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Effect of succinylation on functional and morphological properties of starches from broken kernels of Pakistani Basmati and Irri rice cultivars

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ABSTRACT

Starch extracted from broken kernels of Basmati and Irri rice varieties of Pakistani rice were subjected to modification by addition of succinic anhydride at levels of 2%, 4% and 5% based on dried weight of starch. The succinyl content of Irri rice starch increased with the concentration of succinic anhydride. Scanning electron micrographs revealed presence of dents and fusion of rice starch granules. Swelling power and water retention capacity (WRC) significantly improved after succinylation while on refrigerated storage percent decline in paste clarity of modified rice starches was stable as compared to native Basmati (BC) and Irri (IC) rice starches. Succinylation also reduced solubility, pasting temperature (PT) and gel hardness of starch gels. Improvement was observed in cold storage stability of rice starch succinates as evident from textural profile analysis.

1. Introduction

Almost half of the world's population relies on rice as its staple food. In Asia, rice contributes up to 80% of daily calories intake (Thomas, Wan-Nadiah, & Bhat, 2013). According to FAO global milled rice production in 2013 is 491.3 million tonnes while Pakistan produced 6.8 million tonnes of milled rice. Basmati and non-Basmati milled rice production in Pakistan is 1785 and 3778 tonnes, respectively (FAO Rice Market Monitor, 2014). Rice is one of the most important cereal crop of Pakistan. Basmati kernels are extra-long superfine slender grains with characteristic aroma and traditionally grow in India and Pakistan (Bhattacharjee, Singhal, & Kulkarni, 2002). Irri is non-aromatic rice variety cultivated in Pakistan and is cheaper than Basmati.

Starch is the major component of rice kernel and is almost 90% of the total kernel weight (Shih, 2003). Rice starch is a combination of novel characteristics. Small granular size (3–5 μm), whiteness, odourlessness, hypoallergenicity, blend taste and easy digestibility are some of unique characteristics of rice starch (Singh, Singh, Kaur, Sodhi, & Singh Gill, 2003; Ashogbon & Akintayo, 2012a). Distinctive characteristics of rice starch manifest its usage in food, pharmaceutical, cosmetic and packaging industries. However, native starch lacks some functional aspects. It is prone to syneresis during cold storage and cannot withstand high shear and pH. Therefore, starch is modified to improve and stabilize the functional characteristics. Minor change in starch molecular conformation and starch structure could result in dramatic changes in rheological properties of starch (Shon & Yoo, 2006). Physicochemical properties of starch vary with botanical source, reaction specifications, type of substituent group and degree of substitution (Chun & Yoo, 2007). Succinate starches show numerous desirable properties such as improved paste clarity, low temperature stability, better thickening capability, good film forming property, reduced retrogradation tendency and improved freeze thaw stability, low gelatinization temperature and stability in acidic and saline medium. These characteristics enable succinylated starches to be used in wide range of food and non-food applications. In food, starch succinates are used as binders and thickeners, tablet disintegrants in pharmaceutical sector where as in paper industry it is used as surface sizing agent and coating binder (Bhandari, Singhal, & Kale, 2002; Wu, Liu, Ren, Tong, & Zhou, 2014).

The purpose of the present study was to find differences in morphological, functional and textural characteristics of hitherto unexplored Pakistani rice starch isolated from the broken kernels of two major varieties of Pakistan i.e. Basmati and Irri. Broken rice is available at cheap rates and is usually used as bird feed in Pakistan. Furthermore, the study also aims to tailor the functional characteristics of rice starches through addition of succinic anhydride at 2%, 4% and 5% levels based on dry weight of starch.

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2. Materials and methods

Broken rice kernels from Basmati and Irri varieties were kindly provided by Matco Rice Processing (Pvt) Ltd. The total amylose content in Basmati and Irri was found to be 20.06% and 17.34%, respectively using the method of Hoover and Ratnayake (2001) in combination. All chemicals used were reagent grade.

2.1. Succinylation

Starch slurry 40% (w/w) was prepared in distilled water. The pH was adjusted to 9 using 3% NaOH solution. Succinic anhydride (2%, 4% and 5%, w/w) based on dried weight of starch was specially added to starch slurry while maintaining the pH between 9–9.5. The succinic anhydride reagent was added in small quantities while stirring. After complete addition of modifying reagent the slurry was stirred for two hours after which the reaction was terminated by neutralizing the slurry to pH 7 with 0.5 M HCl solution (Jyothi, Rajasekharan, Moorthy, & Sreekumar, 2005).

2.2. Degree of substitution

Starch (1.0 g, db) was weighed in 250 mL conical flask followed by addition of 50 mL of 75% ethanol (v/v). The starch sample was heated at 50 °C in a water bath with continuous swirling after which the suspension was cooled to room temperature. Then, 40 mL of 0.5 N NaOH was added in each flask with continuous swirling. Flasks were covered with aluminum foil paper and left for 72 h with occasional stirring and were subsequently titrated with 0.5 N HCl solution using phenolphthalein as an indicator. The samples were left for two hours and were then again titrated with 0.5 N HCl solution for complete titer estimation (Bhandari & Singhal, 2002). Percent succinyl content and degree of substitution (DS) was calculated using the formulas.

$$\%\text{Succinyl} = \frac{(\text{Blank titre} - \text{Sample titre}) \times 0.1 \times \text{Normality of acid} \times 100}{\text{Weigh of sample (g)}}$$

$$DS = \frac{162 \times (\%\text{Succinyl}/100)}{100 - (99/100 \times \%\text{Succinyl})}$$

2.3. Scanning electron microscopy (SEM)

The morphology of native and modified starches was studied using scanning electron microscopy (JSM, 6380A, Jeol, Japan). The starch sample was mounted on SEM stub with double sided adhesive tape and afterwards it was coated with gold. The images of all starches were photographed at an accelerating voltage of 6 kV and were studied at 4000× magnification.

2.4. Swelling power and solubility

Aqueous suspension of 1% (w/v) starch was heated at 90 °C for 30 min in pre-weighed centrifuge tubes (W1) using a temperature controlled water bath with occasional swirling. The heated suspensions were cooled to room temperature and subsequently centrifuged at 4448 g for 15 min. The supernatant was decanted and tubes were reweighed (W2) (Carmona-Garcia, Sanchez-Rivera, Méndez-Montealvo, Garza-Montoya, & Bello-Pérez, 2009). Swelling power (SP) calculated as:

$$\text{Swelling power (g/g)} = \frac{\text{W2} - \text{W1}}{\text{Weight of starch (dry basis)}}$$

Solubility was calculated by the method of Ali and Hasnain (2014).

2.5. Water retention capacity

Water retention capacity (WRC) was calculated by method of Ali and Hasnain (2014) with slight modifications. Starch (0.5 g, db) was measured in washed and dried screw capped pre-weighed centrifuge tubes followed by addition of 10 mL of distilled water. The tubes were capped and heated at 90 °C in a temperature controlled water bath for 15 min. Subsequently, the tubes were cooled to room temperature and centrifuged at 4448 g for 15 min. The supernatant was discarded. The centrifuge tubes were weighed with the cakes. The WRC was calculated using the following formula.

$$\text{WRC (g/g)} = \frac{\text{Weight of swollen starch granules} - 0.5}{0.5}$$

2.6. Pasting profile

The pasting properties of isolated and modified rice starches were studied using Brabender micro-viscoamylograph (Model 803201, Brabender, Germany) fitted with a 300 cmg sensitivity cartridge. Starch suspension of 10% (w/w, db) was used to analyze viscosity profile. It was heated from 40 °C to 95 °C at a heating rate of 3 °C/min and after which it was held at 95 °C for 10 min. The slurry was then cooled back to 50 °C at a cooling rate of 3 °C/min following which the starch slurry was kept under isothermal conditions at 50 °C for 10 min. The total program time for the viscoamylography was 55 min. Pasting temperature (PT), peak viscosity (PV), time to reach peak viscosity (TTPV), hot paste viscosity (HPV), breakdown viscosity (BDV), cold paste viscosity (CPV) and setback (SBV) viscosities were recorded from the resulting viscoamylograph.

2.7. Texture analysis

The textural analysis of starch gel prepared by aforementioned method using microviscoamylograph was conducted using testXpert® II program for Universal Testing Machine (Zwick/Roell, GmbH & Co, D-89079 Ulm). The starch gels were filled in plastic cups having 3.5 cm inside diameter The gels were compressed using a two cyclic compression test in order to stimulate the phenomenon of chewing. A 1-cm diameter cylindrical probe was used for the compression test which penetrated at a pre-load speed of 10 mm/min. A two cyclic compression test was used. After penetration, the speed was changed to 5 mm/s (termed as test speed). The deformation of starch gel was kept at 70% of the total compression. The parameters calculated for starch gel were: (i) Hardness, (ii) Cohesion strength, (iii) Gumminess, (iv) Chewiness, (v) Springiness. The starch gels were covered with parafilm and were kept at 6 °C. Textural parameters were measured at 0 hour and after one, three and seven days of refrigerated storage.

2.8. Paste clarity

Paste clarity was measured in terms of percent transmittance (%T). Aqueous suspension of 1% (w/v) starch slurry was heated at 90 °C for 1 h in a temperature controlled water bath with constant swirling. The samples were cooled to room temperature. The sample was stored in refrigerator at 4 °C for a week. The transmittance was determined by using UV–visible Spectrophotometer (JASCO V-670, Jasco Corporation, Tokyo, Japan) at 640 nm. The %T of gelatinized starch solution was measured at 0 h sing water as blank after which the starch slurries were stored in refrigerator at 4 °C and %T was measured at zero hour and after 1st, 2nd and 7th day of cold storage (Singh, Kaur, Sandhu, Kaur, & Nishinari, 2006).

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