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# Influence of water, temperature and sucrose on dynamics in glassy starch-based products studied by low field $^1$H NMR

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ABSTRACT

In this study, the influence of both water content and temperature on the mobility of glassy starch-based matrices (starch alone or mixed with sucrose at the ratio 0% to 20% db) were studied using time domain $^1$H NMR. The 2nd moment $M_2$, and transversal relaxation time $T_2^*$ were used to study the molecular mobility of the rigid and mobile fraction of the NMR signal, respectively.

The molecular mobility of the protons constituting the samples increased with water content (up to 13% wb) at all temperatures. For a given water content, both rigid and mobile protons exhibited a lower mobility in the presence of sucrose. When mobility characteristic parameters, $M_2$ second moment values and spin–spin relaxation times $T_2^*$, were normalized by $T_g$, i.e plotted versus $T_g/T$, the effect of water was no longer visible whereas the effect of sucrose remained marked. The temperature increase induced an increase in both rigid and mobile protons mobility. Whereas no clear change could be observed on the rigid protons mobility around the glass transition temperature the mobile fraction exhibited a marked mobility change in that temperature range.

## 1. Introduction

A glassy matrix is characterized by its relatively low mobility and its high stability. The stability of the glassy state has been shown to be affected by the composition of the material. Water and temperature are known to be very important factors for physical stability of carbohydrate glasses (Champion, Hervet, Blond, Le Meste, & Simatos, 1997; Hancock & Zografi, 1997; Noel, Parker, & Ring, 1996): an amorphous sample may go through its glass transition following an increase of hydration and/or temperature. Water is the most important and the most effective plasticizer (Roos, 1995). A plasticizer (water or small molecules such as sugars or polyols) induces an increase in both the flexibility and molecular mobility of a polymer and a decrease in its glass transition temperature ($T_g$) (Ferry, 1980). Many studies have shown the influence of water on physical properties of glassy starch (Farhat, Mitchell, Blanshard, & Derbyshire, 1996; Farhat, Mousia, & Mitchell, 2003; Kalichevsky & Blanshard, 1992; Kalichevsky, Jaroszkiewicz, Ablett, Blanshard, & Lillford, 1992; Matveev, Grinberg, & Tolstoguzov, 2000). Water does not only decrease $T_g$ but also facilitates the occurrence of secondary relaxations (Poirier-Brulez, Roudaut, Champion, Tanguy, & Simatos, 2006) with an effect more marked in presence of another small molecule (sucrose, glycerol or sorbitol) mixed with the polymer.

Previous studies (Grattard, Salaün, Champion, Roudaut, & Le Meste, 2002; Kumagai, Macnaughtan, Farhat, & Mitchell, 2002; Partanen, Marie, Macnaughtan, Forssell, & Farhat, 2004; Van den Dries, Van Dusschoten, & Hemminga, 1998) have shown, for glassy matrices such as starch, maltose, maltodextrins, a relation between glass transition temperature and proton mobility studied by NMR.

In earlier papers, the macroscopic properties of starch–sucrose blends were considered through texture properties (Valles Pamies, Roudaut, Dacremont, Le Meste, & Mitchell, 2000), and the molecular mobility within these sytems was examined with dielectric (Roudaut et al., 1999) and dynamical mechanical spectroscopies and through structural relaxation studies (Poirier-Brulez et al., 2006).

The aim of the present work is to investigate the dynamic properties (by NMR) of starch–sucrose glasses and compare the effects of water and temperature on proton mobility. This should enable us to complement the study of the relationships between proton mobility and physical state of the matrix. This work is divided into two parts: the proton mobility is first investigated at 25 °C as a function of water and sucrose content, in a second stage, it is then considered as a function of temperature at constant water and sucrose content.

## 2. Experimental materials and methods

### 2.1. Materials

The starch used (PregelFlow CH 20, Roquette Frères) was adipic acid crosslinked, acetic anhydride-stabilized and drum drying-gel-

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atinized. According to the supplier, its substitution degree is around 0.07 (*i.e.* 1 acetate every 15 glucose units), and the cross-linking degree is quite moderate (the maximum being 1 for 4000 glucose units and the minimum 1 for 400 glucose units). Modified starch was chosen for its amorphous state and its stability versus retrogradation. Crystalline sucrose was purchased from Merck.

### 2.2. Samples preparation

Starch was added to a sucrose solution, and the concentrations of starch and sucrose were chosen such as (i) the sucrose content was 0%, 5%, 10% or 20% of the dry matter and (ii) the dry matter of the prepared solution was equal to 5.6% of the total weight. This preparation was thoroughly mixed in order to obtain homogenous systems which were then freeze–dried.

The freeze–dried material was ground to a powder with a household grinder. The water content of the sample was then adjusted at 25 °C in air-tight containers via water vapour phase conditioning over $P_2O_5$ or various concentrations of glycerol–water solutions. The solutions provided controlled equilibrium relative humidity (ERH) between 0% and 65% according to UNIQUAC – LARSEN model (Larsen, Rasmussen, & Fredenslund, 1987). Water activity ($a_w$) equilibrium was considered reached when the sample weight was constant (after over 1 month).

The sample water content was determined from the weight difference of the samples before and after drying for 24 h at 105 °C. The moisture content values are expressed as per cent water on a wet basis (w/w) and standard deviation for each water content was determined from three repetitions.

X-ray diffraction analysis and DSC analysis performed on the equilibrated samples showed no presence of any crystalline material, confirming the amorphous state of all prepared samples (results not shown).

For the $T_g$ measurements, the samples were submitted to two successive DSC heating sweeps in the range [10–170 °C]: the first one to erase the thermal history and the second for the $T_g$ measurement (as in Poirier-Brulez et al., 2006), $T_g$ was determined from the midpoint of the observed heat capacity step change. The $T_g$ values of the different samples versus water content are given in Table 1.

### 2.3. Pulsed nuclear magnetic resonance

$^1$H NMR measurements were performed using a Maran Ultra (Orford Instruments, UK) spectrometer operating at a resonance frequency of 23 MHz. The NMR system was equipped with a temperature control device allowing a ± 0.5 °C temperature regulation. The dead time was 11 μs. Proton free induction decays (FID) were acquired using the following parameters: a 90° pulse of 2.2 μs, a dwell time of 0.1 μs between two successive data points, 64 scans of 10240 data points and a recycle delay of 5 s between each scan. The quantity of powdered samples was controlled (average weight 0.5 g). Internal diameter (8 mm) NMR tubes were used. To avoid water loss, the dead volume in the tube was filled by a glass rod and the tube was sealed. The NMR measurements were performed at 5 °C intervals between 25 and $T \approx T_{g\,\mathrm{sample}} + 20$ °C. Thermal equilibration was ensured by allowing an 8 min-waiting time after each temperature step before the experiment was started.

The signal amplitude was divided by sample weight; this normalization allows the comparison of the experimental data obtained with different samples (Fig. 1). The FID signals were described by two components: each ascribed to one pool of protons: the first one with a short relaxation time (rigid population) and the second with longer relaxation time (mobile population). With the FID sequence, the proton relaxation cannot be detected immediately after the 90° pulse, due the dead time (11 μs). Therefore the number of protons relaxing quickly during this period (rigid protons) cannot be considered.

The NMR signal ($I_{\mathrm{FID}}(t)$) was fitted to a mathematical model according to both a Gaussian-type relaxation process due to rigid protons and a Lorentzian relaxation process due to flexible protons, as suggested by Abragam (1961):

$$I_{\mathrm{FID}}(t) = A\exp\left(-\frac{a^2t^2}{2}\right)\frac{\sin bt}{bt} + B\exp\left(-\frac{t}{T_2^*}\right) \quad (1)$$

where, $A$ and $B$ correspond to the amplitude of the rigid and flexible proton populations respectively, $T_2^*$ (μs) is the spin–spin relaxation time of flexible components and t is the acquisition time. The NMR spectrum of the rigid protons is assumed to have a rectangular line shape with a total width $2b$ (μs$^{-1}$), convoluted with a Gaussian line shape with a standard deviation given by the parameter a (μs$^{-1}$). The rigid and mobile proton populations were characterized with

**Table 1**
Water content and glass transition temperature for starch and starch–sucrose mixtures (Poirier-Brulez et al., 2006). The mean standard deviation is ±2.5 °C.

| $a_w$ | 0.097 | 0.187 | 0.362 | 0.48 | 0.66 |
|---|---|---|---|---|---|
| *Water content (% wb)* | | | | | |
| Starch | 4.3 | 6 | 7.8 | 9.4 | 13.5 |
| Starch–5% sucrose | 4.1 | 5.8 | 7.0 | 9.5 | 12.3 |
| Starch–10% sucrose | 3.9 | 5.5 | 7.0 | 8.8 | 11.9 |
| Starch–20% sucrose | 3.1 | 4.6 | 6.3 | 8.2 | 11.3 |
| *$T_g$DSC (°C)* | | | | | |
| Starch | 149 | 131 | 114 | 100 | 69 |
| Starch–5% sucrose | 135 | 117 | 105 | 83 | 61 |
| Starch–10% sucrose | 124 | 108 | 94 | 78 | 54 |
| Starch–20% sucrose | 100 | 88 | 75 | 62 | 43 |

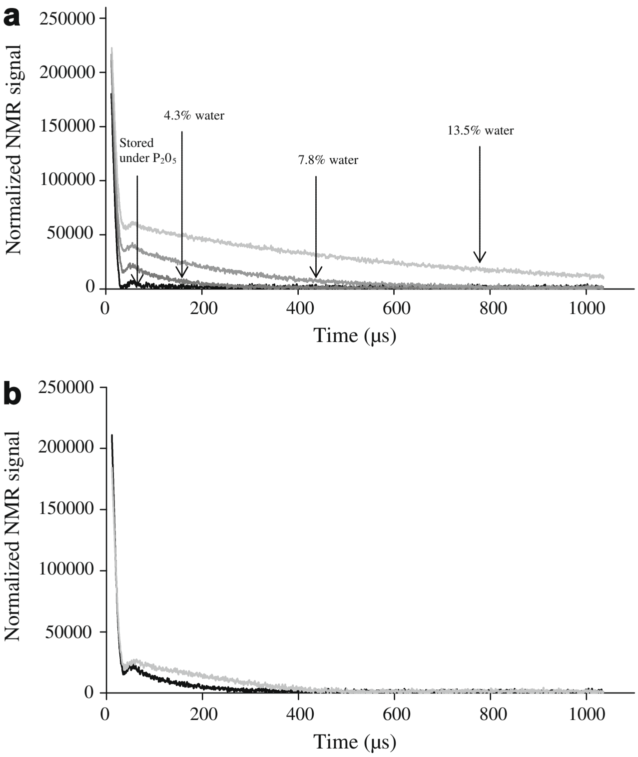

**Fig. 1.** (a) FID signal of starch at different water contents (—: stored under $P_2O_5$; —: 4.3% wb; —: 7.8% wb; —: 13.5% wb). The signals were normalized by sample weight. (b) FID weight-normalized signal of starch (4.3% water) at — 25 °C and — 100 °C.

their 2nd moment $M_2$, and transversal relaxation time, $T_2^*$, respectively.

The second moment, $M_2$ reflects the strength of dipolar interactions in which the rigid protons are involved (Van Den Dries et al., 1998); and thus, it inversely correlates to the molecular mobility of the rigid fraction. It is calculated with the following Eq. (2):

$$M_2 = a^2 + \frac{1}{3}b^2 \qquad (2)$$

All the samples were analysed in triplicate and the reported values ($M_2$, $T_2^*$) are the average of the individual calculated values.

The freeze–drying process resulted in very porous products. Structure collapse occurs during the heat treatment and thus may influence thus the NMR results. A comparative study of the behaviour upon heating (from 25 to 95 °C) was performed on both tabletted (compressed for 5 min under $3 \times 10^8$ Pa at 25 °C) and porous samples. The macrostructure, porous versus compressed tablets, did not affect the NMR data.

## 3. Results and discussion

### 3.1. NMR signal

The FID signals of starch samples, at 25 °C, are shown in Fig. 1. The fast decay of the signal was caused by the "rigid" or non flexible protons (Abragam, 1961) of the matrix, and the slow decaying component was mainly attributed to the mobile protons of the samples. The rigid matrix protons are associated with a proton population with a short relaxation time. The assignment of the mobile protons is more difficult: as according to their rate of mobility in the material, one can observe one or several populations of mobile protons which often cannot be resolved into discrete populations. The relaxation time of this complex population increases with the increasing mobility of the different components, most probably in a differential manner. In presence of increasing amount of water, the system becomes more mobile and previously, several authors (Ablett, Darke, Izzard, & Lillford, 1993; Van Den Dries et al., 1998) attributed the second population solely to water protons; however our observations show that the mobile proton fractions could not be attributed only to water. Indeed at 25 °C, the dry samples stored in desiccant atmosphere exhibited only one population but the thermal agitation caused by heating (at 55 °C) induced the emergence of a second population. Thus, these results confirmed that the second population can be assigned to both water and matrix protons depending on the mobility of the latter (Hills & Pardoe, 1995; Kalichevsky et al., 1992).

The acquired FID signal exhibited for all samples a damped sinusoidal or beat pattern at approximately 50 µs, reflecting strong dipolar interactions between the protons of the rigid component. The second moment $M_2$, which is obtained by fitting this signal according to Eqs. (1) and (2), reports on both the anisotropic mobility and the strength of dipolar interactions between the protons. Such a sinusoidal pattern has been described in many glassy carbohydrates e.g. maltose (Van Den Dries et al., 1998), maltodextrins with different DE (Grattard et al., 2002) or amylose (Partanen et al., 2004). The sinusoidal pattern (Fig. 1) became less pronounced as the water content increased. Partanen et al. (2004) interpreted this as a decrease of the strength of dipolar interactions in the amylose–water blends.

The sinusoidal pattern was found to disappear in maltose and glucose syrups with increasing temperature (Kumagai et al., 2002; Van Den Dries et al., 1998). In these works, the sinusoidal pattern was exhibited up to $T_g$, and disappeared at temperatures above $T_g + 20$ °C (for glucose syrup it disappeared at $T = T_g + 40$ °C). In the present study, the sinusoidal pattern remained very pronounced when sucrose content increased and was unaffected by the temperature increase (Fig. 1b). Sucrose seemed to reinforce dipolar interactions in the starch–sucrose matrix compared to starch alone, for a given water content.

The sinusoidal pattern variations as a function of water or sucrose content or temperature could result from either proton density (which depends on both number and strength of dipolar interactions) or mobility changes (van Den Dries et al., 1998). Hence increasing the sample water content may cause a density decrease and thus a decrease of dipolar interactions, while in the investigated range neither sucrose nor temperature appeared to affect density.

### 3.2. Second moment $M_2$

The fast decay was mainly associated with starch and sucrose (at both low temperature and water content) proton mobility (Choi & Kerr, 2003; Ruan et al., 1999; Tang & Hill, 2000). Fig. 2 shows the effects of both water and sucrose on $M_2$, at 25 °C. $M_2$ values varied for all samples between $5 \times 10^9$ and $7.5 \times 10^9$ s$^{-2}$ and were in the same magnitude range as those published by Partanen et al. (2004) on amylose–glycerol–water samples, in the same water content range. In both the control and the sucrose-containing samples, $M_2$ decreased as water content increased, reflecting the decreasing strength of dipolar interactions, associated with an increased mobility of the rigid protons. For both samples and over the whole investigated hydration range, the addition of 20% sucrose induced an increase in $M_2$ (in dry samples, $M_2 \approx 7 \times 10^9$ s$^{-2}$ for starch and $\approx 7.5 \times 10^9$ s$^{-2}$ for starch–20% sucrose blends), suggesting a sucrose-induced reinforcement in dipolar interactions between the protons of the rigid component (Fig. 2). Such a reinforcement of interactions has previously been suggested for these starch-based systems on the basis of a lower water sorption, a lower secondary relaxation temperature and a structural relaxation of lower amplitude in presence of sucrose (Poirier-Brulez et al., 2006). For sucrose contents lower than 20%, $M_2$ was not significantly different from the value obtained for the starch alone sample.

In addition, for both starch alone and starch–20% sucrose samples, $M_2$ decreased with increasing temperature (Fig. 3a and b). This expected behaviour reflects the increase in rigid proton mobility with temperature. Moreover, at the highest water content (13.5% and 11.3% respectively for starch and starch–20% sucrose) the slope of $M_2$ versus temperature was significantly greater than at the lowest water content (Table 2) suggesting a more effective thermal activation of molecular mobility in water-containing glasses compared to a "dry" polymer one. Moreover, at a given temperature (as previously observed at 25 °C), $M_2$ values were higher in the presence of sucrose, and decreased with increasing water content.

For hydrated starch samples, the decrease of $M_2$ with increasing temperature was followed by a stabilization of $M_2$ at high temperature. The temperature at which $M_2$ leveled off (Fig. 3a) was shifted to-

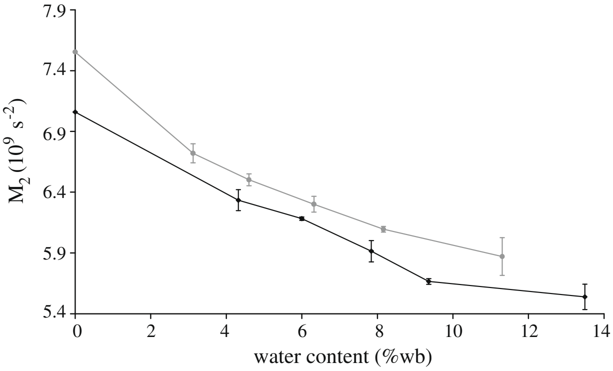

**Fig. 2.** Effect of water on the second moment of gelatinized starch (♦) and starch–20% sucrose (●) at 25 °C.

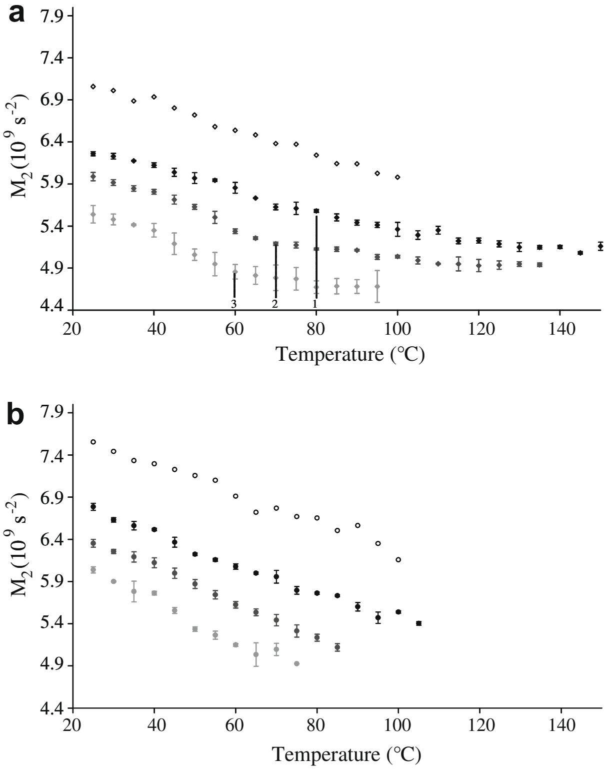

**Fig. 3.** Effect of temperature on the second moment ($M_2$) for starch (a) (◇: stored under $P_2O_5$; ♦: 4.3%; ♦: 7.8%; ♦: 13.5%) and starch–20% sucrose (b) (○: stored under $P_2O_5$; ●: 3.1%; ●: 6.3%; ●: 11.3%) samples at different water contents.

**Table 2**
Linear regression parameter for sucrose and water effects on $T_2$ and $M_2$ evolutions versus temperature.

| Plot | Products | Water content | Slope | Slope error | $R^2$ |
|---|---|---|---|---|---|
| $M_2$ versus $T$ | Starch | 4.10% | −0.0138 | 0.0007 | 0.980 |
| | | 7.80% | −0.0186 | 0.0010 | 0.979 |
| | | 13.50% | −0.0206 | 0.0012 | 0.979 |
| $M_2$ versus $T$ | Starch–20% sucrose | 3.10% | −0.0170 | 0.0005 | 0.987 |
| | | 6.30% | −0.0211 | 0.0004 | 0.996 |
| | | 11.30% | −0.0228 | 0.0014 | 0.967 |
| $M_2$ versus $T_{gDSC}/T$ | Starch | | 0.6013 | 0.0227 | 0.946 |
| | Starch–20% sucrose | Part 1 | 0.7646 | 0.0252 | 0.982 |
| | | Part 2 | 1.0844 | 0.0817 | 0.872 |
| $M_2$ versus $T_{gDSC}/T$ | Starch | | −7.8745 | 0.3753 | 0.954 |
| | Starch–20% sucrose | | −9.5545 | 0.4246 | 0.949 |

wards lower values with increasing water content. Such a 2 phase-behavior and the water sensitive breakpoint have been previously described by Van Den Dries et al. (1998), Grattard et al. (2002) and Kumagai et al. (2002). On the opposite, in dry starch alone and all sucrose–starch samples, $M_2$ decreased continuously (Fig. 3b) in the temperature range considered, without the breakpoints that were observed for the water-containing starch alone samples.

### 3.3. $T_2^*$

By definition, $T_2^*$ is often used as a reflection of molecular mobility, increasing when proton mobility increases. For starch and starch–sucrose samples, $T_2^*$ increased, at 25 °C, with increasing water content (Fig. 4). For all samples, between 3% and 6% of water, the mobility slightly increased, but there was no significant impact of the sucrose content. The increase in $T_2^*$ values versus hydration was more marked above 6% of water (for starch alone, the mobile proton mobility was ≈8 times greater than at lower hydration). Above 6% of water, the evolution of $T_2^*$ values was affected by the sample composition: the mobile protons of starch alone samples were twice more mobile than the mobile protons of starch–20% sucrose blend.

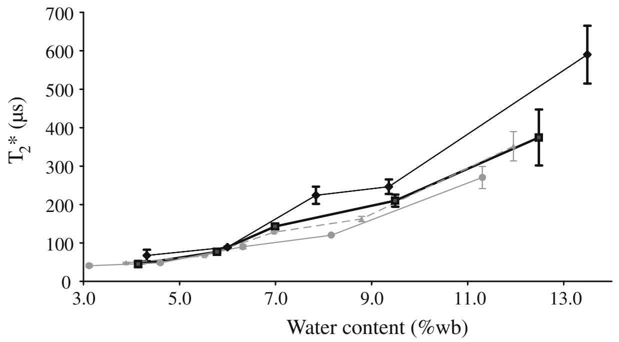

**Fig. 4.** Effect of water content on $T_2^*$ of gelatinized starch at different sucrose contents (♦: starch; ■: starch–5% sucrose; △: starch–10% sucrose; ●: starch–20% sucrose) at 25 °C.

$T_2^*$ values were also studied versus temperature for starch (Fig. 5a) and starch–20% sucrose samples (Fig. 5b). $T_2^*$ increased with increasing temperature reflecting the increase in the mobility of mobile protons. This expected increase in mobility with temperature is in agreement with the results found in literature (Grattard et al., 2002; Kumagai et al., 2002; Van den Dries, Van Dusschoten, Hemminga, & Van der Linden, 2000; Van Den Dries et al., 1998).

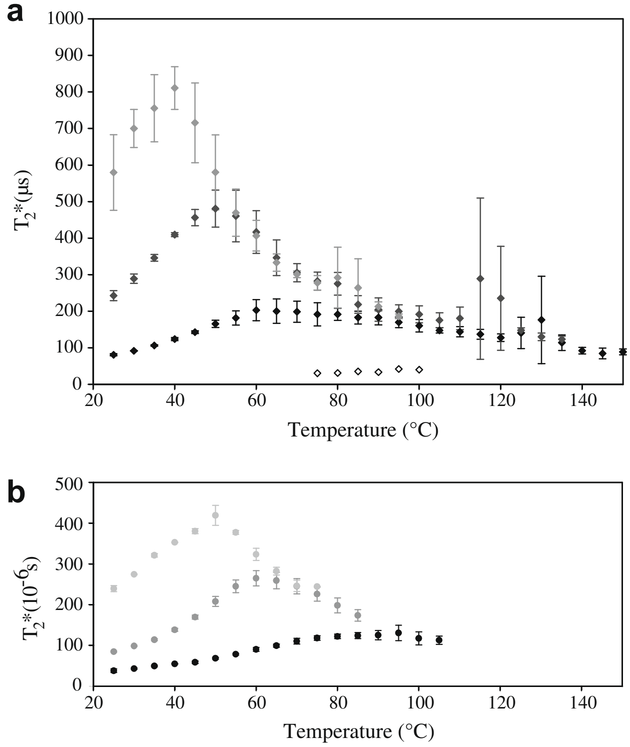

**Fig. 5.** Effect of water content on $T_2^*$ versus temperature on gelatinized starch (a) (◇: $P_2O_5$; ♦: 4.3%; ♦: 7.8%; ♦: 13.5%) and starch–20% sucrose (b) (○: $P_2O_5$; ●: 3.1%; ●: 6.3%; ●: 11.3%) samples.

Following this increase, $T_2^*$ exhibited a decrease at higher temperatures. This $T_2^*$ maximum varied with sample composition: the maximum value decreased with increasing sucrose content, and the temperature at which it was observed shifted to higher values with increasing sucrose content and to lower temperature with increasing water content. A similar maximum was observed in previous works (Ablett et al., 1993; Kalichevsky et al., 1992; Roudaut et al., 1999).

## 4. Discussion

### 4.1. $M_{2.}$ and $T_2^*$ evolutions

Figs. 2–5 have shown that the mobility of the rigid and mobile protons was lower for sucrose-containing samples than for starch alone. Thus, sucrose reduced the rigid and mobile protons mobility by reinforcement of the dipolar interactions strength. Farhat et al. (1996) suggested that sucrose–water interactions could contribute to the decrease of the water mobility (*i.e.* $T_2^*$) above 6% of water.

Low molecular mass compounds or solvents were often mentioned as plasticizers or antiplasticizers on food dry matrices as reported in a recent review from Pittia and Sachetti (2008). These cosolutes may act at relatively high concentration as plasticizer by increasing the flexibility and workability of the otherwise rigid neat polymer. However they may serve as mechanical antiplasticizers when present at low concentrations, resulting instead in the polymer-cosolute blends becoming stiffer than the neat polymer. For example, Lourdin, Bizot, and Colonna (1997) and Chang, Abd Karim, and Seow (2006) have provided experimental data suggesting that glycerol might have an antiplasticizing effect on the yield at break of glassy potato and tapioca starch films. Although the terminology "plasticization and antiplasticization" should be limited to the description of mechanical properties of the material, in the present work, the sucrose effect on mobility in starch-based materials seems analogous: the sucrose addition depressed the calorimetric glass transition ($T_g$) of the starch material but induced a decrease in mobility in the glassy matrix. Different and ill-defined possible factors implied in antiplasticization have been described in literature (Lourdin et al., 1997; Pittia & Sachetti, 2008): a reduction of the free volume of the plasticized system, polymer–cosolute interactions that create steric hindrance and decrease segmental mobility, stiffening action due to the presence of the rigid plasticizer molecules adjacent to polar group of the polymer (Anderson et al., 1995). In our study, the effect observed on the rigid proton mobility might be related to a densification of the product versus sucrose addition. Indeed as suggested for sucrose (Poirier-Brulez et al., 2006) or sorbitol (Gaudin, Lourdin, Forssell, & Colonna, 2000), adding small solutes to starch could cause a glass densification (called antiplasticization when macroscopic mechanical properties are studied) through a decrease of free volume and/or of segmental mobility of starch. Such a free volume-based hypothesis is currently under investigation by positron annihilation spectroscopy.

Considering the second moment $M_2$ of glycerol–amylose mixtures, Partanen et al. (2004) showed that the specific composition of the starch sample in terms of water or glycerol (up to 30%) contents was irrelevant when estimating the molecular mobility of the biopolymer in the glassy state: $M_2$ values of the amylose–glycerol films with different glycerol content were all comparable at temperatures below $T_g$. On the opposite in this study, sucrose addition induced a significant decrease of polymer mobility in the glassy state. These controversial observations may be explained by the physical state of the cosolute in the temperature range studied. According to the $T_g$ of glycerol (−93 °C dry), the latter is expected to be in the liquid state and thus not to contribute to the rigid component, whereas sucrose should affect the rigid proton population whilst it is in vitreous state like starch in the range considered.

According to the temperature study, the increase in temperature caused, first, an increase in the mobile protons' mobility (*i.e.* $T_2^*$) which was characterized by an apparent activation energy. The latter was calculated on the basis of an Arrhenius behaviour of ln $T_2^*$ versus $1/T$, and was found equal to 21 kJ/mol for starch samples and between 18 and 28 kJ/mol for starch–20% sucrose blends, such values are in agreement with Ea value for hydrogen bond breakage $\leqslant$40 kJ/mol. Following this increase, a decrease of $T_2^*$ and finally a stabilization were then observed.

The maximum observed on $T_2^*$ versus temperature plots for all hydrated samples could be related to both a mobility change and/or the onset of proton exchange. The mobility change "effect" could consist in a protons displacement from the rigid to the mobile population: the most mobile protons of the 1st population shifting towards the 2nd population would thus reduce the average mobility of the 2nd population. Because the analysis of the relative intensities of each population did not support this assumption, and due to difficulty to evaluate the intensity of the rigid population, we suggest a change in the relaxation times. When samples were maintained at temperature far below their glass transition, a large density heterogeneity may exist in the sample at the molecular level, which may induce a broad distribution of the relaxation times. The temperature increase was accompanied by an increase in mobility which might allow a homogenization of the relaxation times. This could lead to the loss of the lower molecular density response (as a consequence of structural relaxation facilitated by the vicinity of $T_g$) to the benefits of the response of a higher mean density. Hence, $T_2^*$ would decrease.

### 4.2. $T_g/T$

$M_{2.}$ (Fig. 6a) and $T_2^*$ (Fig. 6b) values were presented as a function of $T_{gDSC}$/T for starch samples and starch–20% sucrose blends

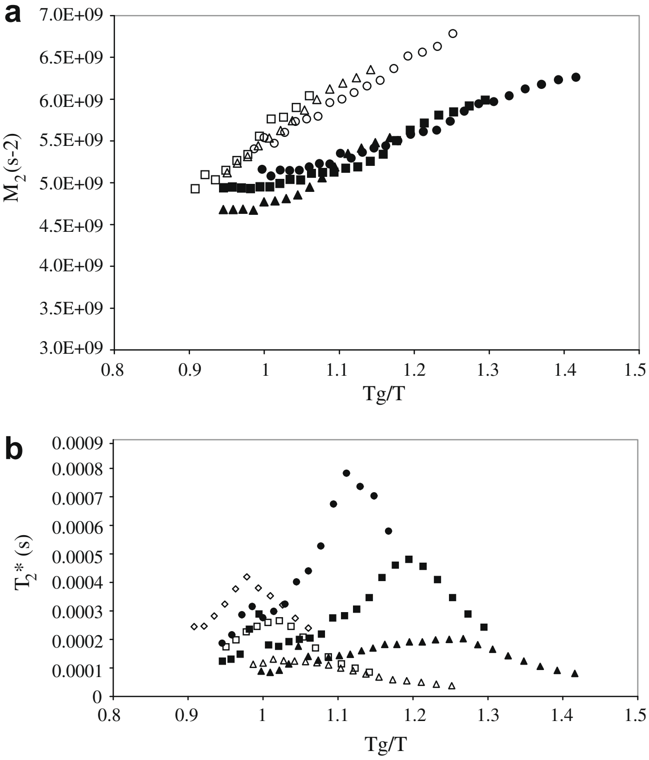

**Fig. 6.** (a) Evolution of $M_2$ versus $T_g/T$ for starch (a) variable temperature results = ○: 4.3%; □: 7.8%; △: 13.5%) and for starch–20% sucrose blends ●: 3.1%; ■: 6.3%; ▲: 11.3% wb). (b) Evolution of $T_2^*$ versus $T_g/T$ for starch (a) ◇: 4.3%; □: 7.8%; △: 13.5%) and for starch–20% sucrose blends = ♦: 3.1%; ■: 6.3%; ▲: 11.3% wb).

at different water contents and temperatures. For the starch alone samples, $M_2$ values followed a unique curve which decreased linearly with decreasing $[T_{gDSC}/T]$ exhibiting no effect of water content for a given $T_{gDSC}/T$ down to $T_g/T = 1.15$, below this value, $M_2$ no longer followed a master curve: the data were then separated as a function of water content: the higher the water content, the lower the $M_2$. The $M_2$ data plotted versus $T_g/T$ for sucrose-containing samples also exhibited a master curve but in this case, over the whole $T_g/T$ range, suggesting that once corrected with regards to $T_g$, water content had no effect on $M_2$. The presence of sucrose could then hinder the effect of water. Moreover, $M_2$ evolved versus $T_g/T$ with a greater slope than for starch alone samples, this greater sensitivity to temperature could be related to the concept of fragility which describes the effect of temperature on the properties of a material through its glass transition (Angell et al., 1994). As previously suggested in Poirier-Brulez et al. (2006), the starch–sucrose blends would be then more fragile than starch alone.

$T_2^*$ values for starch alone at different temperatures and water contents superimposed versus $T_{gDSC}/T$ on a master curve at high $T_{gDSC}/T$ values. Below the $T_{gDSC}/T$ value corresponding to the previously described $T_2^*$ maximum, the values no longer superimposed, but increased with water content for a given $T_g/T$. The evolution of $T_2^*$ versus $T_g/T$ was comparable for starch–sucrose blends and starch alone samples, excepted for the maximum which, for all samples, was observed at lower $T_{gDSC}/T$ values in the presence of sucrose, thus closer to the glass transition temperature of the samples. It is noteworthy that the $T_2^*$ maximum temperature occurred prior to $T_g$, but got closer to it as water content increased. Indeed as water content increased, the probability of matrix-water exchange increased, and at limiting water content the matrix will need to be more mobilized, *i.e.* brought to a lower $T_g/T$, for the onset of exchange to occur. The $T_2^*$ maxima were observed at temperature below $T_g$ for starch alone samples and close to $T_g$ for starch–sucrose samples. These mobility evolutions might also be in relation to the physical aging of the matrix which could induce a densification of the material. In a previous work on the same materials (Poirier-Brulez et al., 2006), the structural relaxation (through enthalpy relaxation) was analyzed at constant temperature difference below $T_g$, using the Cowie–Fergusson semi-empirical model. Physical aging was characterized by both maximum pseudo-equilibrium relaxation enthalpy and the average relaxation time. Our findings showed that the ternary mixtures, starch, sucrose and water samples, exhibited a lower enthalpy relaxation upon aging than starch alone as a sign of lower polymer mobility in the presence of small molecules.

According to Ablett et al. (1993) and Ruan et al. (1999), the mobility of the rigid protons seem controlled by $T_g$, several authors (Grattard et al., 2002; Kumagai et al., 2002; Partanen et al., 2004) mentioned a breakpoint on the $M_2$ evolution around $T_g$. In this study, the breakpoint of $M_2$ did not correspond to $T_{gDSC}$ but occurred before. However, the breakpoint could coincide with "$T_{gNMR}$" which could precede $T_{gDSC}$, since these two techniques probe different distance and time scales. Moreover in Kumagai, et al. (2002) and Partanen et al. (2004), the $M_2$ transition occurred through a temperature range rather than at a precise temperature, which might be in agreement with a spread transition. For the most hydrated samples, it could be argued that the onset of exchange ($T_2^*$ max) occurred closer to $T_g$, possibly through a narrowing of the transition and thus a lower difference between $T_{g\ NMR}$ and $T_{gDSC}$.

The effect of sucrose on both $T_2^*$ and $M_2$ samples is still visible when the data are normalized by their $T_g$, confirming the increased strength of interactions in the starch–sucrose matrix, when a "plasticizing" effect by sucrose could have been expected in agreement with the lower $T_g$ observed with increasing sucrose content. Some authors (Farhat et al., 1996; Gaudin et al., 2000) obtained similar results for starch–sucrose and starch–sorbitol systems, respectively. Very few studies report however the effect of solutes, water, and temperature normalizing the data by $T_g$, which permitted to strengthen the hypotheses on the role of sucrose.

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