Structural Basis for the Slow Digestion Property of Native Cereal Starches

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Native cereal starches are ideal slowly digestible starches (SDS), and the structural basis for their slow digestion property was investigated. The shape, size, surface pores and channels, and degree of crystallinity of starch granules were not related to the proportion of SDS, while semicrystalline structure was critical to the slow digestion property as evidenced by loss of SDS after cooking. The high proportion of SDS in cereal starches, as compared to potato starch, was related to their A-type crystalline structure with a lower degree of perfection as indicated by a higher amount of shortest A chains with a degree of polymerization (DP) of 5−10. The A-type amorphous lamellae, an important component of crystalline regions of native cereal starches, also affect the amount of SDS as shown by a reduction of SDS in lintnerized maize starches. These observations demonstrate that the supramolecular A-type crystalline structure, including the distribution and perfection of crystalline regions (both crystalline and amorphous lamellae), determines the slow digestion property of native cereal starches.

Introduction

Cereal endosperm starch granules are the main energy storage form in cereal grains and the major energy-providing material in human diets. The rate of glucose release from food products may play an important role in human health by helping to maintain proper blood glucose levels and to provide extended energy absorption. Studies[1,2] have shown that obesity, diabetes, and coronary heart disease may be associated with long-term consumption of foods with high glycemic index (GI). Starch, as the main carbohydrate in starchy foods, has been classified as rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) to specify the quality of starch in food products and purported differences in physiological effect.[3,4] The glycemic index (GI) of a starchy food is related to the amount of RDS,[5] whereas the SDS may be more desirable for healthy food products. Therefore, improving food quality with higher amounts of SDS is becoming an area of interest for some food companies, and, due to the low amounts of SDS in processed food products, fundamental research is needed to understand the mechanism and structural bases for SDS.

Enzymatic hydrolysis of starch granules has long been used as a tool to understand the structure of starch granules.[6] Enzymatic hydrolysis of native starch is a solid-solution two-phase reaction in which the enzyme needs first to diffuse toward and binds the solid substrate, and then cleaves the glycosidic linkages. Although both the enzyme binding and the product release from solid substrates affect the overall rate of hydrolysis, the structure of substrate usually dominates the reaction rate as it affects enzyme diffusion (due to starch granule porosity), binding, and bond cleavage. Investigations have shown that starch granule organization has different levels of structure related to enzymatic hydrolysis:[7] granular structure, supramolecular structure, and molecular structure. Granular structure mainly includes shape, size, and porosity (pores and channels within starch granules). Most cereal starches have pores and channels that are considered as the basis for their inside-out digestion patterns. The supramolecular structure includes the arrangement of crystalline and amorphous materials within the starch granule (growth rings), and organization of crystalline and amorphous lamellae in the hard shell of the growth ring,[8] the crystalline type, perfection of crystallites, and degree of crystallinity. For cereal starches, the growth rings comprised of A-type semicrystalline regions and amorphous regions are arranged in concentric layers from the center to the surface of the starch granules. The molecular structure mainly refers to the fine structure of amylopectin and amylose. Normally, amylopectin fine structure determines the crystalline type and its perfection in native starch granules. Because amylopectin is the organizer of starch granules and the major component in normal cereal starches, its fine structure is the key to understanding the structure−digestion relationship. Amylose, on the other hand, as shown from our research results,[9] does not have a significant impact on the slow digestion property of normal maize starch. Depending on the botanical source of starch granules, different levels of structure may govern their hydrolysis pattern and rate. For example, both crystalline type and the surface property of potato starch are associated with its resistance to α-amylase hydrolysis, whereas the supramolecular structure is normally the major controller for enzymatic hydrolysis of native cereal starches.[6]

In our previous study,[9] we showed that native cereal starches are ideal SDS (>50%), and the slow digestion property is realized by a layer-by-layer inside-out (radial) digestion process through a mechanism of side-by-side (tangential) even digestion of amorphous and crystalline regions of starch granules. Although the crystalline regions were indicated to be essential for the slow digestion property of cereal starches, the structural basis has not been studied. This is perhaps due to the complexity

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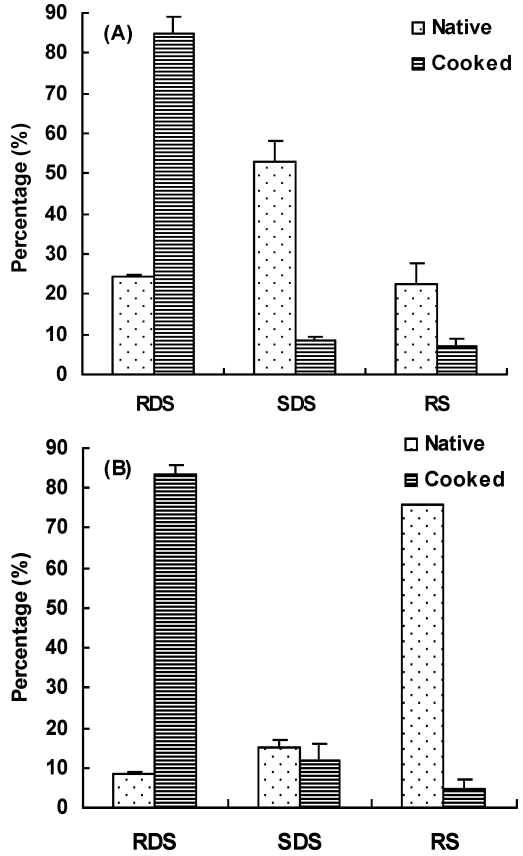

Figure 1. Digestion profiles of native and cooked (A) normal maize and (B) potato starches. RDS, SDS, and RS, respectively, represent rapidly digestible starch, slowly digestible starch, and resistant starch based on the Englyst assay.

Table 1. Englyst Test Results of Cooked (in a Boiling Water Bath for 20 min) Starches

starch type	RDS (%)	SDS (%)	RS (%)
normal maize	84.7 ± 0.62	8.3 ± 1.85	6.9 ± 1.23
waxy maize	88.5 ± 3.39	6.6 ± 1.23	4.9 ± 2.15
rice	88.0 ± 2.16	8.1 ± 4.62	3.9 ± 2.46
wheat	81.3 ± 3.70	13.1 ± 2.47	5.6 ± 1.23
potato	83.4 ± 2.46	11.6 ± 4.62	4.9 ± 2.15

of starch granule structure and organization, particularly the role of amorphous regions, which include the amorphous growth ring (also called the amorphous background) and the amorphous lamellae within the crystalline ring. The main purpose for the current study was to understand the structural basis of native cereal starches that determines their slow digestion property.

Experimental Section

Materials. Normal maize starch, potato starch, and wheat starch were obtained from Tate & Lyle (Decatur, IL), Penford Food Ingredients Co. (Englewood, MO), and MGP Ingredients (Atchison, KS), respectively. Rice and waxy maize starches were purchased from Sigma Chemical Co. (St. Louis, MO). α-Amylase (EC 3.2.1.1) type VI-B from porcine pancreas (19.6 U/mg), amyloglucosidase (EC 3.2.1.3) from Rhizopus mold (21 100 U/g), pepsin (EC 3.4.23.1) from porcine stomach mucosa (1:2500, 51 U/mg), pancreatin from porcine pancreas, invertase (EC 3.2.1.26) grade VII from Bakers yeast (355 U/mg), and guar gum were purchased from Sigma Chemical Co. (St. Louis, MO). Glucose assay reagents and isoamylase (EC 3.2.1.68, 250 U/mL) were from Megazyme International Ireland Ltd. (Wicklow, Ireland).

Methods. *Enzymatic Starch Hydrolysis and Amylose Measurement.* RDS, SDS, and RS starch fractions were measured on the basis of the Englyst test,[3] and values were expressed on a dry weight basis. Starch hydrolysis was also measured using an in vitro enzymatic hydrolysis method developed for this study.[9] Amylose contents were measured using a ConA kit from Megazyme International Ireland Ltd. (Wicklow, Ireland).

Table 2. Percentage of Different Fractions in Total Starch Debranched Profiles of Different Starch Samples[a]

starch type	AM	LC	SC	SC/LC	SAC
normal maize	18.7	25.5	74.5	2.92	12.9
waxy maize	1.2	24.6	75.4	3.07	14.2
rice	12.3	28.3	71.7	2.53	15.2
wheat	18.9	25.2	74.8	2.97	15.6
potato	11.9	40.1	59.9	1.49	10.5

[a] For amylose (AM), the value of percentage is based on total starch, and for other fractions (LC, SC), the value of percentage is based on amylopectin.

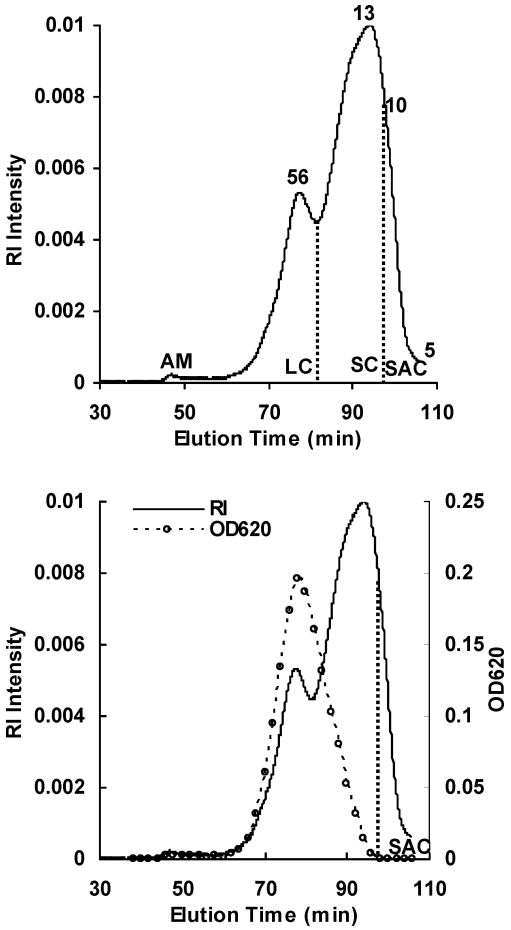

Figure 2. Debranched total starch HPSEC profile of waxy maize starch. AM is amylose, and debranched amylopectin is composed of LC and SC fractions. Iodine reaction with debranched starch is shown in the right panel, and a short A chain (SAC) fraction is delineated from SC fraction based on the iodine reaction reaching baseline.

Starch Lintnerization. Lintnerization of normal native maize and potato starches was based on the procedure of Robin et al.,[10] in which 1.67% starch was incubated in 2.2 N HCl at 35 °C for different periods (3, 7, 15 days) to obtain starch samples with different degrees of lintnerization (for maize, 60%, 75%, and 85% based on weight loss; for potato, lintnerized for 21 days). Samples were centrifuged at 5000 rpm for 10 min to remove the HCl, and the precipitated starch was washed with deionized water until pH was neutralized. Each residue was dehydrated with 100% ethanol and dried in an incubator (35 °C).

X-ray Powder Diffraction. A Kristalloflex diffractometer (Siemens Corp., Munich, Germany) was used to examine the crystalline property

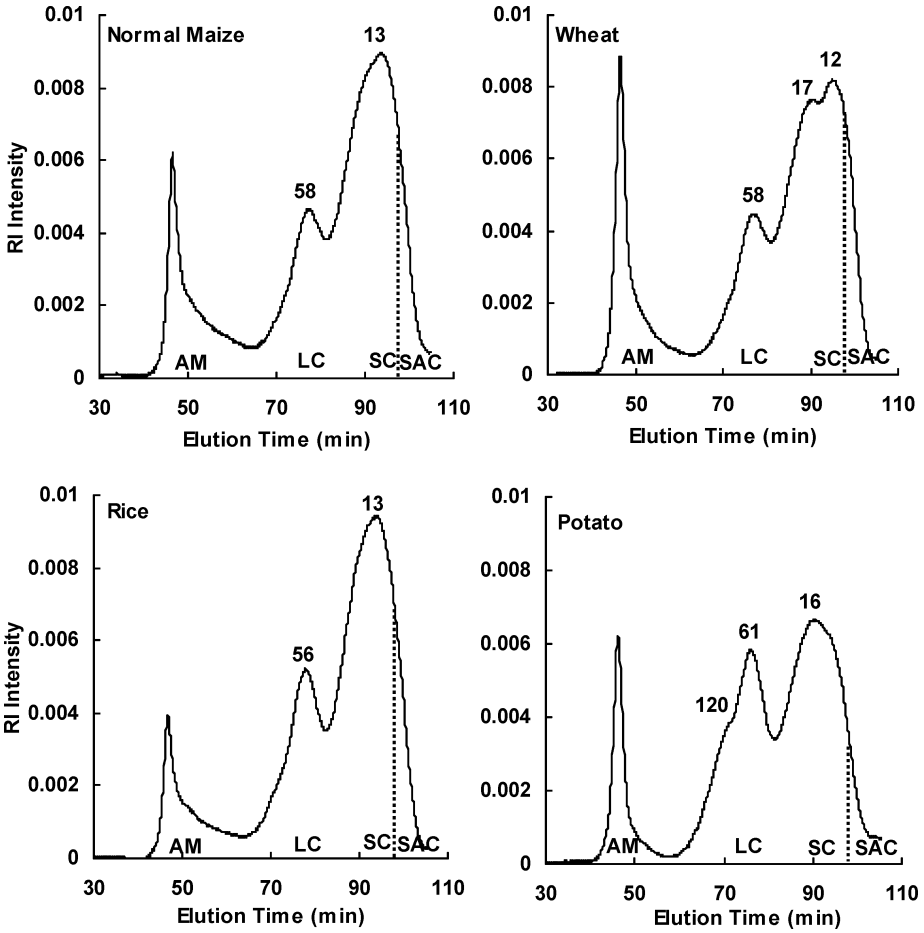

Figure 3. Debranched total starch HPSEC profiles for normal maize, wheat, rice, and potato starches. The number above the peak is the degree of polymerization value (DP). AM, amylose; LC, long B chain fraction; SC, B_1 and A chain fraction; SAC, shortest A chain fraction (DP < 10).

of starch samples (native starches, prehydrolyzed starches, and lintnerized starches) as described by Zhang et al.[9]

Chromatographic Analysis. Chain length distribution profiles of debranched commercial normal maize, waxy maize, wheat, rice, and potato starches, and lintnerized maize and potato starch samples, were analyzed using a high performance size-exclusion chromatography (HPSEC) system based on the method of Zhang et al.[9] The iodine reaction[9] was also carried out to delineate the shortest A chain (SAC) fractions.

Scanning Electronic Microscopy (SEM). Starch samples with different degrees of lintnerization were dehydrated and dried in a hot air oven (50 °C, overnight) and were examined on the basis of the procedure of Zhang et al.[9]

Statistical Analysis. Common statistic analysis was carried out using statistic tools from Microsoft Excel, and the *P* value was obtained by comparing the calculated *t* value:

$$t = \frac{R \times \sqrt{df}}{\sqrt{1 - R^2}}$$

where *R* is the correlation coefficient, and *df* is the degree of freedom (sample number −2), with two tails probability from the table of percentage points of *t* distribution.

Results and Discussion

Digestion Property of Cereal and Potato Starches. Native A-type cereal starches are ideal slowly digestible starches, while B-type potato starch is resistant to enzymatic digestion.[9] However, when the native starch was cooked in a boiling water bath for 20 min before the Englyst test, the slow digestion property was lost with a huge increase of RDS (Figure 1), and the difference in digestion properties between A-type cereal starch and B-type potato starch also disappeared. Similar digestion properties were also shown for rice, wheat, and waxy maize starches after cooking (Table 1). Because the cooking process completely destroys the semicrystalline structure of native starch granules, the loss of SDS and an increase of RDS indicate that the crystalline structure of A-type cereal starches is critical for their slow digestion property.

Starch Debranched Profiles. HPSEC with RI detection showed three major peaks in the debranched profile of waxy maize starch. The eluted fraction at the void volume is amylose (1.2% of total peak area) (Figure 2, AM). The following two fractions (long chain fraction, LC, and short chain fraction, SC) are debranched amylopectin molecules. The shortest A chain (SAC) fraction with DP 5−10 was also delineated from the SC fraction for the purpose of estimating the perfection of crystallites, because these linear chains cannot form stable double helices.[11] Experimentally, a zero reading at 620 nm was observed when the SAC fraction was reacted with iodine solution (Figure 2, right panel).

Similar debranched patterns of amylopectin (LC, SC, SAC fractions) were shown for other starches (Figure 3), and they are consistent with literature reports on these starches.[7,12,13] Normal maize, waxy maize, rice, and wheat starches are A-type starches, and only minor differences are revealed when chain length profiles are compared (Table 2). A ratio of ∼3 and ∼1.5

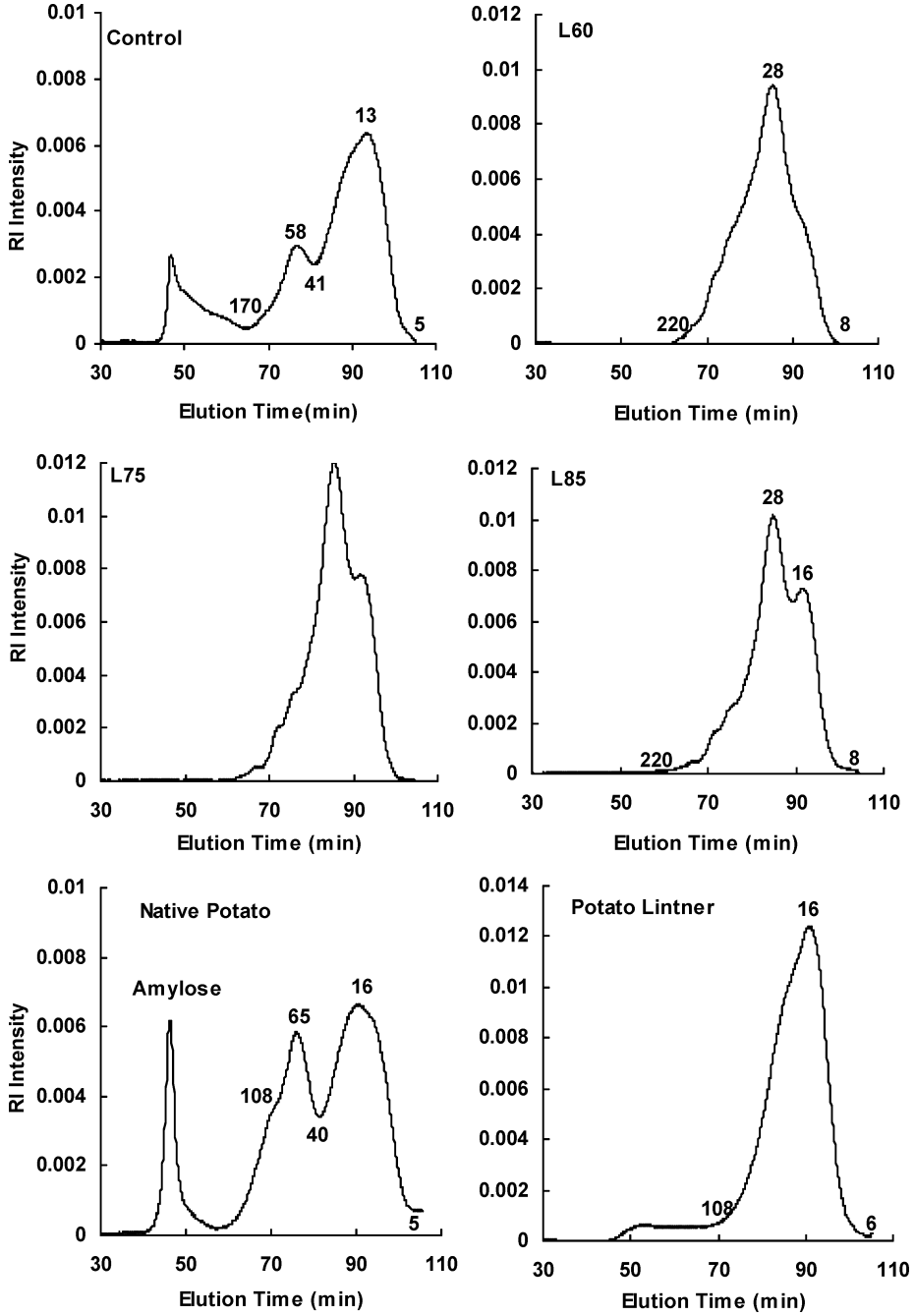

Figure 4. HPSEC profiles of lintnerized normal maize and potato starches. L60, L75, and L85, respectively, represent 60%, 75%, and 85% degrees of lintnerization. The number indicates the DP value at each peak. The control starch was debranched normal maize starch. For potato starch, the degree of lintnerization is 82%.

of fraction SC to fraction LC for cereal and potato starches, respectively, shows that B-type potato starch has a higher percentage of LC chains as compared to A-type starches. The chain length of each fraction is also longer in the B-type potato than in the A-type cereal starches (Figure 3). The difference in chain length distribution is typical of A- and B-type starches and reflects differences in their basic compositions regarding different categories of chains and resulting supramolecular structures.[14]

Amylopectin Chain Length Distribution and Slow Digestion Property. It is well known that amylopectin is the molecule that forms the crystallites in starch granules and that the organization and type of starch crystalline structures are highly correlated with its fine structure. Based on the study of Hizukuri[15] and the cluster model of Robin et al.,[10] amylopectin fine structure includes A, B (B_1–B_4), and C chains in which A and B_1 chains (also called S chains) are the major components of amylopectin crystalline regions. High and low amounts of S chains are associated with A- and B-type X-ray diffraction patterns,[7] respectively. Generally, fraction SC in the total debranched starch profile is composed of A and B_1 chains, and fraction LC is composed of B_2, B_3, and possibly B_4 chains.[15]

The fine structure of amylopectin, especially the A+B_1 (fraction SC) chains that form the crystalline regions, is essential for the slow digestion property of native cereal starches. All of the cereal starches tested showed a higher proportion of SDS (43−53%) and more proportion of fraction SC (Table 2) as compared to potato starch with the lowest SDS (15.2%) and lowest ratio of fraction SC to fraction LC, suggesting SDS is closely associated with the proportion of fraction SC chains that mainly form double helices and crystalline lamellae within the crystalline regions. This result supports our previous prediction

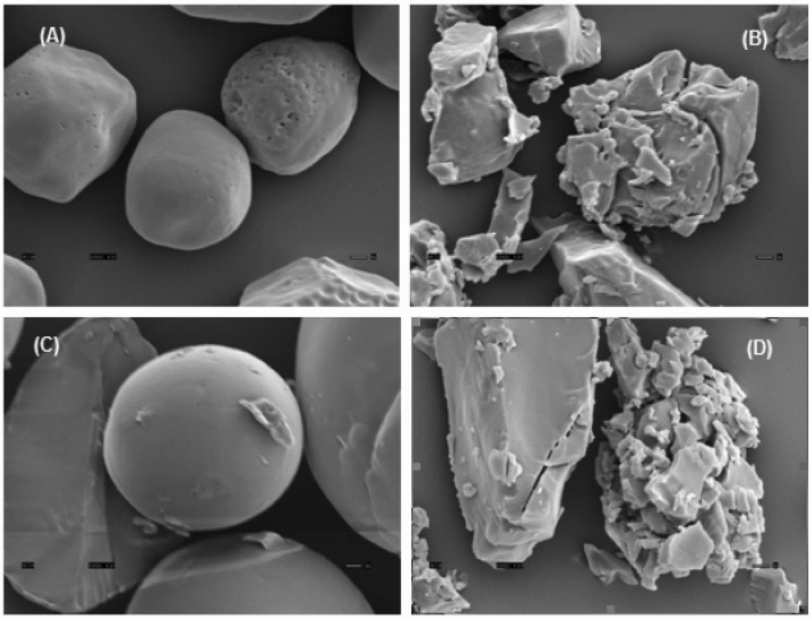

Figure 5. SEM images of normal maize and potato starched after lintnerization. (A) Control maize, (B) lintnerized maize, (C) control potato, and (D) lintnerized potato.

that the crystalline region is the major determinant for the slow digestion property of native cereal starch.[9] However, there was no significant correlation ($R = 0.305$, $P > 0.05$) between the proportion of fraction SC and degree of crystallinity, suggesting not all $A+B_1$ (fraction SC) chains participate in the crystalline lamellae in an ordered crystalline structure. Similar to our previous results,[9] no correlations were found between amylose content and RDS, SDS, or RS.

The shortest A chains with a DP of 5−10 cannot form stable double helices,[11] and thus they are likely to be easily attacked by enzymes leading to a significant correlation with RDS ($R = 0.97$, $P < 0.001$), which is consistent with literature reports.[16,17] The reason is that the shortest A chains may disrupt the formation of an ordered crystalline structure and negatively affect the perfection of amylopectin crystalline structure. Thus, we hypothesize that the proportion of shortest A chains (Figures 2 and 3, fraction SAC) can be considered as a quantitative indicator of crystallite perfection of cereal starches: a higher proportion of the fraction SAC results in less perfect crystallites. According to Gérard et al.,[18] a high amount of short A chains of DP 6−11 suggests an accumulation of dangling chains or defective crystallites that favor a high initial hydrolysis rate. Thus, cereal starches with lower perfection of crystalline structure not only have a relative high amount of RDS, but also their slow digestion property may be affected by the perfection of their crystallites.

B_2, B_3, and possibly B_4 chains (LC), which are used to connect adjacent clusters, are an important component determining the semicrystalline structure of starch granules. B-type starch (potato) has a higher proportion of fraction LC with longer chains, while A-type cereal starches have a lower proportion of LC with shorter chains (Table 2). According to the smectic side-chain liquid-crystalline model of Daniels and Donald,[19] crystallites of B-type starch have shorter flexible spacers as compared to A-type starch. Shorter flexible spacers would decrease the mobility of starch molecules and lead to lower enzyme accessibility and high RS content (lower SDS content). Because the flexible spacers in the liquid-crystalline model[19] correspond to the amorphous lamellae, the effect of flexible spacers on enzyme digestion indicates associations between amorphous lamellae and digestion property of native starch granules.

Starch Lintnerization. The amorphous regions in native starch granules include the amorphous background (the less dense growth ring under the microscope) and amorphous lamellae (branch point regions of B chains) within the dense crystalline region. Starch lintnerization using mild acid (2.2 N HCl) selectively affects the amorphous regions of starch granules and leads to an increase in crystallinity.[20,21] In this study, lintnerized starch was used to understand the effect of amorphous regions (including both the amorphous background and the amorphous lamellae) on the slow digestion property of native cereal starches.

Amylose with high molecular weight was almost completely removed after lintnerization (Figure 4) because amylose is mainly present in the amorphous background or ring,[8,22] which is more sensitive to lintnerization.[21] Amylopectin was also cleaved into smaller molecules (Figure 4) due to susceptibility of long chains to acid hydrolysis.[23] For normal maize starch, moderate lintnerization (60%) led to one fraction with DP 28 at the peak (Figure 4) that is likely composed of singly branched chains and stubs with multiple chains. As lintnerization increased, a peak at DP 16 appeared. For potato starch, extensive lintnerization (~82%) resulted in only one fraction with a peak DP of 16. These results are consistent with literature reports[24,25] and indicate that part of the amorphous lamellae composed of B chains connecting adjacent clusters are hydrolyzed by lintnerization. The different chain length distribution between lintners from normal maize and potato starches demonstrates, as has been shown by others, that A-type amorphous lamellae are more resistant to acid hydrolysis than those of the B-type due to the tight packing with higher density[18,26] and/or high degree of branches scattered into the crystalline lamellae[14] of A-type starches. Additionally, an increase of shortest A chain length (DP = 8 as compared to DP = 5) after lintnerization (Figure 4) indicates that the original shortest chains (DP < 10), which do not form stable double helices,[11] might exist in the amorphous regions[17] as dangling chains that are susceptible to acid hydrolysis.[23] Therefore, lintnerization reduced the SAC

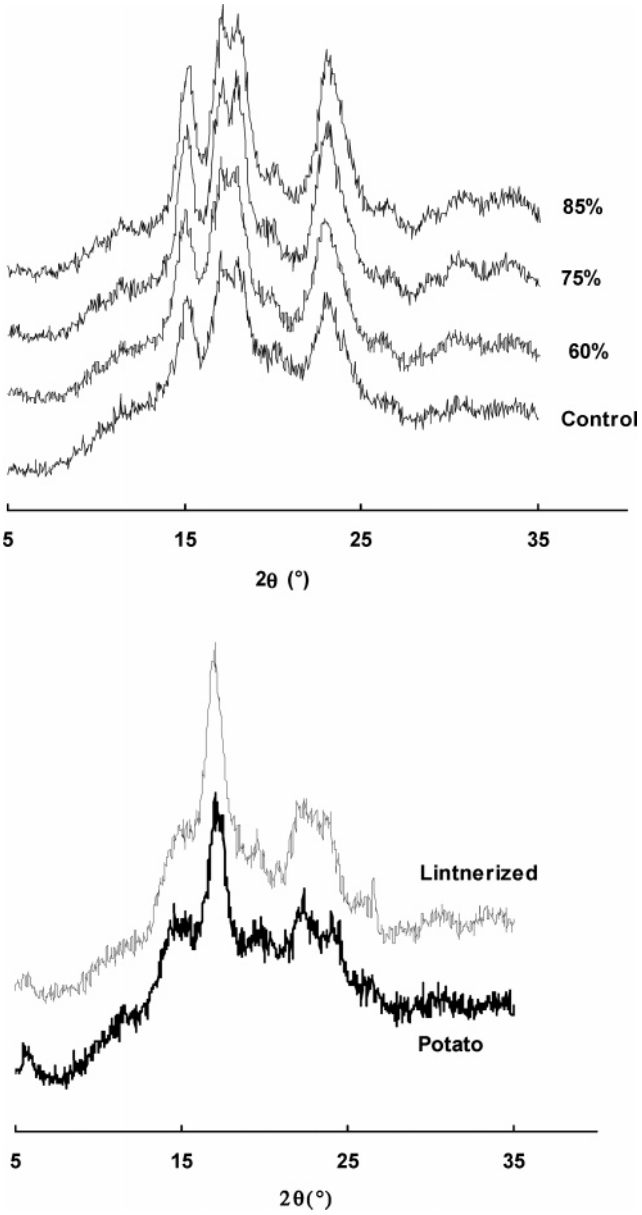

Figure 6. X-ray powder diffraction patterns of lintnerized normal maize for different degrees of lintnerization (top, A-type) and potato starches (bottom, B-type).

fraction and increased the perfection of the residual crystallites. The granular structure of starch (shape, size, surface pore, channels, and cavities) is also completely destroyed based on SEM observation (Figure 5), and large aggregates are formed by small crystalline particles.

Lintnerization also increased the degree of crystallinity (Figure 6, Table 3) without affecting the type of crystallite, which is consistent with the literature.[27] For potato starch, the crystallinity increased by 8.6%, and for maize starch, it increased by 5.5%, 7.7%, and 11.9% for lintnerization degrees of 60%, 75%, and 85%, respectively. However, the increase in degree of crystallinity was less than expected if most hydrolysis occurs only in the amorphous regions during lintnerization. This supports the view that lintnerization not only affects the amorphous regions, but also the crystalline regions, and that all parts of the starch granule might be affected.[23] Based on the study of Biliaderis,[20] there is a range of amorphous domains with structural heterogeneity with different specific orders. Considering this structural heterogeneity and the existence of crystalline lamellae, the supramolecular structure of the starch

Table 3. Englyst Test Results of Native and Lintnerized Maize and Potato Starches[a]

starch sample	RDS (%)	SDS (%)	RS (%)	crystallinity increased (%)[b]
native maize	24.4 ± 0.3	53.0 ± 4.9	22.6 ± 4.9	
L60	64.4 ± 0.0	36.3 ± 0.4	0.0 ± 0.4	5.5
L75	50.2 ± 0.0	40.1 ± 0.8	9.7 ± 0.8	7.7
L85	46.7 ± 0.8	36.3 ± 0.9	17.1 ± 0.4	11.9
native potato	8.7 ± 0.2	15.2 ± 1.8	76.0 ± 2.1	
potato-lin[c]	47.8 ± 0.0	16.5 ± 0.8	35.6 ± 0.8	8.6

[a] For maize, L60, L75, and L85 represent degrees of lintnerization of 60%, 75%, and 85%, respectively. [b] Based on X-ray diffraction, denotes actual percent increase. [c] Potato linters with 82% lintnerization.

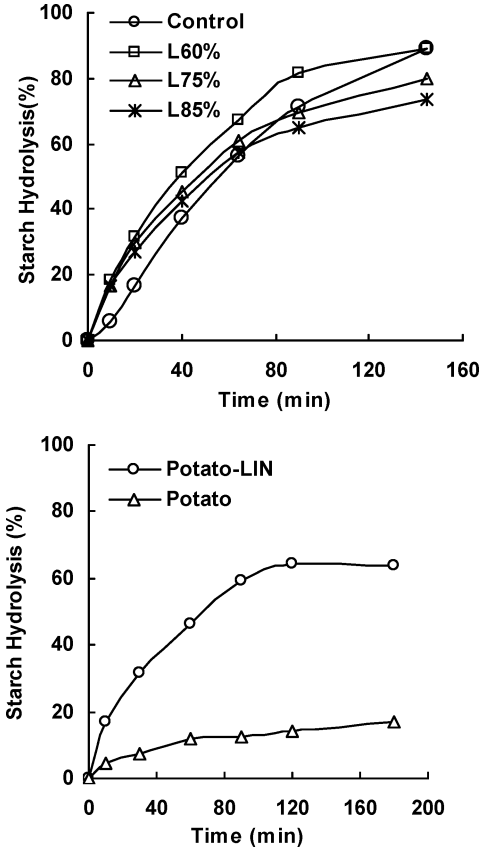

Figure 7. Enzymatic hydrolysis of lintnerized starches at 37 °C. L60, L75, and L85, respectively, represent normal maize starch at 60%, 75%, and 85% lintnerization. Control is the normal maize starch control, and potato-lin is lintnerized potato starch.

granule (i.e., the arrangement of crystalline and amorphous regions, and the perfection and order of crystallites) would greatly affect its enzyme susceptibility.

Slow Digestion Property of Lintnerized Starch. Lintnerization of maize starch granules markedly increased RDS content or initial digestion rate as compared to the control, and somewhat decreased SDS (Table 3, Figure 7). However, within the different degrees of lintnerized maize starches, a higher degree of lintnerization, with a higher perfection of residual crystallites as discussed above, reduced RDS content accompanied by a corresponding increase of RS, while SDS content was kept fairly constant. Similarly, lintnerization dramatically increased the content of RDS for potato starch with little change of SDS (Table 3). It should be noted that the RS from lintnerized normal maize starch, just like that in native normal maize starch, may not be truly resistant to enzyme digestion as RS is removed with longer digestion.[9] Yet the relative proportion of RDS, SDS,

and RS obtained with the Englyst method does suggest the substrate's property related to enzymatic hydrolysis.

Disruption of granular structure caused by lintnerization, and an increase in effective surface area (small particle size linters) for enzyme adsorption and binding, might be the reason for the increased RDS in both maize and potato lintners because initial amylolysis of starch granules is a function of surface area.[28] On the other hand, as compared to the controls, the unchanged SDS content for potato lintners and the significant decrease (~15%) in SDS content for maize lintners (Table 3) demonstrate that granular structure, including granule shape, size, surface pores, and channels, solely provides the opportunity for initial enzyme digestion, but is not the inherent determinant for the slow digestion property of native cereal starches as noted in our previous paper.[9] Although lintnerization increased the degree of crystallinity for both maize and potato starches, no parallel changes in SDS were observed. Our prior study[9] also demonstrated that degree of crystallinity was not correlated with the SDS content of cereal starches. The initial decrease in RS from lintnerization of normal maize starch perhaps was due to disruption of granule structure, while the increased RS proportion (and decreased RDS) coinciding with increase in lintnerization demonstrates that higher crystallite perfection is associated with lower susceptibility to enzyme hydrolysis of cereal starches.

The amorphous lamellar structure is one important component of the crystalline region and appears to contribute to the slow digestion property of cereal starches. That lintnerization increased crystallinity means a corresponding decrease of amorphous regions and, in this study, a concomitant decrease in SDS by about 15% (Table 3). We propose here that SDS is specifically related to the interplay between crystalline lamellae and amorphous lamellae within the crystalline regions. Lintnerization cleaved the shortest A chains (DP < 10) and long B chains, which are structural components of the amorphous lamellae, and resulted in starch crystalline materials with higher perfection and more order, which, with increasing degree of lintnerization, are more resistant to enzyme hydrolysis and have a higher proportion of RS (Table 3). We speculate that the crystalline lamellae might determine the force to resist the enzyme hydrolysis, while the amorphous lamellae might alleviate the resistance by helping enzymes to loosen the tightly packed A-type crystalline structure. Thus, in typical native cereal starches, more SDS would be produced by decreasing the resistance to hydrolysis created by the crystalline lamellae. In lintnerized starch, the decrease of amorphous lamellae might lessen the ability of the enzyme to digest ordered crystalline lamellae, thus resulting in a lower amount of SDS.

Overall, the effect of amorphous lamellae on the slow digestion property of native cereal starches can be explained by two different mechanisms depending on the progress of digestion. At the early stage of digestion, the amorphous lamellae with their dense organization of highly branched B chains[29] might slow amylolysis, while during the later stage, it may help the enzyme to unloosen the tightly packed crystalline lamellae and increase overall digestion. The net result would be the observed large amount of SDS in native cereal starches with less RDS and RS. As for the effect of the amorphous growth ring on the slow digestion property of native cereal starches, it holds the adjacent crystalline shells together, leading to an even digestion of crystalline and amorphous regions,[9] which are also important for the slow digestion property of native cereal starches.

Structural Basis for Slow Digestion Property of Native Cereal Starches. Both in vitro[9] and in vivo data[30] demonstrate that native cereal starches are an ideal source of SDS. Its A-type crystalline structure, determined by the molecular structure of amylopectin, is the major structural basis for its slow digestion property. If the crystalline region is a B-type structure, the slow digestion property is low as shown from the digestibility of native and lintnerized potato starches. Apparently, the A-type crystallites are a hallmark of SDS.

Debranching analysis of amylopectin from A- and B-type starches supports previous evidence that $A+B_1$ chains are generally longer, but in lower proportion, in B-type starch.[7,31] Consequently, B-type crystallites have clusters with higher DP, and fewer chains and fewer branched amorphous lamellae as compared to A-type amorphous lamellae with a higher density of branched points.[32] Second, there is less perfection in A-type crystalline structure due to the higher proportion of shortest A chains (DP < 10) that cannot form stable double helices. Additionally, Vermeylen et al.[33] showed that there is less difference between the density of amorphous and crystalline lamellae of A-type starch as compared to B-type starch, and, further, the A-type amorphous lamellae have a higher degree of branching.[32] Our data suggest that the A-type amorphous lamellae are implicated in the slow digestion property of A-type cereal starch because SDS was reduced with lintnerization. Thus, the fundamental structural basis for the slow digestion property of A-type cereal starches is the A-type crystalline region, including both the crystalline lamellae and the amorphous lamellae.

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