Carbohydrate Polymers 122 (2015) 77–83

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Impact of single and dual modifications on physicochemical properties of *japonica* and *indica* rice starches

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ARTICLE INFO

Article history:
Received 10 June 2014
Received in revised form
24 December 2014
Accepted 5 January 2015
Available online 12 January 2015

Keywords:
Rice starch
Acetylation
Hydroxypropylation
Cross-linking
Dual-modification

ABSTRACT

The *japonica* (JR) and *indica* (IR) rice starches were modified by acetylation, hydroxypropylation, cross-linking, and dual modification (cross-linked acetylation and cross-linked hydroxypropylation) and the effects of single and dual chemical modifications of JR and WR on the physicochemical properties were investigated. The JR had a greater substitution degree of acetyl or hydroxypropyl groups than IR. The dual-modified JR showed broader gelatinization temperature range than corresponding single-modified starches, but narrower it in IR. The dual-modified JR and IR showed higher pasting temperature and lower breakdown than their corresponding single-modified starches. The dual modification with JR and IR induced significant increase in gel hardness as compared to the corresponding unmodified and single-modified starches. The dual-modified JR had a greater hardness, gumminess, and chewiness than the dual-modified IR. The different impact of single and dual modification with JR and IR on the physicochemical properties could be due to the differences in the location and distribution of substituent groups on the starch molecules.

1. Introduction

Rice is a global staple food and is consumed principally as a whole grain. Starch, which is the major component of rice, mainly determines the acceptability of a rice cultivar in terms of its physicochemical properties and cooking characteristics (Sasaki et al., 2009). Although the utilization of rice starch is much less than the other cereal starches from corn and wheat, rice starch has several advantages, including hypoallergenicity, bland flavor, small granules, white color, greater acid resistance, spreadability, and relatively good freeze-thaw stability (Wani et al., 2013). These unique characteristics of rice starch make it ideal for various food applications. Rice starch, like other starches, consists of two polysaccharides, amylose and amylopectin (Hizukuri, 1996). Amylose is an essentially linear molecules of α-(1 → 4)-D-glucopyranosyl units with a few branches, whereas amylopectin has a high molecular weight and highly branched structures consisting of α-(1 → 4)-D-glucopyranosyl units with 5–6% non-randomly distributed α-(1 → 6)-D-glucopyranosyl units (Hizukuri, 1996). These two polymers are organized into a semi-crystalline structure. Rice can be divided into two sub-species, *indica* and *japonica*. Amylose content of *indica* rice starches is generally higher than that of *japonica* rice starches (Takeda, Hizukuri, & Juliano, 1987; Chung, Liu, Lee, & Wei, 2011).

Non-chemically modified starches have been used as food ingredients such as thickening, gelling, stabilizing, and binding agents in the food industry to improve the physical properties. However, non-chemically modified starches do not meet the industrial requirements because of its instability under shear and acidic conditions, retrogradation tendency, and high syneresis (Liu, Ramsden, & Corke, 1999). To overcome the inherent deficiencies of non-chemically modified starches, starch can be structurally modified by various chemical means with acetylation, hydroxypropylation, cross-linking and dual-modification (Liu et al., 1999; Das, Singh, Singh, & Riar, 2010). Starch modification involves alteration of the physicochemical characteristics of starches and can be used to tailor them to specific food applications (Eliasson & Gudmundsson, 1996). Several previous studies have investigated the physicochemical properties of chemically modified starches from different plant starch sources such as corn, tapioca, wheat,

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http://dx.doi.org/10.1016/j.carbpol.2015.01.009
0144-8617/

waxy corn, waxy barley and rice, with a range of modifications including substitution, oxidation and cross-linking, and varied reaction conditions including temperature, pH and concentration of catalyst salts (Lim & Seib, 1993; Wattanachant, Muhammad, Hashim, & Rahman, 2003; Das et al., 2010). However, a comparison of the effectiveness of various chemical modifications in different rice cultivars (*japonica vs. indica*) has not been fully investigated. The objective of this study was to investigate the effects of several single and dual mode chemical modifications (acetylation, hydroxypropylation, cross-linking and dual modification) with different rice starches from *japonica* and *indica* on physicochemical properties.

2. Materials and methods

2.1. Materials

The *japonica* and *indica* rices were obtained from the National Institute of Crop Science (Suwon, Korea) and General Food Products Co. (Nakhorratchasima, Thailand), respectively.

2.2. Starch isolation

Rice starches were isolated from the rice cultivars according to the alkaline steeping method described by Lim, Lee, Shin, and Lim (1999).

2.3. Amylose and protein contents

The amylose contents of the isolated rice starches were measured using high performance size-exclusion chromatography (HPSEC). The HPSEC system consisted of a pump (P2000, Spectra System, San Jose, CA), an injector (Rheodyne 7072, Cotati, CA), the SEC column (Superdex 75HR, Amersham Pharmacia Biotech, Uppsala, Sweden) and a refractive index detector (Shodex RI-71, Tokyo, Japan). The protein contents of the rice starches were measured using a Kjeldahl system (Kjeltec 1026, Tecator, Hoganas, Sweden).

2.4. Preparation of single and dual-modified rice starches

The rice starch slurry was prepared by dispersing the JR and IR (500 g, db) in distilled water (750 mL). For acetylation, acetic anhydride (5% of solid) was added dropwise to the slurry with simultaneously stirring at room temperature while maintaining the pH within 7.8–8.2 using 4% NaOH. The reaction was allowed to proceed for an additional 5 min after the completion of acetic anhydride addition. For hydroxypropylation, propylene oxide (5% of solid) was added to a starch slurry that has been adjusted to pH 11.5 using 1 N NaOH and stirred in a water bath at 45 °C for 24 h. Cross-linked starches were prepared by adding phosphorous oxychloride (0.02%) to a starch slurry with pH 11.5 using 1 N NaOH and stirred in a water bath at 45 °C for 2 h. For dual modification, the rice starch was first cross-linked using phosphorous oxychloride (0.02%) and then reacted with acetic anhydride (5%) or propylene oxide (5%). After the reactions, all starch slurries were neutralized with 1 N HCl, washed with five volumes of distilled water, and dried at 40 °C in a convection oven t for ~12 h to a moisture content of 10–12%.

Acetyl, hydroxypropyl, and phosphorous contents of modified starches were determined and the degree of substitution (DS) was calculated by using the methods reported by Wurzburg (1964), Johnson (1969), and Smith and Caruso (1964), respectively.

2.5. Thermal properties

The thermal properties of the single- and dual-modified rice starches were measured using a differential scanning calorimeter (DSC6100, Seiko Instruments, Chiba, Japan). The starch (3 mg, db) was weighted into a 15 μL aluminum pan (Seiko Instruments, Chiba, Japan) with 6 μL of distilled water. The pan was then sealed and equilibrated at room temperature for 12 h and then heated from 10 to 130 °C at a heating rate of 5 °C/min. An empty pan was used as a reference.

2.6. Pasting properties

The pasting properties of the single- and dual-modified rice starches were analyzed using Rapid Visco-Analyser (RVA-3D, Newport Scientific, Warriewood, Australia). Starch suspensions (7% w/w db, 30 g of total weight) were equilibrated at 50 °C for 1 min, heated to 95 °C at 13 °C/min, held at 95 °C for 3 min, cooled to 50 °C at 13 °C/min, and held at 50 °C for 4 min.

2.7. Swelling power and solubility

The swelling power and solubility of the starches were measured according to the methods reported by Schoch (1964). A starch suspension (0.5 g of starch in 30 mL of water) in a centrifuge tube with a cap was heated at 95 °C for 30 min with continuous shaking (200 rpm). The heated sample was cooled rapidly to room temperature and then centrifuged at 3500 rpm for 20 min. The swelling power was determined by measuring the sedimented paste weight and the solubility with respect to the solid content of the supernatant.

2.8. Gel properties

To prepare gels, starch suspensions (10% w/w db) were heated from 25 to 95 °C at 13 °C/min, held at 95 °C for 10 min and then cooled to 50 °C at 13 °C/min using Rapid Visco-Analyzer. The hot starch paste was transferred into a cylindrical plastic container (50 mm diameter, 0.9 mm height) and stored at 4 °C for 48 h. The texture of the starch gels was determined using a texture analyzer (TA-XT2, Stable Microsystems, Surrey, UK). The gel was compressed using a cylindrical plunger (20 mm diameter) to a depth of 4 mm at a speed of 1.0 mm/s.

2.9. Statistical analysis

The data reported were the means of triplicate measurements. Statistical analyses with Duncan's multiple test ($P < 0.05$) were carried out using SPSS V. 8.2 software (SPSS Institute Inc., Cary, NC).

3. Results and discussion

3.1. Chemical composition and substitution characteristics

The amylose contents of JR determined using size exclusion chromatography (SEC) was lower than that of IR (Table 1). Similar results with higher the amylose content in *indica* rice starch (IR) than *japonica* rice starch (JR) had been reported (Takeda et al., 1987; Chung et al., 2011). The protein contents, which indicate the purity of the isolated starches, were below 1% in JR and IR (Table 1).

The amounts of substituted groups and DS in acetylated and hydroxypropylated starches were greater in JR than IR (Table 1). These results indicate that JR was more easily substituted than IR. Biliaderis (1982) suggested that substitution occurs preferentially in the amorphous domains of amylopectin molecules. Chen, Schols, and Voragen (2004) also claimed that substitution took place in