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State behavior and crystal growth kinetics of sucrose and corn syrup mixtures

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ABSTRACT

Effects of 63DE (dextrose equivalent) commercial corn syrup on the state behavior and crystal growth rate of sucrose and corn syrup mixtures in thin films (1.08 mm) were investigated using DSC and polarized light microscopy. Glass transition temperature (T_g) and solubility temperature increased significantly as moisture content decreased from 16.75% to 3.75%. Additionally, higher levels of corn syrup depressed solubility temperature but at the levels studied, showed no apparent effect on T_g.

Addition of corn syrup significantly decreased sucrose crystal growth rate. For systems containing 14% and 30% corn syrup, growth rates measured between 40 and 120 °C ranged from 5.6 to 3400 μm^2/min and 1.8 to 470 μm^2/min, respectively. Growth rate dispersion (GRD) was observed for all conditions and the extent of the GRD increased with increasing growth rate. By overlaying crystallization rate zones on the state diagram, the competing effects of supersaturation driving force and molecular mobility inhibition on sucrose crystal growth rates were clearly observed.

1. Introduction

The physical characteristics of sucrose systems are dependent on the formulation and processing conditions under which they were prepared. State behavior such as crystallization and glass transition are important to the quality of many food products. The glass transition temperature (T_g) plays a critical role in many food product's quality and storage stability. The understanding of glass transitions of food systems has allowed food material characterization and prediction of their behavior at high solids contents and in the frozen state at varying temperatures and water contents (Roos, 2010). State diagrams, or supplemented phase diagrams (Slade and Levine, 1991), provide useful maps for the observation of changes in glass transition as a function of water content or varying levels of freeze-concentration (Roos and Karel, 1991b).

The state diagram is a map of the different states of a food as a function of water or solids content and temperature (Roos, 1995; Rahman, 2006). As the temperature of a glass increases above the glass transition temperature (T_g), the system becomes unstable and collapses into a liquid-like, rubbery state. Here the system is supersaturated and in a metastable state bounded by the solubility curve and the T_g curve. As the temperature and concentration of such a system approach the solubility curve, the rate of crystallization increases initially and decreases after reaching a maximum due to competition between molecular mobility and supersaturation (Hartel, 2001).

Sucrose crystallization is encountered in many food and pharmaceutical applications. Food products where sucrose crystallization is important include refined sugar, confections, ready to eat cereals, and some snack foods. During processing, nuclei are either formed in situ or added as seeds. Once formed or added, crystal grow at a rate dependent on conditions in their surrounding environment in a series of steps (Mullin, 2001). In sucrose crystallization, diffusion of the sucrose from the bulk solution to crystal surface and integration of the sucrose molecule into the lattice structure are the typical rate-limiting steps (Van Hook, 1981; Hartel, 2013). Many factors can affect the growth rate, including temperature, supersaturation, agitation, and impurities (Hartel and Shastry, 1991). Molecular mobility also influences growth rate. For instance, in a hard candy matrix, crystals imbedded within the metastable glass matrix do not grow, despite the highly supersaturated condition (Hartel et al., 2008).

Growth rate dispersion (GRD) describes the phenomenon whereby individual crystals grow at different rates under identical conditions of supersaturation, temperature and hydrodynamics. It was first seen by White and Wright (1971) in sucrose batch crystallization. Liang et al. (1987a,b) also confirmed that GRD occurs

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in sucrose-water system. Speculations on GRD have centered on two primary mechanisms; differences in the density of dislocation steps on the surface of each crystal, and variations of the crystal perfection (internal lattice strain) of each crystal (Berglund and Murphy, 1986; Hartel, 2001; Pantaraks, 2004).

The primary goal of this work was to study the effects of processing conditions on T_g, solubility temperature and sucrose crystal growth kinetics for sucrose-corn syrup systems. Parameters studied include corn syrup solids level, cooking temperature (moisture or initial concentration inversely), and isothermal crystallization temperature.

2. Materials and methods

Sugar solutions were produced with extra fine granulated sugar (Royal Ingredients, Alkmaar, Netherlands), 63DE (dextrose equivalent) corn syrup (Cargill, Minneapolis, MN), and deionized water. Three formulations were studied, with ratios of 86/14, 78/22, and 70/30 sucrose/corn syrup on wt/wt dry basis. Batch sizes were 25 grams each. All formulations were prepared using the same cooking method. The ingredients were mixed in a 30 ml beaker, heated to completely dissolve all sugar crystals, and then boiled to different temperatures on a PC-420 Stirrer Hot-Plate (Corning Incorporated, Corning, NY). Cooking temperatures of 113 °C, 118 °C, 124 °C, 132 °C, 143 °C, and 154 °C were used to generate different water contents with each level of corn syrup solids.

2.1. Moisture content

A Karl Fischer (KF) Aquametry instrument (795 KFT Titrino, Metrohm Ltd., Herisau, Switzerland) with an automatic pump for the Karl Fischer reagent (Hydranal Composite 5, Riedel deHaën, Sigma–aldrich, Co., St Louis, MO) was used to measure the moisture content of sugar samples. This technique involved titration of the Karl Fischer reagent into a 150 mL titration vessel containing the sample pre-dissolved in a solvent. The solvent, a 4:3 ratio of formamide (Fisher Scientific, Fair Lawn, NJ) and Karl Fischer grade methanol (low water content 0.006%) solution, was used to completely dissolve the sugar glass and release the incorporated water. Three replicates were done for each sample.

2.2. Glass transition and solubility temperature

Measurement of glass transition temperature (T_g) and solubility temperature using differential scanning calorimeter (DSC) is based on the dynamic relationship between enthalpy and temperature (Mohan et al., 2002). In this study, a DSC 8500 (Perkin-Elmer, Inc., Shelton, CT) was used to determine the T_g and solubility temperature of the sugar/corn syrup mixtures cooked to different temperatures. The DSC was connected to a refrigeration system and used the Pyris software program (Version 11, Perkin–Elmer, Inc., Shelton, CT) for analysis. Approximately 20–30 mg of each sugar/syrup blend sample was added to each of three tared, O-ring sealed, large volume stainless steel DSC pans (Perkin–Elmer, Inc., Shelton, CT) and then sealed with a Universal Crimper Press (Perkin-Elmer, Inc., Shelton, CT). The heating and cooling rates were 5 °C/min and 40 °C/min, respectively. The thermal profiles chosen for all conditions were based on their physical properties, which depended on cooking temperatures. The first scan started from a temperature about 25 °C lower than the expected T_g and the highest temperature was 200 °C for all conditions. To eliminate the effects of sample thermal history, each sample was heated through a first heating cycle, cooled quickly back to the start temperature, with T_g and solubility temperature obtained from the second heating scan. The scan temperature range varied depending on sample characteristics, which depended on cooking temperatures. For instance, the thermal profile used for sample cooked to 154 °C was: hold for 1 min at 10 °C, heat from 10 °C to 80 °C, cool from 80 °C to 10 °C and then heat from 10 °C to 200 °C.

2.3. Sucrose crystal growth rates

Amorphous sugar samples were prepared and, while still hot and fluid, were placed in the center of metal washers on preheated microscope slides (Fisher Scientific, Hanover Park, IL) and enclosed with a cover glass (Levenson and Hartel, 2005). The microscope slide coupled with a washer and cover glass were heated in a hot stage (Analysa Peltier-LTS120, Linkam Scientific Instruments, Guildford, UK) prior to the start of each experiment. The washers were used to maintain a uniform volume and height of sugar sample on each slide and had a height of 1.08 mm and an inner diameter of 8.96 mm.

A syringe (BD Brand, Franklin Lakes, NJ) was used to draw approximately 1 ml of the hot sugar syrup, which was injected in the center of a washer. The washer was rapidly enclosed with a cover glass and pressed to provide an even sample surface with no exposure to ambient air and a constant volume and height. The slide was then quickly set in the hot stage and put under the microscope for further image analysis. This process generally took no more than one minute. Based on observations, the sugar samples had already nucleated during the process, so that once injected on the slide, crystal growth was dominant and no additional nuclei were formed.

A Nikon polarized light microscope (Labphot-2, Tokyo, Japan) coupled with a hot stage and a polarizer was used at 4×10× magnification. A digital camera (QICAM Fast1394, QImaging, Surrey, BC, Canada) and QCapture software (QCapture Pro 5.1, QImaging, Surrey, BC, Canada) were used to record crystal growth. The prepared microscope slides were placed in the hot stage set at either 40, 60, 80, 100, or 120 °C, the maximum temperature allowed with this system. A minimum of 3 slides of each formulation and concentration were studied under each temperature. The slides were observed under the microscope and images taken at different time intervals (determined by preliminary experiments) chosen to capture the initial growth rate. For each condition, at least 30 individual crystals were tracked. In order to calculate their surface area by Image Pro Plus software (Version 7.0, Media Cybernetics, Inc., Bethesda, MD), these crystals were manually digitized by outlining them in Paint (Version 6.1, Microsoft Corporation, Redmond, WA). A macro, "Area", written in Image Pro Plus macro language streamlined the process and automatically calculated the surface area. The surface area vs. time was found to be linear and the slope of each line was the growth rate (μm^2/min) for that crystal.

2.4. Data analysis

To determine significant differences in the data, an analysis of variance was conducted with ANOVA using a 95% confidence interval by SAS software (Enterprise Guide V 5.1, SAS Institute Inc., Cary, NC). This analysis was performed for moisture content, T_g, solubility, and growth rate using a comparison of cooking temperature, observation temperature and formulation used. Software R (version 2.15.2, The R foundation for Statistical Computing) was used to generate linear regression models for moisture content, T_g and solubility temperature as a function of cooking temperature and formulation. Linear regression models for growth rates as a function of crystallization temperature, cook temperature and formulation were also performed by R. Growth rates contour plots were generated by JMP software with Contour Plot command in the Graph menu (Pro 10.0.0, SAS Institute Inc., Cary, NC).