Available online at www.sciencedirect.com
ScienceDirect
Thermochimica Acta 471 (2008) 7–13
thermochimica acta
www.elsevier.com/locate/tca

Stop-and-return DSC method to study fat crystallization

Imogen Foubert*, Eveline Fredrick[1], Jeroen Vereecken, Maarten Sichien, Koen Dewettinck

Ghent University, Faculty of Bioscience Engineering, Department of Food Safety and Food Quality, Laboratory of Food Technology and Engineering, Coupure links 653, B-9000 Gent, Belgium

Received 7 September 2007; received in revised form 1 February 2008; accepted 7 February 2008
Available online 15 February 2008

Abstract

Differential scanning calorimeters have frequently been used to study the isothermal crystallization kinetics of fats and oils. In some circumstances (e.g. start of crystallization during cooling to the crystallization temperature, crystallization in emulsion) this straightforward approach is not applicable. This paper describes an indirect DSC method for determination of the crystallization kinetics under these 'difficult' circumstances. The principle is to stop the crystallization at different moments during the isothermal crystallization and raise the sample temperature. The amount of heat released is then used as a measure for the amount of crystallization and plotted as function of time. Combination of the stop-and-return method with the direct method may sometimes be used to save on measurement time. Stop-and-return experiments can furthermore be used to gain more insight in the crystallization mechanism based on the fact that different polymorphic forms and fractions have different melting temperatures.

Keywords: DSC; Fat; Crystallization; Emulsion; Polymorph

1. Introduction

Edible fats are crystallized for various reasons, such as fractionation into certain groups of triglycerides with varying melting and physical properties or to give food products, such as chocolates, confectionary coatings, butter, cream and margarine, a certain texture. The kinetics of fat crystallization, being dependent on the composition and on the processing conditions, are important to produce the desired product characteristics [1]. Polymorphism is another important property since it affects the compliance of fats and oils to thermal and mechanical treatments aimed at preparing specific foods [2].

Differential scanning calorimeters (DSCs) have been used to study the isothermal crystallization kinetics of fats. The time–temperature program used in these investigations in general consists of three stages: first the samples are heated and kept at a high temperature for some time to destroy all homogeneous crystal nuclei, then the samples are cooled at a specified rate to the isothermal crystallization temperature, and finally the samples are kept at that temperature until crystallization is complete. During the isothermal time the instrument monitors the heat flow as function of time [3]. To transform the crystallization peak to a sigmoid crystallization curve representing the fraction of heat released (as a measure for the crystallization degree) as function of time, the DSC peak area must be integrated.

Unfortunately, integration of the crystallization peak is not possible when crystallization starts during cooling to the isothermal temperature or during the equilibration period between the cooling and the isothermal period.

The objective of this paper is to introduce a new, indirect method to extend the application of DSC when direct integration of the crystallization peak is impossible. This stop-and-return method can be combined with the direct method and can provide information about the mechanism of isothermal crystallization (e.g. polymorphic transitions).

After describing the principle of the method, case studies are presented to highlight its possible applications.

2. The stop-and-return method

The principle of the stop-and-return method is schematically illustrated in Fig. 1A–C. Similar to the direct method, the

* Corresponding author. Present address: Katholieke Universiteit Leuven, Campus Kortrijk, E. Sabbelaan 53, 8500 Kortrijk, Belgium. Tel.: +32 56246173.
E-mail addresses: imogen.foubert@kuleuven-kortrijk.be (I. Foubert), eveline.fredrick@UGent.be (E. Fredrick).
[1] Tel.: +32 9 264 61 98; fax: +32 9 264 62 18.

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.02.005

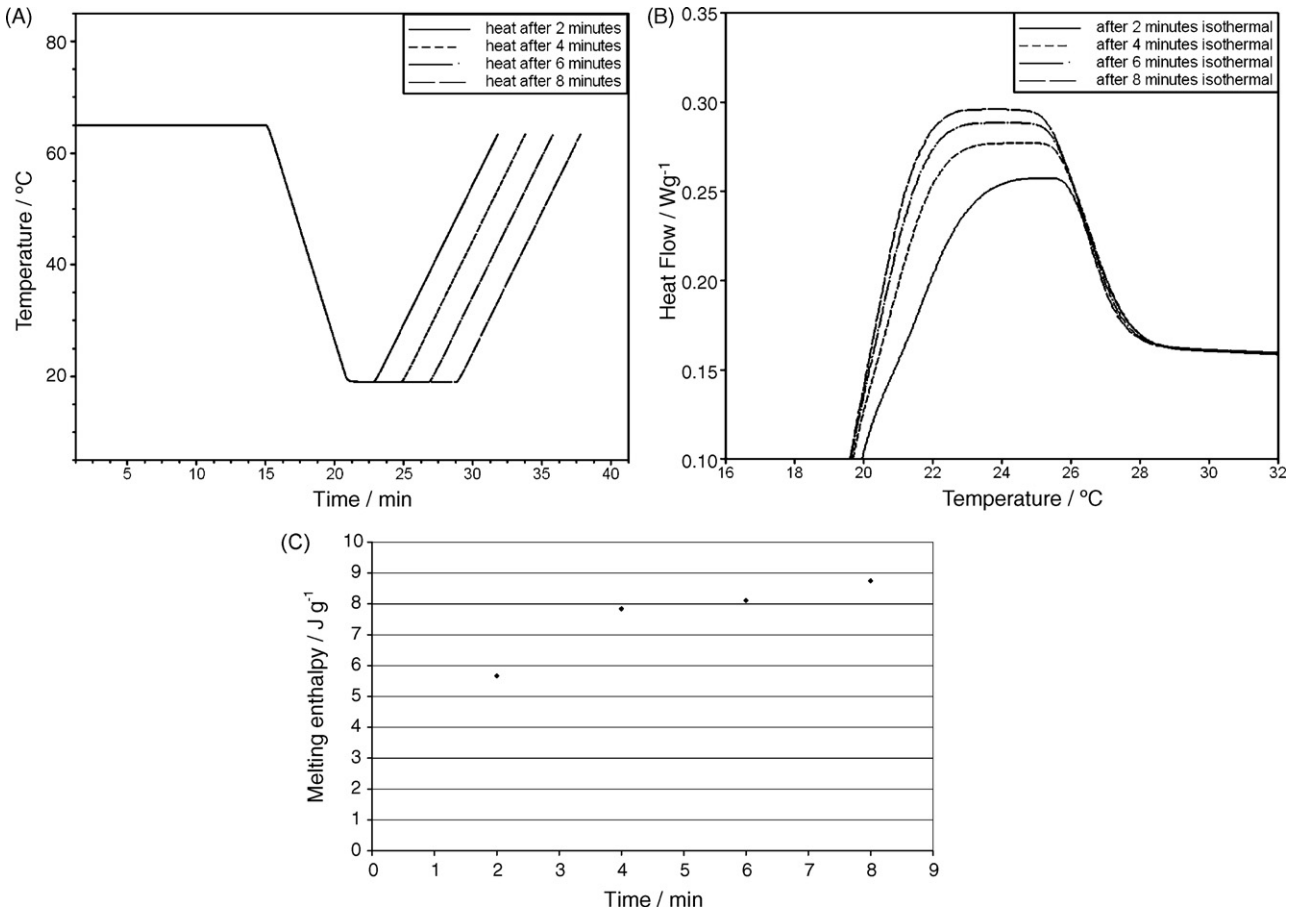

Fig. 1. Principle of the stop-and-return technique: time–temperature program (A), melting profiles (B) and crystallization curve (C).

sample is first melted to remove any memory effect and subsequently cooled to the isothermal crystallization temperature. The isothermal crystallization is interrupted at different times and subsequently the sample is melted (A). The melting profiles (B) are integrated and the area is used as a measure of the amount of crystallized fat at the moment the isothermal crystallization was interrupted. Since different polymorphic forms and fractions have different melting temperatures, the peak temperature gives an idea of the fraction that has crystallized and/or the polymorph in which the fat has crystallized. This is only valid when no polymorphic transitions occur during heating. By plotting the melting areas as a function of time, a crystallization curve (C) can be obtained. This procedure is repeated until the end of the isothermal crystallization is reached. To obtain good repeatability, it is important that the same DSC pan is used for each cycle. Furthermore one has to assure that the sample remains stable during the cycling (see e.g. case 2).

3. Experimental

The isothermal crystallization curves were obtained with a TA Q1000 DSC (TA Instruments, New Castle, USA) with a refrigerated cooling system. The DSC was calibrated with indium (TA Instruments, New Castle, USA), azobenzene (Sigma– Aldrich, Bornem, Belgium) and undecane (Acros Organics, Geel, Belgium) before analyses. Nitrogen was used to purge the system. The sample was sealed in hermetic aluminium pans and an empty pan was used as a reference.

The applied time–temperature program was as follows: holding at 70 °C for 10 min to ensure a completely liquid state, cooling at x °C min^{-1} to the isothermal crystallization temperature (± 0.05 °C) (x was different for the different cases and will be detailed for each case below), holding for the required crystallization time, and then heating at y °C min^{-1} to 70 °C (y was different for the different cases and will be detailed for each case below). The crystallization time before remelting was varied.

The melting curves were integrated using a linear baseline with the end point determined by a calculation algorithm adapted from Foubert et al. [3] and the starting point at the same y-value as the end point.

Three repetitions were performed for each combination of temperature and time.

3.1.1. Case 1

The trans fat based on partially hydrogenated palm oil as well as the trans free alternative based on palm kernel oil were supplied by Loders Croklaan (Wormerveer, Netherlands). Their fatty acid and triglyceride composition is given by Foubert et al. [4].

For the stop-and-return method, a cooling rate of 5 °C min^{-1} and a heating rate of 20 °C min^{-1} was applied.

3.1.2. Case 2

The two different creams used, were produced and supplied by Friesland Foods (Lummen, Belgium) [5].

For the stop-and-return method, a cooling rate of 25 °C min^{-1} and a heating rate of 20 °C min^{-1} was applied.

3.1.3. Case 3

A standard factory product cocoa butter was supplied by Barry Callebaut Belgium (Wieze, Belgium).

For the stop-and-return method, a cooling rate of 8 °C min^{-1} and a heating rate of 5 °C min^{-1} was applied. The time temperature combination to ensure a completely liquid state was in this case 15 min at 65 °C.

3.1.4. Case 4

The refined, bleached and deodorized palm oil and the fully hydrogenated rapeseed oil were supplied by Cargill (Vilvoorde, Belgium). Two percent (w/w) of the fully hydrogenated rapeseed oil was mixed with the palm oil and this mixture was isothermally crystallized at 5 °C.

For the stop-and-return experiments, a cooling rate of 8 °C min^{-1} and a heating rate of 20 °C min^{-1} was applied.

Time resolved synchrotron X-ray diffraction (XRD) measurements were performed on the Dutch-Flemish (DUBBLE) beamline BM26B at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The experiments were done at a fixed wavelength λ of 1.24 Å. A curved 1D microstrip gas chamber detector was used for wide angle X-ray diffraction (WAXD) and a 2D multiwire gas-filled detector for small angle X-ray scattering (SAXS). The samples were enclosed in a perforated aluminium DSC cup and the gap was covered by thin mica. The applied time–temperature program, controlled by a Linkam hot stage, was the same as that applied in DSC. Scattering patterns were taken every 20 s from the start of the isothermal period. The known reflections of silverbehenate and silicon powder were used to calibrate the SAXS and WAXD scattering angles, 2θ, respectively. In the case of SAXS, intensities are presented as a function of s, with $s = 1/d = 2\sin\theta/\lambda$. All scattering patterns were corrected for the detector response and normalized to the intensity of the primary beam, measured by an ionization chamber placed after the sample. The 2D SAXS powder patterns were radially averaged to yield 1D patterns and finally a melt pattern was subtracted as a background. For WAXD only the melt scattering pattern was subtracted.

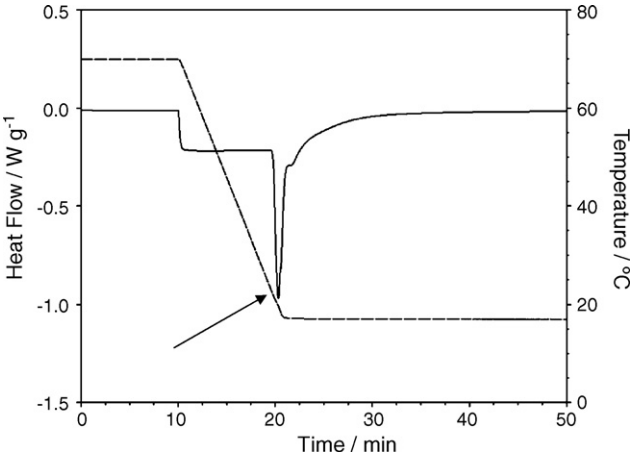

Fig. 2. Isothermal crystallization of trans fat at 17 °C.

4. Results and discussion

4.1. Case 1: isothermal crystallization behaviour of fats used in coatings

The crystallization of two fats (one trans and one trans free), typically used in coatings, in a cooling tunnel was simulated. In some experiments the fats began to crystallize during cooling to the isothermal temperature (which also occurs in a cooling tunnel). This is illustrated in Fig. 2 where the heat flow as well as the temperature as a function of time are depicted. A crystallization peak can clearly be observed at the end of the cooling phase. This peak is superimposed on the heat flow caused by the change of temperature and could therefore not be integrated. To

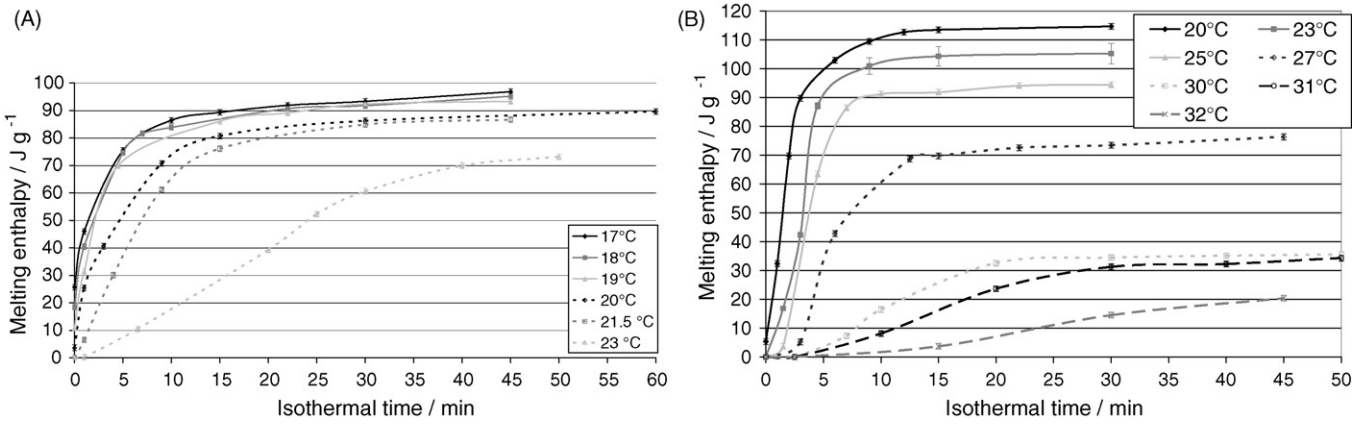

Fig. 3. Melting enthalpy of trans fat (A) and trans free fat (B) as function of isothermal time at different crystallization temperatures.

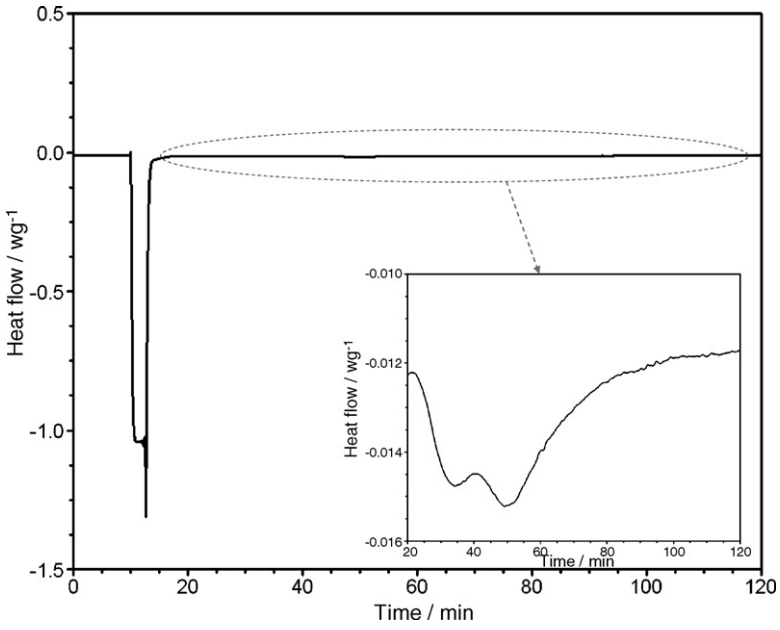

Fig. 4. Isothermal crystallization of natural cream at 5 °C. Inset: magnification of second crystallization peak.

still be able to compare the crystallization kinetics of the two fats as function of temperature, the stop-and-return method was applied.

Fig. 3 shows the crystallization curves. Crystallization of the trans free fat is much faster compared to the trans fat. A very quick crystallization is indeed typical for lauric fats such as the trans free fat. Fig. 3A also shows that the crystallization of the trans fat slows down as the temperature increases and the amount of crystallization at equilibrium also decreases as the temperature increases. The same trends can be observed for the trans free fat in Fig. 3B.

4.2. Case 2: isothermal crystallization of milk fat in an oil-in-water emulsion

Whipping cream is an oil-in-water emulsion of milk fat in which the fat should be partly crystallized to be able to obtain partial coalescence [6], a phenomenon related to the formation of structure in whipped cream [7]. Fig. 4 shows an example of an isothermal crystallization curve at 5 °C of cream. It can be seen that part of the crystallization takes place during the cooling. An additional problem in this case is that, due to the fact that the sample only contains 35% fat, the heat flow is only 35% of the value of bulk milk fat. Combined with the slow crystallization of milk fat, extending the heat release over a broad period of time, this makes that the sensitivity of the apparatus is insufficient to pick up the crystallization peak during the isothermal period. For these reasons it was necessary to develop an alternative method enabling the comparison of the isothermal crystallization of different creams. The stop-and-return method could provide a possible solution if the emulsion remains stable during the repetitive temperature cycles. To check this, the droplet size distribution was determined using a Malvern Mastersizer after several cycles of holding the cream in a hot water bath at 70 °C and a water bath at 5 °C. No shift or broadening of the droplet size distribution took place [5].

Fig. 5 shows the isothermal crystallization curves at 5 °C obtained via the stop-and-return method for two types of cream. Both creams start to crystallize during cooling and show a two-step crystallization curve with a faster first step and a slower second step. However, the second step starts earlier in cream A.

4.3. Case 3: combined method to follow isothermal crystallization of cocoa butter

At temperatures between 19 °C and 23 °C cocoa butter crystallizes in two steps: the first step involves crystallization from the melt to the α polymorph and the second step is a polymorphic transition from α to β′ [8]. The first crystallization step takes place during cooling and/or during the equilibration period between the cooling and the isothermal phase (Fig. 6) and it is thus impossible to integrate the crystallization peak. After this first crystallization step, the heat flow returns to the baseline and

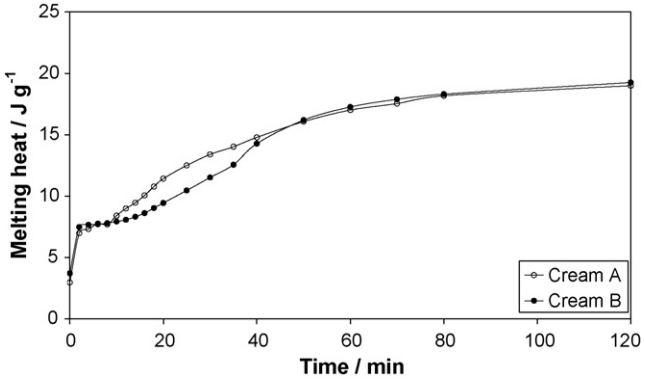

Fig. 5. Melting enthalpy as a function of time for isothermal crystallization at 5 °C of two creams.

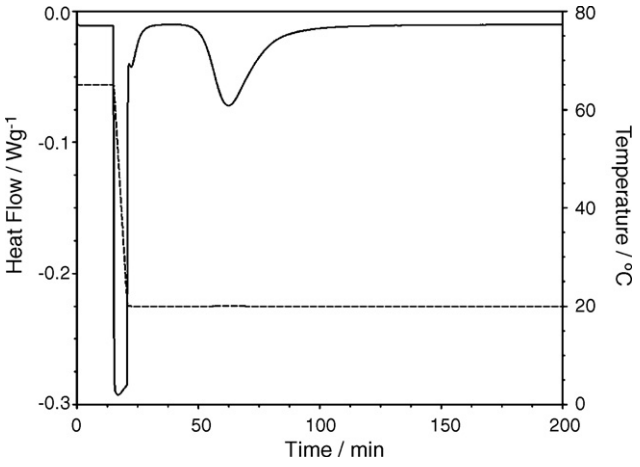

Fig. 6. Isothermal crystallization of cocoa butter at 20 °C.

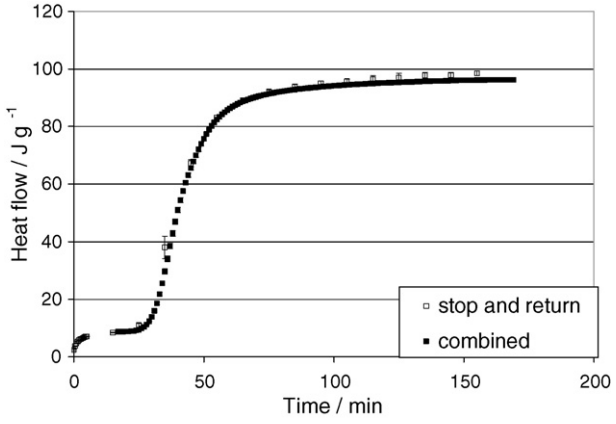

Fig. 7. Comparison of heat flow versus time curves obtained via the stop-and-return method and the combined method.

some minutes later a clear, easy to integrate crystallization peak representing the second crystallization step is visible.

Due to the impossibility to integrate the first crystallization peak, the stop-and-return method had to be applied to obtain and compare crystallization curves of cocoa butter at different temperatures. A disadvantage of this method is however its long analysis time. Based on the fact that the second crystallization peak can be integrated separately, a method combining the stop-and-return and the direct method was developed.

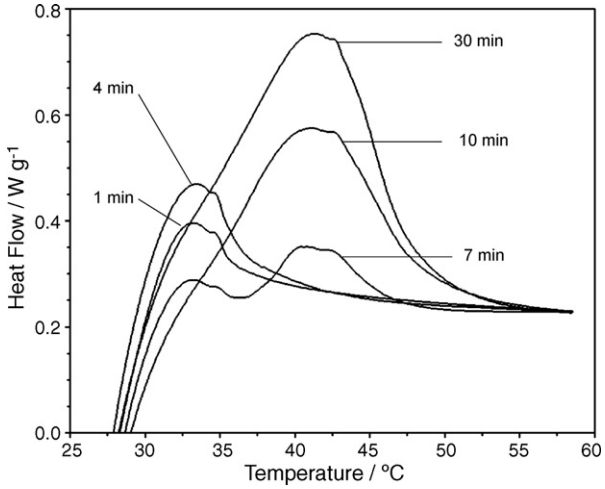

Fig. 9. Melting profiles obtained via stop-and-return method in which the isothermal crystallization at 25 °C of palm oil mixed with hydrogenated fat was interrupted after 1 min, 4 min, 7 min, 10 min and 30 min.

The amount of heat released at a given time t (ΔH_{t_0-t}) can be written as:

$$\text{If } t < \text{ts} \quad \Delta H_{t_0-t} = \Delta H_{\text{S\&R},t}$$

$$\text{If } t > \text{ts} \quad \Delta H_{t_0-t} = \Delta H_1 + \int_{\text{ts}}^{t} \frac{\mathrm{d}Q}{\mathrm{d}t}\mathrm{d}t$$

The variable ts is the start time of the second isothermal peak, $\Delta H_{\text{S\&R},t}$ is the melting enthalpy after a holding time of t minutes determined by the stop-and-return method and ΔH_1 is the total released heat of the first crystallization peak determined by the stop-and-return method with a holding time of ts.

To validate the combination method, heat flow versus time curves obtained by the stop-and-return method for both crystal-

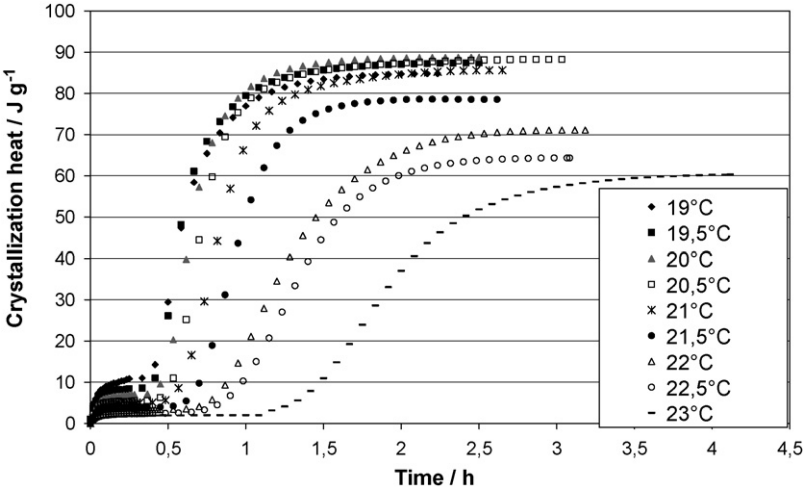

Fig. 8. Influence of temperature on the isothermal cocoa butter crystallization.

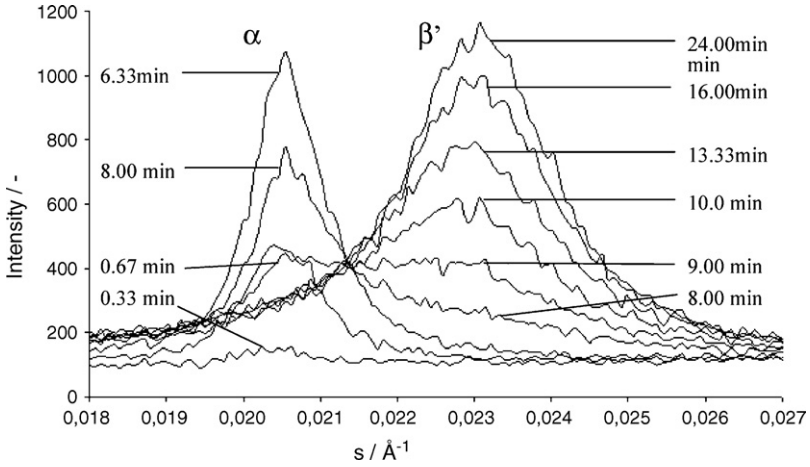

Fig. 10. SAXS curves of isothermal crystallization at 25 °C of mixture of palm oil and hydrogenated fat.

lization steps and for the combined method were compared and shown to be comparable (Fig. 7).

Fig. 8 then shows the isothermal crystallization curves between 19 °C and 23 °C of cocoa butter obtained with the combined method. The amount of released crystallization heat at equilibrium (i.e. after the second crystallization step) decreases as the temperature increases above 21 °C. The amount of α crystallization decreases as the temperature increases. The rate of α crystallization and of the polymorphic transition from α to β′ both decreases as the temperature increases above 20.5 °C. No induction time for α crystallization is present, and the induction time of the polymorphic transition increases with increasing temperature.

4.4. Case 4: information about crystallization mechanism

Since each fraction and each polymorph of a fat has its own melting range, the peak temperatures of the melting curves obtained via the stop-and-return method can also provide information on the isothermal crystallization mechanism.

Fig. 9 shows the melting profiles of palm oil to which 2% hydrogenated fat was added, after isothermal crystallization at 25 °C for 1 min, 4 min, 7 min, 10 min and 30 min. After 1 min isothermal crystallization a pronounced peak with peak temperature at 32.5 °C is visible. After 4 min isothermal crystallization, a larger peak with more or less the same peak temperature is observed, meaning the same fraction/polymorph has crystallized further between 1 min and 4 min isothermal crystallization. After 7 min isothermal crystallization a second, higher melting peak (peak temperature 40.51 °C) appears while the first peak decreases in area. From this it can be concluded that a polymorphic transition from a less stable to a more stable polymorph takes place, and taking into account the polymorphism of palm oil [9], it can be assumed that the first peak coincides with the α polymorph while the second one coincides with the β′ polymorph. After 10 min and 30 min isothermal crystallization, the lower melting α peak has disappeared and the higher melting β′ peak has increased in area, indicating a further polymorphic transition and possibly extra crystallization from the melt directly to the β′ polymorph.

To validate this hypothesis, real-time X-ray diffraction was done. Fig. 10 shows the SAXS-diffraction patterns. At short crystallization times, one peak with a long spacing at 48.69 Å is observed. From 8 min isothermal crystallization onwards a second peak is visible with a long spacing of 43.33 Å. At longer isothermal times, this second peak increases and the first peak decreases. Based on the WAXD-diffraction patterns (detailed results not shown) the two SAXS peaks could be attributed to the α and β′ polymorphs, respectively. The crystallization mechanism (crystallization from the melt to the α polymorph, followed by a polymorphic transition to the β′ polymorph) hypothesized on the basis of DSC stop-and-return experiments was thus justified by XRD.

5. Conclusions

If the standard direct isothermal DSC method is not applicable to obtain isothermal crystallization curves of fats, the stop-and-return method provides a valuable alternative. This technique is based on the determination of the melting profiles at different moments in time during the isothermal crystallization. The melting enthalpy is then used as a measure for the amount of crystallization. Furthermore, the stop-and-return method can be used to gain more information about the crystallization mechanism when real-time X-ray diffraction (the ultimate tool to study crystallization mechanisms) is not readily available.

Acknowledgements

Imogen Foubert is a Postdoctoral Fellow of the Fund for Scientific Research-Flanders (F.W.O.-Vlaanderen). The authors thank F.W.O.-Vlaanderen and Prof. H. Reynaers for their continuous support of the DUBBLE project.

References

[1] S. Metin, R.W. Hartel, J. Am. Oil Chem. Soc. 75 (1998) 1617–1624.

[2] D. Fessas, M. Signorelli, A. Schiraldi, J. Therm. Anal. Calor. 82 (2005) 691–702.
[3] I. Foubert, P.A. Vanrolleghem, K. Dewettinck, Thermochim. Acta 400 (2003) 131–142.
[4] I. Foubert, J. Vereecken, K.W. Smith, K. Dewettinck, J. Agric. Food Chem. 54 (2006) 7256–7262.
[5] E. Fredrick, I. Foubert, K. Dewettinck, Int. Dairy J., in preparation.
[6] K. Boode, P. Walstra, Colloids Surf. A 81 (1993) 121–137.
[7] H.D. Goff, J. Dairy Sci. 80 (1997) 2620–2630.
[8] K. Dewettinck, I. Foubert, M. Basiura, B. Goderis, Cryst. Growth Des. 4 (2004) 1295–1302.
[9] G. Mazzanti, A.G. Marangoni, S.H.J. Idziak, Phys. Rev. E 71. (2005).