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Factors affecting crystallization and crystallization kinetics in amorphous corn starch

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Abstract

The levelling-off extent of crystallization and crystallization behaviour in corn starch were studied using an X-ray diffraction technique, taking into account the glass transition temperature range of amorphous corn starch. Amorphous corn starch samples at 60, 70, or 80% solids were stored at various temperatures giving various temperature differences between storage temperature and glass transition temperature ($T - T_g$). Corn starch was observed to crystallize into the same crystal form, independent of water content and storage temperature and, therefore, of the $T - T_g$. The Avrami equation was found to be useful in modelling of crystallization kinetics in starch. The data obtained can be used in prediction of stability during storage of starch-containing products with various water contents. © 1998 Elsevier Science Ltd. All rights reserved

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1. Introduction

Crystallization of amorphous biopolymers, e.g. starch component molecules, has been suggested to be kinetically controlled by the glass transition (Slade and Levine, 1991). Glass transition is an important change, occurring over a temperature range, in the amorphous state, as it is the transition between the glassy solid and supercooled, viscous liquid-like states. Water plasticizes amorphous biopolymers, resulting in a decrease in the glass transition temperature range. The glass transition (from solid to liquid) results in an increase in translational mobility of molecules. Subsequently, rates of time-dependent changes, e.g. crystallization, increase with the temperature difference between storage temperature and glass transition temperature ($T - T_g$). The glass transition temperature (T_g) is often defined as the onset or midpoint temperature of the glass transition temperature range determined using differential scanning calorimetry (d.s.c.). Crystallization, in most cases, has not been found to occur at temperatures below the T_g (Slade and Levine, 1991; Roos, 1995).

Crystallization in starch-containing foods is often referred to with the term retrogradation. Retrogradation is known to be time dependent. The rate of crystallization in starch was suggested to depend on water content and storage temperature (e.g. Slade and Levine, 1991; Roos, 1995). Numerous methods have been used in studies of crystallization in starch gels. The methods have included thermoanalytical techniques, e.g. differential thermal analysis (DTA) and d.s.c., which detect the melting enthalpy of the crystallized amylopectin fraction (e.g. McIver et al., 1968; Colwell et al., 1969; Longton and LeGrys, 1981; Eliasson, 1983; Russell, 1987; Roulet et al., 1988; Jouppila and Roos, 1997). Development of crystallinity during storage of starch-containing materials can be analyzed using X-ray diffractometry. Increasing intensities and areas of peaks in X-ray diffraction (XRD) patterns describe development of crystallinity (e.g. Marsh and Blanshard, 1988; Roulet et al., 1988). Also, an increase in gel firmness and changes in viscoelastic properties have been related to the changes in crystallinity (e.g. Germani et al., 1983; Roulet et al., 1988; Biliaderis and Zawistowski, 1990). Studies of crystallization in starch have also used Raman spectroscopy (Bulkin et al., 1987), Fourier transform i.r. spectroscopy (Wilson and Belton, 1988; Goodfellow and Wilson, 1990), and n.m.r. (Teo and Seow, 1992; Wu and Eads, 1993).

Crystallization kinetics of synthetic polymers are often modelled using the Avrami equation (Avrami, 1940), as reviewed by Sperling (1986). In some studies, the Avrami equation has been successfully fitted to kinetic data for

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crystallization in starch gels (e.g. McIver et al., 1968; Colwell et al., 1969; Longton and LeGrys, 1981; Eliasson, 1983; Germani et al., 1983; del Rosario and Pontiveros, 1983; Bulkin et al., 1987; Russell, 1987). The equation has also proved to be useful in modelling of bread staling (e.g. Fearn and Russell, 1982; Russell, 1983a; Russell, 1983b; Russell, 1983c). The effect of storage temperature on the values of constants in the Avrami equation, describing kinetics of crystallization in starch, has been studied by Colwell et al. (1969), Longton and LeGrys (1981), del Rosario and Pontiveros (1983), and Marsh and Blanshard (1988).

The objectives of the present study were to investigate the effect of water content and storage temperature on the levelling-off extent of crystallization, as well as crystallization behaviour and kinetics, in corn starch using the XRD technique, taking into account effects of the physical state and glass transition. The Avrami equation was used in modelling of the crystallization data.

2. Experimental

2.1. Sample preparation

Corn starch suspensions containing 5% (w/w) solids were produced using corn starch (Sigma Chemical Co., MO, USA; water content 10.8%) and distilled water. The suspension, in aliquots of 400 ml in a beaker, was heated to boiling under continuous stirring to gelatinize the starch granules. Full gelatinization of starch was confirmed visually using polarized light microscopy. The resulting gels, transferred on Petri dishes (10 g), were frozen at −80°C for at least 20 h and subsequently freeze-dried for at least 72 h at a pressure < 0.1 mbar, using a Lyovac GT2 freeze-dryer (Amsco Finn-Aqua GmbH, Germany). The freeze-dried gels were powdered using a Cyclotec 1093 sample mill (Tecator AB, Sweden), and the powder was further dehydrated to constant weight (at least 5 days) in a vacuum desiccator over P_2O_5 (p.a.; E. Merck, Germany) at 24°C.

2.2. Crystallization conditions

Mixtures of freeze-dried, gelatinized corn starch (about 0.6 g) and distilled water were prepared in glass ampoules (volume, 5 ml; Scherf Präzision GmbH, Germany). Contents of solids in the mixtures were adjusted to be 60, 70, or 80% by adding distilled water with a syringe to the glass ampoules. According to the predicted T_g depression by water (Jouppila and Roos, 1997), the T_g values for the mixtures containing 60, 70, and 80% solids were − 55, − 24, and 22°C, respectively. The ampoules were sealed in an acetylene flame and sterilized in an autoclave at 121°C for 20 min to allow homogeneous water distribution and to avoid microbial spoilage during storage. The autoclaved ampoules were stored for up to 16 days at various temperatures ranging from 10 to 90°C, with respective $T - T_g$ values ranging from 28 to 115°C. Samples containing 60% solids and stored at 10, 30, 50, and 60°C, samples containing 70% solids and stored at 70°C, and samples containing 80% solids and stored at 90°C were used in the evaluation of development of crystallinity during storage. Three replicate samples were taken out of incubators and analyzed at intervals during storage. Samples containing 60% solids and stored at 20 and 40°C, samples containing 70% solids and stored at temperatures ranging from 10 to 60°C, and samples containing 80% solids and stored at temperatures ranging from 50 to 80°C were used in the determination of the levelling-off extent of crystallinity. Storage times used in the determination of levelling-off extents of crystallinity were chosen on the basis of the data for corn starch crystallization determined using d.s.c., and the samples with 60% solids were studied more precisely, because the water content corresponded closely to that in bread (Jouppila and Roos, 1997). After storage, ampoules were opened, frozen at − 80°C for at least 20 h, and then freeze-dried for at least 72 h at a pressure < 0.1 mbar, using a Lyovac GT2 freeze-dryer, as in sample preparation. The freeze-dried samples were stored in a vacuum desiccator over P_2O_5 (p.a.; E. Merck, Germany) at 24°C for at least 1 day, before they were powdered using a mortar and pestle. Powdering of the material was required for the XRD analysis of crystallinity. The powdered samples (three replicates at each solids content, storage temperature, and storage time combination) were placed in 2 ml plastic Eppendorf tubes that were closed and stored for less than 4 h at ambient temperature and relative humidity prior to the XRD measurements.

2.3. Determination of crystallinity

The dehydrated, powdered samples were lightly pressed on aluminium trays, using a 10 mm wide spatula (sample layer, 15 × 20 × 1.5 mm). These trays were exposed to Cu Kα radiation ($\lambda = 0.15418$ nm) in a Philips X-ray powder diffractometer. The X-ray powder diffractometer (PW 1830 generator, PW 1710 diffractometer control, PW 1820 vertical goniometer equipped with a graphite reflected beam monochromator, and PC-APD software for Automatic Powder Diffraction Version 3.0; Philips, Eindhoven and Almelo, The Netherlands) was operated in reflection mode at 40 kV and 50 mA, with a divergence slit for primary beam, a divergence slit for diffracted beam, and a receiving slit for diffracted beam of 1/4°, 1/4°, and 0.1 mm, respectively. The XRD patterns were recorded using diffraction angles (2θ) from 10 to 27° (step size 0.02°; time per step 2.5 s) for most samples, but from 5 to 30° (step size 0.02°; time per step 2.5 s) for one sample at each solids content and storage temperature combination, with the longest storage time used to observe the presence of peaks at smaller diffraction angles. The fit-profile program of the APD software was used to fit a profile to a peak and to obtain peak area.

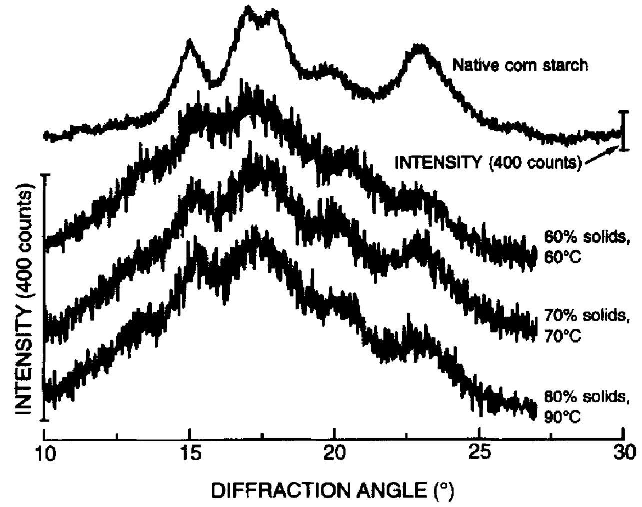

Fig. 1. X-ray diffraction patterns for native corn starch (data from Jouppila and Roos (1997)), and for corn starch at various solids contents crystallized at various storage temperatures. The X-ray diffraction patterns shown are those of samples with the highest extents of crystallinity. Corn starch at 60% solids was stored at 60°C for 12 days, corn starch at 70% solids was stored at 70°C for 8 days, and corn starch at 80% solids was stored at 90°C for 10 days.

Peak areas were $K\alpha 1$ net areas of the fitted profile (in counts).

Modelling of crystallization data was carried out using the Avrami equation (Eq. (1)) (Avrami, 1940), which was written to the form of Eq. (2) for fitting the equation to XRD peak areas, obtained in the present study, and melting enthalpies, reported by Jouppila and Roos (1997), with time of crystallization.

$$\theta = 1 - e^{-kt^n} \qquad (1)$$

where θ is crystallinity, t is time, k is a rate constant, and n is the Avrami exponent.

$$1 - \theta = \frac{A_f - A_t}{A_f - A_0} = e^{-kt^n} \qquad (2)$$

where A_f is the levelling-off value of peak area or levelling-off value of melting enthalpy at which the extent of crystallization in starch ceased at each water content and storage temperature conditions, A_t is peak area or melting enthalpy at time t, and A_0 is the peak area of 0 counts or melting enthalpy of 0 J g^{-1} for a noncrystalline, amorphous material. The levelling-off value of peak area in the present study was calculated as a mean of the six observations for the two longest storage times (three replicates) at each solids content and storage temperature combination.

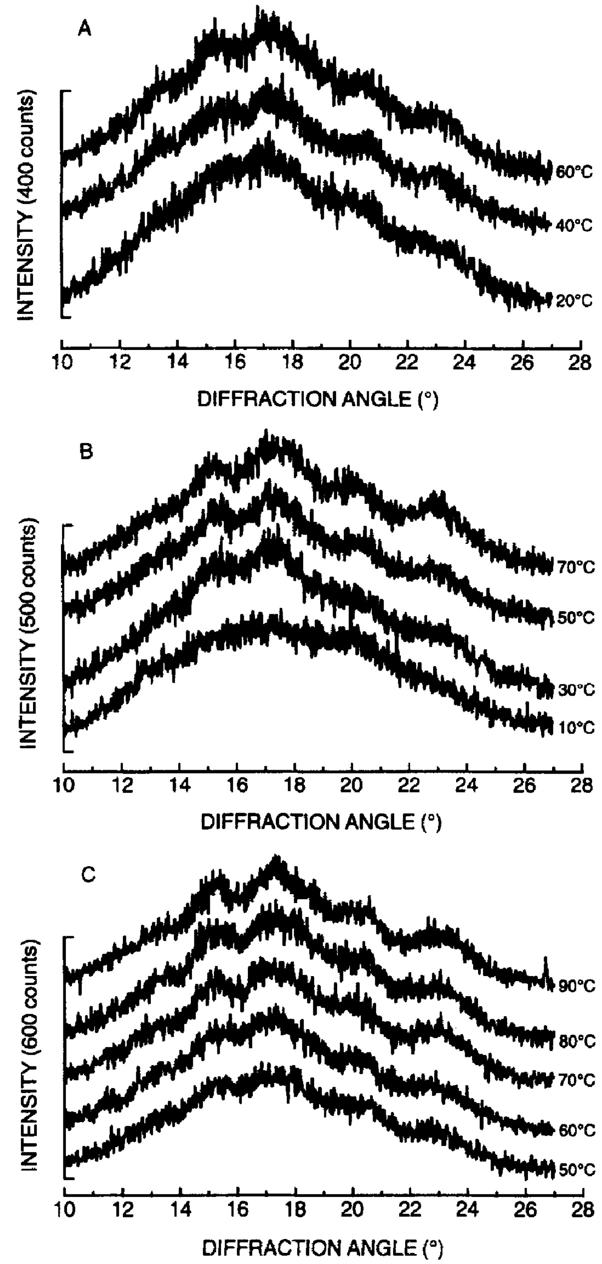

Fig. 2. X-ray diffraction patterns for corn starch containing 60% solids, after storage at 20, 40, and 60°C for 14, 6, and 12 days, respectively (*A*), for corn starch containing 70% solids, after storage at 10, 30, 50, and 70°C for 16, 12, 8, and 8 days, respectively (*B*), and for corn starch containing 80% solids, after storage at 50, 60, 70, 80, and 90°C for 10, 10, 8, 4, and 10 days, respectively (*C*). X-ray diffraction patterns shown suggested that more crystallinity and probably larger crystallites were formed at the higher storage temperatures.

The Avrami equation with $A_0 = 0$ was written to the form of Eq. (3). Fitting of the equation to the data was carried out using a nonlinear regression analysis technique available in a SAS System for Windows computer program (release 6.11, SAS Institute Inc., USA). The program used the least sum of squares method. The iterative algorithm used was the modified Gauss–Newton method, the use of which required specification of the first partial derivates of the model with respect to its constants (Eq. (4) and Eq. (5)).

$$A_t = A_f - A_f\, e^{-kt^n} \qquad (3)$$

$$\frac{\partial A_t}{\partial k} = A_f\, e^{-kt^n} t^n \qquad (4)$$

$$\frac{\partial A_t}{\partial n} = A_f\, k\, e^{-kt^n} t^n \ln t \qquad (5)$$

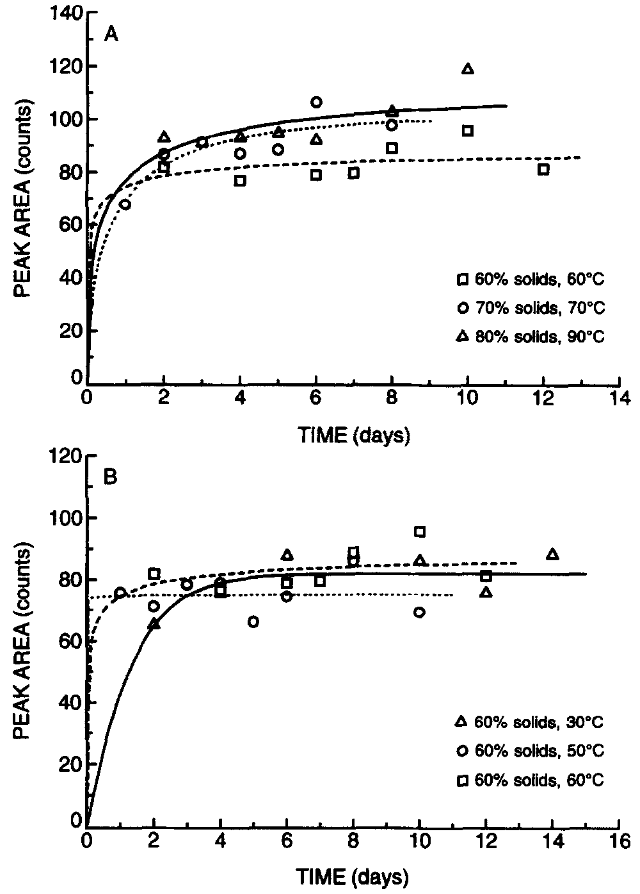

Fig. 3. Peak area (diffraction angle of 17°) in X-ray diffraction pattern, as a function of time, for corn starch at various solids contents after storage at various temperatures. The Avrami equation was fitted to the data, as shown by solid lines (80% solids, stored at 90°C (*A*); 60% solids, stored at 30°C (*B*), dotted lines (70% solids, stored at 70°C (*A*); 60% solids, stored at 50°C (*B*)), and dashed curves (60% solids, stored at 60°C (*A*,*B*)).

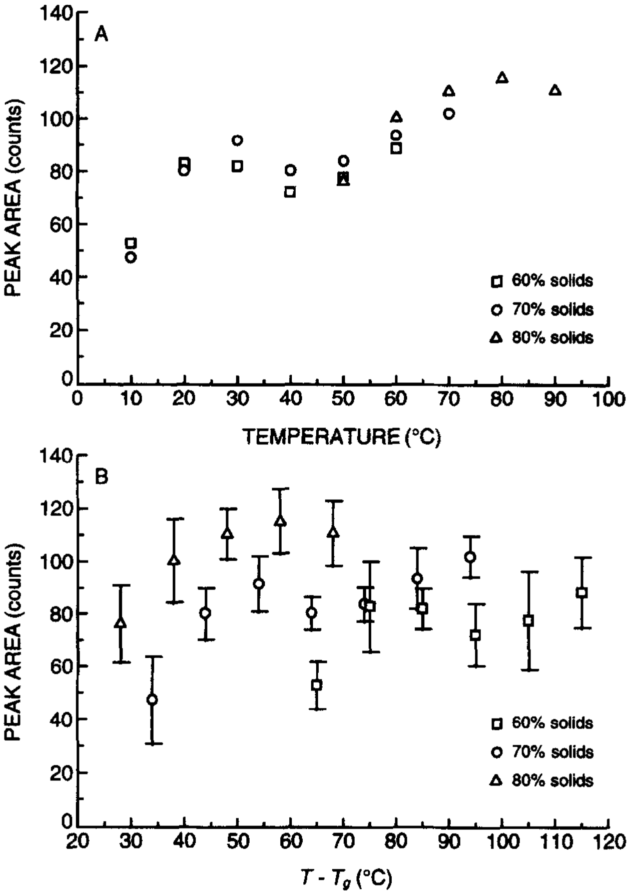

Fig. 4. Levelling-off peak area (diffraction angle of 17°) as a function of storage temperature ((*A*) average levelling-off peak areas) and temperature difference between storage temperature and glass transition temperature, $T - T_g$ ((*B*) average levelling-off peak areas and standard deviations). Levelling-off peak areas indicated the levelling-off extent of crystallinity at each storage temperature.

The values of the constants, k and n, were used to calculate the value of half-time, $t_{1/2}$, for crystallization. Half-time was taken as the time required to achieve 50% of the levelling-off extent of crystallinity, as defined by Eq. (6).

$$t_{1/2} = \left(-\frac{\ln 0.5}{k}\right)^{\frac{1}{n}} \qquad (6)$$

3. Results and discussion

Native corn starch is reported to exhibit the A-type crystallinity of starch, and retrograded starch to exhibit B-type crystallinity (e.g. Roos, 1995). Fig. 1 shows the XRD pattern for native corn starch, which confirms A-type crystallinity. The type of crystallinity could not be clearly determined from the XRD patterns recorded for samples with various water contents after storage at various temperatures in the present study (Figs. 1 and 2), because peaks in XRD patterns were broad and flat. Roulet et al. (1988) similarly reported that signal-to-noise ratio in XRD measurements was low. In particular, the peaks in the XRD patterns for samples stored at the low temperatures were even broader, flatter and, therefore, more difficult to analyze. Jouppila and Roos (1997) reported that crystallites formed at low temperatures had lower melting temperatures than crystallites formed at high temperatures. This finding probably suggested that smaller and/or less perfect crystallites were formed at low temperatures and low $T - T_g$ conditions.

Development of crystallinity during storage, as detected from increasing areas of peaks in XRD patterns at a diffraction angle of 17°, was studied at selected water content and storage temperature combinations (Fig. 3). These combinations were used, because the effect of storage temperature on crystallization kinetics (60% solids and various storage temperatures) and development of crystals with high melting temperatures (highest storage temperature at each solids content; Jouppila and Roos, 1997) were of the main interest. At the highest storage temperatures, samples containing 60, 70, or 80% solids gave clear peaks that could be most precisely analyzed. Different storage temperatures, for samples containing 60% solids, were analyzed to observe differences

Table 1
Values of the constants in the Avrami equation and half-times of crystallization (time to 50% of the levelling-off extent of crystallinity), calculated using the constants, *k* and *n*, for corn starch stored at various temperatures

Solids content (%, w/w)	Storage temperature (°C)	$T - T_g$ (°C)	Levelling-off value (counts)[a]	Values of the constants in the Avrami equation		Half-time (days)
				k (day^{-1})	n	
60	30	85	82.0	7.4×10^{-1}	1.1	9.4×10^{-1}
	50	105	77.6	3.2	3.0×10^{-2}	5.8×10^{-23}
	60	115	88.6	1.8	2.4×10^{-1}	1.7×10^{-2}
70	70	94	101.9	1.1	5.4×10^{-1}	4.0×10^{-1}
80	90	68	110.7	1.2	3.9×10^{-1}	2.5×10^{-1}

Crystallinity was determined using X-ray powder diffractometry

[a] Levelling-off value was calculated as a mean of the six observations for the two longest storage times (three replicates) at each solids content and storage temperature combination

in the rate of crystallization at a constant solids content but varying storage temperature. However, peak areas in XRD patterns, recorded for samples containing 60% solids after storage at 10°C, could not be determined at the beginning of storage, because the peaks were broad and flat. The areas of peaks in XRD patterns at a diffraction angle of 17° were chosen to describe crystallinity, because the area of that peak could also be analyzed in samples stored at the low temperatures, although not at the beginning of storage. For all materials, the extents of crystallization at given intervals are shown in Fig. 3. The increase in crystallinity during storage at 70 and 90°C, in samples containing 70 and 80% solids, respectively, occurred parallel to that found to occur in samples at corresponding solids contents and storage temperatures by Jouppila and Roos (1997). However, the development of crystallinity during storage for samples at 60% solids and various temperatures was more rapid than was found by Jouppila and Roos (1997). The differences between the two studies may have resulted from difficulties in the determination of areas for broad and flat peaks in XRD patterns. This is also in agreement with previous studies (e.g. Longton and LeGrys, 1981; Jouppila and Roos, 1997), suggesting that smaller and less perfect crystallites with lower melting temperatures were formed in starch at low storage temperatures.

Our previous study suggested that crystallization in starch occurred to a levelling-off extent that was dependent on water content and storage temperature. In the present study, the levelling-off extent of crystallization in starch was also found to be a function of storage temperature

Table 2
Values of the constants in the Avrami equation and half-times of crystallization (time to 50% of the levelling-off extent of crystallinity), calculated using the constants, *k* and *n*, for corn starch stored at various temperatures

Solids content (%, w/w)	Storage temperature (°C)	$T - T_g$ (°C)	Levelling-off value (J g^{-1})[a]	Values of the constants in the Avrami equation		Half-time (days)
				k (day^{-1})	n	
60	10	65	4.7	2.1×10^{-2}	2.0	5.7
	20	75	4.5	9.4×10^{-2}	1.3	4.9
	30	85	5.1	1.2×10^{-1}	1.3	4.1
	40	95	4.9	1.9×10^{-1}	1.5	2.4
	50	105	4.7	5.7×10^{-1}	7.5×10^{-1}	1.3
	60	115	4.7	9.0×10^{-1}	4.4×10^{-1}	5.6×10^{-1}
70	10	34	3.1	1.0×10^{-5}	5.6	7.2
	20	44	3.6	2.3×10^{-2}	1.8	6.4
	30	54	3.7	8.6×10^{-2}	1.5	4.0
	40	64	4.6	3.2×10^{-1}	1.1	2.0
	50	74	4.1	5.5×10^{-1}	9.3×10^{-1}	1.3
	60	84	4.6	7.5×10^{-1}	6.2×10^{-1}	8.9×10^{-1}
	70	94	6.1	1.1	6.8×10^{-1}	5.1×10^{-1}
80	50	28	1.2	4.1×10^{-2}	1.7	5.2
	60	38	3.4	3.4×10^{-1}	9.9×10^{-1}	2.1
	70	48	4.7	1.4	5.3×10^{-1}	2.7×10^{-1}
	80	58	5.0	3.0	3.4×10^{-1}	1.4×10^{-2}
	90	68	5.6	8.5×10^{-1}	6.6×10^{-1}	7.4×10^{-1}

Crystallinity was taken from melting enthalpies for crystals formed during storage (Jouppila and Roos, 1997)

[a] The number of observations used in calculations, with corresponding storage time range, was reported by Jouppila and Roos (1997)

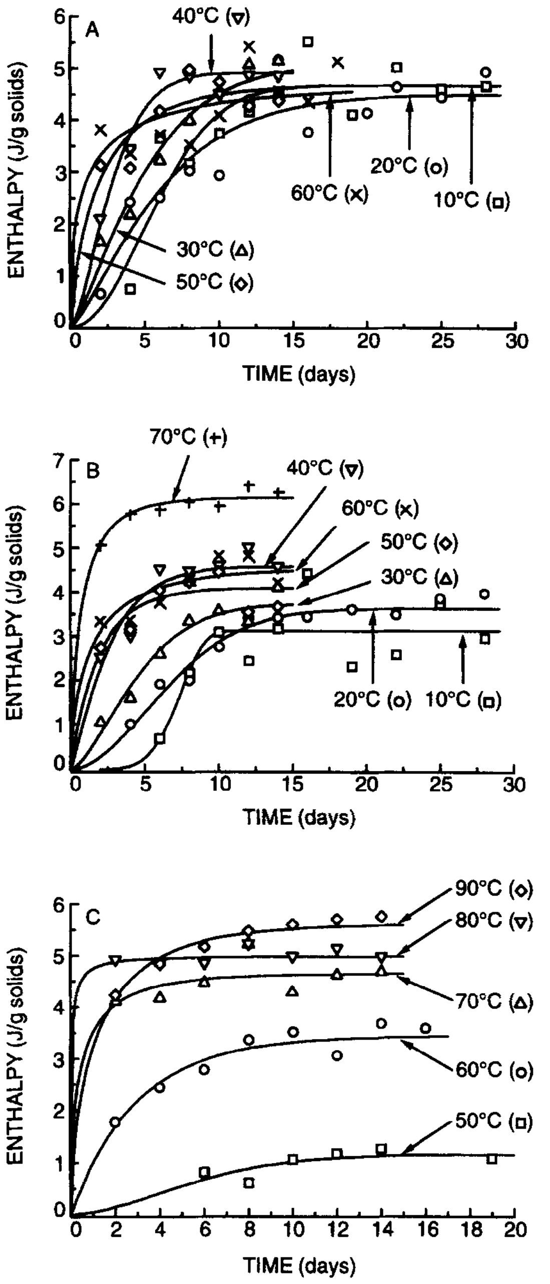

Fig. 5. Melting enthalpies, indicating extent of crystallization, as a function of storage time for corn starch at 60% (*A*), 70% (*B*), and 80% (*C*) solids, after storage at various temperatures (data from Jouppila and Roos (1997)). The Avrami equation was fitted to the data, as shown by solid curves.

and dependent on water content, as shown in Fig. 4*A*. Jouppila and Roos (1997) reported a parabolic relationship between the levelling-off extent of crystallinity and $T - T_g$. Although a parabolic relationship between the XRD peak areas and $T - T_g$ was apparent for samples containing 80% solids (Fig. 4*B*), this behaviour could not be fully confirmed to occur in samples with 60 or 70% solids. However, the determination of areas for broad and flat peaks in XRD patterns was difficult, causing a large scatter in the data.

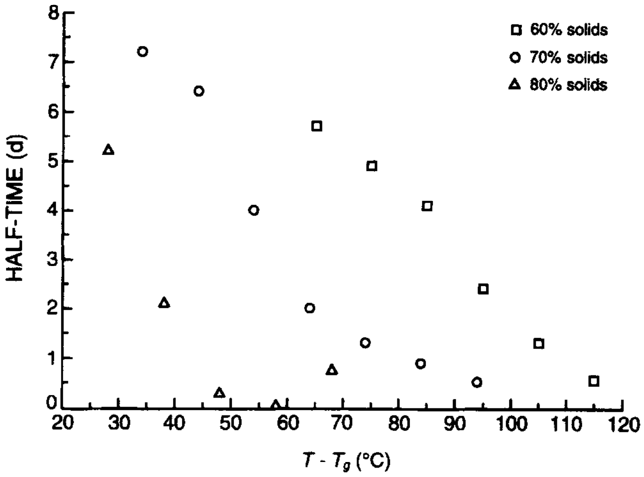

Fig. 6. Half-time for crystallization for corn starch containing 60, 70, or 80% solids, as a function of temperature difference between storage temperature and glass transition temperature, $T - T_g$.

Crystallization data obtained in the present study were modelled using the Avrami equation. The values of the constants, *k* and *n*, in the Avrami equation and half-times for crystallization, $t_{1/2}$ (time to 50% of the levelling-off extent of crystallinity) in starch are given in Table 1. The predicted crystallization kinetics, found using the XRD technique, are shown in Fig. 3. We also fitted the Avrami equation to the crystallization data of Jouppila and Roos (1997). As given in Table 2 and shown in Fig. 5, crystallization kinetics at various temperatures and water contents followed the Avrami equation. The value of the Avrami exponent, *n*, was found to vary and to be higher at the lower storage temperatures and at the low $T - T_g$ conditions, as was also found by del Rosario and Pontiveros (1983) and Wu and Eads (1993). Moreover, Longton and LeGrys (1981) suggested that the degree of crystal perfection was dependent on storage temperature. Therefore, the Avrami exponent, *n*, was dependent on storage temperature, because the value of *n* is generally related to crystallite morphology. However, Colwell et al. (1969) found that the value of *n* was unity over the temperature range from − 1 to 43°C for crystallization of starch gels containing 50% solids. Longton and LeGrys (1981) reported that the Avrami model fitted the crystallization data for starch gels containing 50% solids during storage at 4, 21, and 30°C, but the value of the Avrami exponent, *n*, was less than unity. In agreement with these studies, Teo and Seow (1992) reported that storage temperatures over the range 5 to 25°C did not affect the value of *n* for crystallization in starch gels containing 30% solids. In the present study, the half-time for crystallization, $t_{1/2}$, in samples containing 60 and 70% solids, decreased with increasing storage temperature and $T - T_g$ (Table 2), suggesting that crystallization was more rapid at the higher temperatures and $T - T_g$ conditions. Similarly, half-time for crystallization in samples containing 80% solids decreased with increasing storage temperature and $T - T_g$, but half-time for crystallization was slightly longer, when samples were stored at 90°C and $T - T_g$ of

68°C (Fig. 6). That was possibly a result of decomposition of starch molecules at the high storage temperature.

4. Conclusions

The present XRD study showed that the crystal form produced during crystallization in starch was independent of water content and storage temperature. However, peaks in XRD patterns were more pronounced for samples stored at higher storage temperatures, suggesting that smaller and/or less perfect crystalline regions were formed at low storage temperatures. Development of crystallinity could be detected from increasing peak areas in XRD patterns. Crystallization data obtained from XRD studies and from previous d.s.c. studies could be successfully modelled using the Avrami equation. The rate of crystallization in starch was found to increase with increasing storage temperature and $T - T_g$. However, at 90°C, a slightly slower rate of crystallization was observed, possibly as a result of decomposition of starch component molecules. The values of half-time obtained can be used in prediction of starch crystallization behaviour and stability of products containing amorphous starch.

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