Differential scanning calorimetry to measure the isothermal crystallization kinetics of cocoa butter

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STEP 1:

PREPARATION OF DSC SAMPLE

WHAT IS THE EFFECT OF THE SAMPLE PREPARATION METHOD?

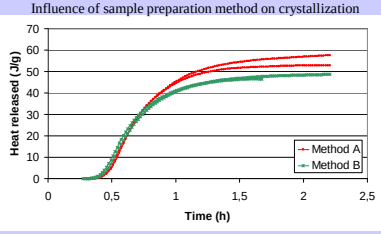
Method A:		sampling with material cleaned with ethanol	in oven at 60°C for 15 min	transfer to DSC pan with plastic micropipette
Method B:	use of desiccator for equilibration to room temperature	sampling with material cleaned with acetone	in oven at 60°C for 15 min	transfer to DSC pan with hot, glass Pasteur pipette

RESULT: Significant differences on *a* parameters of Gompertz and Avrami model

λ parameter of Gompertz model

k parameter of Avrami model

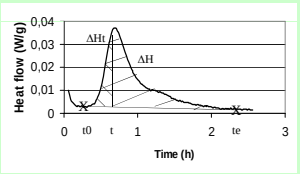
Influence of sample preparation method on crystallization



STEP 2: DSC RUN

Time – temperature program:

- melting the sample to eliminate memory effect
- cooling at 8°C /min to crystallization temperature (17.2°C)
- keep at that temperature until crystallization is complete



WHAT IS THE EFFECT OF THE MELTING PROTOCOL?

Comparison of three melting protocols:

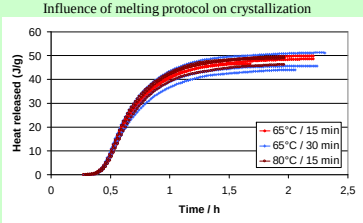
65°C for 15 minutes

65°C for 30 minutes

80°C for 15 minutes

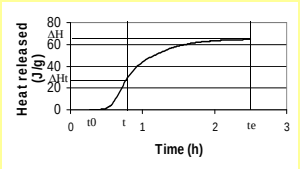
RESULT : No significant differences between the three melting protocols on the Avrami and Gompertz parameters

Influence of melting protocol on crystallization



STEP 3: INTEGRATION

Knowledge of t0 and te is necessary !!



HOW TO DETERMINE t0 AND te?

Suggested method in literature is by visual inspection

At the authors' laboratory eight persons were asked to visually determine the start and end point of a DSC curve:

Operator	Start point (min)	End point (min)
1	37.98	119.04
2	40.18	130.26
3	39.51	111.17
4	39.91	94.49
5	40.01	112.08
6	41.84	100.29
7	41.95	109.95
8	37.99	109.07
Mean	40	110
Standard deviation	1	11
Coefficient of variation (%)	3.7	9.8
Via new algorithm (see right)	37	123

➡ LARGE VARIABILITY!!

NEW OBJECTIVE TIME DETERMINATION ALGORITHM

Preparation step

Determination of slope of curve

Determination of sign changes (n1, n2, …)

Determination of t0

$n_{peak} = 2$?

yes → $t_0 = n_1$

no → $t_0 = n_{neg.-pos.}$ of which heat flow value is lowest

Determination of te

determination of dQ/dt_f

$|dQ/dt\ n_{peak+1} - dQ/dt_f| < 3\sigma$ → yes → $t_e = n_{peak+3}$

no → $|dQ/dt\ n_{peak+2} - dQ/dt_f| < 3\sigma$ → yes → $t_e = n_{peak+1+3}$

no → etc.

Note:

dQ/dt_f = final heat flow value = median of last five values

σ = baseline noise

STEP 4:

MODELING WITH AVRAMI AND GOMPERTZ MODEL

AVRAMI

$$f(t) = a * \left(1 - e^{-k * t^n}\right)$$

f(t): amount of crystallization at time *t* [J/g]

a: value for *f* as *t* approaches infinity [J/g]

k: crystallization rate constant [h^{-n}]

n: Avrami exponent [-]

GOMPERTZ

$$f(t) = a * e^{-e^{\frac{\mu * e}{a} * (\lambda - t) + 1}}$$

f(t): amount of crystallization at time *t* [J/g]

a: value for *f* as *t* approaches infinity [J/g]

μ: maximum increase rate [J/g h^{-1}]

λ: induction time [h]

CONCLUSIONS

- Use of new time determination algorithm leads to objective determination of start and end point of integration
- Sample preparation method has to be kept constant to eliminate influence thereof
- 65°C for 15 min is enough to eliminate any memory effect

Acknowledgements

Imogen Foubert is a research assistant of the Fund for Scientific Research – Flanders (F.W.O. – Vlaanderen).

Barry-Callebaut, Wieze, Belgium is acknowledged for providing the cocoa butter.

Dr. ir. Olivier Thas is acknowledged for the help with the statistics.