Modelling the Temperature Dependency of Crystallization Parameters in View of Describing the Non-Isothermal Crystallization Process

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Foubert et al. (2002) developed a new model able to better describe the isothermal crystallization kinetics of fats compared to the often used Avrami model and the sometimes used Gompertz model. The model describes the crystallization process as if it was a first order forward reaction and a reverse reaction of order n. A lot of industrial processes however take place non-isothermally. Therefore, an extension of this basic isothermal model for application under non-isothermal conditions would be advantageous. To accomplish this, the temperature dependence of the isothermal model parameters was studied and included in the model using so-called secondary models or submodels. Including these in the basic model allows for description of non-isothermal crystallization.

A standard factory cocoa butter was used as a substrate and its isothermal crystallization was followed in the range between 19°C and 23°C. Dewettinck et al. (2004) investigated the crystallization process in this temperature range in more detail and proposed a mechanism for the observed two-step crystallization. In the first step part of the melt crystallizes into the □ polymorph, while in the second step □ crystals transform into □' crystals via a solid-solid transition. Foubert et al. (2006) already presented an extension of the basic model which allows to describe this two-step process.

Before using the two-step isothermal model in this research, a sensitivity analysis (sensitivity functions express how much a variable will change given a change in a parameter value) was performed. From this analysis, it could be concluded that the sensitivity of the amount of crystallization to the parameters $n_{\beta'}$ and $K_{\beta'}$ was comparable which implies that it is useless to estimate both at the same time. Therefore it was decided to fix parameter $n_{\beta'}$ to a value of 6. Furthermore it was also decided to fix t_ind_{α}

to zero as no induction time could be detected. Consequently, the two-step model used in this research had 5 parameters to be estimated.

To be able to follow the two-step crystallization of cocoa butter by means of DSC, the experimental method needed some optimization as the first crystallization step overlaps with the temperature equilibration making it impossible to integrate this peak. Therefore the stop-and-return technique (i.e. stopping the crystallization at several points in time, heating up the sample and using the melting enthalpy as a measure for the amount of crystallization) was applied. To save on analysis time, the stop-and-return technique for the first step was combined with a classical isothermal measurement for the second step.

The isothermal crystallization of cocoa butter could then be measured in fourfold at each crystallization temperature (between 19°C and 23°C with 0.5°C interval). The 5-parameter model as described above was then fitted to all these crystallization curves using the Simplex algorithm and the confidence information on the parameter estimates was obtained using the Nelder & Mead algorithm. For both, the simulation platform WEST (Most4Water, Kortrijk, Belgium) was used. Following, the obtained parameters were plotted as function of temperature and for each parameter a best empirical model to describe the temperature dependency was searched for and calibrated. As much as possible, models with a physical meaning such as the Turnbull-Fisher equation or the Vogel-Fulcher equation were used. These secondary models were then combined with the basic model.

A first validation of the model was performed in WEST using data of cocoa butter sequentially crystallized at two different isothermal temperatures.