ELSEVIER
www.elsevier.nl/locate/carres
Carbohydrate Research 319 (1999) 166–171
CARBOHYDRATE RESEARCH

A calorimetric study of structural relaxation in a maltose glass

Timothy R. Noel *, Roger Parker, Susan M. Ring, Stephen G. Ring

Department of Biochemistry, Institute of Food Research, Norwich Laboratory, Norwich, Research Park, Colney, Norwich NR4 7UA, UK

Received 2 February 1999; accepted 13 May 1999

Abstract

The structural relaxation behaviour of a maltose glass was investigated by differential scanning calorimetry. The ageing of the material, on storage below the calorimetric glass-transition temperature, T_g, was followed, as a function of time, through the measurement of the enthalpy recovered on reheating. The observed relaxation behaviour was well described by the Tool–Narayanaswamy method, which included the effect of non-exponentiality and non-linearity on the observed behaviour. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Maltose; Glass transition; Structural relaxation

1. Introduction

If an organic liquid is cooled below the melting temperature of the crystalline solid T_m, then, providing crystallisation does not intervene, liquid viscosity will increase with increasing undercooling. At the glass-transition temperature T_g, there is a change in material characteristics, from liquid-like to solid-like, with a sharp change in heat capacity, which is dependent on the timescale of the measurement. Typically, a material is considered to be solid-like if the shear stress relaxation time is of the order of 100 s, which occurs when the shear viscosity is about 10^{12} Pa s [1]. On further cooling below the glass-transition temperature, the viscosity and associated relaxation times continue to increase. This increase with undercooling can have two main forms. While network liquids, such as silica, show an Arrhenian dependence, organic molecular liquids, including carbohydrate liquids, generally show a viscosity (η) dependence on temperature, T, described by the semi-empirical Vogel–Tammann–Fulcher (VTF) equation

$$\eta = A \exp[B/(T - T_0)] \tag{1}$$

where A, B and T_0 are constants. For these 'fragile' liquids the viscosity and associated relaxations show a marked temperature dependence in the vicinity of T_g [1].

The structure of an undercooled liquid is time and temperature dependent. At very long times it will have a fully relaxed, 'equilibrium' structure. If this liquid is cooled, further structural relaxations and rearrangements within the undercooled liquid will occur until, given sufficient time, a new 'equilibrium' structure is obtained. This relaxation behaviour has been extensively studied, particularly for polymers and inorganic glasses, and reviewed [2–6]. The

---

* Corresponding author: Tel.: +44-1603-255-000; fax: +44-1603-507-723.
E-mail address: tim.noel@bbsrc.ac.uk (T.R. Noel)

PII: S0008-6215(99)00117-2

changes in bonding between molecules and their configuration are associated with changes in volume, enthalpy, heat capacity and material properties, including mechanical behaviour and transport properties, such as diffusivity [6]. The progress towards 'equilibrium' can be characterised through the notion of a fictive temperature, T_f, the actual temperature at which a particular structure would be fully relaxed at very long times [2–6].

While the relaxation behaviour of the different thermodynamic quantities for the undercooled liquid can differ somewhat, the availability of differential scanning calorimetry has meant that the relaxation behaviour is often characterised through the measurement of heat capacity. There are various phenomenological approaches for describing the observed behaviour, a widely applied one being the Tool–Narayanaswamy method ([2,3,5,6] and references therein).

The dependence of structural relaxation on time, t, can be described by an empirical relaxation function, ϕ, of the form

$$\phi(t) = \exp[-(t/\tau_0)^{\beta}] \tag{2}$$

and 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

$$\tau_0 = A \exp[x\Delta h^*/RT + (1-x)\Delta h^*/RT_f] \tag{3}$$

where A, x ($0 < x \leq 1$) and Δh^* are constants [2,5–9]. These relationships can be used to calculate the time dependence of T_f following a temperature change. During cooling and heating the fictive temperature T_f is related to the temperature, heating or cooling rate and relaxation rate parameters through the relationship [2,8]

$$T_f(T) = T_0 + \int_{T_0}^{T} \mathrm{d}T' \left\{1 - \exp\left[-\left(\int_{T'}^{T} \mathrm{d}T''/Q\tau_0\right)^{\beta}\right]\right\} \tag{4}$$

where T_0 is a starting temperature, well above T_g, where relaxation is sufficiently rapid that, in the initial stages of cooling, equilibration is obtained, Q is the heating or cooling rate, and T' and T'' are dummy temperature variables. In practice, this equation has to be evaluated numerically and so, following the computational approaches described by Hodge and Berens [8], the integrals are replaced by summations. The cooling and heating of a sample can be considered as a succession of n steps in which case

$$T_{f,n} = T_0 + \sum_{j=1}^{n} \Delta T_j \left\{1 - \exp\left[-\left(\sum_{k=j}^{n} \Delta T_k/Q\tau_{0,k}\right)^{\beta}\right]\right\} \tag{5}$$

During annealing the sample is held at a fixed temperature, T_a, for a certain length of time, which was divided into 10 logarithmically spaced steps with Eq. (5) being modified as described [8]

$$T_{f,n} = T_0 + \sum_{j=1}^{n_a} \Delta T_j \left\{1 - \exp\left[-\left(\sum_{k=n_a}^{n} \Delta t_{e,k}/\tau_{0,k}\right)^{\beta}\right]\right\} \tag{6}$$

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

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

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

$T_{f,n}$ 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.

Low-molecular-weight carbohydrate glasses find industrial application as encapsulation matrices for labile molecules including food ingredients, therapeutic proteins and peptides. The time-dependent behaviour of the amorphous matrix is relevant to these applications. While stability to crystallisation is often considered, ageing phenomena related to structural relaxation are also important. Comparatively recently the structural relaxation of amorphous carbohydrates, including sucrose [10], maltitol [11], maltose/water [12], starch/water [13,14] and pullulan/water [14] mixtures, has started to receive attention. As part of our investigations on the glassy behaviour of carbohydrates [15], including the characterisation of localised motions and liquid structure [16,17], we now examine the structural relaxation of liquid maltose by differential scanning calorimetry and its description by the Tool–Narayanaswamy phenomenology.

2. Materials and methods

Sample preparation.—Amorphous maltose was prepared from a 90% w/w aqueous maltose solution (maltose monohydrate dissolved at 140 °C) which was vacuum dried at 60 °C for 48 h over P_2O_5. The product was compacted in an argon atmosphere, collapsed by heating on a metal disc at 130 °C in an oven flushed with dry argon in the presence of P_2O_5, cooled to room temperature and stored in a desiccator over P_2O_5.

Calorimetry.—Samples of glassy maltose (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 robotic autosampler. Three types of DSC experiment were performed: (i) scanning rate studies in which the sample was cooled and re-heated at the same scan rate to determine the effect of scan rate on T_g; (ii) cooling rate studies to study the overshoot observed on re-heating at 10 °C min^{-1}, and (iii) annealing studies. In the annealing studies the samples were subjected to the following thermal history: heated at 40 °C min^{-1} to 120 °C; held for 3 min at 120 °C; cooled at 25 °C min^{-1} to an ageing temperature T_a; held at T_a ($50\ °C \leq T_a \leq 100\ °C$) for a time t_a ($0\ min \leq t_a \leq 160\ min$); cooled at 25 °C min^{-1} to 40 °C; heated at 10 °C min^{-1} to 120 °C. The calorimetric signal of the last stage was logged by computer. Crystallisation during storage of the sample at temperatures close to T_g, as indicated by a fall in the heat capacity increment, ΔC_p, at T_g, was not observed. The calorimeter was calibrated from the melting of indium and the heat capacity of sapphire.

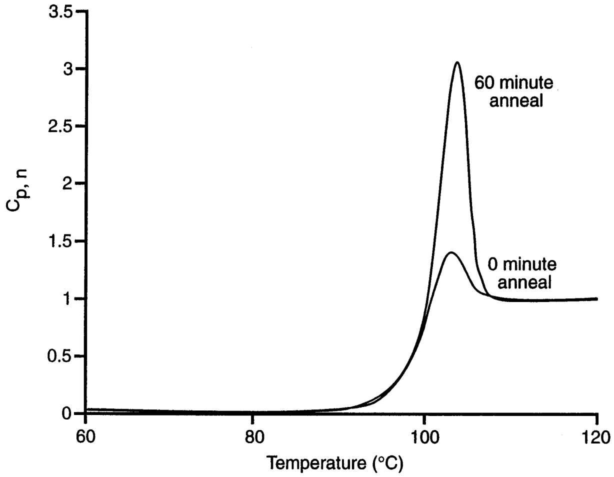

Fig. 1. Plot of normalised heat capacity, $C_{p,n}$ of amorphous maltose as a function of temperature for an 'unaged' sample (0 min anneal) and a sample aged at 85 °C for 60 min (60 min anneal).

Data analysis.—Data analysis was performed using Perkin–Elmer Thermal Analysis software to obtain heat capacity data, which were then normalised after allowance for the temperature dependence of liquid and glass heat capacities. Δh^* was estimated from the dependence of the observed calorimetric T_g on scanning rate [18]. The other parameters describing the relaxation (x, A, β) were estimated from the fitting of the normalised heat capacity data to that generated from Eqs. (5–7) with a FORTRAN program. The structural relaxation was characterised through the determination of the normalised heat capacity maximum of the overshoot, $C_{p,n\ max}$ and its temperature T_{max}.

3. Results and discussion

Fig. 1 shows the observed calorimetric behaviour, plotted as normalised heat capacity, $C_{p,n}$, versus temperature, for an unaged and an aged sample (60 min at 85 °C) of amorphous maltose. A T_g of 98.4 °C was obtained from the midpoint of the heat capacity increment observed on re-scanning an unaged quenched sample, in agreement with previous reports [15,16]. A small recovery peak was also observed. The dependence of the size of the overshoot ($C_{p,n\ max}$) on cooling rate was examined (Fig. 2). Although it decreased in height with increased rate of cooling, even at the fast rate of 80 °C min^{-1} it was still present, and resulted from relaxations occurring during the time spent, during cooling and heating, below T_g. The aged sample had a more prominent relaxation peak.

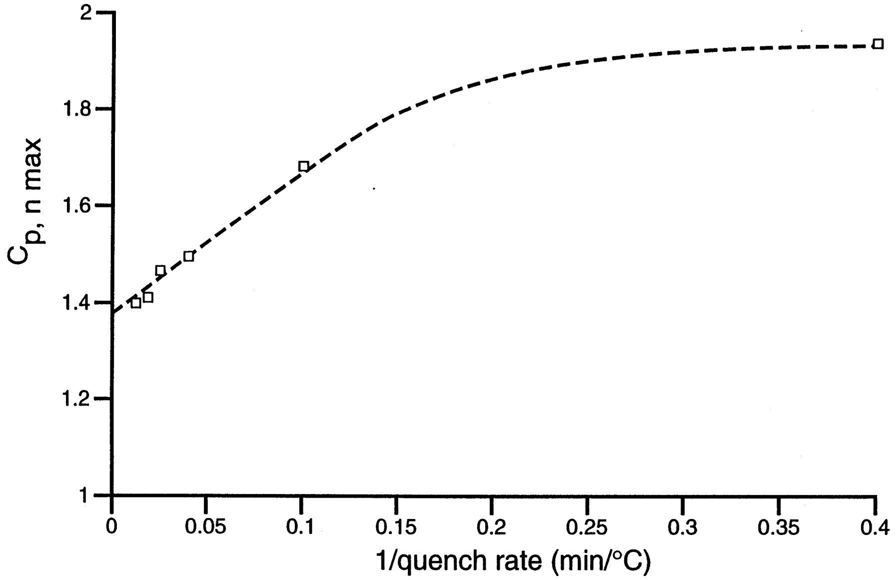

Fig. 2. Effect of quench rate on the normalised heat capacity maximum, $C_{\text{p,n max}}$, for an ‘unaged’ maltose glass.

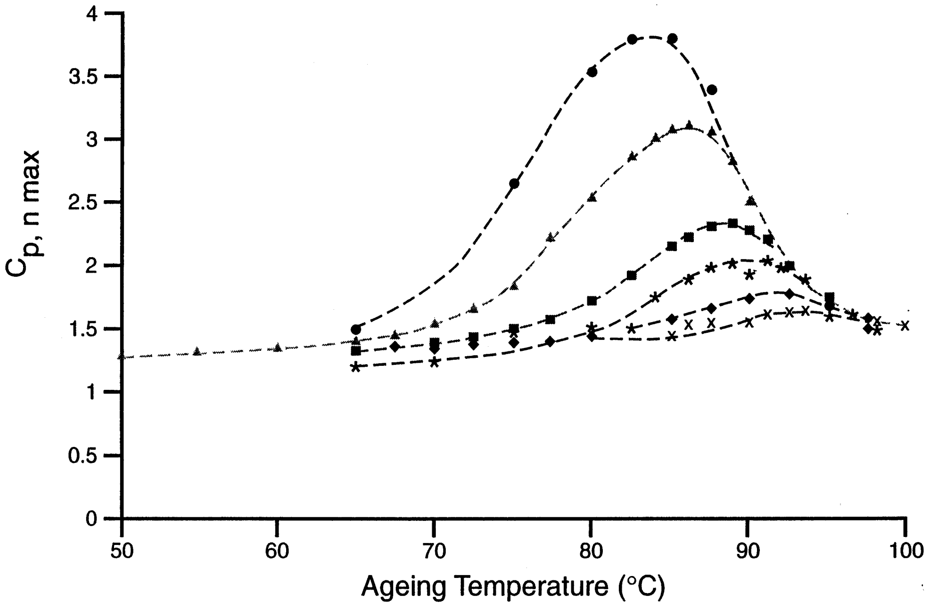

Fig. 3. Plot of normalised heat capacity maximum, $C_{\text{p,n max}}$, as a function of ageing temperature after ageing time (min) of: 1, (×); 3, (◆); 7, (✱); 15, (■); 60, (▲) and 160 (●).

The time and temperature dependence of the structural relaxation during ageing is shown in Fig. 3, where $C_{\text{p,n max}}$ is plotted as a function of ageing temperature, T_a, in a series of isochronal plots for ageing times, t_a, up to 160 min. At a constant ageing time, as T_a decreases, $C_{\text{p,n max}}$ increases, going through a maximum, and then decreasing with further temperature reduction. The temperature of this maximum decreases with increase in ageing time.

For the initial fitting of the relationships described in Eqs. (4) and (5), it is necessary to have an estimate of the various parameters x, A, β and Δh^*. The latter was obtained from the temperature dependence of T_g on DSC scanning rate for samples with an appropriate thermal history and was estimated to be 462 kJ mol^{-1} [18]. This value can be compared to that obtained (240–330 kJ mol^{-1}) from the temperature dependence of the main dielectric relaxation, on frequency in the region of T/

$T_g \sim 1.12$ [16]. This indicates that Δh^* for the structural relaxation is changing as T_g is approached, a characteristic of liquids exhibiting VTF-type behaviour. The former value, obtained calorimetrically, was used for the fitting. To test the applicability of the approach, the usefulness of a single set of parameters to describe the experimentally observed relaxation behaviour was examined. This is shown in a plot of normalised heat capacity, $C_{p,n}$ versus temperature for an ageing time of 60 min at 85 °C (Fig. 4(a)) and 60 °C (Fig. 4(b)). The relationships used provide a good description of the experimentally observed behaviour over the range of temperatures and ageing times examined with $\ln A = -146.5$, $x = 0.58$, and $\beta = 0.86$. The physical significance of the values of the parameters obtained is more difficult to assess. For studies on the same compound the reported values are to some extent variable, in part due to the fitting procedures employed, but also due to differences in experimental protocol and material variations. However, tabulations of the parameters for different materials are becoming available [5]. It is expected that as more carbohydrate liquids are examined, the utility of the approach and the significance of the values of the parameters obtained will be further assessed. From a

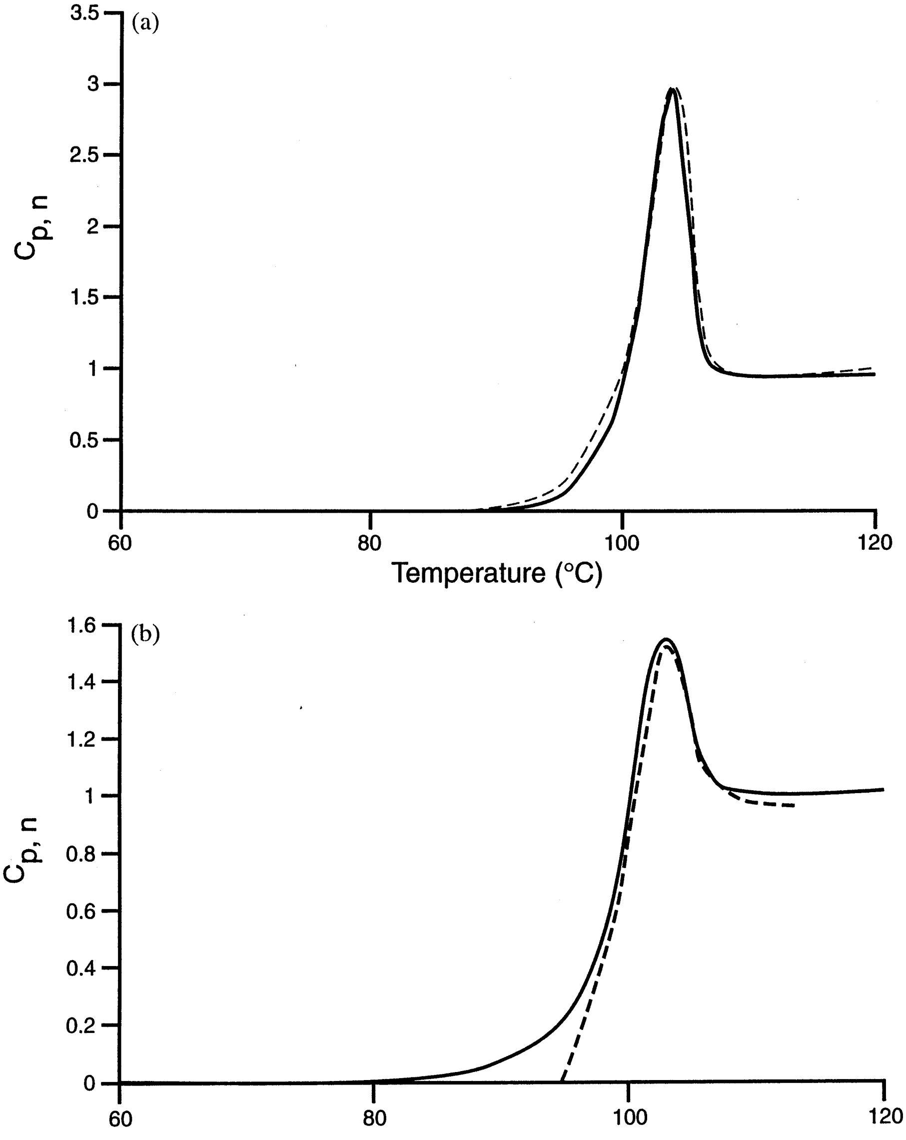

Fig. 4. Comparison of experimental (—) and calculated (---) normalised heat capacity, $C_{p,n}$ as a function of temperature for amorphous maltose after ageing for 60 min at ageing temperatures of: (a) 85 °C and (b) 60 °C. Fitting parameters given in text.

practical viewpoint, the ageing of a maltose glass is well described by the relationships employed, which include the effect of non-linear and non-exponential relaxation on the observed behaviour. There is prospect for the use of this approach to describe the ageing of maltose and dextrins matrices relevant to their industrial use particularly as encapsulation matrices.

4. Conclusions

The ageing of a maltose glass, as assessed calorimetrically, is dependent on thermal history. A phenomenological model of Tool and Narayanaswamy, which included non-exponential and non-linear effects on the structural relaxation, gave a good description of the observed behaviour.

Acknowledgements

The authors would like to thank the BBSRC Competitive Strategic Grant for support.

References

[1] C.A. Angell, *Science*, 267 (1995) 1924–1935.
[2] C.T. Moynihan, P.B. Macedo, C.J. Montrose, P.K. Gupta, M.A. Debolt, J.F. Dill, B.E. Dom, P.W. Drake, A.J. Easteal, P.B. Elterman, R.P. Moeller, H. Sasabe, J.A. Wilder, *Ann. N.Y. Acad. Sci.*, 279 (1976) 15–35.
[3] J.M. Huthchinson, *Prog. Polym. Sci.*, 20 (1995) 703–760.
[4] I.M. Hodge, *Science*, 267 (1995) 1945–1947.
[5] I.M. Hodge, *J. Non-Cryst. Solids*, 169 (1994) 211–266.
[6] C.T. Moynihan, S.N. Crichton, S.M. Opalka, *J. Non-Cryst. Solids*, 131-133 (1991) 420–434.
[7] A.R. Berens, I.M. Hodge, *Macromolecules*, 15 (1982) 756–761.
[8] I.M. Hodge, A.R. Berens, *Macromolecules*, 15 (1982) 762–770.
[9] T. Ho, J. Mijovic, *Macromolecules*, 23 (1990) 1411–1419.
[10] R. Urbani, F. Sussich, S. Prejac, A. Cesaro, *Thermochim. Acta*, 304/5 (1997) 359–367.
[11] A. Faivre, L. David, J. Perez, *J. Phys. II*, 7 (1997) 1635–1650.
[12] S.J. Schmidt, A.M. Lammert, *J. Food Sci.*, 61 (1996) 870–874.
[13] R.L. Shogren, *Carbohydr. Polym.*, 19 (1992) 83–90.
[14] I.A.M. Appelqvist, D. Cooke, M.J. Gidley, S.J. Lane, *Carbohydrate Polymers*, 20 (1993) 291–299.
[15] P.D. Orford, R. Parker, S.G. Ring, A.C. Smith, *Int. J. Biol. Macromol.*, 11 (1989) 91–96.
[16] T.R. Noel, R. Parker, S.G. Ring, *Carbohydr. Res.*, 282 (1996) 193–206.
[17] R.H. Tromp, R. Parker, S.G. Ring, *J. Chem. Phys.*, 107 (1997) 6038–6049.
[18] T.R. Noel, S.G. Ring, M.W. Whittam, *Carbohydr. Res.*, 212 (1991) 109–117.