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COMPOSITIONAL AND DIFFERENTIAL SCANNING CALORIMETRY (DSC) STUDIES OF CRYSTALS OF PALM OLEIN

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The composition and thermal properties of palm olein upon storage have been investigated by numerous techniques such as Differential Scanning Calorimetry (DSC), Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC). DSC melting and crystallization thermograms of crystals separated from palm olein differed in their characteristics, according to the composition of the olein and the storage conditions. A comparison was made between oleins of iodine value (IV) in the range of 56-61 which were stored at conditions of 20°C and 5°C. The more unsaturated olein was stored at 5°C. Oleins with higher unsaturation showed crystals with a group of exotherms and endotherms which generally did not differ much with duration of storage. Crystals of the more saturated types of olein still retained the two exothermic and endothermic peaks, as observed in palm oil. The crystals of unsaturated oleins (IV of 60.6) tended to have a higher proportion of POO than POP, in contrast to the crystals of oleins (IV of 57.7) where the POP content is higher. With longer storage period, these exotherms and endotherms were shifted closer together, depicting polymorphism upon melting. With a long duration of storage, as in ambient storage conditions, another set of olein samples resulted in crystals with harder characteristics and a melting point of about 68°C. These crystals contained high diglycerides, confirming earlier works on the strong role of diglycerides in the crystallization stability of palm olein.

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INTRODUCTION

Palm olein, the liquid fraction resulting from the fractionation of palm oil under controlled conditions, is widely used as cooking oil in the tropics. It has excellent flavour and oxidation stability. Although palm olein is now available in temperate countries, its usage is limited as it becomes cloudy and tends to crystallize during winter when the temperature is low.

Factors influencing the crystallization of palm olein are the presence of fatty acid, diglycerides and triglycerides. However, the influence of diglycerides has much greater impact during crystallization. Characterizations of crystals formed in palm olein have been investigated by Siew and Ng (1995) and Swe *et al.* (1994). Their work showed that the crystals formed at room temperature mainly consisted of a high concentration of diglycerides. The presence of high diglycerides has a role in the crystallization behaviour of palm olein during storage. Samples containing higher amounts of diglycerides tend to crystallize more easily than those with lower amounts (Siew and Ng, 1996b).

DSC is used for the measurement and characterization of the thermal properties of palm olein. When a transition, such as melting or crystallization, occurs in the sample, an endothermic or exothermic reaction takes place and this is recorded as a peak in the chart. The curves and melting peaks in the chart show the melting and crystallization behaviour of the oil. The conditions under which crystallization of oils are carried out have profound effects on the structure and composition of the resulting crystals. Similarities in diglycerides structure with that of triglycerides enable co-crystallization. This is governed by the degree of intersolubility of diglycerides in the triglycerides.

Che Man and Swe (1995) studied the crystallization of palm oil in batch crystallization by DSC techniques and concluded that polymorphic transition of a to β crystals occur at a lower temperature for good quality oils.

In this study, the crystallization of palm oleins under ambient and cold temperatures were studied using DSC, X-ray and microscopic techniques. The composition of the crystals was evaluated by gas liquid chromatography and HPLC.

EXPERIMENTAL

Materials

Palm oleins labelled DF 25 and 9 and another two samples labelled as A and B were obtained from Malaysian refineries. The IVs of DF 25, DF 9, samples A and B were 57.7, 62.3, 57.4 and 60.9, respectively. Storage of palm olein DF 25 and 9 were carried out at 20°C and 5°C in one litre glass bottles. The other two samples A and B were stored at ambient temperatures of 24°C28°C for two months and two years respectively. The crystals obtained from DF 25 and 9 were filtered at different time intervals through Whatman filter paper No. 542. The crystals were characterized by DSC, gas liquid, HPLC, X-ray and microscopy.

Thermal Analysis by DSC

DSC analyses of the samples were performed with a Perkin Elmer 7 DSC (Norwalk, CN, USA) instrument. A sample was completely melted at 80°C before being weighed (10 mg) into an aluminium pan which was then sealed using a sample pan crimper. The previous thermal history of the sample was erased by heating the sample to 80°C in the DSC instrument and holding it for 10 min. The sample was then cooled to -30°C at a rate of 40°C min^{-1}. At the end of the cooling, the sample was heated at 10°C min^{-1} to 80°C for 10 min and then cooled at 10°C min^{-1} to -30°C.

Diglyceride and Triglyceride Analysis by HPLC

HPLC was carried out with Gilson 303 and 302 pumps (Middleton, WI, USA) and Hewlett-Packard 3395 A integrator (Palo Alto, CA, USA). The two columns were of 25 cm length and 4 mm id with 5 µm Lichrosphere RP 18 (Merck Darmstodt, Germany). The columns were kept at a temperature of 30°C in a well insulated column heater. The mobile phase was acetonitrile/acetone (25:75,v/v) at a flow rate of 1.0 ml min^{-1}. Injection was achieved through a Rheodyne valve fitted with a 20 µl loop.

The samples were injected as 10% (w/v> solutions in warm acetone. Identification of the triglyceride was made by comparison with the retention times of triglyceride standards, e.g. triolein (OOO), palmitoyldiolein (POO), oleodipalmitin (POP) and tripalmitin (PPP). Other peaks were identified by comparison with work of Sassano and Jeffrey (1993). Triglycerides having identical fatty acids such as POP, PPO and OPP were not separated. The most unsaturated triglyceride was eluted from the column first. The diglycerides eluted before the triglyceride. The diglycerides were identified by comparison with the standards 1,2-(2,3-) and 1,3-dipalmitoylglycerol, PP; 1,2-(2,3-) and 1,3-dioleoylglycerol, 00 ; 1,2-(2,3-) and 1,3 palmitoyloleoylglycerol, PO.

The coefficient of variations (CV) of the triglyceride peaks were within acceptable limits of those given in the IUPAC procedure (IUPAC, 1987). The IUPAC procedure gave a repeatability CV of <2% for major triglycerides and up to 37% for minor triglycerides in palm oil.

Fatty Acid Composition

The methyl esters were prepared by transesterifying the sample with 1 M sodium methoxide. To the oil sample (6 drops or 50 mg) in a 2 ml vial was added 0.95 ml n-hexane using a graduated pipette. The mixture was well shaken and 0.5 ml sodium methoxide was added. The vial was shaken vigorously for 5 sec with the help of a vortex mixer. The mixture first appeared clear and then turned turbid, as sodium glyceroxide precipitated. After 5 min, the clear upper layer of methyl ester was pipetted off for GC analysis.

Quantification of the peak areas was carried out with a Hewlett-Packard HP 5890 II GC. The conditions were according to Siew and Ng (1996a). A correction based on analysis of a reference mixture or methyl esters of known composition (20A from Nuchek Prep Inc. Elysian, MN, USA) was used for the calculation of percentage by mass.

Crystal Polymorphism by X-ray Diffraction

X-ray analysis was conducted to identify the polymorphic form of the fat samples using a X-ray diffractometer (XRD) Enraf Nonius FR 590 (Delft, The Netherlands). The X-ray pattern was recorded on photographic film with a Guinier camera and the diffraction bands measured with a Enraf Nonius viewer. Identification of the polymorphic form of the crystals was by reference to their short spacing. The stearin samples were smeared on to the flat stainless steel plate of 1 mm thickness with a rectangular hole. The samples were contained in this space with adhesive tape and the XRD patterns taken at 20°C.

Microscope Observation

A polarizing microscope (Axiolab Microscope, Zeiss, Germany) served to identify the types of crystal form. The granular structure and the dimension of the crystals could be easily monitored. These enabled comparison of the crystal structure and size distribution in the samples. A thin smear of the sample was placed on a glass slide. A cover glass was placed on the top without squashing the sample. The sample was then examined under the microscope.

Storage of Palm Olein at 5°C, 20°C and Ambient Conditions (24°C - 28°C)

Storage of the palm olein samples was carried out at 20°C and 5°C for olein DF 25 and 9. Another two samples, sample A (RBD olein) and sample B (blended olein) were stored at ambient conditions for two months and two years respectively. The crystals obtained from DF 25 and 9 were filtered at different time intervals. The amount of crystals increased with time of storage.

RESULTS AND DISCUSSION

DSC Melting and Cooling Thermograms of Crystals

Samples of palm olein were stored at 5°C, 20°C and under ambient conditions. The melting and cooling thermograms of the crystals were obtained with a Perkin-Elmer DSC7. The DSC melting thermograms (Figure 1) for the crystals of DF 9 showed similarity in the profiles. The crystals at 11 hr of storage showed high melting point components up to 56.7°C. These components gradually disappeared in the crystals at 14 and 16 hr of storage. This was due to the crystallization of the more unsaturated triglycerides with time of storage, thus rendering the crystals softer and of lower melting properties. The cooling profiles *(Figure 1)* only showed one exotherm at 3°C4°C.

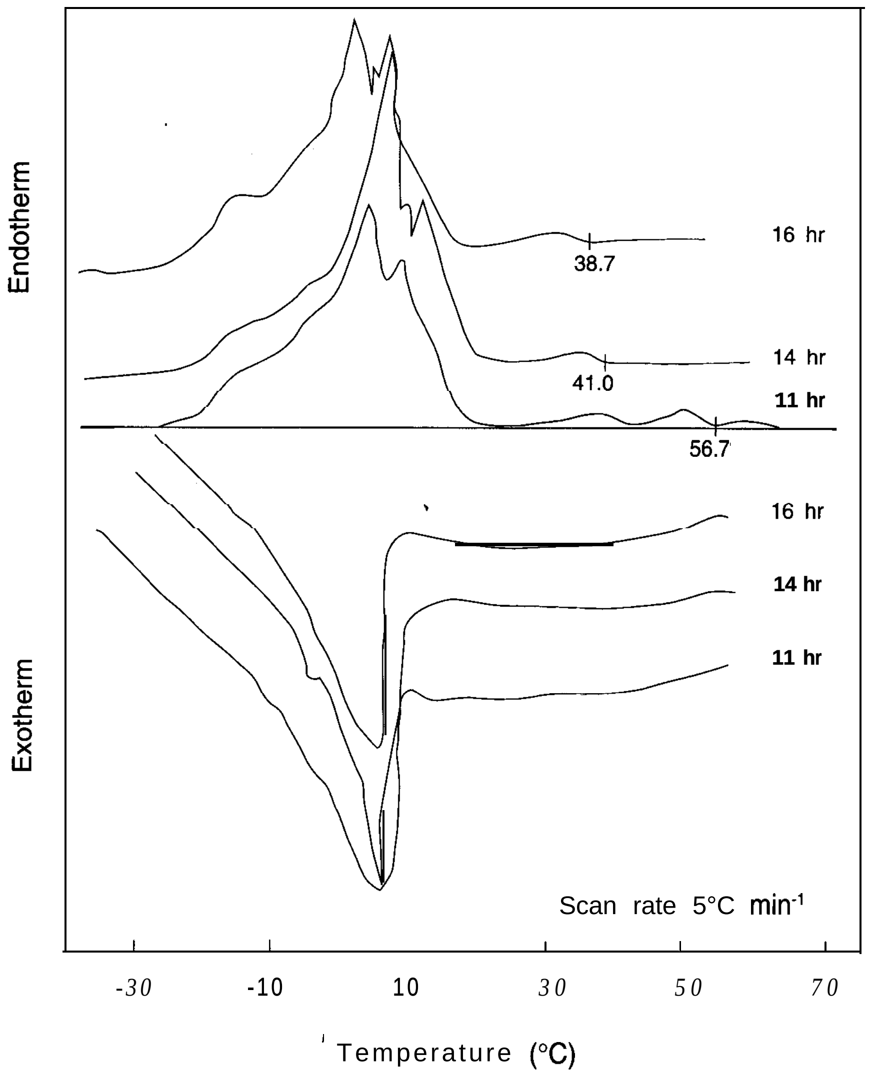

*Figure 1. DSC thermograms **of crystals of** palm olein (at 5°C).*

In comparison, crystals of DF 25 which were obtained at 20°C had more complex melting and crystallization profiles *(Figure 2).* The melting thermograms showed two to three endotherms. The crystals at 24 hr storage period had more softer components, compared to the crystals at only 5 hr. The crystals obtained from 5 hr storage showed a small low melting peak at 12.1°C and a larger high melting peak at 49.7°C. After 11 and 24 hr of storage, the low melting peak was more intense than the peak obtained at 5 hr. The higher melting point (56.4°C) of the crystals from the 5 hr storage programme was noted. However, the crystals from the 24 hr programme melted completely at 50.3°C. Upon cooling the melt *(Figure 2)*, the palm olein crystals showed a large exotherm at 30.3°C and small exotherm at 5.3°C and 8.2°C respectively for both storage at 5 and 11 hr. The cooling thermograms, as in the melting profiles, showed two peaks representing the low and high melting components still present in the crystals. Also, the thermogram was reflective of the polymorphism shown in the endo-

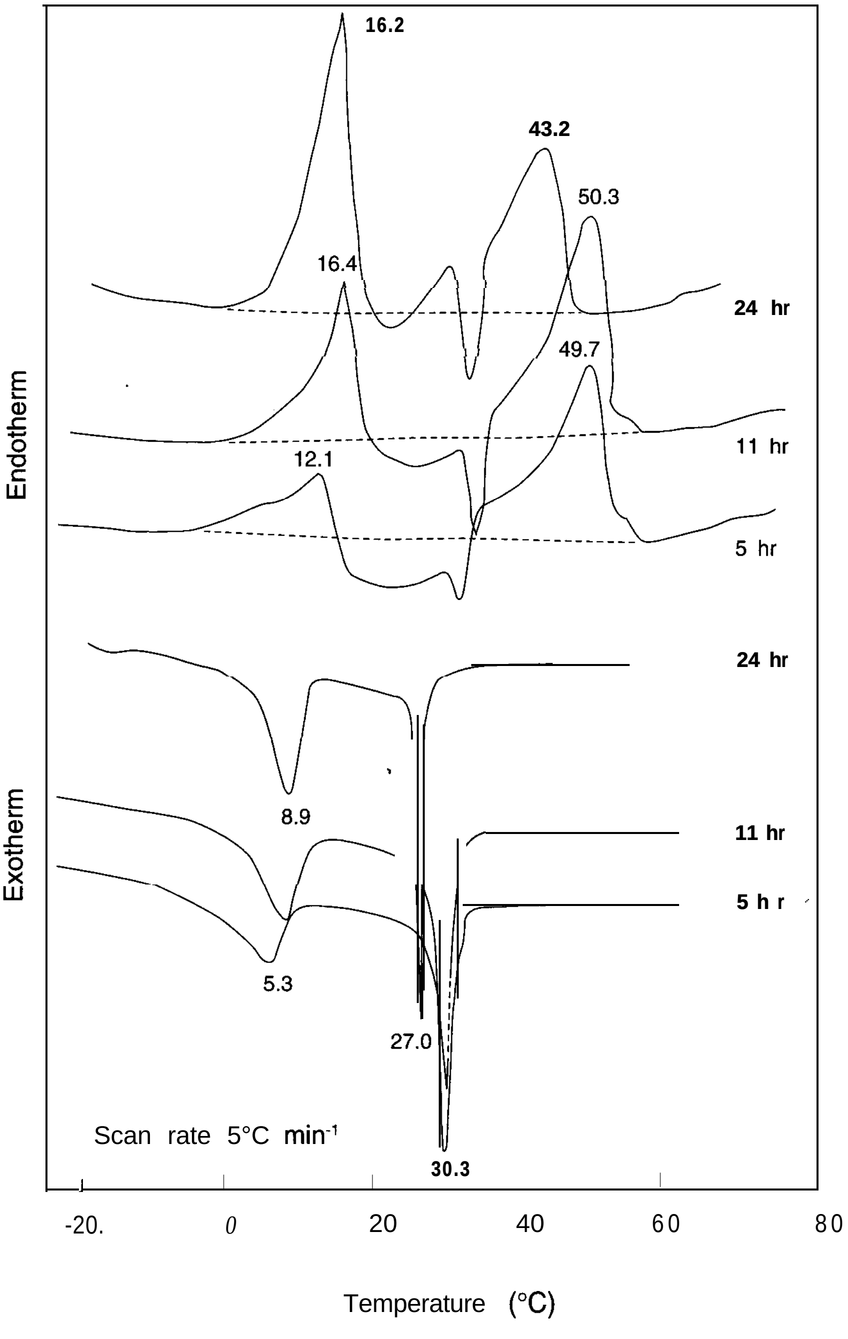

Figure 2. DSC thermograms ***of*** *crystals* ***of*** *palm olein (at 20°C).*

therm at 16°C (alpha crystals), followed by melting to beta prime crystals which remelted to beta crystals at 43°C.

For oleins that were stored at ambient conditions, different observations for both sample A and B were obtained. *Figure* 3 shows similarity in the shapes of the curve for original sample A and its filtered olein. The high melting peak for the original olein at 6.3°C was only slightly shifted to 7.7°C when the olein was filtered. The composition of the filtered and unfiltered olein remained nearly similar. However, the melting thermograms of the crystals showed more complicated profiles. At least five clear peaks were observed in the heating thermograms of sample A, indicative of more

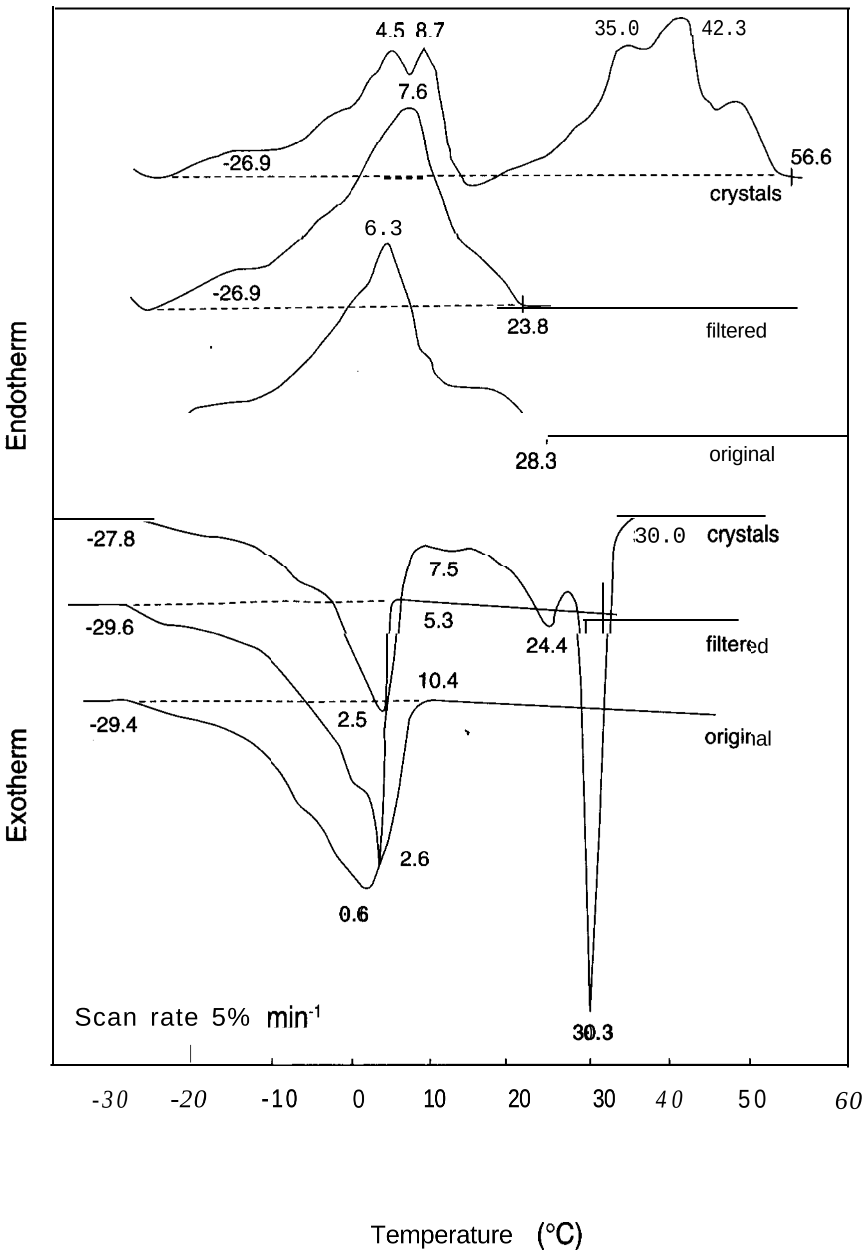

Figure 3. DSC thermograms of original sample A and its crystals (two months at 24°C-28°C).

than five melting forms present in the sample. A small higher melting peak at 49.9% and a small lower melting peak at 4.5°C were obtained. The crystals melted completely at very high temperature at 56.6% compared to the olein. In general, it appeared that the alpha crystals obtained in the cooling conditions remelted to only beta crystals (confirmed by X-ray). These results showed that very high melting components were present in the crystals.

The removal of some saturated triglycerides contributed to a change in the crystallization temperature of the filtered olein when compared to the original olein. Three crystallization exotherms were observed, a sharp exotherm at 30.3°C, a small exotherm at 24.4% and another at 2.5% for the crystals of sample A. The high melting component could be due to the more saturated glycerides.

When two crystals have melting points within 1°C-2°C of each other and are analysed simultaneously on the DSC, a phenomenon known as overlap may occur. *Figure 4* shows the overlap peaks (two shoulders) for both the original and filtered olein B. The shapes of the curves were also nearly similar as sample A *(Figure 3)* and the high melting point for the original sample B was at 6.5°C and after filtration at 6.7%. The crystals showed a larger higher melting peak at 64.1% and small melting peak at 5.6°C. The cooling thermograms indicated a sharp exotherm at 1.8°C for the original oil and at 0.4°C after filtration. The crystallization thermograms indicated a sharp endotherm at 52.9°C and a smaller endotherm at –1.1°C. These thermograms were similar to those observed by Siew and Chong (1998). The high melting component at 64°C could be due to the high proportion of diglycerides in the

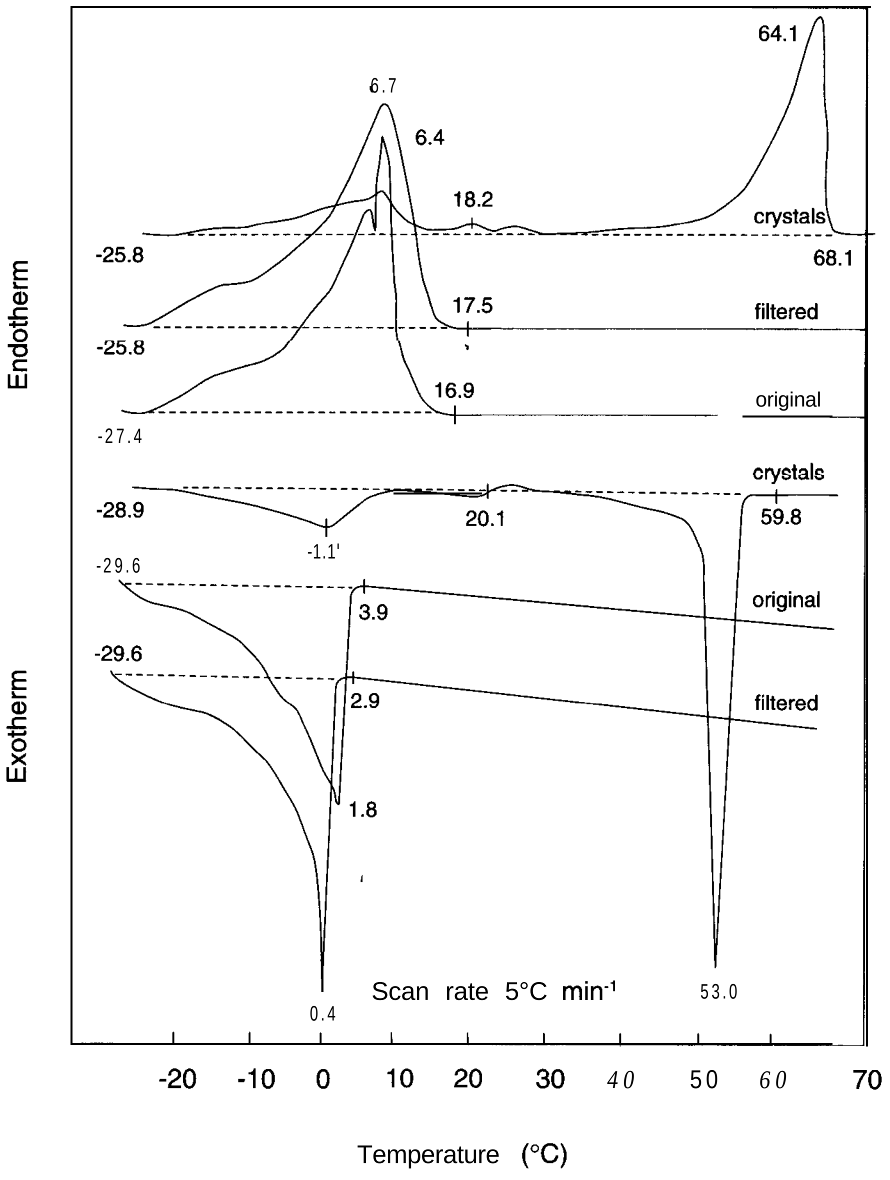

Figure 4. DSC thermograms of original sample B and its crystals (two years at 24°C-28°C).

crystals.

The crystals which contained a high proportion of diglycerides were the contributive factor to the high melting point endotherm. The effects of diglycerides content, especially of 1,3 PP in crystallization of palm oil, are shown in *Figures 5a* and *5b*. *Figure 5a* shows the heating curves of the palm oil, drawn from pure palm oil (a), +5% of 1,3 PP (b), +10% of 1,3 PP (c), +39.7% of 1,3PP (d) and 50% of 1,3 PP (e). This figure confirmed that the high melting peak increased with increasing concentration of 1,3 PP in palm oil. This was seen after the addition of 10% of 1,3 PP (c) - a sharp endotherm at 5.3°C compared to (a) at 4.9°C. Curve (d) showed only one sharp high melting peak at 65.5°C present with 39.7% of 1,3 PP added in the palm oil. Furthermore, curve (e) also showed only one high melting component present in the crystals which showed a sharp peak at 66.0°C and which melted completely at 69.5°C. The other peaks appeared as minor peaks in the lower melting

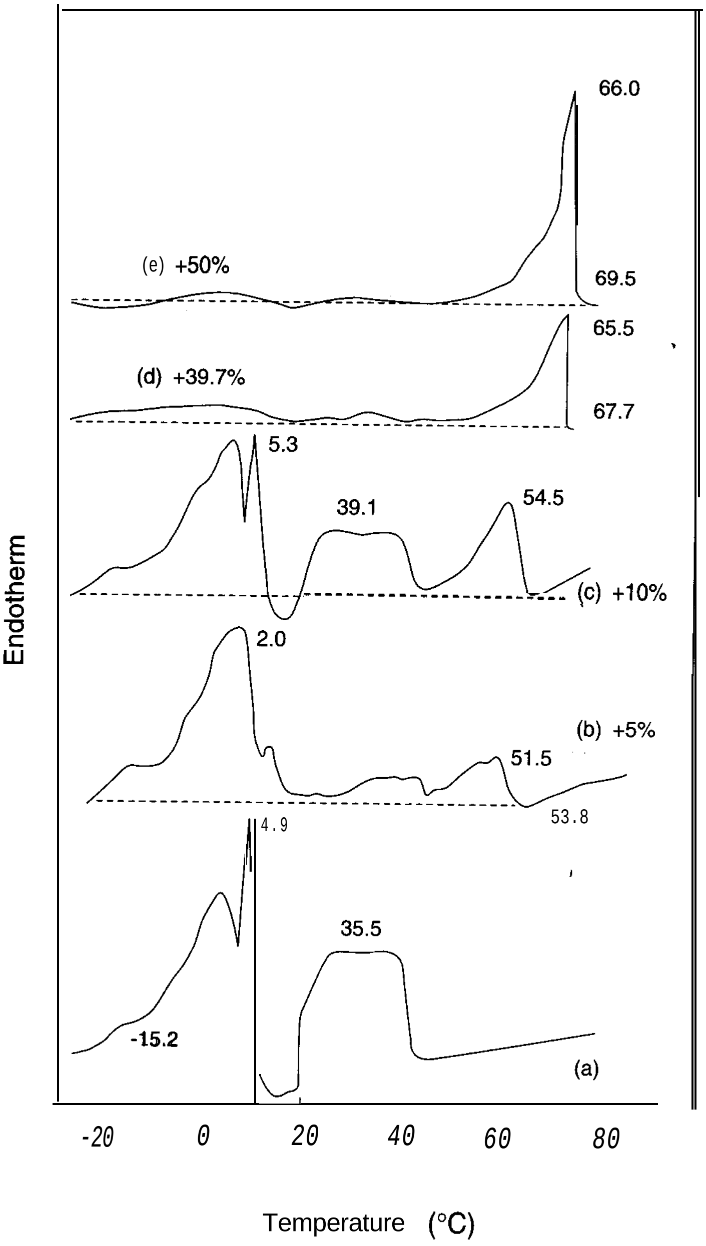

Figure 5a. DSC thermograms shows the ***effects of*** *1,3 PP in palm oil (heating rate 5°C min^{-1}).*

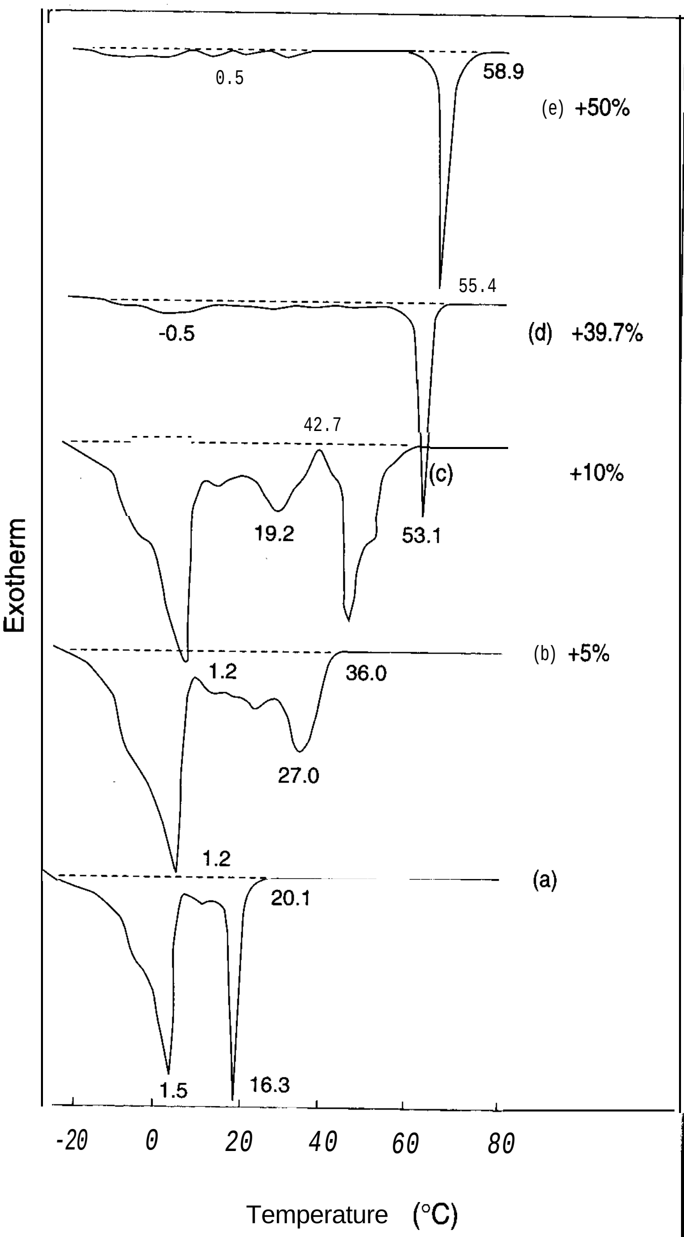

Figure 5b. DSC thermograms shows the ***effects of*** *1,3 PP in palm oil (cooling rate 5°C min^{-1}).*

range and were almost insignificant. These profiles, which had striking similarity to the profiles observed in the crystals, added further confirmation to the conclusion that the high melting component of 64°C in the crystal DSC profile was due to diglycerides.

Figure **5b** shows the cooling curves of (a) pure triglycerides of palm oil with (b) +5% of 1,3 PP (c) +10% of 1,3 PP (d) +39.7% of 1,3PP and (e) +50% of 1,3 PP. The pure triglycerides were obtained by column chromatography as described in Siew and Ng (1999). All the curves show the sharp exotherms (high T peak). Curve (a) illustrates two sharp endotherms at 1.5°C and 16.3°C. This is similar to palm oil cooling curves which consist of low melting and high melting components. After the addition of 5% of 1,3 PP, the sharp high temperature exotherm changed to a broad high temperature exotherm at 27.0°C. The higher the concentration of 1,3 PP added to the pure triglycerides, the larger is the high temperature exotherm. When 50% of 1,3 PP was added to palm oil, crystallization began at the very high temperature of 58.9°C compared to pure palm oil at 20.1°C. The high melting component still existed in the palm oil during the crystallization and gave a peak at 55.4°C. Disappearance of the low temperature exotherms of curves (a), (b) and (c) suggest co-crystallization of the high melting triglycerides with the 1,3 PP, leaving only a small proportion of low melting triglycerides whose DSC crystal profiles show similar patterns.

The thermograms of crystals of palm olein showed higher melting components in these samples. The melting and crystallization behaviour of the crystals obtained from storage of oleins under ambient conditions were very different from the crystals obtained at 5°C and 20°C. This implied that the composition of their crystals was very different. It is thus clear that the crystals obtained from different palm oleins depend on the composition of the olein and the conditions of storage.

Fatty Acid Composition (FAC)

The FAC of the oleins are shown in ***Tables 1*** and ***2.*** In ***Table la,*** the FAC of DF 25 is very different between the olein and its crystals after storage and filtration at 20°C. With initial winterization of 5 hr, the palmitic acid (16:0) content of the crystals was high at 53.8% compared to 39.4% olein. Subsequent storage for longer periods and filtration showed a reduction in palmitic acid. After 24 hr, the palmitic acid content of the crystals decreased to 51.6%. In contrast, oleic acid (18:1) increased from 30.8% in the crystals at 5 hr to 33.9% after storage at 24 hr.

In ***Table 1b***, olein DF 9, which has a palmitic acid content of 37.4%, showed only a slight

TABLE la. FATTY ACID COMPOSITION (wt. %) OF PALM OLEIN DF 25 AND CRYSTALS AT 20°C

Fatty acid (hr)	12:o	14:0	16:0	16:1	18:0	18:1	18:2	18:3	lo:o	Iv
0	0.2	1.0	39.4	0.2	4.3	43.0	11.7	0.2	0.4	57.7
5	0.2	1.3	53.8	0.1	5.9	30.8	7.3	-	0.4	39.0
7	0.2	1.3	51.8	0.1	5.7	32.6	7.7	0.1	0.4	41.6
11	0.2	1.3	54.5	0.1	5.7	31.2	6.5	0.1	0.4	38.3
24	0.2	1.2	51.6	0.1	5.3	33.9	7.2	0.1	0.4	41.8

TABLE lb. FATTY ACID COMPOSITION (wt. %) OF DF 9 AND CRYSTALS AT 5°C

Fatty acid (hr)	12:o	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:o	IV
0	0.3	1.0	37.4	0.2	3.9	43.3	13.2	0.3	0.3	60.6
11	0.4	1.2	38.6	0.2	4.4	42.3	12.4	0.2	0.4	58.2
12	0.3	1.2	40.6	0.2	4.6	40.7	11.7	0.2	0.4	55.6
13	0.3	1.2	41.1	0.2	4.7	40.3	11.6	0.2	0.4	55.1
14	0.4	1.2	40.1	0.2	4.5	41.3	11.9	0.2	0.3	56.5
16	0.3	1.2	39.6	0.2	4.4	41.3	12.2	0.2	0.4	56.9

increase in palmitic acid content in the crystals when stored for 16 hr at 5°C. After 16 hr, the oleic acid of the crystals slightly decreased to 41.3%.

For palm oleins at ambient conditions, the two samples (*Table* 2) showed a higher oleic acid content in the olein compared to their crystals. In both samples A and B, the palmitic acid contents of the crystals were higher than the original. The palmitic acid content of crystals from sample B was higher than those of sample A, even though the starting oil was more unsaturated. This could be due to the longer period of storage of sample B, resulting in more deposition of triglycerides with palmitic acid.

From these two tables, it is noted that the FAC of crystals of palm olein vary according to the length of storage and also according to the composition of the olein. Of course, it will also vary depending on the conditions or temperature of storage. In this experiment, the more unsaturated olein DF 9 was stored at 5°C while DF 25 was stored at 20°C.

Diglyceride Composition

Table 3 (palm olein at ambient condition) indicates that dipalmitoylglycerol, in particular, the 1,3 isomer in both samples, was more effective in causing rapid crystallization of palm olein as indicated by the results of 1,3 PP in the crystals of sample A (8.4%) and sample B (34.8%). However, the 1,3 PP levels in the original samples A and B were only 1.4% and 1.3% respectively. The difference in the 1,3 PP contents of samples A and B crystals was due to the length of storage - one for two months and the other for two years. The role of diglycerides in the short term storage period was less evident.

TABLE 2. FATTY ACID COMPOSITION (wt. %) OF PALM OLEINS A AND B AT AMBIENT CONDITIONS (24°C-28°C)

Sample	12:0	14:o	16:0	16:1	18:0	18:1	18:2	18:3	20:o	Oths	IV
Original sample A[a]	0.3	1.4	39.6	0.2	4.1	43.1	11.2	0.2	0.3	-	57.4
Sample A crystal[b]	0.2	1.3	55.5	0.1	4.9	30.5	6.9	0.1	0.4	0.1	38.6
Original sample B[a]	0.3	1.0	39.6	0.2	3.9	44.6	12.3	0.2	0.4	0.1	60.9
Sample B crystal[b]	0.2	1.0	62.1	0.1	5.1	24.2	6.7	0.1	0.3	0.2	32.9

Notes:
A: stored for two months.
B:stored for two years.
“before storage.
[b]after storage.

TABLE 3. DIGLYCERIDE COMPOSITION (wt. %) OF PALM OLEINS A AND B AT AMBIENT CONDITIONS (24°C-28°C)

Sample code	12 00	13 00	12 PO	13 PO	13 PP	12 PP	Total DG
Original sample A[a]	0.6	0.9	0.8	2.0	1.4	0.2	5.9
Sample A crystals[b]	0.3	0.7	0.4	1.2	8.4	0.0	11.0
Original sample B[a]	0.7	1.1	1.1	2.7	1.3	0.1	7.0
Sample B crystals[b]	0.4	1.7	0.7	2.7	34.8	0.2	40.5

Notes:
A: stored for two months.
B: stored for two years.
“before storage.
[b]after storage.

Triglyceride Composition

The triglyceride composition of palm olein DF 25 (*Table* 4a) shows high POP (28.8%), POO (25.4%), PLO (10.9%) and PLP (9.6%). The other triglycerides are present in minor proportions. The triglyceride content for the crystals after storage of 24 hr was POP (44.6%), POO (14.2%) and PLO (5.4%). POO and PLO triglycerides were lower than their respective palm oleins. An increase in POP (31.6% to 44.6%) was in agreement with the higher content of palmitic acid while the decrease in POO (17.4% to 14.2%) reflected the decrease in C18 fatty acids, which consisted mainly of oleic and linoleic acids (Tan and Oh, 1981). This was illustrated in the DSC thermograms where the melting curves showed that the crystals at 24 hr storage had more softer components, compared to the crystals of only 5 hr storage period.

TABLE 4a. DIGLYCERIDE AND TRIGLYCERIDE COMPOSITION (wt. %) OF PALM OLEIN DF 25 AND THEIR CRYSTALS AT 20°C

Triglyceride (hr)	Dg	OLL	PLL	MLP	OLO	PLO	PLP	OOO	POO	POP	SOO/PPP	POS	PPS	SOS
0	5.2	0.5	2.7	0.6	2.2	10.9	9.6	4.5	25.4	28.8	3.9	5.2	0.2	0.3
5	6.4	0.3	1.6	0.3	0.4	6.7	7.6	2.7	17.4	31.6	13.5	6.0	3.8	0.7
7	5.2	0.3	1.5	0.3	1.4	6.3	8.0	2.5	16.5	35.5	12.1	6.7	3.1	0.6
11	5.0	0.2	0.8	0.3	1.0	4.8	8.2	1.8	13.5	42.3	11.1	7.6	2.7	0.7
24	4.5	0.3	0.8	0.4	1.2	5.4	8.9	2.1	14.2	44.6	7.3	7.8	1.7	0.8

TABLE 4b. DIGLYCERIDE AND TRIGLYCERIDE COMPOSITION (wt. %) OF PALM OLEIN DF 9 AND THEIR CRYSTALS AT 5°C

Triglyceride (hr)	Dg	OLL	PLL	MLP	OLO	PLO	PLP	OOO	POO	POP	SOO/PPP	POS	PPS	SOS
0	8.6	0.7	3.9	0.7	2.7	14.9	10.1	5.4	32.6	14.2	3.6	2.4	0.1	0.1
11	11.6	0.5	3.0	0.7	2.2	12.6	9.9	4.9	29.9	17.5	3.5	3.2	0.2	0.3
12	11.3	0.5	2.9	0.6	2.2	12.1	10.0	4.8	30.1	18.1	3.5	3.3	0.2	0.4
13	10.8	0.7	2.9	0.6	2.3	12.5	10.2	4.8	29.6	18.4	3.4	3.3	0.1	0.4
14	10.6	0.7	3.0	0.7	2.1	12.5	10.4	4.8	29.6	18.5	3.4	3.2	0.1	0.4
16	10.4	0.7	3.0	0.7	2.2	12.3	10.6	4.7	29.2	19.0	3.3	3.4	0.2	0.3

The triglycerides for palm olein DF 9 *(Table 4b)* indicate high POO (32.6%), PLO (14.9%), POP (14.2%) and PLP (10.1%). In general, the increase in the different unsaturated triglycerides was marginal. Larger differences were noted in the PLO, POO and POP contents while the other triglycerides did not differ significantly. The POP content in the crystals was high at 19.0% after storage at 16 hr. The effect of such high melting components was no longer evident in the samples of 16 hr. This was due to the crystallization of more unsaturated triglycerides with time of storage, thus rendering the crystals softer with lower melting properties.

Table 5 shows the triglyceride compositions for samples A and B palm oleins at ambient conditions. The POP content for sample A olein was 29.0% while sample B had only 25.4%. After filtration, the crystals of sample A differed quite significantly from sample B. This was observed in the fact that the POP content of crystal A increased from 29% to 32.1%, while for crystal B, this triglyceride reduced from 25.4% to 16.3%. The POO and PLO content of crystals from both A and B were lower than in their oleins. These results support the FAC data where crystal B had a high palmitic acid content.

TABLE 5. TRIGLYCERIDE COMPOSITION (wt. %) OF PALM OLEIN A AND B AND THEIR CRYSTALS AT AMBIENT CONDITIONS (24°C-28°C)

Samples code	OLL	PLL	MLP	OLO	PLO	PLP	OOO	POO	POP	SOO	PPP	POS	PPS	SOS
Original sample A[a]	0.6	2.8	0.6	2.0	11.1	9.9	4.4	24.4	29.0	2.9	0.9	5.2	0.0	0.6
Sample A crystals[b]	0.3	1.4	0.3	1.0	6.1	7.7	4.1	13.3	32.1	1.4	12.3	5.3	3.4	0.3
Original sample B[b]	0.8	3.0	0.5	2.2	12.3	9.9	4.6	26.4	25.4	3.1	0.0	4.6	0.0	0.2
Sample B crystals[b]	0.6	2.0	0.3	1.4	7.8	6.3	2.9	16.8	16.3	2.0	0.0	3.0	0.0	0.1

Notes:
A: stored for two months.
B: stored for two years.
[a] before storage.
[b] after storage.

X-ray Diffraction Analysis and Microscope Observations

The crystals formed upon winterization were analysed by X-ray diffraction. The X-ray diffraction patterns helped to explain the divergency in properties between the different polymorphic forms.

X-ray diffraction analysis indicated that crystals of sample A were in beta (β) and beta prime (β') forms, while the crystals of sample B were in the beta form. The presence of the beta prime polymorphic form was confirmed by the X-ray short spacings around 3.74, 3.67 and 4.34 Å and two strong spacings at 3.91 and 4.18 A. However, sample B contained only one very strong spacing at 4.65 A. Long spacings were similar for samples A and B at 15.34 A.

The β' form occurs in the case of the 'mixed triglycerides. The melting points are intermediate between the a- and the β- modifications. The β' form in sample A was characterized by small, smooth and fine texture while suspensions of larger particles were noted in sample B.

On microscopical examination with the polarizing microscope, the crystals were found to be of various sizes and shapes. The crystals of sample A were mixtures of tiny and big crystals. This was due to the combination of β and β' polymorphic form. Occasionally, there was formation of a few clusters where the crystals aggregated. In contrast, the crystals of sample B were very large and stacked together to form bundles of β form. The β form was observed to be large, often over 50 µm. The β' form is usually associated with asymmetrical triglycerides, while β crystals are observed with symmetrical triglycerides.

CONCLUSION

The observations of this study showed that the composition and characteristics of crystals of palm olein obtained upon storage is dependent on the composition of the olein and the storage conditions. The triglyceride composition has a major role in the crystallization of palm olein during storage under different conditions. The high content of POP in relation to the lower melting components in palm olein can be a contributing factor to poorer cold stability. This was illustrated by the fact that the crystals not only contain the highest melting point triglyceride, PPP, but also, a substantial amount of POP triglyceride. While the triglyceride composition is the main factor affecting crystallization of the olein, there are nevertheless other factors which contribute to the cloudiness that occurs in the oil. The diglyceride content also has an influence on the crystallization of palm olein. The palm oleins containing higher amounts of diglycerides, especially 1,3 PP, tended to crystallize more easily than those with lower amounts. Furthermore, the crystals which contained a high proportion of diglyceride developed sharp high melting point endotherms.

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