The DSC Thermal Analysis of Crystallization Behavior in Palm Oil

K. KAWAMURA, Food Foods Co., Ltd., Takatsu-ku, Kawasaki-shi, Japan

ABSTRACT
Polymorphic behavior of palm oil crystals was studied by DSC isothermal analysis and microscopic observation. Different crystal forms developed specific spherulites depending on the degree of supercooling from the melt. The A-form crystal was capable of forming a dotted spherulite and the B-form crystal of forming a dendritic spherulite. Experimental results of B-form crystallization studied by the DSC and a microscope under kinetic conditions were evaluated using Avrami's theory, since the behavior of the oil during crystallization related well to that of high polymers. The crystalization process was divided into nucleation and crystal growth phases to facilitate a theoretical treatment similar to that of high polymers, providing crystals possessing overall structural regularity.

INTRODUCTION
Oil crystals have been previously analyzed for their polymorphic behavior using X-ray diffraction, thermallytic methods, etc., but some kinetic aspects like crystal growth have yet to be explained (1-9). However, some researchers have made significant progress toward explaining these aspects (10-13). It could be supposed in a broad sense that oils behave like high polymers when subjected to the crystallization processes from the melt; i.e., they pass through the stages of nucleation, activation, crystal growth and finally reach the end state of a crystal lattice (12). The crystalization process is the spontaneous ordering of the system; i.e., the partial or complete restriction of motion in which triglyceride molecules are being linked with each other by chemical or physical bonds. Differences in crystal forms are the result of different molecular packings (13-15). Hoge (16) has investigated polymorphism and spherulites and suggested that it influences the growth of crystal spherulites resulting in different physical properties of crystal forms. Under iso-thermal conditions, crystals of palm oil are composed of A- and B-forms. A- and B-forms are only used as tentative terms in this report. A form crystals are transformed to the other form under isothermal conditions or during the heating process, e.g., at a rate of 10 K/min, but B-form crystals are stable. The spherulites are shown under a microscope to be identified with these different crystal forms, and the predominant one is dependent on the condition of supercooling.

This paper also attempts to clarify aspects of crystal growth of the B-form in palm oil. The crystalization follows the two main phases of nucleation and crystal growth, but it is very hard to separate them. Theoretically, it is possible to consider these processes relative to crystallization kinetics in high polymers. The theory was initially constructed on low molecular weight materials such as metals by Avrami (17-19) and Evans (20), the base of which was related to the theory of water droplet formation by Volmer et al. (21). It was extended to the crystallization of high polymers by Mandelkern et al. (22,23). These methods were also developed by Takayanagi et al. (24-28) with poly-(ethylene succinate) and poly-(ethylene adipate); by Barnes et al. (29) with poly-(ethylene oxides), and by Kamide et al. (30,31) with isotactic polypropylene.

Barnes' (29) and Takayanagi's analytical methods (24-28) are probably best suited to the case of palm oil crystallization. The triglyceride molecules are combined to form embryos by collision with each other and/or with foreign particles in the supercooled melt of palm oil. When they are charged with a certain activation energy which exceeds a critical level for nucleation, they initiate crystal growth. The crystal growth is composed of surface nucleation and molecular transportation (diffusion), i.e., more molecules are transported to adhere to surface nuclei on spherulites. Daughter crystals are constantly nucleated on the surface of parent spherulites and finally cover them to link with adjacent daughter crystals.

Unfrest polymorphic changes occur; the crystalization which passes through the above process seems to depend on supercooling, which is defined as the difference between the crystallization temperature (T) and the melting point (Tm), by DSC analysis.

EXPERIMENTAL PROCEDURE
Materials
The sample oil was a commercially available whole palm oil from Malaysia with a 54.5% saponification value and with the following fatty acid composition (32): 43.0% of C16:0, 4.5% of C15:0, 39.5% of C18:1 and 11.5% of C18:2. The sample was filtered with a membrane filter (Whatman Filter Unit: 0.20 micron) to eliminate dust and other foreign particles.

DSC Thermal Method
A Perkin Elmer Model DSC-2 was used. A piece of polyethylene terephthalate (12 mg) was sealed in an aluminum sample pan with a lid and used as a reference. Oil samples of ca. 9 mg were also sealed in sample pans and held at 393 K for more than 5 min to destroy crystal nuclei before each DSC scan. The temperature was rapidly dropped under maximum programmed conditions (ca. -80 K/min) and held at the desired temperature (291 K to 305 K) for the isothermal crystallization. The starting point was defined as the time when the indicating (green)

| Plate-like | Linear | Polymorphic |
| 3 | 2 | π G1/2 |
| g | g | 4 g1/2 |
| 2 | 1 | 4 g1/2 |

A: Linear growth rate of crystal-spherulite; t: sporadic nucleation rate in time; d: density of the primary nuclei in the predetermined nucleation; d: width of fiber; n: constant in Avrami's equation; z: rate constant in Avrami's equation.
FIG. 1. DSC isothermal crystallization curves of palm oil. Exothermal rate (mcal/sec) vs. time in min at various temperatures between 291 and 301 °K. 1) Crystallization temperature below 297 °K. Two exothermal peaks -I, -II. 2) Crystallization temperature of 299 °K or higher. One exothermal peak -II.

lamp lit on the DSC front panel, which meant the system was under temperature control. The generated crystals were then heated from that temperature (291 to 305 °K) at a constant rate of 10 °K/min. or 40 °K/min. to obtain the DSC heating curves. The peak temperature (°K) was obtained from DSC heating curves and used for determination of crystal forms.

The bulk crystallization rate was calculated from the DSC isothermal crystallization curves. The area enclosed by a base line and an exothermic peak corresponds to the heat of crystallization, \( \Delta H \). The fraction of crystals (C) at a given time (t) was approximated by the ratio of the integration of the exothermal rate, \( \int_0^t \frac{dA(t)}{dt} \), to the total area, \( \Delta H \), in accordance with the following equation.

\[
C = \left( \int_0^t \frac{dA(t)}{dt} \right) / \Delta H
\]

The equation developed by Avrami (17-19) and Evans (20) was:

\[
1 - C = \exp \left( -z t^n \right)
\]

where z was the rate constant of crystallization and n was the constant defined in accordance with the mechanism of crystallization. The relationship between z and n was derived from the mechanism of nucleation and the morphology of spherulite growth, as designated in Table I.

Equation (II) can be converted to (III):

\[
\log (-\log (1-C)) = \log (z/2.3) + n \log t
\]

The constant terms of \( \log (z/2.3) \) and n can be determined from a linear equation of the relationship between \( \log (-\log (1-C)) \) and log t. Therefore, as the relationship between C and t was calculated from the DSC isothermal crystallization curves of palm oil, the kinetics of oil crystallization could be represented by equation (II).

Microscopic Observation

Oil crystals were observed under a microscope for their morphological changes under isothermal conditions at different temperatures (295, 297, 299, 301, 303, 305 and 307 °K).

A Nikon microscope type S-ke attached to a Nikon camera M-35 S, with a magnification of x 400, was placed in a temperature control chamber at a temperature (within ±1 °K) which was coincident with the DSC isothermal analysis. All equipment was held in the temperature control chamber until an equilibrium was reached at the desired temperature for observation. The experiment started when the melted oil sample (393 °K for 5 min.) was dropped on the glass slide of the microscope within the control chamber. The sample thickness between the cover glass and the glass slide was kept between five to seven microns by using a constant thickness aluminum foil. The thickness was checked after each observation with a micrometer gauge.

The growth of the dendritic spherulites was measured photographically at regular intervals. Three determinations were made at each temperature. Five or more spherulites from different nucleation times were selected from the photographs, and their size was determined as an average of two crossed diameters in a constant direction. The relation between spherulite size and developing time was found to be parabolic. The linear growth rate of the spherulite at each isothermal crystallization temperature was then expressed as the slope of this parabolic curve during the initial phase of crystal growth.

RESULTS AND DISCUSSION

Polymorphic Behavior of Palm Oil

The effect of sample size on crystallization behavior was studied by varying sample quantities from ca. 3 mg to ca. 15 mg. It was found that 2-3 mg of sample was enough to cover the bottom surface of the standard pan (DSC-2). However, sample sizes of 3 to 15 mg had no significant effect on the isothermal crystallization and heating curves except for the thermal peak size. Therefore, a sample size of ca. 9 mg was chosen to apply for DSC studies in this experiment.

Some representative curves of DSC isothermal crystallization are shown in Figure 1. There are two exothermal