A Study of the Kinetics of Nucleation in a Palm Oil Melt[1]

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Nucleation from a supercooled melt of palm oil was studied by optical microscopy and differential scanning calorimetry (DSC). Despite being a multicomponent system, palm oil exhibits a rather simple cooling thermogram with its high- and low-T exotherms exclusively related to the "hard" and "soft" components of the oil. As the "hard" components are being removed, the position of the high-T peak shifts down toward the low-T peak with diminishing peak intensity, while the position of the latter remains virtually unchanged.

At 288°K, nucleation in a palm oil melt is instantaneous. Its induction time-temperature curve shows an abrupt discontinuity at 297°K, which demarcates the occurrence of one polymorph from another. Nucleation data fit very well into the Fisher-Turnbull equation. Its larger activation free energy of nucleation is accompanied by lowering of the melting point and an increase in the crystal/melt interfacial free energy as compared to palm stearin. The slow rate of nucleation in palm oil is attributed to intermolecular interaction between its "hard" and "soft" components.

KEY WORDS: **Nucleation kinetics, palm oil melt.**

Palm oil, which consists largely of triglycerides of palmitic and oleic acid, is a semisolid at room temperature. Its composition and properties can be modified (1,2) by various industrial techniques such as fractionation, hydrogenation and interesterification to yield a wide variety of oils and fats tailored to meet specific uses. The principle of dry fractionation is based on the differences in melting points of the component triglycerides and partial glycerides. Thus, its high-melting (hard) components can be separated from its low-melting (soft) components by crystallization. However, the conditions under which crystallization is carried out have a profound effect on the habit, size, structure and composition of the resulting crystals. Previous investigations concentrated largely on polymorphism (3–5) of the stearin crystals using methods such as photomicrography, calorimetry and x-ray diffraction. It is now generally accepted that palm oil exhibits at least three polymorphs (1,6), designated as α, β' and β in increasing order of melting point and structure stability. Recently there has been a growing interest in the study of its crystallization behavior with respect to nucleation and crystal growth (5,6). However, the crystallization process is quite sluggish (1,3) and remains an unanswered problem. This paper highlights the importance of intermolecular interactions between the "hard" and "soft" components of the oil in influencing its nucleation process.

EXPERIMENTAL PROCEDURES

A typical Malaysian palm oil (I.V. = 52.0) and a commercial palm stearin (I.V. = 39.8) were used for this study. The sample was first melted and homogenized completely at 353°K. This was followed by hot filtration under suction to remove fibrous solid particles. A Perkin Elmer DSC-2 Differential Scanning Calorimeter complete with data station and plotter (Perkin Elmer, Norwalk, CT) was used to obtain thermograms. About 10 mg of sample was placed inside an aluminum pan. For the cooling scan, the sample was first held at 353°K for 30 min before being cooled at 5°K/min to 240°K. This was followed by heating at 5°K/min to the starting temperature to obtain its melting thermogram. The thermogram was calibrated using cyclohexane as a standard. In induction time measurements, glass cover slips containing the sample were prepared and placed on a hot stage of a polarizing microscope. Details of the set-up were described elsewhere (7). Dry fractionation of palm oil was carried out using a Beckman Refrigerated Centrifuge J20 (Beckman Instruments, Fullerton, CA). The filtered and deaerated sample was first placed in eight centrifuge tubes (Corex 8445) which were protected by rubber sleeves. The tubes were then inserted into the holes of a rotor which was previously equilibrated at 288 ± 1°K. Centrifugation was carried out at 10,000 rpm. After each prescribed time interval, two tubes in opposite slots of the rotor were removed. The stearin was well separated from the olein phase as all crystals were accumulated at the bottom of the tube during centrifugation. The melting points of the samples were determined by the capillary method.

RESULTS AND DISCUSSION

High-T and low-T peaks. Despite its multi-component character, palm oil has a relatively simple cooling DSC thermogram (Fig. 1, curve b) with two well separated exotherms. A similar thermogram (curve a) was obtained from palm stearin, except that its high-T peak occurs at a higher temperature. In order to ascertain whether this high-T peak is related to the "hard" components of the oil, a series of palm olein fractions with decreasing "hard" content was prepared. Curves c and d display the cooling thermograms of the olein fractions after the oil had undergone partial crystallization for 15 and 30 min, respectively. The thermograms reveal that whereas the position of the low-T exotherm is almost stationary, the high-T exotherm tends to shift down towards the low-T peaks with diminishing peak intensity as the "hard" content decreases. After 180 min of crystallization and centrifugation, the "hard" components had been totally removed. The cooling thermogram of the resulting olein fraction shows the presence of only the low-T peaks. This result unequivocally confirms that the high- and low-T peaks are due to the "hard" and "soft" components of the oil, respectively.

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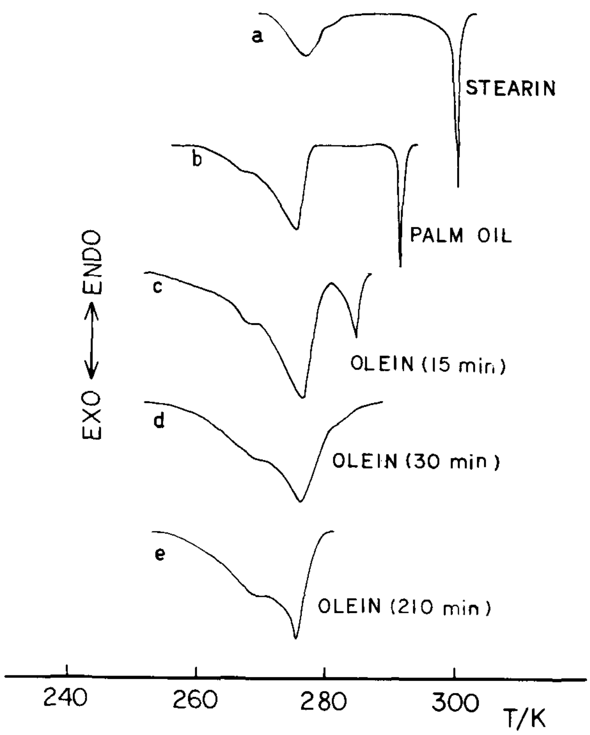

FIG. 1. Crystallization thermograms of palm oil and its various fractions at a cooling scan of 5°K/min. Vertical axis not to scale.

Although the cooling thermograms of either palm oil or palm stearin are relatively simple, there is a considerable broadening and overlapping in the melting thermograms (Fig. 2, curves a and b). For palm stearin, the highest temperature peak falls close to its melting point (325°K). The corresponding peaks for palm oil are, however, obscured by extensive broadening. This broadening effect can be eliminated with successive removal of the "hard" components from the oil (Fig. 2, curves c and d). In the olein fraction, which is devoid of any "hard" component, its thermogram (Fig. 2, curve e) shows a complete absence of the high-T endotherms.

Discontinuity in the nucleation curve. It is interesting to note that the log induction time vs temperature plot (Fig. 3) for nucleation in a palm oil melt shows an abrupt discontinuity at 297°K with a supercooling of 21°K. This discontinuity clearly demarcates the occurrence of one polymorph from another because polymorphism is very common among oil crystals. Its value agrees well with the critical temperature (299°K) of occurrence for α-crystal as observed from the isothermal DSC study (4,5). In that study, the crystals produced above 299°K were designated as the β-form, whereas those below were named α-(mixed with β'-) polymorph. The same designation is used here for the crystals nucleated above and below the discontinuity point. Figure 3 shows that the time needed to bring about nucleation of the β-form in the low temperature region is about three times longer than that for the α-form, so that the latter is readily nucleated (route A) in preference to the former. On the other hand, in the high temperature region, where the α-form is unstable, only the β-crystal (route B) is nucleated.

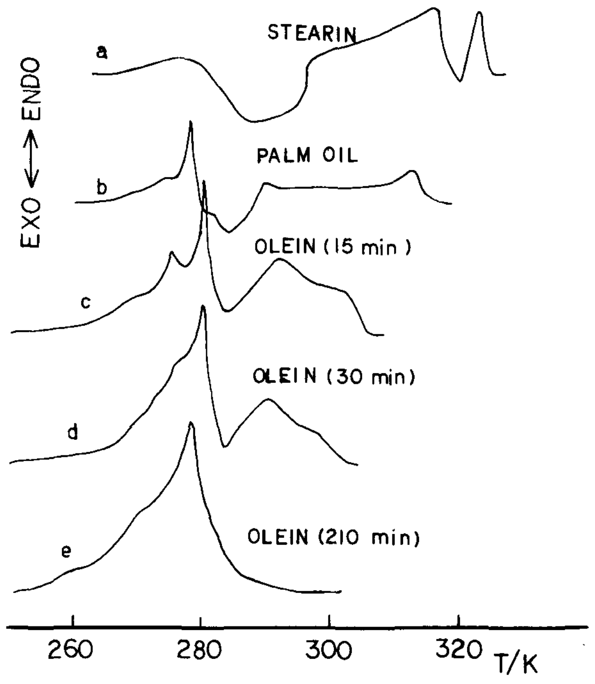

FIG. 2. Melting thermograms of palm oil and its various fractions at a heating scan of 5°K/min.

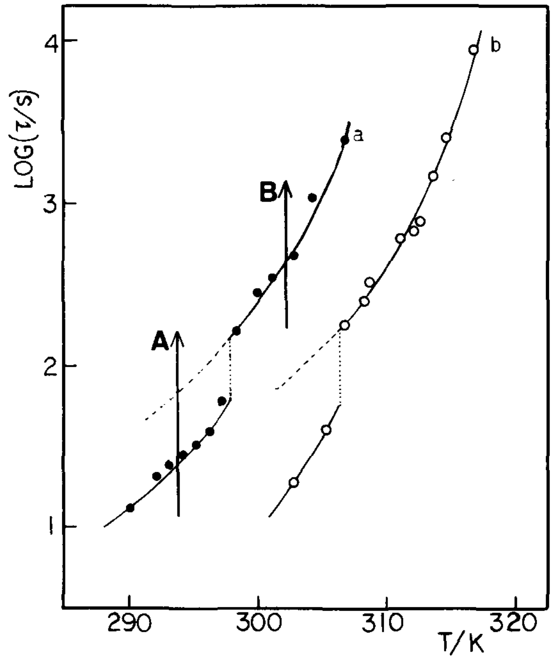

FIG. 3. Nucleation curves (log induction time τ vs temperature T) of a, palm oil; and b, palm stearin; showing discontinuity at 297 and 306°K, respectively.

Nucleation behaviors of palm oil and palm stearin melts are very similar in nature. However, the curve for stearin is displaced towards higher temperatures (curve b) with a discontinuity occurring at 306°K with a supercooling of 19°K. This result shows that at any temperature, nucleation in palm stearin is always easier than in palm oil melt because a much shorter induction time is required.

Activation free energy of nucleation. Palm oil can be fractionated into a so-called "top fraction" (7% of the total oil) that consists mainly of tripalmitin PPP and some dipalmitostearin PPS (1). As co-crystallization and formation of eutectic compounds and solid solutions (mixed crystals) are rather common phenomena (8) in oils and fats, the crystal nucleated may not contain pure PPP and PPS. However, being the highest melting components, it is probable that they are always present in the crystals that are initially nucleated from the oil. Its melting point is affected by the liquid with which it is in contact. The larger melting point depression in palm oil implies that the oil is less susceptible to nucleation. For instance, at 303°K, the induction time of nucleation in palm oil is more than ten times longer than that in palm stearin (Fig. 3).

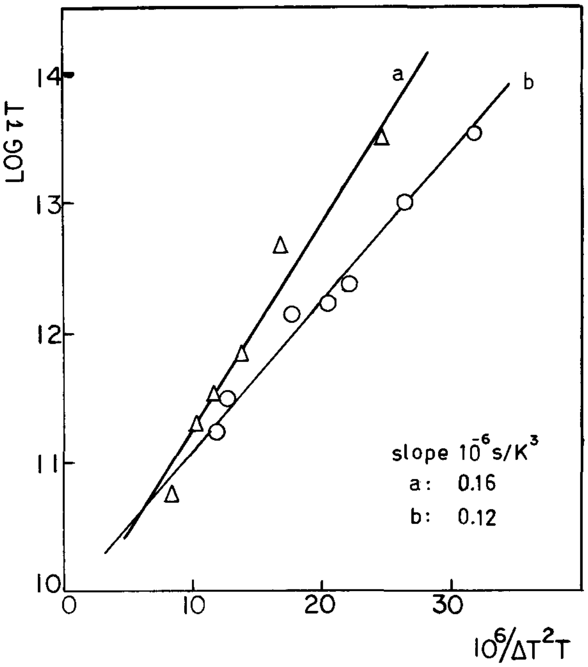

FIG. 4. Fitting of nucleation data to Fisher-Turnbull equation—a, palm oil; and b, palm stearin.

Thermodynamically, a supercooled melt is in a labile state. Such a system may undergo spontaneous nucleation only if there is a decrease in the overall free energy (9) of the system. Although the free energy of the solid phase is lower than that of the liquid phase (10), the formation of a crystal nucleus is always accompanied by simultaneous creation of a crystal/melt interface which increases the free energy of the system. An energy barrier of nucleation ΔG_c (7) therefore exists in the system, and unless local fluctuation in energy is sufficiently large to overcome this barrier, nucleation will not occur and the supercooled system will remain in its metastable state. This energy, which is the activation free energy of nucleation ΔG_c, can be evaluated using the Fisher-Turnbull equation:

$$J = (NkT/h)\exp(-\Delta G_d/kT)\exp(-\Delta G_c/kT) \qquad [1]$$

where J is the rate of nucleation; ΔG_d, activation free energy of diffusion; and the other symbols have their usual meanings. A convenient way of determining J experimentally (11) is to measure the induction time (τ) of nucleation, which is inversely proportional to J. For a spherical nucleus, the activation free energy of nucleation is related explicitly to the surface free energy of the crystal/melt interface σ and the supercooling $\Delta T = (T_m\text{-}T)$ by equation [2]:

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

Plots of log τT vs $1/T(\Delta T)^2$ are given in Figure 4 for both palm oil and palm stearin. A fairly good linearity of the plots shows that the Fisher-Turnbull equation, which is originally derived for a single component system, can also be applied to palm oil, which is a multicomponent system. The corresponding activation free energy of nucleation can then be evaluated (12) from the slope s:

$$\Delta G_c = sk/(T_m\text{-}T)^2 \qquad [3]$$

TABLE 1

Kinetic Parameters in Nucleation

Temperature °K	Palm oil[a]		Palm stearin[b]	
	Δ G_c, kJ/mol	Δ T, °K	Δ G_c, kJ/mol	Δ T, −K
300	4.1	18	—	—
302	5.2	16	—	—
304	6.8	14	—	—
306	9.2	12	2.8	19
308	13.3	10	3.5	17
310	20.8	8	4.4	15
312	37.0	6	5.9	13
314	83.1	4	8.2	11
316	332.6	2	12.3	9
318			20.4	7
320			39.9	5
322			110.9	3

[a] $s = 0.16 \times 10^6$ K^{-3}; $T_m = 318$°K.
[b] $s = 0.12 \times 10^6$ K^{-3}; $T_m = 325$°K.

Table 1 shows that palm oil has a consistently larger activation free energy of nucleation. This much larger value of ΔG_c implies that nucleation of the β-crystal is slower in palm oil than in palm stearin melt at any temperature.

The molar enthalpy of fusion ΔH of the β-crystals could not be determined from its melting thermograms because of extensive broadening and overlapping (Fig. 2) of the peaks. However, assuming ΔH is the same for both palm oil and palm stearin, the crystal/melt interfacial free energy is then estimated from equation [2] to be larger in palm oil by a factor of 1.1. Both crystal/melt interfacial free energy elevation and melting point lowering exert a retardation effect on the kinetics of nucleation in palm oil melt.

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