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Effect of molecular structure and water content on the dielectric relaxation behaviour of amorphous low molecular weight carbohydrates above and below their glass transition

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Abstract

The dielectric relaxation behaviour of several amorphous low molecular weight carbohydrates and their 10% w/w water mixtures has been studied in the supercooled liquid and glassy regions in the frequency range 100 Hz to 100 kHz. The dry carbohydrates show a primary α-relaxation (activation energy 250–405 kJ mol^{-1}) at temperatures above the calorimetric glass transition temperature, T_g, and, in most cases, a secondary β-relaxation (activation energy 42–55 kJ mol^{-1}) at sub-T_g temperatures. Whilst D-mannose showed a β-relaxation similar in strength to D-glucose, its deoxy sugar, L-rhamnose showed a relatively weak β-relaxation. This indicates that the hydroxymethyl group influences relaxation in carbohydrate glasses. Addition of water shifted the α-relaxations to lower temperatures and increased the strength of the β-relaxations. In glucitol this resulted in a merging of the α- and β-relaxations. The β-relaxation increased in strength and decreased in temperature for the series of water mixtures: D-glucose, maltose, and maltotriose.

Keywords: Dielectric relaxation; Glass transition; Water; Mixtures

1. Introduction

Glassy carbohydrates are used in the encapsulation and stabilisation of labile food ingredients [1], therapeutic proteins [2] and pharmaceuticals [3]. Carbohydrate glasses also occur in seeds, pollen and in the dormant states of desiccation-resistant organisms where they are thought to play a similar protective role [4–6]. It has been hypothesised that low water content amorphous carbohydrates stabilise labile species by a reduction in the mobility of reactants, such that reaction rates are negligible over the appropriate time scales [7]. The molecular basis of the kinetics of this behaviour depends upon molecular dynamics in low water content amorphous carbohydrates.

Recent studies of molecular dynamics in low water content amorphous carbohydrates using dielectric, mechanical [8] and NMR relaxation techniques [9,10] show several features in common with other polyhydric alcohols such as glycerol and glucitol, and with glass-forming materials in general. Some motions give rise to frequency-dependent

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dielectric and mechanical properties [8]. In particular, the main structural, primary or α-relaxation gives rise to a loss peak, characterised by a peak relaxation time τ_{max} ($=1/2\pi f_{max}$), which, as the material is cooled through the supercooled region, deviates from Arrhenian behaviour according to the Vogel–Tamman–Fulcher (VTF) equation, $\tau_{max} = A\exp(B/(T-T_0))$ (Fig. 1). At temperatures below the calorimetric glass transition temperature, T_g, the peak relaxation time exceeds experimental time scales (10^2–10^4 s [8,11]) and non-equilibrium glassy states occur. Further secondary or β-relaxations are observed at temperatures close to T_g and in the glassy state [8,12]. The relaxations typically occur over a wide temperature range and have an Arrhenian temperature dependence, $\tau_{max} = A\exp(E_a/RT)$ (Fig. 1).

The relationship between molecular motion and the β-relaxation is somewhat controversial. Johari and Goldstein [13] proposed that the β-relaxation was a universal feature of glasses arising from low-density regions of enhanced mobility. However, recent measurements on glucitol have found no evidence for inhomogeneity [14] though, in common with Johari and Goldstein, these authors maintain that the relaxation does not involve intramolecular degrees of freedom [15]. In contrast, Gangasharan and Murthy [16] rationalise the β-relaxation behaviour of a range of polyhydric alcohols and sugars in terms of the segmental rotations of the linear chain and open ring forms of these molecules. Faivre et al. [8] maintain that both intermolecular and intramolecular interactions contribute to the β-relaxation. To summarise, a fully coherent view of the molecular origin of the β-relaxation is yet to emerge.

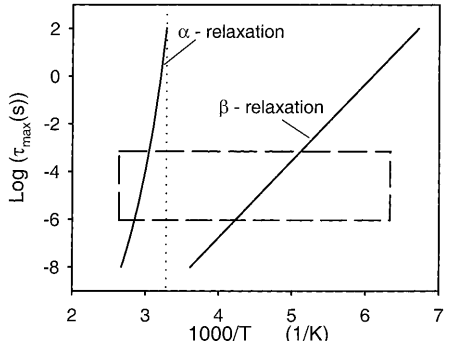

Fig. 1. Schematic showing effect of temperature on peak relaxation times observed in a typical amorphous carbohydrate. Calorimetric glass transition (dotted line) corresponds to a peak relaxation time, $\tau_{max} \sim 100$ s [11]. Dashed box encloses what is observable in a restricted temperature–frequency window.

The aim of the present work is to study the effect of carbohydrate structure on the molecular dynamics in a range of amorphous carbohydrates and their 10% w/w water mixtures through measurements of dielectric relaxation at temperatures above and below T_g. Dielectric relaxation studies readily yield information on mobility within the glassy state, in particular, the β-relaxation process. This extends previous work on dry amorphous carbohydrates [12,16–18]. D-Mannose and L-rhamnose were included to allow a comparison of both a series of hexoses (D-glucose, D-fructose, D-mannose, L-rhamnose) and also between a sugar and its deoxy-sugar (D-mannose, L-rhamnose). L-Rhamnose differs from D-mannose in that C-6 is a methyl group rather than a hydroxymethyl group. The present work extends studies of water mixtures beyond the results for D-glucose and maltose which have previously been reported [17,18] to include other hexoses, a pentose (D-xylose) and a hexitol (glucitol).

2. Experimental

Materials.—D-Glucose, D-fructose, D-mannose, L-rhamnose monohydrate, D-xylose, D-glucitol, maltose monohydrate and maltotriose were purchased from Sigma Chemical Co. (Poole, UK) and used without further purification. All except L-rhamnose and maltotriose were of SigmaUltra grade. Water was obtained from a water purification system (Elgastat Maxima, Elga, High Wycombe, UK) with a conductivity < 1 μS m^{-1}. Dry amorphous samples of L-rhamnose and maltose were prepared by melting the crystalline monohydrates and drying in a vacuum oven over P_2O_5 at 60 °C for 24 h. Other materials were prepared directly from the dry solids and water, as appropriate, as described previously [12].

Table 1
Calorimetric glass transition temperature (T_g) and α- and β-dielectric relaxation peak parameters at 1 kHz for dry amorphous carbohydrates and their 10% w/w water mixtures

	T_g (K)	T_α (K)	Tan δ_{max}	T_β (K)	Tan δ_{max}
Dry carbohydrates					
D-Glucose	312	333	0.24	211	0.037
D-Fructose	284	315	0.26	223	0.045
D-Mannose	311	333	0.28	210	0.036
L-Rhamnose	310	331	0.32	203 [a]	0.017 [a]
D-Xylose	283	304	0.34	[b]	[b]
Glucitol	271	289	0.27	243 [c]	0.082 [c]
Maltose	370	376	0.11	223	0.062
10% w/w water mixtures					
D-Glucose	256	278	0.24	230	0.064
D-Fructose	249	270	0.25	226	0.070
D-Mannose	258	280	0.27	227	0.058
L-Rhamnose	262	282	0.31	216	0.042
D-Xylose	244	263	0.33	[b]	[b]
Glucitol	240	257	0.27	[b]	[b]
Maltose	280	305	0.17	218	0.098
Maltotriose	292	[b]	[b]	208	0.125

[a] Measured at 100 kHz.
[b] Peak not observed.
[c] Measured at 400 Hz.

Glass transition temperatures.—The glass transition temperatures of the amorphous carbohydrates were determined using a Perkin–Elmer DSC2 to measure heat capacity at a heating rate of 10 °C min^{-1} as described previously [19]. T_g was taken to be the temperature at which the heat capacity was midway between the values in the liquid and glassy states measured during a rescan [20]. Duplicate samples of each material were analysed.

Dielectric spectroscopy.—Dielectric measurements were made using a dielectric thermal analyser (Rheometrics Scientific, Loughborough, UK) equipped with a General Radio 1689M Precision RLC Digibridge and stainless steel parallel plate cell (diameter 33 mm, typical gap 0.5 mm) as described previously [12]. Before sample cooling the chamber enclosing the sample cell was purged with nitrogen gas to remove moist air and, for the dry samples, a small container of P_2O_5 was introduced into the chamber. Duplicate samples of each material were analysed.

3. Results and discussion

Glass transition temperatures.—The calorimetric glass transition temperatures of the dry amorphous carbohydrates and their 10% w/w water mixtures are given in Table 1. The values for the dry carbohydrates are similar to previous measurements [21,22] with the exception of L-rhamnose which is higher than previous values, a difference which is probably due to improved drying procedures in the present study. The addition of 10% w/w water depresses T_g (in K) by 11–18% for the monosaccharides and the alditol, by 24% for the disaccharide and by 27% for the trisaccharide (T_g for dry maltotriose is 404 K [23]). This is the well-known plasticisation effect [7,17,23].

Dielectric relaxation behaviour.—The variation of tan δ with temperature, at a frequency of 1 kHz, is shown in Figs. 2 and 3 for the dry carbohydrates. For all the carbohydrates a peak in tan δ was observed at a temperature typically 20 °C above the calorimetric T_g, this is the dielectric α-relaxation. The calorimetric and dielectric techniques probe the same α-relaxation process though shifted in temperature

according to the different relaxation times to which they respond (Fig. 1 and Section 1). The temperature of the peak ($\partial \tan\delta/\partial T = 0$), T_α, and its magnitude, $\tan\delta_{max}$, are given in Table 1. For most of the carbohydrates the ratio $T_\alpha/T_g \sim 1.07$ indicating that the dielectric relaxation time scales with the calorimetric T_g [11]. The ketose, D-fructose, behaves differently with $T_\alpha/T_g \sim 1.11$ which is probably associated with its different isomerisation behaviour [24,25]. The main difference in the magnitudes of the α-relaxation $\tan\delta$ peaks is between the monosaccharides which are in the range 0.24–0.34 and the disaccharide, maltose, which is very much weaker at 0.11 (Table 1).

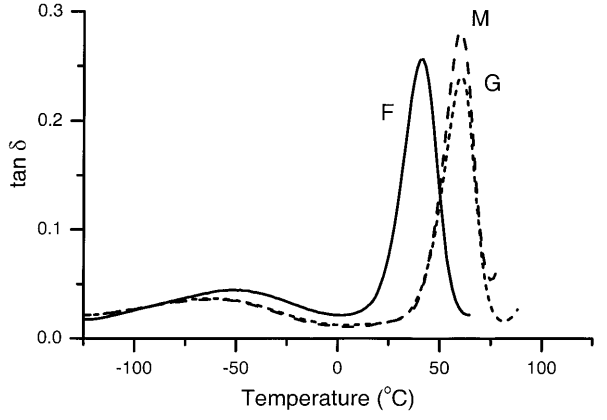

Fig. 2. The variation of $\tan\delta$ with temperature at 1 kHz for dry amorphous hexoses. G, D-glucose; M, D-mannose; F, D-fructose.

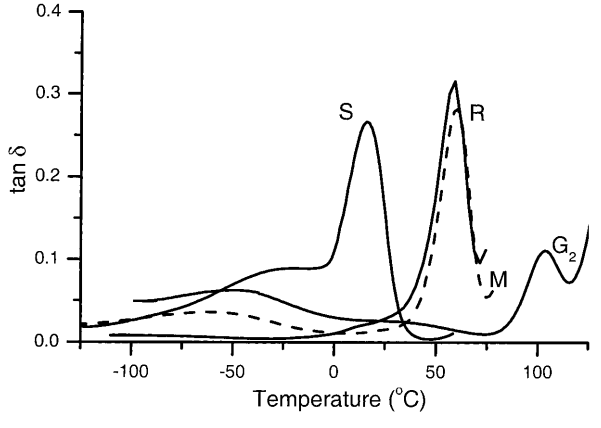

Fig. 3. The variation of $\tan\delta$ with temperature at 1 kHz for dry amorphous carbohydrates. S, glucitol; R, L-rhamnose; M, D-mannose; G_2, maltose.

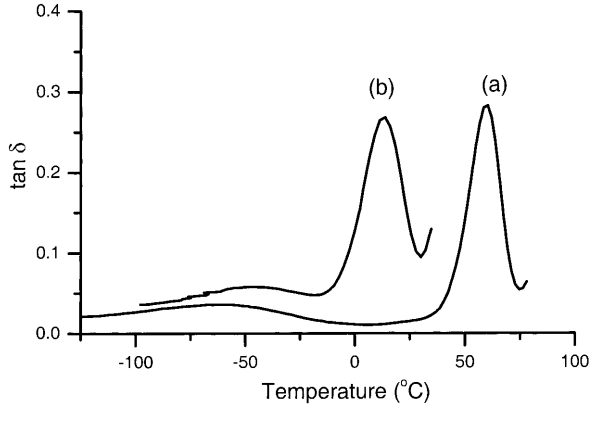

Fig. 4. Comparison of the variation of $\tan\delta$ with temperature at 1 kHz for (a) amorphous D-mannose and (b) its 10% w/w water mixture.

At temperatures below the calorimetric T_g, β-relaxation peaks were observed for all carbohydrates except D-xylose. For the hexoses (Fig. 2) these occur between 90 and 125 °C below the α-relaxations and, as with the α-relaxation, there is greatest similarity between the aldoses, D-mannose and D-glucose. The deoxy sugar (L-rhamnose), alditol (glucitol) and disaccharide (maltose) (Fig. 3) show a wider range of β-relaxation behaviour. For the deoxy sugar, L-rhamnose, the $\tan\delta$ peak was only discernible at the higher frequency of 100 kHz and was weak, with a peak value which is less than half that of D-mannose. In contrast to the hexoses, the β-relaxation of glucitol shows extensive overlap with the α-relaxation, a distinct peak only showing at lower frequencies ($\tan\delta$ peak position at 400 Hz shown in Table 1). Despite its higher T_g the strongest sub-T_g relaxation process of maltose occurs at similar temperature to the monosaccharides. Close examination of the maltose $\tan\delta$ scan (Fig. 3) shows signs of a weaker relaxation process at about 40 °C and so it is not clear whether it is correct to designate the stronger relaxation as the β-relaxation. The temperature, T_β, and magnitude, $\tan\delta_{max}$, of all the β-peaks at 1 kHz are summarised in Table 1. For the mono- and disaccharides (i.e., excluding glucitol) there is an inverse relationship between the $\tan\delta$ peak heights of the α- and β-relaxations e.g., L-rhamnose has the largest α-relaxation peak and the smallest β-relaxation peak and vice versa for maltose.

The effect of the addition of 10% w/w water on the dielectric response is to shift the α-relaxation peak to lower temperatures and increase the strength of the β-relaxations (Table 1 and Figs. 4–7). For all the carbohydrate–

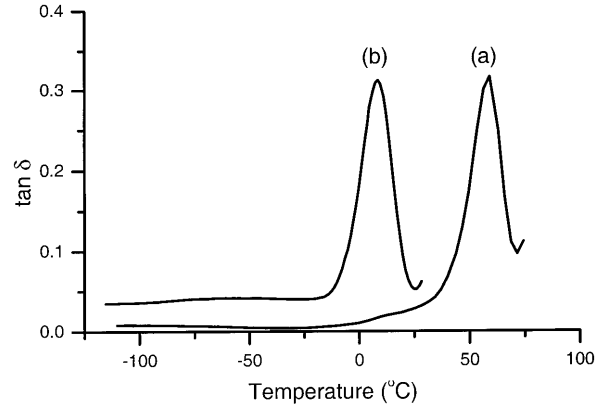

Fig. 5. Comparison of the variation of tan δ with temperature at 1 kHz for (a) amorphous L-rhamnose and (b) its 10% w/w water mixture.

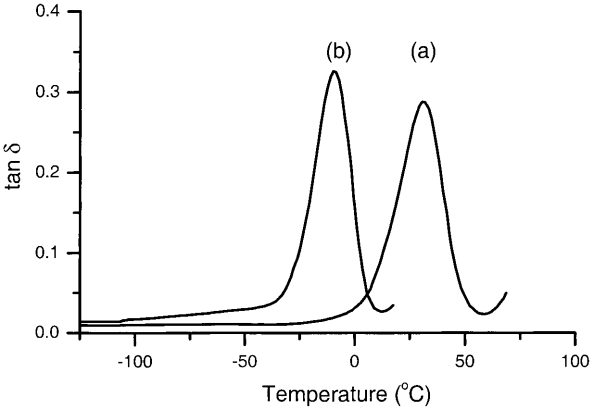

Fig. 6. Comparison of the variation of tan δ with temperature at 1 kHz for (a) amorphous D-xylose and (b) its 10% w/w water mixture.

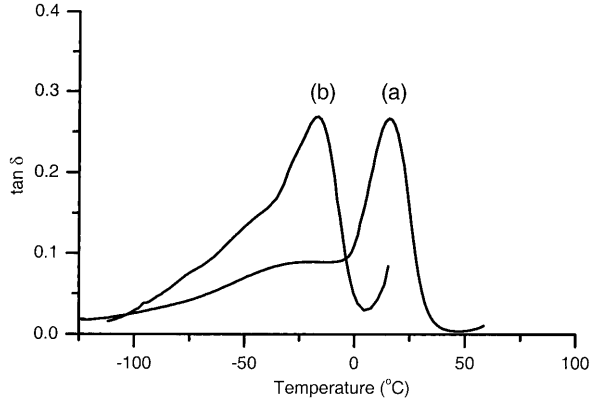

Fig. 7. Comparison of the variation of tan δ with temperature at 1 kHz for (a) amorphous glucitol and (b) its 10% w/w water mixture.

water mixtures the ratio T_α/T_g is in the range 1.07–1.09, indicating that the dielectric α-relaxations scale with the calorimetric T_g and that all the mixtures behave similarly. It follows that the shift in the temperature of the dielectric α-relaxation peak with added water has the same origin as the depression of the calorimetric T_g and is a result of plasticisation [7,17,23]. Fig. 8 shows the trend in the β-relaxations (-100 to -25 °C) for the series of water mixtures (10% w/w): D-glucose, maltose, maltotriose. With the addition of water the α-relaxation loss peak of maltose and maltotriose is obscured by conduction swamping the dielectric relaxation and so at the highest temperatures ($T > 25$ °C) only a steady increase in tan δ due to conduction is observed [19]. Conduction does not affect the β-relaxation, which increases in magnitude with increasing degree of polymerisation.

With the relatively narrow frequency range used in this study the variation of $\log f_{max}$ with $1/T$ is linear, corresponding to (apparent) Arrhenian behaviour, $f_{max} = A \exp(-E_a/RT)$, for both the α- and β-processes and the values of $\log A$ and E_a are given in Table 2 for the dry carbohydrates and their water mixtures. The activation energies of the α-relaxations vary over the range 205–405 kJ mol^{-1} which is typical for amorphous carbohydrates observed over this frequency range [12,18]. The activation energies increase linearly with T_α, with the exception of the glucitol–water mixture, which appears to have a relatively high activation energy. However, this linear variation largely disappears when temperature is scaled with T_α and so the α-relaxations would lie close to a single curve on a scaled-Arrhenius plot [11]. The activation energies of the β-relaxations are relatively small, lying in the

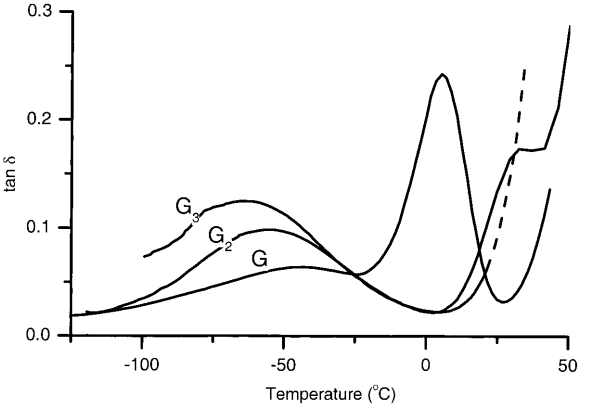

Fig. 8. The variation of tan δ with temperature at 1 kHz for amorphous carbohydrate–water mixtures (10% w/w). G, D-glucose; G_2, maltose; G_3, maltotriose.

Table 2
Arrhenius parameters for the α- and β-dielectric relaxation peaks

	α-Relaxation		β-Relaxation	
	Log A	E_a (kJ mol^{-1})	Log A	E_a (kJ mol^{-1})
Dry carbohydrates				
D-Glucose	51.7	320	13.5	42
D-Fructose	51.0	290	13.1	43
D-Mannose	49.5	295	14.4	46
L-Rhamnose	53.9	320	[a]	[a]
D-Xylose	45.1	250	[a]	[a]
Glucitol	52.5	275	14.0	55 [b]
Maltose	59.5	405	13.8	45
10% w/w water mixtures				
D-Glucose	44.2	220	16.1	59
D-Fructose	46.7	225	15.0	49
D-Mannose	47.4	240	15.6	52
L-Rhamnose	46.9	235	8.5	17 [c]
D-Xylose	44.1	205	[a]	[a]
Glucitol	69.6	330	[a]	[a]
Maltose	53.5	295	18.0	62
Maltotriose	[a]	[a]	16.0	52

[a] Activation energy not determined.
[b] Data only 100 Hz to 1 kHz.
[c] Data only 400 Hz to 4 kHz.

range 42–62 kJ mol^{-1} (as observed previously [12]) with the exception of the L-rhamnose–water mixture which is lower. Wider frequency range studies are needed to show that the α-relaxation process is non-Arrhenian [8,16,17] as illustrated in Fig. 1. Similarly wider frequency and temperature studies are required to detect the weakest β-relaxations e.g., those in D-xylose [16].

The observation of β-relaxations in these different carbohydrate glasses shows that, as in other glass-forming materials, the occurrence of residual mobility is the common behaviour. This study shows that the nature of these β-dielectric relaxations, the temperature at which they occur and their magnitude, depends sensitively upon carbohydrate structure. Previous comparisons of D-glucose and D-xylose [18] and the present comparison of D-mannose and L-rhamnose (Fig. 3) indicate that the presence of a pendant group, and its structure (hydroxymethyl or methyl), influences these relaxation processes. Interpretation of the origin of these relaxation processes, in terms of molecular motions, solely on the basis of dielectric measurements is controversial and will not be attempted. As noted in the introduction, the relative contributions of intramolecular and intermolecular interactions to the β-relaxations is a matter of debate. NMR techniques [9,10] show some promise in resolving this situation. For example, ^{2}H NMR T_1 and T_2 measurements on deuterated glucose–water mixtures [9] yield correlation times ~ 30 μs at T_g which are similar to the β-relaxation times measured using dielectric spectroscopy [17].

One complication when interpreting the relaxation behaviour of sugars is their isomerisation. Both pyranose:furanose and α:β equilibria exist [26]. In dielectric experiments the occurrence of pyranose:furanose isomerisation which gives rise to a more extensive structural rearrangement is likely to be the more important. Only the isomerisation of D-glucose [27–29] and D-fructose [24,25] have been studied in their dry amorphous states. For D-glucose only pyranose forms are reported and, after melting either the α- or β-forms of the crystals, anomeric equilibrium is established within 15 min with α:β ratio being stated as 0.792 [28] and 0.47 [29]. In the present study the crystalline D-glucose comprised mixed anomers and so a shorter equilibration time can be expected. For D-fructose, after melting the β-pyranose crystals, different compositions result depending on subsequent temperature history with melted material containing up to 46% of the furanose forms though reducing to 29% in samples annealed at 25 °C for 48 h [24,25]. The presence of a proportion of furanose isomers may be the reason for the different relaxation behaviour of D-fructose as compared with D-glucose and D-mannose.

The observation of diverse dipolar relaxation behaviour in carbohydrate glasses may have implications for the practical stabilisation of labile species in these materials [3]. It is commonly assumed that deteriorative reactions are strongly coupled to the α-relaxation process, however, as the present study shows, motions exist in carbohydrates glasses which give rise to β-relaxations and it may be these

motions which are coupled to the chemical reactions of interest.

Acknowledgements

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