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GLASS TRANSITION AND CRYSTALLIZATION OF AMORPHOUS TREHALOSE-SUCROSE MIXTURES

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Our objective was to investigate the glass transition and crystallization of trehalose-sucrose mixtures at various moisture contents. Samples were freeze-dried, rehumidified, and scanned with Differential scanning calorimetry (DSC) to obtain T_g values for all mixtures and pure sugars. Amorphous cotton candy samples for crystallization studies were prepared, humidified, and monitored for crystallinity as a function of time using powder X-ray diffraction (XRD). The T_g of pure dry trehalose was found to be 106 °C, while sucrose had a T_g of 60 °C. Glass transition, as expected, occurred at an intermediate temperature for sucrose-trehalose mixtures. Of the dry samples, only those containing less than 16% trehalose showed sucrose crystallization during scanning. In cotton candy made from a 25% trehalose-75% sucrose mixture, humidified to 33%, sucrose did not crystallize after 30 days, whereas pure sucrose cotton candy at that humidity crystallized completely after 11 days. These data show that trehalose may be a useful crystallization inhibitor in foods with high sucrose content, although small amounts of trehalose did not significantly raise the T_g .

Keywords: Glass transition, Trehalose, Sucrose, Crystallization.

INTRODUCTION

Knowledge of and the ability to manipulate sucrose-water state data are important in the effort to increase shelf-life of high-sucrose containing foods, such as cotton candy and soft cookies. Detrimental texture changes, such as stickiness and collapse, in high-sucrose food systems often accompanies the crystallization of the glassy sugar.^[1,2] Furthermore, it is known that the crystallization rates of glasses depend on the temperature in relation to the glass transition temperature, T_g . Amorphous systems subjected to temperatures and humidities that fall on a point above the glass transition line can crystallize. Those systems with a large ($T-T_g$) will crystallize faster than systems close to or below their T_g .^[3] Therefore knowledge of the T_g line of pure or mixed sugar systems is critical to stability prediction. Trehalose has been touted as a special molecule used in nature to protect biological systems in dry or cold environments, perhaps by slowing crystallization.^[4] Thus, due to the relatively high glass transition temperature of trehalose, amorphous sucrose-trehalose mixtures deserve attention from the high-sucrose foods industry. If the presence of trehalose can sufficiently slow crystallization of sucrose under ordinary storage conditions, which can exceed T_g , shelf life can be extended.

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Fig. 1 is a composite state diagram of the trehalose-water system based on data reported in available sources,^[5-25] including those compiled previously by Chen et al., 2000.^[26] The equilibrium lines shown include the liquidus line (freezing point depression line), and the solidus line (solubility or solute crystal melting line). The glass transition curve shows a large variation among different studies, up to ± 20 °C at any given solids content. In these studies the dry T_g of trehalose falls between 75 and 120 °C (see Table 1). As seen in Fig. 1, at low moistures the T_g rises dramatically. Therefore, the range of values in Table 1 could be due to unmeasured, and thus unreported, residual moisture. The same phenomenon can be seen in the case of sucrose-water systems, as shown in Fig. 2, where T_g values taken from publications also do not agree well with each other,^[3,12,20,22,24, 27-41] particularly in the driest region where the glass transition curve has a steep slope.

Fig. 3 shows that in general the reported T_g curve for trehalose is higher than that of sucrose using only those references that reported either onset or midpoint or

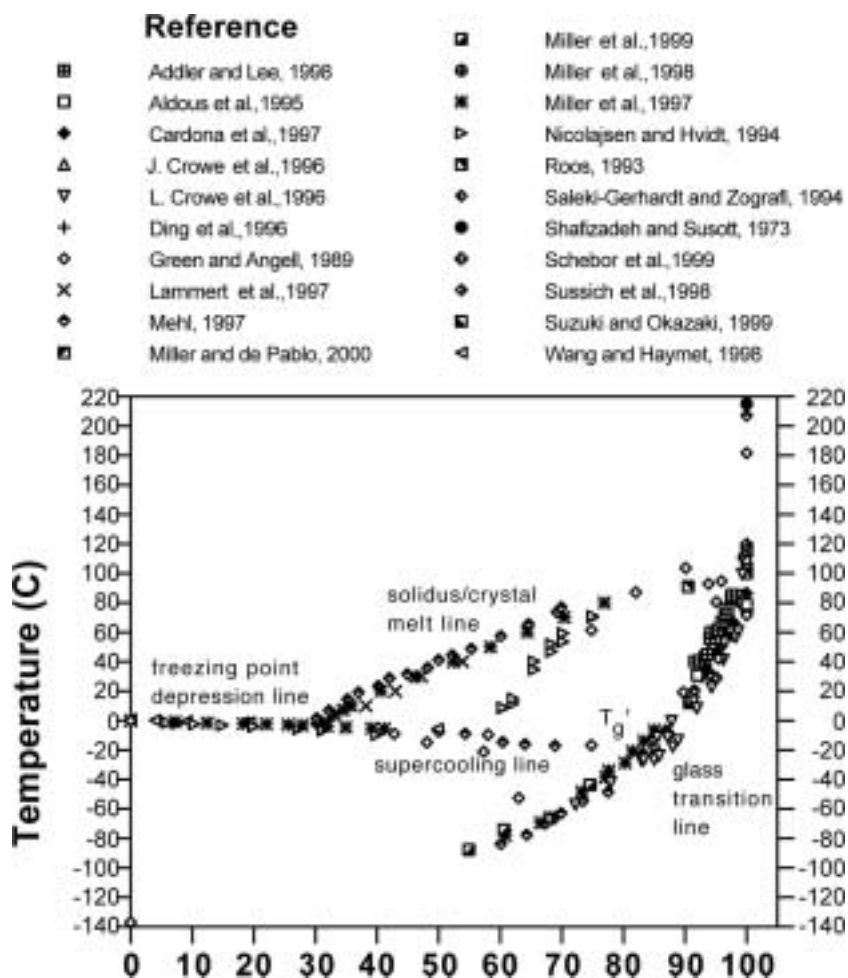


Figure 1 Literature values for the state diagram of the trehalose-water system, including the glass transition line.

Table 1 Literature values for the glass transition temperature of dry amorphous trehalose and sucrose

Reported T_g values in literature for pure, dry trehalose		Reported T_g values in literature for pure, dry sucrose	
T_g (°C)	Reference	T_g (°C)	Reference
75	Green and Angell (1989)	52	Slade and Levine (1988)
79	Aldous <i>et al</i> (1995)	56.6	Roos and Karel (1990)
80	Suzuki and Okazaki (1999)	57	Finegold <i>et al</i> (1989)
85	Cardona <i>et al</i> (1997)	58.8	Suzuki and Okazaki (1999)
90	Saleki-Gerhardt (1993)	59.6	Blond <i>et al</i> (1997)
100	Roos (1993)	60.6	Blond <i>et al</i> (1997)
110	Crowe, J. <i>et al</i> (1996)	62	Roos and Karel (1991a)
112	Mehl (1997)	67.7	Sun <i>et al</i> (1996)
113.9	Crowe, L. <i>et al</i> (1996)	68.5	Urbani <i>et al</i> (1997)
114.9	Miller <i>et al</i> (1997)	70	Orford <i>et al</i> (1990)
115	Miller <i>et al</i> (1998)	70.2	Sun <i>et al</i> (1996)
115	Ding <i>et al</i> (1996)	73.85	Hancock and Zografi (1994)
115	Saleki-Gerhardt and Zografi (1994)	74	Saleki-Gerhardt and Zografi (1994)
116.9	Miller and de Pablo (2000)	75.9	Shamblin and Zografi (1999)
120	Sussich <i>et al</i> (1998)		

both. In no case was the onset of glass transition for trehalose reported as less than the onset for sucrose. The T_g values for dry, amorphous sucrose reported in the literature is also listed in Table 1. As noted above, a factor contributing to inaccuracy in T_g versus moisture reporting may arise from failure to remove all water from the dry samples. In this case presumed dry samples would actually have moisture contents greater than that reported, and thus the reported T_g s would be lower than their true values. Using the Gordon-Taylor model for the trehalose-water system with values derived in Chen *et al.* (2000), ($k = 5.2$), the T_g falls more than 12 °C as the moisture content increases from 0% to 1%.

A variety of methods have been reported for the drying of trehalose and sucrose samples, most of which involve freeze-drying over several days with an increasing temperature program. For trehalose, reports of a dry T_g between 105 and 120 °C—which constitute the upper range of the reported values—come from samples that were dried at high temperature (~60 °C) during the final day of drying.^[10,14,16,17,20,37] Typically, reports of T_g for trehalose below 105 °C were from studies where the samples were dried only at temperatures up to and including room temperature^[3,7,22,24] or even just equilibrated over P₂O₅ at room temperature.^[34] Because inadequate drying is the most prominent source of error in reporting a T_g versus moisture relationship, it follows logically that of the values reported in the literature the lower ones are less likely to be reliable, and the higher ones are perhaps more realistic.

Several papers^[3,7,20,22,37,42,43] have reported data for the moisture content of amorphous sucrose and trehalose as a function of water activity. Fig. 4 shows these data at 25 °C along with a linear regression. The purpose of this study was to evaluate the overall T_g for combined trehalose-sucrose mixtures, as well as the influence of relative humidity and added trehalose on the recrystallization of sucrose in these mixtures.

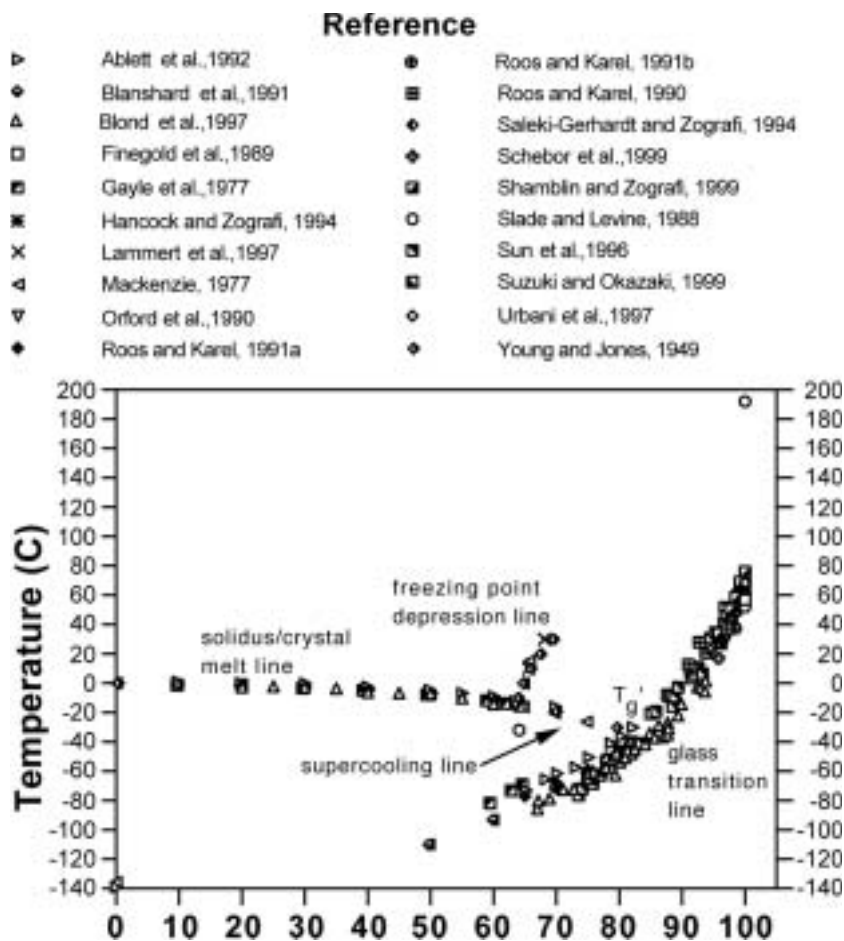


Figure 2 Literature values for the state diagram of the sucrose-water system, including the glass transition line.

METHOD

Freeze-drying

Samples were prepared by first dissolving 10 grams of a pure crystalline sugar mixture in roughly 30 mL of distilled water, and poured into a plastic 40 mm diameter dish. The mixtures consisted of 0, 4, 8, 12, 16, 20, 40, 60, 80 and 100% trehalose mixtures with the balance being sucrose. Each dissolved mixture was rapidly frozen in liquid nitrogen and placed in a Dura-Top bulk tray dryer with a Dura-Dry condenser module (FTS Systems, Inc., Stone Ridge, NY) running at 13.3 Pa vacuum, with a temperature program of -40°C for 24 hours, -20°C for 12 hours, 0°C for 12 hours, 25°C for 24 hours, followed by 50°C for 36 hours. The high-temperature step was not done in the initial trials, resulting in samples with some residual moisture.

After drying, the samples were placed into four desiccators for re-humidification at 25°C . One set of samples were kept dry over P_2O_5 powder, while the other three sets were

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