

Polymorphism of Palm Oil and Palm Oil Products

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Palm oil, palm stearin, hydrogenated palm oil (IV 27.5) and hydrogenated palm olein (IV 28) were crystallized at 5°C, temperature cycled between 5 and 20°C, and kept isothermally at 5°C for 36 days. The polymorphic state of the fats was monitored by X-ray diffraction analysis. Soft laser scanning of X-ray films was used to establish the increase in β crystal content. Palm stearin was least stable in the β' form, followed by palm oil. The hydrogenated oils were very stable in the β' form. Differential scanning calorimeter (DSC) analysis was used to complement the X-ray data.

Palm oil is being used increasingly in foods such as cooking oils, margarines, shortenings and confectionery products. The versatility and adaptability to different food applications of palm oil is the result of its chemical composition. Palm oil differs from many of the common vegetable oils in its high level of palmitic acid, about 44%. In contrast, soybean oil contains 11% and canola oil 5% of palmitic acid. It has been found that addition of palm oil to fats destined for shortening and margarine production has a beneficial effect on their polymorphic stability (1). This stabilizing effect is most likely related to the increased chain length diversity of the fatty acids in these blends. A similar beneficial effect of increased levels of palmitic acid in low erucic acid rapeseed oil obtained by plant breeding has been demonstrated (2).

The incorporation of palmitic acid into the glycerides of a fat should be more effective if the palmitic acid is present mostly in the solid phase of the fat. If this is the case, then the incorporation of suitably modified palm oil might be advantageous. Palm oil is commercially fractionated on a large scale, resulting in a low melting and a high melting fraction known in the trade as palm olein and palm stearin. Palm olein is used as a liquid frying oil; palm stearin can be used as a solid component in margarine and shortening blends (3, 4). Palm oil can also be hydrogenated to yield products with various iodine values and melting points.

This paper deals with the chemical and physical properties of palm oil and modified palm oil and particularly with the polymorphic stability of these fats.

MATERIALS AND METHODS

Refined, bleached and deodorized palm oil, and palm olein and palm stearin were obtained from Palmco Inc., Portland, Oregon. Hydrogenation was carried out in a Parr pressure reaction apparatus with a two-l vessel and a charge of one kg of oil. Nickel catalyst Calsicat E472F (Mallinckrodt Inc., Erie, Pennsylvania) was used at a level of 0.2% by weight of the oil. Reaction temperature was 175°C and hydrogen pressure 103 kPa

(15 psi). Reaction was stopped at IV of about 30. Fatty acid composition of the oils was determined by transesterification and analysis of the methyl esters by gas liquid chromatography (GLC) using a Varian 1400 gas chromatograph with a two-m column packed with 20% DEGS on chromosorb 60–80 mesh operated at 170°C (5).

Iodine value was determined by the Wijs method, AOCS official method Cd 1–25.

Dropping points were determined with the Mettler FP 3 automatic dropping apparatus (6).

Solid fat contents of all fat samples were measured by wideline nuclear magnetic resonance. A Newport Analyzer Mark III and a sample temperature controller WR 2 MK II were used. Tempering of the samples was done at five temperatures with a Praxis Model TU-900 tempering unit.

Trans isomer content was determined by AOCS method CD 14–61 using a Beckman model 4230 infrared spectrophotometer.

To study the polymorphic stability, 10 g of fat samples in 6-cm long and 10-mm diameter tubes were cycled as follows: the fat samples were first heated at 70°C for two hr to destroy any "memory" of earlier crystals, then cooled to 5°C and stored at 5°C for one day, followed by three days at 20°C, one day at 5°C, two days at 20°C, one at 5°C, three days at 20°C and, finally one day at 5°C. For constant temperature studies, the tubes were stored at 5°C for up to 36 days.

X-ray diffraction patterns were obtained with a 601 Diffractis X-ray generator and Guinier camera model FR 552 (Enraf Nonius, Delft, The Netherlands), with a temperature controlled sample holder operated at 10°C. Short spacings on the X-ray film were measured with a Guinier viewer and the relative proportions of the β' and β forms established with a Zeineh soft laser scanning densitometer model SLR-504XL interfaced with an Apple IIe computer (Biomed Instruments, Inc., Fullerton, California). The quantitative evaluation was based on the relative densities of the short spacings at 4.6 and 4.2 Å, which are characteristic of the β and β' forms, respectively. The percentage of β crystals was calculated from:

$$\% \beta = \frac{\text{peak area at } 4.6 \text{ \AA}}{\text{peak areas at } 4.2 \text{ and } 4.6 \text{ \AA}} \times 100$$

At the end of each temperature cycle or storage time, a small sample was taken from the tubes for analysis by DSC with a model 900 DuPont Thermal Analyzer. The samples were heated from 10 to 65°C at 5°C/min.

RESULTS AND DISCUSSION

The properties of palm oil, palm olein, palm stearin, hydrogenated palm oil and hydrogenated palm olein are presented in Table 1. Palm stearin has a higher saturated fatty acid content than palm oil, as evidenced

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TABLE 1

Chemical and Physical Characteristics of Palm Oil, Hydrogenated Palm Oil, Palm Stearin, Palm Olein and Hydrogenated Palm Olein

Fatty acid	Palm oil	Hydrogenated palm oil	Palm stearin fraction	Palm olein fraction	Hydrogenated palm olein
12:0	0.1	—	0.6	0.1	—
14:0	1.0	0.9	1.9	1.0	0.7
16:0	44.7	44.7	60.5	39.6	39.7
18:0	4.0	21.2	4.9	4.0	25.5
18:1	40.1	33.0	26.0	44.0	34.2
18:2	9.5	—	4.8	10.7	—
18:3	0.2	0.2	—	0.5	—
20:0	0.2	—	0.3	—	—
I.V.	51.5	27.5	31.3	57.4	28.0
D.P.	38.6	54.9	53.5	24.4	54.6
% T.I.	0.	12.6	0.	0.	15.7

I.V., Iodine value; D.P., dropping point; T.I., *trans* isomers.

by the higher dropping point and lower iodine value. The chemical composition of hydrogenated palm oil and palm olein were similar. Hydrogenated palm oil contained 12.6% *trans* isomers, hydrogenated palm olein 15.7%. The solid fat contents of the oils are presented in Figure 1. Tables 2 and 3 list the short spacings and their visually estimated intensities. The β' polymorph usually exhibits two strong spacings at 3.8 and 4.2 Å, whereas the β form has one strong spacing at 4.6 Å (7). The β polymorph also shows a weaker spacing at 3.8 Å. For this reason the quantitative evaluation by densitometry involved only the spacings at 4.2 and 4.6 Å. A medium to strong spacing at about 4.3 Å and a weak one at about 4.0 Å may be related to a sub form. Repeated temperature cycling resulted in increased intensity and appearance of the 4.6 Å spacing, indicating a partial transformation to the β form.

An example of a laser densitometer scan of the X-ray films obtained with palm oil at cycle 1 and 4 is

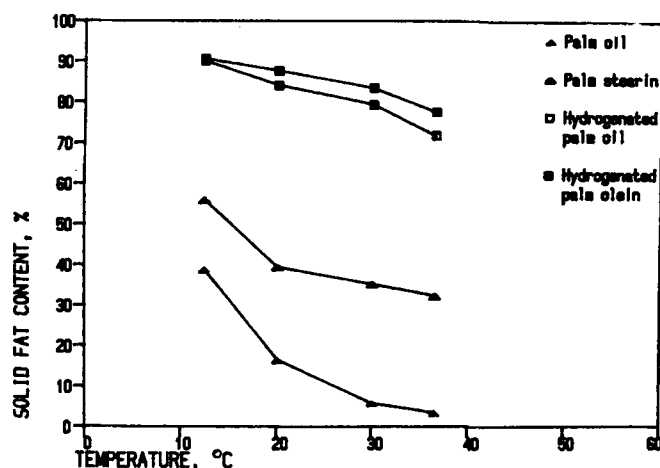


FIG. 1. Solid fat content of palm oil, palm stearin, hydrogenated palm oil and hydrogenated palm olein.

TABLE 2

Short Spacings (Å) of Palm Oil, Palm Stearin, Hydrogenated Palm Oil and Hydrogenated Palm Olein at Different Stages of Temperature Cycling

Cycle ^a	Sample	Form	Short spacings ^{b,c}			
1	Palm oil	β'	—	4.36(s)	4.19(s)	3.88(m)
	Palm stearin	$\beta' \gg \beta$	4.57(m)	4.35(s)	4.20(s)	4.05(w)
	Hydrogenated palm oil	β'	—	4.36(m)	4.22(s)	4.06(w)
	Hydrogenated palm olein	β'	—	4.34(s)	4.19(v.s.)	4.04(m)
2	Palm oil	β'	—	4.35(m)	4.18(s)	4.04(v.w.)
	Palm stearin	$\beta' \gg \beta$	4.60(m)	4.29(m)	4.20(s)	4.03(w)
	Hydrogenated palm oil	β'	—	4.33(m)	4.19(v.s.)	4.04(w)
	Hydrogenated palm olein	β'	—	4.31(s)	4.20(v.s.)	4.03(m)
3	Palm oil	$\beta' \gg \beta$	4.57(v.w.)	4.35(m)	4.20(s)	4.05(v.w.)
	Palm stearin	$\beta' \gg \beta$	4.56(m)	4.34(m)	4.19(s)	4.00(w)
	Hydrogenated palm oil	β'	—	4.36(s)	4.22(s)	4.04(w)
	Hydrogenated palm olein	β'	—	4.31(s)	4.20(v.s.)	4.03(m)
4	Palm oil	$\beta' \gg \beta$	4.56(w)	4.35(m)	4.19(s)	4.00(v.w.)
	Palm stearin	$\beta' \gg \beta$	4.58(m)	4.35(s)	4.18(s)	4.02(w)
	Hydrogenated palm oil	β'	—	4.37(m)	4.23(s)	4.02(w)
	Hydrogenated palm olein	β'	—	4.38(s)	4.22(s)	4.05(m)

^aCycle 1, 5°C for one day; cycle 2, as in cycle 1 with additional 20°C for 3 days and 5°C for one day; cycle 3, as in cycle 2 with additional 20°C for 2 days and 5°C for one day; cycle 4, as in cycle 3 with additional 20°C for 3 days and 5°C for one day.

^bBand intensities are indicated as v.s., very strong; s, strong; m, medium; w, weak; v.w., very weak.

^cPredominate short spacings of β' , 4.2 and 3.8 Å; β , 4.6 Å.

POLYMORPHISM OF PALM OIL

TABLE 3

Short Spacings (Å) of Palm Oil, Palm Stearin, Hydrogenated Palm Oil and Hydrogenated Palm Olein at Different Stages of Storage at 5°C

Day	Sample	Form	Short spacings					
1	Palm oil	β'	—	4.35(s)	4.19(s)	—	—	3.88(m)
	Palm stearin	$\beta' >>> \beta$	4.56(w)	4.35(s)	4.20(w)	4.05(w)	—	3.87(s)
	Hydrogenated palm oil	β'	—	4.36(m)	4.22(s)	4.06(w)	—	3.86(s)
	Hydrogenated palm olein	β'	—	4.34(s)	4.19(v.s.)	4.04(m)	—	3.85(m)
4	Palm oil	β'	—	4.31(s)	4.19(s)	—	3.91(s)	—
	Palm stearin	$\beta' >>> \beta$	4.52(v.w.)	4.31(m)	4.13(s)	—	—	3.75(m)
	Hydrogenated palm oil	β'	—	4.34(m)	4.19(v.s.)	4.04(w)	—	3.84(s)
	Hydrogenated palm olein	β'	—	4.27(s)	4.21(v.s.)	4.05(m)	—	3.76(s)
14	Palm oil	β'	—	4.35(s)	4.19(s)	—	3.90(s)	—
	Palm stearin	$\beta' >>> \beta$	4.54(w)	4.35(s)	4.18(s)	—	—	3.85(s)
	Hydrogenated palm oil	β'	—	4.33(s)	4.19(s)	4.04(w)	—	3.85(s)
	Hydrogenated palm olein	β'	—	4.36(m)	4.21(s)	4.05(w)	—	3.85(m)
36	Palm oil	$\beta' >>> \beta$	4.56(v.w.)	4.34(s)	4.20(s)	—	3.89(s)	—
	Palm stearin	$\beta' >> \beta$	4.67(m)	4.38(s)	4.24(s)	—	—	3.84(m)
	Hydrogenated palm oil	β'	—	4.34(m)	4.21(s)	4.03(w)	—	3.85(m)
	Hydrogenated palm olein	β'	—	4.38(s)	4.20(s)	4.04(w)	—	3.86(m)

presented in Figure 2. Quantitative evaluation of these data are presented in Figure 3 for the temperature cycled fats and in Figure 4 for the isothermally stored fats. Hydrogenated palm oil and palm olein developed no β crystals during cycling, indicating high stability of the β' form. The greatest tendency toward β crystal formation was shown by palm stearin, followed by palm oil.

Palm stearin developed 30% β crystallinity and palm oil 12% in the cycling procedure (Fig. 4). In the isothermal study palm stearin developed 40% β crystallinity and palm oil only 5% (Fig. 5). At 20°C palm oil contains only 17 and palm stearin 38% solid fat; at 10°C these values are 38 and 55% (Fig. 1). This means that temperature cycling between 5 and 20°C results in partial melting of mixed triglycerides. On the other hand, there is little difference in solid fat content of the hydrogenated fats between 10 and 20°C, and little melting takes place during cycling. (Fig. 1). Cooling

will resolidify the higher melting triglycerides into the more stable β form. Comparison of the cycling procedure and the isothermal storage tests indicates that the cycling test can be used as an accelerated stability test for the β' form.

The DSC diagrams illustrate the melting of mixed triglycerides and the resolidification of the higher melting fraction. In the case of palm oil (Fig. 5) the first melting peak gradually increased in size, whereas the second major peak decreased in size. The melting temperature of the first peak was lower in cycle 1 than in cycle 4. In the case of palm stearin and hydrogenated palm oil there was a gradual splitting of the last melting peak (Figs. 6 and 7). The DSC pattern of hydrogenated palm olein was similar to that of hydrogenated palm oil. In all of the fats, the temperature of the last melting peak at cycle 4 was between 4 and 5°C higher than the corresponding dropping points (Table 1).

The greater β tending property of palm stearin

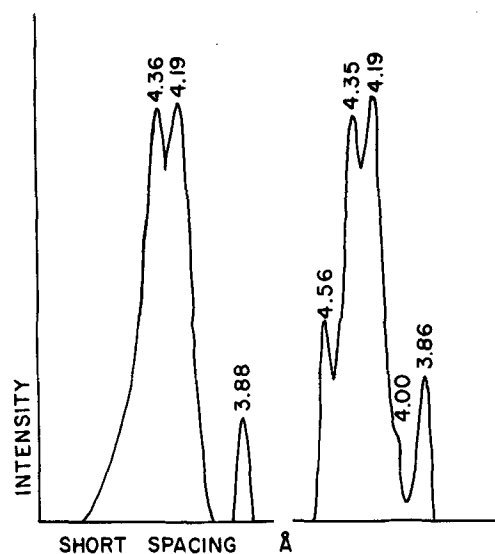


FIG. 2. Laser densitometer scans of the X-ray film obtained with palm oil at (a) cycle 1, and (b) cycle 4.

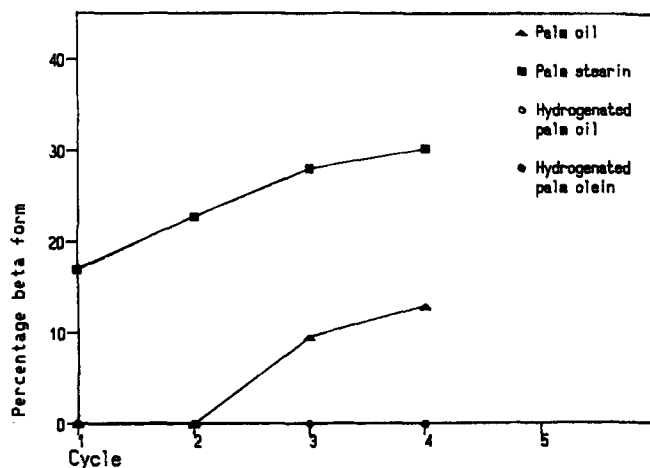


FIG. 3. Development of β crystals in temperature cycled fats.

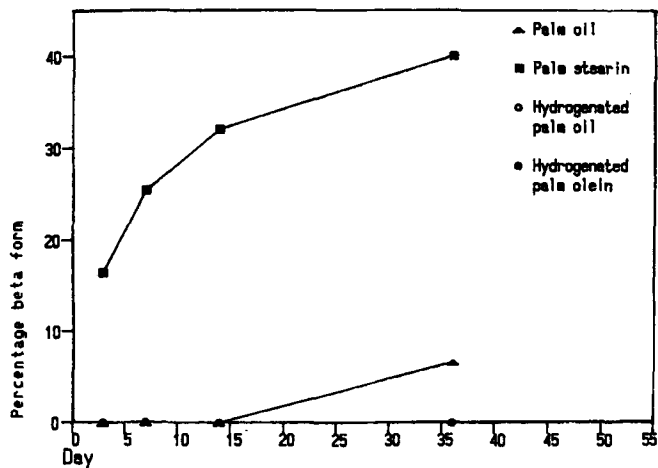


FIG. 4. Development of beta crystals in fats stored isothermally at 5°C.

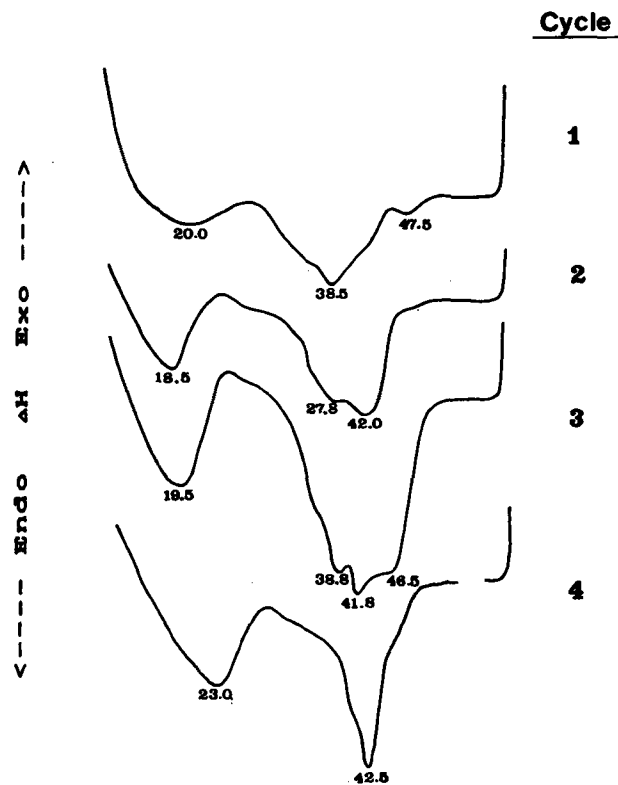


FIG. 5. DSC heating curves of temperature cycled palm oil.

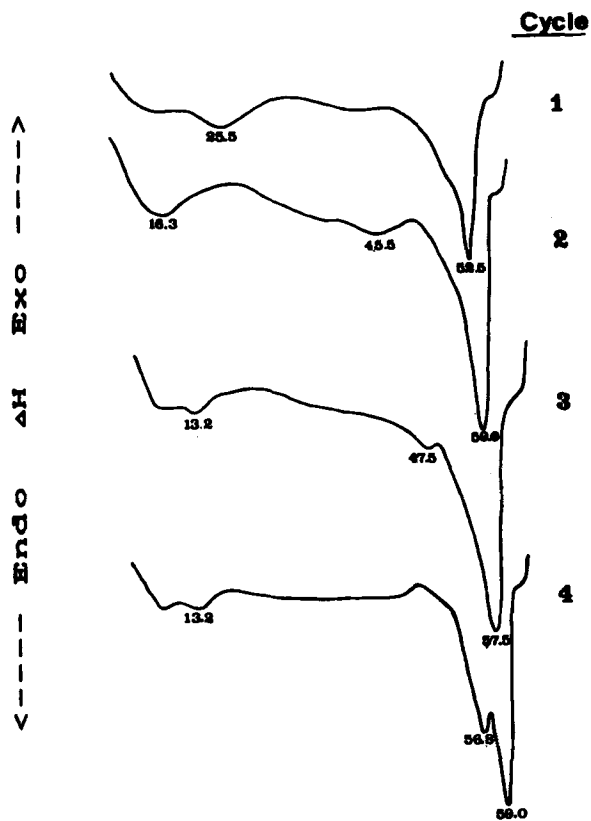


FIG. 6. DSC heating curves of temperature cycled palm stearin.

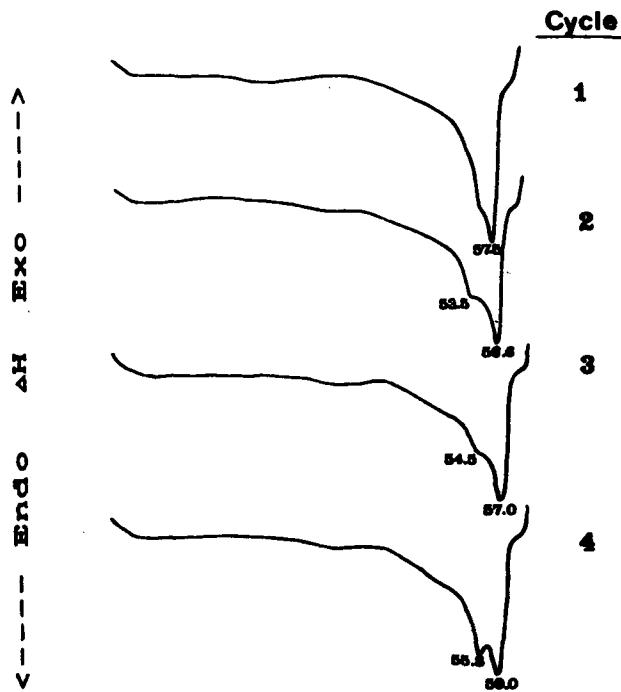


FIG. 7. DSC heating curves of temperature cycled hydrogenated palm oil.

POLYMORPHISM OF PALM OIL

probably can be explained by its higher concentration of tripalmitin, and this triglyceride is a strong β former. Palm oil contains between 5 and 6% tripalmitin, whereas palm stearin may contain from 10 to 32% tripalmitin depending on fractionation conditions (8).

This report has examined the β' stability of palm oil and modified palm oil. The behavior of these products when incorporated into margarine and shortening formulations will be the subject of a future communication.

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