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Thermal evaluation of sucrose-maltodextrin-sodium citrate bioglass: Glass transition temperature

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ABSTRACT

Sucrose-maltodextrin-sodium citrate (SC-MD-NaCit) bioglass model systems were studied using modulated differential scanning calorimetry (DSC) to test the hypothesis that addition of salt to a complex amorphous carbohydrate system at low level of moisture content will significantly affect its glass transition properties. Samples were formulated with different SC/MD ratios (7:3, 5:5 and 3:7, by mass) and NaCit/SC ratios (0, 0.1 and 0.2, by mole) and two levels of residual moisture content, low (0.27–0.35%wb) and high (2.83–4.40%wb). The glass transition characteristics of these systems were strongly dependent on the moisture content and other constituents. On average, glass transition temperature (T_g) of the 7:3, 5:5 and 3:7 SC/MD systems were approximately 77, 84 and 101 °C, respectively. The T_g values tended to increase when NaCit was added, with a noticeable increase occurring in the 7:3 SC/MD system at low moisture content. The increase in moisture content from low to high level had a significant plasticization effect on the bioglass as elucidated based on the decrease in the T_g from approximately 106 to 67 °C. The DSC thermograms suggested that water molecules may interfere with intermolecular interactions between the glass-forming molecules causing changes in the molecular mobility of the bioglass matrix. The findings reveal that addition of NaCit can enhance the stability of low-moisture bioglass by primarily interacting with SC and forming large, less-mobile clusters, which helps to improve the T_g and restrict matrix mobility.

1. Introduction

When a liquid is rapidly cooled the equilibrium crystalline state may be avoided and an amorphous material is obtained. This phenomenon occurs due to a tremendous increase in viscosity during cooling that prevents molecules to rearrange themselves into a crystal lattice. The amorphous material exists as either a highly viscous supercooled liquid or rubbery material or glassy solid, depending on temperature (Allen, 1993; Elliott, Rao, & Thomas, 1986). The temperature at which a material undergoes the transformation from rubbery to glassy state is known as the 'glass-transition temperature (T_g)' (Young & Lovell, 2011). Such a process to convert a material into a glassy solid without any crystalline structure is also known as vitrification. A significantly reduced molecular mobility in the glassy state leads to its relative stability against crystallization while the rubbery state is considerably physically unstable (Roos, 1995).

Food material like sugars can be readily vitrified upon cooling their concentrated solutions. Amorphous sugar systems are capable of preserving seeds, spores, and living organisms under extreme conditions (Buitink & Leprince, 2004; Crowe et al., 2001). Sugars and some other carbohydrates in the glassy state also help modulate the stability of dry and frozen food and pharmaceutical products (Roos, 1995). A number of common food processes, such as drying, freezing, grinding, extrusion etc. yield products in the amorphous or partially amorphous states (Liu, Bhandari, & Zhou, 2007). These products usually face stability issues. In general, water activity of glassy products is considerably low and hence their microbial stability is not a significant concern; however, their chemical and structural stabilities are (Poirier-Brulez, Roudaut, Champion, Tanguy, & Simatos, 2006). The T_g is an important property of amorphous materials; it is related to a number of physiochemical changes in dried food products, for instance crystallization, collapse, stickiness etc. Accordingly, the T_g has become a good indicator of quality changes in food products during storage (Bhandari & Howes, 1999; Le Meste, Champion, Roudaut, Blond, & Simatos, 2002). However, in some cases, temperature and moisture

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content related changes in food and biomaterial properties are not satisfactorily explained using solely the concept of glass transition (Champion, Le Meste, & Simatos, 2000).

Like many other amorphous systems, carbohydrate glasses possess excellent protective property which makes them attractive for numerous food applications. However, materials in the amorphous state are thermodynamically out-of-equilibrium. Their properties change toward equilibrium with time, generally known as 'aging.' Food technologists are then challenged as how to formulate amorphous carbohydrates with desirable functional properties for the designated applications, and substantial degree of stability. Of course, the knowledge about characteristics and parameters that could affect the formulated system is fundamentally indispensable. The use of T_g as a reference temperature for predicting the rate of diffusion-controlled process was found to be relevant (Champion et al., 2000), even though not exclusively since certain reactions can still take place at temperatures below T_g (Hancock & Zografi, 1997).

Among glass-forming food materials, sucrose (SC) can be readily prepared as amorphous matrix. SC is able to form hydrogen bonds with polymers to a greater extent than other sugars having a higher T_g. This ability of SC could be of prime importance for the stabilization of polymers in amorphous SC matrix (Davidson & Sun, 2001; Taylor & Zografi, 1998; Wolkers, van Kilsdonk, & Hoekstra, 1998). The utilization of sugar glasses as an encapsulation matrix could be enhanced by mixing with larger biomolecules such as maltodextrin (MD); this combination could also contribute to certain desirable characteristics. In spray drying, for example, an ideal carrier should have a high degree of solubility, limited viscosity at 30–45% solid content, emulsifying characteristics, good drying properties, bland taste, and non-reactivity. MD serves well for these purposes (Desobry, Netto, & Labuza, 1999; Galmarini, Zamora, Baby, Chirife, & Mesina, 2008). In addition, MD has proven to inhibit crystallization in amorphous SC matrix and provide good product stability to dry powder products (Bhandari & Hartel, 2005). It was also found that glasses which is formulated from the mixtures of SC and MD exhibit stronger hydrogen bonding than pure SC glasses (Oldenhof, Wolkers, Fonseca, Passot, & Marin, 2005). Other interesting functional properties of MD are the ability to bind flavors and fat, and to serve as oxygen barrier (Chronakis, 1998). From economic stand point, both SC and MD are considerably inexpensive and substantially available.

Other than mixing with larger biomolecules, the stability of an amorphous sugar matrix could also be enhanced by the inclusion of small amount of salt. Salts can inhibit crystallization by altering molecular interactions and reducing molecular mobility (Izutsu & Aoyagi, 2005). The result from a SC crystallization study suggested that the presence of salts constrained number of configurations for crystal growth. This could be attributed to the effects of salt on the nucleation mechanism of ion-induced microheterogeneities in the supercooled solutions. It was also found that the crystallization was delayed without affecting the T_g of the system (Longinotti, Mazzobre, Buera, & Corti, 2002). As a result, it was proposed that the salt effect on SC crystallization occurs at a molecular level, but in such a dynamic way that the cooperative relaxations that give rise to glass transitions are not affected (Buera, Schebor, & Elizalde, 2005).

Some recent studies reported the potential of salts to enhance the stability of sugar glasses when residual moisture was less than 2%. It was suggested that the mechanisms that help improve matrix stability are interactions between either ions (You & Ludescher, 2008) or the functional groups (Kets, Ijpelaar, Hoekstra, & Vromans, 2004) of salts and sugar molecules. Sodium citrate (NaCit) is among the salts that is of much of interest from researchers. This type of salts has been widely used in food products for a number of purposes.

Based on these evidences found in the literature we hypothesis that addition of salt to a complex amorphous carbohydrate system at low level of moisture content will significantly affect its glass transition properties. We consider SC, MD, and NaCit are good candidates to utilize as amorphous matrix components for various applications in foods. However, efficient formulation and process control would be made possible only after the characteristics and behaviors of SC-MD-NaCit system have been thoroughly investigated. Thus, our objective was to investigate the dependence of calorimetric properties and behaviors of the SC-MD bioglass systems as a function of SC, MD, NaCit and moisture content.

2. Materials and methods

2.1. Materials

SC (crystalline, $C_{12}H_{22}O_{11}$; molecular weight (Mw), 342.2965 g/mol; melting point, 190 °C; Chemical Abstracts Service (CAS) number, 57-50-1) and NaCit (trisodium citrate dehydrate, $C_6H_5Na_3O_7.2H_2O$; Mw, 294.099568 g/mol; melting point, >300 °C; CAS number, 6132-04-3) were purchased from Fisher Scientific (Fair Lawn, NJ). MD (powder, $H(C_6H_{10}O_5)_2$-OH; Mw, 342.29648 g/mol; dextrose equivalent (DE) maximum 20%; melting point, 240 °C; CAS number, 9050-36-6) was purchased from Spectrum Chemical Manufacturing Corporation (Gardena, CA). All ingredients were used as received without further purification.

2.2. Sample preparation

The experimental factors and their levels studied were as follows: SC/MD ratio: 7:3, 5:5, and 3:7 (by mass); NaCit/SC ratio: 0, 0.1, 0.2 (by mole) and equilibrating relative humidity (RH): low (LRH) and high (HRH). The actual mass values of ingredients used and the experimental design and treatments are listed in Table 1. Two replicates were prepared for each treatment, and the order of experiment was completely randomized. Ingredients were weighed as necessary and dissolved in deionized (DI) water to make a total volume of ~150 mL. These solutions were stirred at 150 rpm using a magnetic stirrer for 3 h at room temperature. Then the sample solutions were held in a glass beaker and continuously stirred while heating over a hot plate while monitoring the solution temperature with a thermometer; heating was increased gradually until the solution temperature reached 175 °C and held there to bring the moisture content decreased to approximately 4.5%–9%, which was the lowest attainable. The progress of moisture reduction was monitored by periodic weighing. The final moisture content of all samples was measured via the Karl Fischer titration technique using the Volumetric Karl Fischer titrator, model 795 KFT Titrino (Metrohm Ltd., Herisau, Switzerland) at 50 °C as recommended for most confectionary products (Hoffmann & Felgner, 2011). Once moisture content reached the level mentioned above, the molten mixtures were poured over a flat surface of a Teflon sheet and spread with a spatula to a thickness of 2–3 mm to rapidly cool them down to room temperature and then transferred to a desiccator to maintain the moisture content.

Glass samples were subsequently ground using a mortar and pestle and sieved through a 170-mesh screen (WS Tyler Sieve 8″-FH-SS-SS-US-170, Sepor Inc., Wilmington, CA), corresponding to a 90 μm opening, to obtain samples as fine powder. Samples were stored in jars containing phosphorus pentoxide (P_2O_5) powder for low relative humidity (RH) of ~1% and lithium chloride (LiCl) solution for high RH of ~11% for at least three months to allow for equilibration.