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Review

Modelling of the crystallization kinetics of fats

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Experimental techniques used to obtain crystallization data are compared. Furthermore, the crystallization models used by different authors are presented in relation to their background. Compared to the mostly used Avrami model, the fit of the Gompertz model seems to be better. The fit of a new model developed at the authors' laboratory is even better for the majority of the samples. The applied parameter estimation methods are also reviewed. Special attention is given to the problems with linearizing the Avrami model. Finally, some future trends are highlighted.

The crystallization of fats has been extensively investigated, probably due to its importance in everyday life. After all, an understanding of the fat crystallization process plays a critical role in determining overall product quality. Products in which fat crystallization is important include chocolates and confectionery coatings, dairy products such as butter and cream, vegetable spreads and peanut butter. Fat crystallization is also important in fat and oil fractionation where lipid products with varying melting and physical properties are manufactured by melt crystallization (Hartel, 1992). Finally, triglyceride crystallization is used to eliminate small quantities of high-melting compounds from an oil so it remains clear at low ambient temperature (Dibildox-Alvarado & Toro-Vazquez, 1997).

A lot of good reviews are published concerning the static properties of fats: Timms (1984) discussed the phase behaviour of fats and their mixtures, Hernqvist (1990) described the structure of the different polymorphic forms of triglycerides and their transition possibilities and Hagemann (1988) treated the thermal behaviour and polymorphism of acylglycerides. However, as was already stated by Timms (1984) and Sato, Ueno, and Yano (1999), the crystallization kinetics of fats (particularly the rate of crystallization and the rate of change from one polymorphic form to another) are equally important since they are relevant to real systems of fat production. After all, understanding when and to what extent fat components crystallize under certain conditions is the basis for controlling operations in which (re)crystallization is of concern (Hartel, 1992). In their review Sato *et al*. (1999) dealt with, among other things, the kinetics of nucleation and polymorphic transformation of triglycerides as examined with time-resolved X-ray diffraction (tr-XRD) measurements. They however did not model the kinetics of the crystallization mathematically. Boistelle (1988) gave a more mathematical approach to the fundamentals of nucleation and crystal growth. The described equations find their basis in thermodynamics, which leads to the disadvantage that they are not always easy to use in practice since a lot of the thermodynamic properties are often not known.

From the late 1970s onwards, but especially in the last few years, quite some articles have been published in which the isothermal crystallization of fats is mathematically modelled to enable quantification of differences in the crystallization behaviour between different products and crystallization circumstances. A model is fitted directly to the experimental data sets and parameters with a physical meaning are extracted.

The aim of this review is to discuss the state of the art in modelling the kinetics of fat crystallization. Attention will be given to the substrates used, the aim of the studies and the experimental techniques used to obtain the required data.

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Box 1 Explanation of symbols used

a_F	maximum amount of crystallization (Foubert model) a_F (% solid fat) or (J/g) depending on measuring technique
a_G	maximum amount of crystallization (Gompertz model) a_G (% solid fat) or (J/g) depending on measuring technique
A, B, D	parameters of the unmodified Gompertz model
C	concentration of particles in the liquid phase at time t (aggregation and flocculation model) (m^{-3})
C_0	initial value of C (aggregation and flocculation model) (m^{-3})
f	absolute amount of crystallization (% solid fat) or (J/g) depending on measuring technique
F	relative amount of crystallization ( )
G	direction averaged rate of growth of r (m/s)
h	remaining crystallizable fat ( )
ΔH	heat of crystallization (J/g)
k	rate constant in Avrami model (s^{-m})
k′	rate constant in modified Avrami model (s)
K_1	rate constant of first order forward reaction (Foubert model) ($time^{-1}$)
K_n	rate constant of nth order reverse reaction (Foubert model) ($time^{-1}$)
K	rate constant of simplified Foubert model ($time^{-1}$)
m	Avrami exponent ( )
m'	exponent in modified Avrami model ( )
n	order of the reverse reaction (Foubert model) ( )
N	number of germ nuclei per unit nucleation region (m^{-3})
$\bar{N}_0$	initial number of germ nuclei per unit nucleation region (m^{-3})
p	probability of occurrence of transformation germ nucleus–growth nucleus (s^{-1})
r	'radius' of a grain ( )
$r(t, y)$	radius at time t of a grain which began growth at time y (m)
$r(\tau, z)$	radius at rescaled time τ of a grain which began growth at time z (m)
t_0	initial value of t (aggregation and flocculation model)
t	time (s)
$t_{w\%}$	time needed to reach w% crystallization (time unit)
t_{ind_x}	induction time (Foubert model) (time unit)
T	transmittance at time t ( )
T_f	minimum transmittance ( )
T_i	transmittance at time zero ( )
$v(\tau, z)$	volume at rescaled time τ of a grain which began growth from a nucleus at rescaled time z (m^3)
v'	non-overlapped volume of a grain (m^3)
v_{ext}	extended volume of a grain (m^3)
V	volume of crystalline phase per unit volume of space ( )
V_{ext}	total extended volume per unit volume of space ( )
x	amount of crystallization in the definition of t_ind_x (Foubert model)
Y	logarithm of relative population size ( )
β	$\frac{6^*\sigma^*G^{3*}\bar{N}_0}{f^3}$ (s^{-3})
τ	rescaled time ( )
$\bar{\tau}$	rescaled time corresponding to exhaustion of germ nuclei ( )
σ	shape factor ( )
μ	maximum specific growth rate (Gompertz model) (%s^{-1}) or (s^{-1} J/g) depending on measuring technique
λ	lag time (Gompertz model) (s)

The main part of this review, however, will describe the different models used and their background. Their quality will be compared and the techniques used for parameter estimation will be discussed (see Box 1 for the terms used).

Aim of the studies and investigated substrates

The aim of the different studies was to quantify differences in crystallization behaviour between different substrates and/or different crystallization conditions (e.g. different isothermal crystallization temperature). As mentioned by Metin and Hartel (1998) very often the crystallization behaviour of a particular substrate has already been studied extensively but very little quantitative data are available. Quantification is thus the main merit of these studies.

Table 1 provides an overview of the substrates used.

Experimental techniques used to obtain the required data

Several experimental techniques can be used to follow the isothermal crystallization of fats as function of time. However, in this review only the methods which have been used in modelling studies are considered: differential scanning calorimetry (DSC) (Foubert, Vanrolleghem, Vanhoutte, & Dewettinck, 2002; Kawamura,

Table 1. Substrates used to study the isothermal crystallization kinetics of fats

Substrate	Author(s)
Cocoa butter	Ziegleder (1990), Kerti (1998), Metin and Hartel (1998), Foubert, Vanrolleghem *et al.* (2002)
Cocoa butter alternatives	Kerti (1998)
Milk fat	Herrera, De Leon Gatti *et al.* (1999), Wright *et al.* (2000), Vanhoutte (2002), Vanhoutte *et al.* (2002)
Blends of cocoa butter and milk fat (fractions)	Metin and Hartel (1998)
Sunflower seed oil	Herrera, Falabella *et al.* (1999)
Palm oil	Kawamura (1979), Ng and Oh (1994)
Solutions of fully hydrogenated palm oil in sunflower oil	Kloek *et al.* (2000)
Tripalmitin in sesame oil	Dibildox-Alvarado and Toro-Vazquez (1997)
Palm stearin in sesame oil	Toro-Vazquez *et al.* (2000)

1979; Kerti, 1998; Metin & Hartel, 1998; Toro-Vazquez, Brinceno-Montelongo, Dibildox-Alvarado, Charo-Alonso, & Reyes-Hernandez, 2000; Vanhoutte, 2002; Vanhoutte, Dewettinck, Foubert, Vanlerberghe, & Huyghebaert, 2002; Ziegleder, 1990), pulsed nuclear magnetic resonance (pNMR) (Foubert, Vanrolleghem, Vanhoutte, & Dewettinck, 2002; Herrera, De Leon Gatti, & Hartel, 1999; Herrera, Falabella, Melgarejo, & Anon., 1999; Kloek, Walstra, & Van Vliet, 2000, Ng & Oh, 1994; Vanhoutte, 2002; Vanhoutte *et al.*, 2002; Wright, Hartel, Narine, & Marangoni, 2000) and transmittance/turbidity measurements (Dibildox-Alvarado & Toro-Vazquez, 1997) are used . Other techniques used to monitor isothermal crystallization, so far without modelling, will be briefly discussed. It can be expected that some of the emerging techniques may, in the future, also be used to model crystallization kinetics.

DSC

In an isothermal DSC experiment, the sample is first molten and then rapidly cooled to the crystallization temperature. Subsequently, the exothermal heat flow induced by the crystallization process is measured as function of time (Simon & Süverkrup, 1995). The exact conditions used to melt the sample and the cooling rate can change between samples and studies.

The relative amount of material crystallized as function of time is calculated by integration of the isothermal DSC curves. The area enclosed by a baseline and the exothermal peak corresponds to the heat of crystallization, ΔH. The relative amount of crystallized material F at a given time t is approximated by the ratio of the integration of the exothermal rate to the total area in accordance with the following equation (Kawamura, 1979):

$$F = \frac{\int_{t=0}^{t} \frac{\mathrm{d}\Delta H(t)}{\mathrm{d}t}\,\mathrm{d}t}{\Delta H} \tag{1}$$

It was shown by Foubert, Vanrolleghem, and Dewettinck (in press) that when the start and end point of the integration are determined visually, the resulting area and thus the model parameters vary when different persons perform the integration but also when the same person performs the integration several times. To eliminate this source of variability, they developed an objective calculation algorithm to determine the start and end point of the integration. The advantages of DSC, as mentioned by Ziegleder (1990) are: (a) the ability to strictly control temperature, (b) the small sample size which makes the presence of foreign nuclei so seldom that they hardly influence the crystallization and (c) the ability to measure free from mechanical effects.

pNMR

With pNMR the solid fat content (SFC) is measured directly. The samples are first molten to destroy any memory effect (the exact conditions can vary between samples and studies) and then transferred to a thermostated water bath at the crystallization temperature. SFC readings are taken at appropriate time intervals.

Wright, Narine, and Marangoni (2001) compared different techniques used in lipid crystallization studies and concluded that pNMR was the best method to characterize the overall crystallization process. The other techniques used, turbidity and light-scattering measurements, tend to become saturated prior to the completion of the crystallization process and therefore it is not possible to obtain reliable data on the later stages

of crystallization. Isothermal DSC was also attempted in this study, but abandoned.

As additional advantages of pNMR the rapid cooling and accurate temperature control of the water bath-based cooling were mentioned by these authors. It has to be remarked however, that these are less efficient when compared to DSC.

Transmittance/turbidity

In a study by Dibildox-Alvarado and Toro-Vazquez (1997) isothermal crystallization curves were obtained by measuring the transmittance (600 nm) of tripalmitin in sesame oil solutions as function of time. A double-beam spectrophotometer with data acquisition system and temperature control was utilized. The fractional crystallization F as a function of time t was calculated as $F = (T_i - T)/(T_i - T_f)$ where T_i is the transmittance of the oil solution at time zero, T is the transmittance at time t and T_f is the minimum transmittance obtained during the crystallization process. However, a few years later the same research group (Toro-Vazquez *et al.*, 2000) also started to use DSC, indicating that crystal birefringence might have affected the transmittance values which modifies the crystallization curve in comparison with the one obtained by DSC. Since heterogeneous nucleation, sporadic nucleation and secondary crystallization are more prevalent as crystallization time proceeds, the intrinsic birefringence of crystals is not constant with time. As a result, events like heterogeneous nucleation and secondary crystallization might be more apparent when measuring transmitted light than when measuring with DSC.

Marangoni (1998) stated that turbidity measurements, which are closely related to transmittance measurements, are not suitable for the kinetic characterization of crystallization processes because: (a) the maximal turbidity does not correspond to the end of crystallization or to the maximal volume or mass of crystallized material achieved, but simply represents the point at which the crystallizing material becomes too opaque and the amount of transmitted light becomes negligible, (b) zero angle scattering is only proportional to the amount of crystals provided that no multiple scattering occurs, an assumption which does not apply when particles become larger than the wavelength divided by 20 and (c) an observed decrease in transmitted light can be due to light refraction.

Other experimental techniques so far not applied for modelling

Time-resolved X-ray diffraction can be used to determine the short spacings of a sample, from which the crystal polymorph can be extracted. Van Malssen, Van Langevelde, Peschar, and Schenk (1999), Kloek *et al.* (2000), MacMillan *et al.* (2002) and Vanhoutte (2002) used this technique to investigate which polymorphic forms are created during isothermal crystallization of cocoa butter, fully hydrogenated palm oil in sunflower oil mixtures, once more cocoa butter and milk fat.

Polarized light microscopy has been used to follow the appearance of the crystals as function of time (Dibildox-Alvarado & Toro-Vazquez, 1997; Herrera, Falabella *et al.*, 1999).

The crystallization process can also be followed by means of viscosity changes as function of time. Before crystallization starts, the melt shows Newtonian behavior. With the formation and growth of crystals, the viscosity increases almost linearly with the amount of crystals in the suspension until it reaches a thermodynamic equilibrium (Breitschuh & Windhab, 1998). This technique has also been used by Loisel, Lecq, Keller, and Ollivon (1998), Toro-Vazquez *et al.* (2000) Chen, Lai, Ghazali, and Chong (2002) to follow the isothermal crystallization of refined palm oil, chocolate and palm stearin in sesame oil, respectively.

Ultrasound velocity measurement appears to be a promising technique for the determination of solid fat contents. The technique is rather simple: a low intensity, high frequency sound wave pulse is emitted through a sample and the time needed for the pulse to travel twice the distance through the sample is measured. From this time the velocity of the ultrasound in the sample is calculated (Kloek, 1998). Since sound travels more quickly in solids than in liquids it is possible to measure the solids content from this velocity (Coupland, 2001). Application of the ultrasound velocity measurement to determine the crystallization kinetics of fats is however only useful for fats with narrow melting ranges and very simple polymorphic behaviour (Kloek, 1998).

Models used to describe the isothermal crystallization

The Avrami model is most frequently used to describe the isothermal crystallization kinetics of fats (Dibildox-Alvarado & Toro-Vazquez, 1997; Kawamura, 1979; Kerti, 1998; Metin & Hartel, 1998; Toro-Vazquez *et al.*, 2000; Vanhoutte, 2002; Vanhoutte *et al.*, 2002; Wright *et al.*, 2000; Ziegleder, 1990). Some authors use a modified Avrami equation, also called the Avrami–Erofeev equation (Herrera, De Leon Gatti *et al.*, 1999; Herrera, Falabella *et al.*, 1999; Ng & Oh, 1994; Toro-Vazquez & Dibildox-Alvarado, 1997). Recently, Kloek *et al.* (2000), Vanhoutte (2002) and Vanhoutte *et al.* (2002) used a reparameterized Gompertz equation to describe their crystallization curves. Berg and Brimberg (1983) proved that empirical equations used for aggregation and flocculation, could also be used to describe fat crystallization. However, to our knowledge the aggregation and flocculation model, was never used by other authors. Very recently, a new model, available in both an algebraic and differential equation form was developed at the authors' laboratory (Foubert, Vanrolle-

ghem, Vanhoutte *et al*., 2002). In the following sections more details concerning these five models is given.

The Avrami model

The Avrami model is the most widely used approach for the description of isothermal phase transformation kinetics. In the 1940s, various authors independently developed this kinetic formulation which is sometimes called the Johnson–Mehl–Avrami–Kolmogorov equation (Wright *et al*., 2000). The theory was initially developed for low molecular weight materials such as metals. Later it was extended to the crystallization of high polymers (Kawamura, 1979).

Avrami (1939, 1940) stated that there is an overwhelming amount of evidence pointing to the conclusion that a phase is nucleated by tiny germ nuclei which already exist in the liquid phase and whose effective number is $\bar{N}_0$ per unit nucleation region. The number of germ nuclei per unit region at time t decreases from $\bar{N}_0$ in two ways: (a) some of them become active growth nuclei in consequence of free energy fluctuations and with probability of occurrence p per unit time and (b) some of them get swallowed by growing grains of the new phase. The number of growth nuclei can increase linearly with time (sporadic nucleation) or the large majority of the growth nuclei can be formed near the beginning of the transformation (instantaneous nucleation). V represents the volume of the crystalline phase per unit volume of space. Avrami also introduced a characteristic time scale, defined by $p\mathrm{d}t = \mathrm{d}\tau$. This characteristic time scale is in fact a rescaled time taking into account the value of p.

Further, Avrami made the assumption that when one grain impinges upon another growth ceases. The volume at rescaled time τ of any grain which began growth from a nucleus at rescaled time z is denoted as $v(\tau,z)$. The number of such grains is given by $N(z)$. Thus, the total extended volume (the term 'extended' refers to the volume the grains would have had, provided that the growth had remained unimpeded) is:

$$V_{\mathrm{ext}} = \int_0^{\tau} v(\tau, z)N(z)\mathrm{d}z \tag{2}$$

Let r, the 'radius', be a one-dimensional measure of the size of a grain and let G be the direction averaged rate of growth of r. Then r, at time t, of a grain which began growth at time y is given by:

$$r(t, y) = \int_y^t G\mathrm{d}x \tag{3}$$

or, if the rescaled time τ is introduced:

$$r(\tau, z) = \int_z^{\tau} \frac{G}{p}\mathrm{d}u \tag{4}$$

The grain volume then becomes:

$$v(\tau, z) = \sigma r^3 = \sigma\left[\int_z^{\tau} \frac{G}{p}\mathrm{d}u\right]^3 \tag{5}$$

where σ is a shape factor, equal to $4\pi/3$ for a sphere.

Since the factors which govern the tendency of the growth nuclei to grow out of the germ nuclei are similar to those which govern further growth, Avrami assumed that p and G are approximately proportional throughout a considerable temperature and concentration range called the isokinetic range. Thus, if G/p is constant for a given substance in the isokinetic range, eqn (2) can be integrated:

$$V_{\mathrm{ext}} = \sigma\frac{G^3}{p^3}\int_0^{\tau}(\tau - z)^3 N(z)\mathrm{d}z \tag{6}$$

In any region, selected arbitrarily, the part of the volume still without crystallized matter is designated as the 'nonoverlapped' volume. Then, on average, the ratio of the nonoverlapped volume v' to the extended volume v_{ext} of a randomly selected region is equal to the density of untransformed matter $1-V$ at that time, i.e.

$$\frac{v'}{v_{\mathrm{ext}}} = 1 - V \tag{7}$$

The same reasoning may be applied, not to the volumes of the single grains, but to the nonoverlapped and extended portions of the increments of these grains in an element of time. The following equation is obtained for the average grain:

$$\frac{\mathrm{d}v}{\mathrm{d}v_{\mathrm{ext}}} = 1 - V \tag{8}$$

since the nonoverlapped decrease of a grain is nothing more than the increment in transformed volume of that grain.

For the unit volume this leads to:

$$\frac{\mathrm{d}V}{\mathrm{d}V_{\mathrm{ext}}} = 1 - V \tag{9}$$

Integrating and rearranging, this gives:

$$V = 1 - e^{-V_{\mathrm{ext}}} \tag{10}$$

Thus the entire problem of determining the kinetics of the crystallization has been reduced to finding V_{ext} in any particular case. To obtain the value for V_{ext} eqn (6) is integrated taking into account that $N(z) = \bar{N}_0 e^{-z}$ and

$$E_q(-x) = \frac{1}{q!}\int_0^x (x-z)^q e^{-z}\mathrm{d}z = (-1)^{q+1}\left[e^{-x} - 1 + x ... (-1)^{q+1}\frac{x^q}{q!}\right] \quad (11)$$

$$V_{\text{ext}} = \frac{6\sigma G^3 \bar{N}_0}{p^3}\left[e^{-\tau} - 1 + \tau - \frac{\tau^2}{2!} + \frac{\tau^3}{3!}\right] = \beta E_3(-\tau) \quad (12)$$

where the following abbreviation has been introduced:

$$\beta = \frac{6\sigma G^3 \bar{N}_0}{p^3} \quad (13)$$

This equation is valid up to $\tau = \bar{\tau}$, the time corresponding to the exhaustion of germ nuclei. Beyond this, the upper limit of the integral should be replaced by $\bar{\tau}$ and the result of integration may be expressed by:

$$V_{\text{ext}} = \beta\left\{E_3(-\tau) - e^{-\bar{\tau}} E_3[-(\tau - \bar{\tau})]\right\} \quad (14)$$

When $\bar{N}_0$ is very large, i.e. exhaustion of the germ nuclei does not occur until the end of crystallization, two limiting cases can be considered. When τ is very small, i.e. when p is very small (and t is not too large), i.e. in the case of sporadic nucleation) the first four terms of the series development of the exponential term $e^{-\tau}$ in (12) cancel against the other terms between the square brackets. Hence, only the term of the fourth power in τ is of importance as the first term, which does not cancel. By inserting the thus obtained equation for V_{ext} in eqn (10) the following equation is obtained:

$$V = 1 - e^{(-\beta\tau^4/4!)} = 1 - e^{(-\sigma G^3 \bar{N}_0 p t^4)/4} \quad (15)$$

Note that a not too large value for p and a very small value for t leads to similar values of τ and therefore supports the same reasoning. However, Avrami did not take this case into account.

On the other hand, for τ very large, i.e. for p very large and t not too small, i.e. instantaneous nucleation, the exponential term $e^{-\tau}$ and the terms up to the order of τ^2 in (12) can be disregarded compared to the last term between square brackets and the following equation for V is obtained:

$$V = 1 - e^{-\beta\tau^{3/3!}} = 1 - e^{-\sigma G^3 \bar{N}_0 t^3} \quad (16)$$

Again, τ can also be very large in the opposite case (t very large and p not too small), a case that Avrami again did not take into account.

For intermediate values of p the dependence of V upon t will lie between eqns (15) and (16).

In general, eqns (15) and (16) can be written as:

$$V = 1 - e^{-kt^m} \quad (17)$$

the equation generally known as the Avrami equation.

For plate-like and linear growth an analysis similar to the previous one leads to other values for k and m (Table 2).

As can be seen from Table 2, the rate constant k is dependent on the nucleation (amount of germ nuclei $\bar{N}_0$ for instantaneous nucleation and rate of nucleation $p\bar{N}_0$ for sporadic nucleation) and on the growth rate. The exact relationship depends on the specific case. The Avrami exponent m depends on the nucleation type (sporadic or instantaneous) and the growth morphology of the crystallizing particles. The meaning of the m value is however not straightforward since an m value of 2 and 3 can have two different meanings.

Theoretically, integer values should be obtained for m. However, it is frequently found by analysis of experimental data that the Avrami exponent is a non-integer. Several causes have been suggested: (a) the ratio of the density of the crystalline phase over the density of the liquid phase varies during the process, (b) the true nucleation rate varies during the process, (c) the growth rate changes during the process, (d) the growth morphology changes during the process and (e) crystalline

Table 2. Summary of the values obtainable for k and m in the Avrami model

Growth morphology	Sporadic nucleation		Instantaneous nucleation	
	k (s^{-m})	m ( )	k (s^{-m})	m ( )
Linear	$\frac{\sigma'' * G^* \bar{N}_0^* p}{2}$	2	$\sigma'' * G^* \bar{N}_0$	1
Plate-like	$\frac{\sigma' * G^{2*} \bar{N}_0^* p}{3}$	3	$\sigma' * G^{2*} \bar{N}_0$	2
Spherical	$\frac{\sigma^* G^{3*} \bar{N}_0^* p}{4}$	4	$\sigma^* G^{3*} \bar{N}_0$	3

aggregates grow concurrently from both instantaneous and sporadic nuclei (Long, Shanks, & Stachurski, 1995; Supaphol & Spruiell, 2000).

Evans (1945), seemingly without knowledge of the prior work of Avrami, obtained the same model based on the problem of expanding waves created by raindrops on a pond.

Modified Avrami model

Apart from the original Avrami model as derived above, some authors also use a so-called modified Avrami model, also called the Avrami–Erofeev model. This modified equation is given by:

$$V = 1 - e^{-(k't)^{m'}} \tag{18}$$

This equation differs from the original Avrami equation in the fact that the rate constant k' is also raised to the power m' which is not the case in the original Avrami equation.

The origin of this modified model can be found, on the one hand, in the work of Ng (1975) who described the development of the Erofeev model and, on the other hand, in the work of Khanna and Taylor (1988) who modified the Avrami model to eliminate the dependence of k on m.

Ng (1975) described the development of the Erofeev model in a work on the thermal decomposition in the solid state. The development was based on the Avrami theory. From eqns (10) and (12) it can be deduced that for three-dimensional growth

$$-\ln(1 - V) = \text{const.}\left[e^{-\tau} - 1 + \tau - \frac{\tau^2}{2!} + \frac{\tau^3}{3!}\right] \tag{19}$$

When returning to the original time scale ($\tau = p^*t$), one obtains:

$$-\ln(1 - V) = \text{const.}\left[e^{-pt} - 1 + pt - \frac{p^2t^2}{2!} + \frac{p^3t^3}{3!}\right] \tag{20}$$

This equation can be transformed into a simplified form in two limiting cases (see also the deduction of eqns (15) and (16)): when pxt is much smaller than 1 eqn (20) turns into:

$$-\ln(1 - V) = \text{const}\left(\frac{p^4t^4}{4!}\right) \tag{21a}$$

or

$$[-\ln(1 - V)]^{1/4} = \frac{\text{const}}{24}pt = \text{const}' \times t \tag{21b}$$

when pxt is much bigger than 1, eqn (20) turns into:

$$-\ln(1 - V) = \text{const}\left(\frac{p^3t^3}{3!}\right) \tag{22a}$$

or

$$[-\ln(1 - V)]^{1/3} = \frac{\text{const}}{6}pt = \text{const}' \times t \tag{22b}$$

These equations can be represented by the generalized Erofeev equation

$$[-\ln(1 - V)]^{1/m' = k't} \tag{23}$$

which equals eqn (18).

Khanna and Taylor (1988) claimed that the value of k obtained from the original Avrami model may not be correct, since k is function of m. This problem may, according to the authors, be eliminated by using a modified equation such as (18). What these authors did, was transform the Avrami constant k from a complex constant of an mth order process to a first order rate constant despite the fact that crystallization is not a first order process. It can be calculated that the k' value of the modified Avrami model is the mth root of the k value of the original model (Marangoni, 1998):

$$k' = k^{1/m} \tag{24}$$

The modified Avrami model thus simply is a reparameterized Avrami model.

Khanna and Taylor (1988) show that by modifying the Avrami model more meaningful values for the reaction rate constant can be obtained. They, for example, compared the overall crystallization rates of virgin nylon 6 and extruded nylon 6. By means of programmed rate DSC, isothermal DSC experiments and optical microscopy they showed that the crystallization rate of virgin nylon 6 is dramatically lower. Thus, if k is an overall rate constant, it should always be a higher number for the extruded nylon 6 resin compared to the virgin material. When calculating k by means of linear regression it appeared that the value was higher for the extruded nylon 6 at temperatures below 200°C but lower at temperatures above 200°C. When calculating k' from the modified Avrami model the value was always higher for the extruded nylon 6, as expected. The authors also cite other work where the original Avrami model has yielded rate constants, which did not coincide with the expected values.

The authors further claim that despite the modification the model retains its original correspondence to nucleation and crystal growth processes. The modification presented simply corrects the value of k by eliminating the influence of m.

Khanna and Taylor (1988) thus conclude that attempts to obtain k values through the original Avrami model may lead to erroneous results, especially when comparing processes that have different values of m.

Marangoni (1998) did not agree with this modified Avrami model. According to him, Khanna and Taylor (1988) arbitrarily suggested a modification of the Avrami model without providing any theoretical justifi-

cation. The only justification the authors provided was their opinion that k and m were correlated and that the transformation would solve this problem. However, no proof of this was given in their paper.

Gompertz model

Kloek *et al.* (2000), Vanhoutte (2002) and Vanhoutte *et al.* (2002) fitted their crystallization curves to a reparameterized Gompertz equation as deduced by Zwietering, Jongenburger, Rombouts, and Van 't Riet (1990). The latter authors compared several sigmoid functions in their ability to describe a bacterial growth curve. Most of these equations contain mathematical fitting parameters rather than parameters with a biological meaning making it difficult to provide initial guesses for the parameters. Moreover, it is difficult to calculate 95% confidence intervals for biologically meaningful parameters if these are not estimated directly from the equation but are calculated from mathematical fitting parameters. Therefore, the growth models were rewritten to substitute the mathematical fitting parameters with biologically meaningful parameters such as a_G (the maximal value reached), μ (the maximum specific growth rate which is defined as the tangent in the inflection point) and λ (the lag time, which is defined as the x-axis intercept of that tangent) (Fig. 1). This reparameterization was performed by deriving an expression for the biologically meaningful parameters as function of the mathematical fitting parameters of the basic function.

The unmodified Gompertz equation is written as:

$$Y = A \times \exp[-\exp(B - D \times t)] \tag{25}$$

with Y being the logarithm of the relative population size.

To obtain the inflection point (at $t = ti$) of the curve, the second derivative of the function with respect to t is set to zero. This leads to:

$$ti = B/D \tag{26}$$

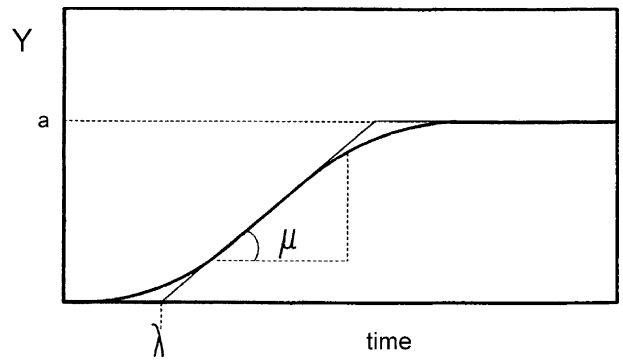

Fig. 1. Visual representation of the Gompertz parameters.

An expression for the maximum specific growth rate can be derived by calculating the first derivative at this inflection point:

$$\mu = \frac{A - D}{e} \text{with e being } 2.718281 \tag{27}$$

The parameter D in the unmodified Gompertz equation can thus be substituted by $\frac{\mu \times e}{A}$.

To obtain an expression for the lag-time, the tangent line through the inflection point is calculated and the intercept with the t-axis deduced:

$$\lambda = \frac{(B - 1)}{D} \tag{28}$$

The parameter B can thus be substituted by $\frac{\mu \times e}{A}\lambda + 1$.

The a_G value equals the A value since Y approaches A when t approaches infinity. The parameter A in the unmodified Gompertz equation can thus be substituted by a_G, yielding the reparameterized Gompertz equation:

$$Y = a_G \times \exp\left\{-\exp\left[\frac{\mu \times e}{a_G}(\lambda - t) + 1\right]\right\} \tag{29}$$

Kloek *et al.* (2000), Vanhoutte (2002) and Vanhoutte *et al.* (2002) used this reparameterized Gompertz equation but replaced Y by f, the amount of crystallization at time t. a_G is then the maximum fraction of solid fat. Kloek *et al.* (2002) used this model because they claimed several analogues between the crystallization of fats and bacterial growth: production of bacteria is comparable with nucleation and growth of crystals and consumption of nutrients is comparable with decrease of supersaturation.

Aggregation and flocculation models

Berg and Brimberg (1983) noticed that the course of fat crystallization is similar to that of aggregation and flocculation of colloids. The authors had previously derived empirical rate formulae for aggregation and flocculation from experimental data. These equations are given below:

$$\text{Aggregation:} \quad C - C_0 = -k_2\sqrt{t - t_0} \tag{30}$$

$$\text{Flocculation:} \quad \ln\frac{C}{C_0} = -k_4\sqrt{t - t_0} \tag{31}$$

Prior to the main phase, an induction period exists where the following equations apply:

$$\text{Aggregation:} \quad C - C_0 = -k_1 \times (t - t_0)^2 \tag{32}$$

$$\text{Flocculation:}\quad \ln\frac{C}{C_0} = -k_3 \times (t - t_0)^2 \tag{33}$$

C is the concentration of particles in the liquid phase at time t, C_0 and t_0 are the initial values of C and t and the k_i constants are rate constants for each phase.

In their study, the authors examined whether the kinetics of fat crystallization could indeed be described by eqns (30)–(33). They used experimental results on palm oil and hardened soy oil obtained from literature.

Since $C-C_0$ is the decrease of the concentration of dispersed particles, this value equals the amount of solid fat. Knowing the solid fat content, the aggregation eqns (30) and (32) can be used. For the flocculation eqns (31) and (33), however, the value of C_0 has to be known. The solid fat content at equilibrium was taken as an estimate for C_0.

Eqns (30)–(33) fitted the literature data well and the authors thus concluded that fat crystallization matches the mechanism of aggregation and flocculation: solid fat is formed by aggregation of dispersed particles and fat crystals also grow by aggregation. It was suggested that the particles are the unit cells of the crystals, which are dispersed in the liquid and that the solid phase grows by addition of unit cells.

Model of Foubert, Vanrolleghem, Vanhoutte *et al.* (2002)

The model developed by Foubert, Vanrolleghem, Vanhoutte *et al.* (2002) is, in contrast to the former models, originally written in the form of a differential equation. This type of equation has the advantage that (i) it is often easier to interpret the equation mechanistically, (ii) it is easier to make minor changes to the equation on the basis of acquired knowledge and (iii) by incorporation of secondary models describing the temperature dependency of the parameters, the model can be used to describe non-isothermal crystallization kinetics. An algebraic solution for isothermal conditions however, offers the advantage that parameter estimation is easier because of more readily available software packages capable of non-linear regression of algebraic equations. Therefore an algebraic solution assuming isothermal conditions was also developed.

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

$$h = \frac{a_F - f}{a_F} \tag{34}$$

where f is the amount of crystallization at time t and a_F is the maximum amount of crystallization. In contrast to f, which increases with time in a sigmoidal way, this variable h is related to the remaining supersaturation (i.e. the driving force for crystallization) and thus decreases in a sigmoidal way with time.

To obtain the model, the crystallization process is represented as if it is a combination of a first-order forward reaction and a reverse reaction of order n with rate constants K_i for each of the reactions. The dynamics of h can then mathematically be written as:

$$\frac{dh}{dt} = K_n \times h^n - K_1 \times h \tag{35}$$

K_1 and K_n are the rate constants of the first order forward reaction and the nth order reverse reaction, respectively.

To calculate the values of h as function of time according to eqn (35), the initial value for h, $h(0)$, needs to be specified:

$$h(0) = \frac{a_F - f(0)}{a_F} \tag{36}$$

$f(0)$ is then the initially present amount of crystals (nuclei?), which can be related to the induction time of the crystallization process.

Extensive parameter estimation studies revealed a relative difference between K_1 and K_n of only around 1.10^{-4}%. Furthermore, the quality of the five-parameter model was found not to be significantly better than that of a four-parameter model for which $K_1 = K_n$. It was thus decided to simplify the model to:

$$\frac{dh}{dt} = K \times (h^n - h) \qquad h(0) = \frac{a_F - f(0)}{a_F} \tag{37}$$

in which a_F is the maximum amount of crystallization (expressed in percent (solid fat potential) when measuring by means of pNMR or expressed in J/g (latent heat) when measuring by means of DSC), K is the rate constant (expressed in time unit^{-1}), n is the order of the reverse reaction (dimensionless) and $f(0)$ is the initially present amount of crystals (expressed in the same units as a).

To simplify parameter estimation the differential equation (four-parameter model) was converted to its algebraic solution. 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.

$$h = \left[1 + \left((1-x)^{1-n} - 1\right) \times e^{-(1-n)\times K \times \left(t - t\_ind_x\right)}\right]^{\frac{1}{1-n}} \tag{38}$$

Parameter estimation

The aim of parameter estimation is to obtain the values of the parameters that give the best fit to a given set of data.

No clear information on parameter estimation for the aggregation and flocculation model of Berg and Brimberg (1983) is given. Kloek *et al.* (2000), Vanhoutte (2002) and Vanhoutte *et al.* (2002) estimated the parameters of the reparameterized Gompertz model by non-linear regression. Herrera, Falabella *et al.* (1999), Herrera, De Leon Gatti *et al.* (1999) and Wright *et al.* (2000) also used non-linear regression to estimate the parameters of the modified Avrami and original Avrami models, respectively. Others (Kawamura, 1979; Ziegleder, 1990; Metin & Hartel, 1998; Toro-Vazquez *et al.*, 2000), however, linearize the Avrami equation by a logarithmic transformation:

$$\ln(-\ln(1 - V)) = \ln k + m\ln t \tag{39}$$

Toro-Vazquez and Dibildox-Alvarado (1997) also linearized the modified Avrami equation. This linearization procedure which makes it possible to estimate the parameters by linear regression using standard spreadsheet programs is, however, statistically questionable (see Box 2 for more details).

Moreover, some authors do not use all collected data to estimate the parameters: e.g. Ziegleder (1990) stated that because of the insecurity in determining the start and end point of the integration, only the data points between

Box 2 Linearization of the Avrami equation to estimate model parameters (Dochain & Vanrolleghem, 2001)

It is common practice to transform a model that is non-linear in its parameters into a model that is linear in its parameters. The linearized form of the Avrami equation given in this review in eqn (39) indeed allows estimating the Avrami parameters by simple linear regression of the logarithmically transformed data.

A classic example of linearization is the Lineweaver–Burk expression that transforms the non-linear Monod-type kinetic equation for microbial growth $\mu = \frac{\mu_{\max} S}{Ks+S}$ into a linear form:

$$\frac{1}{\mu} = \frac{K_s}{\mu_{\max}}\frac{1}{S} + \frac{1}{\mu_{\max}}$$

The rationale for pursuing this type of transformations is that the methods of non-linear regression are much less known with modellers than those of linear regression, which are generally known. The ease of linear regression analysis is, unfortunately, accompanied by fundamental drawbacks:

(a) When data are transformed (e.g. S into $1/S$ in the Lineweaver–Burk expression and V into ln $(-\ln(1-V))$ in the linearized Avrami equation), the measurement errors are transformed too. More particularly, although the measurement errors of the actually measured variables (S or V in the two examples) may be independent and identically distributed normally, the transformed variables will typically not be. The important result is that a wrong assumption is made on the error characteristics, which may lead to biased parameter estimates. It was indeed found by many authors that different linearized forms of the same non-linear model yield different estimates of the same parameters.

(b) Difficulties are encountered when trying to obtain confidence information on the estimated parameters. The parameters that are actually estimated are not the parameters one wants to estimate, but a transformation or combination of parameters. For instance, in the Lineweaver-Burk approximation, the estimated parameters are $\theta_1 = 1/\mu_{\max}$ and $\theta_2 = K_s/\mu_{\max}$ and in the linearized Avrami equation $\theta_3 = \ln k$. It is not at all that easy to accurately calculate the confidence information on $\mu_{\max}$, K_s and k given confidence information on θ_1, θ_2 and θ_3.

(c) The spacing of the data points becomes important. For instance, when applying the Lineweaver–Burk approximation, many data points are located at low values of the variable $1/S$ and only a few are found at large values of $1/S$. This strongly affects the parameter estimates. Similarly, when applying the linearized Avrami equation, many data points are located at high values of the variable $\ln(t)$ and only a few are found at small values of $\ln(t)$. This leads to a very high sensitivity of the parameters to the large values of $1/S$ and the small values of $\ln(t)$, respectively.

To illustrate the influence linearization has on the parameter estimates, the following table gives the 95% confidence intervals of the Avrami parameters k and m obtained with non-linear regression and with linear regression using all data, the data between 10 and 90% crystallization and the data between 25 and 75% crystallization.

Parameter estimation procedure	95% Confidence interval for k (h^{-m})	95% Confidence interval for m ( )
Non-linear regression	$(2.1 < k < 3.3)$	$(3.1 < m < 4.3)$
Linear regression using all data	$(1.07 < k < 2.04)$	$(2.9 < m < 4.5)$
Linear regression using data between 10 and 90% crystallization	$(1.86 < k < 2.45)$	$(2.7 < m < 3.5)$
Linear regression using data between 25 and 75% crystallization	$(2.09 < k < 4.4)$	$(3.0 < m < 4.6)$

$V=0.1$ and $V=0.9$ are taken into account. Kawamura (1979) followed the same reasoning, whereas Toro-Vazquez and Dibildox-Alvarado (1997) even limited the data to the values obtained between 0.25 and 0.75.

Ziegleder (1990) introduced yet another correction. In theory V equals zero at the start point of the integration, but in reality it seemed that already some solid fat has been formed at $t=0$. Based on pNMR results V was put equal to 0.03 at $t=0$ and therefore, the values of V were corrected as follows:

$$V' = \frac{V + 0.03}{1.03} \tag{40}$$

It can be noticed, however, that the value of 0.03 is rather arbitrary and may change between samples and studies.

Parameter estimation of the new model was performed by non-linear regression using Sigmaplot for the algebraic version of the model and using the non-linear parameter estimation available in the WEST dynamic simulator (Hemmis NV, Kortrijk, Belgium, http://www.hemmis.com) for the differential equation version (Foubert, Vanrolleghem, Vanhoutte *et al.*, 2002).

Comparison of models

In this paragraph the quality of fit of the Avrami, Gompertz and Foubert models is compared. The modified Avrami model will not be dealt with since from a curve-fitting point of view, this model does not differ from the original Avrami model. Figure 2 compares the quality of fit of the Avrami, Gompertz and Foubert models for a cocoa butter crystallization followed by means of DSC in the authors' laboratory. It can be seen that the Gompertz model provides a better fit than the Avrami model, a trend that could also be seen when the models were fitted to data series of other cocoa butters at different temperatures and to data series of milk fat (fractions) (data not shown). The Foubert model shows a better fit than both other models. The adequacy of the different models to describe isothermal fat crystallization has been tested statistically by Foubert, Vanrolleghem, Vanhoutte (2002). This study revealed that the Gompertz and Foubert models always perform better than the Avrami model and that the Foubert model performs better than the Gompertz model in the majority of the cases.

Table 3 compares the errors on the parameter estimations for each model. From the table, it can be seen that the errors are largest for the Avrami model. The errors on the Gompertz and Foubert parameters are of

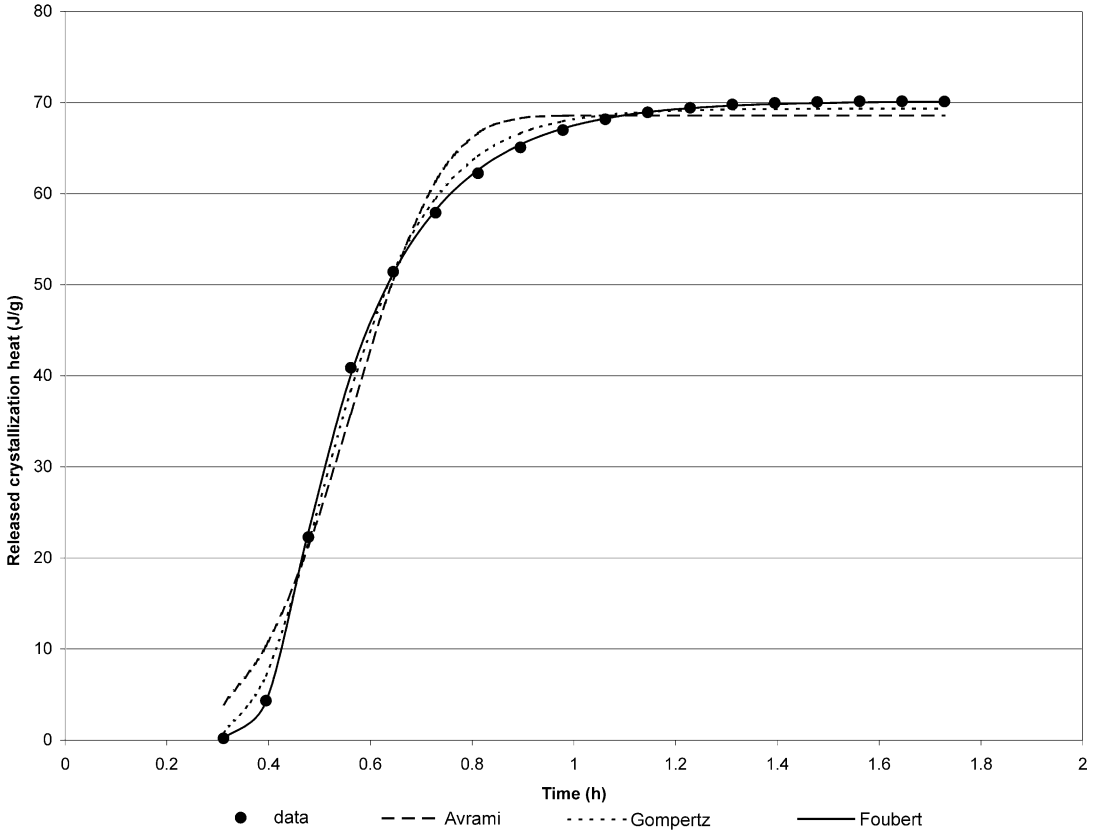

Fig. 2. Visual comparison of fit between the Avrami, Gompertz and Foubert models (isothermal crystallization of cocoa butter as measured by means of DSC).

Table 3. Comparison of the errors on the parameter estimations

Avrami		Gompertz		Foubert	
Parameter	**Error (%)**	**Parameter**	**Error (%)**	**Parameter**	**Error (%)**
k	10	μ	1.5	K	1.5
m	5				
		λ	0.75	t_ind_x	1.5
		a_G	0.25	a_F	0.2
				n	4

Parameters with a comparable meaning are reported on the same line.

similar magnitude, except for the error on the n parameter of the Foubert model, which is higher. This could however be expected since more parameters are estimated.

A benefit of the Gompertz model is that its parameters have a very straightforward physical interpretation. The Avrami model has the advantage that it was especially developed to describe crystallization processes, that it was developed from a theoretical basis and that it has often been used in the field of fat crystallization.

Foubert, Vanrolleghem, Vanhoutte *et al.* (2002) also compared the ability of the three models to fit an asymmetric crystallization curve. The asymmetry of a curve was defined as:

$$\text{asym} = \frac{t_{90\%} - t_{50\%}}{t_{50\%} - t_{10\%}} \tag{41}$$

where $t_{w\%}$ is the time needed to reach w% crystallization. A symmetric curve has a value of 1 for the asym parameter. For the Avrami model it could be concluded from a theoretical analysis that the asymmetry depends on the Avrami exponent m. Estimated m values corresponded to crystallization processes where the start was slower than the end (asym <1) which was not in concordance with the experimental data that show an asym value higher than 1. This inability of the Avrami model to take the proper asymmetry explains why it did not provide very good fits. For the Gompertz model it turned out that the asym value is a fixed value which means that this equation does not offer any flexibility concerning the asymmetry of the curve whereas the data are characterized by clearly different asymmetries. The asym value of the Foubert model is dependent on n, with n values of 2 giving rise to symmetric curves. The ability to fit different asymmetries is an advantage of the Foubert model when compared to the Gompertz model.

Conclusion

The Avrami model is by far the most used model to describe the kinetics of isothermal fat crystallization. The theory is developed on the basis of some assumptions which may not always be satisfied in the case of fat crystallization. Next to the fact that this may lead to non-integer values for the Avrami exponent m, it may raise questions about the applicability of the Avrami model. Importantly, quite some authors linearize this equation to be able to estimate the parameters more easily, a technique which is statistically questionable. The modified Avrami model, advocated by some authors, has been criticized by others as having no theoretical foundation. According to us, the modified Avrami model simply is a reparameterization of the original model, possibly leading to better parameter estimations.

The Gompertz model, generally used to describe the growth of bacteria was used by Kloek *et al.* (2000), Vanhoutte (2002) and Vanhoutte *et al.* (2002) in the field of fat crystallization. The theoretical basis for using the Gompertz model for fat crystallization is however rather weak. Bacterial growth can intuitively be compared with fat crystallization, but this provides no real theoretical justification.

Foubert, Vanrolleghem, Vanhoutte *et al.* (2002) developed a new model which represents the crystallization process as if it is a combination of a first-order forward reaction and a reverse reaction of order n.

The Gompertz and Foubert models always show a better quality of fit than the Avrami model and the Foubert model performs better than the Gompertz model in the majority of the cases. An additional advantage of the Foubert model is its ability to fit different asymmetries.

The very good fits obtained with the Foubert model make it a useful tool to have a better quantitative description of crystallization processes. It will, however, have to be shown in future work whether a true physical mechanism lays beneath this goodness of fit.

Future trends

Most of the published papers dealing with the modelling of the crystallization kinetics of fats use conventional techniques (DSC and pNMR) to follow crystallization. As indicated in the chapter on experimental techniques some other less frequently used or emerging techniques, such as rheology, time-resolved X-ray diffraction and ultrasound measurements are also available. Up to now, they have, to the authors' knowledge, not been used in modelling studies. In the future the possibilities of these techniques for this application can be explored. The models mentioned in this review

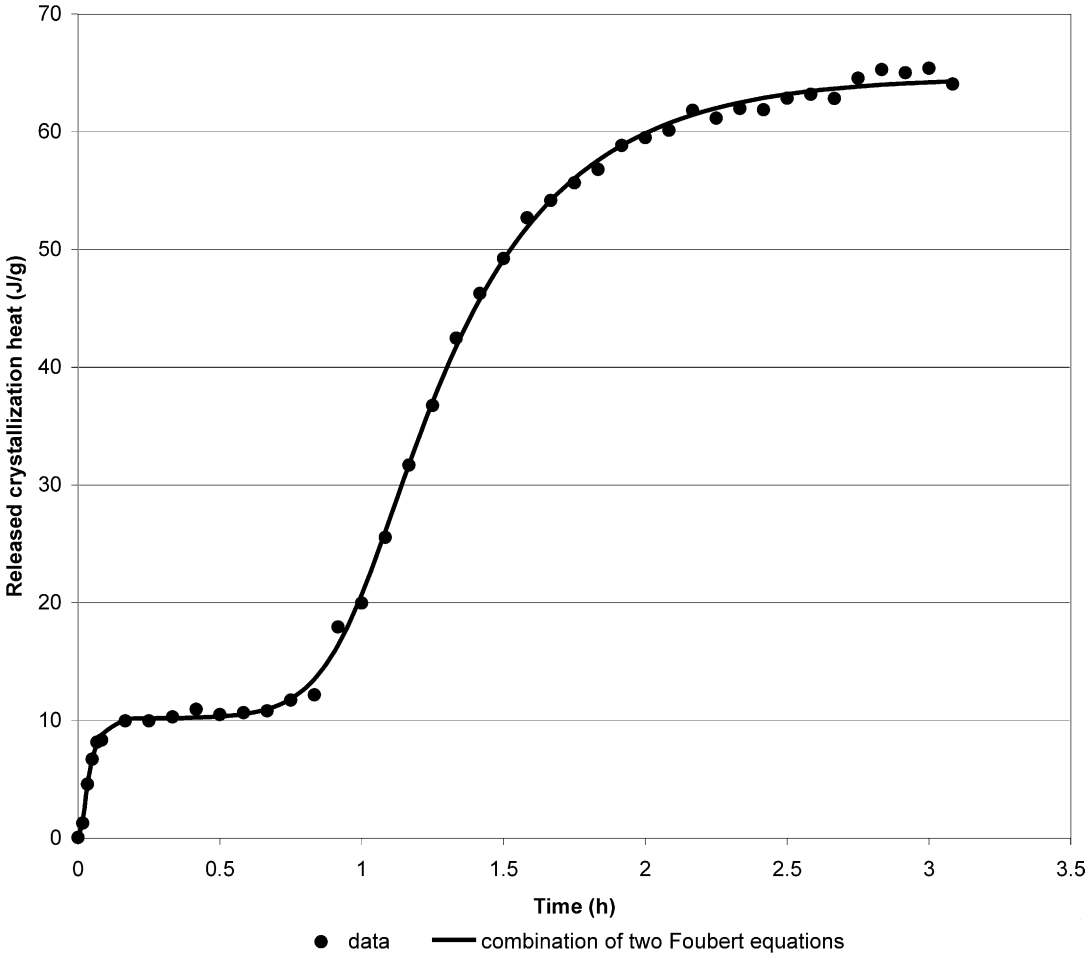

Fig. 3. Example of a two-step process and the fit obtained by combining two Foubert equations.

have, again to the authors' knowledge, not been applied to study the effect of shear on the crystallization kinetics. Some papers are available where the effect of shear on crystallization is studied (e.g. Loisel *et al*., 1998; Macmillan *et al*., 2002), however not in a quantitative way. The effect of shear on the parameters of the different models will probably be investigated in the future.

Since fats are complex mixtures of triglycerides, their crystallization can lead to the formation of many crystal types either due to polymorphism or concomitant growth of several crystal types. This may lead to crystallization curves in which two steps can be identified. This kind of curves were, for example, obtained by Breitschuh and Windhab (1998), Loisel *et al*. (1998), Chen *et al*. (2002), Kalua (2002) and Vanhoutte (2002). Figure 3 shows an example of such a two-step process, which of course, also makes the modelling more complex. To be able to fit a model to this kind of data, Vanhoutte (2002) combined two Gompertz equations. It is also possible to combine two Foubert equations, an example of which is shown in Fig. 3.

A future trend in the modelling of the crystallization kinetics of fats will probably also include the modelling of non-isothermal processes. For this, the Foubert model offers a considerable advantage since it has been developed in the form of a differential equation which can handle time-varying temperatures, for instance. When functions are developed that describe the temperature dependency of the crystallization parameters, these so called secondary models can be combined with the original model, as such allowing the modelling of non-isothermal crystallization. This is not possible for models written in the form of an algebraic solution which was obtained under the assumption of constant temperature.

A model able to describe non-isothermal crystallization will be very interesting for the food industry, since most of their processes are of a non-isothermal kind. In this respect, the study of the effect of shear is interesting too since in a lot of processes some (time-varying) shear forces are applied.

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