Drying and Crystallization of Sucrose Solutions in Thin Films at Elevated Temperatures

T. HOWELL AND R. HARTEL

ABSTRACT: Thin sucrose films were dried over 30-min periods during which sucrose crystal growth rates were monitored by videomicroscopy. Drying parameters and sucrose solution properties were varied to determine their effect on initial sucrose crystal growth rates. Growth rates increased by a factor of 4.5 as temperature increased from 40 to 70 °C. Varying initial sucrose concentration (70 to 80%) and drying air velocity (2 to 5 m/s) produced no change in crystal growth rates. Increases in film thickness from 150 to 450 μm and the presence of moisture in the drying air reduced growth rates by 33% at 70 °C, but had no effect at 50 °C. The addition of invert sugar (up to 5%) reduced growth rates by a factor of 2 to 3.

Keywords: sucrose, crystallization, thin films, drying, invert sugar

Introduction

An abundance of literature exists that details sucrose crystal growth under a variety of conditions, but most of the published work involves batch crystallization systems (Smythe 1967a; Smythe 1971; Van Hook 1969; Van Hook 1981). Although Hartel and Shastry (1991) reviewed the factors that influence sucrose crystallization, a lack of information about crystal growth in thin films still exists.

Shastry and Hartel (1996) studied drying and crystallization of thin films of sucrose solutions under conditions of concern for hard panning of chocolate candies. In their work, syrup concentrations ranged from 70 to 76% initial solids and thin films were crystallized at low temperatures (25 and 30 °C). Other variables included the drying air velocity, relative humidity, and initial seeding density on the films. They found that nucleation did not occur within 60 min in films which were not seeded during drying. Thus, seeding was crucial to crystallization under the conditions of their study. Air velocity and relative humidity did not significantly affect crystallization kinetics. Additionally, initial concentration of the sucrose syrups did not affect initial crystal growth rates, most likely because drying profiles became very similar to each other early in the experiments, regardless of initial concentration.

Shastry and Hartel (1996) described how crystallization and drying processes in thin films compete. Drying of a thin film of concentrated sucrose solution leads to increased concentration and increased supersaturation, the driving force. On the other hand, crystallization of the sucrose in the thin film causes the sucrose concentration in solution to decrease as supersaturation is relieved. Initially, drying is the dominant process but eventually, crystallization becomes more important as the film equilibrates to its saturation concentration. If crystallization does not occur initially, the film may be dried to the amorphous or glassy state, inhibiting future crystallization.

Ben-Yoseph and others (2000) developed a computer model to simulate drying and crystal growth in thin sucrose films. A finite-difference routine was used to solve the heat and mass transfer equations, accounting for changing sucrose diffusivity, crystal growth, and film shrinkage due to drying. This model was used to evaluate the effects of processing conditions such as temperature, initial sucrose concentration, drying air velocity, and initial seed distribution on drying and crystal growth in thin films of sucrose solution. The model predicted that drying air velocity (above 0.3 m/s) did not result in significant increases in crystal growth. Initial sucrose concentration also did not affect the drying profile; the films dried to very similar states over the length of the simulation. The model was also used to predict the effects of temperature and sucrose concentration on crystal growth rates when no drying occurred (Ben-Yoseph 1999). At each temperature (Figure 1), the crystal growth rates increase to a maximum as sucrose concentration increases, but then decrease at higher concentrations due to decreased diffusivity.

The objective of this work was to study the effects of processing parameters on sucrose crystal growth in thin films at higher temperatures than those used by Shastry and Hartel (1996). Parameters which were studied include drying temperature, initial sucrose concentration, surface seeding levels, drying air velocity, drying air relative humidity, film thick-

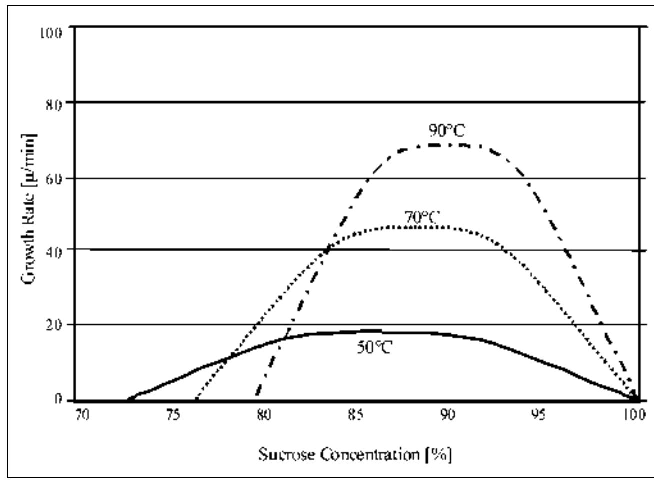

Figure 1—Change in predicted crystal growth rate as a function of temperature and sucrose concentration (adapted from Ben-Yoseph and others 2000)

© 2001 Institute of Food Technologists

ness, and invert sugar level in the sucrose solution.

Materials and Methods

Syrup Preparation

A pilot-scale vacuum evaporator (Groen Mfg., Chicago, Ill., U.S.A.) was used to concentrate sucrose syrups from a stock solution of 30% sucrose (from reagent-grade sucrose, Aldrich Chemical Co., Milwaukee, Wis., U.S.A.). Final syrup concentrations were checked with an Abbe refractometer (Model 3L, Spectronic Instruments, Rochester, N.Y., U.S.A.) to ensure that the syrup was within ± 0.3% of the target syrup concentration (70, 72.5, 75, 77.5, or 80% w/w, depending on the treatment). Approximately 20 to 30 mL of syrup was extracted from the evaporator and transferred to a heated vial in a water bath. The syrup was allowed to equilibrate to the desired experimental temperature in the bath.

Drying Chamber

A "drying cell" with the controlled air conditions was constructed to act as the drying and crystallization chamber. Flow of compressed air through the chamber was regulated through a flow meter and heated through a copper coil in a water bath. The air temperature was controlled by adjusting both the air flow rate and water bath temperature to ensure the correct air velocity and temperature at the sample chamber. When humidified air was required, a separate stream of air was humidified completely by bubbling through water, and mixed at the appropriate flow rates with the dry air (in a fitting) to generate the desired relative humidity. Figure 2 shows the general schematic diagram of the drying system with a top view of the drying chamber. The drying chamber was mounted onto the stage of a Nikon Optiphot (Melville, N.Y., U.S.A.) microscope with polarized lens, equipped with a monochrome video camera (Cohu, Model 4815-2000, San Diego, Calif., U.S.A.). Images were recorded with the video camera directly to the computer hard drive. The microscopic images were magnified 40×.

A microscope slide with appropriate barriers was used to create a trough, or depression, for the sugar film. The depression was approximately 150 µm deep (157 ± 4.4 mm) and 2.5 cm wide. The slide trough was aligned with the air flow, and air was allowed to blow over both top and bottom surfaces of the slide.

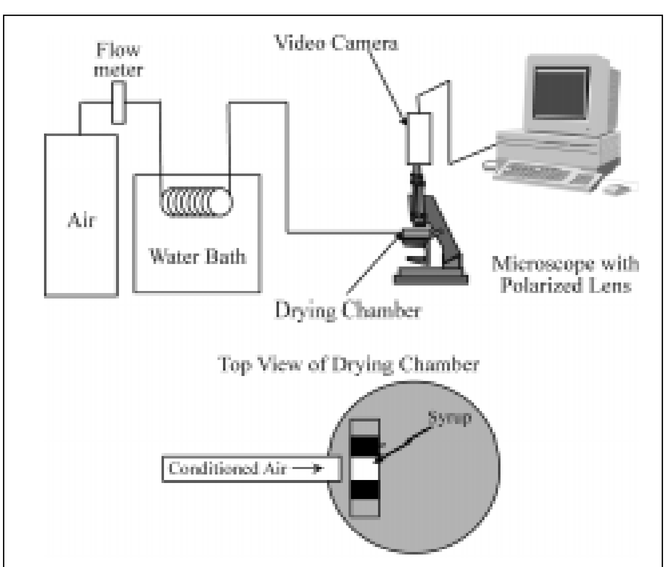

Figure 2—Schematic diagram of drying and crystallization system with top view of drying chamber

Experimental Protocol

Between 0.5 to 1 mL of the syrup was dispensed into the depression of the warmed slide and quickly spread evenly across the depression by removing any excess syrup with a flat surface (usually, another heated glass microscope slide). The sucrose syrups had reduced surface tensions compared to water and formed level surfaces. A sieve with 44-µm mesh size was used to provide "seed" crystals on the surface of the film. Containing the seed crystals, the sieve was held approximately 1 cm above the slide and dropped to the benchtop. The seed crystals were obtained by recrystallizing sucrose in methanol as described by Shastry (1994). The seeded slide was placed on its platform, the cell was closed, microscope focused, and first picture taken in a matter of seconds. A macro in Optimas 6.1 (Media Cybernetics, Seattle, Wash., U.S.A.) image analysis software controlled the image collection for experiments using the video camera.

Syrup samples were analyzed for invert sugar content, using a Glucose LiquiColor enzymatic colorimetric test (Stan-Bio Laboratories, San Antonio, Tex., U.S.A.). For experiments where invert sugar was not expected to be a factor, a sample was taken from 1 in 5 syrups at random and tested. The highest recorded glucose content was 0.06% in syrups which had not been treated with invert sugar. For the experiments where invert sugar was a variable, every sample was tested.

Image Analysis

Images were analyzed to follow individual crystal growth rates of sugar crystals with the differing process and syrup conditions. Individual crystals were "tracked" and their surface areas were digitized by hand from time zero through at least 5 min to calculate initial growth rates for single crystals at each condition. Five to 10 data points were collected for each crystal to obtain initial growth rates. Equivalent circular diameter, or the diameter of a circle with the measured area, was generated from each surface area value. Figure 3 shows typical digital photos of growing crystals under the polarized light, as they progress from time zero to 30 min. An initial growth rate for each individual crystal was calculated as the rate of change in diameter, as the crystal grew.

In addition to measurements on single crystals, the growth of the overall crystal surface area was calculated by summing the areas occupied by all of the crystals within a region of interest (ROI). The ROI was a rectangle encompassing about 3 mm^2 and remained constant for each image that was recorded. The crystal surface area for each image was normalized by dividing the surface area occupied by the crystals by the area of the ROI. A plot of normalized area against time provides an easy way to determine how quickly a "surface" is being covered.

Experimental Design

An initial study was designed to determine the effects of initial sucrose concentration, drying air temperature, and surface seeding levels. Syrups were made at 70.0, 72.5, 75.0, 77.5, and 80.0% initial total solids (TS) and crystallized at 40, 50, and 60 °C. Drying air velocity was 5 m/s; relative humidity was about 0%, and the sucrose seed density was varied from low (less than 10 seeds per mm^2) to high (greater then 30 seeds per mm²). Ten replications at each combination of temperature and initial TS were completed in random order.

A subsequent set of experiments was designed to determine the effects of air temperature, initial sucrose concentration, drying air velocity and relative humidity, film thickness, and invert sugar concentration in the initial syrup. Table 1 shows the range of conditions for these experiments. Thirty-five to 60 crystals were analyzed at each condition.

Table 1—Experimental conditions

Parameter	Conditions Studied
Temperature (°C)	50, 70
Initial Sucrose Concentration (% wt/wt)	75, 80
Air Velocity (m/s)	2, 3, 5
Surface Seeding (seeds/mm²)	Low (<15 seeds/mm²)
Air Relative Humidity (%)	0, 30
Film Thickness (µm)	150, 300, 450
Invert Sugar Level (%)	0, 0.5, 1.0, 5.0

Results and Discussion

Effects of seed density on crystal growth

In the preliminary set of experiments, it was found that the growth of the normalized surface area of crystals was highly dependent on the density of seed crystals at the surface. Figure 4 is a typical example, which shows how the normalized surface areas grew with time as a function of seed density (from low to high). In this case, the film was at 50 °C and the initial sucrose concentration was 80%. As the seed density increased from 1 to 52 seeds/mm², the crystal surface area increased at each time interval. This was seen in each temperature/initial sucrose concentration combination. Under the conditions shown in Figure 4, the films with low seed densities (3 seeds/mm²) reached about 70% surface coverage after 30 min, whereas films with higher seed density (> 6 seeds/mm²) were almost completely covered after 30 min. Thus, seed density is an important parameter for controlling surface area coverage of these films.

Effects of air temperature and sucrose concentration on crystal growth

The effects of drying air temperature and initial sucrose concentration on normalized surface area growth can be seen in Figure 5A (seed densities less than 22 seeds/mm²)

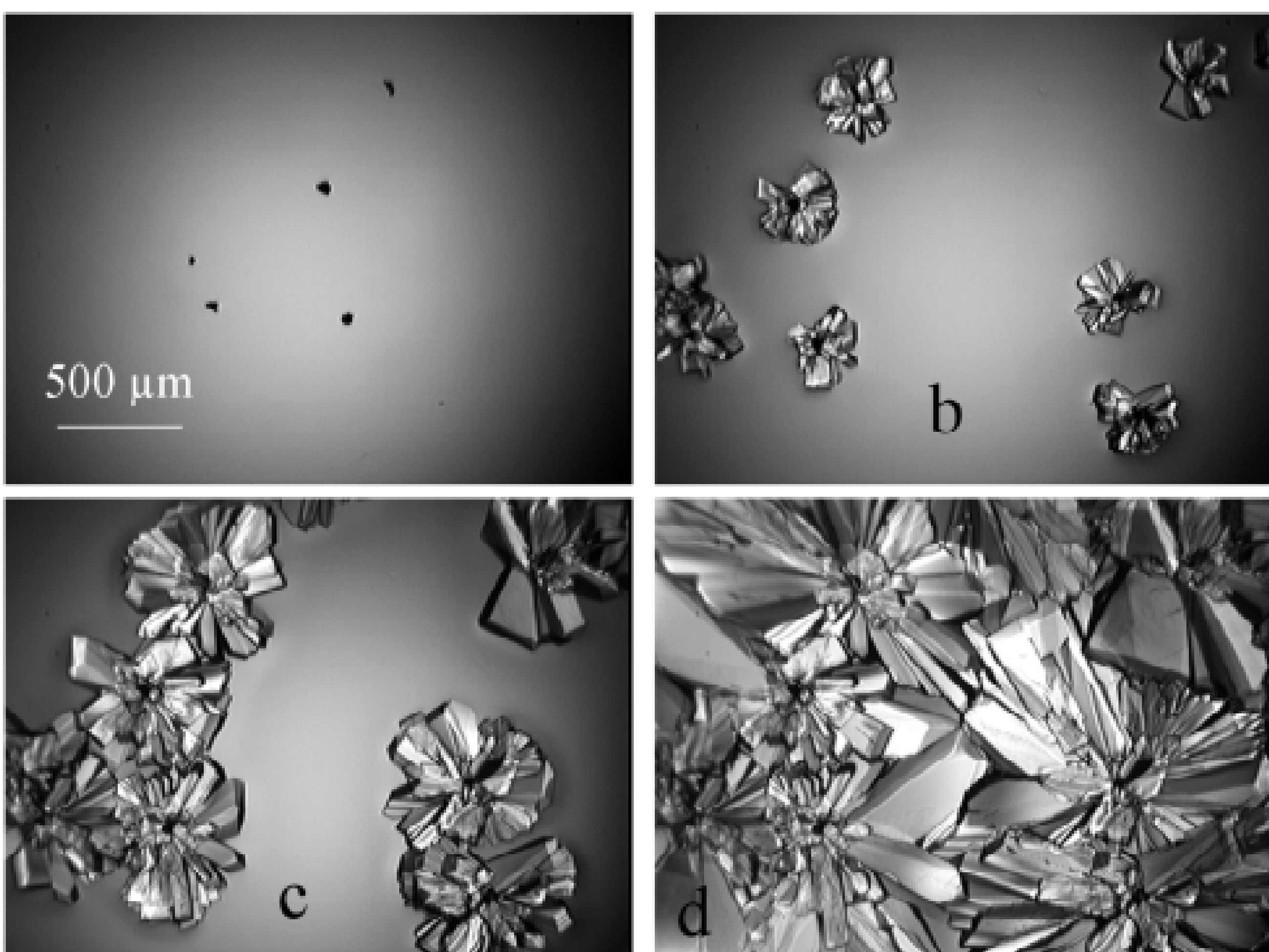

Figure 3—Images of growing sucrose crystals from (a) time zero, (b) 5 min, (c) 10 min, and (d) 30 min, and dried at 70 °C. Initial sucrose concentration was 80% and the solution contained no invert sugar.

and B (seed densities greater than 30 seeds/mm^2). In each case, as initial sucrose concentration increased from 70 to 80% at 40 °C, growth of the crystal surface area did not change appreciably, a result also found by Shastry and Hartel (1996). The rate of drying was sufficiently rapid to create similar driving forces for crystallization (degree of supersaturation), regardless of initial sucrose concentration. As temperature increased from 40 to 60 °C at 80% initial sucrose concentration, the crystal surface areas at each time interval increased substantially. Thus, temperature was very influential on crystal growth in thin films, as also found by Shastry and Hartel (1996).

The growth of individual crystals was analyzed to study the effects of initial concentration and temperature on sucrose crystal growth rates. At each experimental condition, the change in surface area of individual crystals (with low seeding levels) was measured from time zero through 5 min. Figure 6 shows the initial crystal growth rates (in µm/min) plotted against initial concentration. For each temperature, the crystal growth rates remained constant regardless of the initial concentration, in agreement with the normalized surface growth data discussed previously. The high variability of these measurements was primarily due to growth rate dispersion (GRD). Differences in growth rates between individual crystals growing in the same environment have been attributed to differences in internal crystal structure such as dislocations, internal strains, etc. (Fabian and others 1996).

The effect of temperature on initial crystal growth rates of individual crystals may also be seen in Figure 6. As temperature increased, the initial, linear crystal growth rates increased. Growth rates increased from 9 µm/min at 40 °C to 34 µm/min at 60 °C. The variability in the growth rates increased at higher temperatures, primarily since the extent of growth rate dispersion also increases with increasing supersaturation. Liang and others (1987) showed that the variance of the growth rate distribution of sucrose crystals in stagnant and stirred systems increased with the square of the average growth rate. Duncan's multiple range test ($p = 0.01$) confirmed that growth rates were not affected by initial TS, but increased with temperature.

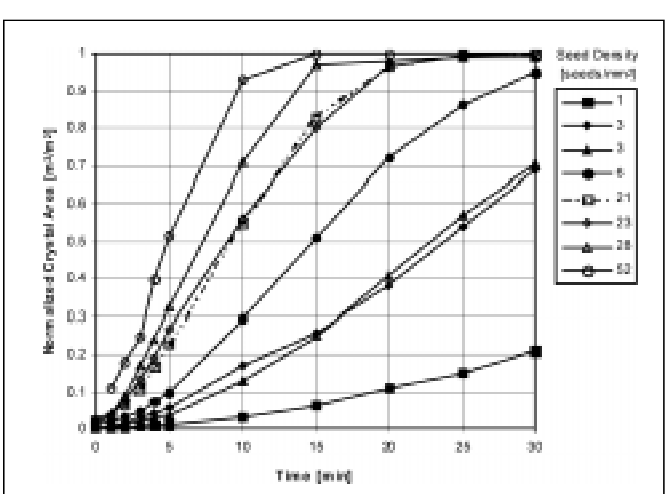

Figure 4—Change in normalized crystal surface area with time as a function of seed density at 50 °C and 80% initial sucrose concentration

Effects of drying air velocity on crystal growth

Figure 7 shows initial crystal growth rates for individual crystals as a function of drying air velocity. In general, increasing the drying air velocity from 2 to 5 m/s did not affect the crystal growth rate. Drying of thin films may be limited by either diffusion of water through the film, or convection away from the film surface. By studying the transport properties at the surface of the film (reducing the drying air velocity), we gain insight into which of these mechanisms controls mass transfer in this process. Altering the drying air velocity did not affect the initial crystal growth rates. If the convection of moisture away from the surface were the rate-limiting step for mass transfer in this instance, the reduced drying air velocity would remove less moisture from the films. The films would contain higher moisture contents and the driving force for crystallization would be reduced. However, since the growth rates were not affected by the reduced drying air velocity, surface convection must not then be the rate-limiting step. This suggests that mass transfer through the film is the rate-limiting step for removal of water in thin films.

Effects of drying air relative humidity on crystal growth

Figure 8 shows that, at 70 °C, the initial crystal growth rate decreased when the films were dried with humidified (30% Relative Humidity (RH)) air. However, at 50 °C, the growth rates were not affected by RH. These results provide further evidence on mass transfer in these thin films. Increasing the humidity at the surface of the film slows drying and increases the water content in the film at any time in comparison to films dried with dry air. The effect of increased water content on growth rate depends on the nature of the growth curve as shown in Figure 1. According to the predictions in Figure 1,

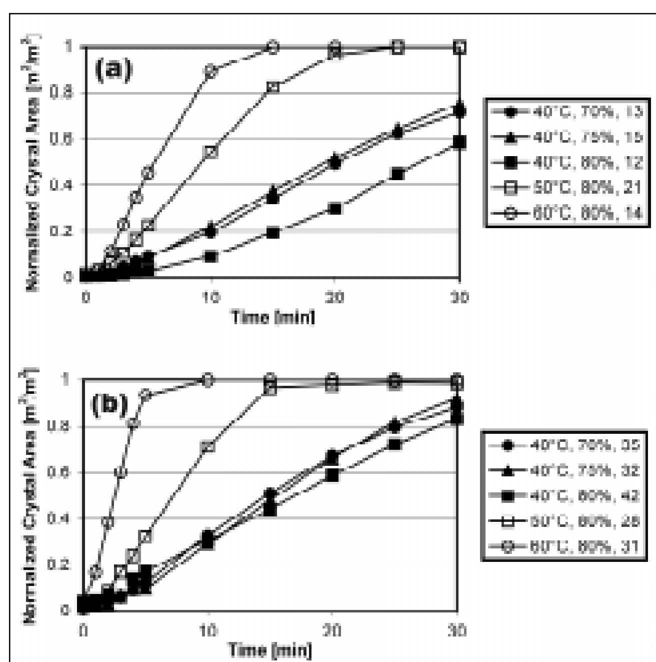

Figure 5—Change in normalized crystal surface area with time at similar seed density levels. Legend denotes drying temperature, initial sucrose concentration (wt%), and seed density (seeds/mm^2). (A) Low seed density (< 22 seeds/mm^2) (B) High seed density (> 30 seeds/mm^2)

at 70 °C, a move from 90% to 80% TS would reduce the average crystal growth rate. At 50 °C, this shift may actually produce a slight increase in average crystal growth rate, although the magnitude is not very large. Thus, the humidified air reduced the sucrose concentration profiles within the drying film such that crystal growth rates decreased at 70 °C and remained consistent at 50 °C (Figure 8).

Effects of film thickness on crystal growth

Initial crystal growth rate as a function of film thickness for films dried at 50 and 70 °C, and with an initial sucrose concentration of 80%, is shown in Figure 9. The individual crystal growth rates at 50 °C did not change with increased film thickness; however, the growth rate at 70 °C dropped from about 45 to 30 μm/min as the film thickness increased from 150 to 300 μm. The growth rate at 450 μm was similar to the growth rate at 300 μm. These results also suggest that the rate-limiting step in mass transfer at 70 °C is the moisture migration through the film (at least for film thicknesses up to 300 μm). As the film thickness increased (increasing the path

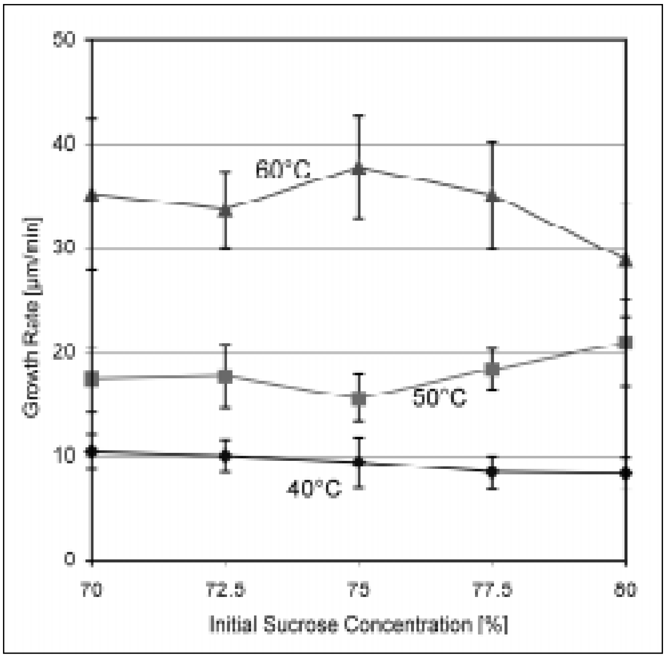

Figure 6—Average initial crystal growth rates as a function of initial sucrose concentration (wt%). Error bars represent standard deviation of individual growth rates.

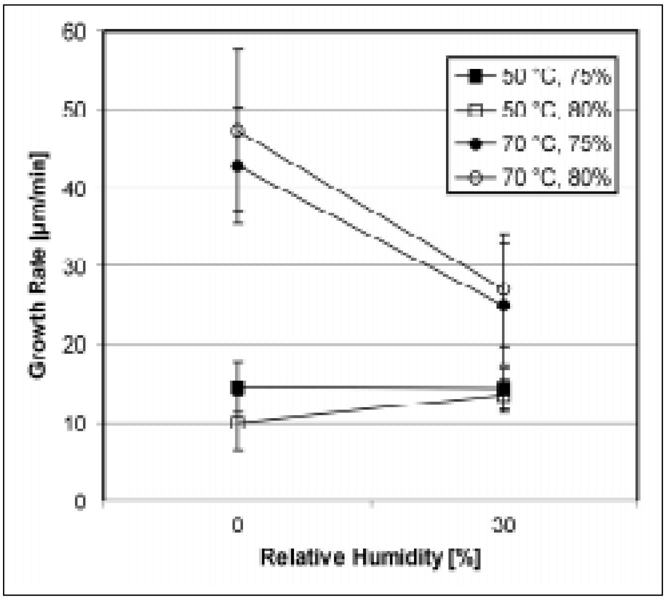

Figure 8—Effect of relative humidity on average initial crystal growth rates. Error bars represent standard deviation of individual growth rates. Legend denotes drying temperature and initial sucrose concentration (wt%).

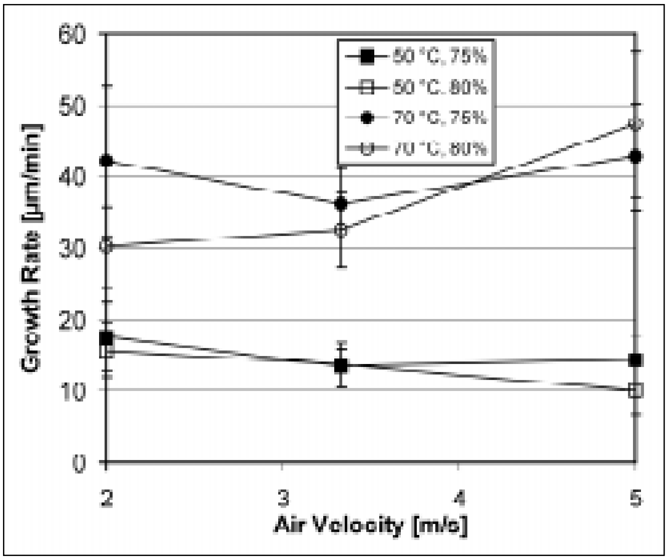

Figure 7—Effect of drying air velocity on average initial sucrose crystal growth rates. Error bars represent standard deviation of individual growth rates. Legend denotes drying temperature and initial sucrose concentration (wt%).

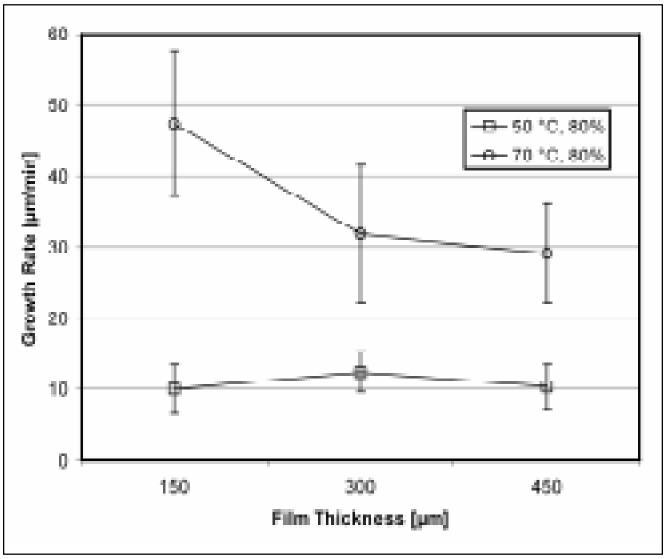

Figure 9—Effect of film thickness on average initial crystal growth rates. Error bars represent standard deviation of individual growth rates. Legend denotes drying temperature and initial sucrose concentration (wt%).

Food Engineering and Physical Properties that the moisture must traverse during drying), the crystal growth rates decreased. Again, a decrease in the average sucrose concentration during drying due to thicker films should result in a decreased crystal growth rate, according to Figure 1. At 50 °C, a similar decrease in sucrose concentration does not result in a significant change in growth rate.

Effects of invert sugar on crystal growth

The effect of invert sugar on initial crystal growth rates of single crystals is shown in Figure 10. At 50 °C, an increase in invert sugar content caused a decrease in initial crystal growth rates, from approximately 15 to 5 μm/min. Lower invert levels (0.5% and 1.0%) did not reduce crystal growth rates appreciably. The addition of 5% invert sugar to the sucrose syrups reduced the crystal growth rates to between 3.5 and 6 μm/min. At 70 °C, the effects of invert sugar were more pronounced. Even at the lowest invert levels (0.5%, 1.0%), crystal growth rates were inhibited. The addition of 5% invert sugar reduced the growth rates by a factor of 3, from about 45 μm/min to 15 μm/min. Note that the presence of invert sugar reduces the solubility of sucrose in solution (Smythe 1967b; Pancoast and Junk 1980). However, at low levels of addition, the effect on solubility is much less than the effect on growth rate.

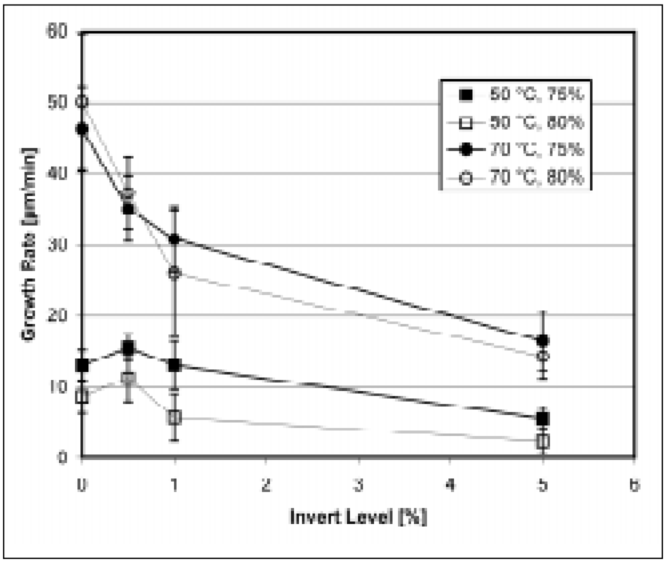

Figure 10—Effect of invert sugar on average initial crystal growth rates. Error bars represent standard deviation of individual growth rates. Legend denotes drying temperature and initial sucrose concentration (wt%).

Conclusions

THE RESULTS OF THIS STUDY HAVE IMPORTANT IMPLICATIONS for food processing operations that require a thin, sugar coating on a food product, such as panned confections or coated cereals. The experimental results (effective growth rates between 15 and 20 μm/min at 50 °C and 40 μm/min at 70 °C) correlate well to the predicted crystal growth theory presented in Figure 1. As temperature increases, crystal growth rates increase. However, the effects of sucrose concentration are more complex. As sucrose concentration increases, crystal growth rates increase until the decreased molecular mobility (high viscosity) inhibits crystal growth rates at higher concentrations. During the drying process, the effect of a change in process conditions (increased film thickness, drying air velocity, and/or relative humidity) on crystal growth rate may be estimated by relating to Figure 1. If the average sucrose concentration increases at any processing temperature, crystal growth rates may be expected to increase, although there may be conditions where growth rate actually decreases.

The distribution of seed crystals and invert content are also important to the rate of crystal growth in thin films. Surface coverage was shown to be highly dependent on seed density levels, which are often generated in practice by sucrose dust from previous processes. High invert sugar levels inhibit crystal growth rates, so inversion (and the conditions that contribute to it) must be monitored carefully.

References

Ben-Yoseph, E. 1999. Computer Modeling of Sucrose Crystallization During Drying of Thin Sucrose Films [DPhil thesis]. Madison, Wis.: University of Wisconsin. 203 p.
Ben-Yoseph E, Hartel RW, Howling D. 2000. Three-dimensional model of phase transition of thin sucrose films during drying. J Food Eng 44(1):13-22.
Fabian J, Hartel RW, Ulrich J. 1996. Growth and Dissolution Rate Dispersion of Sucrose Crystals. In Proceedings of the International Workshop on Crystal Growth of Organic Materials; August 1995; Washington, D.C.: American Chemical Society. p 216-219.
Hartel RW, Shastry AV. 1991. Sugar crystallization in food products. Crit Rev Food Sci Nutr 30(1):49-112.
Liang BM, Hartel RW, Berglund KA. 1987. Contact nucleation in sucrose crystallization. Chem Eng Sci 42(11):2723-2727.
Pancoast HM, Junk WR 1980. Handbook of Sugars.Vol. 2. Westport, Conn.:AVI. 598 p.
Shastry AV, Hartel RW. 1996. Crystallization and drying in thin sucrose films during panning. J Food Sci 61(5):978-981.
Shastry AV. 1994. Sucrose Crystallization of Thin Films of Sucrose Solution During Drying [dissertation]. Madison, Wis.:University of Wisconsin. 296 p.
Smythe BM. 1967a. Sucrose crystal growth. I. Rate of crystal growth in pure solutions. Aust J Chem 20:1087-1096.
Smythe BM. 1967b. Sucrose crystal growth. II. Rate of crystal growth in the presence of impurities. Aust J Chem 20:1097-1114.
Smythe BM. 1971. Sucrose crystal growth. Sugar Tech Rev 1(3):191-231.
Van Hook A. 1969. Sucrose crystallization mechanism of growth from aqueous solution. J Cryst Growth 5:305-311.
Van Hook A. 1981. Growth of sucrose crystals: A review. Sugar Tech Rev 8(1):41-79.
MS 20000818

Author Howell is with the Dept. of Food Science at the University of Arkansas. Author Hartel is with the Dept. of Food Science, University of Wisconsin-Madison, 1605 Linden Dr., Madison, WI 53706. Address inquiries to author Hartel (E-mail: hartel@calshp.cals.wisc.edu).