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Molecular mobility and ageing of sugar glasses

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Abstract

Carbohydrates play an important role in the stabilization of biological components under water stress and, consequently, in the preservation of foods. Water stress is produced either by freezing or drying producing damage in proteins and tissues mainly due to the generation of large gradients of concentration of salts. Some carbohydrates act as protectors but, although some explanations have been proposed, the mechanism is not yet properly known.

We have measured the dielectric relaxation times of aqueous solutions of glucose in the time domain with a custom made device. Some results are presented here for a solution of glucose in water at 88% w/w, in the range of the glass transition temperature, including some data on the rubbery state (above T_g). The curves were fitted with a stretched exponential decay (KWW) with relaxation times in the range of 200–500s and stretching parameter (β) around 0.5.

Keywords: Sugar glasses; Glasses ageing; Dielectric relaxation

1. Introduction

It is well known that carbohydrates play an important role in the stabilization of biological components under water stress and, consequently, in the preservation of foods. Water stress is produced either by freezing or drying, and proteins and tissues are damaged is mainly due to the generation of large gradients of concentration of salts. Although some explanations have been proposed, the mechanism by which carbohydrates act as protectors is not yet properly known. The protection efficiency is not the same for different carbohydrates, and it may be related with particular properties of the glassy state of the carbohydrate–water solutions.

The dynamics of molecular glasses is relevant to the mentioned problem and has been object of a number of studies, from the theoretical and the experimental point of view (Angel, 1988, 1991; Böhmer & Angell, 1994). Properties of molecular glasses depend on its formation process and the time elapsed from its origin (ageing) (Bouchaud, Cugliandolo, Kurchan, & Mézard, 1998; Grigera, Martin-Mayor, Parisi, & Verrochio, 2004). Among the experimental methods to study the dynamics of glasses, dielectric relaxation is one of the most frequently quoted in the literature; however, due to the large relaxation times present in glasses, most of the reported results referred to the super cooled liquids and just a few are for data below the glass transition temperature (Fujima, Furusawa, & Ito, 2002; Pissisy et al., 1998; Wu & Nagel, 1992) which is essential to be able to follow the ageing process (Jérôme & Commandeur, 1997).

In molecular glasses the relaxation process is usually very different from a Debye process and can be described as a stretching relaxation (Ritcher & Blumen, 1994). To define unambiguously the relaxation time it is necessary either to have broadband frequency coverage or to go to

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enough large times, otherwise the incomplete relaxation process prevents from a precise determination of the actual relaxation time.

A reliable measurement in the frequency domain requires a steady state of the system, which means to wait enough time after the frequency is set. While the instrument response is fast enough to provide stability after one cycle, the delay time of the material properties is much slower in reaching equilibrium after a transient impulse. A common 'rule of thumb' would suggest a waiting time of about ten cycles before measurements. For very low frequencies this is a time consuming procedure. Indeed, assuming a relaxation time of the order of 10^{-3} s, a full measurement requires a time of about 30 days even if only one cycle is inserted between each measurement. Even disregarding that this relaxation time may still be too short for molecular glasses, ageing studies cannot be carried out under these experimental conditions as the elapsed time of the measurements falls within the time in which the sample is structurally modified.

In this work we have used a time domain measurement of dielectric relaxation of glucose/water solutions in the range of the glass transition. We were able to observe the changes in the relaxation time as a function of the ageing time (waiting time, t_w) after the thermal equilibration, detecting two relaxation processes.

2. Experimental

Sample preparation: Analytical grade glucose (PARAFARM) was slowly mixed with double distilled and deionised water at 353 K until complete dissolution. The dissolution process is carried out under nitrogen atmosphere to avoid oxidation. The solution is poured in the sample cell, closed, and then immediately immersed in liquid nitrogen. Samples of the solution are taken for the determination of water content and glass transition temperature. A thermometer on the cell allowed following of the temperature change and when it reached the appropriate value, it was transferred to a regulated cryostat. We have recorded the time elapsed from the immersion into liquid nitrogen up to the time the sample reaches the final temperature; then, we set the reference waiting time ($t_w = 0$) at this point.

The water content was determined by drying up to constant weight. A fine sand coating was used to avoid water occlusion in the large clusters of glucose.

Dielectric measurement: We have measured the dielectric properties in the time domain using a custom made equipment. The basic experiment consists on recording the current discharge of the previously charged sample cell. The experimental setup is quite simple; a variable dc power supply provides the necessary current to charge the cell; after the charge period a commuting switch connects the charged cell to an amplifier that provides a virtual short circuit for the cell and produces a measurable tension (proportional to the current). The tension (and hence the current) of the cell is collected at regular intervals until complete discharge of the cell.

We have used a large volume cell of 450 ml with several rectangular parallel plates of anodized aluminium appropriately connected.

Measurements were carried out by applying a 36 V pulse for 20 min and thereafter following the discharge until the current reached its base line. Then, the measurement was repeated after some time.

3. Results

Fig. 1 shows the experimental data points of the decay of the discharging current versus time for an aqueous solution of glucose 88.15% w/w ($T_g = 258.3$) at 257.6 K at different waiting times, t_w. As indicated in the figure the intensity values are normalised against the initial current.

A first attempt to fit the data with a Kohlrausch–Williams–Watts (KWW) stretched relaxation expression gives a very poor fitting for short times; therefore we include another process selecting a single exponential as:

$$F(t) = ae^{-t/\tau_\beta} + be^{-t/\tau_\alpha}. \quad (1)$$

The short time process may not be correctly described by a single exponential and other more appropriated expression may be used. However, it seems that with the present data it is not possible to go into more details.

The parameters obtained from the curve fitting are shown in Table 1 All the fitting parameters appear to be function of the waiting time. The evolution of τ_α and β are shown in Fig. 2.

At very large times no difference between the curves could be appreciated within the resolution of the method, so we consider that the sample has reached a regime of extremely low evolution.

Fig. 3 shows a series of relaxation curves obtained at different temperatures. All curves are at temperatures above the T_g.

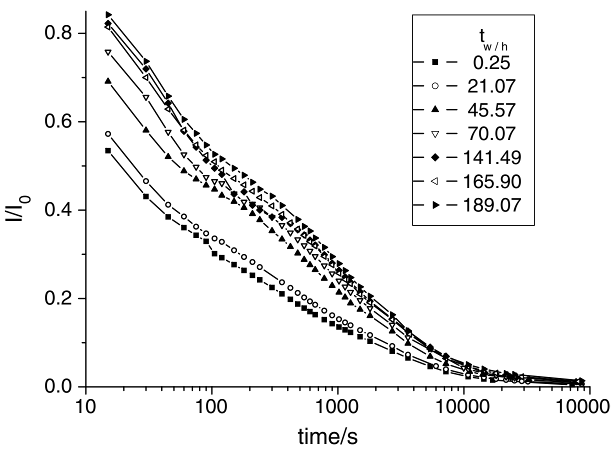

Fig. 1. Normalised discharging current against the time for an aqueous solution of glucose 88.15% w/w; at 257.6 K at different waiting times (indicating in hours). The lines are drawn to guide the eye.

Table 1
Parameters obtained form the curve fitting

t_w/h	a	τ_α/s	β	b	τ_β/s
0.25	0.21	115	0.27	0.06	13.0
21.07	0.19	238	0.30	0.072	14.0
45.57	0.147	763.9	0.43	0.42	13.23
70.07	0.134	1184	0.50	0.08	24.8
141.49	0.124	1641	0.54	0.09	39.29
165.90	0.127	1326	0.63	0.08	30.55
189.07	0.11	1484	0.69	0.08	33.88

The waiting time is indicated as t_w. Other symbols are those indicated in Eq. (1).

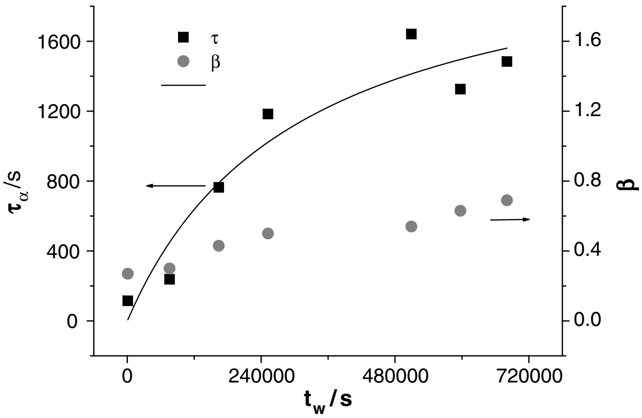

Fig. 2. Evolution of τ_α and β with the waiting time.

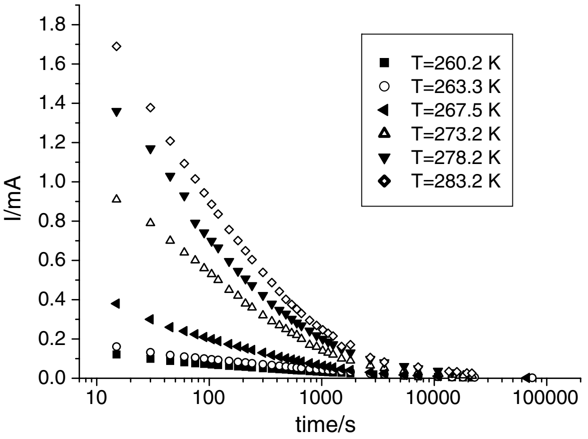

Fig. 3. Relaxation curves at different temperatures. All curves are at temperatures over the T_g.

4. Discussion

From the results of the ageing of the sample below the glass transition temperature we can discriminate between two relaxation processes. The fast one (β process) is not clearly visible at short times after formation but it becomes evident when the ageing process increases. The shifting of the main process to higher relaxation time makes the faster process visible.

It is not easy to assign a very precise relaxation time from the fitting. It may be possible that the ageing will produce a larger stretching than the real one. Such an effect may be suspected since the shorter the waiting time (in which the rate of ageing is faster) the larger the stretching parameter. However, the stretching exponent is always larger than 0.3, which is in agreement with current theories, so we expect that even if the perturbation does exist it will not be of large magnitude. As regards the two relaxation processes, we can see that the relaxation parameters for the main (α) relaxation is three orders of magnitude larger than faster process, which rules out that the observation in the data of two processes was due to a fitting artefact, even if the relaxation times may be affected by some error.

5. Conclusion

We have been able to measure the ageing on the glucose solution in a temperature range close to the glassy state. The measurement system is capable to go to very large relaxation times because the elapsed time of each spectrum is the shortest time needed for complete relaxation. This allows to a direct observation the ageing. Two relaxation processes are detected. The slower one, that shows a stretched relaxation, can be attributed to the structural relaxation while the faster cannot be clearly assigned since the observed variation with the time may be due to the fitting procedure that cannot get a clean separation of both processes. At the larger t_w studied (around six days) is seems that the system has already reached a steady state process.

Acknowledgements

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