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Surface nucleation in complex rheological systems ☆

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ABSTRACT

Forced nucleation induced by suitable foreign seeds is an important tool to control the production of defined crystalline products. The quality of a surface provided by seed materials represents an important variable in the production of crystallizing layers that means for the nucleation process. Parameters like shape and surface structure, size and size distribution of the seed particles as well as the ability to hold up the moisture (the solvent), can have an influence on the nucleation process of different viscous supersaturated solutions. Here the properties of different starch powders as seeds obtained from corn, potato, rice, tapioca and wheat were tested. It could be found, that the best nucleation behavior of a sugar solution could be reached with the use of corn starch as seed material. Here the surface of the crystallized sugar layer is smooth, crystallization time is short (<3 h) and the shape of the product is easily reproducible. Beneficial properties of seed materials are therefore an edged, uneven surface, small particle sizes as well as low moisture content at ambient conditions within the seed materials.

1. Introduction

There are many papers published on the topic of sugar crystallization. Good overviews of these approaches on sugar crystallization are summarized e.g. in books from Hoffman et al. [1], Asadi [2], Wohryzek [3] and Rosenplenter and Nähle [4].

This work focuses on the properties of different seed materials to start the crystallization of coated sweets. Depending on the nucleation behavior of a sugar solution a specific nucleation state must be reached to create, e.g. a reproducible crystallized sugar layer. This work focuses on the use of heterogeneous nuclei (different starch types) to provide a surface where sugar can crystallize. Without initiated nucleation a homogeneous, reproducible crystallized layer is not reachable.

An example from the food industry shows the importance of the issue. In the production of candies from e.g. gels the starch mogul technique is commonly used [1]. Different starch types as powder beds are used in this technique to generate desired shapes of the sweets. Beside the ability to shape the products, these powders can be used to induce the nucleation of supersaturated liquids. Here a sugar solution as supersaturated liquid was used.

Previous works [5] on this topic showed, that the used external seed materials can have an influence on the layer thickness of shelled products produced from sugar solutions.

Effects of the particle shape and surface structure, the ability to hold up moisture as well as the particle size distribution on the crystallization behavior of a sugar solution are important in order to estimate the applicability of different seed materials. This properties and applicability of different external seed materials to induce nucleation are not fully described and represent an interesting challenge, especially, in combination with viscous supersaturated liquids.

The overall aim is to identify the conditions which must be fulfilled and which parameters are negligible to start nucleation and finally receive a uniform layered product.

2. Material and methods

The nucleation behavior of a supersaturated ($\beta \approx 1.16$ at 20 °C) sugar solution induced by different external seed materials (corn, potato, rice, tapioca and wheat starch) was tested. As external seed materials commercial starches which can be purchased in many supermarkets were used. Here potato starch from the company "Frießinger Mühle GmbH", rice starch from the company "Naturkornmühle Werz", wheat starch from the company "Unilever Deutschland" and tapioca and corn starch from the company "Cargill" were used. Starches are an energy store of many plants. All used materials are pure starches without any other declared ingredients.

To prepare this supersaturated sugar solution, white sugar was dissolved in hot water. Starch molds were prepared to produce crystallized end products with a desired shape (see Fig. 1).

Therefore the starch was sieved into starch powder molds (e.g.

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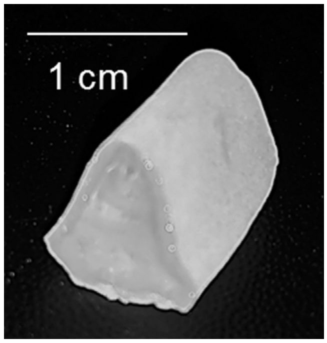

Fig. 1. Bisected end product with a crystallized layer and triangular shape.

big petri dishes). A typical starch powder mold can be seen in a previous publication of Herfurth et al. [5]. After creating a smooth surface of the filled starch molds these molds are dried for 24 h at 50 °C. Thereafter negative imprints were made with special shaped stamps to create cavities in the starch molds. The supersaturated sugar solution is poured into negative imprints in the starch molds. The negative imprints can have any desired shape but here sticks were shaped with a triangular basic shape (dimensions: 1.0 cm x4.2 cm x1.0 cm). The sugar solution is enclosed by the external seed material at all sides of the product (see Fig. 4).

Before starting the experiments all samples (starches) were sieved and dried at 50 °C for 24 h to avoid clumping and agglomeration of the starch particles.

To describe the properties of different seed materials the size distribution was described by measurements of a Mastersizer 2000 (Malvern). The samples were measured in dry state (Scirocco 2000) with an air pressure of 2 bar. Feed rates to achieve an optimal sample supply were 47% for corn, 63% for potato, 50% for rice, 52% for tapioca and 53% for wheat starch. Three measuring cycles were applied with a measuring time of 8 s. The used refractive index was 1.53 for all starch materials.

Scanning Electron Microscope images of different seed materials were taken to observe the surface properties as well as the shape of the particles. The materials were not modified for this measurement and a low accelerating voltage of 2 kV was used. Literature from Tegge [6] shows similar microscopic images from different starches (e.g. corn and tapioca) so that it can be assumed that the used materials are undamaged and in a good state.

The moisture of the seed materials was measured by a Moisture Analyzer MA 50 (Sartorius) after storage of the samples at ambient temperature (22 °C) and 50 °C for different times (24 h or longer). The principle of the Moisture Analyzer is a detection of the material weight during heating (till 150 °C) with an infrared lamp. The measurement stops when a constant weight is reached. The moisture values were determined by a triple measurement and a sample amount of 3–5 g per measurement.

3. Results and discussion

The following section will show the results of different properties of starch particles to initiate the crystallization of a supersaturated sugar solution. Basic requirements to induce the nucleation and to estimate the nucleation behavior of a sugar solution are the dimension of energy input into a supersaturated solution to build nuclei. This energy input can be mechanical by irritation of molecules in a supersaturated sugar solution with sharp and edged surfaces (provided by different external starch materials).

3.1. Properties of different seed materials

Fig. 2 shows the particle size distribution of the seed materials. Here different starches obtained from different plants were used. Corn and tapioca starch have similar size distributions (dashed line and dotted line) from 6 μm to 30 μm. Rice starch is a little bit smaller and tends to form agglomerates due to its small size. Rice starch shows a noticeable wide range of the particle sizes (2–125 μm) due to agglomeration (see Fig. 2 gray line). Wheat starch (dotted and dashed line) and potato starch (black line) are with an average size of mostly 20 μm and 40 μm, respectively, a little bit larger compared to the other seed materials (size 10–14 μm) (see Fig. 2). The average size distribution is with a range of approximately 46 μm for tapioca starch and 85 μm for potato starch wider compared to the other measured particle size distribution of starches (see Fig. 2).

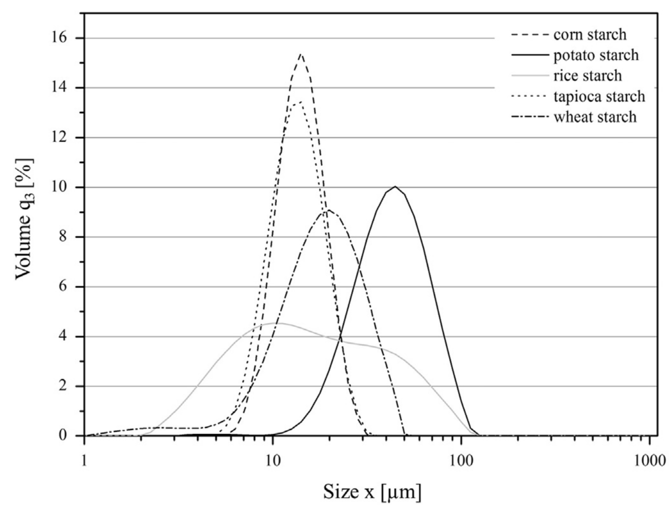

Fig. 2. Volume-weighted particle size distribution density, q_3, of different seed materials.

All measured data show comparable values to the literature (see second column with data at Table 1). Only rice starch shows bigger values due to a very wide measured particle size distribution. Fig. 3 (image top right) confirms the characteristic of forming agglomerates. During the measurement in dry state with the Mastersizer the air flow is not able to separate the single particles from each other so the agglomerates were measured as bigger particles (20–100 μm). Therefore mode, mean size and median values of rice starch differ more than for the other tested starch materials (see Table 1).

Fig. 3 illustrates the surface of the different seed materials. Whereas corn and rice starch appear more edged/polygonal, potato, tapioca and wheat starch show more rounded particles with an even and regular surface. The image (top right) of rice starch illustrates clearly the tendency to form agglomerates. Corn and tapioca starches differ in their surface appearance but have similar sizes. That is why different results concerning the crystallization of sugar can be ascribed to the surface appearance of the starch particles. Round and even surfaces of tapioca starch particles are not effective in starting the nucleation of a supersaturated sugar solution. More edged surfaces (as e.g. for corn starch particles) are necessary to initiate the nucleation process, independent form the particle size of the starch materials (similar sizes of corn and tapioca starches). The wheat starch particles seem to be pressed flat and are not as round as potato starch particles.

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