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The Nature of Starch in Popped Rice

G. Murugesan & K. R. Bhattacharya*

Discipline of Grain Science and Technology, Central Food Technological Research Institute, Mysore — 570 013, India

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ABSTRACT

Brown rice and popped rice flours were fractionated on a Sepharose CL-2B column. The high-molecular-weight fraction of starch was reduced in amount and that of the low-molecular-weight fraction was increased in popped rice as compared to brown rice. In conjunction with the lowering of the λ_{max} of the second fraction, this showed thermal degradation of starch during popping. The difference in popping expansion between varieties could not be related to the relative amounts or molecular weights of the two fractions. X-ray diffraction analysis showed that the A-type pattern of raw rice was changed to the E-type pattern of extruded starch, which changed to a V-type pattern on moistening and tempering. Popped rice flour swelled more than brown rice flour when heated in water at temperatures below 70°C, but less than brown rice flour above 70°C. Popped rice flour was more soluble in water than brown rice flour at all temperatures. Compact and polygonal starch granules in brown rice were blown up into a film arranged in a honeycomb structure in popped rice, as seen by scanning electron microscopy.

INTRODUCTION

Popped rice is a popular snack food in the Indian subcontinent. It is prepared by subjecting moisture-adjusted paddy to high-temperature, short-time (HTST) treatment, when the inner grain expands and is forced out through the opened husk like a flower. The effect of various processing conditions on popping (Murugesan & Bhattacharya, 1986) and associated factors (Murugesan & Bhattacharya, 1988*a*), as well as the reasons for varietal difference in popping expansion (Murugesan &

*To whom correspondence should be addressed.

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Bhattacharya, 1988*b*), were discussed earlier. A study on the hydration and rheological properties of popped rice revealed that it had a high cold-water swelling capacity (Murugesan & Bhattacharya, 1988*c*), suggesting high starch gelatinization and low retrogradation. Further studies on the nature of popped rice, involving starch fractionation, X-ray diffraction, swelling and solubility in water at different temperatures, and scanning electron microscopy (SEM), are reported here.

MATERIALS AND METHODS

Materials

Seven varieties of paddy were selected from the earlier varietal study (Murugesan & Bhattacharya, 1988*b*), representing very high to very low popping expansion. They had been stored at 4–6°C for about 1·5 years.

Processing

Popped rice was prepared as described by Murugesan & Bhattacharya (1986): 25 g of moisture-adjusted — 14% moisture, wet basis (w.b.) — paddy was exposed to air at a temperature of 225°C flowing at a rate of 1·5 m^3/min through a glass jar for about 45 s. The expansion ratio was the ratio of the volume of the popped rice without the husk to that of whole brown rice obtained from 25 g of paddy. To study the effect of the degree of expansion within the same variety, a good-popping variety (GEB24), in addition to being popped at the optimal moisture content of 14% (expansion ratio about 16, abbreviated as POP in Fig. 3), was also popped at 10% moisture to give lower popping (expansion ratio about 6, abbreviated as POP-L in Fig. 3).

Paddy was shelled in a Satake rubber-roll sheller to give brown rice. Brown rice and popped rice were ground first in a Buhler laboratory grain mill (type MLI 204) to about 30 mesh, and then in a Fritsch Pulverisette-14 (Fritsch GmbH, W. Germany) to yield flours that passed through an 80-mesh screen.

To see the effect of moistening and tempering of popped rice flour (to induce starch reassociation, rearrangement or retrogradation) on its X-ray spectra, the flour was moistened to a little above 30% moisture (w.b.), tempered in a plastic pouch overnight, then shade-dried and reground. These samples were arbitrarily termed 'retrograded'.

The flours were defatted, for gel fractionation, with 85% methanol for about 15 h in a Soxhlet apparatus. All samples were exposed to a

constant temperature and humidity room (27°C, 65% RH) for moisture equalization (11–12%, w.b.).

Analytical methods

Gel permeation chromatographic fractionation of brown and popped rice flours was carried out essentially as described previously (Chinnaswamy & Bhattacharya, 1986) with some minor modifications. The flour itself rather than isolated starch was used for chromatography, because isolation of starch from the pregelatinized popped rice was extremely difficult.

About 50 mg defatted flour was dispersed in 3·4 ml 0·25 N KOH under nitrogen, neutralized, diluted to 10 ml and filtered through a prefilter (Sample Clarification Kit, Waters Associates Inc., USA) and G4 sintered glass disc fitted in a syringe. An aliquot of the filtrate containing exactly 10·0 mg (dry weight) of carbohydrate was fractionated by ascending chromatography on a Sepharose CL-2B (Pharmacia Fine Chemicals, Sweden) column (1·6 cm × 70 cm) at a flow rate of 25 ml/h, using distilled water containing 0·02% sodium azide as an eluent. Three-millilitre fractions were collected, 0·5 ml aliquots of which were used to determine polysaccharide by the phenol–sulphuric acid method (Dubois *et al.*, 1956; Lyne, 1976), and the remaining 2·5 ml portions for determining the absorption maximum (λ_{max}) of the iodine–polysaccharide complex. The chromatographic fractionation was carried out in duplicate with most of the samples. Replicates showed good agreement, and the recovery ranged between 94% and 106%. The void volume and the total volume of the gel were determined using blue dextran and potassium chloride, respectively (Bruun & Henriksnas, 1977).

X-ray diffraction spectra were obtained using a Philips X-ray diffractometer system PW 1720 with Cu Kα radiation operating at 30 kV and 10 mA. The spectra were recorded at a chart speed of 3°/3 cm/min. Powders (80 mesh) with about 12% moisture (w.b.) were used.

The total amylose content (Sowbhagya & Bhattacharya, 1979) and hot-water-insoluble amylose content (Shanthy *et al.*, 1980) of rice were determined in rice flour colorimetrically with iodine. Swelling and solubility of brown and popped rice flours, as by Schoch (1964), were determined as described by Unnikrishnan & Bhattacharya (1981).

Scanning electron microscopy of brown and popped rice samples were performed as follows. The popped rice was broken by hand and a portion was fixed on an aluminium stub with the help of double-sided adhesive tape; brown rice was cut longitudinally before fixing. The samples were then coated with gold (about 400 Å) and viewed and

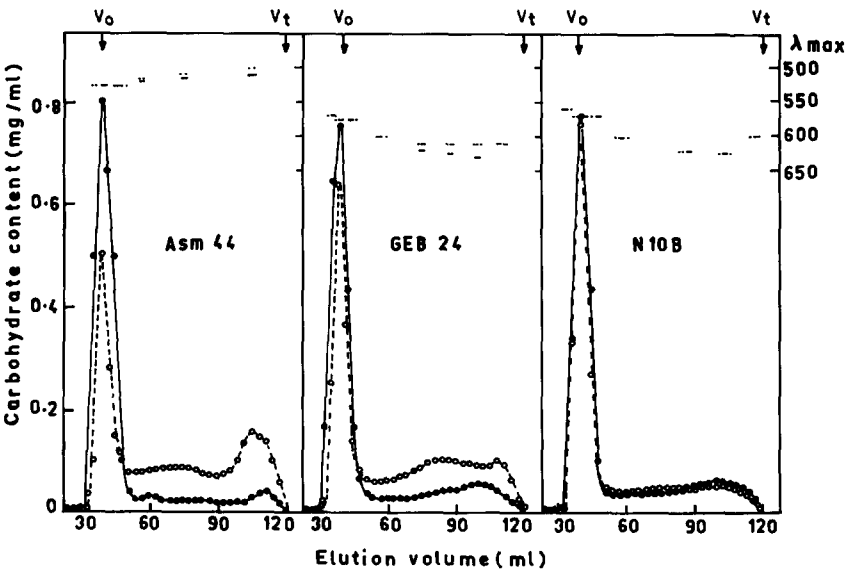

Fig. 1. Elution profiles of brown rice (—●—●—) and popped rice (—○—○—) samples on Sepharose CL-2B column and λ_{max} of iodine complex of the fractions. V_o, void volume; V_t, total volume.

photographed on a Polaroid film in a Jeol JSM-840 SEM at an accelerating voltage of 10 kV.

RESULTS AND DISCUSSION

Fractionation of starch

Gel filtration of brown and popped rice flour on Sepharose CL-2B revealed that there were two main fractions of starch, one eluting in the void volume (fraction I) and the other eluting later (fraction II, which sometimes had a small shoulder that was ignored). A few representative chromatograms are shown in Fig. 1. Full fractionation data pertaining to the different samples are shown in Table 1.

Fraction I (considered as amylopectin) of brown rice flour stained a varying intensity of blue color with iodine depending on the amylose content of the variety. It can be seen that the λ_{max} of this complex increased with increase in the colorimetrically determined amylose content in rice flour. A similar trend, though to a lesser extent, was noticed in fraction II also (Table 1). Identical results have been reported and discussed earlier from this laboratory (Chinnaswamy & Bhattacharya, 1986).

TABLE 1
Fractionation of Rice Flour on Sepharose CL-2B Column

Variety	*Expansion ratio*[a]	*Amylose content (%)*		*Carbohydrate content (mg)*				*Absorption maximum (nm)*				*Fraction I as % of total carbohydrate content*	
				Fraction I		*Fraction II*		*Fraction I*		*Fraction II*			
		Total	*Insoluble*	*BR*[b]	*PR*[c]	*BR*	*PR*	*BR*	*PR*	*BR*	*PR*	*BR*	*PR*
GEB24	16·2	27·8	14·3	6·77	4·72	2·61	5·78	580	580	630	610	72	45
Asm44	15·7	4·8	3·7	7·76	3·78	1·61	6·15	525	525	510	500	83	38
Changlei	14·6	18·7	6·6	7·61	5·24	2·52	4·20	550	550	615	605	75	56
Intan	12·3	26·4	8·9	7·29	5·52	3·36	5·11	560	560	625	610	68	52
Purple puttu	6·3	4·2	3·4	8·29	7·31	1·30	2·03	525	525	515	510	86	78
N1OB	2·5	26·5	10·1	6·75	6·55	3·00	3·15	570	570	625	625	69	68
T(N)1	2.0	29·9	19·4	6·92	6·33	2·51	3·14	580	580	635	635	73	67

[a]Expansion ratio of popped rice.
[b]BR, brown rice.
[c]PR, popped rice.

Comparative fractionation data of brown and popped rice flours revealed that the amount of fraction I decreased and that of fraction II increased upon popping, showing that starch underwent thermal degradation during popping. The extent of degradation was related to the degree of popping expansion. The higher the expansion, the more the degradation (Fig. 1 and Table 1). The absorption maxima of fraction I did not significantly change after popping. However, the λ_{max} of fraction II from popped rice was lower than that of the corresponding brown rice, the extent of fall being positively related to the extent of degradation of fraction I or the degree of popping expansion. Clearly, the amylose (original fraction II) was being contaminated by degraded amylopectin.

It is interesting that gel filtration of native and extruded starches from manioc (Colonna & Mercier, 1983), wheat (Schweizer *et al.*, 1986) and maize (Vergnes *et al.*, 1987) had shown similar molecular degradation of starch upon extrusion. The extent of degradation was proportional to the severity of the treatment. It was reported that drum-dried wheat starch did not undergo any degradation, but extruded wheat starch did (Schweizer *et al.*, 1986).

Relation of starch characteristics to popping expansion

In the case of expanded rice (prepared by puffing milled parboiled rice), it was found earlier from this laboratory that varieties having the combination of 27·5% total amylose and 13·5% hot-water-insoluble amylose gave the highest expansion (Chinnaswamy & Bhattacharya, 1984). Furthermore, the expansion ratio was related to the mean molecular weight of starch (Chinnaswamy & Bhattacharya, 1986).

TABLE 2
Correlation between Popping Expansion and Various Starch Properties ($n = 7$)

Property	*r value*[a]
Total amylose content (%)	−0·242
Insoluble amylose content (%)	−0·367
Carbohydrate content in fraction I	+0·198
Carbohydrate content in fraction II	−0·064
Ratio of carbohydrate content in fraction I to that in fraction II	+0·021

[a]All values are insignificant.

However, neither the amount of fraction I, fraction II, nor their ratio (considered as amylopectin–amylose ratio) had any relationship to the popping expansion (Table 2). Also, the analytical value of

total and hot-water-insoluble amylose contents, as determined colorimetrically in these seven rice flours, showed no correlation to the expansion ratio (Table 2), as already observed earlier with 25 samples (Murugesan & Bhattacharya, 1988*b*).

X-ray diffraction

X-ray diffraction studies of the samples showed that unprocessed brown rice had typical A-type spectra with diffraction peaks around 2θ angles of 15°, 17°, 18° and 23° (Fig. 2). The pattern was changed in popped rice with a peak at slightly over 18°, i.e. the E pattern shown by extruded

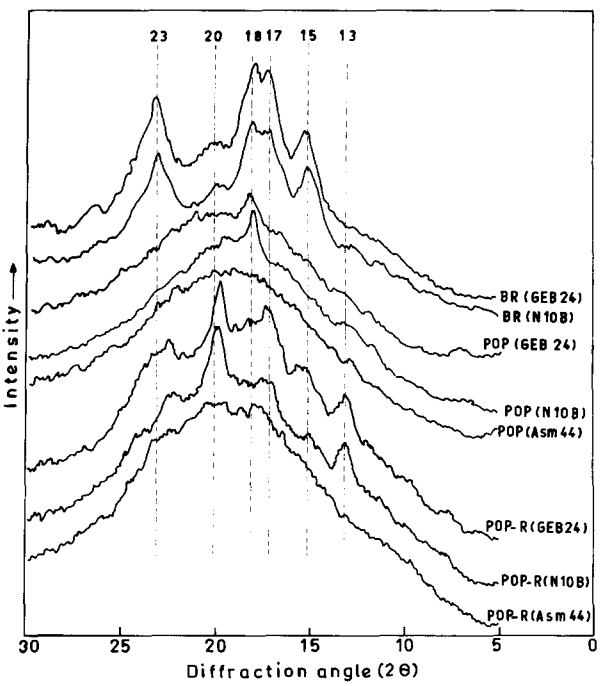

Fig. 2. X-ray diffractograms of brown rice (BR), popped rice (POP) and 'retrograded' (i.e., moistened) popped rice (POP-R). Variety name is given in parentheses.

starch (Mercier *et al.*, 1979). This pattern is said to be similar to the well-known V pattern and, like the latter, is also caused by complex formation between amylose and lipid (Mercier *et al.*, 1979). It changes in extruded starch to the V pattern when the product is hydrated to about 30% moisture (Mercier *et al.*, 1979). Popped Asm44 rice (waxy), which has no amylose, showed an amorphous spectrum as in extruded waxy maize starch (Mercier *et al.*, 1979). Extrusion cooking of manioc starch which

contains only 0·1% lipid also gave an amorphous spectrum (Mercier *et al.*, 1980).

When the samples were moistened and tempered ('retrograded'), here also — as in extruded starch — the E pattern was modified mostly into the V-hydrate pattern (peaks at 2θ values of 13·1° and 20·1°). However, there were also some additional minor diffraction peaks around 15°, 17° and 22°, which may be considered to correspond to the B pattern of retrograded starch (17·2°, 22·2°). The peak combinations might also be thought to simulate the A pattern of untreated starch (15·3°, 17·1°, 18·2°, 23·5° — 2θ) but that would be quite illogical. However, the popped waxy rice (Asm44) continued to remain virtually amorphous even after moisture treatment. While it was not expected to show the V pattern as it had no amylose, it also did not show the B pattern of retrograded starch, probably because the 30% moisture was not high enough. Similar results were obtained for hydrated extruded waxy maize starch (Mercier *et al.*, 1979). These data show close similarity between extruded and popped starch.

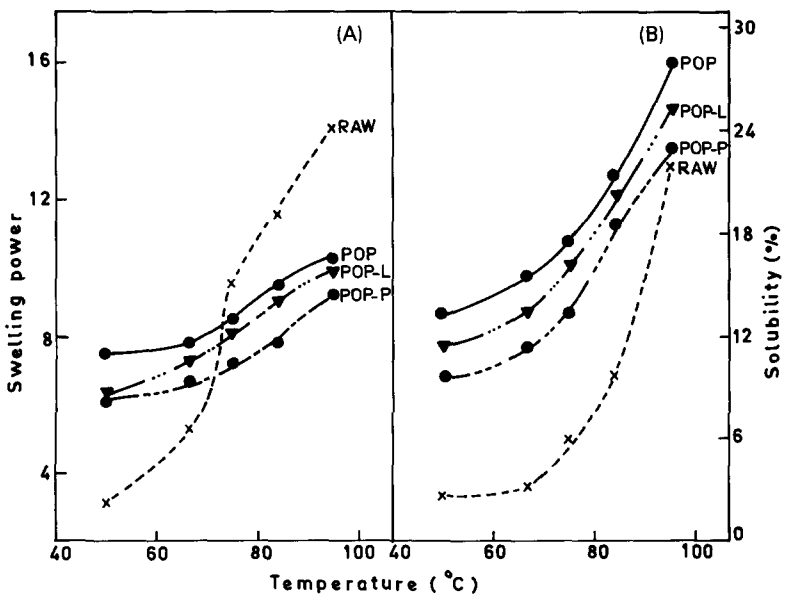

Fig. 3. Swelling power (A) and solubility (B) of brown and popped rice flours in water at various temperatures. Except POP-P, a poor-popping variety (N1OB), all other samples were prepared from GEB24 variety. POP, optimally popped (14% moisture); POP-L, suboptimally popped (10% moisture).

Swelling and solubility

Swelling and solubility behavior of brown rice and popped rice are shown in Figs 3(A) and 3(B), respectively. At low temperatures, swelling was higher in popped rice than in brown rice; but at high temperatures (above 70°C), the reverse was the case (Fig. 3(A)). A similar trend had been observed for parboiled rice, which is pregelatinized (Unnikrishnan & Bhattacharya, 1981). Furthermore, swelling was more in the highly popped sample (POP) then in the suboptimally popped (POP-L) and in the poorly popped one (POP-P, N1OB variety). These results indicate that swelling is influenced by the degree of popping expansion.

However, paradoxical behavior was encountered here. If the pattern of the POP curve in Fig. 3(A) is attributed to extensively gelatinized starch in popped rice, then the less gelatinized POP-L and POP-P samples should have shown a higher swelling than POP at temperatures above 70°C. That is, there should have been a reversal of the order of the samples below and above 70°C, as has been seen in parboiled rice (Unnikrishnan & Bhattacharya, 1981). The reason for this paradox is not clear at this time.

The solubility of popped rice was much higher than brown rice even at low temperatures; the gradation among the samples was maintained at all temperatures (Fig. 3(B)). In variously parboiled rices (Unnikrishnan & Bhattacharya, 1981) and extruded starch products (Mercier & Feillet, 1975; Colonna & Mercier, 1983) also, the solubility increased with increasing severity of treatment.

Scanning electron microscopy

SEM of brown rice (Fig. 4(A)) showed that starch granules, polygonal in shape, were compactly packed in the endosperm. In the case of popped rice, the starch granules were blown up into a film arranged in a honeycomb structure (Fig. 4(B)). It was mostly the endosperm that expanded; the aleurone layer and germ did not (seen visually and under the light microscope). In a study of the microscopic structure of popped cereals (sorghum, popcorn, dent corn, barley and wheat), Reeve & Walker (1969) found that the expansion was mostly confined to the endosperm; the subaleurone portion expanded little and the germ and aleurone not at all; starch granules in cells adjacent to the aleurone layer were either unaltered or only partly gelatinized. Similar observations were made for popped corn (Hoseney *et al.*, 1983) and sorghum (Harbers, 1975).

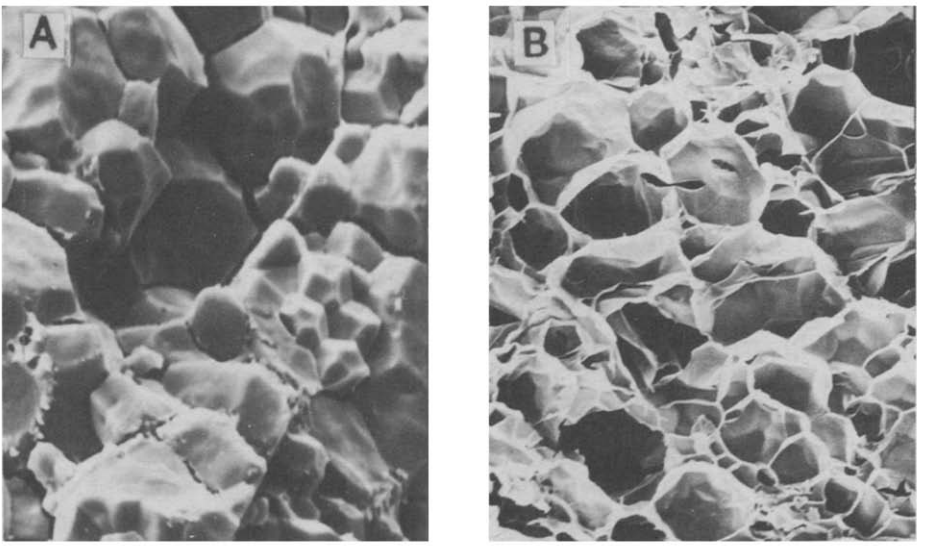

Fig. 4. Scanning electron micrograph of brown rice (A) (× 1600) and popped rice (B) (× 300). GEB24 variety.

The above swelling, solubility and SEM data are in general agreement with the hypothesis made earlier (Murugesan & Bhattacharya, 1988*c*) that starch in popped rice is highly gelatinized but little retrograded or not at all. Clearly mechanical extrusion of heated starch caused by escaping steam leads to disruption (i.e. gelatinization) of starch granules. Thermal degradation of starch has also been shown to occur during popping. What effect this degradation has on the product property is not yet clear.

The above data also show that popped and extruded starches simulate each other in many ways.

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