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Calorimetric analysis of the structural relaxation in partially hydrated amorphous polysaccharides. II. Phenomenological study of physical ageing.

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Abstract

Any glassy material stored at a temperature below its glass transition temperature experiences a structural relaxation that occurs as a function of time and temperature. Using Differential Scanning Calorimetry, enthalpy relaxation was studied on a series of hydrated polysaccharides in comparison with synthetic polymers, poly(methyl methacrylate) (PMMA) and poly(vinyl pyrrolidone) (PVP). The ageing kinetics were evaluated from the relaxation function based on the fictive temperature evolution. While extruded starch equilibrated apparently within the experimental time, amylopectin and phytoglycogen aged slightly faster than PMMA and hydrated PVP without reaching completely their equilibrium. Ageing effects detected after short ageing at very low temperatures ($T_g - 100$°C) revealed the wideness of the relaxation time spectrum. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Differential scanning calorimetry; Glass transition temperature; Fictive temperature; Physical ageing; Structural relaxation

1. Introduction

Glassy materials display mechanical and physical properties similar to those of crystalline solids, while keeping a molecular arrangement more characteristic of a liquid. Being far from the thermodynamic equilibrium, glassy materials are subject to the so-called 'structural relaxation', molecular re-arrangements leading to lower states of energy. These alterations may be of significance for food products since they directly affect enthalpy, volume, mechanical as well as diffusion properties. The term 'physical ageing' was introduced by Struik (1978) to distinguish these effects from other ageing processes such as chemical reactions, degradations or changes in crystallinity.

Following the pioneering works of Kovacs (1963), Struik (1978), physical ageing has been widely studied as related to the evolution of physical properties such as volume (Adachi & Kotaka, 1982; Bero & Plazek, 1991), enthalpy (Berens & Hodge, 1982; Cortes & Montserrat, 1994; Echeverria, Su, Simon & Plazek, 1995), creep compliance (Echeverria et al., 1995; Simon Plazek, Sobieski & McGregor, 1997), relaxation times evaluated from dielectric spectroscopy (Alegria, Goitiandia, Telleria & Colmenero, 1991), reaction of photochromic probes (Royal & Torkelson, 1992), and positron annihilation (Davis & Pethrick, 1998; Ramachandra, Ramani, Ramgopal & Ranganathaiah, 1997). Numerous reviews, papers and books are available on the glassy state description (McKenna, 1989; Scherer, 1990) and structural relaxation (Haward & Young, 1997; Hodge, 1994; Hutchinson, 1997; Kovacs, 1963; Plazek & Andrekanic, 1995; Struik, 1978). Structural relaxation can be essentially described by its non-linearity and non-exponentiality: the former is responsible for the relaxation rate dependence on the sign and magnitude of the initial departure from the equilibrium state, while the latter arises from the wideness of the relaxation times spectrum. This last point is for instance responsible for the so-called memory effects (Adachi & Kotaka, 1982; Struik, 1978).

Enthalpy relaxation phenomena were first observed in differential scanning calorimetry (DSC) experiments as a consequence of the sample storage at room temperature. The corresponding endothermic peaks were observed in the 50–60°C region on fresh samples and disappeared on second scans. This behaviour was observed on a wide variety of products, including wheat gluten (Hoseney, Zeleznak & Lai, 1986), breakfast cereals (Sauvageot & Blond, 1991), hydrated glutenin (Cocero & Kokini, 1991), amylopectin (Kalichevsky, Jaroszkiewicz, Ablett, Blanshard & Lillford,

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1992), hydrated lintners (Le Bail, Bizot & Buléon, 1993) and native rice starch (Seow & Teo, 1993). Different explanations have been put forward for the observed endothermic peak. A few articles appeared in favour of carbohydrate–water interactions (Appelqvist, Cooke, Gidley & Sally, 1993; Gidley, Cooke & Ward-Smith, 1993; Yuan & Thompson, 1994) whereas other studies, following Shogren interpretation (Shogren 1992) favoured enthalpy relaxation associated with the structural relaxation of the amorphous phase (Lawton & Wu, 1993; Le Bail et al., 1993; Livings, Breach, Donald & Smith, 1997; Shogren & Jasberg, 1994; Seow & Vasanti-Nair, 1994). The occurrence of enthalpy relaxation in polysaccharides was definitely assessed by Thiewes and Steeneken (1997), in the light of the phenomenology observed on synthetic polymers.

Probably because of a more simple chemical composition, structural relaxation in small sugars was recognised earlier. Kovacs, for instance, studied the volume relaxation of glucose in 1963. Enthalpy relaxation of sugars such as sorbitol, maltose and sucrose has already been the subject of systematic studies (Chang & Baust, 1990; Faivre, David & Perez, 1997; Schmidt & Lammert, 1996; Urbani, Sussich, Prejac & Cesaro, 1997) involving the use of simulation models (Lammert, Lammert & Schmidt, 1999; Noel, Parker, Ring & Ring, 1999).

Enthalpy relaxation is now clearly recognised as a significant phenomenon occurring during storage of food materials, but there is a lack of an extensive evaluation of its importance. Food products are usually complex mixtures of a variety of components that may be affected by recrystallisation, phase separation or component migration. The study of enthalpy relaxation in these systems should therefore be focused first on their polymeric matrix, in presence of water, its almost unavoidable plasticiser. Among the available techniques, we chose DSC since it permits to control easily thermal histories and to keep constant the water contents during experiments.

Following the first part dealing with the glass transition and its dynamic aspects (Borde, Bizot, Vigier & Buléon, 2001), this paper gives a wide picture of enthalpy relaxation in hydrated polysaccharides as compared to standard synthetic polymers such as poly(methyl methacrylate) (PMMA) and poly(vinyl pyrrolidone) (PVP). Complementary approaches were focused on the low temperature ageing, the impact of the cooling rate and the relevance of the Lagasse method. These data will also provide a basis for further studies involving the use of a simulation model in order to foresee the effect of thermal history on time scales far beyond the experimental window.

2. Materials and methods

2.1. Products

We used waxy maize starch purchased from Roquette Frères (Lestrem-France) as a source of amylopectin. Potato starch from Roquette Frères was destructured by extrusion (twin extruder, 130°C, 30% H_2O, SME: 142 kWh t^{-1}, conditions for little expansion and no degradation). Phytoglycogen was extracted from sugary maize su-1 by aqueous dispersion and alcoholic precipitation. For these three polysaccharides, casting of aqueous solution on a Teflon-coated hot plate produced amorphous material as confirmed by X-ray diffraction analysis. PVP purchased from Sigma ($M_w = 360{,}000$) and PMMA from Goodfellow were used as received. The water content of our samples was adjusted via vapour phase conditioning over saturated salt solutions after complete drying over phosphorus pentoxide at 50°C. All products were hydrated by equilibration over a K_2CO_3 saturated solution ($a_w = 0.43$). Amylopectin was also studied at a higher moisture content, after equilibration on NaBr saturated salt solution. ($a_w = 0.57$). The final moisture contents (m.c) were all determined by Karl Fischer titration and expressed as total weight percentages (i.e. on wet basis).

2.2. Differential scanning calorimetry

2.2.1. Equipment

A differential heat flux calorimeter DSC 121 Setaram (France) was used for calorimetric measurements. Temperature and enthalpy calibrations were checked with Indium ($T_m = 156.6$°C, $\Delta H_m = 28.55$ J g^{-1}) and Gallium ($T_m = 29.9$°C, $\Delta H_m = 80.14$ J g^{-1}). Pressure-tight crucibles ($P_{max} = 15$ MPa) allowed safe manipulations of hydrated products up to high temperatures (100–140°C, typically $T_{g1/2} + 40$°C). Specific funnel and plunger were used for a complete filling of crucibles (up to 120 mg). Due to the thermal inertia of detector and crucibles, the heating rate was kept constant at 3°C min^{-1}. Heat flow data were transformed into specific heat capacity values, after baseline substraction and corrections accounting for differences in masses (alumina from blank and reference, empty crucibles).

2.2.2. Temperatures definitions

The notations we used are defined as follows:

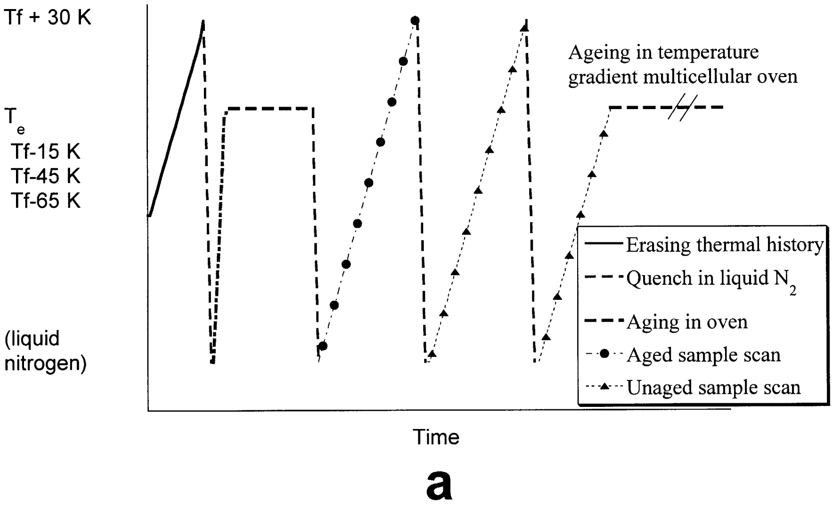
$T_{g1/2}$, temperature of the midpoint of the transition (inflexion point).

$T_f{}'$, fictive temperature characteristic of the structural state of a glass. It was calculated as defined in the preceding paper (Borde et al., 2001) from DSC thermograms recorded on heating ramps (+3°C min^{-1}). This definition of the glass transition temperature was preferred for its higher precision (±0.5°C), especially for aged glasses.

T_{f0}, fictive temperature $T_f{}'$ of the glass at the starting time $t_e = 0$ of the ageing.

T_e and t_e, temperature and duration of isothermal ageing.

The ageing temperature T_e may be defined with respect to the material glass transition in two ways, either by simple



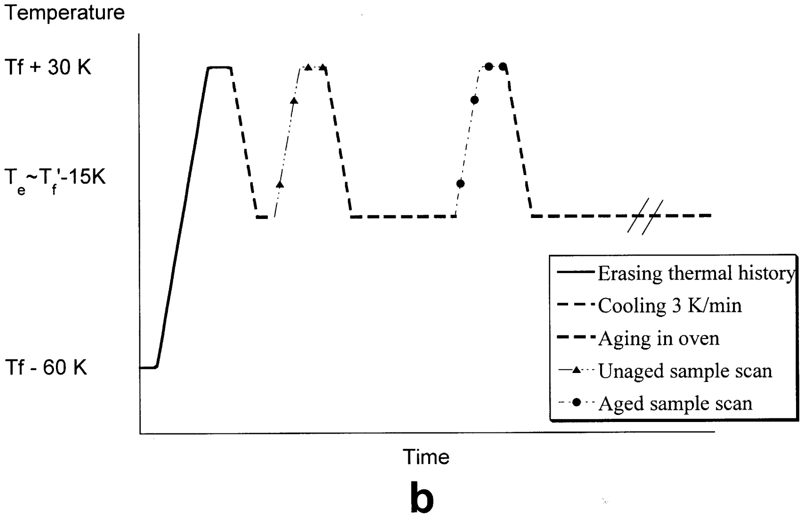


Fig. 1. Thermal history for enthalpy relaxation measurements (a) following classical thermograms difference, (b) following Lagasse's method.

difference $\Delta T_e = T_{f0} - T_e$, or under a reduced form

$$T_{er} = \frac{T_{f0} - T_e}{T_{f0}} = \frac{\Delta T_e}{T_{f0}}.$$

This dimensionless variable T_{er} expresses the relative fractional decrease in available thermal kinetic energy and is more adapted for the comparison of ageing kinetics in the case of products having different glass transition temperatures.

T_{min} and T_{max}, temperatures taken, respectively, in the glassy and liquid domains of the materials thermograms. In both glassy and liquid regions, the experimental heat capacity of our products can be fitted by linear curves.

2.2.3. Thermal history: time–temperature diagrams

All experiments began with a heating ramp to a temperature of $T_f + 30$ K in order to erase the material's previous thermal history. Amorphous glasses were then formed with an imposed cooling rate.

In the first part of our study (Fig. 1a), DSC pans were quenched into liquid nitrogen (effective cooling rate ~60–100°C min^{-1}) and then aged for durations t_e (from 2 h to 12 days), at different ageing temperatures T_e, corresponding to $\Delta T_e \sim 15$, 45 and 65°C. The isothermal ageing experiments were performed in the calorimeter for t_e shorter than 48 h (error on $T_e < 0.1$°C), and in an external oven for longer experiments (error on $T_e < 0.2$°C). After ageing, samples were quenched again and DSC thermograms, $Cp_{aged}(t_e, T_e)$ were recorded. Second scans were performed immediately after a new quench yielding the Cp_{unaged} of our samples.

In the second part of this work, a slower cooling rate was

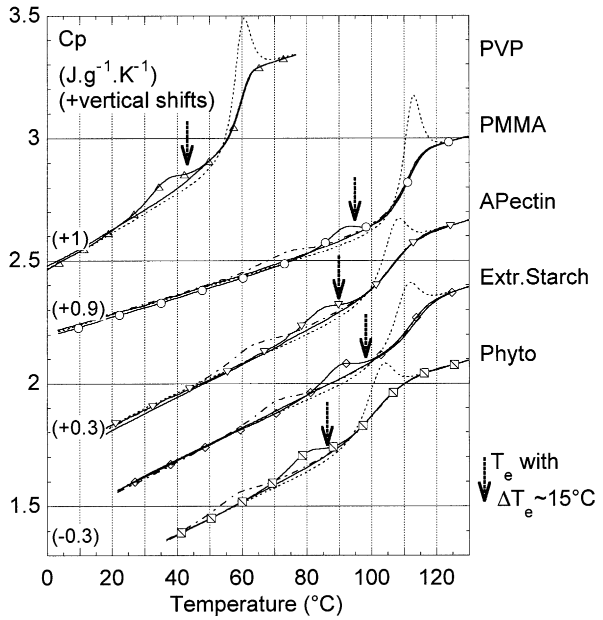


Fig. 2. Enthalpy recovery thermograms for the series of selected polymers aged for $t_e = 24$ h at $\Delta T_e \sim 15, 45, 65°$.

used, 3°C min^{-1}. Within the Lagasse method (Lagasse, 1982) the same rate was also used for heating ramps (Fig. 1b). In that case, the cooling ended at the ageing temperature T_e, and the Cp_{aged} thermograms were recorded on heating ramps beginning from that same temperature. The transitory regimes of the thermograms were fully kept for the calculations.

2.2.4. Enthalpy relaxation

The amount of enthalpy relaxed during ageing (and thus recovered during the DSC heating scans) was evaluated by integration of the difference between thermograms of aged and unaged (second scan) samples.

$$\Delta H_{relax} = \int_{T_{min}}^{T_{max}} (Cp_{aged} - Cp_{unaged})\,dT.$$

Some adjustments (vertical shifts) were sometimes used to force equality of the Cp's in the liquid region in order to allow difference and integration calculations. Such experimental discrepancies can be explained by variations in thermal contacts, baseline or sample position. When calculating ΔH_{relax} on data obtained from the Lagasse method, T_e was the low temperature integration limit and the unaged sample was stabilised for 700 s at T_e.

The enthalpy recovery peak and its evolution with ageing were also determined from the difference curves, $Cp_{aged} - Cp_{unaged}$. The temperature corresponding to the peak maximum was noted T_{peak} and its maximal amplitude, $Cp_{aged} - Cp_{unaged}(T_{peak})$ was noted A_{peak}.

The limiting value of the enthalpy that would be relaxed in the case of a complete equilibration of the glass, $\Delta H_{relax\ \infty}$, was evaluated with the following formula

$$\Delta H_{relax\ \infty}(T_e) = \int_{T_e}^{T_{max}} \left[Cp_{liquid}(T) - Cp_{unaged}(T)\right]dT$$

$$= \Delta Cp(T_{f0})(T_{f0} - T_e)$$

with $Cp_{liquid}(T)$ and $Cp_{glass}(T)$ the best fitting straight lines for the experimental Cp in its liquid and glassy state respectively, and $\Delta Cp(T)$ the difference $Cp_{liquid} - Cp_{glass}$.

During ageing, the fictive temperature of the glass, initially equal to T_{f0}, tends to decrease towards the ageing temperature T_e, fictive temperature of the metastable equilibrium that may finally be attained by the glass. We therefore expressed the ageing process in the normalised form of a relaxation function, $F_{H\ relax}$ taking the value zero at $t_e = 0$ and 1 after complete equilibration of the glass.

$$F_{H\ relax} = \frac{T_{f0} - T_f(t_e)}{T_{f0} - T_e}.$$

3. Results and discussion

3.1. Enthalpy relaxation during ageing at $\Delta T_e = 15, 45, 65°C$

In this part, glasses were prepared by quenching in liquid nitrogen as described in Fig. 1a. This drastic cooling was intended to produce samples further from equilibrium, thus more likely to undergo structural relaxation, possibly yielding a higher signal to noise ratio. Experiments were carried out after isothermal ageing at temperatures corresponding approximately to $\Delta T_e = 15$, 45 and 65°C. Hydrated PVP having a very low glass transition temperature, we performed the study for $\Delta T_e = 15$ and 45°C only.

The thermograms recorded after 24 h of ageing with $\Delta T_e = 15$, 45, 65°C are presented on Fig. 2 for all products (dotted arrows indicate T_e for each sample). The enthalpy recovery peaks obtained for these samples are analysed in Table 1 for the case $\Delta T_e = 15$°C. The peak shape is described by its amplitude A_{peak}, half height width and area ΔH_{relax} whose values were measured on differences between aged and unaged thermograms, $Cp_{aged}(T) - Cp_{unaged}(T)$. Hydrated polysaccharides display similar symmetric peaks, extruded starch presenting the wider one. PVP and PMMA show thinner peaks with a high amplitude A_{peak} for similar areas ΔH_{relax}. The high $\Delta H_{relax\ \infty}$, estimated from ΔT_e and $\Delta Cp(T_{f0})$ and compared with ΔH_{relax}, indicate that these glasses are still far from equilibrium.

The peak position and amplitude are clearly related to the ageing temperature. After 24 h, the enthalpy recovery peak maximum temperatures T_{peak} are roughly situated at $T_e + 18$°C for $\Delta T_e = 15$°C, and $T_e + 25$°C for $\Delta T_e = 45$ and 65°C. Extruded starch behaves a little differently, with lower T_{peak}'s equal to $T_e + 14$°C and $T_e + 22$°C for $\Delta T_e = 15$°C and (45 and 65°C), respectively. Peaks are all

Table 1
Enthalpy recovery peaks characteristics of quench cooled products after ageing 24 h at $\Delta T_e \sim 15°C$

Product	Moisture content %H_2O	A_{peak} (J g^{-1} °C^{-1})	Half height width(°C)	ΔH_{relax} (J g^{-1})	ΔH_{relax} (J g^{-1})
Amylopectin	10.9	0.16	7.9	1.0	3.4
Phytoglycogen	10.6	0.16	7.9	1.0	3.1
Extruded starch	12.2	0.19	8.1	1.2	3.5
PMMA	0.6	0.29	5.3	1.0	4.3
PVP	15.1	0.30	5.0	1.0	5.3

the more developed, as the ageing temperature is closer to the glass transition temperature: this observation stems from the fact that the structural relaxation is mainly governed by molecular mobility.

Increasing the ageing time t_e, both amplitude and position on the temperature scale of the enthalpy recovery peak are observed to increase. This is illustrated in Fig. 3 where T_{peak} and A_{peak} are reported as a function of the logarithm of ageing time, for amylopectin (10.9% H_2O). The development of the enthalpy recovery peak is linear with the logarithm of ageing time: storage temperatures being quite low, the glasses are not yet equilibrated (even after 96 h ageing) and the final regime where ΔH_{relax} should reach a plateau and its final value $\Delta H_{relax\ \infty}$ remains out of our experimental window. The regression coefficients of the linear fits are given in Table 2 for all samples. The fictive temperature variations can be precisely followed in the case of high T_e only, they have been fitted by the same laws.

The ageing behaviour of amylopectin, extruded starch, phytoglycogen and PMMA are illustrated on Fig. 4 for $\Delta T_e = 15°C$. Extruded starch behaves differently from other samples, its peak increases in amplitude with ageing time, but T_{peak} remains almost constant, thus yielding poor fitting values. When extruded starch is aged at lower temperatures, this peculiarity disappears. PVP and PMMA display large increases of peak amplitude with ageing time but, their peaks being thinner, peak areas are not very different from those found for hydrated polysaccharides (Table 1 and Fig. 4).

The enthalpy recovery peak develops less markedly (amplitude and area) for the lower ageing temperatures, but the shift on the temperature scale is larger as may be checked on the evolution of t_1 in Table 2. In the case of low ageing temperatures, ($\Delta T_e = 45$, 65°C), the enthalpy recovery peaks appear as simply superimposed on the trace corresponding to the unaged glass. Chen and Wang (1981) obtained similar results by ageing a nearly monodisperse polystyrene at $T_g - 62°C$ and such ageing effects were also observed by Chen and Kurkjian (1983) for B_2O_3 glasses at temperatures lower than $T_g - 100°C$. This fact can be surprising since the non-linear character of structural relaxation might induce a coupling between the glass transition and the changes induced by annealing. Hodge (1994) explained these observations by the high difference in the effective reduced times associated with the sub-T_g ageing and the glass transition. In this view, the DSC response (glass transition and sub-$T_g$peak) can be considered as a Boltzmann superposition of two separated perturbations:

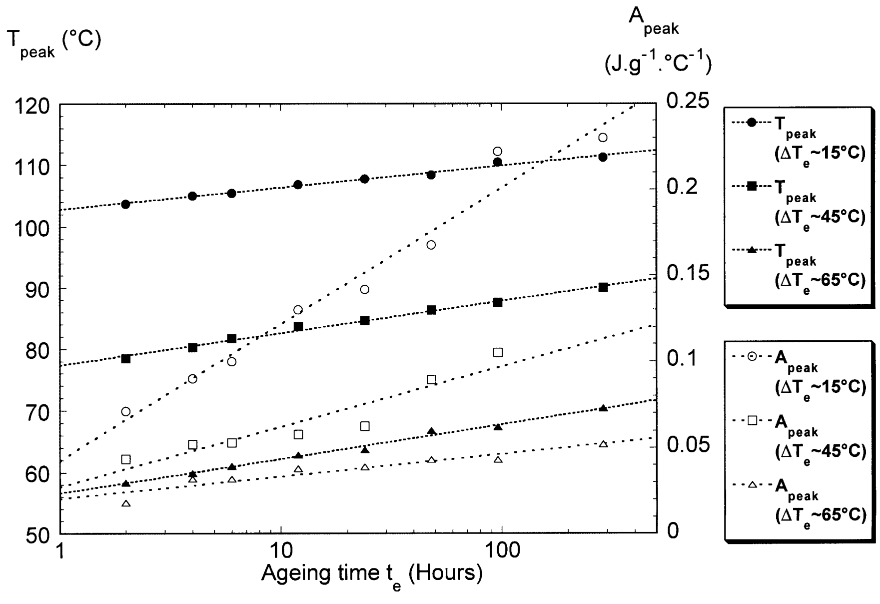


Fig. 3. Evolution of peak maximum and peak amplitude for amylopectin (10.9% H_2O) aged for $\Delta T_e \sim 15$, 45, 65°.

Table 2
Characteristics of enthalpy relaxation kinetics for quenched samples

Product	Moisture content %H_2O	T_{f0} (°C)	T_e (°C)	T_{er} (T in K)	$T_{max} = T_0 + t_1 \log(t_e)$ (°C)			$A_{peak} = A_0 + a_1 \log(t_e)$ (J g^{-1} °C^{-1})		$T_f = T_{f0} - t_f \log(t_e)$	
					T_0	t_1	R^2	a_1	R^2	t_f	R^2
Amylopectin	10.9	107.0	90	0.047	102.9	3.530	0.98	0.084	0.96	2.009	0.93
			60	0.124	77.3	5.245	0.99	0.035	0.88		
			40	0.176	56.6	5.569	0.99	0.013	0.89		
Amylopectin	12.7	85.0	71	0.039	85.8	2.485	0.99	0.067	0.98	2.22	0.97
			41	0.123	57.3	4.783	0.99	0.042	0.86		
			21	0.179	36.8	5.208	0.98	0.016	0.79		
Phytoglycogen	10.6	102.0	86	0.043	98.5	3.403	0.99	0.067	0.99	2.796	0.99
			56	0.123	73.9	4.683	0.92	0.022	0.99		
			36	0.176	51.1	5.207	0.99	0.018	0.98		
Extruded starch	12.2	113.8	98	0.041	110.3	0.44	0.29	0.096	0.96	11.3	0.97
			68	0.118	83.8	4.964	0.98	0.048	0.97		
			48	0.170	62.8	5.678	0.98	0.009	0.85		
PMMA	0.6	109.2	94	0.040	107.8	3.596	0.99	0.200	0.99	1.481	0.95
			64	0.118	83.8	5.515	0.99	0.042	0.97		
			44	0.170	62.0	8.121	0.99	0.01	0.84		
PVP	15.1	58.4	43	0.046	55.7	3.495	0.98	0.231	0.91	1.917	0.99
			13	0.137	28.2	6.265	0.97	0.025	0.93		

cooling through the glass transition and isothermal ageing at low temperatures. Some authors still consider such pre-peaks as completely independent of the structural relaxation, and relate them to the relaxation of mechanical constraints, associated with drastic quenching or high deformations. Studies have indeed shown that strain release in glasses prepared under pressure could produce such endotherms in the sub-T_g region of thermograms (Wunderlich, 1994). Having investigated a large range of ageing temperatures, we did not observe any discontinuity in the behaviour of ΔH_{relax} peaks, either pre-peaks or overshoots in the glass transition region. Our observations are therefore the consequence of the wide distribution of the characteristic times associated with the structural relaxation. The narrowing of this distribution during isothermal ageing may explain the retarded and more cooperative glass transition observed for aged glasses. On contrary, the unaged samples, highly disequilibrated by the quench, show a wide transition because of a large and uniform relaxation times spectrum.

For the higher ageing temperature, specific heat capacities of aged and unaged samples did not perfectly match in the glassy state, even at very low temperatures (Fig. 4). Consequently, negative areas on the thermograms differences were sometimes recorded, and defining the low temperature integration limits for the calculation of ΔH_{relax} was quite hazardous. These difficulties may have a physical origin. The differences in specific heat capacities of glass and crystal of a same substance have been known for a long time (Guttman, 1972) and were estimated for instance at 3% for cyclodextrins (Tsukushi, Yamamuro & Suga, 1994). Although this may be expected as a consequence of the structural rearrangement, there is less evidence for structural relaxation to influence the glassy heat capacity. A decrease of 0.1–0.2% of the Cp_{glass} induced by a decrease of the cooling rate from 20 to 0.625°C min^{-1} was mentioned by Richardson and Savill (1975). On the other hand, Tsukushi et al. (1994) found similar glassy heat capacity values for glasses prepared by various methods (cooling from the liquid state or grinding of crystals), while their enthalpy relaxation behaviours showed some differences. Using standard DSC equipment, we were not able to reach a sufficient precision for a clear assessment of these effects, but the differences we observed indicate lower heat capacities for aged or slowly cooled glasses.

3.2. Enthalpy relaxation kinetics

Quenched glasses are characterised by high fictive temperatures reflecting their structural disorder. During structural relaxation, the glass reaches a state of lower energy, characterised by lower fictive temperature and molecular mobility. Because of this reduced mobility, DSC thermograms of aged samples display increasing apparent T_g values (if one takes $T_{g1/2}$ for instance) for increasing t_e (see for instance Fig. 4). As a misleading consequence, T_g's move in the opposite direction with respect to the fictive temperatures along the ageing process. The fictive temperature is calculated from the whole thermogram taking into accounts pre-peaks and overshoots, it

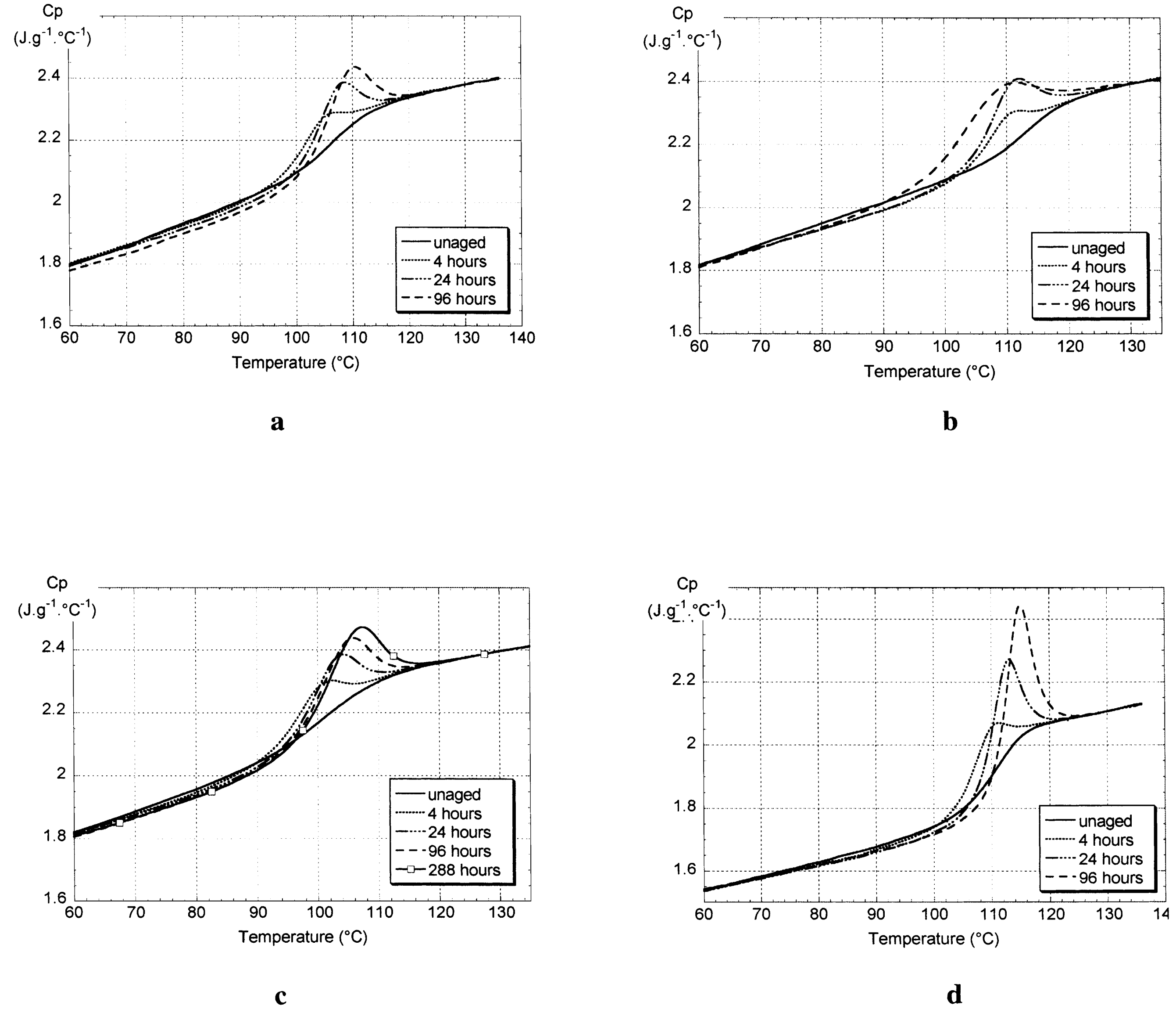


Fig. 4. Enthalpy recovery profiles upon ageing at $\Delta T_e \sim 15$ for quench cooled (a) amylopectin (10.9% H_2O), (b) extruded starch (12.2% H_2O), (c) phytoglycogen (9.6% H_2O) and (d) PMMA (0.6% H_2O).

gives a much more reliable information and can be used for the description of ageing kinetics.

The whole scheme of the ageing process may be represented by a relaxation function $F_{\mathrm{H\ relax}}$ calculated from T_f' values (it could also be done from $\Delta H_{\mathrm{relax}}$ values). After complete equilibration of the glass, T_f' should reach T_e the ageing temperature (and $\Delta H_{\mathrm{relax}}$ should reach $\Delta H_{\mathrm{relax}\ \infty}$). Fig. 5 presents the results we obtained for all our samples with $\Delta T_e = 15$°C. The ranking of the samples in terms of ageing kinetics is similar to that observed from T_f' values in Table 2: it is yet more rigorous to consider this normalised curve. Phytoglycogen ages a little more rapidly than amylopectin, the water possibly enhancing the ageing process in that latter. PVP and PMMA seem to be the less prone to fast enthalpy relaxation. They have also the highest heat capacity increments at the glass transition, respectively, 0.34 and 0.28 J g^{-1} $°C^{-1}$ against typically 0.2 J g^{-1} $°C^{-1}$ for polysaccharides, as described previously (Borde et al., 2001). This value being proportional to $\Delta H_{\mathrm{relax}\ \infty}$, those products are expected to display larger peaks than the others do for similar ΔT_e. Surprisingly, extruded starch seems to be equilibrated after 96 h ageing. At this ageing temperature, a complete equilibration was not expected given the short ageing time. Moreover, it shows strange large peaks developing quite rapidly but moderately influenced by the ageing time (Table 2, Fig. 4). Mixture of roughly 80% amylopectin and 20% amylose, this sample could be more heterogeneous than the others. Macromolecular disentanglements and

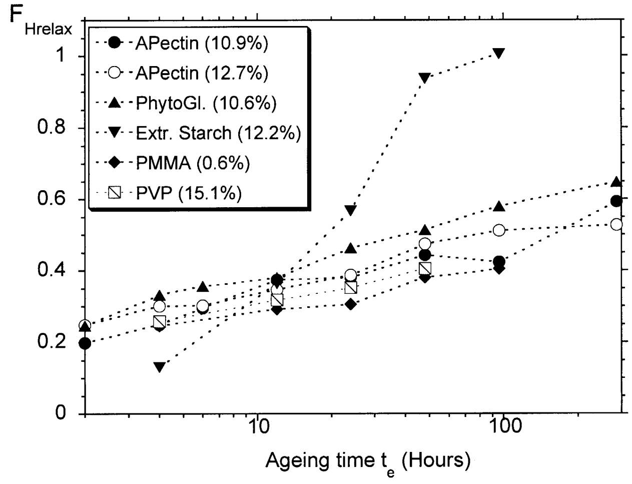


Fig. 5. Structural relaxation function $F_{\mathrm{H\,relax}}$ for $\Delta T_e \sim 15$ for all products.

degradations induced by extrusion, in presence of water, may have favoured a fast rearrangement in the glass. Shogren and Jasberg (1994) compared a normal (28 % amylose) and a high amylose (70%) corn starch and found that a high amylose content was favourable to the slowing down of enthalpy relaxation of extruded products. These results cannot be directly compared to those obtained here because of different storage conditions (time for complete equilibration > 100 days for storage at room temperature with 80% relative humidity and T_g around 45–50°C) but they may have the same origin as our observations: the mixture of two incompatible biopolymers, after possible disentanglement and macromolecular degradation could have a synergetic effect and modify their ageing behaviour.

The data shown in Fig. 5 are quite scattered and concern glasses that are still far from equilibrium. The linearity observed for the evolution of T_{peak}, A_{peak} and T_f' as a function of the logarithm of the ageing time indicated that the products were not so far from exponentiality in the first stages of the ageing process. This fact has been often reported for other polymers in such conditions (Berens & Hodge, 1982; Cortes & Montserrat, 1994; Gomez Ribelles & Monleon Pradas, 1995; Hodge, 1994; Shogren, 1992). The expected non-exponential behaviour of our polymers may influence their relaxation for ageing times longer than those presented here.

In our approach, the fictive temperature reached by the glass at the equilibrium was taken as equal to the ageing temperature. Such a choice was done earlier by Moynihan, Macedo, Montrose, Gupta, DeBolt and Dill et al. (1976); Narayanaswamy (1971) for simulations of structural relaxation, and also later by Hodge (1987), Scherer (1984). The validity of such an hypothesis has been recently debated because of the large discrepancies often reported between the experimentally integrated values for the relaxed enthalpy and the values that should be reached at the equilibrium (Cowie & Ferguson, 1986; Cowie, Harris & McEwen, 1997; Gomez Ribelles, Diaz Calleja, Ferguson & Cowie, 1987). Gomez Ribelles, Ribes Greus and Diaz Calleja, (1990) tried various methods to improve the evaluation of $\Delta H_{\mathrm{relax}}$. They systematically found lower values than those calculated from models such as those from Narayanaswamy (1971) or Adam–Gibbs–Vogel (see for instance Hodge, 1987). A few years later, in the framework of the configurational entropy Adam–Gibbs theory (Adam & Gibbs, 1965), Gomez Ribelles, Monleon Pradas, Vidaurre Garayo, Romero Colomer and Mas Estelles, (1995) developed the idea of an intermediate equilibrium state, characterised by higher enthalpy and fictive temperature than those obtained from simple extrapolation of the metastable equilibrium liquid line to the ageing temperature. This peculiarity of polymers was attributed to mobility restrictions due to topological constraints such as entanglements. The modelling of the structural relaxation process was found to be better (Gomez Ribelles, Monleon Pradas, Vidaurre Garayo, Romero Colomer & Mas Estelles, 1997) when taking into account this intermediate state. High molecular weight polymers such as polysaccharides should also be affected by such entanglements. Except for extruded starch, the T_f' of our aged samples were still far from reaching the ageing temperature T_e but the quasi-exponential ageing kinetics we observed indicate also that equilibrium was still far from being reached, we can therefore not assess this hypothesis.

3.3. Physical ageing at low temperatures

For a more systematic approach of the formation of sub-T_g peaks, amylopectin (10.9 % H_2O) was submitted to 4 h isothermal ageing at temperatures corresponding to ΔT_e comprised between 0 and 100°C. The thermograms are presented on Fig. 6 and the corresponding fictive temperatures are drawn as a function of T_e on Fig. 7. The change in the fictive temperature with respect to the unaged glass, even after only 4 h and at low temperature (for instance, $T_e = 0$°C, $T_f' - T_{f0} = 2.5$°C) is noticeable. Some fast relaxing entities, still mobile despite a limited thermal activation, are present in the quenched material. The effect of T_e on the ageing kinetics is obvious, despite the large errors bars. The higher the T_e, the larger is the decrease in T_f'; this tendency was observed for low T_e up to $T_e = 90$°C ($\Delta T_e \sim 15$°). When ageing temperatures are closer to the initial fictive temperature, the main driving force for enthalpy relaxation (the thermodynamic disequilibrium) is weaker, and becomes a limiting factor, slowing down the decrease of T_f'. At higher T_e ($\Delta T_e < 5$°C), 4 h are sufficient for the sample to reach its equilibrium state, and thus the measured T_f' are on the line $T_f' = T_e$.

Our low temperature experiments allowed us to assert the following points:

the presence of a large relaxation times spectrum allowing ageing even at temperatures as low as 100°C below the glass transition temperature.

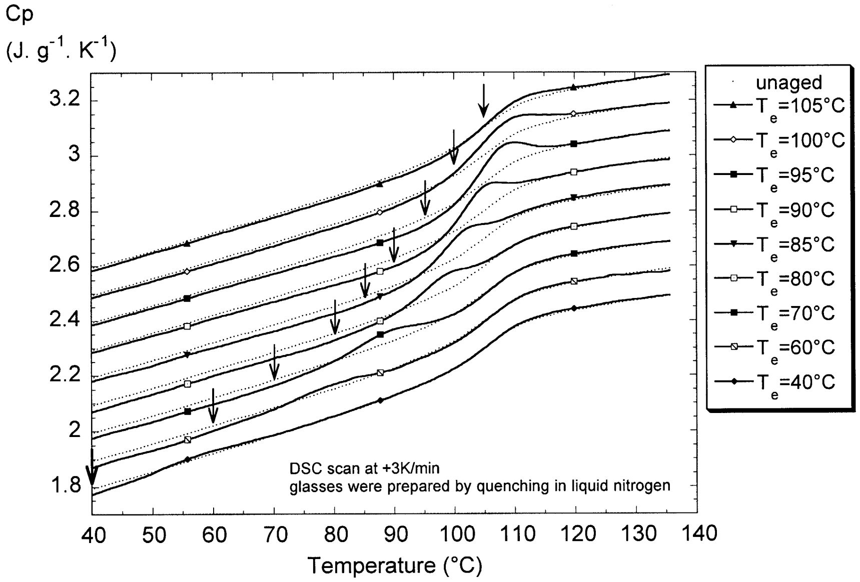


Fig. 6. Enthalpy recovery profiles of amylopectin (10.9% H_2O) for $t_e = 4$ h at various T_e's (arrows indicate T_e).

the existence of an optimal ageing temperature for maximal enthalpy relaxation corresponding to a compromise between the available thermal energy for the molecular mobility on one side (low T_e), and the driving force for structural relaxation ('distance' towards equilibrium) on the other side.

the indication that the studied products' fictive temperature can reach the ageing temperature upon equilibration, within the experimental error bars.

3.4. Influence of cooling rate

As already stated, quenching is favourable to a higher signal to noise ratio on the ΔH_{relax} measurements. Because of the mechanical constraints possibly provoked by such a drastic treatment, we investigated the behaviour of our products after cooling at lower rate (3°C min^{-1}). The thermograms obtained after ageing were similar to those obtained with the quenching technique and differences in the glassy heat capacities with the unaged sample were still obvious. The observed exothermal drifts observed for aged quenched glasses were therefore not linked to the quenching procedure.

The relaxation kinetics are presented for quenched and slowly cooled phytoglycogen glasses on Fig. 8 as $T_f{}'$ versus the logarithm of t_e. For the slowly cooled glass, two ageing conditions are illustrated, $T_{er} \sim 0.04$ (as for the quenched glass) and $T_{er} \sim 0.03$. As was observed for quenched glasses, the relaxation rate is

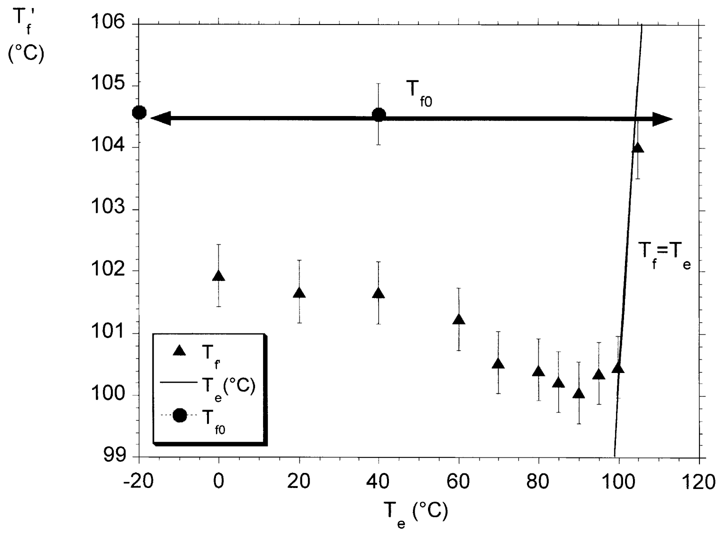


Fig. 7. Evolution of the fictive temperatures of amylopectin (10.9% H_2O) glasses aged for 4 h at various T_e's.

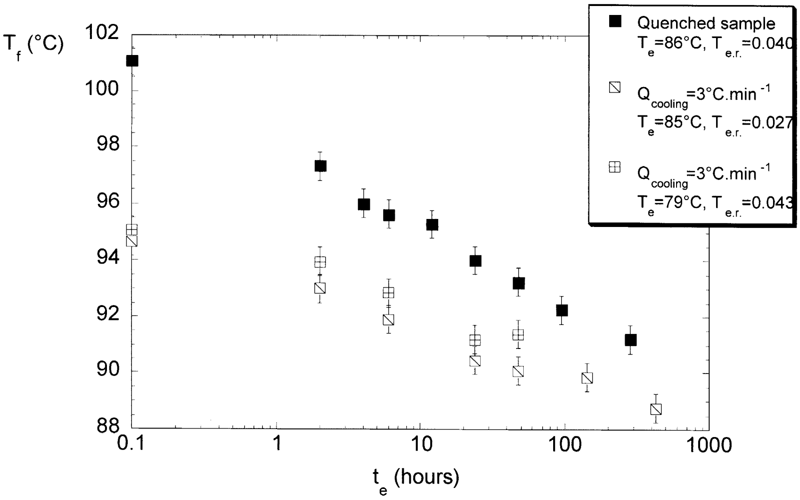


Fig. 8. Influence of cooling/quenching conditions on fictive temperature changes upon ageing of phytoglycogen (9.6% H_2O) for various T_e and T_{er}.

sensitive to the ageing temperatures (79 or 86°C on Fig. 8), the necessary time to reach equilibrium being obviously longer for the lower T_e.

A difference of 6°C is noted between the fictive temperatures of the quenched and slowly cooled glasses. $T_f' = f(\log(t_e))$ is almost linear for the quenched glass. Aged at the same reduced temperature $T_{er} \sim 0.04$, the quenched glass relaxes more rapidly than the slowly cooled glass. This behaviour is related to a larger thermodynamic driving force (departure from equilibrium) in the case of the higher initial T_f'. After 288 h ageing, $F_{H\ \mathrm{relax}}$ was evaluated to 0.65 and 0.28 for quenched and slowly cooled glasses respectively. The same tendency was observed for ageing kinetics at the same ageing temperature ($T_e \sim$ 85–86°C) with $F_{H\ \mathrm{relax}} = 0.65$ and 0.55 for quenched and slowly cooled glasses, respectively. The progress in ageing is higher for the slowly cooled glass due to lower T_{er} (0.027). Such observations were already reported, for instance for polyetherimide (Echeverria et al., 1995). The rate of enthalpy relaxation was described to be higher for the rapidly cooled glasses, but the time to reach equilibrium upon ageing at equal temperature was roughly independent on the cooling rate. The time scale to reach equilibrium is indeed finally governed by the time scale of the equilibrium state rather than by the former cooling history. The small differences in the $F_{H\ \mathrm{relax}}$ measured for quenched and slowly cooled glasses aged at 85–86°C indicate that our products should obey to the same 'law'.

3.5. Following ΔH_{relax} with the Lagasse method

The Lagasse method (Fig. 1b) was used to evaluate more precisely the amount of enthalpy relaxed during ageing. The method requiring similar heating and cooling rates, a rate of 3°C min^{-1} was used. Resulting glasses were shown to undergo a quite slow structural relaxation upon ageing. The lower accuracy associated with this moderate response should be balanced by an improved thermal history. Thermograms were recorded immediately after the end of ageing isotherms, thus minimising the possibility for an evolution of the sample during cooling from T_e to T_{min}, or during the DSC experiment.

The resulting $\Delta H_{\mathrm{relax}}$, are presented on Fig. 9 versus the logarithm of ageing time, in comparison to data from the quenched samples (phytoglycogen). The relaxed enthalpy increases linearly with $\log(t_e)$ up to around 100 h, but the last experimental point (192 h) obviously indicates the occurrence of a less rapid relaxation regime when approaching the equilibrium. At that point, $\Delta H_{\mathrm{relax}}$ has reached 70% of its total value. Apart from higher scattering, the quenched sample behaves similarly, but the values are surprisingly low with respect to the Lagasse data. For similar ageing times, the amount of enthalpy relaxed by the quenched glass should be higher than for the 'Lagasse glass', the limiting values for $\Delta H_{\mathrm{relax}}$ being 3.5 and 2.0 J g^{-1}, respectively, for the quenched and Lagasse glass. Our observations coincide with the results of Gomez Ribelles et al. (1990) who compared the Lagasse protocol with standard procedures. Significant evolutions probably occurred within the aged material between the end of ageing and the subsequent DSC heating (exothermic drifts), they resulted in large errors on the evaluation of $\Delta H_{\mathrm{relax}}$ by thermogram differences.

The Lagasse method revealed the classical linear evolution of the relaxed enthalpy with the logarithm of the ageing time. Moreover, the experimental values seemed to converge reasonably towards the theoretical values estimated for equilibration. Apart from the higher precision it brings on $\Delta H_{\mathrm{relax}}$ values, the Lagasse method has the drawback of truncating the thermograms in such a manner that they cannot be exploited for other purposes. The use of the whole thermogram is more convenient for the simulation of enthalpy relaxation response and therefore for the prediction of long term ageing behaviour.

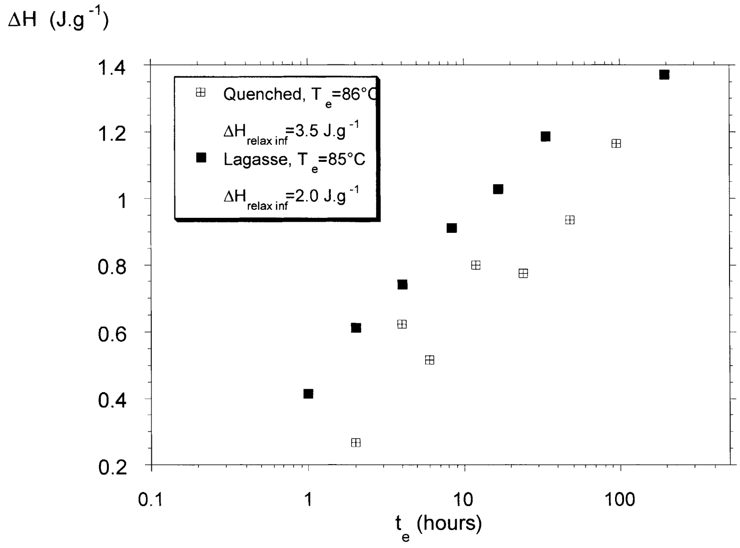


Fig. 9. Enthalpy recovery obtained using Lagasse method upon ageing at $\Delta T_e = 15°$ for phytoglycogen (9.6% H_2O).

4. Conclusion

Enthalpy relaxation phenomenology and kinetics were found to be similar for hydrated polysaccharides and synthetic polymers such as PMMA or hydrated PVP. Structural relaxation during storage yielded either sub-T_g enthalpy recovery peaks or overshoots in the glass transition region evidencing the wideness of the relaxation time spectrum. As expected, the kinetics of physical ageing was found dependent on:

the molecular mobility of the glassy state, e.g. the storage temperature, T_e.

the degree of metastability of the initial state, e.g. the cooling rate. Rapid cooling enhanced enthalpy relaxation by increasing structural disorder and thermodynamic instability.

to lesser extent, the chemical structure and the degree of advancement of structural relaxation.

In contrast to the other products, extruded starch equilibrated apparently within the experimental time scale. Further studies would be necessary for a better understanding of the effect of extrusion and amylose/amylopectin composition with respect to physical ageing as was initiated in the Shogren's study (1994). Hydrated polysaccharides were found to age a little more rapidly than synthetic PMMA and PVP.

Enthalpy relaxation is a significative phenomenon-occurring along storage of starch derived products. Given the evolution of mechanical and physical properties such as storage modulus, volume, molecular mobility and diffusivity that accompany structural relaxation, the simulation of this process would be of great interest. Modelling enthalpy relaxation should allow a more systematic comparison of the samples behaviour and should also provide an efficient tool for the foreseeing of the material evolution along long term storage. A large set of experimental data is available here for such an attempt in a future work.

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