Isothermal Crystallization Kinetics of Refined Palm Oil

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ABSTRACT: The induction times for the crystallization, under isothermal conditions, of refined, bleached, and deodorized palm oil from the melt were studied by viscometry. At temperatures below 295 K, the crystallization of palm oil was observed to occur in a two-stage process. This two-stage process was caused by the fractionation of palm oil, most probably into the stearin and olein fractions. At temperatures higher than 295 K, only a single-stage crystallization process was observed. As seen under polarized light microscopy, spherical crystals were initially formed from the first fraction at temperatures from 287 to 293 K. The diameters of these spherical crystals decreased as the temperature increased. After that, needle-shaped crystals were formed from the second fraction and continued to grow from the surface of these spherical crystals until the spherical crystals were fully enclosed, i.e., the cocrystallization of two polymorphs was observed. At temperatures higher than 293 K, the needle-shaped crystals formed from a mixture of the two fractions were found to be the only polymorphs developed with the onset of crystallization. X-ray diffraction results showed that for temperatures below 295 K, the spherical crystals formed from the first fraction were in α form, whereas the needle-like crystals that nucleated later from the second fraction were in β′ form. β′ crystals were the only polymorphs formed for temperatures above 295 K. The results obtained were in good agreement with the discontinuity observed in the induction time vs. temperature curve. Activation free energies for nucleation were calculated according to the Fisher–Turnbull equation for the various polymorphic forms. Viscometry was observed to be a sensitive method for characterizing the overall crystallization process. This technique is suitable for induction time studies of palm oil crystallization, especially at lower temperatures and with viscous oil.

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KEY WORDS: Activation free energy, Fisher–Turnbull equation, induction time, isothermal crystallization, microscopy, nucleation, palm oil, viscometry, X-ray diffractometry.

Palm oil is a multicomponent system with a large number of TAG. At least 25 TAG types are present in significant amounts, and each has its own polymorphism and melting behavior (1). Under normal ambient conditions (293–303 K), palm oil appears as a heterogeneous slurry of crystals in liquid oil. Palm oil is a prominent fat and oil resource for the food industry, as it is used as cooking oil, margarine, shortening, and in confectionery products.

Early studies on the physical properties of palm oil focused mainly on the polymorphic behavior of crystals by means of DSC (2,3), X-ray diffractometry (XRD) (4–6), photomicroscopy (7), NMR spectroscopy (8), or a combination of these methods. Some of these techniques have been used in kinetic studies, with particular interest given to the determination of induction times (7–11).

Using photomicroscopy, Ng (7) determined induction times for the isothermal crystallization of palm oil and showed that the Fisher–Turnbull equation is applicable to heterogeneous systems such as palm oil. The method used was direct but had the disadvantage of being dependent on the operator's perception. Hererra *et al.* (9) studied the induction time of hydrogenated sunflower seed oil by both polarized light microscopy and laser optical turbidimetry. The laser method was found to be more sensitive and accurate. Light microscopy, which uses white light as the light source, can detect a minimum crystal size of 0.2 μm, whereas a laser source, which is monochromatic and can be polarized, can detect nuclei of smaller sizes (9). The laser method is more objective and accurate, making it especially suited to induction time studies of low-viscosity oil at high temperatures where the nuclei formed are very small in size.

Both Metin and Hartel (10) and Dibildox-Alvarada and Toro-Vazquez (12) used DSC to determine induction times in their studies. DSC measures heat-flow changes during isothermal crystallization. It is very sensitive but more suitable for fats and oils with long induction times, such as cocoa butter. Short induction periods may lead to instantaneous signal changes to the DSC that can cause the results obtained to be inaccurate. Wright and coworkers (11) investigated the induction time of milk fat by using turbidimetry and ^{1}H NMR (pNMR) methods. They reported that the presence of minor components increased the induction time of milk fat. They also concluded that turbidimetry is a much more sensitive technique in terms of determining the induction time for nucleation than pNMR. This is because tiny crystals are sometimes visible in the melt before the pNMR signal can detect the presence of a crystal mass.

The aim of the present study is to introduce a new method for the determination of induction times for the onset of palm oil crystallization. The kinetics of palm oil crystallization was studied under various isothermal crystallization conditions by following the changes in viscosity at a fixed stirring rate. Information on the polymorphic state of the crystals was obtained by XRD and polarized microscopy.

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MATERIALS AND METHODS

Refined, bleached, and deodorized RBD palm oil was supplied by the Malaysian Palm Oil Board (MPOB). The oil was filtered when hot through Whatman No. 1 filter paper prior to use.

(i) Isothermal crystallization. The induction times for crystallization (τ) were determined with a Haake (Karlsruhe, Germany) Rotovisco RV20 viscometer using an M10 measuring system and an NV St (low viscosity) sensor. Viscosity output was recorded automatically. The temperature of the measuring system was controlled by means of water circulated from two water baths *via* three-way valves. One of the bath temperatures was set at 343 K to melt the crystallized oil, whereas the other was held at the crystallization temperature, T_c, which was controlled to within ±0.2 K. The palm oil (17.0 ± 0.5 mL) in the sample holder was heated at 343 K for 15 min to destroy any preexisting nuclei and its crystallization memory. The temperature of the viscometer sample holder was then lowered to T_c and the viscometer controller was started. The water baths could achieve a cooling rate of 15.0 ± 2.0 K/min. Shear rate of the sensor system was increased from 0 to 100 s^{-1} within 2 min. Shear rate was maintained at 100 s^{-1} until the end of the run. We assumed that the effect of shearing on induction time was minor at this slow shear rate. The shear rate used in the present study was much lower than those encountered in commercial tempering devices where shear rates of typically 500–12,000 s^{-1} can be generated (13). Furthermore, all samples were agitated using the same shear rate, which would keep any shearing effect constant.

After starting the cooling process and increasing the shear rate, the viscosity was observed to increase until a shear rate of 100 s^{-1} and the T_c were reached, where it stabilized. When the sample was supercooled sufficiently, nucleation was observed to occur, and the viscosity of the crystallizing suspension increased. The viscosity continued to increase as the crystals grew and finally reached an equilibrium value. Cell temperature lag time was the time needed for the oil to reach the preset T_c from 343 K. A maximum lag time of 2.9 ± 0.2 min was observed at 287 K. The induction time was defined as the interval from the lag time to the onset of crystallization (first deviation from the viscosity–time plot baseline).

Isothermal T_c between 287 and 303 K were investigated. Below 287 K, the oil was found to crystallize before T_c was reached. Three replicates at each crystallization temperature were made, and the mean of the induction times was reported.

(ii) Melting point determination. The melting point of the refined palm oil was measured with a PerkinElmer DSC 7 (Norwalk, CT), equipped with 1020 series Thermal Analysis System software. Five milligrams of the melted sample was weighed into an aluminum pan and sealed. An empty covered sample pan was used as the reference. For the heating run, the sample was held at 353 K for 10 min, then cooled at a rate of 5 K/min to 233 K and held for 10 min at this temperature. It was then heated from 233 to 353 K at a heating rate of 5 K/min. The melting point, T_m, was established as the temperature at which melting was completed.

(iii) XRD. The polymorphic forms of the fat crystals in palm oil were determined with an FR592 Enraf-Nonius Diffractis X-ray generator (Delft, The Netherlands) and an Enraf-Nonius model FR 552 Guinier camera equipped with a customized single-compartment cell with the temperature controlled by an external-circulating thermostated bath. Melted oil (333 K) was placed in the cell, which was already set at the T_c. Samples were held isothermally until all the polymorphic phases were fully observed. Kodak (Eastman Kodak Co., Rochester, NY) diagnostic film with direct exposure (cat. no. 155 8162) was used, and the diffracted line spacings on the X-ray film were measured with an Enraf-Nonius Guinier Viewer Camera capable of reading to the nearest 0.001 nm under illuminated magnification.

(iv) Polarized light microscopy. An Olympus AX 70 (Nagoya, Japan) microscope equipped with a THMS 600 Temperature Control Stage was used to study the crystals formed. Temperature was controlled by a Linkam TMS 93 Multiramp Temperature Programmer and LNP 93/1 Automatic Cooling System (Tadworth, Surrey, United Kingdom). Liquid nitrogen was used as the coolant. The samples were melted at 343 K and pipetted onto a circular slide as a thin layer before being covered with a slide cover. The slide was first heated to 343 K for 10 min and then rapidly cooled (50 K/min) to the T_c. The crystals formed were carefully examined under the microscope at 200 and 500× magnification. Photographs were taken with a PM-C35DX Fully Automatic 35-mm Camera back-mounted on the U-Photo photo tube in the system.

(v) Calculation of the activation free energy for nucleation. The activation free energies for nucleation (ΔG_n) were evaluated from the Fisher–Turnbull equation described in detail elsewhere (7). From the τ, determined at various T_c, a graph of log τT vs. $1/T_c(\Delta T)^2$ can be plotted. The corresponding ΔG_n can be evaluated from the slope, s:

$$\Delta G_n = sk/(\Delta T)^2 \qquad [1]$$

where k is the gas constant per molecule and $\Delta T = (T_m - T_c)$ is the degree of relative supercooling.

(vi) Statistical analysis. Data were statistically analyzed by a two-way ANOVA using an SAS (14) software package. Significant differences ($P < 0.05$) between means were further determined by Duncan's multiple range test.

RESULTS AND DISCUSSION

Two different types of viscosity vs. time curves were observed. At T_c lower than 295 K, a two-stage crystallization process was observed (Fig. 1). As the onset of crystallization was defined as the point from lag time to the point when the viscosity deviated from equilibrium, it was possible to assign two induction times (τ_1 and τ_2) to each stage of the crystallization process. At 295 K and higher temperatures, only a single-stage crystallization process was observed (Fig. 2). The induction times are shown in Table 1.

Figure 3 shows viscosity vs. time curves at different T_c. At lower T_c, the change in viscosity was greater compared to those at higher T_c. In fact, at temperatures above 303 K, the

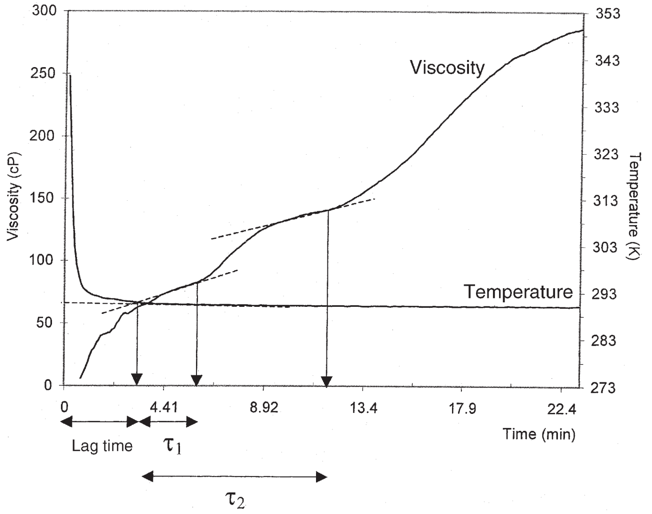

FIG. 1. Viscosity vs. time curves for isothermal crystallization of palm oil at 18°C (291 K). Induction times of first (τ_1)- and second (τ_2)-stage crystallization are indicated.

TABLE 1
First- and Second-Stage Crystallization Induction Times for Isothermal Crystallization of Palm Oil[a]

Temperature (K)	Induction time [τ (min)]	
	First (τ_1)	Second (τ_2)
287.4	$1.10 \pm 0.20^{C,b}$	$5.13 \pm 0.12^{E,a}$
289.1	$1.67 \pm 0.15^{C,b}$	$6.43 \pm 0.29^{E,a}$
291.0	$3.03 \pm 0.21^{B,b}$	$7.90 \pm 0.30^{E,a}$
293.2	$5.17 \pm 0.76^{A,b}$	$11.93 \pm 0.25^{D,E,a}$
295.2	ND	17.53 ± 0.40^{D}
297.0	ND	28.30 ± 0.17^{C}
299.1	ND	32.40 ± 3.64^{C}
301.2	ND	58.97 ± 1.33^{B}
303.2	ND	107.43 ± 6.28^{A}

[a] Each value in the table represents the mean ± SD of triplicate measurements. Means within each column with different capital roman superscripts are significantly different ($P < 0.05$). Means within each row with different lowercase roman superscripts are significantly different ($P < 0.05$). ND, not detectable.

change in viscosity was so small that the induction time could not be established. As T_c was increased from 287 to 293 K, the first crystallization stage became less apparent. At 295 K, it was undetectable. This implies that at higher temperatures the crystallization that occurs is a single-stage process.

The log induction time, τ, vs. temperature, T, plot (Fig. 4) shows an abrupt discontinuity near 295 K demarcating the occurrence of different polymorphic behavior at this temperature, similar to the discontinuity observed by Ng (7). However, in the studies of Ng (7) and Ng and Oh (8), the reported temperatures were below 297 K, whereas in Kawamura's (2) isothermal DSC studies of palm oil, the temperatures for the occurrence of a different polymorph were below 299 K. This slight difference in the discontinuity temperature for polymorphic transition could be due to the sensitivities of the monitoring systems used. The present study also showed that a single-stage crystallization had replaced the mixture of two-stage crystals as T_c was increased (Fig. 3 and Table 2).

In the studies by Kawamura (2,3) and Ng (7), the crystals produced below the discontinuity temperature (curve A in Fig. 4) were designated as α (mixed with β′), whereas those above the discontinuity temperature were designated as β (curve C). Curve B was not detected, probably due to the techniques they used, which could not determine the various crystallization stages shown in the present study. However, it was observed from the present study that curve B (Fig. 4) could actually form a smooth curve with curve C from the lower temperatures to the higher temperatures without any discontinuity. Based on the definition that discontinuity of the plot is due to the occurrence of different polymorphic forms, this could only imply that the crystals formed during the second stage of crystallization at lower temperatures (<295 K), curve B, were actually similar to those crystallized at higher temperatures, i.e., curve C. Palm oil seemed to crystallize initially in the α form followed by the β′ form at lower temperatures (<295 K) whereas at higher temperatures, only β′ crystals were formed.

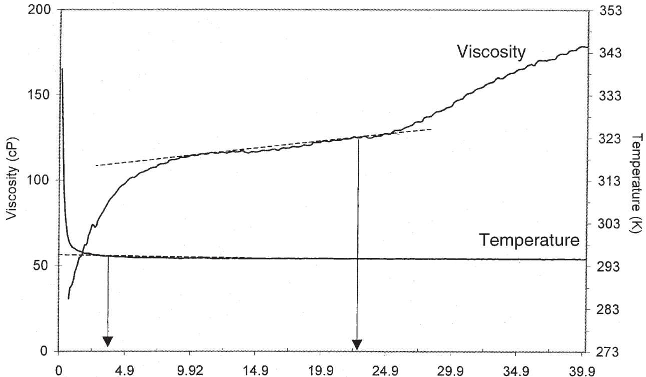

FIG. 2. Viscosity vs. time curves for isothermal crystallization of palm oil at 22°C (295 K).

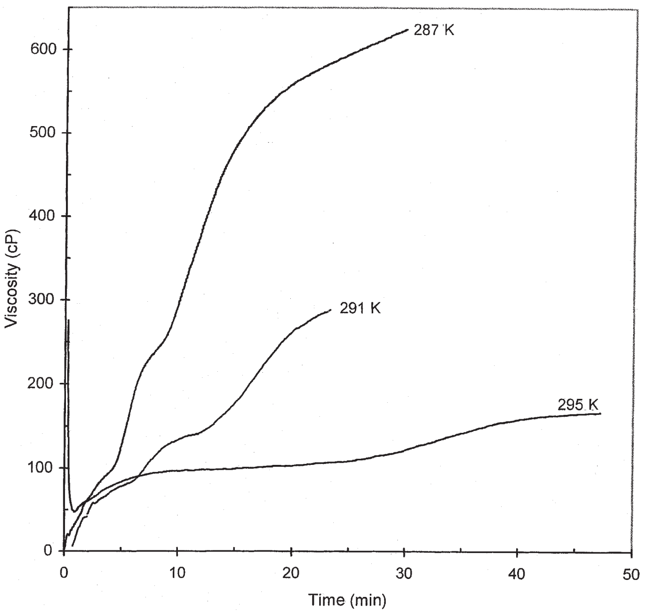

FIG. 3. Viscosity vs. time curves of palm oil at different crystallization temperatures (T_c).

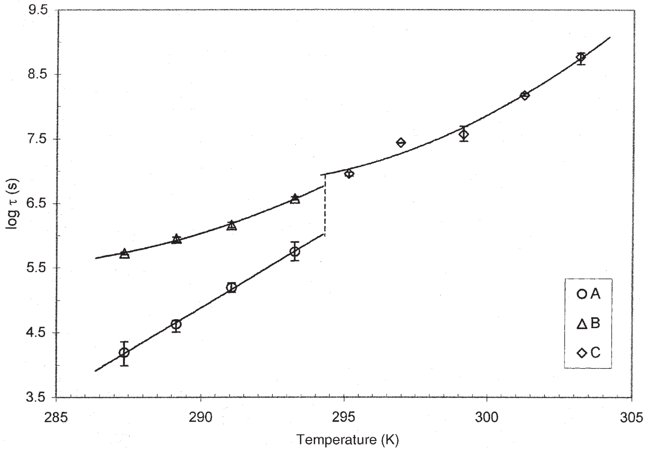

FIG. 4. Log induction time (τ) vs. temperature (T) plot for isothermal crystallization of palm oil. Curves A, B, and C show the occurrence of different polymorphic crystals.

It is well known that fats and oils are mixtures of different TAG (1). When oils are cooled, the highest-melting TAG (i.e., the stearin fraction) will crystallize as solids in a liquid phase of lower-melting TAG (i.e., the olein fraction). Therefore, different stages of crystallization can be observed with the changes in viscosity. The presence of high- and low-melting TAG in palm oil was well documented by Ng and Oh (8), who showed that the high-melting TAG of palm oil are made up of mainly trisaturated TAG that represent 5–11% of its composition (15). In the present study, the first and second fractions of palm oil (most probably the stearin and olein fractions) crystallized at different induction times for each T_c below 295 K in different polymorphic forms. The first fraction (curve A) initially crystallized in the α form, whereas the second fraction (curve B) crystallized later in the β′ form. At T_c of 295 K and above, both fractions crystallized together as the β′ polymorph. This is possible since the stearin fraction, made up of mainly trisaturated TAG (8) such as tripalmitin, is α-tending at lower temperatures (7,16). This fraction is always present in the crystals that are initially nucleated from the oil, whereas the mixed TAG are β′-tending (1). This hypothesis correlates well with the finding of Persmark and coworkers (5). They showed that α crystals initially appeared with rapid cooling followed by β′ crystals at T_c below 293 K, whereas for T_c above 293 K, only β′ crystals were observed.

To confirm this hypothesis, samples obtained by isothermal crystallization from the melt were analyzed for their polymorphic behavior by XRD and polarized light microscopy at various T_c as a function of time. The samples were kept isothermally under X-ray exposure from the melt to ensure that no other polymorphic crystals were present before the induction period. The results are listed in Table 2. The diffraction pattern of palm oil at T_c of 287, 291, and 293 K showed a single diffraction line at 4.13 Å at the onset of crystallization, indicating the presence of α crystals. However, after the second-stage induction time, wide diffraction lines with low intensities attributable to the overlapping of diffraction lines were observed. This indicated a mixture of α and β′ crystals (6). Further crystallization indicated the predominance of β′ crystals. For T_c of 295 K and above, two strong short-spacing lines at 3.83 and 4.16 Å were observed, indicating that the palm oil crystals were in the β′ form, even at the onset of crystallization. For T_c of 303 K, the crystals formed were determined to be in the β′ form.

As observed under polarized microscopy, spherical crystals were formed initially at 293 K and below (Fig. 5A). From the XRD results, these were shown as α crystals. At T_c of 287 K, α crystals grew in a less organized form. As T_c increased, the α crystals became more spherical in shape. The diameters of these spherical crystals decreased as T_c increased. After the second-stage induction times (τ_2), β′ crystals with needle-like shapes were observed to nucleate at the edge and surface of the α crystals (Fig. 5B). The β′ crystals continued to grow rapidly and eventually covered the α crystals (Figs. 5C and 5D). However, for T_c above 295 K, β′ crystals were found to be the only polymorphs developed (Figs. 6A–C). Results from both XRD and microscopy studies support the proposed hypothesis.

Another question that needs to be resolved is whether curves A and B indicate the cocrystallization of the two different polymorphs (i.e., mixtures of α and β′) or the transition from one polymorph to another (i.e., α → α + β′ → β′). From the changes in the XRD diffraction pattern and their intensities, XRD results appear to indicate that curves A and B are the transition stages of these two different polymorphs, which is in line with the literature (5,17). In fact, it is well established that the α crystal is metastable and can easily be transformed to a more stable β′ crystal, either under constant heating or isothermal condition (5,17).

However, the polarized light microscopy observations gave a different point of view. Toward the end of crystal growth for

TABLE 2
X-Ray Diffraction Results for Crystallization of Palm Oil at Different T_c and Times from the Melt[a]

Temperature (T_c/K)	Time (min)	Short spacing (Å)					Polymorphic form
287	13	—		4.13m		—	α
	30, 45	3.83s	4.00vw	4.16s	4.32s	4.54vw	β′ + β (β′ → β)
291	10, 15, 20	—	—	4.13w	—	—	α
	25, 30	3.83w	—	4.16w	4.32w	—	α + β′
293	12	—	—	4.13vw	—	—	α
	30, 45	3.83w	—	4.16w	4.32w	—	β′
295	45	3.83w	—	4.16w	4.32w	—	β′

[a]vw, very weak; w, weak; m, medium; s, strong; T_c, crystallization temperature.

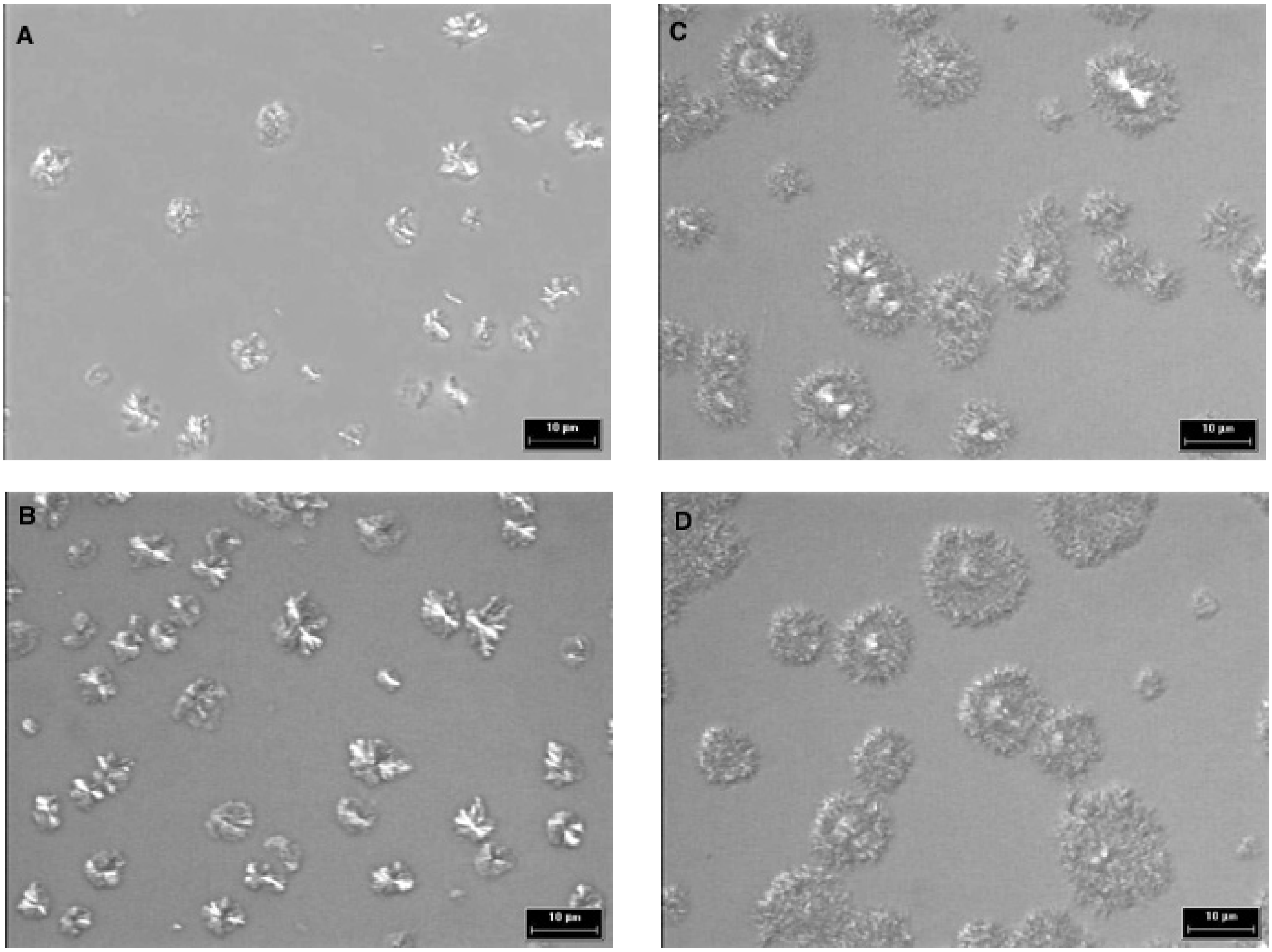

FIG. 5. Isothermal crystallization of palm oil at 291 K at different time intervals: (A) initial stage of crystallization; (B) after second induction period; (C) and (D) toward the end of the crystal growth stage.

T_c below 295 K, spherical crystals could still be observed (Fig. 7), indicating perhaps the existence of α crystals inside β′ crystals (the cocrystallization of α and β′). This contradicts the XRD results and also the results from the literature. The misleading XRD results could be caused by the overlapping of α short spacings by β′ short spacings. Hence, it is difficult in practice to confirm the presence of α crystals when β′ are present. However, an alternative explanation could be that the XRD could not detect the existence of α crystals when the α crystals were fully enclosed by the β′ crystals (Fig. 7). The X-ray beams could not penetrate the thick layer of the β′ crystal shield, thus causing the misinterpretation that α crystals were metastable and had transformed to β′ crystals during the isothermal crystallization process. This is plausible because during isothermal crystallization, no external heat was provided to the α crystals to enable the transformation. Figure 8 shows a simple illustration of the hypothesis of how XRD could not detect the α crystals when fully enclosed by the β′ crystals. This hypothesis is certainly worth further study.

DSC isothermal crystallization studies of palm oil by both Kawamura (2) and Ng and Oh (8) best support our hypothesis that the α crystals did not transform to β′ crystals. Both their works showed that for isothermal crystallization at lower T_c (Kawamura, 291–297 K; Ng and Oh, 271–295 K), two exothermal peaks could be distinguished. At higher T_c, only one exothermal peak was observed, which correlates well with the present study. Ng and Oh concluded that each exothermal peak was actually characteristic of its own crystal produced. If their observation is correct, then the exothermal peaks represent the α and β′ polymorphs in our present study. In both their DSC scans, the rise of the second peak (β′ crystals) was not preceded by adequate endothermal changes that could allow the melting of the first peak (α crystals) for the transformation. In the literature, changes in peak height and enthalpies in dynamic (constant heating and cooling) and isothermal DSC scans had been interpreted as transformations of the polymorphs. However, unlike constant heating conditions, both isothermal and constant cooling conditions may not lead to melting and the recrystallization of crystals formed. This could only imply that both the α and β′ crystals coexisted even when the crystallization process was complete.

Persmark and coworkers (5) studied the lifetime of α crystals of palm oil under isothermal crystallization with a diffrac-

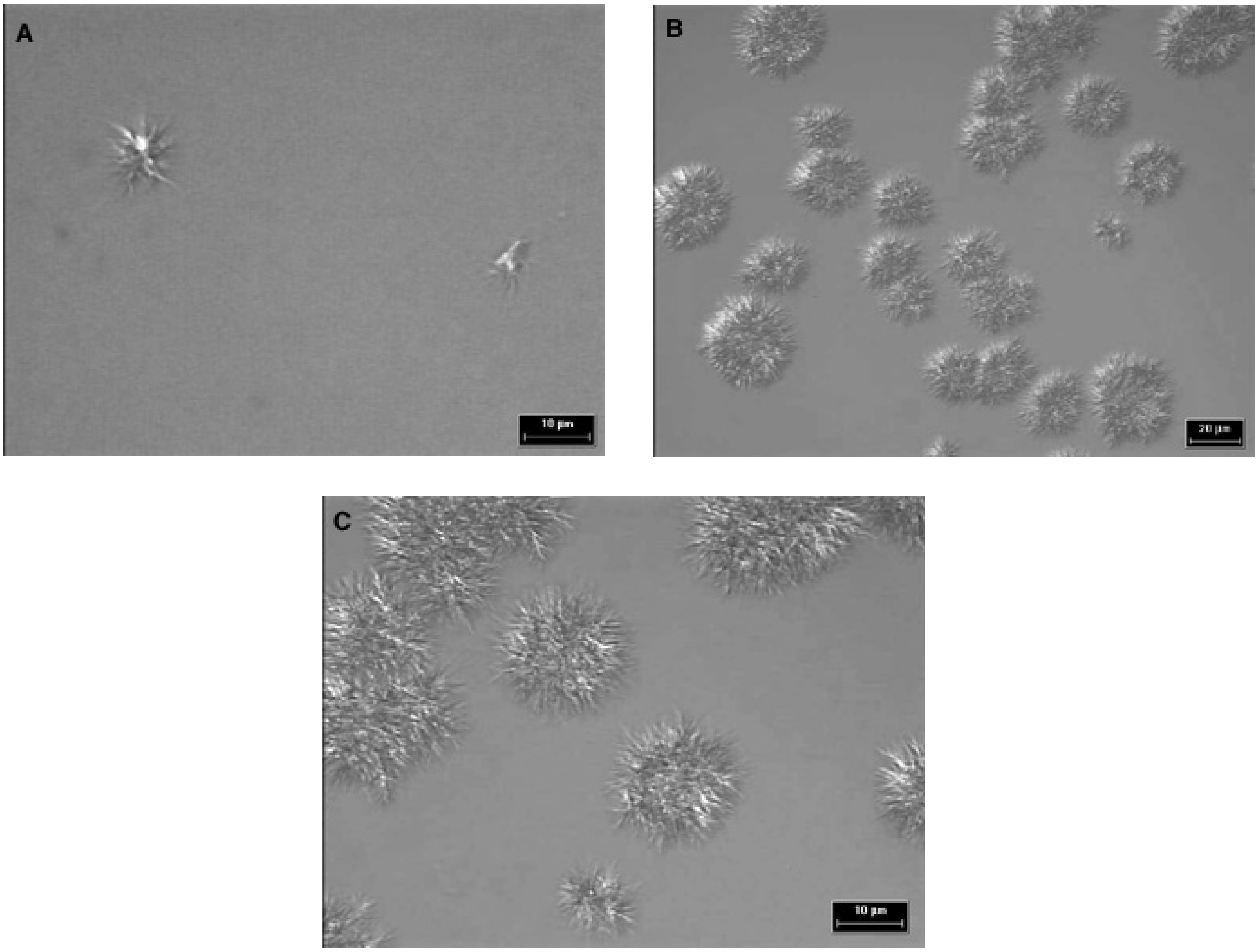

FIG. 6. Isothermal crystallization of palm oil at 301 K at different time intervals. Only needle-like shaped crystals were observed.

tion programmable temperature (DPT) camera. They reported that the α lifetime was maximum at about 283 K and gradually decreased when T_c increased, based on their definition that α lifetime is the time from its formation to the time of appearance of the β′ phase. Their definition and the DPT camera results may have led them to conclude that the α crystal is metastable. Prolonged storage might cause the transformation of the α crystal, but it is not possible at this stage to discuss more about the α lifetime until further work is conducted.

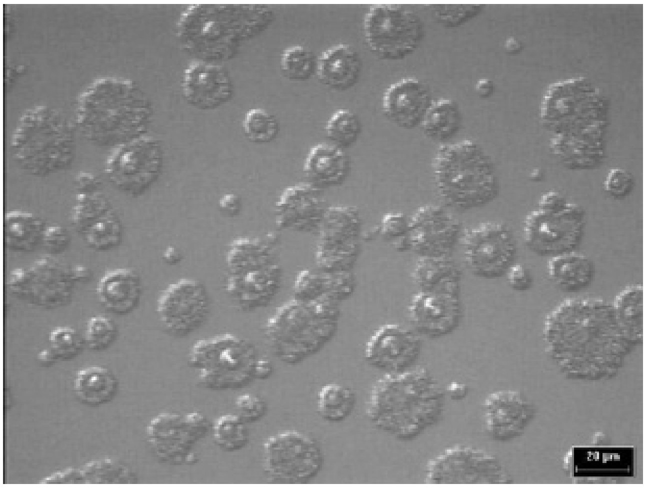

FIG. 7. Isothermal crystallization of palm oil at 291 K at the end of the crystallization process. The spherical crystals (α crystals) are still visible although being enclosed.

Plots of log τT vs. $1/T(\Delta T)^2$ for all the crystallization stages are shown in Figure 9. For palm oil, good linearities for both the α and β′ crystal regions imply that the Fisher–Turnbull equation is applicable to this oil, although the equation was originally derived for a single-component system. The calculated activation energies for nucleation, ΔG_n, of palm oil are shown in Table 3, and good agreement was found with the values given by Ng (7). The results showed that ΔG_n for both α and β′ crystals increased as temperature increased from 287 to 293 K. At 295 K, ΔG_n for β′ was lower since α crystals were not detected. β′ Crystals with lower ΔG_n are more stable; thus, nucleation in this form is favored. Changes of ΔG_n also imply that β′ crystals formed at T_c above 295 K may be different from those of lower T_c. This could be because the β′ crystals formed at these two different ranges of T_c were of different TAG mixtures. At T_c below

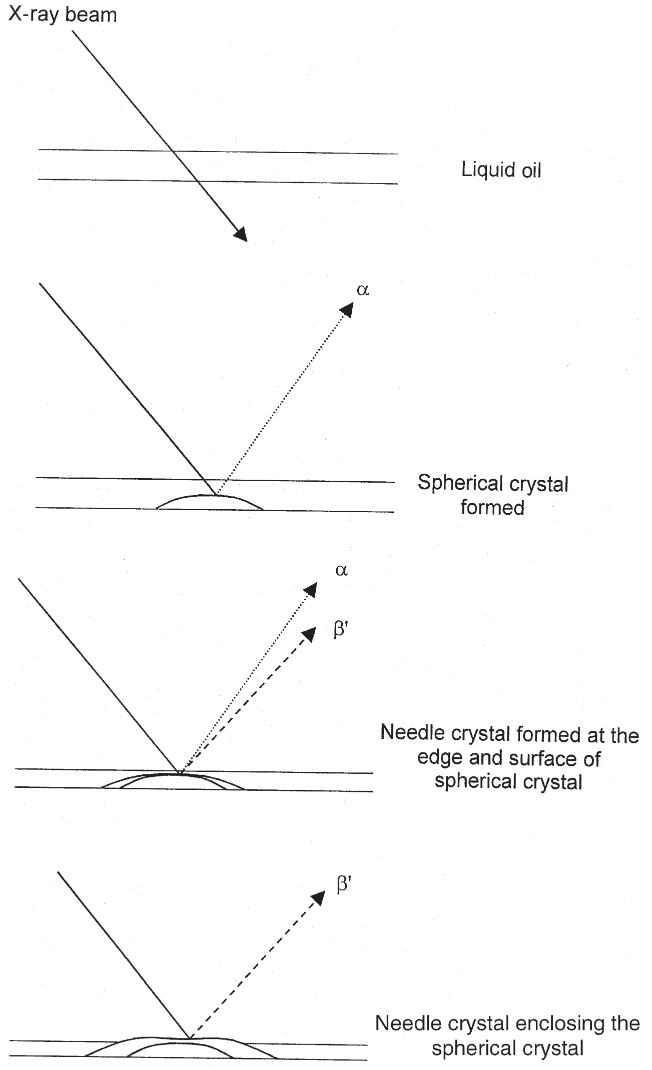

FIG. 8. Illustration of how X-ray diffraction results could be misleading. At (D), when α crystals are fully enclosed by β′ crystals, the X-ray beam is unable to penetrate and reach the α crystal enclosed by the thick layer of β′ crystals.

TABLE 3
Nucleation Activation Free Energies for Isothermal Crystallization of Palm Oil[a]

Temperature (K)	ΔG_n (kJ mol^{-1}) α Region	ΔG_n (kJ mol^{-1}) β′ Region	ΔT (K)
287.4	$7.49 \pm 1.13^{B,a}$	$4.01 \pm 0.36^{D,E,b}$	30.3
289.1	$8.44 \pm 1.35^{B,a}$	$4.51 \pm 0.48^{C,D,b}$	28.6
291.0	$9.72 \pm 1.48^{A,B,a}$	$5.20 \pm 0.50^{B,b}$	26.6
293.2	$11.49 \pm 1.78^{A,a}$	$6.15 \pm 0.53^{B,b}$	24.4
295.2		3.21 ± 0.21^{F}	22.5
297.0		$3.77 \pm 0.26^{E,F}$	20.7
299.1		4.75 ± 0.27^{C}	18.5
301.2		6.00 ± 0.42^{B}	16.4
303.2		7.71 ± 0.49^{A}	14.5

[a] Each value in the table represents the mean ± SD of triplicate measurements. Means within each row with different capital roman superscripts are significantly different ($P < 0.05$). Means within each column with different lowercase roman superscripts are significantly different ($P < 0.05$). Melting temperature, $T_m = 317.65$ K.

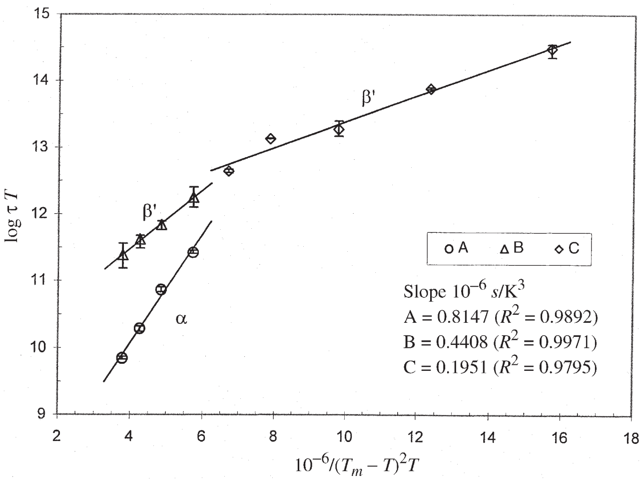

FIG. 9. Log τT vs. $1/T(\Delta T)^2$ for the isothermal crystallization of palm oil. τ, induction time; T_m, melting temperature; T, preset isothermal temperature.

295 K, β′ crystals were formed from the second (most probably the olein) fraction of palm oil, whereas at T_c of 295 K and above, they were formed from both the first and second (stearin and olein) fractions. Ng and Oh (8) reported that the lower the supercooling, the faster the nucleation rate, a finding which contradicts the normal kinetic theory. Their reasoning was that the crystals produced in that temperature range had a wider range of melting points (i.e., a wider range of different TAG). Our present work was able to support their hypothesis, whereby the broad DSC peak observed by Ng and Oh (8) was most probably due to the crystallization of the two fractions together with lower ΔG_n (Table 3).

As shown in Table 3, the second-stage β′ crystals formed at the lower temperature range (from 287 to 293 K) were nucleated with lower activation energies than those of the α crystals. This could be because the surface of the α crystal initially crystallized is a favorable site for the nucleation of β′ crystals, and therefore less energy is required (Fig. 5). Alternatively, it could also be possible that the mixed TAG crystallizing at these conditions have a preference for the β′ form with a lower activation free energy for nucleation.

Results from the present study showed that viscometry can be used to determine induction times for the crystallization of oil, especially for a highly viscous sample at low temperatures. In addition to determining the induction time, the method is sensitive enough to detect the various stages of the crystallization process that are due to changes in polymorphic forms. The capability of viscometry to characterize the overall crystallization process is an advantage over the other techniques discussed. However, the method is not sufficiently sensitive to detect the onset of crystallization at higher temperatures (>303 K) owing to the relatively small change in viscosity at these temperatures.

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