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Variation in crystalline type with amylose content in maize starch granules: an X-ray powder diffraction study

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Abstract

Comparative studies of native maize starches with different amylose contents were carried out using X-ray powder diffraction. The results show a transition of crystalline type from A through C to B, accompanying a decrease in degree of crystallinity from 41.8% to 17.2% across a range of apparent amylose content from 0% to 84%. Hydration induces an increase in degree of granule crystallinity, but does not change the transition of crystal type. Progressively from A-type to C-type, crystallinity decreases rapidly with an increase in amylose content. From C-type to B-type, overall crystallinity decreases more slowly. The crystal type is strongly dependent on amylose content and on average chain length of the respective amylopectin. Waxy A-types have an average chain length of about 20, while in high amylose B-types this rises to ≈ 35. The proportion of short chains ($\sim$10–13 glucose units) appears to affect crystal type significantly. Some V-type material was detected at high amylose levels. The proportion of this increased after prolonged exposure of the granules to iodine vapour. Implications for the arrangement of starch components in the granule are discussed.

Keywords: Maize starch granules; Amylose content; X-ray diffraction; Degree of crystallinity; Average chain length

1. Introduction

Starch is an important reserve polysaccharide in higher plants. A widely accepted model of a typical cereal starch granule involves alternating amorphous and crystalline lamellae, in which the two main components, amylose and amylopectin, are embedded. Amylose is an α-(1 → 4)-D-glucopyranosyl polymer, with linear or lightly branched molecules or a mixture of both. The residues in amylopectin are α-(1 → 4)-D-glucopyranose units with α-(1 → 6)-linkages at intervals of approximately 20 units, depending on the source. Typically, natural starch granules range in degree of crystallinity from about 15% to 45% (Zobel, 1988).

Much of the information about starch granule crystalline properties has been acquired from X-ray powder diffraction studies. According to several such studies, starch can be classified to A, B and C forms. In the native granular forms, the A pattern is associated mainly with cereal starches, while the B form is usually obtained from tuber starches. The C pattern is a mixture of both A and B types, but also occurs naturally, e.g. smooth-seeded pea starch and various bean starches. The V-type conformation is a result of amylose being complexed with substances such as aliphatic fatty acids, emulsifiers, butanol and iodine. The main difference between A and B types is that the former adopt a close-packed arrangement with water molecules between each double helical structure, while the B-type is more open, there being more water molecules, essentially all of which are located in a central cavity surrounded by six double helices (Wu & Sarko, 1978; Imberty & Pérez, 1988; Imberty et al., 1988).

Hizukuri studied the distribution of chain lengths in the amylopectins of starches from 20 species by HPLC, and found that there is a close relationship between the weight-average chain lengths of the amylopectins and crystal type of starch granules. Short chain lengths display A-type crystallinity, while long chain lengths show B-type crystallinity and intermediate chain length is associated with C-type crystallinity (Hizukuri, 1985; Hizukuri et al., 1983).

We have determined the effect of amylose content (0%–84%) on amylose molecular size and average chain length of amylopectin in maize starches (Cheetham & Tao, 1997). Results show that amylose content has a significant correlation with average chain-length of amylopectin, and the ratio of short chains (F2) to long chains (F1). The higher-amylose granules have in their

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amylopectin (i) a greater average chain length ($\overline{CL}$), (ii) a lower F2/F1 than the lower-amylose samples. These relationships suggested to us that there might be a crystal type transition in maize starch across the range of amylose contents. To date, A-type and B-type crystallinity has been reported. To our knowledge, C-type crystallinity in maize starch has not been described.

The amylose content in maize starch affects many significant physical, chemical and functional properties such as pasting temperature, birefringence end point temperature (BEPT), viscosity, gel stability, the water solubility and the degree of resistance of the starch granules to 'in vitro' digestion by amylases. These in turn affect the range of industrial applications of a starch. The objective of work described here was to compare crystal types and crystallinity levels in maize starch granules of differing amylose content, and to characterise the relationship between crystal type, amylose content, and average chain length of amylopectins. Detailed knowledge of such relationships should be of assistance, e.g. to plant geneticists, in the development of 'tailor-made' starches for specific applications.

2. Materials and methods

2.1. Sources and pretreatment of starch samples

Native maize starch (MS) granules with different amylose contents (WMS, MSA, MSB, MSC, MSD and MSE) and potato starch were provided by Starch Australasia Ltd., Australia. Their apparent amylose contents are 0%, 28%, 40%, 56%, 65% and 84%, respectively, as determined by amperometric iodine binding, and 0%, 26%, 39%, 51%, 58% and 62% by HPSEC of debranched starches, respectively. The hydrated starch samples were obtained by maintaining starch at 100% relative humidity in a desiccator for several days or weeks. Water contents of the hydrated starch samples were calculated from the weight difference before and after drying at 130°.

2.2. The preparation of iodine-treated samples of starches

Maize starch (600 mg) on a watch glass in a thin layer, was exposed to iodine vapour in the desiccator for at least 4 months until the weight became constant. The samples before and after iodination were weighed in order to calculate the amount of absorbed iodine. The process of iodination was carried out at room temperature in order to avoid possible degradation of starch (Murdoch, 1992).

2.3. X-ray powder diffraction measurements

Monochromatic Cu-K_α radiation (wavelength = 1.542 Å) was produced by a SIEMENS X-ray powder diffractometer. The starch powders were packed tightly in an rectangular aluminium cell (20 × 20 mm, thickness 0.15 cm), The samples (density about 1.10 × 10 g/cm^3) were exposed to the X-ray beam with the X-ray generator running at 40 KV and 30 mA. The scanning regions of the diffraction angle 2θ were 4°–30°, which covers all the significant diffraction peaks of starch crystallites. The other operation conditions were as follows: Step interval 0.02, scan rate 2°/min, Sollet and divergence slit, 1°, receiving slit, 1°, and scattering slit, 0.15°. One sample needed 13 min scanning. The 'd' spacings were computed according to Bragg's law. Duplicate measurements were made at ambient temperature.

2.4. Determination of the degree of crystallinity

The degree of crystallinity of samples was quantitatively estimated following the method of Nara & Komiya (1983). A smooth curve which connected peak baselines was computer-plotted on the diffractograms (Fig. 1). The area above the smooth curve was taken to correspond to the crystalline portion, and the lower area between the smooth curve and a linear baseline which connected the two points of intensity at 2θ of 30° and 5° in WMS and MSA and three points of 4°, 8°, 30° in the samples of MSB, MSC, MSD and MSE was taken as the amorphous section. The upper diffraction peak area and total diffraction area over the diffraction angle 5°–30° 2θ were integrated on Smadchrom software (Morgan and Kennedy Research, Australia). The ratio of upper area to total diffraction area was taken as the degree of crystallinity.

3. Results and discussion

3.1. The effect of amylose content on crystal patterns of maize starch

The X-ray diffractograms of native maize starch samples of differing amylose content are presented in Fig. 1. The corresponding X-ray diffraction parameters and crystallinity level calculated from the ratio of diffraction peak area and total diffraction area are given in Table 1. The scattering angle, at which the diffraction intensities can be observed was 2θ, and the d spacing was used to discriminate the planes of different sites. The spectra were compared to those presented by Gernat et al. (1993) and found to be equally or better resolved.

The X-ray diffraction patterns were compared with reported standard diffraction patterns of different crystalline types (Zobel, 1964; 1988). Previously, waxy, normal maize and high amylose maize starch X-ray diffraction patterns have been reported (Zobel, 1964; Gernat et al., 1993), but very little work has been reported on the spectra and crystallinity of maize starches across a series of differing amylose contents (0%–84%). Waxy maize starch (WMS) and MSA show a typical A-type pattern, with strong reflections at 2θ

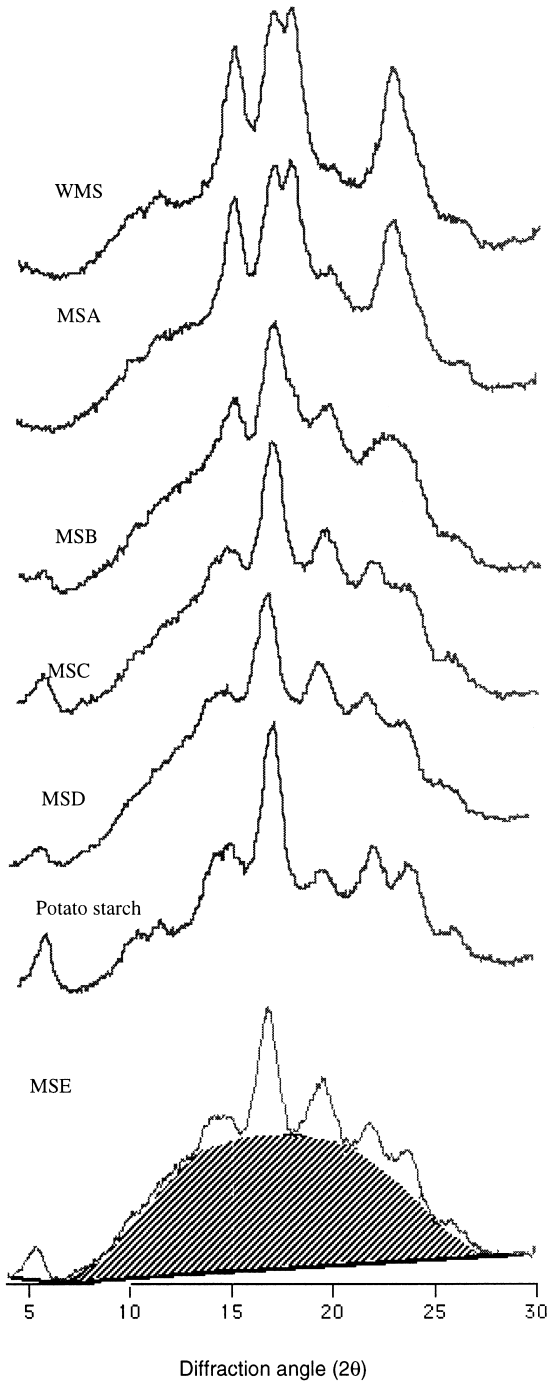

Fig. 1. Wide-angle X-ray powder diffraction spectra for maize starches with different amylose contents, showing crystalline (upper region) and non-crystalline regions.

about 15° and 23°, and an unresolved doublet at 17°, 18° 2θ. High amylose starches from MSC to MSE give the strongest diffraction peak at around 17° 2θ and a few small peaks at around 2θ values of 23°, 22° and 20°. An additional peak appeared at about 5° 2θ with a d spacing of 5.4 Å. These latter spectra are basically the same as that of potato starch, which is a characteristic B type. MSB generally showed the presence of a B-pattern (Fig. 1 and Table 1). However, the

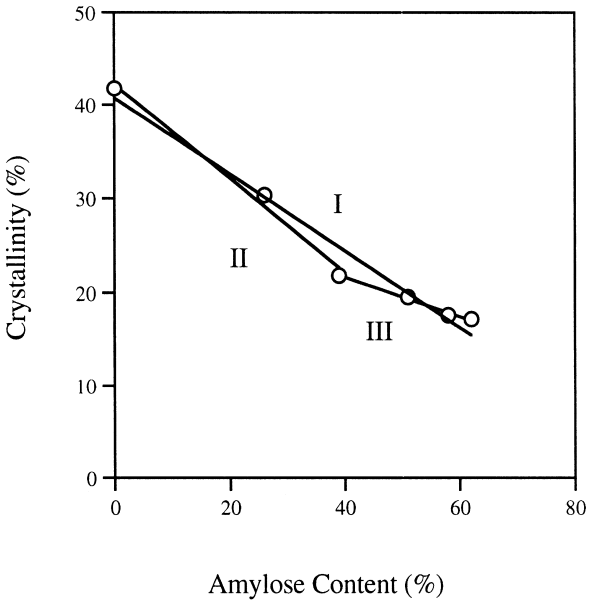

Fig. 2. The crystallinity and amylose content relationship in maize starch samples.

presence of some additional A type peaks indicate that it lies between the A- and B-type pattern. At 23° 2θ, only one peak appears and the peak at ~18° is converted into a shoulder. These are indicative of the A pattern, while the peaks at 5° 2θ are characteristic of the B pattern. Thus MSB is classed as C-type. Overall, with an increase in amylose content, the peak at 15° 2θ becomes progressively weaker and broader, while the peaks at 17° and 18° 2θ merge to a large peak, and line-widths are significantly attenuated. Similarly, the peak at 22° decreases in intensity and splits into two peaks. With continuing increase in amylose content, the peak at $2\theta = 22°$ undergoes further enlargement of line-width and split down. These results clearly indicate that a transition of crystallinity types in maize starch granules from A to B via a C type occurrs at approximately 40% amylose.

It is noteworthy that when amylose content increases, scattering intensity for almost every diffraction peak decreases, except that at $2\theta = 20°$. By comparison of this trend with the pattern for potato starch (Fig. 1) we conclude that there is an increasing amount of V-type amylose across the range 40%–84% amylose. Because the peak is common to B and V patterns, the increase in intensity suggests that the proportion of V-type in maize starch increases with increased amylose content, but the B-type is still predominant.

3.2. The effect of amylose content on degree of crystallinity of maize starches

The degree of crystallinity of the samples was measured by the method of Nara & Komiya (1983). For this evaluation, we used starch samples which had almost identical moisture contents (~10%) in order to minimize the effect of different moisture contents on crystallinity. The

Table 1
X-ray powder diffraction data of various maize starch samples

Samples	Amylose(%)	Diffraction peaks at 2θ value (° angle)							Degree of crystallinity (%)	Crystal pattern
		5°	15°	17°	18°	20°	22°	23°		
WMS	0	–	14.86* (5.96 Å)**	16.70 (5.3 Å)	17.84 (5.02 Å)	19.70 (4.50 Å)	–	22.86 (3.89 Å)	41.8	A
MSA	28	–	14.96 (5.91 Å)	16.96 (5.22 Å)	17.78 (4.98 Å)	19.70 (4.50 Å)	–	22.86 (3.89 Å)	30.3	A
MSB	40	5.24 (16.85 Å)	14.66 (6.04 Å)	16.80 (5.27 Å)	–	19.46 (4.56 Å)	–	22.60 (3.90 Å)	21.8	C
MSC	56	5.30 (16.66 Å)	14.46 (6.12 Å)	16.74 (5.29 Å)	–	19.50 (4.55 Å)	21.84 (4.07 Å)	23.60 (3.77 Å)	19.5	B
MSD	65	5.60 (15.77 Å)	14.68 (6.03 Å)	16.96 (5.22 Å)	–	19.60 (4.53 Å)	21.98 (4.04 Å)	23.78 (3.74 Å)	17.6	B
MSE	84	5.40 (16.35 Å)	14.42 (6.14 Å)	16.94 (5.23 Å)	–	19.60 (4.53 Å)	21.90 (4.05 Å)	23.80 (3.74 Å)	17.2	B

*Relative intensity.
**The figures in parentheses represent interplar spacings.

calculated crystallinities show a strong correlation with amylose content (Table 1), the degree of crystallinity being inversely proportional to the amylose content. WMS, which has no amylose, has the highest crystallinity (41.8%), while MSE with 84% amylose content has the lowest (17.2%). Fig. 2 is a plot of crystallinity vs amylose content.[1] Three regression curves were made from different amylose ranges in order to compare the correlation between amylose content and crystallinity. This analysis reveals that the decrease in crystallinity with increased amylose content exhibits a two stage correlation pattern (Fig. 2 and Table 2). A linear relationship between crystallinity and amylose content was found with amylose content ranging from 0% of WMS to 40% of MSB. Crystal type changed from A to C, and crystallinity decreased rapidly [slope of line II (Fig. 2) in regression equation is -0.503]. The high correlation factor ($r = 0.995$) suggests that amylose content plays a role in reducing crystallinity, or at least is not involved in crystallite formation up to 40%. When amylose content further increases from 40% (MSB) to 84% (MSE), the crystal type alters from C to B, crystallinity also decreases, but to a lesser degree (slope of line III (Fig. 2) in the regression equation is -0.208, the correlation factor $r = 0.995$). These results of course also indicate that the amylopectin content has a significant positive correlation with the degree of crystallinity. This is to be expected, as crystallinity in a typical cereal starch ($\approx$ 28% amylose) has been attributed largely to the formation of double helices in amylopectin (Zobel, 1988). Why should these be such a change in slope? From the lower correlation factor ($r = 0.985$) for a linear decrease in crystallinity (line I, Fig. 2), we conclude the change is real, although the number of data points is limited. Apparently, amylose is less effective in reducing the crystallinity of B-type, compared to A-type starch. This will be discussed later.

3.3. The effect of hydration on crystallinity and crystal types of maize starches

In Fig. 3 X-ray diffraction spectra of hydrated maize starch with different amylose content are displayed. Although these hydrated starch samples still have the same X-ray diffraction types as the original examples (cf. Fig. 1), the diffraction peaks become sharper. There is a decrease in the amorphous regions. This striking improvement in resolution and calculated results indicates that the crystallinities have increased significantly (Fig. 3 and Table 3). With increased amylose, the shoulder at 24° 2θ becomes more prominent and finally develops into a peak. At a high hydration level (~30%), the C-type pattern of MSB still retains the transition between A- and B-types. The shoulder peak at 18° 2θ and broad peak still retain A type characteristics, and the peak at 5° 2θ strongly shows the B pattern. The degree of hydration does not change the crystal type, indicating that the C type is an inherent characteristic of MSB rather than being caused by environment factors.

Fig. 4 compares the change of the degree of crystallinity of the maize starches before and after hydration. The crystallinity is the highest in WMS and lowest in MSE before and after hydration. Though the degree of increase differed considerably among the starches

Table 2
Correlation between crystallinity and amylose content over different ranges of amylose content in maize starches

Line	Amylose range	Equation	r
I	WMS–MSE	$y = -0.407x + 40.725$	0.985
II	WMS–MSB	$y = -0.503x + 42.193$	0.995
III	MSB–MSE	$y = -0.208x + 29.930$	0.995

[1] Amylose content determined by HPSEC of debranched starches. We have shown (Cheetham & Tao, 1997) that the iodine binding method significantly overestimates amylose levels in high-amylose starches.

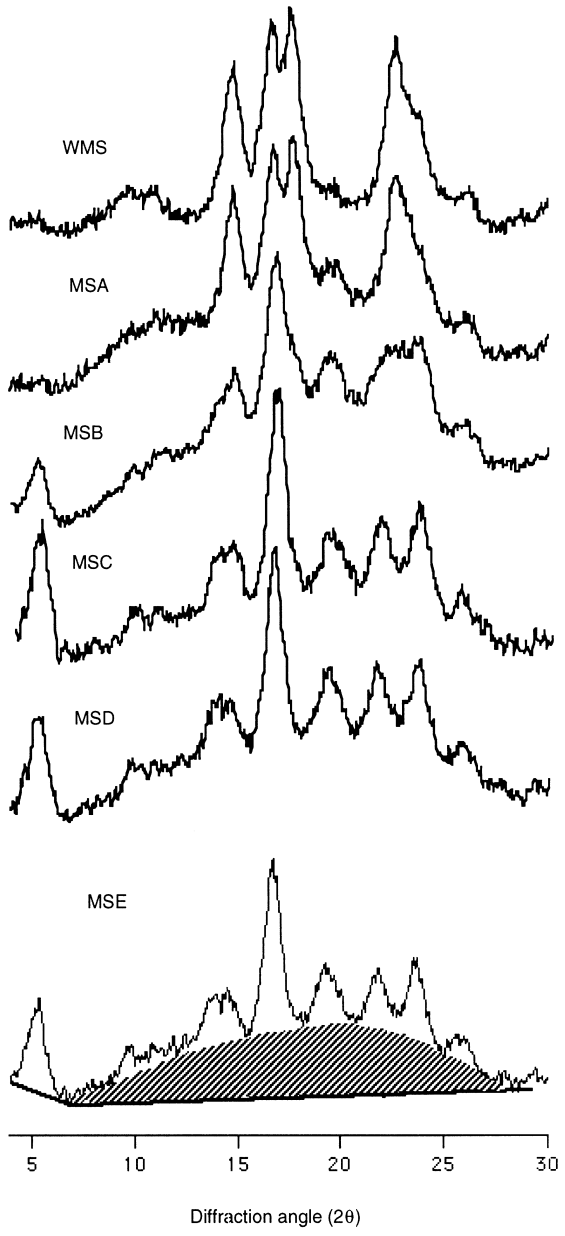

Fig. 3. Wide-angle X-ray powder diffraction patterns for maize starches with different amylose contents after 18 days hydration.

(WMS > MSA > MSB > MSC > MSD > MSE) the two curves are almost parallel, i.e. the absolute differences are similar. This is a reflection of the fact that each starch hydrates to almost exactly the same equilibrium moisture value (≈ 30%) from the same starting value (≈ 10%) and also indicates that crystallinity increases linearly with moisture content, i.e. the 'driving force' for increased water uptake is the formation of crystallites.

3.4. The effect of iodination on the degree of crystallinity

The X-ray powder diffractograms for MSA, MSE, and WMS and their iodine complexes are presented in Fig. 5. Crystallinities and X-ray diffraction data are shown in Table 3. Iodine vapour was maintained in the desiccator during the entire period (4 months) of treatment. There was no further uptake after this period. Iodine treated WMS was light yellow in colour. Its increase in weight was about 0.5%, while MSA and MSE were dark brown, and increased in weight by 2.8% and 9.4%, respectively, i.e. closely proportional to their amylose content.

After iodination, all maize starches still presented the same X-ray patterns. However, the degree of crystallinity decreased, presumably with the formation of a V-type complex. The influence of iodination on crystallinity of starch varied with amylose content. WMS, which is free of amylose, after iodination, retained its native X-ray diffraction spectrum, with little change (1.4%) in the degree of crystallinity. There is a small difference between MSA and MSA-iodine, though Fig. 5 shows that the intensity of each diffraction peak decreases slightly. In MSE, several diffraction peaks disappear. Only two distinct peaks at $2\theta = \sim 20^\circ$ and 17° survive. The loss of the peak at 5°2θ (Fig. 5d) indicates possible conversion of crystal types. An increase in relative intensity of the peak at $2\theta = \sim 20^\circ$ is attributed to the presence of the V-type complex, by comparison with literature V-type values (Zobel, 1964). It has also been demonstrated that maize starch, exposed to iodine vapour and moisture, develops the V-pattern (Zobel, 1992). The degree of crystallinity in MSA decreased from 30.3% to 26.3% (about 13.2%), and that of MSE from 17.2% to 13.4% (about 22.1%) (Table 3). Induction of the amylose-iodine complex apparently disrupts the

Table 3
Comparison of X-ray diffraction data of various maize starch samples before and after iodination

Samples	2θ values (° angle)							Degree of crystallinity (%)	Crystal pattern
	23°	22°	20°	18°	17°	15°	5°		
WMS	22.66 (3.89 Å)	–	19.70 (4.50 Å)	17.84 (5.02 Å)	16.70 (5.29 Å)	14.86 (5.96 Å)	–	41.8	A
WMS-I_2	22.86 (3.89 Å)	–	19.70 (4.50 Å)	17.56 (5.05 Å)	16.78 (5.28 Å)	14.74 (6.01 Å)	–	41.2	A
MSA	22.86 (3.88 Å)	–	19.70 (4.50 Å)	17.78 (4.98 Å)	16.96 (5.22 Å)	14.96 (5.91 Å)	–	30.3	A
MSA-I_2	22.98 (3.86 Å)	–	19.88 (4.46 Å)	18.02 (4.92 Å)	17.12 (5.18 Å)	15.04 (5.89 Å)	–	26.3	A
MSE	23.80 (3.74 Å)	21.90 (4.05 Å)	19.60 (4.53 Å)	–	16.94 (5.23 Å)	14.42 (6.14 Å)	5.40 (16.35 Å)	17.2	B
MSE-I_2	–	–	19.684 (4.51 Å)	–	16.98 (5.22 Å)	–	–	13.4	B + V

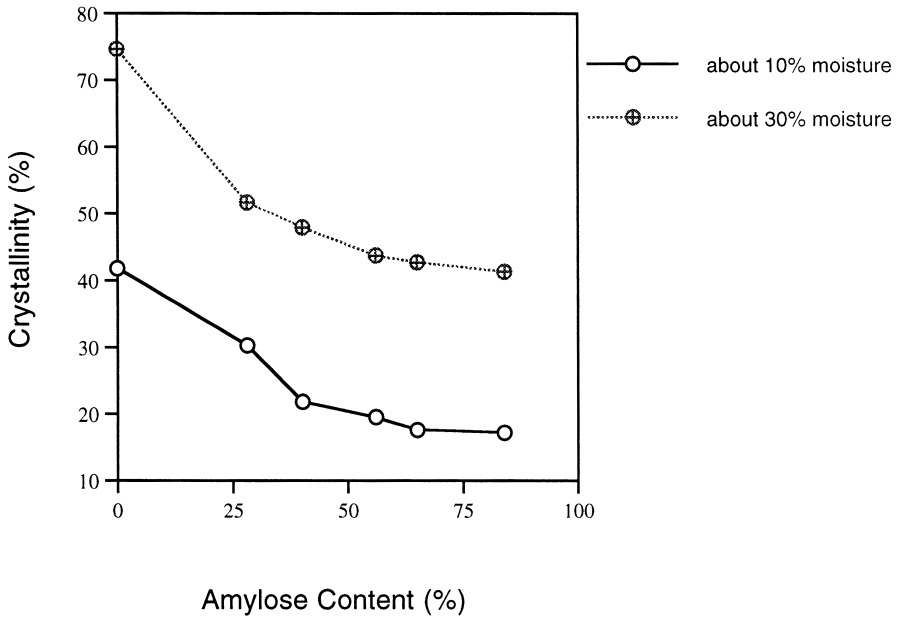

Fig. 4. The effect of amylose content on crystallinity of maize starch at different moisture contents.

crystallinity of the granules. In support of this, iodine has been shown displace water from V-amylose readily and the iodine complex is stable at high humidity (Saitô et al., 1991). Alternatively, if iodine molecules are incorporated into crystallite regions, they could cause disruption of some of the existing double helical structures, lead to reorganisation of the crystallite region, and thus change the crystalline to amorphous ratio in starch granules. This latter explanation seems unlikely, however, as there is little effect on the highly crystalline WMS.

3.5. The relationship between average chain length of amylopectin and crystal types

In our previous work, WMS, MSA, MSB, MSC, MSD, MSE were studied in order to establish the correlation between amylose content and amylose molecular size, and the fine structure of corresponding amylopectin (Cheetham & Tao, 1997). Table 4 shows these maize starch crystal types and some data on chain length of the respective amylopectins. From these data, we conclude that chain length has a significant effect on crystal form. From WMS to MSB, the average chain length of amylopectins changes from 20 to 25, and the crystal type changes from A to C, i.e. a small change in average chain-length of amylopectin causes a large change in crystal type and crystallinity. In contrast, from MSB to MSE, the transition from C to B type involves an average chain length increase from 25 (MSB) to 35 (MSE). MSB, with amylopectin of average chain length of about 25, appears to be the boundary for A and B type starch, containing some common features of A and B (Fig. 1). This indicates that long chains favour formation of B type crystallinity and short chains benefit A type. The transition of crystal type A → C → B accompanying the increase in average chain length is in agreement with Hizukuri's conclusions (Hizukuri, 1985).

The F2/F1 ratio has a strong correlation with crystallinity, the correlation factor being 0.99 and 0.93 at two moisture contents (Fig. 6). The higher the F2/F1 ratio, the higher the crystallinity. As determined by our previous work

Table 4
The relationship between crystal type, degree of crystallinity, and hydration levels of maize starches

Sample	Moisture content about 10%		Moisture content about 30%		Amylopectin * %	Amylopectin average chain-length	F2/F1 * (mole% basis)
	Crystal type	Crystallinity (%)	Crystal type	Crystallinity (%)			
WMS	A	41.8	A	74.6	100 (100)	20	10.6
MSA	A	30.3	A	51.6	72 (74)	23	8.33
MSB	C	21.8	C	47.9	60 (61)	25	5.07
MSC	B	19.5	B	43.7	44 (49)	27	4.95
MSD	B	17.6	B	42.7	35 (42)	30	3.93
MSE	B	17.2	B	41.3	16 (38)	35	3.77

* The data was derived from our previous work (Cheetham & Tao, 1997). Amylopectin contents were obtained from amperometric iodine binding and HPSEC of debranched starches (the data in brackets), respectively. F2 and F1 represent short chain and long chain fraction of debranched amylopectin, respectively.

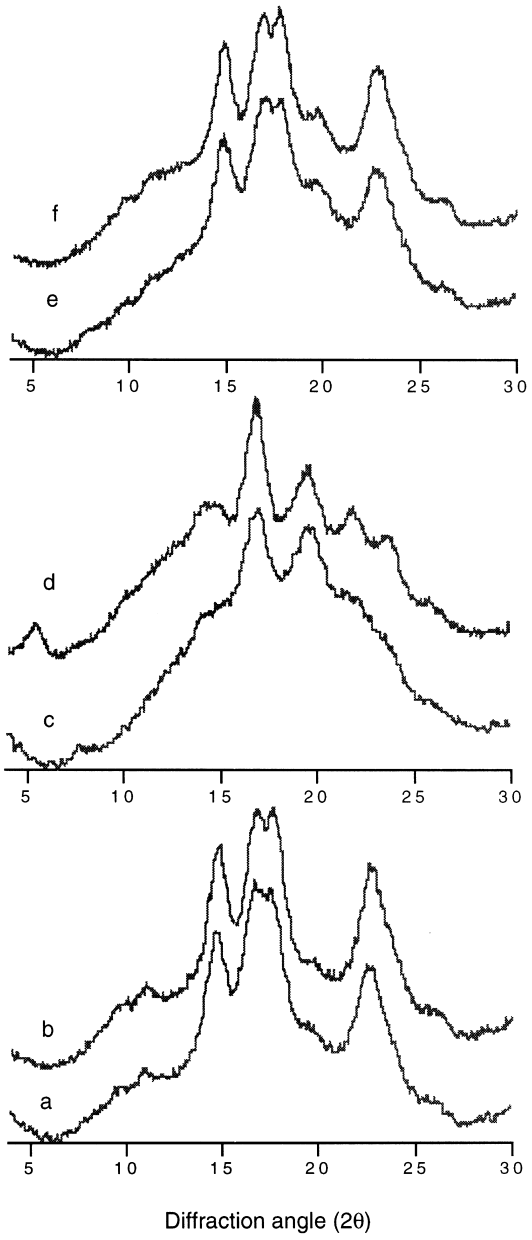

Fig. 5. The effect of iodination on the X-ray powder diffraction spectra of maize starches with different amylose contents. (a) WMS-iodine; (b) WMS; (c) MSE-iodine; (d) MSE; (e) MSA-iodine; (f) MSA.

(Cheetham & Tao, 1997), F2 is composed of dp 10–13 short chains, so these results suggest that short chain fraction of the amylopectin plays an important role in the formation of crystallinity. Consistent with such a proposal are the studies on lintnerisation (heterogeneous mild acid hydrolysis) of potato starch granules. This leaves a crystalline residue essentially consisting of linear chains of $\overline{DP}$ 15 (Robin et al., 1974). Similar material has been obtained after lintnerisation of an amylopectin gel (Ring et al., 1987). The former authors proposed that these are the short chains of amylopectin, and are largely responsible for crystallinity in the original granules.

A recent study on the influence of amylose content on granule structure used small-angle X-ray scattering to measure differences in electron density profiles of granules (Jenkins & Donald, 1995). The authors concluded that: (i) the amylopectin cluster size was invariant ($\approx$ 9 mm) across the range of amylose contents, i.e. though these was a significant variation in the relative sizes of crystalline amorphous lamellae, the combined repeat distance remained constant; (ii) the crystalline region size increased with increasing amylose content (despite the fact that amylopectin is generally accepted as being responsible for granule crystallinity). The explaination was based on the relative chain length of the amylopectins involved in the crystalline lamellae. Amylopectin A-chain length has been shown in a range of species to increase as the amylose content increases (Hizukuri, 1985; Hizukuri et al., 1983). Similar results have been obtained by ourselves (Cheetham & Tao, 1997). Thus where the A-chain length is small (low amylose, A type), the crystalline lamellae are small, and the amorphous lamellae are relatively large. Where A chains are large (high amylose, B-type), crystalline lamellae are relatively large, and the amorphous portion relatively smaller. Jenkins and Donald also propose that amylose disrupts the crystalline packing of amylopectin, quoting as supporting evidence the apparent reduction in crystalline lamellae electron density with increasing amylose content.

To this we add our conclusions based on the different effects of amylose content on A- and B-type crystallinity mentioned above. The A-type crystallinity decreases linearly in native starches with amylose levels between 0% (WMS) and 40% (MSB). In MSB, A-type is greatly reduced, being largely replaced by B-type, to yield a C-type diffraction pattern. From MSB-MSE the decrease in crystallinity is again linear, but of different slope. The same pattern is evidence in fully-hydrated ($\approx$ 30% moisture) samples (Fig. 4).

4. Conclusions

The crystal type of maize starches changes from A to B via C with an increase in amylose content, the transition occurring at about 40% amylose. The degree of starch crystallinity decreases with the increase in amylose content and average chain length in amylopectin, and appears to be directly proportional to the mole percent of short chain fraction of dp 10–13. Hydration of the granules leads to increases in crystallinity, but does not change the original crystal types. These results indicate that the observed crystal types are inherent to the molecular properties of granular maize starches, and are direct results of (i) the amylose content and (ii) the average chain length in the corresponding amylopectins. We believe that the results presented here have implications for the control of maize starch biosynthesis, and for geneticists wishing to produce ‘tailor-made’ starches. The trends in amylose molecular weight, and

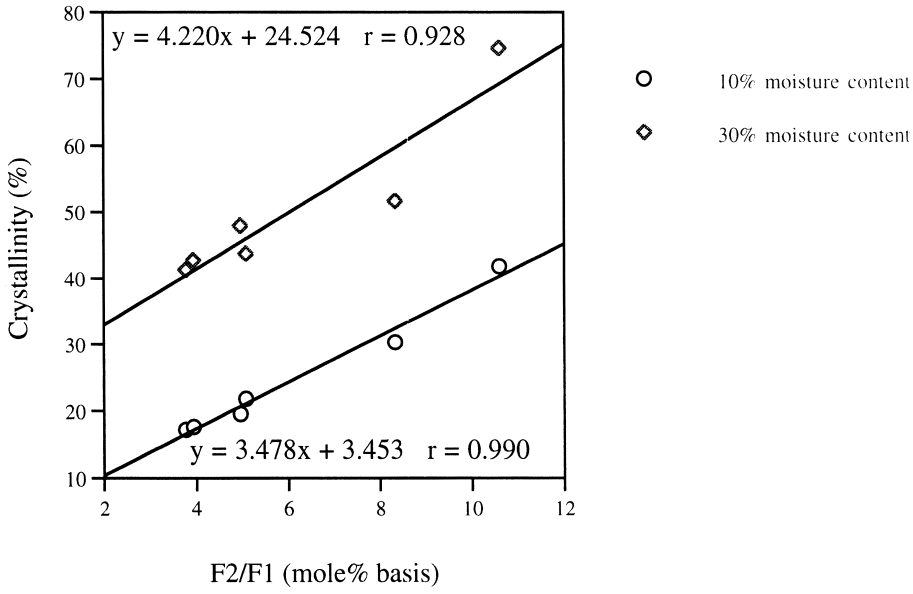

Fig. 6. The correlation between F2/F1 and crystallinity.

chain-length of amylopectin surely reflect the pattern of genetic control over these parameters.

Why there should be a change from A-type through C-type to B-type across the range of maize starches is open to speculation. The fact that the same structural features control the type of crystallinity over a range of 20 plant species (Hizukuri, 1985) is significant. Physical properties of the starch components, and especially the mole percent of the DP 10–13 short-chain fraction, appear to be more influential in determining crystalline type than the species of origin. This could be due to (i) the relative energies of double helix packing in A and B types, (ii) the inability of the enzymes involved in double helix formation to handle longer-chain amylopectins, or (iii) the disrupting influence of high levels of amylose on crystallinity. These aspects are worthy of further study.

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