

Reprinted from *Lipid Technology*, Vol.17, No.11, Pages 247–250 (November 2005) with permission from the publisher. ©PJ Barnes & Associates, 2006; e-mail: sales@pjbarnes.co.uk; web: www.pjbarnes.co.uk

FEATURE

Crystallization of 1,3-dipalmitoyl-2-oleoylglycerol (POP) studied using non-isothermal DSC

Geoff Talbot, Kevin Smith and Fred Cain

Geoff Talbot is a consultant to the food industry at The Fat Consultant, Suite 250, St Loyes House, 20 St Loyes Street, Bedford MK40 1ZL, UK; tel: +44-7850-605719; email: geoff@thefatconsultant.co.uk; web site: www.thefatconsultant.co.uk; Kevin Smith is Lead Scientist, Lipids, in the Life Science group of Unilever Research Colworth, Sharnbrook, Bedfordshire MK44 1LQ, UK; tel: +44-1234-222786 email: kevin.w.smith@unilever.com; and Fred Cain is Science Director at Loders Croklaan, Hogeweg 1, 1520AA Wormerveer, The Netherlands; tel: +31-75-6292-911.

Summary

With the increasing emphasis on replacing hydrogenated and trans fats in food, oils and fats processors and food manufacturers are looking to palm oil and its fractions as alternative fats. Crystallization is of major importance in the processing of food and food ingredients and differential scanning calorimetry (DSC) has been widely used in studying such crystallization. This article discusses the use of non-isothermal DSC in modelling the crystallization of 1,3-dipalmitoyl-2-oleoylglycerol, one of the main triacylglycerol components of palm oil. Various kinetic crystallization models were used to fit the data, thus allowing the calculation of crystallization parameters. A similar approach may be used in the future to model crystallization in real systems.

Introduction

The crystallization of fats is important for oils and fats processors and for manufacturers using oils and fats in their end-products. As manufacturers move away from hydrogenated fats and fats containing trans fatty acids, palm oil has taken on particular importance and is providing the basis for many of the alternatives.

Some of these alternatives are based on fractions of palm oil, which means that a knowledge of the kinetics of palm oil crystallization is vital for both the processor and the food manufacturer. A major triacylglycerol in palm oil is 1,3-dipalmitoyl-2-oleoylglycerol (POP) and it is probably the main triacylglycerol to crystallize from this oil in most processes. An understanding of the crystallization kinetics of this triacylglycerol will greatly assist processors and manufacturers in using this oil.

A further reason for studying POP is that it is also one of the three main triacylglycerols in cocoa butter. Since the optimal crystallization of cocoa butter is critical to obtaining good quality chocolate, further awareness of the crystallization kinetics of POP will also help chocolate manufacturers.

The way in which POP in palm oil will crystallize in an industrial fractionation process will differ from the way in which POP in a palm fraction will crystallize when used in margarines and spreads. Furthermore, these will differ also from the way in which POP will crystallize when part of a cocoa butter equivalent in chocolate. For these reasons, it is useful to have a model of the crystallization kinetics to use as a basis for predictions of crystallization behaviour.

Microscopy, pulse NMR, ultrasound, and X-ray diffraction have been used to obtain the basic experimental data for crystallization models but in these studies we have chosen to use differential scanning calorimetry (DSC).

Differential scanning calorimetry (DSC)

In terms of measuring the crystallization of fats, DSC has been used in two ways — isothermally and non-isothermally. In the isothermal method the sample is rapidly cooled to a temperature below its freezing point and crystallization is then measured as a function of time. In the non-isothermal method the sample is cooled from liquid at a constant rate through the freezing point and below.

With the isothermal method, the rate of crystallization is dependent only on the degree of crystallization. However, selection of the correct temperature is critical — if it is too high, then crystallization will be slow and the signal may be lost within the baseline noise; if it is too low, then crystallization could be so rapid as to have started even before the crystallization temperature is reached. The use of non-isothermal DSC allows the measurements to be made within a reasonable time-frame and overcomes the need to find an appropriate isothermal crystallization temperature.

As far as kinetic modelling of crystallization is concerned, this has normally been done using data from isothermal DSC measured at a range of temperatures. In contrast, the application of non-isothermal DSC data to kinetic crystallization

Box 1. Mathematical models for the kinetics of crystallization.

The expression for the rate of a simple reaction (including crystallization) can be given by:

$$\frac{d\alpha}{dt} = f(\alpha)g(T) \quad (1)$$

where $f(\alpha)$ represents the kinetic model of the process and $g(T)$ accounts for the temperature dependence of the reaction rate.

The most common relationship used to model the kinetics of crystallization is the Avrami model. Although this was developed by Avrami in the late 1930s, other workers were at the same time developing the same relationships and so the model is now referred to as the Johnson-Mehl-Avrami-Erofeev-Kolmogorov, or JMAEK, model. The JMAEK equation is:

$$\alpha = 1 - \exp(-(Kt)^n) \quad (2)$$

where n is the Avrami exponent, dependent on the mode of nucleation and crystal growth, and K is the temperature-dependent rate constant. This leads to $f(\alpha)$ being defined as:

$$f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n} \quad (3)$$

In the JMAEK equation $g(T)$ is defined by the Arrhenius equation:

$$g(T) = K = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where R is the universal gas constant, A is the pre-exponential factor and E_a is the activation energy.

An extension of this model, the Vogel-Fulcher equation, has been defined which references the temperature to a constant temperature, T_0 :

$$g(T) = A \exp\left(-\frac{E_a}{R(T-T_0)}\right) \quad (5)$$

Replacing T in the Arrhenius equation [Equation 4] with $(T-T_0)$ allows for a Vogel-Fulcher temperature dependency.

models is unusual. We have therefore chosen to study crystallization of pure POP at a number of different cooling rates using non-isothermal DSC. The data were analysed using models ranging from those based on DSC peak information to those using iso-conversional techniques. We have also carried out further analysis using the non-parametric kinetics (NPK) method of Serra and colleagues (1). This method has the advantage of not making any assumptions regarding the dependence of crystallization speed on either the temperature or the degree of solidification, but separates out these factors allowing them to be analysed individually.

Kinetic crystallization models

In the literature, a range of models has been proposed for the kinetics of crystallization and many of these have been examined in the context of this study. The models considered in this paper are briefly outlined in **Box 1**. For a more thorough, mathematical description and explanation of the models, we refer the reader to our recent paper (2).

Equation 1 tells us that the rate of crystallization at any time is dependent only on the degree of crystallization, α , and the temperature, T . This means that the rate of crystallization can be represented in three-dimensional space as a surface of crystallization plotted against temperature and degree of crystallization. This can then be analysed by matrix mathematics using the NPK method referred to above.

Crystallization of POP

The POP used in our studies was greater than 99.5% pure. It had a fatty acid composition of 66.7% 16:0 and 33.3% 18:1, and a triacylglycerol composition of 99.6% C50 (along with 0.1% C48 and 0.3% C52). Silver-ion HPLC showed the presence of 99.9% SatOSat (plus 0.1% SatSatSat).

It was crystallized (as samples of approximately 10 mg) in a Perkin-Elmer Pyris 1 DSC. The samples were heated to 100°C and held at that temperature for 2 minutes before cooling at 50°C/minute to 50°C. The samples were then cooled from 50°C to -30°C using cooling rates of 2.5, 5, 7.5, 10, 12.5, 15 and 17.5°C/minute. These rates enabled full temperature control during cooling and also allowed the POP to crystallize in only one polymorphic form. After crystallization, the samples were held for 2 minutes at -30°C and were then re-heated at a rate of 5°C/minute to 60°C.

The DSC thermograms collected at these different cooling rates are shown in **Figure 1**. In the representation in Figure 1a, the area of the peak appears to increase with cooling rate when heat flow is shown as a function simply of temperature. When

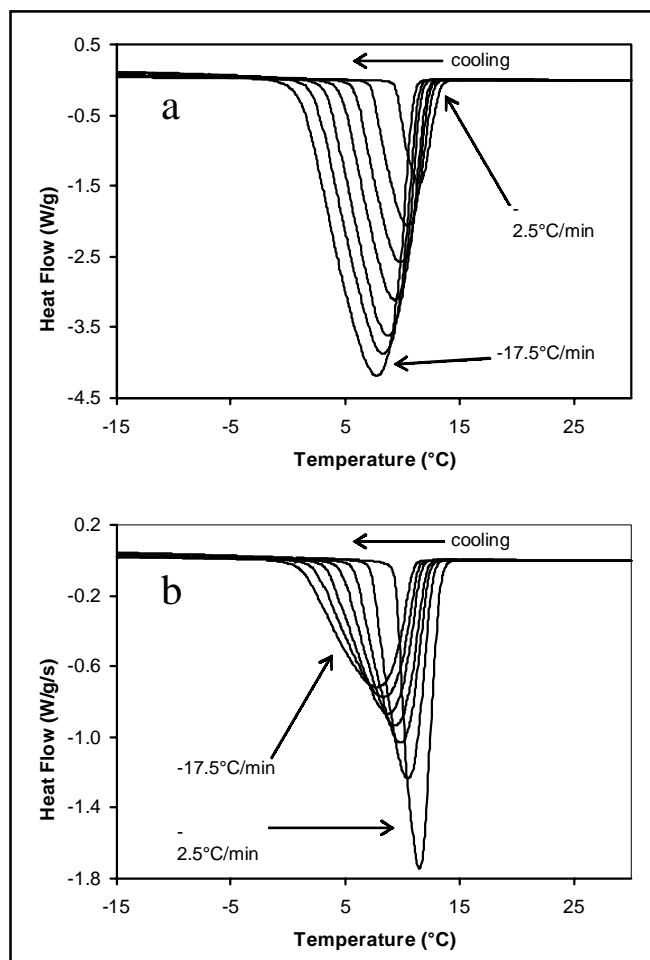


Figure 1. DSC crystallization curves of POP at cooling rates of 2.5, 5, 7.5, 10, 12.5, 15 and 17.5°C/minute. (a) Standard thermogram of normalized heat flow against temperature; (b) normalized heat flow per second against temperature (showing that peak areas are the same). Figure reproduced from *J. Agric. Food Chem.*, 2005, 53, 3031–3040 © 2005, American Chemical Society.

we bring a time factor into account and show the thermograms with normalized heat flow per second as a function of temperature (Figure 1b), then it is clear that the peak areas are the same for all cooling rates. However, as cooling rate increases, we do see a shift in both the onset temperature and the peak temperature. The onset temperature shifts because of the induction time of the crystallization; the peak temperature shifts because of both induction time and crystallization rate. The peak area for all the cooling rates was the same, at 89.1 J/g (SD 2.77). This also agreed with the area found on subsequent reheating, at 89.9 J/g (SD 3.03) and is the heat of fusion of the α polymorph.

By integrating these peaks we can show a representation of the degree of crystallization as a function of temperature (Figure 2).

The NPK method defined by Serra *et al.* allows us to separate the temperature dependency and the degree

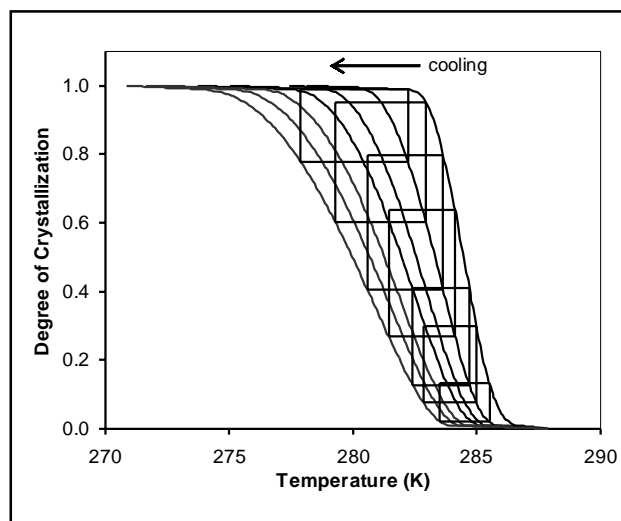


Figure 2. Integrated DSC crystallization curves of POP at cooling rates of 2.5, 5, 7.5, 10, 12.5, 15, 17.5°C/min. (The overlapping rectangles define the sub-matrices used for the NPK analysis). Figure reproduced from *J. Agric. Food Chem.*, 2005, 53, 3031–3040 © 2005, American Chemical Society.

of crystallization dependency before then going on to evaluate various kinetic models. To do this, we divide the data into a series of overlapping matrices, which are shown as overlapping rectangles in Figure 2. This method allows us to separate the two main parts, $f(\alpha)$ and $g(T)$, of Equation 1.

Crystallization models

Taking firstly $f(\alpha)$, various crystallization models were fitted as determined experimentally. One of the best-fitting models was the Johnson-Mehl-Avrami-Erofeev-Kolmogorov (JMAEK) model referred to in Box 1. In this model $f(\alpha)$ is defined as in Equation 3. In fitting the data to this model, the Avrami exponent, n , has a value of 1.303 (SE 0.006) with a root mean squared error of 0.0075.

In theory, Avrami exponents can range from 0.5 (which is characteristic of linear or rod-like crystal growth, spontaneous nucleation and a growth rate limited by diffusion) to a value of 4 (which is characteristic of spherical crystal growth, sporadic nucleation and a growth rate limited by nucleation). The calculated exponent of 1.3 could indicate either sporadic nucleation or spontaneous nucleation, the former being characterized by linear growth and the latter by spherical growth, in each case with a growth rate limited by diffusion.

In fitting the data to the JMAEK model a scaling multiplier is also defined (0.322). This is used to 'correct' the temperature dependent vector $g(T)$. If we plot $g(T)$ against temperature, either as $\ln(g(T))$ against $1000/T$ or simply as $g(T)$ versus T , then we find that the standard Arrhenius relationship

Table 1. Pseudo-induction times at different cooling rates.

Scanning rate (°C/minute)	Induction time (seconds)
2.5	45.4
5.0	35.3
7.5	26.5
10.0	20.1
12.5	19.8
15.0	17.6
17.5	16.9

(Equation 4) does not fit the data particularly well. However, if the Vogel-Fulcher modification (Equation 5) is used, then a much better fit is found. In the Vogel-Fulcher model there is a reference to a constant temperature, T_0 . The value obtained by fitting this parameter was 288.77 K. This was very close to the average onset of melting following crystallization at various cooling rates, which was 288.22 K.

Using the Vogel-Fulcher model we arrive at a pre-exponential factor for the crystallization of $2.278 \times 10^{-1} \text{ s}^{-1}$ and an apparent activation energy of 76.7 J/mol.

We can use the parameters calculated from the JMAEK and Vogel-Fulcher models to calculate the DSC curves at different cooling rates. In order to obtain a good match between the calculated and the observed curves it is necessary to bring in an induction time factor — or, at least, a pseudo-induction time factor. This is the shift needed to bring the calculated curves into line with the observed curves. These pseudo-induction times for each cooling rate are shown in Table 1. As would be expected, the pseudo-induction times decrease as the cooling rate increases because of the shorter times spent at the higher temperatures. Using these pseudo-induction times allows us to obtain an excellent fit between the calculated DSC curves and the observed DSC curves. These are shown for cooling rates of 2.5°C/minute and for 17.5°C/minute in Figure 3.

Conclusions

By applying a combination of non-parametric kinetics (NPK) modelling with various crystallization models (especially JMAEK model) and the Vogel-Fulcher modification to the Arrhenius relationship, it is possible to model the crystallization kinetics of a pure triacylglycerol such as POP, providing that care is taken to ensure that the triacylglycerol crystallizes in the same polymorph throughout.

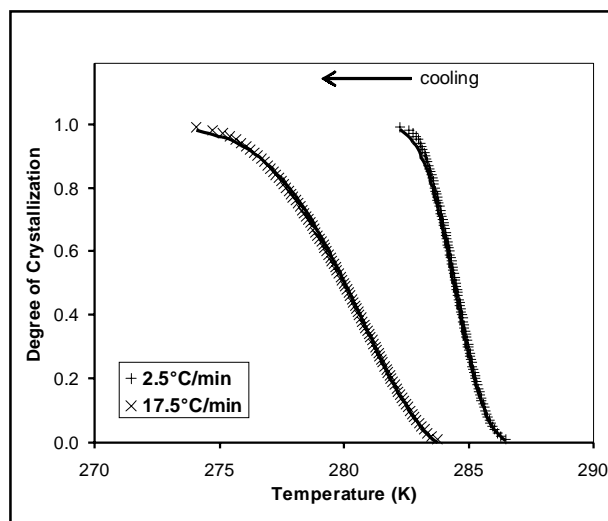


Figure 3 . Calculated crystallization curves and measured data points from DSC. Figure reproduced from *J. Agric. Food Chem.*, 2005, 53, 3031–3040 © 2005, American Chemical Society.

References

- Serra, R., Sempere, J. and Nomen, R. (1998) A new method for the kinetic study of thermoanalytical data: The non-parametric kinetics method. *Thermochim. Acta*, 316, 37–45; Serra, R., Nomen, R. and Sempere, J. (1998) The non-parametric kinetics. *J. Therm. Anal.*, 52, 933–943.
- Smith, K.W., Cain, F.W. and Talbot, G. (2005) Kinetic analysis of non-isothermal differential scanning calorimetry of 1,3-dipalmitoyl-2-oleoylglycerol. *J. Agric. Food Chem.*, 53, 3031–3040.

CONFECTIONERY FATS HANDBOOK

Written by Ralph E. Timms.
ISBN 0-9531949-4-9, 2003,
441 pages, 90 tables, 146 figures,
725 references.



Fat is the most expensive component in confectionery such as chocolate. It may comprise cocoa butter, milk fat, palm oil, lauric oil, exotic fats etc. This handbook, with a large number of figures and tables, provides a comprehensive guide to all aspects of confectionery fats. The author is recognized worldwide as a leading expert in the practical as well as the theoretical aspects. The following topics are covered.

- Introduction • Physical chemistry • Analytical methods • Raw materials • Processing of raw materials • Production and properties • Applications • Bloom, rancidity, migration • Adulteration, detection and quantification • Legislation and regulatory aspects • Appendices: Suppliers and products.

To order a copy, see: www.pjbarnes.co.uk/op/cf.htm
or contact: sales@pjbarnes.co.uk