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Production of starch nanoparticles using normal maize starch via heat-moisture treatment under mildly acidic conditions and homogenization

Eun Young Park[b], Min-Jung Kim[a], MyoungLae Cho[a,c], Ju Hun Lee[d], Jong-Yea Kim[a,*]

[a] Department of Food Science and Biotechnology, Kangwon National University, Chuncheon 24341, South Korea
[b] Department of Biotechnology, College of Life Sciences and Biotechnology, Korea University, Seoul 02841, South Korea
[c] Present address: Applied Product Development Team, National Development Institute of Korean Medicine, Gyeongsan 38540, South Korea
[d] College of Liberal Arts, Shinhan University, Uijeongbu-Si 11644, South Korea

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ABSTRACT

Normal maize starch was subjected to heat-moisture treatment (HMT) under mildly acidic conditions (0.000, 0.050, or 0.075 M H_2SO_4) for various treatment times (3, 5, or 8 h) followed by homogenization up to 60 min to prepare nanoparticles. The combination of HMT (0.075 M, for 8 h) and homogenization (60 min) produced nanoparticles with diameters of less than 50 nm at a yield higher than 80%. X-ray diffractometry and size-exclusion chromatography revealed that HMT under mildly acidic conditions selectively hydrolyzed the starch chains (especially amylose and/or long chains of amylopectin) in the amorphous region of the granules without significant damage to the crystalline structure, however, modification of the molecular structure in the amorphous region increased fragility of the granules during homogenization. Homogenization for 60 min caused obvious damage in the long-range crystalline structure of the HMT starch (0.15 N, for 8 h), while the short-range chain associations (FT-IR) remained intact.

1. Introduction

Nano-sized starch is a type of modified starch that has potential applications, such as the use as a reinforcing nano-filler, in food science and food industries because the specific surface area increases as the size of a starch particles decreases; furthermore, the surface, which has hydroxyl groups, is highly reactive (Dufresne, 2015). Nano-sized starch particles can be prepared with various strategies, however the physicochemical properties of the nanoparticles, such as the crystalline structure and morphology, depend on the preparation method (Dufresne, 2015). Acid hydrolysis is one of most convenient and most investigated procedure for preparing nano-sized starch particles with highly crystalline structures. Dufresne, Cavaillé, and Helbert (1996) found that microcrystalline starch with agglomerated particles of 10 nm could be obtained via the hydrolysis of potato starch granules in a 2.2 N HCl suspension for 15 days, after which various studies have reported methods for producing starch nanocrystals via acid hydrolysis (García, Ribba, Dufresne, Aranguren, & Goyanes, 2009; Kim, Lee, Kim, Lim, & Lim, 2012; Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003). Transmission electron microscopy (TEM) revealed that the starch nanocrystals are individual platelet nanocrystals with lengths of 20–40 nm and widths of 15–30 nm (Putaux et al., 2003). It has been believed that acid hydrolysis of all starch granules consist of two stage, (1) a fast initial hydrolysis, presumably due to the erosion of the amorphous region of the starch granules, and (2) a second slower phase, which results in the hydrolysis of the crystalline region (Jayakody & Hoover, 2002). However, degradation of the crystalline region and the amorphous area of the starch granules during acid hydrolysis is concomitant (Putaux et al., 2003). Consequently, it is thought that the lengthy duration of the acid hydrolysis for the starch nanocrystals resulted in a low yield of less than 5%, which is possibly due to the transformation of the inherent amorphous and/or crystalline structures in the starch granules into soluble sugars by the end of the long batch production process (LeCorre, Bras, & Dufresne, 2011). Although the optimized conditions for the production of starch nanocrystals were achieved using a response surface methodology, these conditions resulted

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* Corresponding author.
E-mail address: jongkim@kangwon.ac.kr (J.-Y. Kim).

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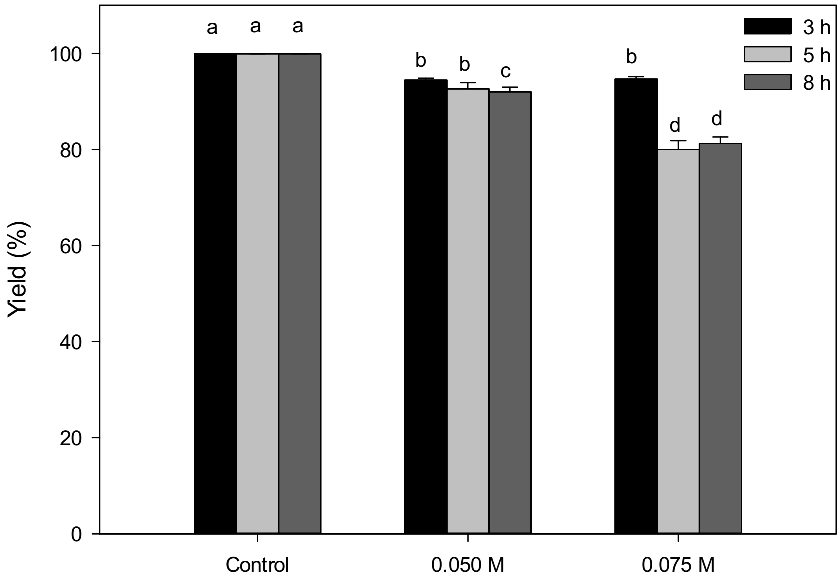

Fig. 1. The yield of starch after the HMT under various acid concentrations (0.000 [control], 0.050 or 0.075 M) and treatment times (3, 5 or 8 h) (the bars along the x-axis denoting a common letter are not significantly different, $p < 0.05$).

Table 1
Debranched chain profiles of heat-moisture treated starch samples relative to native starch.

Sample			Fraction of starch chains[a,b]			
			F-1	F-2	F-3	F-4
Native		$\mathrm{CL_w}$[c]	170.84a	43.80a	16.04a	12.97ab
		%	21.61A	26.62C	22.00C	29.78CD
Control	3 h	$\mathrm{CL_w}$[c]	165.84a	43.65a	16.22a	13.04ab
		%	22.38A	27.01BC	20.84C	29.78CD
	5 h	$\mathrm{CL_w}$[c]	167.52a	43.68a	16.07a	13.01ab
		%	22.32A	27.20BC	21.69C	28.80D
	8 h	$\mathrm{CL_w}$[c]	169.82a	45.68a	16.35a	13.26a
		%	22.73A	26.72C	21.66C	28.89D
0.050 M	3 h	$\mathrm{CL_w}$[c]	155.56b	44.33a	16.36a	13.06ab
		%	13.50B	27.52BC	27.64B	32.85B
	5 h	$\mathrm{CL_w}$[c]	155.06b	44.64a	16.31a	13.23a
		%	12.12B	29.37ABC	26.51B	32.02BC
	8 h	$\mathrm{CL_w}$[c]	106.88c	43.86a	16.10a	12.59ab
		%	8.74C	28.04ABC	30.01A	33.22B
0.075 M	3 h	$\mathrm{CL_w}$[c]	149de.67b	43.43a	15.90a	12.85ab
		%	7.56C	31.18A	29.90A	31.36BC
	5 h	$\mathrm{CL_w}$[c]	101.54c	44.03a	16.21a	12.72ab
		%	9.50C	30.30AB	27.99B	32.22BC
	8 h	$\mathrm{CL_w}$[c]	102.18c	44.77a	16.46a	12.22b
		%	7.91C	29.01ABC	26.72B	36.37A

[a] Values within same column sharing a common upper or lower letter are not significantly different ($p < 0.05$).

[b] Fractions are defined as follows: F-1, amylose; F-2, amylopectin long chains; F-3, amylopectin short chains; F-4, amylopectin short chains.

[c] $\mathrm{CL_w}$, weight average chain length.

in a yield of 14.69% (Angellier, Choisnard, Molina-Boisseau, Ozil, & Dufresne, 2004). Therefore, it is thought that there are some limitations for the practical application of starch nanocrystals in their related industries due to the relatively low yield of the particles via the current procedure.

Several studies have reported alternative procedures for preparing starch nanocrystals, such as the combination of acid treatment, continuous extraction and/or physical fragmentation (Kim, Han, Kweon, Park, & Lim, 2013; Kim, Park, Kim, & Lim, 2013; LeCorre et al., 2011). These procedures, however, employ the traditional acid hydrolysis procedure (acid hydrolysis in aqueous media), and it is thought that they may require relatively complicated and/or careful processes to overcome the inherently low recovery obtained from traditional acid hydrolysis. HMT of the starch granules with limited moisture levels (<35% w/w) at temperatures between the glass transition and the gelatinization of the starch granules (84–150 °C), can induce structural rearrangements of the starch molecules within the amorphous and/or crystalline region of the starch granules without disturbing the granular structure. Kim and Huber (2013) reported that an alternative HMT under mildly acidic conditions may primarily cleave the branching points of the starch chains. It is expected that the HMT under mildly acidic conditions may alter the granular structure without the severe loss of the starch substance because limited moisture content may inhibit the formation and/or loss of soluble sugars during the acid hydrolysis procedure. The primary objective of this study was to prepare starch nanoparticles using a combination of HMT under mildly acidic conditions and physical treatment and to evaluate their molecular and crystalline structures.

2. Materials and methods

2.1. Starch and chemical sources

Normal maize starch was obtained from Samyang Genex Inc. (Seoul, South Korea). Isoamylase (EC 3.2.1.68; 1000 U/mL) was purchased form Megazyme International Ireland Ltd. (Wicklow, Ireland). All other chemicals used were of analytical grade or better.

2.2. Preparation of starch nanoparticles

2.2.1. HMT under mildly acidic condition

Starch was modified using the method described by Kim and Huber (2013) with minor modifications. Starch (15 g, dry basis [DB]) was dispersed in distilled water (150 mL), and then an aliquot of a 0.000 [control], 0.050, 0.075 or 0.100 M sulfuric acid solution (6 mL) was added to the starch suspension. The resulting mixtures were stirred for 1 h at an ambient temperature, after which the treated starch was recovered using vacuum filtration (Whatman filter paper 40, GE Healthcare Life Science, Piscataway, NJ, USA). The recovered starch was allowed to dry at 35 °C for 12 h and was subsequently ground to pass through a No. 120 sieve. The treated starch samples were equilibrated in a thermo-