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Characteristics of acetylated starches prepared using starches separated from different rice cultivars

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Abstract

The physico-chemical properties of acetylated starches from different rice cultivars were evaluated. The acetylation of starches from different cultivars showed different acetyl (%) and degrees of substitution (DS). The FT-IR spectral analysis confirmed the introduction of acetyl moiety in the acetylated starches through a band at 1730.8 cm^{-1}. The scanning electron microscopy did not show any significant difference between the external morphology of native and acetylated starches. The acetylated rice starches showed slightly higher amylose contents than their native counterparts. Acetylation increased swelling power and solubility and decreased T_o, T_p, T_c and ΔH_{gel} of all starches. In all starches, acetylation decreased pasting temperatures, but increased peak viscosities. Acetylation brought greatest change in T_o of the starch showing highest DS and least in the starch showing lowest DS. Acetylation caused weakening of the starch gels, which was observed to be dependent on degrees of substitution. Starch gels stored at 4 °C showed a significant decrease in syneresis (%) upon acetylation. The effectiveness of acetylation in reducing retrogradation was more evident from syneresis data than from setback viscosities observed by RVA.

Keywords: Rice starch; Acetylation; Physico-chemical; Morphological; Thermal; Pasting; Gel texture; Retrogradation

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1. Introduction

Starch, nature's most abundant polysaccharide, is a major food reserve providing energy often at low cost in the human diet. Starches have many diverse applications both in food production and industrial applications. But the native starches present limitations that reduce their use at the industrial level. They have low shear stress resistance, thermal decomposition, high retrogradation, and syneresis (Betancur & Chel, 1997). These facts motivated the employment of modified starches (Fleche, 1985) as important functional ingredients in processed foods in recent years because of their improved functional properties over unmodified starches (Wurzburg & Szymanski, 1970). Numerous chemical modifications may be applied to starch to impart properties that are useful for particular applications. One common starch modification is acetylation, which is the esterification of starch polymers with acetyl groups to form starch acetates (Jarowenko, 1986). Acetylation of starches has been applied to starches to impart the thickening needed in food applications. Acetylated starches have improved properties over their native counterparts and have been used for their stability and resistance to retrogradation (Wurzburg, 1986). Rutenberg and Solarek (1984) reported that the introduction of acetyl groups upon acetylation reduces the bond strength between starch molecules and thereby increases the swelling power and solubility of the starch granule, decreases the coagulation of the starch, and

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provides improved freeze-thaw stability. The extent of physico-chemical property changes in the acetylated starch compared to the native starch is proportional to the degree of acetylation or degree of C=O substitution incorporated into the starch molecules (Phillips, Huijum, Duohai, & Harold, 1999). Acetylated starches are extensively used in a large variety of foods including baked goods, canned pie fillings, sauces, retorted soups, frozen foods, baby foods, salad dressings, and snack foods (Wurzburg, 1995).

The availability of corn to the Indian starch industry is decreasing, day by day, because of increased demand by industries involved in the production of breakfast cereals and snacks. The broken rice, which is cheaper than corn and is available in abundance, can be used in the production and modification of starch. No studies have been reported that characterize the acetylated starches from Indian rice cultivars. So, the present study was undertaken to evaluate the effect of acetylation on the physico-chemical properties of rice starches isolated from different Indian cultivars.

2. Materials and methods

2.1. Materials

Five *indica* paddy cultivars (cv.) i.e. PR-106, PR-114, IR-8, PR-103 and PR-113, commonly grown in Punjab State, were procured from Punjab Agricultural University, Ludhiana, India. PR-106, PR-114, IR-8 and PR-113 had a maturity period of 144 days while PR-103 had 125 days. All the varieties have 30 days of grain filling period. Analytical grade acetic anhydride, sodium hydroxide and hydrochloric acid were procured from Glaxo India Limited, Mumbai. Ethanol was purchased from Hayman Ltd., Essex (UK).

2.2. Dehusking and milling

The paddy samples were dehusked and milled to remove 6% bran as described earlier (Singh, Singh, Kaur, & Bakshi, 2000). The paddy samples were dehusked on McGill sample sheller (Rapsco, Brookshire, TX, USA). The brown rice samples obtained were polished in McGill mill No. 2 (Rapsco, Brookshire, TX, USA) to obtain 6% degree of milling.

2.3. Starch isolation

Starch was isolated from various rice cultivars by alkali extraction of the protein. Milled rice was steeped in 5–6 volumes of sodium hydroxide (0.2–0.3%) solution at 25 °C for 24 h to soften the endosperms. The steep liquor was drained off and the endosperms were ground lightly in successive small fractions with a mortar and pestle. The slurry was then diluted to the original volume with sodium hydroxide (0.2–0.3%). The mixture was stirred for 10 min. and allowed to settle overnight. The cloudy supernatant was drained off, and the sediment was diluted to the original volume with sodium hydroxide solution. The process was repeated until the supernatant became clear and gave a negative reaction to the biuret test for protein. Starch was suspended in distilled water, passed through a 100–200 mesh nylon cloth, and repeatedly washed with water until the supernatant no longer showed any pink colour with the phenolphthalein. The starch was collected by sedimentation, and the white middle portion was collected and dried in cabinet drier at 40 °C (Nikuni & Hizukuri, 1958).

2.4. Acetylation of isolated rice starches

The method described by Phillips et al. (1999) was used to prepare acetylated starches. Starch (100 g) was dispersed in distilled water (225 ml) and stirred for 1 h at 25 °C. NaOH (3%) solution was used to adjust the suspension pH to 8.0. Acetic anhydride (6 g) was added drop-wise to the stirred slurry, while maintaining the pH within the range of 8.0–8.4 using 3% NaOH solution. The reaction was allowed to proceed for 10 min after the completion of acetic anhydride addition. The slurry was then adjusted to pH 4.5 with 0.5 N HCl. After sedimentation, it was washed free of acid, twice with distilled water and once with 95% ethanol, and then oven-dried at 40 °C.

2.5. Acetyl (%) and degree of substitution

The percent acetylation (% acetyl) and degree of substitution (DS) were determined titrimetrically following the method of Wurzburg (1978). Acetylated starch (1.0 g) was placed in a 250 ml flask and 50 ml of 75% ethanol in distilled water was added. The loosely stoppered flask was agitated, warmed to 50 °C for 30 min, cooled and 40 ml of 0.5 M KOH was added. The excess alkali was back-titrated with 0.5 M HCl using phenolphthalein as an indicator. The solution was stood for 2 h, and then any additional alkali, which may have leached from the sample, was titrated. A blank, using the original unmodified starch, was also used.

$$\text{Acetyl\%} = \frac{[(\text{Blank} - \text{Sample}) \times \text{Molarity of HCl} \times 0.043 \times 100]}{\text{Sample weight}}$$

Blank and sample were titration volumes in millilitre, sample weight was in gram. DS is defined as the average number of sites per glucose unit that possess a substituent group (Whistler & Daniel, 1995).

$$\text{DS} = \frac{(162 \times \text{Acetyl\%})}{[4300 - (42 \times \text{Acetyl\%})]}$$