

REGULAR ARTICLE

Effect of cross-linking on physicochemical and *in vitro* digestibility properties of potato starch

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ABSTRACT

This study was carried out to elucidate the physical, chemical and *in vitro* digestibility characteristics of potato starch cross-linked with sodium trimetaphosphate (STMP)/sodium tripolyphosphate (STPP). These properties were evaluated by swelling factor, light transmittance, X-ray diffraction, and *in vitro* digestibility tests. X-ray diffraction patterns showed cross-linking using STMP/STPP took place mostly in the amorphous area and did not alter the crystalline area in potato starch granules. The light transmittance and swelling factor for native potato starch (NPS) were significantly decreased after cross-linking. *In vitro* digestibility results showed that cross-linking significantly decreased the contents of rapid digestible starch and significantly increased the contents of resistant starch (RS). The RS contents of NPS were augmented significantly with an increase in the degree of cross-linking. Cross-linked potato starch with STMP/STPP can be used as a replacer for dietary fibers in the food industry.

Keywords: Cross-linking; *In vitro* digestibility; Potato starch; Sodium trimetaphosphate; Sodium tripolyphosphate

INTRODUCTION

Potato starch has been widely used in the food industry and is the outstanding source of nutrition. It has been known that the starch possesses functional characteristics, including encapsulation, gelling, thickening, coating, and adhesion (Pedreschi, 2009). However, potato starch is limited by its physicochemical characteristics, like thermal decomposition, low shear strength, and acid susceptibility. Accordingly, to enlarge the range of the starch usages in the food industry, an effective technique, such as chemical modification of starch, is necessary (Hong et al., 2016).

Cross-linking can enhance the hydrogen bonds already present in the granules of starch with a new covalent bonding, and the cross-linked starch is less sensitive to heat, shearing, and acid; thus, it is suitable for use in salad dressing, hot chilled food, and canned food (Maningat et al., 2009). Sodium tripolyphosphate (STPP), phosphorus chloride (POCl_3), epichlorohydrin (EPI), and sodium trimetaphosphate (STMP) are the most frequently utilized food quality cross-linking reagents (Rutenberg and Solarek, 1984).

Chemical modification of starch includes the changes in the physicochemical properties of native starch to improve its functional properties and may be utilized to customize starch for particular food usages (Singh et al., 2007). Such modifications of native starches substantially alter their pasting, retrogradation, gelatinization, and *in vitro* digestibility characteristics. These properties of modified starch depend on the starch source, distribution of the substitutions, type of substituent, and extent of substitution in the starch granules (Park et al., 2004; Adebawale and Lawal, 2003).

When it comes to the nutrition, starches can be divided into three sections: Resistant starch (RS), rapidly digestible starch (RDS), and slowly digestible starch (SDS), according to their extent and rate of digestion in human being (Englyst et al., 1992). Among them, RS was recognized as an essential food ingredient, like dietary fiber, for human nutrition, due to consumers' increased demand for functional foods (Aparicio-Saguilán et al., 2008). In particular, cross-linked pea starch (Shi et al., 2013), cassava starch (Jyothi et al., 2006), and corn starch (Koo et al., 2010; Chung et al., 2008) inhibited their *in vitro* digestibility.

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Many of the earlier literatures on starch modification with STMP/STPP were performed on wheat and corn starches (Kahraman et al., 2015; Koo et al., 2010; Sang et al., 2007; Van Hung and Morita, 2005; Chung et al., 2004; Lim and Seib, 1993). When using STMP alone, the amount of substitution is restricted to 0.04% phosphorus (P) content. On the other hand, when native starch is reacted with a mixture of STMP and STPP, the permitted P amounts are ten times higher (CFR, 2013). According to Lim and Seib (1993), the mixture of STMP/STPP provided better outcomes than utilizing only STMP for preparing the cross-linked starches. However, there is little information regarding the *in vitro* digestibility and physicochemical properties of potato starch cross-linked using STMP/STPP. Therefore, this study aimed to elucidate the physicochemical and *in vitro* digestibility characteristics of potato starch cross-linked with STMP/STPP.

MATERIALS AND METHODS

Materials

Potatoes (Goun) were obtained from the National Institute of Highland, Pyeongchang, Korea. Sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), and porcine pancreatin (P-7545, activity $8 \times \text{USP/g}$) were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Amyloglucosidase (AMG 300 L, 300 AGU/mL) was purchased from Novozymes (Basvaerd, Denmark). The total starch assay kit was obtained from Megazyme International Ireland Ltd (Bray, Ireland). All other chemical reagents were of analytical grade.

Isolation of potato starch

Potato starch was isolated following the method of Djabali et al. (2009) and Huang et al. (2015), with slight modifications. Potatoes were washed, peeled, and cut into cubes. Cubes were steeped in 0.1 % (w/v) sodium bisulfite solution, smashed in a blender, filtered with distilled water through a 100-mesh sieve (Chung Gye Sang Gong Sa, Seoul, Korea), and centrifuged at 3,500 rpm for 10 min (VS-5000N, Vision scientific Co., Seoul, Korea). Centrifugation was repeated until pure white starch was obtained. The starch was dried at 45 °C for 48 h. The dried starch was then milled and sieved through a 100-mesh sieve.

Preparation of cross-linked potato starch

Cross-linked potato starch (CLPS) samples were prepared according to the method of Woo and Seib (2002), with some modifications. Potato starch (100 g, db), sodium sulfate (10 g), and different amounts (0.0125, 0.025, 0.05, 0.5, 5, and 10 g) of a 99:1 mixture of STMP and STPP were mixed in distilled water (140 mL). After the pH was adjusted to 11.0 with 1 N NaOH, the slurry was kept at

45 °C for 3 h using a magnetic stirrer equipped with a temperature controller (PS-1000, EYELA, Tokyo, Japan). The suspension was neutralized to pH 6.5 with 1 N HCl to stop the reaction and centrifuged, with distilled water washing, five times. After drying at 45 °C for 48 h, the dried samples were ground and passed through a 100-mesh sieve. Based on the different amounts of STMP/STPP, the samples cross-linked by STMP/STPP at 0.0125, 0.025, 0.05, 0.5, 5, and 10 % (w/w, based on the potato starch) were designated as CLPS-0.0125, CLPS-0.025, CLPS-0.05, CLPS-0.5, CLPS-5, and CLPS-10, respectively. The flow chart for cross-linking potato starch is shown in Fig. 1.

Chemical composition analysis

The chemical composition of the native potato starch (NPS), including moisture, crude ash, crude protein, and crude lipid contents, was determined according to AACC Approved Methods 08-01, 30-10, 44-15A, and 46-13, respectively. The total starch content in the NPS was determined based on AACC method 76-13.01 (AACC, 1995). The amylose content was determined according to the procedure described by Williams et al. (1970).

Determination of phosphorus content and degree of substitution

Phosphorus (P) contents of NPS and CLPS samples were determined by inductively coupled plasma optical emission

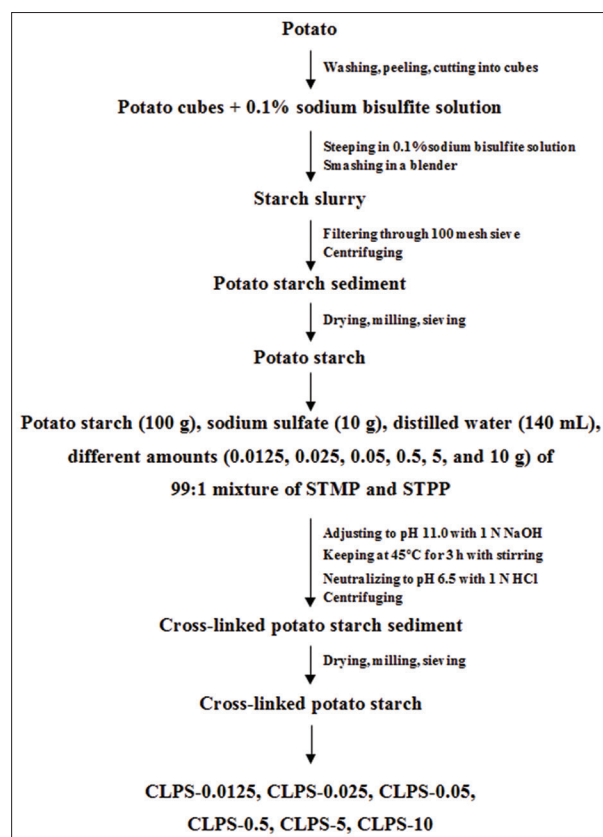


Fig 1. Flow chart for isolation and cross-linking of potato starch.

spectrometry (ICP-OES(Agilent Technologies, Mulgrave, Australia)) after hot nitric acid digestion. Starch samples (0.3 g) were digested with 10 mL 60 % nitric acid at 180 °C for 2 h. After cooling, they were diluted with 30 mL of distilled water and analyzed using an Agilent 5100 ICP-OES instrument. The degree of substitution (DS) was calculated as follows (Wongsagonsup et al. 2005):

$$DS = 324P/3100 - 96P \quad (1)$$

P: phosphorus content (%)

X-ray diffraction

X-ray diffraction patterns of NPS and CLPS samples were investigated using a D8 Advance X-ray diffractometer (Bruker Co., ÖstlicheRheinbrückenstr, Germany). The samples were scanned from 5° to 40° (2θ).

Fourier transform infrared spectroscopy

The Fourier transform infrared (FT-IR) spectra of NPS and CLPS samples were determined using a Fourier transform infrared spectrophotometer (Spectrum One System, Perkin-Elmer, Waltham, MA, USA). Samples were mixed with 100 mg of KBr under anhydrous conditions and recorded over a range of wave numbers from 400 to 4000 cm⁻¹.

Swelling factor

The swelling factors of the NPS and CLPS samples were determined based on the procedure of Tester and Morrison (1990), with some modifications. The sample (100 mg) was combined with 5 mL of distilled water and incubated in a water bath at 50, 60, 70, 80, and 90 °C for 30 min. The mixture was vortexed thoroughly for 5 min. After cooling the sample in an ice bath, 0.5 mL of blue dextran solution (5 mg/mL) was added. The solution was centrifuged at 3,000 × g for 15 min, and the absorbance of the supernatant was measured at 620 nm. The swelling factor (SF) was calculated using the following equation:

$$SF = 1 + \frac{7,700}{w} \times \frac{A_S - A_R}{A_S} \quad (2)$$

w: sample weight (mg)

A_S: absorbance of the supernatant

A_R: absorbance of the reference (without starch)

Light transmittance (% T)

The clarity of the NPS and CLPS samples was determined according to the method of Reddy and Seib (1999). Starch (0.05 g) was suspended in 5 mL of distilled water in a 15-mL centrifuge tube and placed in a boiling water bath for 30 min, with vortexing every 5 min. After cooling the sample at room temperature, the light transmittance (% T) was read at 650 nm against a distilled water blank.

In vitro digestibility

The *in vitro* digestibilities of native and cross-linked potato starches were determined based on the method of Englyst et al. (1992), with slight modifications. To prepare the enzyme solution, pancreatin (1 g) was dissolved in distilled water (12 mL), stirred for 10 min, and then centrifuged at 1500 × g for 10 min. The supernatant (10 mL) and amyloglucosidase (2 mL) were transferred into a beaker and mixed well. The enzyme solution was freshly prepared for each digestibility test. The digestibilities of native and cross-linked potato starches were measured as follows: Sodium acetate buffer (0.1 M, pH 5.2, 0.75 mL), and a glass bead were added to each of the 2 mL micro tubes containing starch samples (30 mg). After equilibration at 37 °C for 10 min, the enzyme solution (0.75 mL) was added to each tube and incubated in the shaking water bath (185 rpm) at 37 °C. The tubes were taken at intervals of 10 and 240 min, boiled for 10 min to stop the enzyme reaction, and centrifuged at 5000 × g for 10 min. The glucose content in the supernatant was measured by the dinitrosalicylic acid (DNS) method (Miller, 1959). The percentage of hydrolyzed starch was calculated by multiplying the glucose content by a factor of 0.9. The percentages RD, slowly SDS, and RS in the samples were calculated using the following equations:

$$RDS (\%) = G_{10} \times 0.9 \quad (3)$$

$$SDS (\%) = (G_{240} - G_{10}) \times 0.9 \quad (4)$$

$$RS (\%) = 100 - RDS - SDS \quad (5)$$

Where, G₁₀ and G₂₄₀ are the glucose contents released after 10 and 240 min, respectively.

Statistical analysis

All statistical analyses were performed using SAS version 9.1 (SAS Institute Inc., Cary, NC, USA). Analysis of variance (ANOVA) was performed according to the general linear models (GLM) procedure to determine the significant differences among the samples. Means were compared according to Fisher's least significant difference (LSD) procedure. Significance was defined at the 5 % level.

RESULTS AND DISCUSSION

Chemical analysis and degree of substitution

The chemical composition of the NPS is shown in Table 1. The starch contained 9.47 % moisture, 0.20 % crude ash, 0.50 % crude protein, 0.31 % crude fat, and 86.80 % total starch. The very low contents of protein and fat indicated that the obtained potato starch was very pure and that the residual protein had been thoroughly removed during isolation. The isolated potato starch contained 32.52% amylose and 67.48% amylopectin. The amylose content

of potato starch varies from 23 to 31% for potato starch genotypes (Kim et al., 1995; Wiesenborn et al., 1994).

The DS was calculated using the phosphorus content of the CLPS and Eq. (1). The DS values for the CLPS samples increased from 5.561 to 36.136 as the concentration of STMP/STPP increased from 0.0125 to 10 % (Table 2).

Light transmittance (% T)

The light transmittance of the NPS and CLPS pastes is presented in Table 2. The NPS paste showed the highest light transmittance (85.55 %) among all samples. The light transmittance of the CLPS pastes cross-linked with different concentrations (0.0125–5%) of STMP/STPP decreased significantly with increasing concentrations of STMP/STPP; however, no significant differences were found for the starch pastes treated with more than 5 % of STMP/STPP. These results were consistent with the reports for starches cross-linked with STMP/STPP, such as corn starch (Koo et al., 2010) and tapioca starch (Wongsagonsup et al., 2014). According to Kaur et al. (2006) and Reddy and Seib (1999), the reduced clarity of cross-linked starch pastes might be partly responsible for their reduced swelling factor (Table 3).

X-ray diffraction

The X-ray diffraction patterns of the NPS and CLPS prepared with different STMP/STPP concentrations are presented in Fig. 2. There were no obvious changes between the NPS and CLPS samples. All samples showed similar diffraction patterns, with peaks at angles 5.6°, 15°, 17°, 22° and 24° (2 θ), which are the typical characteristics of a B-type structure (Zhu et al., 2012). The results

suggested that cross-linking with STMP/STPP up to 10 % occurred primarily in the amorphous regions and did not change the crystalline region of the potato starch granules (Koo et al., 2010; Hoover and Sosulski, 1986).

Fourier transform infrared spectroscopy

The FT-IR spectra of the NPS and CLPS samples are presented in Fig. 3. For the potato starch spectrum, a wave number of approximately 3400 cm⁻¹ could be ascribed to the presence of O-H bonds. The observed bands in the 1365–1413 cm⁻¹ region are related to C-H bending vibrations and the peak at 2945 cm⁻¹ is caused by C-H stretching. Intramolecular hydrogen bonds cause the peak at 1642 cm⁻¹. In particular, the peak at 1160 cm⁻¹ represents C-O stretching (Gao et al., 2014).

However, no significant changes were detected in the FT-IR spectroscopy pattern among the NPS and CLPS samples (Fig. 3). The characteristic absorption peaks inherent to P=O (1150–1400 cm⁻¹) and P-O-C (995–1050 cm⁻¹) did not appear in the spectra of the CLPS samples, probably because of the low content of cross-linking agents. Gao et al. (2014) also reported that the FT-IR spectrum of cross-linked porous corn starch prepared with STMP (8 %) was not remarkably different from the native starch.

Swelling factor

The swelling factors of the NPS and CLPS samples between 50 and 90 °C are shown in Table 3. The swelling

Table 1: Chemical composition of native potato starch (NPS)

Chemical composition	NPS (%)
Moisture	9.47±0.08
Ash	0.20±0.12
Protein	0.50±0.05
Fat	0.31±0.06
Total starch	86.80±0.30
Amylose	32.52±0.29
Amylopectin	67.48±0.25

Table 2: Degree of substitution (DS) and light transmittance of native (NPS) and cross-linked potato starches (CLPS) prepared with different STMP/STPP concentrations

Sample	DS (10 ⁻³)	Light transmittance (%T)
NPS	-	85.55±0.70 ^a
CLPS-0.0125	5.561 ^e	69.87±2.80 ^b
CLPS-0.025	6.029 ^d	60.91±1.06 ^c
CLPS-0.05	6.031 ^d	36.74±2.83 ^d
CLPS-0.5	6.264 ^c	10.20±0.03 ^e
CLPS-5	19.489 ^b	6.44±0.02 ^f
CLPS-10	36.136 ^a	6.12±0.05 ^f

^{a-f} Values with different letters within the same column differ significantly ($p < 0.05$)

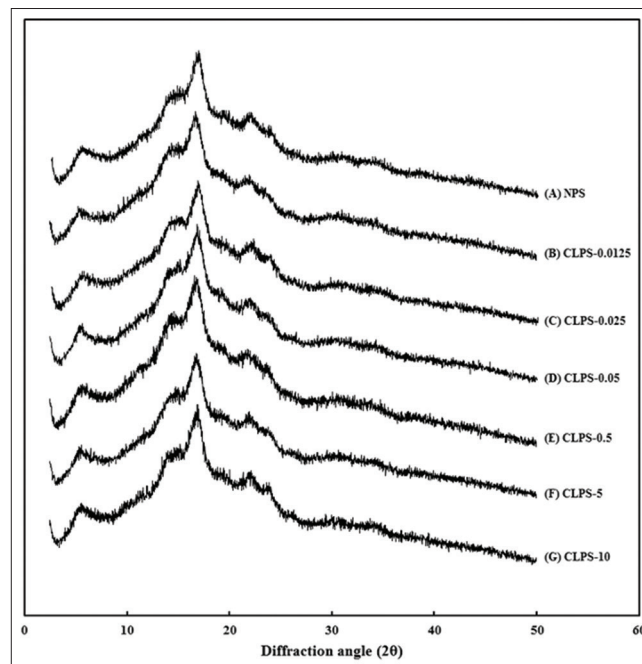


Fig 2. X-ray diffraction patterns of native (NPS) and cross-linked potato starches (CLPS) prepared with different STMP/STPP concentrations. (A) NPS (B) CLPS-0.0125 (C) CLPS-0.025 (D) CLPS-0.05 (E) CLPS-0.5 (F) CLPS-5 (G) CLPS-10.

Table 3: Swelling factor of native (NPS) and cross-linked potato starches (CLPS) prepared with different STMP/STPP concentrations

Sample	Temperature (°C)				
	50	60	70	80	90
NPS	^A 1.30±0.53 ^d	^A 3.34±0.71 ^c	^A 18.24±0.71 ^b	^A 32.70±1.43 ^a	N.D.
CLPS-0.0125	^A 1.30±0.52 ^e	^A 2.98±0.48 ^d	^B 15.85±0.08 ^c	^B 26.15±0.93 ^b	^A 46.57±0.28 ^a
CLPS-0.025	^A 1.00±0.00 ^e	^A 3.30±1.55 ^d	^B 16.69±0.19 ^c	^B 25.10±0.88 ^b	^B 42.12±0.48 ^a
CLPS-0.05	^A 1.59±0.51 ^e	^A 2.91±1.12 ^d	^C 13.25±0.34 ^c	^C 19.03±0.47 ^b	^C 29.94±0.58 ^a
CLPS-0.5	^A 1.28±1.00 ^c	^A 2.65±1.06 ^c	^D 7.34±0.62 ^b	^D 8.88±0.41 ^{ab}	^D 9.65±1.02 ^a
CLPS-5	^A 1.29±0.51 ^d	^A 3.49±0.56 ^c	^E 5.51±0.91 ^b	^E 6.78±0.67 ^a	^E 6.92±0.61 ^a
CLPS-10	^A 1.29±0.51 ^d	^A 3.32±1.35 ^c	^E 5.43±0.72 ^b	^E 6.57±0.92 ^{ab}	^E 7.08±0.37 ^a

^{A-E}Values with different letters within the same column differ significantly ($p < 0.05$), ^{a-e}Values with different letters within the same row differ significantly ($p < 0.05$), ND: Not detected

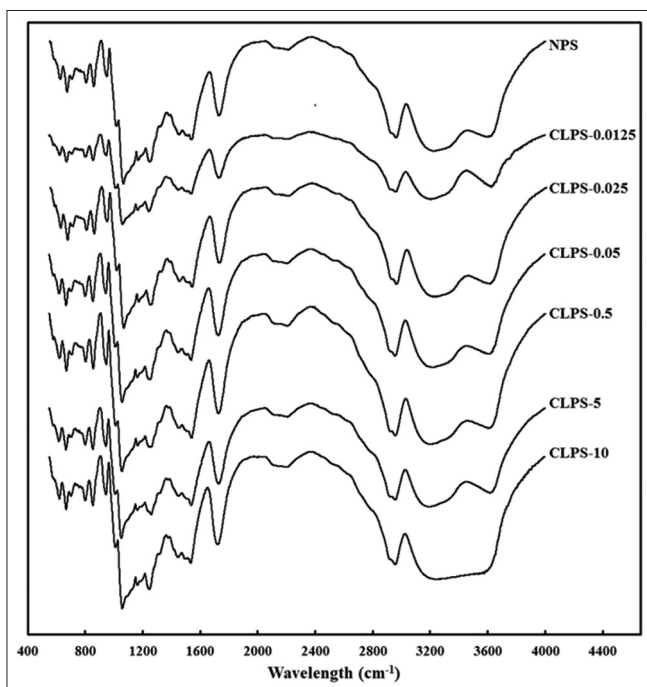


Fig 3. Fourier transform infrared spectroscopy of native (NPS) and cross-linked potato starches (CLPS) prepared with different concentrations.

factors of all starch samples increased significantly as the temperature increased from 50 to 90 °C ($p < 0.05$). It was difficult to measure the swelling factor of the NPS at 90 °C, because the NPS granules were completely ruptured at 90 °C and existed as cloudy solids, which were not separated clearly from the supernatant.

There were no significant differences between the NPS and all CLPS samples at 50 and 60 °C. However, all CLPS samples showed significantly lower swelling factors at 70 and 80 °C compared with those of the NPS. In the lower temperatures (50-60 °C), all samples were not gelatinized; therefore, the swelling factors for all samples were not different. However, in the higher temperatures (70-80 °C), the NPS had the higher swelling factor than CLPS samples because the NPS was easily gelatinized. Cross-linking reinforces starch granules with new covalent bonds that

can act as a bridge between starch molecules, leading to reduced swelling compared with native granules (Maningat et al., 2009).

The swelling factor decreased in the CLPS samples with increasing concentrations of the cross-linking reagents. The results were consistent with those of cross-linked cassava starch (Jyothi et al., 2006), waxy maize starch (Hirsch and Kokini, 2002), and taro starch (Hazarika and Sit, 2016).

***In vitro* digestibility**

Table 4 shows the contents of RDS, SDS, and RS in the NPS and CLPS samples. When STMP/STPP concentrations were elevated from 0 to 10%, RDS contents significantly reduced from 24.33 to 11.89 %, respectively, but RS contents were significantly increased from 73.49 to 86.63 % ($p < 0.05$). There were no significant changes in SDS contents among the NPS and CLPS samples ($p > 0.05$), indicating that cross-linking of NPS with STMP/STPP did not remarkably affect SDS contents in NPS. Furthermore, Chung et al. (2004) indicated that RS contents in corn starch cross-linked with 0 to 10 % STMP/STPP increased from 0.36 to 81.58 %. The extent of *in vitro* digestibility can be related to not only the degree of cross-linking but also the swelling factor (Koo et al., 2010). According to Huber and BeMiller (2001), after cross-linking, cereal starch can prevent the penetration of α -amylase through the channels that result in the inside of the starch, leading to decreased enzymatic digestibility. According to Yeh and Yeh (1993), α -amylase finds it very hard to digest highly cross-linked starch because cross-linking stabilizes the starch granules and regulates their swelling. Therefore, in the present study, the increase in the RS content could be associated with increase starch cross-linking, which would increase resistance to α -amylase digestion.

Additionally, a negative relationship for RS ($R^2 = 0.9228$) and a positive relationship for RDS ($R^2 = 0.9248$) were observed when the starch fractions (RDS and RS) were plotted against the swelling factor (Fig. 4). The swelling of starch molecules can improve the access of digestive

Table 4: Starch fractions of native (NPS) and cross-linked potato starches (CLPS) prepared with different STMP/STPP concentrations

Sample	Starch fraction (%) ¹		
	RDS	SDS	RS
NPS	24.33±0.91 ^a	2.19±0.80 ^a	73.49±0.11 ^e
CLPS-0.0125	23.59±0.04 ^a	1.51±0.01 ^a	74.90±0.06 ^{de}
CLPS-0.025	21.98±0.33 ^b	2.84±0.45 ^a	75.19±0.11 ^d
CLPS-0.05	18.60±0.01 ^c	2.99±1.35 ^a	78.42±1.34 ^d
CLPS-0.5	17.01±0.76 ^d	2.66±0.39 ^a	80.34±1.15 ^c
CLPS-5	13.05±0.06 ^e	2.38±0.33 ^a	84.57±0.27 ^b
CLPS-10	11.89±0.86 ^e	1.49±0.13 ^a	86.63±0.98 ^a

Values with different letters within the same column differ significantly ($p < 0.05$). ¹ RDS (%) = $G_{10} \cdot 0.9$, ¹ SDS (%) = $(G_{240} - G_{10}) \cdot 0.9$, ¹ RS (%) = $100 - RDS - SDS$, ¹ G_{10} and G_{240} are the glucose contents released after 10 and 240 min, respectively

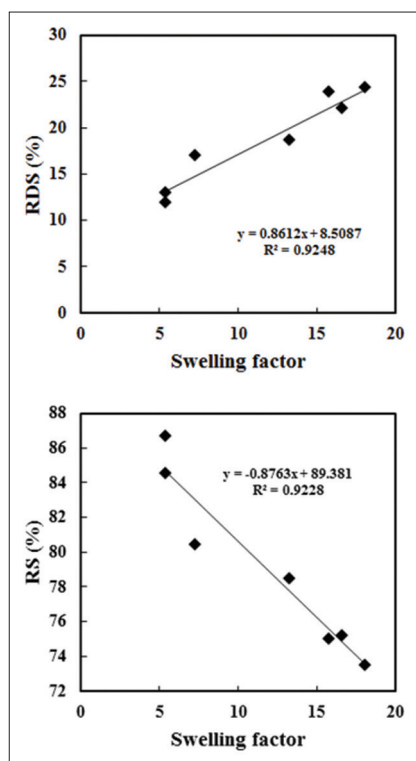


Fig 4. Linear regression of swelling factor and starch fractions (rapid digestible starch; RDS and resistant starch; RS) of native (NPS) and cross-linked potato starches (CLPS) prepared with different STMP/STPP concentrations.

enzymes, such as α -amylase, β -amylase, and glucoamylase, to its inner structure. Therefore, it was suggested in the present study that CLPS samples with the lower swelling factors can be less susceptible to the degradation by digestive enzymes, consequently leading to a reduction in RDS contents. However, RS contents were associated negatively with the swelling factor, because the limited swelling induced by cross-linking may diminish the degradation by digestive enzymes. Based on the results, the increased RS contents in the CLPS samples may have been influenced by a decrease in swelling factors and an increase in the degree of cross-linking. In addition, the

findings suggested that the potato starch cross-linked by STMP/STPP (0.0125–10 %) could be used for functional food ingredients, such as dietary fiber, because of its reduced digestibility.

CONCLUSIONS

Cross-linking with STMP/STPP resulted in remarkable changes in the physicochemical and *in vitro* digestibility properties of potato starch. There were no pronounced changes in the X-ray diffraction patterns among the NPS and CLPS samples, indicating that cross-linking occurred in the amorphous regions. The swelling factor of the CLPS samples decreased significantly as the concentration of STMP/STPP increased. The *in vitro* digestibility analysis of the CLPS samples showed significantly decreased RDS contents and significantly increased RS contents. In addition, the RDS content correlated positively with the swelling factor and the RS content correlated negatively. In conclusion, cross-linking using STMP/STPP could improve the RS content of potato starch, and the cross-linked potato starch could be used as a replacement for dietary fiber in the food industry.

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Authors' contributions

All authors contributed to the work presented in the manuscript. Hyemi Heo conducted the experiments, analyzed the data, and wrote the manuscript. Yun-Kyung Lee participated in the experiments and reviewed the manuscript. Yoon Hyuk Chang planned the overall experiments and reviewed the manuscript.

Abbreviations used

CLPS, cross-linked potato starch; DS, degree of substitution; FT-IR, Fourier transform infrared; NPS, native potato starch; P, phosphorus; RDS, digestible starch; RS, resistant starch; SDS, slowly digestible starch; SF, swelling factor; STMP, sodium trimetaphosphate; STPP, sodium tripolyphosphate

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