

Polymorphic Behavior of Palm Oil and Modified Palm Oils

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Refined, bleached and deodorized palm oil, its purified palm triacylglycerol (PTG), palm olein (PO), palm stearin (PS) and high melting palm stearin (HMPS) fractions as well as randomized palm oil (RP) and its high melting randomized palm stearin (HMRPS) fractions were solidified at 5°C and kept isothermally at 10, 20 and 30°C for 60 days. X-ray diffraction showed that PTG was in β' form crystals, while palm oil and RP were in both α and β' forms at 5°C. In HMPS and HMRPS, the higher percentage of β -transformation was observed with a higher content of trisaturated triacylglycerols and at a higher temperature. RP transformed from β' to the intermediate form crystals during prolonged storage. Other fats were stable in β' form crystals. Palm oil, RP, HMPS and HMRPS exhibited long-spacing values between those of tripalmitin and tristearin in α , β' and β modifications, respectively. This confirms that palm oil and its modified oils form a double-chain-length conformation.

Keywords: fractionation, interesterification, olein, palm oil, polymorphic transformation, stearin

Palm oil is a vegetable oil that has been widely used in the manufacture of products such as margarines, shortenings, cooking oils and confectionery fats (Kheiri, 1985; Murase, 1986; D'Souza *et al.*, 1991; Ohfuji & Fujiwara, 1994). The use of palm oil in foods, however, has been limited by its physical properties, namely, the presence of granular crystals (Ishikawa *et al.*, 1980; Watanabe *et al.*, 1992) and its low rate of crystallization (van Putte & Bakker, 1987; Ng, 1990). In margarines and shortenings, solid fats should consist of β' form crystals, which confer a smooth texture to the products. On the other hand, the β form crystals confer a rough texture to the products. The crystal forms depend on the triacylglycerol composition of blended oils and the rate of crystallization. Interesterification has been adopted to change the triacylglycerol composition. Random interesterification involves rearrangement of fatty acids within and between triacylglycerols. Rearrangement of acyl residues in triacylglycerols results in oils with new physical properties and different polymorphic behavior. Today, interesterification is used as frequently as fractionation in various areas. The interesterification of triacylglycerols has been extensively reviewed (Husted, 1976; Matsui, 1979; Laning, 1985; Mori, 1989).

D'Souza *et al.* (1992) studied the polymorphic behavior of solid fats found in commercially available soft margarines and suggested that solid fats can be provided by interesterified palm oil products. Duns (1985) studied the properties of palm oil before and after interesterification and concluded that the application of interesterification techniques, although useful, was restricted. However, little is known about fundamental research on the polymorphic behavior of modified palm oils.

In this study, we have dealt with modified palm oils formed by random interesterification and solvent-fractionation and investigated the effect of the triacylglycerol composition of these oils on their polymorphic behavior when placed at a constant temperature for a given period.

Materials and Methods

Refined, bleached and deodorized palm oil, and its palm olein (PO) and palm stearin (PS) fractions were obtained from The Nisshin Oil Mills, Ltd. (Tokyo). The purified palm triacylglycerol (PTG) fraction was separated from palm oil by thin-layer chromatography. The high melting palm stearin (HMPS) fraction was obtained by solvent-recrystallization as follows: PS was dissolved in acetone at the ratio of 1 : 5 (w : v). The solution was left overnight in a water bath at 20°C to allow crystallization. The liquid fraction was then removed by filtration. The solvent was removed from the crystals under vacuum.

Random interesterification of palm oil was carried out at 80°C in an 1 l vessel. Sodium methoxide was used at a level of 0.3% by weight of the oil. High melting randomized palm stearin (HMRPS10, HMRPS20) fractions were obtained from randomized palm oil (RP) by solvent-crystallization (at 10 and 20°C, respectively, in acetone). For comparison of polymorphic behavior, tripalmitin and tristearin (Sigma Chemical Co., St. Louis, MO) were used as standard trisaturated triacylglycerols.

The fatty acid compositions were determined by transesterification and analysis of methyl esters in a Hewlett-Packard gas chromatograph (Model 5890, Wilmington, DE) equipped with a flame ionization detector. Separations of the methyl esters were performed on a SP-2380 fused-silica capillary column (30 m×0.32 mm i.d.; Supelco, Inc., Bellefonte, PA). The temperatures were 250°C for injection, 260°C for the detector, and 170°C for the column.

The diacylglycerol content in palm oil and PTG was measured with a TLC/FID Iatrosan TH-1000 (Iatron Labo., Inc., Tokyo).

The iodine value was determined according to the Wijs method, AOCS official method Cd 1-25.

The solid fat content (SFC) was measured by pulsed nuclear magnetic resonance (pNMR) in an NMR analyzer

(Model SFC-900, Praxis Corp., San Antonio, TX) according to AOCS official method Cd 16-81.

Triacylglycerol compositions were determined by HPLC. The apparatus for HPLC was a Waters LC Module 1 equipped with a Waters differential refractometer (Model 410). Separation was performed on a Nova-Pak C18 column (300 mm×3.9 mm i.d.; Waters, Millipore Corp., Milford, MA). The mobile phase was a mixture of acetone/acetonitrile (50:50), and the flow rate was 1 ml/min at 45°C. Peak identification was based on the relative retention times reported in the literature (Defense, 1984, 1985).

X-ray diffractometry (CuK α ; RAD-III A, Rigaku Co., Ltd., Tokyo) was employed to measure the short and long spacings. The fat samples were first heated at 80°C for 1 h, then cooled to 5°C for 1 h, and finally stored at 10, 20 and 30°C until analyzed. Quantitative evaluation of the β form was based on the relative densities of the short spacings at 4.2 Å and 4.6 Å, which are characteristic of the β' and β forms, respectively (Yap *et al.*, 1989). The percentage of the β form was calculated from:

$$\beta\% = (\text{peak height at } 4.6 \text{ \AA}) / (\text{peak heights at } 4.2 \text{ and } 4.6 \text{ \AA}) \times 100$$

Results and Discussion

Chemical and physical characteristics The fatty acid composition and iodine value of palm oil and modified palm oils are shown in Table 1. Palmitic acid (16:0) tended to predominate in the stearin fraction while the fatty acid composition of PTG and PO was similar to that of the original palm oil. On the other hand, the iodine value of the high melting stearin fractions varied within a wide range. As shown in Table 2, the solid fat content of palm oil was markedly lower than that of PTG at 10 and 20°C, probably because partial acylglycerols and free fatty acids form eutectic compounds with triacylglycerols (Jacobsberg & Oh, 1976).

Palm oil and fractions The short and long spacings for various fats are shown in Table 3. Palm oil cooled rapidly

to 5°C showed a mixture of α and β' form crystals, then maintained the β' form crystals at 10 and 20°C. PTG was in β' form crystals at 5, 10 and 20°C. The crystal form observed at 5°C depended on the diacylglycerol content of palm oil and PTG (1.7% and 0.0%, respectively). Persmark *et al.* showed that the lifetime of α form crystals is considerably increased by the presence of partial acylglycerols (Berger, 1975; Persmark *et al.*, 1976).

X-ray diffraction lines over $d=8$ Å (CuK α : $2\theta<10$) are called long spacings. Chapman (1962) reported that the lines are closely related to the length of the fatty acid in triacylglycerol, mainly the carbon number. On the other hand, each of the chain-packing subcells is characterized by X-ray diffraction lines in a wide-angle region, that is, between 3.6 Å and 5.0 Å (CuK α : $2\theta=25-18$, short spacings). In long spacings, palm oil solidified from the melt exhibited a strong line at 47.2 Å and a weak line at 43.3 Å. It is assumed that the crystallized palm oil consists mainly of α form crystals in which the unit cells are perpendicular to the methyl end-group plane and the hydrocarbon chains are hexagonally closed packed (Persmark *et al.*, 1976). When the crystallized palm oil was stored at higher temperatures of 10 and 20°C, the α form crystals quickly transformed into β' form crystals with short spacings at 4.37, 4.23, 3.90 Å within 1 day. Palm oil contains a high proportion of POP (symmetric 1,3-di-palmitoyl-2-oleoyl glycerol). Sato *et al.* (1989) reported that the α , pseudo- β_2' and pseudo- β_1' form crystals of POP had a double-chain-length structure; whereas, the γ , δ , β_2 and β_1 crystals had a triple-chain-length structure. The long spacing value of 43.3 Å in the β' form corresponded to the double-chain-length structure, and palm oil containing many triacylglycerols exhibited one modification. HMPS (IV 14) showed α form crystals at 5°C and transformed to β form crystals at 10, 20 and 30°C. From the triacylglycerol composition (Table 4), HMPS which consisted mainly of trisaturated triacylglycerols, PPP (60%) and PPS (11%) crystallized initially in α form crystals which transformed into β form crystals when the storage temperature was increased, like a monoacid triacyl-

Table 1. Fatty acid composition (%) and iodine value of palm oil and its fractions.

Fatty acid	Palm	PTG ^(a)	PO ^(b)	PS ^(c)	HMPS ^(d)	RP ^(e)	HMRPS10 ^(f)	HMRPS20 ^(g)
12:0	0.2	0.2	1.4	0.1		0.2	0.1	0.1
14:0	1.2	1.1	1.6	1.5	1.9	1.1	1.0	1.0
16:0	45.9	45.4	40.1	47.6	73.1	43.6	60.0	72.5
16:1	0.4	0.3	0.3	0.3			0.2	0.2
18:0	4.4	4.6	5.0	10.5	8.4	4.8	6.1	6.7
18:1	37.8	38.3	41.7	32.6	13.3	39.5	24.8	15.4
18:2	9.4	9.5	9.6	7.3	2.8	9.8	6.0	3.4
20:0	0.7	0.6	0.3	0.4	0.5	0.7	1.2	0.5
Iodine value	53.0	53.1	56.0	45.1	14.4	53.4	35.3	22.5

^(a) Purified palm triacylglycerol fraction, ^(b) palm olein, ^(c) palm stearin, ^(d) high melting palm stearin (20°C, acetone), ^(e) randomized palm oil, ^(f) high melting randomized palm stearin (10°C, acetone), ^(g) high melting randomized palm stearin (20°C, acetone).

Table 2. Solid fat content (%) of palm oil and its fractions.

	Palm	PTG ^(a)	PO ^(b)	PS ^(c)	HMPS ^(d)	RP ^(e)	HMRPS10 ^(f)	HMRPS20 ^(g)
10°C	51.7	66.6	34.5	60.4	100	47.9	100	100
20°C	20.1	24.4	6.0	34.3	100	30.0	74.4	100
30°C	11.0	11.9	1.5	25.3	100	18.8	66.2	100

^(a) Purified palm triacylglycerol fraction, ^(b) palm olein, ^(c) palm stearin, ^(d) high melting palm stearin (20°C, acetone), ^(e) randomized palm oil, ^(f) high melting randomized palm stearin (10°C, acetone), ^(g) high melting randomized palm stearin (20°C, acetone).

Table 3. Short and long spacings (Å) of palm oil and its fractions at different temperatures.

Condition	Fat	Short spacings			Long spacings ^{a,b}			Form		
5°C, 1 h	Palm	4.35(s)	4.23(w)	3.90(w)	47.2(s)	43.3(w)	15.9(w)	14.4(w)	$\alpha > \beta'$	
	PTG ^c	4.35(s)	4.23(s)	3.90(m)		43.3(s)			β'	
	PO ^d	4.35(s)	4.23(m)	3.90(m)		43.5(w)			$\alpha \ll \beta'$	
	HMPS ^e			4.15(s)	46.0(s)		15.5(s)	14.1(w)	α	
	RP ^f	4.35(s)	4.23(s)	3.90(m)	47.2(m)	43.3(m)	15.9(w)	14.5(m)	$\alpha + \beta'$	
	HMRPS10 ^g	4.62(w)	4.39(s)	4.27(s)	3.90(s)	43.9(s)			$\beta' \gg \beta$	
	HMRPS20 ^h	4.62(s)	4.35(s)	4.27(s)	3.90(s)	43.7(s)			$\beta' > \beta$	
	Tripalmitin			4.15(s)	46.0(s)		15.3(m)		α	
10°C, 60 days	Palm	4.37(s)	4.23(s)	3.90(s)		43.3(s)		14.4(m)	β'	
	PTG	4.37(s)	4.23(s)	3.90(s)		43.3(s)		14.4(m)	β'	
	PO	4.37(s)	4.23(s)	3.90(s)		43.3(m)		14.4(m)	β'	
	HMPS	4.60(s)		3.90(s)	3.77(m)	42.0(s)		14.1(m)	β	
	RP	4.62(s)	4.37(s)	4.23(s)	3.90(s)	43.3(s)		14.5(m)	$\beta' > \beta$	
	HMRPS10	4.62(s)	4.37(s)	4.27(s)	3.88(s)	43.3(s)		14.3(m)	$\beta' < \beta$	
	HMRPS20	4.62(s)	4.37(m)	4.23(m)	3.88(s)	42.4(s)		14.2(m)	$\beta' < \beta$	
20°C, 60 days	Palm	4.37(s)	4.23(s)	3.90(s)		43.3(s)		14.4(m)	β'	
	PTG	4.37(s)	4.23(s)	3.90(s)		42.9(s)		14.3(m)	β'	
	PO	4.37(s)	4.23(s)	3.90(s)		42.9(s)		14.4(m)	β'	
	HMPS	4.60(s)		3.90(s)	3.75(s)	41.3(s)		13.8(m)	β	
	RP	4.62(s)	4.37(m)	4.23(m)	3.88(m)	3.78(w)	42.9(s)	14.4(m)	$\beta' \ll \beta$	
	HMRPS10	4.62(s)	4.39(s)	4.25(s)	3.88(s)	42.9(s)		14.3(m)	$\beta' < \beta$	
	HMRPS20	4.62(s)		3.90(s)	3.80(m)	42.2(s)		14.2(m)	β	
30°C, 60 days	HMPS	4.60(s)		3.90(s)	3.74(s)	41.3(s)		13.8(m)	β	
	HMRPS10	4.62(m)		3.92(m)	3.80(m)	42.2(s)		14.1(m)	β	
	HMRPS20	4.62(s)		3.90(s)	3.77(m)	42.0(s)		14.0(m)	β	
		Tripalmitin	4.60(s)		3.86(s)	3.70(s)	40.6(s)		13.7(m)	β

^a Band intensities are indicated as s, strong; m, medium; w, weak.

^b Predominate short spacings of β' , 4.37, 4.23 and 3.90 Å; β , 4.60, 3.86 and 3.70 Å.

^c Purified palm triacylglycerol fraction, ^d palm olein, ^e high melting palm stearin (20°C, acetone), ^f randomized palm oil, ^g high melting randomized palm stearin (10°C, acetone), ^h high melting randomized palm stearin (20°C, acetone).

Table 4. Triacylglycerol composition (%) of palm oil and its fractions as determined by HPLC.

Triacylglycerol	Palm	PO ^a	HMPS ^b	RP ^c	HMRPS10 ^d	HMRPS20 ^e
PPP	6.8	0.8	59.8	9.3	31.1	47.0
PPS	1.5	—	11.4	2.6	8.4	12.7
POP+PPO	31.5	32.8	17.2	24.7	25.0	19.2
POS	5.7	5.6	2.1	4.6	4.6	2.9
POO+OPO	21.5	24.1	0.8	21.0	8.5	4.2
PLO+POL	9.5	11.2	—	11.3	4.5	2.0
SOO	2.6	2.8	—	2.3	—	—
PPL+PLP+MOP	10.4	11.7	3.0	8.1	6.0	4.0
OOO	3.4	3.8	—	5.4	2.0	—
OOL	1.5	1.8	—	4.3	1.7	—

^a Palm olein, ^b high melting palm stearin (20°C, acetone), ^c randomized palm oil, ^d high melting randomized palm stearin (10°C, acetone), ^e high melting randomized palm stearin (20°C, acetone).

glycerol.

Randomized palm oil and fractions RP showed a mixture of α and β' form crystals at 5°C, like palm oil. On the other hand, it exhibited a weak line at 4.6 Å after 1 day at 10 or 20°C. During the period at 10 or 20°C, there was a transformation to β form crystals. The crystals, however, did not show a perfect β form but an intermediate form. As for the long spacings of RP, the length of the *c*-axis in the unit cell was the same as that of palm oil in β' form crystals. In case of HMRPS (IV 35, 23), the X-ray diffraction data indicated that they had transformed from β' to β form crystals. Especially, the higher melting fraction HMRPS20 changed to β form crystals in a short time.

Chain-packing in each modification The long and short spacings in each modification are summarized in Table 5. Tripalmitin showed the shortest long spacing for each

polymorph among the samples analyzed, and tristearin showed the longest ones. Palm oil, RP and other fractions exhibited intermediate values between tripalmitin and tristearin. This confirms that palm oil and RP form double-chain-length conformation, because they had the same long spacings in the α and β' modifications.

Relation between triacylglycerol composition and β -transformation We investigated the relation between the percentage of β form crystals and the content of trisaturated triacylglycerols in higher melting stearins and tripalmitin stored at various temperatures for different periods of time (Figs. 1, 2). High melting stearin fractions easily transformed from β' to β form crystals as the trisaturated triacylglycerol content and storage temperature increased. However, the development of β form crystals in HMPS was low when stored at 10°C for 1 day. On the other hand, tripalmitin was

Table 5. Characteristic long and short spacings (Å) of various fat samples.

Polymorph	Fat	Short spacings		Long spacings		
α	Tripalmitin	4.15		46.0	15.3	
	HMPS ^{a)}	4.15		46.0	15.5	
	Palm	4.20		47.2	15.9	
	RP ^{b)}	4.20		47.2	15.9	
	Tristearin	4.15		50.6		
β'	Tripalmitin	4.20	3.80	42.6		
	Palm	4.37	4.23	43.3	14.4	
	RP	4.37	4.23	43.3	14.4	
	Tristearin	4.20	3.80	47.2		
β	Tripalmitin	4.60	3.86	3.70	40.6	13.7
	HMPS	4.60	3.90	3.74	41.3	13.8
	HMRPS20 ^{c)}	4.62	3.90	3.77	42.0	14.0
	HMRPS10 ^{d)}	4.62	3.92	3.80	42.2	14.1
	Tristearin	4.60	3.86	3.70	44.6	

^{a)} High melting palm stearin (20°C, acetone), ^{b)} randomized palm oil, ^{c)} high melting randomized palm stearin (20°C, acetone), ^{d)} high melting randomized palm stearin (10°C, acetone).

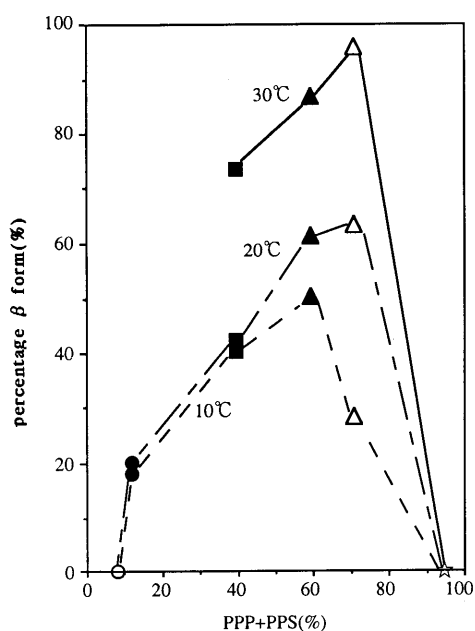


Fig. 1. Relation between the percentage of β form crystals and the trisaturated triacylglycerol content (1 day after solidification). \circ palm oil, \triangle high melting palm stearin, \bullet randomized palm oil, \blacksquare high melting randomized palm stearin (10°C, acetone), \blacktriangle high melting randomized palm stearin (20°C, acetone), \star tripalmitin.

in α form crystals when stored at 10 or 20°C but transformed to β form crystals when stored at 30°C for 60 days.

Data on triacylglycerol composition, polymorphic transformation, and the length of long spacings in β form crystals can be summarized as follows. High melting stearin fractions transformed into β form crystals in proportion to the trisaturated triacylglycerol content. The length of long spacings in β form crystals approached that of tripalmitin as the trisaturated triacylglycerol content increased. Lower fractionation temperature yielded more middle melting triacylglycerols in fractionated solid fats: POP, PPO, POS. Hence the long spacings of original fats were longer than those of high melting stearin fractions. On the other hand, RP transformed from β' to β form crystals faster than HMRPS10 when stored at 20°C for 60 days in spite of its lower trisaturated triacyl-

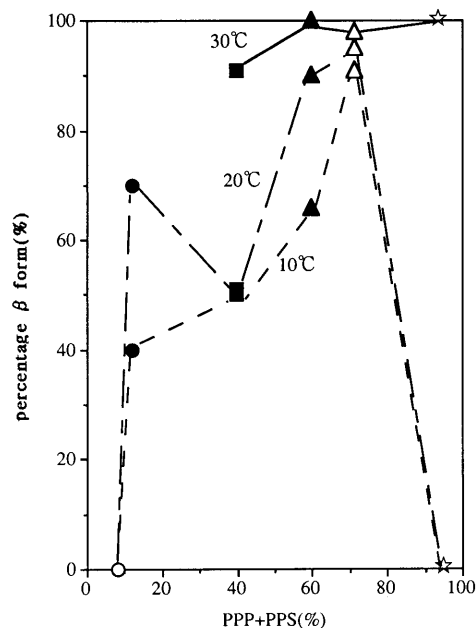


Fig. 2. Relation between the percentage of β form crystals and the trisaturated triacylglycerol content (60 days after solidification). \circ palm oil, \triangle high melting palm stearin, \bullet randomized palm oil, \blacksquare high melting randomized palm stearin (10°C, acetone), \blacktriangle high melting randomized palm stearin (20°C, acetone), \star tripalmitin.

glycerol content. We assumed that diunsaturated and triunsaturated acylglycerols in RP accelerated the transformation at 20°C by behaving as a solvent, thus causing the migration of molecular chains in the lattice.

When the content of monoacid trisaturated triacylglycerols such as tripalmitin was extremely high, the percentage of transformation from α to β form crystals under 30°C was lower than that of other stearin fractions.

The results obtained from this study indicated that the β -transformation of modified palm oils can be affected by the trisaturated triacylglycerol content and storage temperature. However, the physical characteristics and polymorphic behavior of these oils when incorporated into a margarine formula would be considerably influenced by other factors such as the triacylglycerol composition of blended oils, the presence and kind of emulsifiers, and the processing conditions.

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