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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

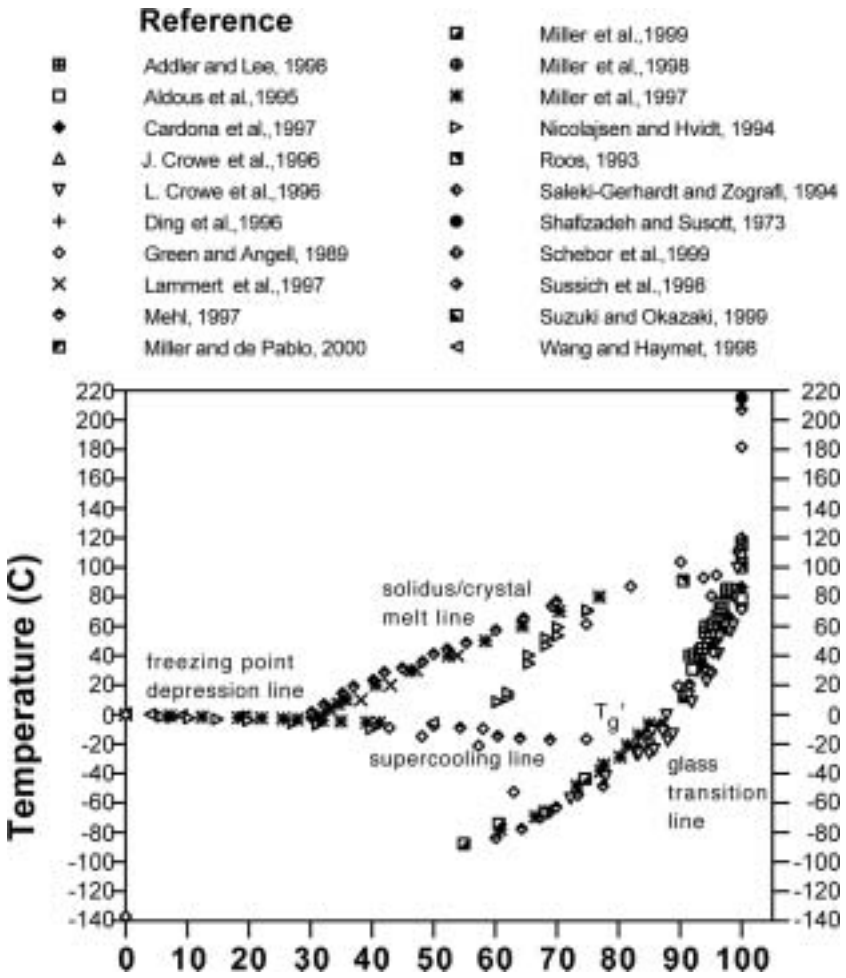


**Figure 1** Literature values for the state diagram of the trehalose-water system, including the glass transition line.

**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 *et al* (1995) | 56.6 | Roos and Karel (1990) |
| 80 | Suzuki and Okazaki (1999) | 57 | Finegold *et al* (1989) |
| 85 | Cardona *et al* (1997) | 58.8 | Suzuki and Okazaki (1999) |
| 90 | Saleki-Gerhardt (1993) | 59.6 | Blond *et al* (1997) |
| 100 | Roos (1993) | 60.6 | Blond *et al* (1997) |
| 110 | Crowe, J. *et al* (1996) | 62 | Roos and Karel (1991a) |
| 112 | Mehl (1997) | 67.7 | Sun *et al* (1996) |
| 113.9 | Crowe, L. *et al* (1996) | 68.5 | Urbani *et al* (1997) |
| 114.9 | Miller *et al* (1997) | 70 | Orford *et al* (1990) |
| 115 | Miller *et al* (1998) | 70.2 | Sun *et al* (1996) |
| 115 | Ding *et al* (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 *et al* (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 Tgs 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 $P_2O_5$ 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.

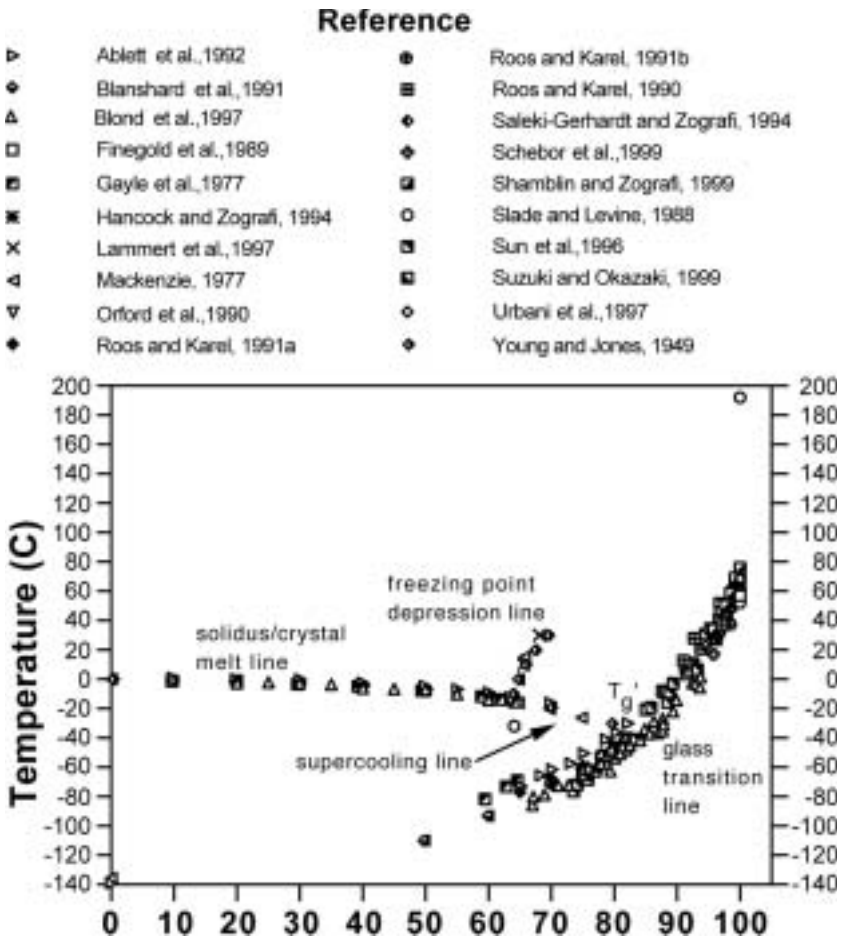


**Figure 2** Literature values for the state diagram of the sucrose-water system, including the glass transition line.

## 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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