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Changes in physicochemical properties of rice starch during steeping in the parboiling process

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ABSTRACT

Isolated rice starch, milled rice, and paddy rice kernels of the same variety (18% amylose) were examined after steeping at temperatures (60–75 °C) below and above the onset of rice starch gelatinization temperature for different durations in a 2:1 (w/w) ratio of water to kernel or starch. Changes in gelatinization temperatures were greater for resultant isolated starch >> milled rice > paddy rice. Annealing above its original T_o caused partial gelatinization, loss of crystallinity, and birefringence of the isolated starch as determined by X-ray diffraction, differential scanning calorimetry, and light microscopy. However, starch granules in milled rice and paddy rice, which are surrounded by non-starch components, maintained their granule integrity. Scanning electron microscopy revealed morphological differences between starch granules within native and steeped rice kernels. Rice starch granules and kernel characteristics were significantly altered during steeping and changes in isolated starch differed from those inside the rice kernels.

1. Introduction

Parboiling is a three-step hydrothermal process involving steeping, heating, and drying of rice. Parboiling can effectively change physical (e.g. resistance to breakage) and textural characteristics as well as improve nutritional values (Bhattacharya, 2004; Buggenhout et al., 2013a). Parboiling conditions affect the physicochemical properties of rice such as color formation via Maillard reactions (Lamberts et al., 2006a,b) and cooked rice texture because of differences in polymorphic forms of starch: residual starch, reassociated starch, and amylose-lipid complexes (Ong and Blanshard, 1995). With limited water and restricted space in rice kernels during parboiling, starch granules may lose their crystallinity but are still birefringent and display Maltese cross (Sittipod and Shi, 2016; Slade, 1984). The extent of Vh–type crystallite formation via amylose-lipid complexes has been found to be highly dependent on the moisture content of the kernel, moisture distribution within the kernel, steaming temperature (Derycke et al., 2005) and rice variety, which determines starch gelatinization onset temperature (Biliaderis et al., 1993). The extent of formation of retrogardated B-type crystallites originating from crystalline amylopectin and crystalline amylose greatly depends on the parboiling condition and amylose content (Lamberts et al., 2009).

Miah et al. (2002a,b) studied milling properties and the degree of starch gelatinization of parboiled rice using hot-soaking temperatures and found that accelerated water penetration into the kernel helped improve the quality of subsequent parboiled rice kernels and the efficiency of parboiling. Because starch makes up more than 80% of a rice kernel, it is important to understand not only how the kernels are altered, but also how the starch changes during steeping. When starch is heated in excess amounts of water at a temperature slightly below its gelatinization temperature for prolonged periods, it undergoes several physiochemical changes as a consequence of annealing (Jacobs and Delcour, 1998; Shi, 2008; Slade and Levine, 1991; Tester and Debon, 2000). This process is known to increase gelatinization temperature, decrease swelling power, and alter the pasting properties of starches. Many researchers have studied annealing effects on isolated starches (Jacobs and Delcour, 1998; Shi, 2008; Slade and Levine, 1991; Tester and Debon, 2000) but the changes in starch when annealed as whole rice kernels have not been well studied.

Non-starch components in rice kernels and the integrity of the whole kernel may affect the starch in rice kernels during the steeping step of the parboiling process. Protein, which makes up around 7% of the entire grain, is the second largest component in rice. Protein is known to contribute to the gelatinization and

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pasting properties of rice flour (Hamaker and Griffin, 1990; Zhu et al., 2010). The removal of proteins by buffer extraction or enzyme treatments tends to decrease the gelatinization temperature of starch in rice flour (Marshall et al., 1990). The disulfide bonds of proteins restrict starch granules from swelling, and prevent shearing disruption (Hamaker and Griffin, 1993). Without these proteins, starch granules break more easily under high shear and swell more under low shear, because intact proteins provide protection under high shear and act as barriers that restrict swelling under low shear. After disulfide bonds were destroyed with DL-dithiothreitol, waxy rice starch becomes more exposed and susceptible to alpha-amylase degradation (Zhu et al., 2010).

Lipids and waxes also contribute to rice's native barrier. Brown rice is higher in wax content than white rice and has a lower rate of water absorption, which explains why a higher degree of milling and lipid extraction samples have a lower gelatinization peak temperature (T_p) (Champagne et al., 1990). Similarly, Bello et al. (2004) studied the effects of bran level and hull on the rate of kernel water absorption, and found that the water diffusivity of white rice was higher than that of brown rice, which was higher than that of paddy rice. These authors concluded that the hull and bran fractions provided a diffusion barrier to water and reduced solid leaching. Normand and Marshall (1989) also noted the impact of kernel integrity on gelatinization, observing that producing flour destroys natural barriers and makes starch granules more accessible to water, thus lowering gelatinization temperatures.

We hypothesized that the differences in water absorption due to physical barriers would cause different annealing effects on starch granules in rice kernels than in flour or isolated starch. In this study, using thermal and microscopic techniques, we examined changes in isolated rice starch, milled rice and paddy rice kernels of the same long-grain variety during steeping at 60–75 °C. The starting materials represent three different physical forms with different morphologies and physical barriers. Our goal was to understand the effects of annealing on the changes in rice kernels during the steeping process of parboiling.

2. Materials and methods

2.1. Materials

Long-grain paddy rice (rough rice with hulls) was obtained from Mars Incorporated (McLean, VA). Foreign matter was removed by sifting through 10-mesh and 16-mesh standard test sieves (Fisher Scientific, Pittsburgh, PA), and rice was dehulled with a McGill Sheller (McGill Inc., Houston, TX). Bran was removed using a One-Pass Rice Pearler (Model No. 66939396, Satake, Tokyo, Japan) for 30 s to obtain milled rice kernels (degree of milling = 15%), which were then ground with a coffee grinder for 30 s at high speed to obtain milled rice flour. Chemicals were of analytical grade.

2.2. Isolation of starch

Rice starch isolation was based on an alkaline-protease method on milled rice kernels (Zhu et al., 2011).

2.3. Composition analysis

Amylose content was determined by a modified concanavalin (ConA) method and total starch was determined by AACC Method 76-13, each with an assay kit from Megazyme International Ltd. (Wicklow, Ireland). Moisture content was measured according to AACC Air Oven Method 44-19 in a convection oven (Model 160DM Thelco, Precision Scientific, Chicago, IL) at 135 °C for 2 h. Crude protein content was determined by the nitrogen combustion method using a Nitrogen Determinator (LECO FP-528, St. Joseph, MI) according to AOAC standard method 990.03. Nitrogen (N) values were converted to protein content using an N × 5.95 conversion factor. Total ash was based on AACC international method 946.05. All tests were done in duplicate.

2.4. Annealing

Thirty grams each of paddy rice kernels, milled rice kernels, and isolated starch were placed in glass jars, adjusted to a 2:1 (w/w) ratio of water to kernel or starch, and placed in a water bath (reciprocal shaking bath model 50: Precision Scientific, Chicago, IL) kept at a constant temperature of 60, 65, 70 or 75 °C. The jars were removed at time intervals of 0.5, 1, 2, 4, 8, and 16 h. Paddy and milled rice was then drained and air dried to about 12% moisture content. Isolated starch solutions annealed at 60, 65, and 70 °C were centrifuged (Beckman, model J2-21) at 3000*g* for 15 min and air-dried at 30 °C for 24 h. Isolated starch solution annealed at 75 °C was added to absolute ethanol (200 ml) with agitation. The mixture was centrifuged at 15,300*g* for 15 min and washed once with acetone. The starch was then dried using a vacuum pump equipped with a condenser system to trap the acetone solvent. Dried starch was then hand ground into fine powder using a mortar and pestle. Dried kernels were ground into flour using a coffee grinder (Model CM08, Hamilton Beach Brands, Inc., Richman, VA). Annealed paddy rice flour refers to flour from steeped paddy rice kernels. Annealed milled rice flour refers to flour from steeped milled rice kernels.

2.5. Kernel water absorption

Steeped paddy rice and milled rice were drained and lightly blotted with filter paper to remove excess water before being placed in a conventional oven (Model 160DM Thelco, Precision Scientific, Chicago, IL) at 105 °C for 24 h to determine moisture content. Isolated starch was centrifuged at 3000*g* and decanted before determining moisture content using the same procedure. Tests were done in duplicate.

2.6. Granule particle size

Particle size distribution of starches was measured using a Laser Scattering Particle Size Distribution Analyzer (Model LA-910, Horiba, Ltd., Japan). Starch (~10 mg) was suspended in 2 ml of distilled water and slowly introduced into the water reservoir until the light transmittance requirement reached around 85%. The suspension was sonicated for 60 s to prevent agglomeration before analysis. Three replicates were done per sample.

2.7. Differential scanning calorimetry (DSC)

Thermal properties were determined in duplicate using DSC (Q100, TA Instruments, New Castle, DE). Approximately 9 mg of starch were accurately weighed into a high-volume stainless steel DSC pan. Distilled water was added to obtain a starch to water ratio of 1:2 (w/w). The sample pans were hermetically sealed and heated from 10 °C to 120 °C at the rate of 10 °C/min. The transition temperatures reported were the gelatinization onset (T_o), peak (T_p), and conclusion (T_c) temperatures. The enthalpy of gelatinization (ΔH) was calculated using Universal Analysis software (TA Instruments) and normalized to the dry weight of the sample.

2.8. X-ray diffraction (XRD)

X-ray diffraction was conducted with an X-ray diffractometer (APD 3520, Philips, Eindhoven, Netherlands) with Cu Kα radiation