

Dynamic mechanical thermal analysis of aqueous sugar solutions containing fructose, glucose, sucrose, maltose and lactose

Isabel B. Cruz,¹ Jorge C. Oliveira^{2*} & William M. MacInnes³

¹ Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Rua Dr António Bernardino de Almeida, 4200-Porto, Portugal

² Department of Food Science and Technology, University College Cork, Cork, Ireland

³ Nestlé, Lausanne Research Centre, CH 1000 Lausanne 26, Switzerland

Summary The glass transition of glucose, fructose, lactose, maltose and sucrose solutions at maximum cryo-concentration was studied by Dynamic Mechanical Thermal Analysis (DMTA), using the disc bending technique. The glass transition temperatures were determined from the peaks in the loss modulus E'' , which corresponds theoretically to the resonance point (Maxwell model) for several input frequencies. The frequency dependence was well described by both an Arrhenius-type model and by the WLF (Williams, Landel and Ferry) equation, yielding glass transition temperatures for an average molecular vibration time of 100 s, which were similar to published midpoint temperatures determined by DSC scans. Some sugar mixtures were studied, yielding results that were well described by the Gordon–Taylor equation, using literature data. The frequency dependence of the viscoelastic ratio was also well approximated by an Arrhenius-type equation, with activation energies similar to those of the glass transition temperature and corresponded well to published values of the endset of glass transition.

Keywords Biomaterials science, frequency-response analysis, glass transition, molecular mobility, WLF equation.

Introduction

According to the Ehrenfest (1933) classification, glass transition has the properties of a second order phase transition that occurs over a temperature range, in which an amorphous glassy material (rigid and brittle) is transformed to a rubbery viscous liquid state (soft and flexible). This phenomenon is found in amorphous or semi-amorphous biopolymer matrices, which is the case for most concentrated food products.

Molecular mobility increases significantly above the glass transition, with important implications for the physical and chemical stability of foods (e.g. microbial growth, crystallization and recryst-

tallization, collapse of dried structures; Slade & Levine, 1991). The glass transition is conventionally identified by a single temperature, designated glass transition temperature (T_g). It is usually identified from DSC scans, but there is some controversy in the literature as to what T_g should stand for: onset, endset or midpoint, as will be discussed later in the text. The standard for pure components, which is the intercept of the two asymptotes of the variation of a property such as entropy or volume with temperature (Scherer, 1991), has not been generally applied to foods and complex matrices in general.

One of the most important applications of this concept concerns food stability studies, as the reaction/decay rates of many quality/safety factors are found to be well related to molecular mobility and hence to glass transition (Slade

*Correspondent: Fax: 353 21 4276398;
e-mail: j.oliveira@ucc.ie

& Levine, 1993). Most foods are in a rubbery or liquid state and can reach glassy state on cooling or water removal. On glass transition, the molecular conformation of a rubbery amorphous matrix reaches its lower limiting entropy (or close to zero free volume – Doolittle, 1951). The average molecular vibration time of the matrix increases drastically as the glass transition is approached and the molecular mobility decreases. In the glassy state, matrices show only molecular vibration and muta-rotation, with viscosity in the region of 10^{12} Pa s, and hence have a great stability.

The average molecular relaxation times of supercooled liquids above the glass transition have been shown to follow generally the empirical Vogel law (Mansfield, 1993), which can be directly transformed into the more usual empirical equation applied in biomaterials science (Slade & Levine, 1993), the WLF (Williams, Landel and Ferry) equation (Williams *et al.*, 1955; Mansfield, 1993):

$$-\log\left(\frac{\tau}{\tau_g}\right) = \frac{C_1(T - T_g)}{C_2 + T - T_g} \quad (1)$$

where \log stands for decimal logarithm (base 10), τ is the average molecular vibration time at temperature T , and τ_g the respective value at T_g . C_1 and C_2 are model parameters. C_1 would be, in principle, the difference in order of magnitude between the average atomic vibration time (*c.* 10^{-13} s) and the average molecular vibration time in the glassy state (*c.* 10^3 s), that is, around 16. Williams *et al.* (1955) proposed the universal values of 17.44 for C_1 and 51.6 °C for C_2 by fitting data from many polymers. However, some authors have cautioned against the use of universal constants, as specific systems may show quite a variation (Mansfield, 1993). Peleg (1992) collected C_1 values from the literature ranging from 13.7 to 34 and C_2 values between 24 and 80 °C, although even lower C_1 values were collected by Roos (1995). From the comprehensive work of Angell *et al.* (1994), it is clear that while C_1 could indeed be a universal constant with a value around 16, C_2 is a system-dependent value and should be determined for the specific matrix in question.

The Arrhenius equation has also been applied with success in a number of cases:

$$-\log\left(\frac{\tau}{\tau_g}\right) = \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_g}\right) \quad (2)$$

where \ln stands for natural logarithm (base e), E_a is the activation energy and R the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). As shown by Angell *et al.* (1991, 1994), systems designated as ‘strong’ (as opposed to ‘fragile’) would show a behaviour close to the Arrhenius model, even around the glass transition (these are liquids with high resistance to thermal degradation). However, this is not the case for most food systems, which would show a break in the Arrhenius plot (MacInnes, 1993). Nevertheless, the Arrhenius equation might still give reasonable results in a sufficiently small temperature range, on either side of such a breakpoint. It is particularly noteworthy that in the vicinity of the glass transition, in the rubbery state, viscosity can be described by the so-called Adam–Gibbs equation, developed from a thermodynamic approach proposed by Adam & Gibbs (1965), which can be reduced to the simple Arrhenius form. Hence, there would be a sound theoretical foundation for using an Arrhenius-type equation close to the glass transition.

The difference between WLF or Arrhenius models can be ultimately related to the viscosity model that one is inherently assuming (as the average relaxation time and the viscosity are proportional): following the free volume theory of molecular mobility (Cohen & Turnbull, 1959) one obtains the VTF (Vogel, Tamman and Fulcher) equation, which is interconvertible with the WLF model (Angell *et al.*, 1994), while if one assumes an isostructural viscosity model, the Arrhenius equation is obtained (Scherer, 1991).

There is quite a lot of physical evidence for many liquids showing that the value of τ_g is around 100–1000 s, and mostly close to 200 s (Angell *et al.*, 1991), but this cannot be generalized to complex food matrices without further experimental verification. Fixing the value of τ_g at 100 s has been used by Moynihan *et al.* (1971) and Angell *et al.* (1994).

Diffusion-dependent phenomena can also be expected to follow a WLF model, given the relationship between viscosity and diffusivity. Thus, the WLF equation has been successfully applied to microbial death and quality decay rates,

showing particularly better fits than the Arrhenius equation as the glass transition is approached (Slade & Levine, 1993; Kerr *et al.*, 1993).

Therefore, it could be argued that a useful indicator for T_g should be the parameter that corresponds to the WLF equation (1), particularly for stability studies, where the WLF equation, in the above or a modified form, would be used to describe the influence of temperature and water content on reaction rates.

The water content dependency results from the plasticizing effect of water, as T_g decreases significantly with water content (Slade & Levine, 1991). This effect has been successfully described, particularly in binary mixtures, by the Gordon–Taylor equation (Gordon & Taylor, 1952):

$$T_g = \frac{kwT_{g(\text{water})} + (1-w)T_{g(\text{dry matrix})}}{kwT_g + (1-w)} \quad (3)$$

where w is the water content (in $g_{\text{water}}/g_{\text{water} + \text{solid}}$), and k is a system parameter, to be obtained from model fitting of experimental data for several water contents. This is in fact a derivation of the theoretically based Couchman–Karasz equation (Couchman, 1978), with the empirical parameter k replacing the ratio of the specific heat increase for water, because of the glass transition, and that for the dry matrix. Although the equation becomes empirical, the added flexibility allows for a wider application. With the empirical constant k determined by data regression, the equation has been applied with success to several food systems (Roos & Karel, 1991; Roos, 1995; Frias *et al.*, 1998), with k values ranging roughly between 2 and 10.

For aqueous solutions below the maximum cryo-concentration (that is, the concentration above which no ice crystallization is possible and the solution vitrifies), as the solution cools below the freezing point, it cryo-concentrates as ice crystals are formed and the freezing temperature of the cryo-concentrated solution decreases while its glass transition temperature increases. The value of T_g for the maximally freeze-concentrated solution is denoted T'_g , and the corresponding concentration C'_g , while the freezing/melting temperature is T'_m . Whether T'_g and T'_m are equal, or the former is lower, is a debatable issue (a good discussion is provided by Slade & Levine, 1995), but evidently, the endset of the glass transition

should be roughly equal to T'_m , whatever the definitions used.

The determination of T_g according to equation (1) can be made rather straightforwardly by Dynamic Mechanical Thermal Analysis (DMTA).

The objective of this work was to apply DMTA measurements and compare the results with literature data, thereby establishing the usefulness of DMTA for obtaining objective indicators of the glass transition, suitable for stability studies of frozen food matrices. Sugar solutions, which are among the most widely reported (model) food systems in published studies, were used.

Glass transition analysis by DMTA

Dynamic Mechanical Thermal Analysis is a frequency-response test, which can be theoretically interpreted in terms of system dynamics theory, well known in process engineering (Luyben, 1990).

The DMTA measures the rheological properties of a system continuously, while the temperature is changed, usually by linear increase or decrease scans. The rheological measurements are normally made by compression or bending tests, which quantify the modulus of elasticity of the matrix by measuring the stress caused by a given input strain.

The concept of dynamic or frequency-response tests is to cause a sinusoidal input strain. It is fairly simple to demonstrate theoretically that in the linear viscoelastic range the response of any stable system will tend to an output sinusoidal stress that has the same frequency as the input strain (Luyben, 1990), although with a phase angle, which can vary from 0° for an ideal solid body to 90° for an ideal liquid (Darby, 1975). Furthermore, it can also be demonstrated that in the linear viscoelastic range, the phase angle (δ) and the ratio of the amplitudes of the output and input sinusoidal waves, which are independent of the amplitude of the input wave, allow for the quantification of the fraction of mechanical energy input which is stored (elastic behaviour) and the fraction which is dissipated (plastic behaviour). The relationships between the measuring and system variables are the following:

Input strain wave	$\varepsilon = \varepsilon_0 \sin(\omega t)$
Output stress wave	$\sigma = \sigma_0 \sin(\omega t + \delta)$
Complex elastic modulus	$E^* = E' + i E''$;
	$ E^* = \sigma_0/\varepsilon_0$
	$= (E'^2 + E''^2)^{1/2}$

Storage modulus	$E' = E^* \cos \delta$
Loss modulus	$E'' = E^* \sin \delta$
Phase angle	$\tan \delta = E''/E'$

where ε is the strain at time t , ε_0 the strain amplitude, σ the stress at time t , σ_0 the stress amplitude, ω the frequency, δ the phase angle ($\tan \delta$ is the visco-elastic ratio), E^* the complex elastic modulus, E' the storage elastic modulus (mechanical energy storage), E'' the loss elastic modulus (mechanical energy dissipation) and i is the imaginary unit (square root of -1). E^* is the system transfer function in the frequency-response domain. Thus, it can be easily demonstrated that for a first-order system (e.g. the Maxwell model of viscoelasticity), the maximum loss modulus E'' (maximum of energy dissipation) occurs when the input frequency and the system frequency (reciprocal of the average relaxation time) are in resonance (Luyben, 1990; Allen, 1993).

Therefore, the peak of the E'' vs. temperature plot for a given frequency will indicate the temperature at which the average molecular relaxation time of the matrix is the reciprocal of the input frequency. Measurements at different frequencies should therefore allow one to apply equation (1) in order to estimate T_g . Arrhenius plots can also be constructed. MacInnes (1993) found the breakpoint in the Arrhenius plot at frequencies around 20 Hz for sucrose solutions; at lower frequencies an Arrhenius model with high activation energy fitted the data well.

Other features of the glass transition can also be identified with the DMTA results. As in the glassy state, E' is relatively unaffected by temperature, the onset of the glass transition corresponds to an initial drop in the E' vs. T plot. The end of the glass transition would occur at a point where E' becomes less sensitive to temperature again (having fallen by 2–3 orders of magnitude), and thus could be identified by a peak in the $\tan \delta$ plot. If solute crystallization occurs, the patterns can be greatly affected in this region.

Materials and methods

Materials

Binary systems of water + sucrose, fructose, lactose, maltose or glucose were prepared with 30% ($g_{\text{solid}}/g_{\text{water} + \text{solid}}$) total solids. Equal proportions

of the solutes were used to produce ternary and quaternary solutions of water + (fructose + glucose), (fructose + lactose), (glucose + lactose), (glucose + maltose) or (fructose + glucose + lactose), so that the final solids concentration was also 30%. Bi-distilled water and sugars of analytical purity (Merck, Whitehouse station, NJ, USA) were used to make the solutions.

Methods

A DMTA unit (RSAII, Rheometrics, Piscataway, NJ, USA), equipped with a disc-bending sample holder specially constructed for this purpose (Fig. 1), was used to measure the viscoelastic properties.

The upper and lower rings of the sample holder clamp two plastic discs and the centering ring, and were rigidly attached to the DMTA. The bottom shaft that causes the sinusoidal strain operates the rings, and the upper shaft, where the stress is measured, is attached to the centre of the sample holder. The liquid samples were injected into the space between the plastic discs, through a 1.2 mm diameter hole in the centering ring (Fig. 1).

The centre of the disc was subjected to an oscillatory small-amplitude deflection (strain amplitude 0.001 m) by the DMTA drive shaft, and the corresponding stress measurements were made at several frequencies with a frequency sweep test. The following multi-wave frequency programmes were used: 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8 and 0.1, 1.0, 10 Hz. In such tests, the equipment measures the same sample at the different programmed

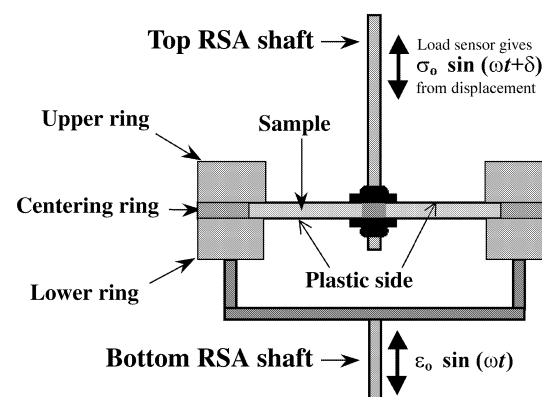


Figure 1 Sketch of the DMTA tool designed for analysing aqueous solutions in a Rheometrics DMTA.

frequencies at each temperature step. Preliminary experiments were made to verify that such a procedure yielded similar results to taking one frequency measurement at a time. Between two and three replicates were made (except for maltose, which was not replicated).

The sample temperature was measured with a thermocouple located inside the sample. Temperature was scanned, at $0.4\text{ }^{\circ}\text{C min}^{-1}$ by the DMTA temperature controller, from -70 to $0\text{ }^{\circ}\text{C}$.

Data regressions were performed, with Excel software (Excel 97, Microsoft, Seattle, WA, USA) and KaleidaGraph software (KaleidaGraph 3.0, Synergy Software, Reading, PA, USA), on the equations obtained by manipulating equation (1) or (2) to yield T vs. ω , as the former is the measured response and the latter the input factor.

Results and discussion

Some preliminary scans were made with the binary solutions at different heating rates from 0.3 to $1.2\text{ }^{\circ}\text{C min}^{-1}$. No significant differences were found below $0.8\text{ }^{\circ}\text{C min}^{-1}$, with 1 and $1.2\text{ }^{\circ}\text{C min}^{-1}$ showing a consistent tendency to yield significantly higher peak temperatures. Various heating and cooling (from 0 to $-70\text{ }^{\circ}\text{C}$) scans with the same sample were also performed. It was clear that if cooling was sufficiently fast to avoid crystallization, the scans were perfectly reversible. However, there was a significant difference in the peak temperatures between heating and cooling scans for all solutions, with the peak temperatures for cooling scans being around $2\text{--}5\text{ }^{\circ}\text{C}$ lower than those for the heating scans. The variation of T_g with the heating rate and the existence of hysteresis (the measurements follow a different path in heating than they do in cooling) stem from the nonexponential nature of structural relaxation, and suitable theories exist to describe these influences (Scherer, 1991) – attention is drawn to Narayanaswamy's work (1971). However, as this is outside the scope of the present work, it was decided to use sufficiently low heating rates to have a negligible effect of this parameter on the measurements and to analyse only the data from heating scans.

A typical DMTA response is shown in Fig. 2, where the influence of the frequency can be well observed. The glass transition is a second-order phase transition and, as such, is influenced by

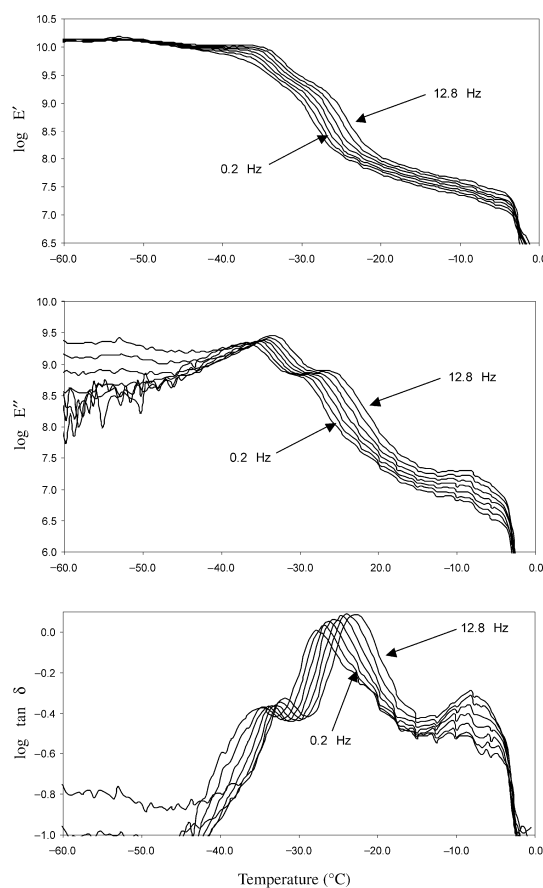


Figure 2 Typical DMTA thermograms (glucose). Curves from left to right indicate the system response for the frequencies of 0.2, 0.4, 0.8, 1.6, 3.2, 6.4 and 12.8 Hz.

frequency, while changes caused by first-order transitions (such as crystallization) should be frequency-independent. Thus, it is clear that the peaks in $\tan \delta$ are indicators of the end of the glass transition and not of T_m .

Figure 3a–e show the plots of the WLF equation for the binary water–sugar matrices. It may be noted from manipulation of equation (1) that, with these co-ordinates, the WLF model is not a straight line, but slightly curved, tending to a straight line as T approaches T'_g and τ/τ_g tends to unity. The values of T'_g , assuming the relaxation time at the glassy state (τ_g) to be 100 or 1000 s, are indicated as dashed horizontal lines. As can be seen, the value measured at 0.1 Hz is an outlier point in most of the graphs (which was, therefore, not used in the fits). This may be because of the

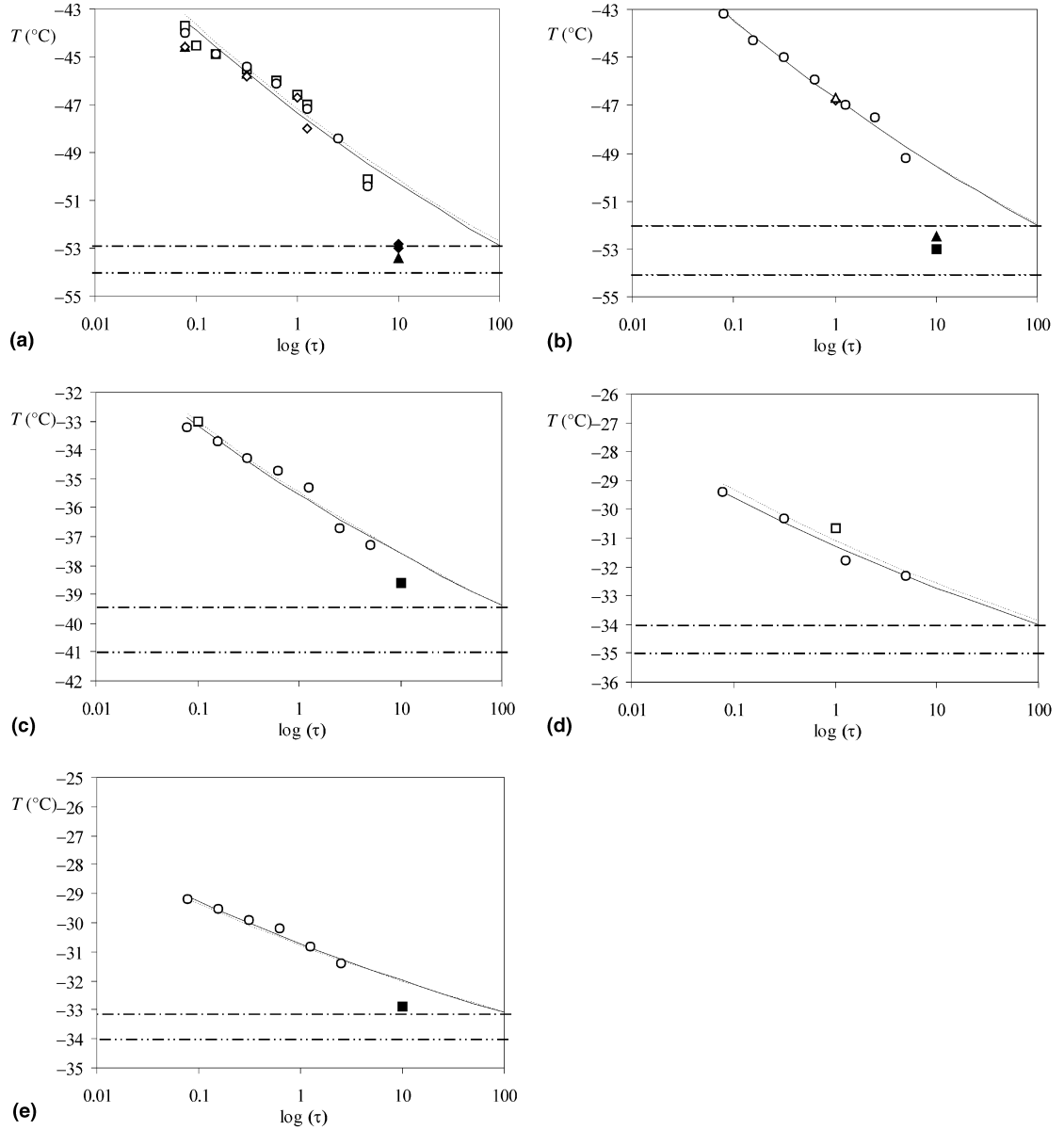


Figure 3 WLF plots of the E'' peak temperatures and model fit for $C_1 = 16$ and $\tau_g = 100$ s (solid line) or $\tau_g = 1000$ s (dashed line) for binary (water-sugar) matrices. Open symbols indicate points used in the model regression, while closed symbols were considered outliers. Different symbols correspond to replicate samples. The top horizontal dashed line indicates the T'_g estimated by the model regression for $\tau_g = 100$ s (solid line), and the bottom horizontal line the T'_g for $\tau_g = 1000$ s. (a) fructose; (b) glucose; (c) sucrose; (d) maltose; (e) lactose.

equipment precision, as the temperature at that frequency is already close to T'_g (it can be seen in Fig. 2 that as the frequency decreases, the peak in E'' becomes more imperceptible). However, the impact of the τ_g value is small, as in the range of

interest (100–1000 s), the resulting T'_g varies generally by < 2 °C. Figure 4 shows the pooled data for the sugar mixtures tested. The WLF parameters obtained by fixing C_1 at 16 and τ_g at 100 or 1000 s are shown in Table 1.

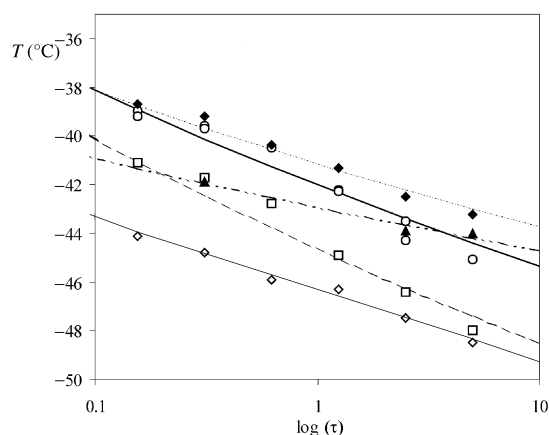


Figure 4 The WLF plots of the E'' peak temperatures and model fit for $C_1 = 16$ and $\tau_g = 100$ s for sugar mixtures. \circ : fructose + lactose; \diamond : glucose + fructose; \blacklozenge : glucose + lactose; \blacktriangle : glucose + maltose; \square : gluc. + fruct. + lact.

The Arrhenius equation could also be fitted to the data with similar success, in agreement with the findings of MacInnes (1993) for sucrose, as all frequencies were below 20 Hz. Again, the lower point at 0.1 Hz is generally an outlier. Figure 5 shows the Arrhenius plots for the E'' peak temperatures, and Fig. 6 those of the peak $\tan \delta$ temperatures for the binary water–sugar matrixes. The Arrhenius parameters are shown in Table 2.

It is interesting to note that the activation energies of the binary water sugar matrixes for the E'' peak temperatures are not statistically different from those for the peak $\tan \delta$ temperatures. This is another indication that $\tan \delta$ peaks may be taken as measurements of the endset of the glass

transition. However, curiously, this cannot be said for all the sugar mixtures.

It is noteworthy that for the binary water–sugar matrixes, C_2 decreases with increasing T'_g (inversely, E_a increases with T'_g in the Arrhenius model). This indicates that generally, the sugars with higher T'_g showed a higher sensitivity to temperature. Such a relationship was not clear in the sugar mixtures.

It is important to compare the values obtained here with those reported in the literature. Because of the application of slightly different concepts and nomenclature, there is some confusion in data collected from the literature; some authors indicate T_g as the onset temperature, others as the midpoint, still others as the endset, or close to the endset; some authors designate a T'_m that is above T'_g and maybe even above the endset of the glass transition, while others say that T'_m is no more than the end of the glass transition. An emerging consensus points to the use of T'_m as T'_g , the critical temperature below which a food matrix is stable, regardless of whether this does indeed correspond to a glass transition parameter or not (Slade & Levine, 1995). The most relevant data collected from the literature are shown in Table 3. The data were pooled according to their overall consistency – some authors (e.g. Slade & Levine, 1991) designated simply as T'_g values which were included in Table 3 as endset, by comparison with the results of other authors that distinguished between onset, midpoint and endset or T'_m . It is evident that there is no significant difference between T'_m and endset of the glass transition. The authors who distinguished between endset and T'_m obtained values for the latter that are

Table 1 Glass transition temperature (T'_g) and system constant C_2 for maximally freeze-concentrated aqueous solutions (obtained by WLF fitting)

Solids	C_2	C_2	T'_g (°C)	T'_g (°C)
	$\tau_g = 100$ s	$\tau_g = 1000$ s	$\tau_g = 100$ s	$\tau_g = 1000$ s
Fructose	39 ± 5	34 ± 4	-52.9 ± 0.8	-55.0 ± 0.9
Glucose	37 ± 2	32 ± 2	-52.0 ± 0.3	-54.1 ± 0.4
Sucrose	27 ± 2	24 ± 2	-39.4 ± 0.4	-41.0 ± 0.5
Maltose	19 ± 4	17 ± 3	-34.0 ± 0.6	-35.0 ± 0.8
Lactose	17 ± 2	14 ± 1	-33.1 ± 0.3	-34.0 ± 0.4
Glucose 50%–Fructose 50%	35 ± 2	28 ± 2	-51.4 ± 0.4	-52.8 ± 0.5
Glucose 50%–Lactose 50%	34 ± 3	29 ± 2	-46.0 ± 0.5	-47.9 ± 0.6
Fructose 50%–Lactose 50%	44 ± 4	38 ± 3	-48.3 ± 0.6	-50.8 ± 0.8
Glucose 50%–Maltose 50%	23 ± 2	20 ± 2	-46.2 ± 0.3	-47.5 ± 0.4
Glucose 33%–Fructose 33%–Lactose 33%	51 ± 5	44 ± 5	-51.9 ± 0.9	-55 ± 1

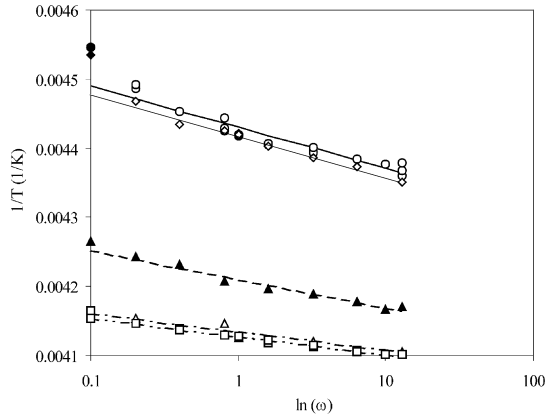


Figure 5 Arrhenius plots of the E'' peak temperatures for the binary (water-sugar) matrices. Closed symbols indicate outliers. ○: fructose; ◇: glucose; ▲: sucrose; △: maltose; □: lactose.

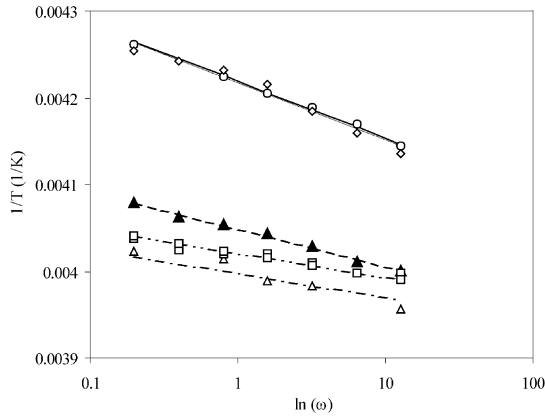


Figure 6 Arrhenius plots of the $\tan \delta$ peak temperatures for the binary (water-sugar) matrices. ○: fructose; ◇: glucose; ▲: sucrose; △: maltose; □: lactose.

close to what other authors indicated as endset of the glass transition. There is quite some variation among published data on the endset of the glass transition, reaching as much as 10 °C, which is most likely because of not only the different measuring methods, but also the different ways of treating and interpreting the data, even when the method (mostly DSC) is the same.

The T_g' values obtained in this work, whether from the WLF or Arrhenius models, with a relaxation time of 100 s, are very close to the midpoint values in the existing literature (mostly from Roos, Karel and co-workers), being at least 2–3 °C lower than what some other authors

designated as the glass transition temperature. The $\tan \delta$ peak temperature for a relaxation time of 100 s seems to be a good measurement of the endset of the glass transition, falling in the lower range of literature values shown in Table 3, close to those suggested by Slade & Levine (1991), except for maltose, where the value obtained here is about 3 °C lower.

The results obtained for sugar mixtures permit an important test: the applicability of the Gordon–Taylor equation to predict the glass transition temperature of sugar mixtures, or to estimate C_g' , just like the WLF equation was used to estimate T_g' from the DMTA data. This is an interesting option because the experimental determination of C_g' is also complex and not at all straightforward, because of the difficulty in estimating accurately the exact amount of ice that exists at maximum cryo-concentration. Reid *et al.* (1993) have discussed this subject clearly and the limitations of existing methods. With a more correct approach, albeit based on a hypothetical procedure, they obtained values of C_g' around 79–80%, while earlier literature references suggested values around 53–65%, because of an apparent underestimation of the ice content. It is important to note that if C_g' is estimated from the value of concentration where T_g equals T_g' , combining the data presented by Roos & Karel (1991) with those of Noel *et al.* (1996) (for maltose), Chan *et al.* (1986) (for glucose), Ablett *et al.* (1993a) (for fructose) and Roos (1995) (for sucrose), also yields C_g' values around 79–81% for these sugars. Roos & Karel (1993) also considered, from various studies, that the maximum cryo-concentration of sugar solutions is around 80%. Values between 78 and 81% were reported for malto-oligomers by Ablett *et al.* (1993b).

By manipulation of equation (3), the maximum cryo-concentration for each solution can be determined from the glass transition temperatures of the pure sugars, water and the k values. From the Couchman–Karasz concept, equation (3) could be generalized for ternary solutions, as

$$T_{g(i+j)} = \frac{wT_{g(\text{water})} + x_i(T_{gi}/k_i) + x_j(T_{gj}/k_j)}{w + (x_i/k_i) + (x_j/k_j)} \quad (4)$$

where i and j represent any two sugars, x_i and x_j are the mass fractions, k_i and k_j the Gordon–Taylor parameters of equation (3) for each sugar,

Table 2 Arrhenius parameters of the average molecular relaxation times and $\tan \delta$ peaks for maximally freeze-concentrated sugar solutions

Solids	T_{p1} (°C) ($\omega = 1$ Hz)	E_{ag} (kJ mol ⁻¹ × 0.1)	$T_{\delta 1}$ (°C) ($\omega = 1$ Hz)	$E_{a\delta}$ (kJ mol ⁻¹ × 0.1)
Fructose	-47.3 ± 0.1	33 ± 2	-35.9 ± 0.1	30 ± 2
Glucose	-46.7 ± 0.1	31 ± 1	-35.9 ± 0.1	28 ± 3
Sucrose	-35.5 ± 0.1	46 ± 3	-26.0 ± 0.1	44 ± 4
Maltose	-31.2 ± 0.2	69 ± 9	-22.8 ± 0.2	68 ± 8
Lactose	-30.7 ± 0.1	78 ± 6	-24.2 ± 0.1	70 ± 8
Glucose 50%–Fructose 50%	-46.4 ± 0.1	36 ± 2	-35.0 ± 0.1	36 ± 2
Glucose 50%–Lactose 50%	-41.1 ± 0.1	36 ± 2	-30.4 ± 0.2	39 ± 3
Fructose 50%–Lactose 50%	-42.0 ± 0.2	28 ± 2	-30.5 ± 0.2	40 ± 4
Glucose 50%–Maltose 50%	-42.9 ± 0.1	53 ± 5	-32.2 ± 0.3	33 ± 4
Glucose 33%–Fructose 33%– Lactose 33%	-44.5 ± 0.3	23 ± 2	-32.4 ± 0.3	41 ± 2

Manipulating equation (2), the Arrhenius model for the E'' peak temperatures is $\frac{1}{T} = \frac{1}{T_{p1}} - \frac{R \ln \omega}{E_{ag}}$, where T_{p1} is the E'' peak temperature at the input frequency of 1 Hz, E_{ag} is the activation energy, R is the ideal gas constant and ω is the input frequency. Similarly, the Arrhenius model for the $\tan \delta$ peak temperatures is $\frac{1}{T} = \frac{1}{T_{\delta 1}} - \frac{R \ln \omega}{E_{a\delta}}$, where $T_{\delta 1}$ is the E'' peak temperature at the input frequency of 1 Hz and $E_{a\delta}$ is the activation energy.

Table 3 Temperatures (°C) extrapolated by Arrhenius and WLF models to a relaxation time of 100 s and glass transition temperatures reported in the literature

Solids	Arrhenius peak E''	WLF, T_g	Arrhenius peak $\tan \delta$	Literature			
				Onset	Midpoint	Endset	T_m
Fructose	-53.2	-52.9	-43.1	-57 ²	-53 ²	-50 ² -48 ^{13,14} -43 ⁵ -42 ^{1,7}	-46 ²
Glucose	-52.6	-52.0	-43.0	-57 ²	-53 ²	-50 ² -44 ⁹ -43 ^{7,10} -40 ⁵	-46 ²
Sucrose	-40.1	-39.4	-31.3	-46 ^{2,8,16} -49 ^{11,12}	-40 ^{2,8,13}	-37 ¹¹ -36 ² -35 ^{8,9,12} -34 ¹ -32 ^{5,6,7,15}	-32 ²
Maltose	-34.2	-34.0	-26.3	-42 ^{2,3}	-37 ² -35 ³	-32 ^{1,2} -31 ³ -30 ⁷ -29 ⁵	-32 ² -29 ³
Lactose	-33.8	-33.1	-27.7	-41 ²	-36 ² -33 ⁴	-30 ² -28 ⁷	-30 ²

Literature references: ¹Kerr *et al.* (1993), ²Roos & Karel (1995), ³Roos & Karel (1991), ⁴Her *et al.* (1994), ⁵Wang & Jane (1994), ⁶Schenz *et al.* (1993), ⁷Slade & Levine (1991), ⁸Karel *et al.* (1994), ⁹Kerr & Reid (1994), ¹⁰Maurice *et al.* (1991), ¹¹Blond *et al.* (1997), ¹²Shalaev & Franks (1995), ¹³Ablett *et al.* (1993a), ¹⁴Carrington *et al.* (1996), ¹⁵Levine & Slade (1989), ¹⁶Roos (1995).

and T_{gi} and T_{gj} the glass transition temperatures of the pure sugars. It is noted that in the present case, as the sugars are mixed in equal parts, $x_i = x_j = (1 - w)/2$. A similar equation can be written for the quaternary solution.

Table 4 shows the values obtained. It can be seen that the T'_g values experimentally determined for the sugar mixtures are very consistent with the literature data concerning the Gordon–Taylor equation for the binary sugar–water

Table 4 Maximum cryo-concentrations estimated from the Gordon–Taylor equation (T'_g in °C, C'_g in weight percentage – $g_{\text{solids}}/100 g_{\text{solids}} + \text{water}$)

Sugar	Binary sugar solutions				Solutions of sugar mixtures		
	$k^{(L)}$	$T_g^{(L)}(\text{dry})$	$T_g^{(\text{exp})}$	$C_g^{(\text{eq})}$	Mixture	$T_g^{(\text{exp})}$	$C_g^{(\text{eq})}$
Fructose	3.70 ¹	16 ²	–52.9	81.5	Glucose 50%–Fructose 50%	–51.4	81.1
Glucose	4.52 ¹	38 ³	–52.0	80.7	Glucose 50%–Lactose 50%	–46.0	81.3
Sucrose	5.42 ¹	70 ³	–39.4	82.6	Fructose 50%–Lactose 50%	–48.3	80.9
Maltose	6.15 ¹	95 ³	–34.0	82.8	Glucose 50%–Maltose 50%	–46.2	81.0
Lactose	6.56 ¹	101 ⁴	–33.1	83.3	Glucose 33%–Fructose 33%– Lactose 33%	–51.9	79.7

^(L) Obtained from the literature (references indicated according to legend below);

^(exp) Experimental (from the WLF equation for $\tau_g = 100$ s);

^(eq) Estimated from the Gordon–Taylor equation;

Literature references: ¹Roos (1995), ²Simatos *et al.* (1996) (midpoint), ³Orford *et al.* (1990), ⁴Loyd *et al.* (1996).

matrices. Curiously, the C'_g values obtained from equation (3) for the disaccharides are slightly higher. The C'_g values of the ternary matrices differ by <1–2% from the arithmetic average of C'_g of the individual sugars used, while the quaternary solution shows a slightly larger deviation (2.6%).

Conclusions

The E'' peaks from DMTA measurements show a frequency dependence that is coherent with their interpretation as a resonance point. By application of the WLF equation to data obtained at several frequencies, the values of T'_g for several sugar solutions were obtained, being similar to literature values for the glass transition midpoint. The $\tan \delta$ peaks could also be related to the endset of the glass transition given in the literature. In both cases, this good agreement suggests average molecular relaxation times around 100 s. The data for sugar mixtures were very consistent with the application of the Gordon–Taylor equation, indicating maximum cryo-concentrations around 80–83% for the various matrices studied. This suggests the adequacy of using the glass transition temperatures determined with the WLF equation (corresponding to the DSC midpoint) in quantitative analysis of the glass transition.

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