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Enthalpy relaxation and glass transition behaviour of sucrose by static and dynamic DSC[1]

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Abstract

The relaxation process of the sucrose in the glassy state and its glass transition are studied by differential scanning calorimetry in both the conventional and the dynamic mode. The data on the kinetics of glassy relaxation are experimentally evaluated by measuring the enthalpy relaxation peaks as a function of the ageing times at three different ageing temperatures, namely 45, 55 and 60°C. It is shown that the ageing process is a complex phenomenon with a rather large distribution of relaxation times. The value of the breath of the distribution of relaxation processes, β, is 0.32 and it is in the lower range of the distributions commonly observed. The dynamic components of the heat capacity (C'_p and C''_p) have been obtained from the experiments carried out at different frequency of temperature modulation (ν=8.3–83 mHz). These components are unaffected by the ageing process and therefore are more reliable for the correct T_g determination. The activation energies for the relaxation process and for the glass transition process are also evaluated. © 1997 Elsevier Science B.V.

1. Introduction

Amorphous states are of great importance in the field of food science for their behaviour, structure and interactions in food systems with particular relevance to food storage and processing. In the last twenty years, the study of the glassy state and glass transitions in food molecules has involved a growing number of scientists and technologists [1,2]. The peculiarity that distinguishes amorphous solids from the liquids is their departure from equilibrium. They have very long relaxation times and if kept at a suitable temperature may remain almost indefinitely in a metastable state. Slightly below the glass transition temperature, T_g, a glassy system can slowly approach a quasi-thermodynamic equilibrium undergoing structural relaxations upon ageing with a reduction in molecular mobility. All these important features were recognised about 50 years ago by Kauzmann [3].

Many processed or prepared foods are far from a thermodynamic equilibrium and their glassy state is the most common one in which the non-equilibrium systems are quasi-stabilized. Since the physical ageing implies a progressive change (time dependence) not only in the thermodynamic properties (such as enthalpy, specific volume or refractive index), but also in the physico-mechanical and texture properties, these changes are of relevant practical importance as they concern the stability and shelflife of the products. The amorphous state of sugars (fructose,

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glucose, lactose and sucrose) is widely known and formed by dry-milling, rapid quenching from the melt or by removal of water molecules from concentrated solutions, e.g., during dehydration or freezing processes, extrusion or baking. The presence of water molecules is at the origin of the phase transitions that may be induced in sugar-based foods because of the higher mobility of water with respect to other larger molecules. For example, the glass transition temperature may change as much as some 10° for mixtures containing only 1% of water moisture.

Among the various sugars extensively studied in both the solution state and the solid state, sucrose is by far the most important and is the largest commodity in the world trade [4]. Unlike other unstable glassy systems, anhydrous sucrose can be brought to the amorphous glassy state also by conventional cooling. However, despite the apparent simplicity of obtaining the glass form of this important sugar, the T_g of amorphous sucrose is reported in the literature to range between 50 and 70°C (see Table 1). In this paper a preliminary report of an investigation dealing with the thermal glassy properties and the relaxation phenomena of sugars and other food components is presented. In particular, it shows that the Dynamic Differential Scanning Calorimetry (DDSC) can be very useful for studying these phenomena, without some of the problems encountered in the conventional DSC.

2. Experimental conditions

Calorimetric measurements were carried out with a Perkin-Elmer DSC 7 (power compensation) differential scanning calorimeter, connected to a computer via a TAC7/DX Thermal Analysis Instrument Controller. The calorimeter was equipped with the Dynamic DSC (DDSC) Accessory [5] and the 7 Series/UNIX DDSC software by Perkin-Elmer was used. The thermal unit

Table 1
Values of T_g of sucrose reported or quoted in the literature

T_g	Reference
52	F. Franks and J. R. Grigera, Water Science Reviews, Cambridge University Press, 1990, The molecules of life, 187, Vol. 5.
52	F. Franks, Process. Biochem., 24 (1989) R3–R7.
52	J.M.V. Blanshard and F. Franks, Food Structure and Behaviour, J.M.V. Blanshard and P. Lillford, eds., Academic Press, London, 1987, 51.
53	H. Levine and L. Slade, Cryo-Lett., 9 (1988) 21.
55	R.H.M. Hatley and A. Mant, Int. J. Biol. Macromol., 15 (1993) 227.
55	F. Franks and A. Hatley, U.S Patent 5, 098 (1992) 893.
57	F. Franks, Cryo-Lett., 11 (1990) 93.
57	Y. Roos and M. Karel, J.Food Sci., 56 (1991) 38.
57	Y. Roos and M. Karel, J.Food Sci., 56 (1991) 266.
57	Y. Roos and M. Karel, Biotechnol. Prog., 6 (1990) 159.
58	R.H.M. Hatley, C.van den Berg and F. Franks, Cryo-Lett., 12 (1991) 113.
61	S.S.N. Murthy, Gangasharan and S.K. Nayak, J. Chem. Soc. Faraday Trans., 89 (1993) 509.
62	Y. Roos, Handbook of Food Engineering, D.R. Heldman and D.B. Lund, eds., Marcel Dekker, New York, 1992, 145.
66	J.L. Green and C.A. Angell, J. Phys. Chem., 93 (1989) 2880.
67	T. Soesanto and M.C. Williams, J. Phys. Chem., 85 (1981) 3338.
67	Y. Roos, Carbohydr. Res., 238 (1993) 39.
67	Y.Roos and M. Karel, Cryo-Lett., 12 (1991) 367.
67	M.P.W.M. te Booy, R.A. de Ruiter, and A.L.J. de Meere Pharmaceut. Res., 9 (1992) 109.
69.5	C. van den Berg, Carbohydr. in the Netherlands, 8 (1992) 23.
70	P.D. Orford, R. Parker and S.G. Ring, Carbohydr. Res., 196 (1990) 11.
70	C. van den Berg, F. Franks and P. Echlin, The Glassy State in Food, J.M.V. Blanshard and P.J. Lillford, eds., Nottingham University Press, Loughborough, 1993, p. 249.
70	F. Franks and R.H.M. Hatley, Stability and Stabilization of Enzymes, W.J.J. van den Tweel, A. Harder and R.M. Buitelaar, eds., Elsevier, Amsterdam, 1993, p. 45.
70	F. Franks, Pure Appl. Chem., 65 (1993) 2527.

was thermostatted with an external thermocryostat in which the coolant was kept at 0°C. Calibrations were made using indium and zinc at the same scan rates used in the experiments, a nitrogen flux was used as a purge gas for the furnace. The DSC scans were run on samples of weight ranging between 15 and 25 mg and sealed in the Perkin-Elmer DSC aluminium pans. An empty aluminium pan was used as reference cell. Experiments were carried out by heating the sample from the starting temperature of 30°C to 95°C with an underlying heating rate of 0.5 K min^{-1} and a temperature amplitude T_p of 0.3 K for the thermograms of the annealed samples. The conditions of an underlying scan rate of 0.5 K min^{-1} and T_p=1 K were used to study the frequency effect on the glass transition, by changing the frequency of the temperature modulation between 8 and 83 mHz. The heat flux signal was treated according to the linear response theory approach included in this software, obtaining simultaneously the static C_p, and by a deconvolution procedure the components of the (dynamic) complex specific heat capacity C_p^*, i.e., the storage (C_p'), and the loss (C_p'') heat capacity, respectively [6,7]. In addition, the data files were transferred in a suitable format to an external work-station to perform independent data analysis and processing, as well as graphic plotting of the results.

The sucrose sample used was purchased from Carlo Erba and was of analytical grade. The water content of 0.15% was determined by Karl–Fischer measurements using a Mettler DL18 Karl–Fischer titrator.

3. Enthalpy relaxation phenomena

A typical glassy state is not in the equilibrium state, but with sufficient ageing at a temperature close to T_g the properties will eventually approach some equilibrium values. This non-equilibrium condition is also the underlying reason of the fact that the determination of T_g values is strongly affected by the time scale of measurement, on whether the cooling or heating mode is used and on the previous thermal history of the sample. For example, in the cooling mode the glass transition occurs at different temperatures, the faster the scan rate, the lower the T_g observed.

It has been repeatedly pointed out that when a glassy substance is heated, the changes in its properties may overshoot those of the "equilibrium" fluid because of the lag of the property gradient with respect to the temperature gradient. However, the non-equilibrium properties are subjected to the ageing process, e.g., the enthalpy of the glassy state decreases with ageing and, therefore, the experimentally determined curve of the specific heat vs. temperature shows a greater overshoot peak with increasing ageing time. The effect in the heating thermogram is the recovery of the enthalpy lost during the ageing at $T<T_g$. The phenomenon, known as enthalpy relaxation, results from the slow relaxation of the glass from its initial non-equilibrium state towards its final thermodynamic state and it can be experimentally studied by annealing the sample as a function of the time t_a at an ageing temperature, $T_a<T_g$. Physical ageing is commonly carried out on amorphous samples in which any previous thermal treatment has been erased. This can be done by annealing the permanently amorphous compound at a temperature of at least 40 K greater than T_g or, in the case of crystallisable materials as in this work, by melting the sample and cooling it in the amorphous phase at a suitable cooling rate. In the latter case, care has to be taken as to whether any decomposition occurs in these conditions.

Theoretical approaches have been made to describe the rate at which the glassy state undergoes the physical ageing [8]. However, the number of variables and molecular parameters (often semiempirical) which enter into a theoretical treatment makes the exact solution of the problem very difficult to reach in practice. In the original treatment proposed by Petrie and Marshall [9], the kinetics of relaxation involved was analyzed by using a model with a single relaxation time. Due to the physical complexity of a relaxing glass, it is now recognised that an improvement in the description of the extent of the enthalpy relaxation with time can only be reached by introducing the concept of a distribution of relaxation processes, the breadth of which is defined by the value of β, as was reported by Williams and Watts in the empirical approach to the dielectric relaxation [10].

In principle, at any given ageing temperature T_a, the measurable quantities of the enthalpy relaxation process are the $\Delta H(t_a,T_a)$ values as a function of the ageing time t_a and the maximum extent of enthalpy relaxation $\Delta H(t_\infty,T_a)$. These two quantities enter into the equation which relates the extent of the enthalpy relaxation to the Williams-Watts function:

$$\Phi(t_a) = [1 - \Delta H(t_a, T_a)/\Delta H(t_\infty, T_a)], \quad (1a)$$

$$= \exp[-(t_a/\tau_{eff})^{\beta}], \quad (1b)$$

where $\Phi(t_a)$ is the decay function and τ_{eff} is some effective relaxation time of the system, which depends on the ageing temperature T_a but also on the departure of the system from the final equilibrium state. This latter (and "unfortunate") dependence can be easily, but only intuitively, understood by noting that the size of the domains undergoing the transformation increases with ageing and that the relaxation times depend on the size of these domains.

The values of the enthalpy loss $\Delta H(t_a,T_a)$ can be obtained from DSC experiments by integrating the ΔC_p difference $[\Delta C_p = C_{p(aged)} - C_{p(un)}]$ of the curves of aged and unaged samples between two temperature limits not too close to the glass transition region:

$$\Delta H(t_a, T_a) = \int_{T<T_g}^{T>T_g} [C_{p(aged)} - C_{p(un)}]\,dT. \quad (2)$$

Similarly, the $\Delta H(t_\infty,T_a)$ value is commonly obtained by the integration of the area defined by the extrapolation of the C_p line of the liquid and the C_p curve of an unaged sample, within the integral limits T_a and $T>T_g$, i.e.,

$$\Delta H(t_\infty, T_a) = \int_{T_a}^{T>T_g} [C_{p(liq)}(T) - C_{p(un)}(T)]\,dT, \quad (3)$$

where $C_{p(liq)}(T)$ is obtained by linear fit of the heat capacity of the sample in the liquid state and $C_{p(un)}(T)$ is the experimental heat capacity of the unaged sample.

The primitive model proposed by Petrie and Marshall [9] is based on the concept of a single relaxation time (effective relaxation time τ_{eff}), i.e., the value of $\beta=1$ is imposed in Eq. (1b). With this somehow crude hypothesis the dependence of the τ_{eff} on the ageing temperature and on the ageing time t_a can easily be explored. In fact, by setting $\beta=1$, the effective relaxation time of the system as a function of t_a and T_a is obtained by [11,12]:

$$1/\tau_{eff} = -1/\Phi(t_a)\,d\Phi(t_a)/dt_a. \quad (4)$$

The same authors [9] then proposed an equation to relate the relaxation times calculated by Eq. (4) and the temperature of ageing and to evaluate the apparent activation energy of the relaxation process, E^*, by the linear fit of the $\ln(1/\tau_{eff})$ as a function of $\delta H = \Delta H(t_\infty,T_a) - \Delta H(t_a,T_a)$:

$$\ln(1/\tau_{eff}) = \ln(A') + C\delta H, \quad (5)$$

with

$$A' = A\exp[-E^*/RT_a], \quad (6)$$

where the parameters C and A are constants. Therefore, the Arrhenius-like plot of $\ln(A')$ vs. $1/T_a$ gives the activation energy and the pre-exponential factor.

More recently, in two papers dealing with polymer blends, Cowie–Ferguson have applied a more detailed model [13] in which the relaxation process is described in terms of a summation of many different elementary processes, each one having a characteristic relaxation time τ_i, this determines a distribution of relaxation times, $g(\tau)$, which is related to the relaxation function $\Phi(t)$ by the integral trasformation:

$$\Phi(t) = \int g(\tau)\exp(-t/\tau)\,d\tau. \quad (7)$$

Their approach takes into account the fact that the kinetics of the glass transition and ageing phenomena are usually non-exponential in the sense that the relaxation toward the equilibrium has to be described using a non-exponential decay function $\Phi(t)$. The same concept was also implicit in the empirical function used by Williams and Watts [10], as reported in the Eq. (1b), which includes the presence of several components of τ and gives a fairly good fit for many relaxation processes in a large variety of amorphous materials.

In the Cowie–Ferguson model [13], four parameters are calculated by non-linear fittings of $\Delta H(t_a,T_a)$ vs. $\ln(t_a)$ data at different ageing temperatures. The three parameters of interest here are $\Delta H(t_\infty,T_a)$, τ_c (characteristic time) and β. This self-consistent approach therefore requires very accurate data on a large range of the variables T_a and t_a in order to extract reasonable values of the fitting parameters from the non-linear fittings.

Alternatively, using the graphical methods to evaluate $\Delta H(t_a,T_a)$ and $\Delta H(t_\infty,T_a)$ from the experimental curves and therefore to calculate $\Phi(t_a)$ one may reduce the number of fitting parameters and determine τ_{eff} and β by the linearised form of Eq. (1b) as a double logarithm of $\Phi(t_a)$:

$$\ln[-\ln\Phi(t_a)] = \beta\ln(t_a) - \beta\ln(\tau_{\mathrm{eff}}). \tag{8}$$

From Eq. (8), the values of τ_{eff} and β are obtained by linear least-square fitting of the $\ln[-\ln(t_a)]$ data as a function of $\ln(t_a)$, with the further assumption that τ_{eff} is independent of ageing time.

It is worth noting that the careful analysis of Cowie and Ferguson [13] has shown some discrepancy between the values calculated with the different methods, mainly (but not exclusively) due to the more or less arbitrary way of extracting $\Delta H(t_\infty, T_a)$ from the experimental curves and furthermore to the assumed independence of τ_c from the ageing time. However, the non-linear least-square analysis made by the authors requires a large number of experiments (very time consuming). Therefore care has to be taken to avoid a possible acritical use of their approach in the absence of an appropriate statistical analysis.

4. Results and discussion

4.1. *Assessment of the experimental conditions of the dynamic differential scanning calorimeter*

The DSC furnace system is characterized by a time response (or dynamic time constant) due to the finite thermal conductivity and heat capacity of all the components (cells, temperature sensors and thermoelectric parts). This causes a distortion in the shape of the heat capacity function characteristic of every instrumental set-up which therefore has to be properly corrected (desmeared). The desmearing procedure commonly used comes directly from the theory of linear response [14], according to which the output of any apparatus can be described as the convolution product of an input power and the so-called Green's function of the apparatus, $G(t)$:

$$\Phi_{\mathrm{out}}(t) = G(t) * \Phi_{\mathrm{in}}(t) = \int G(t-t')\Phi_{\mathrm{in}}(t')\,\mathrm{d}t'. \tag{9}$$

In addition to the heat transfer contributions, the $G(t)$ function also contains terms which depend on the thermal behaviour of the sample, i.e., the total Green's function is the convolution product of the function of the DSC apparatus and that due to the sample:

$$G(t) = G_{\mathrm{s}}(t) * G_{\mathrm{dsc}}(t).$$

Therefore, the response of the instrument changes from one experiment to another and has to be evaluated for each combination of sample/temperature range/scan rate [15]. The function $\Phi_{\mathrm{in}}(t)$ can be thought of as the true heat flow into a thermally ideal sample.

In our instrument (the Dynamic Differential Scanning Calorimeter, DDSC-7), as a first approximation, the Green's functions as a function of the scan rate were obtained experimentally from the relaxation behaviour of the DSC apparatus at the beginning (switching-on the scan rate) and at the end (switching-off) of a run [16]. The time response constants were evaluated as the equivalent temperature shift, ΔT, as a function of the scan rate (Fig. 1). A linear but different dependence of ΔT was observed for samples having different C_p (indium, water, sucrose) and for empty pans. For the latter case, the same results have been obtained from a standard DSC run as well as from a modulated run, by using different frequencies and amplitudes.

The thermal treatments to which the sucrose was subjected inside the DSC apparatus before the modulated temperature scans were: (a) a scan from 30°C to

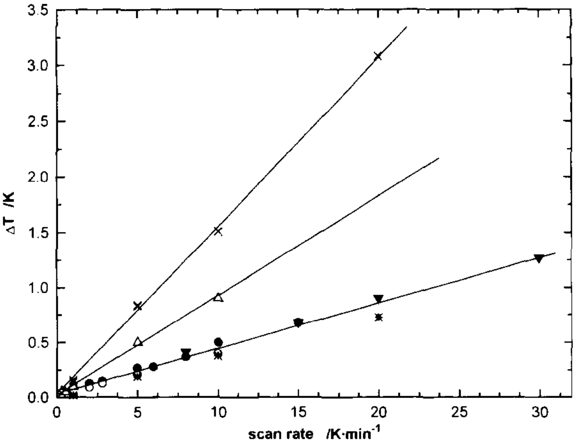

Fig. 1. Temperature delays, ΔT, as a function of scanning rate for samples with different C_p (*: indium, △: sucrose, ×: water) and for empty pans (with temperature amplitude T_p and initial temperature T_0 (°C): ● $T_p = 2$, $T_0 = 50$; ▼ $T_p = 4$, $T_0 = 50$; ○ $T_p = 2$, $T_0 = 150$).

205°C (above the melting temperature) with a heating rate of 10 K min^{-1}, in order to erase any crystalline order, (b) cooling the sample to 30°C with a scanning rate of 50 K min^{-1} and then holding it at this temperature for 5 min, (c) heating to the ageing temperature T_a with a heating rate of 200 K min^{-1} and then ageing for t_a minutes, (d) cooling it (scan rate 200 K min^{-1}) to the starting temperature of 50°C and dynamic scan at a given underlying scan rate, β°, frequency ν, and amplitude T_p. For the step (b), the ageing temperatures considered in this work were 45, 55 and 60°C and the longest ageing time was 17 h. Within the range of instrumentally controlled conditions, the heating scan (step (d)) was carried out from 50°C to 95°C with an underlying heating rate of 0.5 K min^{-1} and a temperature amplitude T_p=0.3 K. Different conditions (underlying heating rate 0.5 K min^{-1} and T_p=1 K) were used to study the effect of the frequency on the glass transition, by changing the frequencies of the temperature modulation in the range of 8–83 mHz.

4.2. Enthalpy relaxation by annealing experiments

The heating thermograms carried out on sucrose samples aged at a temperature T_a below its T_g for several ageing times t_a show an endothermic overshoot which is a function of t_a. In Fig. 2, the static component C_p vs. T for different ageing times t_a at T_a=60°C is reported (note that the static C_p is equivalent to that measured by conventional DSC). The size and the position of the specific heat overshoot affect the apparent onset of the glass transition, T_{ons} and are almost linear with the ageing time, ranging the T_{ons} from 62°C to 65°C.

The enthalpy effects, $\Delta H(t_a,T_a)$ (defined in Eq. (4)), were obtained by graphical integration of the thermogram of the aged and unaged sucrose samples, while the $\Delta H(t_\infty,T_a)$ were computed by extrapolation of the C_p liquid curve, as mentioned in the preceding section. The logarithm of the relaxation functions $\Phi(t_a)$ as a function of time (i.e., a linearization of Eq. (1b)) is reported for the three T_a in Fig. 3. The non-linearity of these data reveals the presence of shorter and longer relaxation time components (i.e., the non-simple exponential nature of the kinetics) and, therefore, reflects the complexity of the sucrose relaxation process which cannot be described by the elementary mechanism as in the Petrie–Marshall model, with, β=1 in the Eq. (1b). However, continuing in the same order of approximation (β=1) and using Eq. (4) to calculate the values of $1/\tau_{\mathrm{eff}}$, the plot of Fig. 4 can be constructed, in which the logarithm of $1/\tau_{\mathrm{eff}}$ as a function of δH for each annealing temperature T_a is reported. Each line describes the dependence of the relaxation time as a function of the departure from the

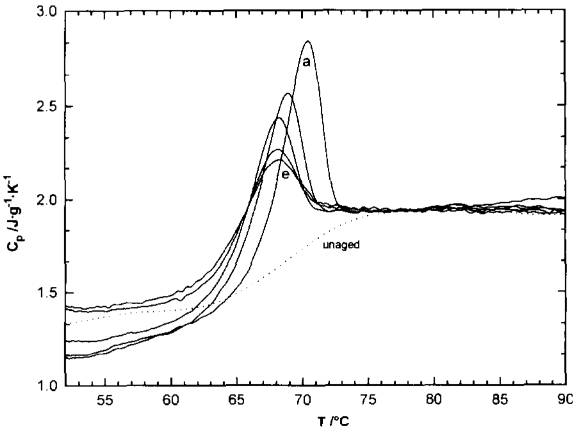

Fig. 2. DSC thermograms of sucrose at different ageing times, t_a at 60°C (from the top to the bottom t_a ranges from 905 (a) to 30 (e) minutes with intermediate ageing times of 300, 180 and 60 min).

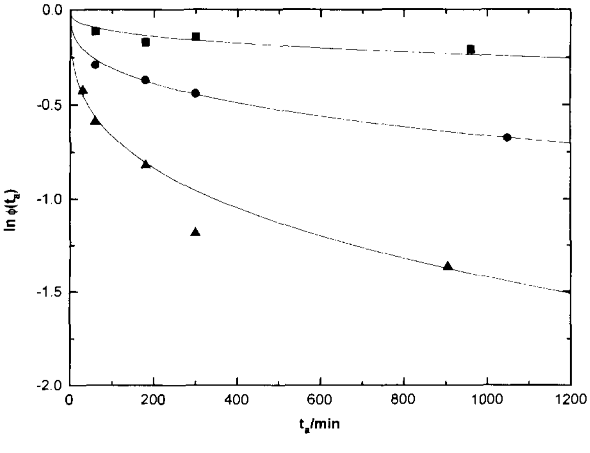

Fig. 3. Dependence of ln $\phi(t_a)$ on ageing time, t_a at three ageing temperatures, T_a (▲ T_a=60°C; ■ T_a=55°C; ● T_a=45°C). Curves are the fitting of the experimental data according to Eq. (1b), with, β=0.32 and τ_{eff}=345 min. (T_a=60°C), τ_{eff}=3480 min. (T_a=55°C) and τ_{eff}=75400 min. (T_a=45°C).

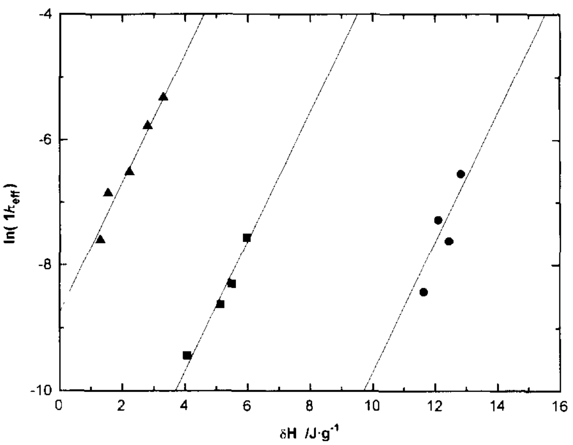

Fig. 4. Plot of $\ln(1/\tau_{eff})$ derived from Eq. (4) vs. δH for three temperatures (▲T_a=60°C; ■ T_a=55°C; ● T_a=45°C).

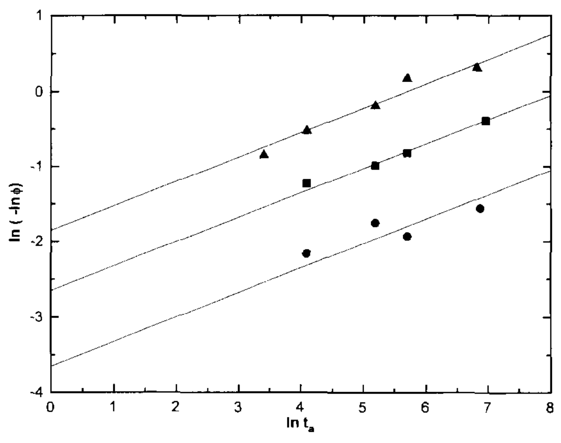

Fig. 5. Plot of $\ln[-\ln \phi(t_a)]$ vs. $\ln(t_a)$ according to Eq. (8) for T_a=60°C (▲), T_a=55°C (■) and T_a =45°C (●). The slope of the fitting lines imposed to be constant gives β=0.32.

equilibrium state, expressed through the quantity δH. The plot clearly shows that the apparent relaxation times depend on both the ageing temperature and on the ageing time, with some time-temperature correspondence. For this reason, bearing in mind a sort of master curve for time–temperature superposition principles, the lines of Fig. 4 have been drawn with the same slope, that is the constant C in Eq. (5). With the same data, the extrapolated values of the intercept $\ln(A')$ at δH=0 have been used in the Arrhenius plot vs. $1/T_a$ to calculate the activation energy of the relaxation process, E^*=640 kJ mol^{-1}. Note that, although the relaxation times are a function of the ageing time, the way the lines are drawn (i.e., parallel to each other) gives one constant value only for the activation energy.

In the preceding section it has been mentioned that a more accurate analysis of the relaxation process would involve the direct fitting of all the parameters from the set of experimental data, according to the suggestion of Cowie and Ferguson [13]. Unfortunately, the number of data does not allow us to extract simultaneously meaningful values for the parameters $\Delta H(t_\infty,T_a)$, τ_{eff} and β, from the non-linear least-square fittings of $\Delta H(t_a,T_a)$ vs. $\ln(t_a)$ data at different ageing temperatures. However, by taking for granted the data of $\Delta H(t_\infty,T_a)$ obtained by graphical integration, Eq. (8) can be used to explore the appropriate value of β which gives the non-linearity of the plot of Fig. 3. Fig. 5 shows the linear least-square fittings of the experimental data by using Eq. (8). Once again, given the little information available on the possible dependence on the temperature, the fitting value of β=0.33 has been "set" as constant. In no way does this mean that, β is independent from the ageing temperature, but simply that the reported value is the average value in the range of T_a considered. The values for β and $\ln(\tau_{eff})$ determined from the slope and the intercept, respectively, have been used to simulate the fitting lines reported in Fig. 3.

We are not able, with the present data, to discriminate whether the function $\Phi(t)$ obtained with Eq. (1a) by using graphically determined values of $\Delta H(t_\infty,T_a)$, could be subject to modification by using different methods to obtain the $\Delta H(t_\infty,T_a)$ values. Cowie and Fergurson have reported that their method provides value of the $\Delta H(t_\infty,T_a)$ which are significantly smaller than those obtained by graphical methods. If so, then the ageing enthalpy data would refer to conditions of higher level of ageing. In all cases, the question raised by Cowie and Ferguson is intriguing and worth studying on a suitable system.

4.3. Dynamic analysis of the glass transition

Thermograms of sucrose carried out with the dynamic accessory are useful for obtaining more information than the usual parameters about glass transition and enthalpy relaxation. The deconvolution of the heat capacity gives the storage (C_p') and loss

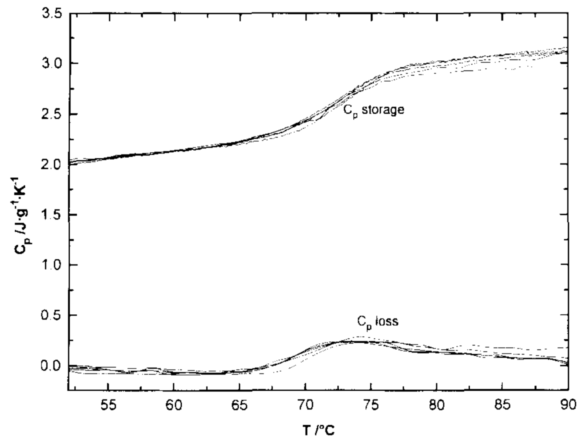

Fig. 6. Storage (C'_p) and loss (C''_p) heat capacity curves of sucrose aged at 60°C. The curves with different ageing times are indistinguishable from each other.

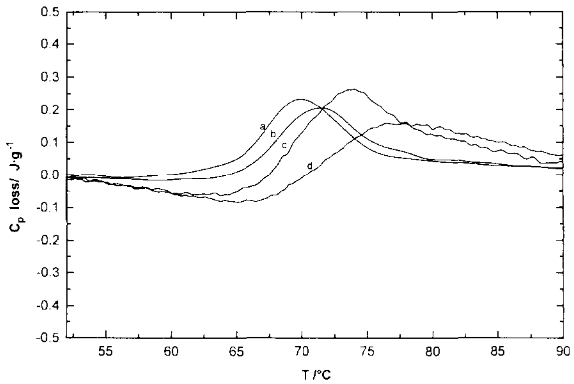

Fig. 7. Loss heat capacity (C''_p) thermograms obtained with different frequencies of temperature modulation (a=8 mHz, b=17 mHz, c=42 mHz and d=83 mHz).

(C''_p) heat capacities. Despite the fact that the total heat capacity gives rise to a well defined peak for the enthalpic relaxation, in both the dynamic components only a change in the heat capacities due to the glass transition process is observed while the relaxation peaks are absent. This result is a direct consequence of the algorithm used to calculate C'_p and C''_p, since they are extracted from the modulated part and therefore are phase-dependent, while the enthalpy relaxation is clearly a thermodynamically irreversible process of the system approaching the equilibrium state. This irreversible part of the process can only be calculated as a difference between the total component and the reversible component (i.e., as $C_p^{irr}=C_p^{tot}-C_p^{rev}$). A thermodynamically irreversible process, therefore, does not appear as part of the oscillating response and is not revealed in the dynamic components C'_p and C''_p, as reported in Fig. 6.

The glass transition temperature, T_g, is therefore more easily calculated by analysing the dynamic response than by using the total heat capacity curve. From inspection of the Fig. 6 (and from mathematical treatment of the curves therein reported) it appears evident that the T_g of sucrose determined by the dynamic components becomes independent of the thermal history (i.e., ageing) of the sample, irrespective of the component used (either the storage or the loss). This is a non-trivial result of great practical importance (see the data quoted in Table 1). It is based on the fact that only the actual thermodynamic part of the transition is examined (or rather the part that is reversible in the time scale considered). The value of T_g=68.5±0.5°C is therefore obtained as an average of the experimental data (13 measurements) with different ageing times and different ageing temperature. It should, however, be noted that the T_g calculated in this way is still a function of the frequency (8.3, 17, 42 and 83 mHz) used in the modulation of temperature, similarly to any other transition process explored in the frequency–temperature domains (e.g., dynamico-mechanical and dielectric measurements). As a preliminary example of this dependence the C_p loss component is reported in Fig. 7 at four different frequencies for the sucrose aged at T_a=60° and t_a=180 min. The range limits of ν=8.3–83 mHz are instrumentally set by the other two experimental conditions, the underlying scan rate (β°=0.5 K min^{-1}) and the amplitude of the temperature modulation (T_p=1 K), which depend on the nature of the thermal event and on quasi-isothermal conditions required by the method [17].

The dependence of the "dynamic" glass transition temperatures (onset and peak), with the frequency suggests the use of these data to calculate the corresponding activation energy for the transition from the glassy state to the fluid state (Fig. 8). All the data points (i.e., the onset temperature, T_g(ons) and the mid-point temperature, T_g(mid) of the C'_p and C''_p components) can be used in a plot of ln ν vs. 1/T_g, giving an average value of 350 kJ mol^{-1} for the

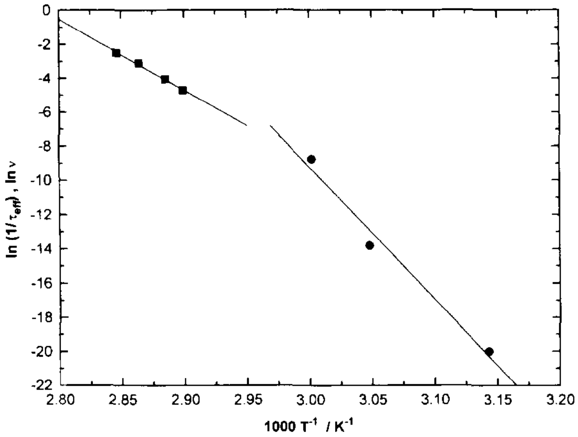

Fig. 8. Arrhenius plot of the relaxation times (plotted as $\ln(1/\tau_{\text{eff}})$, ●) and of the frequencies modulation (plotted as $\ln \nu$, ■), respectively, as a function of the inverse of ageing temperature and of glass transition, $T_{\text{g(ons)}}$.

activation energy. This value is smaller than the activation energy obtained for the ageing process (Fig. 8).

5. Conclusion

The physical ageing phenomenon of sucrose has been investigated with two purposes: (a) to assess the kinetic behaviour of the ageing process and (b) to attempt a more accurate definition of the glass transition temperature. The first aim has been only partially achieved, since the complexity of the glass relaxation (with a value of β=0.33) makes impossible a linearisation of a kinetic exponential equation. Therefore, only a partial description of the process has been obtained and a larger number of more accurate data seems to be necessary for this task. The second aim has been achieved inasmuch as the dynamic components of the thermograms of the glass transition region are independent of the ageing processes. Therefore, the glass transition temperature is quantitatively defined by using the temperature modulation mode.

Other unclear transitions ascribed to either glass transition or to recrystallisation during melting detected in water–food systems will benefit of these dynamic procedures.

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