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Crystallization behavior of lactose/sucrose mixtures during water-induced crystallization

Mona Edrisi Sormoli *, Debolina Das, Timothy A.G. Langrish

Drying and Process Technology Group, School of Chemical & Biomolecular Engineering, Building J01, The University of Sydney, Darlington, NSW 2006, Australia

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ABSTRACT

The crystallization behavior of lactose/sucrose mixtures during water-induced crystallization was studied to gain more insight about their crystallization during storage. Solutions with different ratios of lactose and sucrose, 75:25 and 50:50, were spray dried to produce amorphous powders. The powders were kept at a controlled temperature and humidity to study their sorption–desorption behavior. X-ray diffraction and light microscopy analysis were performed to study their crystallization behavior. Two-step desorption was observed after sieving the powders as sample preparation. Sieving decreased the crystallization time for lactose/sucrose mixture 75:25 from 22 days to 2.5 days. Based on the X-ray diffraction analysis during this two-step process of water desorption, it was concluded that lactose crystallizes first and more quickly than sucrose. The degree of crystallization for the lactose crystals increases by 89% (relative to their final level of crystallinity), whereas sucrose crystals increase their level of crystallinity by only 28% during the first step of crystallization in the lactose/sucrose (75:25) mixtures. The light microscopy images also suggested that the crystallization of amorphous lactose/sucrose powders during water-induced crystallization may occur as a solution rather than in the solid phase.

1. Introduction

Crystallization of sugars during storage has received extensive attention during recent years. Lactose and sucrose are two of the most common and widely used sugars in the food and pharmaceutical industries. The presence of these two sugars in food formulations can be either in the crystalline or the amorphous form. In the case of amorphous sugars, their tendency to crystallize causes difficulties in industry, both in processing and in storage. Crystallization of amorphous sugars during storage occurs mainly by adsorption and desorption of water vapor existing in the environment. This phenomenon has been addressed in many studies, and the glass-transition temperature has been proposed and accepted to be the key property responsible, according to the Williams–Landel–Ferry (WLF) equation (Hancock and Dalton, 1999; Roos and Karel, 1992). During this crystallization process, water acts as a plasticizer and increases the molecular mobility of sugars, which results in a decrease in the viscosity and the glass-transition temperature, which all lead to crystallization (Levine and Slade, 1986; Roos and Karel, 1991b). The WLF equation has been suggested to be used for estimating the rate of crystallization during storage (Roos and Karel, 1992). The WLF equation suggests that the rate of solid-phase crystallization depends on the difference between the crystallization temperature and the glass-transition temperature of the amorphous material. Accordingly, a low glass-transition temperature will enhance the rate of crystallization.

At the glass-transition temperature, a transition from an amorphous solid (a glass) to an amorphous liquid (rubber) occurs, and the viscosity decreases. This critical transitional viscosity is reported to be 10^{11}–10^{14} Pa s (Buckton and Darcy, 1999; Levine and Slade, 1986) and therefore an equal or lower viscosity may facilitate crystallization.

It has been reported that most sugars interfere with sucrose crystallization due to viscosity or surface effects (Roos and Karel, 1991b). Roos and Karel (1991b) have also observed that some additives like fructose and Amioca (a high amylopectin starch) will delay sucrose crystallization. They attributed this delay to the possibly increased viscosity of the mixture above the glass-transition temperature.

Due to the importance of lactose and sucrose in the food and pharmaceutical industries, there have been extensive studies on these sugars, their crystallization behavior (Hancock and Dalton, 1999; Herrington, 1934; Herrington and Branfield, 1984; Nickerson and Patel, 1972; Roos and Karel, 1991a) and the dependence of the crystallization behavior on the glass-transition temperature (Jouppila et al., 1997, 1998). However, there is little known about the crystallization behavior for powder mixtures of these amorphous sugars during storage. These sugars exist in many food formulations together, such as ice cream and sweetened

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* Corresponding author. Tel.: +61 02 9351 3714; fax: +61 02 9351 2854.
E-mail address: mona.edrisi@sydney.edu.au (M. Edrisi Sormoli).

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condensed milk (Peter, 1928). Additions of various marine and vegetable gums to ice cream have been used to inhibit the crystallization of lactose (Gänzle et al., 2008). Ice cream powder mixes obtained from spray drying also contain both lactose and sucrose in their formulation, together with fat (Bassett, 1965). Hence, understanding their crystallization behavior as mixtures may help to improve the storage properties of these powders, without the addition of extra additives. Water-induced crystallization has been used by many authors to stimulate the crystallization of amorphous sugars during storage (Imtiaz-Ul-Islam and Langrish, 2008; Jouppila et al., 1997; Roos and Karel, 1992). The same approach has been applied here.

The objective of this study has been to determine the crystallization behavior of powders consisting of lactose and sucrose in the same particles during water-induced crystallization to gain more insight about their crystallization during storage and processing.

2. Materials and methods

2.1. Materials

Sucrose, laboratory chemical, Labchem, Ajax Finchem Pty Ltd., Australia, and lactose monohydrate, analytical grade reagent, from Chem-supply, Australia, were used.

2.2. Sample preparation

The required amounts of sucrose and lactose to have solutions with lactose/sucrose ratios of 95:5, 75:25 and 50:50 (w/w), and a total solid concentration of 10%, were added to deionized water. All solutions were magnetically stirred for at least 30 min to achieve a clear solution. The clear solutions were then spray dried.

2.3. Operating conditions for spray drying

Spray drying was performed using a mini spray dryer Buchi-290 (Buchi, Switzerland) at an inlet air temperature of 130 °C, a pump rate of 6 mL/min, an aspirator flow rate of approximately 35 m^3/h, and an atomizing air flow rate of 601 L/h. All experiments were performed in triplicate.

2.4. Powder characterization

2.4.1. Moisture sorption behavior and moisture content

The sorption behavior of the spray-dried powders was observed using a sealed sorption box (80 cm × 52 cm × 40 cm), in which there was a NaCl salt saturated solution to produce a constant 75% relative humidity at 25 °C and a four figure (±0.0001 g) analytical balance (Mettler Toledo AB204-S, Switzerland) to record the mass change of the sample. Sufficient and different amounts of the powders to create a monolayer of particles were placed on a Petri dish and put on the balance in the box. Prior to each experiment, the empty Petri dish was oven-dried for 24 h to ensure that there was no surface moisture present. A stainless steel sieve with a 53 μm aperture was used when sieving was needed. For recording the mass change the same approach as Imtiaz-Ul-Islam and Langrish (2009) was applied. The mass change was recorded (by computer) every minute until a constant mass was achieved for more than 6 h. The moisture content of the powders was then determined using the gravimetric method and oven drying.

2.4.2. X-ray diffraction analysis

The crystallinity of the spray-dried powders was determined using a Shimatzo D6000 X-ray diffractometer. The scanning range for 2θ was set to 5–30°, the step size was 0.02° with a scanning rate of 1 step/s, and the operating conditions were 40 kV and 30 mA. The data analysis for computing peak areas was performed using the DIFFRAC^{plus} EVA (version 3, BRUKER AXS) software. Pure non-processed samples of both individual components were analyzed as reference standards for confirming the associated peaks. The characteristic peaks for α-lactose crystals was confirmed to be at $2\theta = 12.4°$, 19.07°, 19.5°, 19.9° and 16.2° and for sucrose $2\theta = 8.3°$, 11.8°, 12.8°, 16.7°, 25.2°, as also found in the literature (Chinachoti and Steinberg, 1986). The percentage crystallinity of each component in the mixtures was defined as the ratio between the sums of the areas under the characteristic peaks of that component to the area for that component in the final and totally crystalline mixture. The crystalline composition of the mixture was again calculated with the same approach described by Drapier-Beche et al. (1997).

2.4.3. Light microscopy

Light microscopy was performed with a LEICA DM2500 light microscope, equipped with a Leica DFC290 HD series digital camera, a SCHOTT KL 1500 LED *plus* cold light source and objectives at 2.5×, 5× and 10× primary magnifications. Leica Application Suite (version 2.8.1) software was used for image processing (Leica Microsystems Limited, Switzerland).

3. Results and discussion

3.1. Moisture sorption behavior and moisture content

Fig. 1 shows the effect of composition on sorption–desorption behavior of spray-dried lactose/sucrose mixtures. The sorption–desorption curves, which also indicate the crystallization of these amorphous sugars, have been plotted against time and normalized with respect to their final equilibrium moisture contents for comparison purposes. It is known from the literature that amorphous sugars adsorb water vapor from the surrounding environment initially (Jouppila and Roos, 1994; Mathlouthi and Rogé, 2003). This water acts as a plasticizer that helps the sugars to crystallize and desorb the excess moisture in the second stage, until the equilibrium moisture content is reached (Lehto et al., 2006; Jouppila and Roos, 1994; Buckton and Darcy, 1995). The plateau part of the curve is considered to be the end of the crystallization process, where a constant and supposedly equilibrium moisture content is reached (Jouppila and Roos, 1994). Hence, the time-dependent lactose crystallization was observed from the rate of the sorbed water loss.

As shown in Fig. 1, the rate of lactose crystallization is decreased by the presence of sucrose. It takes nearly 500 min for pure lactose to be crystallized during water-induced crystallization, whereas this time increases to 2500 and 33,000 min for mixtures containing 5% (w/w) and 25% (w/w) sucrose, respectively. The rate of crystallization was determined to be 0.0070 ± 0.0010 kg/kg min for pure lactose, decreasing to 0.0032 ± 0.0019 kg/kg min for mixtures containing 5% (w/w) sucrose, and 0.0003 ± 0.0001 kg/kg min for the 25% (w/w) sucrose mixtures.

As far as the glass-transition temperature is concerned, adding sucrose with a lower glass-transition temperature is expected to decrease the crystallization time.

Some salts have been previously reported to delay lactose crystallization (Omar and Roos, 2007). In 2008, Imtiaz-Ul-Islam and Langrish also observed the changes in moisture sorption curves of lactose and a delay in water desorption, when adding salts such as NaCl and KCl to lactose in different ratios. Omar and Roos found that, during water-induced crystallization, $CaCl_2$ decreased the rate of crystallization significantly and more than the other studied salts. They attributed this phenomenon to the higher glass-transition temperature of the mixture compared with pure lactose.