

# Digestibility of retrograded starches with A- and B-type crystalline structures

Min Ah Kim · Seung Jun Choi · Tae Wha Moon

Received: 13 February 2015 / Accepted: 6 April 2015 / Published online: 10 April 2015  
© The Korean Society for Applied Biological Chemistry 2015

**Abstract** This study investigated whether the crystalline structure of the retrograded starch affects the contents of slowly digestible starch (SDS) and resistant starch (RS). When the relative crystallinities were similar, there was no difference in RS content between the retrograded starches with A- and B-type crystallites. However, the SDS content in A-type crystalline structure was constantly higher than B-type, contradicting the observation that the granular starches with B-type crystallites were more enzyme resistant. Therefore, the primary factor that accounts for the digestibility of granular starch is not the crystalline structure, but the granular properties, including the surface pores and the size.

**Keywords** Gelatinized starch · Retrogradation · Starch crystal type · Digestibility · Structural properties

## Introduction

Starch is generally classified into three categories, rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) based on the rate and extent of

in vitro starch digestion (Englyst et al. 1992). RS is further subclassified into four different types (RS type I, II, III, and IV) according to the mechanism of resistance to enzymatic digestion.

Starch exists as semi-crystalline matrices. The double helices of the amylose and/or amylopectin chains are packed into either A- or B-type crystalline structure (Wang et al. 1998; Hizukuri et al. 2006). These two polymorphs differ in the geometry of their single cell units, the packing density of their double helices, and the amount of bound water within the crystal structure. However, starches in pea and green banana show the C-type crystalline structure, which is a combination of the A- and B-types (Buléon et al. 1998). Generally, the crystalline structure of native granular starches is mainly dependent on its vegetal source, including the amylopectin structure. Amylopectin structures of A- and B-type starches are different. The amylopectin of A-type starches generally shows a greater average branched chain length than that of the B-type starches, because the amylopectin of A-type starches has a larger proportion of short branched chains and a smaller proportion of long branched chains compared to the amylopectin of the B-type starches (Hizukuri 1985). The amylopectin of the A-type starches has a few branching points located in the crystalline region, but the amylopectin of the B-type starches has most of branching points located in the amorphous region (Jane et al. 1997). Therefore, more porous structure is observed in the A-type starch granules compared to the B-type starches granules.

The enzymatic digestion rate of granular starch depends primarily on its crystalline structure, amylose content, and the granule size. Especially, its crystal structure has a significant influence on its enzymatic resistance (Planchot et al. 1997). It is generally accepted that starch granules with the A-type crystalline structure (found in cereal

M. A. Kim · T. W. Moon (✉)  
Department of Agricultural Biotechnology, Seoul National University, Seoul 151-921, Republic of Korea  
e-mail: twmoon@snu.ac.kr

S. J. Choi  
Department of Food Science and Technology, Seoul National University of Science and Technology, Seoul 139-743  
Republic of Korea

T. W. Moon  
Center for Food & Bioconvergence, Seoul National University, Seoul 151-921, Republic of Korea

starches) are more readily and quickly hydrolyzed than are the starch granules with the B-type crystalline structure (found in tuber starches) (Planchot et al. 1997). The easy and rapid digestion of A-type starch granules could be attributed to the fact that their amylopectin has a larger proportion of short branched chains and that the branching points are located in both the crystalline and amorphous regions. The less perfect crystalline structure could be formed with amylopectin in A-type starch granules, resulting in the porous internal structures, such as pinholes and channels (Fannon et al. 1992). However, the starch granules with B-type crystalline structure do not possess the porous structures that the starch granules with A-type crystalline structure have. The different susceptibility between A- and B-type granular starches could result in the higher SDS content and lower RS content of A-type granular starches compared to the B-type granular starches (Zhang et al. 2006a).

In starch granules, the structure of amylopectin would determine their degrees of resistance to enzymatic digestion. When a starch has amylopectin molecules that could form A-type crystalline structure, its retrograded form could have either an A- or B-type crystallite, depending on the retrogradation conditions, and the reverse is also possible. Therefore, this study examined the relationship between the crystalline structure of the retrograded starch and its digestibility.

## Materials and methods

### Preparation of recrystallized starches having A- or B-type crystalline structure

Corn starch (Samyang Genex, Incheon, Korea) was completely gelatinized by boiling for 60 min in excess water, then dried in an air-dried oven at 40 °C for 24 h. Starch was weighed into a glass container, and its moisture content was adjusted to the desired value by adding an appropriate amount of distilled water. After equilibrium, starch was stored at various temperatures for the desired period. After storage, samples were dried in an air-dried oven to reach a final moisture content of around 11 %. All samples were ground and passed through a 150- $\mu$ m sieve.

### Determination of crystalline pattern and relative crystallinity

The crystalline structure of the starches was determined using an X-ray diffractometer (Model D5005, Bruker, Karlsruhe, Germany) and the degree of relative crystallinity was calculated according to the method of Nara and Komiya (1983).

### In vitro starch digestibility

In vitro digestibility was determined by the method of Song et al. (2014). Starch fractions were classified based on the rate of hydrolysis. RDS was measured based on the glucose value after enzyme reaction for 10 min. SDS was obtained as the amount digested between 10 and 240 min. RS was defined as the amount left undigested after 240 min.

## Results and discussion

### X-ray diffraction patterns and relative crystallinity

Retrograded starches with different crystalline structures but similar relative crystallinities were prepared by storing the fully gelatinized starches under various conditions (Table 1). Raw starch showed the typical A-type crystalline structure (Hizukuri et al. 2006), and the gelatinized starch did not exhibit any specific crystalline structure, suggestive of an amorphous state to a great extent. Although various conditions were applied to prepare the retrograded starches with different relative crystallinities, the highest relative crystallinity was 17.3 %, slightly higher than half of raw starch ( $31.1 \pm 0.7$  %). This value was higher or similar to the previous reports that the retrograded corn starch showed the relative crystallinity ranged from 6 to 17 % (Bai et al. 2013). Since the relative crystallinity of 17 % shown in the previous study was obtained from the retrograded corn starch with 25 % amylose (Bai et al. 2013), it could be difficult for direct comparison of the relative crystallinity of this study to the previous studies.

Depending on the retrograded conditions, starches having A- or B-type crystallite were obtained. The A-type retrograded starches were obtained by storing at high temperature (100 °C), and starches having B-type crystalline structure were obtained by storing at low temperature (below 10 °C). It was consistent with the previous findings by Eerlingen (1993). This result also demonstrated that the retrogradation at high temperature generally favors the formation of more stable A-type, rather than B-type polymorphs.

### Starch digestibility

The digestibility of starch samples is presented in Table 2. The amounts of RDS, SDS, and RS in raw starch were 26.0, 48.0, and 26.0 %, respectively. The gelatinized starch was mostly digested, and its RDS content reached 74.8 %. The slow digestion properties were mostly lost, with a significant increase in RDS after gelatinization (Zhang et al. 2006b). The enzymatic digestibility of the retrograded

**Table 1** Relative crystallinity of recrystallized corn starches and their types of crystalline structure

Sample no.	Recrystallization condition			Relative crystallinity (%)	Type of crystalline structure
	Moisture content (%)	Storage temperature (°C)	Storage time (h)		
1	30	100	48	16.4 ± 0.7 <sup>a</sup>	A type
2	25	100	48	16.6 ± 0.5 <sup>a</sup>	A type
3	25	100	168	17.3 ± 0.6 <sup>a</sup>	A type
4	60	10	90	16.3 ± 0.5 <sup>a</sup>	B type
5	60	4	168	16.9 ± 0.1 <sup>a</sup>	B type
6	80	4	90	17.1 ± 0.6 <sup>a</sup>	B type

Least significant difference values were computed at the 5 % level. The different letter in a column indicates a significant difference ( $p < 0.05$ )

**Table 2** Relationship between the crystalline properties of recrystallized starches and their digestibilities

Sample no.	Type of crystalline structure	RDS	SDS	RS
1	A type	64.3 ± 0.0 <sup>b</sup>	5.3 ± 0.8 <sup>b</sup>	30.4 ± 0.8 <sup>a</sup>
2	–	62.3 ± 0.1 <sup>c</sup>	8.1 ± 0.4 <sup>a</sup>	29.6 ± 0.2 <sup>b</sup>
3	–	63.4 ± 0.0 <sup>b</sup>	6.4 ± 0.4 <sup>b</sup>	30.1 ± 0.3 <sup>a</sup>
4	B type	68.9 ± 0.2 <sup>a</sup>	2.5 ± 0.0 <sup>a</sup>	28.6 ± 0.2 <sup>c</sup>
5	–	70.0 ± 0.1 <sup>a</sup>	3.2 ± 1.1 <sup>a</sup>	26.7 ± 1.2 <sup>d</sup>
6	–	69.1 ± 0.4 <sup>a</sup>	0.4 ± 0.1 <sup>c</sup>	30.5 ± 0.5 <sup>a</sup>

RDS, SDS, and RS denote rapidly digestible, slowly digestible, and resistant starch fractions, respectively

Least significant difference values were computed at the 5 % level. The different letter in a column indicates a significant difference ( $p < 0.05$ )

starches was reduced, as reported by Chung et al. (2006), which decreased the proportion of RDS and increased SDS and RS contents. Although there was a significant difference in RS content between the retrograded starches with A- and B-type crystallites, the extent of difference was negligible. However, interestingly, there was a substantial difference in SDS content between A- and B-type crystalline structures in retrograded starches. Although there was no significant difference in RS content between the retrograded starches with A- and B-type crystallites, the higher SDS content of the A-type retrograded starch compared to B-type retrograded starches suggests that the retrograded starches with A-type crystalline structure could be more resistant to enzymatic hydrolysis than B-type retrograded starch. This observation was not in agreement with the general knowledge on the digestive pattern of raw starch granules. As described earlier, the starch granules with B-type crystallite are more resistant to enzymatic hydrolysis compared to those with A-type crystallite, mostly found in raw cereal starches. It is well known that A-type crystalline structures accommodate densely packed double helices, while the double helices in B-type crystalline structure are loosely packed (Leach et al. 1959). Previous studies also described that digestion by enzymes would have a more significant impact on the loosely packed internal region of starch than the densely packed

structure (Miao et al. 2009). Therefore, for retrograded starches with profoundly analogous morphological characteristics, the crystalline structure could determine their digestibility in terms of the SDS and/or RS contents. In other words, the type of crystalline structure in the retrograded starch could account for the SDS content, but did not significantly affect the RS content. However, for granular starch, although its crystalline structure could affect digestibility to a certain extent, digestibility might be determined mainly based on the shape, size, and porosity.

**Acknowledgments** This work was supported by both the BioGreen 21 Program (No. PJ007192) and the “Cooperative Research Program for Agriculture Science & Technology Development (Project No. PJ008575)”, Rural Development Administration, Republic of Korea.

## References

- Bai X, Dong Z, Wu X, Tong J, Zhou J (2013) Changes in crystalline structure of microspheres of corn starch and amylose under isothermal and temperature cycling treatments. *Ind Crops Prod* 51:220–223
- Buléon A, Gérard C, Riekel C, Vuong R, Chanzy H (1998) Details of the crystalline ultrastructure of C-starch granules revealed by synchrotron microfocus mapping. *Macromolecules* 31:6605–6610
- Chung HJ, Lim HS, Lim ST (2006) Effect of partial gelatinization and retrogradation on the enzymatic digestion of waxy rice starch. *J Cereal Sci* 43:353–359

- Eerlingen R (1993) Enzyme-resistant starch. I. Quantitative and qualitative influence of incubation time and temperature of autoclaved starch on resistant starch formation. *Cereal Chem* 70:339–344
- Englyst HN, Kingman S, Cummings J (1992) Classification and measurement of nutritionally important starch fractions. *Eur J Clin Nutr* 46:S33
- Fannon JE, Hauber RJ, BeMiller JN (1992) Surface pores of starch granules. *Cereal Chem* 69:284–288
- Hizukuri S (1985) Relationship between the distribution of the chain length of amylopectin and the crystalline structure of starch granules. *Carbohydr Res* 141:295–306
- Hizukuri S, Abe J-I, Hanashiro I (2006) Starch: analytical aspects. In: Eliasson A-C (ed) *Carbohydrates in food*, 2nd edn. CRC Press, Boca Raton, pp 305–390
- Jane J-L, Wong KS, McPherson AE (1997) Branched-structure difference on starches of A- and B-type X-ray patterns revealed by their Naegeli dextrans. *Carbohydr Res* 300:219–227
- Leach HW, McCowen L, Schoch T (1959) Structure of the starch granule. *Cereal Chem* 36:534
- Miao M, Zhang T, Jiang B (2009) Characterisations of kabuli and desi chickpea starches cultivated in China. *Food Chem* 113:1025–1032
- Nara S, Komiya TT (1983) Studies on the relationship between water-saturated state and crystallinity by the diffraction method for moistened potato starch. *Starch/Stärke* 35:S407–S410
- Planchot V, Colonna P, Buleon A (1997) Enzymatic hydrolysis of  $\alpha$ -glucan crystallites. *Carbohydr Res* 298:319–326
- Song HY, Lee SY, Choi SJ, Kim KM, Kim JS, Jung HG, Moon TW (2014) Digestibility and physicochemical properties of granular sweet potato starch as affected by annealing. *Food Sci Biotechnol* 23:23–31
- Wang TL, Bogracheva TY, Hedley CL (1998) Starch: as simple as A, B, C? *J Exp Bot* 49:481
- Zhang G, Ao Z, Hamaker BR (2006a) Slow digestion property of native cereal starches. *Biomacromolecules* 7:3252–3258
- Zhang G, Venkatachalam M, Hamaker BR (2006b) Structural basis for the slow digestion property of native cereal starches. *Biomacromolecules* 7:3259–3266