

ARE CHARACTERISTICS OF SOFT PALM STEARINS SIMILAR TO SOFT PALM MID FRACTIONS?

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ABSTRACT

The aim of this assessment was to determine the variation between soft palm mid fractions (sPMF) and soft palm stearins (sPOs) which are the co-fractions (solid fractions) obtained from two different fractionation processes which yield palm olein of iodine value (IV) 60. The sPMF and sPOs are not governed by any official standard specifications and are traded based on contractual specifications. Furthermore, the physical and chemical characteristics of sPOs lack documentation as it falls into the general category of palm stearin. Hence, users who are unaware of the differences between these two fractions are misinformed and misguided, leading to dysfunctional application of these fractions in food products. This assessment of sPMF and sPOs evaluated the triacylglycerol composition, fatty acid compositions (FAC), IV, dropping point (DP), solid fat content (SFC) profiles and thermal behaviours in order to establish parameters which can be used as quality qualifiers, which are able to distinctively discriminate both fractions. The triacylglycerol compositions differed significantly between sPMF and sPOs. sPMF contained high amounts of monounsaturated triacylglycerols ranging from 61.83% to 80.07% with 1,3-dipalmitoyl-2-oleoyl-glycerol (POP) ranging from 43.53% to 55.95%. Lesser amount of monounsaturated triacylglycerols were present in sPOs, ranging from 55.56% to 57.33% (POP from 38.36% to 41.81%). The trisaturated triacylglycerols ranged from 2.45% to 5.41% in sPMF and higher values were detected in sPOs ranging from 10.46% to 18.52%. SFC profiles of sPMF and sPOs varied significantly. The sPMF exhibited a sharp decrease in the percentage of solids from 20°C to 30°C which were not exhibited by sPOs. The DP of sPMF ranged between 24.3°C to 31.8°C and sPOs varied between 40.3°C to 50.1°C. sPMF and sPOs exhibit unique and distinctive crystallisation and melting profiles which can be used to differentiate these two fractions. Fatty acid composition and iodine values exhibited overlapping values, hence, are inadequate indicators to differentiate these fractions. The assessment concludes that triacylglycerol composition, DP, SFC profile and thermal behaviour (crystallisation and melting) are indicative parameters that are able to assist in differentiating the physical and chemical characteristics of sPMF and sPOs.

Keywords: soft palm mid fraction, soft palm stearin, 1-3-dipalmitoyl-2-oleoyl-glycerol (POP).

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INTRODUCTION

Oil palm has emerged as a major economic crop feeding the world with an overwhelming production

of 67.92 million tonnes in 2017. A major portion of palm oil amounting to 80% of production is channelled towards supporting the global demand of the food sector (Kushari *et al.*, 2018). Refined palm oil to a great extent is fractionated to olein (liquid) and stearin (solid) fractions, as these fractions have distinctive roles in the food sector. Palm olein and palm stearin undergo single or multiple

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fractionation steps to fulfil the specific application and functionality requirements of the food sector.

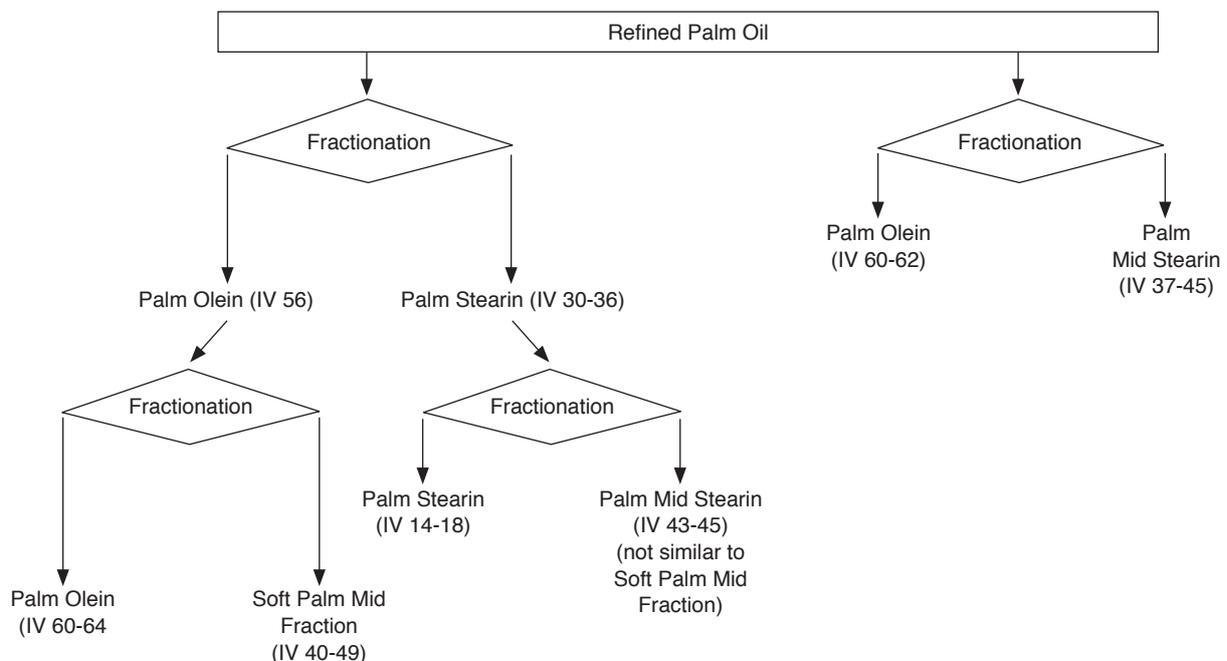
Soft palm mid fraction (sPMF) and soft palm stearin (sPOs) are co-fractions (solid fractions) obtained from the fractionation process to produce palm olein of iodine value (IV) 60. Figure 1 shows the flow charts of the two routes for obtaining palm olein of IV 60, the common routes practiced by the Malaysian fractionation plants. The first route is fractionation of palm olein IV 56, which will yield palm olein IV 60 and sPMF (Danthine *et al.*, 2017; Gijs *et al.*, 2007; Calliauw *et al.*, 2007; Hashem *et al.*, 2018; Kellens *et al.*, 2007). The second route is single fractionation of palm oil (IV 50 to 52) which yields palm olein IV 60 and sPOs. The latter is cost-effective and is preferred by the industry, as this process shortens the production time, hence, improves productivity. Nevertheless, sPMF is a premium grade product, in contrast to sPOs which is traded as the general grade of palm stearin.

The sPMF and sPOs are not governed by any official standard specifications and are traded based on contractual specifications. The concern arises as some of the contractual specifications are not able to discriminate between sPMF and sPOs. Iodine values are generally included in the contractual specifications for trading of sPMF and sPOs. The non-significantly difference iodine values of sPMF and sPOs stands as a challenge to the potential buyers as it may cause confusion. Hence,

sPMF and sPOs are two solid fractions which are sometimes misinterpreted by food formulators, who are unaware of the differences between these two fractions, which in some cases have led to dysfunctional application of these fractions in food products.

Palm mid fractions (PMF) are categorised as specialty fats due to their unique sharp melting characteristic which suits special functional applications in food formulations (Gee, 2007; Sonwai *et al.*, 2014). PMF are widely used as cocoa butter equivalent, coating fats, fat component of margarine and shortening (Kellens *et al.*, 2007; Lumor *et al.*, 2010; Biswas *et al.*, 2017; Jahurul *et al.*, 2014). The fractionation process increases the crucial triacylglycerol which is 1,3-dipalmitoyl-2-oleoyl-glycerol (POP) content from approximately 27% in palm olein to above 40% in the sPMF. The characteristics of sPMF are dominated by the amount of POP present in the fractions. Nevertheless, the presences of other triacylglycerols have an impact on the overall characteristics of the fractions. The sPMF is further fractionated to obtain solid fraction which is known and traded as hard palm mid fraction, a value-added premium fraction. The key variation between these two fractions is the amount of POP, the amount of POP in hard palm mid fractions are more than 65%.

The sPOs are least documented as these fractions are categorised as general grade of palm stearin.



Note: IV - iodine value.

Source: Information from the Malaysian fractionation plants operators: Sime Dardy Jomalina Sdn Bhd, Agri Asia Refinery Sdn Bhd, Sawit Raya Sdn Bhd, SOP Edible Oils Sdn Bhd, Premium Vegetable Oil Sdn Bhd, Mewah Oils Sdn Bhd Malaysia, Ecolex Sdn Bhd and Moi Foods Malaysia Sdn Bhd.

Figure 1. Fractionation process flow of production of soft palm mid fraction (sPME) and soft palm stearin (sPOs).

Most palm stearin from Malaysia is traded based on the Palm Oil Refiners' Association Malaysia (PORAM) specifications, which specifies palm stearin as fractions with IV of 48 maximum and melting point value of 44°C minimum (PORAM Specification., 2013). Palm stearins are very cost-effective, natural and non-hydrogenated fats which are commonly and widely used in the production of frying fats, shortening, margarine, vegetables ghee (vanaspati), dairy fat replacers and animal fat replacers (Adhikari *et al.*, 2010; Sivaruby *et al.*, 2018).

The application of fats in products such as in cocoa butter alternatives, margarine, shortenings, replacers of dairy fats and replacers of animal fats to a large extent is influenced by the triacylglycerol compositions (Biswas *et al.*, 2017). Triacylglycerol composition determines the characteristics of the fats with respect to their macroscopic properties such as overall texture which in turn affects the compatibility of the fats into various food systems. It is well documented by other researchers that small variation in triacylglycerol composition gives significant changes to the overall functionality and application of the fats in the final food products. Changes in triacylglycerol composition will cause changes in melting and crystallisation behaviour, which determines the structure, crystal morphology and polymorphic transitions of the crystals, hence, leads to variation in the crystal network (Narine and Marangoni, 1999; Marangoni, 2005). Triacylglycerols are basically structural component of fats, thus, variation in triacylglycerol composition will lead to major changes in the characteristics of the functionality of the fats (Vereecken *et al.*, 2010). Hence, structure to functionality relationship is of great importance in the selection of fats for food formulation.

The aim of this evaluation was to determine and discuss the variations and similarities in the physical and chemical characteristics of sPMF and sPOs. The analyses of interest in determining the physical and chemical characteristics of sPMF and sPOs were triacylglycerol composition, fatty acid composition (FAC), IV, dropping point (DP), solid fat content (SFC) profile and thermal behaviour of the fractions. These analyses were able to indicate and identify the variations and similarities of these fractions. Hence, enables differentiation of these fractions by establishing their unique characteristics.

MATERIALS AND METHODS

Materials

The sPMF and sPOs samples were obtained from the Malaysian fractionation plants. The samples obtained were produced via dry fractionation process.

Triacylglycerol Composition Analysis

Triacylglycerol analysis was determined using the method reported in Ramli *et al.* (2008). Samples were prepared by dissolving 0.015 g litre⁻¹ in acetone. Solid impurities were removed by filtering the samples through a 0.2 µm nylon membrane filter. High performance liquid chromatography (Agilent 1100 Series, USA) was used to determine the triacylglycerol composition. Two Purospher® STAR RP-18 end-capped column (25 cm length x 4 mm i.d with of 5 µm particle size) (Merck KGaA, Darmstadt, Germany) were connected in series. Sample of 10 µl was injected into the column and column was kept in an oven at 30°C. The mobile phase used was acetone:acetonitrile (75:25% vol/vol), at a flow rate of 1.0 ml min⁻¹ under isocratic conditions. The individual peaks were identified by a refractive index detector and the total run time was 45 min per sample. The chromatograms were identified by comparing retention times with standards and quantified using the area normalisation method (Ramli *et al.*, 2008).

Fatty Acid Composition

FAC was determined as fatty acid methyl esters. The samples (0.05 g) were weighed and dissolved in 1 ml hexane. The mixture was then added with sodium methoxide solution, 0.2 ml of NaOCH₃ (2M), in anhydrous methanol and then mixed for 1 min with a vortex mixer. After sedimentation of sodium glycerolate, 1 µl of clear supernatant was injected into Rtx 2330 fused silica capillary column (60 m x 0.25 mm x 0.25 mm) (Restex Corporation, USA) and analysed using a Burker Gas Chromatography system Model 430-GC (Burker Daltonics, CA, USA) equipped with a flame ionisation detector (FID) and Galaxie Chromatography Data System. Injection and detection temperatures were set at 240°C. The oven temperature was set at 190°C. The column temperature was isothermal at 185°C. The carrier gas was helium with a flow rate of 1 ml min⁻¹. The peaks were identified by comparing retention times with FAME standards and quantified using peak area normalisation methods.

Iodine Value

The IV denotes the degree of unsaturation of fatty acids in oils and fats. Determination of IV was carried out according to the MPOB Test Method MPOB p3.2:2004 (Kuntom *et al.*, 2005). The 20 g of totally melted and homogenised sample and 20 ml of solvent (1:1 cyclohexane:glacial acetic acid) were weighed into a conical glass flask fitted with a round glass stopper. Followed by 25 ml of Wijs reagent was added, the stopper was placed, the solution swirled by hand and was placed in a dark

room for 1 hr. A blank test was prepared by omitting the test portion. At the end of the reaction time, 20 ml of potassium iodide and 150 ml of water were added. The solution was then titrated with standard sodium thiosulphate solution. The blank test was similarly treated and titrated. Calculation of the IV was carried out and the IV were expressed as g of I₂/100 g of oil.

$$IV = \frac{12.69 C (V_1 - V_2)}{M}$$

C is concentration of sodium thiosulphate.

V₁ is volume, in millilitres, of sodium thiosulphate solution used in blank test.

V₂ is volume, in millilitres, of sodium thiosulphate solution used in determination of sample.

M is the mass, in grams, of sample.

Dropping Point

The DP indicates the temperature where the frozen samples become liquid and are able to flow. Determination of DP was carried out in accordance to MPOB Test Method f1.2 (Kuntom *et al.*, 2005). A Mettler Toledo DP analysing system with central processor FP90 (AG, Schwerzenbach, Switzerland) was used to determine the DP of the samples. The sample cup (inner diameter 2.8 mm Mettler No. 18732) was placed in the freezer (below -5°C) for 10 min. The sample was melted, homogenised and filled into the sample cup. The filled cup was kept in the freezer for 15 min. The DP analyser was set at 10°C below the expected DP. The heating rate was set at 1°C min⁻¹. The sample was removed from the freezer and immediately placed into the DP measuring cell and the DP values were recorded (Sivaruby *et al.*, 2013; Kuntom *et al.*, 2005).

Solid Fat Content

SFC denotes the amount of solid present at a specific temperature. Determination of SFC was performed according to the MPOB Test Method p4.8:2004 (Kuntom *et al.*, 2005). The SFC was measured with Bruker Minispec PC 120 pulse-NMR. Samples were totally melted at 80°C to erase all crystal memory. The totally melted samples were homogenised and filled into tubes (10 mm o.d x 75 mm length) up to 3 cm in height. The samples were tempered at 70°C in a water bath for 30 min, before chilling at 0°C for 90 min. These tubes were conditioned in pre-equilibrated thermostated baths for 30 min prior to the measurement. The measuring temperatures were 0°C, 5°C, 10°C, 15°C, 20°C, 25°C, 30°C, 35°C, 40°C, 45°C, 50°C, 55°C and 60°C. The direct method was employed for the measurements.

Thermal Behaviour

Differential scanning calorimetry (DSC) analyses were carried out using a Perkin Elmer DSC Model DSC-7 with refrigerated cooling system (Perkin Elmer, Norwalk, CT). The instrument was attached to a data processing unit, Perkin Elmer Thermal Data Station. Calibration was carried out with an indium standard. The 4 to 5 mg of a precisely weighed (± 0.1 mg) fat sample was placed in the DSC pan and hermetically sealed. The cooling and heating profiles of samples were defined by using two different temperature programs. The samples were subjected to the following temperature profile: 70°C for 5 min, cooled at a cooling rate of 10°C min⁻¹ to -40°C and the cooling thermogram was recorded. The same samples were held at -40°C for 5 min then heated from -40°C to 70°C at a heating rate of 10°C min⁻¹ and the melting thermogram was recorded.

Statistical Analysis

All measurements were performed in triplicate unless stated and data were reported as mean \pm standard deviations of independent analysis. The significant difference of the samples was analysed using a one-way analysis of variance (AVONA) by Tukey's test at a significance level of 0.02. All statistical analyses were computed using Minitab 16.0 (Minitab Inc, Pennsylvania, USA).

RESULTS AND DISCUSSION

Triacylglycerol Composition

The eight sPMF samples collected from the Malaysian fractionation plants were produced via fractionation of palm olein IV 56. sPMF contain high amounts of monounsaturated triacylglycerols ranging from 61.83% to 80.07% with the most abundant triacylglycerol being POP ranging from 43.53% to 55.95%, as shown in *Table 1*. The amount of POP reported by Sonwai's team was 51.8%, Biswas's team reported 50.7% and Calliauw's team reported two values, which were 40.75% and 48.90% (Sonwai *et al.*, 2014; Biswas *et al.*, 2017; Calliauw *et al.*, 2007). POP is the crucial triacylglycerol in PMF, as it dominantly contributes to the unique characteristics of PMF (Kellens *et al.*, 2007; Calliauw *et al.*, 2007; Son *et al.*, 2010; Hashimoto *et al.*, 2001). POP level is usually set as more than 40% to qualify as sPMF. The percentage of diunsaturated triacylglycerols ranged from 14.33% to 30.57% and triunsaturated triacylglycerols from 3.19% to 5.16%. The percentage of trisaturated triacylglycerols detected in this category was very low, ranging from 2.45% to 5.41%. This combination of triacylglycerols with a very high ratio of unsaturated triacylglycerols to

TABLE 1. TRIACYLGLYCEROL COMPOSITION OF SOFT PALM MID FRACTIONS

	sPMF 1	sPMF 2	sPMF 3	sPMF 4	sPMF 5	sPMF 6	sPMF 7	sPMF 8
LLL	0.30±0.02	0.30±0.01	0.46±0.09	0.30±0.07	0.22±0.11	0.23±0.07	0.15±0.04	0.25±0.04
PLL	1.87±0.01	1.74±0.31	1.68±0.06	1.41±0.07	1.37±0.10	1.57±0.16	1.39±0.23	1.37±0.12
MLP	0.51±0.03	0.58±0.19	0.34±0.02	0.37±0.05	0.51±0.06	0.61±0.14	0.72±0.03	0.40±0.17
OOL	1.34±0.08	1.34±0.13	1.17±0.02	0.96±0.16	1.11±0.04	0.88±0.04	0.99±0.02	0.78±0.04
POL	7.66±0.29	6.96±0.11	5.99±0.04	5.52±0.09	5.97±0.02	5.52±0.01	4.94±0.01	4.73±0.18
PLP	9.02±0.48	8.90±0.08	8.72±0.06	8.26±0.24	9.01±0.20	8.38±0.26	9.03±0.05	7.31±0.15
MPP	1.76±0.18	1.82±0.07	2.00±0.04	2.13±0.11	1.94±0.08	1.95±0.07	2.35±0.01	1.65±0.03
OOO	3.52±0.54	2.98±0.06	2.72±0.00	2.58±0.30	2.42±0.15	2.79±0.19	2.23±0.03	2.16±0.31
POO	19.29±0.48	16.59±0.01	14.58±0.11	15.72±0.09	14.73±0.05	15.75±0.08	12.28±0.09	11.90±0.07
POP	43.53±0.19	45.65±0.12	48.27±0.40	49.20±0.16	49.33±0.24	49.64±0.16	51.56±0.22	55.95±0.10
PPP	0.69±0.04	2.37±0.04	2.26±0.05	1.44±0.01	1.49±0.20	1.55±0.02	2.57±0.04	0.76±0.04
SOO	1.73±0.06	1.50±0.03	1.52±0.08	1.39±0.07	1.59±0.18	1.42±0.05	1.05±0.05	1.06±0.07
POS	7.73±0.10	7.84±0.06	8.69±0.05	9.32±0.49	9.12±0.03	8.48±0.02	9.23±0.05	10.46±0.01
PPS	0.00±0.00	0.55±0.00	0.45±0.02	0.35±0.04	0.00±0.00	0.32±0.01	0.48±0.02	0.00±0.00
SOS	1.03±0.04	0.87±0.10	1.12±0.05	1.06±0.11	1.20±0.01	0.90±0.04	1.02±0.11	1.21±0.03
PSS	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
SSS	2.45 ± 0.22	4.75±0.12	4.72±0.12	3.91±0.06	3.44±0.29	3.83±0.10	5.41±0.03	2.41±0.07
SUS	61.83 ± 0.15	63.85±0.16	67.15±0.11	68.21±0.13	69.16±0.06	68.01±0.06	71.55±0.17	80.07±0.13
SUU	30.56 ± 0.23	26.79±0.17	23.77±0.07	24.04±0.13	23.66±0.35	24.25±0.18	19.66±0.27	14.33±0.12
UUU	5.16 ± 0.44	4.61±0.10	4.36±0.11	3.84±0.21	3.74±0.00	3.91±0.15	3.37±0.02	3.19±0.23

Note: sPMF - soft palm mid fraction, SSS - trisaturated triacylglycerol, SUS - monounsaturated triacylglycerol, SUU - diunsaturated triacylglycerol, UUU - triunsaturated triacylglycerol, M - myristic, P - palmitic, S - stearic, O - oleic, L - linoleic. Each value in the table represents the mean ± standard deviation of triplicate analyses (n=3).

saturated triacylglycerols influenced the DP of these sPMF. These fractions are considered to be medium melting solid fractions by food formulators at the application temperature of 20°C to 30°C (Braipson and Gibon, 2007).

The four sPOs samples collected from the Malaysian fractionation plants were by-products from the production of palm olein IV 60 via single fractionation of palm oil. The monounsaturated triacylglycerols ranged from 55.56% to 57.33%, with POP content ranging from 38.36% to 41.81%. The percentage of diunsaturated ranged from 20.07% to 28.70% and triunsaturated triacylglycerols ranged from 4.28% to 6.28%. The trisaturated triacylglycerols ranged from 10.46% to 18.52% with 6.31% to 13.88% of tripalmitoyl-glycerol (PPP), as shown in Table 2.

A significant difference was observed ($p < 0.02$) among the monounsaturated triacylglycerols and POP values in sPMF and sPOs as shown in Table 3. Monounsaturated triacylglycerols were 4.5% to 24.51% lesser in sPOs than in sPMF. The amount of POP were 1.68% to 17.35% lesser in sPOs than the values detected in sPMF. Significant difference ($p < 0.02$) was observed among the trisaturated triacylglycerols and PPP values in sPMF and sPOs as shown in Table 3. The percentage of trisaturated triacylglycerols were very much higher in sPOs, approximately 5.41% to 16.07% higher than detected in sPMF. The triacylglycerol compositions of sPMF differed from the compositions of sPOs. Hence, triacylglycerol values can be used to differentiate these two fractions.

Fatty Acid Composition

The FAC of sPMF in Table 4 shows that the percentages of saturated fatty acids were the highest, ranging from 51.91% to 58.29% with 45.89% to 51.55% palmitic acid. The percentages of monounsaturated fatty acids which consisted mostly of oleic acid were 34.38% to 39.03%. The percentages of polyunsaturated fatty acids ranged from 6.24% to 8.90%. The percentages of saturated fatty acids were the highest in sPOs ranging from 56.19% to 63.08% with 49.74% to 56.57% of palmitic acid as shown in Table 5. The percentages of monounsaturated fatty acids which consisted mostly of oleic acid were 30.98% to 35.57%. The percentages of polyunsaturated fatty acids were in the range of 5.75% to 8.04%.

No significant difference ($p < 0.02$) was observed among the palmitic and oleic fatty acids in sPMF and sPOs as shown in Table 3. The FAC of sPMF and sPOs have overlapping ranges; the percentage of palmitic acid in sPMF was 45.89% to 51.55% and sPOs was 49.74% to 56.57%. In the case of oleic acid, it was 34.49% to 38.88% in sPMF and 30.41% to 35.41% in sPOs. It is noteworthy that the arrangement of the fatty acids in the triacylglycerols in sPMF and sPOs varied substantially. The arrangement of the fatty acids in the triacylglycerol structure to a great extent determines the characteristics of the fats. Hence, in differentiating of sPMF from sPOs consideration of triacylglycerol composition will be a better reference as compared against FAC.

TABLE 2. TRIACYLGLYCEROL COMPOSITION OF SOFT PALM STEARIN

	sPOs 1	sPOs 2	sPOs 3	sPOs 4
LLL	0.24±0.03	0.66±0.20	0.23±0.01	0.19±0.04
PLL	1.62±0.19	1.71±0.24	1.44 ±0.05	1.33±0.11
MLP	0.51±0.03	1.07±0.05	0.36±0.02	0.46±0.07
OOL	1.30±0.02	1.83±0.22	1.09±0.12	0.87±0.10
POL	7.33±0.33	6.55±0.50	5.94±0.11	4.69±0.14
PLP	8.43±0.23	7.63±0.25	7.80±0.06	7.21±0.14
MPP	1.70±0.05	1.92±0.02	1.57±0.02	1.64±0.04
OOO	3.8 ±0.02	3.79±0.29	3.54±0.07	3.22±0.17
POO	18.14±0.07	15.59±0.24	14.86±0.08	12.99±0.38
POP	39.77±0.22	38.36±0.25	38.61±0.02	41.81±0.03
PPP	6.31±0.18	9.32±0.01	13.39±0.03	13.88±0.16
SOO	1.62±0.02	1.54±0.19	1.29±0.02	1.06±0.06
POS	6.19±0.04	6.51±0.14	6.25±0.02	6.96±0.07
PPS	2.05±0.01	2.35±0.12	2.66±0.04	2.73±0.08
SOS	0.66±0.11	0.72±0.08	0.65±0.02	0.88±0.12
PSS	0.39±0.05	0.44 ±0.01	0.33±0.05	0.27±0.02
SSS	10.46±0.09	14.03±0.13	17.94±0.03	18.52±0.30
SUS	55.56±0.13	56.00±1.28	53.68±0.10	57.33±0.28
SUU	28.70±0.13	23.69±0.21	23.53±0.04	20.07±0.35
UUU	5.41±0.01	6.28±0.26	4.86±0.17	4.28±0.23

Note: sPOs - soft palm stearin, SSS - trisaturated triacylglycerol, SUS - monounsaturated triacylglycerol, SUU - diunsaturated triacylglycerol, UUU - triunsaturated triacylglycerol, M - myristic, P - palmitic, S - stearic, O - oleic, L - linoleic.

Each value in the table represents the mean ± standard deviation of triplicate analyses (n=3).

TABLE 3. QUALITY PARAMETRS OF SOFT PALM MID FRACTION AND SOFT PALM STEARIN

	sPMF	sPOs
Triacylglycerols (TAG)		
Trisaturated TAG	3.87±1.08 ^a	15.24±3.75 ^b
Tripalmitoyl-glycerol	1.64±0.71 ^a	10.73±3.58 ^b
Monounsaturated TAG	68.73±5.49 ^a	55.64±1.51 ^b
1,3-dipalmitoyl-2-oleoyl-glycerol	49.14±3.72 ^a	39.64±1.57 ^b
Dropping point	28.58±3.23 ^a	45.80±4.91 ^b
Fatty acid composition		
Palmitic acid	49.59±1.82 ^a	53.17±2.94 ^a
Oleic acid	36.20±1.66 ^a	32.93± 2.20 ^a
Iodine value	44.79±2.53 ^a	41.34±3.56 ^a

Note: S - saturated, sPMF - soft palm mid fraction, sPOs - soft palm stearin.

For each quality parameter, means within each column with same superscripted letter ^{a-b} are not significantly different at p = 0.02.

Iodine Value

Iodine values are directly related to FAC of the oils or fats. The increase in the amount of saturated fatty acids, will in turn decrease the iodine values of the fractions. The iodine values of sPMF ranged from 40.91 to 49.50 as shown in *Table 4*. sPMF 7 recorded the lowest IV of 40.91, consisted of 58.07% saturated, 35.54% monounsaturated and polyunsaturated 6.24% fatty acids. In contrast, sPMF 1 with the highest IV of 49.50, consisted of higher amount of monounsaturated and polyunsaturated fatty acids, the composition was

51.91% saturated, 39.03% monounsaturated and 8.90% polyunsaturated fatty acids. The iodine values of sPOs ranged from 37.05 to 45.69 as shown in *Table 5*. The iodine values of sPOs decreased as the amount of saturated fatty acids increased and the amount of monounsaturated and polyunsaturated fatty acids decreased. sPOs 4 recorded the lowest IV of 37.05, consisting of 63.08% of saturated fatty acids and sPOs 1 had the highest IV of 45.69 as it consisted the lowest amount of saturated fatty acids of 56.19%.

TABLE 4. FATTY ACID COMPOSITION, IODINE VALUE AND DROPPING POINT OF SOFT PALM MID FRACTIONS

	sPMF 1	sPMF 2	sPMF 3	sPMF 4	sPMF 5	sPMF 6	sPMF 7	sPMF 8
C12:0	0.17±0.00	0.17±0.00	0.33±0.04	0.26±0.00	0.20±0.00	0.15±0.00	0.44±0.05	0.13±0.00
C14:0	0.96±0.00	1.06±0.00	0.76±0.12	1.08±0.00	1.02±0.00	1.00±0.00	1.12±0.08	0.84±0.01
C16:0	45.89±0.06	48.79±0.03	50.64±0.52	49.78±0.06	49.17±0.02	49.38±0.08	51.53±0.04	51.55±0.41
C16:1	0.15±0.01	0.14±0.00	0.81±0.14	0.12±0.00	0.12±0.01	0.13±0.01	0.54±0.61	0.10±0.00
C18:0	4.52±0.01	4.57±0.01	5.15±0.04	4.87±0.01	4.90±0.00	4.55±0.01	4.83±0.31	5.17±0.04
C18:1	38.88±0.05	36.92±0.07	33.57±0.63	36.36±0.04	36.74±0.02	37.16±0.01	34.49±0.40	35.44±0.51
C18:2	8.64±0.00	7.66±0.04	7.54±0.03	6.61±0.01	7.16±0.01	6.94±0.07	6.47±0.46	6.13±0.02
C18:3	0.25±0.09	0.16±0.00	0.76±0.16	0.09±0.00	0.13±0.00	0.11±0.00	0.08±0.00	0.11±0.20
C20:0	0.38±0.00	0.36±0.00	0.35±0.01	0.37±0.00	0.38±0.00	0.38±0.00	0.37±0.02	0.39±0.01
Others	0.16±0.02	0.17±0.00	0.10±0.00	0.46±0.00	0.16±0.00	0.19±0.02	0.15±0.02	0.15±0.01
Saturated	51.91±0.05	54.95±0.04	57.22±0.63	56.35±0.05	55.67±0.025	55.47±0.09	58.29±0.51	58.07±0.47
Monounsaturated	39.03±0.04	37.06±0.08	34.38±0.77	36.48±0.04	36.87±0.013	37.30±0.02	35.04±1.00	35.54±0.51
Polyunsaturated	8.90±0.00	7.82±0.04	8.30±0.13	6.70±0.01	7.30±0.011	7.05±0.07	6.54±0.47	6.24±0.03
Others	0.16±0.02	0.17±0.00	0.10±0.00	0.46±0.00	0.16±0.01	0.19±0.02	0.15±0.02	0.15±0.01
Iodine value (I ₂ /100 g)	49.50±0.13	45.83±0.23	45.98±0.09	43.27±0.08	44.38±0.17	45.18±0.08	40.91±0.20	43.26±0.12
Dropping point (°C)	23.4±0.21	31.6±0.14	31.8±0.10	28.3±0.21	28.0±0.14	27.6±0.14	32.5±0.10	25.4±0.14

Note: sPMF - soft palm mid fraction.

Each value in the table represents the mean ± standard deviation of triplicate analyses (n=3).

TABLE 5. FATTY ACID COMPOSITION, IODINE VALUE AND DROPPING POINT OF SOFT PALM STEARINS

	sPOs 1	sPOs 2	sPOs 3	sPOs 4
C12:0	0.19±0.00	0.19±0.01	0.68±0.01	0.15±0.00
C14:0	1.22±0.00	1.84±0.00	1.17±0.02	1.19±0.00
C16:0	49.74±0.05	52.04±0.01	54.33±0.47	56.57±0.06
C16:1	0.15±0.02	0.13±0.00	0.49±0.54	0.10±0.00
C18:0	4.66±0.00	5.09±0.01	4.86±0.02	4.79±0.01
C18:1	35.41±0.01	32.16±0.02	31.23±0.22	30.87±0.05
C18:2	7.79±0.00	6.64±0.00	6.72±0.14	5.70±0.04
C18:3	0.25±0.00	0.10±0.00	0.10±0.01	0.05±0.07
C20:0	0.38±0.00	0.37±0.00	0.31±0.02	0.38±0.00
Others	0.21±0.05	0.47±0.00	0.11±0.02	0.20±0.00
Saturated	56.19±0.06	59.53±0.00	61.35±0.43	63.08±0.07
Monounsaturated	35.57±0.03	33.28±0.01	31.72±0.32	30.98±0.05
Polyunsaturated	8.04±0.01	6.74±0.01	6.82±0.13	5.75±0.11
Others	0.21±0.05	0.47±0.00	0.11±0.02	0.20±0.00
Iodine value (I ₂ /100 g)	45.69±0.08	41.93±0.15	40.68±0.15	37.05±0.18
Dropping point (°C)	40.3±0.10	42.5±0.10	49.9±0.10	50.1±0.10

Note: sPOs - soft palm stearin.

Each value in the table represents the mean ± standard deviation of triplicate analyses (n=3).

The iodine values reflect the composition of the fatty acids, hence, it is not an advisable comparison parameter to differentiate between sPMF and sPOs. The iodine values of sPMF and sPOs was not significantly different, sPMF with 40.91 to 49.50 and sPOs with 37.05 to 45.69. No significant difference ($p < 0.02$) was observed among the iodine values in sPMF and sPOs (Table 3). Iodine values are not able to reflect the actual characteristics of these two very varied fractions. IV determines the level of unsaturation of the fatty acids and independent of the arrangement or position of the fatty acids in the triacylglycerol structure. Hence, IV should not

be considered as a quality parameter to differentiate these two fractions.

Dropping Point

The DP of sPMF ranged from 23.4°C to 32.5°C as shown in Table 4. The variation in the DP is attributed to the triacylglycerol composition of these fractions. The low amount of trisaturated triacylglycerols in sPMF 1 (2.45%) and sPMF 8 (2.41%), resulted in lower DP values of 23.4°C and 25.4°C, respectively. In contrast, sPMF 2 and sPMF 3 with higher amount of trisaturated triacylglycerols

of 4.75% and 4.72%, gave higher DP values of 31.6°C and 31.8°C, respectively. The DP of sPOs varied between 40.3°C to 50.1°C as shown in Table 5. The high DP values of sPOs were caused by the higher amount of trisaturated triacylglycerols present in the fractions. Sample sPOs 1 contained 10.46% of trisaturated triacylglycerols which gave a DP value of 40.3°C and sPOs 4 with 18.52% of trisaturated triacylglycerols gave a higher DP value of 50.1°C. Although the IV overlapped in the range of 40 to 46 between the two types of palm solid fractions, the DP varied distinctively. The DP of sPMF ranged between 24.3°C to 31.8°C and sPOs varied between 40.3°C to 50.1°C, a substantial difference of 8.5°C to 25.8°C. This difference is due to the varied triacylglycerol compositions in the fractions. DP values were able to express the physical variation between sPMF and sPOs. The DP values obtained for these fats were high ranging from 40.3°C to 50.1°C. Similar values were reported by Rashid *et al.* of palm stearin with IV of 40.8 gave an slip melting point of 49.6°C (Rashid *et al.*, 2012).

Significant difference ($p < 0.02$) was observed among the DP values in sPMF and sPOs as shown in Table 3. DP of sPMF ranged from 23.4°C to 32.5°C,

in contrast sPOs exhibited much higher DP values of 40.3°C to 50.1°C. Hence, DP can be used to differentiate these two fractions.

Solid Fat Content

The SFC profiles of sPMF showed similar trends even though the triacylglycerol compositions differed (Figure 2). The SFC values of sPMF were from 48% to 65% at 15°C and from 34% to 51% at 20°C. These fractions experienced a drastic decrease in SFC between 20°C to 25°C (a mere increase of 5°C), SFC decreased from 34% to 51% at 20°C to below 15% at 25°C. The substantial difference in SFC was 15% to 35% between the temperatures of 20°C to 25°C. This sharp decrease in the percentage of SFC values were in the range of 20°C to 25°C, which denotes the melting of the monounsaturated triacylglycerols, which are a major component of sPMF. The percentage of monounsaturated triacylglycerols present in sPMF are from 61.83% to 80.07%. SFC values were from 0.0% to 5% at 30°C. Composition of triacylglycerols strongly influences the SFC profile patterns. The main monounsaturated triacylglycerol is POP (46% to 52%), hence, the SFC

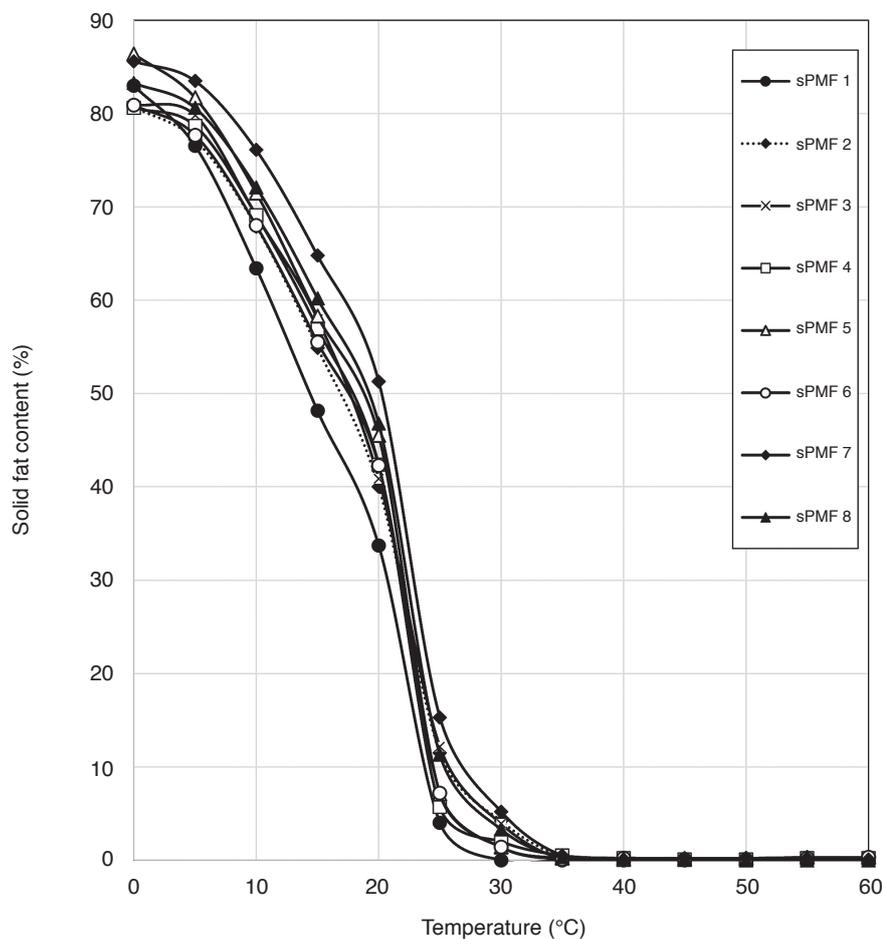


Figure 2. Solid fat content of soft palm mid fractions (sPMF).

profile pattern was dominated by the characteristic of POP that has a DP of 30.5°C (β') to 35.5°C (β). This unique SFC profile is preferred by the chocolate industry, hence, it is widely used as a cocoa butter equivalent (Bootello *et al.*, 2012). POP rich fats are usually blended with exotic crops such as shea, sal and illipe fats (source of palmitoyl-oleoyl-stearoyl-glycerol and distearoyl-oleoyl-glycerol), to obtain fat blends that are compatible to cocoa butter.

The SFC profiles of sPOs varied in the degree of SFC present at individual temperatures reflecting the variation in the triacylglycerols present (Figure 3). The variation was due to the level of trisaturated triacylglycerols present, as the percentage of trisaturated triacylglycerols increased, the percentage of SFC at the respective temperatures increased. The SFC profiles of sPOs did not exhibit a sharp drop over the temperature range evaluated, rather a gradual decrease in SFC values was experienced with the increase in temperature. A decrease of 28% to 32% of SFC was observed between 20°C to 30°C (sPOs 1 dropped from 42% to 14%, sPOs 2 from 49% to 20%, sPOs 3 from 59% to 28% and sPOs 4 from 63% to 30%). This drop in SFC was due to the melting of monounsaturated

triacylglycerols which were 54% to 57% (POP 38% to 42%) of the triacylglycerol composition. The percentage of SFC present at 45°C ranged from 0.3% to 10%.

The SFC profile of sPMF and sPOs differed at the temperature range of 15°C to 30°C. The point to emphasise is that sPOs did not mimic the SFC profiles of sPMF although they have a high percentage of POP but on the contrary, exhibited a 'tail effect' due to the presence of trisaturated triacylglycerols, that ranged from 10% to 18%. Hence, SFC profiles for sPMF and sPOs can be established and used to differentiate these two fractions.

Crystallisation and Melting Behaviour

The crystallisation and melting curves of sPMF are as shown in Figure 4. The position of the peaks in the crystallisation and melting profiles are very much dominated by the triacylglycerol composition that is strongly related to the content of low melting, medium melting and high melting triacylglycerols (Braipson and Gibon, 2007; Marangoni and Lencki, 1998). The onset temperature of the crystallisation profile is characterised by the beginning of fat

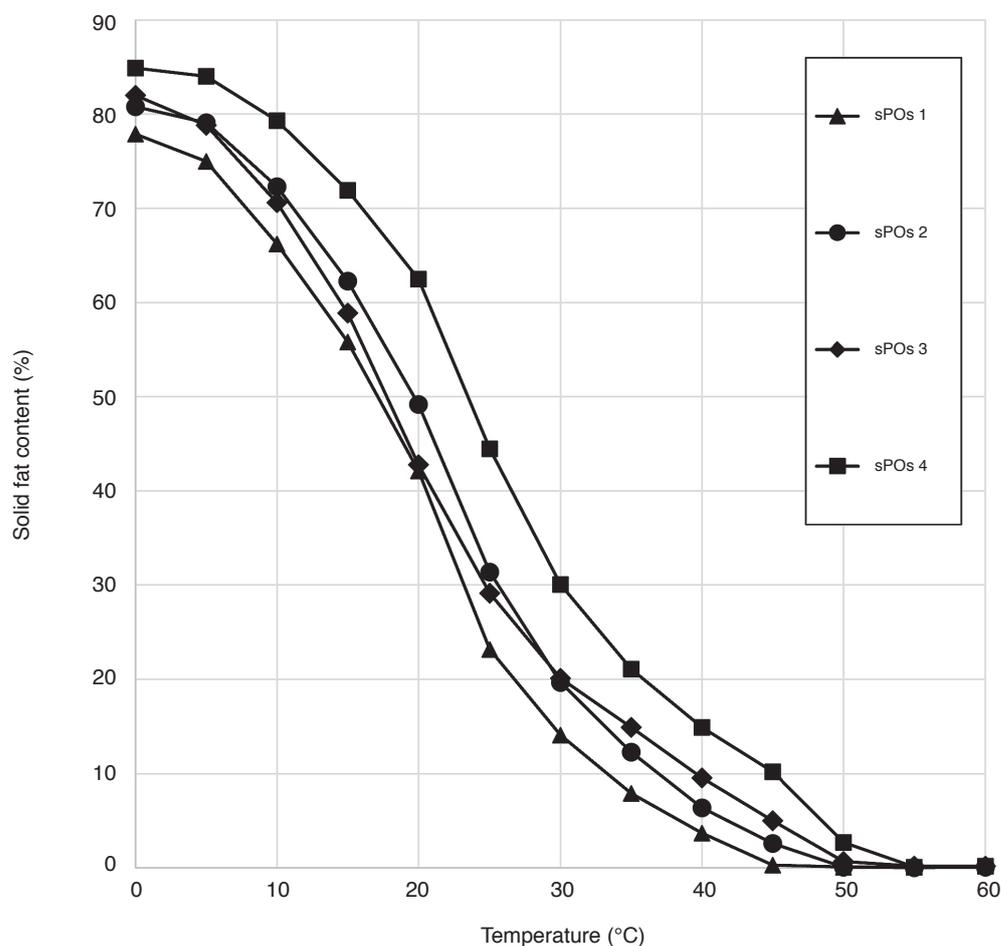


Figure 3. Solid fat content of soft palm stearins (sPOs).

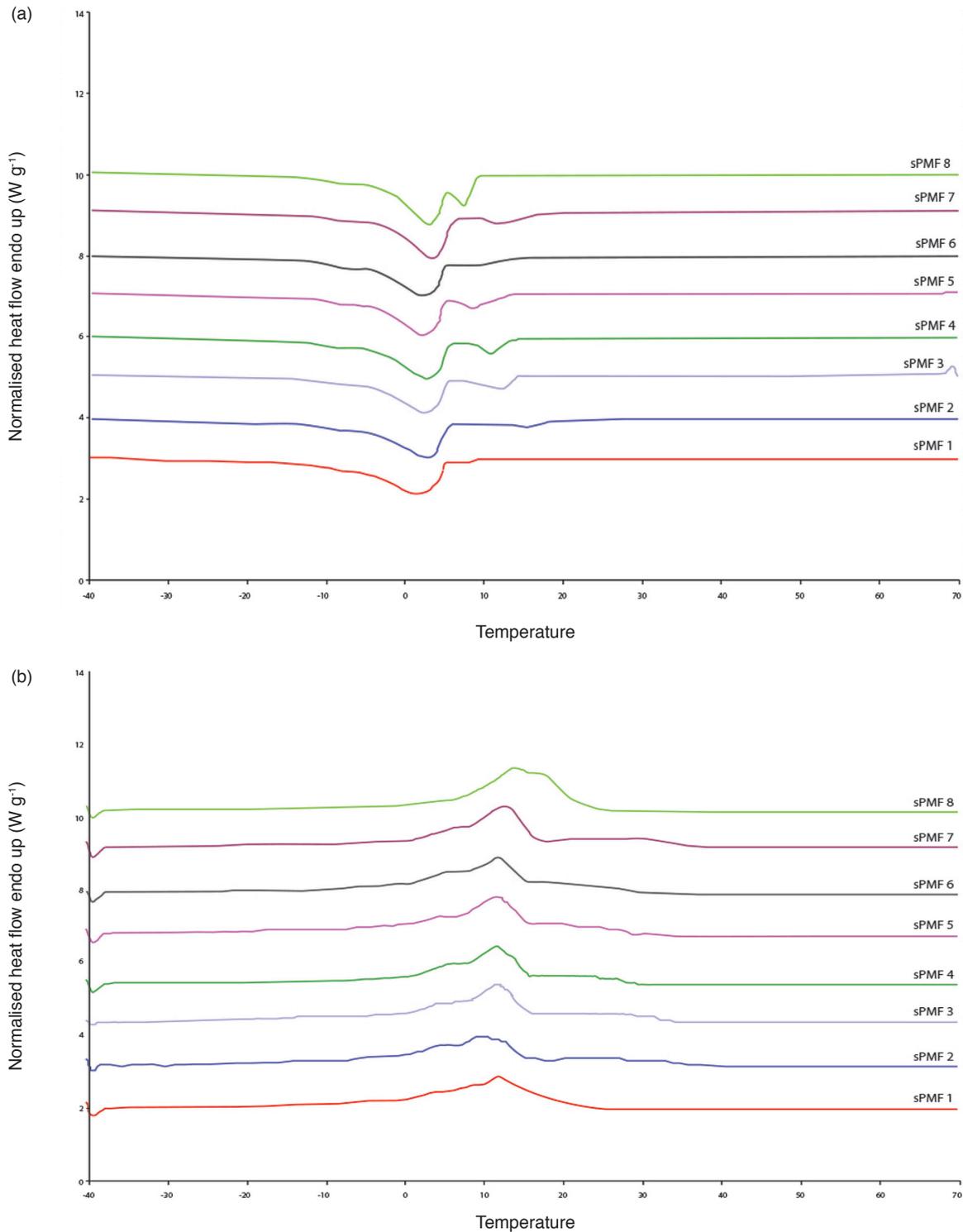


Figure 4. Differential scanning calorimetry (DSC) thermograms of (a) cooling (crystallisation) and (b) heating (melting) of soft palm mid fractions (sPMF).

crystal formation, which is greatly influenced by the content of saturated triacylglycerols combined with rapid cooling and the offset temperature explains the end of crystallisation (Saadi *et al.*, 2012). The onset temperature of sPMF differed with the amount of saturated triacylglycerols present in the fractions.

Fraction sPMF 1 exhibited a single exothermic peak, displaying the homogenous crystallisation and formation of crystals. sPMF 2 to sPMF 8 exhibited a well-defined two stage crystallisation. The events indicated initial crystallisation of trisaturated triacylglycerols and continued with the crystallisation

of monounsaturated and diunsaturated triacylglycerols. The offset crystallisation temperature of sPMF 1 to sPMF 8 were between -29°C to -31°C , indicating the delayed crystallisation of triunsaturated triacylglycerols. The melting profiles of sPMF exhibited a major endothermic peak accompanied by a broad endothermic peak. sPMF 8 had the highest peak attributed by its high monounsaturated triacylglycerols level of 80% and this was closely followed by sPMF 7 with 71% of monounsaturated triacylglycerols. sPMF 3, sPMF 4, sPMF 5 and sPMF 6 exhibited a very similar pattern of endothermic melting peaks. This trend was aligned to the composition of monounsaturated triacylglycerols present in these fractions which varied from 67.15% to 68.01% with approximately 48.27% to 49.64% of POP. The lowest peak was exhibited by sPMF 1, which was related to the lowest percentage of monounsaturated triacylglycerols of 61.83% with 43.53% of POP. sPMF 1 and sPMF 8 had only one endothermic peak present without a tailing broad peak. These fractions had low percentage of trisaturated triacylglycerols of 2.4%, hence, the endothermic broad peak indicating the crystallisation of these trisaturated triacylglycerols were not evident as compared to sPMF 2 to sPMF 7. sPMF 2 and sPMF 7 had 3.44% to 5.41% of trisaturated triacylglycerols, with 2.4% and 2.6% of tripalmitin (PPP), respectively. Hence, sPMF 2 and sPMF 7 showed broader secondary endothermic peaks indicating melting of high melting trisaturated triacylglycerols. Similar observations were reported in binary mixtures of PPP/POP with a blending ratio of 10:90. It was reported that the lowering and broadening of peaks denoting the melting behaviour of PPP is caused by level of solubility of PPP in the presence of liquid POP (Minato *et al.*, 1996). These phenomena also explain the complete melting of PPP at temperatures below 40°C .

The sPOs crystallisation profile exhibited two exothermic peaks, as shown in *Figure 5*. The onset temperature of the first exothermic peak varied with the percentage of trisaturated triacylglycerols. As the percentage of trisaturated triacylglycerols increased, the onset temperature increased. The lowest onset temperature was exhibited by sPOs 1 at 18°C with 10% trisaturated triacylglycerols, followed by sPOs 2 at 22°C with 14% trisaturated triacylglycerols. The highest onset temperature was by sPOs 3 and sPOs 4 at 24°C with 18% trisaturated triacylglycerols. The sPOs were crystallised rapidly at the rate of $10^{\circ}\text{C min}^{-1}$, hence, crystallised instantaneously. High melting triacylglycerols were rapidly cooled which initiated rapid crystallisation, forming solids within a liquid phase. This occurrence was accompanied by a rapid increase in viscosity, thus, severely limiting mass transfer, hence, a single major peak was observed representing the combined crystallisation of trisaturated, monounsaturated and diunsaturated

triacylglycerols (Campos *et al.*, 2002; Toro-Vazquez *et al.*, 2001). The second endothermic peak was a broad peak stretching from approximately 5°C to -30°C , indicating the combined crystallisation of low and medium melting triacylglycerols.

The melting profiles of sPOs fractions presented in *Figure 5* exhibit two significant endothermic peaks. The positions of the two endothermic peaks were, one below 20°C and the other above 20°C (Anais *et al.*, 2010). The two endothermic peaks corresponded to melting transitions of low melting triacylglycerols (low temperature endotherm is from -30°C to 20°C) and the second peak indicating the melting of the medium melting and high melting triacylglycerols (medium and high temperature endotherm is from 20°C to 50°C) (Anais *et al.*, 2010; Tan and Che Man, 2002). In sPOs 3 and sPOs 4, a third endothermic peak was observed; which corresponded to the presence of higher amount of high melting saturated triacylglycerols. The amount of trisaturated triacylglycerols in sPOs 3 and sPOs 4 were 17.94% and 18.52%, respectively as compared to sPOs 1 and sPOs 2 with 10.46% and 14.03%, respectively.

The sPMF and sPOs exhibit unique and distinctive crystallisation and melting profiles. The crystallisation and melting profile reflect the triacylglycerol composition of the fractions. Hence, crystallisation and melting profile can be established and used to differentiate these two fractions.

CONCLUSION

Specific chemical and physical characteristics of sPMF differ from sPOs. sPMF contained higher amounts of monounsaturated triacylglycerols than sPOs. The monounsaturated triacylglycerols of sPMF ranged from 61.83% to 80.07% (POP from 43.53% to 55.95%) and sPOs from 55.56% to 57.33% (POP from 38.36% to 41.81%). The trisaturated triacylglycerols ranged from 2.45% to 5.41% in sPMF and 10.46% to 18.52% in sPOs. SFC profile of sPMF and sPOs varied significantly. The sPMF exhibited a sharp decrease in the percentage of solids from 20°C to 30°C . The SFC values of these fractions were 34% to 51% at 20°C and below 0.0% to 5% at 30°C . In contrast, sPOs did not exhibit a sharp decrease between 20°C to 30°C temperature and had 0.3% to 10% of solids at 45°C giving the fraction a tailing effect. The DP of the fractions also varied significantly. The DP of sPMF ranged from 24.3°C to 31.8°C and that of sPOs ranged from 40.3°C to 50.1°C . sPMF and sPOs exhibit unique and distinctive crystallisation and melting profiles which can be used to differentiate these two fractions. Thus, triacylglycerol composition, DP, SFC and thermal behaviour (crystallisation and melting) are indicative parameters that are able to assist in

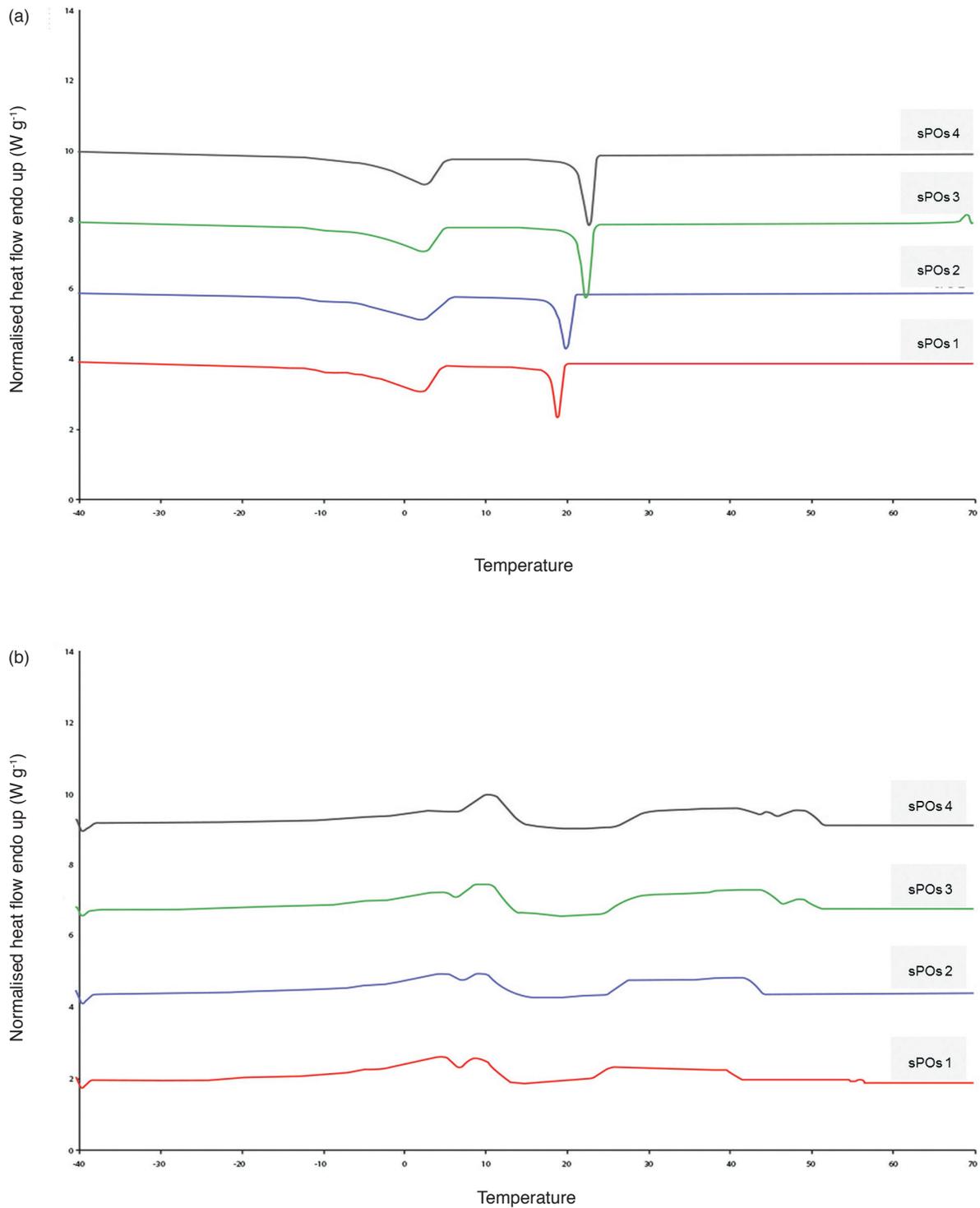


Figure 5. Differential scanning calorimetry (DSC) thermograms of (a) cooling (crystallisation) and (b) heating (melting) of soft palm stearins (SPOs).

determining the variations in the characteristics of sPMF and sPOs. In contrast, FAC and iodine values are objectionable indicators to differentiate these two solid fractions. The specification on the sPMF and sPOs should be addressed and established to avoid confusion in sales and purchase transactions.

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