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Insight in model parameters by studying temperature influence on isothermal cocoa butter crystallization

The aim of this research was to get more insight into the crystallization parameters of the model of Foubert *et al.* (2002) by examining the isothermal crystallization of two cocoa butters at different temperatures. The nucleation in the α polymorph was studied by scanning diffusive light scattering and was shown to agree with the Turnbull–Fisher equation. In accordance with the solubility principle, the amount of α crystals decreases as a function of temperature. The four parameters of the crystallization model were used to describe the influence of temperature on the β' crystallization. The parameter a_F decreases from temperatures of 20.5 °C onwards. The induction time increases with temperature while the rate constant *K* decreases as the temperature increases, especially at higher temperatures. Three hypotheses on the nature of the reverse reaction as described in the model were formulated and tested based on the temperature and cocoa butter dependency of the reverse reaction order *n*. The temperature dependence itself does not allow us to rule out one of the hypotheses, but the clear temperature dependence of the influence of the chemical composition is in favor of the hypothesis that the reverse reaction is dominantly either a re-melting or a redissolving reaction, depending on the crystallization temperature.

Keywords: Cocoa butter, fat, crystallization, temperature, mathematical modeling.

1 Introduction

The crystallization process may be separated into two steps: nucleation and crystal growth. However, both steps often occur simultaneously, making it difficult to determine the kinetics for each process. Yet, the crystallization kinetics is important for controlling operations in the food industry and thus to produce the desired product characteristics. The kinetics of fat crystallization depends on the triacylglycerol composition, the level of minor components and processing conditions (temperature, cooling rate, agitation rate, *etc.*) [1]. From the late 1970's onwards, but especially in the last few years, quite a number of articles have been published in which the isothermal crystallization of fats is mathematically modeled to enable quantification of differences in the crystallization behavior between different products and crystallization circumstances [2].

To obtain the model of Foubert *et al.* [3], the crystallization process was represented as if it is a combination of a first-order forward reaction and a reverse reaction of order *n*.

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The differential equation of this model is expressed in terms of a variable *h* (–), which is the relative remaining crystallizable fat:

$$h = \frac{a_F - f}{a_F} \tag{1}$$

where *f* (in J/g) is the amount of crystallization at time *t* (in h), and a_F (in J/g) is the maximum amount of crystallization. The dynamics of *h* can then mathematically be written as:

$$\frac{dh}{dt} = K \times (h^n - h) \qquad h(0) = \frac{a_F - f(0)}{a_F} \tag{2}$$

in which *K* is the rate constant (in h^{-1}) and *f(0)* (in J/g) is related to the initially present amount of crystals. To simplify parameter estimation, the differential equation was converted to its algebraic solution for isothermal conditions (Eq. 3). Since the physical interpretation of a parameter 'induction time' is more straightforward than that of the parameter *h(0)* (or the equivalent *f(0)*) and since the induction time can be more easily extracted from a crystallization curve, it was decided to represent the equation as a function of t_ind_x instead of *h(0)*. The parameter t_ind_x is defined as the time needed to obtain *x*% of crystallization, and *x* was chosen to be 1.

$$f(t) = a_F \times \left[1 - \left[1 + ((0.99^{1-n} - 1) \times e^{-(1-n)\times K\times(t-t\_ind_x)}\right]^{\frac{1}{1-n}}\right] \tag{3}$$

Although this model provided a superior fit than the often used Avrami and Gompertz models, the exact physical interpretation of the different crystallization parameters has not yet been completely elucidated. Therefore, it was the aim of this research to get more physical insight into the crystallization parameters, and especially in the parameter *n* of the model of Foubert *et al.* [3], by examining the isothermal crystallization of two types of cocoa butter at different temperatures.

Cocoa butter is a major component of the fat phase of chocolate. In fact, it contributes 30–40% by weight to finished chocolate and is responsible for texture, gloss and mouth feel of the chocolate products. Ziegleder [4] studied the isothermal cocoa butter crystallization by differential scanning calorimetry (DSC) and established a strong temperature dependency in the range of 19–23 °C. A plot of the logarithm of the Avrami rate constant *versus* temperature shows a decreasing straight line at temperatures from 20 °C onwards. This was attributed to the strong temperature dependence of the nucleation rate since the crystal growth rate is only very slightly dependent on temperature in the studied range. At temperatures below 20 °C, the rate constant increases less than expected from the linear relationship. According to the author, this is caused by an increase in the melt viscosity at these lower temperatures. The logarithm of the onset time, giving an indication of the start of the process, is also linearly correlated with temperature. This was again explained by the exponentially increasing nucleation rate at decreasing temperatures.

From the isothermal phase transition scheme developed for statically crystallized cocoa butter by Van Malssen *et al.* [5], it could be concluded that both the start of the α crystallization and the occurrence of the first β' crystals take place later, when the temperature is higher.

Marangoni and McGauley [6] used pulsed nuclear magnetic resonance (pNMR) to study the effect of temperature on the isothermal crystallization kinetics of cocoa butter. Both the induction time and the level at which the curves level off are a function of temperature: the former increases while the latter decreases with increasing temperature.

A second aim of this study was to describe the influence of temperature on the isothermal, static crystallization of different kinds of cocoa butter, not so much different in triacylglycerol composition, as described by, *e.g.*, Ziegleder [4], but differing in the amounts of minor components. This influence was studied based on isothermal DSC measurements between 19 and 23 °C. Supplementary information was obtained by scanning diffusive light scattering (SDLS) and pNMR experiments.

Summarized, the goal of this research was thus twofold: to gain more insight into the crystallization parameters of the model of Foubert *et al.* [3], while studying the effect of temperature on the isothermal crystallization of cocoa butters differing in their content of minor components.

2 Materials and methods

2.1 Cocoa butters

A mixture of cocoa butters from different origin (CB A) and a Nigerian cocoa butter (CB B), both supplied by Barry Callebaut (Wieze, Belgium), were used. Their composition is given in Tab. 1.

Tab. 1. Chemical composition of the studied cocoa butters.

Chemical composition variable	Mixture (CB A)	Nigerian (CB B)
Palmitic acid [%]	25.0 ± 0.2	26.5 ± 0.0
Stearic acid [%]	37.7 ± 0.2	37.1 ± 0.2
Oleic acid [%]	33.6 ± 0.0	33.1 ± 0.1
Linoleic acid [%]	2.72 ± 0.1	2.25 ± 0.05
Arachidic acid [%]	1.01 ± 0.06	1.03 ± 0.06
Trisaturated triacylglycerols [%]	1.63	2.10
POP + POS + SOS [%]	84.5	87
POO + SOO [%]	5.7	3.89
Diacylglycerols [%]	0.72	1.1
Free fatty acids [%]	1.38 ± 0.01	2.77 ± 0.02
Soap [ppm]	195 ± 53	3.05 ± 0.01

2.2 Isothermal crystallization experiments by pNMR

The pNMR experiments were performed with a Minispec pc 20 (Bruker, Karlsruhe, Germany). Liquefied cocoa butter was transferred to pNMR tubes, and these were warmed up to 65 °C for 1 h to eliminate any thermal history. Then, they were placed in a thermostatic water bath at crystallization temperature. The sample temperature decreased exponentially with an initial rate of 25 °C/min. Readings of the amount of solid fat were taken at appropriate time intervals, and a separate tube was used for each measurement.

2.3 Isothermal crystallization experiments by SDLS

An NK60-CPA (Phase Technology, Richmond, Canada) light-scattering analyzer was used to follow the initial phases of the isothermal cocoa butter crystallization.

Liquefied cocoa butter (150 μL) was placed in the sample compartment, heated up to 65 °C at 25 °C/min and held at that temperature for 15 min. Next, the sample was cooled at 8 °C/min to the crystallization temperature, where it was kept until saturation of the signal (*i.e.* a value of 250). The induction time for α crystallization (t_ind_α) was determined as the time needed for the crystal signal to increase 5 units above the minimum value.

2.4 Isothermal crystallization experiments by DSC

The DSC experiments were performed with a 2010 CE DSC (TA Instruments, New Castle, USA) with a Refrigerated Cooling System (TA Instruments). The DSC was calibrated with indium (TA Instruments), azobenzene (Sigma-Aldrich, Bornem, Belgium) and undecane (Acros Organics, Geel, Belgium) before analyses. Nitrogen was used to purge the system. Cocoa butter (2.7–15.3 mg) was sealed in hermetic aluminum pans using sample preparation procedure B as described in Foubert *et al.* [7], and an empty pan was used as a reference. The applied time-temperature program was as follows: holding at 65 °C for 15 min to ensure a completely liquid state, cooling at 8 °C/min to the isothermal crystallization temperature, and keeping at that temperature until crystallization had finished. The crystallization peaks were integrated using a horizontal sigmoid baseline, and the starting and end points were determined using the calculation algorithm as described in Foubert *et al.* [7]. In between the starting and end points, the area (and thus the amount of heat released up to that moment) was calculated at 5-min intervals. The integration was performed with the Universal Analysis software version 2.5 H (TA Instruments).

2.5 Parameter estimation

The model of Foubert *et al.* [3] was fitted to the data series by non-linear regression using the Sigmaplot 2000 software (SPSS Inc., Chicago, USA). The same software was used to fit the Turnbull–Fisher equation to the data obtained by SDLS.

2.6 Stop-and-return experiments using DSC

Stop-and-return experiments using DSC were applied to estimate the amount of α crystallization. For these experiments the same pan as for the isothermal crystallization experiment at that crystallization temperature was used. Such an experiment is basically identical to the isothermal crystallization experiment, except that the sample is heated (at 5 °C/min) after a given time, but prior to completion of the crystallization. For cocoa butter, the heating rate of 5 °C/min is fast enough to prevent polymorphic transitions from taking place during heating, and slow enough to eliminate effects of thermal lag. As melting starts as soon as heating is initiated, no stable baseline was available at the low-temperature side. Accordingly, it was decided to integrate the peaks using a linear baseline with the end point at the visual end of the melting peak and the starting point at the same y value as the end point. It has to be stressed that this method only gives an approximation of the area of the melting peak. The integration was performed with the Universal Analysis software version 2.5 H (TA Instruments).

2.7 Detection of statistically significant differences

To check the general influence of the independent variable temperature on the different crystallization parameters, ANOVA was performed (SPSS for Windows 10.0.5; SPSS Inc., Chicago, USA). A significance level of 0.05 was used at all times. To check what temperatures differed significantly (*post-hoc* tests), the adapted *t*-test as described in Foubert *et al.* [7] was used. This test takes into account that the calculated model parameters themselves are estimates. A significance level of 0.05 was also used here. The same adapted *t*-test was used to check whether the type of cocoa butter has a significant influence on the model parameters at each temperature.

3 Results and discussion

3.1 Influence of temperature as measured by pNMR

Fig. 1 shows the amount of solid fat as a function of time for CB A at temperatures between 19 and 23 °C. Comparable curves were observed for CB B. At these temperatures, the crystallization clearly is a two-step process.

Dewettinck *et al.* [8] investigated this process in more detail by means of pNMR, DSC (stop-and-return experiments) and real-time X-ray diffraction. They proposed a mechanism for the two-step crystallization based on the observed isosbestic behavior. In the first step, part of the melt crystallizes into the α polymorph, while in the second step α crystals transform into β' crystals. This second step starts before the melt-to-α transition is complete. In the late stage of the process, the α crystallization stops and only the polymorphic transition from α into β' is observed. The crystallinity increase during the conversion

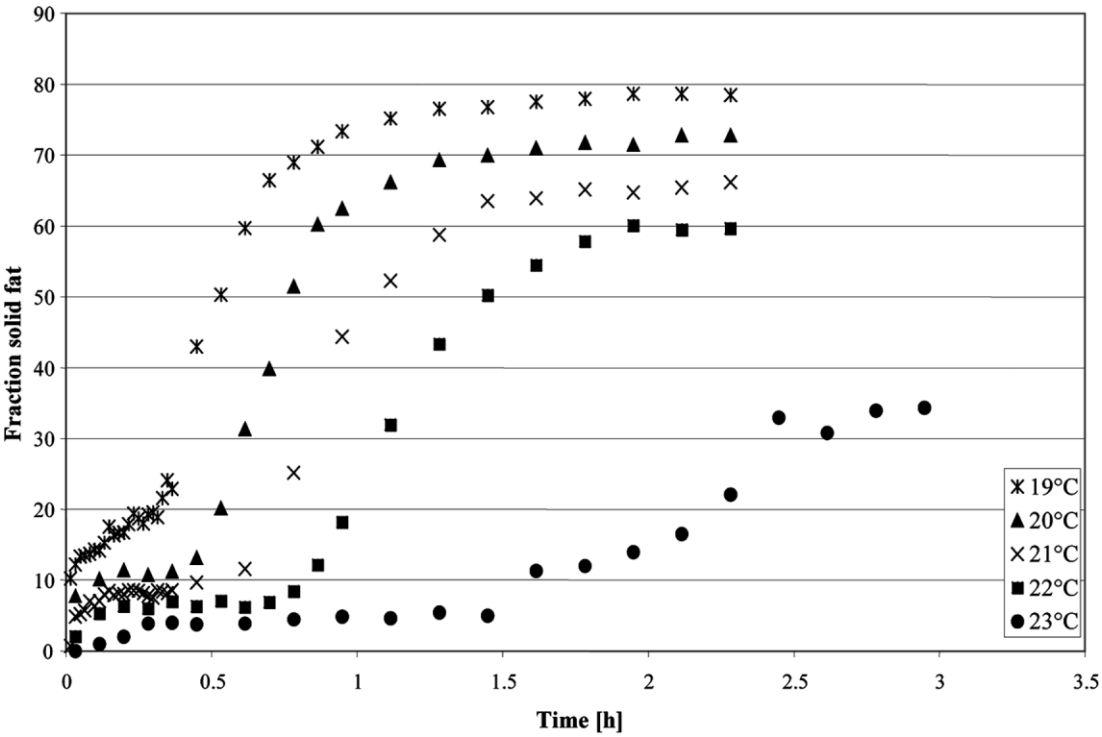


Fig. 1. Influence of the isothermal crystallization temperature on the amount of solid fat *versus* the time curves as obtained by pNMR for CB A. (*) 19 °C, (▲) 20 °C, (X) 21 °C, (■) 22 °C, (◆) 23 °C.

from α to β' is related to the transformation of the typical liquid-like layers of the α polymorph into β' crystalline material.

From Fig. 1 it can be seen that both the rate of the first step (rate of α crystallization) and the height of the plateau after the first step (amount of α crystallization) decrease as the crystallization temperature increases. Also, the second step (induction time for polymorphic transition of α to β') starts later and the crystallization occurs more slowly. Furthermore, the equilibrium amount of solid fat decreases as the temperature increases.

It has to be remarked that the β' crystals formed during this two-step crystallization are metastable crystals that will, over a long period of time, transform into a stable β_V polymorph. This transition was, however, not studied in the framework of this research.

3.2 The α induction time as determined by SDLS

SDLS was used to study the initial phase of the first crystallization step, *i.e.* the crystallization of part of the melt in the α polymorph. Since the crystal signal saturates very quickly, no information about the later stages of crystallization could be obtained using this experimental technique. Fig. 2 shows that the α induction time (t_ind_α) increases exponentially with temperature. No jump in the curve can be observed, meaning that the same polymorph was formed [9] in the whole temperature range studied. This was expected as it was already demonstrated that α crystals are formed first at all investigated temperatures [8].

Taking account of the rather low supercooling at which crystallization occurs, heterogeneous nucleation can be suspected to take place [10]. The temperature dependence of heterogeneous nucleation is, however, the same as for homogeneous nucleation, and the latter is described by the Turnbull–Fisher equation [10]. Considering that the induction time is inversely proportional to the nucleation rate and neglecting the volume diffusion term of the Turnbull–Fisher equation, the induction time can thus be written as a function of temperature as:

$$t\_ind_\alpha = \frac{h_P}{N_m k_B T_K} e^{\left(\frac{-16\pi V_m^2 \gamma^3 \times T_{Km}^2}{3k_B \Delta H \times \Delta T^2 \times T_K}\right)} \quad (4)$$

with T_K being the absolute temperature (in K), T_{Km} the absolute melting temperature (K), and $T_{Km} - T_K = \Delta T$ being the supercooling (K). The other parameters in the equation have the following meaning: h_P is the Planck's con-

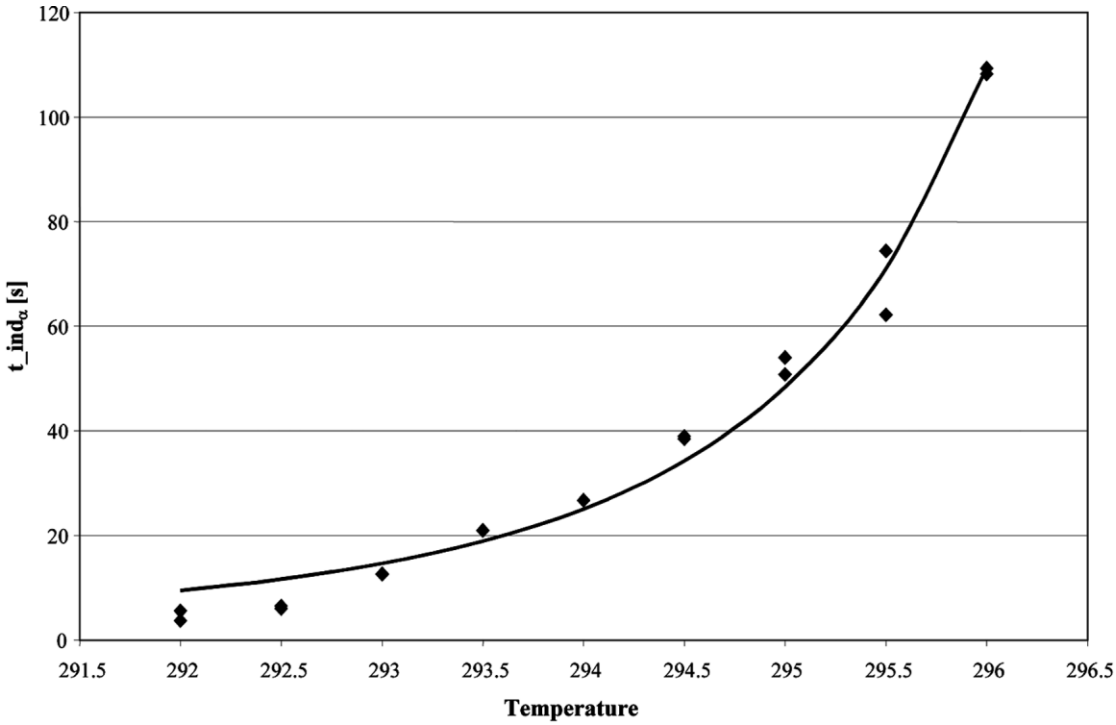


Fig. 2. Influence of temperature on the α induction time as measured by SDLS (CB A) and the Turnbull–Fisher equation fitted to these data (T_{Km} = 309 K).

stant (J s), N_m is the number of molecules per m^3 (m^{-3}), k_B is the Boltzmann constant (J K^{-1}), V_m is the molar volume (m^3 $mole^{-1}$), γ is the surface free energy per unit surface area (J m^{-2}), and ΔH is the molar enthalpy variation in the system during the transition (J $mole^{-1}$). For fitting purposes, some parameters are summarized in *cst1* and *cst2*, leading to Eq. 5. Eqs. 6 and 7 then give the definition of these constants.

$$t\_ind_\alpha = \frac{cst1}{T_K} e^{\left(\frac{cst2 \times T_{Km}^2}{\Delta T^2 \times T_K}\right)} \quad (5)$$

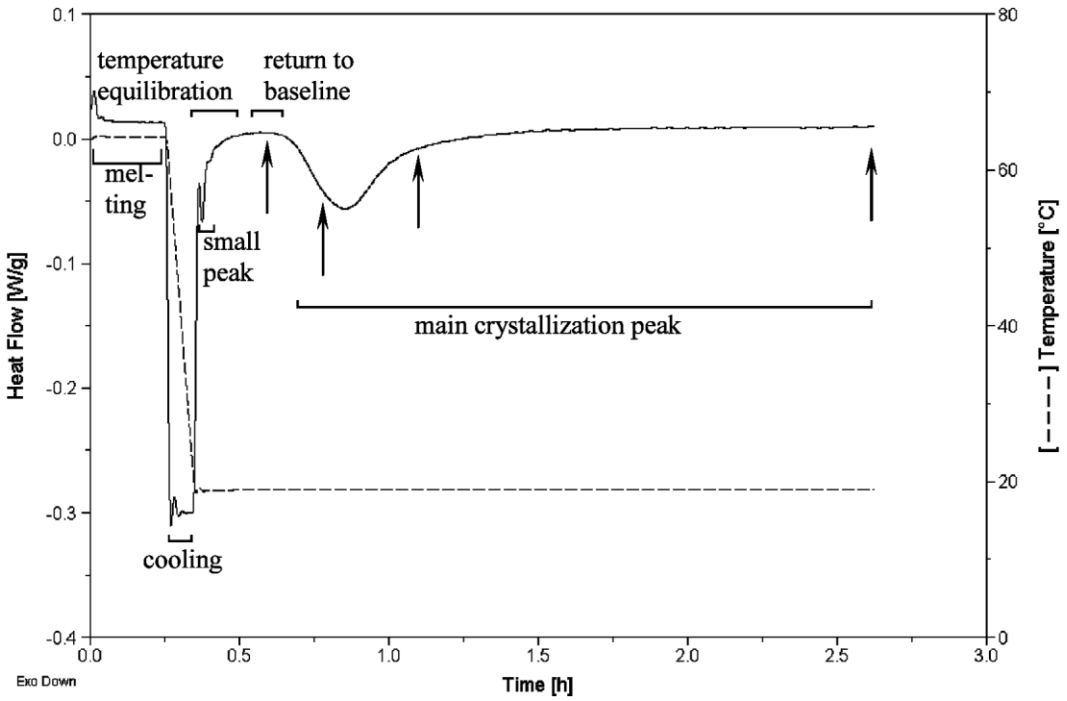
$$cst1 = \frac{h_P}{k_B N_m} \quad (6)$$

$$cst2 = \frac{16\pi V_m^2 \gamma^3}{3 k_B \Delta H} \quad (7)$$

It was investigated whether Eq. 5 could be fitted to the data points in Fig. 2. Using the definition for T_{Km} proposed by Litwinenko *et al.* [11], as being the peak maximum of a DSC melting profile (heating at 5 °C/min) of the stable sample (stored for months, thus most probably in the β_V polymorphic form), the melting point of CB A was established at 36 °C or 309 K. A good fit (R^2 = 0.984) to Eq. 5 was then obtained, as the curve in Fig. 2 shows. The obtained parameter values are: 75 K s for *cst1* and 3.2 K for *cst2*. Using the value of *cst2*, a value of 1.46×10^{-20} J per molecule was obtained for ΔG^* for a crystallization temperature of 19 °C. This value is equivalent to 8.8 kJ $mole^{-1}$, a value of the same order of magnitude as reported in the literature by Toro-Vazquez *et al.* [12] for tripalmitin in sesame oil, by Herrera *et al.* [13] and Wright and Marangoni [14] for milk fat (fractions), and by Litwinenko *et al.* [11] for palm-based shortening.

3.3 Isothermal crystallization as measured by DSC

An example of a DSC thermogram is shown in Fig. 3A. In the isothermal DSC experiments, the first crystallization step was visible as a small peak at the start of the isothermal period. However, due to overlap with the temperature equilibration, it is impossible to integrate this peak. Therefore, only the main crystallization peak was integrated and the model of Foubert *et al.* [3] was fitted to the data series. Taking into account the above proposed mechanism, this main peak represents the polymorphic transition of already formed α crystals into β' and the α-mediated β' crystallization. As will be demonstrated



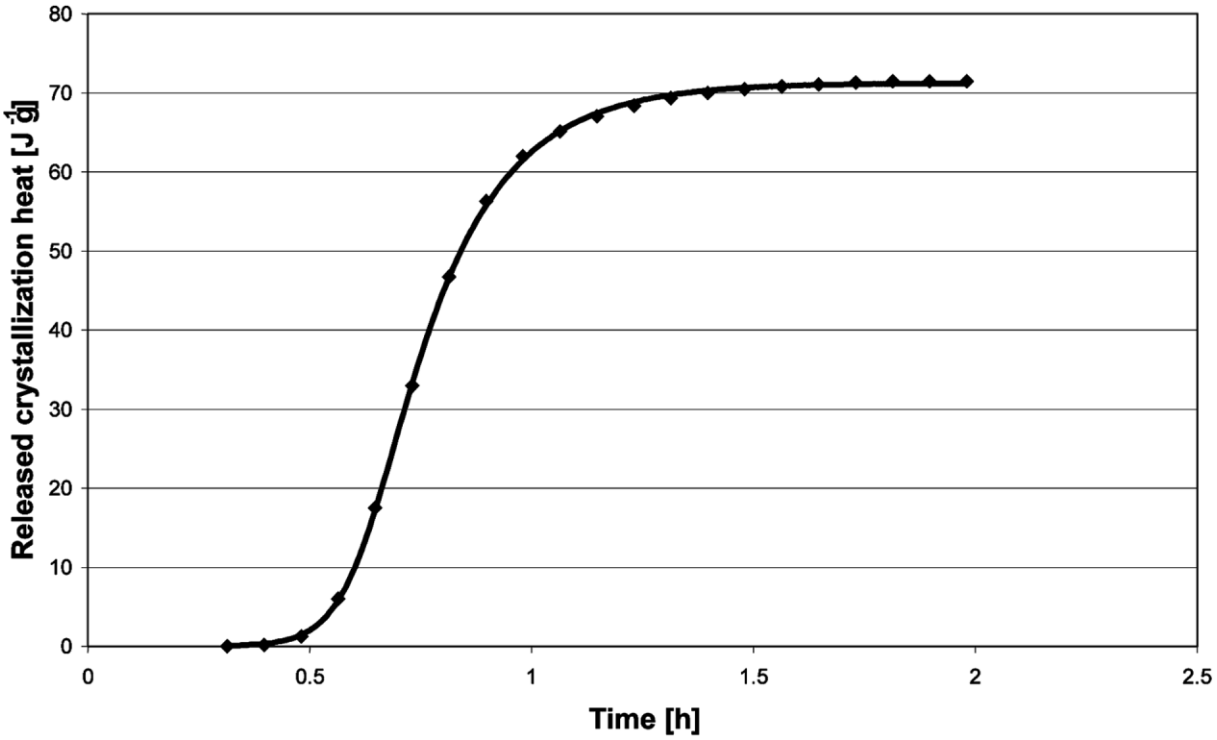


Fig. 3. (**A**) Example of isothermal cocoa butter crystallization at 20 °C as measured by DSC. (**B**) Example of an integrated curve of isothermal cocoa butter crystallization at 20 °C together with a fit of the model of Foubert *et al.* [3]. (◆) Experimental data points, (___) as predicted by the model.

further (paragraph stop-and-return experiments by DSC), the contribution of the polymorphic transition of already formed α crystals into β' is negligible compared to the contribution of the α-mediated β' crystallization. Fig. 3B shows an example of an integrated main crystallization peak and the excellent quality of the model fit. To have an idea of the amount of α crystals formed before the main crystallization peak, stop-and-return experiments were conducted at each temperature.

3.4 Stop-and-return experiments by DSC

The amount of α crystallization was estimated by DSC by holding the sample at the crystallization temperature up to the starting point of the integration of the main peak and then heating up the sample.

Considering that the latent heat of the α polymorph is around 80 J g^{-1} [15], the mass fraction α crystals can be calculated from the area of the melting peak. For CB A this mass fraction decreases from 14.7% at 19 °C to 2.4% at 22 °C, while for CB B a decrease from 16.4% at 19 °C to 2.8% at 22.5 °C was observed. The same decrease of the mass fraction of α crystals as a function of temperature for CB A can also be observed in Fig. 1.

Comparable results for the mass fraction of solid fat after the first step were obtained by Herrera *et al.* [13] for milk fat and by Ng and Oh [16] for palm oil. The result can be explained by the higher solubility at higher temperatures as described by the Hildebrand equation.

Using the mass fractions of α crystals formed in the first crystallization step, the contribution to the main DSC crystallization peak of their transformation to β' can be calculated taking account of the heat of polymorphic transition of approximately 20 J g^{-1}. The contribution appears to be 3.3 J g^{-1} at the most and is thus negligible compared to the total area of the main peak, which is between 50 and 80 J g^{-1}.

3.5 Model parameter a_F

Fig. 4 shows the influence of temperature on the a_F parameter for both cocoa butters. Taking into account that the latent heat of the β' polymorph is about 100 J g^{-1} [15], the a_F value equals the mass fraction β' crystals formed in the second step of crystallization, neglecting the heat released by the polymorphic transition of the already formed α crystals (see former section).

ANOVA detected a significant effect of temperature on a_F for both cocoa butters. For CB A, the value remains constant until 20.5 °C and then starts to decrease (although not all differences are significant). For CB B, the a_F value slightly increases up to a temperature of 20.5 °C and then decreases as the temperature further rises. At temperatures up to 21 °C, the amount of crystallization is significantly higher for CB A compared to CB B. For the higher temperatures, the same trend is visible, although the difference is not always significant. This difference cannot be explained by the difference in triacylglycerol composition, since one would then expect that CB A, with its higher amount of di-unsaturated triacylglycerols which do not crystallize at temperatures around room temperature, has a lower a_F value, which does not coincide with the observations. However, CB B, although having a lower amount of di-unsaturated triacylglycerols, contains a larger amount of diacylglycerols and free fatty acids, which have been reported to decrease the amount of solid fat [17, 18]. From the above it is clear that not only the triacylglycerol composition is important to judge the physical properties of cocoa butter.

By adding the mass fraction α formed in the first step (obtained by the stop-and-return experiments) to a_F, an equivalent to the equilibrium amount of solid fat could be calculated from the DSC experiments. This value decreases as a function of temperature in the same way as the equilibrium amount of solid fat, as depicted in Fig. 1.

3.6 Model parameter t_ind_x

Fig. 5 shows the influence of temperature on the t_ind_x parameter for both cocoa butters. This parameter represents the induction time of the second step of crystallization, *i.e.* the α-mediated β' crystallization. This induction time is defined as the time needed to obtain 1% of β' crystallization in terms of released crystallization heat; it is thus the time where the released crystallization heat equals 1% of the final amount of released crystallization heat. This means that t_ind_x reflects the time needed to initiate the polymorphic transition from α to β'. However, the induction time as measured by DSC will also be associated with crystal growth, since a considerable heat flow is only measured when the β' crystals are growing.

It is obvious that t_ind_x increases as a function of temperature in a more or less exponential way. No jump is observed in Fig. 5, indicating that always the same polymorph (*i.e.* the β' polymorph) is formed in the studied temperature range [9]. This again agrees with the mechanism proposed by Dewettinck *et al.* [8].

ANOVA showed that temperature has a significant influence on t_ind_x for both cocoa butters. As already stated in the introduction, Ziegleder [4] also crystallized cocoa

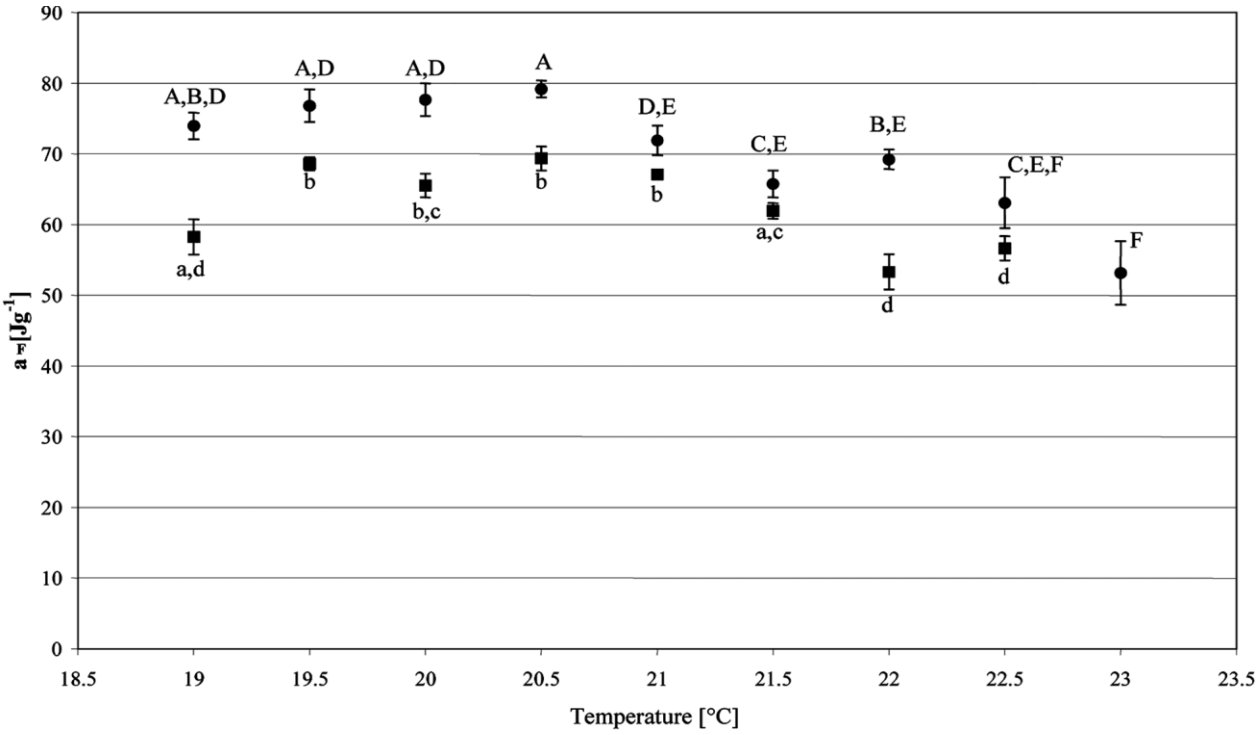


Fig. 4. Influence of temperature on a_F. Adapted *t*-tests were used to obtain more details on what temperatures differ significantly, and the results are indicated by letters. Values with the same letter are not significantly different at the 5% level. (●) CB A, (■) CB B.

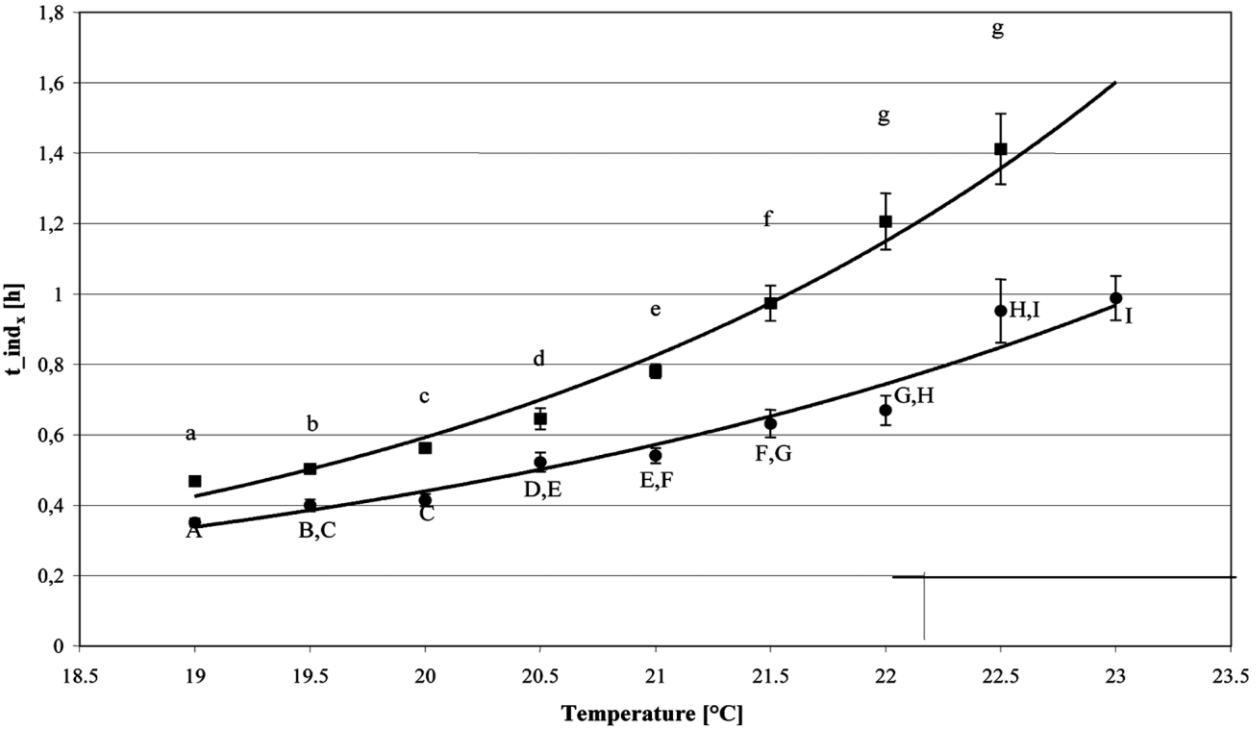


Fig. 5. Influence of temperature on t_ind_x and an exponential curve fitted to the data. Adapted *t*-tests were used to obtain more details on what temperatures differ significantly, and the results are indicated by letters. Values with the same letter are not significantly different at the 5% level. (●) CB A, (■) CB B.

butter isothermally at different temperatures. He obtained a linear relation between the logarithm of the onset time (the intersection of the baseline with the line tangent to the curve at the inflection point) and the crystallization temperature. The onset time gives an indication of the start of a process and is thus related to the induction time t_ind_x. The linear correlation between the logarithm of the onset time and the crystallization temperature obtained by Ziegleder [4] would correspond with an exponential relationship between t_ind_x and temperature. For CB A, a rather good exponential relationship was obtained ($R^2 = 0.87$). In contrast to the results of Ziegleder [4], no deviation from the exponential relationship was observed at temperatures between 19 and 20 °C. For CB B, an R^2 of 0.93 was obtained, also without a deviation at the lower temperatures.

Marangoni and McGauley [6] and Van Malssen *et al.* [5] also obtained increasing induction times for polymorphic transition at higher temperatures. However, ten Grotenhuis *et al.* [19] stated that the stability of the α polymorph of milk fat is higher at lower temperatures, leading to a diminished driving force for polymorphic transition and thus a later start of the transition at lower temperatures. Sato and Kuroda [20] showed that the rate of the isothermal polymorphic transition from α (formed by rapid cooling of the melt to 0 °C) to β in tripalmitin increases with rising temperature.

A possible explanation for this contradiction is that due to the very low supercooling for the β' polymorph (only about 5 °C at the highest isothermal crystallization temperature) the crystal growth may be retarded, especially at the highest temperatures. This would mean that it takes a longer time before a considerable amount of heat is released. Still, it is possible that β' nuclei already exist quite some time before the moment when the β' crystals have grown enough to release enough heat to be detected by DSC. It is thus also possible that the first β' nuclei appear earlier at higher temperatures. In milk fat and tripalmitin, the difference between the melting points of both polymorphs is higher, causing the smallest possible supercooling for β' formation by polymorphic transition to be higher (α polymorphs can only be formed up to the melting point of α). This may mean that crystal growth is not that much retarded and that is why the faster nucleation in the more stable polymorph at higher temperatures may predominate.

At all temperatures the induction time is significantly higher for CB B compared to CB A. This can probably be explained by the larger amount of diacylglycerols in CB B, which are known to hinder polymorphic transitions [21, 22].

3.7 Model parameter K

Fig. 6 shows the influence of temperature on the *K* parameter for both cocoa butters. This parameter represents the rate constant of the crystallization process. ANOVA showed a significant influence of temperature on *K* for both cocoa butters.

It is obvious that for CB A, the *K* value remains more or less constant up to 20 °C, but decreases strongly at higher temperatures. For CB B, the *K* value at the lowest temperatures is much lower than the values of CB A (significantly higher value for CB A up to a temperature of 21.5 °C) while at higher temperatures the difference is less pronounced (no significant difference at temperatures 22 and 22.5 °C). As a consequence, the decrease at higher temperatures is less clear for CB B.

As already mentioned in the introduction, Ziegleder [4] observed a linear dependence of the logarithm of the Avrami rate constant *k* on temperature from 20 °C onwards. This corresponds with an exponential relationship between *k* and temperature from 20 °C onwards. He attributed the lower than expected values for temperatures lower than 20 °C to the increase of the melt viscosity. A similar result was obtained by Supaphol and Spruiell [23] for melt crystallization of polymers. They described the temperature dependency of the crystallization rate constant with a bell-shaped curve and ascribed this type of curve to the nucleation control effect at low supercooling and the diffusion control effect at high supercooling.

The data for CB A can be described rather well by the right side of such a bell-shaped curve, which shows that, as expected, the viscosity influence is not that pronounced in the temperature interval studied. The data of CB B can hardly be described by a bell-shaped curve. Possibly, the rate constant *K* only starts to decrease strongly at higher temperatures.

The higher values for CB A at most of the temperatures cannot be explained by the triacylglycerol composition. CB A contains a higher amount of di-unsaturated triacylglycerols, and one would thus expect a slower crystallization rate for this type of cocoa butter. However, CB B contains more diglycerides and free fatty acids, which have a negative influence on the growth rate, as shown, *e.g.*, by Pontillon [24], Shukla [25], Ziegleder [26] and Wright *et al.* [27]. When diacylglycerols become incorporated in the solids, they create irregularities in the growing crystal because of the hydroxyl group they contain instead of a fatty acid chain. This polar region, or the structural vacancy created in the lattice, may hinder the incorporation of triacylglycerol molecules into the crystal and thus the subsequent crystallization. This effect may

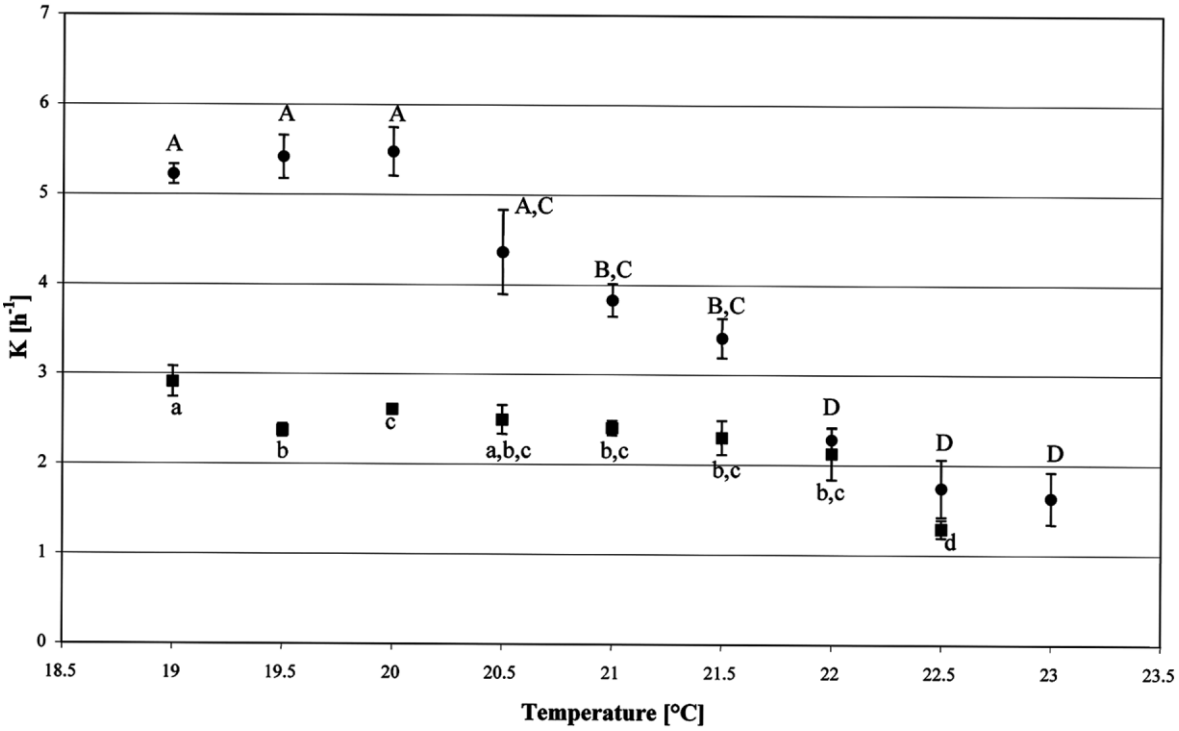


Fig. 6. Influence of temperature on *K*. Adapted *t*-tests were used to obtain more details on what temperatures differ significantly, and the results are indicated by letters. Values with the same letter are not significantly different at the 5% level. (●) CB A, (■) CB B.

be less pronounced when the crystallization proceeds more slowly as the incoming triacylglycerols have more time to incorporate into the crystal lattice. This may explain why the difference between CB A and CB B becomes less pronounced at higher crystallization temperatures and thus lower growth rates.

3.8 Model parameter *n*

Fig. 7 shows the influence of temperature on the *n* parameter for both cocoa butters. This parameter represents the order of the reverse reaction of the crystallization process, reflecting for how long this reverse reaction affects the crystallization process. The higher *n*, the shorter is its influence.

Several hypotheses concerning the detailed nature of the reverse reaction can be formulated:

(i) As crystallization takes place, latent heat of crystallization is released. Locally, this causes the temperature to rise, which may lead to a local melting of crystals if the local temperature rises above the melting point of these crystals.

(ii) Formed crystals may redissolve. This possibility was proposed by Smith *et al.* [28] who showed that, at thermal equilibrium, an exchange of molecules between pools in solid and dissolved form takes place. Their experiments were performed on a model system of β crystals of tripalmitin as the solid phase, and tripalmitin dissolved in a medium-chain triacylglycerol oil as the liquid phase. A surface specific exchange rate of 11 mg h^{-1} m^{-2} was obtained. It could be argued that a similar phenomenon takes place during crystallization.

(iii) A combination of several processes takes place, *e.g.*, a combination of re-melting, redissolving and diffusion of the molecules away from the crystals. It is possible that the importance of each process depends on the crystallization temperature. The values of *n* well above 1 are an argument in favor of this hypothesis. For a simple re-melting or redissolving reaction, a reaction order around 1 would be expected.

ANOVA showed a significant influence of temperature on *n*. It is clear that the *n* value initially decreases, but remains more or less constant from 20.5 °C (CB A) or 21.5 °C (CB B) onwards. The difference between CB A and CB B is strongly dependent on the crystallization temperature: At the lowest temperatures (19, 19.5 and

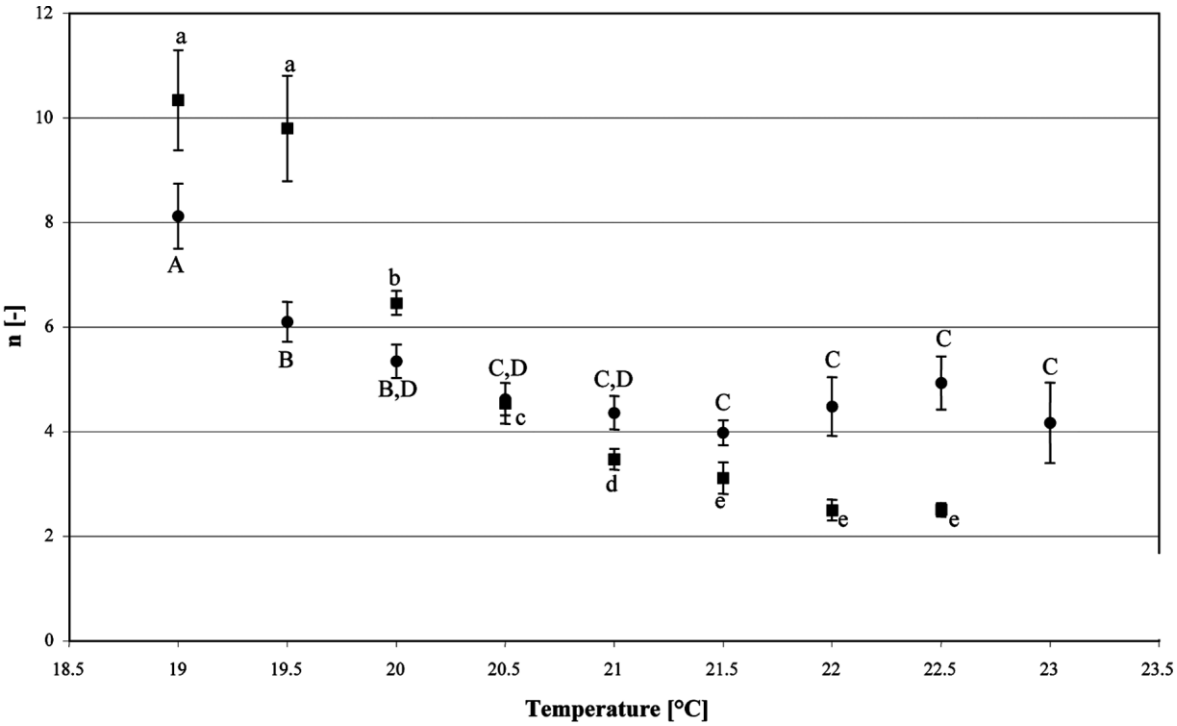


Fig. 7. Influence of temperature on *n*. Adapted *t*-tests were used to obtain more details on what temperatures differ significantly, and the results are indicated by letters. Values with the same letter are not significantly different at the 5% level. (●) CB A, (■) CB B.

20 °C) the value of *n* is higher for CB B, at intermediate temperatures (20.5, 21 and 21.5 °C) there is no significant difference, and at the highest temperatures (22 and 22.5 °C) the value of *n* is higher for CB A.

The plausibility of the three hypotheses mentioned above can be checked by taking into account the temperature and cocoa butter dependency of the parameter *n*.

Re-melting may be suspected to be less plausible at lower temperatures, as the temperature has to increase more before the melting point is reached. This would cause the reverse reaction to lose its effect faster and thus lead to higher *n* values at lower temperatures. This agrees with the observed results.

When redissolution of molecules from the crystals takes place, the expectation is that, at lower temperatures, when more nuclei are formed and the crystals remain smaller, the rate of the reverse reaction decreases less and thus lower *n* values are obtained. This is in contrast to the observations. However, it is also of importance that the solubility is higher at higher temperatures, and for that reason, redissolution may be more favored at these higher temperatures, leading to a lower value of *n*.

A reverse reaction only caused by one process, either re-melting or redissolving makes it, however, very hard to explain the clear temperature dependence of the influence of the chemical composition, as both processes are expected to be more pronounced for one of both cocoa butters, and this independent of the crystallization temperature.

A combination of several processes was a third hypothesis. The temperature influence may then be explained by a different dominating process, leading to another order of the reaction. Re-melting may dominate at higher temperatures due to the smaller temperature difference between crystallization and melting temperature, whereas at lower temperatures redissolving may be favored because of the smaller crystal size. Redissolving may be considered then as a more complex reaction, depending directly on *h*, but also on several variables (*e.g.* the size of the crystals), which are in turn affected by *h*. This may explain the higher order of the overall reaction. Such a different dominating process at different temperatures could then also explain why the influence of chemical composition is different at lower crystallization temperatures compared to higher crystallization temperatures, as re-melting may be more pronounced in one cocoa butter while redissolving is more pronounced in the other.

4 Conclusions

The influence of temperature is more or less comparable for both cocoa butters. It was determined that the nucleation in the α polymorph, as measured by SDLS, agrees with the Turnbull–Fisher equation describing a higher induction time at higher temperatures. Furthermore, the amount of α crystals was shown to decrease as a function of temperature, in accordance with the Hildebrand equation. The parameter a_F decreases from temperatures of 20.5 °C onwards. Also, the induction time of the polymorphic transition to β' (however, possibly also influenced by the growth rate of β' crystals) (t_ind_X) increases with temperature. The rate constant K decreases as the temperature increases, especially at higher temperatures. The order of the reverse reaction n decreases up to a certain temperature and then remains equal. This does not allow us to select one of the three introduced possible explanations for the reverse reaction. The temperature dependence of the influence of the chemical composition, on the other hand, is in favor of the third hypothesis stating that the dominating type of reverse reaction (re-melting *versus* redissolving) differs at different crystallization temperatures. The influence of the chemical composition on the model parameters also made clear that not only the triacylglycerol composition but also the content of minor components is important to estimate the crystallization properties of cocoa butter.

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