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Structure-Functionality Changes in Starch Following Rough Rice Storage

The molecular-level features of starch in relation to the changes in rice functionality during storage are not yet fully elucidated. This work investigated the effects of rough rice storage conditions on starch fine structures and physicochemical properties. Dried rough rice samples (medium-grain Bengal and long-grain Cypress) were stored at 4, 21, and 38°C in temperature-controlled chambers and then periodically removed and evaluated after 1, 3, 5, 7, and 9 months. Flour (powdered head rice) and starch (extracted from head rice by alkali steeping) samples were evaluated for pasting and thermal properties. High-performance size-exclusion chromatography and high-performance anion exchange chromatography were used to characterize starch molecular size and amylopectin chain-length distribution, respectively. Significant changes in starch fine structure were observed primarily on the 38°C lots, and to some extent on the 21°C lots. The decreased amylose: amylopectin ratio, shortened amylopectin average chain length, and the shift in chain-length distribution to shorter branch chains were implicative of molecular-level starch degradation. The flour and starch samples showed inconsistent trends in pasting and thermal properties, thus suggesting the role of not only starch but also its interaction with non-starch components in rice aging.

Keywords: Amylopectin; Amylose; Fine structure; Rice starch; Storage and aging

1 Introduction

In the United States and other temperate rice growing countries, rice is grown once a year, harvested within a short period, but used year-round. Hence, part of the rice needs to be stored for an extended duration to provide a year-round supply before it is processed for specific end-uses. Stored rough rice is subject to a variety of physical, chemical, and biological changes, which are collectively termed as aging. Aging generally results in a higher head rice yield on milling [1–3], higher volume expansion and water absorption upon cooking [1–2, 4–7], and harder, less sticky cooked rice [4, 6, 8–12]. The changes in cooked rice texture associated with aging are enhanced by high storage temperatures [1, 4, 10–12]. The pasting and gelatinization properties of rice flour or starch pastes also change following storage. Amylograph peak and final viscosities tend to increase after a few months of storage [1, 8, 13, 14] but eventually decrease in the long term [15–17]. These changes, that accompany rice storage, may be favorable to some processors/end-users but may be unfavorable to others, depending on the intended applications and the ethnic background of the end-users.

Despite the many studies on the subject, the exact mechanism of aging is still not clear and some findings have been contradictory. *Moritaka* and *Yasumatsu* [18] proposed an aging mechanism involving lipids, starch, and proteins. Lipids form free fatty acids, that can complex with amylose and long chains of amylopectin. Carbonyl and hydroperoxide products of lipid oxidation can accelerate protein oxidation and condensation coupled with the accumulation of volatile carbonyl compounds [18]. *Mod* et al. [19] inferred that during storage, the ferulate esters of hemicellulose are oxidized, which leads to cross-linking and increased strength of cell walls and overall grain integrity. *Chrastil* [6, 7] hypothesized that many of the physicochemical and functional changes, that occur during storage, are caused by oryzenin-starch interactions. The molecular weight of oryzenin and its subunits increased substantially through disulfide bridge formation and the equilibrium binding ratio and binding constant between oryzenin and starch decrease appreciably, resulting in decreased rice stickiness [6, 7]. The foregoing suppositions simply reflect the complexity of the rice aging process.

The functionality of rice has long been ascribed to starch because starch constitutes about 90% of milled rice on a dry weight basis. However, studies regarding the structural changes of the starch molecule (amylose and amylopectin) following rough rice storage are limited. The fine

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structures of starch (including molecular-weight distribution of amylose and amylopectin, degree of branching, and chain-length distribution in amylopectin) have been suggested to influence cooked rice texture [20–23], gelatinization and pasting characteristics [24–29], and other functional properties [23, 28, 29]. The purpose of this study was to examine the effects of storage temperature and duration on starch fine structures and the relations of structure-function changes in the rice aging process. A study of the changes in the structural features of starch during rough rice storage may provide valuable insights regarding the mechanisms in rice functionality changes associated with aging.

2 Material and Methods

2.1 Materials and experiment design

This study was conducted for two consecutive crop years. The long-grain rice, Cypress (2001 crop), and the medium-grain rice, Bengal (2002 crop), were used for the first and second year, respectively. Clean, gently dried rough rice samples (at 20°C and 50% RH to ~12.5% moisture content) of each cultivar were provided by the University of Arkansas Rice Processing Program. For each cultivar, five bags of 150-g rough rice were placed in a tightly closed bucket. Two buckets of rice samples were stored at 4, 21, and 38°C in separate temperature-controlled chambers. One bag of rough rice was randomly removed from each bucket after 1, 3, 5, 7, and 9 months of storage for milling and evaluation of starch and other physicochemical properties.

2.2 Milling of sample

Samples were allowed to equilibrate to room temperature for 2 h prior to milling. A Satake THU-35 dehusker (Satake Corporation, Hiroshima, Japan) was used to dehull each 150-g rough rice sample. The brown rice recovered was milled for 30 s in a McGill No.2 Mill (RAPSCO, Brookshire, TX). Head rice was separated from the broken kernels through a double-tray sizing device (GrainMan Machinery Mfg. Corp., Miami, FL). Total milled rice and head rice yields were calculated as percentages by weight of rough rice.

2.3 Preparation of flour and starch samples

Flour samples were obtained by grinding head rice in a Udy cyclone sample mill (Udy Corp., Fort Collins, CO) fitted with a 0.5 mm sieve. Starch samples were prepared based on the alkali-steeping method of *Yang* et al. [30] with slight modifications. A 10-g milled rice sample was soaked in 40 mL 0.1% NaOH for 24 h. The soaked sample was then wet-milled in an Osterizer blender for 4 min at speed 6, filtered though a US standard test sieve #230 (63 μm), and centrifuged at 1,500 × *g* for 15 min. The supernatant was transferred into a waste bottle while the top yellow, curd-like layer of the residue was discarded by carefully scraping it off with a spatula. The remaining starch residue was washed with 0.1% NaOH, centrifuged at 1,500 × *g* for 10 min, and the supernatant and yellow curd were discarded as before. The pH of the starch residue was then adjusted to pH 6.5 with 0.2 M HCl, and washed with 40 mL deionized water three times with centrifugation. The starch residue was dried in a convection oven at 40°C for 24 h, and ground into powder using a mortar and pestle to pass through a standard 100-mesh sieve. Starch yield was calculated on a dry-weight basis. A portion of the starch sample was defatted with water-saturated 1-butanol by a procedure described by *Patindol* and *Wang* [28].

2.4 Starch characterization

The relative amounts of amylose, amylopectin, and intermediate material in defatted starch samples were analyzed by high-performance size-exclusion chromatography (HPSEC) following the method of *Kasemsuwan* et al. [31] as modified by *Wang* and *Wang* [32]. The HPSEC system (Waters, Milford, MA) consisted of a 515 HPLC pump with an injector of 100 μL sample loop, an in-line degasser, a 2410 refractive index detector maintained at 40°C, and a series Shodex OHpak columns (KB-802 and KB-804) maintained at 55°C. Amylopectin, intermediate material, and amylose content were calculated automatically from the area of their corresponding peaks. The chain-length distribution of amylopectin was determined by high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) according to the method of *Kasemsuwan* et al. [31] with modifications [32]. The HPAEC system (Dionex DX500, Sunnyvale, CA) consisted of the following components: GP50 gradient pump, LC20–1 chromatography organizer, ED40 electrochemical detector, 4 × 50 CarboPac PA1 guard column, 4 × 250-mm CarboPac PA1 analytical column, and AS40 automated sampler.

2.5 Pasting properties

The pasting properties of 10% flour or starch slurries (50 g, 12% moisture, in 450 mL deionized water) were measured according to Approved AACC Method 61–01 [33] with a Brabender Viskograph-E (C.W. Brabender Instruments, Inc., South Hackensack, NJ). The slurry was first held at 35°C for 5 min, heated to 95°C at a rate of 1.5°C/min, held at 95°C for 20 min, and cooled to 50°C at 1.5°C/min. Viscosity values were expressed in arbitrary Brabender units (BU). Pasting temperature was estimated as the point where the amylograph curve crossed the 20-BU viscosity line. Paste breakdown was calculated as the difference between peak hot-paste viscosity and minimum hot-paste viscosity (amylograph trough). Peak hot-paste viscosity was subtracted from the final (cooled paste) viscosity to obtain setback viscosity.

2.6 Thermal properties

Thermal properties were assessed by a Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC) (Perkin-Elmer Co., Norwalk, CT) following the method of *Wang* et al. [34]. The instrument was calibrated with indium and an empty pan was used as reference. Starch (4.0 mg, dry basis) was weighed into an aluminum DSC pan and then moistened with 8 μL of deionized water using a microsyringe. The pan was hermetically sealed and allowed to stand for 1 h prior to thermal analysis. Thermal scanning was done from 25 to 120°C at a heating rate of 10°C/min.

2.7 Statistical analysis

The experimental data from each crop year were analyzed in a split-plot statistical model with storage temperature as main-plot factor (with two nested replicates) and storage duration as sub-plot factor. JMP version 5 (SAS Software Institute, Inc., Cary, NC) was used in the statistical analyses. Analysis of variance was done to detect any significant contribution of the treatment factors and factor interactions. Significantly different means were identified by Least Significance Difference test *($P <$ 0.05)*.

3 Results and Discussion

3.1 Starch yield

Fig. 1 presents the data on starch yield from Bengal and Cypress head rice as affected by the storage conditions examined in this study. The medium-grain cultivar, Bengal, generally had a lower starch yield than the long-grain cultivar, Cypress. It was observed for Bengal that a larger amount of residue, although not quantified, could not pass through the 63-μm sieve upon the filtration of the wet-milled, alkali-rice slurry. Bengal kernels were thicker (average thickness of 1.78 mm) than Cypress (average thickness of 1.66 mm) and their difference in thickness may cause the difference in starch recovery by the alkali-steeping method. Although both cultivars were subjected to the same NaOH concentration and steeping time, the penetration of the alkali solution into the core of the milled rice endosperm and the dissolution of the non-starch matrix, that holds starch granules together, may be less efficient for the thicker-kernel cultivar. Fig. 1 also shows an evident decrease in the amount of starch recovered from head rice on the batch stored at 38°C for both cultivars following storage and the decrease became significant on the fifth month. It was noted that during the alkali-extraction of starch, the amount of residue retained on the sieve and the yellow curd recovered in the centrifugation step tended to increase during storage, which corresponded to a decrease in the amount of starch recovered. The decrease in starch yield and increase in the amount of yellow curd and residue are indicative of enhanced interaction between the starch granules and the matrix of protein and non-starch components, that hold the individual starch granules together as a result of aging. Because of the enhanced interaction, isolation of the starch granules from the matrix became more difficult.

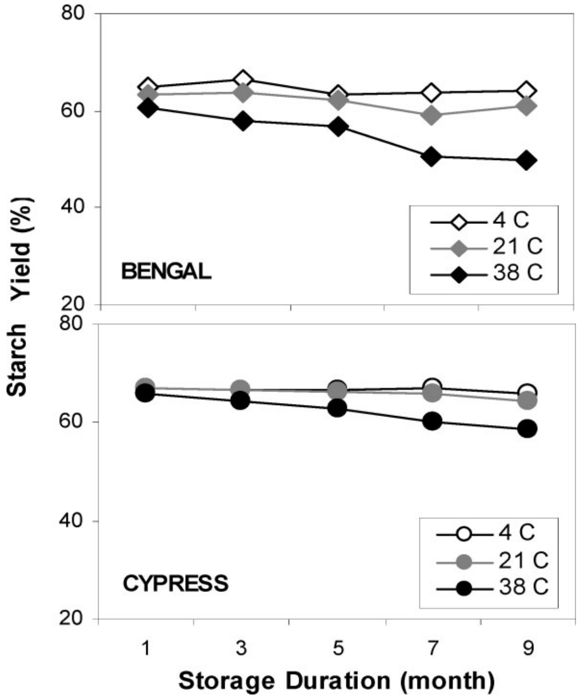

Fig. 1. Starch extraction yields (%) from Bengal and Cypress milled head rice following rough rice storage.

3.2 Changes in starch molecular size distribution

Fig. 2 shows representative chromatograms of starch samples resolved by HPSEC. Based on the area of the chromatogram peaks, the relative proportion of amylo-

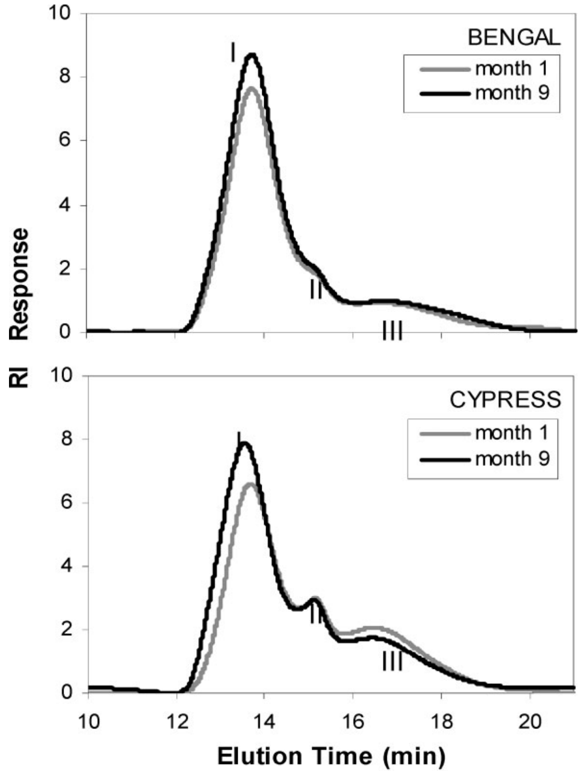

Fig. 2. High-performance size exclusion chromatographs of the native starches from Bengal and Cypress after 1 and 9 months of rough rice storage: I: amylopectin, II: intermediate material, and III: amylose.

pectin (I), intermediate material (II), and amylose (III) in the starch samples were calculated and expressed as percentage as summarized in Tab. 1. For Bengal, a significant change in the relative proportion of amylose and amylopectin occurred after 7 and 9 months for the lots stored at 21 and 38°C. The area of the amylopectin peak on the HPSEC chromatogram increased while that of amylose decreased. Starch molecular size distribution did not change for the Bengal samples stored at 4°C. For Cypress, only the lot stored at 38°C showed a significant change in starch molecular size distribution. The area of the amylopectin peak increased, while that of amylose decreased after 9 months (Tab. 1).

It has been reported that amylolytic enzymes remain active during rough rice storage although their activity tends to decrease over time [6, 35, 36]. *Awazuhara* et al. [36] reported that the starch degrading enzymes in the inner rice endosperm had a higher optimum temperature than those in other parts of the kernel. Hence, the observed changes in starch molecular size distribution especially on the batches stored at a higher temperature may be attributed to starch hydrolysis by amylolytic enzymes. The present results agree with an earlier inference that some hydrolysis or degradation may occur during rough rice storage, leading to a significant increase in reducing sugars and a decrease in non-reducing sugars and starch [6, 37]. Furthermore, *Chrastil* [6] also

Tab. 1. Molecular size distribution of Bengal and Cypress starch following rough rice storage[a].

Storage		Bengal			Cypress		
Temp. [°C]	duration [month]	AP [%]	IM [%]	AM [%]	AP [%]	IM [%]	AM [%]
4	1	74.9 gh	9.7 abc	15.4 ab	66.1 b	13.8 a	20.2 a
	3	75.1 efgh	9.5 bcd	15.4 ab	66.3 ab	13.8 a	20.0 ab
	5	75.2 defg	9.4 cde	15.4 ab	66.6 ab	13.4 a	20.0 ab
	7	75.3 defg	9.5 bcd	15.2 ab	66.8 ab	13.2 a	20.0 ab
	9	75.5 cdef	9.3 cde	15.2 ab	66.5 ab	13.4 a	20.1 a
21	1	74.8 gh	9.7 abc	15.5 a	65.9 b	14.1 a	20.0 ab
	3	74.7 gh	9.9 ab	15.4 ab	66.3 ab	13.5 a	20.2 a
	5	75.1 efgh	9.5 bcd	15.4 ab	66.8 ab	13.4 a	19.9 ab
	7	75.6 bcd	9.5 bcd	14.9 cd	66.6 ab	13.3 a	20.1 a
	9	76.0 b	9.1 e	14.9 cd	66.7 ab	13.6 a	19.6 abc
38	1	74.6 h	10.0 a	15.4 ab	66.2 b	13.8 a	20.0 ab
	3	76.6 bcd	9.3 cde	15.1 bc	66.6 ab	13.6 a	19.8 abc
	5	75.8 bc	9.3 cde	14.9 cd	66.3 ab	14.0 a	19.8 abc
	7	76.8 a	9.3 cde	13.9 d	67.0 ab	13.6 a	19.4 bc
	9	76.8 a	9.2 de	14.0 d	67.4 a	13.4 a	19.2 c

[a] Values are means of two replicates. Means in a column followed by a common letter are not significantly different based on Least Significance Difference ($P < 0.05$). Abbreviations: AP, amylopectin; IM, intermediate material; AM, amylose.

noted that the molecular weight of starch slightly decreased with storage. The amylose: amylopectin ratio remained fairly constant on the lots stored at 4 and 21°C but decreased noticeably on the lots stored at 38°C (Fig. 3). The decreasing trend in amylose: amylopectin ratio suggested that amylose might be hydrolyzed faster than amylopectin at an elevated storage temperature. This is being thought of considering that the amylose molecules are generally confined in the amorphous layers of the starch granules which are more susceptible to enzymatic attack and other chemical changes than the amylopectin-rich crystalline layers.

3.3 Changes in amylopectin chain-length distribution

The data on amylopectin chain-length distribution (Tab. 2, Fig. 4) indicated that the amylopectin fraction of starch was also degraded during rough rice storage. The amylopectin molecule seemed to undergo some trimming of the long chains, as the short branch chains (A chain or DP 6–12) tended to increase while the long branch chains (B2 chain or DP 25–36 and B3 chain or DP 37+) tended to decrease. The changes in amylopectin chain-length distribution were significant only on the lots stored at 38°C after 7 months (for both Bengal and Cypress) and with Bengal samples stored at 21°C after 9 months. Average amylopectin chain length also decreased significantly on the lots stored at 38°C. The average length changed from 20.5 to 19.5 glucose units for Bengal and from 21.92 to 20.31 glucose units for Cypress (Fig. 4). This agrees with the findings of *Chrastil* [6, 7] that the molecular weight of amylopectin slightly decreased following storage. The change in amylopectin chain-length distribution and average chain length may also be attributed to amylolytic enzyme activity as previously suggested.

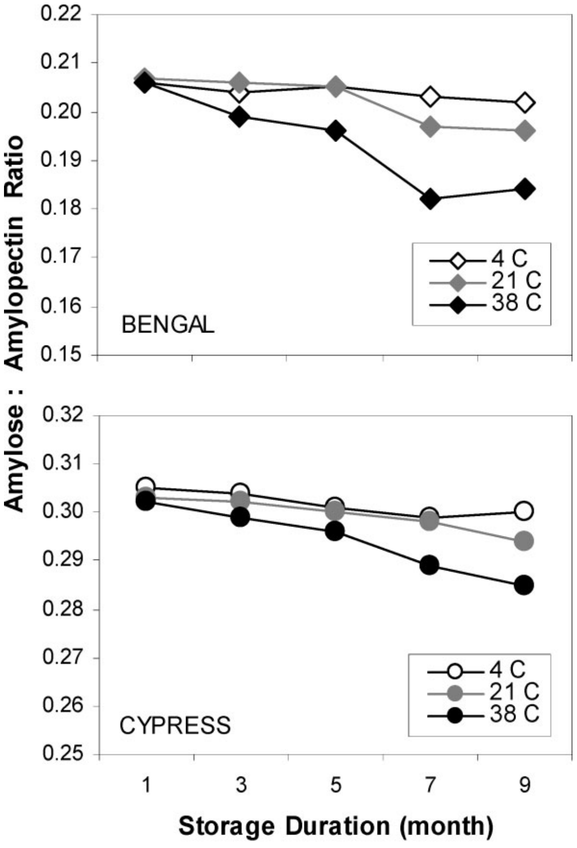

Fig. 3. Changes in the amylose: amylopectin ratio of the starches from Bengal and Cypress following rough rice storage as determined by high-performance size-exclusion chromatography.

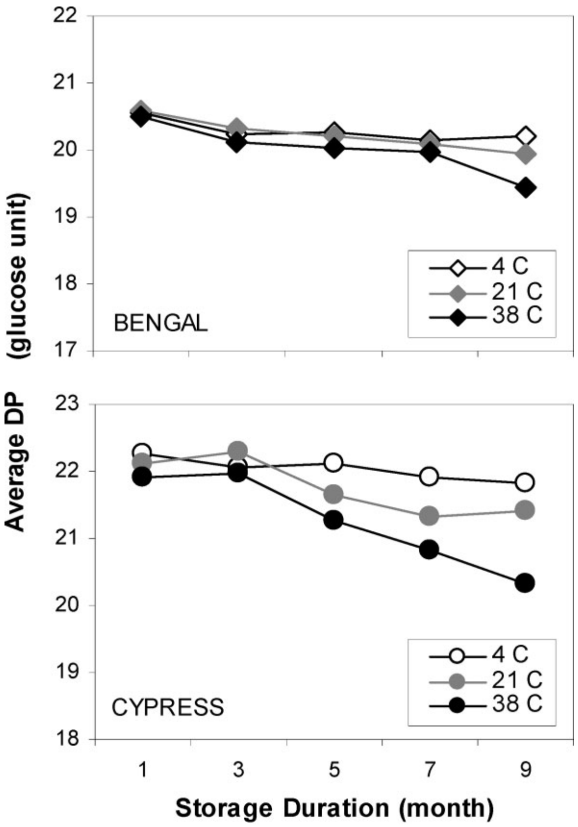

Fig. 4. Changes in the average amylopectin chain length (no. of glucose units) of the starched from Bengal and Cypress following rough rice storage as determined by high-performance anion exchange chromatography with pulsed amperometric detection.

3.4 Starch structure and changes in pasting properties

The pasting properties of starch and flour samples were evaluated side by side to account for the importance not only of starch itself but also of the other rice endosperm

Tab. 2. Amylopectin chain length distribution following rough rice storage[a].

Storage		Bengal				Cypress			
Temp. [°C]	Duration [month]	DP 6–12 (A chain)	DP 13–24 (B1 chain)	DP 25–36 (B2 chain)	DP 37+ (B3 chain)	DP 6–12 (A chain)	DP 13–24 (B1 chain)	DP 25–36 (B2 chain)	DP 37+ (B3 chain)
4	1	26.1 h	50.7 a	12.1 f	11.1 abc	18.2 ef	52.0 abc	15.6 ab	14.2 ab
	3	26.2 fgh	50.6 ab	12.1 f	11.1 abc	19.5 bcde	51.3 abc	15.0 abcde	14.2 ab
	5	26.4 efgh	50.2 abc	12.4 ef	11.0 abc	19.9 bcd	51.9 abc	14.4 def	14.0 abc
	7	26.5 efgh	50.0 abcd	12.5 cdef	11.0 abc	19.8 bcd	51.1 c	15.7 a	13.4 bcde
	9	26.9 def	49.9 abcd	12.2 f	11.0 abc	20.0 abcd	52.9 ab	13.9 f	13.2 cde
21	1	25.9 h	49.3 cdef	13.5 a	11.2 abc	17.9 f	53.0 a	15.1 abcd	14.0 abc
	3	26.2 gh	48.9 efgh	13.6 a	11.3 ab	18.7 def	52.5 abc	15. 5 abc	13.3 bcde
	5	26.4 efgh	49.1 defg	13.4 ab	11.1 abc	19.9 abcd	53.2 a	14.0 ef	12.9 de
	7	26.8 defg	49.5 cdef	13.0 bcde	10.7 cd	20.3 abc	52.5 abc	14.0 ef	13.2 cde
	9	27.9 bc	48.6 fghi	12.4 def	11.1 abc	20.7 ab	52.9 ab	13.9 f	12.5 e
38	1	26.3 fgh	49.1 defg	13.2 abc	11.4 a	17.4 ef	52.2 abc	14.8 bcdef	14.6 a
	3	26.9 def	48.3 ghi	13.4 ab	11.4 a	19.0 cdef	52.0 abcd	15.0 abcd	14.2 ab
	5	27.4 cd	48.1 hi	13.6 a	10.9 abc	19.0 bcde	52.0 abc	15.0 abcd	13.5 bcd
	7	28.2 b	48.0 i	13.0 bcde	10.8 bcd	20.0 abcd	52.2 abc	14.7 cdef	13.3 bcde
	9	29.1 a	48.1 hi	12.5 cdef	10.3 d	21.2 a	51.8 abc	14.0 ef	13.0 cde

[a] Values are means of two replicates. Means in a column followed by a common letter are not significantly different based on Least Significance Difference ($P < 0.05$).

Tab. 3. Brabender viscosity of flour and starch pastes following rough rice storage[a].

Storage		Bengal				Cypress			
Temp. [°C]	Duration [month]	Flour		Starch		Flour		Starch	
		Peak [BU]	Final [BU]	Peak [BU]	Final [BU]	Peak [BU]	Final [BU]	Peak [BU]	Final [BU]
4	1	720 g	550 e	1,262 ab	928 ab	705 gh	705 gh	945 d	1,095 bc
	3	728 fg	572 cde	1,258 ab	925 abc	698 gh	698 gh	968 cd	1,095 bc
	5	730 fg	552 de	1,260 ab	925 abc	682 h	682 h	1,008 bcd	1,040 c
	7	728 fg	578 cde	1,290 ab	910 bcde	715 ef	715 ef	1,030 bcd	1,042 c
	9	732 fg	578 cde	1,268 ab	905 bcde	758 de	758 de	1,015 bcd	1,040 c
21	1	748 f	587 cd	1,255 ab	932 a	740 ef	740 ef	990 cd	1,128 ab
	3	778 e	600 c	1,270 ab	925 abc	725 fg	725 fg	990 cd	1,122 ab
	5	780 de	580 cde	1,250 b	928 ab	780 cd	780 cd	975 cd	1,030 c
	7	782 de	582 cde	1,280 ab	905 bcde	790 c	790 c	1,045 bcd	1,035 c
	9	800 d	595 c	1,305 ab	898 de	856 a	856 a	1,055 bcd	1,055 c
38	1	845 c	678 b	1,272 ab	922 abcd	838 b	838 b	1,065 abcd	1,185 a
	3	868 b	680 b	1,255 ab	905 bcde	855 ab	855 ab	1,057 abcd	1,082 bc
	5	942 a	838 a	1,260 ab	900 cde	856 a	856 a	1,128 ab	1,035 c
	7	938 a	852 a	1,300 ab	898 de	872 a	872 a	1,072 abc	1,055 c
	9	940 a	858 a	1,322 a	855 e	872 a	872 a	1,185 a	1,038 c

[a] Values are means of two replicates. Means in a column followed by a common letter are not significantly different based on Least Significance Difference ($P < 0.05$).

components removed in the alkaline extraction of starch. The trends in pasting property changes following rough rice storage are depicted in Tab. 3, Fig. 5 and Fig 6. Changes were generally minimal and statistically non-significant on the lots stored at 4°C for both Bengal and Cypress (flour and starch samples). Notable changes were observed mainly on the lots stored at 38°C and to some extent, on the lots stored at 21°C.

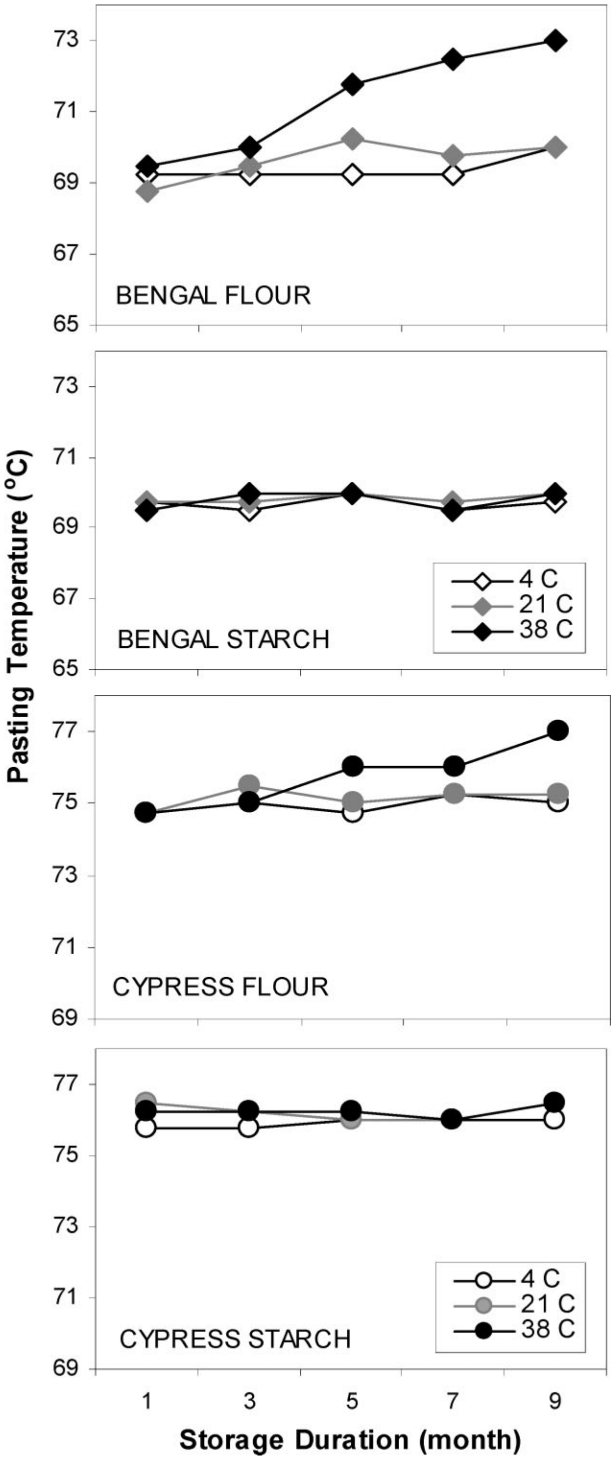

Fig. 5. Changes in the pasting temperature of Bengal and Cypress flour and starch pastes following rough rice storage as measured by a Brabender viscoamylograph.

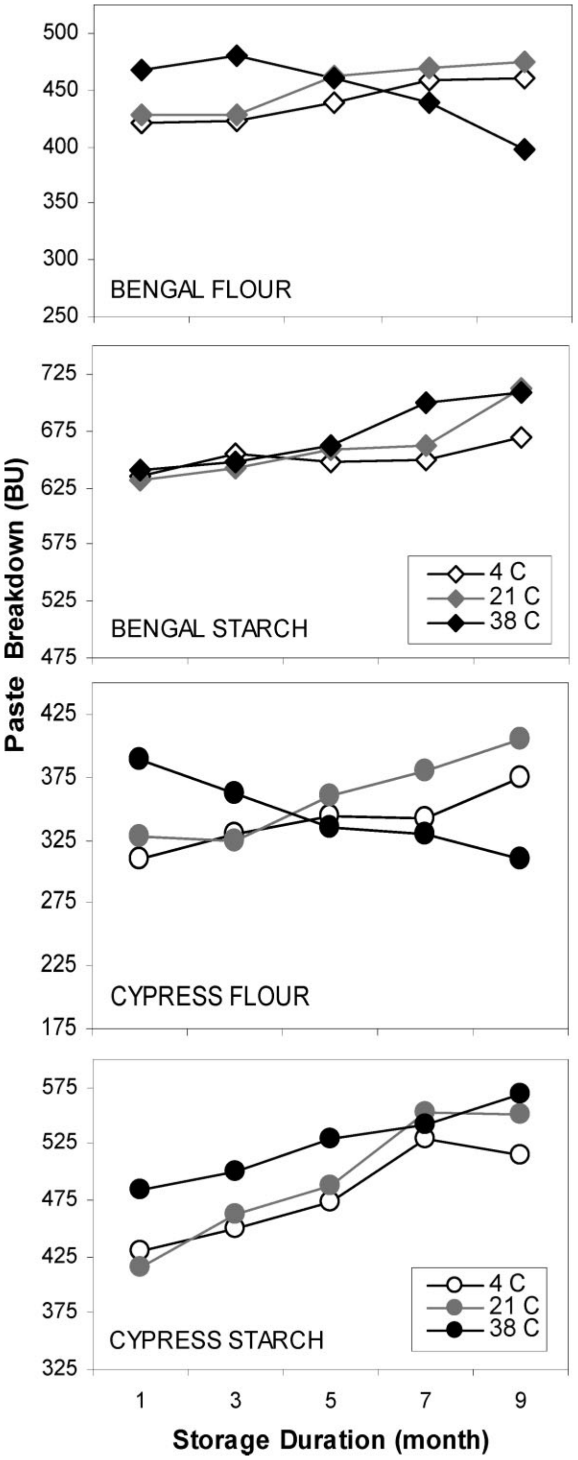

Fig. 6. Changes in the paste breakdown of Bengal and Cypress flour and starch pastes following rough rice storage as measured by a Brabender viscoamylograph.

Increases in pasting temperature were observed on the flour samples stored at 38°C but not on the 4 and 21°C lots; but for starch, pasting temperature remained fairly constant for all lots (Fig. 5). *Showbhagya* and *Bhattacharya* [17] suggested that an increase in pasting temperature was indicative of increased organization. However, the increased kernel organization as indicated by increasing pasting temperature following aging was not noted for starch samples, suggesting that the kernel components removed during starch isolation may be highly involved with the increase in the pasting temperature of flour samples.

Flour peak and final viscosity gradually increased up to month 9 for the 21°C lots (both Bengal and Cypress). For the 38°C lots, peak and final viscosity increased from month 1 to month 5 and then leveled off on further storage (Tab. 3). Previous works [1, 13, 14, 17, 35] also reported the initial increase and eventual tapering off of flour peak and final viscosity. In contrast, the peak viscosity of starch pastes, although generally higher than that of the flour counterparts, did not change with storage duration for all the temperature lots and for both Bengal and Cypress. The final viscosity of the 4°C lots also remained fairly constant while those of the 21 and 38°C lots tended to decrease, with the magnitude apparently dependent on storage temperature. *Shibuya* and *Iwasaki* [38] also reported a slight change in amylogram characteristics of rice starch pastes during storage. *Teo* et al. [14] did not observe amylographic changes during the storage of purified rice starch samples presumably due to insufficient amylolytic enzyme activity in the samples.

Paste peak viscosity measures the extent by which starch granules swells in the presence of water, heat, and sometimes shear. Starch swelling is mainly a property of amylopectin. On the other hand, amylose and protein are known to restrict swelling [39–41]. Hence, the flour pastes showed a lower peak viscosity than the starch counterparts due to the presence of protein. The increase in flour paste peak viscosity following storage may be ascribed to enhanced polysaccharide leaching as a result of starch degradation particularly at elevated storage temperatures. *Shin* et al. [42] attributed the increase in peak viscosity during the storage of brown rice to amylase activity while *Shibuya* and *Iwasaki* [38] ascribed the storage-related changes on flour paste amylograms to the decomposition of cell wall structure by endo-xylanase. Paste final viscosity is often associated with the retrogradation of amylose upon cooling [5]. Therefore, the decrease in the final viscosity of starch paste on the lots stored at an elevated temperature agreed with previous results (Tab. 1) that the starch samples from these lots contained a lower proportion of amylose.

Another distinguishing change in pasting property, that accompanies aging, is paste breakdown (Fig. 6). Flour breakdown viscosity did not change for the 4°C lots, increased slightly for the 21°C lots, and decreased progressively for the 38°C lots. On the other hand, starch paste breakdown did not change for the 4°C lots, and increased gradually for both 21 and 38°C lots. Breakdown viscosity measures the tendency of swollen starch granules to rupture when held at high temperatures and continuous shearing. The decreasing trend in flour paste breakdown of the 38°C lots suggested the presence of a

Tab. 4. Gelatinization temperatures (by differential scanning calorimetry) of flour and starch following rough rice storage[a].

Storage		Bengal				Cypress			
		Flour		Starch		Flour		Starch	
Temp. [°C]	Duration [month]	Onset [°C]	Peak [°C]	Onset [°C]	Peak [°C]	Onset [°C]	Peak [°C]	Onset [°C]	Peak [°C]
4	1	66.2 f	71.8 e	66.0 ab	71.2 a	66.2 f	71.8 e	74.5 ab	79.0 a
	3	66.4 ef	72.0 de	66.0 ab	71.2 a	66.4 ef	72.0 de	74.3 abc	78.8 ab
	5	66.3 f	72.6 bcde	65.8 abcd	71.1 ab	66.3 f	72.6 bcde	74.2 abcd	79.0 a
	7	66.6 ef	72.9 bcd	65.6 bcd	70.9 abcd	66.6 ef	72.9 bcd	74.2 abcd	78.9 a
	9	66.8 cdef	73.9 bc	65.6 bcd	70.7 abcd	66.8 cdef	73.9 bc	74.0 bcd	78.4 abcd
21	1	66.2 f	71.9 e	66.1 a	71.3 a	66.2 f	71.9 e	74.8 a	79.2 a
	3	66.1 f	72.4 cde	65.8 abc	71.3 a	66.1 f	72.4 cde	74.2 abcd	78.9 a
	5	66.8 cdef	73.0 bc	65.5 cde	70.9 abcd	66.8 cdef	73.0 bc	74.1 bcd	78.7 ab
	7	67.5 bc	74.6 a	65.4 def	71.1 ab	67.5 bc	74.6 a	74.0 bcd	78.1 cde
	9	67.6 ab	74.4 a	65.2 ef	70.5 bcd	67.6 ab	74.4 a	73.5 cd	77.8 de
38	1	67.0 bcde	72.6 bcde	65.7 abcd	71.0 ab	67.0 bcde	72.6 bcde	74.2 abcd	78.6 abc
	3	67.8 cdef	72.7 bcde	65.7 bcd	71.1 ab	67.8 cdef	72.7 bcde	73.8 bcd	78.4 abcd
	5	67.3 bcd	73.3 b	65.2 ef	70.7 abcd	67.3 bcd	73.3 b	73.8 bcd	78.6 abc
	7	68.2 a	74.4 a	65.0 f	70.3 d	68.2 a	74.4 a	73.6 cd	77.6 e
	9	68.2 a	75.2 a	65.0 f	70.5 bcd	68.2 a	75.2 a	73.4 d	77.8 de

[a] Values are means of two replicates. Means in a column followed by a common letter are not significantly different based on Least Significance Difference ($P < 0.05$).

stabilizing factor, that protects the swollen starch granules from disintegrating. The stabilizing factor was proposed to consist of proteins and/or non-starch components removed during starch isolation. It was also possible that with heat and water, the leached glucans may interact with proteins and/or other non-starch components to provide the stabilizing effect on the swollen starch granules, which was based on the observation that starch degradation was only evident on the 38°C lots and the 38°C lots exhibited the decreasing paste breakdown. Although flours from the 4°C and 21°C lots also contain protein and/or other non-starch components, the decreasing trend in paste breakdown was not clearly manifested, considering that the starch fine structure in these lots was not extensively degraded (Tabs. 1–2). For starch pastes, the increasing trend in paste breakdown may be attributed to the increase in the amount of shorter amylopectin branch chains (Tab. 2). *Han* and *Hamaker* [27] found that the proportion of short-chain and long-chain amylopectins correlated with paste breakdown positively and negatively, respectively. A greater proportion of short branch chains in amylopectin may render the swollen starch granules more fragile, and vice versa. It was noted that elevated temperature storage slightly shifted the amylopectin chain-length distribution to shorter branch chains (Tab. 2, Fig. 4), therefore the starch paste breakdown tended to increase over time.

3.4 Starch structure and changes in thermal properties

Changes in DSC thermal properties following storage are presented in Tab. 4 and Fig. 7. Flour gelatinization temperatures (onset and peak) and gelatinization enthalpy increased for the 21 and 38°C lots, with the change more pronounced in the latter. *Fan* and *Marks* [43] and *Teo* et al. [14] observed this similar trend. The isolated starches generally had higher gelatinization enthalpy values than the flour counterparts. The 4°C lots showed negligible changes in the thermal properties but the 21 and 38°C lots showed slight decreases in gelatinization temperature (onset and peak) and enthalpy. *Teo* et al. [14] found that the thermal properties of purified rice starch remained unchanged upon storage and concluded that the non-starch constituents, particularly protein, were responsible for the increased gelatinization temperature and enthalpy in rice flour and the aging process. It should be emphasized that in this study, rice was stored as rough rice and starch samples were prepared periodically according to the set storage duration. Changes in thermal properties may also be related to changes in starch structure. Gelatinization has been described as the melting of the crystalline region of starch granules. Higher gelatinization temperatures and enthalpies are associated with larger amounts of long branch chains in amylopectin [24, 26, 29, 44]. The long branch chains in amylopectin may enhance the integrity of starch structure primarily through the formation of double helices that improves crystalline struc-

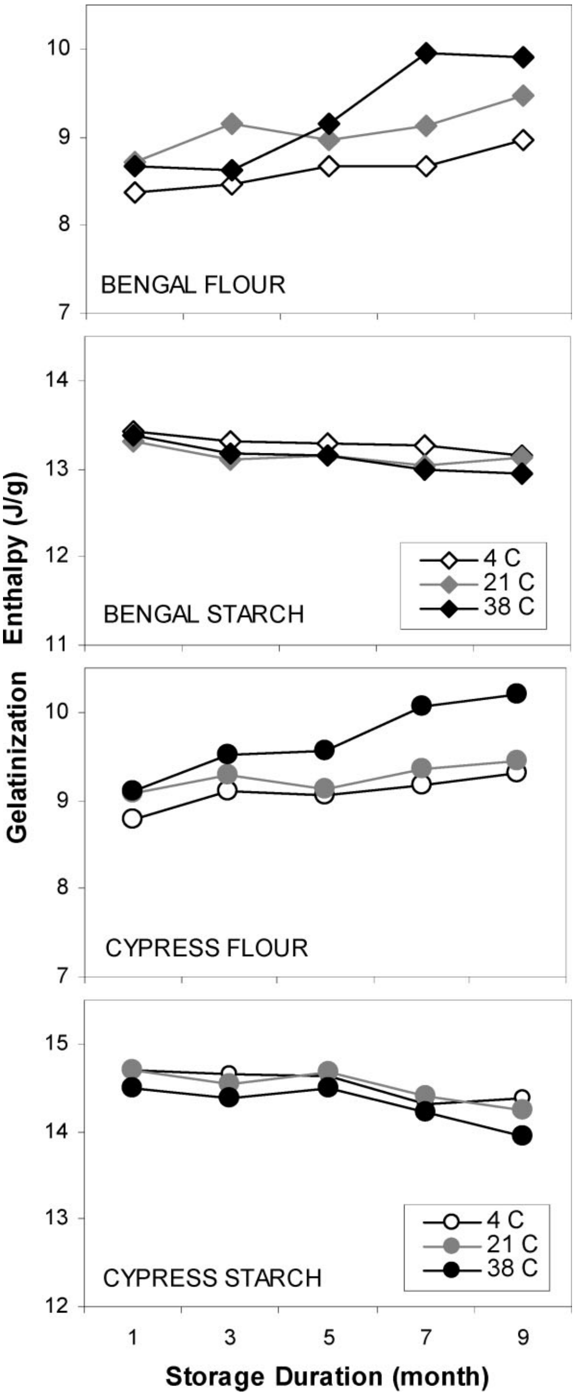

Fig. 7. Changes in the gelatinization enthalpy of Bengal and Cypress flour and starch following rough rice storage as measured by a differential scanning calorimeter.

ture [24, 26, 44]. Thus, the gelatinization temperature and enthalpy of the starch samples prepared from the 38°C lots tended to decrease over time due to the observed shift in the amylopectin chain-length distribution to shorter branch chains (Tab. 2).

4 Conclusions

The changes in starch structure and physicochemical properties following rough rice storage were distinctly temperature-dependent and implicative of molecular-level starch degradation. At elevated storage temperatures, amylose was preferentially degraded over amylopectin. Amylopectin structure also changed as evidenced by the decreased average chain length and the shift in chain-length distribution to shorter branch chains. The decrease in starch yield and increase in extraction residue and tailing (yellow curd) were indicative of enhanced interaction between starch and non-starch components, making it more difficult to isolate the starch granules from the non-starch matrix, that hold them together. The trends in pasting and thermal properties of flour and starch samples were inconsistent. Therefore non-starch endosperm constituents (e.g. protein, lipid, non-starch polysaccharides) and their interaction with starch and starch degradation products were also important in the rice aging process.

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