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# Calorimetric analysis of the structural relaxation in partially hydrated amorphous polysaccharides. I. Glass transition and fragility

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**Abstract**

The glass transition of low moisture food products is now widely recognised as a key-concept regarding their stability and processability. Differential Scanning Calorimetry is an efficient technique for the measurement of the glass transition temperatures $T_g$'s on hydrated products. Thanks to the control of thermal history, this technique can bring more information on the relaxational behaviour of products around the glass transition. Simple thermograms (cooling rate = heating rate = 3°C min$^{-1}$) were recorded, allowing a preliminary characterisation of various hydrated polysaccharides (amylopectin, phytoglycogen, extruded starch, pullulan and dextran): $T_{g1/2}$, $T_f$, $\Delta C_p$ and other related parameters were determined. After following the cooling rate dependence of the fictive temperatures of different glasses, we calculated their fragility parameter. The significance of the parameters extracted from DSC thermograms was discussed and compared with the fragilities. The influence of the water content on thermal properties was studied on amylopectin. Finally, we attempted to discuss our results in a structure/property perspective developed for polymers. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords*: Differential scanning calorimetry; Amorphous polysaccharides; Glass transition; Fragility

## 1. Introduction

The interest in the glassy state in foods and pharmaceutical products has grown up during the last decades, stimulated by the application of concepts from polymer science and strongly supported by industrial demand (Blanshard & Lillford, 1993; Slade & Levine, 1995). Many processes such as extrusion, baking, drying or milling yield amorphous products whose stability on storage has to be controlled. A wide number of models and theories has been developed in an attempt to describe the molecular dynamics around the glass transition temperature: they range from free volume theory (Turnbull & Cohen, 1961; Curro, Lagasse & Simha, 1982) to the more recent coupling model, (Ngai, Rendell, Rajagopal & Teitler, 1986) or quasi-point-defect model (Perez, 1988). Following more pragmatic approaches with the aim of improving polymer processing, studies dealing with polymer/diluent properties have been carried out and the related concepts were also used in the food area. The peculiar role of water as plasticizer of biopolymers has been widely recognised and its importance regarding food structure, quality and safety has given rise to series of seminars and congresses (Roos, Leslie & Lillford, 1999: ISOPOW 7).

Differential scanning calorimetry (DSC) is frequently used for the characterisation of the glass transition, especially in food science because it allows easy routine measurements with a good control of hydration thanks to the confined geometry of samples (Bizot, Le Bail, Leroux, Davy, Roger & Buleon, 1997; Noel & Ring, 1992). Because of the kinetic aspects of the glass transition, the measurement conditions are crucial for the precision of results: the differences in reported glass transition temperatures for similar products are often due to discrepancies in the experimental procedures.

### *1.1. Glass formation and fictive temperature (Moynihan, Easteal, DeBolt & Tucker, 1976a; Moynihan, Macedo, Montrose, Gupta, Debolt, Dill et al., 1976b; Scherer, 1986; McKenna, 1989; Hodge, 1994)*

When a liquid is cooled through the glass transition region, it reaches a temperature at which the time required for structural rearrangement becomes too long to be experimentally observed: below the glass transition temperature, it is kinetically arrested. The limiting structure obtained after cooling depends on the imposed cooling rate; it may be

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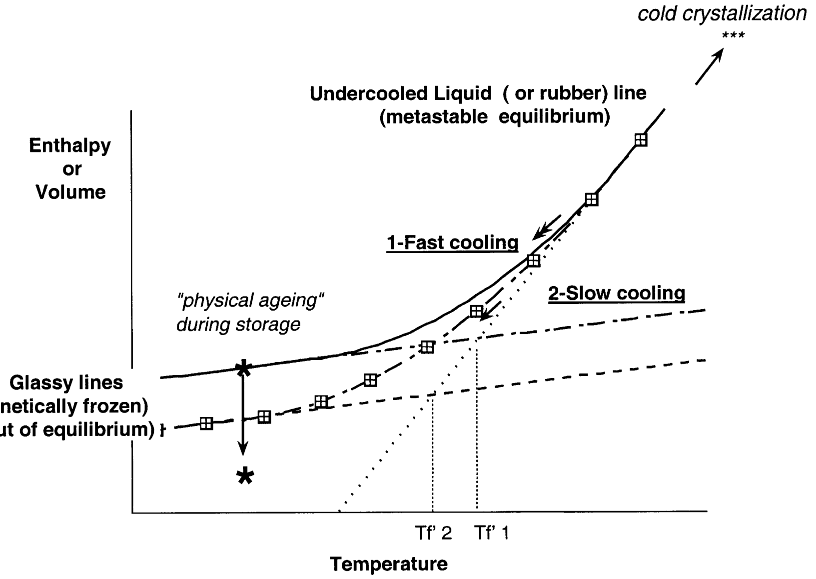

Fig. 1. Effect of cooling rate on the final glassy states and corresponding fictive temperatures.

represented in terms of a fictive temperature, $T_f'$, a concept first introduced by Tool and Eichlin (1931). Considering a given macroscopic property (enthalpy or volume, for instance) for a vitreous system, $T_f'$ is defined as the temperature of intersection between the equilibrium liquid curve and the linear extrapolation of the glassy line (see Fig. 1). Depending on the imposed cooling kinetics, various glasses may be obtained, characterised by a more or less high degree of disorder and therefore having different enthalpy and volume values as illustrated on Fig. 1. Temperature calibration being less easy to perform on cooling (Menczel & Leslie, 1993; Menczel, 1997) than on heating, in the classical use of DSC, heat flows are recorded during heating scans. Therefore glasses are characterised a posteriori.

### *1.2. Fragility (Angell, 1985, 1991)*

The concept of fragility was developed by Angell (1985) for simple glass forming liquids in order to account for their various behaviours. In this view, strong liquids are characterised by stable structures (local to intermediate range order) and properties that do not change dramatically from the liquid state to the glassy state. On the other hand, for fragile liquids, such structures are unstable and property changes are more evident. This is also valid for the thermodynamic response (e.g. specific heat capacity) and the transport properties (e.g. viscosity). Generally, the fragility can be defined from the relaxation time associated with the glass transition, plotted as a function of $T_g/T$: in this representation, it describes the departure from the linear Arrhenius behaviour (strong liquid). The fragility parameter, m, first defined as 'steepness index' (Plazek & Ngai, 1991) corresponds to the limiting slope of the curve described above. It can also be related to the apparent conventional Arrhenius activation energy, $\Delta H^*$:

$$m = \left. \frac{\mathrm{d}\log_{10}(\tau)}{\mathrm{d}\dfrac{T_g}{T}} \right|_{T=T_g} = \frac{\Delta H^*}{2.303RT_g}$$

The evaluation of fragility parameter $m$, and the apparent activation energy of the glass transition, $\Delta H^*$, from DSC measurements find their origin in Ritland's work (Ritland, 1954). He showed that the fictive temperature dependence on the cooling rate was governed by the same parameters that describe the temperature dependence of the structural relaxation times near equilibrium. Years later, using the Narayanaswamy expression (Narayanaswamy, 1971) for relaxation times and assuming a temperature independent relaxation time spectrum, Moynihan et al. (1976a) rederived Ritland's expression and established the following formula which is now widely used:

$$\frac{\mathrm{d}\ln|q|}{\mathrm{d}\left(\dfrac{1}{T_f'}\right)} = -\frac{\Delta H^*}{R}$$

with $T_f'$ the limiting fictive temperature as described above, $q$ the cooling rate and $R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$.

The activation energy, $\Delta H^*$ is used in many models for the description of structural relaxation (Tool–Narayanaswamy–Moynihan model: Narayanaswamy, 1971; Moynihan et al., 1976b; Kovacs–Aklonis–Hutchinson–Ramos model: Kovacs, Aklonis, Hutchinson & Ramos, 1979; Hutchinson, 1987). It is usually determined from DSC measurements with varying cooling and/or heating rates (Hodge, 1983; Godard & Saiter, 1998).

The present work follows a former study on the calorimetric evaluation of the glass transition in hydrated polysaccharides (Bizot et al., 1997). Dealing with similar products, we propose here a standard procedure for the analysis of the glass transition region by classical DSC, and complete this view by a more dynamic approach, with the determination of the fragility parameter and the apparent activation energy of the glass transition. A series of amorphous partially hydrated polysaccharides was treated, products were chosen either for their wide presence in food products (amylopectin, extruded starch) or for their varying chain structure (phytoglycogen, dextran and pullulan) for a better assessment of structure/properties correlation. PMMA [poly(methyl methacrylate)] was also considered as a canonical synthetic polymer as well as PVP [poly(vinyl pyrrolidone)], a water soluble polymer widely used in pharmaceutical industry.

## 2. Materials and methods

### 2.1. Materials

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: $142\ \mathrm{kW\,h\,t^{-1}}$, 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. Dextran T500 was purchased from Pharmacia Chemicals (batch no. 230306). Pullulan PF20 (technical grade) produced by Hayashibara (Japan) was provided by Pr Biliaderis in the framework of MMF European project. PVP was purchased from Sigma ($M_w = 360\,000$, $K \sim 80$–$100$) and used without further purification. PMMA from Goodfellow was used as received. The water content of all samples was adjusted via vapour phase conditioning over saturated salt solutions (water activities $a_w = 0.32$, 0.43, 0.57 and 0.75) after complete drying over phosphorus pentoxide at 50°C. PMMA was used after drying and PVP was hydrated by equilibration over a $K_2CO_3$ saturated solution ($a_w = 0.43$). The final water contents were all determined by Karl Fischer titration and expressed as total weight percentages (i.e. on wet basis).

### 2.2. Differential scanning calorimetry

A differential heat flux calorimeter DSC 121 Setaram (France) was used for calorimetric measurements. Temperature and enthalpy calibrations were checked with Indium ($T_m = 156.6°C$, $\Delta H_m = 28.55\ \mathrm{J\,g^{-1}}$) and Gallium ($T_m = 29.9°C$, $\Delta H_m = 80.14\ \mathrm{J\,g^{-1}}$). Pressure-tight crucibles ($P_{max} = 15$ MPa) allowed safe manipulations of hydrated products up to high temperatures (typically 100–140°C, $T_{g1/2} + 40°C$): 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 $3°C\ \mathrm{min}^{-1}$. 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, inox of empty crucibles). Multiple identical scans recorded on some samples showed a good reproducibility. Different cooling kinetics were necessary for the determination of fragility parameters: cooling rates between 3 and $30°C\ \mathrm{min}^{-1}$ were performed in the calorimeter whereas slower rates (0.3 and $1°C\ \mathrm{min}^{-1}$) were programmed by an external cooling bath.

### 2.3. Thermogram analysis

We recorded for each sample simple DSC sequences, with constant heating and cooling rates equal to $3°C\ \mathrm{min}^{-1}$. The previous thermal history was erased in a first scan, the glass was formed with the imposed cooling rate, and the final thermogram was recorded. These data were taken as reference scans and analysed for a precise characterisation of the glass transition region.

In the first part of our study, the glass transition temperature was defined either by $T_{g1/2}$, taken at the mid-point of the transition (inflexion point) or by $T_f'$ the fictive temperature. $T_f'$, was obtained by integration of the normalised heat capacity measured during heating:

$$T_f = T_{max} - \int_{T_{min}}^{T_{max}} \left( \frac{dT_f}{dT} \right) dT \approx T_{max} - \int_{T_{min}}^{T_{max}} \left( \frac{C_p - C_{p\ \mathrm{glass}}}{C_{p\ \mathrm{liquid}} - C_{p\ \mathrm{glass}}} \right) dT$$

with $T_{min} \ll T_g \ll T_{max}$.

The integration bounds $T_{min}$ and $T_{max}$ were taken far from the transition region in the linear zone of $C_p(T)$ corresponding to the glassy and liquid states respectively. $C_{p\ \mathrm{glass}}(T)$ and $C_{p\ \mathrm{liquid}}(T)$ were the linear fitting curves for the glassy and liquid $C_p$. The slopes of these lines, respectively $dC_{p\ \mathrm{glass}}/dT$ and $dC_{p\ \mathrm{liquid}}/dT$ were also collected. Slight differences in absolute specific heat capacities were sometimes observed and corrected by small vertical shifts: varying positions in the calorimeter and in the thermal contacts can be responsible for such variations. Calculation of $T_f'$ was then exclusively based on the fitting procedure of $C_{p\ \mathrm{glass}}(T)$ and $C_{p\ \mathrm{liquid}}(T)$: we estimated at 0.5°C the error on $T_f'$s.

$\Delta C_p$, the specific heat capacity jump, was measured at $T_{g1/2}$. $\Delta C_p/C_{p\ \mathrm{glass}}$, the fractional increase, was also calculated, the normalisation by the glassy heat capacity value allowing a better comparison of results between different materials or compositions (Angell, Bressel, Green, Kanno, Oguni & Sare, 1994). $\Delta T$, the broadness of the transition region, was measured on the temperature scale using a criterion proposed by Donth, Korus, Hempel and Beiner (1997). $\Delta T$ was taken as $T_{84} - T_{16}$ with $T_x$, the temperature at which $x\%$

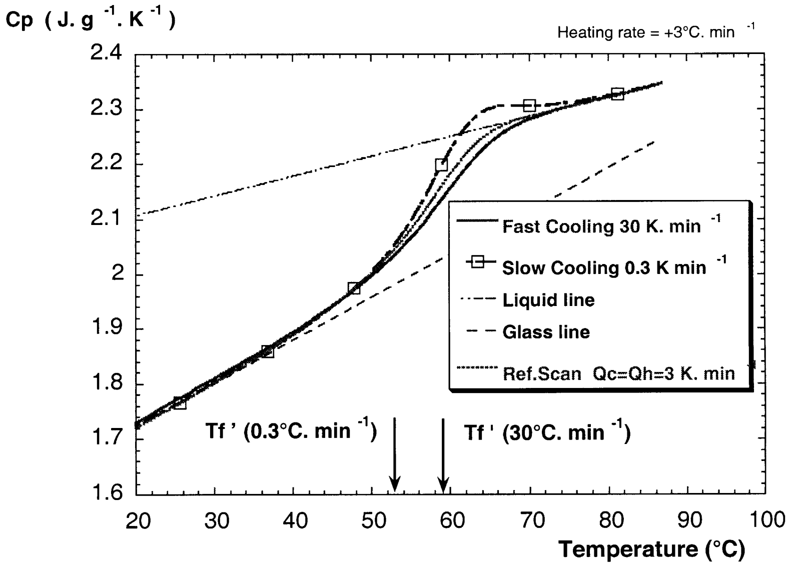

Fig. 2. Effect of cooling rate on the shape of subsequent DSC curves (amylopectin 16.1% $H_2O$).

of the glass transition has been achieved. This method was particularly relevant for our materials whose transitions were broad and smooth. The slope of the specific heat capacity was also taken in this region as an indicator of the steepness of the transition, $\Delta C_{p\ 84-16}/\Delta T = (C_{p\ 84} - C_{p\ 16})/(T_{84} - T_{16})$.

Couchmann (1978) proposed a classical thermodynamic analysis for the treatment of binary mixtures. Considering the glass transition as a quasi-second-order phase transition and using the continuity of entropy at $T_g$, he derived an expression for the glass transition of mixtures as a function of pure component properties.

$$T_{g\ (\text{mixture})} = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}},$$

$\Delta C_{pi}$: heat capacity change of component $i$, $w_i$: weight fraction of component $i$, $T_{gi}$: glass transition temperature of component $i$.

The Gordon Taylor formula (Gordon & Taylor, 1952) has sometimes been preferred for the fitting of $T_g$ values as a function of mixtures composition: it is equivalent to the Couchman equation but uses the ratio of pure components heat capacity change, $\Delta C_{p2}/\Delta C_{p1}$ as an adjustable variable. Using the same notations as above, the equation becomes:

$$T_{g\ (\text{mixture})} = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad \text{with } k = \frac{\Delta C_{p2}}{\Delta C_{p1}}$$

## 3. Results and discussion

### 3.1. Glass transition analysis of hydrated polysaccharides

#### 3.1.1. Cooling rate influence

The consequences of the cooling rate on subsequent DSC traces are shown for amylopectin (16.1% $H_2O$ w.b.) on Fig. 2. The scan performed when the heating rate matches the former cooling rate (3°C $\text{min}^{-1}$ in our case) can be taken as a reference scan. The slower cooling rate (0.3°C $\text{min}^{-1}$) yields a lower glass transition temperature $T_{g1/2}$ and presents a small overshoot in the transition region. The quenched glass is characterised by higher fictive temperature and relaxational enthalpy values, both associated with a higher degree of disorder. For the slowly cooled glass, the fictive temperature as well as molecular mobility are lower, therefore on heating the glass reverts to the liquid state with a little delay, marked by the overshoot (Fig. 2).

#### 3.1.2. Glass transition of hydrated polysaccharides

For the characterisation of our products' glass transition, we chose to use the 'reference scans' obtained with equal cooling and heating rates (±3°C $\text{min}^{-1}$). The effect of chain structure on the glass transition characteristics and sorption isotherms of the products under study has already been discussed in a former publication (Bizot et al., 1997). We confirm here these results and take benefit of an increased precision on a wider range of products for further interpretation and confrontation with the literature.

*Macromolecular structure*: the polysaccharides under study can be briefly described as follows. Amylopectin and phytoglycogen are highly branched anhydroglucose polymers with α(1–4) linkages in the main chain, and short external glucan chains grafted on the backbone by α(1–6) linkages. The amount of α(1–6) is 5.6% for amylopectin and 8.3% for phytoglycogen with an average external chain length smaller for phytoglycogen (DP 6) than for amylopectin (DP 12 to 15). Extruded potato starch, mainly composed of amylopectin, contains also 23% of linear amylose (α(1–4) linkages). Dextran is essentially formed by contiguous α(1–6)-linked glucose residues in the main

Table 1
Glass transition data of hydrated polysaccharides (m.c. ~ 10–12% $H_2O$) and PMMA, PVP

| Product | m.c. (%w,b) | $T_{\mathrm{fictive}} \pm 0.5$ (°C) | $T_{g1/2} \pm 0.5$ (°C) | $\Delta C_p$ at $T_{g1/2} \pm 0.015$ ($J\ g^{-1}\ °C^{-1}$) | $\Delta C_p/C_{p\ \mathrm{glass}}$ at $T_{g1/2}$ | $T$-range $\Delta T$ (°C) | Steepness $\Delta C_{p\ 84-16}/\Delta T$ ($10^{-2}\ J\ g^{-1}\ °C^{-2}$) | $\Delta C_p^* T_{g1/2}$ ($J\ g^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| Amylopectin | 10.9 | 101.9 | 102.9 | 0.201 | 0.09 | 8.5 | 1.55 | 76 |
| Phytoglycogen | 10.6 | 95.1 | 96.5 | 0.197 | 0.10 | 8.5 | 1.57 | 73 |
| Extruded Starch | 12.2 | 13.8 | 104.9 | 0.219 | 0.10 | 8.4 | 1.72 | 83 |
| Pullulan | 11.6 | 65.7 | 66.5 | 0.279 | 0.15 | 6.8 | 2.56 | 95 |
| Dextran | 10.8 | 71.1 | 72.5 | 0.522 | 0.29 | 6 | 5.9 | 180 |
| PMMA | 0 | 110.7 | 111.9 | 0.282 | 0.16 | 7 | 2.66 | 109 |
| PVP | 15.1 | 55 | 56.6 | 0.344 | 0.18 | 6.5 | 3.55 | 113 |

chain with about 5% of α(1–3) branch linkages bearing either single glucose or a few long lateral chains. Pullulan is considered as linear, constituted of maltotriose monomers associated by α(1–6) linkages. The pullulan used was found to have an average molecular weight $M_w$ of $2.74 \times 10^5\ g\ mol^{-1}$ and a polydispersity of 1.634.

*Assessment of a glass transition temperature $T_{g1/2}$ or $T_f'$?*: the glass transition temperatures are given in Table 1 for polysaccharides in the humidity range 10–12% $H_2O$ w.b. and for PMMA and hydrated PVP. Values obtained for $T_{g1/2}$ and $T_f'$ usually do not differ by more than 2°C, $T_f'$ being lower. The heating rate being equal to the former cooling rate, we obtained rather stable glasses and thus reliable values of $T_{g1/2}$. The determination of $T_f'$ is illustrated on Fig. 3 for glassy amylopectin (16.1% $H_2O$ w.b.) cooled at $0.3°C\ min^{-1}$. After determining the equations of glassy and liquid extrapolated $C_p$'s and the limits for integration, $T_f'$ is calculated using the equation presented in Section 2.3. Thanks to the use of $T_f'$, it is easier to make a difference between various glasses, the area of the relaxation 'overshoot' being taken into account in the calculation. It is also interesting to note that the fictive temperature does not depend on the heating rate as earlier pointed out by Richardson and Savill (1975).

The fictive temperature may also have some limitations. Ritland (1956) showed that glasses which are structurally different may have the same fictive temperature, depending on their former thermal history. More generally, the non-exponentiality of structural relaxation implies the necessity for more than one order parameter to fully describe the glassy state. Nevertheless, when the thermal history is perfectly known or controlled, the fictive temperature remains a convenient way to characterise unambiguously the structural state of a glass.

*Glass transition of polysaccharides 10–12% $H_2O$*: considering our different polysaccharides in the humidity range 10–12% $H_2O$ (Table 1), we note comparable $T_{g1/2}$ values for glassy amylopectin (102.9°C), extruded starch (104.9°C) and phytoglycogen (96.5°C). Amylopectin and phytoglycogen both have highly branched structures but internal plasticisation by the more numerous and shorter external chains can account for the slightly lower $T_{g1/2}$ of phytoglycogen. The non-negligible amylose content of extruded starch could explain its higher $T_{g1/2}$ notwithstanding a higher water content. For similar water contents, dextran (72.5°C) and pullulan (66.5°C) display very low glass transition temperatures with respect to these branched starch-derived polymers. This important difference may be attributed to more linear structures with less steric hindrance as well as to lower chain stiffness related to the nature of glycosidic linkages.

Amylopectin, phytoglycogen and extruded starch have similar $\Delta C_p$ values, (typically $0.2\ J\ g^{-1}\ °C^{-1}$), transition width (~8.5°C) and steepness ($\sim 1.6 \times 10^{-2}\ J\ g^{-1}\ °C^{-2}$). The value obtained for $\Delta C_p$ of hydrated pullulan ($0.270\ J\ g^{-1}\ °C^{-1}$) approaches a value reported for dry pullulan ($0.245\ J\ g^{-1}\ °C^{-1}$ — Ratto & Schneider, 1998). Unlike these authors, we were not able to determine this value on dry pullulan as thermograms showed exothermal drifts (probably due to thermal degradation or changes in the thermal contacts between the sample and the DSC pan) before any endothermic step potentially associated with a glass transition. Surprisingly, dextran displays a very high $\Delta C_p$ for comparable $T_{g1/2}$ by comparison with pullulan at equivalent water content. The specific heat capacities of dextran, pullulan and amylopectin in their dry glassy state at 47°C (Table 2) are very similar thus indicating that the most important discrepancies in heat capacities of our products are in the liquid state. This similarity of $C_p$ values in the dry glassy state was expected for polymers whose chemical structures are very close to each other: the total vibration spectra of these products in their solid state should not differ significantly. Dextran, pullulan and amylopectin range in similar order in terms of heat capacity increments at the glass transition and steepness of the transition (dextran > pullulan > amylopectin). Dextran shows the highest $\Delta C_p$ at $T_{g1/2}$ but the transition occurs very rapidly on a small temperature range and therefore the 'transition steepness' is really higher. Amylopectin and pullulan behave closer to each other and show less marked glass transitions. The nature of the glycosidic linkages constituting the monomers seems to be particularly relevant for the explanation of the heat capacity increment, chain branching having apparently little influence. The higher conformational freedom provided by α(1–6) linkages with respect to α(1–4) (supplementary degree of freedom) has often been discussed (Rees, 1977) and can explain the increasing $\Delta C_p$ observed for the series amylopectin, pullulan and dextran.

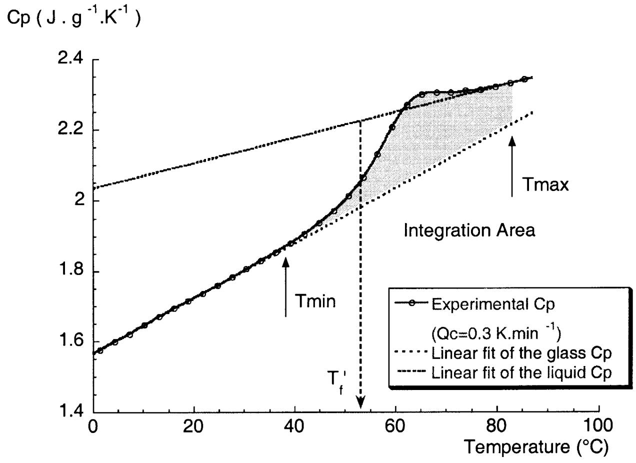

Fig. 3. Thermogram analysis for $T_f'$ calculation.

Dextran and pullulan are also very different in their ability to crystallise, dextran may crystallise in different forms according to the water content (Guizard, Chanzy & Sarko, 1984) whereas pullulan is known to be amorphous. Irregularities in the sequences [α(1–4), α(1–4), α(1–6)] of the maltotriose monomer, could explain high barriers for crystalline arrangements in the case of pullulan. For dextran, the slight branching was not sufficient to prevent crystallisation in some of our experimental conditions (e.g. 16% $H_2O$ and slow cooling rates $<3$°C min$^{-1}$). Apart from the geometrical considerations, this point can also be interpreted as a higher mobility of the dextran chains in the rubbery state. Amylopectin can't be really considered in this discussion, as crystallisation usually occurs in the small grafted chains.

Comparative studies on the conformations of polysaccharides in solution have shown a higher extension of the dextran macromolecules compared to that of the amylose chains (Ruddick & Goodall, 1998). Can this be related to the higher heat capacity of rubbery dextran compared to amylopectin and pullulan? One could also invoke the persistence of hydrogen bonding thanks to the $CH_2OH$ lateral groups present in amylopectin and to a lesser extent in pullulan to explain these differences in mobility in the rubbery state and the varying solution behaviour. Considering the respective heat capacities of liquid water and ice, one can see that the breaking of hydrogen bonds may increase drastically the heat capacity (Rowland, 1979). In both cases, because of the presence of water and of the fluctuating character of hydrogen bonds, it remains difficult to draw clear conclusions from these observations.

Table 2
Glassy heat capacity of dry polysaccharides at 47°C

| Product | $C_p$ at 47°C (J g$^{-1}$ °C$^{-1}$) |
|---|---|
| Amylopectin | 1.283 |
| Pullulan | 1.306 |
| Dextran | 1.289 |

The synthetic polymers under study, dry PMMA and hydrated PVP present DSC traces that are very similar to those of hydrated polysaccharides. The characteristics of dry PMMA agree with those given by the ATHAS databank[1] ($T_g = 105$°C and $\Delta C_p = 0.333$ J g$^{-1}$ °C$^{-1}$ for atactic PMMA). The low $T_g$ value we recorded for PVP is explained by its high hydration level: PVP is a well-known water-plasticised polymer (Tan & Challa, 1976; Hancock, Shamblin & Zografi, 1995).

*Heat capacity increments and glass transition theories*: after the analysis of the glass transition region of hydrated amylopectin, dextran and pullulan, the most striking result concerns the differences in heat capacity increments at the glass transition. The monomers of dextran and pullulan differ only in one glycosidic linkage but the consequence on the $\Delta C_p$ is very important (+85%). Our results covering various polysaccharides need to be considered in the light of the theoretical interpretation that was given in earlier works on synthetic polymers.

The heat capacity jump at the glass transition is a sensitive indicator for the evaluation of crystallinity in semi-crystalline materials, but for purely amorphous products its amplitude reflects also the changes in molecular mobility. Treating the glass transition with the 'hole theory' developed for liquids by Hirai and Eyring, (1958), the heat capacity increment at the glass transition was first associated with the formation of holes in the material (Wunderlich, 1960). The 'rule of constant heat capacity increment' was also established. Regarding the glass as built from beads (a bead being 'the smallest chain unit whose movement may change the hole equilibrium'), the value $\Delta C_p(T_g) = 11.3$ J °C$^{-1}$mol$^{-1}_{\text{bead}}$ was found to be representative of a great number of glasses either polymeric or molecular. Similarly, the product $\Delta C_p(T_g) \times T_g$ seemed to be roughly constant and equal to 115 J g$^{-1}$ for different high polymers (Boyer, 1973). Other relations can be found in the literature where the $\Delta C_p$ was evaluated from the cohesive energy and $T_g$ (Mathot 1984). For polymers, the Boyer's formula can also be rationalised in the frame of the Gibbs–DiMarzio theory of the glass transition as it predicts an increase in $T_g$ with the chain stiffness (Gibbs & DiMarzio, 1958). The chain stiffness can be supposed to decrease the mean square fluctuations in configurational entropy: from the statistical mechanical relation $k_B C_p = \langle \Delta S^2 \rangle$, one can therefore also expect $\Delta C_p$ to decrease (Donth, 1992; Hodge, 1994). A more complete description of the glass transition was given by DiMarzio and Dowell (1979). They were able to predict fair $\Delta C_p$ values from the chemical structure and without any adjustable parameter. In this approach, the following contributions to the heat capacity increment were taken into account: two configurational terms arising either from changes in shape of macromolecules (~50% of total $\Delta C_p$) or from

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[1] ATHAS databank http://web.utk.edu/~athas.

volume expansion related to changes in hole number (~30%), and a vibrational term accounting for changes in vibrational frequencies and anharmonicity of vibrational modes (~20%). Goldstein (1976) indicated also the possibility for 'thermodynamic contributions of molecular rearrangement processes that give rise to secondary relaxations below $T_g$'.

In an attempt to relate our data with the law of 'constant heat capacity jump', (Wunderlich, 1960), we encounter difficulties for the definition of the so-called beads, the studied samples being all anhydroglucose polymers and differing only in their glycosidic linkages. A strict application of the law (11.4 J °C$^{-1}$bead$^{-1}$) would yield the following values: three beads for the amylopectin monomer, four for pullulan, and eight for dextran. Such a decomposition of chemical structures is obviously difficult to justify, the varying flexibility of bonds in the main chain seems to be more relevant in our case to justify the variations in heat capacity increments. Analysis in the frame of DiMarzio and Dowell prediction (1979) would certainly bring more accuracy. The contribution of secondary relaxations to the heat capacity jump at $T_g$ is debatable since they have been reported by some authors as giving rise to heat capacity increments in the glassy region using adiabatic calorimetry on molecular glasses (Fujimori & Oguni, 1995), standard DSC on synthetic polymers (Bershtein & Egorov, 1994). Nevertheless they can certainly not explain the important differences observed between dextran and pullulan (sub-$T_g$ relaxations of similar intensity were observed for both products by dielectric spectroscopy, Borde, 1999). Regarding the values obtained for $\Delta C_p^* T_g$ (Table 1), hydrated synthetic polymers match almost perfectly the 'universal' value of 115 J g$^{-1}$ given by Boyer (1973), whereas hydrated polysaccharides render really lower values, typically 80/90 J g$^{-1}$. Dextran exhibits another peculiarity, with a very high value 180 J g$^{-1}$.

Further this qualitative discussion, our results underline the incidence of the polysaccharide structure (namely type of glucosidic linkage) on the values of $\Delta C_p$ observed at the glass transition.

### 3.1.3. Water plasticisation: amylopectin

*Thermograms shapes $T_{g1/2}$, $T_f'$ and $\Delta C_p$*: we focused our study of the effect of water content on amylopectin. The detailed analysis of amylopectin glasses obtained after equal cooling and heating rate (3°C min$^{-1}$) is reported in Table 3 and the corresponding thermograms are presented on Fig. 4. Data for dry amylopectin show only the glassy heat capacity, as degradation would occur before the glass transition. As expected for any polymer/diluent mixtures, increasing water contents decrease considerably the glass transition temperatures: the measured $T_f'$s span from 149.9°C for 6.9% $H_2O$ to 38.9°C for 19% $H_2O$. The $T_{g1/2}'$s were reported on Fig. 5 for different water contents and fitted with a Gordon Taylor formula with the following parameters: $T_{g\ water} = -139°C$, $T_{g\ amylopectin} = 266°C$ and $\Delta C_{p\ amylopectin}/\Delta C_{p\ water} = 0.181$.

The total heat capacity increment increases slowly with growing water content in the range we studied, the same evolution is observed on the heat capacity jump normalised by the glassy value of $C_p$. The reverse tendency was reported by Noel and Ring (1992) for hydrated amylopectin whereas a linear increase in $\Delta C_{p\ (mixture)}$ with increasing water content was observed in studies on pullulan (Ratto & Schneider, 1998), galactose, PVP (Blond & Simatos, 1991), sucrose and stachyose (Hatley & Mant, 1993).

The presence of water affects the shape of the transition, the width of the glass transition $\Delta T$ decreases slowly with increasing water content whereas the steepness of the transition increases more rapidly. Usually the introduction of a plasticizer in synthetic polymers has a reverse effect on the glass transition region, smoothing the heat capacity curve and broadening the glass transition (Bair, 1997). Water modifies also the temperature dependence of the glassy heat capacity, the slope $dC_p/dT$ (Table 3) increases linearly with the water content. Obviously this observation is not compatible with a simple additivity of both components heat capacities. The heat capacity for dry amylopectin being linear with respect to increasing temperature (Fig. 4), one would need an additional heat capacity increasing linearly with temperature to account for the observed variations in slopes with the water content. The specific heat capacity of water (atmospheric pressure) displays a minimum at 35°C and is almost constant and less than 4.2 J g$^{-1}$.°C$^{-1}$ in the range 10–90°C (Robinson, Zhu, Singh & Evans, 1996). These results indicate a non negligible excess heat capacity arising from non ideal mixing, it would roughly be represented by a straight line with positive slope of 0.025 J g$^{-1}$°C$^{-2}$. The influence of water on the heat capacity of amylopectin is really less marked above the glass transition region, than in the glassy state.

*Glassy heat capacities*: as illustrated by Figs. 4 and 5, the effect of water on the glassy heat capacity of hydrated amylopectin is noticeable: in the range 0–19%, the $C_{p\ glass}$ is observed to increase approximately linearly with the water content. Our fitting straight line agrees with the data given by Noel and Ring (1992) except for the higher water content (Fig. 5). The specific partial heat capacities of water and amylopectin can be derived from the total heat capacity of the mixture by means of the following equation:

$$\left(1 + \frac{m_{water}}{m_{amylopectin}}\right) \times C_{p\ mixture} = C_{p\ amylopectin} + \frac{m_{water}}{m_{amylopectin}} C_{p\ water}$$

Plotting $(1 + m_{H_2}0/m_{AP}) \times C_{p\ mixture}$ vs. $m_{H_2}O/m_{AP}$ gives the specific partial heat capacity of amylopectin as the ordinate intercept and $C_{p\ water}$ as the slope if a linear curve is obtained. The curve drawn for amylopectin/water mixtures at $T = 25°C$ is linear (with $R^2 > 0.998$) and gives 1.19 and

4.81 J $g^{-1}$ °$C^{-1}$ respectively for the specific partial heat capacities of amylopectin and water (Fig. 6). The experimental value for dry amylopectin is well taken into account by the equation ($C_{p\ \mathrm{amylopectindry}\ (T=25°\mathrm{C})} = 1.185$ J $g^{-1}$ °$C^{-1}$) and the specific partial $C_p$ obtained for water is 15% higher than the $C_p$ for liquid water at the same temperature (4.179 J $g^{-1}$ °$C^{-1}$).

Similar results are obtained when drawing the same curve for $T = 47$°C. Values are higher than those determined at 25°C (Fig. 6), specific heat capacities values determined for amylopectin and water being 1.29 and 5.31 J $g^{-1}$ °$C^{-1}$ respectively. In this case, for the higher water contents, values for glassy heat capacities are extrapolations of the linear variations observed at lower temperatures since additional heat capacity contributions are brought by the glass transition.

*Amylopectin/water interactions*: the large effect of water on the thermogram shapes as well as on the heat capacity absolute values indicates a non-ideal mixing for amylopectin and water. The additivity laws cannot therefore be applied to the heat capacity increments as was sometimes done for carbohydrate mixtures to rationalise the increase in $\Delta C_p$ with the water content. In polymer/water mixture, the notions of bound (sorbed water) and freezable (clustered) water have often been considered (Hoeve, 1979; Yoshida, Hatakeyama & Hatakeyama, 1992; Bair, 1997). In our case, freezable water was not observed, except for the most hydrated amylopectin sample and cooling rates inferior to 4.5°C $min^{-1}$. Water can therefore be considered as 'bound' to the polymer chain. Specific interactions between water and biopolymers are very probable, hydrogen bonds being favoured by the presence of numerous hydroxyl groups. Water may therefore change the thermal properties of amylopectin itself, by modifying intermolecular interactions and consequently increasing the chain mobility. This may change the total vibration spectra of the macromolecule and thus make the comparison with the dry amylopectin properties impossible.

*Heat capacity increment of hydrated amylopectin*: our experimental data for the heat capacity jump at $T_{g1/2}$ of amylopectin are 50% smaller than those measured with an incremental procedure by Noel and Ring (1992). As illustrated by Fig. 5, discrepancies are observed, for 14% $H_2O$ $T_g$ is equal to 39°C while we obtain $T_g = 74$°C with the same water content. The ratio between the very slow heating rate from incremental method (+1°C $h^{-1}$, unknown cooling rate) and our heating rate (+3°C $min^{-1}$, same cooling rate) is about $5.10^{-3}$. As can be checked on Fig. 7 in the Section 3.2, for amylopectin, two or three decades frequency difference cannot reasonably explain a difference in $T_g$ amounting to more than 6°C.

Semi-crystallinity could be invoked as an explanation for a reduced heat capacity jump as well as for different $T_g$ values. Anyway, for such a high difference, X-ray diffraction would not have given the observed amorphous patterns. Although other unknown differences linked with the product origin or preparation may be responsible for scattered data, the main problem seems to reside in the experimental procedures. The application of incremental methods in the glass transition region may be questionable as very low scanning rates favour structural relaxation during the experiment.

*Heat capacity increments of dry polysaccharides*: the Couchman formalism has been widely used as an empirical equation for the prediction of the plasticising effect of water in food materials (Noel & Ring, 1992; Kalichevsky & Blanshard, 1993). The values of $T_g$ and $\Delta C_p$ of the pure components, necessary for these predictions, are not accurately known for both polysaccharides and water. Dry polysaccharides have a very high $T_g$ and usually undergo degradation before the glass transition. Properties of pure amorphous solid water have proven to be very difficult to determine: a $T_g$ value of −139°C seems reliable whereas given values for $\Delta C_p$ range between 0.092 (liquid quenched water, Hallbrucker, Mayer & Johari, 1989) and 1.94 J $g^{-1}$ °$C^{-1}$ (vapour deposited water, Sugisaki, Suga & Seki, 1968). The values reported for $\Delta C_{p\ \mathrm{water}}$ in mixtures span in a large range: 0.93 J $g^{-1}$ °$C^{-1}$ for highly concentrated galactose solutions and 1.39 J $g^{-1}$ °$C^{-1}$ for PVP/water mixtures, (Blond & Simatos, 1991), 1.06 to 1.39 J $g^{-1}$ °$C^{-1}$ for electrolyte aqueous solutions, (Angell & Tucker, 1980), 1.83 J $g^{-1}$ °$C^{-1}$ for freeze-concentrated carbohydrate solutions (Hatley & Mant, 1993) and less than 0.3 J $g^{-1}$ °$C^{-1}$ for hydrated amylopectin (Noel & Ring, 1992). Additional contributions of the mixture components were usually considered since the $\Delta C_p$ varied linearly in function of the water content.

$T_g$ and $\Delta C_p$ of pure amylopectin were respectively estimated at 227°C and 0.47 J $g^{-1}$ °$C^{-1}$, by extrapolation from malto-oligomer series (Orford, Parker, Ring & Smith,

Table 3
Glass transition data of hydrated amylopectin as a function of the moisture content ($Q_{\mathrm{cooling}} = 4.5$°C $min^{-1}$ to prevent crystallisation of freezable water)

| m.c. (%w.b.) | $T_{\mathrm{fictive}}$ ± 0.5 (°C) | $T_{g1/2}$ ± 0.5 (°C) | $\Delta C_p$ at $T_{g1/2}$ ±0.015 (J $g^{-1}$ °$C^{-1}$) | $\Delta C_p/C_{p\ \mathrm{glass}}$ at $T_{g1/2}$ | $T$ range $\Delta T$ (°C) | Steepness $\Delta C_{p84-16}/\Delta T$ ($10^{-2}$ J $g^{-1}$ °$C^{-2}$) | $\left(\frac{dC_p}{dT}\right)_{\mathrm{glass}}$ ±0.2 ($10^3$ J $g^{-1}$ °$C^{-2}$) | $\left(\frac{dC_p}{dT}\right)_{\mathrm{liquid}}$ ±0.2 ($10^3$ J $g^{-1}$ °$C^{-2}$) |
|---|---|---|---|---|---|---|---|---|
| 0 | | | | | | | 4.41 | |
| 6.9 | 149.9 | 148.9 | 0.204 | 0.096 | 8.5 | 1.63 | 5.31 | 1.32 |
| 10.9 | 101.9 | 102.9 | 0.201 | 0.090 | 8.5 | 1.55 | 6.58 | 3.47 |
| 12.7 | 81.1 | 82 | 0.218 | 0.110 | 8.4 | 1.70 | 6.86 | 3.55 |
| 16.1 | 56.7 | 57.5 | 0.225 | 0.110 | 7.7 | 1.94 | 7.85 | 3.57 |
| 18.9 | 38.9 | 39.9 | 0.233 | 0.116 | 7.7 | 2.00 | 8.5 | 3.4 |

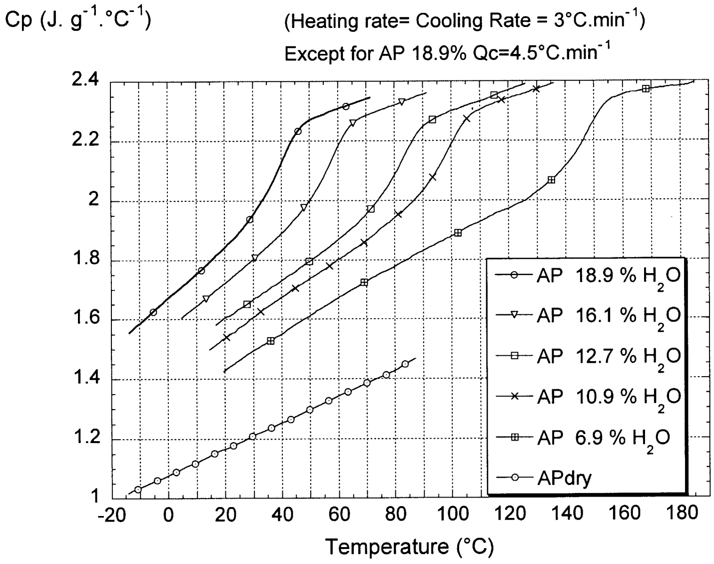

Fig. 4. Influence of water content on amylopectin thermograms.

1989). These values applied well for the prediction of $T_g$ amylopectin/water mixtures with $T_{g\ \mathrm{water}} = -139°C$ and $\Delta C_p$water = 1.94 J g$^{-1}$ °C$^{-1}$ (Kalichevsky, Jaroszkiewicz, Ablett, Blanshard & Lillford, 1992). For ternary mixtures of amylopectin, water and fructose, the values $T_g = 229°C$ and $\Delta C_p = 0.41$ J g$^{-1}$ °C$^{-1}$ were successfully used for amylopectin (Kalichevsky & Blanshard, 1993). Incidentally, the authors also mentioned the possibility of using $\Delta C_{p\ \mathrm{water}} =$ 1.04 J g$^{-1}$ °C$^{-1}$and $\Delta C_{p\ \mathrm{amylopectin}} = 0.22$ J g$^{-1}$ °C$^{-1}$, noticing that this low value was generally measured for amylopectin in the presence of water. Ratto and Schneider (1998) found that the high value of $\Delta C_{p\ \mathrm{water}} = 1.94$ J g$^{-1}$ °C$^{-1}$ overestimated the $T_g$ depression in pullulan/water mixtures. They obtained a good Couchman regression of their data using $\Delta C_{p\ \mathrm{water}} = 1.000$ J g$^{-1}$ °C$^{-1}$ and the experimental value $\Delta C_{p\ \mathrm{pull}} = 0.245$ J g$^{-1}$ °C$^{-1}$. This value could help fixing the contribution of water to the heat capacity of hydrated polysaccharides. While this experimental $\Delta C_{p\ \mathrm{pull}}$ is very lower than the one proposed for amylopectin by Orford et al. (1989), the structural differences between pullulan and amylopectin should rather play in favour of a higher $\Delta C_p$ for the more flexible pullulan. We believe that the flexibility of the Couchmann formula has erroneously accredited the $\Delta C_p$ value first given for dry amylopectin: 0.47 J g$^{-1}$ °C$^{-1}$ is surprisingly

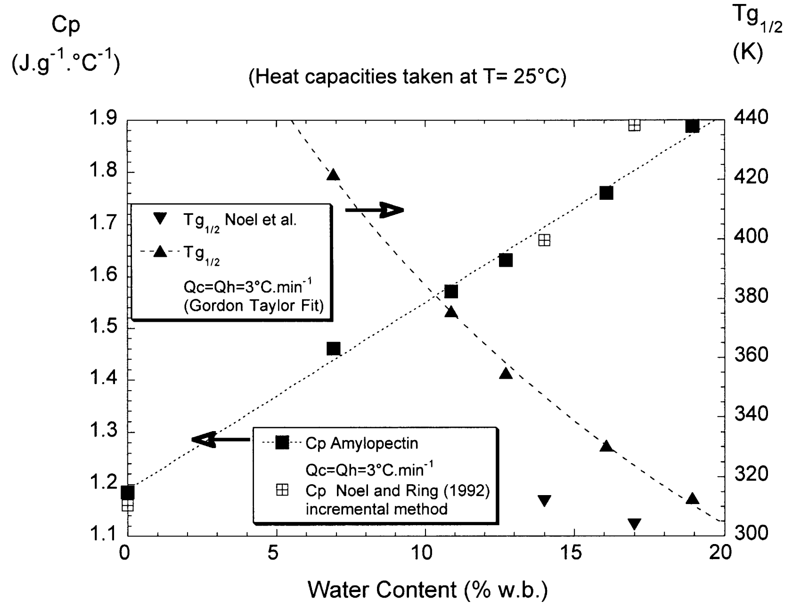

Fig. 5. Amylopectin heat capacity and $T_{g1/2}$ as a function of the water content.

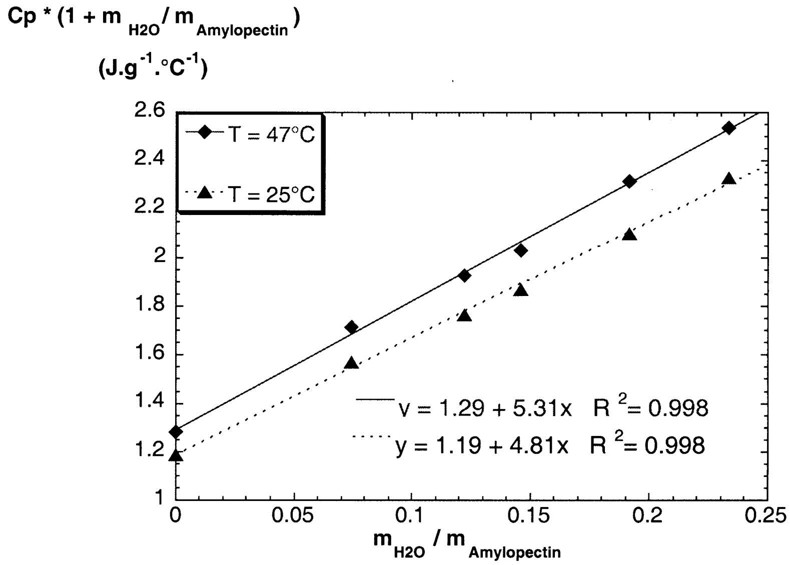

Fig. 6. Evaluation of the partial heat capacities for hydrated amylopectin.

high compared to the typical 0.22 J g$^{-1}$ °C$^{-1}$ measured for hydrated amylopectin.

The determination of pure components properties being difficult, the Gordon-Taylor formula (1952) has also been used for the fitting of $T_g$ values as a function of water content (Bizot et al., 1997; Roos & Karel, 1991). The results presented on Fig. 5 are comparable to those found by Jouppila, Ahonen and Roos (1995) for amylopectin. For the Gordon Taylor regression, $\Delta C_{p\ \mathrm{amylopectin}}/\Delta C_{p\ \mathrm{water}} = 0.185$ J g$^{-1}$ °C$^{-1}$ and $T_{\mathrm{g\ amylopectindry}} = 243$°C were determined, in agreement with a former study by Zeleznak and Hoseney (1987). The best parameters we find for the Gordon Taylor regression, $T_{\mathrm{g\ water}} = -139$°C, $T_{\mathrm{g\ amylopectin}} = 266$°C and $\Delta C_{p\ \mathrm{Ap}}/\Delta C_{p\ \mathrm{water}} = 0.181$ would also fit in a Couchmann approach with $\Delta C_{p\ \mathrm{amylopectin}} = 0.181$ J g$^{-1}$ °C$^{-1}$ and $\Delta C_{p\ \mathrm{water}} = 1.000$ J g$^{-1}$ °C$^{-1}$, both values being in agreement with recent results of Ratto and Schneider (1998).

### 3.2. Fragility and activation energy of structural relaxation

Recent works dealing with the fragility of some carbohydrates (sorbitol, fructose: Simatos, Blond, Roudaut, Champion & Perez, 1996; Mehl, 1998) have been published but no data were yet available for polysaccharides: this approach provides a new insight into the dynamics of the glass transition. As underlined by Böhmer, Ngai, Angell and

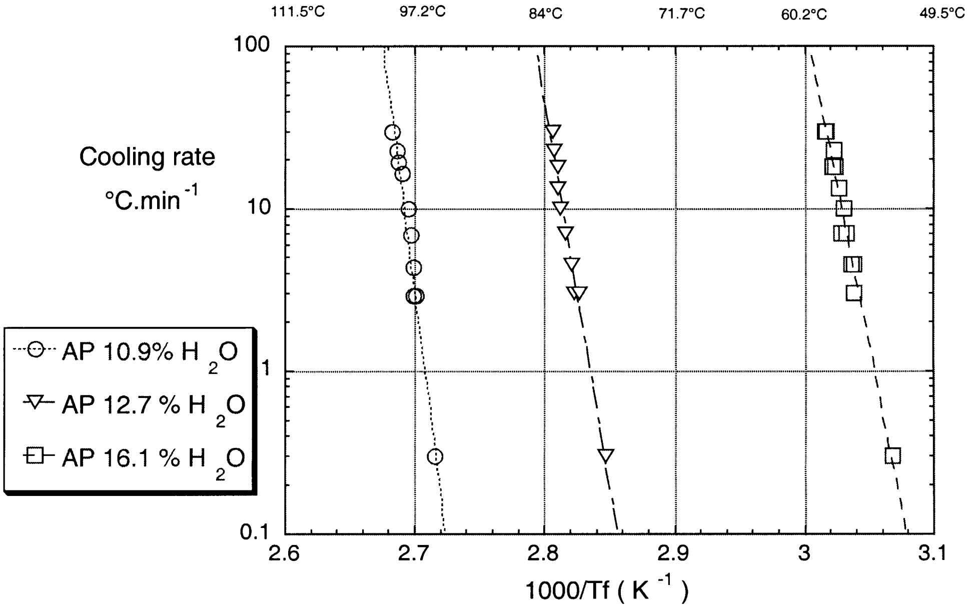

Fig. 7. Determination of the activation energy $\Delta H^*$ for hydrated amylopectin.

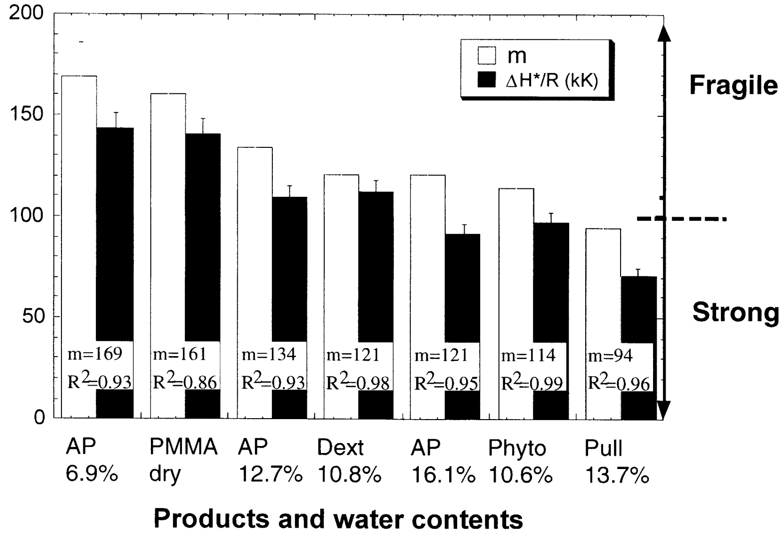

Fig. 8. Fragility parameters m and activation energy $\Delta H^*$ of polysaccharides.

Plazek (1993), the best methods for the determination of the fragility parameter are those operating in the linear regime, thus able to resolve the dynamic properties in the vicinity of $T_g$. Nevertheless, a good agreement was observed for the activation energy $\Delta H^*$ determined by linear and non-linear calorimetric experiments (Moynihan, Crichton & Opalka, 1991). Spectroscopic methods such as dielectric or mechanical spectroscopy are difficult to apply to hydrated polysaccharides in the glass transition region because of their conductivity and poor mechanical properties (Borde, 1999).

### 3.2.1. Experimental results

A series of thermograms was recorded and analysed after cooling at rates ranging between 0.3 and 30°C min$^{-1}$. The determination of the activation energy $\Delta H^*$ is illustrated for amylopectin at three water contents on Fig. 7 (see Section 1.2). The corresponding values of fragility $m$ and $\Delta H^*/R$ are presented for amylopectin (6.9–16.1% $H_2O$), phytoglycogen, dextran, pullulan and PMMA on Fig. 8. The presence of freezable water for slow cooling rates prevented us from treating the highest humidity level of amylopectin. The slopes of Arrhenius lines are expressed directly as $\Delta H^*/R$, sometimes used as a fitting parameter in enthalpy relaxation models such as KAHR model (Kovacs et al., 1979). The products are presented by order of decreasing fragility parameter; m was calculated from $\Delta H^*$ and $T_{g1/2}$ (reference scan), the correlation coefficients $R^2$ of the exponential fittings are also indicated (drawn after elimination of obvious outlying points). Errors bars were estimated at 10% of the $m$ and $\Delta H^*$ values.

In the strong/fragile classification, amorphous partially hydrated polysaccharides are fragile liquids ($m \geq 100$). The fragility parameter of amylopectin decreases with growing water content ($m = 169–114$), phytoglycogen and dextran are a little bit stronger than amylopectin whereas pullulan is the strongest liquid of our series ($m = 94$). Dextran and phytoglycogen would range differently if one considered the activation energies, but differences remain in the experimental uncertainty. The parameter $\Delta H^*$ is strictly the activation energy of the relaxation in the range of ‘frequency’ under investigation whereas the fragility parameter introduces a normalisation with respect to $T_g$. The fragility found for dry PMMA is similar to the one of low hydrated amylopectin, $m_{\mathrm{PMMA}} = 161$. This value is a little high compared with values found in the literature: $m = 145$ obtained from creep measurements (Böhmer et al., 1993), $m = 120$ determined by calorimetry from $T_f$ cooling rate dependence (Godard & Saiter, 1998). Differences in the experimental procedures and cooling rate ranges could explain these differences, the activation energy determined in this way being dependent on the chosen temperature interval, as polymers dynamics usually follow Vogel–Tamman–Fulcher laws in that region.

### 3.2.2. Strong/fragile classification and other properties

In the original paper given by Angell (1985), the strong/fragile classification is described for a wide variety of glass forming liquids and correlations between fragility and configurational thermodynamic properties are found. Strong liquids ($16 < m < 100$) exhibit only small changes in heat capacity at the glass transition, a behaviour related with stability in the short and intermediate range order. On the other hand, the structure of fragile liquids degrades rapidly with the increase of temperature above the glass transition temperature, their heat capacity increment at $T_g$ is large. Their average relaxation time follows Arrhenius law both in the high and low temperature domains, with an intermediate region strongly non-Arrhenian. For fragile liquids, typical values are $100 < m < 200$ and $C_{p\ \mathrm{liquid}}/C_{p\ \mathrm{glass}} < 1.1$. Most polymeric liquids are fragile and show the well known Vogel–Fulcher behaviour, polyvinyl (chloride) being one of the most fragile ($m = 191$).

The strong/fragile behaviour of liquids has also been interpreted in terms of differences in configurational space potential energy (Angell, 1988). Fragile liquids have a high density of configurational states, leading to rapid thermal excitation whereas strong liquids, structurally better defined, have a lower number in minima on their potential energy surface. Alcohols are frequently found to escape from the general tendency, showing large heat capacity increments and intermediate viscosity behaviour. The breaking of hydrogen bonds between molecular units being necessary for the structural rearrangement of these liquids, their potential energy surface is thought to present a high density of minima with large energy barriers in-between (Angell, 1991).

Discussing the significance of the 'steepness index', Ngai and Plazek (1995) pointed out that polymers might display different normalised temperature dependences for structural reasons modifying their ability for intermolecular coupling or cooperativity. A clear correlation between the steepness index and the cooperativity parameter determined in the coupling theory was found (Plazek & Ngai, 1991). Experimental data on polybutadiene showed that the fragility increased with the number of pending vinyl chain units: the simultaneous increase of the coupling parameter n was attributed to steric constraints or coupling between the rearranging segments. In this view, symmetric and compact chemical structures, with less steric hindrance and intermolecular interactions will be less fragile than others will. In a more recent review on 14 synthetic polymers, Colucci and McKenna (1997) similarly classified as fragile those containing oxygen or ringed structures in the backbones.

### 3.2.3. Hydrated polysaccharides: fragile liquids

Dealing with mixtures, the importance of the water content on the parameters measured has to be kept in mind. For amylopectin, the addition of water reduces the thermal energy necessary for promoting the cooperative chain motions associated with the glass transition; it increases the transition steepness and decreases the fragility parameter. These effects seem to indicate a structuring role of water, reducing the hindrance and heterogeneities associated with branched chains. Here again, the presence of hydrogen bonds, reinforced by increasing water contents, can be invoked to account for our observations.

The ranking of our products on the strong/fragile scale is not consistent with the general idea that strong liquids should present a small heat capacity increment at $T_{g1/2}$. Pullulan shows an intermediate $\Delta C_p$ value and is found to be the strongest. This may be attributed to its linear and rather flexible structure, cooperativity at the glass transition may be less important than for the highly branched amylopectin. Complementary results covering a wider range of hydration for pullulan and dextran would be necessary, but pullulan may be expected to be even stronger with respect to others products, given the high humidity tested here. In spite of its intrinsic defects (e.g. non-linearity), DSC allows a classification of hydrated polysaccharides on the strong/fragile scale. Comparisons remain difficult (experimental devices are still poorly adapted for the study of hydrated products) with results obtained from other spectroscopic methods, but as a whole this study brings already a self consistent characterisation of our products and new elements for a deeper comprehension of their structural relaxation.

## 4. Conclusion

We present a systematic study of the calorimetric glass transition of a series of hydrated polysaccharides. Using simple thermal cycles, classical DSC can yield detailed information on the material relaxational behaviour in the region of the transition. The fictive temperature is shown to be an efficient characterising parameter which provides a reliable value for the definition of a glass transition temperature. Its dependence on the cooling rate can be used to evaluate the activation energy of the structural relaxation as well as the fragility parameter. Such an approach could be used for a 'routine' characterisation of a wide variety of glassy food products as was already proposed by Simatos et al. (1996) for sugars. Our results also illustrate well-defined effects of the thermal history on the behaviour of polysaccharide glasses, either pure or water-plasticised, similarly to synthetic polymers.

The influence of water as a plasticizer of amylopectin is complex, including depression of the glass transition temperature, non-ideal mixing contributions to the heat capacity in the glassy state, increase of the transition steepness and slight reduction of the fragility. These observations indicate water-biopolymer interactions at a molecular level, strong enough to modify the dynamics of the mixture around the glass transition.

Concerning the structural relaxation of hydrated polysaccharides, we now possess sufficiently detailed data to begin an investigation of the behaviour on storage. The effect of isothermal ageing at sub-$T_g$ temperatures will be the subject of the following paper. Complementary studies with modulated DSC would also be useful for comparison with our fragility parameters. The investigation of the effect of water on thermal properties of dextran and pullulan could also generate more information on the importance of the nature of glycosidic linkages.

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## References

Angell, C. A., & Tucker, J. C. (1980). Heat capacity changes in glass-forming aqueous solutions and the glass transition in vitreous water. *Journal of Physical Chemistry*, *84*, 268–272.

Angell, C. A. (1985). Strong and fragile liquids. In K. Ngai & G. B. Wright, *Relaxations in complex systems* (pp. 3–11). Springfield, VA: National Technical Information Service, US Department of Commerce.

Angell, C. A. (1988). Perspective on the glass transition. *Journal of Physical Chemistry Solids*, *49* (8), 863–871.

Angell, C. A. (1991). Relaxations in liquids, polymers and plastic crystals — strong/fragile patterns and problems. *Journal of Non-Crystalline Solids*, *131-133*, 13–31.

Angell, C. A., Bressel, R. D., Green, J. L., Kanno, H., Oguni, M., & Sare, E. J. (1994). Liquid fragility and the glass transition in water and aqueous solutions. *Journal of Food Engineering*, *22*, 115–142.

Bair, H. E. (1997). Thermal analysis of additives in polymers. In A. Turi, *Thermal characterization of polymeric materials* (pp. 205–482). San Diego, USA: Academic Press.

Bershtein, V. A., & Egorov, V. M. (1994). *Differential scanning calorimetry of polymers: physics, chemistry, analysis, technology*, Chichester, UK: Ellis Horwood.

Bizot, H., Le Bail, P., Leroux, B., Davy, J., Roger, P., & Buleon, A. (1997). Calorimetric evaluation of the glass transition in hydrated, linear and branched polyanhydroglucose compounds. *Carbohydrate Polymers*, *32*, 33–50.

Blanshard, J. M. V., & Lillford, P. J. (1993). *The glassy state in food*, Loughborough, UK: Nottingham University Press.

Blond, G., & Simatos, D. (1991). Glass transition of the amorphous phase in frozen aqueous systems. *Thermochimica Acta*, *175*, 239–247.

Böhmer, R., Ngai, K. L., Angell, C. A., & Plazek, D. J. (1993). Non exponential relaxations in strong and fragile glass formers. *Journal of Chemical Physics*, *99* (5), 4201–4209.

Borde, B. (1999). Mobilité moléculaire et processus de relaxation dans des polysaccharides amorphes partiellement hydratés. PhD Génie des Matériaux INSA de Lyon, 364 p.

Boyer, R. F. (1973). $\Delta C_pT_g$ and related quantities for high polymers. *Journal of Macromolecular Science Physics Part B*, *7* (3), 487–501.

Colucci, D. M., & McKenna, G. B. (1997). Fragility of polymeric liquids: correlations between thermodynamic and dynamic properties. In C. A. Angell, K. L. Ngai, Kieffer, T. Egami & G. U. Nienhause, *Structure and dynamics of glasses and glass formers* (pp. 171–176). Pittsburgh, USA: Material Research Society.

Couchmann, P. R. (1978). A classical thermodynamic discussion of the effect of composition on glass-transition temperatures. *Macromolecules*, *11* (1), 117–119.

Curro, J. G., Lagasse, R. L., & Simha, R. (1982). Diffusion model for volume recovery in glasses. *Macromolecules*, *15* (6), 1621–1626.

DiMarzio, E. A., & Dowell, F. (1979). Theoretical prediction of the specific heat of polymer glasses. *Journal of Applied Physics*, *50* (10), 6061–6066.

Donth, E. (1992). *Relaxation and thermodynamics in polymers*, *Glass transition*. Berlin: Akademie.

Donth, E., Korus, J., Hempel, E., & Beiner, M. (1997). Comparison of DSC heating rate and HCS frequency at the glass transition. *Thermochimica Acta*, *304–305*, 239–249.

Fujimori, H., & Oguni, M. (1995). Correlation index ($T_g\alpha - T_g\beta/T_g\alpha$) and activation energy ratio Δεαα/Δεαβ as parameters characterizing the structure of liquid and glass. *Solid State Communications*, *94* (2), 157–162.

Gibbs, J. H., & Dimarzio, E. A. (1958). Nature of the glass transition an the glassy state. *Journal of Chemical Physics*, *28* (3), 373–383.

Godard, M. E., & Saiter, J. M. (1998). Fragility and non-linearity in polymethyl(α-*n*-alkyl)acrylates. *Journal of Non-Crystalline Solids*, *235–237*, 635–639.

Goldstein, M. (1976). Viscous Liquids and the Glass Transition. V. Sources of the excess specific heat of the liquid. *Journal of Chemical Physics*, *64* (11), 4767–4774.

Gordon, M., & Taylor, J. S. (1952). Ideal copolymers and the second-order transition of synthetic rubbers. *Journal of Applied Chemistry*, *2*, 493–499.

Guizard, C., Chanzy, H., & Sarko, A. (1984). Molecular and crystal structure of dextrans: a combined electron and X-ray diffraction study-I the anhydrous high temperature polymorph. *Macromolecules*, *17*, 100–107.

Hallbrucker, A., Mayer, E., & Johari, G. P. (1989). The heat capacity and glass transition of hyperquenched glassy water. *Philosophical Magazine*, *60* (2), 179–187.

Hancock, B. C., Shamblin, S. L., & Zografi, G. (1995). Molecular mobility of amorphous pharmaceutical solids below their glass transition temperatures. *Pharmaceutical Research*, *12* (6), 799–806.

Hatley, R. H., & Mant, A. (1993). Determination of the unfrozen water content of maximally freeze-concentrated carbohydrate solutions. *International Journal of Biological Macromolecules*, *15*, 227–232.

Hirai, N., & Eyring, H. (1958). Bulk viscosity of liquids. *Journal of Applied Physics*, *29* (5), 810–816.

Hodge, I. M. (1983). Effects of annealing and prior history on enthalpy relaxation in glassy polymers 4: comparison of five polymers. *Macromolecules*, *16* (6), 898–902.

Hodge, I. M. (1994). Enthalpy relaxation and recovery in amorphous materials. *Journal of Non-Crystalline Solids*, *169*, 211–266.

Hoeve, C. A. J. (1979). The Structure of Water in Polymers. In Water in polymers (vol. 127). ACS Symposium Series, 178th Meeting of the American Chemical Society (pp. 135–146) Washington, DC: ACS.

Hutchinson, J. M. (1987). *Thermal cycling of glasses: a theoretical and experimental approach*, *Molecular dynamics and relaxation phenomena in glasses. Lecture notes in physics*, vol. 277. Berlin: Springer (pp. 172–187).

Jouppila, K., Ahonen, T., & Roos, Y. (1995). *Adsorption and plasticization of amylopectin glasses*, *Food macromolecules and colloids*. Cambridge: Dickinson and Lorient (pp. 556–559).

Kalichevsky, M. T., & Blanshard, J. M. V. (1993). The effect of fructose and water on the glass transition of amylopectin. *Carbohydrate Polymers*, *20*, 107–113.

Kalichevsky, M. T., Jaroszkiewicz, E. M., Ablett, S., Blanshard, J. M. V., & Lillford, P. J. (1992). The glass transition of amylopectin measured by DSC, DMTA and NMR. *Carbohydrate Polymers*, *18*, 77–88.

Kovacs, A. J., Aklonis, J. J., Hutchinson, J. M., & Ramos, A. R. (1979). Isobaric volume and enthalpy recovery of glasses. II. A transparent multiparameter theory. *Journal of Polymer Science: Polymer Physics Edition*, *17*, 1097–1162.

Mathot, V. B. F. (1984). Temperature dependence of some thermodynamic functions for amorphous and semi-crystalline polymers. *Polymer*, *25*, 579–599.

McKenna, G. B. (1989). *Glass formation and glassy behavior*, *Polymer properties: comprehensive polymer science*, vol. 2. Oxford: Pergamon Press (pp. 311–362).

Mehl, P. M. (1998). Fictive glass-transition temperature and fragility for the phase diagram of the system fructose/water. *Thermochimica Acta*, *324*, 215–221.

Menczel, J. D., & Leslie, T. M. (1993). Temperature calibration of an electrical compensation DSC on cooling using thermally stable high purity liquid crystals. *Journal of Thermal Analysis*, *40*, 957–970.

Menczel, J. D. (1997). Temperature calibration of heat flux DSC's on cooling. *Journal of Thermal Analysis*, *49*, 193–199.

Moynihan, C. T., Easteal, A. J., DeBolt, M. A., & Tucker, J. (1976a). Dependence of the fictive temperature of glass on cooling rate. *Journal of the American Ceramic Society*, *59* (1-2), 12–16.

Moynihan, C. T., Macedo, P. B., Montrose, C. J., Gupta, P. K., DeBolt, M. A., Dill, J. F., Dom, B. E., Drake, P. W., Easteal, A. J., Elterman, P. B., Moeller, R. P., Sasabe, H., & Wilder, J. A. (1976b). Structural relaxation in vitreous materials. *Annals of the New York Academy of Science*, *279*, 15–35.

Moynihan, C. T., Crichton, S. N., & Opalka, S. M. (1991). Linear and non linear structural relaxation. *Journal of Non-Crystalline Solids*, *131-133*, 420–434.

Narayanaswamy, O. S. (1971). A model of structural relaxation in glass. *Journal of the American Ceramic Society*, *54* (10), 491–498.

Ngai, K. L., & Plazek, D. J. (1995). Identification of different modes of molecular motion in polymers that cause thermorheological complexity. *Rubber Chemistry Technology*, *68*, 376–434.

Ngai, K. L., Rendell, R. W., Rajagopal, A. K., & Teitler, S. (1986). Three coupled relations for relaxations in complex systems. *Annals of the New York Academy of Science*, *484*, 150–184.

Noel, T. R., & Ring, S. G. (1992). A study of the heat capacity of starch/water mixtures. *Carbohydrate Research*, *227*, 203–213.

Orford, P. D., Parker, R., Ring, S. G., & Smith, A. C. (1989). Effect of water as a diluent on the glass transition behaviour of malto-oligosaccharides, amylose and amylopectin. *International Journal of Biological Macromolecules*, *11*, 91–96.

Perez, J. (1988). Defect diffusion model for volume and enthalpy recovery in amorphous polymers. *Polymer*, *29*, 483–489.

Plazek, D. J., & Ngai, K. L. (1991). Correlation of polymer segmental chain dynamics with temperature-dependent time-scale shifts. *Macromolecules*, *24* (5), 1222–1224.

Ratto, J. A., & Schneider, N. (1998). The effect of water interactions on the thermal transition behavior of pullulan. *ACS Proceedings Polymeric Materials Science and Engineering*, *79*, 469–470.

Rees, D. A. (1977). *Polysaccharide shapes*, London: Chapman & Hall.

Richardson, M. J., & Savill, N. G. (1975). Derivation of accurate glass transition temperatures by differential scanning calorimetry. *Polymer*, *16*, 753–757.

Ritland, H. N. (1954). Density phenomena in the transformation range of a borosilicate crown glass. *Journal of the American Ceramic Society*, *37* (8), 370–378.

Ritland, H. N. (1956). Limitations of the fictive temperature concept. *Journal of the American Ceramic Society*, *39* (12), 403–406.

Robinson, G. W., Zhu, S. B., Singh, S., & Evans, M. W. (1996). *Water in biology, chemistry and physics, Experimental Overviews and Computational Methodologies*. Singapore: World Scientific.

Roos, Y., & Karel, M. (1991). Water and molecular weight effects on glass transition in amorphous carbohydrates and carbohydrate solutions. *Journal of Food Science*, *56* (6), 1676–1681.

Roos, Y. H., Leslie, R. B. & Lillford, P. J. (1999). Water management in the design and distribution of quality foods: ISOPOW 7. International Symposium on Water Management in the Design and Distribution of Quality Foods, Helsinki, Finland, 30th May–4th June 1998. Lancaster, USA: Technomic.

Rowland, S. P. (1979). Water in polymers. ACS Symposium Series, 178th Meeting of the American Chemical Society (vol. 127). Washington, DC: ACS.

Ruddick, A., & Goodall, D. M. (1998). Use of capillary electrophoresis for the determination of the conformation and size of individual components in a biopolymer distribution. 1. Theory and application to amylose and dextran. *Macromolecules*, *31* (24), 8638–8643.

Scherer, G. W. (1986). *Relaxation in glass and composites*, New York: Wiley.

Simatos, D., Blond, G., Roudaut, G., Champion, D., & Perez, J. (1996). Influence of heating and cooling rates on the glass transition temperature and the fragility parameter of sorbitol and fructose as measured by DSC. *Journal of Thermal Analysis*, *47*, 1419–1436.

Slade, L., & Levine, H. (1995). Polymer science approach to water relationships in foods. In G. V. Barbosa-Canovas & J. Welti-Chanes, *Food preservation by moisture control. Fundamentals and applications* (pp. 33–132). Lancaster, USA: Technomic.

Sugisaki, M., Suga, H., & Seki, S. Y. (1968). Calorimetric study of the glassy state. IV. Heat capacity of glassy water and cubic ice. *Bulletin of the Chemical Society of Japan*, *41*, 2591–2599.

Tan, Y. Y., & Challa, G. (1976). The glass transition temperature of poly (*N*-vinyl pyrrolidone) and the effect of water. *Polymer*, *17*, 739–740.

Tool, A. Q., & Eichlin, C. G. (1931). Variations caused in heating curve of glass by heat-treatment. *Journal of the American Ceramic Society*, *14* (4), 276–308.

Turnbull, D., & Cohen, M. H. (1961). Free-volume model of the amorphous phase: glass transition. *Journal of Chemical Physics*, *34* (1), 120–125.

Wunderlich, B. (1960). Study of the change in specific heat of monomeric and polymeric glasses during the glass transition. *Journal of Physical Chemistry*, *64*, 1052–1056.

Yoshida, H., Hatakeyama, T., & Hatakeyama, H. (1992). Effect of water on the main chain motion of polysaccharide hydrogels. In W. G. Glasser & H. Hatakeyama, *Viscoelasticity of biomaterials. ACS Symposium Series* (pp. 217–230). Washington, DC: ACS.

Zeleznak, K. J., & Hoseney, R. C. (1987). The glass transition in starch. *Cereal Chemistry*, *64* (2), 121–124.