Physical Properties of Oils and Mixtures of Oils

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ABSTRACT

The physical properties of palm, palm kernel and coconut oils are reviewed and compared and contrasted with the properties of other oils and fats. More information is available for palm oil than for the other two. The properties of mixtures of the oils also are considered, especially mixtures of palm and palm kernel oils in which a eutectic interaction occurs.

Basic physical properties considered are density, specific heat, heat of fusion and viscosity. Where appropriate, data is tabulated in SI and Imperial units.

Experimental methods used for determining melting points and solid fat contents are discussed and the empirical nature of the results emphasized. Wiley melting points and Slip melting points, and Solid Fat Content by NMR and Solid Fat Index by dilatometry, are compared and comparative data given. For palm oil, detailed olein and stearin information is presented.

The phase behavior and polymorphism of the three oils is reviewed. Special attention is given to the post-hardening phenomenon in palm oil and the effects of diglycerides and storage time on phase behavior.

INTRODUCTION

Physical properties of an oil or fat are of critical importance in determining its use. This is particularly true of the large quantity and variety of oils and fats used in various forms as food. Indeed, the separate words "oil" and "fat" occur in most languages and show that one fundamental physical property—whether the fat is liquid at ambient temperatures —has been recognized from the earliest times as of great importance.

A fat is a material that is composed of an intimate mixture of liquid and solid phases whose main constituents are triglycerides. The physical state of a fat may vary from a liquid to a viscous fluid to a plastic solid to a brittle solid. The three oils palm oil (PO), palm kernel oil (PK) and coconut oil (CN), together with their commercially available fractions, span the whole range of physical states. Furthermore, although they are called oils, presumably because they are mostly liquid at the ambient tropical temperatures where they are produced, they are mostly solid and treated as fats in the more temperate climates of the major industrial countries. These two features make their physical properties of particular interest and have resulted in their use in a wide range of special applications (1).

In this paper I propose to consider the basic physical properties, empirical physical properties and phase behavior and polymorphism. This is not an exhaustive list but will encompass most of the properties which are of interest. More detailed and extensive information can be found in various reviews and textbooks (2-4).

BASIC PHYSICAL PROPERTIES

Density

The density* of an oil depends on its saponification value (molecular weight), iodine value (unsaturation), free fatty acid content, water content and temperature. Approximately, density changes by $(4,5) + 0.3 \text{ kg/m}^3$ for each unit increase in saponification value; $+0.14 \text{ kg/m}^3$ for each unit increase in iodine value; -0.68 kg/m^3 for each degree C increase in temperature; -0.2 kg/m^3 for each 1% increase in free fatty acids, and $+0.8 \text{ kg/m}^3$ for each 1% increase in water.

These corrections refer only to determinations at the usual ambient and measuring temperatures, e.g. 20-60 C. Thus, for practical purposes the temperature is the most important variable.

Data for PO, PK and CN is limited and is reported at a variety of temperatures, sometimes as density and sometimes as specific gravity, so that comparison is difficult: PO, 0.891 g/ml at 50 C (6), 0.8919-0.8932 sg 50 C/25 C (7), 0.8957-0.8766 kg/l at 42-70 C (5); PK, 0.860-0.873 sg 99 C/15.5 C (4), 0.9195-0.8913 kg/l at 20-60 C (5); CN, 0.917-0.919 sg 25 C/15.5 C (4), 0.869-0.874 sg 99 C/15.5 C (4), 0.9219-0.8934 kg/l at 20-60 C (5), 1.12-7.06 $\times 10^{-4}$ T (g/cm³) over 30-60 C where T is temperature in K (40).

The most comprehensive study of the density of palm oil has been made by PORIM (8). Crude and RBD palm oil and olein were studied over the temperature range 25-75 C. Statistical analysis of the data showed no significant difference between the various oils, and the density could be expressed as density (g/ml) = 0.9244 - 0.00067 T, where T is the temperature in degrees Celsius. Typical Malaysian crude palm oil has a moisture content of 0.25% and free fatty acid content of 3%. Thus, the difference in density between RBD and crude oils would be expected to be only 0.0004 g/ml, and this small difference was not statistically significant compared with experimental error and natural variability of the various oils studied.

For reference purposes the available data has been referred to common temperatures and units using a temperature coefficient of -0.68 kg/m^3 and conversions between specific gravity and density as given by Cocks and van Rede (5) (Table I).

Densities of triglycerides in the solid state are approximately 10% greater than in the liquid state. Thus, on melting, expansion occurs which is the principle of the dilatometric method for determining solid fat content (9).

Specific Heat

Much data has been reported on specific heats of oils and fats, but none refers specifically to PO, PK or CN (4,7). In the solid state there is little change in the specific heat as the molecular weight varies, but there is an increase in specific heat with increase in iodine value (unsaturation). In the liquid state specific heat increases slightly with

TABLE I

Densities of Palm, Palm Kernel and Coconut Oils

Temperature		PO		Р	ĸ	CN		
С	F	kg/m³	lb/ft ³	kg/m³	lb/ft ³	kg/m³	lb/ft ³	
50	122	891	55.6	898	56.1	901	56.2	
75	167	874	54.6	881	55.0	884	55.2	
100	212	857	53.5	864	53.9	867	54.1	
200	392	789	49.3	796	49.7	799	49.9	

^{*}In this discussion the term density refers to the apparent density or weight by volume, assuming the oil is weighed in air. This is the most useful definition for practical purposes. The absolute density refers to the oil weighed in vacuum. The specific gravity = (weight in air of volume of oil at a given temperature $(T_1)/(weight$ in air of same volume of water at reference temperature (T_1)) and usually is written as sg T_1/T_2 to indicate the particular temperature. If T_1 and T_2 are the same, they often are omitted. A full discussion of this topic is given in reference (5).

molecular weight, but decreases slightly with iodine value. Overall, there is little variation among the natural oils and fats. For practical purposes the specific heats of liquid oils and fats, including PO, may be taken as:

0.47 + 0.00073T kcal/kg

where T is the temperature in degrees Celsius. Note: 1 Btu/ lb = 0.252 kcal/kg. There is no data available for PK and CN, but the above equation is probably satisfactory for practical purposes since the variation of specific heat with molecular weight is small.

Heat of Fusion

Although there is much published data on heats of fusion of pure triglycerides (10), there is only limited data on the heats of fusion of natural oils and fats. Recent work at PORIM (11) has provided useful data on the heats of fusion of PO, PK and CN, as shown in Table II. These values should be compared with milk fat (12) 17.7-22.3 kcals/kg, fully hardened milk fat (12), 24-31 kcal/kg, and cocoa butter (13) in the β' polymorph, 26-29 kcal/kg. As usually measured, heats of fusion are an empirical physical property dependent on the thermal pre-treatment or tempering given to the oil. The tempering procedure applied in the PORIM study would be expected to transform all the sample to the β' polymorph, but this was not checked independently.

Viscosity

Oils and fats show the flow behavior of true Newtonian liquids. Near the melting point non-Newtonian behavior may occur due to the presence of fat crystals. The viscosities of natural oils and fats do not differ greatly (4,40). Viscosity increases with molecular weight but decreases with increasing unsaturation and temperature. The viscosity of an oil decreases by approximately 30% for each 10 C rise in temperature.

Frying increases the viscosity of oils (14), and recently a viscosity test has been proposed for screening used frying oils (15). A viscosity of 45 cP at 50 C has been proposed as the maximum permissible for a used frying oil. For this test to be applied it is important to know the viscosity of freshly refined oils. Table III gives our recently determined data. By this criterion, the viscosity of an oil would approximately double before it would be rejected.

Blends of palm and palm kernel oils also were studied. Although blends of lauric and non-lauric oils are not normally used for frying, such blends show interesting and potentially useful eutectic effects (1,16). It was of interest to see if the interactions between the lauric and non-lauric oil also affect the viscosity. In Figure 1, viscosity and solid fat content (SFC) data are shown for blends of palm oil and palm kernel oil and palm olein and palm kernel oil. At all compositions the viscosity of the blend is lower than the viscosity expected by linear interpolation (dashed line), but the effect is unrelated to the eutectic interaction as shown by the SFC curves.

EMPIRICAL PHYSICAL PROPERTIES

Melting Point

Since fats are mixtures of many compounds, they exhibit a broad melting range rather than a clearly defined melting temperature. The melting point of a fat is thus an empirical property related to the experimental method of determination and not a basic physical property, like the melting point of a pure compound. The two commonest methods

TABLE II

Heats of Fusion of Palm, Palm Kernel and Coconut Oils (11)

	ΔH _f (kcal/kg)
RBD PO	22.6
RBD PK	29.7
RBD CN	26.0
Fully hardened PK	31.6
Fully hardened CN	31.2

Instrument: Perkin-Elmer DSC-2. Tempering procedure: 353K (10 min), cooled 10K/min to 293K and held 30 min, cooled 10K/ min to 223K and held 10 min. Measuring procedure: heated at 10K/min to 353K, reference indium.

TABLE III

Viscosity (cP) of Various Oils

	Temperature (C)						
Oil	20	25	30	35	40	45	50 ^b
Palm Palm olein Palm kernel Coconut	>100 ^a 85.3 >100 ^a >100 ^a	>100 ^a 69.2 >100 ^a 48.1	>100 ^a 56.3 44.0 39.8	96.3 ^a 43.4 35.6 32.9	40.4 38.6 30.0 27.4	33.3 32.6 25.4 23.3	27 26.5 21 19
Soybean	63.6	51.6	43.1	36.8	31.7	26.8	22.5

^aTurbulent, non-Newtonian flow occurred.

^bBy extrapolation, log(viscosity) vs. T.



FIG. 1. Viscosity and Solid Fat Content of blends of Palm Oil and Palm Kernel Oil, top, and Palm Olein and Palm Kernel Oil, bottom.

for determining the melting point (MP) of a fat are:

Slip Melting Point—The temperature at which fat in a capillary tube placed in water becomes soft enough to slip or rise up the tube. Also called open tube MP, rising point or softening point and exemplified by AOCS Method Cc 3-25.

Wiley Melting Point-The temperature at which a disc of fat becomes spherical when heated in an alcohol-water mixture. AOCS Method Cc 2-38.

The Wiley MP is very popular in the USA, but little used elsewhere. The Slip MP is used commonly in Europe and has been adopted in Malaysia as the preferred method for palm and palm kernel oil. Comparative values for Slip and Wiley MP's are shown in Table IV. Wiley MP's frequently are several degrees higher than Slip MP's. In the Slip MP test the fat slips in the capillary tube when about 5% solid fat is present. In the Wiley MP test the fat is sufficiently fluid to form a sphere only when the fat is almost fully liquid with about 1% solid fat still present.

Because there are substantial differences in MP's determined by different methods, it is important to distinguish carefully between the methods. Too often, papers in the literature or at conferences refer simply to Melting Point.

TABLE IV

Comparison	of Slip	(AOCS	Cc 3-25)	and	Wiley
(AOCS Cc 2	-28) Me	elting Po	oints		

	Slip	MP	Wil	ey MP
	С	F	С	F
RBD palm oil	36.3	97.3	41 9	107.4
RBD palm olein	22.8	73.0	25.8	78.4
RBD palm stearin	54.0	129.2	54.4	129.9
RBD palm kernel oil	27.6	817	32.1	89.8
NBD palm kernel stearin	32.0	89.6	34.2	93.6
RBD coconut oil	24.1	75.4	26.0	78.8
Hydrogenated palm kernel oil	40.0	104.0	45.1	113.2
Hydrogenated coconut oil	35.6	96.1	41 7	107 1
Hydrogenated palm oil	50.4	122.7	50.8	123.4
Cocoa butter substitute based on hydrogenated				
PK stearin	35.9	96.6	38.8	101.8

TABLE V

Variation of Slip Melting Point (C) of Palm Oil, Palm Olein, Palm Stearin and Palm Kernel Oil

Oil	Source of data	No. of samples	Mean	Range	
Crude palm kernel	PORIM (39)	118	27.3	25.9-28.0	
Crude palm oil	PORIM (37)	102	36.0	32.3-39.0	
Crude palm oil	MARDI (37)	215	34.2	30.8-37.6	
Crude palm oil	KEO (36)	300	35.6	33.6-37.2	
RBD palm oil	KEO (36)	36	36.1	34.0-39.0	
Crude & RBD palm olein ^a	PORIM (38)	193	21.6	19.4-23.5	
Crude palm olein ^b	KEO (36)	40	20.3	17.2-26.1	
RBD palm olein ^b	KEO (36)	35	21.5	19.0-23.0	
Crude & RBD palm stearin ^a	PORIM (38)	150	_	44.5-56.2	
Crude palm stearin ^b	KEO (36)	29	52.6	51.2-54.2	

^aAll fractionation processes.

^bDetergent fractionation only.

In Figure 2, Slip and Wiley MP's of blends of palm and palm kernel oils are compared. The substantially different shape of the two curves indicates that caution should be used in converting from one MP to the other by any "rule of thumb" method. Figure 2 also clearly demonstrates the empirical nature of the MP determination as discussed above.

There is little information available on the natural variation of coconut oil. In our experience, Malaysian coconut oil has a Slip MP of 23.5-25.5 C. Ranges of 23-26 C (17) and 20-28 C (18) have been given in the literature for the natural variation, but the latter range is not found in commercial samples.

Much more information is available for palm oil, olein and stearin and for palm kernel oil (Table V). The results from my own company (KEO) refer to weekly composite samples collected over a 12-month period. All means from



FIG. 2. Comparison of Slip and Wiley Melting Points for blends of Palm and Palm Kernel Oils.

this study are weighted according to the tonnage. For crude palm oil the KEO results agree closely with the PORIM results, suggesting that the MARDI results are too low. For palm olein, the KEO and PORIM results are similar again. For palm stearin, the PORIM survey covered all the fractionation processes used in Malaysia. The result is a very wide spread of MP's. The KEO results refer only to stearins produced by detergent fractionation and therefore show a narrower variation, with results at the upper end of the PORIM range.

In the PORIM and MARDI surveys, no systematic differences in MP (or other properties) were found between crude PO from different parts of Malaysia. In the KEO study, over 90% of the oils studied originated in Johore. The close agreement between the KEO and the PORIM data confirms PORIM's conclusions of little regional variation for Malaysian PO. Furthermore, except for one small parcel of PO from Sabah, there was no significant difference in the MP's or the iodine values of oils received from 10 major suppliers in the KEO study. This is further confirmation that Malaysian crude palm oil is a very uniform product.

In the KEO study, no significant correlation was found between MP's and iodine values for crude palm oils. This somewhat surprising result is attributed to (a) the effect of free fatty acids, (b) the possible effects of the introduction of the weevil, (c) a trend increase in the MP over the year studied (see below), (d) lack of homogeneity in a supplier's tank coupled with blending practices to keep the FFA of delivered oil below 5%. It should be noted that the period under study, from June 1982 to June 1983, was a period of tremendous change in Malaysian crude PO production and supply due to the combined effects of the introduction of the weevil and of the weather.

Although, as noted, Malaysian crude palm oil varies over a narrow range of properties, day to day and week to week fluctuations can be large and cover the whole range observed. In Figure 3 the variations of MP of crude PO received at KEO over the year studied are shown. Each point refers to the weighted mean MP for a week's deliveries of oil. A substantial part of the daily and weekly variation is due to inhomogeneity in a supplier's tank. After several weeks of storage, which happens all too frequently, stearin crystals sink to the bottom of the tank and the first oil to be pumped out is enriched in stearin and has a higher melting point.

Apart from these daily and weekly fluctuations there was a statistically significant upward trend in MP during the period. The trend regression line is shown in Figure 3. The trend line slope was 0.9 C rise per yr, and the average MP in the second six mo was 0.6 C higher than in the first six mo. This increase may have been due to the combined effects of the weevil and the weather. There is some evidence that a higher MP for Malaysian PO has persisted, leading to lower yields of palm olein on fractionation.

When palm stearins are considered, a relationship between MP and iodine value becomes clear. Results for palm oil and palm stearin are shown in Figure 4. PORIM has proposed using this relationship to assist in distinguishing between palm oil and stearin and to detect adulteration of PO with palm stearin.

The results in Table V and other results by PORIM and other workers show that MP's rise on refining.

Solid Fat Contents

The solid fat content (SFC) of a fat at a given temperature has until recent years been determined mainly by dilatometry (5,9).

European practice has been to use dilatations themselves in units of mm³ per 25 g. American practice has been



FIG. 3. Variation of Slip Melting Point for crude Palm Oil received over a year; weekly-composite analyses.



FIG. 4. Relationship between Slip Melting Point and Iodine Value for Palm Stearin and Palm Oil samples (taken from ref. 38).

to divide this dilation by 25 to give a "solid fat index" (SFI), which all too frequently is confused with the actual percentage of solid fat present. The American procedure assumes that all fats have the same total melting dilation (TMD), that it is $2500 \text{ mm}^3/25 \text{ g}$, and that its variation with temperature can be ignored. All these assumptions have long been known to be incorrect (9). In addition, American tempering practice was designed especially for hardened oils and includes a tempering at 80 F (26.7 C). This tempering procedure tends to lower the solid fat content at temperatures below 80 F and raise it above 80 F. It is generally unsuitable for PO, PK and CN and has not been adopted widely in Malaysia. Furthermore, the use of a TMD of 2500 means that SFI's for PO and PK based fats often are only about 80% of the true solid fat content and

even the hardest PK-based cocoa butter substitutes, with actual solid fat contents above 90%, do not show SFC's above about 75%.

In the last 10 yr, nuclear magnetic resonance spectrometry (NMR) has been used widely for the determination of SFC (19-23). The NMR method is quicker, more precise and closer to the absolute solid fat content than dilatometry. Laboratory instruments suitable for routine use in



FIG. 5. Comparison of Solid Fat Index by dilatometry (SFI), Solid Fat Index by NMR (SFI(N)) and Solid Fat Content by NMR (SFC).

TABLE VI

factory production and quality control became available in the early 1970's. In Europe, NMR has replaced dilatometry almost entirely, but in North America the adoption of NMR appears to have proceeded more slowly. In Malaysia, dilatometry has never become well established. Research institutes and refinery laboratories immediately adopted the new technology. Indeed in my own laboratory we only resort to dilatometry to provide results for potential American customers.

All the results given below as SFC's were obtained by NMR and used a "European" series tempering procedure as adopted by PORIM and used widely in Malaysia (0 C for 90 min, then 30 min at each measuring temperature, 10 C, 20 C, 25 C, etc.).

Figure 5 shows typical results for PK and hydrogenated PK comparing SFI, SFC by NMR and an SFI/NMR procedure in which the tempering was as SFI (AOCS Cd 10-57) but measurement was by NMR. At temperatures above 26.7 C there is little difference between the three methods, but at lower temperatures the differences are substantial.

In Table VI SFC data for PK and PO products is given. It should be compared with the MP data in Table V. As with the MP, refining increases the SFC of palm oil and fractions. This is due partly to the removal of free fatty acids, since adding back fatty acid distillate lowers the SFC's (Fig. 6). However, in some cases it appears that other changes due to refining are important, such as some rearrangement of the triglycerides or removal of phospholipids and monoglycerides, since we find that adding back the fatty acid distillate does not fully account for the change on refining.

There is no published data on the variation of the SFC of coconut oil. From experience at my own company, typical Malaysian CN has SFC at 10 C, 68-72%; at 20 C, 32-40%, at 25 C, 0-3%.

PHASE BEHAVIOR AND POLYMORPHISM

The phase behavior of fats (including palm, palm kernel and coconut oils) has been reviewed recently (2). This review should be referred to for more detailed information.

Palm Oil

Palm oil is unique among vegetable oils because of its high saturated acid content with a significant amount (10-16%) of saturated acids at the 2-position of its triglycerides. In

Solid Fat Content (% by NMR) of Palm Oi	, Palm Olein, Palm Stearin and Palm Kernel Oil

	Source of data	Temperature (C)							
		10	20	25	30	35	40	45	50
Crude palm kernel oil	PORIM (39)	67.6	40.1	17.1	0	_		-	-
Crude palm oil	PORIM (37)	48.5	21.8	13.4	9.3	6.6	4.2	_	-
Crude palm oil	MARD1 (37)	49.6	22.5	13.5	9.2	6.6	4.0	-	
Crude palm oil	KEO (36)	49.2	21.5	13.8	7.9	4.5	2.1	0.7	0.1
RBD + NBD palm oil	PORIM (37)	50.3	23.2	13.7	8.5	5.8	3.5	_	-
RBD palm oil	KEO (36)	53.1	24.7	15.5	9.1	5.7	2.0	1.1	0.1
Crude palm olein	PORIM (38)	33.6	3.2			-		-	-
Crude palm olein	KEO (36)	36.9	1.8	0.2	0	-		_	-
RBD + NBD palm olein	PORIM (38)	37.0	5.9		_				-
RBD palm olein	KEO (36)	37.6	4.5	0.9	0.3	0		-	-
Crude palm stearin	PORIM (38)	54.2 91.1	31.3 87.4	20.2 81.9	16.4— 73.5	12.5- 65.0	7.4 56.6	2.7- 48.6	0 39.7
Crude palm stearin	KEO (36)	76.8	68.0	61.2	50.3	42.6	35.7	29.3	19.0



FIG. 6. Effect of palm oil fatty acid distillate on the Solid Fat Content of RBD Palm Oil.

consequence, PO consists of three main types of triglyceride: trisaturated (mainly PPP), disaturated (mainly POP) and monosaturated (mainly POO). PO also contains appreciable amounts of diglycerides (5-8%) and free fatty acids (24-25), which can have a substantial effect on its physical properties.

Under normal ambient conditions (20-30 C), PO appears as a heterogeneous slurry of crystals (mainly PPP + POP) in a liquid oil (mainly POO + POP) (26,27). The separation of these phases is the basis of the large-scale fractionation processes applied to PO. These fractionation processes are relatively easy to operate, because the phases are more distinct than in other fats. If the fractionation process uses a solvent, three fractions roughly corresponding to the three main types of triglyceride may easily be separated.

A most useful and comprehensive study of the phase behavior of PO has been reported by Persmark, Melin and Stahl (28). In unfractionated PO three polymorphs were found:



Similar polymorphic behavior was found by Riiner (29) and by Berger and Wright (30). For practical purposes, when PO is used for margarines and shortenings and most other food uses, only the α -2 and β'_1 -2 polymorphs are

important. An important consideration here is that the time for the α polymorph to transform to β' (i.e. the α lifetime) is unusually long in PO, which has been shown to be due to the high level of diglycerides (28-31).

It is recognized that crystallization and development of an equilibrium SFC and hardness is relatively slow in PO compared to other oils, especially hardened oils, with similar MP. This phenomenon is called post-hardening and is a serious disadvantage in some applications of PO. The cause of post-hardening is not fully understood, but it is related to the peculiar triglyceride and phase composition of PO and to the presence of high levels of diglycerides. The rate of crystallization and polymorphic transformation in PO has been studied using differential scanning calorimetry and microscopy and a theoretical treatment developed (32,33).

As well as affecting the rates of crystallization and polymorphic transformation, diglycerides also affect the equilibrium solid fat contents (30,31). However, at the average level of diglycerides found in our study of Malaysian PO, 6.3%, the results of Berger and Wright (Fig. 7) showed no substantial effect. However, when the oil was stored for a long time there was a clear effect of diglycerides on the rate of crystallization, even at the levels normally found in PO (Fig. 8). (In fact, the oils used by Berger and Wright had



FIG. 7. Solid Fat Content after 10 days at 21 C of mixtures of triglycerides and diglycerides isolated from Palm Oil (taken from ref. 30).

FIG. 8. Effect of diglycerides on the rate of crystallization of palm oil triglycerides (taken from ref. 30). Sample worked in mini-votator •-•-•, Sample crystallized in NMR tube -----.

unusually low amounts of diglycerides, 3.7% and 5.4%, one oil being expressed directly from the fruit in the laboratory and the other a specially selected, Lotox, palm oil).

The results in Figure 8 also show that the final level of SFC and the rate at which it is attained are substantially affected by the crystallization method. Other oils do show a similar effect, but it seems to be particularly pronounced in PO.

Recent results from PORIM also show the post-hardening effect clearly and its strong dependence on the method of crystallization and the amount of working given to the sample (Fig. 9).

One practical consequence of the post-hardening of PO is shown in Figure 10, where the creaming power of a palmbased margarine is shown to be strongly dependent on storage time.

The rate of crystallization can be increased and the posthardening problem largely eliminated by interesterification.

Palm Kernel and Coconut Oils

These two lauric oils contain mainly saturated triglycerides, with the medium chain acids lauric and myristic predominating. The result is a very complex mixture of triglycerides with properties changing only slightly with fatty acid chain length from one triglyceride to the next, e.g. LMM, LMP, MMP and MMM. Both oils behave like a single phase and, although both can be fractionated, there is no clearcut phase separation as is found with PO. The polymorphism is correspondingly simple with a β' -2 polymorph occurring under almost all circumstances. An α phase can be obtained only by rapid cooling, and it easily transforms to the stable β' polymorph (29). It is possible that a β phase develops after several months (34). Hydrogenated PK and CN and their stearins show similar behavior. All lauric fats crystallize rapidly (35), which makes them ideally suited for confectionery coatings and molded compound chocolate products.

Mixtures of Palm, Palm Kernel and Coconut Oils

Because of molecular size differences, PO and the two lauric oils are incompatible with each other and form

FIG. 9. Penetration of RBD Palm Oil on storage at 20 C (taken from ref. 11).

eutectic mixtures (1,16). The eutectic interaction is clearly shown by the minima in the SFC and Slip MP curves in Figures 1 and 2.

Figure 11 shows a response surface diagram of the SFC of blends of palm stearin, palm olein and palm kernel oil. The eutectic interaction is indicated by the maximum in the iso-SFC lines, and it can be used to advantage in the blending of fats for many food uses. Formerly, lauric oils were used extensively in margarines. Now they are little

FIG. 10. Creaming power of margarine on storage (Creaming power = specific volume of standard batter after 6 min whipping under test conditions).

FIG. 11. Solid Fat Content at 10 C for blends of palm stearin, palm kernel olein and palm oil. Response curves calculated by multiple regression from blends prepared at 5-10% intervals (taken from ref. 1).

used due to their high prices relative to non-lauric oils.

It has been suggested that the eutectic interaction be used to advantage in the blending of oils for frying (16). Blends of PO and lauric oils were found to have lower MP's and better cold stability than the base oils. However, although the lower MP is potentially useful, blends of lauric and non-lauric oils are not usually recommended for frying because of excessive foaming.

Blends of PO and palm stearin and palm olein and palm stearin are used for shortenings, especially in Malaysia. However, even though all the components originate from PO it should not be expected that the physical properties of the blends are linearly related to the properties of the components. In theory, a logarithmic curve is expected (9). A curve is observed in practice, as shown in Figure 12.

FIG. 12. Slip Melting Points of blends of Palm Olein and Palm Stearin.

ACKNOWLEDGMENTS

I am grateful to E. M. Goh, F. H. Foo, N. C. Wong and their staff for experimental work, and to F.C.H. Oh (PORIM) for determining heats of fusion.

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Session II Discussion

The following questions, answers and comments were presented during the informal discussion held at the conclusion of the session.

- Q: When you measure "carotene" content, what do you mean? What analytical method was used?
- Goh: Carotenoids have to be analyzed by chromatography and UV visible measurement.
- Q: Would you kindly dwell a little further on the possible anticancer agent found in the minor constituents of palm oil? What is it specifically? What are the prospects so far? What types of cancer are affected by this/these agents?
- Goh: Anticancer agents in a protective sense are possible from carotenes and precursors of carotenes. There are many long term and short term experiments being carried out at PORIM for palm oil and for carotene rich foods in other countries.
- Q: The tocopherol contents in PFAD were given as 150-8500 ppm in one of your slides. Could you let us know what could be the causes of such wide variation?
- Goh: Tocopherols can be degraded thermally and by oxidation. Obviously, great care should be exercised during refining.
- Comment, K.G. Berger: The refining process affects the tocopherol level to a different extent due to a different deodorizer and the way it was used, especially the temperature. In the States, high deodorization temperature is used to remove the pesticides, but this is not necessary for palm oil.
- Q: We have observed in Honduras and Colombia the following: If one adds a little 85% phosphoric acid to a neutralized bleached palm oil and then centrifuges (in a laboratory), a dark precipitate forms. What kind of material can this be?
- Goh: The thing to note is that colloidal impurities are destabilized and can be precipitated. As to composition of the centrifuged product, one normally finds inorganic impurities (Fe, Ca, Mg, PO_4^2 , etc.) as well as organic impurities (cellulase, phenolic materials, etc.).
- Q: Is to copherol determination by the DPPH Method suitable for deodorized oil? If not, why?
- Goh: The DPPH method measures the total amount of reducing substances in the oil. It therefore may not indicate the true level of tocopherols and tocotrienols in palm oil in view of the fact that palm oil contains a number of unknown substances and also the possibility of the formation of reducing substances during the refining process.
- Q: The SFI and SFC data for palm oil and palm oil fractions are very different from each other. Since in formulation SFI is a very important parameter one would like to have comparable results. The AOCS SFI method states that it is valid only for fats having an SFI of less than 50 at 10 C, and most palm oil fractions have SFI over 50 at 10 C. Is there a modified SFI method for palm oil?

If so, please give details. What data are most representative of solid content at 40 C, SFI or SFC? Also, is there any correlation already established between SFI and SFC? Please comment.

- Timms: First, as far as I know there is no modified method for fats with SFI above 50. We and other people just use the method as given. Second, SFC by NMR is closer to the absolute content of solid than SFI, as explained in my talk. Data on SFI and SFC by NMR have been given in JAOCS by Madison and Hill, and others. Data on dilatometry and SFC have been given by workers from Unilever in Fette, Seifen, Anstrichmittel. (Detailed references and comments are given in my recent review in Progress in Lipid Research.)
- Q: In your slide showing variation in slip melting points, did you investigate if the lower melting points were due to lack of stabilization on account of higher FFA or diglycerides (DG)?
- Timms: No, we did not investigate if lower melting points (MPs) were due to lack of stabilization due to higher FFA and DG. However, it is not likely because there was no statistical correlation between DG and MP or FFA and MP, and we find that 4 hrs stabilization is adequate for palm oil; we used 16 hrs as recommended by PORIM.
- Comment, Dr. M.S.A. Kheiri: There is a correlation between C₄₈ and melting point.
- Q: The viscosity figures you show are up to 50 C only. At this temperature palm oil will still have some "memory" of its crystalline state. Viscosity is important for the drainage of fried foods, and is assessed at 100 C or higher for this purpose. Do you have any figures?
- Timms: All our 50 C data was obtained on oils previously heated to 80 C, so no internal memory should persist. We have not measured viscosity at 100 C because of the danger of oxidation. However, results up to 80 C have shown that the theoretical log (viscosity) vs. 1/T relationship is observed and so the results could be extrapolated to 100 C.
- Q: Has the speaker any views on the different NMR approaches adopted by Praxis and Bruker? Has he any view on the recently published AOCS method for SFC by pNMR?
- Timms: There are three instruments for NMR measurement: Praxis pulse; Newport continuous wave; and Bruker pulse. Both the Praxis and the Newport measure only the liquid fat signal. Therefore, the sample has to be weighed, a reference oil has to be used and the SFC result is obtained only at the end of a series of readings at different temperatures. This is the so-called indirect method. The Bruker measures both solid and liquid fat signals. Therefore, there is no need to weigh the sample, and the SFC result is available immediately. This is the direct method and has been developed with and adopted by Unilever in Europe. The direct method uses an approximation in the calculation, but for practical purposes this does not produce significant errors. In any case the Bruker also may be used for indirect measurements. The AOCS tentative method for "SFI" by NMR refers only to the use of the Praxis instrument.