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RESEARCH ARTICLE

Porous rice powder from the precipitation of gelatinized flour or starch paste with ethanol*

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Hot paste obtained by autoclaving (130°C, 25 psi, 20–30 min) a 5–7% w/w rice flour or starch slurry was precipitated with ethanol (three extractions) to produce a dry, porous, pregelatinized powder with an average particle size of 75.0 μm (flour-derived powder) and 41.6 μm (starch-derived powder). The microstructure of the individual particles was characterized by an interconnecting lattice of irregularly shaped vesicles, and with cavities of varying size and shape. The vesicular network was relatively thinner and finer for the starch-derived products compared with the flour-derived ones. In comparison with native flour and starch, the bulk density of pregelatinized powders decreased; solvent uptake (water, oil, and alcohol), swelling power, and in vitro starch digestibility increased; whereas, gel consistency, freeze–thaw stability, and AAM content sparingly changed. Changes in morphological and physicochemical properties were generally more evident on the starch-derived products compared with the flour-derived counterparts. To some extent, changes in properties were also affected by severity of the gelatinization treatment (varying slurry concentration and autoclaving duration). The pregelatinized rice products as developed may be useful in food and non-food applications.

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1 Introduction

Native starches (or flours) are often modified by physical and/or chemical methods for enhanced functionality in various food and non-food applications. Research has demonstrated the production of modified gelatinized starch (or flour) containing a porous structure with increased specific surface area for improved food characteristics. Several studies investigated enzymatic hydrolysis [1] or digestion [2] on the properties of rice starch. However, these methods require long reaction times and

heating. Among the physical methods to modify rice starch, gelatinization is the simplest and is typically achieved either by drum-drying [3], spray-drying [4], or extrusion [5] techniques. Gelatinization results in starch granule-swelling, loss of birefringence and crystallinity, disruption of granule structure, and some level of molecular depolymerization [6–9]. These changes make pregelatinized flour or starch higher in water absorption and water solubility upon dispersion in cold water compared to its native counterpart [7]. With heat, pregelatinized products exhibit lower paste viscosity parameters as examined by viscoamylography [5–7, 10, 11]. Pregelatinized starch can be incorporated into food and non-food ingredients without heating to provide thickening, bulking, binding, and other properties [3–7, 10, 11]. It is

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Abbreviations: **BD**, breakdown; **FV**, final viscosity; **HPV**, hot paste viscosity; **PV**, peak viscosity; **RVA**, rapid visco analyzer; **SB**, setback; **TSB**, total setback

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useful in the preparation of many food products like instant pudding, breakfast cereal, soup mix, pie filling, cake frosting, salad dressing, baby food, among others [3, 5, 11]. The improved flowability of pregelatinized starch makes it suitable for use as a matrix in the manufacture of pharmaceutical tablets [12]. Improvements in dispersibility and viscosity properties make pregelatinized cereal flours more effective in paper and flocculation applications [10]. Pregelatinized starch also imparts desirable characteristics to drilling mud used in oil wells [13]. It is also a valuable matrix for the efficient auto-encapsulation of pesticides [14].

Aside from botanical origin, the physicochemical properties of pregelatinized powder from flour or starch highly depend on the gelatinization and drying conditions used [7–11, 15–17]. Pregelatinized wheat starch obtained by twin-screw extrusion exhibited lower cold-water swelling, higher solubility, and thinner pastes than did drum-dried counterparts [7–8]. SEM revealed that the particles of pregelatinized starch manufactured by extrusion technology appeared like irregularly-shaped stones with lots of holes; whereas, those produced by drum-drying showed irregular laminar structure [15]. Steam jet cooking of cereal flours increased paste dispersibility, and decreased paste viscosity and setback (SB) to greater extents than did water bath or amylograph cooking [10]. Wheat starch modified by gelatinization/freezing-drying had inferior flow properties compared with those prepared by spray-drying [12]. Significant starch molecular degradation was observed in pregelatinized rice flour prepared by gun-puffing process; whereas, hot air puffing did not degrade starch molecules [11]. Hu *et al.* [16] compared the properties of rice starch gelatinized by heat and high hydrostatic pressure and reported that retrogradation rate was slower for the latter. Gelatinization by autoclaving followed by slow cooling and freeze-drying increased the percentage of RS as a result of retrogradation [17]. In contrast, amorphous and non-fragmented pregelatinized starch was obtained from common corn by precipitation of hot, completely gelatinized paste with acetone, indicating the absence of retrogradation [9].

This work examined the morphological and physicochemical properties of pregelatinized rice flour and starch powders obtained by ethanolic precipitation of hot, gelatinized pastes. Autoclaving was employed to prepare the pastes. Our goal in this work was to modify the characteristics of rice flour and starch in order to be more readily used in both food and non-food uses. Of particular importance is the development of a simple method to produce pregelatinized powders that have a porous structure with increased specific surface area to improve food usage characteristics. The pregelatinized powder would vary in particle size and pore size when compared to native, commercially available rice flour and starch. The literature

is still limited regarding the viability and impact of employing such an alternative process of preparing pregelatinized powder. The results presented here provide insights on the product's potential food and non-food end-uses.

2 Materials and methods

2.1 Preparation of pregelatinized powder

Rice flour (Remyflo R7-150) with an amylose content of 25.2%, and rice starch (Remy B7) with an amylose content of 35.3%, were provided by A&B Ingredients (Fairfield, NJ). A 5% w/w flour or starch slurry in deionized water was prepared in a beaker and stirred continuously for 30 min with a magnetic stirring bar at speed 5 using a Corning hot plate/stirrer. The slurry was transferred into a stainless rectangular basin, covered with aluminum foil and placed in an autoclave (Cyclomatic Control, American Sterilizer Company, Erie, PA). For maximum gelatinization, the slurry was autoclaved at a temperature of 130°C and a pressure of 25 psi for 30 min. The hot paste was passed through a 100-mesh sieve and then transferred into a reagent bottle containing an equal volume of technical-grade ethanol. The mixture was shaken vigorously for 2 min for fine particles to form, and allowed to settle for an hour. The liquid layer was carefully decanted off the precipitate, replaced with the same amount of fresh ethanol, shaken vigorously as before and allowed to settle for 2 h. Decanting, replacement with fresh ethanol, and vigorous shaking were repeated once more and the mixture was allowed to stand overnight at room temperature. After decanting off the liquid layer, the precipitate was suction-filtered in a large Büchner funnel lined with a Whatman filter paper #4 to remove excess ethanol. The powdery precipitate was again washed with a minimal volume of ethanol, transferred into a plastic tray, allowed to further dry at room temperature for 24 h, and then ground with mortar and pestle to pass through a standard 80-mesh sieve. Powder was then stored in an airtight glass jar. To examine the effect of slurry concentration and autoclaving time, a batch of samples was prepared starting with a 7% slurry instead of 5% (flour or starch). Another batch was prepared by cutting down the autoclaving time from 30 to 20 min. All experiments were repeated twice.

2.2 Scanning electron microscopy (SEM)

Powder microstructure was visualized by an environmental SEM (Phillips XL-30, FEI-Phillips, Hillsboro, OR). The samples were mounted as follows. A double-sided adhesive tape was placed on a stub. The stub was gently dipped into the sample and tapped to remove loose particles. The mounted specimen was coated with Pd/

Au using an ion sputter (Hummer II Sputter Coater, Technics Inc, Alexandria, VA) to facilitate contrast imaging.

2.3 Particle size analysis

Particle size analysis was carried out with a small volume particle size analyzer (Model LS230, Coulter Corporation, Miami, FL). Powder (200 mg) was added with 5 mL of reagent grade methanol and vortexed for 30 s. The slurry was poured drop by drop into the sample port using a transfer pipet until the instrument read 45% PIDS (polarization intensity differential scattering) or 10–14% obscuration. Methanol was used as dispersant because pregelatinized starch and flour have high solubility in water.

2.4 Bulk density

A pre-weighed, 15-mL plastic graduated centrifuge tube was filled with powder sample to the brim. The tube was tapped continuously on the bench top until reaching a constant volume reading. The volume reading was recorded and the tube with the powder was weighed. Bulk density was expressed as grams per cubic centimeter.

2.5 Solvent uptake

Solvent uptake was evaluated with water, vegetable oil, and alcohol. For water uptake, a 0.2 g powder (db) was added with 10.0 mL of deionized water in a 15-mL pre-weighed centrifuge tube. The mixture was vortexed for 30 s, incubated for 15 min in a 30°C water bath, and followed by centrifugation at $1000 \times g$ for 10 min. Excess water was decanted off with a transfer pipet and the amount of absorbed water was calculated. Water uptake was expressed as grams of water absorbed per gram of powder (g/g). For oil absorption, a 0.5 g powder (db) was added with 2.5 mL peanut oil and the remaining steps of the water absorption test were followed as is. Peanut oil was replaced with reagent grade ethanol for the alcohol absorption test.

2.6 Pasting/gelling properties

Pasting characteristics were assessed with a rapid visco analyzer (model RVA-Super 4, Perten Instruments, Springfield, IL). Rice flour or starch (3.0 g, 12% moisture) was weighed into an aluminum canister and 25 g of distilled water was added. The mixture was initially stirred at 960 rpm for 10 s, held for 1.0 min at 30°C and a stirring speed of 160 rpm, heated to 95°C at 12°C/min, held for 2.5 min at 95°C, cooled to 30°C at 12°C/min, and finally held for 1.0 min at 30°C. Viscosity values were recorded in centipoise (cP). Variables measured were: peak viscosity (PV), hot paste viscosity (HPV or trough), final viscosity

(FV), breakdown (BD), SB, and total setback (TSB). BD was calculated as PV minus HPV; SB as FV minus PV; and TSB as FV minus HPV.

Gel consistency was determined according to Cagampang et al. [18] with modifications [19]. A 25-mg powder was weighed into a 10×75 mm test tube, wetted with 50 μ L of thymol blue solution (0.03% thymol blue in 85% ethanol) and vortexed for 10 s. It was immediately added with 0.5 mL of 0.2 N KOH, covered with a marble, and heated in a boiling water bath for 7 min. The water level of the bath was maintained to cover the lower 1/3 of the tube's length to avoid overflowing of the contents. The tube was taken out, cooled at room temperature for 5 min, and then chilled in an ice water bath (8–9°C) for 10 min. The chilled test tube was laid horizontally on a table for 30 min and gel consistency was measured as the extent of gel spreading (i.e. length in millimeter from the bottom of the tube to the top of the gel).

2.7 Swelling power

Swelling power was evaluated at 85°C according to the method of Leach et al. [20] with modifications. Starch sample (0.20 ± 0.01 g, db) was weighed into a 15 mL disposable centrifuge tube to which distilled water (6 mL) was added using a rapid dispensing pipette. The screw cap was replaced and vortexed immediately for 30 s. The tube was then placed in a constant temperature water bath at 85°C and mixed by inverting twice at regular intervals (20 s intervals initially for the first 5 min until the contents were fully gelatinized, and every 5 min thereafter, for a total time of 30 min). The tube was cooled rapidly in iced water bath for 15 min and then centrifuged at $\sim 2500 \times g$ for 15 min. The supernatant was carefully removed by suction, evaporated and dried at 105°C for 3 h. Swelling power was calculated as the weight of sedimented gel, divided by the original dry weight of starch less soluble dry matter.

2.8 Freeze–thaw stability

A gram of powder (db) was weighed into a 50-mL screw-cap test tube. A magnetic stirring bar and 25 mL deionized water were added, vortexed for 20 s to disperse, and heated in a boiling water bath for 20 min with stirring (speed 5). The tube was removed from the bath, opened, and the hot paste was mixed thoroughly with a stirring rod. Five pre-weighed 15-mL disposable centrifuge tubes were each filled with the hot paste up to the 4–5 mL mark. The tubes were capped and allowed to cool for 2 h and the weight of the cooled paste was taken. One freeze–thaw cycle involved storing at -20°C for 24 h and thawing in a water bath at 30°C for 2 h. The freeze–thaw cycle was repeated nine times. After 1, 3, 5, 7, and 9 cycles, one tube

was centrifuged for 15 min at $2500 \times g$ and the expelled water decanted off and the weight of the residual paste was taken. Syneresis was expressed as percentage ratio of expelled-water weight to the cooled-paste weight.

2.9 Starch digestibility

Starch digestibility was determined *in vitro* [19]. A 0.30 g powder was added with 3 mL of deionized water, vortexed for 30 s, heated in a boiling water bath for 15 min with magnetic stirring at 150 rpm, and cooled for 10 min to reach room temperature. The mixture was added with 7.0 mL of acetate buffer (0.1 M, pH = 5.2), incubated in a water bath at 37°C for 10 min with magnetic stirring, and added with 2.5 mL of amylase cocktail (3800 U/mL pan-creatin, 13 U/mL amyloglucosidase, and 188 U/mL invertase). Enzymatic hydrolysis was allowed to proceed for a period of 2 h, collecting a 0.25 mL aliquot every 20 min. The aliquots were transferred into separate tubes, each containing 20 mL of 66% ethanol to deactivate the enzymes. The tubes were vortexed for 30 s, centrifuged at $2500 \times g$ for 10 min, and the glucose in the supernatant was quantified with a D-glucose oxidase–peroxidase assay kit (Megazyme, Wicklow, Ireland). Rapidly available glucose was taken as the amount of glucose released after 20 min of enzymatic digestion. For comparison, the assay was repeated without the 15-min heating step to get an idea as to the extent of retrogradation or recrystallization that molten starch molecules undergo upon precipitation and drying.

2.10 Statistical analysis

Statistical analyses were done using JMP software version 8 (SAS Institute, Cary, NC). Analysis of variance was used to evaluate the effects of the different treatments. Significantly different means were identified by Tukey's HSD (Honestly Significant Differences) Test.

3 Results and discussion

3.1 Morphology and physical properties

The microstructure of the particles that compose the different powder samples are shown in Fig. 1. Native rice flour particles were polyhedral (Fig. 1A and B), consisting primarily of starch granules congregated by a protein coating. Alcohol-dried pregelatinized rice flour particles appeared like vesicular rocks (Fig. 1C and D). The surfaces consisted of interconnecting lattices of irregularly shaped vesicles, and cavities of variable size and shape. The starch granules were completely disintegrated and seemed to have fused with the denatured protein moiety.

Figure 1. Low (1000 $\times$) and high (2500 $\times$) magnification scanning electron micrographs, respectively, for native rice flour (A and B), porous rice flour (C and D), native rice starch (E and F), and porous rice starch (G and H) powder.

Native starch particles consisted of clusters of uncoated polyhedral granules with relatively smooth surface (Fig. 1E and F). Alcohol-dried pregelatinized rice starch powder resembled pregelatinized flour but the vesicles and cavities were slightly sharper and finer possibly due to the absence of protein (Fig. 1G and H). The microstructure of the powder samples in this work was noticeably different from those obtained by drum [3], spray [4], or freeze-drying [21] techniques. Drum-drying resulted in starch granule disintegration and the dried powder exhibited laminar structure [3]. Although spray drying did not cause starch granule disintegration, the granules became larger, deformed, and had dents on their surfaces [4]. On the other hand, freeze-drying of rice starch paste resulted in the formation of coarse honeycomb-like structure [21].

Average particle size of the pregelatinized powder after passing through a standard 80-mesh sieve (opening = 177 μm) was 75.0 and 41.6 μm for flour and starch, respectively (Table 1). The values were evidently higher than those of the native flour (63.2 μm) and native starch (10.3 μm) samples. The presence of protein moiety in flour

Table 1. Properties of native and pregelatinized starch rice flour and starch powder^{a)}

Property	Flour		Starch	
	Native	Pregel ^{b)}	Native	Pregel ^{b)}
Particle size (μm)	63.2 ^b	75.0 ^a	10.3 ^d	41.6 ^c
Bulk density (g/cm^3)	1.02 ^a	0.43 ^c	0.71 ^b	0.33 ^c
Water uptake (g/g)	2.5 ^c	12.1 ^b	1.0 ^d	14.9 ^a
Oil uptake (g/g)	1.0 ^d	2.5 ^b	1.6 ^c	3.2 ^a
Alcohol uptake (g/g)	0.7 ^d	1.6 ^b	1.0 ^c	2.2 ^a
Swelling power (g/g)	9.2 ^b	19.8 ^a	10.6 ^b	25.2 ^a
Gel consistency (mm)	28.5 ^b	64.5 ^a	55.5 ^a	66.5 ^a
Syneresis (%)	28.9 ^a	26.1 ^a	12.0 ^b	9.5 ^b
AAM (%)	25.2 ^b	26.9 ^b	35.3 ^a	35.1 ^a
Rapidly available glucose (%)	61.5 ^{ab}	60.8 ^b	63.1 ^a	62.8 ^a

a) Means in a row followed by a common superscript letter are not significantly different based on Tukey's honestly significant difference test ($p < 0.05$).

b) Pregelatinized flour or starch was prepared by autoclaving at a temperature of 130°C and a pressure of 25 psi for 30 min.

(~9.0%) may be responsible for the observed difference in particle size. Autoclaving and subsequent alcohol dehydration caused a reduction in bulk density by >50% for both flour and starch. Hagenimana et al. [5] also reported a decrease in bulk density for rice flour modified by extrusion. The decrease in bulk density may be associated with the extent of starch gelatinization and the destruction of crystalline structure. Water absorption increased by about 5 times for flour and nearly 15 times for starch. Oil and alcohol uptake, and swelling power at 85°C were more than doubled as a result of the treatments. These profound changes in solvent uptake and swelling power may be indicative of macromolecular disorganization and some level of molecular degradation due to autoclaving [3, 5, 7, 9].

3.2 Functional and physicochemical properties

With the exception of BD viscosity, the pregelatinized flour and starch powder exhibited lower paste viscosity parameters when examined with a RVA (Fig. 2) and these observations are in agreement with previous works [5–7, 10, 11]. Peak, hot paste, and FV values were 2538, 1893, and 5470 cP, respectively, for native flour; 1802, 882, and 2215 cP for pregelatinized flour; 1985, 1550, and 4085 cP for native starch; and 1651, 459, and 2036 cP for pregelatinized starch. BD viscosity was 645 and 920 cP, respectively, for native and pregelatinized flour; and 435 and 1192 cP, respectively, for native and pregelatinized starch. The increase in BD viscosity of the pregelatinized samples is indicative of poorer ability to withstand heating and stress during cooking, and can be attributed to the autoclaving treatment.

Pastes (~4%) prepared from the different powder samples showed poor freeze–thaw stability according to the syneresis data presented in Table 1 and Fig. 3. Syneresis already occurred even after the first freeze–thaw cycle. Variations were primarily between flour and starch samples; the effect of autoclaving/alcohol-dehydration treatment itself was minimal; and the level of syneresis increased after nine freeze–thaw cycles. The poor freeze–thaw stability may be attributed to the samples' relatively high amylose content (25.2–35.1%). The flour sample had about 9% protein and its lower freeze–thaw stability (or higher syneresis) in comparison with starch may be ascribed to the inferior water-retention capacity of

Figure 2. Rapid visco analyzer (RVA) pasting profiles of native and pregelatinized (pregel) rice flour and starch samples in comparison with a corn starch standard.

Figure 3. Freeze–thaw stability of native and pregelatinized rice flour and starch.

rice protein. The surface hydrophobicity of rice flour protein increases with denaturation by heat [22].

Differences in enzymatic starch digestibility were minimal at the initial stage of the assay. Rapidly available glucose, which is the amount of glucose (%) determined after 20 min of enzymatic digestion, did not differ among the samples except for pregelatinized rice flour (Table 1). Repeated exposure to ethanol should have removed the free sugars and short-chain polysaccharides in this particular flour sample, hence, there was an initially lower percentage of total glucose. After 2 h of digestion, the amount of glucose released was 86.5 and 85.5% for native and pregelatinized flour, respectively; and 95.0 and 93.3% for native and pregelatinized starch, respectively (Fig. 4). The effect of heating the samples prior to the enzymatic assay is also evident in Fig. 4. Uncooked native flour and starch were found susceptible to amylolytic digestion, although incomplete and at a slower rate (Fig. 4A and C). The digestibility of uncooked native flour was higher than the uncooked native starch possibly due to inherent damaged starch formed during its preparation by pin-milling. For the pregelatinized powders, starch digestibility of unheated samples was relatively slower during the first hour of the assay, but approached that of the heated counterparts at the end of the test (Fig. 4B and D). The slower rate indicates that the pregelatinized powders were not totally amorphous and some crystalline structure may have developed through starch–ethanol complex formation. XRD analysis revealed that precipitation of starch paste with ethanol and 2-propanol resulted in the formation of some starch–organic solvent complexes and some crystallinity [9].

Figure 4. In vitro starch digestibility of unheated and heated native rice flour (A); unheated and heated pregelatinized rice flour (B); unheated and heated native rice starch (C); and unheated and heated pregelatinized rice starch (D).

Table 2. Effect of slurry concentration and autoclaving duration on some properties of porous rice powder^{a)}

Condition/property	Flour				Starch			
Powder sample	I	II	III	IV	I	II	III	IV
Slurry concentration (%)	5	5	7	7	5	5	7	7
Autoclaving time (min)	20	30	20	30	20	30	20	30
Bulk density (g/cm ³)	0.47 ^a	0.46 ^{ab}	0.49 ^a	0.48 ^a	0.38 ^{bc}	0.33 ^c	0.43 ^{ab}	0.34 ^c
Particle size (μm)	89.0 ^a	88.5 ^a	95.8 ^a	94.6 ^a	71.2 ^b	41.6 ^c	90.0 ^a	43.2 ^c
Water uptake (g/g)	10.0 ^b	12.09 ^{ab}	11.95 ^{ab}	13.40 ^{ab}	13.70 ^{ab}	14.88 ^{ab}	13.85 ^{ab}	15.45 ^a
Oil uptake (g/g)	2.20 ^{bc}	2.50 ^{abc}	1.98 ^c	2.42 ^{abc}	2.70 ^{abc}	3.17 ^a	2.61 ^{abc}	3.06 ^{ab}
Alcohol uptake (g/g)	1.25 ^c	1.64 ^{bc}	1.23 ^c	1.53 ^{bc}	1.68 ^{bc}	2.20 ^a	1.37 ^c	2.01 ^{ab}
Swelling power (g/g)	17.7 ^c	17.4 ^{bc}	20.2 ^{abc}	21.7 ^{abc}	23.4 ^{abc}	24.7 ^{ab}	25.0 ^{ab}	26.8 ^a
Gel consistency (mm)	60.5 ^b	70.0 ^a	63.0 ^{ab}	70.5 ^a	62.5 ^{ab}	69.5 ^a	68.5 ^a	67.0 ^a
AAM (%)	27.3 ^b	26.9 ^b	27.6 ^b	28.2 ^b	35.3 ^a	35.2 ^a	36.0 ^a	35.4 ^a
Rapidly available glucose (%)	59.0 ^{ab}	60.80 ^{ab}	57.6 ^b	59.2 ^{ab}	61.4 ^{ab}	62.8 ^a	60.8 ^{ab}	61.0 ^{ab}

a) Means in a row followed by a common superscript letter are not significantly different based on Tukey's honestly significant difference test ($p < 0.05$).

3.3 Effects of amylose, slurry concentration, and autoclaving time

Precipitation of hot paste with ethanol worked well with high-amylose rice but not with waxy rice (amylose content ± 0.0). Adding ethanol to a hot waxy rice flour or starch paste resulted in the formation of a gummy, cohesive mass instead of the powdery, fine precipitates (data not shown). The same observation was reported by Amelia and BeMiller [9] with waxy corn starch paste when precipitated with a polar solvent like acetone. Preliminary trials were done by varying the starting flour or starch-in-water slurry concentration from 5 to 8% w/w. It was noted that with 8% slurry, a thicker paste was formed after autoclaving and was difficult to handle for ethanol precipitation. The precipitates appeared like milk curds. Upon air-drying at room temperature after a series of ethanol extraction and washing, the precipitates aggregated like coarse bread crumbs, and were tough to grind with mortar and pestle. Consequently, the data presented here are only for 5 and 7% slurry (Table 2). Autoclaving duration was also varied from 20 to 30 min. The idea of this work was to attain maximum starch gelatinization such that an autoclaving time shorter than 20 min was not attempted; autoclaving time beyond 30 min was also considered impractical in terms of energy requirement.

The effect of varying slurry concentration or autoclaving duration on the product's physicochemical properties was more evident for the starch-derived samples rather than the flour-derived counterparts, particularly average particle size and bulk density. The starch powder obtained by using a 7% slurry and autoclaved for 20 min had the highest average particle size; whereas, the sample obtained using a 5% slurry and 30 min autoclaving had the lowest. An opposite trend was observed for bulk

density; the 7%-slurry-20 min-autoclaving starch powder had the highest and 5%-slurry-30 min-autoclaving had the lowest. Such differences may be attributed to the severity of treatment that a sample was subjected to per total solids weight. The 5%-slurry-30 min-autoclaving combination was the more severe gelatinization treatment. As to the other physicochemical properties examined, the effect of varying slurry concentration or autoclaving duration was minimal. The observed differences were between flour and starch, and not necessarily due to the variation in processing conditions. Solvent uptake (water, oil, and alcohol), swelling power, gel consistency, amylose content, and rapidly available glucose of the flour powder samples were generally lower than those of the starch counterparts.

4 Conclusions

Autoclaving followed by alcohol precipitation/dehydration may be employed as an alternative process of producing dry, porous, pregelatinized powder from high-amylose rice flour or starch. The process resulted in some profound changes on powder morphological and physicochemical properties, the extent of which depended upon the severity of the gelatinization treatment. Accompanying changes were also more remarkable on the starch-derived powders than the flour-derived ones. The product's surface morphology was characterized by an interconnecting lattice of irregularly shaped vesicles, with cavities of varying size and shape. These features are different from those described in the literature for gelatinized powder prepared by drum-drying, spray-drying, or extrusion techniques. The process is not suitable for waxy samples (flour or starch that predominantly consists of amylopectin) because amylopectin–ethanol interaction resulted in

the formation of gummy, cohesive mass instead of fine, powdery precipitates. The process outlined in this work provides a low-cost, easy to manufacture, unique porous rice powder (flour and starch) that is ideal for many food uses.

The authors have declared no conflict of interest.

5 References

- [1] Xiao, H., Lin, Q., Liu, G.-Q., Effect of cross-linking and enzymatic hydrolysis composite modification on the properties of rice starches. *Molecules* 2012, 17, 8136–8146.
- [2] Yao, W. R., Yao, H. Y., Adsorbent characteristics of porous starch. *Starch/Stärke* 2002, 54, 260–263.
- [3] Nakorn, K. N., Tongdang, T., Sirivongpaisal, P., Crystallinity and rheological properties of pregelatinized rice starches differing in amylose content. *Starch/Stärke* 2009, 61, 101–108.
- [4] Laovachirasuwan, P., Peerapattana, J., Srijesdaruk, V., Chitropas, P., Otsuka, M., The physicochemical properties of a spray dried glutinous rice starch biopolymer. *Colloids Surf. B: Biointerfaces* 2010, 78, 3–35.
- [5] Hagenimana, A., Ding, X., Fang, T., Evaluation of rice flour modified by extrusion cooking. *J. Cereal Sci.* 2006, 43, 38–46.
- [6] Zobel, H. F., in: Whistler, R. L., BeMiller, J. N., Paschall, E. F. (Eds.), *Starch: Chemistry and Technology*, 2nd Edn. Academic Press, London 1984, pp. 285–309.
- [7] Colonna, P., Doublier, J. L., Melcion, J. P., de Monredon, F., Mercier, F., Extrusion cooking and drum drying of wheat starch. I. Physical and Macromolecular modifications. *Cereal Chem.* 1984, 61, 538–543.
- [8] Doublier, J. L., Colonna, P., Mercier, C., Extrusion cooking and drum drying of wheat starch. II. Rheological characterization of starch pastes. *Cereal Chem.* 1986, 63, 240–246.
- [9] Amelia, I., BeMiller, J. N., Preparation of nonfragmented, completely amorphous, pregelatinized maize corn starches and determination of the effects of fragmentation on the adhesiveness of their pastes. *Starch/Stärke* 2007, 61, 696–701.
- [10] Rankin, J. C., Phillips, B. S., Doane, W. M., Russell, C. R., Steam jet cooking of unmodified and modified cereal flours. Evaluation of paste properties, papermaking uses and flocculation activity. *Starch/Stärke* 1976, 28, 174–179.
- [11] Lai, H. M., Cheng, H. H., Properties of pregelatinized rice flour made by hot air or gun-puffing. *Int. J. Food Sci. Tech.* 2004, 39, 201–212.
- [12] Sanchez, L., Torrado, S., Lastres, J. L., Gelatinized/freeze-dried starch as excipient in sustained release tablets. *Int. J. Pharm.* 1995, 115, 201–208.
- [13] Zhang, L. M., A review of the starches and their derivatives for oilfield applications in China. *Starch/Stärke* 2001, 53, 401–407.
- [14] Trimnell, D., Shasha, B. S., Autoencapsulation: A new method for entrapping pesticides within starch. *J. Control. Release* 1988, 7, 25–31.
- [15] Yan, H., Zhengbao, G. U., Morphology of modified starches prepared by different methods. *Food Res. Int.* 2010, 43, 767–772.
- [16] Hu, X., Xu, X., Jin, Z., Tian, Y. et al., Retrogradation properties of rice starch gelatinized by heat and high hydrostatic pressure. *J. Food Eng.* 2011, 106, 262–266.
- [17] Björck, I., Nyman, M., Pedersen, B., Siljestrom, M. et al., Formation of enzyme resistant starch during autoclaving of wheat starch: Studies *in vitro* and *in vivo*. *J. Cereal Sci.* 1987, 6, 159–172.
- [18] Cagampang, G. B., Perez, C. M., Juliano, B. O., A gel consistency test for eating quality of rice. *J. Sci. Food Agric.* 1973, 24, 1589–1594.
- [19] Patindol, J. A., Guraya, H. S., Champagne, E. T., McClung, A. M., Nutritionally important starch fractions of rice cultivars grown in southern United States. *J. Food Sci.* 2010, 75, H137–144.
- [20] Leach, H. W., McCowen, L. D., Schoch, T. J., Structure of the starch granule. I. swelling and solubility patterns of various starches. *Cereal Chem.* 1959, 36, 534–544.
- [21] Lee, S. W., Rhee, C., Effect of condition and starch concentration on the structure and properties of freeze-dried rice starch paste. *Food Res. Int.* 2007, 40, 215–223.
- [22] Ju, Z. Y., Hettiarachchy, N. S., Rath, N., Extraction, denaturation, and hydrophobic properties of rice flour proteins. *J. Food Sci.* 2001, 66, 229–232.