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Thermal and Physicochemical Properties of Rice Grain, Flour and Starch

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Three types of rices, namely, Thailand rice (Indica), Nipponbare (Japonica), and Himenomochi (Japonica waxy), in grain, flour, and starch forms have been studied for their thermal and physicochemical properties. In grain form, Indica was slender and Japonica rices were bold and thick. Indica had the highest protein and amylose equivalent. Protein contents in isolated starches varied from 0.2 to 0.9%. Cooked Indica grain was hardest and waxy rice was softest; stickiness was highest in Japonica rice. Glass transition temperature (T_g) was highest in Indica rice flour (∼222 °C) and almost the same in Japonica rice flours. Melting point was highest for Japonica (∼264 °C) and almost the same for Japonica waxy and Indica rice flours. T_g values of starches were almost the same in Indica and Japonica waxy (∼237 °C); defatting caused reduction in this property in all of the starches. Highest melting point was shown by Indica starch (∼276 °C) and was almost the same for the other two starches. Protein and fats play a critical role in glass transition and melting points of rice flours and their respective starches. Viscosities of the cooked pastes of flour and starch during cooking in an RVA instrument and their gel and other properties have been discussed.

Keywords: *Differential scanning calorimetry; Tensipresser; Rapid Visco analyzer; glass transition temperature; amylose equivalent absorbance; percent transmission*

INTRODUCTION

Rice is a staple food for Asian countries. There are various types of rice. Different countries will use different types of rice. For instance, Indians prefer Indica rice, which has a higher amylose equivalent to a greater extent with some exceptions. In Japan, generally, Japonica rice is preferred, which is of low to intermediate amylose equivalent. Waxy rice is generally accepted especially in Japan for ready-to-eat products such as rice crackers and rice cakes, although other types of rice are also used. Here we notice three different types of rice, namely, Indica, Japonica, and Japonica waxy. These are used generally as whole grains or in powdered form after cooking. Quality aspects of rice have been studied by Bhattacharya et al. (1982), who grouped various rices of the world into eight groups depending on their physicochemical properties, mainly amylose content, insoluble amylose content, and viscographic pattern. Ohtsubo et al. (1998) have discussed the merits of traditional and modern equipments in rice quality evaluation, and Radhika Reddy et al. (1993) have studied the texture of cooked rice and described the finer structure of amylopectin in rice starch and related this to the texture of cooked rice. Zeleznak and Hoseney (1987) have studied the glass transition in wheat starch and clarified the degree to which crystallinity plays a key role in granule and nongranule form. Shogren (1992) has studied the effect of moisture content on the melting of corn starch by using differential scanning calorimetry and the calorimetric peak characteristics of enthalpy changes due to structural relaxation. Biliaderis et al. (1986) reported the thermal characterization of rice starches by using DSC and thermal mechanical analysis and discovered that all non-waxy rice starches exhibit two-stage swelling: the first stage indicates onset of the gelatinization phenomenon, and the second coincides with melting of starch crystallites. Kainuma et al. (1968) studied the changes in starch granule during gelatinization with photopastegraphy method. Singh (1996) studied the isolation of starches from various food grains and measured the changes in these starches after acid modification at the granular and molecular level. We find scant literature on simultaneous studies on the properties of rices in grain, flour, and starch form. Hence, this study was undertaken to characterize their thermal and physicochemical properties under simultaneous experimental conditions.

MATERIALS AND METHODS

Materials. Commercial Thailand rice (an Indica rice) was procured from the market. Japonica rice, viz. Nipponbare (nonwaxy), and waxy rice, viz. Himenomochi, in the form of brown rice was procured from National Agricultural Research Center, Tsukuba, Japan; their brief storage history was as follows: harvested in 1997; after shelling, the rices were stored in the form of brown rice under low temperature (5 °C). Standard amylose used was from potato, Sigma Chemical Co. (A 0512). Amylopectin (from Mochi rice) was a gift from Shimada Kagaku Co. Ltd., Nagaoka, Japan. All chemicals used were of analytical grade. Unless otherwise mentioned, deionized water was used for all studies.

Methods. *Sample Preparation.* The rice samples were milled using a Yamamoto polisher, Rice Pal 31(Tendo, Japan), to an extent of 10% (degree of polish) or 90% milling yield, by keeping a flow rate of 4 (fourth among five grades of flow rate,

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which is rather faster than average three) and resistance at 3. Indica rice was slightly polished as it was already available as polished rice. Length, width, and thickness of the grains were measured by using Mitutoyo digital slide calipers, made in Japan. Milled rice was powdered by using a Cyclone sample mill from UDY Corp., Ft. Collins, the powder was passed through a 100-mesh sieve, and −100 mesh powder was used for studies.

Protein content was estimated by using a fully automated Kjeldahl vapor still from Mitamura Riken Kogyo (MRK), Tokyo, Japan. Equilibrium moisture content in the milled rice was determined according to the method of Indudhara Swamy et al. (1971). A known weight of the sample was soaked in water for ∼18 h at room temperature, the water was decanted, adhering moisture was removed by a filter paper, and the moisture of this wet rice was estimated by keeping it in an air oven at 135 °C for l h. Ash content in flour and starch was estimated at 550 °C according to the procedure of Singh and Ali (1987a).

Swelling and Solubility. Swelling and solubility of these samples were determined according to the procedure of Schoch (1964) as modified by Unnikrishnan and Bhattacharya (1981). About 500 mg (db) of sample was cooked in ∼20 mL of water at various temperatures ranging from 50 to 90 °C for 30 min. They were weighed and made equivalent to 25 g by the addition of water. They were centrifuged at 3000 rpm for 15 min. Supernatant was decanted carefully, and residue was weighed for swelling power determination. Ten milliliters of the supernatant was pipetted out to a wide-mouth Petri dish and kept on a boiling water bath for evaporation. Afterwards, the dishes were dried at 105 °C for 3 h, cooled, and weighed. Solubility and swelling power was estimated with the following formulas:

$$\text{swelling power} = \text{wt of the wet residue}/500 - \text{wt of the dried sample} \quad (1)$$

$$\text{solubility} = \text{wt of the dry residue} \times 2.5 \times 100/\text{wt of the sample (db)} \quad (2)$$

Sample Preparation for Physicochemical Properties. Defatting of samples was carried out by making use of 85% methanol with a Soxhlet apparatus for 18−24 h. The defatted samples were exposed to room temperature for ∼48 h. Milled rice grains were cooked in excess water for their optimum time with an addition of 2−3 min. The optimum time was determined by cooking the grains in excess water at boiling temperature and testing them at 2−3 min intervals by taking a few grains and pressing them between two glass plates; time was taken into consideration when the chalkiness or white portion disappeared in the cooked grains (Ranghino, 1966). Afterwards, excess water was decanted, and grains were kept on a filter paper to remove adhering moisture, transferred to a Petri dish, covered with another Petri dish, and placed in a Polythene [low-density polyethylene sheet (LDPE) from which covers were made] cover for ∼2.5 h at room temperature in a plastic box; their texture was measured according to the method of Okadome et al. (1996) by using a Tensipresser supplied by Taketomo Denki Co., Tokyo, Japan. The Tensipresser was used to measure the physical properties of cooked grain; the capacity of the load cell of this device was a maximum of 10 kg force. In this experiment, low-compression test and high-compression test measured the physical properties of a single cooked grain. In the low-compression test, the cooked grain was deformed to 25% for measuring the surface physical property, and in the high-compression test, it was deformed to 90% for measuring the overall physical property of the grain. Averages based on the results of 10 grains are reported.

Isolation of Starch. Starch was isolated as described by Singh and Ali (1987 b). Briefly, ∼1 kg of the polished rice was soaked in ∼0.05 N sodium hydroxide for 3−4 h, washed once with tap water, and next ground in a mixer and passed through a 100 mesh sieve; the plus portion (retentate) was again ground and filtered, and the minus portions were pooled and centrifuged at 3000 rpm for 15 min. The supernatant was discarded, the top brownish portion of protein was scraped out, and the residue was again ground using a mixer; these operations were continued several times until the plus portion (retentate) did not give any whitish filtrate on addition of water. After centrifugation, the residue was taken and the procedure was repeated with 200 mesh, 390 mesh, and finally 420 mesh sieve. At the end of grinding, that is, when 420 mesh was used, tap water had been replaced with deionized water. At the end of these operations starch so obtained was treated with toluene and a common salt (sodium chloride) solution in the proportion of 3:05 by volume and kept in a shaker overnight at 250 rpm. The next day it was removed from the shaker and again ground in the mixer and passed through a 420 mesh sieve; only filtrate was taken, a negligible portion of residue on the top of the sieve was discarded, and the filtrate was filtered using a Büchner funnel; the residue was washed for a minimum of four to five times with deionized water and filtered. The residue so obtained was broken, and it was dried either at room temperature for ∼3 days or dried at 40 °C for ∼18 h with occasional stirring. The dried residue so obtained was ground using a Retsch ultracentrifugal mill/pulverizite from MRK, Tokyo, Japan, using a 1 mm screen. The protein content of these starches was estimated according to the micro-Kjeldahl method, and the pH of the starch was determined by taking a 20% slurry as per the procedure of Smith (1967).

Amylose Equivalent Estimation. Amylose was estimated according to the procedure ISO 6647 (1987). Briefly, ∼100 mg (db) of sample was treated with 1 mL of ethyl alcohol in a 50 mL conical flask, slowly stirred, treated with 9 mL of 1 N sodium hydroxide, and heated in boiling water for 10 min with occasional stirring. The sample was cooled to room temperature, transferred to a 100 mL volumetric flask, washed, transferred, and finally made up to volume with water. Five milliliters of the dispersion was taken, ∼50 mL of water was added, 1 mL of 1 N acetic acid was added, and the whole contents were shaken; 2 mL of 0.2% iodine in 2% potassium iodide solution was added, made up to volume with water, and kept at 27 °C for 20 min. Color was read at 620 nm in a UV-2010 spectrophotometer (Hitachi, Hitachi, Japan) with a blank (without sample). A standard graph was prepared by using different proportions of amylose and waxy rice starch [0% amylose and 100% waxy starch (amylopectin), similarly different proportions, and finally 100% amylose and 0% waxy starch (amylopectin)], wetted with 1 mL of alcohol followed by 9 mL of alkali and following the same procedure as above for developing the color. A standard graph was drawn with absorbance on the *y*-axis and amylose content on the *x*-axis. A regression equation was prepared for estimating amylose content in the unknown sample.

Transmission Experiments. For these experiments, 0.1% (db) sample concentration was considered. About 50 mg (db) of respective sample was cooked in ∼30 mL of water at different temperatures ranging from 50 to 90 °C in a water bath for 30 min at each temperature. They were cooled to room temperature and transferred to a 50 mL volumetric flask after being made up to volume with water; the transmission of the dispersion was measured at 650 nm according to the procedure of Wilson et al. (1978) by using a UV-1600 spectrophotometer (Shimadzu, Kyoto, Japan). After this, the remaining dispersion was centrifuged at 3000 rpm for 15 min, and the supernatants were carefully transferred to a beaker. Five milliliters of this was taken for the measurement of soluble amylose equivalent at an absorbance of 620 nm after the color had been developed as before.

Viscoamylography. A Rapid Visco-Analyzer model 3D (RVA) (Newport Scientific Pty. Ltd., Narrabeen, Australia) was employed to determine the pasting properties of various rice flour and rice starch samples. The sample (3.5 g) was made equivalent to 14% moisture and mixed with water in an RVA aluminum canister (supplied by Newport Scientific Pty Ltd.) to make the total weight of the slurry 28 g. A programmed heating and cooling cycle was followed as outined in the procedure of Toyoshima et al. (1997); the sample was installed on the rotor of the RVA and heated from 50 to 93 °C (at 50 °C for 1 min and 4 min to reach 93 °C). It was held at 93 °C for

Table 1. Some Physicochemical Properties of Rice and Its Flour and Starch

property	sample	Indica (commercial)	Japonica (Nipponbare)	Japonica waxy (Himenomochi)
protein content (%)	brown rice	ND	5.6 ± 0.04	6.7± 0.08
	milled rice	6.87 ± 0.17	5.2 ± 0.03	6.1 ± 0.09
	starch	0.45 ± 0.02	0.9 ± 0.02	0.2 ± 0.05
milled rice	1000 grain wt (g)	20.9 ± 0.18	19.82 ± 0.50	18.8 ± 0.41
	length (mm)	7.3 ± 0.04	4.80 ± 0.14	4.6 ± 0.19
	width (mm)	2.1 ± 0.08	2.80 ± 0.09	2.9 ± 0.14
	thickness (mm)	1.7 ± 0.03	1.7 ± 0.01	2.1 ± 0.05
amylose equivalent (% d·b)	flour	27.7 ± 0.24	19.9 ± 0.06	0.0 (1.5)
	defatted flour	32.9 ± 0.13	25.6 ± 0.22	0.0 (1.5)
	starch	34.6 ± 0.17	25.6 ± 0.16	0.0 (1.2)
	defatted starch	36.5 ± 0.20	26.5 ± 0.20	0.0 (1.3)
pH of slurry (20%)	starch	6.6 ± 0.12	8.5 ± 0.12	7.9 ± 0.08
fat (%)	flour	0.74 ± 0.005	0.9 ± 0.007	1.4 ± 0.003
	starch	0.08 ± 0.001	0.24 ± 0.005	
Emc-s[a] (w·b)	milled rice	27.8 ± 0.29	30.0 ± 0.26	35.0 ± 0.24
ash (%)	flour	0.41 ± 0.04	0.54 ± 0.07	0.48 ± 0.04
	starch	0.22 ± 0.06	0.20 ± 0.06	0.10 ± 0.02

[a] Emc-s is the maximum moisture picked up by the respective rice grains when soaked in water at room temperature, on wet basis (generally the grains are soaked overnight, but maximum moisture will be picked by the grains within 4−5 h).

7 min, cooled from 93 to 50 °C in 4 min, and allowed to stand at 50 °C for 3 min. Parameters recorded were peak viscosity (P), hot paste viscosity (H), and cold paste viscosity (C). The gel so obtained was immediately removed, mixed with a spatula, transferred to an aluminum cup of 40 mm diameter and 10 mm depth, covered with aluminum foil, and kept for 4 h at room temperature.

For the comparison of flour and starch, starch concentration was determined according to the method of Bhattacharya et al. (1978a). In this experiment 3.5 g of sample is equivalent to 12.5% concentration, weight adjusted to 14% moisture basis as described in the procedure of operation instructions of the RVA. Three and a half grams was converted into starch equivalent, where the protein content of the rice flour was taken into consideration. This proportion of isolated starch was taken as maximum concentration. Viscograms were run at different concentrations (e.g., 3.1%, 5.6%, 8.1%, 10.6%, and 12.5% for respective flours). Starch concentrations were different and are shown on the respective figures. A graph was drawn with concentration on the x-axis and viscosity in RVA units on the y-axis. At a fixed peak viscosity value, various ratios of breakdown (H/P), setback (C/P), and total setback (C/H), where P is peak viscosity, H is hot paste viscosity, and C is cold paste viscosity, and relative breakdown (BDr) were calculated by taking the ratio of $P - H$ to $C - H$. The quality of the present rices was predicted by making use of the standard graphs as shown in the publication of Bhattacharya and Sowbhagya (1979b).

Measurement of Gel Texture. The gel so obtained after viscography analysis in RVA was cooled for 4 h, and then its texture was measured by a Tensipresser. The gel was compressed to 9.8 or 0.2 mm clearance by means of a plunger of 10 mm diameter into the cup of dimensions mentioned above, and measurements were based on the texture profile method of Bourne (1978). Textural parameters such as hardness, stickiness, adhesiveness, and cohesiveness were determined. In the calculation of these parameters, some of the values were divided by the area of the plunger in order to express the values as dynes per square centimeter.

Differential Scanning Calorimetry. Thermal analysis was performed with a DSC 220C instrument from Seiko Instruments Inc. (Japan). Silver crucible of P/N 560-004 AG15 capsule was used for the experiments. About 5 mg of the sample was used in each experiment. Heating was carried out from 30 to 350 °C at the rate of 10 °C/min. The sample was placed in the silver cup, covered with the silver lid, and sealed very carefully with the sealer supplied by the manufacturers. Another empty cup was used after sealing as before, making this the reference (air). The instrument was calibrated using melting temperature and enthalpy of indium. Mainly glass transition, melting point, and dextrinization or degradation or decomposition point were measured.

All experiments were carried out in replication except DSC, where the melting point and decomposition point were reproducible even by carrying out experiments two or three times. Hence, only one experiment was carried out in this instrument.

RESULTS AND DISCUSSION

Physicochemical Properties of Rice Grain, Flour, and Starch. Table 1 depicts some of the physicochemical properties of these rices and their different forms. The demarcation of protein presence in brown rice, milled rice, and starch is clearly seen. Highest protein content is seen in Indica milled rice and lowest in Japonica rice, although this should not be taken as a generalized statement (as studies were carried out in only one variety of each category). Protein content in starch depends on the method of isolation. It is generally required to have <0.5%. In the case of Japonica rice, great care had been taken during the isolation; still, the protein content could not be brought down to <0.9%, the expected level of protein content in Indica rice starch and Japonica waxy rice starch could be achieved.

The 1000 grain weight was highest in Indica rice followed by Japonica and waxy rice. Indica rice, a long-grain rice, was significantly longer compared to the other two, and it was slenderer compared to the other two, as they were bolder grain varieties. Thickness was least in Indica and highest in waxy rice with Japonica rice intermediate. This is clear from the photographs of these three rice varieties (Figure 1).

Amylose equivalents of respective flours are shown. The highest value was found for Indica followed by Japonica, and there was negligible amylose content in waxy rice. In waxy rice flour as well as starch, the value of amylose equivalent is shown as zero, which has been found from the standard graph prepared from amylose and amylopectin as mentioned under Methods. The values in parentheses, which are all <2%, were estimated by using the procedure of Sowbhagya and Bhattacharya (1971), in which the standard readings are taken by combination of amylose and amylopectin. Hence, two values are shown in Table 1. After defatting,

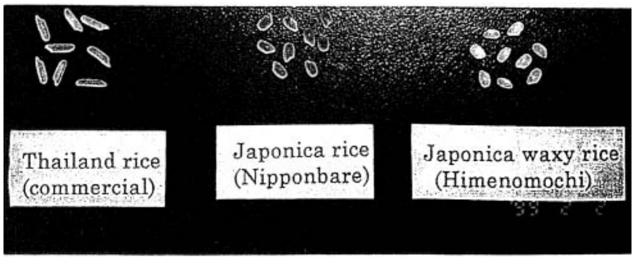

Figure 1. Photographs of three types of rices: (left to right) Thailand rice (Indica rice, commercial); Japonica rice (Nipponbare); Japonica waxy rice (Himenomochi).

the amylose equivalent increased, indicating the role of lipids in binding the linear polymer of each type of rice. Before and after defatting of the starches, the values further increased as seen from Table 1. In waxy rice, a value of almost zero was seen, probably because Japonica waxy rice starch does not contain lengthy linear chains in the amylopectin molecule of starch granule, which can freely take a helical form to receive the iodine molecule and by resonance blue color can develop; as is well-known, to develop blue color, a minimum chain length of 40 glucose residues is required.

Although starch was isolated from all of the rices under identical conditions, the pH of the slurry varied: Indica rice starch was acidic, and the other two were alkaline, implying that the hydrogen ion concentration varies in different starches. It has been observed by Oosten (1990) that upon sodium chloride treatment of starch, the pH becomes acidic. Also, the p*K* value of water is 14, but that of a starch suspension in water is 12.6. In the present study, isolation of starches involves salt treatment at the end, and, because of Donnan potential between starch and water, the variation in H ion concentration is seen. Hence, there are variations in pH in different starches, and even different varieties of starches also play a role. Indica starch becomes acidic, whereas Japonica starch suspensions in water become alkaline under the conditions of starch isolation mentioned above. Ash content in rice flours varied from 0.41 to 0.53%, whereas in starch it varied from 0.14 to 0.22%. It is obvious, in rice flour, that the mineral content will be concentrated on the surface of the endosperm and hence it was high, whereas starch was free from the cell wall material and the ash content was low. In waxy starch the value was least (0.14%) compared to the other two. Fat content was highest in Japonica waxy rice flour followed by Japonica nonwaxy and Indica, and this high content of fat in Japonica waxy is well documented. This depends to a greater extent on the removal of bran from the outer surface (although all steps had been taken to polish all types of brown rices under identical conditions, still some differences existed in these). In starch, the fat was almost negligible in Indica, but in Japonica it is ~0.24%. In the case of waxy starch, it was difficult to estimate, although attempts were made.

Equilibrium moisture content on soaking in water at room temperature (Emc-s) was highest in waxy rice and lowest in Indica rice; Japonica rice was intermediate. This observation holds agrees with the work of Bhattacharya et al. (1979a), who noticed that Emc-s is inversely related to the amylose equivalent on a broad classification of high-, intermediate-, and low-amylose waxy rice varieties. In our work, the highest value is shown by waxy, as it consists of mainly branched amylopectin molecules in its starch granule, which has absorbed the greatest amount of moisture at room temperature compared to the other two, which consist of different proportions of linear and branched polymers. This explanation holds true when only starch is taken into consideration, but Emc-s has been estimated in rice grains where constituents of rice play an important role.

Table 2. Textural Properties of Cooked Grains of Three Types of Rices[a]

name of rice	surface property		overall property	
	H_1 (dyn)	$-H_1$ (dyn)	H_2 (dyn)	$-H_2$ (dyn)
Indica	1.68×10^5	6.77×10^3	2.13×10^6	3.73×10^5
Japonica	1.10×10^5	9.59×10^3	1.55×10^6	4.75×10^5
Japonica waxy	5.50×10^4	6.39×10^3	1.36×10^6	3.91×10^5

[a] H_1, surface hardness; $-H_1$, surface stickiness; H_2, overall hardness; $-H_2$, overall stickiness.

Textural Properties of Cooked Rice Grains. Table 2 shows some of the textural properties of the cooked grains of these rices. In the surface properties, Indica, having the highest amylose equivalent content, had the highest hardness (H_1), and the least was shown by Japonica waxy. This clearly indicates that the higher the linear component content, the higher will be the hardness. With respect to surface stickiness ($-H_1$) Japonica showed the highest stickiness followed by waxy and Indica. This may be one of the reasons for the preference of Japonica variety nonwaxy rice by the Japanese population, as they consume the cooked rice with chopsticks. In the overall physical property, overall hardness of the grain (H_2) followed the same trend as surface hardness. However, overall stickiness followed a different pattern, where, as usual, Japonica had the highest stickiness followed by waxy and then Indica, which is different in surface stickiness.

Differential Thermogram Analysis. Figure 2 shows some of the thermograms of native and defatted rice flours and starches. Table 3 shows some of the thermal analysis properties of these three types of rice flours and their starches before and after defatting. Special care was taken to measure glass transition points. According to Maurice et al. (1985), the glass transition occurs just before melting, as they had observed in the study of waxy corn starch by thermomechanical and differential scanning calorimetry. The work of Zeleznak and Hoseney (1987) suggests that the glass transition is ill-defined below 13% moisture. In our work, there were sharp peaks before melting, but in some cases very weak peaks were seen. Therefore, the scales were enlarged, and the peaks before the melting points were taken into consideration for comparison purposes. Also, there is no perfect method; there are several literature reports of different methods of addition of moisture and measurement of glass transition. Hence, in this method samples per se were taken for experiment and the observations have been made. Moisture content varied from 9 to 11% in the isolated starches and from 13 to 14.5% in respective rice flours. Preliminary experiments revealed that great variations in the results were not seen in these moisture ranges. Melting point and degradation peaks were very clear and sharp. The very first melting point of rice flour in all three types remained almost the same; the highest was shown by Japonica rice flour followed by waxy rice flour and Indica rice flour, indicating that the presence of protein and fat does not have significant effect on this property. After defatting, the melting points increased marginally in each flour. Thus, the highest increase was observed in Indica followed by Japonica and the least in the case of waxy

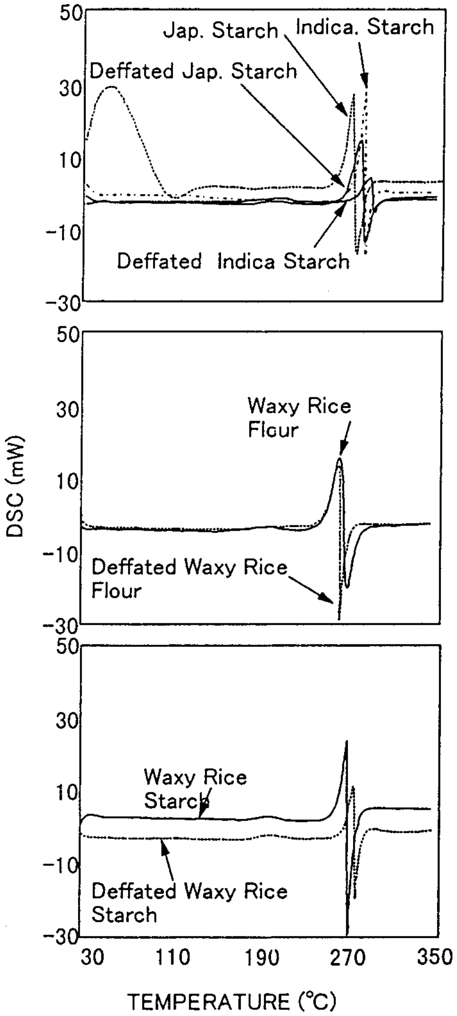

Figure 2. DSC thermograms of some of native and defatted rice flours and starches.

Table 3. Some of the Parameters Derived from the Thermograms of the DSC Instrument for Various Rice Flours and Their Starches before and after Defatting[a]

type of rice	mp (°C)	dp (°C)	T_g (°C)	ΔH top peak (mJ/mg)	ΔH bottom peak (mJ/mg)
Indica					
flour	259.8	278.6	221.8	−318.0	320.8
defatted flour	262.0	269.9	227.7	−232.2	263.3
starch	276.2	278.0	235.8	−059.3	119.4
defatted starch	284.4	288.4	212.3	099.3	055.0
Japonica					
flour	264.1	273.6	210.7	−210.9	276.2
defatted flour	265.1	274.6	204.6	−206.5	193.8
starch	268.5	272.8	215.5	−202.8	125.9
defatted starch	276.4	281.4	209.8	−213.3	132.7
Japonica waxy					
flour	261.4	269.2	209.3	−335.1	178.1
defatted flour	261.3	262.8	226.5	−041.7	266.3
starch	267.0	268.4	237.6	−034.1	109.4
defatted starch	273.5	274.9	214.2	−017.7	190.9

[a] mp, melting point; dp, degradation or decomposition point; T_g, glass transition temperature; ΔH, exothermic DSC peak (top peak, melting); ΔH, endothermic DSC peak (bottom peak, endothermic).

rice flour, indicating that the presence of the lipids may interfere with the starch and protein matrix of each type of flour. The degradation or dextrinization point of flour after melting occurs generally at 18 °C higher than the melting point in the case of Indica rice flour, around 10 °C higher in Japonica, and around 8 °C higher in waxy rice flour. Hence, both protein and fat have a tremendous effect on the degradation point of these types of rice flours. After defatting, an 8−9.5 °C rise was shown in Indica and Japonica, but there was less of an increase in waxy rice flour, indicating the least effect of fat in the case of waxy rice flour and substantial effect on Japonica and Indica rice flours.

Glass transition (T_g) was highest in Indica rice flour and almost the same in Japonica nonwaxy and waxy rice flours (Table 3). After defatting, the T_g value decreased for Japonica but increased in Indica by ~5 °C, and that for waxy rice flour by 15 °C, although the peak was not sharp in the case of this waxy rice flour, indicating the presence of amylopectin and protein; that is, defatted waxy rice flour behaves differently. The change in T_g can be taken as a type of cross-linking between starch and protein or fat or both, although they exist as globules or protein matrix along with starch granule in the cell compartments of the endosperm of rice grain, and it is well documented that cross-linking increases T_g (Armeniades and Baer, 1977).

Starches have higher melting points compared to their respective flours, probably because they are free from protein to a greater extent, although not completely. The highest melting point was shown by Indica starch followed by Japonica and waxy starch (Table 3). Degradation or dextrinization takes place at just 2−5 °C above their respective melting points. After defatting, in starch, the melting point of Indica and Japonica increased to the same extent (~8 °C), but the increase in waxy was only 6.5 °C, indicating that the absence of protein and fat enhances the melting point of starches (defatted) to a greater extent, whereas the presence of these did not have much effect, as seen by the melting point of respective flours. However, after defatting, degradation occurs at a higher temperature compared to the non-defatted ones. The degradation point increased by 1.4 to 5 °C after defatting in all three types of starches compared to the melting points of defatted ones. These interesting observations indicate the influence of protein and fat (or lipids) on the physical properties of these rice flours and their starches.

The T_g values among the starches were almost the same in Indica and waxy but were lower in Japonica starch (Table 3). These values decrease after defatting; the extent of decrease varied, by 23.5 °C in Indica, by 6 °C in Japonica, and by 23.4 °C in waxy starch. These observations lead to some speculations. If these fat or lipid globules are attached to the starch granules or encapsulated to granules, in flexible types of side groups, their T_g could decrease after defatting as reported by Armniades and Baer (1977).

Moreover, starch consists of two major chemically distinguishable polysaccharides, amylose and amylopectin. Amylopectin is a highly branched molecule. The crystalline nature of starch seems to be associated with the amylopectin molecule (Singh et al., 1993). If this is the case, the melting point of waxy starch which is fully amylopectin is supposed to be correct, because crystalline molecules will have a sharp melting point. A similar explanation can be given for the amorphous nature of linear polymer present in Indica and Japonica starches. In previous work, Zeleznak and Hoseney (1987) observed that the glass transition is mainly due to the amorphous polymer (linear, i.e., amylose), where the molecules slide over each other, when thermal energy is supplied, becoming more viscous, rubbery, and flexible, which leads to glass transition in the starch.

Exothermic and Endothermic Behaviors of Rice Flours and Starches. Table 3 also shows the exothermic and endothermic values in millijoules per milligram of DSC melting and endothermic peaks of the respective rice flours and starches before and after defatting. Generally, top melting peaks were exothermic and bottom ones were endothermic in nature. In Indica rice flour, under exothermic peak, 318 mJ/mg was heat liberated, but after defatting, it reduced to ~232 mJ/mg, indicating the presence of fat makes the system hold heat; under endothermic peak, absorption of heat was higher in the presence of fat and lower in the absence of fat by ~60 mJ/mg. Evolution or absorption of heat in starch was lower compared to that in its flour. The phenomenon was the opposite in starch: exothermicity was lower in the presence of fat but higher in the absence of fat. In contrast, in endothermic peaks, absorption of heat was higher in un-defatted ones but lower in defatted ones. This property was different in Japonica rice flour compared to Indica rice flour. In the presence or absence of fat, heat evolution was almost the same, whereas in endothermic peaks, the absorption of heat was higher in the presence of fat (~276 mJ/mg) and lower in the absence of fat (~194 mJ/mg). In starch, the presence or absence of fat did not play any significant role except to cause slightly higher evolution and higher absorption. In waxy rice flour there was a very high evolution of heat; after defatting, the evolution of heat was decreased. In waxy starch before defatting, ~34 mJ/mg was heat evolved, but after defatting, evolution reduced by ~50%. Under endothermic peaks, in flour after defatting excess heat was absorbed (~100 mJ/mg) compared to its flour and a similar phenomenon occurred in starch also.

Among the flours, the exothermicity was higher in all types of rices. In the presence of protein and the absence of lipids (i.e., defatted flour) exothermicity reduces, whereas in waxy rice flour, exothermicity occurs to a greater extent, indicating the special property or behavior of the defatted waxy rice flour, implying that in the presence of fat and protein, waxy rice holds more heat compared to other rice flours.

Among the starches, highest exothermicity was seen in Japonica starch (~203 mJ/mg) followed by Indica starch and waxy starch (Table 3). In the absence of protein and fat (i.e., defatted starch) exothermicity behavior was observed in all three types of starches.

Among native starches absorption of heat was highest in Japonica followed by Indica and waxy starch. After defatting, the absorption increased to a greater extent in waxy starch and to a lesser extent in Japonica, but in Indica starch the amount of absorption decreased. We notice from these results the key role played by fat or lipids in the case of rice flour and their starches, before and after defatting.

Pasting Behavior and Gel Texture. Figure 3 shows RVA viscograms obtained for Japonica rice flour at different concentrations, which is shown for a specific rice variety to depict the pattern of RVA curves. Figure 4 shows viscogram patterns of various rice flours and their starches. The drawing patterns are similar in to those of Bhattacharya and Sowbhagya (1978b), who clearly discuss and interpret high-amylose, intermediate-amylose, and waxy varieties of rices, viscosity behaviour, on cooking.

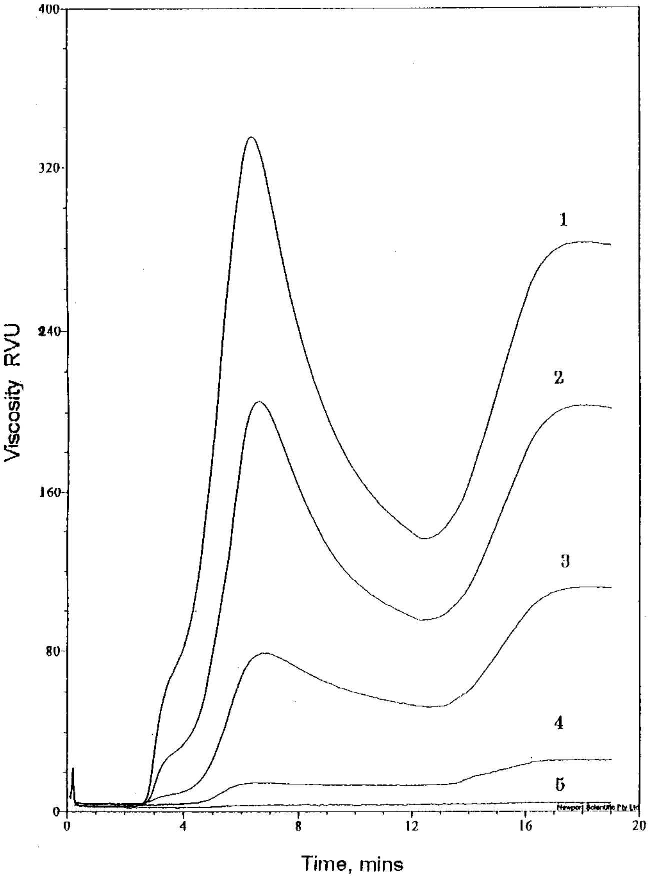

Figure 3. Rapid Viscogram patterns of Japonica rice flour at various concentrations: (1) 12.5%; (2) 10.6%; (3) 8.1%; (4) 5.6%; (5) 3.1%.

Table 4 shows various viscographic parameters. In this table *P* is the peak viscosity observed when the slurry is heated and the granules swell; highest viscosity will be recorded as peak viscosity *P*. *H* is the hot paste viscosity, which is an indication of granules breaking down after reaching maximum viscosity (generally at higher concentrations of slurry the value of *P* will be greater than *H*), and *C* is the cold paste viscosity, which is obtained while the hot paste slurry is cooled from *H* onwards. $P - H$ is the breakdown; instead of this, as per the description of Bhattacharya and Sowbhagya (1979b), the ratio has been expressed. The breakdown ratio of *H*/*P* was high in the case of Indica rice flour. From the standard graphs of Bhattacharya and Sowbhagya (1979b), taking into consideration only *H*/*P* values, Indica rice comes under group III rice quality as enumerated by Bhattacharya et al. (1982), Japonica rice comes under group VI, and waxy rice flour fits authentically very well in group VIII. [Depending on the total, soluble, and insoluble amylose equivalents, equilibrium moisture content on soaking in water at room temperature, alkali score, stickiness, consistency, and relative breakdown, Bhattacharya et al. (1982) have tentatively classified rice varieties in the world into eight quality groups: group I cooks flaky and hard, whereas group VIII cooks extremely sticky and soft, and group IV is scented rice varieties.] Other values do not shed much light except relative breakdown for waxy rice flour, which very well fits into the quality profile of rices. Probably, conditions with RVA and Brabender amylograph need to be standardized in a separate study, as Bhattacharya et al. (1979b) studied the quality profile

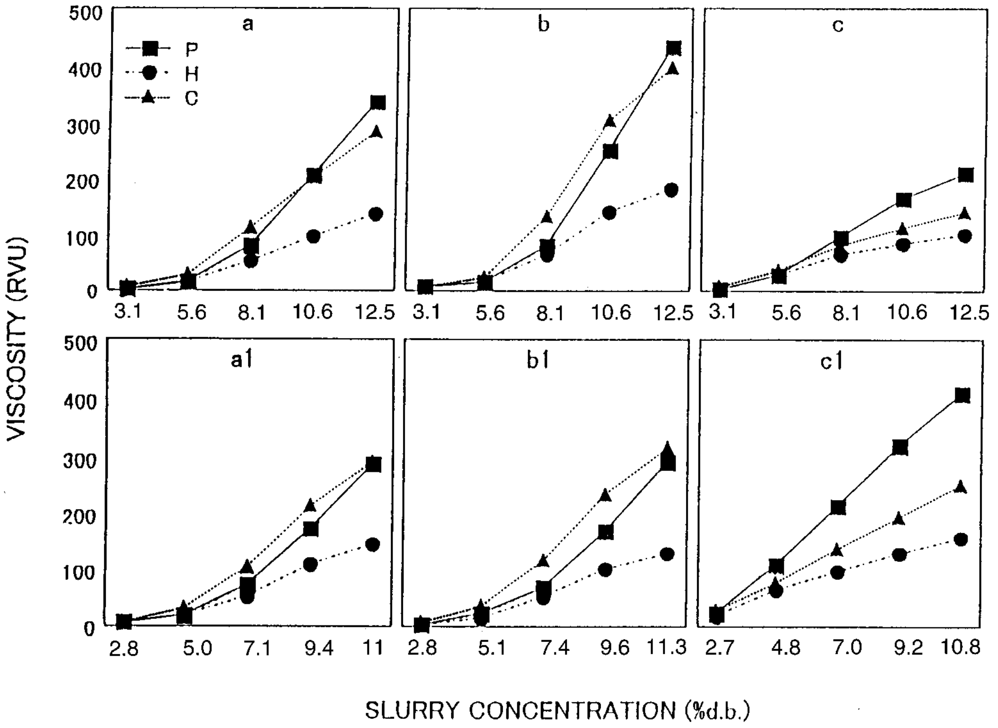

Figure 4. Viscogram parameters of three types of rice flour and their starches at various concentrations: (a) Indica flour; (a1) Indica starch; (b) Nipponbare flour; (b1) Nipponbare starch (Japonica nonwaxy); (c) Himenomochi flour; (c1) Himenomochi starch (Japonica waxy); (*P*) peak viscosity; (*H*) hot paste viscosity or trough viscosity; (*C*) cold paste viscosity.

Table 4. Pasting Characteristics and Viscography Indices of Rice Flour and Respective Rice Starches at a Peak Viscosity of 200 RVA Units[a]

rice/form	*H*/*P*	*C*/*P*	*C*/*H*	BDr
flour				
Indica	0.61	1.00	1.63	1.00
Japonica	0.48	1.00	2.10	1.00
Japonica waxy	0.49	0.68	1.57	2.78
starch				
Indica	0.54	1.00	1.85	1.00
Japonica	0.60	1.00	1.60	1.00
Japonica waxy	0.60	0.63	1.60	2.66

[a] *H*/*P*, breakdown ratio; *C*/*P*, setback ratio; *C*/*H*, total setback ratio; BDr, relative breakdown (*P* − *H*)/(*C* − *H*).

by making use of Brabender amylograph. Among corresponding starches, there was a remarkable difference in the case of Japonica, for which the *H*/*P* value was high compared to its flour and the value for waxy rice starch for *C*/*H* (total setback ratio) was almost the same as that of its flour. In fact, the comparison has been made by equalizing the concentration of starch in the flour along with the pure isolated starch; still, some differences have been shown, which may be due to the presence of fat and a negligible quantity of protein. This pasting behavior illuminates peculiar properties of Japonica nonwaxy and waxy rice starch, which demands further testing by other experimental data.

At the end of the RVA run, the texture of the gel was measured using the Tensipresser, and some of the parameters are shown in Table 5. Among the three types of rice flour and starch, at lower concentrations, the gel texture could be measured only in Indica and Japonica. However, in waxy rice flour, it was not possible to measure even at higher concentrations up to 10.6% except its flour at 12.5% concentration, which is 3.5 g in the present experiment. In the case of Indica flour and starch, starch shows a higher hardness, lesser stickiness, higher adhesiveness, lower cohesiveness, and lower balance degree (balance degree is the ratio of hardness to stickiness) compared to its rice flour. Japonica starch showed higher hardness, lesser stickiness, higher adhesiveness, lesser cohesiveness, and lesser balance degree compared to its rice flour. Waxy rice starch could not register any measurement under the conditions employed here. However, waxy rice flour showed lower hardness, higher stickiness, almost the same adhesiveness, higher balance degree, and higher cohesiveness compared to other rice flours. Further work is needed to reach generalized conclusions in the case of Japonica nonwaxy and waxy rices.

Table 5. Some Textural Parameters of the Gels of Different Rice Flours and Their Corresponding Starches[a]

name	H_1	$-H_1$	adh	balance	coh
Indica					
flour	1.51×10^5	7.07×10^4	1.29×10^6	0.47	0.52
starch	2.89×10^5	6.27×10^4	2.87×10^6	0.22	0.46
Japonica					
flour	1.63×10^5	7.21×10^4	1.21×10^6	0.40	0.54
starch	2.08×10^5	7.09×10^4	1.41×10^6	0.31	0.46
Japonica waxy					
flour	9.98×10^5	7.18×10^5	1.23×10^5	0.72	0.74

[a] H_1, hardness in dyn/cm^2; $-H_1$, stickiness in dyn/cm^2; adh, adhesiveness in dyn/cm^2; coh, cohesiveness.

Swelling and Solubility. The most important property of starch in a commercial application is its ability to swell and produce a viscous paste when heated with water (Leach, 1965). It is clear from Figure 5 that the swelling power increased in Indica flour slowly from 50 to 70 °C and remained almost constant up to 90 °C, but in its starch this property increased from 50 to 90 °C; the increase was gradual up to 80 °C, and there was a sudden jump from 80 to 90 °C. Swelling power was high in Indica starch compared to its flour at 90 °C. It can be seen in Figure 5 that the swelling power in starch was less from 50 to 60 °C compared to its flour; in Indica

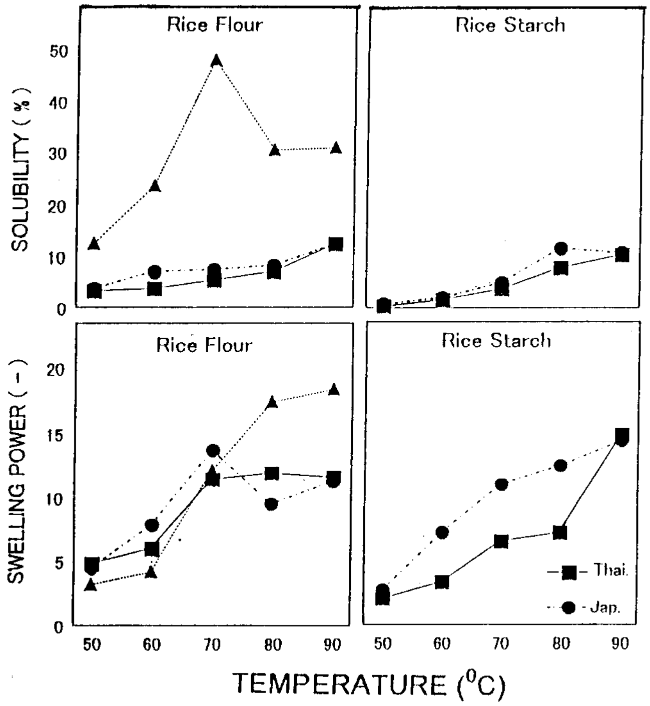

Figure 5. Swelling power and solubility patterns of Indica, Japonica, and Japonica waxy rice flour and their starches, respectively, at different temperatures except waxy rice starch: (■) Indica; (●) Japonica; (▲) Japonica waxy.

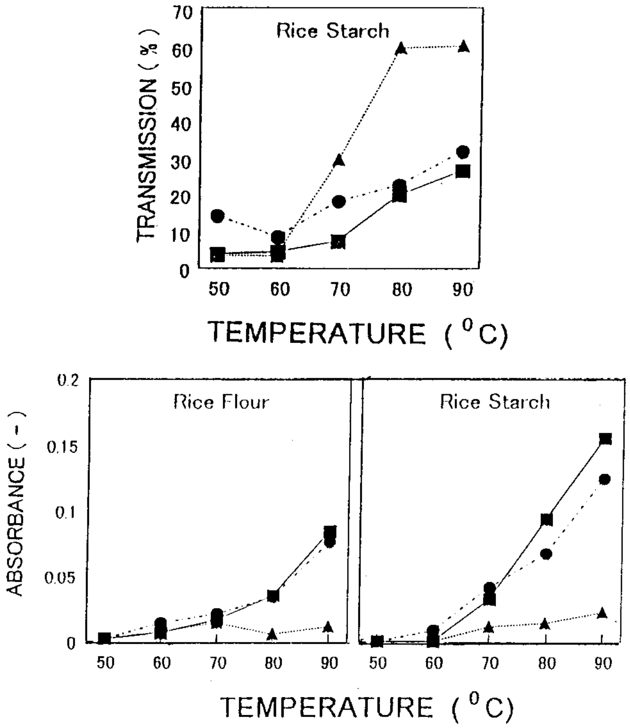

Figure 6. Percent transmission of various rice starches (0.1% concentration) and amylose equivalent absorbance of solubles of various rice flours and their starches at different temperatures: (■) Indica; (●) Japonica; (▲) Japonica waxy.

flour a jump occurred from 60 to 70 °C, but in its starch the jump was from 80 to 90 °C. In Japonica flour, this property increased slowly and reached its highest value at 70 °C and then fell, but in Japonica starch it continuously rose from 50 to 90 °C. It can also be seen from Figure 5 that the jump in Indica starch was double from 80 to 90 °C, but the jump in Japonica starch was only one-sixth that from 80 to 90 °C. In waxy rice flour this property continuously increased from 50 to 90 °C and reached its highest value at 90 °C, indicating restricted swelling in Indica and Japonica nonwaxy flour as well as to some extent in starches. Under these conditions, it was difficult to measure the swelling power in waxy rice starch.

Among the three flours, the highest swelling power was shown by waxy rice flour and the lowest by Japonica and Indica flours (Figure 5). Cereal flours are known to swell in two stages, reflecting the properties of linear and branched polymers (Leach, 1965) Amylopectin molecules swell to a greater extent along with protein and fat as individual components, but in combination with a linear polymer (i.e., amylose), it is more resistant to swelling, as seen in Indica and Japonica flours (Figure 5). The effect may be due to either a combination of linear and branched molecules or linear branched molecules along with protein and fat, which demands further studies in these starches.

The extent of solubility for rice flour and starch is shown in Figure 5. In Indica flour, the solubility increased from 50 to 90 °C, but the extent of solubility in the corresponding starch was comparatively less. In Japonica, the solubility in flour increased slowly, but in its starch the increase is sudden from 70 to 80 °C and then comes down, which was not so in Indica starch. In waxy rice flour, starting from 50 °C the solubility was very high, and an almost 4.5 times jump was observed at 70 °C and then falls down. This is the peculiarity of Japonica waxy rice flour. Hence, flour and starch of Japonica and Indica have less swelling and solubility compared to waxy rice flour. Also, it is seen from Figure 5 that at 70 °C the swelling power was high for Japonica rice flour, and at the same time the solubility was high for waxy flour. Solubility is high in Japonica waxy flour, probably due to leaching of linear portions of branched molecules, and maybe this is true if this waxy flour is pregelatinized, which is not the case in the present study; it is generally well documented that pregelatinized flours or starches will have high solubility.

Transmission and Amylose Equivalent Absorbance. In the case of respective rice flours there were difficulties in the measurement of the transmission, as irrespective of the temperature of cooking the values were abnormal; hence, the values of these are not shown. It is seen from Figure 6 that respective starches showed a particular pattern. Up to 70 °C the opacity was higher, as transmission was lower and dramatic changes have taken place after 70 °C, which was in and around the gelatinization temperature of all three types of starches, indicating the cooking of the starch granules, loss of their crystallinity, and reaching the birefringence end point temperature. Again we observe the highest transmission value in waxy rice starch, indicating the peculiar nature of the amylopectin molecules and clear clarity of this starch. At 50 °C the transmission was high in Japonica starch, decreases, and then again increases, which is a peculiar observation. In other words, percent transmission was inversely related to the amylose equivalent of these starches, as is clearly seen from Figure 6; waxy had the highest value and Indica the lowest, with Japonica in between.

It is also clear from Figure 6 that amylose equivalent absorbance of solubles was highest in Indica starch followed by Japonica and then waxy rice starch. These observations suggest that the higher the amylose equivalent, the higher will be leaching of the linear polymer from each type of starch while cooking. Thus, 50% less leaching occurred in the case of rice flours, especially at 90 °C, when compared to their respective starches. Leaching of linear polymer was very high in starches compared to that in their respective flours, as it is seen from Figure 6 that absorbance was high in starches. Again, for the contents of amylose, although negligible in the case of waxy flour and its starch, there is a change at a particular temperature (70 °C), which was the same in the swelling and solubility experiments of this rice. It appears protein and lipids hinder the leaching of linear polymers, as it is seen in respective rice flours that amylose equivalent absorbance was less in these flours compared to their respective starches, where fat is present to a greater extent but proteins to a negligible extent, which may be one of the reasons for the easy leaching of linear polymers; hence, there is higher amylose equivalent absorbance in starches and in a rice of higher amylose equivalent.

ABBREVIATIONS USED

DSC, differential scanning calorimeter; T_g, glass transition temperature; mp, melting point; dp, decomposition point or dextrinization point; RVA, Rapid Visco analyzer; db, dry basis; wb, wet basis; P, peak viscosity; H, hot paste viscosity; C, cold paste viscosity; BD_r, relative breakdown; H/P, breakdown ratio; C/P, setback; C/H, total setback; amylose equiv, amylose equivalent; Emc-s, equilibrium moisture content on soaking rice at room temperature; H_1, surface hardness; $-H_1$, surface stickiness; H_2, overall hardness; $-H_2$, overall stickiness; adh, adhesiveness in dyn/cm^2; coh, cohesiveness.

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LITERATURE CITED

Armeniades, C. D.; Baer, E. Transition and relaxations in polymers. In *Introduction to Polymer Science and Technology: An SPE Text Book*; Kaufman, H. S., Ed.; Wiley: New York, 1977.

Bhattacharya, K. R.; Sowbhagya, C. M. On viscograms and viscography, with special reference to rice flour. *J. Texture Stud.* **1978b**, *9*, 341−351.

Bhattacharya, K. R.; Sowbhagya, C. M. Pasting behaviour of Rice: A New Method of Viscography. *J. Food Sci.* **1979b**, *44*, 797−800.

Bhattacharya, K. R.; Sowbhagya, C. M.; Indudhara Swamy, Y. M. Importance of Insoluble Amylose as a Determinant of Rice quality. *J. Sci. Food Agric.* **1978a**, *29*, 359−364.

Bhattacharya, K. R.; Indudhara Swamy, Y. M.; Sowbhagya, C. M. Vareital difference in equilibrium moisture content of rice and effect of kernel chalkiness. *J. Food Sci. Technol.* **1979a**, *16*, 1−2.

Bhattacharya, K. R.; Sowbhagya, C. M.; Indudhara Swamy, Y. M. Quality profile of rice: A tentative scheme for classification. *J. Food Sci.* **1982**, *47*, 564−569.

Biliaderis, C. G.; Page, C. M.; Maurice, T. J.; Juliano, B. O. Thermal characterization of rice starches: A polymeric approach to phase transitions of granular starch. *J. Agric. Food Chem.* **1986**, *34*, 6−14.

Bourne, M. C. Texture Profile Analysis. *Food Technol.* **1978**, *7*, 62−67, 72.

Indudhara Swamy, Y. M.; Ali, S. Z.; Bhattacharya, K. R. Hydration of raw and parboiled rice and paddy at room temperature. *J. Food Sci. Technol.* **1971**, *8*, 20.

International Standard. Rice—Determination of amylose content. 1987(E); ISO 6647, 2−3.

Kainuma, K.; Oda, T.; Suzuki, S. Observation on the changes of Starch Granules during Gelatinization with the novel Photopastegraphy. Part 1. Design and produce of photopastegraph. Denpun Kogyo Gakkaishi. *Journal of Starch Technology* **1968**, *16*, 51−54.

Leach, H. W. Gelatinization of Starch. *STARCH: Chemistry and Technology, Vol. I, Fundamental Aspects*; Whistler, R. L., Paschall, E. F., Eds.; Academic Press: New York, 1965.

Maurice, T. J.; Slade, L.; Sirett, R. R.; Page, C. M. Polysaccharide-water interactions—Thermal behaviour of rice starch. In *Influence of Water on Food Quality and Stability*; Simatoa, D., Multon, S. L., Eds.; Martinus Nijhoff: Dordrecht, The Netherlands, 1985.

Ohtsubo, K.; Toyoshima, H.; Okadome, H. Quality Assay of Rice using Traditional and Novel Tools. *J. Cereal Sci.* **1998**, *43*, 203−206.

Okadome, H.; Toyoshima, H.; Ohtsubo, K. Many sided Evaluation of Physical Properties of Cooked Rice Grains with a Single Apparatus. (Development of Advanced Physical Measurement Method for Individual Cooked Rice). Part I. *Nippon Shokuhin Kagaku Kogakukaishi* **1996**, *43*, 1001−1004.

Oosten, B. J. Breda (The Netherlands), Interaction Between Starch and Electrolytes. *Staerke* **1990**, *42*, 327−330.

Radhika Reddy, K.; Zakiuddin, Ali S.; Bhattacharya, K. R. The fine structure of rice-starch amylopectin and its relation to the texture of cooked rice. *Carbohydr. Polym.* **1993**, *22*, 267−275.

Ranghino, F. Valuation of rice resistance to cooking. *RISO* **1966**, *15*, 117−127.

Schoch, T. J. In *Methods in Carbohydrate Chemistry*; Whistler, R. L., Ed.; Academic Press: New York, 1964; Vol. IV, pp 106−108.

Shogren, R. L. Effect of moisture content on the melting and subsequent physical aging of corn starch. *Carbohydr. Polym.* **1992**, *19*, 83−90.

Singh, V. Studies on Modified Starches. Ph.D. Thesis submitted to and awarded by the University of Mysore, Karnataka, India, 1996.

Singh, V.; Ali, S. Z. Estimation of Phosphorus in Native and Modified Starches. Improvement in the Molybdovanado phosphoric Acid Methodology. *Staerke* **1987a**, *39*, 277−279.

Singh, V.; Ali, S. Z. Comparative acid modification of various starches. *Staerke* **1987b**, *39*, 402−405

Singh, V.; Ali, S. Z.; Divakar, S. ^{13}C CP/MAS NMR Spectroscopy of Native and Acid Modified Starches. *Staerke* **1993**, *45*, 59−62.

Smith, R. J. Characterization and Analysis of Starches. In *STARCH Chemistry and Technology. Vol. II, Industrial Aspects*; Whistler, R. L., Paschall, E. F., Eds.; Academic Press: New York, 1967.

Sowbhagya, C. M.; Bhattacharya, K. R. A simplified colorimetric method for determination of amylose content in rice. *Staerke* **1971**, *23*, 53−56.

Toyoshima, H.; Okadome, H.; Ohtsubo, K.; Suto, M.; Horisue, N.; Inatsu, O.; Narizuka, A.; Aizaki, M.; Okawa, T.; Inouchi, N.; Fuwa, H. Cooperative Test on the Small-scale Rapid Method for the Gelatinization Properties Test of Rice Flours with a Rapid-Visco-Analyser (RVA). Nippon Shokuhin Kagaku Kogakukaishi **1997**, *44*, 579−584.

Unnikrishnan, K. R.; Bhattacharya, K. R.: Swelling and Solubility behaviour of parboiled rice flour. *J. Food Technol.* **1981**, *16*, 403−408.

Wilson, L. A.; Birmingham, V. A.; Moon, D. P.; Snyder, H. E. Isolation and Characterization of starch from mature soyabeans. *Cereal Chem.* **1978**, *55*, 661−670.

Zeleznak, K. J.; Hoseney, R. C. The Glass Transition in Starch. *Cereal Chem.* **1987**, *64*, 121−124.

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