The Malaysian Journal of ANALYTICAL SCIENCES ISSN 1394-2506

EFFECTS OF CHEMICAL INTERESTERIFICATION ON THE PHYSICOCHEMICAL PROPERTIES OF PALM STEARIN, PALM KERNEL OIL AND SOYBEAN OIL BLENDS

(Kesan Interesterifikasi Kimia ke atas Fizikokimia Minyak Stearin Sawit, Minyak Isirong Sawit dan Minyak Kacang Soya serta Adunannya)

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Abstract

Palm stearin (PS), palm kernel oil (PKO) and soybean oil (SBO) blends were formulated according to Design Expert 8.0.4 (2010). All the sixteen oil blends were subjected to chemical interesterification (CIE) using sodium methoxide as the catalyst. The effects of chemical interesterification on the slip melting point (SMP), solid fat content (SFC), triacylglycerol (TAG) composition and polymorphism were investigated. Palm based *trans*-free table margarine containing PS/PKO/SBO [49/20/31, (w/w)], was optimally formulated through analysis of multiple ternary phase diagrams and was found to have quite similar SMP and SFC profiles as compared with commercial table margarine. This study has shown that blending and chemical interesterification are effective in modifying the physicochemical properties of palm stearin, palm kernel oil, soybean oil and their blends.

Keywords: chemical interesterification, ternary blends, palm stearin, palm kernel oil, soybean oil

Abstrak

Aduanan antara minyak stearin sawit (PS), minyak isirong sawit (PKO) dan minyak kacang soya (SBO) telah dirangka mengikut *Design Expert* versi 8.0.4 (2010), menghasilkan enam belas aduanan minyak yang diinteresterifikasi secara kimia (CIE) menggunakan sodium metoksida sebagai pemangkin. Kesan interesterifikasi kimia pada takat gelincir (SMP), kandungan lemak pejal (SFC), komposisi trigliserida (TAG) dan polimorfisme dikaji. *Table margarine trans* bebas berasaskan kelapa sawit yang mengandungi nisbah campuran PS/PKO/SBO [49/20/31, (w/w)], telah diformulasi secara optimum melalui kaedah *multiple ternary phase diagrams* dan didapati mempunyai persamaan melalui analisis SMP dan SFC apabila dibandingkan dengan *table margarine* komersial di pasaran. Kajian ini telah menunjukkan bahawa pencampuran dan interesterifikasi kimia adalah berkesan dalam mengubah sifat-sifat fizikokimia minyak stearin sawit, minyak isirong sawit, minyak kacang soya serta adunannya.

Kata kunci: interesterifikasi kimia, campuran pertigaan, stearin sawit, minyak isirong sawit, minyak kacang soya

Introduction

Palm oil and their fractions (palm olein and palm stearin) are becoming important natural source of raw material and alternative for food manufacturers. Palm stearin (PS) is a cheap high-melting fraction from palm oil, can be used as a source of fully natural hard component in the manufacture of solid fat products such as shortenings, margarines and fat spreads. Palm stearin is also an excellent substitute for partially hydrogenated oil since it does not require any hydrogenation process. Furthermore, it provides strength or structure which enhances the plasticity of the products [1]. However, because of its high melting point (44-45°C), palm stearin poses problems in manufacture of solid fat products as it confers low plasticity to the products and does not completely melt at body temperature. To improve its melting properties, palm stearin (PS) may be blended and/or interesterified (IE) with polyunsaturated soft oils that have a good melting profile such as palm kernel oil (PKO), soybean oil (SBO), sunflower oil (SFO) and others in order to impart plasticity to the final interesterified product [5].

Interesterification (IE) has received much interest in the edible oil industry as an alternative method to improve the physical properties of fats and oils. Interesterification creates new fatty acids distribution of glyceride molecules, which in turn affects the physical characteristics of oils and fats, including melting point, hardness and crystallization behavior of the product. Unlike hydrogenation, interesterification neither effects the degree of saturation nor cause isomerization of the fatty-acid double bond. The stability of oils and fats also remains essentially unchanged [9].Through interesterification, a coarse-crystal, grainy-texture fat can be changed into one with lower melting point, finer crystal size, more plastic, smoother in texture and mouth feel. It can be either chemically- or enzymatically- catalyzed. Chemical interesterification (CIE) is a random process. Depending on the lipase used, enzymatic interesterification (EIE) can be random, regioselective, or fatty acid specific [7].
The recent interest of minimizing the *trans* fatty acid content of fat products especially in production of margarine has focused attention on palm oil products as a source of solid fat in placed of hydrogenated fats. Partially hydrogenated products have been proven to be detrimental to human health due to the formation of *trans* fatty acids (TFA) [4]. The United States and part of Latin America implemented labeling regulation for TFA on food products in January and August 2006 respectively [2, 8]. Those regulations have also prompted food industries to find alternatives in producing healthier foods and *trans*-free fats.

In this study, ternary blends of refined, bleached and deodorized palm stearin (PS), palm kernel oil (PKO) and soybean oil (SBO) was modified by chemical interesterification (CIE). The modified blends prepared will be formulated to achieve desirable properties of *trans*-free table margarine fats. Hence, the objectives of this work were: (i) to modify the physical and chemical properties of palm stearin (PS), palm kernel oil (PKO) and soybean oil (SBO) by blending at certain ratios according to the Design Expert version 8.0.4 (2010), (ii) to compare the physicochemical and microstructural properties of ternary blends before and after chemical interesterification, and (iii) to determine the most suitable interesterified ternary blends for *trans*-free table margarine formulation.

Materials and Methods

Materials

Refined, bleached, and deodorized (RBD) palm stearin (PS) (SMP 53.4°C, IV 40.3) and palm kernel oil (PKO) were obtained from Golden Jomalina Sdn Bhd, Klang, Malaysia, while RBD soybean oil (SBO) was purchased from local hypermarket at Shah Alam, Selangor, Malaysia. The oils and fats were stored at 0°C prior to use. All the chemicals used were either analytical or high-performance liquid chromatography (HPLC) grade.

Blend Preparation

The PS, PKO and SBO were melted at 60°C in an oven prior to use. Based on the Design Expert 8.0.4 (2010), sixteen blends of PS, PKO and SBO were prepared as indicated in Table 1.

Chemical Interesterification (Cie)

The chemical interesterification process was carried out according to the MPOB Test Method (2004) [6]. The fat blend was dried under nitrogen at 100°C for 60 minutes. After lowering the temperature to 80°C, 0.2% sodium methoxide powder (catalyst) was added. The mixture was heated to 110°C under nitrogen for 60 minutes with vigorous stirring. It was then cooled to 70°C and 5% citric acid solution was added to inactivate the catalyst. After the mixture was stirred mechanically at 70°C for 15 min, the excess citric acid and sodium methoxide were removed with warm water washes. Finally the interesterified oil was filtered through a Whatman #4 filter paper. The non-interesterified oil is abbreviated as NCIE and interesterified oil as CIE.

Table 1. Compositional design of the blends

Sample (PS/PKO/SBO)*	Components (g/100g)		
	Palm Stearin	Palm Kernel Oil	Soybean Oil
A (1/0/0)	100.00	0.00	0.00
B (1/0/0)	100.00	0.00	0.00
C (1/0/0)	100.00	0.00	0.00
D (0/1/0)	0.00	100.00	0.00
E (0/1/0)	0.00	100.00	0.00
F (0/0/1)	0.00	0.00	100.00
G (0/0/1)	0.00	0.00	100.00
H (1/0/1)	50.00	0.00	50.00
I (0/1/1)	0.00	50.00	50.00
J (1/1/0)	50.00	50.00	0.00
K (1/1/0)	50.00	50.00	0.00
L (0/2/1)	0.00	66.66	33.33
M (0/1/2)	0.00	33.33	66.66
N (1/0/2)	33.33	0.00	66.66
O (1/1/1)	33.33	33.33	33.33
P (4/1/1)	66.66	16.66	16.66

*PS, Palm stearin; PKO, Palm kernel oil; and SBO, Soybean oil

Slip Melting Point (SMP)

The SMP of the NCIE and CIE blends was determined according to MPOB Test Method (2004) [6]. Three replicates of this analysis were performed.

Solid Fat Content (SFC)

The SFC of the NCIE and CIE blends was measured using a Bruker Minispec pulse Nuclear Magnetic Resonance (pNMR) spectrometer (Karlsruhe, Germany). The parallel [6] method was used. Three replicates of this analysis were performed for every blend, and the reported value is the average of the three values.

Triacylglycerol (TAG) composition

The TAG profiles of the NCIE and CIE blends were analysed in a reversed- phase high-performance liquid chromatography (Gilson, Villiers-el-Bel, France). A Lichrosphere RP-18 column (250 mm x 4 mm) of 5-µm particle size (Merck, Darmstadt, Germany) with acetone/acetonitrile (75:25% v/v) as the eluent at a flow rate of 1.0 ml/min and a refractive index detector was used. Identification of TAG was done by comparison of retention time with those of commercial TAG standards.

Polymorphism

The polymorphic forms of fat crystals in the NCIE and CIE blends were determined by X-ray diffraction, using an Enraf Nonius Model FR592 (Delft, The Netherlands). The instrument was fitted with a fine copper X-ray tube. The sample holders were flat stainless-steel plates with rectangular holes. Samples were melted at 70°C and tempered at 20°C for 30 minutes. Short spacings on the X-ray film were measured with a Guinier viewer (Enraf Nonius, Delft, Netherlands). 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 [6]. Levels of β' and β crystals in mixtures were estimated by the relative intensity of the short spacings at 4.2 and 4.6 Å.

Experimental Design and Statistical Analysis

An optimal mixture design consisting three variables was used in this study. The three mixture components and palm stearin is represented by *X1*, palm kernel oil by *X2* and soybean oil by *X3*, where $X1 + X2 + X3 = 1$ or 100%. SFC at 5-45°C and SMP were used as responses. This experimental design was formulated with Design-Expert Software version 8.0.4 (2010) (Minneapolis, Minnesota, USA). Total number of sixteen design points (blends) was suggested by the software and ternary diagrams at each temperature were built by mixture design.

Optimization of ternary mixture components for production of *trans*-free table margarines formulation was conducted through graphical multiple responses optimization tool in Design-Expert 8.0.4 (2010) software. All experiments were carried out in a randomized order to minimize the effect of unexplained variability in the observed response due to extraneous factor.

Results and Discussion

Slip Melting Point (SMP)

As observed in Figure 1a palm stearin, PS had the highest SMP (45°C), followed by palm kernel oil, PKO (26°C) and soybean oil, SBO (10°C). The highest melting point of PS was due to the presence of long-chain saturated fatty acids. The PKO contains short- and medium-chain saturated fatty acids, while SBO had the lowest melting point as it contains high amount mono- and polyunsaturated fatty acid such as oleic and linoleic acids. The SMP of both NCIE and CIE of the original oils did not much change as much as in binary and ternary blends as shown in Figures 1a-c. This could be due to intraesterification which involves reshuffling of fatty acid moieties within the triacylglycerols (TAGs) molecule, and hence the melting point was hardly altered.

The slip melting point of all CIE binary blends decreased with an increase in the proportion of SBO in PS/SBO and PKO/SBO blends. This could be due to the decrease of highly saturated TAGs presence in PS and PKO, diluted by mono- and polyunsaturated SBO. The effects of diluting factor of SBO before and after chemical interesterification can be observed in Figure 1b. As expected, binary blend of interesterified PS/PKO, shown in Figure 1b, had lower slip melting point (35°C) than NCIE (40°C). This finding has demonstrated that CIE could provide a better alternative for producing new tailored-fats with desired melting profile that meets consumer preferences.

The slip melting point of ternary PS/PKO/SBO blends before and after CIE (Figure 1c) also differed, depending on the amounts of PS, PKO and SBO in the blends. Blends with high proportions of PS (coded P) tended to have the higher slip melting points than others. The CIE blends of 4PS/PKO/SBO had SMP 39°C compared to its NCIE blends with SMP of 45°C, while PS/PKO/SBO which had an equi-mixture of ternary blends, showed a reduction of 6°C in the slip melting point after CIE.

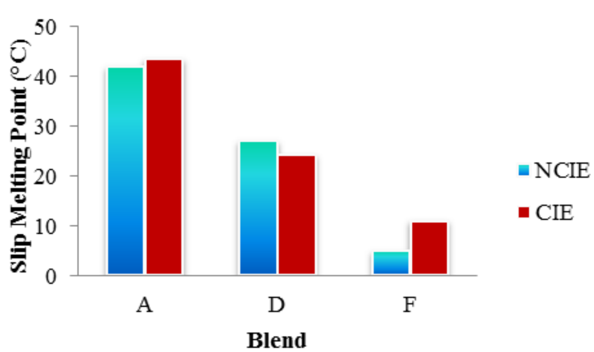

Figure 1a. The slip melting point (SMP) of original oil-PS (coded A), PKO (coded D) and SBO (coded F).

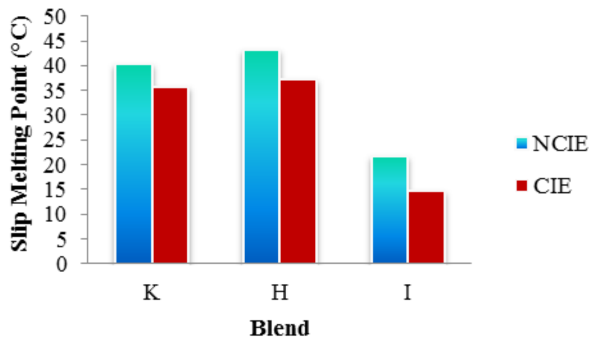

Figure 1b. The slip melting point (SMP) of binary blends –PS/PKO (coded K), PS/SBO (coded H) and PKO/SBO (coded I)

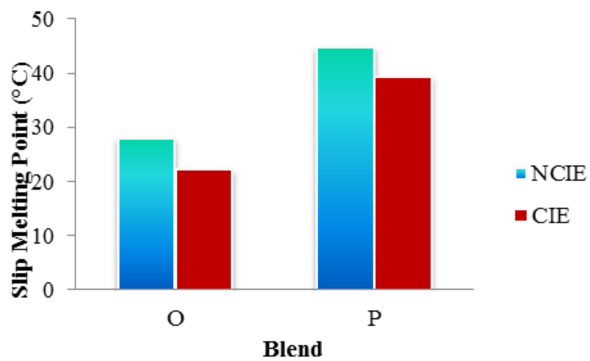

Figure 1c. The slip melting point (SMP) of ternary blends –PS/PKO/SBO (coded O), and 4PS/PKO/SBO (coded P)

Solid Fat Content (SFC)

Figure 2a shows palm stearin (coded A) had high SFC at low temperature and melted completely above 45°C. Soybean oil (coded F) was fully liquid at measured temperature as it is very rich in monounsaturated (oleic) and polyunsaturated (linoleic) fatty acids. Palm kernel oil (coded D) had a very sharp melting profile as it contained high proportions of medium-chain fatty acids. The largest reduction in the SFC of PS (coded A) occurred from 25–30°C, and that of PKO (coded D) occurred from 20–25°C, which was most likely due to the large proportion of TAGs that liquefy and solubilize in these temperature ranges. The chemical interesterification (CIE) reduced the SFC of PKO (coded D) throughout the temperature range investigated.

The SFC of binary blends of PS/PKO, PS/SBO and PKO/SBO are shown in Figure 2b. Interesterified blends (CIE) tended to have lower SFC values than the starting blends (NCIE). For the binary blends of PS/SBO (coded H), substantial changes in SFC were observed at temperatures starting at 15°C, whereas for the binary blends of PKO/SBO (coded I), apparent changes in their SFC values occurred at all measured temperatures. The decrease in the SFC values of the interesterified blends of PS/SBO (coded H) could be attributed mainly to the decreased proportion of the high-melting S_3 and S_2U TAG of PS, mainly PPP (S_3) and POP (S_2U), concomitant with the formation of more U_2S TAG of SBO such as PLL and PLO (Table 2b). For the binary blends of PKO/SBO (coded I), the reduction in the SFC values could be most likely attributed to the decrease in the proportion of the S_3 medium-chain TAG of PKO such as LaLaLa, CaLaLa and CLaLa simultaneously with the formation of several species of low-melting TAG as observed in Table 2b. The formation of the low-melting TAG could be due to the replacement of saturated fatty acid (FA) in the TAG of PS and PKO with the unsaturated FA of SBO TAG, which are mainly U_2S and U_3.

Interesterified binary blends (CIE) of PS/PKO (coded K) had higher SFC values at temperatures from 20-25°C compared to the starting blends (NCIE) as shown in Figure 2b. The most plausible explanation for this is that the eutectic interaction that occurred between PS and PKO in the binary blends of PS/PKO, which makes the blends much softer than they should be, was eliminated after CIE, demonstrating a better miscibility between the two fats, as shown by the isosolid diagram in Figure 2d and 2e. This result is consistent with that reported by Timms (1984) [10], which showed that IE would eliminate or at least reduce eutectic interactions in a eutectic mixture.

The SFC of ternary PS/PKO/SBO blends (coded O and P) before (NCIE) and after (CIE) are shown in Figure 2c. As observed, interesterified ternary blends of PS/PKO/SBO (coded O and P) were also different from those of the starting blends. Adding SBO to PS and PKO lowered their SFC proportionally at all measuring temperatures. As observed from starting temperature to 25°C, the CIE PS/PKO/SBO had 44% of SFC reduction as compared with NCIE PS/PKO/SBO with 40%, while CIE 4PS/PKO/SBO with 56% of SFC reduction and its NCIE with 48%. The results of percent SFC reduction proved that SFC of CIE blends were lower compared to its NCIE blends. This study has demonstrated that a combination of blending and CIE of PS with SBO and/or PKO could provide an alternative for producing new fat products with the desired SFC profiles. Chemical interesterification is also the method of choice to improve miscibility among the blended oils and fats.

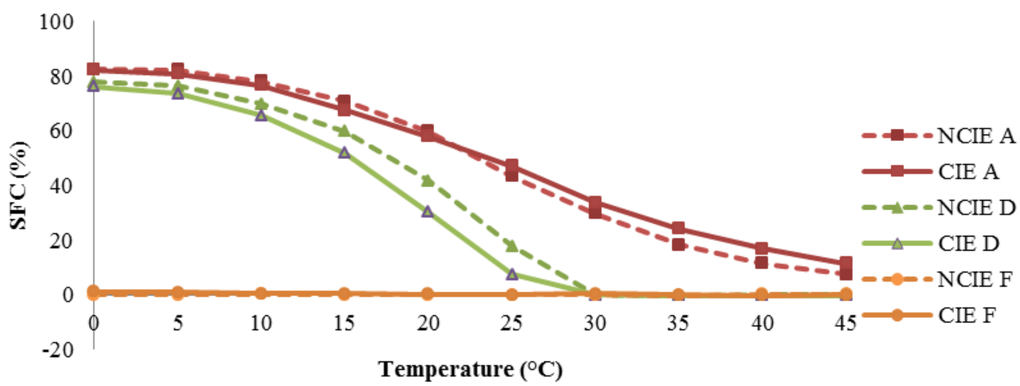

Figure 2a. The solid fat content (SFC) of original oil-PS (coded A), PKO (coded D) and SBO (coded F)

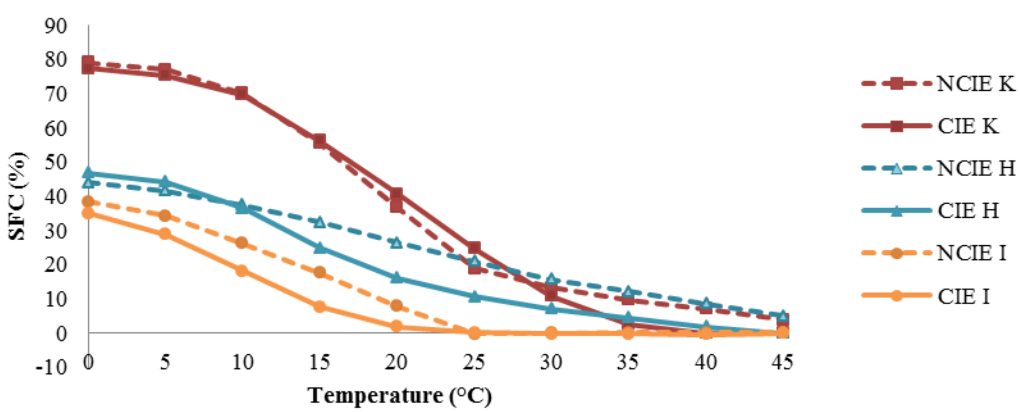

Figure 2b. The solid fat content (SFC)) of binary blends –PS/PKO (coded K), PS/SBO (coded H) and PKO/SBO (coded I)

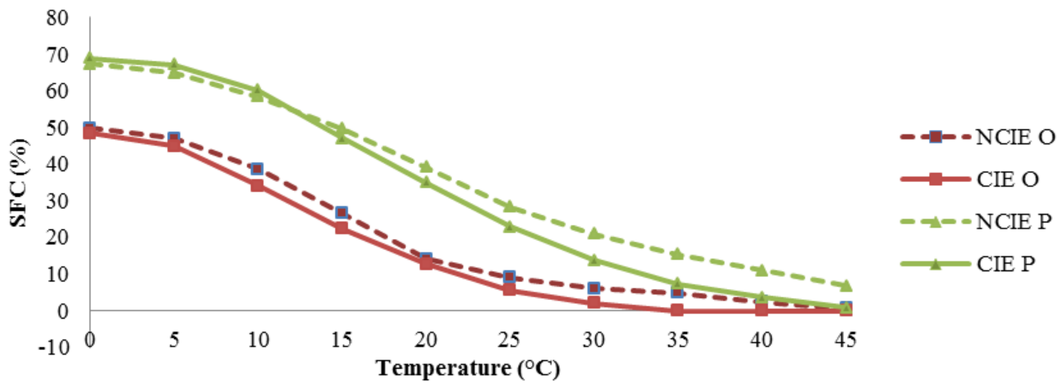

Figure 2c. The solid fat content (SFC) of ternary blends –PS/PKO/SBO (coded O), and 4PS/PKO/SBO (coded P)

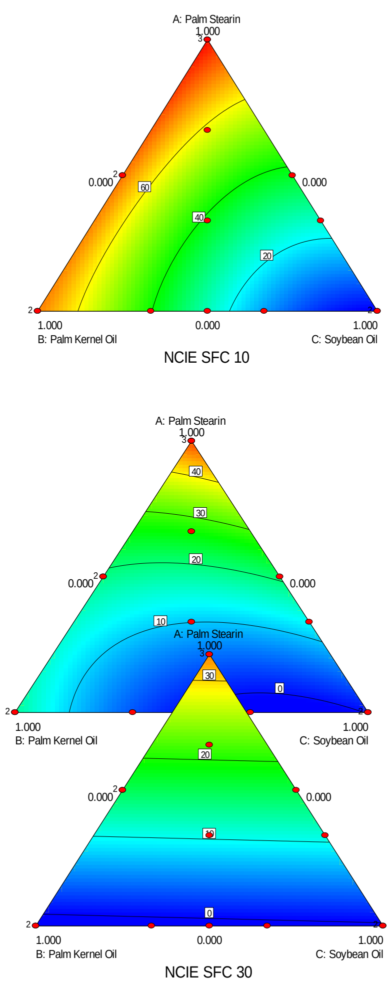

Figure2d. Eutectic effects in SFC (%) were observed in NCIE of PS/PKO blends at 10, 25, and 30°C

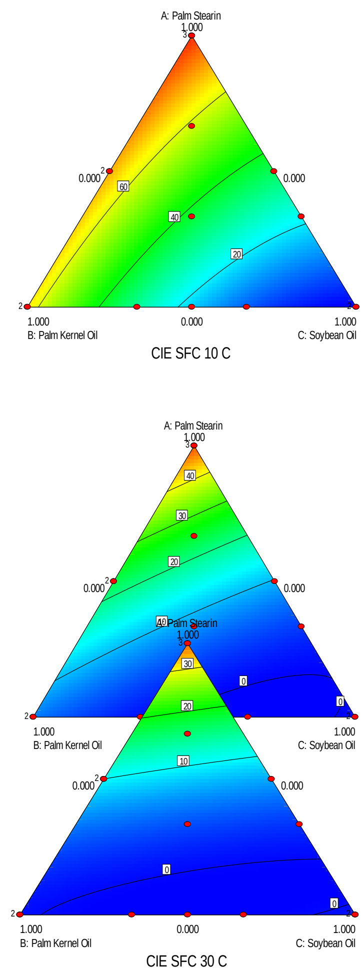

Figure 2e. Eutectic effects in SFC (%) were reduced after CIE for all blends at 10, 25, and 30°C

Triacylglycerol (TAG) composition

Table 2a-c shows the TAG composition of palm stearin (PS), palm kernel oil (PKO) and soybean oil (SBO) as well as their blends before and after chemical interesterification. The main triacylglycerol of PS were PPP, POP and PLO where P is palmitic acid, L is linoleic acid, S is stearic acid and O is oleic acid. Palm stearin (PS) also contained noticeable amounts of POS, PLO and OLO. Palm kernel oil (PKO) contained a wide range of medium-chain TAG species. The major TAG classes of PKO were S_3 and S_2U such as LaLaLa, LaLaM, CaLaLa, CLaLa, LaLaP, and LaLaO, where La is lauric acid, M is myristic acid, Ca is caprylic acid and C is capric acid. While SBO consists mainly of U_3 and SU_2 classes such as LLL, OLL, OLO, PLO and PLL.

Chemical interesterification (CIE) generated few changes in the TAG composition of PS, PKO and SBO. For example, the proportions of the main TAG of NCIE PS, such as POS, PLP and PPS had reduced from 5.5%, 7.5% and 3.6% to 3.5%, 6.2% and 3.0% after CIE, concomitantly the proportions of other TAGs such as PPP and POP had increased from 18.7% and 33.5% to 25.8% and 34.5%, respectively. The proportions of TAG in PKO after CIE also generated noticeable changes with LaLaLa, CaLaLa and CLaLa were reduced and simultaneously proportions of LaLaO, LaLaP and LaOM were increased following CIE. Meanwhile, TAGs of SBO were hardly changed after the CIE, only small changes of TAG such as LLL and OLL were reduced while OLO was increased after interesterification reaction. The single blend of PS, PKO and SBO after CIE generated only few changes of TAG as compared to the NCIE. This presumably because of intraesterification and randomization of same proportion blend hence did not result in much change in the TAG composition. The changes of TAG proportions due to interesterification reaction were more pronounced for binary and ternary blends due to the presence of varied TAG species in the mixtures.

Randomization led to the formation of a new number of TAG that could not be identified due to the complex interaction via the phase of mixture blends. However, the TAG profile of the interesterified blends showed an even peak distribution than the starting blends, as the relative concentration of several TAG increased; while others decreased. This result is consistent with findings reported by Zainal & Yusoff (1999) [11].

Table 2a. TAG composition (area %) of palm stearin, palm kernel oil, and soybean oil before and after chemical interesterification[a]

	PS		PKO		SBO	
TAG	**NCIE**	**CIE**	**NCIE**	**CIE**	**NCIE**	**CIE**
CLaLa	-	-	9.0	4.5	-	-
CaLaLa	-	-	12.3	5.5	-	-
LaLaLa	-	-	25.5	20.0	-	-
LaLaM	-	-	14.0	15.0	-	-
LaLaO	-	-	5.5	13.5	-	-
LaLaP	-	-	7.5	10.0	-	-
LLL	-	-	-	-	32.0	28.0
LaOM	-	-	4.0	8.0	-	-
LaPM	-	-	3.8	5.5	-	-
OLL	-	-	-	-	30.5	28.5
PLL	0.8	-	-	-	8.0	7.5
LaOO	-	-	2.8	3.0	-	-
LaOP	-	-	5.0	4.1	-	-
LaPP	-	-	0.8	2.5	-	-
OLO	1.0	1.0	-	-	9.8	10.5
PLO	5.0	2.5	-	-	9.5	9.0
MOO	-	-	1.0	1.0	-	-
PLP	7.5	6.2	-	-	1.0	0.6
MOP	-	-	2.3	1.8	-	-
OOO	2.0	1.5	1.2	0.5	3.0	2.5

POO	17.5	17.0	1.0	1.0	3.8	4.0
POP	33.5	34.5	0.5	0.5	0.5	0.8
PPP	18.7	25.8	0.1	0.1	1.0	1.5
SOO	1.0	1.0	-	-	0.5	0.5
POS	5.5	3.5	-	-	0.2	0.4
PPS	3.6	3.0	-	-	0.2	0.2
Others	3.9	4.0	3.7	3.5	0.0	6.0
Total	96.1	96.0	96.3	96.5	100.0	94.0

Notes: NCIE, non-interesterified; CIE, interesterified oil; C, capric acid; La, lauric acid; Ca, caprylic acid; M, myristic acid; O, oleic acid; P, palmitic acid; L, linoleic acid; S, stearic acid.

Table 2b. TAG composition (% area) of binary blends before and after chemical interesterification

	PS/PKO		**PS/SBO**		**PKO/SBO**	
TAG	**NCIE**	**CIE**	**NCIE**	**CIE**	**NCIE**	**CIE**
CLaLa	5.0	2.0	-	-	4.5	2.5
CaLaLa	6.0	5.0	-	-	5.8	5.0
LaLaLa	8.0	5.0	-	-	11.4	10.0
LaLaM	6.5	2.5	-	-	7.8	6.0
LaLaO	3.0	2.0	-	-	1.9	2.0
LaLaP	3.7	2.0	-	-	5.0	3.0
LLL	-	-	15.0	6.5	10.0	12.5
LaOM	2.0	1.5	-	-	3.0	3.0
LaPM	1.5	1.5	-	-	-	-
OLL	-	-	18.0	10.0	15.8	5.0
PLL	0.5	2.5	5.0	12.0	5.0	6.8
LaOO	1.5	3.0	-	-	2.1	1.0
LaOP	2.0	13.5	-	-	2.5	1.0
LaPP	-	10.0	-	6.5	-	-
OLO	1.0	1.0	5.0	20.0	6.8	18.0
PLO	2.5	2.0	7.3	-	6.2	15.0
MOO	3.0	2.0	-	-	-	-
PLP	5.0	3.8	4.5	11.5	-	-
MOP	3.0	2.5	-	-	-	-
OOO	1.5	2.0	2.5	1.5	2.0	3.0
POO	8.5	6.3	8.0	9.0	2.3	1.7
POP	20.5	7.6	18.5	13.0	0.5	1.0
PPP	10.0	5.5	8.0	4.5	0.5	0.2
SOO	0.8	2.0	1.0	1.0	0.2	0.1
POS	4.0	3.7	4.0	1.5	0.1	0.1
PPS	0.5	3.0	2.5	1.5	0.1	0.1
Others	0.0	8.1	0.7	1.5	6.5	3.0
Total	100.0	91.9	99.3	98.5	93.5	97.0

Table 2c. TAG composition (% area) of ternary blends before and after chemical interesterification

	4PS/PKO/SBO		PS/PKO/SBO	
TAG	**NCIE**	**CIE**	**NCIE**	**CIE**
CLaLa	3.0	2.8	3.0	2.0
CaLaLa	3.5	4.5	4.0	5.0
LaLaLa	2.8	4.0	7.5	5.0
LaLaM	2.0	2.0	4.5	4.5
LaLaO	3.5	2.0	2.3	6.7
LaLaP	-	-	-	5.5
LLL	5.0	7.0	10.6	3.5
LaOM	2.3	2.0	1.0	3.0
LaPM	-	-	-	-
OLL	5.0	5.8	11.5	5.0
PLL	4.0	5.0	3.0	3.0
LaOO	1.0	1.0	1.1	4.5
LaOP	1.5	1.0	1.7	7.7
LaPP	-	-	-	-
OLO	3.6	3.0	5.2	4.0
PLO	4.5	3.7	6.0	5.5
MOO	-	-	-	-
PLP	3.0	5.8	3.3	6.8
MOP	-	-	-	-
OOO	4.0	-	1.5	5.8
POO	4.8	8.4	6.0	3.0
POP	10.0	9.5	15.0	8.3
PPP	11.3	9.0	5.0	3.5
SOO	1.7	2.0	1.0	1.0
POS	10.8	8.5	2.5	2.0
PPS	12.0	8.0	1.2	1.5
Others	0.7	5.0	3.1	3.2
Total	99.3	95.0	96.9	96.8

Table 3. Polymorphic forms of the non-interesterified (NCIE) and interesterified (CIE) original oil (PS, PKO, and SBO), binary (PS/PKO, PS/SBO and PKO/SBO) and ternary (PS/PKO/SBO) blends

	Polymorphic form(s)	
	NCIE	**CIE**
Original oil		
PS (coded A)	β' + β	β' + β
PKO (coded D)	-	β'
SBO (coded F)	-	-
Binary blends		
PS/PKO (coded K)	β' + β	β' + β
PS/SBO (coded H)	β' + β	β'
PKO/SBO (coded I)	-	-
Ternary blends		
PS/PKO/SBO (coded O)	β' + β	β' + β
4PS/PKO/SBO (coded P)	β' + β	β' + β

Optimization of Ternary Mixture Components for *Trans*- Free Table Margarine Formulation

As mentioned before, optimization of ternary mixture of PS, PKO and SBO for table margarine formulation was conducted through graphical multiple responses optimization tool in Design-Expert 8.0.4 (2010) software. This tool is able to predict all possible proportions of blend constituents having similar SFC profile with table margarine and to determine as an area in a ternary diagram. In doing so, it is necessary to enter the SFC range at each temperature suitable for table margarine. The acceptable SFC range for each temperature was selected based on SFC profile of oils extracted from commercial table margarine. Figure 4 shows possible fat blend formulations for table margarine made from PS, PKO and SBO (red area).

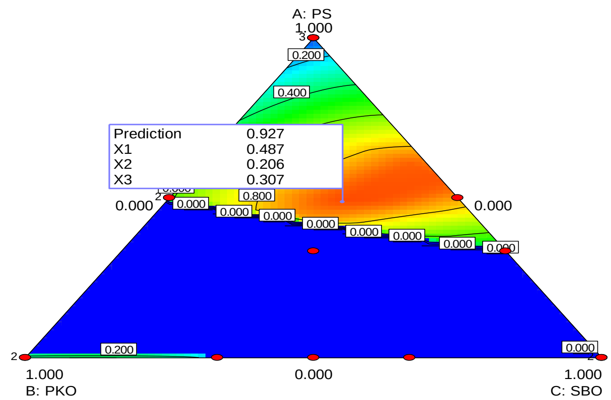

Figure 4. Multiple isosolid diagrams using Design-Expert 8.0.4 (2010) software resulted in successful prediction of various possible formulations of *trans*-free table margarine formulation which having similar SFC profile and SMP with commercial table margarine

Conclusion

Ternary phase diagram of PS, PKO and SBO provided valuable information through analysis of complicated solution behaviors of these three oils and their influence on the physical properties of final product. Simultaneous analysis of multiple isosolid diagrams using Design-Expert 8.0.4 (2010) software resulted in successful prediction of various possible formulations of *trans*-free table margarine formulation having similar SFC profile and SMP with commercial table margarine. *Trans*-free table margarine formulation containing PS/PKO/SBO [49/20/31, (w/w)] not only has beneficial effect due to the presence of high proportions of palm fraction but it also free from *trans*-FA. Design-Expert 8.0.4 (2010) software was found to have a valuable tool to optimize the new fat blend formulation using the minimum number of blend preparation. By using this tool, assessment of complicated interactions among the blend components through construction of the corresponding phase diagrams which are critical for optimization purpose would also be possible.

Acknowledgement

The authors would like to acknowledge financial support of Universiti Teknologi MARA Malaysia.

References

1. Aini, I. N., & Miskandar, M. S. (2007). Utilization of palm oil and palm products in shortenings and margarines. *European Journal Lipids Science Technology, 109(4),* 422-432.
2. Biotimes. (2006). www.novozymes.com
3. de Man, L., & de Man, J. M. (1994). Functionality of palm oil and palm kernel oil in margarine and shortening. *PORIM Occasional Papers, 32,* 1-14.

4. Katan, M. B., Zock, P. L., & Mensink, R. P. (1995). *Trans* fatty acids and their effect on lipoproteins in humans. *Annual Review of Nutrition, 15,* 473-493.
5. Lai, O. M., Ghazali, H. M., & Chong, C. L. (1998). Effect of enzymatic transesterification on the melting points of palm stearin-sunflower oil mixtures. *Journal of the American Oil Chemists' Society, 75*, 881-886.
6. Malaysian Palm Oil Board Test Methods (MPOB). (2004). A compendium of tests on palm oil products, palm kernel products, fatty acids, food-related products and others. Ministry of Primary Industries, 310-317.Kuala Lumpur, Malaysia.
7. Marangoni, A. G., & Rousseau, D. (1998). Chemical and enzymatic modification of butterfat and butterfat–canola oil blends, *Food Research International, 31(8),* 595–599.
8. Moss, J. (2005). Labeling of *trans* fatty acid content in food, regulations and what limits, pros and cons- the FDA view. First International Symposium on *Trans* Fatty Acids and Health, Copenhagen, Denmark.
9. Rousseau, D., Forestiére, K., Hill, A. R., & Marangoni, A. G. (1996). Restructuring butterfat through blending and chemical interesterification. 1. Melting behavior and triacylglycerol modifications. *Journal of the American Oil Chemists' Society, 73*, 963-972.
10. Timms, R. E. (1984). Phase behavior of fats and their mixtures. *Progress in Lipid Research, 23,* 1–38.
11. Zainal, Z., & Yusoff, M. S. A. (1999). Enzymatic interesterification of palm stearin and palm kernel olein. *Journal of the American Oil Chemists' Society, 76*, 1003-100.