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Journal of Food Engineering 75 (2006) 551–559
JOURNAL OF FOOD ENGINEERING
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Modelling two-step isothermal fat crystallization

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Received 22 December 2004; accepted 27 April 2005
Available online 1 July 2005

Abstract

Since fats are complex mixtures of triglycerides, multiple steps may be identified in their crystallization curves, due to polymorphism or crystallization of different fractions. This kind of curve, which was already observed in several studies, is more complex to model than single step crystallization curves. Therefore it is the aim of this research to present an extension of the Foubert model which facilitates the description of two-step processes. The data used in this study are from isothermal crystallization of milk fat (fractions) and cocoa butter examined by time-resolved X-ray diffraction (XRD) where the first crystallization step involves crystallization of part of the melt in the α polymorph while the second step is an α mediated β′ crystallization with no β′ crystals formed directly from the melt. The model is built based on these assumptions, that are based on the occurrence of an isosbestic point. Simulation experiments are performed to show the role of the different model parameters. Parameter estimation on the different data sets is performed with a very good fit as a result.

Keywords: Mathematical modelling; Time-resolved X-ray diffraction; α mediated β′ crystallization; Fat; Two-step crystallization

1. Introduction

Since crystallized fat is an important part of many food products, a detailed understanding of the crystallization process is desirable. Both the evolution of the amount of crystallization as a function of time, i.e. the crystallization kinetics, and the type of polymorph(s) formed, are valuable information for the food industry. This knowledge can be applied to better control processing steps that involve (re)crystallization of the fat fraction, thus ensuring the desired product quality. Factors influencing the crystallization process are the chemical composition of the product and the crystallization conditions.

In order to quantify the differences in crystallization behaviour caused by these influencing factors, mathematical modelling can be applied. A model is constructed to describe the crystallization process as closely as possible. By fitting an adequate model directly to experimental datasets, parameters with a physical meaning can be extracted.

The Foubert model (Foubert, Vanrolleghem, Vanhoutte, & Dewettinck, 2002) can be used to describe isothermal fat crystallization when it is a one-step process. It was shown that it performs better than the Avrami and Gompertz models, two more traditionally used models.

However, since fats are complex mixtures of triglycerides, their crystallization can be a two-step process. This can be either due to the formation of different polymorphic forms or due to the crystallization of different

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doi:10.1016/j.jfoodeng.2005.04.038

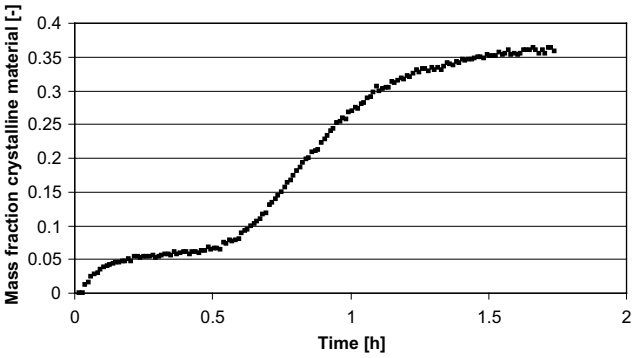

Fig. 1. Example of a two-step crystallization curve (cocoa butter isothermally crystallizing at 20 °C).

fractions. This leads to curves which rise to an intermediate plateau and then increase again to a second plateau. Fig. 1 shows an example of such a curve.

In their study of the static isothermal crystallization of cocoa butter from the melt, Marangoni and McGauley (2003) observed two-step curves for crystallization temperatures below 20 °C. They fitted the Avrami model to all SFC curves, including those representing a two-step crystallization. Nothing was mentioned on the quality of fit in case of such a two-step curve. It was however observed that the Avrami exponent increased significantly in the vicinity of 20 °C. It would thus appear that the Avrami exponent is very sensitive to differences in crystallization behaviour between metastable and stable polymorphs (α versus β′). It however has to be stressed that it is not mathematically correct to fit a one-step model to a two-step curve and the obtained results should thus not be taken into account.

Herrera, de Leon Gatti, and Hartel (1999) found that isothermal milk fat crystallization becomes a two-step process below 25 °C. For the mathematical analysis, they also used the same Avrami model as for the one-step crystallization curves, which is thus, as mentioned above not mathematically correct.

Vanhoutte (2002) found two-step crystallization curves of milk fat at a supercooling higher than 15 °C. An algebraic sum of an exponential function and the Gompertz model was used to fit the curves. This model is given in Eq. (1):

$$\mathrm{SFC}(t) = \mathrm{SFC}_1 * \left(1 - \exp\left(-\frac{2\mu_1}{\mathrm{SFC}_1}\cdot t\right)\right) + \mathrm{SFC}_2 * \exp\left(-\exp\left(\frac{\mu_2 * e}{\mathrm{SFC}_2}(\lambda - 1) + 1\right)\right) \quad (1)$$

where SFC_1 represents the amount of solid fat crystallized in the first step [%], μ_1 is the growth rate of the first step [%/min], SFC_2 corresponds to the additional amount of solids that is crystallized in the second step [%], μ_2 is related to the maximal growth rate for the second step [%/min] and λ is the induction time [min].

The aim of this research was to extend the original Foubert model in such a way that multi-step processes can be described as a whole, with a model that has physically meaningful parameters. To build the model, information on the details of the crystallization process obtained by time-resolved X-ray diffraction was used. Through simulation experiments, the physical meaning of the model parameters was verified and finally, the proposed model was validated by fitting it to real data sets and estimating the parameters.

2. Materials and methods

2.1. Data acquisition

The data used in the framework of this research originate from two types of fat. On the one hand, data on milk fat and its fractions were obtained from Vanhoutte (2002). He used three commercial products supplied by Aveve Dairy Products (Klerken, Belgium): a standard anhydrous milk fat (AMF1), a low melting anhydrous milk fat fraction ($\mathrm{AMF_{LMP}}$) and a high melting anhydrous milk fat fraction ($\mathrm{AMF_{HMP}}$). On the other hand, data on cocoa butter were obtained by Dewettinck, Foubert, Basiura, and Goderis (2004). They used a standard factory product supplied by Barry Callebaut (Wieze, Belgium). All data sets were acquired by means of time-resolved X-ray diffraction (XRD) performed on the Dutch–Flemish (DUBBLE) beamline BM26B at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The scattering patterns at small angles (representing the long spacings) (SAXS) and wide angles (representing the short spacings) (WAXD) were detected. Fig. 2 shows the SAXS diffraction patterns as function of time for cocoa butter crystallizing at 20 °C. The mass fractions pertaining to the three different phases encountered during the crystallization process (liquid, α and β′), were extracted from the WAXD patterns as described by Dewettinck et al. (2004). An example of the thus obtained data as function of time is shown in Fig. 3.

2.2. Modelling

All modelling work was performed in WEST (Hemmis NV, Kortrijk, Belgium). For the simulation experiments the adaptive step size Runge–Kutta integration (RK4ASC) algorithm was used to solve the differential equations. The simulations were performed in a time interval from 0 to 4 h. The other settings for the simulation experiments are detailed in Table 1.

For the parameter estimation the Simplex algorithm was used. The accuracy was set to 1×10^{-6} and the maximum number of iterations to 1000.

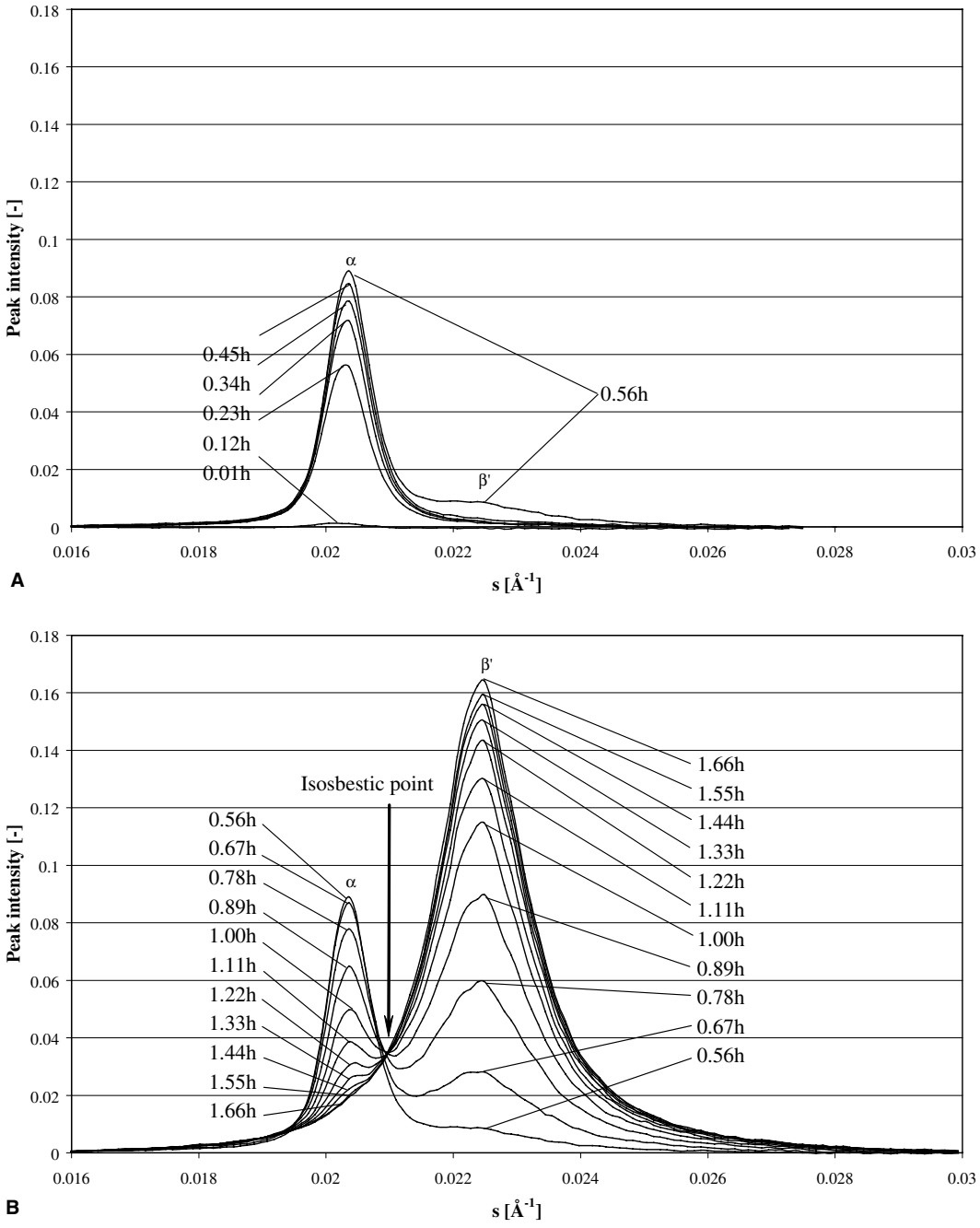

Fig. 2. Isothermal crystallization of cocoa butter at 20 °C: SAXS diffraction patterns as function of time. (A) Time span 1, up to 0.56 h. (B) Time span 2, from 0.56 h onward.

3. Results and discussion

3.1. Modelling assumptions

The two-step crystallization process that is described in this research occurs when milk fat (fractions) and cocoa butter are crystallized isothermally at a high supercooling. The crystallization temperature is in this case below the melting point of a metastable polymorphic form, and since this form has a lower activation free energy of nucleation and thus a higher nucleation rate, it is formed first. In the second step, polymorphic transformation to a more stable polymorph occurs. Dewettinck et al. (2004) investigated this process in more detail by means of pNMR, DSC (stop and return experiments) and time-resolved X-ray diffraction. They proposed a mechanism for the two-step crystallization based on the observed isosbestic behaviour, i.e. the fact that the diffraction patterns of all frames pass through one single point (see also Fig. 2). Such an isosbestic

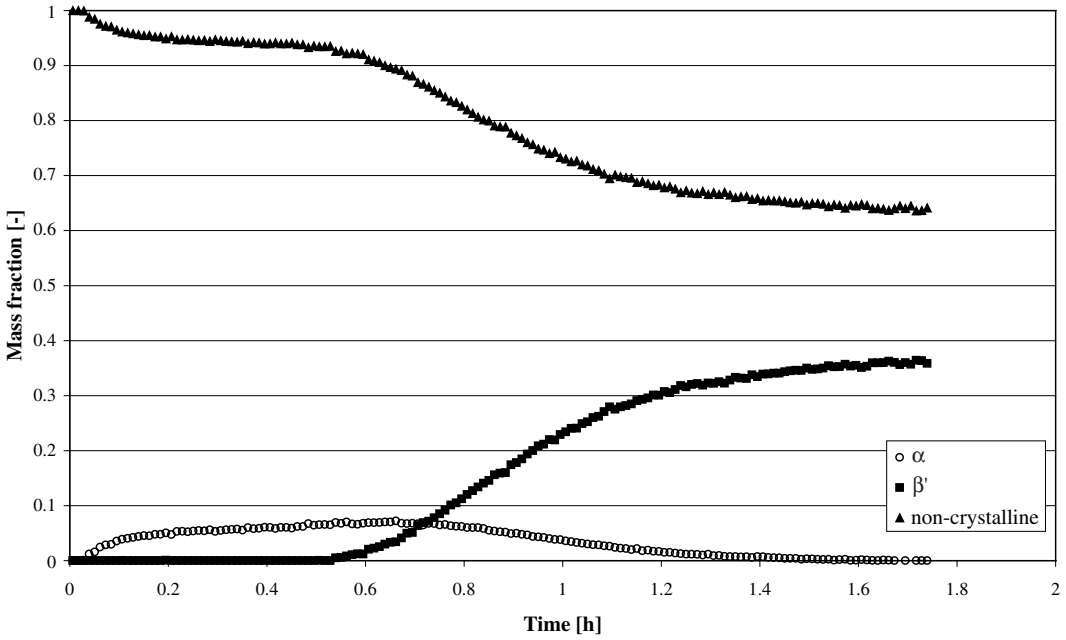

Fig. 3. Mass fraction of α and β′ polymorphs and noncrystalline fraction during isothermal crystallization of cocoa butter at 20 °C as measured by WAXD.

Table 1
Settings for the numerical integration

Accuracy	1e−06
Initial step size	1e−06
Min. step size	1e−06
Max. step size	0.001

point indicates that the α phase characteristic layer structure is transformed into the β′ phase layer without a change of the total volume occupied by α layer stacks and β′ layer stacks. This leads to the proposed mechanism in which in the first step part of the melt crystallizes into the α polymorph, while in the second step α crystals transform into β′ crystals via a solid–solid transition. In the case of cocoa butter crystallizing at low temperatures this second step starts already before the melt-to-α transition is complete. In the late stage of this solidification process the α crystallization stops and only the polymorphic transition from α into β′ is observed. An important assumption, based on the isosbestic behaviour, is that no β′ crystals are formed directly from the melt after the conversion has come to an end. The crystallinity increase during the conversion from α to β′ is related to the transformation of the α polymorph typical liquid-like layers into β′ crystalline material. The presence of liquid-like end group regions with disordered chains in the α polymorph was first suggested by Hernqvist and Larsson (1982). When a polymorphic transition from α to β′ takes place the chains in the liquid-like end group regions of the α polymorph order themselves leading to a higher crystallinity of the β′ polymorph. This increase in crystallinity can be observed in Fig. 2 knowing that from 0.85 h onwards only a polymorphic transition takes place. In the case of the isothermal crystallization of milk fat, the complete second step of crystallization coincides with only a polymorphic transition from α to β′.

This knowledge leads to the following assumptions on which the development of the two-step model is based: (1) one α crystal transforms into one β′ crystal, or in other words, no extra material from the melt is involved in the formation of β′ crystals and (2) both steps are described by the Foubert model.

It has to be stressed that if for other fats and/or processing conditions the crystallization mechanism would be different, the assumptions to the model and also the model itself can be quite easily adapted due to the fact that the original model is written as a differential equation.

The original Foubert model is expressed in terms of a variable h [–], which is the relative remaining crystallizable fat:

$$h = \frac{a - f}{a} \tag{2}$$

where f [% solid fat when measured by means of pNMR or J/g when measured by means of DSC] is the amount of crystallization at time t [h] and a [% solid fat or J/g] is the maximum amount of crystallization. Furthermore, the crystallization process is represented as if it is a combination of a first-order forward reaction and a reverse

reaction of order n [–]. The dynamics of h can then mathematically be written as

$$\frac{dh}{dt} = K \times (h^n - h) \quad h(0) = \frac{a - f(0)}{a} \tag{3}$$

in which K is the rate constant [h^{-1}] and $f(0)$ [% solid fat or J/g] is related to the initially present amount of crystals. 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 where x is chosen to be 1%. Eq. (4) mathematically shows the relation between $f(0)$ and t_ind_x.

$$t\_ind_x = \frac{-\ln\left(\frac{(1-x)^{1-n}-1}{\left(1-\frac{f(0)}{a}\right)^{1-n}-1}\right)}{(1-n)\times K} \tag{4}$$

To develop the two-step model, the Foubert model was reformulated in terms of f, the absolute amount of crystallization:

$$\frac{df}{dt} = K * (a - f) - a * K * \left(\frac{a-f}{a}\right)^n \tag{5}$$

This Eq. (5) forms the basis from which the proposed two-step model is built.

3.2. The fractional model

As discussed in the assumptions, an increase in crystallinity is observed, although only a polymorphic transition takes place and no new material crystallizes from the melt. Both steps in the two-step curve therefore incline towards a different maximum value, while one α crystal is assumed to transform into one β′ crystal. The first step in building the two-step model is a fractional model that does not take into account these different maximum values and where both steps thus have the same maximum value of 1.

The change in fraction of α and β′ crystals, fr_α and $fr_{\beta'}$, as function of time can be written as function of the rate of formation of α crystals from the melt r_α and the rate of transformation of α to β′ crystals $r_{\beta'}$. To describe the change in the fraction of α crystals over time $(\frac{dfr\alpha}{dt})r_{\beta'}$ has to be subtracted from r_α, since the change in fr_α as function of time is not only determined by the rate at which α crystals are formed from the melt (r_α) but also by the rate at which α crystals are transformed into β′ crystals ($r_{\beta'}$). On the other hand, the change in the fraction of β′ crystals over time $(\frac{dfr\beta'}{dt})$ is simply equal to $r_{\beta'}$. indicating that β′ crystals can only be formed through a polymorphic transformation of α crystals.

$$\frac{dfr_\alpha}{dt} = r_\alpha - r_{\beta'} \tag{6}$$

$$\frac{dfr_{\beta'}}{dt} = r_{\beta'} \tag{7}$$

The rate of formation of α crystals from the melt, r_α can be defined as

$$r_\alpha = K_\alpha * \left[1 - (fr_\alpha + fr_{\beta'})\right] - 1 * K_\alpha * \left(\frac{1 - (fr_\alpha + fr_{\beta'})}{1}\right)^{n_\alpha} \tag{8}$$

in which K_α is the rate constant [h^{-1}] and n_α is the order of reverse reaction [–] in the first step.

Compared to Eq. (5) two adaptations have been made to obtain Eq. (8). Firstly, the parameter a has been replaced by 1 in order to have a fractional model with a maximum of 1. Secondly, as the rate of formation of α crystals from the melt is not only influenced by the fraction of α crystals at a time t, but also by the fraction of β′ crystals at a time t, f has been changed to $(fr_\alpha + fr_{\beta'})$. Basically, this term refers to the remaining melt, $[1 - (fr_\alpha + fr_{\beta'})]$, the driving force for crystallization.

The rate of formation of β′ crystals from the melt, $r_{\beta'}$ can be defined by a 'standard' Foubert model:

$$r_{\beta'} = K_{\beta'} * \left(1 - fr_{\beta'}\right) - 1 * K_{\beta'} * \left(\frac{1 - fr_{\beta'}}{1}\right)^{n_{\beta'}} \tag{9}$$

in which $K_{\beta'}$ is the rate constant [h^{-1}] and $n_{\beta'}$ is the order of reverse reaction [–] in the second step.

In this case only the adaptation putting a equal to 1 has to be made.

For completion, initial values have to be specified for fr_α and $fr_{\beta'}$ in order to start up the differential equations. Based on Eq. (4) the induction times are introduced into the proposed two-step model in order to calculate the initial values $fr_\alpha(0)$ and $fr_{\beta'}(0)$. The value of x was put equal to 0.01.

$$fr_\alpha(0) = 1 - 1 * \sqrt[(1-n_\alpha)]{1 + \frac{0.99^{(1-n_\alpha)} - 1}{e^{((n_\alpha - 1) * K_\alpha * t\_ind_\alpha)}}} \tag{10}$$

$$fr_{\beta'}(0) = 1 - 1 * \sqrt[(1-n_{\beta'})]{1 + \frac{0.99^{(1-n_{\beta'})} - 1}{e^{((n_{\beta'} - 1) * K_{\beta'} * t\_ind_{\beta'})}}} \tag{11}$$

in which t_ind_α [h] is the time needed to reach 1% of α crystallization and $t\_ind_{\beta'}$ [h] is the time needed to reach 1% of β′ crystallization.

Fig. 4 shows an example of the crystallization curves obtained with this model given the following values for the parameters: $K_\alpha = 6\ h^{-1}$, $K_{\beta'} = 3\ h^{-1}$, $n_\alpha = 100$, $n_{\beta'} = 4$, $t\_ind_\alpha = 0.01$ h and $t\_ind_{\beta'} = 0.5$ h.

3.3. Conversion to complete two-step model

The crystallization data show that in reality both steps tend towards a different maximum value

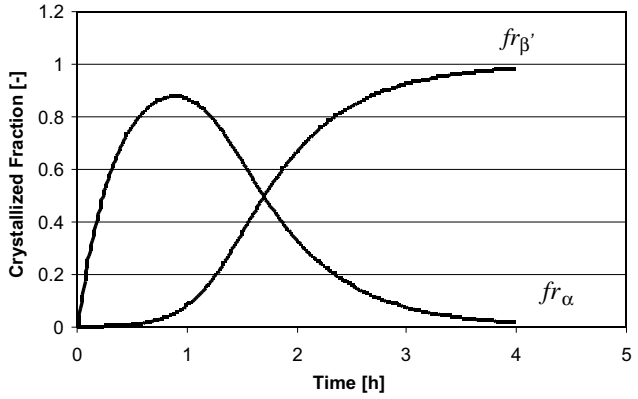

Fig. 4. Example of crystallization curves obtained by fractional model using the following parameter values: $K_\alpha = 6\ h^{-1}$, $K_{\beta'} = 3\ h^{-1}$, $n_\alpha = 100$, $n_{\beta'} = 4$, $t\_ind_\alpha = 0.01$ h, $t\_ind_{\beta'} = 0.5$ h.

(see Fig. 1). The fractional model must thus be converted into a model for real data by multiplying the fractional amounts (fr_α and $fr_{\beta'}$) with the respective maximum values (a_α and $a_{\beta'}$ [% solid fat or J/g]).

$$f_\alpha = a_\alpha * fr_\alpha \tag{12}$$

$$f_{\beta'} = a_{\beta'} * fr_{\beta'} \tag{13}$$

in which f_α and $f_{\beta'}$ [% solid fat or J/g] are the amount of α and β′ crystallization at time t, respectively.

The total amount of crystallization is then given by the sum of f_α and $f_{\beta'}$.

$$f\_out = f_\alpha + f_{\beta'} \tag{14}$$

Fig. 5 shows the curves of f_α, $f_{\beta'}$ and f_out when $a_\alpha = 10\%$, $a_{\beta'} = 50\%$, $K_\alpha = 6\ h^{-1}$, $K_{\beta'} = 3\ h^{-1}$, $n_\alpha = 100$, $n_{\beta'} = 4$, $t\_ind_\alpha = 0.01$ h, $t\_ind_{\beta'} = 0.5$ h.

3.4. Influence of model parameters on the two-step crystallization curve

The proposed two-step model contains eight parameters, which are summarized in Table 2. In order to examine the influence of these parameters on the shape of the two-step crystallization curve and thus check the validity of the physical interpretation of the parameters, simulation experiments were performed. The results are presented in Figs. 6–13.

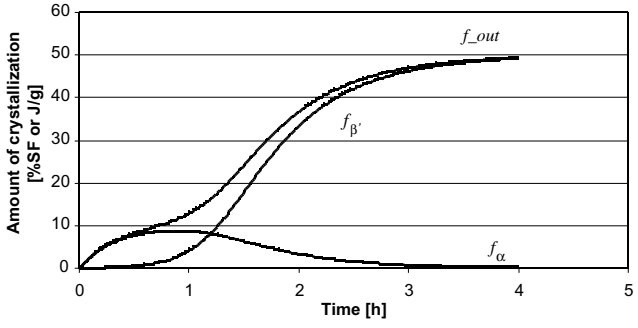

Fig. 5. Example of crystallization curves obtained by two-step model using the following parameter values: $a_\alpha = 10\%$, $a_{\beta'} = 50$, $K_\alpha = 6\ h^{-1}$, $K_{\beta'} = 3\ h^{-1}$, $n_\alpha = 100$, $n_{\beta'} = 4$, $t\_ind_\alpha = 0.01$ h, $t\_ind_{\beta'} = 0.5$ h.

Table 2
Summary of the parameters in the proposed two-step model

Name	Description	Unit
a_α	maximum amount of α crystallization	% solid fat or J g^{-1}
$a_{\beta'}$	maximum amount of β′ crystallization	% solid fat or J g^{-1}
K_α	rate constant of the first step	h^{-1}
$K_{\beta'}$	rate constant of the second step	h^{-1}
n_α	order of reverse reaction in the first step	–
$n_{\beta'}$	order of reverse reaction in the second step	–
t_ind_α	time needed to reach 1% of α crystallization	h
$t\_ind_{\beta'}$	time needed to reach 1% of β′ crystallization	h

The parameters a_α and $a_{\beta'}$ determine the height of the plateau of the first and second step, respectively, and

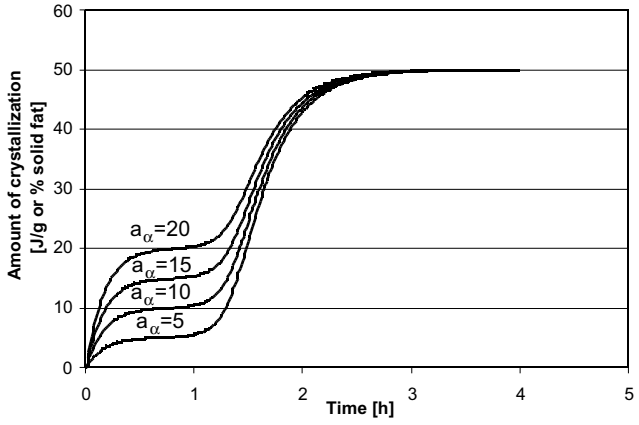

Fig. 6. Influence of varying a_α [J/g or % solid fat] on the crystallization curve ($a_{\beta'} = 50\%$, $K_\alpha = 6\ h^{-1}$, $K_{\beta'} = 3\ h^{-1}$, $n_\alpha = 100$, $n_{\beta'} = 4$, $t\_ind_\alpha = 0.01$ h, $t\_ind_{\beta'} = 1$ h).

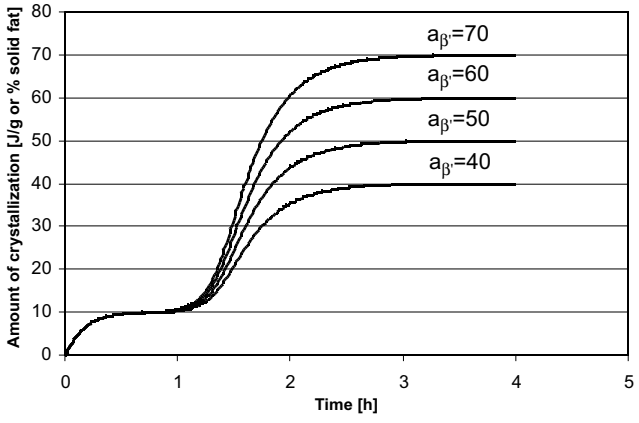

Fig. 7. Influence of varying $a_{\beta'}$ [J g^{-1} or % solid fat] on the crystallization curve ($a_\alpha = 10\%$, $K_\alpha = 6\ h^{-1}$, $K_{\beta'} = 3\ h^{-1}$, $n_\alpha = 100$, $n_{\beta'} = 4$, $t\_ind_\alpha = 0.01$ h, $t\_ind_{\beta'} = 1$ h).

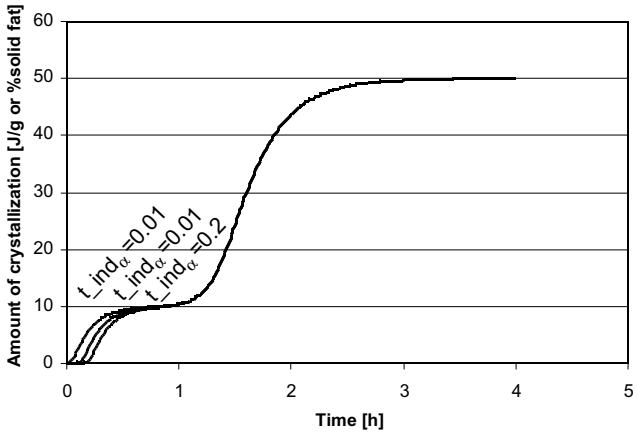

Fig. 8. Influence of varying t_ind_α [h] on the crystallization curve ($a_\alpha = 10\%$, $a_{\beta'} = 50\%$, $K_\alpha = 6\ \mathrm{h}^{-1}$, $K_{\beta'} = 3\ \mathrm{h}^{-1}$, $n_\alpha = 10$, $n_{\beta'} = 4$, $t\_\mathrm{ind}_{\beta'} = 1$ h).

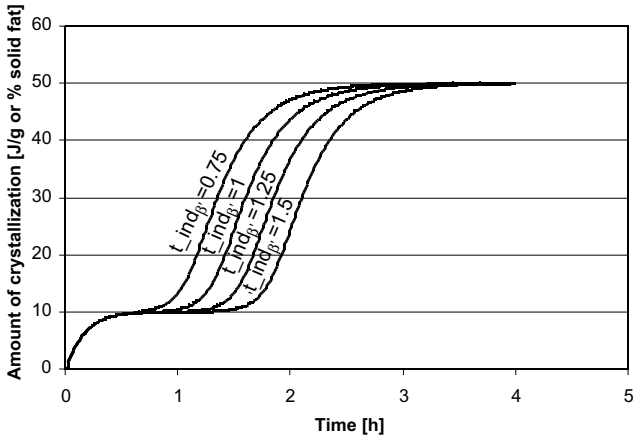

Fig. 9. Influence of varying $t\_\mathrm{ind}_{\beta'}$ [h] on the crystallization curve ($a_\alpha = 10\%$, $a_{\beta'} = 50\%$, $K_\alpha = 6\ \mathrm{h}^{-1}$, $K_{\beta'} = 3\ \mathrm{h}^{-1}$, $n_\alpha = 100$, $n_{\beta'} = 4$, $t\_\mathrm{ind}_\alpha = 0.01$ h).

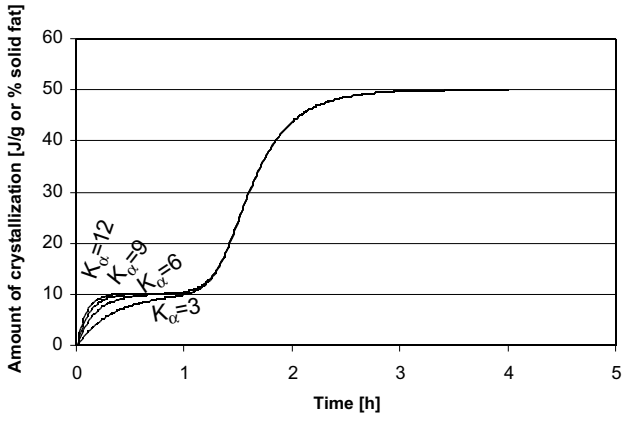

Fig. 10. Influence of varying K_α [h^{-1}] on the crystallization curve ($a_\alpha = 10\%$, $a_{\beta'} = 50\%$, $K_{\beta'} = 3\ \mathrm{h}^{-1}$, $n_\alpha = 100$, $n_{\beta'} = 4$, $t\_\mathrm{ind}_\alpha = 0.01$ h, $t\_\mathrm{ind}_{\beta'} = 1$ h).

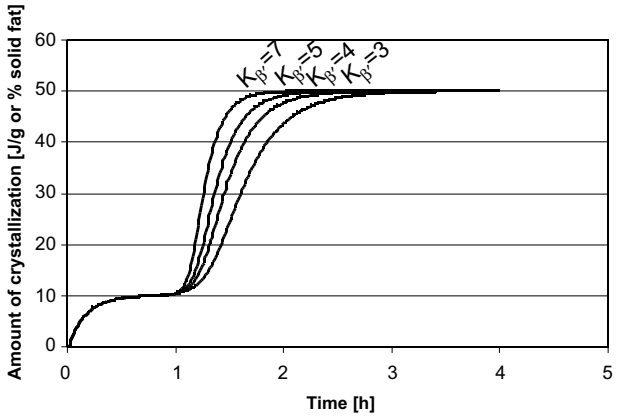

Fig. 11. Influence of varying $K_{\beta'}$ [h^{-1}] on the crystallization curve ($a_\alpha = 10\%$, $a_{\beta'} = 50\%$, $K_\alpha = 6\ \mathrm{h}^{-1}$, $n_\alpha = 100$, $n_{\beta'} = 4$, $t\_\mathrm{ind}_\alpha = 0.01$ h, $t\_\mathrm{ind}_{\beta'} = 1$ h).

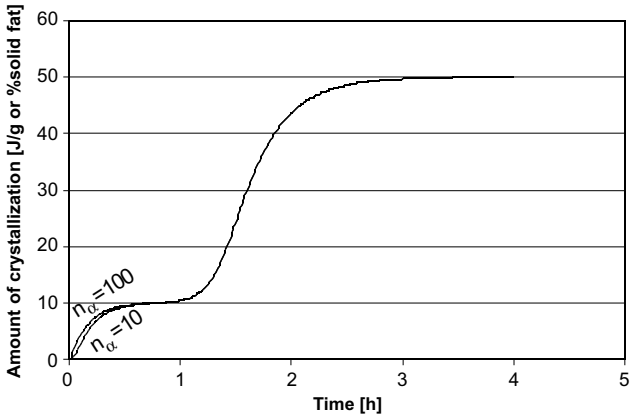

Fig. 12. Influence of varying n_α [–] on the crystallization curve ($a_\alpha = 10\%$, $a_{\beta'} = 50\%$, $K_\alpha = 6\ \mathrm{h}^{-1}$, $K_{\beta'} = 3\ \mathrm{h}^{-1}$, $n_{\beta'} = 4$, $t\_\mathrm{ind}_\alpha = 0.01$ h, $t\_\mathrm{ind}_{\beta'} = 1$ h).

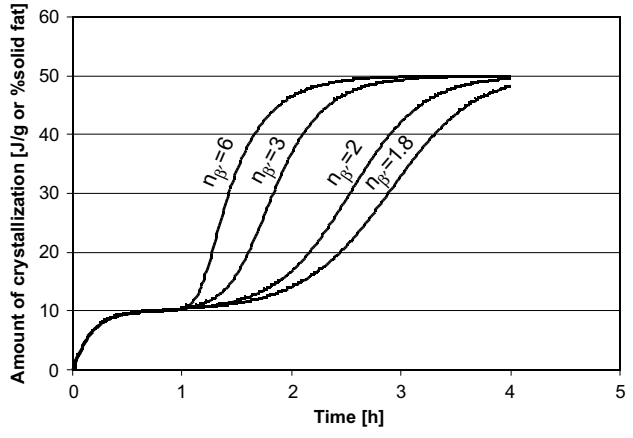

Fig. 13. Influence of varying $n_{\beta'}$ [–] on the crystallization curve ($a_\alpha = 10\%$, $a_{\beta'} = 50\%$, $K_\alpha = 6\ \mathrm{h}^{-1}$, $K_{\beta'} = 3\ \mathrm{h}^{-1}$, $n_\alpha = 100$, $t\_\mathrm{ind}_\alpha = 0.01$ h, $t\_\mathrm{ind}_{\beta'} = 1$ h).

thus represent the maximum amount of α and β′ crystallization, respectively.

Parameters t_ind_{α} and $t\_ind_{\beta'}$ represent the induction times of the first and second step, respectively: the higher the value, the later the crystallization begins.

Increasing the values K_{α} and $K_{\beta'}$ results in a faster crystallization during the first or second step of crystallization as shown by the steeper curve. These parameters thus undoubtedly embody the rate constant of the two steps.

Fig. 12 shows the outcome of changing n_{α} from 10 to 100. According to the proposed model, increasing the order of the reverse reaction n_{α} would decrease the importance of the reverse reaction, causing crystallization to occur faster. This can indeed be seen in the figure. The results are not that pronounced though, since the first step actually follows an exponential function. Because of this the order of the backward reaction n_{α} is fixed at a value of 100, almost reducing the Foubert model to a simple exponential equation.

In Fig. 13, the differences resulting from varying $n_{\beta'}$ between 1.8 and 6 are much more apparent than in the case of n_{α}. Increasing $n_{\beta'}$ brings about a faster crystallization due to the reduction of the importance of the reverse reaction. In Fig. 13, the effect of the order of the reverse reaction on the curve shape, as described by Foubert et al. (2002) becomes clear too. When $n_{\beta'}$ is equal to 2, the second part of the crystallization curve is perfectly symmetric. When $n_{\beta'}$ is larger than 2, crystallization in the beginning of the second step occurs faster than crystallization in the end. On the other hand, when $n_{\beta'}$ is smaller than 2, crystallization in the beginning of the second step occurs slower than crystallization in the end.

3.5. Parameter estimation on selected data-sets

Parameter estimation was performed on three data sets acquired by time-resolved X-ray diffraction as described in the materials and methods section: AMF crystallizing at 19 °C, AMF_{HMP} crystallizing at 24 °C and cocoa butter crystallizing at 20 °C. The f_out and $f_{\beta'}$ data were fitted simultaneously. Fig. 14 shows an example of the obtained fit for AMF crystallizing at 19 °C. From the figure it can be deduced that the data can be fitted well by the proposed two-step model. The quality of fit for the other two data sets is comparable, which means that the underlying assumptions seem to hold. The parameters and their confidence information obtained for the three data sets are given in Table 3. For the three data sets the value of t_ind_{α} is not significantly different from zero, which means that α crystallization starts immediately without an induction time. The error on the parameter estimate of K_{α} is always higher than that of the other parameters. This can probably be explained by the fact that less data points are available for the estimation of this parameter, since the α crystallization is very fast and the data points are taken at equal intervals.

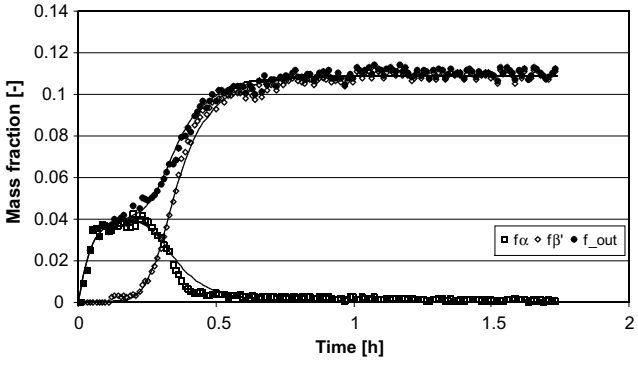

Fig. 14. Fit of proposed two-step model to data of AMF isothermally crystallized at 19 °C.

Table 3
Parameters estimates of proposed two-step model for three example data sets

Name	AMF at 19 °C	AMF_{HMP} at 24 °C	Cocoa butter at 20 °C
a_{α} [–]	0.04 ± 0.0008	0.06 ± 0.002	0.08 ± 0.001
$a_{\beta'}$ [–]	0.11 ± 0.0002	0.17 ± 0.0004	0.37 ± 0.001
K_{α} [h^{-1}]	22.55 ± 1.8	25.17 ± 2.23	4.18 ± 0.24
$K_{\beta'}$ [h^{-1}]	9.15 ± 0.28	29.62 ± 0.88	3.23 ± 0.03
$n_{\beta'}$ [–]	4.30[a]	4.42 ± 0.20	5.74 ± 0.08
t_ind_{α} [h]	[b]	[b]	[b]
$t\_ind_{\beta'}$ [h]	0.17 ± 0.00	0.09 ± 0.002	0.50 ± 0.004

[a] No confidence information can be calculated.
[b] Means not significantly different from zero.

4. Conclusion

A model was developed to describe two-step isothermal fat crystallization. The assumptions to build the model were based on the presence of an isosbestic point indicating that the first step involves crystallization from the melt to α and the second step involves a polymorphic transformation from α to β′ without a direct crystallization from the melt in β′. The model was shown to fit well to data sets obtained by time-resolved XRD for cocoa butter and milk fat (fractions), meaning that the underlying assumptions seem to hold. The model parameters could also be estimated with acceptable accuracy. The developed model thus allows to describe the often occurring two-step processes with one model, which has not been described before for fat crystallization.

Acknowledgments

Imogen Foubert is a Postdoctoral Fellow of the Fund for Scientific Research-Flanders (Belgium) (F.W.O. Vlaanderen). Stijn Van Hulle and Dirk De Pauw

(BIOMATH) are acknowledged for the help with the WEST software.

References

Dewettinck, K., Foubert, I., Basiura, M., & Goderis, B. (2004). Phase behaviour of cocoa butter in a two-step isothermal crystallization. *Crystal Growth and Design, 4*, 1295–1302.

Foubert, I., Vanrolleghem, P. A., Vanhoutte, B., & Dewettinck, K. (2002). Dynamic mathematical model of the crystallization kinetics of fats. *Food Research International, 35*, 945–956.

Hernqvist, L., & Larsson, K. (1982). On the crystal structure of the β' form of triacylglycerols and structural changes at the phase transitions $\mathrm{LIQ} \rightarrow \alpha \rightarrow \beta' \rightarrow \beta$. *Science Technology, 84*, 349–354.

Herrera, M. L., de Leon Gatti, M., & Hartel, R. W. (1999). A kinetic analysis of crystallization of a milk fat model system. *Food Research International, 32*, 289–298.

Marangoni, A. G., & McGauley, S. E. (2003). Relationship between crystallization behaviour and structure in cocoa butter. *Crystal Growth and Design, 3*, 95–108.

Vanhoutte, B. (2002). *Milk fat crystallisation: fractionation and texturisation*. PhD thesis, Ghent University, Belgium.