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Structural relaxation and physical ageing of starchy materials

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Abstract

The structural relaxation during the ageing of an amorphous maltose and a starch–sorbitol mixture was examined using a range of physical techniques. Heat capacity, measured by differential scanning calorimetry, showed an overshoot in the glass-transition region, the size of which was temperature and time dependent. Volume relaxation measurements were made at different ageing temperatures in the range $T_g - 15$ to -30 K. The volume decreased with increasing ageing time, in an essentially linear fashion with log time. The mechanical behaviour of the materials showed a progressive embrittlement on ageing. For both materials, the mechanical relaxation time increased with ageing, and the material became stiffer. Investigation of the effect of physical ageing on transport properties was also performed using conductivity measurements on a maltose–water–KC1 mixture. A decay in conductivity, which was almost linear with log time, was observed. The structural relaxation was modelled using the Tool–Narayanaswamy approach to describe the calorimetric data. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Starch; Maltose; Glass transition; Physical ageing

1. Introduction

Starch and its hydrolysis products have widespread industrial use, often in low moisture systems where the materials are glassy. In the vicinity of the glass transition, there can be large changes in properties for relatively small changes in temperature. As a polymer in a rubbery state is cooled to a temperature below the calorimetric glass-transition temperature, T_g, the local viscosity of the polymer chain progressively increases, leading to reduced molecular mobility and vitrification. T_g is commonly determined from the sharp change in heat capacity occurring at the transition, as a result of a change from liquid-like to solid-like behaviour over the experimental timescale. When most polymer liquids are cooled, their density will increase. Below T_g, this structural relaxation occurs very slowly as a result of reduced mobility, and gives rise to the phenomenon of physical ageing, which is associated with a change in material properties[1,2] including their mechanical[3] and diffusional behaviour.[4] These changes have important practical consequences for the stability of glassy materials, and have been extensively studied, particularly for synthetic polymers.[5–8]

Structural relaxation can be probed by measurements of enthalpy or volume change. Fig. 1 shows a schematic of the dependence of volume and enthalpy on temperature, as an undercooled liquid is cooled below T_g. At T_g there is a sharp change in behaviour as the liquid structure becomes arrested over the timescale of the cooling. If the cooling is slower, there is more time available for the structure to relax, and the appearance of T_g will occur at a lower temperature. The structure of the glass will slowly evolve with time to that of the 'equilibrium' liquid. This relaxation will, in part, be dependent on temperature and partly on liquid structure, characterised on a temperature scale through the notion of a fictive temperature, T_f, the temperature at which a particular structure would be fully relaxed (Fig. 1).

Although dilatometry is a direct way of measuring the densification of the liquid, its use is rather restricted. Densification also affects the energetics of in-

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teraction between molecules, and the accessibility of liquid configurations, both of which can be probed in a calorimetric experiment where structural relaxation is observed as a peak in heat capacity preceding T_g, or an overshoot at T_g. There is not necessarily a simple relationship between the observed time-dependent behaviour of enthalpy and volume and their associated effect on mechanical behaviour.[9,10]

There are various phenomenological approaches for describing the observed time-dependent behaviour, a widely applied one, which has a potentially useful predictive capability, is the Tool–Narayanaswamy method,[11–14] which has been applied to polymeric systems. The dependence of structural relaxation on time, t, can be described by an empirical relaxation function, ϕ, of the form

$$\phi(t) = \exp[-(t/\tau_0)^\beta] \tag{1}$$

where β $(0 < \beta \leq 1)$ is a measure of its non-exponentiality. τ_0 is a characteristic time which is dependent on both temperature, T, and to an extent, liquid structure (characterised by T_f) and has been successfully obtained using the expression

$$\tau_0 = A\ \exp[x\Delta h^*/RT + (1-x)\Delta h^*/RT_f] \tag{2}$$

where A, x $(0 < x \leq 1)$ and Δh^* are constants.[12,13,15] These relationships can be used to calculate the time dependence of T_f following a temperature step. The cooling and heating of a sample can be considered as a succession of n such steps in which case

$$T_{f,n} = T_0 + \sum_{j=1}^{n} \Delta T_j \left\{1 - \exp\left[-\left(\sum_{k=j}^{n} \Delta T_k/Q\tau_{0,k}\right)^\beta\right]\right\} \tag{3}$$

where Q is a heating or cooling rate, and T_0 is a starting temperature where relaxation is sufficiently rapid that in the initial stages of cooling, equilibration is obtained. During annealing, the sample is held at a fixed temperature, T_a, for a certain length of time, this was divided into ten logarithmically spaced steps with Eq. (3) being modified as described

$$T_{f,n} = T_0 + \sum_{j=1}^{n_a} \Delta T_j \left\{1 - \exp\left[-\left(\sum_{k=n_a}^{n} \Delta t_{e,k}/\tau_{0,k}\right)^\beta\right]\right\} \tag{4}$$

where $n_a + 10 \geq n > n_a$ and

$$\Delta t_{e,k} = t_e^{1/10} \quad k = n_a + 1 \tag{5}$$

$$\Delta t_{e,k} = t_e^{(k-n_a)/10} - t_e^{(k-n_a-1)/10} \quad k > n_a + 1 \tag{6}$$

For a calorimetric experiment, $T_{f,n}$ is then related to a normalised heat capacity, $C_{p,n}$ by

$$C_{p,n} = (T_{f,n} - T_{f,n-1})/(T_n - T_{n-1}) \tag{7}$$

These predicted values of $C_{p,n}$ can then be compared with those determined calorimetrically.

There is a need to predict the time-dependent behaviour of starchy materials. Although there is an abundant literature on the effects of starch crystallisation, physical ageing has received much less attention. This study aims to characterise the structural relaxation behaviour of starch and a low molecular-weight analogue of starch–maltose. The study examines the usefulness of the Tool–Narayanaswamy approach for describing the observed time-dependent behaviour.

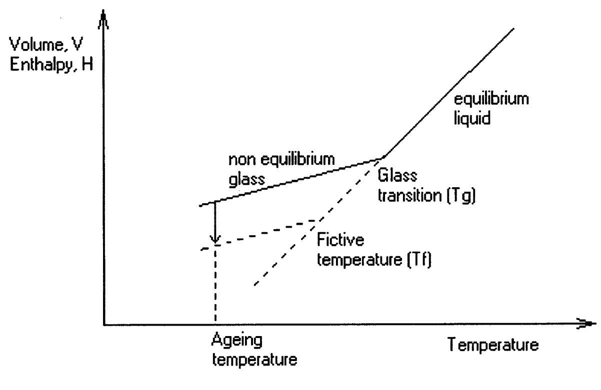

Fig. 1. Schematic of the dependence of volume and enthalpy on temperature as an undercooled liquid is cooled below T_g.

2. Experimental

Materials.—Maltose monohydrate was purchased from Sigma and used without further purification. For dilatometry, maltose cylinders (0.5 × 3 cm) were formed in plastic syringes after quenching the hot liquid (80 °C) to rt. Sorbitol-plasticised amorphous starch was prepared by extrusion of native potato starch containing 25% water with sorbitol. For the dilatometric study, extruded starch rods were granulated. Samples were conditioned at a relative humidity of 57% and the water content was determined gravimetrically after drying in a vacuum oven over P_2O_5 at 80 °C for 12 h.

Dilatometry.—A dilatometer of borosilicate glass was used. The design of the apparatus consisted of a capillary with a precision bore (0.2 mm diameter) between two side arms which act as the sample chamber. The arms were sealed with Teflon taps. The whole dilatometer was filled with degassed decane and the sample introduced into the decane. The solvent had no effect on the T_g of the sample. The sample mass was ~ 20 g. The dilatometer was initially equilibrated to a temperature 15 °C above the calorimetric T_g of the sample for 10 min. The dilatometer was then immersed in a water bath maintained at the ageing temperature, controlled to ± 0.001 °C, and measured using a quartz thermometer (Hewlett–Packard 2804A), calibrated from the triple point of water. The measured time for temperature equilibration was ~ 0.28 h. Time zero for the physical ageing experiment was taken as the time at which the dilatometer was quenched to the ageing

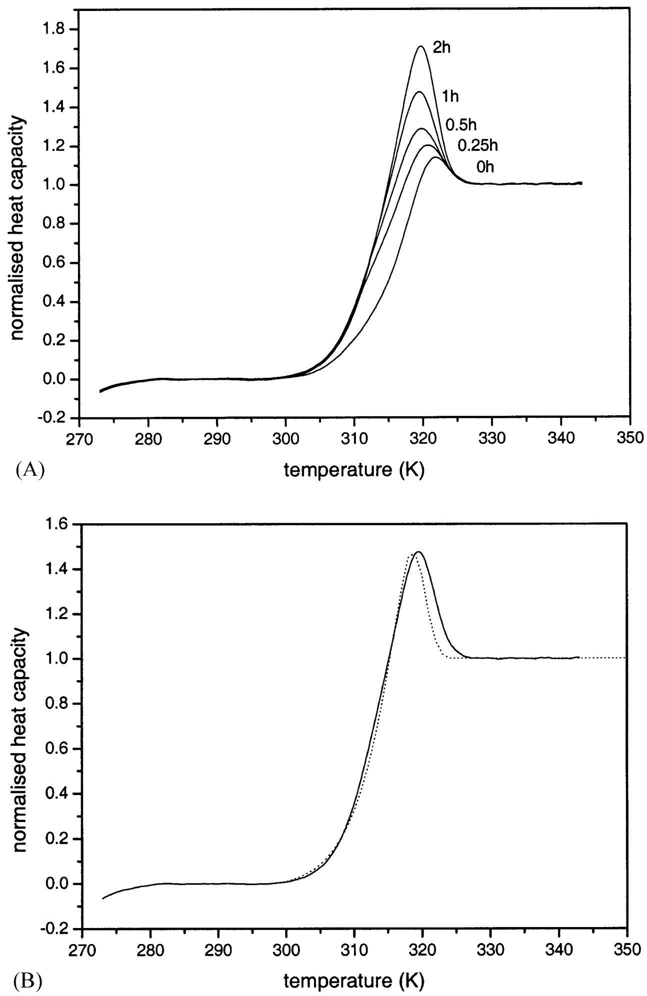

Fig. 2. (A) Plot of experimental normalised heat capacity of amorphous maltose containing 5% water as a function of temperature for various ageing times (0, 0.25, 0.5, 1 and 2 h) at 298 K. (B) Superposition of fitted and experimental data for an ageing time of 2 h at 298 K, using the following values of the parameters: $\Delta h^* = 400{,}000$; $\ln A = -150$; $x = 0.58$; $\beta = 0.65$.

temperature by placing in the water bath. After initial thermal equilibration, one tap was closed and the other limb pressurised to introduce decane into the capillary and then the other tap closed. The contraction or expansion of the sample was followed through the movement of decane in the capillary using a cathetometer to permit the measurement of a volume change of 3×10^{-9} m^3.

Calorimetry.—Samples (~ 10 mg) were sealed in pre-weighed aluminium pans in an argon atmosphere. DSC experiments were performed using a Perkin–Elmer DSC 7 fitted with a robotic autosampler. The DSC was calibrated for temperature, at each heating rate used, from the melting points of indium (156.6 °C) and dodecane (-9.65 °C). The heat flow was calibrated from the heat of melting of indium (28.45 J/g), and the calibration for heat capacity checked against a sapphire standard. Ageing was performed in the DSC at the ageing temperature, the instrument was then cooled to 0 °C at 10 °C/min and then measurements made in the temperature range 0–80 °C, using a scanning rate of 10 °C/min. Data analysis was performed using Perkin–Elmer thermal analysis software to obtain the heat capacity data. An estimate of the parameter Δh^*, was obtained by measuring the dependence of the glass-transition temperature on scanning rate, with cooling into the glass performed at the same rate.[16] The calorimetric behaviour after ageing and rescanning was compared to the initial behaviour to confirm that the T_g of the 'unaged' material had not changed.

Mechanical measurements.—Amorphous maltose–water mixtures were pressed into blocks 2 × 6 × 30 mm, and amorphous starch–sorbitol mixtures extruded into 6 mm diameter rods of the same length. The mechanical properties of these materials were examined on an Instron 1122 in a three-point bend test over a total sample length of 26 mm, at a temperature of 27.7 °C. In order to avoid water loss, mechanical measurements were made on samples immersed in a temperature controlled bath of silicone oil. Immersion in silicone oil had no effect on T_g for the experimental timescales used.

Conductivity measurements.—A mixture of maltose containing 5% w/w water and 0.74% w/w KC1 was examined. Conductivity measurements were made using a two-stainless steel parallel-plate cell with circular electrodes (diameter 33 mm) (Rheometric Scientific, Loughborough, UK) with an electrode separation of 0.5 mm. The cell was enclosed in a controlled temperature chamber. Direct current (DC) measurements were performed with a sensitivity of 0.1 pA and a response of 0.36 s. After thermal equilibration, a voltage step was applied for 1 min (0. 1 V) and the current recorded, a reversing voltage was then applied in order to minimise electrode polarisation. The conductivity experiments were performed isothermally across the temperature range 70–25 °C, with decreasing temperature to reduce the time-dependent effects of electrode polarisation.

3. Results and discussion

Calorimetric behaviour.—A plot of normalised heat capacity, $C_{p,n}$ as a function of temperature is shown in Fig. 2(A) for the 19:1 maltose–water mixture. There is a sharp change in heat capacity in the region of 318 K indicative of a glass transition. The samples were aged at 298 K for different times for up to 2 h. With increasing ageing time there is an increasing overshoot in heat capacity at the glass transition. The observed behaviour was modelled using Eqs. (4)–(7).[16] A good fit to the data was obtained with $\Delta h^* = 400{,}000$ (ob-

Table 1
Ageing dependence of mechanical and calorimetric relaxation times for a maltose–water mixture at 300.7 and 300 K, respectively

Mechanical behaviour			Calorimetric behaviour	
Ageing time (h)	β	$\tau_m(s) \times 10^{-2}$	Ageing time (h)	$\tau_0(s) \times 10^{-3}$
0.28	0.50	1.20	0.28	2.80
1.16	0.50	2.80	0.56	3.45
1.76	0.45	3.00	1.00	4.23
4.76	0.45	4.00	1.75	5.27
20.40	0.45	6.00	4.80	8.05
			20.40	14.80

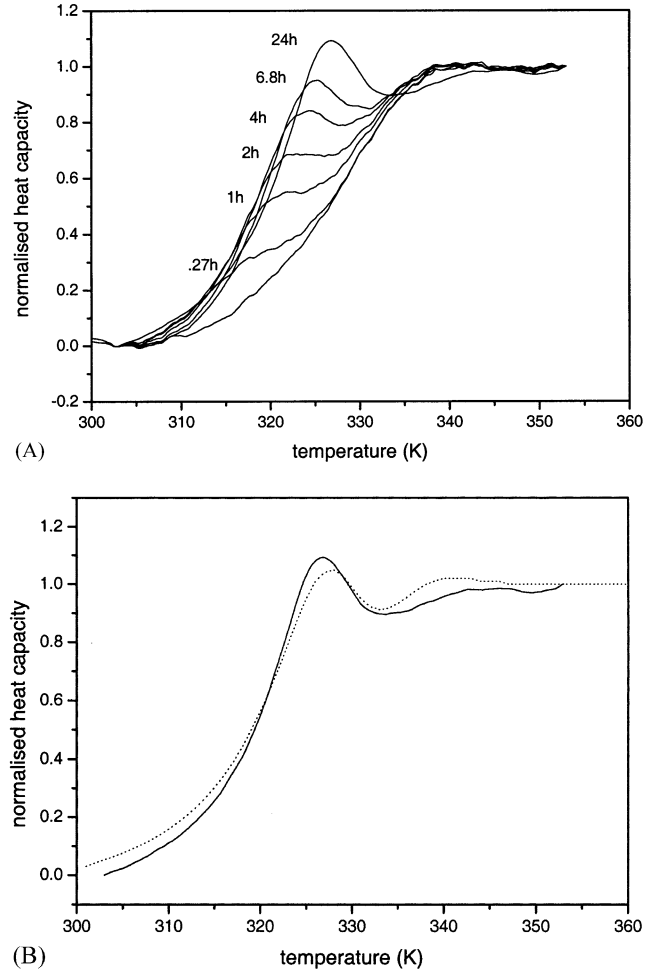

Fig. 3. (A) Plot of experimental normalised heat capacity of amorphous starch containing 15% sorbitol and 5% water as a function of temperature for various ageing times (0.27, 1, 2, 4, 6.8 and 24 h) at 300 K. (B) Superposition of fitted and experimental data for an ageing time of 24 h at 300 K, using the parameters: $\Delta h^* = 400{,}000$; $\ln A = -143$; $x = 0.48$; $\beta = 0.32$.

Table 2
Ageing dependence of mechanical and calorimetric relaxation times for a starch–sorbitol–water mixture at 300.7 and 300 K, respectively

Mechanical behaviour			Calorimetric behaviour	
Ageing time (h)	β	$\tau_m(s) \times 10^{-4}$	Ageing time (h)	$\tau_0(s) \times 10^{-5}$
0.26	0.35	0.13	0.27	0.80
1.00	0.33	0.27	1.00	1.00
2.00	0.31	0.40	2.00	1.35
4.00	0.30	0.73	4.00	1.41
6.80	0.28	1.00	6.80	1.65
24.60	0.26	3.70	24.00	2.55
48.00	0.26	6.90		
78.00	0.26	7.50		

tained from the dependence of T_g on scanning rate), $\ln A = -150$, $x = 0.58$ and $\beta = 0.65$. These values are similar to those obtained on pure maltose[16] with a decrease in the parameter β from 0.86 to 0.65, indicating a greater spread in the distribution of relaxation times as water is added. The fit to the experimental data at the ageing time of 2 h is shown in Fig. 2(B). In preparation for dilatometric and mechanical measurements, these parameters were then used to predict the extent of ageing at different temperatures and the effect of ageing on relaxation time. For example, the calculated characteristic relaxation time, τ_0 (Eq. (2)), progressively increased from 2.8×10^3 to $\sim 1.48 \times 10^4$ on ageing from 0.28 to 20.4 h (Table 1).

The calorimetric behaviour obtained on ageing a 16:3:1 starch–sorbitol–water mixture is shown in Fig. 3(A). A change in heat capacity, indicative of a glass transition is observed at 323 K. Compared to the maltose–water mixture the transition is broader. On ageing at 300 K there was a progressive appearance of an overshoot in heat capacity, although not nearly as marked as for the maltose–water mixture. For example, after 20 h the overshoot in calculated $C_{p,n}$ for the maltose–water mixture is ~ 4, while for the starch mixture it is only ~ 1.1. A fit to the data was obtained with $\Delta h^* = 400{,}000$, $\ln A = -143$, $x = 0.48$ and $\beta = 0.32$ (Fig. 3(B)). The change in the latter two parameters characterises the broadening of the transition in the ternary starch–sorbitol–water mixture. After 24 h the calculated relaxation time (Table 2) had increased to 2.55×10^5 s reflecting the effect of ageing at a lower temperature with respect to T_g.

Volume relaxation.—The change in volume, $\Delta V/V$, with ageing time is shown in Figs. 4 and 5 for 19:1 maltose–water and 16:3:1 starch–sorbitol–water mixtures, respectively. The quantity $\Delta V/V$ was calculated from

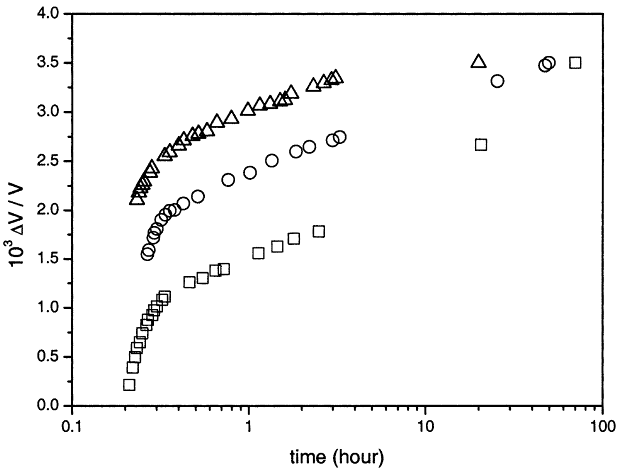

Fig. 4. Relative volume change as a function of time for maltose–5% water at 297 K (□), 300 K (○) and 303 K (△). The data at 300 and 303 K are displaced upwards by 0.5 and 1.0 ordinate units, respectively.

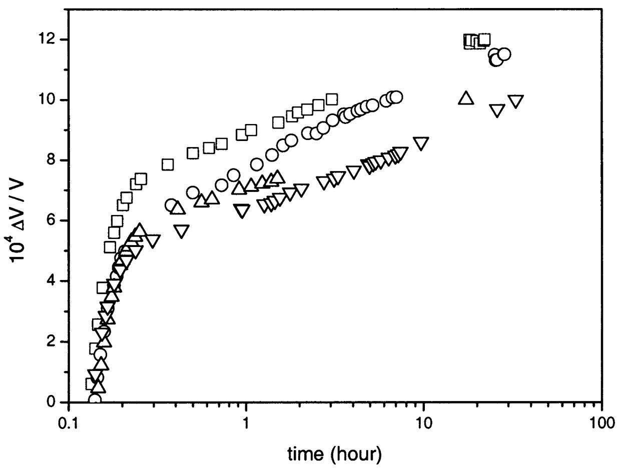

Fig. 5. Relative volume change as a function of time for starch–15% sorbitol–5% water at 294.5 K (▽), 298 K (△), 300.5 K (○) and 303 K (□). The data at 298, 300.5 and 303 K data are displaced upward at 0.5, 1.0 and 1.5, respectively.

$$\Delta V = |V_{(t)} - V_{(0)}|/V_{(0)}$$

where $V_{(t)}$ is the specific volume at time, t, and $V_{(0)}$ is the initial specific volume measured by pycnometry after quenching and thermal equilibration at the ageing temperature. The calorimetric T_g of the mixtures was 318 and 323 K for maltose and starch, respectively. Volume relaxation measurements were made at different ageing temperatures in the range $T_g - 21$ to -15 K for the maltose–water mixture, and in the range $T_g - 29$ to -20 K for the starch–sorbitol–water mixture. The volume decreases with increasing ageing time. For both materials the initial behaviour, up to ~0.3 h, is dominated by the effects of thermal equilibration. After this time, the volume change is essentially linear with log t. The slope of $\Delta V/V$ versus log t does not show a significant dependence on temperature within the range examined.

To estimate whether equilibration of liquid structure was achieved within the experimental timescale of 100 h, the thermal expansion coefficient, α, of an 4:1 maltose–water mixture was measured using densimetry. At 20 °C α was found to be 4.3×10^{-4}/°C compared to 3.25×10^{-4}/°C for water. If the volumetric properties of maltose–water mixtures are additive this would give a value of 4.49×10^{-4}/°C for a 19:1 maltose–water mixture. As a consequence, the predicted relative volume change on quenching the maltose–water mixture to 297 K ($T_g - T$ of 21 K) is 9.4×10^{-3}, and 8.1×10^{-3} and 6.7×10^{-3} at 300 and 303 K, respectively. For all temperatures, the observed relative volume change during ageing for ~100 h (after thermal equilibration) is substantially less, indicating that the equilibration of liquid structure was not achieved during this time. The densification occurring during physical ageing is comparable to that arising from the non-ideality of mixing carbohydrates and water suggesting that the latter effect could also have a significant impact on material properties in these systems and would be relevant to antiplasticisation phenomena.[17–19]

Mechanical relaxation.—The mechanical behaviour of the 19: 1 maltose–water and 16:3:1 starch–sorbitol–water mixtures was examined in a three-point bend test at a crosshead speed of 2 mm/min. As for the dilatometric experiment, samples were initially equilibrated at a temperature 15 °C above the T_g of the sample for 10 min; samples were then rapidly cooled to 300.7 K. The force at break and the deformation was recorded for samples aged to different extents at 300.7 K (Table 3).

Table 3
Ageing dependence of mechanical properties for maltose–water and starch sorbitol–water mixtures at 300.7 K

Maltose			Starch		
Ageing time (h)	Strength at break (Newton)	Deformation at break (mm)	Ageing time (h)	Strength at break (Newton)	Deformation at break (mm)
0.08	284 ± 7.1	0.39 ± 0.08	0.08	112 ± 9	5.8 ± 1.2
96.00	4.0 ± 14	0.04 ± 0.01	24.00	124 ± 13	3.0 ± 0.9
			1440.00	150 ± 12	1.9 ± 0.7

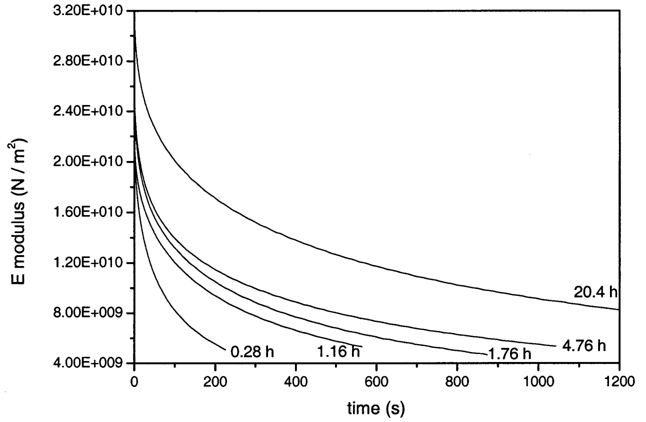

Fig. 6. Plot of mechanical relaxation at 300.7 K of amorphous maltose containing 5% water, aged for different times with the ageing time given in hours.

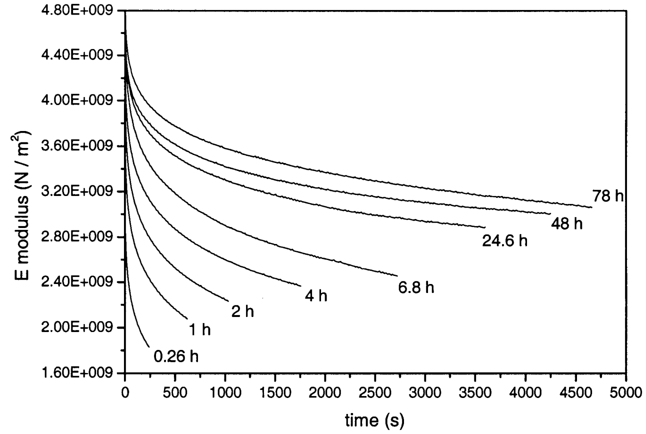

Fig. 7. Plot of mechanical relaxation at 300.7 K of amorphous starch containing 15% sorbitol and 5% water. Different curves correspond to various ageing time (indicated in hours) of the same sample.

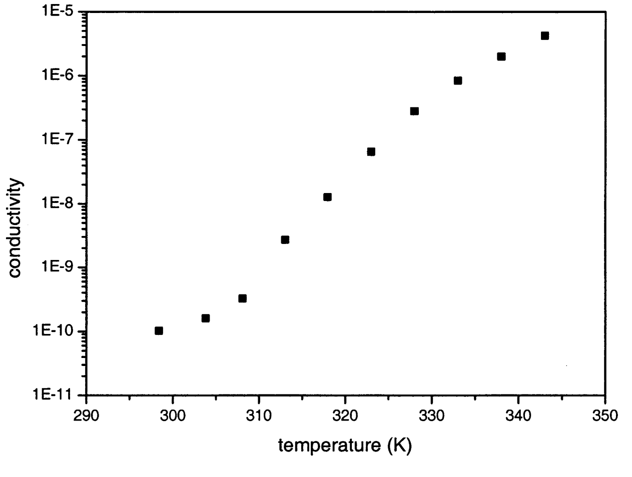

Fig. 8. Plot of the conductivity of maltose–5% water–KCl mixture as a function of temperature.

Each point was an average of five determinations. With ageing, the deformation at break decreases, indicating a progressive embrittlement on ageing and is particularly marked for the maltose–water mixture. Figs. 6 and 7 show the mechanical relaxation behaviour for maltose–water and starch–sorbitol–water mixtures as a function of ageing time. The load was applied at t_0, and the load required to maintain the deformation was recorded as a function of time. The initial load of 15 and 30 N, determined for the maltose and starch samples respectively, was within the linear region of the stress–strain behaviour. As recommended by Struik,[6] the duration of each mechanical test was less than 10% of the total ageing time to ensure that the time dependence of ageing could be obtained. The different curves show the mechanical relaxation of Young's modulus (E) on ageing at 300.7 K. For both materials the mechanical relaxation time shows a progressive increase with ageing. This behaviour is broadly similar to that obtained for amorphous synthetic polymers. In order to extract characteristic mechanical relaxation times (τ_m), the experimental data was fitted to a relaxation function of the same form as Eq. (1).

$$\phi(t) = \exp[-(t/\tau_m)^\beta] \qquad (1')$$

The mechanical relaxation data for the maltose–water mixture and the starch–sorbitol–water mixture are summarised in Tables 1 and 2. For both materials, with increased ageing, τ_m is shifted to longer times. Although τ_m is much shorter than that obtained from calorimetry, the timescale over which the mechanical behaviour changes is similar to that for both the calorimetric and volumetric behaviour.

Conductivity.—Fig. 8 is a plot of the conductivity of a maltose–water–KCl mixture measured as a function of temperature. On decreasing temperature, the conductivity decreases although the effect is not as marked as the corresponding increase in viscosity. Ten degrees below the calorimetric glass transition of 318 K, the temperature dependence of conductivity changes and is an experimental indication of 'frozen' liquid structures which are not fully 'equilibrated'. The difference in temperature of the structural arrest observed in calorimetric and conductometric experiments was attributed to differences in the thermal history of the two samples. This arrested structural relaxation was investigated in more detail through performing an ageing experiment at 303 K. After heating to 353 K, the sample was quenched to 303 K and the conductivity measured as a function of time (Fig. 9). The large change in conductivity in the first 20 min is influenced by the thermal equilibration, thereafter the decay in conductivity is almost linear with log t. This experiment shows that translational mobility, as assessed through ionic conductivity, is affected by the slow structural relaxation

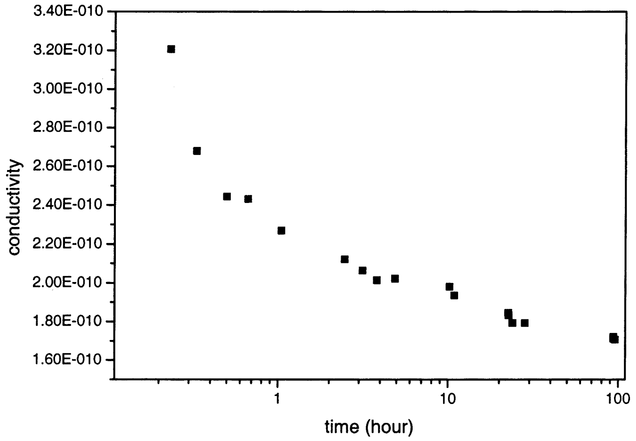

Fig. 9. Plot of the conductivity of maltose–5% water–KCl mixture as a function of time at 303 K.

which occurs during ageing below the calorimetric glass transition temperature.

4. Conclusions

The effects of structural relaxation on the material properties of amorphous carbohydrates (maltose, starch) was observed using a range of physical techniques. During ageing of the glassy solids, the materials became less compliant with the mechanical relaxation time progressively increasing. A progressive slowing of transport in the maltose mixture was also observed. The progressive change in material properties occurred over a similar timescale to the slow densification of the amorphous glasses, characteristic of structural relaxation in the glassy state. We have shown that the Tool–Narayanaswamy model gave a good description of the observed calorimetric behaviour and has predictive potential for describing the time dependence of the structural relaxation.

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