

The glass transition and the sub- T_g endotherm of amorphous and native potato starch at low moisture content

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The glass transition temperature (T_g) of amorphous and native potato starch with 16% moisture was investigated by means of DSC. The glass transition in amorphous potato starch could be observed in a rescan of native potato starch, after heating to 210°C and quenching. The T_g -onset was 40°C, in agreement with literature data. The T_g of native potato starch is partly obscured by a so-called sub- T_g endotherm. It was demonstrated by means of aging experiments that this endotherm is related to enthalpy relaxation rather than to carbohydrate–water interactions. After erasing the thermal history of the sample by a short treatment at 90°C, a distinct glass transition with an onset at 80°C was observed. This was confirmed by additional aging and annealing experiments. © 1997 Elsevier Science Ltd

INTRODUCTION

Almost any application of starch involves the gelatinization or melting of the granule structure. Therefore, much research has been done on the structural changes in starch granules induced by heating, as a function of moisture content, using techniques such as differential scanning calorimetry (DSC) (Kalichevsky *et al.*, 1992; Liu *et al.*, 1991; Noel & Ring, 1992; Shogren, 1992; Gidley *et al.*, 1993; Appelqvist *et al.*, 1993; Le Bail *et al.*, 1993; Yuan & Thompson, 1994; Shogren & Jasberg, 1994), infra-red spectroscopy (IR) (Gidley *et al.*, 1993), dynamic mechanical thermal analysis (DMTA) (Kalichevsky *et al.*, 1992; Appelqvist *et al.*, 1993), nuclear magnetic resonance (NMR) (Kalichevsky *et al.*, 1992; Shogren, 1992), microscopy (Liu *et al.*, 1991) and small- and wide-angle X-ray scattering (SAXS, WAXS) (Liu *et al.*, 1991; Cameron & Donald, 1993; Le Bail *et al.*, 1993; Jenkins *et al.*, 1994). In such studies, starch granules are often considered as semi-crystalline polymer entities, where water molecules form an integral component of the crystalline domains (Imberty *et al.*, 1988; Imberty & Pérez, 1988).

In the thermal analysis of aqueous starch systems, four types of events may be encountered, depending on the moisture content: the so-called sub- T_g endotherm, the glass transition, various crystal melting processes

(M1 and M2), and finally, the so-called high-temperature endotherm (HT), which marks the transition into a thermoplastic melt (Tomka, 1990, 1991; Willenbücher *et al.*, 1995). However, the explanations which were given for the different observed phase transitions are ambiguous. This is also the case for the glass transition temperature (T_g).

From a practical point of view, the T_g marks the transition in mechanical properties between ductile and brittle. This transition is reversible and is characterized by a change in heat capacity (C_p) and viscosity (Liu & Lelievre, 1991; Slade & Levine, 1988a, b, 1995; Roos & Karel, 1991). In general, the temperature location of the T_g is dependent on the thermal history of the material, the molecular weight of the polymer chains, the presence of a plasticizer (e.g. water), the degree of crystallinity and the composition of a sample (e.g. miscible polymer blends) (Liu & Lelievre, 1991; Roos & Karel, 1991; Slade & Levine, 1995; Oudhuis, 1995). Modification of polymer properties by physical treatments such as crystallization or annealing is possible only above the T_g . Below the T_g , only slow thermoreversible physical aging occurs (Struik, 1978), which is reflected by the phenomenon of enthalpy relaxation, to be discussed below. Slade & Levine (1988a, 1995) have emphasized the importance of the T_g to the properties and handling of carbohydrate-based food products.

Unlike for most polymers, the glass transition of

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starch is still a matter of much debate. One reason for this is that starch is invariably associated with moisture, and its T_g is reported to be strongly dependent on the moisture content. Furthermore, the thermal events giving rise to the sub- T_g endotherm and the gelatinization endotherm may interfere with the glass transition. Until now, unambiguous values for the T_g have only been published for amorphous starch (Zelezna & Hoseney, 1987; Shogren, 1992; Noel & Ring, 1992), but not for native starches.

Biliaderis *et al.* (1986, 1991, 1992) observed a T_g for native rice starch with 50% moisture just below the gelatinization endotherm. Zeleznak & Hoseney (1987) ascribed the findings of Biliaderis to the beginning of granule expansion and the initiation of the starch crystallite melting process. Slade & Levine (1988a) found a T_g at -5°C in DSC rescans of native wheat and maize starch with 50% moisture. Values for the T_g of native wheat starch at moisture contents between 13 and 22% were reported by Zeleznak & Hoseney (1987). However, these authors heated their samples in the DSC to 127°C , or even to 152°C , prior to the actual measurement, presumably to erase the disturbing sub- T_g endotherm. At those temperatures, partial melting may well occur. Their repeated DSC scans of samples with 13.0–18.7% moisture content were terminated before a visible melting transition, which precludes the possibility to ascertain whether or not the native structure in those samples was preserved.

Therefore, we have attempted to measure the glass transition of native potato starch at a moisture content of 16%, by exploiting the fact that enthalpy relaxation related to physical aging occurs only below the T_g , whereas annealing is possible only above the T_g . In order to do so, it was necessary to examine in detail the nature of the sub- T_g endotherm and to establish whether or not this endotherm is due to enthalpy relaxation.

SOME REMARKS ON ENTHALPY RELAXATION AND ANNEALING

Enthalpy relaxation, or physical aging, of glassy materials is a thermoreversible phenomenon, well-known in synthetic polymer science (Struik, 1978; Hodge & Berens, 1981, 1982; Oudhuis, 1995). When an amorphous or semi-crystalline polymer is cooled below the T_g , its mobility decreases suddenly, and its thermodynamic properties can no longer follow the change in temperature. Consequently, the system is frozen into a metastable state that has an effectively infinite lifetime at low temperatures (Struik, 1978; Mathot, 1994). From a kinetic point of view, there will be a deviation in the linear decrease in enthalpy, which is shown in Fig. 1A (Shogren, 1992). When the sample is kept at a temperature T_e below the T_g for a certain time t_e , there

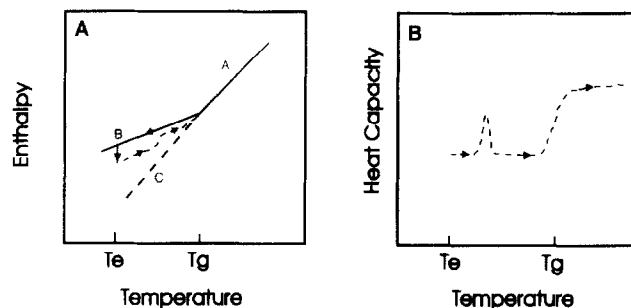


Fig. 1. Schematic illustrations of the changes in (A) enthalpy (H) and (B) heat capacity (dH/dT) for a polymer glass after rapid quenching from the melt (A) to a temperature T_e below the T_g , isothermal aging at T_e , and reheating to above the T_g . The initial enthalpy of the glass after quenching to below the T_g is given by the line B, while the equilibrium enthalpy is given by the dotted line C. [Reprinted from: Shogren (1992)].

will be a decrease in enthalpy and in volume [a decrease in conformational entropy (Adam & Gibbs, 1965)], because the system will slowly approach equilibrium. During this aging process, there will be a rearrangement of the polymer structures to an energetically more favorable conformation. It is stated that this relaxation process occurs only between the T_g and the T_β (Struik, 1978). The T_β is defined as the limiting temperature for polymer side-chain mobility. The relaxation times of the material increase during aging (Struik, 1978). When the sample is heated in the DSC after a certain storage period t_e below the T_g , the absorption of thermal energy will occur, as soon as the mobility of the relaxed polymer segments attains a threshold value. Because the heating rate in the DSC is relatively high, this results in a sudden endothermic event in the DSC scan, during which the loss in enthalpy due to aging is recovered and its equilibrium value is attained (Fig. 1B). After the enthalpy has been compensated, the amorphous system as a whole is mobilized, and the T_g is passed. Because the magnitude and location of this so-called sub- T_g endotherm depend on the aging conditions, this endotherm provides a fingerprint of the thermal history of the material. The foregoing shows that the enthalpy relaxation is a thermoreversible event. Occasionally, this so-called sub- T_g endotherm is superimposed on the glass transition (Oudhuis, 1995).

Hodge & Berens (1981, 1982) have developed a kinetic four-parameter model, to describe relaxation at and below the T_g . This model is based on the Williams–Watts equation for relaxation processes in polymers, and takes into account the Gordon–Narayanaswamy equation to express the non-linearity of the relaxation kinetics (Mathot, 1994). With this model, the following properties of the sub- T_g endotherm were derived and verified experimentally for several polymers: (1) the sub- T_g endotherm is asymmetrical; (2) the endotherm increases in magnitude and shifts to a higher tempera-

ture when t_e and T_e are increased; (3) at long t_e and high T_e , the sub- T_g endotherm will be superimposed on the glass transition; and (4) the peak temperature of the endothermic event, T_{max} , is a linear function of both $\ln(t_e)$ and T_e . The second property can be explained by an increase in relaxation times. Aging is accelerated at higher T_e (if $T_e < T_g$). Therefore, more heat input and heating to a higher temperature are required to compensate for this.

During fast crystallization processes of semi-crystalline polymers, lots of imperfections in the crystalline domains are obtained. These crystalline imperfections will be eliminated, when the material is kept at a temperature not too far below the melting transition (T_m). This process is called annealing. During this treatment, small crystallites enlarge and become more stable, so that they will melt at a higher temperature. The increased homogeneity of crystalline domains results in a narrower melting endotherm. Annealing only takes place at temperatures between the glass and the melting transition temperatures of a semi-crystalline polymer (Wunderlich, 1976; Krueger *et al.*, 1987; Larsson & Eliasson, 1991; Stute, 1992; Jacobs *et al.*, 1995).

EXPERIMENTAL

Material

Native potato starch (harvest, 1994; type, OKO; batch number, 5001-474-32-4372-0019) was obtained from AVEBE B.A., Veendam, The Netherlands. The moisture content of this starch was determined to be 16.1%.

Methods

The moisture content was calculated from the weight loss of the starch sample, after heating the material for 2 h at 130°C in a free-ventilating oven.

The DSC experiments were performed with a Perkin-Elmer DSC 7 PC-series apparatus. The measuring unit was cooled by means of a Perkin-Elmer Intracooler II. The DSC apparatus was calibrated with indium ($T_{m,onset} = 156.60^\circ\text{C}$ and $\Delta H = 28.45 \text{ J/g}$) and cyclohexane ($T_{m,onset} = 6.54^\circ\text{C}$). A maximum deviation of $\pm 0.1^\circ\text{C}$ for $T_{m,indium}$ was allowed. All experiments were carried out in duplicate, using large volume pans with a sample weight of 52 mg. An empty large volume pan was used as the reference. All experiments were performed with a heating or cooling rate of 10°C/min . Amorphous starch samples were obtained by heating the native material in the DSC to 210°C , followed by quenching to -20°C at 200°C/min . Annealing and aging experiments at longer times ($t_e = 15, 20, 96, 100 \text{ h}$) were performed in various ovens and refrigerators. Experiments of short duration ($t_e = 1 \text{ h}$) were performed within the DSC.

RESULTS AND DISCUSSION

The glass transition of amorphous potato starch

To locate the glass transition of amorphous potato starch with 16% moisture, native starch was first made amorphous by heating to 210°C and quenching, as described in the Experimental Section. The amorphous starch was subsequently heated from 10 to 100°C and thereafter cooled from 100 to -10°C with a scan rate of 10°C/min .

The heating and cooling scans in Fig. 2 clearly show that this transition is reversible. Furthermore, it can be seen that the glass transition is spread over a temperature range of 40°C , from 30 to almost 70°C , which is rather broad in comparison with other semi-crystalline polymers. This is not astonishing in light of the heterogeneous nature of starch (Biliaderis, 1992). Starch consists of two different polymers, amylose and amylopectin, which differ in molecular weight. Also, polymer blends often have broad glass transitions, which are caused by heterogeneities in the mixture. The T_g -onset for our starch sample is located at about 40°C . Here, the onset is defined as the intersection of the tangents to the baseline and the ascending part of the DSC heating scan.

The T_g -onset observed for amorphous potato starch at 16% moisture content is in the same range as determined values for amorphous maize starch with 16.1% moisture [50°C (onset value), Shogren, 1992] and waxy maize amylopectin with 17% moisture [24°C (onset value), Noel & Ring, 1992]. The lower value for the latter is most probably due to a low scanning rate in combination with a higher moisture content. This result suggests that the T_g of amorphous starch is not strongly dependent on starch type.

Sub- T_g endotherm

The sub- T_g endotherm, first described by Kalichevsky *et al.* (1992), has the following features: the endotherm is

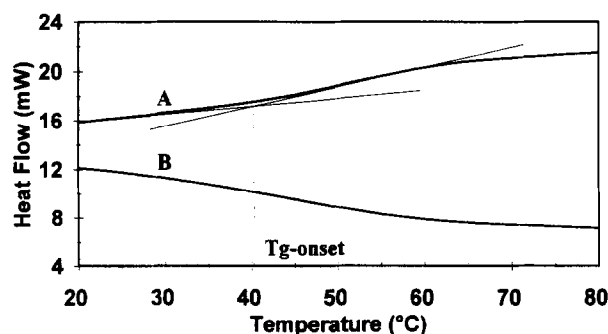


Fig. 2. DSC traces for amorphous potato starch with 16% moisture. Amorphous starch was prepared in the DSC by heating to 210°C , followed by quenching: (A) heating; (B) cooling after heating the amorphous sample to 100°C .

observable only at moisture contents lower than 25%, the temperature location of the endotherm is independent of the moisture content, and the endotherm is not immediately regained in a second heating scan in DSC (Shogren, 1992; Gidley *et al.*, 1993; Appelqvist *et al.*, 1993; Yuan & Thompson, 1994). Two explanations have been put forward for this transition: enthalpy relaxation (Shogren, 1992; Le Bail *et al.*, 1993; Shogren & Jasberg, 1994; Slade & Levine, 1995) and carbohydrate–water interactions (Gidley *et al.*, 1993; Appelqvist *et al.*, 1993; Yuan & Thompson, 1994).

Shogren studied the aging at 22°C of extruded maize starch at 10–50% moisture contents by means of DSC and CP/MAS ^{13}C NMR. He interpreted his results with the aid of the properties of enthalpy relaxation found by Hodge & Berens (1981, 1982) for synthetic polymers. A sub- T_g endotherm was only observed in samples with moisture contents up to 25%. The magnitude of the endotherm increased with the aging time and moisture content. The effect of moisture content can be explained by a decrease in $(T_g - T_c)$. At moisture contents exceeding 25%, the T_g becomes lower than T_c , and slow relaxation does not occur. Equilibrium values of thermodynamic properties are attained instantaneously. As the CP/MAS ^{13}C NMR spectrum was not changed by aging, it was concluded that structural changes are not involved.

On the other hand, Gidley *et al.* (1993) and Appelqvist *et al.* (1993) ascribed the sub- T_g endotherm to the melting of carbohydrate–water interactions. These authors studied various polysaccharides with moisture contents between 5 and 25% by means of DSC, IR-spectroscopy and DMTA. Gidley *et al.* (1993) used IR-spectroscopy as a probe for detecting water–carbohydrate interactions. However, the authors observed no changes in the IR-spectra before and after a heat-treatment at 70°C for amorphous potato starch, guar-gum and κ -carrageenan, whereas the DSC traces had been changed significantly. These apparently contradictory results were explained by noting that IR typically probes short-range effects, whereas thermal effects as measured by DSC involve much longer distance scales.

In DMTA, both the glass transition and the enthalpy recovery are expected to be frequency-dependent (Appelqvist *et al.*, 1993). Moreover, in the case of enthalpy relaxation, the sub- T_g endotherm should shift to higher temperatures at increasing t_e in the DSC. Because neither a frequency dependence of the DMTA signal in the region of the sub- T_g endotherm nor a shift in the temperature location of this endotherm on storage were observed, the authors concluded that the sub- T_g endotherm has its origin in the disruption of interactions between carbohydrate and water, rather than in enthalpy relaxation.

In our opinion, these arguments are not very convincing. No changes were found in the IR-spectra

(Gidley *et al.*, 1993), whereas the DMTA plot [Fig. 9 of Appelqvist *et al.* (1993)] is rather flat in the region of the sub- T_g endotherm, which makes it difficult to decide whether or not this transition is frequency-dependent. Furthermore, the absence of a noticeable shift in the location of the sub- T_g endotherm in the DSC could also be due to the narrow time window of their aging experiments, which spanned only a factor 2. The increase in magnitude of the endotherm with moisture content can be explained equally well by carbohydrate–water interactions as by enthalpy relaxation, as described above. However, a role for carbohydrate–water interactions as a cause for the sub- T_g endotherm is difficult to reconcile with its disappearance at moisture contents higher than 25%. Other results presented by Appelqvist *et al.* (1993) (Figs 4, 5, and 7), can be readily explained by enthalpy relaxation: the shift of the endotherm to lower temperatures coinciding with the glass transition at increasing water content, the absence of the endotherm in the case of storage at temperatures far below the T_g , and the increase in size and shift to higher temperature of the endotherm at increasing T_c .

Yuan & Thompson (1994), in their study on amorphous waxy maize starch, its β -limit dextrin, and its triacetate, also argued in favour of carbohydrate–water interactions. Their key experiment involved a two-step procedure: aging of amorphous waxy maize starch at constant moisture content, followed by drying to 2% moisture at constant temperature. The sub- T_g endotherm that appeared after conditioning at constant relative humidity disappeared after the drying treatment. Because physical aging in the first step cannot be affected by subsequent drying, this observation was presented as evidence for carbohydrate–water interactions as the origin of this endotherm. However, in our opinion the lack of enthalpy recovery after drying was due to a shift of the glass transition to a higher temperature, so that $T_c \ll T_g$. This suggestion is confirmed by the fact that no glass transition was noticeable in their DSC scan up to 160°C.

In order to decide whether the sub- T_g endotherm is due to enthalpy relaxation or to carbohydrate–water interactions, we conducted a series of aging experiments, with careful control of the thermal history of the samples. We started our investigations with amorphous potato starch, making use of the characteristic property that relaxation of amorphous polymeric conformations is strongly delayed below the T_g (Struik, 1978; Hodge & Berens, 1981, 1982; Oudhuis, 1995). Aging experiments were performed at different aging temperatures T_e (–21, 5, 20, 30°C) and aging times t_e (1, 15, 100 h). The amorphous samples were prepared by heating native potato starch to 210°C, followed by quenching to the aging temperature. The mean endothermic T_{\max} -values vs the T_c and t_e are summarized in Table 1.

In Fig. 3, thermograms are shown which illustrate the

Table 1. T_{\max} of the sub- T_g endotherm for amorphous potato starch with 16% moisture vs the aging temperature (T_e) and aging time (t_e)

T_e ($^{\circ}\text{C}$)	t_e (h)		
	1	15	100
-21 ^a	—	—	—
5	22.5	28.5	36.2
20	38.9	46.2	48.1
30	48.9	53.5	56.6

^a:no endothermic event.

development of the sub- T_g endotherm at $t_e = 100$ h as a function of T_e . It is seen that the temperature location and the magnitude of the aging endotherm depend on the choice of T_e and t_e . The peak temperature of the aging endotherm is shifted to a higher temperature, when at a given T_e , a longer t_e is used, and when at a given t_e , a higher T_e is used. The endotherm also increases in size, when T_e is raised at constant t_e . The increase in magnitude of the endotherm at higher T_e [smaller $(T_e - T_g)$] is caused by an acceleration of the aging process. A longer t_e allows the relaxation process to proceed, which also results in an increase in the size of the endotherm.

In Table 1, it can be seen that at $T_e = -21^{\circ}\text{C}$, no endotherm is obtained. This is probably due to the very low aging temperature (60°C below the T_g), at which the relaxation is too slow to be noticeable within the time scale of the experiment. Figure 4 shows that the results of our aging experiments on amorphous potato starch are in good agreement with the predictions of Hodge & Berens (1981, 1982) for enthalpy relaxation: T_{\max} varies linearly with $\ln(t_e)$ and T_e .

The DSC thermogram for native potato starch with a moisture content of 16% (Fig. 5A) exhibits four endothermic events: at 64°C (sub- T_g); 126°C (M1); 156°C (M2); and 192°C (HT); which are in good agreement with earlier results of Tomka (1990). The M1 and M2 endotherms are credited to melting of B- and A-type crystallites, respectively (Zobel, 1988; Tomka, 1990, 1991). The origin of the HT endotherm is still unknown.

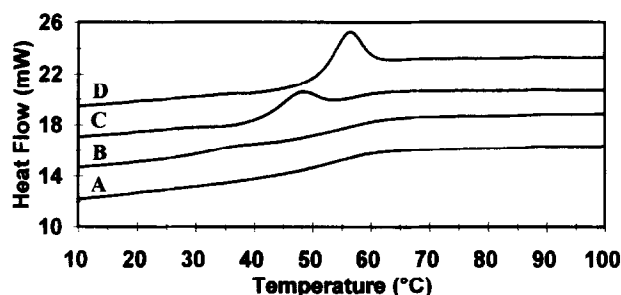


Fig. 3. DSC traces (heating mode) for freshly prepared amorphous potato starch with 16% moisture after aging for 100 h at $T_e = 5^{\circ}\text{C}$ (B); 20°C (C); and 30°C (D). A sample not subjected to aging is shown for comparison (A).

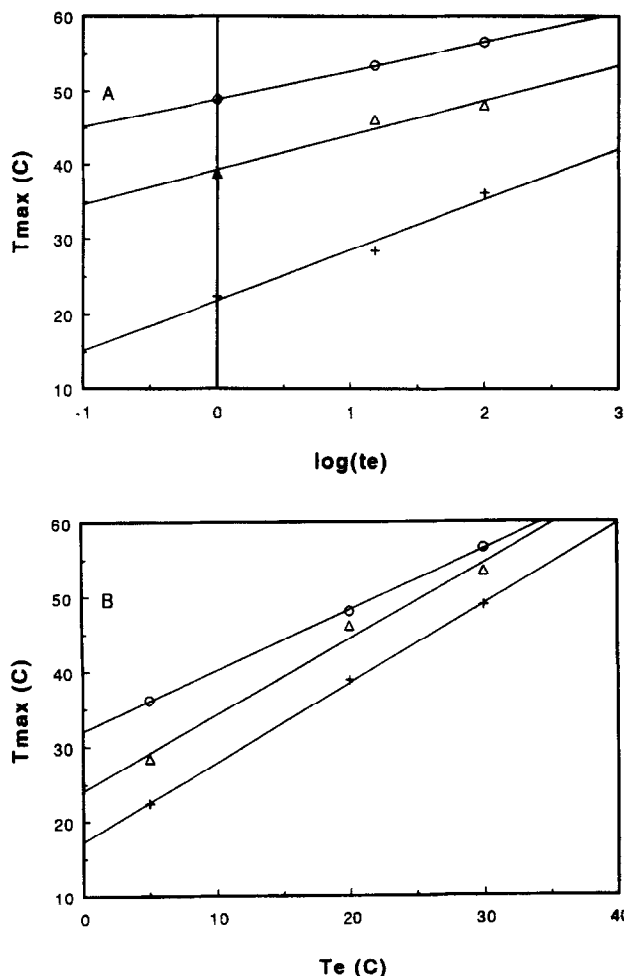


Fig. 4. Maximum of sub- T_g endotherm (T_{\max}) vs aging time (t_e) and temperature (T_e) for amorphous potato starch with 16% moisture: (A) T_{\max} vs $\ln(t_e)$ at $T_e = 5^{\circ}\text{C}$ (+), 20°C (Δ) and 30°C (\circ); (B) T_{\max} vs T_e at $t_e = 1$ h (+), 15 h (Δ) and 100 h (\circ).

Furthermore, a barely noticeable shift of the baseline is observed at ca 90°C , which might be associated with the T_g . Several relaxation experiments were performed with native potato starch at different aging temperatures below the vague transition mentioned above. Here, T_e was 5, 30, 50 and 70°C at $t_e = 0, 1, 20$ and 100 h. In experiments at $T_e = 5, 30$ and 50°C , the thermal history was first removed by heating the starch samples for 20 s at 90°C . After the aging of the starch samples, the materials were scanned from -20 to 210°C at $10^{\circ}\text{C}/\text{min}$. The mean endothermic T_{\max} values as a function of T_e and t_e are shown in Table 2. It is obvious that the transition temperature of the endothermic event as well as its magnitude are dependent on the choice of T_e and t_e , as expected for enthalpy relaxation.

In Fig. 5B–E, aging endotherms are shown as a function of different aging temperatures after aging for 100 h. During aging under these conditions, the M1 and M2 endotherms were not narrowed and were not shifted to higher temperatures, indicating that no annealing

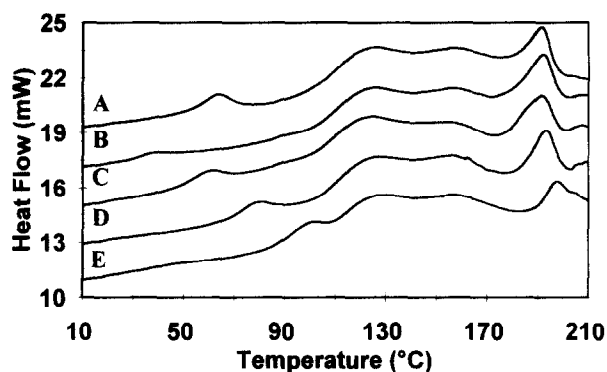


Fig. 5. DSC traces (heating mode) for native potato starch with 16% moisture, showing the sub- T_g , M1, M2, and HT endotherms (from left to right). Samples were aged for 100 h at $T_e = 5^\circ\text{C}$ (B); 30°C (C); 50°C (D); and 70°C (E); after a short treatment at 90°C (B, C and D only). Untreated native potato starch (A) is also shown.

had occurred. So, it can be concluded that all these experiments had been performed below the T_g . A similar result was reported by Appelqvist *et al.* (1993) in their experiments on aging of pullulan at different T_e values. Figure 6 shows the linear relationships of T_{\max} vs $\ln(t_e)$ and T_{\max} vs T_e for native potato starch, in agreement with the model of Hodge & Berens (1981, 1982) for enthalpy relaxation.

One further experiment to discriminate between enthalpy relaxation and carbohydrate-water interactions was performed, involving a two-stage aging procedure at different temperatures. Here, we assume that carbohydrate-water interactions at a given moisture content melt at a fixed temperature, and that the melting enthalpy is constant, regardless of previous thermal treatment. Native potato starch samples with a moisture content of 16% were aged at 70°C for 0, 20 and 96 h, followed by aging at 30°C for 100 h. The thermograms are shown in Fig. 7. It is clearly seen that two sub- T_g endotherms are present in curves B and C. One endotherm at c. 60°C is due to the aging at 30°C which decreases in magnitude, when the aging times at $T_e = 70^\circ\text{C}$ are increased. On the contrary, the second endotherm at c. $90\text{--}100^\circ\text{C}$ due to the aging at 70°C increases in magnitude. Furthermore, this endotherm shifts to higher temperature (Fig. 7B, C).

Table 2. T_{\max} of the sub- T_g endotherm for native potato starch with 16% moisture vs the aging temperature (T_e) and aging time (t_e)

T_e ($^\circ\text{C}$)	t_e (h)		
	1	20	100
5	23.7	35.5	37.7
30	50.0	57.6	60.3
50	71.5	76.8	80.4
70	84.8	92.4	102.1

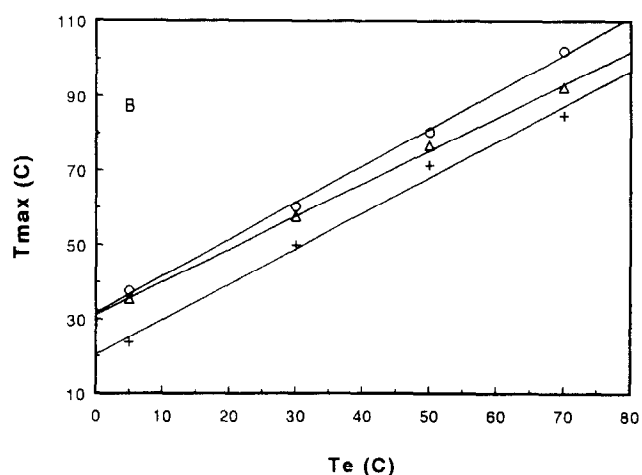
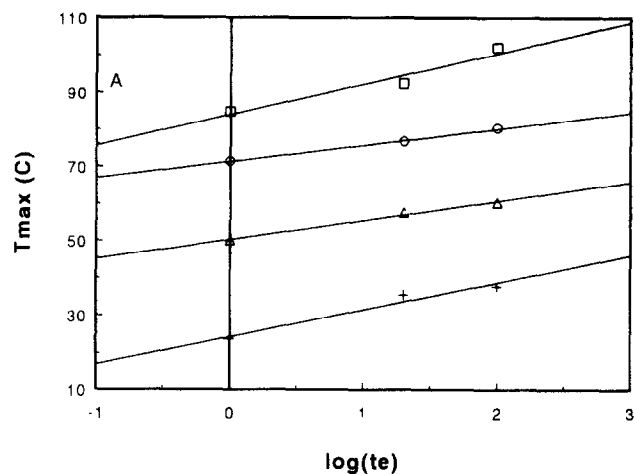


Fig. 6. Maximum of sub- T_g endotherm (T_{\max}) vs aging time (t_e) and temperature (T_e) for native potato starch with 16% moisture: (A) T_{\max} vs $\ln(t_e)$ at $T_e = 5^\circ\text{C}$ (+), 30°C (Δ), 50°C (\circ), and 70°C (\square); (B) T_{\max} vs T_e at $t_e = 1$ h (+), 20 h (Δ), and 100 h (\circ).

This tendency can hardly be explained otherwise than by enthalpy relaxation. Struik (1978) has stated that aging of a polymeric material is accompanied by an increase in relaxation times. Because aging processes are accelerated at a higher T_e , the relaxation times

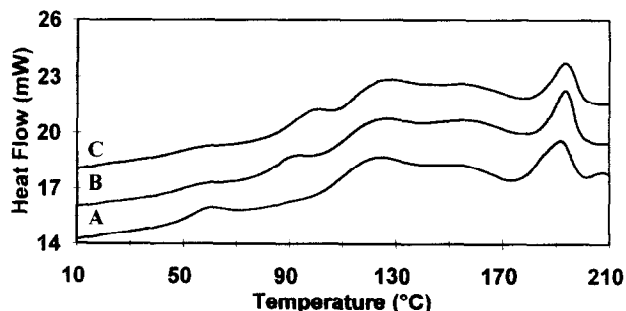


Fig. 7. DSC traces (heating mode) for native potato starch with 16% moisture after aging at 70°C for 0 h (A); 20 h (B); and 96 h (C); followed by aging at 30°C for 100 h. Sample (A) was subjected to a short treatment at 90°C .

are increased so much after aging at 70°C that subsequent relaxation at 30°C is delayed. This leads to a decrease in size of the endotherm due to aging at 30°C. In the case of melting of carbohydrate–water interactions, the endotherms would have been expected to be of similar size and to be located at the same temperature, regardless of the treatment at 70°C. It can be concluded that, for amorphous as well as for native starch, the sub- T_g endotherm has its origin in enthalpy relaxation, rather than in the melting of carbohydrate–water interactions.

The glass transition of native potato starch

Zeleznač & Hoseneý (1987) reported the only available data for the glass transition of native starch at low moisture contents. These data were obtained after heating the samples up to 127°C, or even to 152°C. This was the main reason for us to re-examine those results critically. In a first scan of native potato starch at 16% moisture (Fig. 8A), only a very indistinct transition at 86°C is noticed. According to Biliaderis *et al.*, (1986, 1991) the absence of a clearly visible glass transition in native starch is due to three possible factors: (1) amorphous chains are surrounded by crystalline domains; (2) physical crosslinks inhibit the movements of the amorphous chain segments; and (3) the presence of intercrystalline phases that do not show normal thermal behaviour. In addition, the glass transition appears to be obscured by the sub- T_g endotherm.

In order to reveal the glass transition of native starch, the thermal history of the sample was erased by a short thermal treatment, much in the same way as was done by Zeleznač & Hoseneý (1987), but under less severe conditions (Fig. 8). The sample was heated in the DSC at maximum rate to 90°C, held at that temperature for 20 s and then quenched to –20°C. Figure 8B shows a clearly visible glass transition with an onset temperature of c. 80°C. The melting endotherms M1 and M2 appear to be unchanged by this treatment.

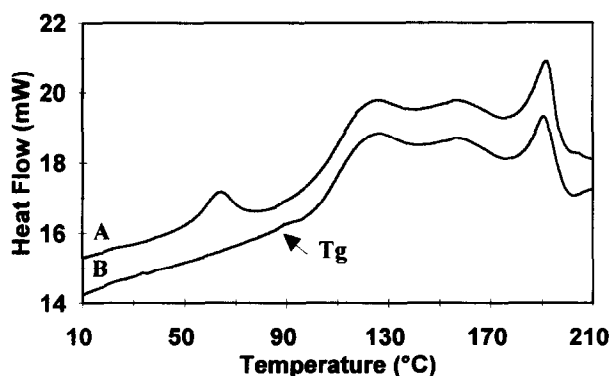


Fig. 8. DSC traces (heating mode) for native potato starch with 16% moisture: (A) untreated sample; (B) after short treatment at 90°C. The arrow marks the glass transition.

A final, albeit indirect, way to locate the glass transition of a semi-crystalline polymer exploits the fact that physical aging occurs only below the T_g , whereas annealing can be achieved only above the T_g . Recalling former aging experiments, we note that aging at 70°C hardly affects the temperature location and magnitude of M1 and M2 (Fig. 5E). The very small shifts to higher temperature of these endotherms are due to loss of moisture, which does not exceed 0.8–0.9%. These losses could be avoided by reducing the aging time at 70°C to 3 h (Fig. 9B). The development of a sub- T_g endotherm, together with the absence of annealing during aging at 70°C, point to the conclusion that the T_g of native potato starch exceeds 70°C. On the other hand, storing the sample at 95°C for 3 h leads to a marked narrowing of M1, indicative of annealing with at the same time, no sign of appearance of a sub- T_g endotherm (Fig. 9C). This indicates that the T_g of native potato starch with 16% moisture is located between 70 and 95°C, in agreement with the result shown in Fig. 8. In Fig. 9C, a glass transition of the annealed starch sample can be distinguished. The slight shift of M1 to a higher temperature could be partly due to a very small loss of moisture during aging at 95°C. The magnitude and transition temperature of M2 remained unchanged on storage at 95°C, which would mean that the transition from B-type to A-type crystallites took place during the DSC experiment. This has also been suggested by Le Bail *et al.* (1993).

The T_g -onset of native potato starch at 16% moisture is higher than the value for wheat starch (40°C) reported by Zeleznač & Hoseneý (1987). It is not known whether this is due to the different starch type, or to inadvertent melting of the native starch structure by the heating protocol employed by those authors. The T_g for native potato starch is also higher than that for amorphous starch (40°C). This is probably due to motional restrictions of amorphous polymer chains and a higher concentration of physical crosslinks in native starch granules, as was also proposed by Zeleznač & Hoseneý (1987).

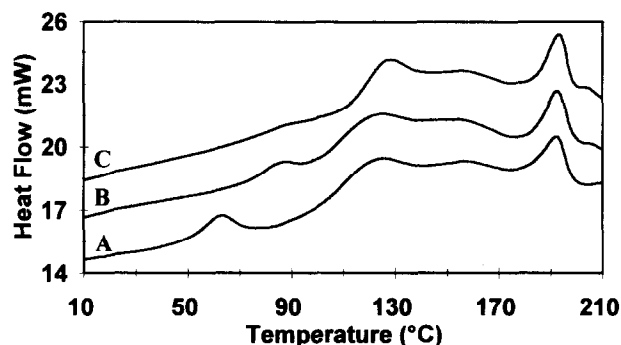


Fig. 9. DSC traces (heating mode) for native potato starch with 16% moisture: (A) untreated sample; (B) after storing for 3 h at 70°C; (C) after storing for 3 h at 95°C.

CONCLUSIONS

By means of aging experiments with careful control of thermal history, we have been able to demonstrate that the so-called sub- T_g endotherm in DSC scans of amorphous and native potato starch is not due to carbohydrate-water interactions, as stated by Gidley *et al.* (1993), Appelqvist *et al.* (1993), and Yuan & Thompson (1994), but rather to enthalpy relaxation, in agreement with the conclusion of Shogren (1992), and with the suggestion of Le Bail *et al.* (1993) and Slade & Levine (1995).

After erasing the thermal history by a short heat treatment at 90°C, we observed a glass transition in native potato starch at 16% moisture, with an onset temperature of 80°C. This is appreciably higher than the measured T_g -onset of amorphous potato starch and the value reported for native wheat starch by Zeleznak & Hoseney (1987). The T_g -onset of amorphous potato starch was in the same range as that reported for amorphous maize starch.

A second way to estimate T_g of native starch involved a combination of aging and annealing experiments. This approach may be used as a general and fruitful strategy for semi-crystalline polymers, in which the T_g is difficult to determine directly.

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