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Relationship of starch changes to puffing expansion of parboiled rice

Charu Lata Mahanta • Bhattacharya K. R.

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Abstract 'Intan' variety of paddy (Oryza sativa) was tested for puffing. It was parboiled under a wide range of paddy moisture content, steaming pressure and time, as also temperature and time of sand heating. The resulting milled rices were studied for their diverse properties including puffing. Indices of starch changes in the samples were calculated as: (1) gelatinisation index from the solubility of amylose in 0.2 N KOH; (2) amylopectin retrogradation from the post-production drop in room-temperature hydration power of the parboiled paddy during air-drying, (3) thermal breakdown of starch from the drop in gel permeation chromatographic fraction I of starch; lipid-amylose complexation indirectly from (4) drop in rate of water uptake during cooking and (5) cooked-rice firmness. It was found that the puffing expansion was very highly correlated with the combined above 5 indices of starch changes, as much as 90% of the variation in puffing being explainable on that basis. Puffing was promoted by gelatinisation as well as lipid-amylose complexation, but was retarded by amylopectin retrogradation and probably starch breakdown.

 $\label{eq:constraint} \begin{array}{l} \textbf{Keywords} \quad \mbox{Parboiled rice} \cdot \mbox{Puffed rice} \cdot \mbox{Gelatinisation} \\ \mbox{index} \cdot \mbox{Amylopectin retrogradation} \cdot \mbox{Thermal breakdown} \\ \mbox{of starch} \cdot \mbox{Water uptake} \end{array}$

Mahanta C. L. • Bhattacharya K. R. Department of Grain Science and Technology, Central Food Technological Research Institute (Council of Scientific and Industrial Research), Mysore - 570 020, India

Bhattacharya K. R. (⊠) E-mail: krb@rrdc.net

Introduction

A characteristic property of parboiled rice is that when it is subjected to high-temperature-short-time (HTST) heat treatment, it puffs out to yield puffed (or expanded) rice (Roberts et al. 1954). The degree of puffing expansion is affected by the conditions of HTST treatment (Chinnaswamy and Bhattacharya 1983a), the rice variety, i.e., mainly its amylose content (Chinnaswamy and Bhattacharya 1983b) and the parboiling conditions.

The effect of parboiling conditions remains to be fully understood. Three broad types of parboiling processes can be distinguished (Bhattacharya 2004). One is conventional parboiling, where paddy is soaked to saturation (about 30% moisture) and then steamed to gelatinise the starch. A second has been termed pressure parboiling, but is better called low-moisture (LM) parboiling, where paddy is only partially hydrated (12–22% moisture) but is then gelatinised by steaming under elevated pressure. The third is dry-heat (DH) parboiling, where fully soaked paddy is conductionheated with or without hot sand. Within each type, again, the actual process parameters can be varied, resulting in product-quality variation.

The effect of the type as well as the conditions of parboiling on puffing expansion of rice had been studied in this laboratory earlier (Chinnaswamy and Bhattacharya 1983a, 1984, 1986). Substantial variation in puffing with the processing conditions had been observed, but the reasons thereof could not be understood. An attempt was again made to explore this aspect as part of a larger study to understand the fundamental nature of parboiled rice. A large number of parboiled rices were prepared from a single variety under a very wide range of processing conditions and studied for various properties, including puffing, already partly reported (Mahanta and Bhattacharya 1989, Mahanta et al. 1989). Unfortunately these results too could not be fully interpreted at that time primarily due to lack of proper understanding of the nature of starch changes during parboiling, and hence were not fully reported.

Recent studies on starch polymorphism in various starchy foods under different conditions of heat-moisture treatment (Biliaderis et al. 1986, Mesters et al. 1988, Biliaderis and Galloway 1989, Biliaderis 1992) have now substantially clarified the nature of starch changes during parboiling. The understanding that has emerged, as summarised by Bhattacharya (2004), is that parboiled rice contains different polymorphs of starch depending on the conditions of processing: viz., gelatinised starch, retrograded amylopectin (melting temperature, ~55°C), lipid-amylose complex ($\geq 100^{\circ}$) and annealed starch ($\sim 80^{\circ}$). Mahanta and Bhattacharya (1989) also obtained clear evidence of thermal degradation of starch in parboiled rice produced under severe heat treatment. Based on these understandings, the earlier data of the above study have been reexamined and have been now found to provide a fair idea of what promotes or retards puffing. These results are presented here.

Materials and methods

The experimental samples were the same as in Mahanta and Bhattacharya (1989) and Mahanta et al. (1989), as briefly presented below. All data are also taken from the same work carried out with these samples at that time.

An intermediate-amylose (25.6%) rice (Oryza sativa) variety, 'Intan', was parboiled under a wide range of grain moisture contents (12-30%, all moisture data being on wet basis, wb, unless indicated), steam pressures (0-3 kg/cm², gauge), steaming times (10-60 min), sand temperatures (200-275°C), and sand-heating times (1-4 min). To facilitate their easy identification without repeatedly quoting the processing conditions, the large number of samples were identified by a system of code, as listed in Table 1. Each code consisted of 3 parts. The first numeral indicated the nominal paddy moisture (%, wb) before steaming or heating, the second numeral showed the steam pressure (kg/ cm², gauge); and the last numeral indicated the time (min) of steaming. In the case of DH-parboiled rice, the first item showed the sand temperature (°C), the second showed the time of sand heating (min) and the third item the nominal paddy moisture (%, wb) to which the paddy was dried during heating. For instance code 17-3-10 indicated that paddy adjusted to nominally 17% moisture was steamed under 3 kg/cm² gauge pressure for 10 min. Similarly 250°-2-16 indicated that fully soaked paddy (~30% moisture) was heated with 250°C sand for 2 min until the paddy reached a nominal moisture content of 16%.

Several very low-moisture-paddy parboiled samples (especially in 12 and 17% moisture series) had huge white bellies (ungelatinised opaque core) and hence were not properly parboiled (Table 1). These samples were nevertheless retained for the study to provide a total picture, but their properties were to be viewed with caution.

In addition to the above parboiled rice samples as such, properties of the same samples were also studied after "moisture treatment". Milled parboiled rice was mixed with calculated amount of water to raise its moisture content to 25–30%, filled in bottles and tempered for 24 h. The rice was then carefully air-dried in the room in thick layers. This moisture treatment was done to induce starch reassociation (Ali and Bhattacharya 1976, Bhattacharya 2004).

The hydration power of parboiled rice at room temperature (RT, $27 \pm 2^{\circ}$ C) was determined from the equilibrium moisture content (EMC) attained by it when soaked in water at RT (EMCS) (Indudhara Swamy et al. 1971). Two values of EMCS were determined, both expressed on dry basis (db). One was the 'immediate EMCS' (EMCS-I), viz., the EMCS of the parboiled paddy determined immediately after steaming or sand heating before drying (Ali and Bhattacharya 1976). This value expressed the hydration power of the parboiled rice before amylopectin reassociation set in. The other was the 'final EMCS' (EMCS-F), viz., the EMCS of the parboiled rice determined after the parboiled paddy had been air-dried and milled. This value expressed the hydration power of the same sample after it underwent partial amylopectin reassociation during slow drying of the paddy. Water uptake (WU) by the samples during cooking at 96°C for 1 h was determined as per Bhattacharya and Sowbhagya (1971). The starch of rice samples was fractionated by gel permeation chromatography (GPC) over Sepharose CL-2B into a large molecular fraction (Fr I) and a small molecular fraction (Fr II) as already reported (Mahanta and Bhattacharya 1989). For alkali solubility of amylose, 100 mg of rice flour was extracted with 50 ml of 0.2 N or 0.5 N KOH for 1 h with intermittent stirring and then centrifuged. An aliquot of the extract was neutralised with 1 N acetic acid and the blue colour developed with iodine (0.2% in 2%)KI solution) was read at 600 nm against an iodine blank. The cooked-rice texture of the samples was determined as per Sowbhagya et al. (1987): Rice was cooked with 2.5 times its weight of water and the texture was measured with a Chopin-INRA viscoelastograph. The thickness of a cooked grain when pressed with a 500 g weight, expressed as per cent of the original grain thickness, was expressed as its firmness (F).

Milled parboiled rice was puffed by optimum HTST treatment as follows (Chinnaswamy and Bhattacharya 1983a): The rice was adjusted to 10.5–11.0% moisture by exposing to saturated magnesium nitrate atmosphere, and 10 g of it was heated with 300 g sand, previously heated to 255°C, for 9–10 sec in a small laboratory rotating roaster. The ratio of bulk volumes of rice before and after puffing gave the puffing expansion (E).

For assessing the relationship of starch changes in rice during parboiling to its puffing expansion (E), indices of 5 types of starch changes were calculated from the above data as follows:

Rice ^a	White belly area ^b , %	Amylose in 0.2 N KOH ^c (O.D. X 1000)	Starch in Fr I ^d , % of total	EMCS, % db		Water uptake, g/g	Cooked-rice firmness (F), %	Puffing expansion, E
				Immediate	Final	-		
Raw rice		50	69.5	39.3	39.3	3.87	32	1.8
12-1-10	95	66 (98.5) ^e	61.1	70.4	74.3 (74.0)°	3.54 (99.7)°	51 (103.9) ^e	—
12-1-20	90	65 (96.9)	-	57.9	81.1 (65.2)	3.47 (97.4)	55 (101.8)	_
12-2-10	80	71 (95.8)	_	84.0	93.1 (63.2)	3.37 (96.4)	57 (112.3)	_
12-2-20	50	82 (97.6)	59.2	122.9	124.0 (52.0)	3.07 (95.4)	57 (114.0)	_
12-3-10	25	96 (96.9)	53.5	175.3	176.5 (42.4)	3.14 (92.4)	60 (108.3)	6.4 (82.4) ^e
12-3-20	0	108 (96.3)	38.4	226.8	187.0 (41.9)	3.04 (97.0)	59 (101.7)	7.9 (93.4)
17-1-10	40	85 (97.6)	55.8	123.1	114.5 (61.5)	3.50 (91.7)	53 (109.4)	_
17-1-20	10	98 (96.9)	_	185.5	134.8 (60.8)	2.94 (94.1)	56 (107.1)	_
17-2-10	5	104 (99.0)	53.5	214.5	166.8 (47.8)	2.90 (93.1)	54 (113.0)	6.8 (91.2)
17-2-20	0	106 (98.1)	49.3	267.1	169.5 (46.9)	2.86 (93.7)	58 (110.3)	6.7 (89.6)
17-3-10	0	112 (98.2)	43.1	254.6	192.6 (41.3)	3.04 (91.8)	51 (121.6)	6.8 (86.8)
17-3-20	0	118 (94.9)	20.9	235.0	211.4 (45.1)	2.89 (97.9)	42 (150.0)	6.6 (86.4)
22-1-10	0	112	47.4	228.1	134.3	3.02	56	_
22-1-20	0	112	45.0	229.3	138.0	2.94	58	6.6
22-2-10	0	113	-	242.5	144.9	3.12	58	_
22-2-20	0	115	40.2	220.8	155.2	3.10	56	6.0
22-3-10	0	118	35.4	268.2	171.0	3.19	51	—
22-3-20	0	123	16.1	263.1	195.5	2.92	24	5.6
30-0-10	0	83	68.5	110.8	69.5	3.51	35	2.7
30-0-20	0	95	_	153.6	66.7	3.28	38	_
30-0-60	0	95	52.8	189.6	79.1	3.21	41	4.0
30-1-10	0	108	53.8	246.7	95.7	3.08	56	_
30-1-20	0	107	53.0	252.7	96.5	2.96	59	5.6
30-2-10	0	109	-	257.4	109.6	3.24	58	_
30-2-20	0	116	47.1	291.1	95.7	3.15	50	5.3
30-3-10	0	118	38.0	314.9	110.5	3.46	26	—
30-3-20	0	122	33.0	361.0	113.4	3.23	22	4.9
200°-2-20	0	76 (98.7)	_	121.6	97.3 (76.9)	3.88 (92.5)	35 (142.9)	_
200°-4-16	0	78 (97.4)	67.1	141.8	111.5 (70.5)	3.21 (90.7)	44 (125.0)	3.4 (82.4)
250°-1-20	0	92 (97.8)	-	233.7	159.9 (47.7)	3.77 (91.8)	36 (147.2)	5.1 (90.2)
250°-2-16	0	97 (96.9)	_	244.7	196.4 (41.5)	2.94 (94.2)	47 (121.3)	6.0 (80.0)
275°-0.75-20	0	94 (97.9)	_	237.8	183.4 (42.1)	3.61 (96.9)	39 (141.0)	5.2 (88.5)
275°-1.5-16	0	111 (88.3)	51.6	249.5	201.5 (40.6)	3.43 (95.6)	43 (132.6)	5.8 (93.1)

Table 1Properties of parboiled rice samples

^aThe parboiled samples are identified by a code as explained under materials and methods

^bProperties of samples with huge white bellies (ungelatinised opaque core), which are not properly parboiled, are to be viewed with caution

^cThe absorbance value of amylose extracted by 0.5 N KOH was remarkably constant at 0.125 ± 0.0018 for all the samples

^dThese gel permeation chromatography data are quoted from Mahanta and Bhattacharya (1989)

^eThese values in parentheses represent properties of the same samples after they had been "moisture treated" to induce starch reassociation (expressed as per cent of respective moisture-untreated samples)

The index of starch gelatinisation (G) was the ratio of dissolved amylose calculated as per Birch and Priestley (1973):

G = (amylose dissolved in 0.2 N KOH/amylose dissolved in 0.5 N KOH) \times 100%

The index of amylopectin retrogradation (R) was derived from the per cent fall in the final EMCS value (EMCS-F) as compared to the immediate value (EMCS-I) of the parboiled rice (Ali and Bhattacharya 1976):

 $R = (1 - \text{final EMCS}/\text{immediate EMCS}) \times 100\%$

The index of thermal starch depolymerisation or breakdown (B) was obtained from the GPC fractionation of starch. The per cent fall in the amount of Fr I in a parboiled sample as compared to that in the untreated raw rice gave the value of B:

 $B = (1 - Fr I in parboiled rice/Fr I in raw rice) \times 100\%$

The resistance to cooking was calculated from the drop in water uptake (WU) of a given sample, when cooked in water at 96°C for 1 h, as compared to that of the unparboiled raw rice (W):

 $W = (1 - WU \text{ of parboiled rice/WU of raw rice}) \times 100\%$

The textural hardness of the cooked rice was determined from the Chopin-INRA viscoelastograph firmness value, i.e.,

 $F = (cooked-rice thickness after pressing/thickness before pressing) \times 100\%.$

All estimations were done in duplicate.

Results and discussion

Values of primary properties of the large number of samples along with those of the untreated raw rice are presented in Table 1. Also presented are the values of the properties after the samples had been "moisture treated". As already explained, several low-moisture-paddy parboiled samples, especially from the 12%-moisture series as well as sample 17-1-10, had huge white bellies (ungelatinised opaque core). Properties of these samples often deviated from the norm, so these results are to be viewed with caution.

The case of amylopectin retrogradation (R) was fairly straight forward. Earlier work from this laboratory, as reviewed by Bhattacharya (2004), clearly showed that moistening of parboiled rice to 25-30% moisture (wb) and tempering the same for a few hours ("moisture treatment") invariably resulted in substantial lowering of hydration power (EMCS) of the samples. Initially it had been thought to be caused by some strong complexation. But the fact that such moistening and tempering resulted in a substantial drop in EMCS but not in that of water uptake during cooking showed that the association was light and largely reversed at boiling temperature. It will be noticed in the present case also (Table 1) that moisture treatment led to substantial reduction in EMCS but only to a marginal $(\sim 5\%)$ reduction in water uptake. In other words, this must be due to the formation of retrograded amylopectin; this product is said to melt at around 55°C (Biliaderis 1992) and hence cause little reduction in boiling-temperature hydration although showing much reduction in EMCS.

As for gelatinization (G), Birch and Priestley (1973) suggested that the ratio of amylose dissolved in 0.2 N KOH to that in 0.5 N KOH gave a good index of it. The data in Table 1 strongly support this contention. First, the ratio increased with increasing heat treatment, when the degree of gelatinisation would be expected to go up. Second, the fact that amylose dissolved in 0.2 N KOH virtually approached the value of that dissolved in 0.5 N KOH in very high-pressure steamed samples, where a very high degree of gelatinisation can be expected, is also an indirect evidence of the validity of this index. Third, moisture treatment hardly affected the value of the index (mean drop of 3%), supporting the contention that the ratio is not affected by any reassociation of starch.

The case of thermal breakdown of starch (B) is again straight forward. When the starch is fractionated by GPC, the progressive fall in the proportion of the larger-molecule Fr I with progressively severe heat treatment is presumptive evidence of starch breakdown.

There was no way to estimate the degree of formation of either annealed starch or of lipid-amylose complex, for our GPC data (Mahanta et al. 1989) could not provide unambiguous and quantitative information on these polymers. Therefore an indirect approach was adopted. It was reasoned that the formation of lipid-amylose complex (melting point $\geq 100^{\circ}$ C) is what led to both the resistance to cooking of parboiled rice (i.e., the drop in water uptake index, W) as well as the increasing hardness (Chopin-INRA viscoelastographic firmness, F) of cooked rice. On that basis, both W and F were thought to indirectly represent the lipid-amylose complex.

The above five indexes of starch polymorphism in the samples calculated from the results in the Table 1 along with the results of expansion ratio, E, for 16 samples are presented in Table 2.

Statistical calculation of progressive multiple correlations, selected values of which are given (Table 3), showed very strong relationship between puffing expansion index E and the other five starch indices. It is clear from Table 3 that the R² value is virtually identical and very high in the last four cases. Virtually 90% of the variation in puffing expansion of the samples could be explained on the basis of 3 starch indices G (gelatinisaton), R (amylopectin retrogradation) and F (cooked-rice firmness). But B (starch breakdown) and W (index of drop in water uptake) also probably did play some part as seen from other correlations. It appears that B as well as W would have been partly included in the index F. It can be seen from Table 2 that wherever starch breakdown became excessive (e.g., 22-3-20, 30-3-20), the trend of

Table 2Indices of starch polymorphs^a and puffing expansion(E) of selected parboiled rices

(E) of selected parooned files						
Rice	G	R	В	W	F	Е
12-3-10	76.8	-0.7	23.0	18.9	60	6.4
12-3-20	86.4	17.5	44.7	21.4	59	7.9
17-2-10	83.2	22.2	23.0	25.1	54	6.8
17-2-20	84.8	36.5	29.1	26.1	58	6.7
17-3-10	89.6	24.4	38.0	21.4	51	6.8
17-3-20	94.4	10.0	70.0	25.3	42	6.6
22-1-20	89.6	39.8	35.2	24.0	58	6.6
22-2-20	92.0	29.7	42.2	19.9	56	6.0
22-3-20	98.4	25.7	76.8	24.6	24	5.6
30-0-10	66.4	37.3	1.4	9.3	35	2.7
30-0-60	76.0	58.3	24.0	17.1	41	4.0
30-1-20	85.6	61.8	23.8	23.5	59	5.6
30-2-20	87.2	67.1	32.2	18.6	50	5.3
30-3-20	97.6	68.6	52.5	16.5	22	4.9
200°-4-16	62.4	21.4	3.5	17.1	44	3.4
275°-1.5-16	88.8	19.2	25.8	11.4	43	5.8

^aG: gelatinisation; R: amylopectin retrogadation; B: thermal breakdown; W: drop in water uptake during cooking; F: cooked-rice firmness

Starch indices ^a	R ² against E ^b		
G	0.360		
W	0.462		
G, F	0.792		
B, F	0.810		
G, B, F	0.834		
R, B, F	0.829		
G, R, F	0.894		
G, R, B, F	0.896		
G, R, W, F	0.904		
G, R, B, W, F	0.904		

^aSee Table 2

 ${}^{b}n = 16$

decrease in W within the moisture group got reversed and F declined. The relevant regression equation was

E = 0.0995 G - 0.0219 R + 0.0665 F - 5.1665.

While the expansion was promoted by the degree of gelatinisation and by the formation of lipid-amylose complex and annealed starch [as presumably indexed by retardation in water uptake (W) and cooked-rice firmness (F)], it was retarded by amylopectin retrogradation (R) and probably also by thermal breakdown of starch (B).

The above relationships help to confirm some observations made earlier, as follows. In conventional steam-parboiled rice of a given variety, there was an optimal steam pressure which gave the best expansion (Chinnaswamy and Bhattacharya 1983a). Such optima are visible within each paddy-moisture steamed samples in the present results (Table 1) also. The above mentioned optimum however had been found to vary with the rice variety, specifically with its amylose content. The optimal steam pressure increased as amylose content of the variety increased. Conversely there was an optimum amylose content for each given steam pressure. Thus the optimum steam pressure for best expansion was approximately 3, 2, 1, 0.5 and 0 kg/cm² (gauge) for 28–30%, 26–28%, 22–26%, 16–22% and <5% amylose rice, respectively (Chinnaswamy and Bhattacharya 1984). The present results with 'Intan' rice (25.6% amylose), puffing best at ~1 kg/cm steam pressure, again agreed with this gradation. Under optimal conditions of processing within each parboiling type, LM-parboiled rice (pressure parboiled) gave the highest expansion, DH-parboiled rice the next, and conventional parboiled rice the least (Chinnaswamy and Bhattacharya 1986). Again, it is evident that, the present data (Table 1) are also to some extent in agreement with this conclusion.

The above observations could not be explained at that time, but can now be largely explained on the basis of the latest results presented in Table 3. The reason why the puffing expansion in conventional steam parboiled rice first increased and then decreased with increasing steam pressure could be due to the increasing promoting effect of gelatinisation and lipid-amylose complexation at the beginning and the retarding effect of starch breakdown later as the steam pressure increased. The reason why the above optimum steam pressure itself increased in varieties with increasing amylose content could be explained if it is assumed that lower-amylose rice is apparently more susceptible to starch breakdown than higher-amylose rice. Finally, the reason why puffing was best in LM-parboiled rice, next in DH-parboiled rice and the least in conventional parboiled rice could be due to the different combinations of four starch polymers in them. Probably LM-parboiled rice had the highest gelatinization (G) and starch complexation (W, F) along with the least amylopectin retrogradation (R), even though having rather high breakdown (B). DH-parboiled rice probably had low R as well as B.

These results thus provide a reasonable picture of what promotes or retards the puffing of parboiled rice. There was some direct evidence of the deleterious influence of amylopectin staling (R) on puffing. The data presented within parentheses in the last column of Table 1 show that 'moisture treatment' of the parboiled rice samples led to a uniform fall of their expansion ratio by 10-20% compared to the ratio of the untreated rice. Clearly amylopectin retrogradation hindered puffing. This is somewhat intriguing, for this amylopectin complex is said to melt at ~55°C, and yet it hindered puffing that involved heating to ~250°C. Perhaps the absence of moisture during puffing may explain this apparent anomaly. Another interesting paradox is that while amylopectin retrogradation hindered puffing, lipidamylose complex (and possibly annealed starch) seemed to facilitate it. Better knowledge of the molecular organisation of these complexes is needed to explain these apparent anomalies.

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