Observing and modeling the evolution of starch granules size distribution

Giana Almeida, Artemio Plana-Fattori, Gabrielle Moulin, Camille Michon, Denis Flick

Title

Observing and modeling the evolution starch granules size distribution

Authors & Affiliations

ALMEIDA Giana[1,2], PLANA-FATTORI Artemio[1 2], MOULIN Gabrielle[1 2], MICHON Camille[1 2], FLICK Denis [1 2]

[1] *AgroParisTech, UMR1145, Ingénierie Procédés Aliments, F-91300 Massy*
[2] *INRA, UMR1145, Ingénierie Procédés Aliments, F-91300 Massy*

Corresponding author email: denis.flick@agroparistech.fr

Abstract:

Introduction: Starch granules undergo structural changes under thermal treatment, and the subsequent viscosity increase of starch suspensions allows many applications in the food industry. For instance, dairy cream products consist of milk mixed with starch and carrageenan as gelling agent. Prediction of the starch transformation and of the associated rheological evolution is a challenging task, even for a suspension of starch granules in water. Current models define the starch swelling degree in terms of the mean diameter of granules, with no information regarding the observed diversity of size and swelling onset. To our knowledge, no models exist for predicting the evolution of the size distribution of starch granules under thermal treatment.

Materials & Methods: Modified waxy maize starch is considered (no disruption of swollen granules, no amylose release). Three modeling approaches are compared with experimental results, in which an optical microscope (Olympus BX51, objective x50) coupled to a Linkam warming plate is used to continuously observe the starch granules behavior during thermal treatments. Three tests were performed; for each one, the evolution of about 15 granules could be followed. The heating rate was of 5°C/min from 50 to 90°C, then, the temperature was maintained at 90°C during 2 min. At given time steps, the images were analysed using ImageJ. The plugging ABSnake (Andrey et Boudier, 2006) was used to automatically contour starch granules of each image. Major and minor diameters were measured by fitting an ellipse. The geometric mean value of the ellipse axes was considered as the characteristic size; in the following it is simply called 'granule diameter'.

The first model considers that all the granules swell with the same 2[nd]order kinetics (Lagarrigue *et al* 2008). The cumulative size distribution (csd) is related to the swelling degree: $S=(d-d_0)/(d_{max}-d_0)$.

$$csd_1 = \frac{1}{2}\left(1+\mathrm{erf}\left(\frac{d-(1+\alpha S_{(t)})d_{m0}}{\sqrt{2}(1+\alpha S_{(t)})\sigma_0}\right)\right) \text{ with } \frac{dS}{dt} = -k_{1(T)}(1-S)^2 \rightarrow S_{(t)} = 1 - \frac{1}{1+\int_0^t k_{1(T)}dt'}$$

The second model considers that a granule has a probability $k_{2(T)}$ to completely swell (very quickly) during the next time unit. For a high number of granules this corresponds to a first order kinetics for the proportion of not swollen granules: n. The size distribution becomes the weighted sum of two Gaussians: $n \cdot G(d_{m0},\sigma_0)+(1-n)\cdot G(\alpha d_{m0},\alpha\sigma_0)$

$$csd_2 = \frac{1}{2}\left(1+n_{(t)}\mathrm{erf}\left(\frac{d-d_{m0}}{\sqrt{2}\sigma_0}\right)+(1-n_{(t)})\mathrm{erf}\left(\frac{d-(1+\alpha)d_{m0}}{\sqrt{2}(1+\alpha S)\sigma_0}\right)\right) \text{ with } \frac{dn}{dt} = -k_{2(T)}n \rightarrow n_{(t)} = 1-\exp\left(-\int_0^t k_{2(T)}dt'\right)$$

The third model considers diffusive swelling, it implies than the smallest granules swell more rapidly than the largest ones. The size distribution is obtained by calculating the relative inflation: $Z=d/d_0$ for a set of initial diameters using the following equations (Singh and Weber 1996).

$$\frac{dZ}{d\tau} = \frac{\alpha^3-1}{Z}\left.\frac{\partial\theta}{\partial z}\right|_{z=1} \quad \text{with } \tau = \int_0^t D_{(T)}dt' \Big/ (d_0/2)^2$$

$$\frac{\partial\theta}{\partial\tau} = \frac{z}{Z}\frac{dZ}{d\tau}\frac{\partial\theta}{\partial z} + \frac{1}{Z^2}\left[\frac{2}{z}\frac{\partial\theta}{\partial z}+\frac{\partial^2\theta}{\partial z^2}\right] \text{ with } \theta\begin{pmatrix} t=0 \\ 0<z<1 \end{pmatrix} = 0;\ \theta\begin{pmatrix} t>0 \\ z=1 \end{pmatrix} = 1;\ \frac{\partial\theta}{\partial z}\begin{pmatrix} t>0 \\ z=1 \end{pmatrix} = 0$$

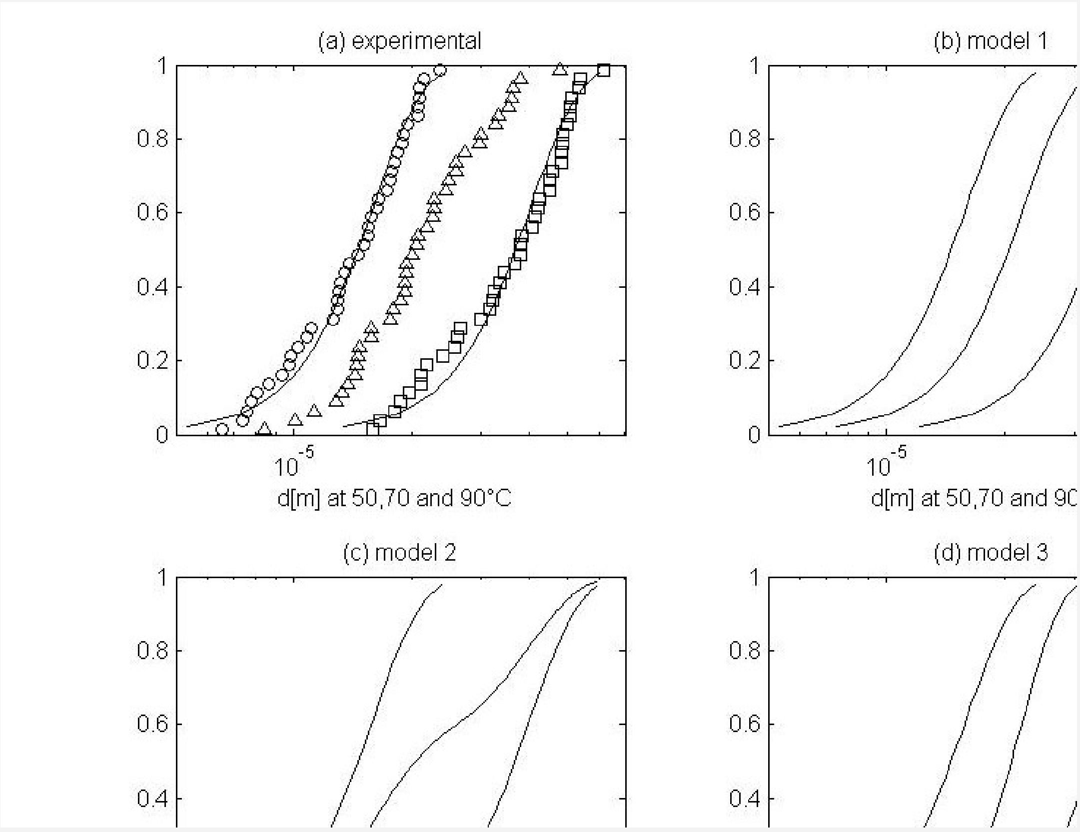
In this preliminary study, the kinetic parameters k_1, k_2 and D are assumed to be zero as long as the

temperature is lower than the gelatinisation onset temperature (60°C) and, then, increase linearly with temperature. The slope was adjusted in order to obtain the same median diameter as observed experimentally at the intermediate temperature of 70°C.

Results and discussion

The initial granule size distribution (at 50°C) was approximately Gaussian with a mean value of d_{m0}=14.6 µm and a standard deviation of σ_0=4.6 µm. The final distribution (after 2 min at 90°C) was also about Gaussian with a mean value of d_{mf}=36,7 µm and a standard deviation of 12.4 microns. After 2 min at 90°C, it can be considered that all the granules were completely swollen. The inflation ratio was averagely of $\alpha=d_{mf}/d_{m0}$=2.51 in diameter which corresponds to 15.9 in volume. The relative standard deviation remained almost the same: 31% for initial distribution and 34% for the final one. This suggests that the inflation ratio is independent of the initial granule size. Figure 1a shows the cumulative size distributions at 50°C, at 70°C (4 min) and at 90°C (10 min); the abscissa represent the diameter (logarithmic scale) the ordinate the percentage (in number) of the granules smaller than this diameter. We observe a simple translation between the initial and final distributions (constant inflation ratio) whereas the intermediate distribution presents a slightly different shape.

Figure 1 compares the experimental and simulated results. The shape of the size distribution at intermediate temperature (70°C) does not really match with one of the simulated distributions. Visual observation (following individual granules) suggest than swelling mechanism is in between model 2 and 3. All the granules do not begin to swell at the same time (same temperature); as formulated in model 2. The beginning of swelling is rather quick, then, it becomes slower especially for the largest granules; as represented in model 3. Further work is necessary: more granules should be followed in various conditions (other heating rates) and a stochastic-diffusive model could be developed.



Literature cited :

Andrey, P. and Boudier, T. (2006) Adaptive Active Contours, ImageJ Conference

Lagarrigue S., Alvarez G., Cuvelier G. and Flick D. (2008) *Swelling kinetics of waxy maize and maize starches at high temperatures and heating rates.* Carbohydrate Polymers 73, 148-155

Singh J. and Weber M.E. (1996) *Kinetics of one-dimensional gel swelling and collapse for large volume change.* Chemical Engineering Science 51, 4499-4508