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Comparing different models of starch swelling

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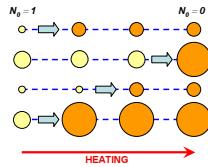
Swelling models

Starch granules undergo structural changes under thermal treatment. The subsequent increase of the viscosity associated with starch suspensions allows many applications in the food industry. To our knowledge, no models exist for predicting the evolution of the size distribution of starch granules under thermal treatment.

The first model considers: a) that each granule can exhibit two possible states only, namely not-swollen and fully-swollen; and b) that there is a probability per unit of time, P , of quick transition between these states. For a high number of granules, this can be expressed as one first-order kinetics for the proportion N_0 of starch granules which remain not-swollen:

$$dN_0/dt = -P N_0$$

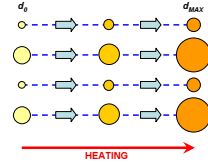
At a given time, the actual granule size distribution is estimated as the weighted-average of the size distributions which characterize not-swollen and fully-swollen granules.



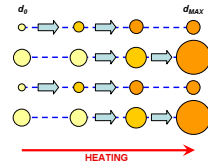
The second model considers that the size of each granule can continuously increase with the time. The evolution of granules sizes can be assumed to follow a second-order kinetics for the swelling degree S (e.g. Lagarrigue *et al.*, 2008):

$$dS/dt = k(1-S)^2, \quad S = (d - d_0) / (d_{MAX} - d_0)$$

Here k is the swelling kinetics rate, assumed to be the same for all the starch granules. For each granule, d_0 is its diameter at a given time, while $d = d_0$ is associated with uncooked starch (not-swollen granule) and $d = d_{MAX}$ with starch after maximum thermal treatment (fully-swollen granule).



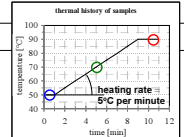
The third model considers diffusive swelling: starch granules swell while taking surrounding water. Hence, the inflation d/d_0 associated with smaller granules increases more rapidly and reach earlier its respective maximum value, than that associated with the larger granules. The diffusivity D for water inside starch granules is the key parameter. The problem can be solved following the approach proposed by Singh and Weber (1996).



In this preliminary study, the key parameters P , k , and D are assumed to be zero as long as the temperature is lower than the swelling onset value (60°C); above the latter, they are assumed to increase linearly with temperature. The slope is chosen in order to allow the same median diameter as observed experimentally at the intermediate temperature 70°C.

Observations

An optical microscope (Olympus BX51, objective x50) coupled to a Linkam warming plate was used to continuously observe the starch granules behavior during a selected thermal treatment.



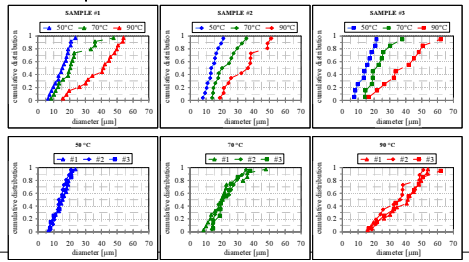
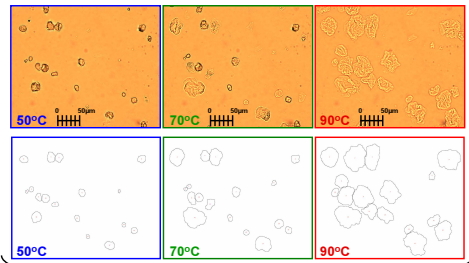
Modified waxy maize starch was chosen; starch granules swell without rupture or release of soluble species in water.

Starch in water at very low mass concentration (0.05 wt.%) was studied, allowing the monitoring of each granule along its thermal history.

Image analysis was performed through the public domain Java processing program ImageJ. The software component AB-Snake was used to automatically contour starch granules in each image.

Major and minor diameters were estimated 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".

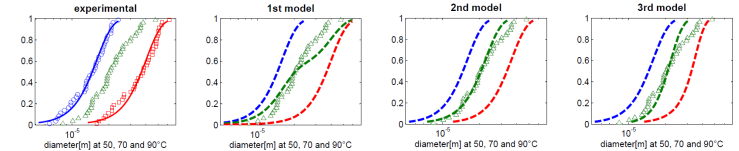
The distribution of diameters evolves along the thermal history of the sample. The whole experiment has been replicated.



Models and observations

Symbols summarize experimental data from the three samples. Forty granules were followed. Granule diameters at 50°C (uncooked starch) and 90°C (after thermal treatment) were associated with mean values of 14.8 and 37.0µm, and with standard deviations of 4.6 and 12.4µm respectively. Relative standard deviations were similar (about 32% at 50°C and 34% at 90°C); corresponding distributions exhibit very similar shape. Maximum inflation d_{MAX}/d_0 ranged from 2.2 to 2.7.

Full lines indicate cumulative size distributions built by assuming log-normal distributions for the granule diameter. Dashed lines indicate distributions predicted by the swelling models, whose parameters were estimated from experimental data at 50 and 90°C.



Conclusions and future work

The shape of the observed size distribution at the intermediate temperature (70°C) does not really match with one of the predicted distributions. Visual observation of individual granules suggests that swelling mechanism seems to be in between the stochastic and the diffusive models. On one hand, all the granules do not start to swell at the same time (say, at the same temperature) as formulated in the stochastic model. On the other hand, the beginning of swelling is rather quick, then it becomes slower especially for the largest granules. Such a behavior can be interpreted with the help of the diffusive model.

Forthcoming efforts include:
i) observation of a larger number of starch granules under different heating rates, and
ii) further model development, for instance by combining the stochastic and the diffusive approaches.

Lagarrigue, S., Alvarez, G., Cuvelier, G., Flick, D. – 2008 – Swelling kinetics of waxy maize and maize starches at high temperatures and heating rates. *Carbohydrate Polymers*, 73: 146-155.
Singh, J., Weber, M. E. – 1996 – Kinetics of one-dimensional gel swelling and collapse for large volume change. *Chemical Engineering Science*, 51: 4489-4508.