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# AN EXPERIMENTAL STUDY OF THE SWELLING BEHAVIOR OF STARCH GRANULES UNDER HEAT TREATMENT

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## **ABSTRACT**

Current models for predicting the transformation state of starch suspensions define the swelling degree in terms of the mean diameter of granules, with no information regarding the observed diversity of size and swelling onset.

This article analyzes the thermal history of 143 granules as obtained from images captured during hot-stage normal light microscopy of droplets of a modified waxy maize starch suspension. The evolution of 0.5 mL samples was studied under heat treatment from 50 to 90 °C at rate of 5 °C/min.

No relationship was found between initial granule diameter and swelling onset temperature. Changes in the starch swelling state were relatively weak below 60 °C and above 80 °C. Simultaneous occurrence of uncooked starch and swollen granules was observed at intermediate temperatures.

## **Keywords**

Starch, swelling, size distribution, heat treatment, thermal history, hot-stage microscopy

## **1. INTRODUCTION**

The mechanisms driving the transformation of ingredients along the processing pathway need to be understood as a necessary step for manufacturing food products in a reproducible manner. To predict the product transformation and the associated rheological evolution represents a challenging task, even for a simple liquid product like an aqueous suspension of starch granules submitted to heat treatment.

Efforts have been devoted, since the early 1800s, in understanding the structural changes of starch granules heated in water (Ratnayake and Jackson, 2008). Modifications experienced by starch under heating have been summarized as: disruption of crystalline and molecular order

of starch granules, swelling and rupture of the granules, and reorganization of the disordered molecules (Matignon and Tecante, 2016). Swelling of granules plays a major role in driving the flow behavior of dilute starch suspensions (Lagarrigue and Alvarez, 2001). Current models for predicting the transformation state of starch suspensions define the swelling degree in terms of the mean diameter of granules, with no information regarding the diversity of size and swelling onset. Starch phase transition processes have been studied through a number of techniques, including: normal and polarized light microscopy, scanning electron microscopy, differential scanning calorimetry, X-ray diffraction, high-performance size exclusion chromatography, and confocal laser scanning microscopy (e.g. Ratnayake and Jackson, 2007; Chen et al., 2011; Schirmer et al., 2013). Some techniques allow the real-time monitoring of the starch suspension while it is submitted to heat treatment; they enable the assessment of swelling kinetics with no additional starch transformation between the end of the heat treatment and laboratory analysis. This is the case of hot-stage microscopy, a standard technique employed since the 1960s (Carlson, 2011).

The study of the granule size distribution along its thermal history constitutes the first step towards the prediction of transformation state and flow behavior of starch suspensions. This article analyzes the thermal history of individual granules as obtained from images captured during hot-stage normal light microscopy of droplets of a starch suspension.

## 2. EXPERIMENTAL METHODS AND DATA PROCESSING

The liquid product is a 0.5 g/kg starch suspension in water. Chemically-stabilized and cross-linked waxy maize starch (acetylated adipate distarch, C\*Tex 06205) was kindly provided by Cargill (Baupte, France). It consisted of at least 99% of amylopectin (less than 1% of amylose). For this type of starch neither disruption of swollen granules nor release of amylose is expected (Matignon et al., 2014). The product was prepared by adding the starch powder to a 0.1 M NaCl aqueous solution. Before heat treatment, the resulting liquid remained at 50 °C for 30 min under continuous gentle stirring.

Samples of 0.5 mL were placed on a Linkam LTS120 stage (Linkam Scientific Instruments, Surrey, UK) and observed under 50X magnification using an optical Olympus BX-51 microscope (Olympus Optical Co. Ltd., Tokyo, Japan). Adhesive spacers (total thickness of 250 µm) were fixed on the microscope slides in order to ensure free swelling of starch granules. The Linksys32 temperature control software was used for programming the hot-stage operation. The evolution of samples of the starch suspension was studied under the following heat treatment: firstly one minute at 50 °C, then heating from 50 to 90 °C at rate of

5 °C/min, and finally one minute at 90 °C. Images were captured every second with a Basler A102fc digital camera (Basler AG, Ahrensburg, Germany). Images at selected temperatures were retained for this study, namely: a) after one minute at 50 °C, b) at 60, 68, 70, 75, 80 and 90 °C during heating, and c) after one minute at 90 °C. Image processing was applied only to the starch granules which were recognized at all these temperatures. The characterization of each granule was performed through the public domain Java image processing program Image-J (version 1.42q, National Institutes Health, Bethesda, Maryland, USA), including the plug-in component that implements the active contour method AB-Snake (Andrey and Boudier, 2006). After manual recognition of granules, the software automatically contoured and measured them. The geometric mean of major and minor diameters of the ellipse with the same area than the surface occupied by the granule is hereafter called granule diameter. In a final processing step, conducted through routines written in MATLAB code (Mathworks, Natick, Massachusetts, USA), each granule was associated with the same numbering order over the set of images at different temperatures.

In this article we discuss the results obtained for 143 starch granules, satisfactorily monitored after submitting 17 samples to the prescribed heat treatment. Figure 1 illustrates one of the samples at 50, 70, and 90 °C, as captured by the camera coupled to the microscope and after image processing through Image-J and MATLAB routines.

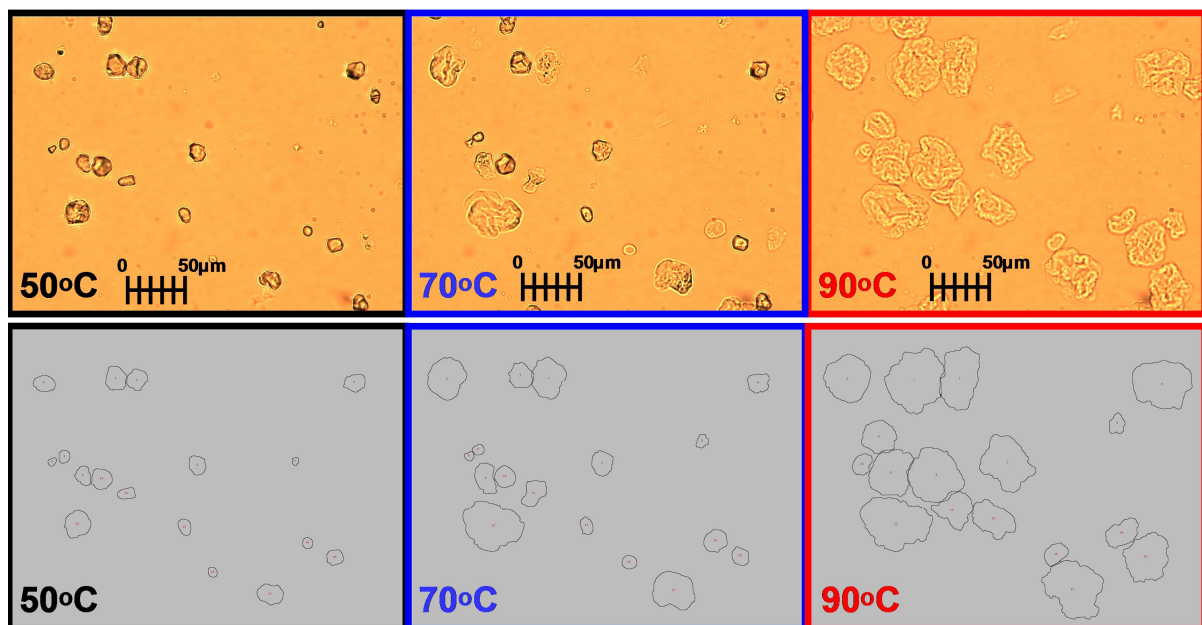


Figure 1: One sample at three selected temperatures, as captured by the digital camera (top), and after processing through Image-J and MATLAB routines (bottom).

### 3. RESULTS

All the observations considered in this study are shown in Figure 2A. Thin lines connect observations associated with a same thermal / swelling history. Selected histories are presented in Figure 2B. Firstly, starch granules associated with quite similar diameter at 50 °C (as granules #50, #80 and #110) can evolve differently under a same heat treatment. Secondly, the final swelling state (say, the diameter observed after one minute at 90 °C) can be reached quite early during the heat treatment (between 60 and 68 °C in the case of granule #20). Lastly, in many cases, swelling is relatively weak above 75-80 °C.

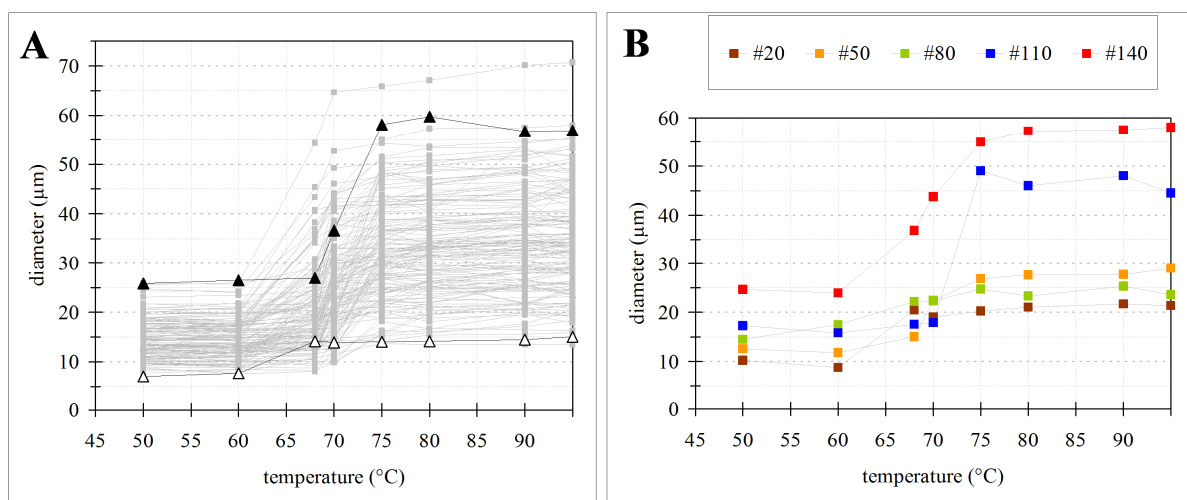


Figure 2: A) All the observations under consideration; white and black triangles indicate the thermal histories associated with the smallest (rank #1) and the largest (rank #143) granule diameter at 50 °C, respectively. B) Selected thermal histories, labeled by their rank. The right-most points correspond to the observation performed after one minute at 90 °C.

Figure 3A presents all the observations corresponding to the temperatures at the start (50 °C), at the middle (70 °C) and at the end (90 °C) of the 8-min heating period (i.e. from 50 to 90 °C at rate of 5 °C/min). Observations are ordered increasingly with the granule diameter at 50 °C. Observations are less scattered at 90 °C (near the end of the heat treatment) than at 70 °C. Figure 3B put in evidence that there are cases where there is no starch swelling at 70 °C (#103 and #110), cases where swelling is weak at 70 °C (#102, #107, #108), and cases where the granule diameter has almost already reached its final value at 70 °C.

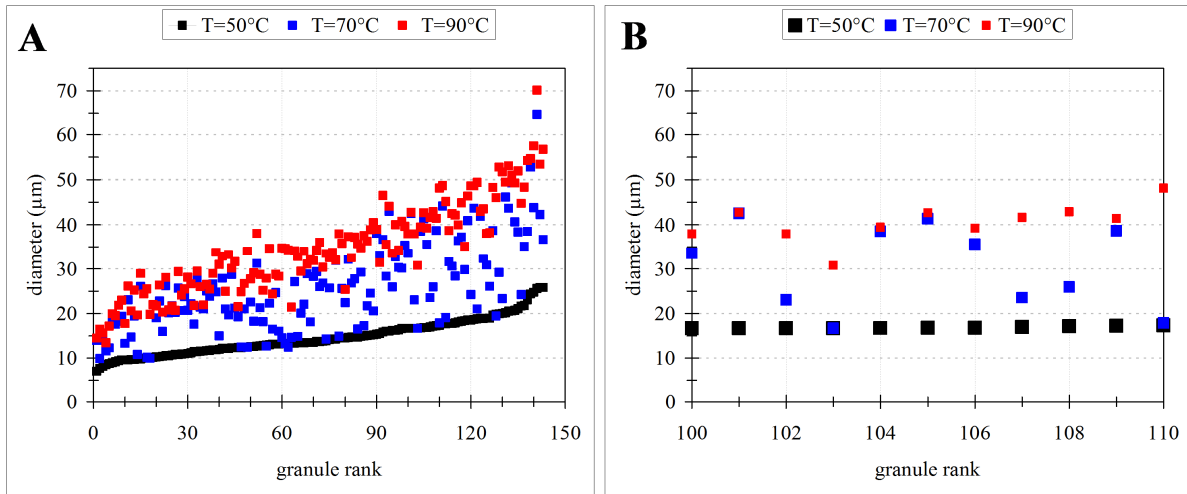


Figure 3: A) All the observations at three temperatures, showing granule diameters ordered increasingly with their value at 50 °C. B) The same, but for a selection of thermal histories.

The granule diameter at a given temperatures can be presented as a function of its value at the beginning of the heat treatment, as shown in Figures 4A and 4B. There are a lot of starch granules that exhibit similar diameters at 50 and 70 °C; such situation corresponds to the points situated near the line  $d_{70} = d_{50}$  on Figure 4A. Looking for the mean relative increase of granule diameter (with respect to its value at 50 °C), we obtained a regression line intercepting zero for each scatter diagram.

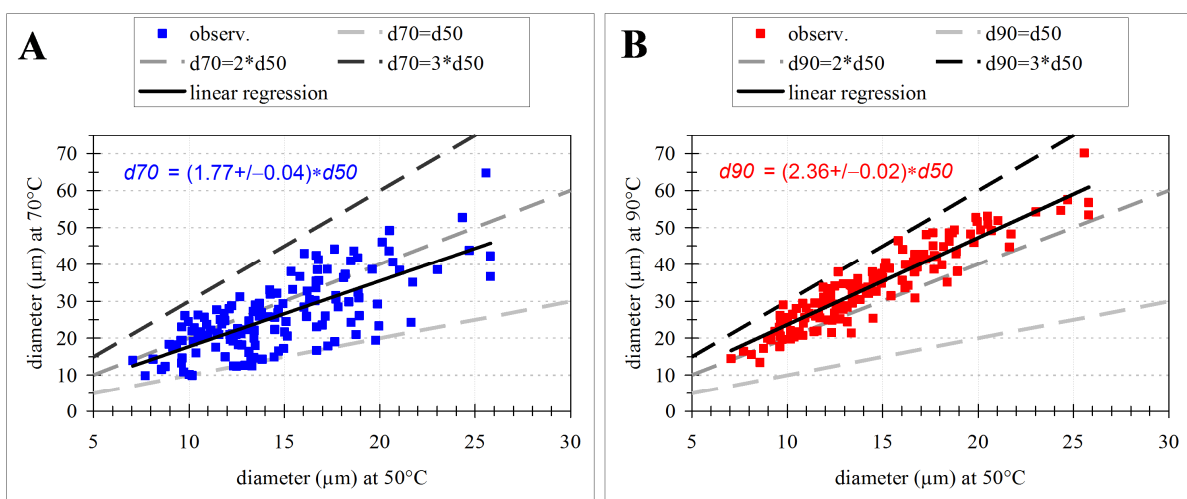


Figure 4: Granule diameter  $d_{70}$  at 70 °C (A) and  $d_{90}$  at 90 °C (B) as a function of its value  $d_{50}$  at 50 °C. Dashed lines correspond to three hypothetical values for the increase. Bold continuous lines indicate linear regressions intercepting zero.

The regression lines shown in Figure 4 constitute zero-order models for predicting the granule diameter at a selected temperature, provided that the diameter is known at 50 °C. A higher-order predictive model might consider the relative increase  $d\{T\}/d50$  in function of the diameter at 50 °C. Figure 5A presents the diameter increase values up to 70 and 90 °C, ordered increasingly with the diameter at 50 °C. The increase  $d90/d50$  exhibits higher average (2.34) and smaller standard deviation (0.28) than the increase  $d70/d50$  (1.77 and 0.45, respectively). Figure 5B displays the observations as function of the diameter at 50 °C, as well as the regression lines  $d\{T\}/d50 = \alpha*d50 + \beta$ . In the case of  $d70/d50$ , the standard error of  $\alpha$  ( $0.01 \mu\text{m}^{-1}$ ) is many times larger than the  $\alpha$  value itself ( $0.0006 \mu\text{m}^{-1}$ ); the probability of null value for  $\alpha$  is high (about 95%). The dependence of the increase  $d70/d50$  with the diameter at 50 °C is overwhelmed by its own variability (Figure 5A), which is associated in a large extent with the variability of diameters at 70 °C (Figures 3A and 4A). Contrarily, in the case of the increase  $d90/d50$ , the standard error of  $\alpha$  ( $0.006 \mu\text{m}^{-1}$ ) is smaller than the  $\alpha$  value ( $0.011 \mu\text{m}^{-1}$ ) and the probability of null value for  $\alpha$  is relatively low (about 6 %). The dependence of the increase  $d90/d50$  with the diameter at 50 °C is significant: on average, larger is the granule before the heat treatment, higher is the increase between 50 and 90 °C; nevertheless, this dependence remains weak. The variability of  $d90/d50$  can be explained for a small part by the initial diameter ( $r^2 = 0.03$ ).

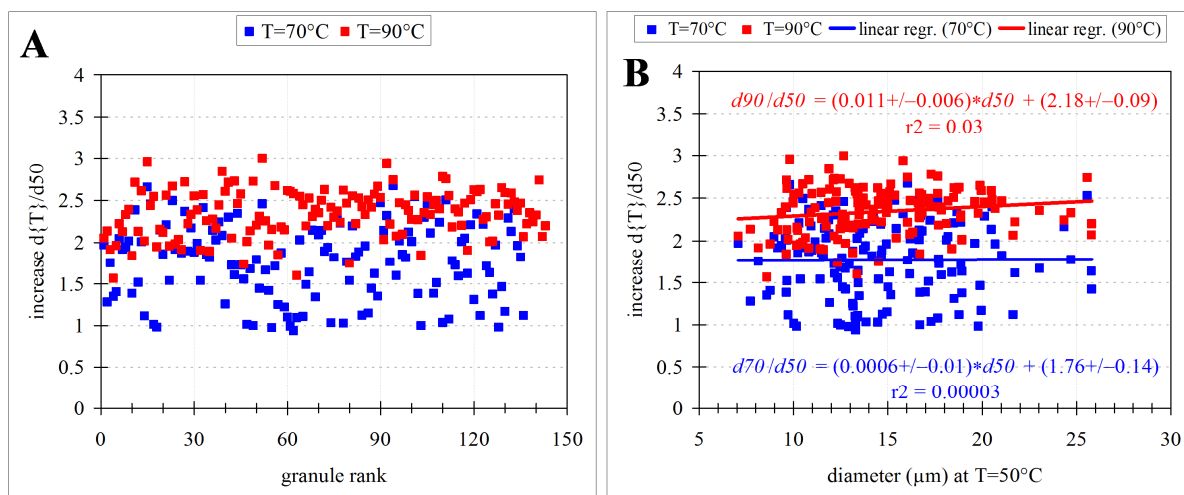


Figure 5: Diameter increase from 50 °C up to two selected temperatures, as a function of the granule rank (A), and of the granule diameter at 50 °C (B). Bold lines indicate linear regressions; equation parameters are presented plus/minus one standard error.

Figures 6A and 6B show the cumulative distribution of granule diameters. In increasing the temperature, the distribution of diameters becomes progressively wider and associated with larger median values. Early steps of the heat treatment are summarized by the distributions at 50 and 60 °C; their relative proximity indicates that, on average, starch swelling is weak below 60 °C. Final steps of the heat treatment are summarized by the three last distributions: they span over the last 3 minutes of the treatment and suggest that maximum swelling is essentially concluded at about 80 °C. Between these two groups of results, the distributions at 68 and 70 °C are clearly distinct despite their proximity in time; following a 5 °C/min heating rate, images at 70 °C were captured 24 seconds after than those at 68 °C. Starch swelling can, for a great number of granules, be pictured as a somewhat "explosive" transformation phenomenon. Figure 6B employs a logarithmic scale for granule diameters: they can be supposed to follow log-normal distributions. Observations at 50 °C correspond to a mean of 14.6  $\mu\text{m}$  and a standard-deviation of 4.0  $\mu\text{m}$ ; observations at 90 °C correspond to a mean of 34.5  $\mu\text{m}$  and a standard-deviation of 11.2  $\mu\text{m}$ . Relative standard deviations are a little different: about 27 % at 50 °C and 33 % at 90 °C.

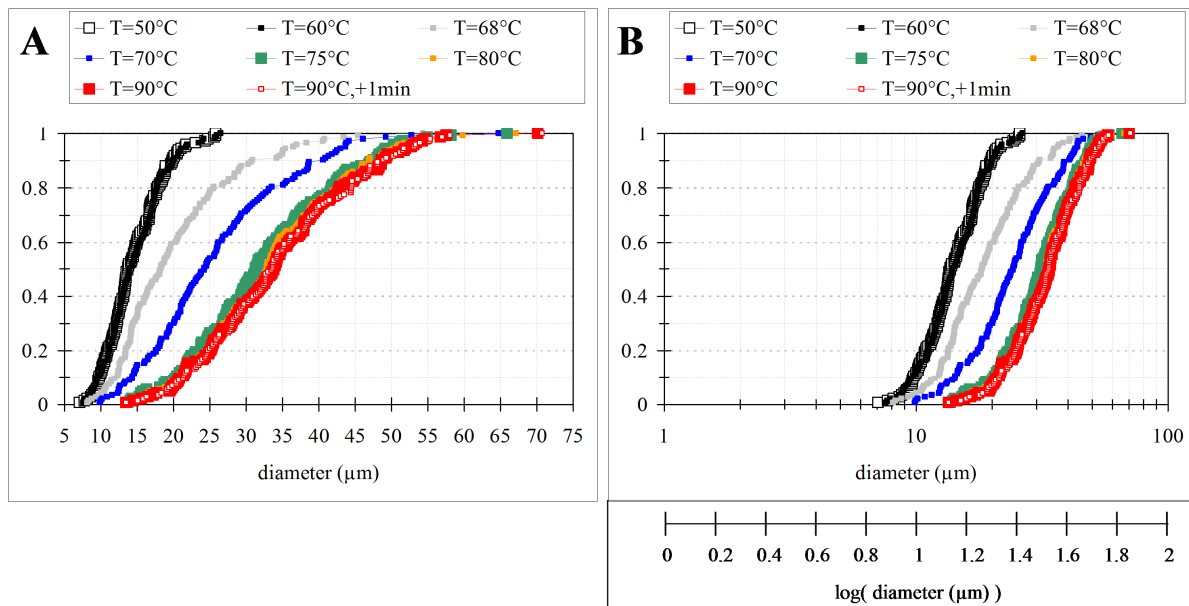


Figure 6: Cumulative distribution of the granule diameter (A) and of its logarithm (B) at each temperature considered.

Figure 7A presents the cumulative distribution of the diameter increase from 50 °C up to each temperature considered. The distributions corresponding to 60, 68 and 70 °C start below the



unity. One may ask the influence of experimental errors on such a finding. The estimation of granule diameters can be affected by random errors due to the automatic acquisition of images and to the human-made recognition of the granule of interest in each image. The occurrence of bias between samples is expected to be negligible, firstly because the prescribed heat treatment was repeated to droplets of starch suspensions which were prepared following the same protocol, and secondly because the same image processing method was applied to all the available observations.

Figure 7B focus the attention on values near to the unity. A range of diameter increase values is indicated, centered at the unity; its half-width equals 0.14, which corresponds to the difference between the unity and the smallest value observed at 60 °C (about 0.86). Changes in the granule size distribution of cross-linked waxy maize starch under heating rate close to 5 °C/min are not expected to be important for temperatures below 60 °C (Ziegler et al., 1993). Therefore, the shape of the cumulative distribution corresponding to 60 °C cannot be attributed to changes in starch swelling state.

A plausible explanation for these patterns near the unity is that starch granules do not remain immobile during the heat treatment. Once in diluted aqueous suspension, they are free to change their orientation with respect to the observing device. Starch granules are not spherical; if one granule is assimilated to an axi-symmetrical ellipsoid, its projection becomes an ellipse: one axis length is the equatorial diameter, while the other varies between the later and the pole-to-pole distance depending on the orientation. Hence, from an image to its following, even if no starch swelling occurs, the visible area of a given granule can either increase or decrease. Such an explanation turns easier to understand why the diameter value may (apparently) decrease not only between 50 and 60 °C but also elsewhere in the granule history (for instance, granules #80 and #100 in Figure 2A).

We argue that observations associated with increase values smaller than the 1.14 correspond to conditions where granule orientation, and not starch swelling, dominates the diameter increase value. The distribution corresponding to 60 °C falls almost entirely into the range indicated in Figure 7B; actually, only 3 observations (over 143) are associated with values higher than 1.14 for the diameter increase from 50 up to 60 °C. At higher temperatures, the fraction of diameter increase values higher than 1.14, which can only be explained by starch swelling, becomes significant: 78/143 ~ 55 % at 68 °C and 123/143 ~86 % at 70 °C. The influence of granule orientation is secondary for all the observations at 75 °C and higher temperatures.

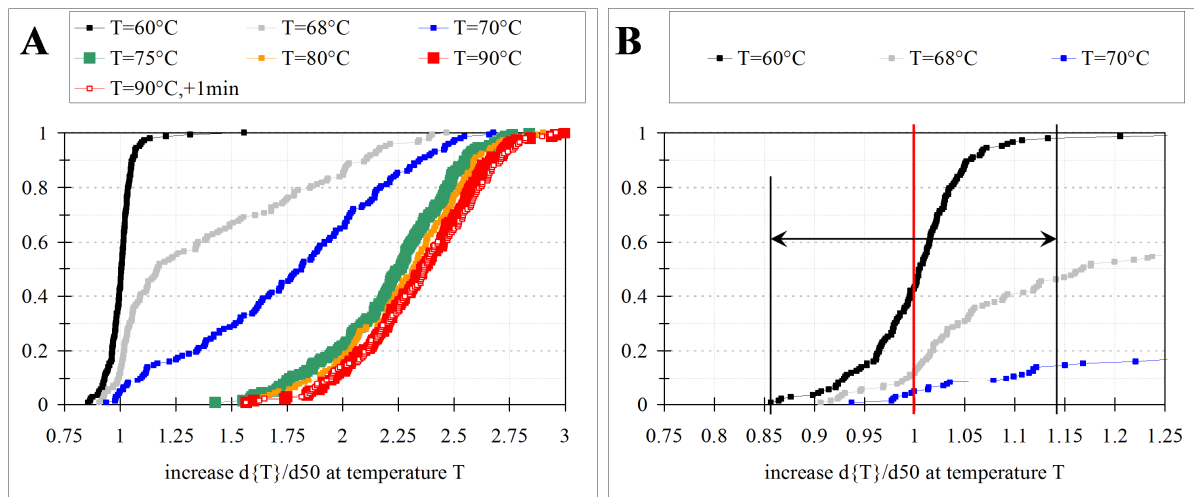


Figure 7: A) Cumulative distribution of the diameter increase from 50 °C up to each temperature considered. B) The same, but focusing on diameter increase near to the unity.

#### 4. CONCLUSIONS AND FUTURE WORK

The study of the thermal history experienced by 143 granules of a modified waxy maize starch suspension, exposed to the same heat treatment, confirmed the diversity of granule size and temperature associated with swelling onset. No simple relationship emerges between initial size and swelling onset.

Secondly, changes in the starch swelling state were relatively weak under temperatures below 60 °C, as well as above 80 °C. At the intermediate temperatures, distinct populations of granules co-existed: starch swelling can be negligible at 70 °C for some granules but significant for others.

Thirdly (and consequently), the diameter increase from 50 °C up to 70 °C exhibited more important variability than up to 90 °C; under such conditions it appears more difficult to predict the diameter increase from 50 °C up to 70 °C than up to 90 °C.

Lastly, the analysis of diameter increase values near the unity revealed that a great number of observations below 70 °C corresponded, actually, to a diameter decrease. This was interpreted as being due to changes of granules orientation with respect to the observing device, the granules being not spherical. Combined effects of starch swelling and granule orientation are intrinsically included in all the observations resulting from our experimental approach.

Looking for the development of predictive models for the starch granule size distribution, ongoing efforts are devoted to the influence of the heat treatment (both intensity and duration) as well as to the role played by granule orientation on observations.

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