TAG Composition and Solid Fat Content of Palm Oil, Sunflower Oil, and Palm Kernel Olein Blends Before and After Chemical Interesterification

H.M.D. Noor Lida^{*a*,*}, K. Sundram^{*a*}, W.L. Siew^{*a*}, A. Aminah^{*b*}, and S. Mamot^{*b*}

^aMalaysian Palm Oil Board, Bandar Baru Bangi, 43000 Kajang, Selangor, Malaysia, and ^bUniversiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

ABSTRACT: Modification of the characteristics of palm oil (PO), sunflower oil, and palm kernel olein (PKOo) according to conventional three-component mixture designs was undertaken by a combination of blending and chemical interesterification (CIE) techniques. TAG composition and solid fat content (SFC) profile of the starting blends were analyzed and compared with those of the interesterified blends. Upon CIE, extensive rearrangement of FA among TAG was evident. Concentrations of several TAG were increased, some were decreased, and several new TAG were formed. The resulting changes in TAG profile were reflected in the SFC of the blends. The SFC values of the chemically interesterified blends, except binary blends of PO/PKOo, revealed that they were softer than their respective starting blends. SFC data also indicated that eutectic interaction occurred between PO and PKOo in the starting blends and that this interaction was diminished after CIE.

Paper no. J10270 in JAOCS 79, 1137–1144 (November 2002).

KEY WORDS: Chemical interesterification, palm-based fat blends, solid fat content, triacylglycerol composition.

Palm oil (PO) is a vegetable oil high in saturated FA content with a significant amount of the saturated FA at the 2-position of its TAG. PO consists of trisaturated (S₃) (mainly PPP), disaturated (S₂U) (mainly POP), and monosaturated (U₂S) (mainly POO) TAG, where P is palmitic acid and O is oleic acid. PO also contains appreciable amounts of DG (5–7%) and FFA, which could have substantial effects on its physical characteristics. Under normal ambient conditions (20–30°C), PO is a semisolid fat appearing as a heterogeneous slurry of crystals (mainly PPP and POP) admixed in liquid oil (mainly POO and POP) (1).

PO is an important edible oil source for the food industry because of its numerous advantageous properties, such as its high thermal and oxidative stability and its plasticity at room temperature (2). As it tends to crystallize as β' , PO is an attractive option for yellow-fat spread production. However, in temperate regions, PO should be added with other oils and/ or fats, as the characteristic solid fat content (SFC) of PO alone does not result in products that melt quickly on the

palate (3). Moreover, the relatively slow crystallizing properties of PO can result in a rather brittle structure, a phenomenon that is known as "posthardening," owing to the formation of granular crystals. Posthardening is particularly profound when the product is stored, after processing, at refrigeration temperatures (4). The formation of granular crystals can be eliminated by reducing the content of symmetrical TAG, notably POP, through interesterification (IE) with other oils and/ or fats low in saturated long-chain FA (2). Hence, to improve its melting and crystallization properties, PO may be blended and/or interesterified with palm kernel olein (PKOo), a lauric fat that contains short- and medium-chain FA. PO and PKOo may also be blended and/or interesterified with a liquid vegetable oil such as sunflower oil (SFO), which is high in PUFA, to give blends with better functional properties such as good spreadability at refrigeration temperatures (5).

IE is one of three important processes currently utilized for modifying the physicochemical characteristics of oils and fats. The other two processes are hydrogenation and fractionation. IE causes randomization of the FA distribution within (intraesterification) and among (interesterification) TAG molecules in oils and fats until a thermodynamic equilibrium is reached (6). Thus, it leads to modifications in TAG composition and, consequently, in its physical characteristics. The FA interchanges resulting from IE lead to changes in the physical characteristics of oils and fats because in nature FA are not randomly distributed between the TAG present. In most oils and fats, the 2-position of the TAG molecules is preferentially occupied by unsaturated FA. In its most commonly used form, IE produces a truly random distribution of FA that leads to an increased number of TAG species. This results in changes in the physical characteristics of the oils and fats, such as melting and crystallization behavior. The rearrangement process does not change the degree of unsaturation or the isomeric state of the FA as they shift from one position to another. The stability of the oils and fats also remains essentially unchanged (7,8). Two types of IE are available, i.e., chemical (CIE) and enzymatic (EIE). CIE produces a complete positional randomization of acyl groups in TAG, by using chemical catalysts. EIE uses lipases as catalyst. Each type of IE possesses advantages and disadvantages. CIE is preferred over EIE because of the lower investment and production costs of the finished products. Chemical catalysts are

^{*}To whom correspondence should be addressed at Product Development and Advisory Services Division, Malaysian Palm Oil Board, No. 6 Persiaran Institusi, Bandar Baru Bangi, 43000 Kajang, Selangor, Malaysia. E-mail: nlida@mpob.gov.my

much less expensive 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 readily available. On the other hand, EIE reactions are more specific, require less severe reaction conditions, produce less waste than CIE, and may represent the way of the future (9).

The aim of this work was to investigate the effect of CIE on the TAG composition and SFC of PO, SFO, PKOo, and blends thereof in various ratios. The interaction of these oils and fats and their compatibility are also discussed.

EXPERIMENTAL PROCEDURES

Materials. PO, SFO, and PKOo were obtained from Lam Soon Malaysia Sdn. Bhd. (Petaling Jaya, Selangor, Malaysia).

Preparation of blends. Blends of PO, SFO, and PKOo were prepared in the following mass (by wt) 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).

CIE. Each fat blend (250 g) was dried for 30 min at 110°C. A steady stream of nitrogen was maintained throughout the process. Sodium metal (0.2%) was then added as catalyst. After 60 min of stirring at a constant speed of 2000 rpm, the mixture was cooled to 60-70°C. A citric acid solution (20%) was then added to deactivate the residual catalyst. The mixture was then transferred into a separating funnel with a bottom opening for washing. Excess hot water was added, and the mixture was stirred mechanically for 15-20 min and then allowed to settle for 10 min to separate the oil and the water phase before discarding the water phase. The washing process was repeated several times to ensure that the sample was completely clean of citric acid, residual catalyst, and the resulting soaps formed by the reaction between sodium ion and any free FFA present or produced during the process. Finally, the fat blend was dried by filtering through anhydrous sodium sulfate (Merck, Darmstadt, Germany). The filtration was performed under gravity in an oven. The oven temperature was set at slightly higher than the expected melting temperature of the fat blend.

FA composition (FAC). FAC was determined as FAME. FAME were prepared by dissolving 50 mg of fat blend in 950 µL hexane (Merck, Darmstadt, Germany) in a 2-mL screwcapped vial, to which was added 50 µL of 1 M sodium methoxide (Merck, Darmstadt, Germany). The mixture was then mixed vigorously with a vortex mixture for 1 min or until it became cloudy. One milliliter of distilled water was added and the mixture was mixed thoroughly. It was then allowed to settle and separate into two distinct layers. The upper clear supernatant, i.e., the FAME, was decanted and a small amount of anhydrous sodium sulfate (Merck) was added to remove traces of moisture. One microliter of the FAME was injected into a gas chromatograph fitted with a polar SP 2340 fused-silica capillary column (60 m length × $0.25 \text{ mm i.d.} \times 0.2 \mu \text{m film thickness}$ (Supelco, Bellefonte, PA). A FID was used to detect the FA. The detector and TAG composition. TAG composition was determined by reversed-phase HPLC. The fat blend (before and after CIE) was used as it was and was not purified prior to analysis. The mobile phase was acetone/acetonitrile (Merck) at a gradient composition beginning with 65% acetone and increasing to 85% acetone in 30 min. The mobile phase flow rate was 1.5 mL/min. Two commercially packed Genesis C18 HPLC columns (15 cm length × 4.6 mm i.d) of 4 μ m particle size (Jones Chromatography, Mid Glamorgan, United Kingdom) were used to separate the TAG. The TAG were detected by an ELSD. Individual peaks were identified by comparing the retention times with those of pure TAG standards and common vegetable oils of known TAG composition. The equivalent carbon number of each TAG was calculated according to AOCS Official Method Ce 5b-89 (10).

SFC. SFC was determined by a pulse NMR analyzer according to the procedures described in PORIM Test Method p4.9 (11).

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 (12). R^2 values, which indicate model fits for each of the constructed ternary diagrams, were determined and were found to be greater than 0.95.

RESULTS AND DISCUSSION

FAC. Table 1 shows the FAC of PO (coded A), SFO (coded E), and PKOo (coded I) and their blends in various ratios. PO and blends containing a high proportion of PO were characterized by a high content of palmitic ($C_{16:0}$) and oleic ($C_{18:1}$) acids. SFO and blends containing a high proportion of SFO were rich in oleic and linoleic ($C_{18:2}$) acids. Lauric ($C_{12:0}$), myristic ($C_{14:0}$), and oleic acids were the major FA in PKOo and blends containing a high proportion of PKOo. They also contained appreciable amounts of short-chain FA, e.g., caprilic ($C_{8:0}$) and capric ($C_{10:0}$) acids. FAC of the interesterified blends are not shown, as IE neither affects the degree of saturation nor causes isomerization of the FA double bonds. Thus, IE does not alter the FA composition of the starting material (7).

TAG composition. The TAG composition of PO, SFO, and PKOo before and after CIE is tabulated in Table 2. The main TAG of PO were POP, POO, PLP, and PLO, where L is linoleic acid. PO also contained appreciable amounts of PPP, POS, OOO, SOO, and PLL TAG, where S is stearic acid. SFO consisted mainly of OLL, LLL, OLO, PLO, PLL, POO, and OOO. PKOo contained a wide range of medium-chain TAG species. The major TAG of PKOo were LaLaLa, LaLaM, CaLaLa, CLaLa, LaLaP/LaMM, and LaLaO, where La is lauric acid, M is myristic acid, Ca is caprylic acid, and C is capric acid. PKOo TABLE 1

Code	PO/SFO/PKOo	FAC (wt%)									
	ratios	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	1.0	42.9	4.4	40.8	10.2	0.5	
3	(3:1:0)	_	_	0.1	0.8	33.7	4.3	36.8	23.9	0.4	
С	(1:1:0)	_	_	0.1	0.5	24.6	4.1	32.6	37.8	0.3	
D	(1:3:0)	_	_	_	0.4	15.5	3.9	28.6	51.3	0.3	
-	(0:1:0)	_	_	_	0.1	6.3	3.7	24.3	65.1	0.5	
-	(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	
	(0:0:1)	4.7	3.8	44.5	13.7	8.4	2.8	18.1	2.9	1.1	
	(1:0:3)	3.5	2.8	33.7	10.4	17.2	3.2	23.9	4.7	0.6	
<	(1:0:1)	2.4	1.9	22.4	7.1	25.7	3.6	29.7	6.6	0.6	
-	(3:0:1)	1.2	1.1	11.4	3.6	34.5	3.9	35.4	8.4	0.5	
Л	(4:1:1)	0.8	0.7	7.6	2.7	31.1	3.9	34.6	18.2	0.4	
1	(1:4:1)	0.8	0.7	7.6	2.5	12.9	3.6	26.1	45.5	0.3	
)	(1:1:4)	3.1	2.5	30.0	9.5	13.9	3.1	23.0	14.4	0.5	
Ç	(1:1:1)	1.6	1.3	14.9	5.0	19.3	3.7	27.8	26.0	0.4	

^aFAC, FA composition; PO, palm oil; SFO, sunflower oil; PKOo, palm kernel olein; $C_{8:0'}$ caprylic acid; $C_{10:0'}$ capric acid; $C_{12:0'}$ lauric acid; $C_{14:0'}$ myristic acid; $C_{16:0'}$ palmitic acid; $C_{18:0'}$ stearic acid; $C_{18:1'}$ oleic acid; $C_{18:2'}$ linoleic acid. Others include caproic ($C_{6:0}$), linolenic ($C_{18:3}$), and/or arachidic ($C_{20:0}$) acids.

TABLE 2 TAG Composition (area %) of Palm Oil, Sunflower Oil, and Palm Kernel Olein Before and After Chemical Interesterification^a

			DB			CIE	
TAG species	ECN	PO	SFO	PKOo	PO	SFO	PKOo
CLaLa	32.0	_	_	8.4	_	_	5.4
CaLaLa ^a /CLaM ^a	34.0/34.0	_		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
LLL	39.9	_	27.2	_	0.2	27.1	_
LaLaP ^b /LaMM ^b	40.0/40.0			7.8	_		9.0
LLM	40.6	—	_	0.3	_		0.6
LMM ^c /LaOM ^c	41.3/41.4	—	_	5.0	_		7.6
MMM ^d /LaPM ^d	42.0/42.0	—	_	3.3	_		4.7
OLL	42.0	0.4	29.5		0.4	30.1	_
PLL	42.6	1.2	9.6		0.6	8.4	_
LMO ^e /LaOO ^e	42.7/42.8	—	_	3.5	_		3.3
MPL ^f /LaOP ^f /MMO ^f	43.3/43.4/43.4	—	_	5.1	_		4.2
LaPP ^g /MMP ^g	44.0/44.0	—	_	1.1	—		1.8
OLO	44.1	1.5	11.0		3.7	10.0	_
PLO	44.7	8.9	10.0		9.3	8.5	_
MOO	44.8	—	_	1.1	—		0.7
PLP	45.3	9.2	0.6		6.6	0.4	_
MOP	45.4	—	_	1.9	_	_	1.5
PPM	46.0	0.2	—	0.2	0.3	—	0.5
000	46.2	3.9	3.0	0.9	6.0	1.9	0.2
POO	46.8	23.3	3.5	1.4	22.5	3.6	0.4
POP	47.4	30.2	0.5	0.7	26.9	0.8	0.4
PPP	48.0	6.7	0.8	0.1	10.0	1.4	0.1
SOO	48.8	2.9	1.1	_	2.1	1.2	_
POS	49.4	6.7	0.4		5.4	0.4	_
PPS	50.0	1.1	0.4		2.5	0.8	_
Others		3.8	2.4	3.3	3.5	5.4	4.6

^aDB, 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; S, stearic acid. TAG with the same roman supercript a–g are TAG with similar or very similar ECN; hence, their peaks emerged at the same or almost the same retention times. Others include DAG and/or unidentified TAG. For other abbreviations see Table 1.

		PO/SF	O/PKOo	PO/SFO/PKOo	PO/SFC)/PKOo	PO/SFO/PKOo	
		(1:1:0)	(coded C)	(0:1:1) (coded G)	(1:0:1) (coded K)		(1:1:1) (coded Q)	
TAG species	ECN	DB	CIE	DB	DB	CIE	DB	
CLaLa	32:0	_	_	4.3	4.4	1.9	2.7	
CaLaLa ^a /CLaM ^a	34:0/34.0	_		6.0	6.2	4.2	4.1	
LaLaLa	36:0	—	_	11.4	11.6	6.1	7.9	
LaLaM	38:0	—	_	7.2	7.1	2.2	5.2	
LaLaO	39.4	_	_	2.8	2.6	6.3	1.8	
LLL ^b /LaLaP ^b /LaMM ^b	39.9/40.0/40.0	13.8	4.3	17.0	3.6	5.2	11.8	
LLM	40.6	_	_	0.2	0.2	1.5	0.1	
LMM ^c /LaOM ^c	41.3/41.4	_	_	1.8	2.2	6.3	1.6	
OLL ^d /LaPM ^d /MMM ^d	42.0/42.0/42.0	14.5	11.4	16.6	2.0	4.8	11.7	
PLL ^e /LMO ^e /LaOO ^e	42.6/42.7/42.8	5.5	10.0	4.8	2.6	6.1	4.6	
MPL ^f /LaOP ^f /MMO ^f	43.3/43.4/43.4	_	_	2.2	2.5	13.0	1.4	
LaPP ^g /PMM ^g /OLO ^g	44.0/44.0/44.1	5.9	11.4	7.1	1.4	8.0	4.6	
PLO ^h /MOO ^h	44.7/44.8	10.1	21.3	6.6	5.3	1.0	6.7	
PLP ⁱ /MOP ⁱ	45.3/45.4	4.5	7.4	1.0	5.7	6.0	3.8	
PPM	46.0	0.1	_	0.2	0.2	2.7	0.1	
000	46.2	3.2	3.1	2.1	2.4	1.6	2.6	
POO	46.8	14.2	11.4	2.6	13.0	6.5	10.3	
POP	47.4	16.0	8.9	0.4	16.2	6.8	11.8	
PPP	48.0	3.5	1.3	0.3	3.2	2.2	2.3	
SOO	48.8	2.0	1.0	0.5	1.3	0.5	1.2	
POS	49.4	3.3	1.6	0.2	3.4	1.1	2.0	
Others		3.4	6.9	4.7	2.9	6.0	1.7	

TABLE 3 TAG Composition (area %) of the Blends of Palm Oil, Sunflower Oil, and Palm Kernel Olein in Various Ratios Before and After Chemical Interesterification^a

^aTAG with the same supercript a-i are TAG with similar or very similar ECN; hence, their peaks emerged at the same or almost the same retention times. For other abbreviations see Tables 1 and 2.

also contained appreciable amounts of other medium-chain TAG such as LaOM, LaPM, LaOP/MMO, LaPP, MOO, and MOP. CIE generated only small changes in the TAG composition of PO, SFO, and PKOo. Two of the main TAG in PO, i.e., POP and PLP, were reduced from 30.2 and 9.2% before CIE to 26.9 and 6.6% following CIE, whereas POP was hardly altered. Concomitantly, an increase in the proportion of several other TAG, such as PPP, OOO, OLO, and PPS, was observed. Each of these TAG was increased from 6.7, 3.9, 1.5, and 1.1% to 10.0, 6.0, 3.7, and 2.5%, respectively. The proportions of the TAG of SFO were hardly changed after CIE. In the case of PKOo, medium-chain S3 TAG, i.e., LaLaLa, CaLaLa/CLaM, and CLaLa, were reduced from 22.7, 11.8, and 8.4% to 18.6, 6.6, and 5.4%, respectively. Correspondingly, LaLaO, LMM/LaOM, and LaLaP/LaMM TAG were increased from 6.4, 5.0, and 7.8% to 13.6, 7.6, and 9.0%, respectively.

The TAG composition of the binary and ternary fat blends represents a linear combination of the fat component in the blends (Table 3). For example, as the proportion of PO was increased in the blends, the proportion of POP, POO, PLP, PLO, and other TAG present in PO was increased. CIE induced large changes in the TAG composition of PO/SFO/PKOo blends, as shown in Table 3. For example, in the 50% PO and 50% SFO blend (coded C), the proportion of the main TAG, i.e., POP, POO, and LLL, was reduced from 16.0, 14.2, and 13.8% to 8.9, 11.4, and 4.3%, respectively. Concomitantly, the proportion of other TAG, such as PLO, OLO and PLL, was increased from 10.1, 5.9, and 5.5% to 21.3, 11.4, and 10.0%, respectively.

HPLC chromatograms of the blend before and after CIE are shown in Figure 1. Because of the presence of a high proportion of medium-chain (e.g., lauric and myristic) and unsaturated long-chain (e.g., linoleic and oleic) FA, many individual TAG in the interesterified binary blend of PKOo/SFO (coded F, G, and H) and the ternary blend of PO/SFO/PKOo (coded M, N, P, and Q) could not be identified. Randomization led to the formation of a number of TAG having combinations of lauric, myristic, linoleic, and oleic acids in varying permutations. These tended to have equivalent carbon numbers that were very similar, thereby making their identification (based on relative retention times) extremely difficult and uncertain. The problem was further confounded by the lack of authentic standards for such TAG. However, the TAG profile of the interesterified blends showed a more balanced or even peak distribution than the starting blends, as the relative concentration of several TAG increased, others decreased, and several new TAG might also have been synthesized. This result is consistent with findings reported by Zainal and Yusoff (13).

SFC. SFC greatly influences the suitability of oils and fats for a particular application. Generally, the SFC of the constituent oils and fats is responsible for many of a product's characteristics, including its general appearance, ease of packing, spreadability, oil exudation, and organoleptic properties (14). SFC also can also be used to study the compatibility of fats by determining the changes in the percent solids at different fat proportions. The result is a graphic indication of the loss of solids due to dilution of existing solids with liquid oil or an

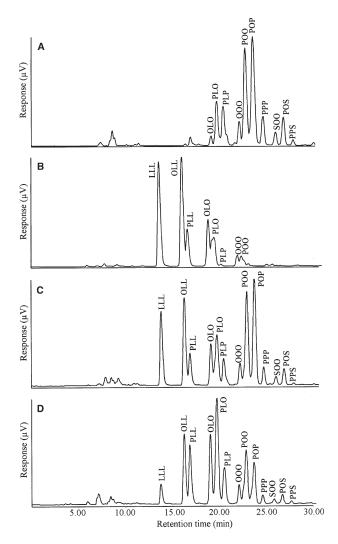


FIG. 1. TAG gas chromatograms of palm oil (PO), sunflower oil (SFO), and the blends of PO/SFO in the ratio of 1:1 before and after chemical interesterification (CIE). (A), PO; (B), SFO; (C), PO/SFO (1:1) before CIE; (D), PO/SFO (1:1) after CIE. O, oleic acid; P, palmitic acid; L, linoleic acid; S, stearic acid.

incompatibility due to eutectic interaction (15). SFC of PO, SFO, PKOo, blends thereof in various ratios, and their respective chemically interesterified products are shown in Table 4. The SFC profiles of all fats and their blends were significantly different from each other. The rate of SFC evolution was dependent on both temperature and the proportion of each fat in the blend. PO had a high SFC at low temperature but melted completely between 35 and 40°C. SFO was fully liquid at the lowest measuring temperature, as it is very rich in monounsaturated (oleic) and polyunsaturated (linoleic) FA (Table 1). PKOo had a very sharp melting profile, as it contained high proportions of medium-chain FA. As a result of its FAC, PO had a lower SFC than PKOo at low temperatures $(5-15^{\circ}C)$, but at higher temperatures, the SFC of PKOo was lower than that of PO. The largest reduction in the SFC of PO occurred from 15–20°C, and that of PKOo occurred from 15–25°C, which was most likely due to the large proportion of TAG that liquefy and solubilize in these temperature ranges.

Adding SFO to PO and PKOo lowered their SFC proportionally at all measuring temperatures. The blends of PO/SFO (coded B, C, and D) and PKOo/SFO had physical characteristics representing linear combinations of the two components. The softening effect was due to the liquid triunsaturated (U_2) TAG in SFO that diluted the amount of solid S_2U and S₃ TAG in PO and PKOo. On the other hand, the SFC of PO/PKOo blends (coded J, K, and L) did not represent linear combinations of the PO and PKOo. According to Dieffenbacher (16), if the physical characteristics of components of a fat blend do not represent linear combinations of the components, this indicates the presence of some interaction between the components. In this case, the interaction that occurred between PO and PKOo was eutectic (15), and this interaction occurred at 5-10°C for blends coded K and L; at 15-20°C for blends coded J, K, and L; and at 25°C for blends coded J and K. Eutectic interaction is always observed in fat mixtures and defines one of the criteria for the degree of compatibility of fats. This kind of interaction tends to occur when the fats differ in molecular volume, shape, or polymorph. A mixture with a eutectic effect will have a lower SFC than either one of the two pure fats, showing that the two fats are not compatible with each other (15,17). Eutectic effects are usually undesirable, but in the case of margarine and shortenings, the effect can be beneficial (4). The eutectic effect between PO and PKOo was most evident at 10-20°C, as shown by the isosolid diagrams in Figure 2. The SFC reaches its minimum at about a 3:1 blending ratio at 10 and 15°C, and at a 1:1 blending ratio at 20°C, which is coincidental with the proportion that defines the maximum eutectic effect. At these temperatures, TAG with short- and medium-chain FA begin to crystallize independently in the systems and tend to show eutectic effects due to immiscibility. Timms (1) previously demonstrated similar eutectic interaction in the binary system of PO and PKOo.

Changes in the TAG composition of the fats and their blends following CIE were accompanied by changes in their SFC values. It was observed that although randomization of PO by CIE produced only modest changes in the SFC at low temperature $(5-10^{\circ}C)$, more significant increases in the SFC were observed above 10°C. This was due to the increase in S₃ TAG, i.e., PPP and PPS, consistent with that reported by Laning (18), as well as a simultaneous significant decrease in some S_2U (PLP, POP, and POS) and U_2S (POO and SOO) TAG. PPP and PPS increased from 6.7 and 1.1% before CIE to 10.0 and 2.5% after CIE. On the other hand, the PLP, POP, POS, POO, and SOO were reduced from 9.2, 30.2, 6.7, 23.3, and 2.9%, respectively, before CIE to 6.6, 26.9, 5.4, 22.5, and 2.1%, respectively, after CIE. CIE reduced the SFC of PKOo throughout the temperature ranges investigated. This was probably due to an increase of TAG species with intermediate degrees of unsaturation. There were no changes in the SFC of SFO after CIE. This is presumably because SFO is very rich in unsaturated long-chain FA (Table 1), and randomization did not result in much change in its TAG composition. As a result, its SFC was hardly altered.

TABLE 4

	PO/SFO/PKOo		SFC (%)							
Code	ratios		5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
A	(1:0:0)	DB	63.1	50.3	36.6	20.5	11.3	8.6	2.6	0.8
		CIE	62.2	53.9	42.5	30.2	21.3	13.8	8.3	3.4
В	(3:1:0)	DB	43.9	34.3	24.9	13.3	7.1	5.6	1.5	_
		CIE	36.8	30.2	20.5	11.7	7.7	3.8	1.6	_
С	(1:1:0)	DB	21.6	15.1	8.9	5.2	2.7	1.7		
		CIE	19.7	13.5	5.9	2.8	1.0	_		
D	(1:3:0)	DB	6.4	3.2	0.7	_				
		CIE	3.5	0.2	_					
E	(0:1:0)	DB	_							
		CIE	_							
F	(0:3:1)	DB	8.4	2.2	_					
		CIE	2.3							
G	(0:1:1)	DB	26.9	16.4	8.8	_				
		CIE	17.3	6.2	0.5	_				
Н	(0:1:3)	DB	46.9	35.8	23.8	9.0				
		CIE	41.6	27.5	13.6	0.9	_			
I	(0:0:1)	DB	70.2	60.3	44.1	23.0	3.6	_		
		CIE	65.0	53.8	36.3	14.7	1.3	_		
J	(1:0:3)	DB	65.6	51.6	31.8	10.7	_			
		CIE	59.6	48.2	32.9	17.7	5.2	_		
К	(1:0:1)	DB	59.7	42.1	23.7	7.5	1.7	0.8		
		CIE	55.0	41.2	29.4	16.4	7.7	0.8		
L	(3:0:1)	DB	58.3	39.0	22.4	10.3	6.1	4.7		
		CIE	54.0	43.5	30.6	20.2	12.8	6.3	1.1	_
М	(4:1:1)	DB	42.0	28.2	17.4	8.3	4.7	2.7		
		CIE	44.6	33.8	22.2	12.5	7.3	3.3		
Ν	(1:4:1)	DB	9.8	1.9	_					
		CIE	7.0	1.1	_					
Р	(1:1:4)	DB	51.1	37.4	20.9	5.8				
		CIE	43.8	30.8	17.7	6.5				
Q	(1:1:1)	DB	32.5	18.4	7.2	_				
		CIE	27.9	16.0	7.5	2.5				

Solid Fat Content of Palm Oil, Sunflower Oil, Palm Kernel Olein, and Their Blends in Various Ratios
Before and After Chemical Interesterification ^a

^aSFC, solid fat content. For other abbreviations see Tables 1 and 2.

SFC of the binary blends of PO/SFO and PKOo/SFO were changed dramatically following CIE. Interesterified blends tended to have lower SFC values than the starting blends. For the binary blends of PO/SFO, substantial changes in SFC were observed at lower temperatures (below 15°C), whereas for the binary blends of PKOo/SFO, apparent changes in their SFC values occurred at all measured temperatures. The decrease in the SFC values of the interesterified blends of PO/SFO could be attributed mainly to the decreased proportion of the high-melting S_3 and S_2U TAG, mainly PPP (S_3) and POP (S_2U), concomitant with the formation of more U_2S TAG such as PLL and PLO. For the binary blends of PKOo/SFO, the reduction in the SFC values can most likely be attributed to the decrease in the proportion of the S_3 medium-chain TAG such as LaLaLa, CaLaLa, CLaLa, and LaLaM simultaneously with the formation of several species of low-melting TAG. The formation of the low-melting TAG could be due to the replacement of saturated FA in the TAG of PO and PKOo with the unsaturated FA of SFO TAG, which were mainly U_2S and U_3 .

Despite having almost equal amounts of the high-melting

 S_3 and S_2U TAG (Table 3), interesterified binary blends of PO/PKOo had higher SFC values at temperatures above 10°C compared to the starting blends. The most plausible explanation for this is that the eutectic interaction that occurred between PO and PKOo in the binary blends of PO/PKOo, 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 3. This result is consistent with that reported by Timms (17), which showed that IE would eliminate or at least reduce eutectic interactions in an eutectic mixture. The SFC values of interesterified ternary blends of PO/SFO/PKOo were also different from those of the starting blends. It appeared that the ternary blend containing a high proportion of PO (coded M) tended to have higher SFC values than the starting blends at all measuring temperatures, which most probably was due to the increase in S₃ TAG, i.e., PPP and PPS. Other ternary blends seemed to have lower SFC values than their corresponding starting blends.

This study has demonstrated that a combination of blending and CIE of PO with SFO and/or PKOo could provide an

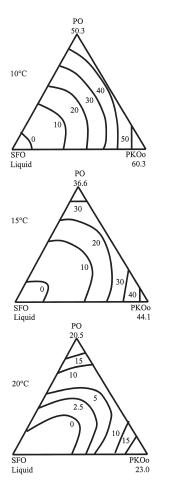


FIG. 2. Isosolid diagram of solid fat content (%) of the simple blends of PO, SFO, and PKOo in various ratios at 10, 15, and 20°C. For abbreviations see Figure 1.

alternative for producing new fat products with the desired SFC profiles. CIE is also the method of choice to improve miscibility among the blended oils and fats, and hence could assist in eliminating the posthardening phenomena, which are profound in PO-based yellow-fat products.

ACKNOWLEDGMENTS

The authors thank the Director General of MPOB, Datuk Dr. Yusof Basiron, for his permission to publish this paper, Rosnah Mat Nor, Noraini Mohamad and Mohd. Adrina Malek for TAG analysis, Nik Mahani Nik Salleh for FAC analysis, and Nasoikhieddinah Md. Purdi for SFC analysis. This work was partially sponsored by the Malaysian Government under the Intensification of Research in Priority Areas programme (IRPA No:03-04-03-0004).

REFERENCES

- 1. Timms, R.E., Physical Properties of Oils and Mixtures of Oil, J. Am. Oil Chem. Soc. 62:241–248 (1985).
- Watanabe, A., I. Tashima, N. Matsuzaki, J. Kurashige, and K. Sato, On the Formation of Granular Crystals in Fat Blends Containing Palm Oil, *Ibid.* 69:1077–1080 (1992).
- 3. Moran, D.P.J., Reduced Calorie Spreads, PORIM Technology

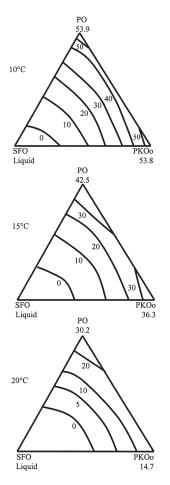


FIG. 3. Isosolid diagram of solid fat content (%) of the chemically interesterified blends of PO, SFO, and PKOo in various ratios at 10, 15, and 20°C. For abbreviations see Figure 1.

No. 15, Palm Oil Research Institute of Malaysia, Bandar Baru Bangi, 1993.

- DeMan, L., and J.M. DeMan, Functionality of Palm Oil, Palm Oil Products and Palm Kernel Oil in Margarine and Shortening, PORIM Occasional Paper No. 32, Palm Oil Research Institute of Malaysia, Bandar Baru Bangi, 1994.
- Noor Lida, H.M.D., and A.R. Md. Ali, Physicochemical Characteristics of Palm-Based Oil Blends for the Production of Reduced Fat Spreads, *J. Am. Oil Chem. Soc.* 75:1625–1631 (1998).
- 6. Sreenivasan, B., Interesterification of Fats, *Ibid.* 55:796–805 (1978).
- Rozendaal, A., Interesterification of Oils and Fats, in *Edible Fats and Oils Processing: Basic Principles and Modern Practice*, edited by D.R. Erickson, American Oil Chemists' Society, Champaign, 1989, pp. 152–157.
- Rousseau, D., K. Forestière, A.R. Hill, and A.G. Marangoni, Restructuring Butterfat Through Blending and Chemical Interesterification. 1. Melting Behavior and Triacylglycerol Modifications, J. Am. Oil Chem. Soc. 73:963–972 (1996).
- Konishi, H., W.E. Neff, and T.L. Mounts, Chemical Interesterification with Regioselectivity for Edible Oils, *Ibid.* 70:411–415 (1993).
- Official Methods and Recommended Practices of the American Oil Chemists' Society, 4th edn., edited by D. Firestone, AOCS Press, Champaign, 1995, Method Ce 56–89.
- 11. *PORIM Test Methods*, Palm Oil Research Institute of Malaysia, Bandar Baru Bangi, 1995, Method p4.9.

- Md. Ali, A.R., and P.S. Dimick, Thermal Analysis of Palm Mid-Fraction, Cocoa Butter, and Milk Fat Blends by Differential Scanning Calorimetry, J. Am. Oil Chem. Soc. 71:299–302 (1994).
- Zainal, Z., and M.S.A. Yusoff, Enzymatic Interesterification of Palm Stearin and Palm Kernel Olein, *Ibid.* 76:1003–1008 (1999).
- Krawczyk, G.R., G.S. Buliga, D.T. Bertrand, and W.M. Humpreys, Reviewing the Technology of Low-Fat Spreads, *IN-FORM* 7:635–639 (1996).
- Bigalli, G.L., Practical Aspects of the Eutectic Effect on Confectionery Fats and Their Mixtures, *Manuf. Confect.* 53:65–80 (1988).
- Dieffenbacher, A., *The Optimal Use of Oils and Fats in Foods*, Nestec Ltd. Technical Assistance, Vevey, Switzerland, 1988, pp. 21–31.
- 17. Timms, R.E., Phase Behavior of Fats and Their Mixtures, *Prog. Lipid Res.* 23:1–38 (1984).
- Laning, S.J., Chemical Interesterification of Palm, Palm Kernel, and Coconut Oils, J. Am. Oil Chem. Soc. 62:400–405 (1985).

[Received March 11, 2002; accepted July 14, 2002]