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Characteristics of Simple and Chemically Interesterified Blends Containing Palm Stearin, Sunflower Oil and Palm Kernel Olein and Potential Application of the Blends in Fats Spread Formulations

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The above biopolymers could be further processed to produce derivatives *e.g.* micro-crystalline cellulose (MCC) from cellulose, lignin sulphonic from lignin, *etc*.

ABSTRACT

Palm stearin (POs), sunflower oil (SFO) and palm kernel olein (PKOo) were blended in various ratios and subjected to chemical interesterification (CIE). Fatty acid composition, triacylglycerol (TAG) composition, solid fat content (SFC) and polymorphic behaviour of the interesterified blends were analysed and compared with the properties of the unreacted blends. Upon CIE, extensive rearrangement of fatty acids among TAGs was evident. New TAGs were formed and concentrations of several TAGs were changed. These changes in TAG profiles resulted in some changes in the physical properties of the blends. The SFC of the interesterified blends, except binary blends of POs/PKOo, were softer than their respective unreacted blends. All the unreacted blends, except blends with high proportion of SFO which were liquid at measurement temperature, stabilized exclusively in ß' crystal or as a mixture of ß' and β crystals with the ß' crystals dominating. More ß crystals were observed in the binary blends of POs/SFO following CIE. Other blends especially blends containing high proportion of PKOo were still dominated by ß' crystals. Based on the SFC profile, 16.2%-22.5% POs, 0.0%-22.5% PKOo and 57.5%-81.2% SFO blends could be used directly to formulate tub type spreads for temperate countries and 20.0%-25.0% POs, 18.8%-47.5% PKOo and 32.5%-60.0% SFO are suggested for tropical countries. Simple blends of POs/SFO/PKO are not suitable for block type spread formulation. After CIE, more POs and PKOo could be incorporated into the fat spread formulations. Interesterified blends of 41.2%-53.1% POs, 0.0%-23.8% PKOo and 35.0%-51.2% SFO are suitable for tub type spread formulations for tropical countries. For block type spreads, 47.5%-52.5% POs, 0%-15.0% PKOo and 37.5%-47.5% SFO are recommended. However, interesterified blends of POs/SFO/PKOo are not suitable for tub type spreads for temperate countries.

ABSTRAK

Stearin sawit (POs), minyak biji bunga matahari (SFO) dan minyak olein isirong sawit (PKOo), diadun dalam pelbagai nisbah dan diberi perlakuan penginteresteran secara kimia (CIE). Komposisi asid lemak, komposisi triasilgliserida (TAG), kandungan lemak pejal (SFC) dan kelakuan penghabluran bagi adunan-adunan lemak yang terinterester dianalisis dan dibandingkan dengan ciri-ciri fiziko-kimia adunan-adunan langsung lemak. Pengaturan semula asid-asid lemak pada molekul-molekul TAG dikesan selepas CIE. Beberapa TAG baru terhasil dan kepekatan beberapa TAG tertentu berubah. Perubahan dalam profil TAG menyebabkan perubahan ke atas sifat-sifat fizikal adunan-adunan lemak. SFC bagi adunan-adunan yang terinterester, kecuali adunan-adunan perduaan POs/PKOo, adalah lebih rendah berbanding dengan adunan langsung masing-masing. Kesemua adunan langsung, kecuali adunan yang kaya dengan SFO yang bersifat cecair pada suhu pengukuran, stabil dalam bentuk 100% hablur ß' atau dalam bentuk campuran hablur-hablur ß dan ß' dengan hablur ß' mendominasi. Selepas CIE, lebih banyak hablur ß hadir dalam adunan POs/SFO. Adunan-adunan lain terutamanya adunan yang mengandungi PKOo dalam nisbah yang tinggi masih stabil dalam bentuk hablur ß' mendominasi. Berdasarkan kepada profil SFC, adunan langsung 16.2%-

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22.5% POs, 0.0%-22.5% PKOo and 57.5%-81.2% SFO; dan 20.0%-25.0% POs, 18.8%-47.5% PKOo dan 32.5%-60.0% SFO setiap satunya dicadangkan untuk pemformulasian sapuan lemak jenis tub untuk negara iklim sederhana dan sapuan lemak jenis tub untuk negara tropika. Adunan langsung POs/SFO/PKO tidak sesuai digunakan untuk pemformulasian sapuan lemak meja jenis blok. Selepas CIE, lebih banyak POs dan PKOo boleh digunakan dalam pemformulasian sapuan lemak. Adunan 41.2%-53.1% POs, 0.0%-23.8% PKOo and 35.0%-51.2% SFO yang terinterester sesuai untuk pemformulasian sapuan lemak jenis tub untuk negara tropika. Untuk sapuan lemak jenis blok, 47.5%-52.5% POs, 0%-15.0% PKOo dan 37.5%-47.5% SFO adalah dicadangkan. Bagaimanapun, adunan POs/SFO/PKOo yang terinterester tidak sesuai digunakan untuk pemformulasian sapuan lemak jenis tub untuk negara iklim sederhana.

Keywords: palm stearin, palm kernel olein, blending, chemical interesterification, fat spreads.

INTRODUCTION

Palm stearin (POs), the cheaper, high melting fraction from palm oil, can be used as a source of fully natural hard component in the manufacture of fat spreads. Its high melting point (³ 44°C -56°C), however poses problems for the manufacture of fat spreads as it confers low plasticity to the products and is not completely melted at body temperature (Pantzaris, 1985). Furthermore, because the solids in POs consist mainly of tripalmitin (PPP), where P = palmitic acid, a TAG with 48 carbon atoms, it is a strong β crystal promoter as TAGs with 48 and 54 carbon atoms are β formers. When diluted with liquid oils, the β forming tendency increases (de Man, 2000).

As fat spreads should be stiff in the refrigerator but spread easily upon removal, melt quickly in the mouth and should also crystallize as a β' polymorph (de Man, 2000; Gunstone and Norris, 1983), POs by itself is not a good hard stock for fat spreads. To improve its melting properties and crystallization behaviour, POs may be blended and/or interesterified with fats that contain shorter-chain fatty acids, such as PKOo with a slip melting point of about 26°C. PKOo is a by-product from the fractionation of palm kernel oil. PKOo is rich in short- and medium-chain fatty acids and has a good β' stability. Blending and/or interesterifying POs with PKOo results in blends with sharp melting characteristic and this gives a cool sensation when the fat blends melt in the mouth (Pantzaris, 1985). The resulting blends are also β' stable. POs and/or PKOo may also be interesterified with liquid vegetable oils such as SFO, to give blends with better functional properties.

Interesterification is a useful tool for altering the natural physical characteristics of a fat or fat blend to produce a product offering greater functionality for certain specific applications. It involves an interchange of fatty acids within (intraesterification) and among (interesterification) TAG molecules, which make up fats and oils, until a thermodynamic equilibrium is reached (Sreenivasan, 1978). Two types of interesterificaton are in commercial use, *i.e.* enzymatic interesterification (EIE) involves CIE. CIE produces a complete positional randomization of acyl groups in TAGs, with chemicals (such as sodium metal or sodium methoxide) as catalyst. EIE involves microbial lipases as catalyst. Each type of interesterification possesses advantages and disadvantages. The advantages of CIE over EIE primarily involve cost recovery and initial investment. Chemical catalysts are much cheaper than lipases. CIE is also a tried-and-true approach, as it has been around for a long time, and industrial procedures and equipment are available. On the other hand, EIE reactions are more specific, require less severe reactions and produce less waste than CIE and may represent the way of the future (Konishi *et al.*, 1993).

The objectives of this study were to study the physico-chemical characteristics of simple and chemically interesterified blends containing POs, SFO and PKOo and to produce suitable blends for the formulation of fat spreads that have all the inherent qualities of a good table spread, yet are free of *trans* fatty acids.

EXPERIMENTAL PROCEDURES

Materials

POs (with iodine value of 40), SFO and PKOo were obtained from Lam Soon Malaysia Sdn. Bhd., Petaling Jaya, Selangor, Malaysia.

Preparation of Blends

Blends of POs, SFO and PKOo were made in the following mass (w/w) ratios: A[1:0:0], B[3:1:0], C[1:1:0], D[1:3:0], E[0:1:0], F[0:3:1], G[0:1:1], H[0:1:3], I[0:0:1], J[1:0:3], K[1:0:1],

L[3:0:1], M[4:1:1], N[1:4:1], P[1:1:4] and Q[1:1:1].

Chemical Interesterification (CIE)

The fat blend (250 g) was dried for 30 min at 110°C. A steady stream of nitrogen was maintained throughout the process. About 0.2% sodium metal was then added as catalyst. After 60 min of stirring at a constant speed of 500 rpm, the mixture was cooled below 80°C. About 20% citric acid solution was then added to deactivate the catalyst while the mixture was stirred mechanically for 30 min, followed by washing the mixture a few times with hot water to remove the citric acid, catalyst and soap. Finally, the fat blend was dried by filtering it through anhydrous sodium sulphate.

Fatty Acid Composition (FAC)

FAC was determined according to the official AOCS method Cd 14c-94 (AOCS, 1992). The fat blend was esterified into fatty acid methyl ester (FAME). About 1 µl of the FAME was injected into a Hewlett-Packard 5890 II (Palo Alto, CA) gas chromatograph fitted with a polar SP 2340 (Supelco, Bellefonte, PA) capillary column (0.25 mm i.d. x 60 m x 0.2 µm). The detector and injector port temperatures were 240°C. Carrier gas was helium at 0.8 ml min^{-1}. The column temperature was isothermal at 190°C.

Triacylglycerol (TAG) Composition

TAG composition was determined by non-aqueous reversed-phase high performance liquid chromatograph (RP-HPLC) (Jasco, Japan). The mobile phase was acetone/acetonitrile (Merck, Darmstadt, Germany) at a gradient composition from 65% acetone increasing to 95% acetone in 30 min. The mobile phase flow rate was 1.5 ml min^{-1}. Two commercially packed Genesis C18 columns (15 mm x 4.6 mm i.d) of 4 µ particle size were used to separate the TAGs. The TAGs were detected by an Alltech 500 (Deerfield, IL) evaporative light scattering detector. Individual peaks were identified by comparing the retention times with those of commercial TAG standards and common vegetable oils of known TAG composition. The equivalent carbon number of each TAG was calculated according to the official AOCS method Ce 5b-89 (AOCS, 1995).

Solid Fat Content (SFC)

SFC was determined using a Bruker Minispec PC 120 pulse nuclear magnetic resonance (Karlsruhe, Germany) according to the procedures described in PORIM Test Method (1995).

Polymorphism

The polymorphic forms of fat crystals in fat blends were determined by X-ray diffraction using an Enraf Nonius Diffractic X-ray generator Model FR592 (Delft, the Netherlands) and an Enraf Nonius Guinier camera Model FR552 with temperature controlled sample holder operated at 5°C. Samples were heated at 70°C for 30 min to destroy any *memory* of earlier crystals, followed by crystallization at 0°C for 90 min. The samples were then tempered at room temperature for five days and at 5°C for two days before measurement. Short spacings on the X-ray film were measured with an Enraf Nonier Guinier viewer. The short spacings of the β' form are at 4.2 and 3.8Å and that of the β form is at 4.6 Å (de Man, 1992). The levels of β' and β crystals are estimated by the relative intensity of the short spacings at 4.2 and 4.6 Å.

Statistical Analysis

Analyses of general linear models and response surfaces were performed using the SAS® (Cary, NC) statistical package as described by Md Ali and Dimick (1994). The R^2 values which indicate model fits of each of the constructed ternary diagrams were determined and found to be greater than 0.95.

Comparison of the SFC profiles was made with oil blends extracted from fat spread samples purchased from supermarkets in the United States and Malaysia.

RESULTS AND DISCUSSION

Fatty Acid Composition (FAC)

Table 1 shows the FAC of POs, PKOo and SFO, and their blends. POs and blends containing a high proportion of POs were characterized by a higher content of palmitic and oleic acids. Lauric, myristic and oleic acids were the major fatty acids in PKOo and blends containing a high proportion of PKOo. They also contained appreciable amounts of short-chain fatty acids, *e.g.* caprylic and capric acids. The SFO and blends containing high proportions of SFO were high in oleic and linoleic acids. The FAC of the interesterified blends are not shown as CIE neither affects the degree of saturation nor causes isomerization of the fatty acid double bond. Thus, it does not change the fatty acid profile of the

TABLE 1. FATTY ACID COMPOSITION OF PALM STEARIN, SUNFLOWER OIL, PALM KERNEL OLEIN AND THEIR BLENDS IN VARIOUS RATIOS

Code	POs:SFO:PKOo ratios	FAC (wt %)								
		$C_{8:0}$	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	Others
A	[1:0:0]	-	-	0.2	1.2	55.6	4.8	30.3	6.9	1.0
B	[3:1:0]	-	-	0.1	1.0	43.8	4.4	28.8	21.2	0.7
C	[1:1:0]	-	-	0.1	0.7	31.2	4.2	27.4	36.0	0.4
D	[1:3:0]	-	-	-	0.4	18.6	4.0	25.7	50.7	0.6
E	[0:1:0]	-	-	-	0.1	6.3	3.7	24.3	65.1	0.5
F	[0:3:1]	1.2	1.1	11.5	3.6	7.0	3.5	22.8	48.6	0.7
G	[0:1:1]	2.4	1.9	22.8	7.2	7.4	3.2	21.2	33.3	0.6
H	[0:1:3]	3.7	2.9	33.8	10.5	7.8	3.0	19.6	18.2	0.5
I	[0:0:1]	4.7	3.8	44.5	13.7	8.4	2.8	18.1	2.9	1.1
J	[1:0:3]	3.5	2.8	33.7	10.8	19.8	3.5	21.1	4.1	0.7
K	[1:0:1]	2.4	1.9	22.9	7.7	31.6	3.6	24.2	4.9	0.8
L	[3:0:1]	1.2	1.1	12.0	4.4	43.4	3.9	27.4	6.0	0.6
M	[4:1:1]	0.8	0.7	7.7	3.2	39.3	4.0	27.6	16.1	0.6
N	[1:4:0]	0.8	0.7	7.6	2.6	14.9	3.8	24.2	44.9	0.5
P	[1:1:4]	3.1	2.5	30.0	9.4	15.8	3.1	21.2	14.3	0.6
Q	[1:1:1]	1.6	1.3	15.1	5.2	23.3	3.9	24.0	24.8	0.8

Notes: FAC = fatty acid composition, POs = palm stearin, SFO = sunflower oil, PKOo = palm kernel olein, $C_{8:0}$=caprylic, $C_{10:0}$=capric, $C_{12:0}$=lauric, $C_{14:0}$=myristic, $C_{16:0}$=palmitic, $C_{18:0}$=stearin, $C_{18:1}$=oleic and $C_{18:2}$=linoleic acid. Others include caproic ($C_{6:0}$) and/or linolenic ($C_{18:3}$) and/or arachidic ($C_{20:0}$) acids.

starting material (Allen, 1996; Haumann, 1994; Rozendaal, 1989).

Triacylglycerol (TAG) Composition

TAG composition of POs, SFO and PKOo before and after CIE is tabulated in *Table 2*. The main TAGs in POs were POP (35.9%), PPP (17.9%), POO (15.3%), PLP (8.1%), POS (7.1%) and PLO (5.1%), O=oleic, S=stearic and L=linoleic acid. SFO consisted of 29.8% OLL, 28.2% LLL, 11.0% OLO, 10.0% PLO and 9.6% PLL. PKOo contains a wide range of TAG species. The major TAGs of PKOo were LaLaLa (22.7%), LaLaM (15.0%), CaLaLa/CLaM (11.8%), CLaLa (8.4%), LaLaP/LaMM (7.8%), LaLaO (6.4%), LaOP/MMO (5.1%) and LaOM (5.0%), where La=lauric, M=myristic, Ca=caprylic and C=capric acid. Generally, CIE generated only small changes in the TAG composition of POs, SFO and PKOo.

Table 3 shows the TAG composition of some of the binary and ternary blends of POs/SFO/PKOo. TAG composition of the simple blends of POs/SFO/PKOo represents a linear combination of the fat component in the blends. For example, as the proportion of POs increases in the blends, so does the proportion of POP, PPP, POO, PLP and POS. CIE induced enormous changes in the TAG composition of the fat blends. For example, the proportions of the main TAGs in the blend containing 50% POs and 50% SFO (coded C), *i.e*., the POP, OLL, LLL and PPP had respectively reduced from 18.5%, 14.4%, 13.8% and 9.4% before CIE to 12.8%, 9.9%, 6.0% and 4.6% after CIE. Concomitantly, the proportions of other TAGs, such as PLO, PLP and PLL had increased from 7.8%, 4.3% and 4.5% to 18.4%, 11.7% and 11.7% respectively. The HPLC chromatograms of the respective blends before and after CIE are shown in *Figure 1*. Due to the presence of a wide range of fatty acids, from short-, medium- and long-chain fatty acids, the TAG species in the chemically interesterified blends containing PKOo could not be identified, as the TAG composition of the blends had become very complicated. However, the TAG profile of the interesterified blends generally showed a more balanced or even peak distribution than the starting blends, as the relative concentrations of several TAGs increased, others decreased, and several new TAGs might also have been synthesized. These results are consistent with the findings reported by Zainal and Yusoff (1999) and Lai *et al*. (1998).

Polymorphic Behaviour

X-ray data revealed that except for blends E, F and N, which were liquid at 5°C due to the presence of high amounts of SFO, other simple blends were stable exclusively in β' form or with the β' form dominating (*Figure 2a*). POs consisted primarily of β' crystals with a small amount of β crystals, PKOo was stable exclusively in the β' crystalline form and SFO was liquid at the measuring temperature. Incorporation of SFO into the blends in-

TABLE 2. TRIACYLGLYCEROL COMPOSITION (% area) OF PALM STEARIN, SUNFLOWER OIL AND PALM KERNEL OLEIN BEFORE AND AFTER CHEMICAL INTERESTERIFICATION

TAG species	ECN	DB			CIE		
		POs	SFO	PKOo	POs	SFO	PKOo
CLaLa	32.0	-	-	8.4	-	-	5.4
CaLaLa/CLaM	34.0	-	-	11.8	-	-	6.6
LaLaLa	36.0	-	-	22.7	-	-	18.6
LaLaM	38.0	-	-	15.0	-	-	16.2
LaLaO	39.4	-	-	6.4	-	-	13.6
LaLaP/LaMM	40.0	-	-	7.8	-	-	9.0
LLL	39.9	-	28.2	-	-	26.8	-
LaOM	41.4	-	-	5.0	-	-	7.6
LaPM	42.0	-	-	3.3	-	-	4.7
OLL	42.0	-	29.8	-	-	28.8	-
PLL	42.6	0.2	9.6	-	-	8.7	-
LaOO	42.8	-	-	3.5	-	-	3.3
LaOP/MMO	43.4	-	-	5.1	-	-	4.2
LaPP/MMP	44.0	-	-	1.1	-	-	1.8
OLO	44.1	0.6	11.0	-	0.3	10.9	-
PLO	44.7	5.1	10.0	-	2.7	9.5	-
MOO	44.8	-	-	1.1	-	-	0.7
PLP	45.3	8.1	0.6	-	5.9	0.5	-
MOP	45.4	-	-	1.9	-	-	1.5
OOO	46.2	2.2	3.0	0.9	1.7	2.2	0.2
POO	46.8	15.3	3.5	1.4	15.4	4.6	0.4
POP	47.4	35.9	0.5	0.7	35.3	0.8	0.4
PPP	48.0	17.9	0.8	0.1	23.8	1.4	0.1
SOO	48.8	1.4	1.1	-	0.7	1.2	-
POS	49.4	7.1	0.4	-	5.1	0.4	-
PPS	50.0	3.3	0.4	-	5.1	0.8	-

Note: TAG=triacylglycerol, PO=palm oil, SFO=sunflower oil, PKOo=palm kernel olein, DB=before chemical interesterification, CIE=after chemical interesterification, ECN=equivalent carbon number, C=capric acid, La=lauric acid, Ca=caprylic acid, M=myristic acid, O=oleic acid, P=palmitic acid, L=linoleic acid and S=stearic acid.

creased the tendency of the desirable β' polymorphic form to convert to the β form, consistent with what was reported by de Man (2000). On the other hand, addition of PKOo to the blends promoted stabilization in the β' crystalline form. According to Timms (1990), lauric fats tend to posses a stable β' polymorphic because of their mixed chain length TAG, which are due, in turn, to the presence of various chain length fatty acids. When POs, SFO and PKOo were blended, the TAG mixture of the blends became more complex and the tendency of the blends to crystallize in β polymorphic form declined.

In the absence of PKOo, more β crystals were observed in the chemically interesterified POs/SFO/PKOo blends (*Figure 2b*). This could be due to the fact that POs was rich in POP. According to Duns (1985), the molecular rearrangement that takes place during interesterification reduces the proportion of the native symmetrical TAG of POP, and that of PPO increases. This phenomenon facilitates the development of β-2 compound formation attributed to interaction between the POP (stable in β-3 polymorph) and PPO (stable in β'-3 polymorph), as described by Timms (1984). Compound formation may be regarded as the transformation of a mixture of two TAGs of different polymorphs into a single new polymorph. Interesterified blends which contain PKOo were found to stabilize in the β' crystalline form for reasons discussed earlier.

Solid Fat Content (SFC)

The SFC profiles of the simple and chemically interesterified POs, SFO, PKOo and blends thereof in various ratios are shown in *Figure 3*. The SFC profiles of all the fats and their blends were significantly different from each other. The rate of SFC evolution was dependent on both temperature and proportion of each fat in the blends. POs was the hardest fat with SFC of 14.8%-23.4% at 35°C. This was due to the high proportion of saturated TAG with respect to the content of fatty acids as described in *Table 1*. SFO was fully liquid at temperatures as low

TABLE 3. TRIACYLGLYCEROL (% area) COMPOSITION OF THE BLENDS OF PALM STEARIN, SUNFLOWER OIL AND PALM KERNEL OLEIN IN VARIOUS RATIOS BEFORE AND AFTER CHEMICAL INTERESTERIFICATION

TAG species	ECN	POs/SFO/PKOo [1:1:0] (DB)	POs/SFO/PKOo [0:1:1] (DB)	POs/SFO/PKOo [1:0:1] (DB)	POs/SFO/PKOo [1:1:1] (DB)	POs/SFO/PKOo [1:1:0] (CIE)
CLaLa	32:0	-	4.4	4.3	2.6	-
CaLaLa/CLaM	34:0	-	6.0	6.1	4.1	-
LaLaLa	36:0	-	11.6	11.7	7.9	-
LaLaM	38:0	-	7.2	7.3	5.4	-
LaLaO	39.4	-	2.7	2.6	1.8	-
LaLaP[a]/LaMM[a]	40.0	-	18.0[a]	3.6	11.5[a]	-
LLL[a]	39.9	13.8		-		6.0
LaOM	41.4	-	2.5	2.4	1.6	-
LaPM[b]	42.0	-	16.6[b]	1.4	10.6[b]	-
OLL[b]	42.0	14.4		-		9.9
PLL	42.6	4.5	4.8	0.2	3.0	11.7
LaOO	42.8	-	1.8	1.7	0.9	-
LaOP/MMO	43.4	-	2.4	2.5	1.7	-
LaPP[c]/PMM[c]	44.0	-	7.1[c]	0.9[c]	4.9[c]	-
OLO[c]	44.1	6.5				6.6
PLO[d]	44.7	7.8	6.1[d]	3.3[d]	5.8[d]	18.4
MOO[d]	44.8	-				-
PLP[e]	45.4	4.3	1.2[e]	5.0[e]	3.6[e]	11.7
MOP[e]	45.4	-				-
OOO	46.2	2.4	1.9	1.6	1.6	1.4
POO	46.8	9.0	2.6	8.3	6.6	8.9
POP	47.4	18.5	0.6	19.3	13.5	12.8
PPP	48.0	9.4	0.5	10.1	6.8	4.6
SOO	48.8	1.2	0.2	0.8	0.7	0.8
POS	49.4	3.8	0.2	3.6	2.8	2.8
PPS	50.0	1.8	0.2	1.6	1.2	1.4

Notes: abbreviations as in *Table 2*. TAGs with the same superscript [a, b, c, d] and [e] are TAGs with similar/almost similar ECN and hence their peaks emerged at almost the same retention time.

as 5°C, as it was rich in polyunsaturated fatty acids. PKOo had a very sharp melting profile, as it contained a high proportion of medium-chain fatty acids.

The altered TAG composition of the interesterified blends was reflected in the SFC. However, since there was not much change in TAG composition for POs, SFO and PKOo after CIE, there was also not much change in their SFC profiles (*Figure 3a*). All the interesterified blends, except the binary blends of POs/PKOo (*Figure 3c*), appeared to have lower SFC values than their respective unreacted blends (*Figures 3b* and *d*). The decrease in the SFC values can be explained by the decrease in high melting TAGs, *e.g.* PPP and POP. Chemically interesterified binary blends of POs/PKOo have higher SFC values than the simple blends, although there was a reduction in the proportion of the high melting tri- and di-saturated TAGs in the blends following CIE. The only plausible explanation could be that there was an eutectic interaction between POs and PKOo in the simple binary blends of POs/PKOo that made the blends softer. Eutectic (from the Greek Eutektos which means easily melted) interaction is always observed in fat mixtures and defines one of the criteria for the degree of compatibility for the two fats (Timms, 1984). Eutectic interaction tends to occur when the components differ in molecular volume, shape or polymorph. Interesterification of the blends eliminated eutectic interactions (Bigalli, 1988).

Applications

Figure 4 shows the superimposed iso-lines of SFC at 5°C, 25°C and 35°C, for the simple and chemically interesterified POs/SFO/PKOo blends

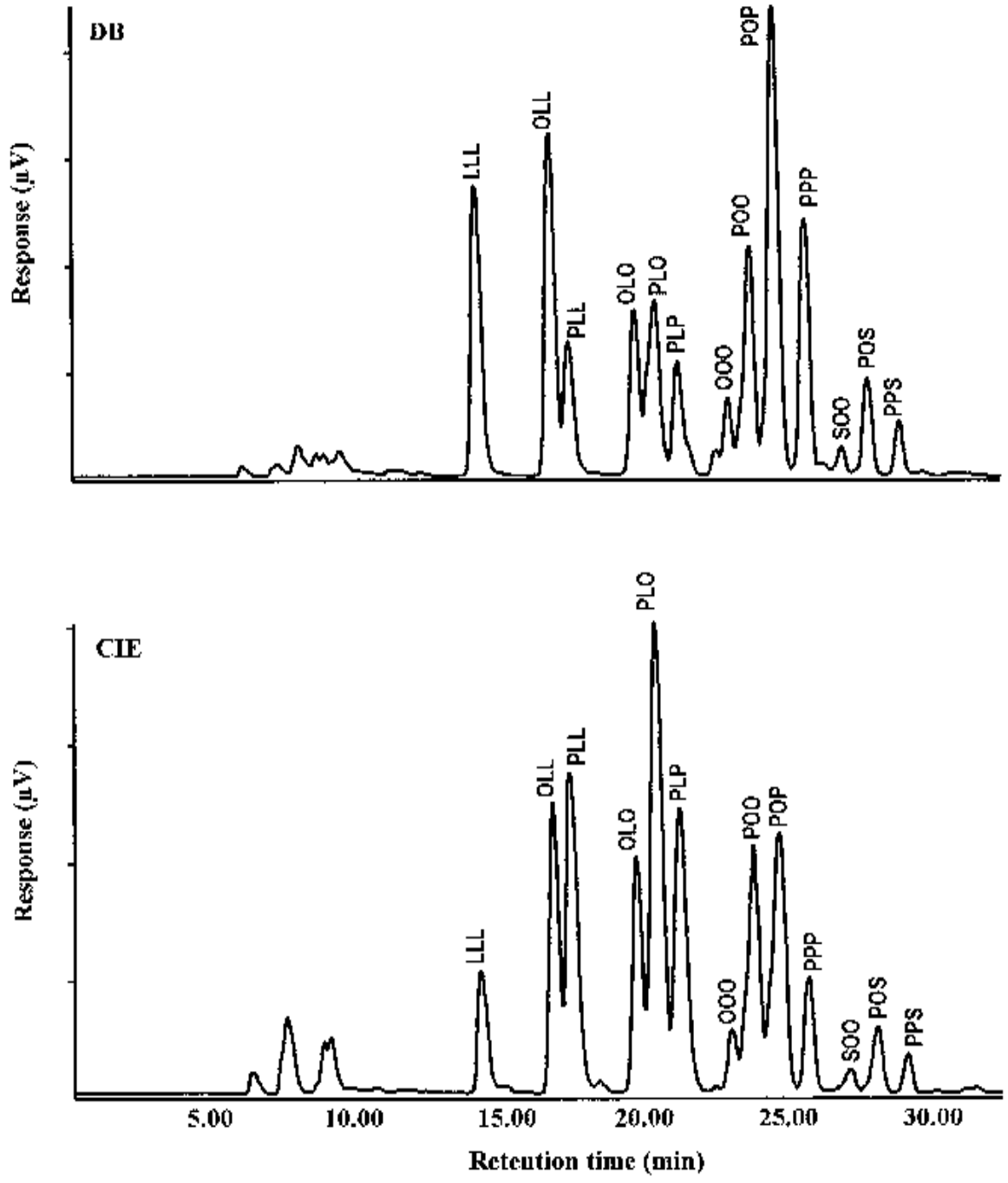

Figure 1. Triacylglycerol chromatogram of the blend of palm stearin and sunflower oil in the ratio of 1:1 before (DB) and after chemical interesterifaction (CIE).

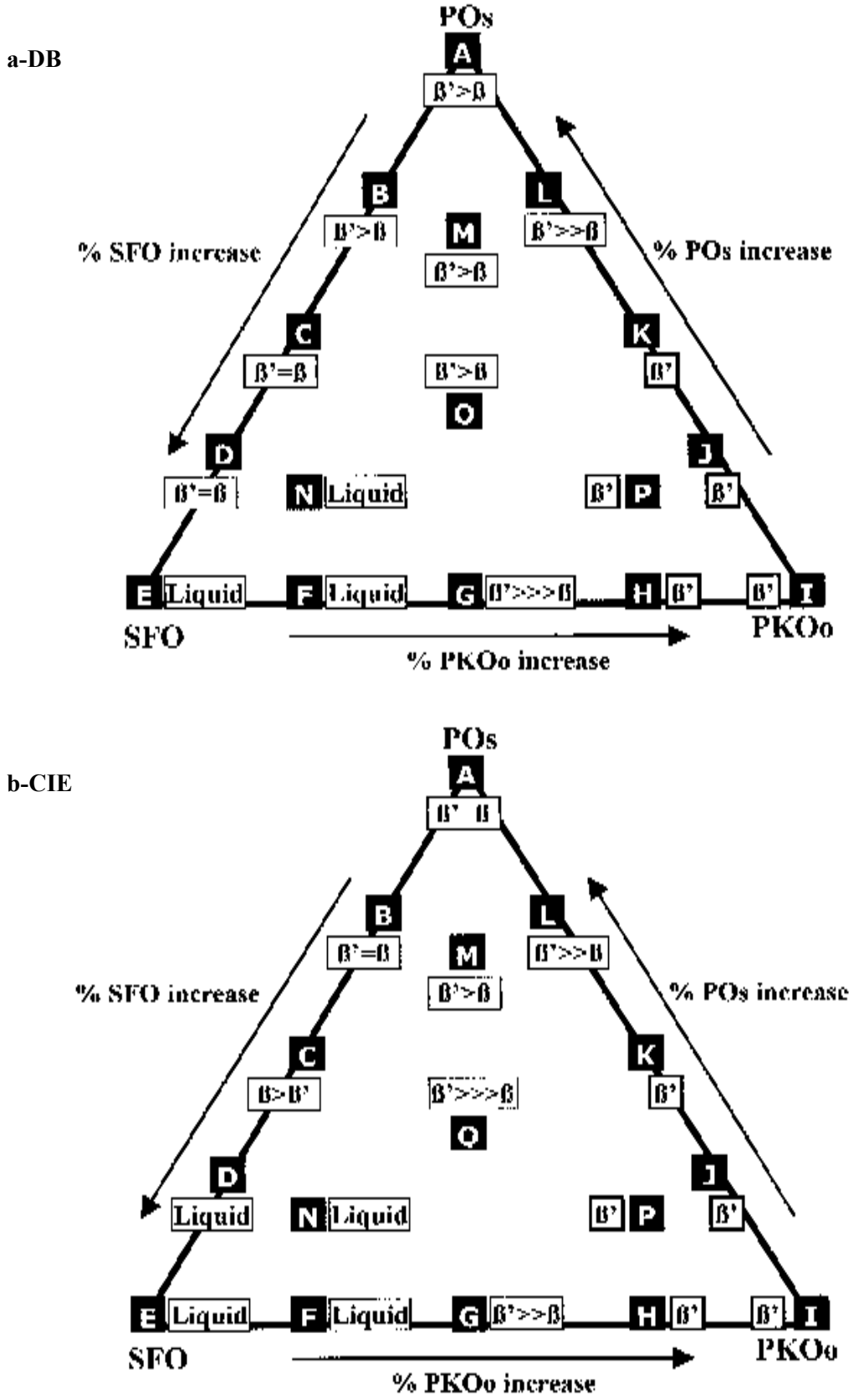

Figure 2. Polymorphic behaviour of blends of palm stearin (POs), sunflower oil (SFO) and palm kernel olein (PKOo) in various ratios before (DB) and after chemical interesterification (CIE).

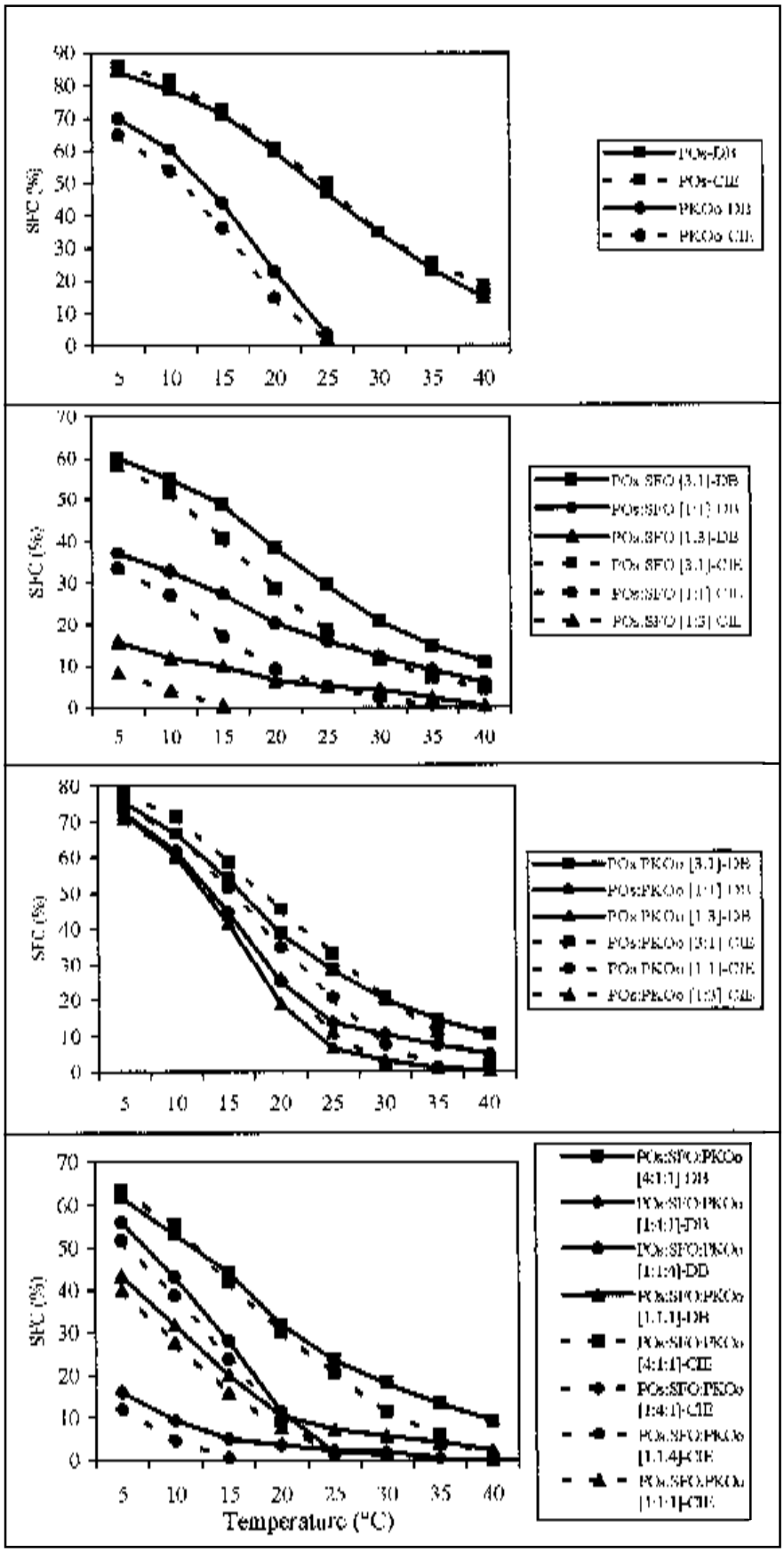

Figure 3. Solid fat content (SFC) profiles of palm stearin (POs) and palm kernel olein (PKOo) (a), POs and sunflower oil (SFO) in various ratios (b), POs and PKOo in various ratios (c) and POs, SFO and PKOo in various ratios (d) before (DB) and after chemical interesterification (CIE).

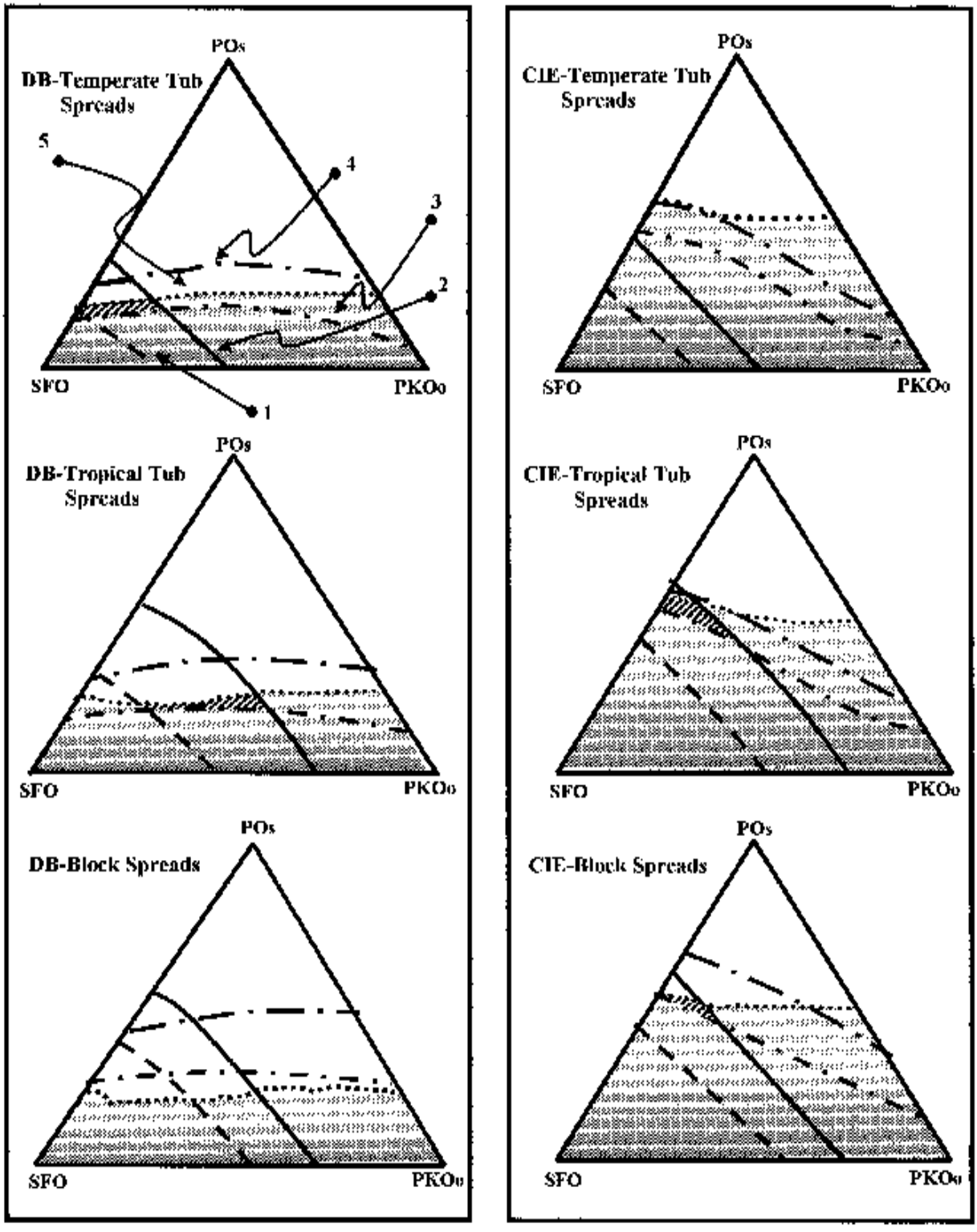

Figure 4. Superimposed iso-lines of solid fat content (SFC) at 5°C, 25°C and 35°C of the simple (DB) and chemically interesterified (CIE) ternary blends of palm stearin (POs), sunflower oil (SFO) and palm kernel olein (PKOo) for the formulation of tub type fat spreads for temperate (temperate tub spreads) and tropical (tropical tub spreads) countries and block type fat spreads (block spreads). Shaded areas indicate the possible formulation for each type of fat spreads. 1=SFC min. at 5°C, 2=SFC max. at 5°C, 3=SFC min. at 25°C, 4=SFC max. at 25°C and 5=SFC max. at 35°C.

that delineate the range of commercial tub for temperate and tropical countries, and block fat spreads. The SFC, *i.e*., the amount of fat crystals in a blend, is responsible for many of the fat spread characteristics including general appearance, ease of packing, organoleptic properties and oil exudation. The SFC at 5°C determines the ease of spread of the product at refrigeration temperature. The SFC at 25°C determines the product's stability and resistance to oil exudation at room temperature. The SFC at 35°C determines the thickness and flavour release properties of the fat spreads in the mouth (Krawczyk *et al*., 1996). Considering the SFC profile, in order to produce tub fat spreads for temperate and tropical countries, 16.2%-22.5% POs, 0.0%-22.5% PKOo and 57.5%-81.2% SFO; and 20.0%-25.0% POs, 18.8%-47.5% PKOo and 32.5%-60.0% SFO blends could be directly used, respectively. Simple blends of POs/SFO/PKO are not suitable for block type spread formulations. After CIE, more POs and PKOo could be incorporated into the fat spread formulations. Chemically interesterified blends of 41.2%-53.1% POs, 0.0%-23.8% PKOo and 35.0%-51.2% SFO are suitable for tub type spread formulation for tropical countries. For block type spreads, 47.5%-52.5% POs, 0%-15.0% PKOo and 37.5%-47.5% SFO are recommended. However, chemically interesterified blends of POs/SFO/PKOo are not suitable for tub type spreads for temperate countries.

CONCLUSION

This study showed that CIE significantly modified the properties of blends of POs, SFO and PKOo. CIE of POs with SFO and PKOo can be used as an alternative to partial hydrogenation to produce a plastic fat phase that is suitable for the production of tub or block type fat spreads. The final products would have comparable physical properties as good table spreads and yet be free of *trans* fatty acids.

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REFERENCES

ALLEN, D A (1996). Interesterification - a vital tool for the future*? Lipid Technology*: 11-15.

AOCS (1992). *Official Methods and Recommended Practices of the American Oil Chemists' Society* (Firestone, D ed.). Fourth edition. AOCS Press, Champaign, IL.

AOCS (1995). *Official Methods and Recommended Practices of the American Oil Chemists' Society* (Firestone, D ed.). AOCS Press, Champaign, IL.

BIGALLI, G L (1988). Practical aspects of eutectic effect on confectionery fats and their mixtures. *Proc. of the 42nd P.M.C.A. Production Conference.* p. 66-71.

de MAN, J M (2000). Use of palm stearin as a component of interesterification. *Society of Chemical Industry (SCI) Lecture Papers Series.*

de MAN, J M (1992). X-ray diffraction spectroscopy in the study of fat polymorphisms. *Food Res. Int., 25*:471-476.

DUNS, M L (1985). Palm oil in margarine and shortening. *J. Amer. Oil Chem. Soc., 62*:408-410.

GUNSTONE, F D and NORRIS, F A (1983). *Lipid in Foods, Chemistry, Biochemistry and Technology* (Maxwell, R ed.). Pergamon Press, Oxford.

HAUMANN, B F (1994). Tools: hydrogenation and interesterification. *INFORM*, *5*:668-678.

KONISHI, H; NEFF, W E and MOUNTS, T L (1993). Chemical interesterification with regioselectivity for edible oils. *J. Amer. Oil Chem. Soc., 70*:411-415.

KRAWCZYK, G R; BULIGA, G S; BERTRAND, D T and HUMPHREYS, W M (1996). Reviewing the technology of low fat spreads. *INFORM*, *7*:635-639.

LAI, O M; GHAZALI, H M and CHONG, C L (1998). Physical properties of *Pseudomonas* and *Rhizomucor miehei* lipase-catalyzed transesterified blends of palm stearin: palm kernel olein. *J. Amer. Oil Chem. Soc*., *75*:953-959.

MD ALI, A R and DIMICK, P S (1994). Thermal analysis of palm mid fraction, cocoa butter and

milk fat blends by differential scanning calorimetry. *J. Amer. Oil Chem. Soc*., *71*:299-302.

PANTZARIS, T P (1985). *Pocketbook of Palm Oil Uses*. PORIM, Bangi. p. 23-47.

PORIM (1995). *PORIM Test Methods*. PORIM, Bangi. p. 134-142.

ROZENDAAL, A (1989). Interesterification of oils and fats. *Proc. Edible Fats and Oil: Basic Principle and Modern Practice*. p. 152-157.

SREENIVASAN, B (1978). Interesterification of fats. *J. Amer. Oil Chem. Soc., 55*:796-805.

TIMMS, R E (1990). Crystallization behaviour of palm oil. *Symposium Proceeding: New Developments in Palm Oil* (Berger, K G ed.). PORIM, Bangi. p. 38-44.

TIMMS, R E (1984). Phase behaviour of fats and their mixtures. *Prog. Lipid Res*., *23*:1-38.

ZAINAL, Z and YUSOFF, M S A (1999). Enzymatic interesterification of palm stearin and palm kernel olein. *J. Amer. Oil Chem. Soc*., *76*:1003-1008.