

EFFECT OF BLENDING ON PHYSICO-CHEMICAL PROPERTIES OF PALM OIL AND PALM OIL PRODUCTS WITH SOYABEAN OIL

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ABSTRACT

Palm stearin is a co-product of olein production. There is a considerable potential for the use of palm stearin in the edible food industry if the physical and chemical properties can be modified. In this study, palm oil, soft and hard stearins were blended with 10% to 90% (w/w) of soyabean oil. The slip melting point (SMP), iodine value (IV), solid fat content (SFC), fatty acid composition (FAC), polymorphic form and morphological properties of the blends were determined. Results showed that there was an increase in linoleic acid (C18:2) content and a decrease in palmitic acid (C16:0) in all the blends. The SMP of the blends decreased while the IV increased with the addition of soyabean oil. A gradual decrease in % SFC was also observed in the blends containing hard stearin with higher amount of soyabean oil. The crystals obtained were observed to be stabilised in the β polymorphic form and became more plate-like with higher ratios of soyabean oil added.

Keywords: palm stearin, solid fat content, slip melting point, polymorphism, morphological properties.

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INTRODUCTION

Palm oil is usually fractionated into olein (liquid) and stearin (solid) fractions, and occasionally into a palm-mid fraction. Olein is mainly used as cooking oil and for soft margarine formulations. Palm stearin is a saturated fat with slip melting point (SMP) in the range of 46°C-50°C. At room temperature (~25°C) palm stearin is a solid which lacks in the spreadability characteristics required for products like margarine and shortening. The composition and properties of palm oil and palm stearin, however, can be modified by various processing techniques to produce a series of different products that can be

tailored for specific uses (Gulla *et al.*, 2012; Taylor, 1976; Rusell, 1975).

Blending of palm oil with other vegetable oils is commonly used in the industry to achieve specific properties in the products for food and other applications. According to Yap *et al.* (1989a), the high content of palmitic acid and unique polymorphic properties of palm oil and its products may be used to advantage by blending with different types of oils and fats for the manufacturing of margarine and shortening. Margarine and shortening made using oils that tend to crystallise in the β form, such as canola and soyabean, when blended with palm oil would stabilise in the β' polymorphic form (Ward, 1988). Moreover, due to the *trans* fatty acids issues that have an adverse effect on the condition of blood vessels and heart problems, consumers are encouraged to take low *trans* fatty acid fats. Therefore, palm stearin fractions could be used widely in the future to replace the hydrogenated vegetable fats either by blending with other liquid

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oils, or interesterification, or fractionation and also by other new techniques. Blending and chemical interesterification are effective in modifying the physicochemical properties of palm stearin, palm kernel oil, soyabean oil and their blends (Fauzi *et al.*, 2013).

The polymorphism of fat greatly affects the consistency, plasticity, graininess and other physical properties of many important products such as butter, margarine, shortening, *etc.* The three basic polymorphs are designated as α , β' and β . The α is the least stable and has the lowest melting temperature; β is the most stable and has the highest melting temperature and the three polymorphic forms exhibit distinct properties which are largely dependent on the crystallisation conditions (Timms, 1985). DeMan *et al.* (1989) reported that palm hard fat was the most stable. The stabilisation effect increased with the increased in the amount of palm oil added (Yap *et al.*, 1989b). The stability also relates to its unique triacylglycerols composition. Palm oil contains a high percentage of palmitic acid (44%) which is distributed mainly between the 1, and 3-position of the triacylglycerol molecule. DeMan (1992) reported that oil blends that contain high levels of palmitic acid (above 30%) possess better polymorphic stability.

In this work palm oil, hard and soft palm stearins were blended with 10% to 90% of highly unsaturated soyabean oil. The physical and chemical characteristics of the blends were investigated through their SMP, solid fat content (SFC), fatty acid composition (FAC), polymorphic form and morphological properties.

MATERIALS AND METHODS

Materials

Commercial refined, bleached and deodorised palm oil (RBDPO) of iodine value (IV) 53.7, hard palm stearin (HPS) of IV 25.4, soft palm stearin (SPS) of IV 41.9 and 100% pure commercial soyabean oil (SBO) of IV 135.2 were used. Palm oil and palm stearin were purchased from Lam Soon Oils and Fats, Petaling Jaya, Selangor, Malaysia. Soyabean oil (Mazola brand) was bought from CPC/AJI (Malaysia) Sdn Bhd, Segambut, Selangor, Malaysia.

Blending Method

The RBDPO, HPS, and SPS were melted at 70°C and homogenised by thoroughly shaking before individually blended with 10%-90% (w/w) of SBO. The blends were abbreviated as PO: SBO, HPS: SBO and SPS: SBO.

Analytical Methods

The blends were subjected to various analyses as mentioned below. Triplicate measurements were carried out for each analysis.

Slip Melting Point (SMP)

This was determined according to AOCS Method Cc.3.25 (AOCS, 1990). Capillary tubes (i.d. 1.1-1.3 mm; o.d. 1.4-1.7 mm; 50-60 mm length) were filled with a 1 cm high column of melted fat. The capillary tubes were then rolled against a piece of ice before being chilled in a refrigerator at 10±1°C for 16 hr to solidify the fat. The tubes were subsequently attached with a rubber band to a thermometer and suspended in a 600 ml beaker of boiled distilled water. The bath temperature was adjusted 8°C-10°C below the slip melting point of the sample and heat was applied using a heating coil element to increase the bath temperature at a rate of 1°C min⁻¹. A magnetic stirrer was used to stir the water. The temperature at which the fat column rises was reported as the SMP. Samples were run in triplicate and the mean values were calculated.

Iodine Value (IV) by Wijs' Method

IV were determined using AOCS Official Method Cd 1-25 (AOCS, 1990). Samples weighing 1 g were placed into a 500 ml flask and 15 ml of carbon tetrachloride was added to dissolve the fat. Then 25 ml of Wijs' solution was added and the flask was shaken gently. After standing in the dark for 1 hr, 20 ml of 10% potassium iodide solution and 150 ml distilled water was added. The solution was titrated with 0.1 N sodium thiosulphate until the yellow colour disappeared. One to 2 ml of starch indicator solution was added and the titration was completed when the blue colour just disappeared after vigorous shaking. Blank and triplicate determinations were carried out under the same conditions. The IV was calculated as below:

$$\text{Iodine value} = \frac{12.69N(V_2 - V_1)}{W}$$

where

N = exact normality of the sodium thiosulphate solution used.

V₁ = volume (ml) of sodium thiosulphate solution used for the blank test.

V₂ = volume (ml) of sodium thiosulphate solution used for the determination.

W = weight (g) of the test portion.

Fatty Acid Composition (FAC)

FAC were measured as methyl esters, which were prepared according to MPOB Test Method (2005). Analyses were conducted by using a capillary column (60 x 0.25 mm i.d.) with a split ratio of 1:100 and a flow rate of 0.85 ml N₂ min⁻¹, the oven temperature was set at 230°C under isothermal conditions on a Hewlett Packard 5890 gas chromatograph (Avondale, PA).

Solid Fat Content (%SFC)

The SFC of oil is a measure (in percentage) of the amount of solid fat present in the oil at any temperature. It was measured by means of pulsed Nuclear Magnetic Resonance Spectrometry (Bruker minispec P20:20 Mhz, Karlsruhe, Germany). The measurement was conducted according to MPOB Test Method (2005). The sample was melted at 70°C for 30 min, chilled at 0°C for 90 min and then kept at the desired temperatures for 30 min in thermostatted water baths prior to measurements.

Fat Blend Crystal Morphology

Crystal morphology study was carried out by using a Leica DML polarised light microscope (Wetzlar, Germany), equipped with a Linkam THMS 600 temperature controller stage and a JVC 3-CCD colour video camera. The temperature was thermostatically controlled by Linkam TP 94 multiramp temperature programmer and LNP automatic cooling system (Linkam, Tadworth, Surrey, United Kingdom). Liquid nitrogen was used as the coolant. The samples were placed on a heat controlled stage. For sub-ambient temperatures, a water bath circulator was used. The samples were heated to 80°C and kept for 10 min before being cooled down to the desired crystallisation temperatures. Different heating and cooling treatments would give rise to different types of crystal in terms of size, distribution and appearance.

Polymorphic Forms of the Blends by X-ray Diffraction Diffractometry

X-ray diffraction (XRD) was carried out using an Enraf Nonius model FR 592 (Enraf Nonius, Delft, The Netherlands) XRD. The instrument was fitted with a fine focus copper X-ray tube. The sample holders were flat stainless-steel plates with rectangular holes. Samples were melted at 80°C and then tempered at 10°C for 1 hr. The short spacings of the β' form are at 4.2 and 3.8 Å and that of the β form is at 4.6 Å (D'Souza *et al.*, 1990). Levels of β' and β crystals in the mixtures were estimated by the relative intensities of the short spacings at 4.2 and 4.6 Å.

RESULTS AND DISCUSSION

Slip Melting Point (SMP) and Iodine Value (IV) by Wijs' Method

The increase in the amount of SBO added into RBDPO, SPS and HPS blends results in a gradual decrease of their SMP except for blends with 90% SBO as shown in *Table 1*. A drastic drop in SMP and an increase in IV values of the blends were observed when more than 80% of SBO was added to RBDPO, SPS and HPS. This could be due to the higher solubility of RBDPO and stearins in the SBO compared to the solubility of the soft and hard stearins. IV is another useful parameter and could be an indicator for the hardness and oxidative stability of oils and fats. It is a measure of the degree of unsaturation of oil and fat (Weiss, 1983). According to Forsell *et al.* (1992), changes in the TAG profiles of a fat and oil mixture are always accompanied by a change in the SMP. Hence, the saturation of the blends is increased with the addition of SBO.

Fatty Acid Composition (FAC)

Table 2 shows the FAC of the blends at various ratios. The addition of 90% SBO into RBDPO resulted in a gradual decrease of palmitic acid (C16:0) of the blends from 41.5% to 13.8% and C18:1 content decreased from 42.9% to 23.8%. On the other hand, the C18:2 content increased from 9.5% to 50.2%. There was hardly any change observed in C18:1 content of HPS blends with the addition of SBO. This could be due to the equal amount of C18:1 in both the original oils (HPS and SBO). The addition of SBO in the all systems reduced the C16:0 and increased their C18:2 contents due to the high content of C18:2 (55.3%) present in SBO. As expected, hard stearin blends had the highest C16:0 followed by the soft stearin and refined palm oil.

Solid Fat Content (%SFC)

Figures 1, 2 and 3 show the SFC of RBDPO, HPS and SPS blends as a function of temperature, respectively. For hard stearin and SBO mixtures (HPS:SBO), a gradual decrease in SFC was observed due to the large concentration of high melting triacylglycerols in HPS. The SFC of the RBDPO:SBO blends decreased with SBO added and almost melted at 30°C.

At 40°C, with 80% of SBO added, RBDPO blends showed the lowest SFC (1.4%) compared to those of HPS blend (39.2%) and SPS blend (17.5%). This is due to the presence of higher amounts of C16:0 in hard and soft stearins and higher C18:2 in the RBDPO blends. This indicated that the addition of the stearins of different iodine values has a great influence on the solubility of the fat blend for a

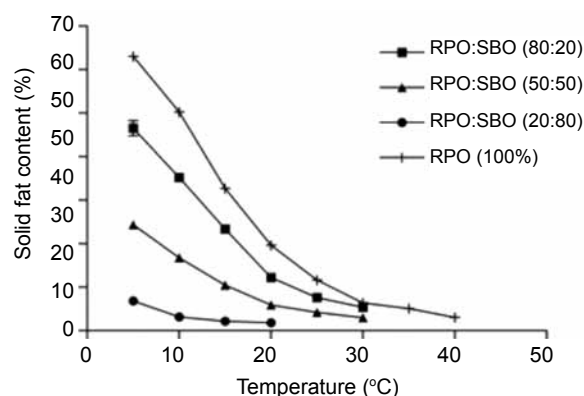


Figure 1. Solid fat content (SFC %) as a function of temperature for RPO:SBO blends.

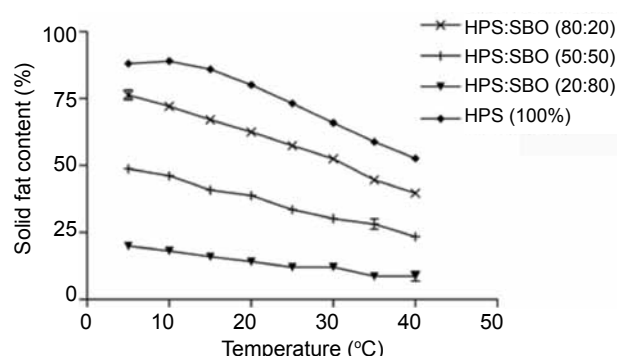


Figure 2. Solid fat content (SFC %) as a function of temperature for HPS:SBO blends.

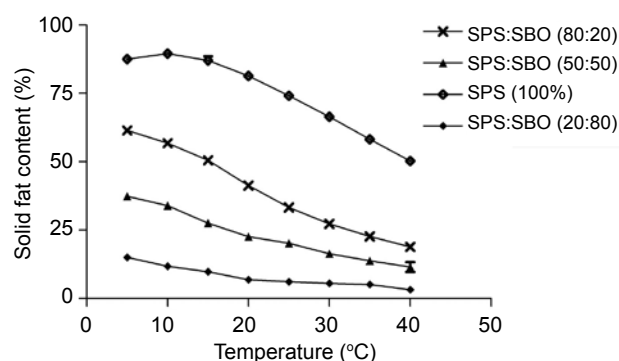


Figure 3. Solid fat content (SFC %) as a function of temperature for SPS:SBO blends.

particular application. Dian *et al.* (2007) reported that the SFC is responsible for many product characteristics in margarines, shortenings and fat spreads, including their general appearance, ease of packing, spreadability, oil exudation and organoleptic properties.

Blend Crystal Morphology

Polarised light microscopy was used to elucidate information on the types of crystal structure formed by the blends. The photomicrographs of the blends are shown in Figures 4, 5 and 6. When less than

TABLE 1. SLIP MELTING POINT (SMP) OF THE BLENDS

Sample	Slip melting point (SMP°C)	Iodine value (Wijs')
RBDPO:SBO		
100:0	32.6 ± 0.4	52.69 ± 0.2
80:20	29.3 ± 0.2	69.81 ± 0.4
50:50	25.3 ± 0.3	93.87 ± 0.5
20:80	18.3 ± 0.2	117.65 ± 0.7
10:90	0.2	126.75 ± 0.5
0:100	< 0.0	134.20 ± 0.6
HPS:SBO		
100:0	57.9 ± 0.2	25.40 ± 0.4
80:20	50.4 ± 0.3	48.29 ± 0.6
50:50	49.9 ± 0.2	79.81 ± 0.5
20:80	44.4 ± 0.3	116.72 ± 0.3
10:90	37.2 ± 0.3	124.68 ± 0.4
SPS:SBO		
100:0	56.6 ± 0.2	41.90 ± 0.5
80:20	49.9 ± 0.3	57.98 ± 0.3
50:50	46.0 ± 0.3	86.58 ± 0.4
20:80	37.0 ± 0.2	115.83 ± 0.6
10:90	27.3 ± 0.2	125.58 ± 0.4

Note: RBDPO - refined, bleached and deodorised palm oil.
HPS - hard palm stearin.
SPS - soft palm stearin.
SBO - soyabean oil.

80% of SBO added into RBDPO the crystals tend to decrease in size. At higher temperatures (>25°C), less crystals are formed. These crystals are less aggregated and more spherulitic in shape. This could be due to the SBO crystals and low melting triacylglycerols of RBDPO totally melted at this temperature. The spherulitic crystals might be due to the RBDPO crystals which are known to be β' polymorph. A similar trend was observed for the stearin and SBO blends. However, with more than 80% of SBO added, the crystals became more plate-like as shown in photomicrograph D of Figures 4, 5 and 6. This could be due to dilution effect as observed by DeMan and DeMan (1994) where the β polymorphic form tends to dominate the more the fat is diluted with liquid oil.

Polymorphic Forms of the Blends

Table 3 shows the polymorphic forms of the blends tempered at 10°C for 1 hr before exposure to X-ray. SBO is stable in the β form due to the high content of unsaturated fatty acids (C18:1 and C18:2). Palm oil and palm stearin, however, are β' stable due to the high levels of palmitic (C16:0) and stearic (C18:0) acids present. The HPS is more dominated by the β' form ($\beta' \gg \beta$) than SPS due to its higher palmitic acid content as indicated in Table 2. DeMan (1992) reported that oil blends that contain high levels of palmitic acid (above 30%) possess better β polymorphic stability. The HPS: SBO blends are

TABLE 2. FATTY ACID COMPOSITION OF THE BLENDS

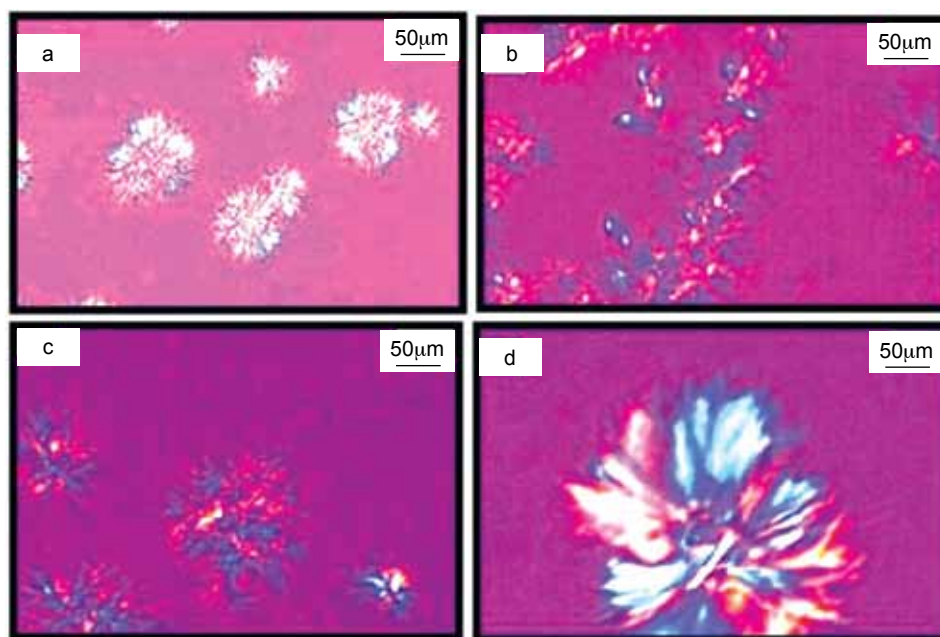
Sample	C12:0	C14:0	C16:0	C18:0 % wt.	C18:1	C18:2	C18:3
RBDPO:SBO							
RBDPO	0.3	1.1	41.5	4.1	42.9	9.5	0.2
80:20	0.2	0.9	35.3	3.9	38.7	18.5	1.9
50:50	0.2	0.6	25.9	4.0	32.5	32.2	4.4
20:80	0.1	0.3	16.9	3.9	25.7	45.9	6.8
10:90	0.1	0.2	13.8	3.9	23.8	50.2	7.7
SBO	0.1	0.1	10.5	3.82	21.4	55.3	8.4
HPS:SBO							
HPS	0.2	1.3	67.2	4.6	21.7	4.2	0.1
80:20	0.2	1.1	55.7	4.7	21.2	15.0	4.2
50:50	0.1	0.7	38.2	4.4	21.7	30.2	1.5
20:80	0.1	0.3	21.6	4.1	21.6	45.0	6.8
10:90	0.1	0.2	16.2	4.0	21.6	49.9	7.5
SPS:SBO							
SPS	0.2	1.3	53.9	4.7	32	7.2	0.1
80:20	0.2	1.0	45.3	4.3	29.6	16.9	1.7
50:50	0.1	0.7	32.1	4.2	26.6	31.7	4.0
20:80	0.1	0.4	23.8	3.9	24.8	41.1	5.1
10:90	0.1	0.2	14.9	4.7	22.0	50.8	7.0

Note: C12:0 - lauric acid; C14:0 - myristic acid; C16:0 - palmitic acid.
 C18:0 - stearic acid; C18:1 - oleic acid; C18:2 - linoleic acid; C18:3 - linolenic acid.
 RBDPO - refined, bleached and deodorised palm oil.
 HPS - hard palm stearin.
 SPS - soft palm stearin.
 SBO - soyabean oil.

TABLE 3. SHORT SPACINGS AND POLYMORPHIC FORMS OF THE BLENDS

Sample	Polymorphic form
RBDPO:SBO	
100% RBDPO	β'
(80:20)	β'
(50:50)	β'
(20:80)	$\beta + \beta'(\beta >>> \beta')$
SBO	β
HPS: SBO	
100% HPS	$\beta + \beta'(\beta' >>> \beta)$
(80:20)	$\beta + \beta'(\beta' >>> \beta)$
(50:50)	$\beta + \beta'(\beta' > \beta)$
(20:80)	$\beta + \beta'(\beta >>> \beta')$
SPS:SBO	
100% SPS	$\beta + \beta'(b = \beta')$
(80:20)	$\beta + \beta'(b = \beta')$
(50:50)	$\beta + \beta'(\beta >> \beta')$
(20:80)	$\beta + \beta'(\beta >>> \beta')$

Note: RBDPO - refined, bleached and deodorised palm oil.
 HPS - hard palm stearin.
 SPS - soft palm stearin.
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Note: RBDPO - refined, bleached and deodorised palm oil.

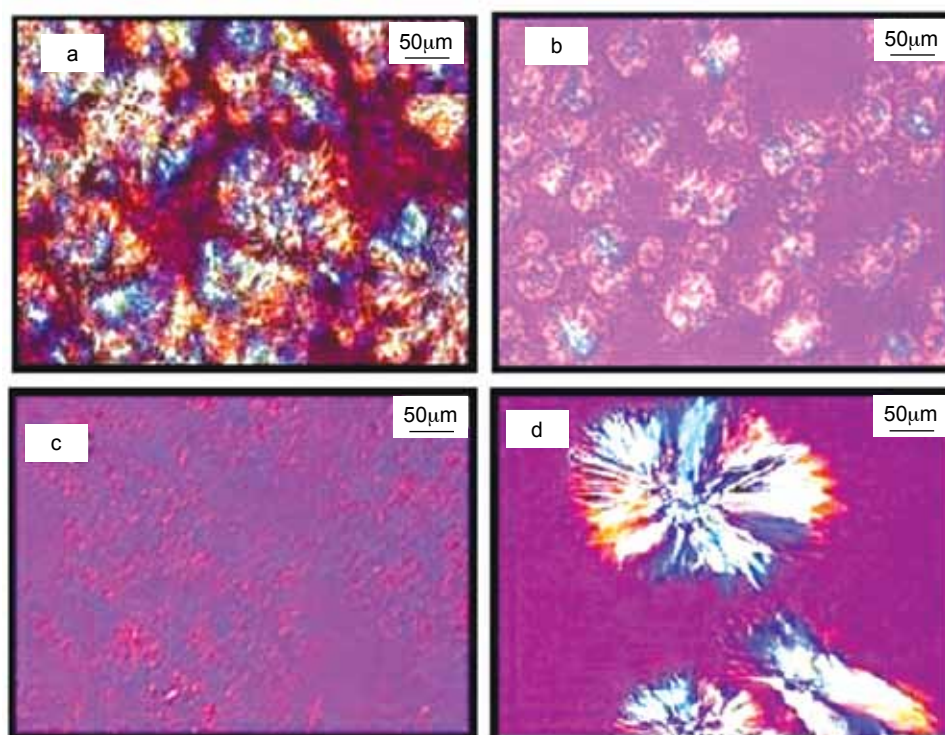
HPS - hard palm stearin.

SPS - soft palm stearin.

SBO - soyabean oil.

Figure 4. Crystals of RBDPO:SBO blends at 27°C at different ratios.

a. RBDPO, b. RBDPO:SBO (80:20), c. RBDPO:SBO (50:50), d. RBDPO:SBO (20:80).



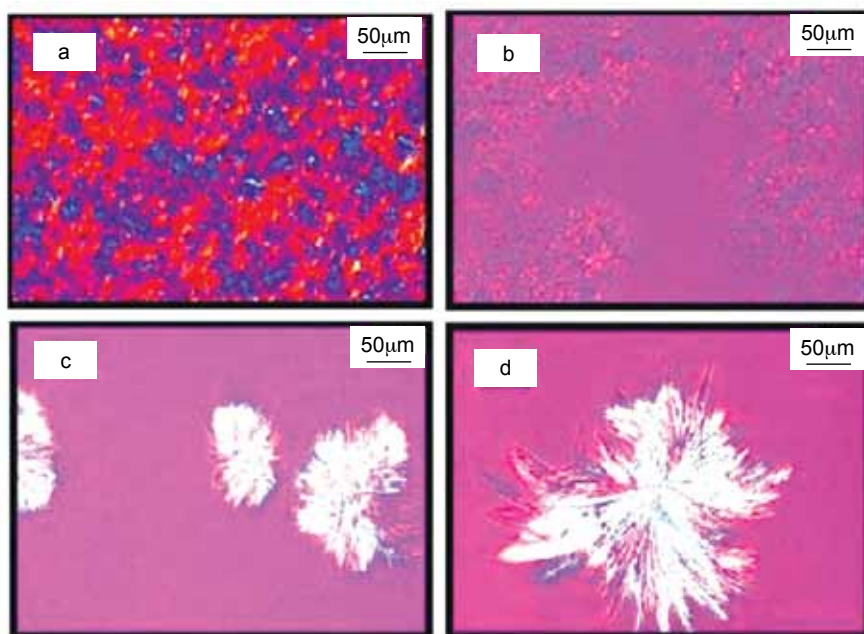
Note: HPS - hard palm stearin.

SPS - soft palm stearin.

SBO - soyabean oil.

Figure 5. Crystals of HPS:SBO blends at 35°C at different ratios.

a. HPS, b. HPS:SBO (80:20), c. HPS:SBO (50:50), d. HPS:SBO (20:80).



Note: HPS - hard palm stearin.
SPS - soft palm stearin.
SBO - soyabean oil.

Figure 6. Crystals of SPS:SBO blends at 27°C at different ratios.
a. SPS, b. SPS:SBO (80:20), c. SPS:SBO (50:50), d. SPS:SBO (20:80).

more stable in the β' form. The SPS:SBO blends consist mixture of β' and β polymorphic forms with form β dominating. The addition of SBO to palm oil and palm stearin caused the transition of β' polymorphic form to a mixture of β' and β . At high amounts of SBO added (up to 80%), RBDPO, HPS and SPS blends tend to be stabilised in the β polymorphic form. This shows that the polymorphic form of the major component became the dominant polymorphic form of the blends.

CONCLUSION

The addition of SBO to palm oil, hard and soft stearins at different concentration resulted in the changes of their SMP, FAC, SFC, polymorphic forms and morphological properties. This could be due to the dilution effect of unsaturated SBO. Hence, the plasticity of the stearins can be modified by blending with SBO.

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