

# Measuring and interpreting the glass transition in frozen foods and model systems

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Many frozen foods contain an unfrozen phase with a very low freezing point, due to the process of freeze-concentration of the solutes as water is removed in the form of ice. Hence, many reactions that are diffusion-controlled, such as enzymatic degradation or ice recrystallization, can occur within this unfrozen phase even at very low temperatures, giving frozen foods a finite shelf-life. Recent research in the area of low-temperature stability of foods has focused on the importance of the viscosity of the frozen solution and the rates of diffusion of water and solutes within the unfrozen phase (Goff, 1992). At very high viscosities ( $>10^{12}$  Pa s), an amorphous solid state or glass may form within this unfrozen phase, thus tremendously decreasing the rates of molecular diffusion and rendering the frozen food stable for much longer periods of time. Awareness of this glass formation emphasizes the importance of appropriate freezing and storage temperatures to stability and may also allow formulation of foods with a higher glass transition temperature or reduced molecular diffusion rates to improve shelf life. The measurement and interpretation of this glass transition will be discussed.

**Keywords:** glass transition, frozen foods, storage stability, thermal analysis, polysaccharide stabilizers.

## INTRODUCTION

A common amorphous or non-crystalline metastable state of solids is termed the 'glassy' or vitreous state. A glass can also be characterized as a liquid with extremely high viscosity ( $10^{12}$ – $10^{14}$  Pa s) that will flow but has an extremely low molecular diffusion rate (Slade & Levine, 1991). The glass/rubber transition is a kinetic phenomenon that is dependent upon the type and concentration of the solute and the temperature. In Figure 1, a glass transition line as a function of temperature and concentration is shown. Above and to the left of the glass transition line, solutions or complex systems such as foods are in the rubbery or liquid state, in which they are unstable and reactive, so that ice-crystal growth can occur in time-frames significant to food storage. Below and to the right of the glass transition curve, the system transforms to the glassy state as a result

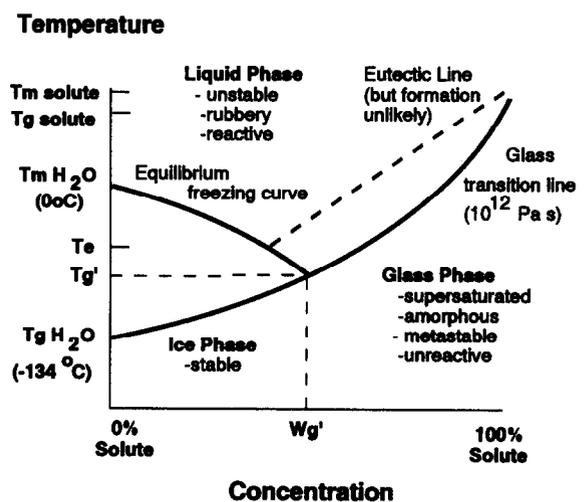


Fig. 1. Temperature-concentration state diagram for an aqueous solution, showing the glass transition line, defined by viscosity, the equilibrium freezing curve, the theoretical eutectic line, and a description of the reactivity of the various 'states'. The glass transition ( $T_g$ ), melting ( $T_m$ ), and eutectic ( $T_e$ ) temperatures of the solute and water are shown. Point  $T_g'$  represents the glass transition temperature of the maximally freeze-concentrated solution and  $W_g'$  represents the amount of unfrozen water which becomes trapped in the glass. (From Goff, 1992).

of extremely high viscosity and exists as an unreactive, amorphous solid (Roos, 1992). The hypothesis has recently been stated that this transition greatly influences resulting food stability, as the water in the concentrated serum phase becomes kinetically 'immobilized' and therefore does not support or participate in reactions (Levine & Slade, 1992). Regions exist (not shown) on this state diagram that correspond to the dried foods area, the intermediate moisture foods area, and the frozen foods area (Noel *et al.*, 1990).

If foods are subjected to an 'equilibrium' freezing process in which they become maximally freeze-concentrated, the viscosity of this unfrozen concentrated phase, supersaturated beyond the solute eutectic point, becomes so high that a metastable glass will form. This glass forms at a characteristic glass transition temperature lower than the eutectic temperature, designated the  $T_g'$ , and the amount of unfrozen water present in the glass, designated  $W_g'$ , will be minimal but still substantial. Glass transitions are most often determined by differential scanning calorimetry (DSC) (Levine & Slade, 1990; Hatley *et al.*, 1991) and by thermomechanical analysis (TMA) (Goff *et al.*, 1993).

## RESULTS AND DISCUSSION

In this laboratory, we have used several techniques for measuring the glass transition and low-temperature thermal events in model systems of sucrose and polysaccharides, including DSC, TMA, dielectric analysis (DEA), nuclear magnetic resonance (NMR), and low-temperature parallel-plate rheometry. Our objective is to determine the influence of polysaccharides, when used in concentrations of commercial relevance, on low-temperature thermal events as a means of explaining their demonstrated behaviour in cryostabilization. Figure 2 shows a typical DSC plot for a 20% sucrose solution. Several transitions in the curve can be seen. These transitions have been the subject of some debate amongst scientists (Blond & Simatos, 1991), particularly the large baseline shift just prior to the melting endotherm, described by Levine and Slade (1990) as the  $T_g'$ . Other instrumental techniques have revealed further information about the nature of the frozen substance at temperatures above and below this transition. This transition is most likely a combination of a glass relaxation and the onset of ice melting. There are also a number of other glass relaxations

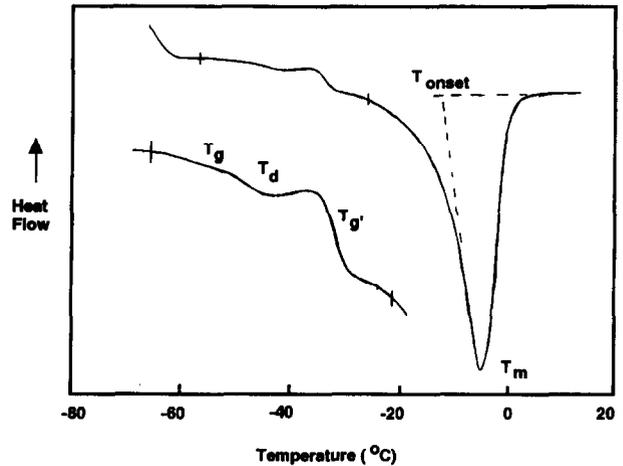


Fig. 2. A typical differential scanning calorimetry plot of a 20% sucrose solution showing the various thermal events occurring between  $-60$  and  $0^{\circ}\text{C}$ , generated with a DuPont 2000 Thermal Analyzer with a DuPont 2910 Cell Base. The temperature axis refers to the upper curve. The lower curve is an expansion of the upper curve from  $-55$  to  $-25^{\circ}\text{C}$ , as indicated by the vertical slash marks on the curve.  $T_g'$  = glass transition temperature of a maximally freeze-concentrated solution, as the midpoint of the baseline shift;  $T_g$  = thermal event at temperatures less than  $T_g'$ , possibly a glass transition temperature of glass formed during a non-equilibrium freezing process, as a result of partial freeze-concentration;  $T_d$  = devitrification temperature of a glass formed during the non-equilibrium freezing process, resulting in a small exotherm;  $T_{\text{onset}}$  = temperature of the onset of the melting endotherm, obtained by extrapolation back to the baseline (although the actual onset of melting may be at much lower temperatures);  $T_{\text{melt}}$  = melting temperature taken as the peak temperature of the melting endotherm. (From Goff *et al.*, 1993).

occurring at temperatures below this transition. However, it is likely, and on this point most scientists concur, that this is the technologically significant transition which has the greatest influence on low-temperature stability. At temperatures above this point, foods can suffer from reactions and quality loss that are related to molecular diffusion phenomena (Goff, 1992).

Polysaccharides are used in a number of frozen products due to their perceived effect on frozen stability. In frozen dairy dessert products, for example, they are used to retard the size and growth of ice crystals. Our research has confirmed that the size and growth rate of ice crystals in stabilized ice creams is less than in non-stabilized ice creams. We have attributed this to the enhanced viscosity created by the stabilizers in the unfrozen phase, although no significant difference in the  $T_g'$  of the two ice cream mixes existed. Thus it appears that the decreased mobility of molecules leading up to the formation of a glass is sufficient to alter the stability of the system.

## CONCLUSIONS

The understanding that has been gained from this research and from that of other scientists in the last five years in the area of low-temperature stability in foods will undoubtedly lead to exciting new developments in the processing and development of frozen foods in the near future. Research is currently underway to elucidate mechanisms by which cryo-stabilizing agents exert their protective effects and to determine practical means of manipulating the  $T_g$  in frozen foods to increase their storage stability, using ingredients such as dextran or gelatin, for example.

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