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The physical state of amorphous corn starch and its impact on crystallization

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Crystallization of amorphous polymers is affected by their physical state and molecular mobility. In the present study, crystallization behaviour of amorphous corn starch was related to its physical state and glass transition. Amorphous corn starch was produced by freeze-drying a gelatinized 5% (w/w) starch suspension. State diagram and sorption properties were determined to characterize the material. Amorphous corn starch samples containing 60, 70, and 80% solids were stored at various temperatures that gave various temperature differences between storage temperature and glass transition temperature ($T-T_g$). The melting behaviour of crystallites formed was determined using differential scanning calorimetry. Crystallization in starch samples occurred with a rate that was dependent on storage temperature, water content, and $T-T_g$. In addition, the melting temperature and the extent of crystallization were affected by storage temperature, water content, and $T-T_g$. The data reported allow the prediction of crystallization in starch, as a physical state-dependent phenomenon and, therefore, stability of starch-containing products during storage. © 1997 Elsevier Science Ltd

INTRODUCTION

Native starch exists as semicrystalline granules consisting mostly of starch component polymers, i.e. highly branched amylopectin and essentially linear amylose. Crystalline regions in starch granules are those of partially crystalline amylopectin (e.g. Morris, 1990). Amorphous regions contain linear amylose and branching points of amylopectin (e.g. Morris, 1990). Molecular order within native starch granules can be disrupted by gelatinization, which often occurs as a result of melting of the crystalline regions, as reviewed by Roos (1995).

Gelatinization of starch in dilute suspensions at appropriate temperatures results in formation of amorphous starch with molecular disorder, which can be retained by dehydration. Changes toward an equilibrium in the physical state of amorphous biopolymers, e.g. crystallization, are strongly dependent on water content and storage temperature (Slade & Levine, 1991; Roos, 1995). The most important change in the amorphous state occurs over the glass transition range, i.e. the transition between the solid, glassy and supercooled, viscous liquid-like rubbery states. The transition occurs over a temperature range, but it is often referred to with a single temperature value (T_g). Water plasticizes amorphous biopolymers, thereby decreasing the glass transition temperature range. This results in a higher molecular mobility, when the transition is depressed to below ambient temperature. Crystallization of amorphous biopolymers has been suggested to be kinetically controlled by the glass transition (Slade & Levine, 1991). Crystallization does not occur or is extremely slow at temperatures below T_g, but it can occur at temperatures above T_g, at a rate depending on $T-T_g$ (Slade & Levine, 1991; Roos, 1995).

Crystallization of amylopectin in starch gels is known to be time-dependent, and it often occurs during storage with a rate depending on water content and storage temperature, as reviewed by Roos (1995). The effect of storage temperature on crystallization in starch has been investigated in numerous studies (e.g. Colwell *et al.*, 1969; Longton & LeGrys, 1981; Marsh & Blanshard, 1988; Laine & Roos, 1994; Jouppila & Roos, 1996). These studies have shown that the melting temperature of crystallized starch increases with increasing storage temperature, suggesting formation of a more perfect crystalline structure. Longton & LeGrys (1981), and Zeleznak & Hoseney (1986) reported that starch concentration affected the extent of crystallization in starch gels. The maximum extent of crystallization was attained in starch gels containing 50 and

60% solids and stored at 4° and 25°C, respectively. Laine & Roos (1994), and Jouppila & Roos (1996) related crystallization in corn starch to its physical state and T_g. They found that the extent of starch crystallization increased with increasing temperature difference between storage temperature and glass transition temperature ($T-T_g$), as previously predicted (Slade & Levine, 1991).

The objectives of the present study were to investigate the effect of storage temperature on the extent of crystallization and melting behaviour of the crystallites formed in corn starch with various water contents, and to relate the observed crystallization behaviour to the physical state and glass transition of corn starch.

EXPERIMENTAL

Sample preparation

Starch suspensions containing 5% (w/w) solids were prepared using corn starch (Sigma Chemical Co., MO, USA; water content 10.8%) and distilled water. Suspensions were heated to boiling with continuous stirring, in order to gelatinize starch granules. Gelatinization was confirmed visually using polarized light microscopy. The resulting gels (10 g in Petri dishes) were frozen (at least 20 h at −80°C) and then freeze-dried for at least 72 h at a pressure < 0.1 mbar, using a Lyovac GT2 freeze-dryer (Amsco Finn-Aqua GmbH, Germany). Dried gels were powdered using a Cyclotec 1093 Sample mill (Tecator AB, Sweden) and stored in vacuum desiccators over P_2O_5 (p.a.; E. Merck, Germany) at 24°C, until a constant weight was achieved (at least 5 days).

The crystallinity of native corn starch (water content 10.8%) and amorphous state of powdered, gelatinized corn starch (dehydrated) were checked from X-ray diffraction (XRD) patterns (Fig. 1) that were obtained using a Philips powder X-ray diffractometer (PW 1830 generator, PW 1710 diffractometer control, PW 1820 vertical goniometer equipped with graphite reflected beam monochromator, and PC-APD software for Automatic Powder Diffraction Version 3.0; Philips Analytical, The Netherlands). The X-ray diffractometer was operated in reflection mode at 40 kV and 50 mA. Samples on aluminium trays (sample layer, 15 mm × 20 mm × 1.5 mm) were exposed to Cu*Kα* radiation (λ = 0.15418 nm) at diffraction angles (2θ) from 10 to 30° (step size 0.02, time per step 2.5 s). Divergence slit for the primary beam was 1°. The divergence and receiving slits for the diffracted beam were 1° and 0.2 mm, respectively.

Sorption properties

Water sorption properties of amorphous corn starch were determined gravimetrically by equilibrating duplicate samples (sample size, ~1.2 g) in glass vials, weighed at intervals, for up to 859 h in vacuum desiccators over saturated salt solutions (Fig. 2). The salts used were LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, NaCl, KCl, and KNO_3 (p.a.; E. Merck, Germany), with respective relative humidities of 11.5, 23.9, 33.0, 44.4, 53.8, 66.2, 76.4, 85.8, and 93.6% (Labuza *et al.*, 1985; Greenspan, 1977), giving water activity values of 0.01 × % relative humidity at steady-state. The water content of samples after storage was calculated as the average weight gain at each relative humidity. Steady-state water contents were achieved in 24 h at relative humidities below 66.2% (Fig. 2). At higher relative humidities levelling-off of water sorption was slower. Water contents after 95 h of storage were used in modelling of water sorption.

The Guggenheim–Anderson–deBoer (GAB) sorption isotherm model (van den Berg & Bruin, 1981; Roos, 1993) was chosen to model water sorption, using linear and nonlinear regression analysis techniques. Modelling of water sorption by fitting linearized models to obtain

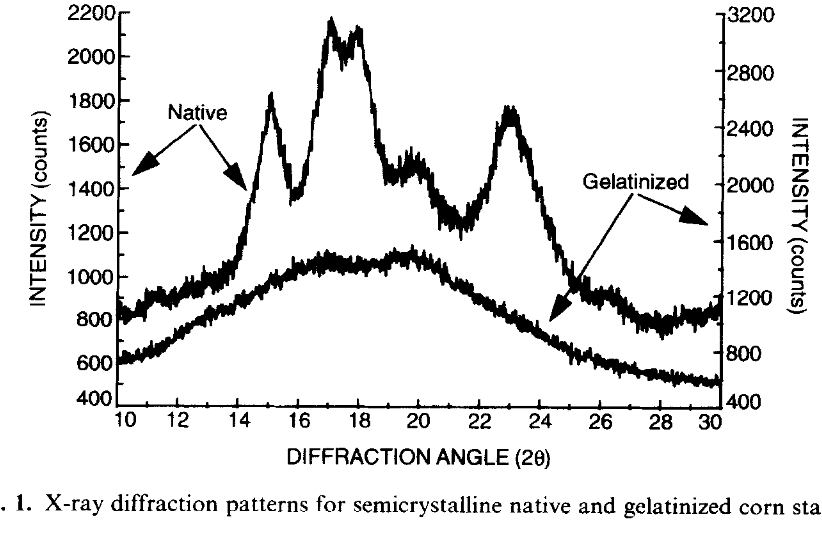

Fig. 1. X-ray diffraction patterns for semicrystalline native and gelatinized corn starch.

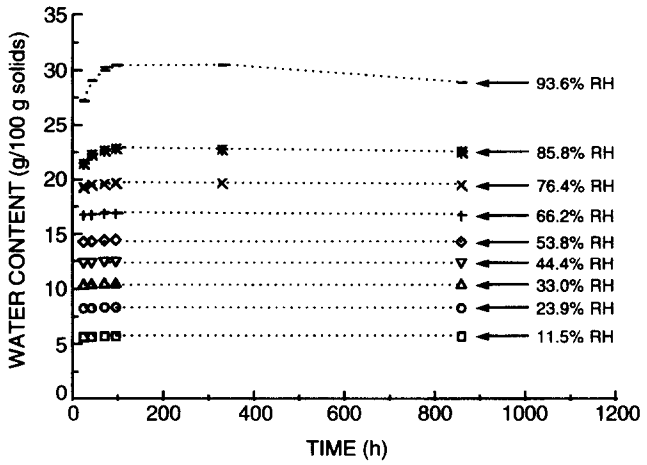

Fig. 2. Water content of amorphous corn starch stored at various relative humidities as a function of storage time.

parameter values, using linear regression analysis, has been the most traditional and general method (e.g. Schär & Rüegg, 1985; Roos, 1993). However, the use of nonlinear regression analysis to obtain parameter values has also been recommended (e.g. Schär & Rüegg, 1985). Linear regression analysis was done using a Statistix 4.0 computer program (Analytical Software, USA), and nonlinear regression analysis was done using a SAS System for Windows 3.10 computer program (SAS Institute Inc., USA).

State diagram

Glass transition temperatures (T_g) were determined for amorphous corn starch samples, stored at various relative humidities ranging from 53.8 to 93.6%, having corresponding water contents from 14.5 to 30.5 g/100 g solids. Determinations were carried out using a Mettler TA 4000 differential scanning calorimeter (DSC) analysis system with DSC-30 low temperature cell, TC10A TA processor, and GraphWare TA72AT.2 thermal analysis software (Mettler-Toledo AG, Switzerland). The DSC was calibrated for temperature using *n*-hexane (T_m = −95.0°C; reference substance for gas chromatography, minimum content 99.7%; E. Merck, Germany), distilled water (T_m = 0.0°C), and indium (T_m = 156.6°C; Mettler-Toledo AG, Switzerland), and for heat flow using indium ($\Delta H_m = 28.5$ J/g). Triplicate samples (~3 mg) in open DSC pans (aluminium pans, inner volume 40 μl; Mettler-Toledo AG, Switzerland) were stored in vacuum desiccators over saturated salt solutions for 24 h. After storage, the pans were hermetically sealed and scanned at 5°C/min from at least 30°C below the observed onset of the glass transition to at least 30°C above the glass transition temperature range. An immediate rescan over the same temperature range was run for each sample. The T_g was taken from the onset temperature of the glass transition. The reported T_g values are average values of the triplicate first and second scan-onset temperatures at each water content. An endothermic enthalpy relaxation occurred in the first scan of samples stored at relative humidity of 85.8%.

The T_g values and corresponding water contents (calculated as weight fraction of water, w_2; weight fraction of solids, $w_1 = 1 - w_2$) obtained from the sorption study were modelled using the Gordon–Taylor equation (Gordon & Taylor, 1952), where a T_{g2} of −135°C (Johari *et al.*, 1987) was used for amorphous water and the predicted T_{g1} of 243°C (Roos & Karel, 1991) was used for anhydrous starch:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}$$

As a result, the average value for the constant, $k = 5.6$, was obtained. The predicted T_g values for mixtures containing 60, 70, and 80% solids were calculated to be −55°, −24°, and 22°C, respectively.

Glass transition (T_g') (Slade & Levine, 1991) and onset temperature of ice melting (T_m') (Roos & Karel, 1991), within maximally freeze-concentrated solutions, were determined using DSC, as reported by Roos & Karel, (1991) for corn starch dispersions containing 10 and 20% amorphous corn starch, and 90 and 80% distilled water, respectively. Dispersions (1 g) were prepared in beakers by mixing with a glass rod. Triplicate samples (~20 mg) in hermetically sealed DSC pans (aluminium pans, inner volume 40 μl; Mettler-Toledo AG, Switzerland) were first scanned at 10°C/min from −70° to −10°C and then annealed for 15 min at −10°C to allow maximum ice formation. Then, the mixtures were cooled at 20°C/min to −70°C and scanned at 5°C/min from −70° to 0°C for the determination of T_g' and T_m'.

Crystallization conditions

Mixtures of freeze-dried amorphous corn starch and distilled water were prepared in glass ampoules (volume, 2 ml) containing about 0.5 g freeze-dried corn starch. Solids contents of the mixtures were adjusted to 60, 70, and 80% by adding distilled water with a syringe to the glass ampoules. The ampoules were sealed in an acetylene flame and sterilized in an autoclave at 121°C for 20 min to avoid microbial spoilage during storage. The autoclaved ampoules were stored for 2 to 4 weeks at various temperatures ranging from 10° to 90°C, with respective temperature differences between the storage temperature and the predicted glass transition temperature ($T - T_g$) ranging from 28° to 115°C.

Determination of crystallinity and melting behaviour

The effects of storage temperature and $T - T_g$ on formation of crystallites and melting behaviour of the crystallites were determined using DSC at intervals of 2 to 3 d. The water contents of duplicate samples were

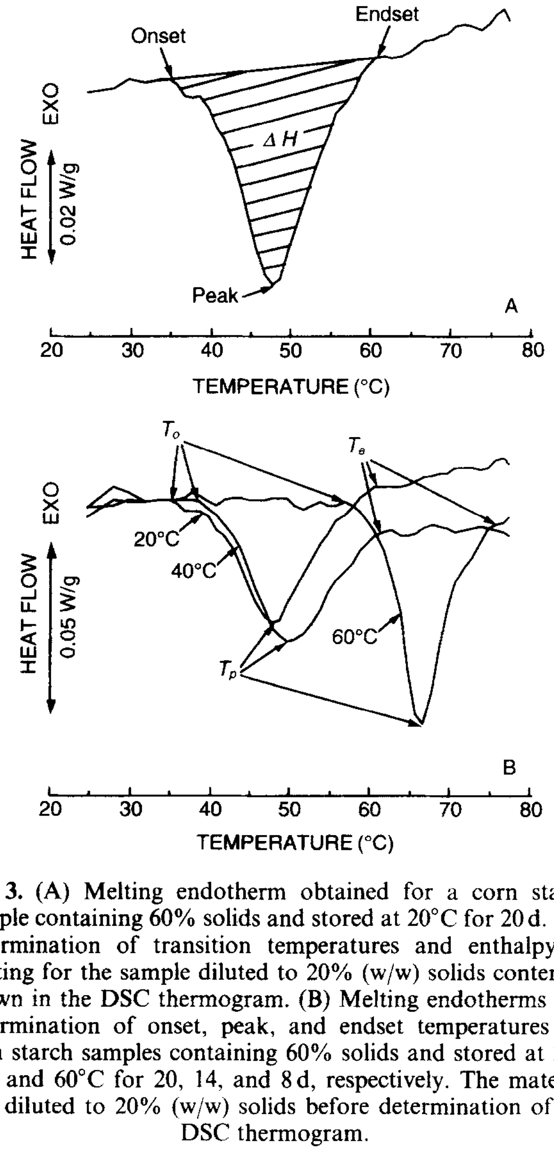

Fig. 3. (A) Melting endotherm obtained for a corn starch sample containing 60% solids and stored at 20°C for 20 d. The determination of transition temperatures and enthalpy of melting for the sample diluted to 20% (w/w) solids content is shown in the DSC thermogram. (B) Melting endotherms and determination of onset, peak, and endset temperatures for corn starch samples containing 60% solids and stored at 20°, 40°, and 60°C for 20, 14, and 8 d, respectively. The material was diluted to 20% (w/w) solids before determination of the DSC thermogram.

adjusted to 80%, by adding distilled water with a syringe to crystallized starch in a beaker at room temperature, before DSC scanning from 10° to 95°C at 5°C/min, to ensure full dissolution of the crystalline regions over the melting temperature range observed in the DSC scans. The melting behaviour and extent of crystallization after storage were determined from the location and size of the melting endotherm (Fig. 3). The gelatinization enthalpy for the native corn starch with 80% water was found to be 12.4 J/g solids, and the onset temperature for gelatinization was 62°C.

RESULTS AND DISCUSSION

State diagram and water sorption of amorphous corn starch

State diagram and water sorption isotherm were determined for amorphous corn starch, because knowledge of the physical state was required for the crystallization studies. The state diagram of amorphous corn starch describes its plasticization by water (Fig. 4). The T_g (onset) values determined for amorphous, gelatinized corn starch containing 14.5–30.5 g water/100 g solids decreased with increasing water content. This relationship could be successfully predicted using the Gordon–Taylor equation, in which the constant, $k = 5.6$, was used. Comparable T_g (midpoint) values were previously reported for native wheat starch and for amorphous amylopectin from waxy corn starch (Fig. 4) by Zeleznak & Hoseney (1987a) and Kalichevsky *et al.* (1992), respectively. Also, Jouppila *et al.* (1995) reported comparable T_g (onset) values for amorphous amylopectin from waxy corn starch, using corresponding water contents (Fig. 4). Unfortunately, only this narrow water content range can be used to determine T_g for starch using DSC. When the water content was lower than 15 g/100 g solids, a broad and ill-defined transition was detected (Zeleznak & Hoseney, 1987a). At higher water contents, which depress T_g to below 0°C, ice formation during a DSC scan can change solids content, due to freeze-concentration.

Onset temperature of glass transition and ice melting within maximally freeze-concentrated solutions was determined to be -11°C. It has been suggested that T_g' is equal to T_m' for high molecular weight carbohydrate polymers, such as starch (Roos & Karel, 1991). The T_g' as well as T_m' were independent of the initial solids concentration (Roos & Karel, 1991; Slade & Levine, 1991). Concentration of solids in the maximally freeze-concentrated unfrozen material (C_g') was estimated to be 73% (w/w). Slade and Levine (1988) reported a higher T_g' (midpoint) value for gelatinized wheat starch (-5°C), but the same C_g' value. Roos & Karel (1991) determined T_g' and calculated C_g' for gelatinized waxy corn starch to be -6°C and 73%, respectively. Our results suggested a lower T_g' for the starch used, but the C_g' was in agreement with previously reported values. The differences in T_g' and T_m' may reflect differences in sample preparation and possible depolymerization, e.g. freeze-dried after gelatinization of starch in a beaker vs starch gelatinization in a DSC pan.

Water sorption of amorphous corn starch could be modelled using the GAB sorption isotherm model. Linear and nonlinear regression analysis techniques produced almost identical sorption isotherms for amorphous corn starch (Fig. 5). Although the critical values indicated in Fig. 5 were determined using the GAB isotherm obtained by nonlinear regression analysis, both methods can be considered to be equally applicable. Obviously, the standard deviation in experimental data from water sorption studies is often higher than the difference in isotherms predicted by the linear and nonlinear methods. The critical relative humidity and corresponding steady-state water content were previously defined to be those values that depress T_g of amorphous corn starch to 25°C (Roos, 1993). The criti-

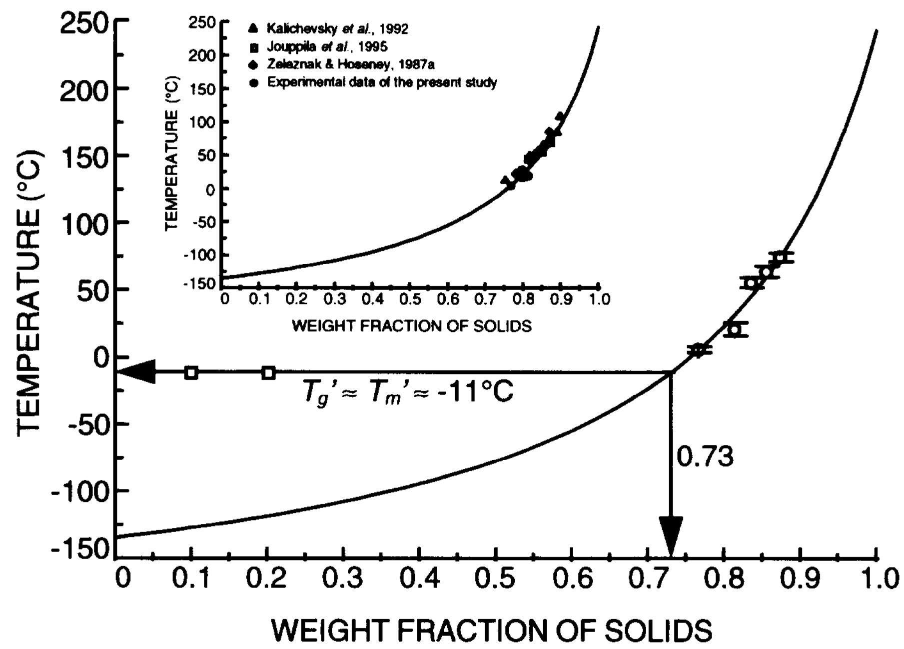

Fig. 4. State diagram of amorphous, gelatinized corn starch, with average values and standard deviations for experimental onset temperatures for the glass transition (T_g). The T_g curve indicates estimated T_g calculated with the Gordon–Taylor equation (constant, $k = 5.6$). The glass transition (T_g') and onset temperature of ice melting (T_m') within the maximally freeze-concentrated solutions was found to be −11°C. The corresponding concentration of the solids in the maximally freeze-concentrated material (C_g') was estimated to be 73% (w/w). Inset figure shows a comparison between previously reported data and the results obtained in the present study.

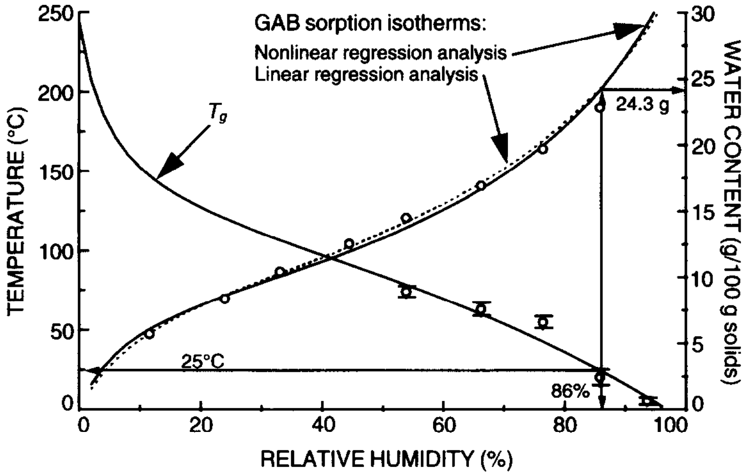

Fig. 5. Relationships between onset temperature of glass transition (T_g), water content, and relative humidity at steady-state conditions for amorphous, gelatinized corn starch. The critical T_g of 25°C for storage, corresponding critical relative humidity, and critical water content are indicated with small-headed arrows.

cal relative humidity was estimated to be 86% and the respective critical water content 24.3 g/100 g solids. If these critical values are exceeded at 25°C, physical changes, e.g. crystallization, may occur in an amorphous material as a result of increased molecular mobility, due to T_g depression to below ambient temperature (Roos, 1993). According to Jouppila *et al.* (1995), critical relative humidity and water content for amorphous amylopectin from waxy corn starch were 90% and 25.2 g/100 g solids, respectively, which were close to the values estimated for amorphous corn starch in the present study. Zeleznak & Hoseney (1987a) suggested that the glass transition of native wheat starch occurred below room temperature at water contents greater than 28.2 g/100 g solids, a value slightly higher than the critical water content predicted for corn starch in the present study.

Melting behaviour of crystallites

Corn starch samples stored under various crystallization conditions showed differences in the melting behaviour

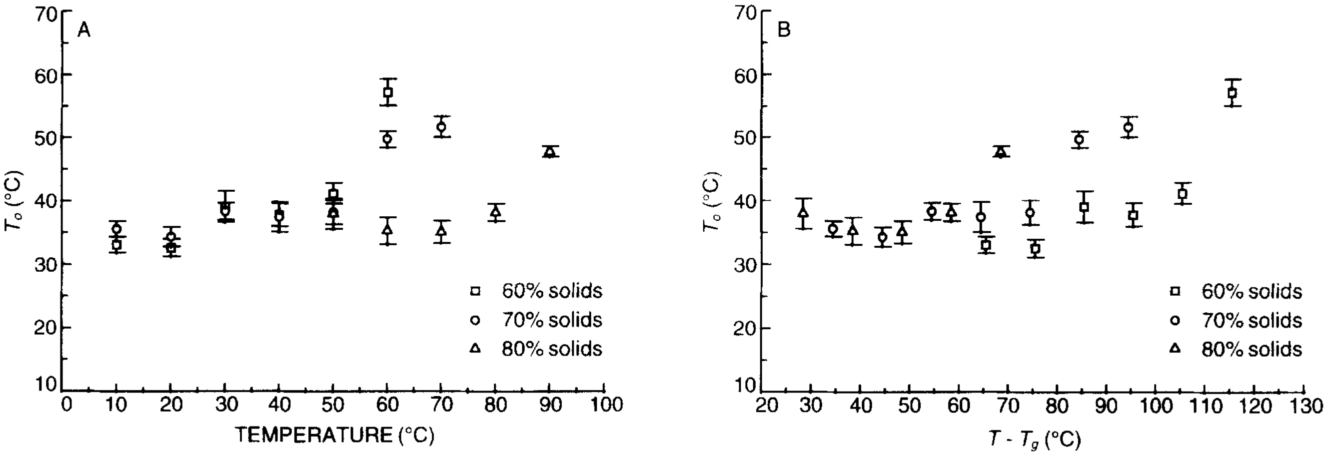

Fig. 6. Onset temperatures (average values and standard deviations) of melting endotherms for corn starch samples, containing 60, 70, and 80% solids during storage, as a function of storage temperature (A) and temperature difference between storage temperature and glass transition temperature, $T-T_g$ (B). The values were determined after the samples were diluted to 20% (w/w) solids content.

of the crystallites formed (Fig. 3). Onset temperatures of melting increased in samples having the same water content, when the storage temperature, and correspondingly, the temperature difference between storage temperature and glass transition temperature ($T-T_g$) was increased (Fig. 6). The increase in the melting temperatures suggested that smaller and/or less perfect crystalline regions were formed at the lower $T-T_g$ values. Also, peak and endset temperatures increased with increasing storage temperature (Table 1). The temperature range of melting (~27°C) was observed to be slightly narrower, when the crystallites were formed at the higher storage temperatures.

A number of researchers (e.g. Colwell *et al.*, 1969; Longton & LeGrys, 1981; Nakazawa *et al.*, 1984; Eliasson, 1985; Nakazawa *et al.*, 1985; Jankowski & Rha, 1986; Zeleznak & Hoseney, 1987b; Eliasson & Ljunger, 1988; Chang & Liu, 1991) have studied the effect of storage temperature on melting behaviour of crystallites formed in gelatinized starch. In all these studies, melting temperatures of the crystallites decreased with decreasing storage temperature, if the storage temperature was well above the T_g' of amorphous starch. Most of these studies reported melting behaviour for starch samples that contained 30–50% solids and were stored at refrigeration and room temperatures. However, comparison

Table 1. Onset, peak, and endset temperatures (average value ± standard deviation) of melting endotherms obtained for corn starch samples containing 60, 70, and 80% solids and stored at various temperatures (T) and $T-T_g$ conditions

Solids content (% w/w)	T (°C)	$T-T_g$ (°C)	Samples used in calculation					
			Storage time (d)	Number of observations	T_o (°C)	T_p (°C)	T_e (°C)	ΔT (°C)
60	10	65	12–28	28	33±1	46±2	59±1	26
	20	75	12–28	28	33±1	47±1	64±1	31
	30	85	10–38	16	39±2	52±1	65±2	26
	40	95	6–20	24	38±2	51±1	68±2	30
	50	105	6–56	24	41±2	54±2	66±2	25
	60	115	10–18	20	57±2	67±0	77±2	20
70	10	34	10–28	32	36±1	48±2	60±2	24
	20	44	12–28	28	34±2	48±1	64±2	30
	30	54	8–38	20	38±1	48±1	62±3	24
	40	64	6–27	24	37±2	48±1	66±2	29
	50	74	6–56	22	38±2	51±1	63±2	25
	60	84	8–14	16	50±1	60±1	69±1	19
	70	94	6–14	20	52±2	64±0	78±1	26
80	50	28	10–19	16	38±2	48±2	61±2	23
	60	38	8–16	20	35±2	48±2	64±2	29
	70	48	6–14	20	35±2	50±1	68±1	33
	80	58	2–14	28	38±1	54±1	69±1	31
	90	68	8–14	16	48±1	62±0	77±1	29

Results for samples with various storage times after levelling-off value was reached were included in the number of observations and used in the calculation of the average levelling-off value.
The average temperature range of melting (ΔT) is the difference between T_e and T_o.

of reported melting temperatures is fairly difficult because of differences in sample materials (e.g. origin of starch, starch/water ratio) and preparation techniques (e.g. heating rate, heating time, temperature range) that may affect the degree of gelatinization. Moreover, differences in determination of melting temperatures (e.g. DSC scanning rate) may result in additional variation of the melting temperatures.

The increasing melting temperatures of crystallized starch with increasing storage temperature and $T-T_g$ could be explained by polymer crystallization theory (Slade & Levine, 1991). According to Flory (1953), crystallization of a polymer for a long period of time at temperatures close to its melting temperature results in a higher degree of order and larger average size of the crystallites. The degree of perfection of the crystallites may be quite low, if proper annealing conditions have not been employed (Flory, 1953). Such improper annealing conditions may occur during storage at temperatures close to the T_g. Colwell *et al.* (1969), and Longton & LeGrys (1981) reported that storage of wheat starch gels at higher temperatures resulted in the formation of a more perfect crystal structure. Zeleznak & Hoseney (1987b) and Chang & Liu (1991) found that the crystals formed in wheat and rice starch gels, respectively, at a higher temperature had a more perfect crystalline structure, due to annealing of the material in the vicinity of the melting temperature during storage. They also found that the melting range of crystallized starch with a more perfect structure was narrower, in agreement with the results obtained in the present study.

The rate and extent of crystallization

Time needed for levelling-off of melting enthalpies of the crystallites increased at the lower storage temperatures (Fig. 7). This behaviour could be observed most clearly in starch samples containing 80% solids, which were stored at temperatures ranging from 50° to 80°C. Nakazawa *et al.* (1985) reported similar results for potato starch samples containing 50% solids, but the difference in crystallinity of samples stored at 5° and 23°C was quite small. In contrast, Colwell *et al.* (1969), Longton & LeGrys (1981), Eliasson (1985), Jankowski & Rha (1986), and Marsh & Blanshard (1988) observed that crystallization in wheat starch samples containing 50% solids occurred more rapidly at refrigeration temperatures (−1° to 10°C) than at room temperature. Colwell *et al.* (1969) suggested that crystal formation occurred more rapidly at low temperatures, because the degree of supercooling was greater. However, differences in concentration and starch origin presumably affect $T-T_g$, which has not been considered in most previous studies.

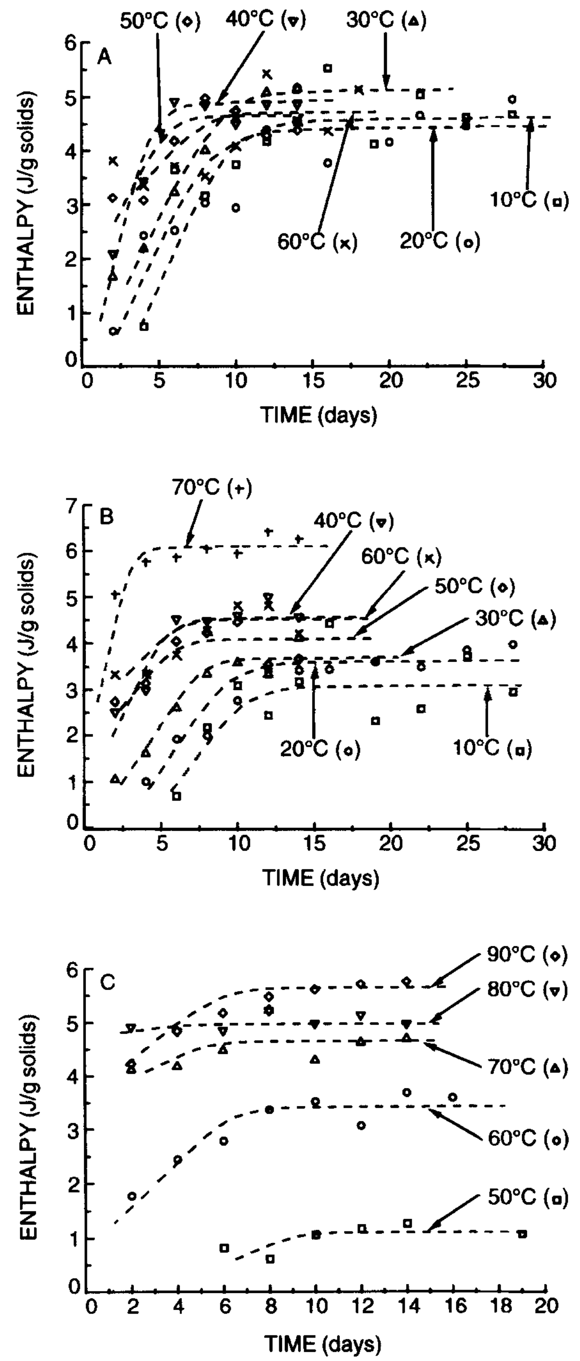

Fig. 7. Melting enthalpies as a function of storage time for corn starch samples stored at various temperatures and containing 60% (A), 70% (B), and 80% (C) solids. Levelling-off of melting enthalpies, determined after the samples were diluted to 20% (w/w) solids content, is indicated by dotted lines.

Melting enthalpies after levelling-off were presumed to indicate the extent of crystallization. The melting enthalpies used in calculations of the average levelling-off melting enthalpies were from the same endotherms that were included in the number of observations and used in calculations of levelling-off values for onset, peak, and endset temperatures (Table 1). The extent of crystallization was observed to be dependent on storage temperature and $T-T_g$ conditions (Fig. 8). The relationship between the extent of crystallization and $T-T_g$ was observed to be parabolic, as suggested by Slade and

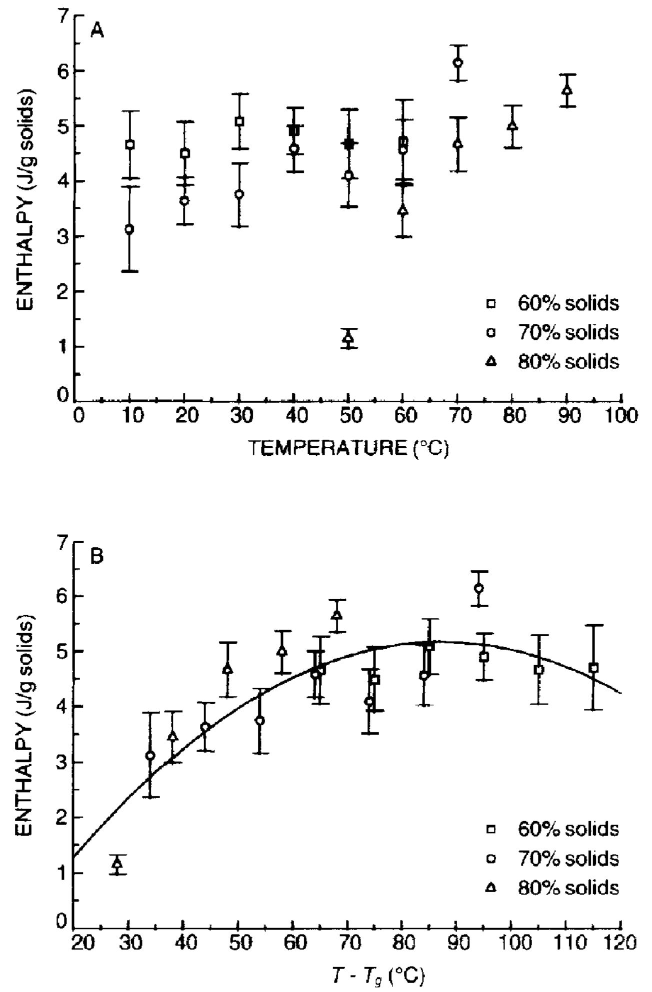

Fig. 8. Levelling-off melting enthalpies (average values and standard deviations), for corn starch samples containing 60, 70, and 80% solids during storage, as a function of storage temperature (A) and temperature difference between storage temperature and glass transition temperature, $T-T_g$ (B). The values were determined after the samples were diluted to 20% (w/w) solids content. A second-order polynomial ($\Delta H = -0.00086 \cdot [T-T_g]^2 + 0.15 \cdot [T-T_g] - 1.38$) was fitted to experimental data, giving a coefficient of determination, R^2, of 0.71.

Levine (1991). The extent of crystallization under low $T-T_g$ conditions was proposed to be low because, while nucleation was fast, crystal growth was kinetically restricted and slow, because molecular mobility was low. Under high $T-T_g$ conditions, crystal growth was fast, but nucleation occurred slowly. Flory (1953) stated that a wide range of degrees of order was typical of the semicrystalline state in polymers. The crystals formed at the beginning of storage under low $T-T_g$ conditions may inhibit later crystallization by formation of rigid amorphous regions next to these early crystallites. As a consequence, a polymer chain in such a stiff region is not able to take part in crystallization, and, thus, the crystallites formed are quite small (Flory, 1953). Laine & Roos (1994) reported corresponding extents of crystallization for corn starch samples containing about 80% solids, after storage under various $T-T_g$ conditions.

In other studies (e.g. Colwell *et al.*, 1969; Longton & LeGrys, 1981; Eliasson, 1985; Jankowski & Rha, 1986; Marsh & Blanshard, 1988; Roulet *et al.*, 1988), the extent of crystallization was also observed to be dependent on storage temperature. All those workers reported that the extent of crystallization in wheat starch samples containing 50% solids decreased with increasing storage temperature. These results agree with ours, if the extents of crystallization are examined as a function of $T-T_g$, and T_g is predicted to be −78°C (50% solids). We observed a slight decrease in the extent of crystallization with increasing storage temperature in corn starch samples containing 60% solids, when the storage temperature was above 30°C. However, the differences in starch samples, water contents, and experimental conditions do not allow further comparison of our and previous results. Colwell *et al.* (1969) suggested that the lower extent of crystallization at higher temperatures was due to the formation of a more symmetrically perfect crystal structure, which could impose limitations on the availability of suitable material for crystal formation and thus lead to a lesser extent of crystallization. The results of the present study suggest that the extent of crystallization has a maximum, above which formation of crystallites presumably occurs close to the melting temperature for the respective solids content. Crystallization above this maximum results in a higher melting temperature of probably more perfect crystallites.

Similarly, the effect of starch concentration on the extent of crystallization at constant temperature could be related to $T-T_g$. Longton & LeGrys (1981), and Zeleznak & Hoseney (1986) reported that a maximum extent of crystallization occurred when the wheat starch content was 50% at a storage temperature of 4°C (our estimate for the corresponding $T-T_g$, 82°C) or 60% at a storage temperature of 25°C (our estimate for the corresponding $T-T_g$, 80°C), respectively. In the present study, the maximum extent of crystallization was calculated to occur at $T-T_g$ of 87°C, which suggests that the maximum extent of crystallization for corn starch samples containing 50% solids (predicted T_g = −78°C) occurs at 9°C ($T = T_g + [T-T_g] = [-78 + 87]$°C = 9°C). Although there are differences in the melting temperatures and perfection of the crystallites after storage under various $T-T_g$ conditions, our preliminary XRD results suggest that crystallization to the same crystalline form occurs (as also reported, e.g. by Zeleznak & Hoseney, 1987b; Marsh & Blanshard, 1988; Chang & Liu, 1991). It is also interesting to note that the maximum extent of crystallization in samples containing 60% solids, a starch concentration close to that in bread, occurred at 32°C. However, the temperature at which the maximum occurs is very sensitive to small differences in composition and water content. This should be taken into account, when our results are compared with those reported for other systems, e.g. wheat starch gels and bread, in which the maximum may occur below room temperature. Such systems may also be partially amorphous and, therefore, more sensitive to water as water plasticization is likely to occur within the amorphous regions.

CONCLUSIONS

The crystallization behaviour of amorphous starch is similar to the crystallization behaviour of synthetic polymers. The temperature difference between storage temperature and glass transition temperature ($T-T_g$) for gelatinized starch affects both the extent of crystallization and the melting behaviour of the crystallites formed. Crystallization under low $T-T_g$ conditions appears to produce smaller and less perfect crystallites than those produced under high $T-T_g$ conditions, due to lower molecular mobility. The crystallization behaviour can be related to T_g, which allows prediction of starch crystallization behaviour and stability of products containing starch.

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