*Food Sci. Biotechnol.* 24(3): 835-841 (2015)
DOI 10.1007/s10068-015-0108-x

**RESEARCH ARTICLE**

# Forming Rice Starch Gels by Adding Retrograded and Cross-linked Resistant Starch Prepared from Rice Starch

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Received August 16, 2014; revised December 25, 2014; accepted January 26, 2015; published online June 30, 2015

**Abstract** Retrograded and cross-linked resistant starches (RS) were prepared from rice starches through autoclaving-cooling cycles (RS3) and cross-linking using sodium trimetaphophate after annealing (RS4). The RS-added non-waxy rice starch gels were investigated to improve the gel structures of rice products. Rice starch (Nampyeong) isolated by an alkaline steeping method showed 24.25% of the amylose content. The RS levels of RS3, the citric acid added RS3 (CARS3), and RS4, and those of RS (10%) added gels were 9.05, 7.41, and 53.14%, and 3.52, 3.16, and 6.51%, respectively. However, rice starch with less than 12% starch concentration unlikely formed a gel network structure. RS was added to assist the rice starch in forming a gel structure, regardless of RS types. RS added starch gels showed significantly greater lightness, hardness, springiness, and gumminess than the control gel. It was found that RS improved rigidity and textural properties and increased dietary fiber level of gels.

**Keywords:** rice starch, retrograded RS, cross-linked RS, gel structure, textural property

## Introduction

Starch is composed of amylose (linear α-1, 4 glucosidic bond) and amylopectin (linear α-1, 4 glucosidic bond and branched with α-1, 6 glucosidic bond). When a starch granule is heated up to the gelatinization temperature in excess water, the granule swells as a result of the loss of a crystalline order and water absorption, while amylose in the granules simultaneously leaches out (1). Upon cooling of starch paste, the leached-out amylose forms a three-dimensional network with swollen granules embedded in the matrix (2,3). This phenomenon is called starch gelation. Starch gel undergoes structural changes during staling, or retrogradation, which involves the crystallization of amylose and amylopectin. The initial stage of gelation of starch is dominated by the gelation of solubilized amylose (4). The changes of starch granules cause the rheological behavior of starch paste and gel, and swollen starch granules form a closely packed gel structure that possesses high shear resistance (1). Gelatinization parameters and the extent of starch retrogradation are influenced by starch composition and structure, moisture content during gelatinization and storage, storage temperature, and the presence of non-starch polysaccharides (5,6).

Dietary starch is generally classified into the three types: rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS), depending on the extent of in vitro digestion (7,8). RS, the portion of starch and starch products that resist digestion, can be classified into four types: physically inaccessible starch (RS1), B-crystal types of raw starch granules and high amylose starch (RS2), retrograded starch (RS3), and chemically modified starch (RS4) (9,10). RS is not digested in the small intestine and produces short chain fatty acids in the large bowel through fermentation by probiotics, which is beneficial for colon health and protects from colonic diseases (11,12). RS plays important physiological roles and has the potential to improve human health and lower the risk of many diet-related diseases. Compared to traditional insoluble fibers, RS has advantageous features, such as natural white color, bland flavor, and better appearances and textures (13).

Rice is a staple food source throughout the world, especially in Asia, and contains approximately 80% starch.

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Rice starch forms the structural network of rice flour products and is gelatinized and retrograded in an aqueous system. Various types of dietary fiber have been studied to improve functionality of rice flour products, as white rice flour exhibits low dietary fiber content. RS prepared from rice starch is a beneficial additive to rice flour, because of its small granule size, bland taste, white color, and suitable texture for processing (14). RS has been reported to increase dietary fiber in traditional rice cakes, bread, cookies, and noodles (14,15). Moreover, it is well known that properties of RS vary depending on several factors, such as starch source, amylose content (16,17), and treatment conditions (18).

Starch gel structures vary depending not only on starch concentration but also on the structure of swollen starch granules, amount of amylose and amylopectin leached out from granules, and heating conditions (19,20). Non-waxy rice starch is unable to produce a viscoelastic gel, such as *muk* due to the low amylose content (12-20%). Some polysaccharides affect the texture of mixed rice starch gels according to types and concentration (21). When RS is added into starch-containing foods, the structure of RS may change by type. Whereas B-type raw starch granule (RS2) can be gelatinized after heating in excess water, and retrograded RS3 and cross-linked RS4 maintain the same structure during normal cooking, because of the high thermal stability (14,18). The properties of mixed starch-RS gels may be affected by starch source, starch and water ratio, and RS level and type. To the best of our knowledge, the role of RS in starch gelation and the dietary content of mixed gels has not yet been studied.

To understand the effect of RS added to rice flour products, gel formation of rice starch of different types of RS and effects of the addition of RS on the quality of rice starch gels were investigated.

## Materials and Methods

**Materials** Japonica non-waxy Nampyeong rice was purchased from the National Institute of Crop Science, Rural Development Administration (Iksan, Korea). Citric acid (Reagents Duksan, Ansan, Korea), sodium trimetaphosphate (STMP), and sodium polyphosphate (STPP) (Sigma Chemical Co., St. Louis, MO, USA) were used to prepare RS. A total dietary fiber assay kit (Sigma Chemical Co.) was purchased to analyze RS level.

**Preparation of rice starch** Rice starch was isolated from Nampyeong white rice using the alkaline-steeping method (22). The moisture, crude protein, ash, crude lipid, and amylose content of isolated rice starch were 11.78, 0.27, 0.33, 0.04, and 24.25%, respectively.

**Preparation of resistant starch** Retrograded RS3 and cross-linked RS4 were prepared according to the methods by Song *et al.* (22) and Mun and Shin (23). A rice starch and water (1:2) mixture with or without citric acid (CA; 0.1% basis on starch) was autoclaved at 121°C for 1 h, and the paste was then cooled at room temperature and stored for 24 h at 4°C. After three repetitions of the autoclaving-cooling cycle, the sample was dried in an oven at 40°C, ground and passed through a 100 mesh sieve (< 150 μm). To make cross-linked RS4, a mixture of rice starch (100 g, db) and distilled water (100 mL) mixture was annealed at 50°C in a shaking water bath at 80 rpm for 12 h. Annealed starch slurry and sodium sulfate (10%, starch basis) were mixed in a beaker, stirred for 10 min, and then STMP (11.98 g) and STPP (0.02 g) were added by stirring. The mixture was adjusted to pH 11.5 by adding 1.0 M NaOH solution. The slurry was stirred continuously in a 45°C water bath. After 3 h reaction, the slurry was adjusted to pH 6.5 by adding 1.0 M HCl, and neutralized starch was collected by centrifugation, washed with distilled water to remove salt, dried at room temperature, ground, and passed through a 100 mesh sieve. The food grade RS4 which was produced under the same conditions was phosphorylated to ~0.4% phosphorus (24). The RS level was analyzed by the AOAC method (25) using a total dietary fiber kit. RS levels of RS3, citric acid added RS3 (CARS3), and RS4 were 9.05±0.53, 7.41±0.09, and 53.14±1.54%, respectively.

**RVA analysis** The pasting properties of rice starch with different RS samples (10%) were examined in duplicate with a Rapid Visco Analyzer (RVA-4; Newport Scientific, Warriewood, Australia). The sample (3 g, db) and 25 mL distilled water mixed in an aluminum canister before RVA analysis. Each sample suspension was held at 50°C for 1 min, heated at a rate of 12°C/min up to 95°C, maintained for 2.5 min, then cooled down to 50°C at a rate of 12°C/min. RVA parameters, initial pasting temperature, peak viscosity (P), trough viscosity (T), cold viscosity (C), breakdown viscosity (P-T), and setback viscosity (C-T) of each sample were recorded.

**Preparation of rice starch gel with RS** Normal rice starch was gelatinized for 30 min at different concentrations and cooled to set the gel. A 12% rice starch suspension was used to investigate the effect of RS on formation of the normal rice starch gel, as rice starch gel does not form properly at a 12% starch concentration. A mixture of rice starch and different types of RS (10%, starch basis) in distilled water (12%, starch suspension) was gelatinized in a sealed autoclaving bottle in a boiling water bath for 30 min. The paste was poured into a stainless steel column (ϕ 1.8×1.5 cm) on a glass plate without air bubbles and covered with another glass plate. The starch gel (12%) was kept for 6 h at room temperature and removed carefully for use as a sample.

**Color value measurement** The color value of gel samples was measured using a spectrophotometer (CM-3500d; Konica Minolta, Tokyo, Japan) and Spectramagic NX software under the following conditions: specular component SCE, measurement area 30 or 8 mm, UV setting 100% full, a petri dish or 8 mm target mask, source of light D65. White and black calibration was confirmed before the measurement to determine the degree of accuracy in measurement of color value. Lightness (L), +redness/-greenness (a), and +yellowness/-blueness (b) were measured according to the Hunter's Lab color system.

**Morphological properties** The Nampyeong rice starch gel matrix with RS was observed by a scanning electron microscope (SEM) (JSM-7500F+EDS; Jeol Ltd., Tokyo, Japan) with an accelerating potential of 20 kV at 500× magnification. The freeze-dried gel slices were attached to an SEM stub using double-sided carbon tape. Samples were thinly coated with gold under vacuum. Completed samples were examined and photographed.

**X-ray diffraction** X-ray diffractograms of native rice starch, RS and freeze-dried starch gel powders were obtained with an X-ray diffractometer (X'Pert PRO Multi-purpose X-ray diffractometer; Panalytical B.V., Almelo, Netherlands). The working conditions were target Cu-K$\alpha$; filter Ni; voltage of 40 kV and 20 mA, with a scanning speed of 8°/min and a diffraction ($2\theta$) ranging from 5 to 40°.

**Texture profile analysis** A texture analyzer (TA-XT Plus; Stable Micro System, Surrey, UK) was used to measure the force-time curve. A two-bite compression test for texture profile analysis (TPA) was performed with a cylinder probe type ($\phi$ 20 mm) and deformation rate of 50%, pre-test at 2 mm/s, and test and post-test at 1 mm/s. All parameters (hardness, adhesiveness, cohesiveness, springiness, gumminess, and resilience) were determined from the TPA curve.

**Statistical analysis** All samples were analyzed at least in duplicate and mean values and standard deviations were reported. Statistical analyses were performed by Duncan's new multiple range tests with level of significance set at 5%, using SPSS 18.0 (SPSS Inc., Chicago, IL, USA).

## Results and Discussion

**Color values of rice starch, RS, and rice starch with RS** Color values of Nampyeong rice starch, RS prepared from rice starch and rice starch gels with RS are presented in Table 1. The L, a, and b values of native rice starch were 96.79, –0.05, and 1.09, respectively. RS showed significantly different L, a, and b values, and RS4 was whiter than RS3. Color values of the retrograded RS3 with citric acid showed a higher L value and lower a and b values than those of RS3. RS4 had the highest L value and the lowest a value, and did not show significant difference from a native rice starch. The color of RS differed depending on RS types and preparation methods. The color of RS as a dietary fiber may affect characteristics of a product, which would make RS3 (grain flour or flour) and RS4 (white flour) more suitable for products of a similar color. It was reported that wheat flour with RS3 and RS4 increased lightness (L) and decreased redness (a) and yellowness (b) compared to wheat flour with other dietary fibers (26), and product color was one of the important factors for consumer preferences. Color values of rice starch gels were significantly different by type of RS ($p<0.05$). RS4 gel had a higher L value and lower a value than others. Rice starch paste was observed as a clear dispersion after heating stopped, and starch paste became an opaque gel with whiteness. The whiteness of starch gel was affected by the matrix formation and the crystallization of gel. The lightness of RS gel had increased compared to the control, due to a network matrix formation of rice starch gel. The degrees of whiteness of RS and starch gel with RS were in the following order: RS4> CARS3>RS3.

**Table 1. Hunter L, a, and b values of Nampyeong rice starch, resistant starches and gels with different 10% RS**

| Samples | Color values3) | | |
|---|---|---|---|
| | L | a | b |
| Native starch1) | 96.79±0.03$^{a4)}$ | -0.05±0.02$^{c}$ | 1.09±0.01$^{c}$ |
| RS31) | 88.75±0.06$^{c}$ | 0.51±0.05$^{a}$ | 7.15±0.04$^{a}$ |
| CARS31) | 90.35±0.01$^{b}$ | 0.20±0.01$^{b}$ | 5.68±0.14$^{b}$ |
| RS41) | 94.85±0.11$^{a}$ | -0.12±0.02$^{c}$ | 0.98±0.05$^{c}$ |
| Control2) | 27.52±0.73$^{c}$ | -0.81±0.04$^{a}$ | -0.53±0.09$^{a}$ |
| RS32) | 33.01±0.25$^{b}$ | -1.01±0.08$^{b}$ | -6.69±0.57$^{c}$ |
| CARS32) | 38.87±0.20$^{a}$ | -1.31±0.04$^{d}$ | -6.99±0.26$^{c}$ |
| RS42) | 39.68±0.30$^{a}$ | -1.19±0.05$^{c}$ | -6.05±0.04$^{b}$ |

1)Native rice starch, retrograded RS3, citric acid (CA) and RS3, and cross-linked RS4 were prepared from Nampyeong rice starch.

2)Rice starch gel without RS (control), and with RS3, citric acid RS3, and RS4, respectively.

3)Color values represent L (lightness), ±a (redness/greenness), and ±b (yellowness/blueness).

4)Each value represents mean±SD; Mean values in the same column with different letters are significantly different ($p<0.05$) according to Duncan's multiple range test.

**Pasting properties** Table 2 shows a comparison between the pasting properties of Nampyeong rice starch with or without RS. The initial pasting temperature showed no-

**Table 2. Pasting properties of rice starch with 10% RS**

| Properties | Native rice starch[1] | | | |
|---|---|---|---|---|
| | Control | RS3[1] | CARS3[1] | RS4[1] |
| Initial pasting temp. (°C) | 74.45±0.14 | 74.45±0.00 | 74.43±0.04 | 74.38±0.04 |
| Peak viscosity (P, RVU) | 246.50±2.24$^{a}$[2] | 245.56±1.30$^{a}$ | 210.88±1.24$^{b}$ | 215.75±0.35$^{b}$ |
| Trough visc. (T, RVU) | 184.42±0.24$^{a}$ | 184.63±2.89$^{a}$ | 165.75±2.24$^{c}$ | 177.08±2.36$^{b}$ |
| Cold visc. (C, RVU) | 320.21±0.06$^{a}$ | 317.17±5.42$^{ab}$ | 283.17±2.00$^{c}$ | 309.17±3.30$^{b}$ |
| Breakdown visc. (P-T) | 62.08±2.47$^{a}$ | 61.50±2.12$^{a}$ | 45.13±1.00$^{b}$ | 38.67±2.71$^{c}$ |
| Setback visc. (C-T) | 135.79±0.18$^{a}$ | 132.54±2.53$^{a}$ | 117.42±0.24$^{b}$ | 132.08±5.66$^{a}$ |

[1] Native rice starch, retrograded RS3, citric acid (CA) and RS3, and cross-linked RS4 were prepared from Nampyeong rice starch.

[2] Each value represents mean±SD; Mean values in the same row with different letters are significantly different ($p$<0.05) according to Duncan's multiple range test.

significant difference. All paste viscosities of peak, trough, cold, breakdown, and setback were significantly different ($p$<0.05). RS3 did not affect paste viscosities of rice starch, but CARS3 and RS4 decreased peak, trough, cold, and breakdown viscosities of rice starch. RS3 and CARS3 were composed of 92.59-90.95% amorphous polymer, and most RS3 starches were solubilized in heated starch paste. RS3 absorbed water, but did not increase peak viscosity. Therefore RS3 starch maintained paste viscosities of native rice starch. During the cooling of paste, linear soluble glucose chains interacted with starch molecules. Further, the low pH dispersion of CARS3 starch may affect the hydrolytic reaction of gelatinized starch molecules to lower molecular fragments that caused a reduction in viscosity. Consequently, the trough and cold viscosities of CARS3 starch pastes had the lowest values. It has been reported that RS4 maintains almost constant values of swelling power and solubility during heating, as the cross-linked RS4 starch granule does not absorb water when heated in excess water and retained the same size and the shape of a native granule. In other words, the type, solubility, modification method, and RS level of RS affected the pasting viscosity. Unabsorbed small particles of RS4 increased trough viscosity, but did not increase peak viscosity. Breakdown viscosity, which is the difference calculated between peak and trough viscosities, showed the lowest value in RS4 starch. However, the setback viscosity of CARS3 starch was different from a native starch, the RS3, and the RS4 starches. The control starch gel (12% sb) did not form a solid gel, but RS added 12% rice starch gels was rigid enough to form a gel structure (Fig. 1).

**Textural properties** Textural properties of starch gels with or without RS are presented in Table 3. There were significant differences among samples in textural parameters of hardness, springiness, and gumminess ($p$<0.05). Hardness of RS added starch gels was 2.24-4.59 times higher than the control. CARS3 added starch gel had the greatest hardness. The springiness of the control was significantly low, and increased with adding RS. The CARS3 and the RS4 added gels had more springiness than the RS3 added starch gel. The gumminess of gels had tendency to accompany springiness. The CARS3 and the RS4 improved the hardness, springiness, and gumminess of the rice starch gel. Results confirmed that the addition of RS improves textural properties of normal rice starch gels. The addition of citric acid (0.1%, sb) of retrograded RS formation decreased RS level, however CARS3 contributed to the formation of gel structure and improved textural properties. If rice starch in rice flour formed the structure to make rice noodles, rice cakes and rice bakery products, for it would be necessary for to improve quality and functionality to compensate for the hardness, springiness, and gumminess.

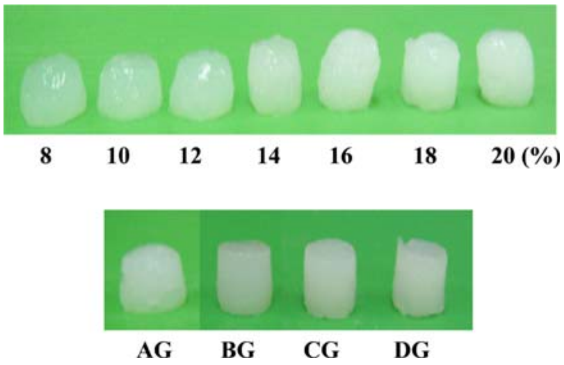

**Fig. 1. Shape of rice starch gels with different starch contents (top) and 12% rice starch gels with different RS types prepared from rice starch (bottom).** The 12% rice starch gels without RS (AG), and with RS3 (BG), CARS3 (CG), and RS4 (DG).

**Morphological properties** The shape of Nampyeong rice starch gels (24.25% amylose content) at different concentrations and gels with different RS (10% starch basis) are presented in Fig. 1. It is known that the formation and strength of starch gel is affected by starch source, amylose content, starch concentration, molecular structure, modification method, the addition of other substances, and rate and extent of heating (27). High amylose rice starch can be made into a gel at 12% starch concentration. However, forming a proper gel from normal Nampyeong

**Table 3. Textural properties of 12% Nampyeong rice starch gels with different 10% RSs**

| Samples | Hardness (g) | Adhesiveness | Springiness | Cohesiveness | Gumminess |
|---|---|---|---|---|---|
| Control[2)] | 76.22±22.44[c1)] | -71.66±46.27 | 0.31±0.06[b] | 0.91±0.06 | 68.64±18.63[b] |
| RS3 | 170.49±20.09[bc] | -69.64±47.83 | 0.45±0.01[b] | 0.93±0.02 | 158.58±15.34[b] |
| CARS3 | 349.89±104.41[a] | -35.39±4.21 | 0.53±0.04[a] | 0.87±0.09 | 297.59±53.15[a] |
| RS4 | 299.58±79.87[ab] | -115.31±86.65 | 0.52±0.07[a] | 0.88±0.03 | 262.57±61.67[a] |

[1)] Each value represents mean±SD; Mean values in the same column with different letters are significantly different ($p$<0.05) according to Duncan's multiple range test.
[2)] Control, Nampyeong rice starch gel without RS

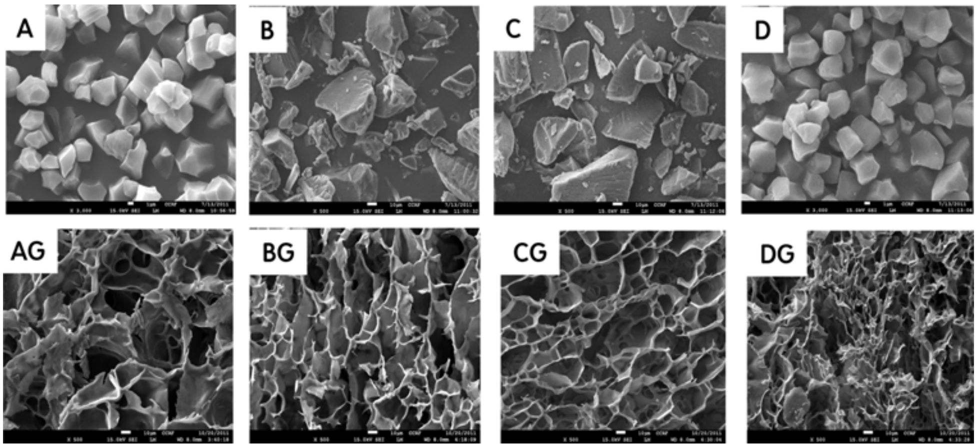

**Fig. 2. Scanning electron microphotographs of native rice starch (A ×3,000), RS3 (B), CARS3 (C), and RS4 (D ×3,000) (top) and 12% rice starch gels without RS (AG), and with RS3 (BG), CARS3 (CG), and RS4 (DG).** Magnification ×500

rice starch is difficult due to small particle size and lower soluble amylose concentration during gelation. The addition of a hydrophilic linear chain such as soluble glucose chains and hydrocolloids can improve the gel structure and texture. The 10% (w/w, sb) addition of the RS3, CARS3, and RS4 may help to form a gel matrix of normal rice starch paste under a 12% concentration. The above 12% rice starch gels showed firm but sticky gel compared to high amylose rice starch gel (The data was not shown).

The shapes of autoclaved-cooled RS3, CARS3, and cross-linked RS4 are shown in Fig. 2. The native rice starch granule ranged from 2-8 μm with a polygonal shape. RS4 was the same shape and size as a native starch granule. RS3 showed an irregular lump, regardless of treatment. RS3 has a thermal stability under 150°C and is composed of amorphous and recrystalline parts that have resistance to an amylolytic enzyme and consist of amylose double helical lamellar structures. The amorphous part of RS3 retained a higher capacity of water and was easily solubilized (13). The RS4 granule was similar to raw starch granules without a change of shape, as it forms on its own internal starch chains or cross-links between starch chains and membrane proteins via a phosphate group. When a starch is annealed, RS level increased with diverting the glucose chain (namely, starch molecular structures). As annealing was conducted below gelatinization temperature, the annealed and cross-linked RS4 did not alter the shape of granules. The network structure of rice starch gels with or without RS is shown as SEM in Fig. 2. Gel structure of the control was irregular with a large hole, and the addition of RS3 and CARS3 improved and transformed it to a three dimensional gel network structure (Fig. 2BG and 2CG). RS4 starch gel had a more compact structure than the control, which may be attributed to the intermingling of granular RS4 with breaking into the linear polymer chains to form a network. The hardness of starch gels with the CARS3 and RS4 was due to a regular linked and an irregular but dense gel structures, respectively (Table 3). Based on these results, it was suggested that RS help to form a three dimensional network of lowly concentrated rice starch gel. However, RS added non-waxy rice gel would improve gel quality in terms of appearance, color, and textural properties.

**X-ray pattern** The X-ray patterns of rice starch, RS and gels with or without RSs are shown in Fig. 3. In general, an A type crystalline is shown in rice starch; a B type crystalline is observed in potatoes, bananas, and high maize starches, and a C type crystalline can be seen in the starch of legumes, roots, fruits, and stems (28). Two crystalline structures of starch have been identified. The A type starches are found in cereal grains, and B type starches are

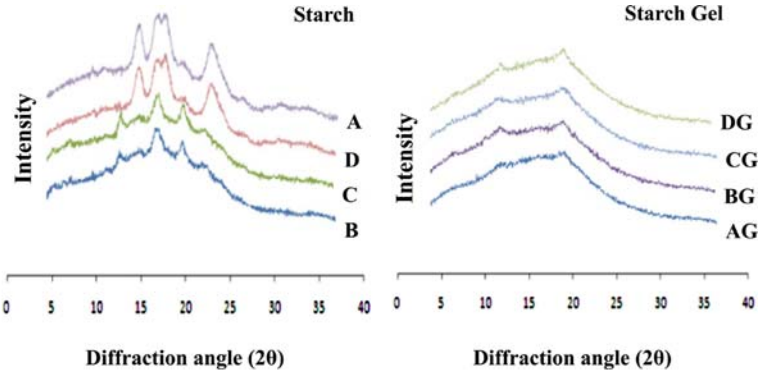

**Fig. 3. X-ray diffractograms of native rice starch (A), RS3 (B), CARS3 (C), and RS4 (D) and 12% rice starch gel powder without RS (AG), and with RS3 (BG), CARS3 (CG), and RS4 (DG).**

found in tubers and amylose-rich starches. A third type, called C type, appears to be a mixture of both A and B and is found in legumes (14). Native rice starch was shown an A type pattern (Fig. 3) and matched the diffraction angle of peaks at 2θ-15.0, 17.1, 18.0, and 23.0° in cereal starches. X-ray patterns of RS3 and CARS3 were the same as B and V type crystalline peaks at 2θ=12.7, 16.7, and 20°. An amylose-lipid complex peak was formed at 2θ=20° during the heating of starch paste. RS4 exhibited an A type crystallinity that was the same as native starch. It was suggested that annealing and cross-linked treatment were unaffected by the crystalline type of native starch. For example, a maize starch and high amylose maize starch prepared by annealing and cross-linking methods presented A type X-ray patterns (29).

X-ray diffraction of gel powders showed a peak at 2θ= 20°, which indicates that all have a V type crystalline. Rice starch paste was made from heating rice starch slurry (rice starch:RS:water=10.8-12:0-1.2:88), and gel was set at a cold temperature. The gelation process involves an amorphous polymer chain forming a three-dimensional network structure in diluted starch dispersion. Because the relative crystallinity of RS starch gel was low, the peak at 2θ=16.9° in the X-ray diffractogram was not found. It was difficult to make a gel structure with rice starch at a 12% concentration, because linear starch molecules in the paste cannot form double helix like retrograded amylose. RS levels of RS added gels were 3.52% in RS3, 3.16% in CARS3, and 6.51% in RS4 added starch gels, compared to 1.12% in control gel. The RS levels of RS3 and CARS3 added starch gels increased 2.6-2.9 times more than expected values. But in case of RS4, the RS level was similar to the expected values. In conclusion, RS3 and RS4 addition to rice starch gel (below~12% concentration) not only increased the total dietary fiber content but also improved the textural properties of the gel.

**Acknowledgment** This research was supported by High Value-added Food Technology Development Program, Ministry of Agriculture, Food and Rural Affairs.

**Disclosure** The authors declare no conflict of interest.

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