Determination of glass transition temperatures during cooling and heating of low-moisture amorphous sugar mixtures

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A B S T R A C T

Glass transition temperatures (Tg) of amorphous sugar samples, prepared from 0% to 14% (wb) moisture content, were determined during both cooling and heating using differential scanning calorimetry (DSC). The DSC protocol used involved heating, cooling, and reheating the sugar samples, where Tg was obtained during both cooling and reheating steps. The Gordon-Taylor equation modeled the water plasticization effect, where the Tg of anhydrous solids and constant (k) values were determined simultaneously. No significant difference was found between the cooling and heating glass transition temperature values, with both values significantly influenced by sugar composition ($p < 0.05$). No significant effect of sugar composition was observed for the k values, resulting in discrepancies displayed by the Gordon-Taylor model for solid mass fractions below 0.84. Thus, k values should be estimated from measured Tg data at low solid mass fractions rather than extrapolated from high solid mass fractions, for prediction of Tg curve at high moisture contents.

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1. Introduction

The glass transition is a state transition between the glassy and rubbery states (or reverse) of a substance as it experiences changes in temperature and/or moisture. The temperature at which this transition occurs is well known as the glass transition temperature or simply Tg (Rhaman, 2010; Roos, 2010; Sablani et al., 2010). In recent years, the study of the relationship between Tg and water mass fraction (x_w) or solid mass fraction (x_s) has received considerable attention and is useful for construction of simplified stability/mobility diagrams or supplemented state diagrams of several sugar-rich products, such as dried fruit and fruit juice powders (Rahman, 2006; Jaya and Das, 2009; Rhaman, 2010; Roos, 2010; Sablani et al., 2010; Buera et al., 2011).

For instance, undesirable physical changes in foods occurring during storage and distribution, such as collapse, re-crystallization, stickiness, caking due to the glass transition phenomena can be predicted using the simplified water activity/temperature state diagrams (Tg vs a_w) or simplified water content/temperature state diagrams (Tg vs x_w) (Thomsen et al., 2005; Moraga et al., 2006; Rahman, 2006; Kasapis, 2006; Jaya and Das, 2009). On the other hand, a supplemented state diagram is a map of the different states of a food as a function of temperature over the entire solid mass fraction scale. Supplemented state diagrams are very helpful for developing food formulations, processing strategies, or storage procedures to optimize the stability of foods, which contain freezable or unfreezable water (Schmidt, 2004; Rhaman, 2010; Sablani et al., 2010).

In this context, state diagrams concerning dried fruit or fruit juice powders, have been reported in the literature for selected fruits such as raspberry, blueberries, strawberries, kiwifruit, grape, tomato, mango, pineapple, apple, persimmon, camu–camu, acai, borojó (Sá and Sereno, 1994; Welti-Chanes et al., 1999; Khalloufi et al., 2000; Bai et al., 2001; Sobral et al., 2001; Telis and Sobral, 2001, 2002; Moraga et al., 2004, 2006; Silva et al., 2006; Goula et al., 2008; Wang et al., 2008; Syamaladevi et al., 2009; Jaya and Das, 2009; Tonon et al., 2009; Mosquera et al., 2011).

Differential scanning calorimetry (DCS) is the most extensively used technique for Tg analysis of sugar solutions and sugar-rich foods. In general, samples containing freezable and unfreezable water are cooled from room temperature to a temperature well below zero ($\approx -100\,°C$) and then heated to a selected temperature, dependent upon the composition and water content of the food. Scan rates of 10 °C/min during heating are commonly used for Tg determination (Schmidt, 2004; Rhaman, 2010; Sablani et al., 2010). Freeze-dried or spray-dried samples are reconstituted by adding appropriate amounts of water or equilibrated over

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Nomenclature

a_w	water activity (dimensionless)
C_P	heat capacity (J/g °C)
HTR	heating temperature range (°C)
k	Gordon-Taylor parameter (dimensionless)
R^2	determination coefficient (dimensionless)
T	temperature (°C)
Tg	glass transition temperature (°C)
x	mass fraction (dimensionless)

Subscripts

C	cooling
F	fructose
G	glucose
H	heating
m	mixture
s	solid
S	sucrose
w	water

saturated salt solutions to prepare samples in the low and high moisture domains. However, freeze-dried or spray-dried partially crystalline/partially amorphous systems in the reduced-moisture domains can be obtained; however, sometimes, the Tg values of these samples are difficult to obtain because DSC was not sensitive enough to separate thermal transitions displayed in partially crystalline-amorphous samples (Orlien et al., 2003; Ronkart et al., 2007; Sablani et al., 2009; Wang and Weibiao Zhou, 2012).

The creation of reduced-moisture amorphous materials through crystal melting and fast cooling (termed melt quench) is another alternative for determining the Tg of sugar-rich foods (Vanhal and Blond, 1999; Liu et al., 2006; Jiang et al., 2008; Saavedra-Leos et al., 2012). Additionally, glass transition temperatures displayed during both cooling and heating by polymers and sugar glasses can be observed using a melt quench DSC protocol (Schawe, 1998; Schmidt, 2004; Badrinarayanan et al., 2007; Hutchinson, 2009).

Sugar-rich products, such as hard caramels, dried fruit products and fruit juice powders, are predominantly in a glassy amorphous form and low molecular weight sugars, such as fructose, glucose, and sucrose, constitute over 90% of the solids of these products, which are characterized to have low glass transition temperatures in the range of 5 and 68 °C (Bhandari and Howes, 1999). Therefore, the technical difficulties of processing and storage of the above sugar-rich products are generally associated with the basic physical characteristics of the mixtures of these low molecular weight sugars (Bhandari and Howes, 1999; Khalloufi et al., 2000; Jaya and Das, 2009). Also, the amount of low molecular weight sugars such as fructose, glucose and sucrose can vary drastically from one fruit to another and the number of possible fruit combinations is great. Thus, there is a need to understand the transition states of model food systems, including low molecular sugars and their mixtures at low moisture content, to predict and optimize processing strategies or storage procedures of sugar-rich products. Therefore, the objective of this research was to determine the glass transition temperatures during cooling and reheating of reduced-moisture model food systems prepared with several fructose/glucose/sucrose mass fractions.

2. Materials and methods

2.1. Crystalline sugars

Analytical grade fructose (Product No F2543), glucose (Product No G7528), and sucrose (Product No S0389) were purchased from Sigma–Aldrich Co. (St. Louis, MO). In order to obtain uniform mixing for the sugar mixtures, crystals with similar particle sizes in all the sugars were used. Each sugar was ground separately using mortar and pestle and were then screened using Tyler sieves (W.S. Tyler, Mentor, Ohio), where only particles size of ⩽0.212 micrometers were collected and used.

2.2. Sample preparation for DSC measurement

The mass fraction of fructose (x_F), glucose (x_G), and sucrose (x_S) in the sugar mixtures was established using a user-defined distance-based experimental design for mixtures of the three components (Table 1). A total of 16 anhydrous sugar mixtures, including pure components, as well as binary and ternary mixtures, were studied. Samples of about 5–12 mg were accurately weighted into Tzero aluminium pans (TA instruments) in a Mettler-Toledo microbalance (AG245: RS232, ±0.1 mg/0.01 mg). For binary and ternary mixtures, the amount of each sugar required in the mixture, was weighted directly into the same pan using the microbalance Mettler-Toledo with a readability of ±0.1 mg. The open pans were immediately stored over Drierite® in desiccators at room temperature for at least 4 weeks to completely dry the sugar samples at the same environmental conditions. Additional sugar samples of approximately 2 g were prepared and equilibrated in a similar way over Drierite® in desiccators, after which they were dried in a vacuum oven at 60 °C for 24 h (AOAC, 1990) to determine the initial moisture content of each sugar. For each of the 16 model systems listed in Table 1, about 20–24 samples of varying water contents were prepared by exposing the Drierite® equilibrated sugar samples to 100% relative humidity using distilled water. At regular time intervals, pans were withdrawn, sealed and reweighted. Water content was determined from weight gain after equilibration. This procedure was not time-consuming, because samples with moisture contents between 0% and 14% (wet basis) were prepared in about 1 h. Samples in the sealed pans were left at room temperature for a minimum of 24 h to allow for equilibration of moisture throughout the sample before DSC measurements were made.

2.3. Glass transition temperature measurement

The calorimetric methodology proposed by Saavedra-Leos et al. (2012), tested and suitable for determining the glass transition temperatures during cooling and heating of several sugar mixtures, was used in this study to produce the amorphous structure from crystalline sugars with subsequent Tg determination. The experiments were carried out by using a Differential Scanning Calorimetry (DSC Q2000, TA Instruments, Lukens Drive, New Castle, Delaware 19720, United States) with a temperature and sensitivity accuracy of ±0.1 °C and ±0.2 μW, respectively. The experiments were carried out in an inert atmosphere using nitrogen (ultra-pure, grade 5.0, 99.99% pure) at a flow of 50 ml/min. An empty pan was used as a reference.

In brief, samples in sealed pans were heated at 20 °C/min to a selected heating temperature, dependent upon the specific sample composition and water content (Table 1), and were then cooled at 20 °C/min to −60 °C to achieve the amorphous state. Samples were then reheated at 10 °C/min to their same corresponding heating