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✱ Factors Affecting Slip Melting Point of Palm Oil Products

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ABSTRACT

The effect of different factors affecting the slip melting point of palm oil has been evaluated. The most important factor appears to be the difference in tempering temperatures. The influence of different tempering temperatures on slip point values is, however, dependent on the nature of the sample. For hydrogenated oils and for some high-melting palm stearins, tempering has no effect. For palm oil and palm olein, higher melting points were obtained when tempering at the higher temperatures in the range of 4-15 C. For some soft stearins, however, lower melting points were obtained at the higher tempering temperatures. These effects are investigated with differential scanning calorimetry and an explanation is offered, based on phase diagrams. A secondary effect on the slip melting point was the height of fat in the capillary tube. Effects of using different methods of determination are also shown. Collaborative trials on a standard testing procedure, AOCS Cc3-25, revealed the inadequacy for palm oil of the temperature range of 4-10 C specified in the procedure and its fractions. Strict adherence to a fixed tempering temperature produced better precision and reproducibility among laboratories. Tempering at 10 ± 1 C is recommended.

INTRODUCTION

A number of standard procedures is available for the determination of the slip melting point of fats, e.g., AOCS Cc 3-25 and Cc 1-25 (1), British Standard 684 (2), Indian Standard 548 (3) and as described by Cocks and Van Rede

(4). The methods differ in important details as shown in Table I.

For some fats, pretreatment has an important effect on the value obtained, particularly when the fat shows polymorphic behavior. For example, the British Standard method 2 (2) recommends a special procedure for such fats, and it is well known that an elaborate procedure must be followed in the case of cocoa butter. The melting point of fats is an important item of many specifications used in trade and, in some countries, is an element of the legal definition of food products. Widespread conformity in methods and in the results obtained is therefore of importance to the oils and fats industry worldwide. This study was prompted by the large interlaboratory variations found in ring tests of the AOCS method Cc 3-25 (1) when applied to palm oil products.

EXPERIMENTAL PROCEDURES

Samples

Commercial samples of refined palm oil, palm olein, hydrogenated palm oil (IV 44.6), palm stearin of different iodine values, hydrogenated rapeseed (IV 79.9) and soybean oils (IV 75.8) and of Indian vanaspati were examined. The palm olein and stearin samples were obtained from the fractionation of palm oil on the commercial scale.

TABLE I
Differences Among Slip Point Methods

Methods	Internal diam. of capillary tubes	Tempering procedure	
		Initial treatment	Further treatment
Cocks and Van Rede	0.9-1.1 mm	Chill against ice until solid	Hold at -10 C for 5 min
AOCS Cc 3-25	1 mm	Chill against ice until solid	Hold at 4-10 C for 16 hr
British Standard 684 Method 1	1.1-1.3 mm	Cool to 15 C	Hold at 15-17 C for 16 hr
	Method 2	Cool with stirring until a paste is formed Fill capillary tube with paste.	Hold at 15-19 C for at least 24 hr
Indian Standard 9.1	0.8-1.1 mm	Chill against ice until solid	Hold at 4-10 C for 1 hr

TABLE II

Slip Point Values (C) Using Different Methods

Methods	Palm oil	Palm olein	Palm stearin (high melting point)	Hydrogenated		
				Soyabean	Rapeseed	Palm oil
1. Cocks & Van Rede	40.4, 39.0, <u>41.7</u>	20.7, 10.5	50.9, 50.4	32.4	<u>33.1</u>	40.9, 40.8
2. AOCS Cc 3-25	36.2, 35.2, <u>37.5</u>	<u>21.8</u> , 19.9	<u>51.4</u> , 50.7	<u>32.4</u>	33.8	<u>41.5</u> , 40.9
3. BS 1.3						
Method 1	36.5, 35.9, 38.0	— —	51.2, <u>49.3</u>	33.1	34.0	<u>40.1</u> , 40.3
4. BS 1.3						
Method 2	34.5, <u>33.0</u> , 35.6	— —	50.9, 49.4	<u>33.5</u>	<u>34.7</u>	40.6, 40.7
5. IS 9.1	36.4, 35.8, 38.0	20.4, <u>10.0</u>	51.1, 51.0	<u>32.4</u>	<u>33.9</u>	40.9, 41.0

Methods

Slip melting points were determined according to the methods quoted, but using tubes of internal diameter (id) 1.1-1.2 mm throughout.

The AOCS method Cc 3-15 was studied in detail by varying the diameter of tubes, the height of fat in the tubes and the tempering temperature and time.

Differential scanning calorimeter (DSC) melting curves were determined using the Perkin Elmer DSC II calorimeter fitted with Intracooler II. Samples (10-mg) were sealed into volatile sample pans and pretreated by the chosen tempering procedures. Melting thermograms were obtained by heating the sample from the tempering temperature to complete melting at 1.25 C/min.

The triglyceride composition was analyzed according to carbon number using a glass column (46 cm × 3 mm id) of 1% Dexsil 300 on 100-120 mesh Supelcoport (Supelco) in a Pye 104 gas chromatograph. Column temperature was programmed from 255 to 355 C at 6 C/min with a nitrogen flow rate of 80 cm³/min. The injector temperature was set at 310 C. The detector temperature was set at 350 C, i.e., 10 C above the elution temperature of the last peak. Peak areas of the triglycerides were estimated by multiplying the peak height by the peak width at half-height. For calibration, an interesterified palm oil mixture was used. Typical molar response factors obtained were C46 (1.33), C48 (1.31), C50 (0.93), C52 (0.90) and C54 (1.21). The precision of the method from 10 replicate analyses of the standard mixture is shown by the following results in terms of peak area percentage:

	Mean	SD	CV (%)
C46	0.68	0.078	11.5
48	9.35	0.259	2.8
50	37.42	0.249	0.7
52	41.11	0.354	0.9
54	11.44	0.291	2.5

RESULTS AND DISCUSSION

Different Methods

The slip melting point of palm oil products determined by the different methods is shown in Table II. For each sample, the highest and the lowest figure of each set of results is underlined. It is concluded that the variation among methods is unsatisfactorily large for palm oil and palm olein, but is probably acceptable for the other samples. It is of interest to note that for palm oil the quick method of Cocks and Van Rede (4) gives the highest results. For palm olein, it is evident that the short tempering periods of Cocks and Van Rede and of the Indian Standard do not always allow for adequate crystallization. The tempering temperature of the British Standard methods is too high to be suitable for oleins (mostly melting at 17-23 C).

Height of Fat Column

Melting points determined with different heights of the fat column in the capillary tube are shown in Table III. For all the samples examined, the higher fat columns gave higher results, and this effect was particularly significant in the case of palm oil, where a difference of only 2 mm is important.

Effect of Tube Diameter

Two sizes of capillary tube were compared, differing widely in id and wall thickness. The results are given in Table IV. No significant effect was obtained.

Effect of Tempering Time

Very little difference was observed in slip melting point when tempering times were varied between 1 and 16 hr for all samples except palm oleins. Here, as already stated, 1 hr proved insufficient but 8 hr or more was adequate.

Effect of Temperature of Tempering

Samples were tempered for 16 hr under the following conditions: (a) -10 C, freezer; (b) 4 C, thermostated waterbath; (c) 10 C, refrigerator; (d) 10 C, thermostated waterbath; (e) 15 C, thermostated waterbath. A range of 4-10 C is specified by the AOCS Cc 3-25, whereas 15 C is specified by the British standards.

Results for various palm oil products and for vanaspati are summarized in Figure 1. The melting point of vanaspati (see curves V1 and V2) was insensitive to tempering, as were the various hydrogenated oils (not shown in Fig. 1). Palm stearin of high melting point is also insensitive to tempering (see curve marked IV 36.5). On the other hand, palm stearin of lower melting point falls into 2 classes, some of which are insensitive to tempering (curves marked IV 46.4 and 46.1), whereas others give higher melting points at the lower tempering temperatures (curves marked IV 46.0, 48.0, 49.5).

Palm oils and palm oleins, on the other hand, show significantly higher melting points after the higher temper-

TABLE III

Effect of Different Levels of Fat Column in Capillary Tubes^a on Melting Point (C)

Sample				Difference between 7 mm + 12 mm
	7 mm	10 mm	12 mm	
Palm oil 1	33.9	35.1	35.6	1.7
Palm oil 2	35.2	36.3	36.9	1.7
Palm olein 1	20.6	20.3	20.9	0.3
Palm olein 2	20.2	20.8	20.7	0.5
Palm stearin	39.9	40.5	40.8	0.9

^aUsing AOCS Cc 3-25.

ing temperatures. This behavior was further studied by obtaining DSC melting thermograms of these samples after the relevant treatments. Figure 2 shows the thermograms obtained for palm oil. While there is little change in the temperature of complete melting, there are large differences in the amount of crystalline solid developed during the tempering process. A progressive increase in the proportion of solid phase is seen, the developing phase apparently being of intermediate melting point with a peak at about 26 C.

Figure 3 shows the melting curves for palm olein, where there is only ill-defined solid formation at tempering temperatures below 10 C. Figure 4 shows the melting thermograms for those soft stearins with anomalous tempering behavior. It appears that, at the low tempering

temperature, a high melting phase is produced, which is responsible for the higher melting points observed under these conditions. A possible explanation of this behavior can be deduced from consideration of simple binary phase diagrams for the α and β' forms (Fig. 5).

If we assume that the palm stearin tempered at the lower temperature has solidified with a high proportion of α phase, then, in the course of heating in the DSC experiment, the α phase will give rise to a liquid and a solid phase of different compositions as it begins to melt, as indicated by the dotted lines. The liquid phase is metastable, recrystallizes in β' form and gives rise to the low melting point phase. The α solid, upon continued heating, transforms into a β' solid phase of a higher melting point.

On the other hand, palm stearins tempered at the higher

TABLE IV

Effect of Different Tube Diameter and Thickness on Slip Point^a

Sample	Size of capillary tubes		Difference
	Internal diam. 1.2 mm; wall thickness 0.20 ± 0.02 mm	Internal diam. 2 mm; wall thickness ca. 0.4 mm	
Palm oil			
3	37.5	37.3	+0.2
4	36.4	36.2	+0.2
Palm olein			
3	22.0	22.3	-0.3
4	21.3	21.3	0
Palm stearin			
A	51.5	52.3	+0.2
B	51.9	52.2	-0.3
Hydrogenated palm oil			
A	41.5	41.4	+0.1
B	40.9	40.6	+0.3
C	43.9	44.1	-0.2

^aUsing AOCS Cc 3-25.

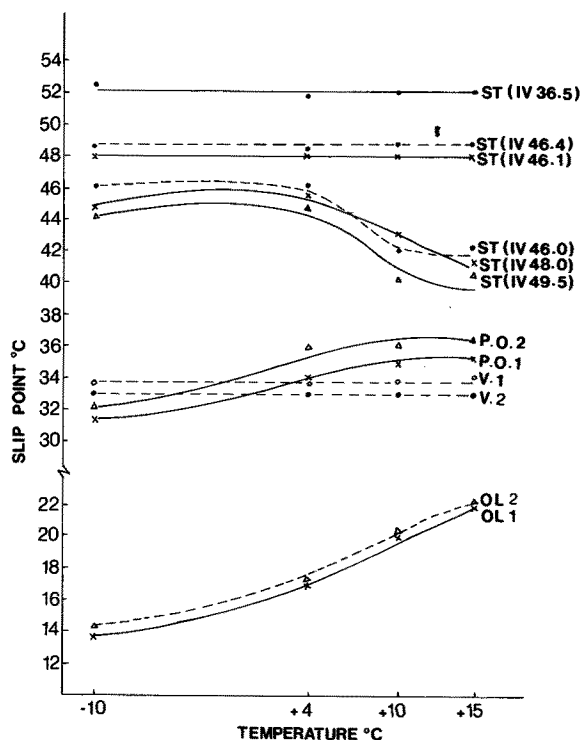


FIG. 1. Effect of tempering temperature on slip melting point. ST = palm stearin, PO = palm oil, V = vanaspati, OL = palm olein.

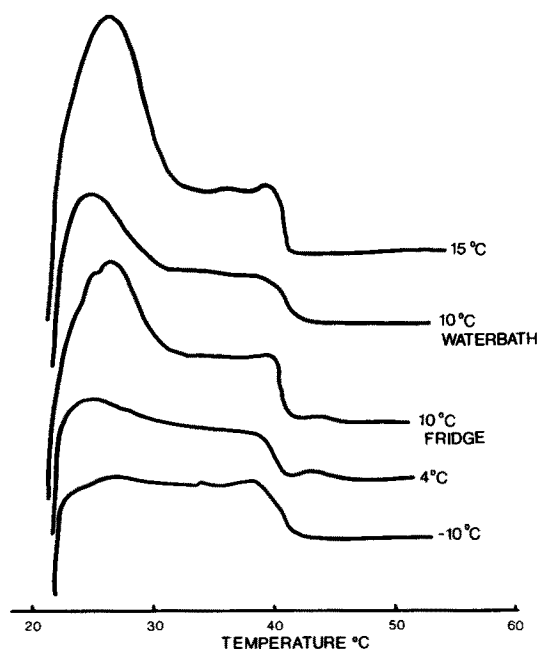


FIG. 2. DSC melting thermograms of palm oil. The palm oil was tempered under the conditions specified at the right-hand side.

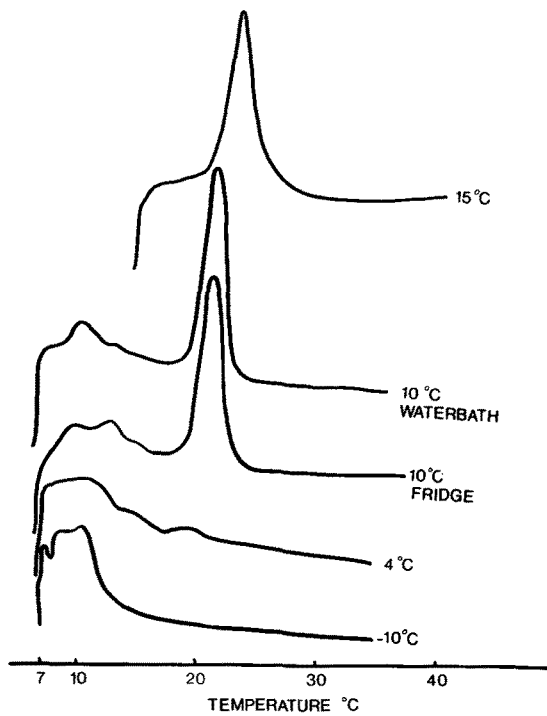


FIG. 3. DSC melting thermograms of palm olein. The palm olein was tempered under the conditions specified at the right-hand side.

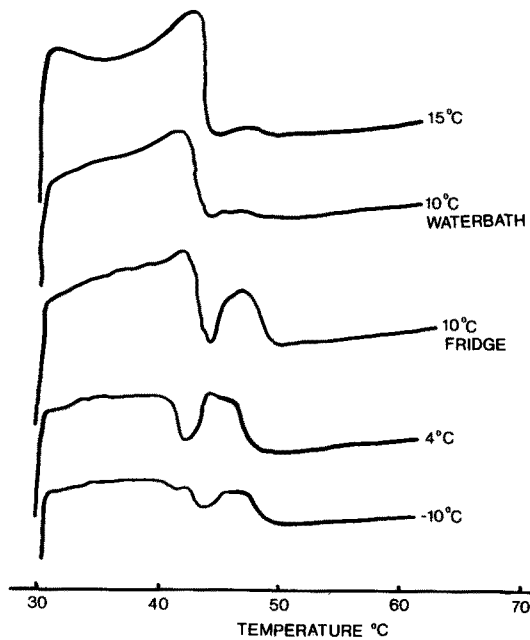


FIG. 4. DSC melting thermograms of soft stearin sample A. The palm stearin was tempered under the conditions specified at the right-hand side.

temperature, indicated by X in Figure 5, will be mainly in a β' phase of intermediate composition and lower melting point. The difference between the curves obtained by tempering in a refrigerator, with temperature cycling over a fairly wide range, and by tempering in a more closely controlled waterbath is noteworthy.

Figure 6 shows the thermograms obtained for a soft stearin whose slip melting point was insensitive to tempering. A substantial amount of high melting phase was developed at all temperatures, although the treatments at 10 and

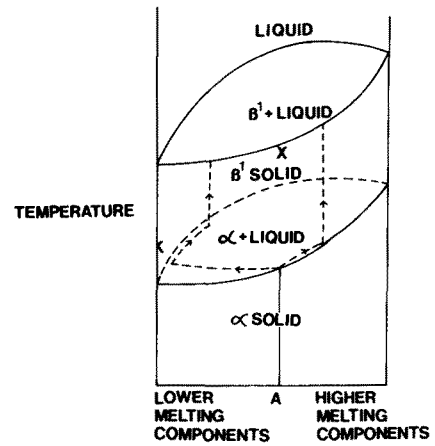


FIG. 5. Binary phase diagram of α and β' forms. A sample of composition A, tempered in the α form, follows the path indicated by the continuous and dashed lines as temperature rises. X indicates the starting point of a sample of the same composition, tempered in the β' state.

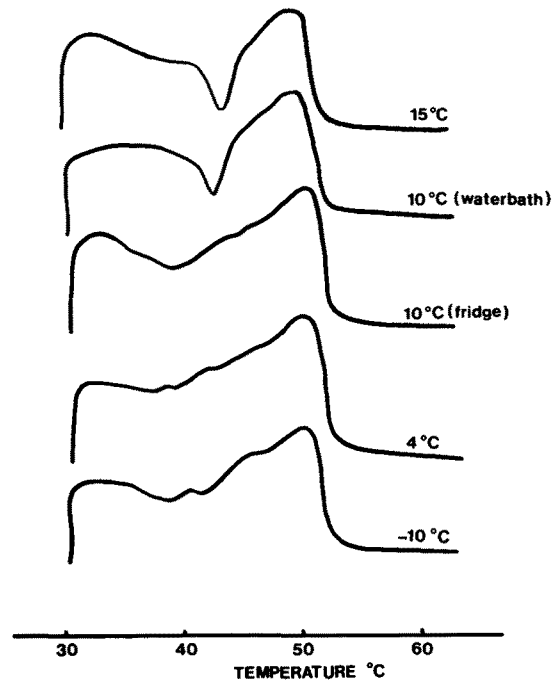


FIG. 6. DSC melting thermogram of soft stearin sample 81CS. The palm stearin was tempered under the conditions specified at the right-hand side.

15 C have also enabled a more pronounced lower temperature phase to develop, presumably of a similar composition to the phase noted in Figure 4. Thermograms of the high melting point stearin showed only one sharp peak, independent of tempering procedure.

The 2 types of soft stearin were analyzed for their triglyceride composition by GLC of the whole triglycerides. The analyses of a number of samples, including those shown in Figures 4 and 6, are given in Table V. The most significant compositional differences between the 2 types are in the C48 and C52 contents.

The "sensitive" stearins have a lower C48 content representing mainly tripalmitin, and a higher C52 content. The latter, representing mainly POO, would probably encourage the development of α crystallinity, whereas the higher C48 content of the second group of stearins would

TABLE V

Triglyceride Composition of Soft Palm Stearins:
(a) Slip Point Sensitive to Tempering

Triglyceride carbon number	Stearins IV 48-49			Stearins IV 46-47		
	63CS	143CS	65CS	A ^a	127CS	128CS
C46	0.8	0.8	1.6	1.1	1.0	1.1
C48	12.8	8.2	12.2	10.8	9.9	12.4
C50	42.2	48.9	43.4	43.0	49.8	48.0
C52	36.0	35.7	35.5	36.6	33.9	33.2
C54	8.2	6.3	7.2	8.5	5.4	5.2
Slip point after tempering at 4 C	45.1	44.2	46.0	45.5	44.6	45.8
at 10 C	41.8	40.0	42.4	40.4	39.7	43.7

(b) Slip Point Not Sensitive to Tempering

Triglyceride carbon number	Stearins IV 46-47		
	125CS	98CS	81CS ^a
C46	1.2	1.5	1.3
C48	14.0	16.2	19.4
C50	47.5	45.4	41.8
C52	32.3	30.0	30.9
C54	5.0	6.9	6.6
Slip point after tempering: at 4 C	46.1	48.0	48.2
at 10 C	46.1	48.1	49.6

^aDSC Melting Thermogram is shown in Figs. 4 and 5.

TABLE VI

Precision of Slip Point of Palm Oil and Its Fractions:
**(a) Tempering at 10 C in a Refrigerator and (b) Tempering at
 10 C in a Thermostated Waterbath**

	Palm oil		Palm stearin		Palm olein	
	(a)	(b)	(a)	(b)	(a)	(b)
Mean	37.5	37.2	52.3	52.9	20.4	20.9
Standard deviation	0.27	0.18	0.19	0.09	0.14	0.08
Coeff. of variation	0.72	0.47	0.36	0.18	0.68	0.37
Least significant difference (95% confidence)	0.75	0.50	0.52	0.25	0.39	0.22

TABLE VII

Reproducibility of Slip Melting Point

	Expected agreement of single determinations ^a	
	Within laboratory	Between laboratories
Palm oil		
1st test 41 results	1.8	6.4
1st test 35 results ^b	0.8	3.9
2nd test	0.8	2.4
Palm olein		
1st test 41 results	0.6	5.9
1st test 35 results ^b	0.6	6.1
2nd test	0.5	1.9
Palm stearin		
1st test 41 results	1.3	1.9
1st test 35 results ^b	0.8	2.6
2nd test	0.5	1.6

^aCalculated according to AOCS MI-59.

^bEliminating those laboratories using freezer for tempering.

encourage earlier crystallization at a higher temperature and formation of more stable crystalline phases. The composition of these groups of products therefore seems to be poised on either side of a critical point regarding crystallizing behavior. Even a small change in composition will encourage earlier crystallization.

Precision of Slip Melting Point of Palm Oil Products

A comparison was made between the use of an accurate thermostat bath and a refrigerator set at 10 C. The results of 10 replicates are shown in Table VI. It is clear that a significant improvement in repeatability is obtained by using the thermostat.

Results Obtained in Ring Test

The results of 2 ring tests of slip melting point done on palm oil products are summarized in Table VII. In the first test, 41 laboratories reported. The AOCS method Cc 3-25 was circulated to them, but no special emphasis was placed on tempering, and subsequently it was found that some laboratories tempered samples in a freezer at -10 C. In the second test, 13 laboratories took part, all using a thermo-

stat bath for tempering. Table VII records the expected agreement between 2 single determinations within and between laboratories calculated according to AOCS M1-59. For the first ring test, the results for all laboratories are compared with those for laboratories not tempering at freezer temperatures. A significant improvement in the expected agreement is obtained. A further improvement resulted in the second ring test in which a thermostat bath was used.

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