A Kinetic Study on Isothermal Crystallization of Palm Oil by Solid Fat Content Measurements

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Isothermal crystallization of palm oil was studied by means of differential scanning calorimetry (DSC) as well as by nuclear magnetic resonance spectrometry to monitor its solid fat content (SFC). The temperature of crystallization (Tc) varied from 0 to 30°C, depending on the method used. The plot of %SFC vs. time at 25°C was sigmoidal in shape. However, at lower temperatures, two consecutive curves were clearly visible. Results from DSC experiments showed the following interesting features. At each Tc, the crystals produced were of different compositions. From 0 to 8°C, the thermogram showed three peaks, with the first two peaks (I and II) sharp, and the third (III) rather broad. At elevated temperatures up to 20°C, peak II disappeared totally while peak III tended to shift toward peak I. Above 20°C, both peaks shifted downward to longer times. Peak I continued to be broadened, and then suddenly disappeared at Tc above 24°C. The melting thermograms of the crystals obtained above and below this cut-off point were distinctly different. Kinetic studies on isothermal crystallization based on the data of SFC measurements showed that the data fit well into the Avrami-Erofeev equation with n = 3 over the first 70% of the crystallization.

KEY WORDS: Crystallization, kinetics, palm oil, solid fat content.

Palm oil is a multicomponent natural product comprised of more than twelve different triglycerides, which make up as much as 94% by weight of the oil. In addition, it also contains 5% diglycerides. Despite its complexity in composition, its crystallization behavior is rather simple. For instance, its differential scanning calorimetry (DSC) cooling thermogram exhibits only two exotherms (1). The high-T and low-T exotherms correspond to the "hard" and "soft" components, respectively, of the oil. Previous investigations on crystallization of the oil focused mainly on polymorphism of the crystal by means of DSC, X-ray diffraction and photomicroscopic techniques (2–5). Three polymorphic crystals, designated as α, β′ and β with increasing melting points, were identified. There has been a growing interest in the kinetics of crystallization by measurement of induction time (1), both in nucleus formation (6) and in the enthalpy change (5,7). This paper describes the kinetics of isothermal crystallization of palm oil by measurements of its solid fat content from 0 to 30°C.

EXPERIMENTAL PROCEDURES

A typical Malaysian palm oil [iodine value (IV) = 52.5] was used. Pretreatment of the sample was previously described (1). A Perkin-Elmer DSC-2 differential scanning calorimeter, complete with a data station and plotter (Perkin-Elmer, Norwalk, CT), was used to obtain thermograms that were calibrated with cyclohexane as a standard. For isothermal runs, the sample at 353°K (80°C) was cooled rapidly to a preset temperature (0–30°C) and held at that temperature for crystallization. A chart recorder was used to display the signals. At the end of crystallization, the sample was then heated at a rate of 5°K/min to obtain its melting thermogram. For solid fat content (SFC) measurements, a Newport Analyzer MK IIIA wide-line NMR spectrometer with an analogue computation unit (Newport Instruments Ltd., Newport Pagnell, Buckinghamshire, England) was used. Optimum instrument settings have been described elsewhere (8). Triolein, 99% pure (Sigma Chemical Co., St. Louis, MO), was used as reference. The %SFC was calculated from the formula:

$$\%\text{SFC} = 100[1 - (\frac{R_{80}}{S_{80}R_T})\, S_T] \qquad [1]$$

where R and S denote reference and sample, respectively, and the subscript indicates the temperature in °C. Readings were taken with an integration time of 8 s.

RESULTS AND DISCUSSION

Degree of supercooling. A pure tripalmitin, when supercooled to a temperature (Tc, temperature of crystallization) well below its β melting point (Tm), undergoes crystallization easily (9) because the system is in a labile state. The driving force for a supercooled melt to undergo crystallization is provided by the degree of supercooling ΔT, which is the difference between Tm and Tc. Figure 1 shows the

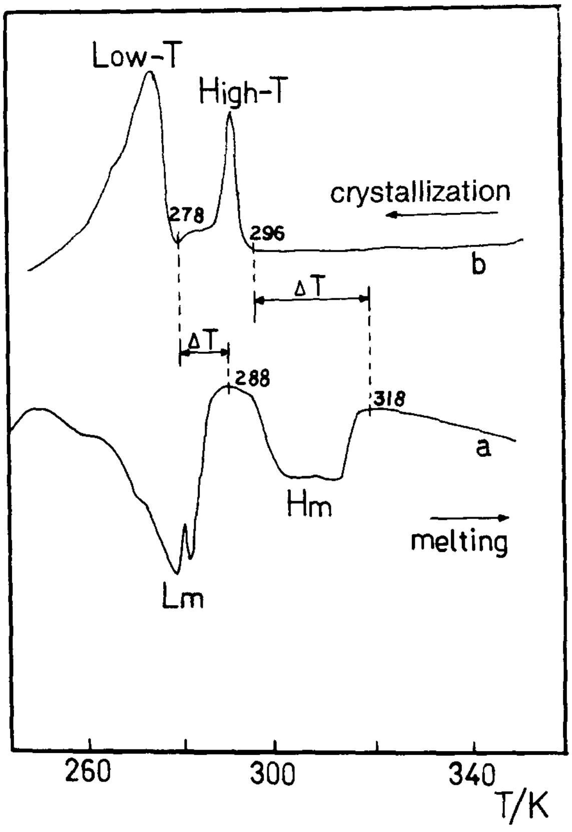

FIG. 1. Dynamic differential scanning calorimetry melting (curve a) and cooling (curve b) thermograms at a rate of 5°K/min.

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melting profile (curve a) of solid palm oil, which was heated up from 240°K at a rate of 5°K/min. Two broad endotherms, barely separable at 288°K, are clearly visible. They probably correspond to the low-T and high-T exotherms, respectively, in curve b. Although the high-T exotherm in its cooling profile (curve b) is rather sharp, its melting endotherm shows considerable broadening, which covers a wide range (30°) of temperatures. On the other hand, the broadening of the low-T endotherm is even more extensive, ranging from 240 to 288°K. Based on the result of Figure 1, palm oil can thus be considered to be made up of two distinct fractions of different melting range. We label them as the low-melting (Lm) fraction and the high-melting (Hm) fraction in increasing order of their melting range (see curve a, Fig. 1). The highest melting points for the Lm and Hm fractions were 288 and 318°K, respectively. This was determined by the interception of the tangent to the endotherm and the base line (curve a, Fig. 1). In the dynamic cooling experiment at a rate of 5°K/min, crystallization began when the oil temperature reached 296°K. This corresponds to a supercooling of 22°K with respect to the Hm fraction. The presence of this Hm crystal could then serve as seeding (10) in the Lm melt, causing the latter to undergo heterogeneous nucleation. Thus, the second crystallization occurred at 278°K, which corresponds to a much smaller supercooling of only 10°K, with respect to the Lm fraction.

Isothermal thermogram. The kinetics of isothermal nucleation (1) above 300°K conformed closely to the Fisher-Turbull equation:

$$J = (NkT/h) \exp(-\Delta Gd/kT) \exp(-\Delta Gc/kT) \qquad [2]$$

where ΔGd and ΔGc are, respectively, the activation free energy of diffusion and nucleation. In general, ΔGc depends on the enthalpy of fusion ΔH and melting point Tm, as well as on the supercooling ΔT as given by (11):

$$\Delta Gc = (16/3)\, \pi\sigma^3 Tm^2/(\Delta H)^2(\Delta T)^2 \qquad [3]$$

When its isothermal crystallization was conducted at much lower temperatures, crystals of widely differing composition were produced at different Tc's. Thus, each thermogram depicted in Figure 2 is actually characteristic of its own crystal produced. In general, the thermograms show the occurrence of three exotherms that are well separated from each other. At 0°C, peak I is almost instantaneous, and peak II follows immediately after it. They are both sharp and are followed by a broad peak, peak III. Peak I remained unchanged while peak II continued to diminish in intensity. It finally vanished at Tc values above 8°C. In the meantime, peak III moved steadily toward longer time. Figure 3 shows the unusual behavior of peak III. It moved upward to a shorter time even though crystallization was conducted at elevated Tc. Kinetically, this means that for a crystal of peak III, the lower the supercooling, the faster the nucleation rate. This is in contradiction to normal kinetic theory unless the crystals produced in this temperature range are all having different melting points. However, it is not possible at this stage to offer any explanation until further work has been done to isolate the crystals and fully characterize their compositions.

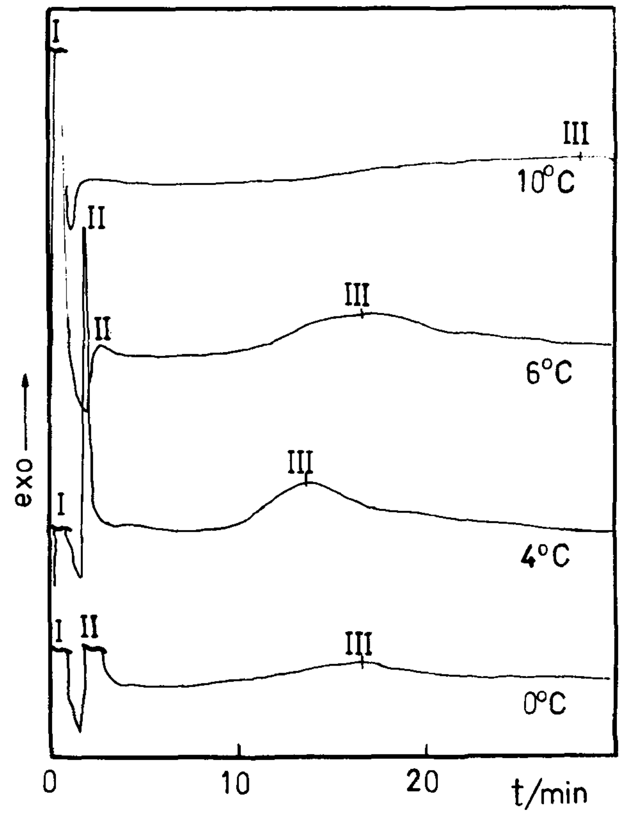

FIG. 2. Isothermal differential scanning calorimetry crystallization thermogram of palm oil at various temperatures from 0 to 10°C. There are two sharp exothermic peaks (I and II) and a broad peak (III). A short vertical bar marks the position of the peak.

In Figure 4, both peaks I and III begin to broaden and shift steadily downward to longer time. Finally, at 24°C, peak I disappears totally, leaving peak III as the only exotherm remaining in the isothermal crystallization profile. At higher temperatures, peak III continues to broaden. This peculiar behavior can be understood in light of the composition of the crystals produced. At the end of each crystallization, the sample was heated to obtain its melting profile. Table 1 summarizes the position of the peaks that appear in the Hm fraction of its melting thermograms. Figure 5 shows the melting thermograms of the crystals produced at the end of each crystallization. The high-melting endotherm is basically made up of at least four peaks, which, though overlapping, are clearly discernible. They are labelled as P, Q, R and S in increasing order of temperature. The relative height of these peaks varies greatly and is Tc-dependent. For instance, at lower Tc, there is a larger proportion of P and Q at the expense of R and S, while the reverse is true for crystals produced at a higher Tc. At 25°C and above (see Table 1), crystals do not have component Q, whereas those created below it contain all the four components. Thus, component Q is exclusively associated with peak I, and components R and S are responsible for peak II. This cut-off temperature of 24°C, as seen in Figure 2, for the disappearance of peak I, is supported by induction time measurements (1), which also display a discontinuity in the nucleation plot of palm oil at 25°C.

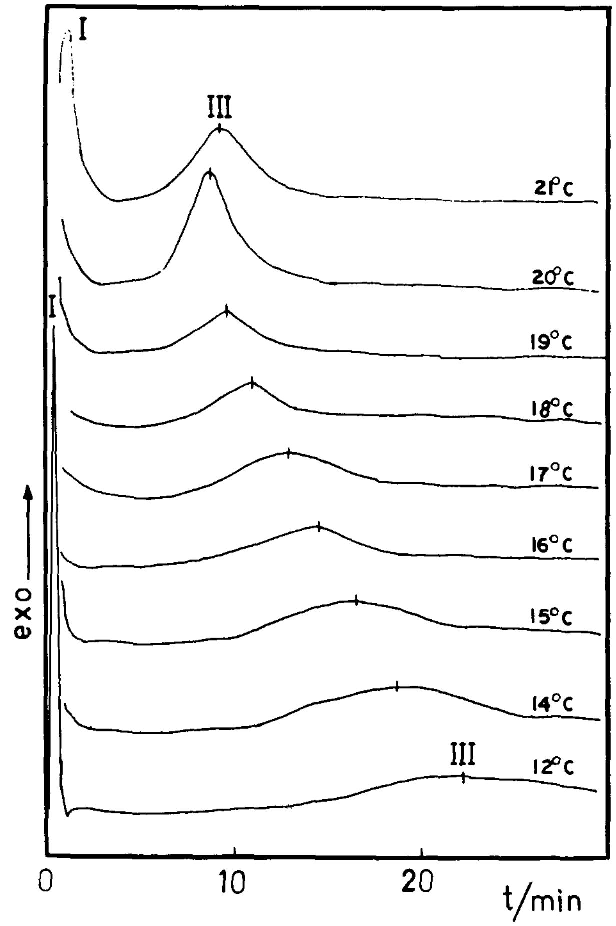

FIG. 3. Isothermal differential scanning calorimetry crystallization thermogram of palm oil at various temperatures from 12 to 21°C.

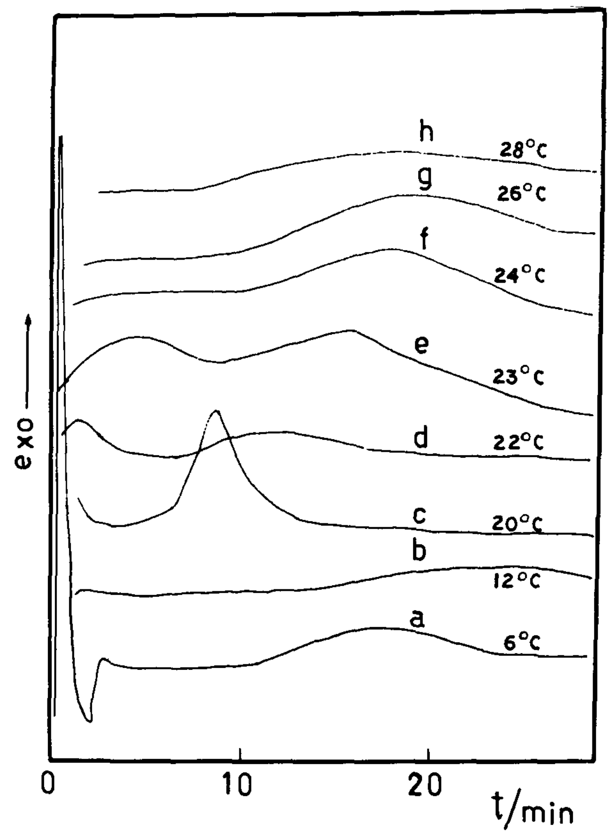

FIG. 4. Isothermal differential scanning calorimetry crystallization thermogram of palm oil at various temperatures from 6 to 28°C.

Crystallization curve by SFC. Figure 6 is a plot of %SFC vs. time for the various isothermal runs from 5 to 25°C. A step is clearly visible in all curves except in the one at 25°C. The first step decreases steadily both in rate and height as Tc is raised. It finally disappears at 25°C. This cut-off point coincides with that found in our DSC findings of 24°C, as described earlier. The second step of crystallization is sigmoidal in shape. This tends to suggest that its kinetics might follow that of Avrami (12), which is based on three-dimensional random nucleation, followed by a uniform linear growth of the nuclei:

$$-\ln(1 - f) = (6\sigma N_o k_2{}^3/V_o k_1{}^3)\exp(-k_1 t) - 1 + k_1 t - (k_1 t)^2/2! + (k_1 t)^3/3! \quad [4]$$

where f is the fractional crystallization, V_o the final volume of the crystal and N_o the total number of potential nucleus forming sites at t = 0. This nonlinear equation can be simplified under two limiting conditions of $k_1 t << 1$ or $k_1 t >> 1$. The final version is known as the Avrami-Erofeev equation (13):

$$-\ln(1 - f) = (k_n t)^n \quad [5]$$

where n = 3 or 4 and represents the index of the reaction.

TABLE 1

Melting Thermogram of Palm Oil After Isothermal Crystallization at Temperatures of Crystallization (Tc)

	Melting peaks (°K)			
Tc (°C)	P[a]	Q[a]	R[a]	S[a]
0	288	292	310	318
4	289	296	312	319
8	288	297	312	319
12	290	299	313	318
17	294	304	313	318
25	—	304	310	319
27	—	306	312	—
30	—	—	310	316

[a] See text for further details.

We have tried to determine the value of n by plotting $\ln[-\ln(1 - f)]$ vs. ln t for all the runs below 25°C. The plot gave a good straight line. The value of n, as determined from the slope, fell between 3.0–3.2. Because n has to be an integral number, its value was then rounded off to 3. Fitting of the experimental data to the kinetic equation was then carried out by plotting $[-\ln(1 - f)]^{1/n}$ vs. t. Figure 7 shows that the SFC data fit the equation well over the range of fractional crystallization, f, from 0 to 0.7. The kinetic parameters are summarized in Table 2. The rate constant decreases initially between Tc = 5°C and Tc = 9°C. However, between 9 and 20°C, its value

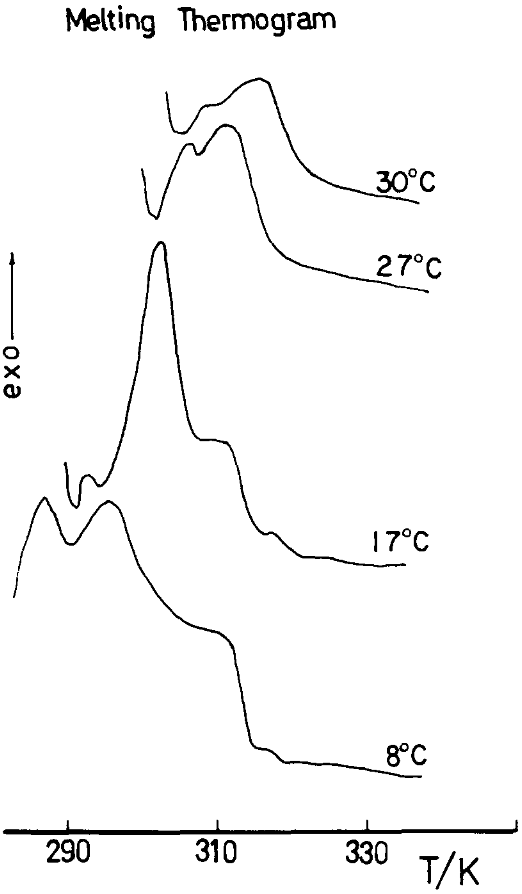

FIG. 5. Melting thermogram at 5°K/min on palm oil at the end of isothermal crystallization at various temperatures of crystallization.

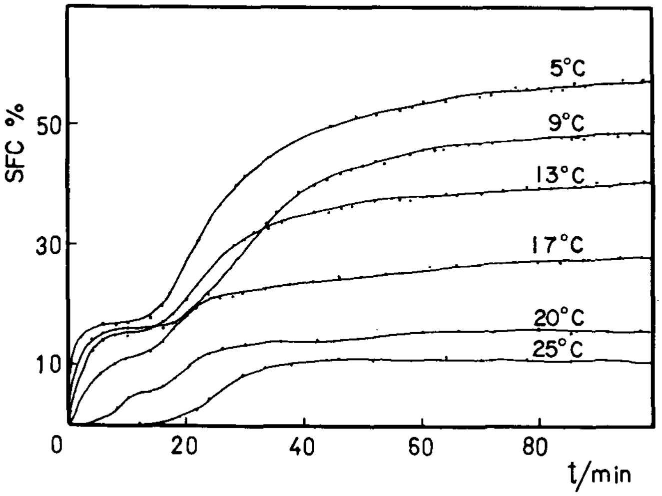

FIG. 6. A plot of percent of solid fat content (%SFC) vs. time at various temperatures of crystallization as indicated on the curves.

increases from 0.053 to 0.081 min^{-1}. This means that the rate increases with decreasing supercooling, which confirms our earlier DSC results over the same temperature range studied (i.e., between 8–20°C).

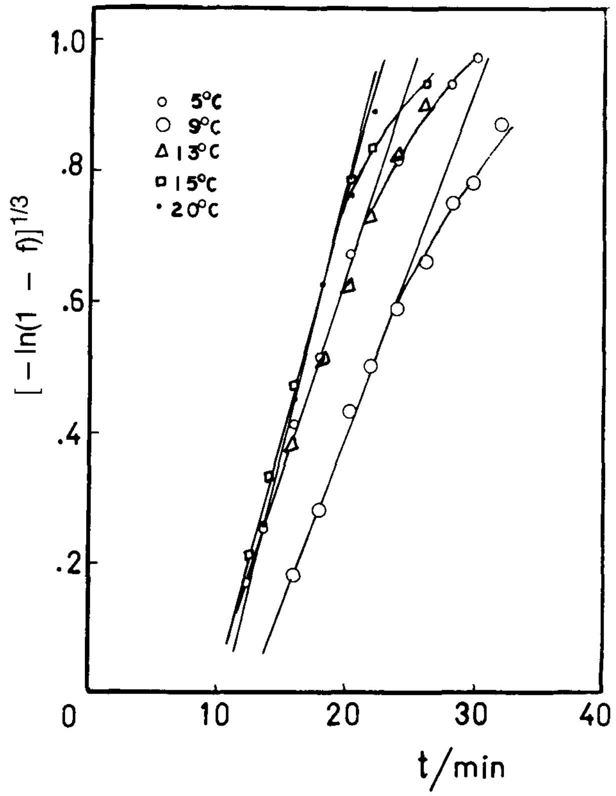

FIG. 7. Fitting of solid fat content data to the Avrami-Erofeev Equation with n = 3.

TABLE 2

Parameters in the Avrami-Erofeev Equation with n = 3 for the Crystallization Curves by Solid Fat Content Measurements

Tc[a] (°C)	f-Range	k_n/min^{-1}	ΔT (°K)
5	0–0.70	0.062	40
9	0–0.66	0.053	36
13	0–0.73	0.062	32
15	0–0.78	0.075	30
20	0–0.76	0.081	25

[a] See Table 1 for abbreviation.

Despite the fact that palm oil shows relatively simple dynamic cooling and melting thermograms (Fig. 1), its isothermal behavior is rather complicated, as revealed by the present SFC and DSC studies. This is not unexpected because palm oil is such a complex system and comprises more than twelve different triglycerides of widely differing melting points, which are known to exhibit various degrees of intermolecular interactions.

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