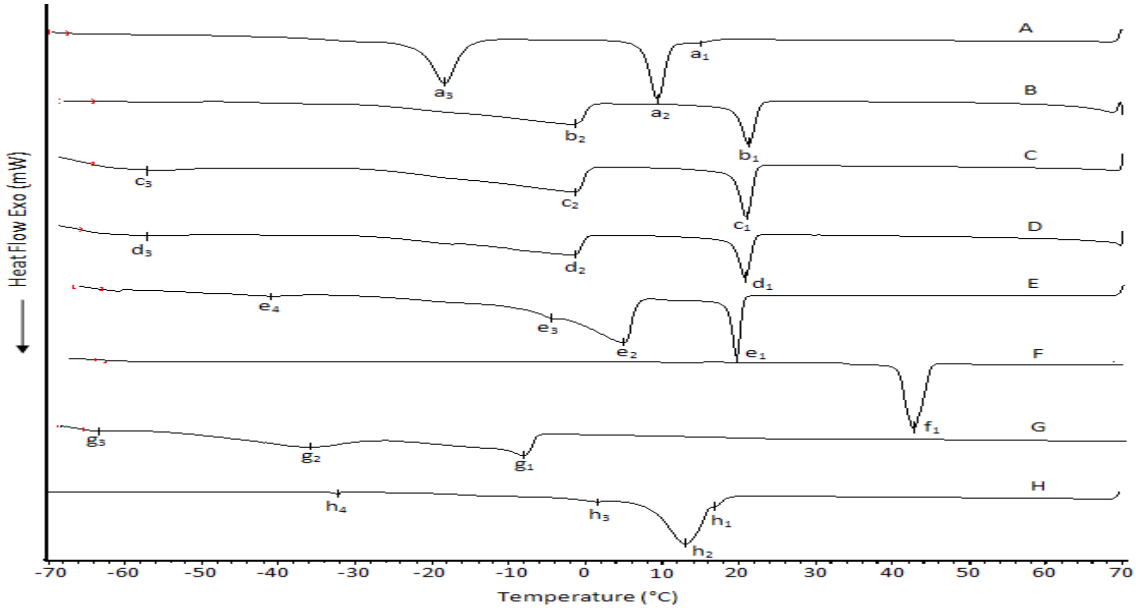

Figure 1a: DSC cooling thermograms of LD (A), quaternary mixtures of PO:PS:SBO:CB (B=38:5:52:5; C= 36:5:54:5; D=34:5:56:5), PO (E), PS (F), SBO (G) and CB (H)

Abbreviations: LD, lard; PO, palm oil; PS, palm stearin; SBO, soybean oil; CB, cocoa butter

The melting behaviors of PO, PS, SBO, CB, PO:PS:SBO:CB mixtures and LD were depicted in Figure 1b. The melting profile of LD (curve A) has five endothermic transitions, which could be classified into two distinct regions namely, low-melting region below 0 °C (a_1, a_2) and high-melting region above 0 °C (a_3, a_4, a_5). The native PO sample (curve E) had seven endothermic transitions; two major endothermic regions, corresponding to low-melting fraction known as olein and high-melting fraction known as stearin. These were largely confirmatory with the findings reported previously. The high-melting region (above 10 °C) consisted of a plateau with a pair of shoulder peaks (c_6 and c_7), while the low-melting region (below 10 °C) contained five overlapping peaks (c_1, c_2, c_3, c_4 and c_5). PS (curve F) and CB (curve H), on the other hand, had one major sharp peak at 59.0 (f_1) and 20.4 °C (h_2). In addition, CB had one shoulder peak at 14.8 °C (h_1). In the meantime, SBO (curve G) had four endothermic transitions at low-temperature region; the profile was comparably similar to that reported previously by TAN and CHE MAN (2000). This could be due to the fact that SBO was a liquid oil that contained a high amount of USFA (Table 1) and UUU TAG molecules (Table 2). The major peak was found at -27.7 (g_2) °C with two shoulder peaks at -20.1 (g_3) and -6.5 °C (g_4). The minor peak was found at -38.2 °C (g_1). Generally, the melting profile of mixtures (curve B, C, D) has six endothermic transitions, which could be classified into three distinct regions namely, low-melting region below -20 °C (peaks at position 1 and 2), middle melting region between -10 to 20 °C (peaks at position 3, 4 and 5) and high-melting region at around 40 °C (peaks at position 6).

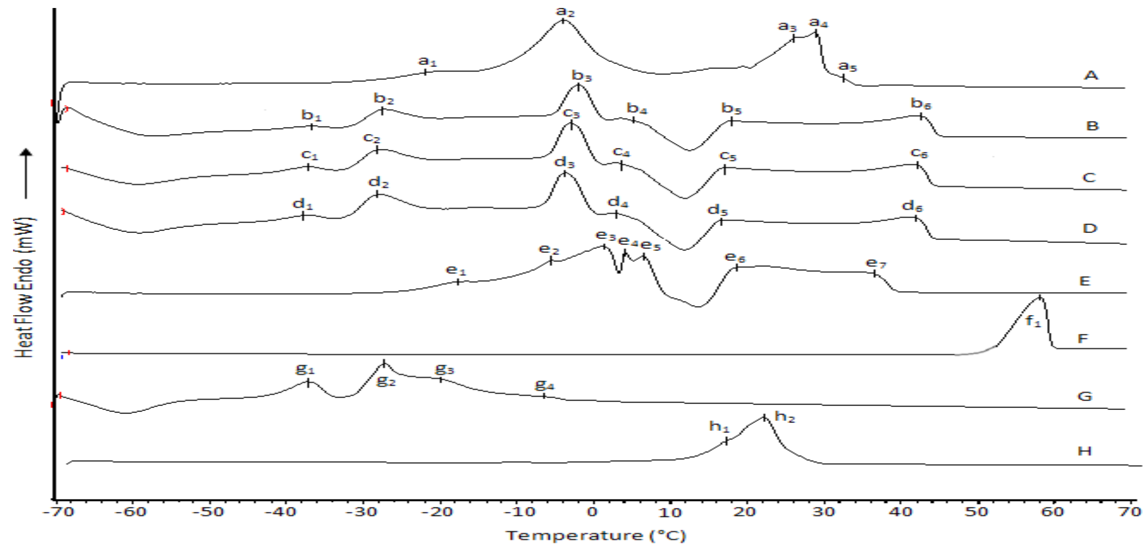

Figure 1b: DSC melting thermograms of LD (A), quaternary mixtures of PO:PS:SBO:CB (B=38:5:52:5; C= 36:5:54:5; D=34:5:56:5) PO (E), PS (F), SBO (G) and CB (H)

Abbreviations: LD, lard; PO, palm oil; PS, palm stearin; SBO, soybean oil; CB, cocoa butter

According to Figure 1b, the thermal profiles displayed by the quaternary mixtures were considerably different from the melting profile of original sample of PO. The melting profiles of mixtures were found to have one additional minor peak (b_2, c_2 and d_2) with a shoulder peak (b_1, c_1 and d_1) at below -20 °C could be attributed to the presence of SBO, which had all of its thermal peaks in the low-melting region. With respect to the original sample, T_{endset} of all quaternary mixtures were found to be shifted to higher temperature region after addition of PS and CB into PO. When compared to LD (T_{endset} =37.5 °C), all three quaternary mixtures had higher end-set of melting (T_{endset}) (at around 44 °C) and lower on-set of melting T_{onset} (at around -45 °C). Although there were much differences in melting transitions between lard and the mixtures, a closer similarity between them was seen at the peak-maximum of (b_3, c_3 and d_3) and (a_2) at -3.59 °C.

3.5 Solidification behavior

A comparison of the SFC profiles of the quaternary fat mixtures and LD was given in Figure 2. The SFC of LD and PO at 0 ºC was 30.8 and 68.63%, respectively and tended to decrease gradually until they become 0% at 40 and 55 ºC, respectively. As mentioned previously by YANTY (2016), the SFC values of PS and CB were found to drop dramatically at 25 ºC and above 55 ºC, respectively. This unique behaviour of PS and CB was largely in agreement with the observed thermal events in their respective DSC curves where the occurrence of single sharp peak was indicative of the meltdown of the entire TAG groups within a narrow temperature range. This rapid meltdown behaviour of these fats was also further discussed in other reports (YANTY, 2016). However, the SFC value of SBO at 0 ºC was found to be 0.31% and become 0% at 10 ºC. This phenomenon could be due to the presence of high amount of USFAs (Table 1) and UUU

TAG molecules (Table 2) in SBO. The SFC value of PO was found to be higher than that of LD within the temperature range between 0 and 20 °C. Addition of SBO into PO could probably reduce the amount of SFC in this temperature region. However, addition of 50 % of SBO into PO was resulted in a big slope (below SFC values of LD) within this temperature ranges and the SFC values tended to be higher than that of LD from 30 to 55 °C. Although additions of PS into PO:SBO mixtures were tended to increase the SFC values at 0 to 20 °C, the SFC values were still higher than those of LD at 30 and 35 °C.

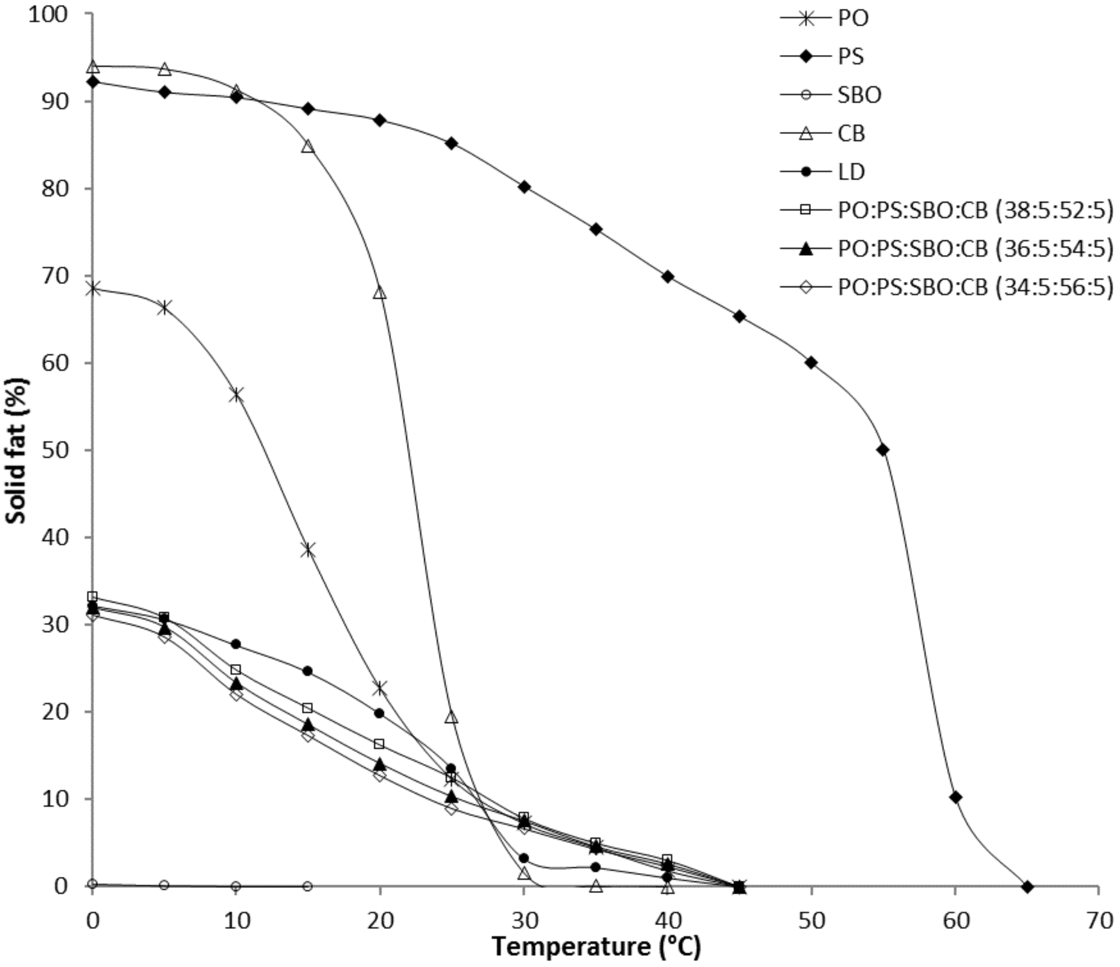

Figure 2: Solid fat content of PO, PS, SBO, CB, quaternary mixtures of PO:PS:SBO:CB and LD

Abbreviations: PO, palm oil; PS, palm stearin; SBO, soybean oil; CB, cocoa butter; LD, lard

According to another set of SFC data not shown here, addition of CB into PO:SBO mixtures did not change the SFC values above 30 °C. Hence, it was assumed that blending PO with an appropriate amount of PS, SBO and CB would help to adjust SFC values of PO to become closer to that of lard at almost all temperature regions. The SFC values of three quaternary mixtures in Figure 2 were found to be lower than that of LD in between 0 to 25 °C. However, the SFC values of the mixtures were tended to be higher than that of lard above 30 °C due to a presence of PS. Out of the three quaternary mixtures, PO:PS:SBO:CB (38:5:52:5) was found to have SFC value somewhat closer to LD at 0, 5 and 25° C. The calculations presented in Table 3 also showed that PO:PS:SBO:CB (38:5:52:5) was found to have the least difference to LD in terms of SFC values throughout the temperature range. Hence, this mixture was found to be the most compatible to LD in term of solidification behavior.

Table 3: Comparing least difference of SFC values of LD and PO:PS:SBO:CB mixtures

Temp (°C)	PO:PS:SBO:CB (38:5:52:5)+/- LD	PO:PS:SBO:CB (36:5:54:5)+/- LD	PO:PS:SBO:CB (34:5:56:5)+/- LD
0	0.96	-0.25	-1.13
5	0.17	-0.92	-2.08
10	-2.87	-4.35	-5.68
15	-4.15	-6.04	-7.31
20	-3.59	-5.71	-7.1
25	-1.05	-3.2	-4.58
30	4.63	4.33	3.44
35	4.28	3.69	3.62
40	2.02	1.61	1.29
Total	**0.4**	**-10.84**	**-19.53**

Abbreviations: PO, palm oil; PS, palm stearin: SBO, soybean oil; CB, cocoa butter; Temp, Temperature

4. CONCLUSIONS

This study demonstrated the possibility of producing a fat mixture to mimic some of the compositional and thermal properties of LD by blending PO with PS, SBO and CB in appropriate ratios. Among the three different mixtures formulated, PO:PS:SBO:CB (38:5:52:5) was found to have the closest similarity to LD in terms of some DSC parameters and SFC behavior. The SFC values of this mixture were found to display the least difference to those of LD throughout the temperature range. Particularly, the closest compatibility in terms of SFC values was seen at 0, 5 and 25°C. In terms of composition, the USFA and SFA contents of this mixture were least difference to those of LD.

ACKNOWLEDGEMENTS

The authors acknowledge partial funding from a research grant (FRGS/2/2013/SG01/UPM/02/5) awarded by Ministry of Higher Education Malaysia

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