Thermal Analysis of Failed-Batch Palm Oil by Differential Scanning Calorimetry

Y.B. Che Man* and **P.Z. Swe**
Department of Food Technology, Universiti Pertanian Malaysia, Serdang, Malaysia

ABSTRACT: Thermal behavior of palm oil samples drawn from the batch crystallizers that failed during crystallization and of a control oil that was drawn from a batch that produced good crystallization were analyzed by differential scanning calorimetry under constant heating and cooling conditions. Four polymorphs—β'_2, α, β'_1, and β_1—were observed, and their temperatures were tabulated. A rapid and sudden surge of heat demand was observed for samples from failed crystallizers. Less supercooling values were obtained from the control oil compared to the higher values for samples from failed crystallizers. In crystallization thermograms, a sharp high-temperature exotherm (high-T peak) and a broad low-temperature exotherm (low-T peak) were observed. Low-T peaks were found almost invariably stationary at −5.1 to −5.6°C, and high-T peaks varied depending on the saturation level of the oil. A new peak, sandwiched between the high-T and low-T peaks, was observed for the control oil.

JAOCS 72, 1529–1532 (1995).

KEY WORDS: Crystallization, DSC, polymorph, super cooling, thermal behavior.

Palm oil, which consists largely of triglycerides of palmitic and oleic acid, is a semi-solid at room temperature. Triglycerides of palm oil are complex, and the presence of partial glycerides adds to the complexity (1). Palm oil has a β′ crystal structure and solidifies from the molten state quite rapidly (2). Fractionation is necessary to meet specific uses. Due to its fatty acid composition, which includes 50% saturated and 50% unsaturated fatty acids, palm oil can be fractionated readily (3). Fractionation separates palm oil into fractions with different melting properties. This process is based on the crystallization of part of the oil, followed by separation of the crystals from the mother liquor. Ng (4) studied nucleation from a supercooled melt of palm oil by optical microscopy and differential scanning calorimetry (DSC) with dry fractionation. He concluded that the conditions under which crystallization was carried out have a profound effect on the habit, size, structure, and composition of the resulting crystals. The report (4) highlighted the importance of intermolecular interactions between the "hard" and "soft" components of the oil in influencing its nucleation process, along with the cooling and melting thermograms of palm oil, palm olein, and palm stearin. Watanabe *et al.* (5) monitored the formation process of granular crystals in fat blends that contained palm oil and concluded that the granular crystals are of the most stable polymorph, β_1, of 1,3-dipalmitoyl 2-oleoyl glycerol with triple chainlength structure.

Factors influencing the crystallization of palm oil are the presence of free fatty acid, partial glycerides (mainly diglycerides), and oxidation products. It was shown that they shift the melting range toward lower temperatures. This is partly due to the formation of mixed crystals (6). This corroborates the findings of other investigators for palm oil and also for other oils (7,8). However, for palm oil, the influence of diglycerides has a much greater practical impact than for seed oils because of the relatively high degree of hydrolysis due to lipase activity in the fruit coat (6). The role and mode of action of diglycerides during crystallization of palm oil were investigated by Okiy (9). Similarities in structure between triglycerides and 1,3-diglycerides suggested that some diglyceride molecules were probably being adsorbed into the crystal lattices of triglycerides. This heterogeneous mixture was unable to pack closely and was more easily disrupted by heat than a structure built entirely of triglyceride molecules. Consequently, there was a reduction in heats of fusion as well as of solid contents. The life of the unstable polymorphic phases, namely β′ and α, was prolonged (9). Oxidation products act in a similar manner as the free fatty acids and partial glycerides, in that they also tend to increase the plasticity and decrease the melting range (3). According to Jacobsberg and Ho (6), melting and solidification of fats are governed by the degree of intersolubility of the glycerides, which is linked to the pattern of imbrication of the triglyceride chains in the crystal.

The DSC is a sophisticated instrument for the measurement and characterization of the thermal properties of materials. When a transition, such as melting or crystallization, occurs in the sample material, an endothermic or exothermic reaction takes place, and this is recorded as a peak in the chart. The effect of sample size on crystallization behavior is insignificant for the sample size of 3–15 mg, except for the changes in the thermal peak size (10).

Depending upon an oil's composition and its past treatment, its triglycerides may crystallize within the mother oil

---

*To whom correspondence should be addressed at the Department of Food Technology, Universiti Pertanian Malaysia, 43400 UPM, Serdang, Selangor, Malaysia.

according to different structures, dense or loose. This phenomenon is known as polymorphism and requires close monitoring. It is now generally accepted that palm oil exhibits at least three polymorphs, designated as α, β′, and β, in increasing order of melting point and structure stability (8,10–14). Crystals that are too soft or too small may bring about an inefficient separation and give poor iodine values (IV). The industries currently are striving toward high-quality, value-added products. It is evident that high-IV palm olein (IV 64 and higher) production is confined to the problem of poor crystal formation, which apparently leads to batch failures. This study was conducted to investigate the probable cause of poor crystallization by DSC thermal analysis.

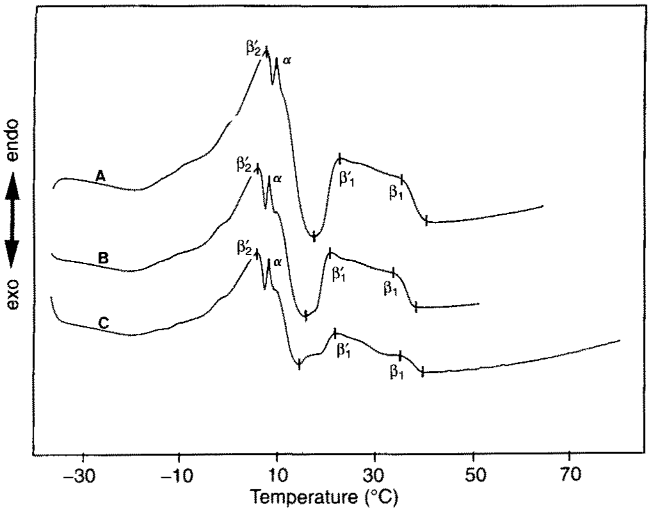

FIG. 2. Differential scanning calorimetry heating curves, analyzed at scanning rate of 10°C/min, for palm oil samples that failed during crystallization (curves A and B) and for control (curve C).

MATERIALS AND METHODS

Palm oil samples from a local refinery were drawn from the batch crystallizers that failed during crystallization prior to fractionation. Samples also were drawn from a batch that produced good crystallization to serve as control oil.

A Perkin Elmer Model DSC-7 (Norwalk, CT) was used for thermal analysis. An empty aluminum sample pan, hermetically sealed with a lid, was used as the reference. Samples of approximately 1.5 mg were sealed in sample pans and placed in the instrument's sample chamber. The temperature was programmed from 30 to 80°C at a rate of 5 or 10°C/min for heating and −5 or −10°C/min for cooling. Before cooling, the sample was first melted in the DSC by commencing the temperature program and was held at 80°C for more than 15 min to destroy crystal nuclei before each scan.

RESULTS AND DISCUSSION

Heating curves. Figures 1 and 2 show the heating curves of palm oil samples, drawn from the batch crystallizers that failed during crystallization (curves A and B) and from the batch that produced good crystallization as control oil (curve C). The scanning rates for Figures 1 and 2 were 5 and 10°C/min, respectively. Table 1 shows the temperature readings of the various points on the DSC heating curves. Higher values are observed for polymorphs at higher scanning rates. A comparison of the control oil with the sample showed that the lowest temperatures were observed for polymorphs β'_2 and α at both scanning rates. However, the highest temperatures were obtained for polymorphs β'_1 and β_1. Control oil's α → β phase transition temperatures (12.9 and 13.9°C) were found to be lowest when compared with the samples. This means that the α → β phase transition takes place at a lower temperature for palm oil with good crystallization behavior. A rather steep slope at

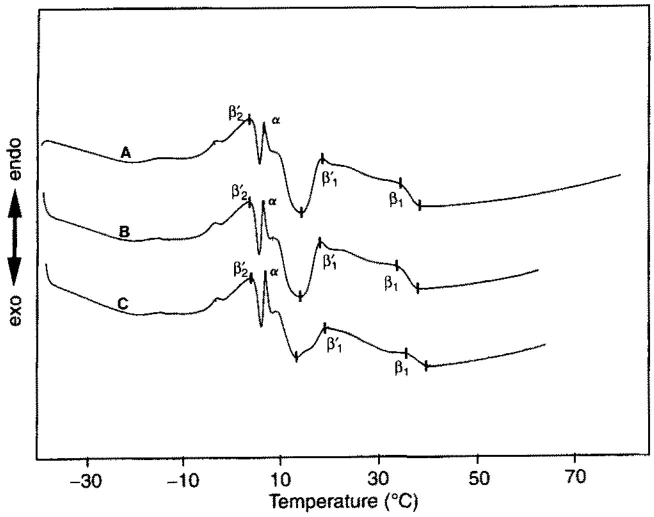

FIG. 1. Differential scanning calorimetry heating curves, analyzed at scanning rate of 5°C/min, for palm oil samples that failed during crystallization (curves A and B) and for the control (curve C).

TABLE 1

Temperature Readings (°C)[a] on the Differential Scanning Calorimetry Curves for Heating and Cooling in Figures 1–4

	Scanning rate	Polymorph form					
Figure	(°C/min)	β'_2	α	—	β'_1	β_1	—
1, curve A	5	3.9	6.9	14.0	18.7	33.1	38.8
1, curve B		3.4	6.2	13.4	18.2	33.5	38.0
1, curve C		3.2	6.2	12.9	18.5	35.0	40.3
2, curve A	10	6.2	8.2	15.7	21.6	33.2	39.9
2, curve B		3.9	6.9	14.0	18.7	33.1	38.8
2, curve C		4.9	7.3	13.9	21.4	34.9	39.5
3, curve A	−5	−5.1	3.4	6.7	14.8	17.0	
3, curve B		−5.1	3.6	9.9	15.9	20.0	
3, curve C		−5.1	2.8	6.7	14.8	17.8	
4, curve A	−10	−5.4	0.9	6.2	12.4	16.9	
4, curve B		−5.1	2.1	8.1	14.4	17.4	
4, curve C		−5.6	1.7	6.4	13.3	15.2	

[a] Values given are read from left to right.

the α → β phase transition represents a sudden surge demand for heat, followed by a rapid change of phase for the oil with poor crystallization behavior. A more precise and efficient cooling method is required to crystallize such oil.

Cooling curves. Figures 3 and 4 show the cooling curves of palm oil samples drawn from the batch crystallizers that failed during crystallization (A and C) and from the batch that produced good crystallization as control oil (curve B). The scanning rates for the figures were at –5 and –10°C, respectively. Palm oil exhibits a simple DSC cooling thermogram despite being a multicomponent system. All curves show a sharp high-temperature exotherm (high-T peak) and a broad low-temperature exotherm (low-T peak). Table 1 shows the temperature readings of the various points on the DSC cooling curves. Basically, fractionation separates these high-T and low-T peaks into stearin and olein, respectively. Low-T peaks were almost invariably stationary at –5.1 to –5.6°C, but high-T peaks varied depending on the saturation degree of the oil. The more the oil is saturated, the higher the high-T peak value. Watanabe *et al.* (5) reported that the high-T peak is due to the tripalmitin (PPP). On the other hand, the high-T peak broadens with reduced intensity and shifts downward toward the low-T peak as the palm olein content increases (15). However, in the crystallization thermograms of control oil (curve B), there is a new peak sandwiched between the two, but it is situated at the shoulder of the low-T peak. Ng and Oh (15) reported that for low PPP concentrations (<8%), this new peak was full-masked by the presence of the adjacent high-T peak, which overlaps with the low-T peak.

The crystallization process can be divided into nucleation and crystal growth phases. 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 a 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 up with adjacent daughter crystals. Unless polymorphic changes occur, the crystallization that passes through the above process seems to depend on supercooling, which is defined as the difference between the crystallization temperature and the melting point by DSC analysis (10). The degree of supercooling values obtained in this study were, at a scanning rate of 5°C/min:sample oil, 21; control, 20.3; and at a scanning rate of 10°C/min:sample oil, 23–23.2; control, 22.1. Lower values were obtained for the control oil; therefore, a lesser amount of activation energy is necessary to initiate crystal growth. This explains the occurrence of batch failure, which is characterized by high viscosity, uneven crystal size, and poor filtration. This is due to formation of too many nuclei in the system as a result of insufficient activation energy given to the crystallizer to start crystal growth. To get good olein yield and better filtration, there must be a small number of nuclei and even crystal size. Too many nuclei in the system also can limit the mobility of crystals, thereby reducing the selectivity.

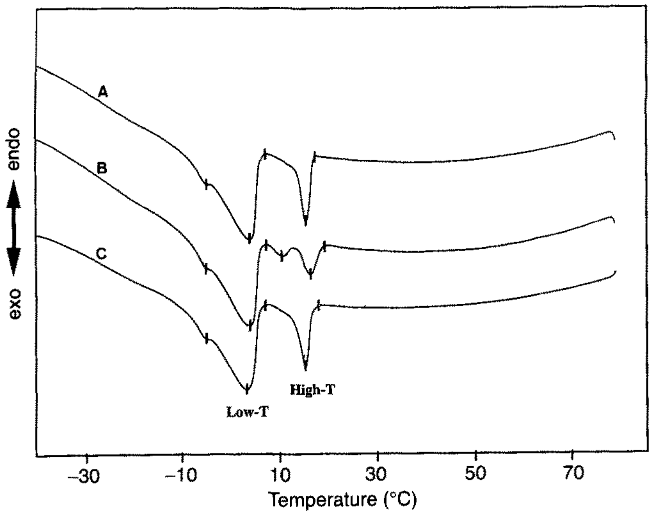

FIG. 3. Differential scanning calorimetry cooling curves, analyzed at scanning rate of –5°C/min, for palm oil samples that failed during crystallization (curves A and C) and for control (curve B). High-T, sharp high-temperature exotherm; Low-T, broad low-temperature exotherm.

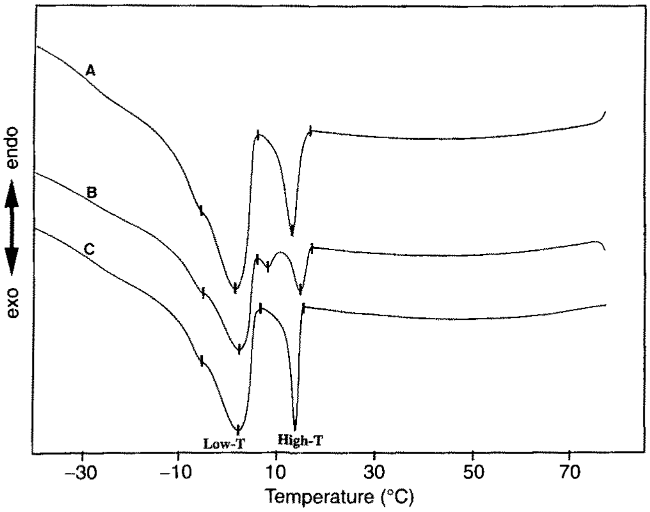

FIG. 4. Differential scanning calorimetry cooling curves, analyzed at scanning rate of –5°C/min, for palm oil samples that failed during crystallization (curves A and C) and for control (curve B). Abbreviations as in Figure 3.

Good or bad crystallization depends mainly on feed oil quality. The purer the oil, the better and faster it crystallizes, and the easier the separation becomes. The feedstock of a fractionation plant based on crystallization should therefore be as free as possible from impurities, such as gums, soap traces, mineral acid traces, and monoglycerides, which act as crystallization inhibitors. Crystallization is a slow process, even when applied to a pure product. Oils have marginal physical conditions, and heat transfer by conduction can be considered negligible although the viscosity is generally high. The transfer of heat takes place solely by convection. This will necessitate efficient agitation, together with a large transfer surface and a slow rate of cooling. This will ensure homogeneity of temperature, which is essential for tight control on the end products. Supercooling is the ability for a liquid to be refrigerated below its melting point without crystallizing or solidifying. This supercooling is always present when crystallizating fats and oils, especially when using fast cooling rates. Intersolubility and polymorphism of crystals also affect the composition of both liquid and solid fractions.

In most crystallizer batch failures, the feed oil (refined, bleached, and deodorized palm oil) quality plays the most important role. The feed oil must be low in color, inorganic impurities, partial glycerides, free fatty acids, and peroxides. All these factors significantly contribute toward improper crystal formation because of their interference in the formation of the crystal lattice, creating a loosely packed crystal structure and subsequent batch failure. A lower percentage of product yield is due to the intersolubility of mixed triglycerides caused by an incorrect rate of cooling. In most failure cases, especially for double-fractionated palm olein, high viscosity is caused by latent heat of crystallization. The latent heat of crystallization, also known as sudden heat release by high melting crystals, is especially likely to occur at the initial nucleation time if the memory of high-melting crystals is not destroyed properly at the heating stage.

The fractionation process basically separates the triglycerides of an oil or a fat into two or more fractions of different physical characteristics. Crystallization of fats and oils is a delicate operation. The feed stock is complex. In addition to triglycerides of a hundred different molecules, free fatty acids, partial glycerides, and a number of various minor components can have a bad or a beneficial effect upon the growth of crystals, even when present in trace amounts (16). The process parameters that influence heat and mass transfer within the oil must be chosen to enhance the selectivity with which each crystal will grow according to the degree of solubility of the triglycerides.

ACKNOWLEDGMENTS

The authors thank the Government of Malaysia for providing the funds under the IRPA scheme (1-07-05-083) to carry out this study, and Zaliha Omar of PORIM for assisting in the DSC analyses.

REFERENCES

1. Jurriens, G., *Analysis and Characterization of Oils, Fats and Fat Products,* Vol. 2, Interscience, London, 1968, pp. 25–34.
2. Weiss, T.J., *Food Oils and Their Uses,* 2nd edn., AVI Publishing Co., Westport, 1983, p. 19.
3. Deffense, E., *J. Am. Oil Chem. Soc. 62*:376–385 (1985).
4. Ng, W.L., *Ibid. 67*:879–882 (1990).
5. Watanabe, A., I. Tashima, N. Matsuzaki, J. Kurashige, and K. Sato, *Ibid. 69*:1077–1080 (1992).
6. Jacobsberg, B., and O.C. Ho, *Ibid. 53*:609–617 (1976).
7. Riiner, U., *Lebensm.-wiss. &Technologie 4*:76–84 (1971).
8. Persmark, U., K.A. Melin, and P.O. Stahl, *Rev. Ital. Del. Sos. Gra. 53*:301–306 (1976).
9. Okiy, D.A., *Oleagineux 33*:625–628 (1978).
10. Kawamura, K., *J. Am. Oil Chem. Soc. 56*:753–758 (1979).
11. Rossell, J.B., *Ibid. 52*:505–511 (1975).
12. Taylor, A.M., *Oleagineux 31*:73–79 (1976).
13. Kawamura, K., *J. Am. Oil Chem. Soc. 57*:48–52 (1980).
14. van Putte, K.P.A.M., and B.H. Bakker, *Ibid. 64*:1138–1143 (1987).
15. Ng, W.L., and F.C.H Oh, in *The Proceedings of the PORIM International Palm Oil Conference,* September 9–14, 1991, Kuala Lumpur, Malaysia, 1991, pp. 298–304.
16. Jacobsberg, B., and D. Jacqmain, in *The Proceedings of the Malaysian International Symposium on Palm Oil Processing and Marketing,* June 17–19, 1976, Kuala Lumpur, Malaysia, 1976, pp. 143–147.

[Received March 15, 1995; accepted September 6, 1995]