

Physicochemical Rheological and Thermal Properties of Njavara Rice (*Oryza sativa*) Starch

CHANDROTH KALYAD SIMI AND THOLATH EMILIA ABRAHAM*

Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST), Council of Scientific and Industrial Research (CSIR), Thiruvananthapuram, India

Njavara rice starch was studied for its morphological, physicochemical, and thermal properties and was found to be different from the native chamba variety of rice. Njavara rice starch has bigger granule and has a high (85 °C) gelatinization temperature and shows high thermal stability. The swelling power, solubility, water absorption capacity, and enthalpy of gelatinization were found to be high compared to the native rice starch. The 6% (w/v) njavara rice starch gel had 87.45% clarity and its pasting properties such as peak viscosity (957 cP), break down viscosity (324 cP), and set back values (421 cP) were also higher. It also had better freeze thaw stability, gel strength, and high springiness against shear stress. Other properties like hardness, gumminess, adhesiveness, cohesiveness, and chewiness of the gel are slightly higher than native rice starch. These inherent high thermal and pasting properties make njavara rice suitable as poultice for the body massage in the panchakarma treatment.

KEYWORDS: Njavara; physicochemical properties; rheology; thermal analysis.

INTRODUCTION

Rice is one of the most important cereals, and more than two thousand varieties of rice are grown commercially throughout the world. It is the main food item in Asia. Njavara rice is a unique, short duration cultivar grown only in certain pockets in Kerala state, south India (1) and belongs to the family *Oryza*. This is the only cultivar traditionally used effectively in the ayurvedic system of medicine in certain specific treatments like Panchakarma. It is interesting to note that this treatment is now getting more and more popular, not only in this region of the country but also in other parts of the nation and even in other countries. Njavara as a special cereal, reported to have properties to rectify the basic ills affecting the circulatory, respiratory, as well as the digestive system. Black glumed njavara has been used in Ayurveda treatment from the age of Charaka, i.e., 600 B.C. Njavara kizhi and njavara theppu are two major treatments in the ayurveda system of medicine for conditions of arthritis, paralysis, neurological complaints, degeneration of muscles, tuberculosis, for children with anemia, for women during lactation, in certain ulcers, and skin diseases. Njavara rice endosperm has around 73% starch.

Starches exhibit difference in various properties in accordance with the source and genotype. The properties mainly depend on physical and chemical characteristics such as amylose amylopectin ratio and the shape and size of starch granules, which is characteristics of their botanical origin (2). Starch exhibits unique viscosity behavior with change of temperature, concentration, and shear rate (3). Many researchers have used

the dynamic rheometer to study the viscoelastic or rheological properties of starches (4). The rheological properties of different starches vary to a large extent as a function of granule structure and physicochemical composition. Several rheological changes occur in starch; when starch–water systems are heated above the gelatinization temperature, the starch granules loose their crystallinity, absorb large amounts of water, and leach out amylose, thereby forming a paste composed of swollen starch granules dispersed in an amylose matrix (5). Here we are reporting the unique physicochemical, thermal, rheological, and textural characteristics of njavara starch compared to the native chamba rice starch.

MATERIALS AND METHODS

Materials. Njavara (black glumed) and chamba (jaya) rice were purchased from a local market, in Trivandrum, Kerala, India. All chemicals used were of reagent grade and purchased from Central Drug House, Mumbai, India.

Starch Isolation. Njavara and chamba rice was separately soaked in water for a few hours and ground well to release the starch granules from the seeds. The slurry was filtered through a double layer of organdy cloth. The milky filtrate was kept for settling of the starch granules. The supernatant was decanted off and the starch residue was washed with distilled water three or four times. The starch granule was deproteinated with protease enzyme (protease from *Bacillus licheniformis*); 500 μ L (>1.2 unit/500 μ L of protein) of enzyme was added into the starch phosphate buffer suspension at pH 7. The mixture stirred for 30 min at 30 °C and was centrifuged at 21 000g for 5 min. The supernatant and upper brown layer were discarded. The deproteinated starch was air-dried at room temperature (25–28 °C). Lipids present were removed by washing with hexane, and the hexane was added to

* Corresponding author. Fax: 0091-471-2491712. E-mail: emiliatea@gmail.com.

the deproteinized starch (0.25% w/v), which was stirred for a few minutes at 30 °C, filtered, air-dried and then oven-dried at 50 ± 2 °C, and stored in airtight containers.

Amylose Content. Amylose content of njavara rice was determined according to the procedure of Sowbhagya and Bhattacharya (6). Njavara amylose was separated by alkali leaching, purified, and used as a standard.

Scanning Electron Microscopy. Morphological characteristics of the starch grains were studied using a scanning electron microscope (JEOL, model JSM 5600 LV, Tokyo, Japan). Starch powder was mounted on the stud using double-sided carbon tape, and the gold-sputtered samples were scanned under the electron beam at an accelerating voltage of 10 kV.

Solubility and Swelling Power. Solubility and swelling power at various temperatures such as 60, 70, 80, 85, and 90 °C were determined (7). Starch (0.1 g) was taken in a previously tared bottle and sufficient distilled water was added to give a total volume of water equivalent to 9 g. The starch was heated in a water bath for 30 min at a constant temperature (60, 70, 80, 85, or 90 °C) with magnetic stirring. After heating, the bottle was rinsed with distilled water to bring the volume to 10 g. The sample was centrifuged at 313g for 15 min. Five milliliters of the clear supernatant was drawn off into a clean, dry dish. The dish was dried in a vacuum oven for 4 h at 120 °C, cooled in a desiccator, and weighed. The supernatant was completely decanted, and the swollen granules were weighed. The percentage solubility and swelling power were calculated using the formula

$$\% \text{ solubility} = \frac{\text{dry weight at } 120 \text{ }^\circ\text{C}}{\text{sample weight}} \times 200$$

$$\text{swelling power} = \frac{\text{weight of swollen granule}}{\text{sample weight}(100 - \% \text{ solubility})} \times 100$$

Light Transmittance or Gel Clarity. Starch suspensions (0.6% w/v in DMSO) were placed in a water bath at 90 °C for 30 min, agitated well, and then cooled to room temperature. The percentage transmittance of this gelatinized starch was determined at 640nm using a spectrophotometer (UV 2100, Shimadzu, Kyoto, Japan). The gel clarity was studied over time (2, 4, 6, 24, 48, and 72 h) (8).

Freeze-Thaw Stability. Fifty milliliters of 6% (w/v) starch solution was heated to 95 °C and was held at this temperature for 15 min, and the gel was cooled down to room temperature. The gel was frozen at <0 °C overnight, thawed to room temperature, and then centrifuged at 604g for 15 min, and measurements were taken for water separation (syneresis) from the starch gels. This process was repeated five times.

Differential Scanning Calorimetry. A differential scanning calorimeter (Perkin-Elmer) was employed to measure the thermal analysis of rice starches. Njavara and native chamba rice starches (about 3 mg) were weighed in to an aluminum pan and the moisture level was adjusted to 70–80% by adding deionized water. The pan was hermetically sealed and left to equilibrate for 2 h at room temperature. The samples were scanned at temperatures from 0 to 130 °C at a rate of 10 °C/min. The gelatinization temperature was determined by automatically computing the initial temperature (T_i), maximum peak temperature (T_p), final temperature (T_f), and gelatinization enthalpy (ΔH) from the resulting thermogram (9). After conducting the thermal

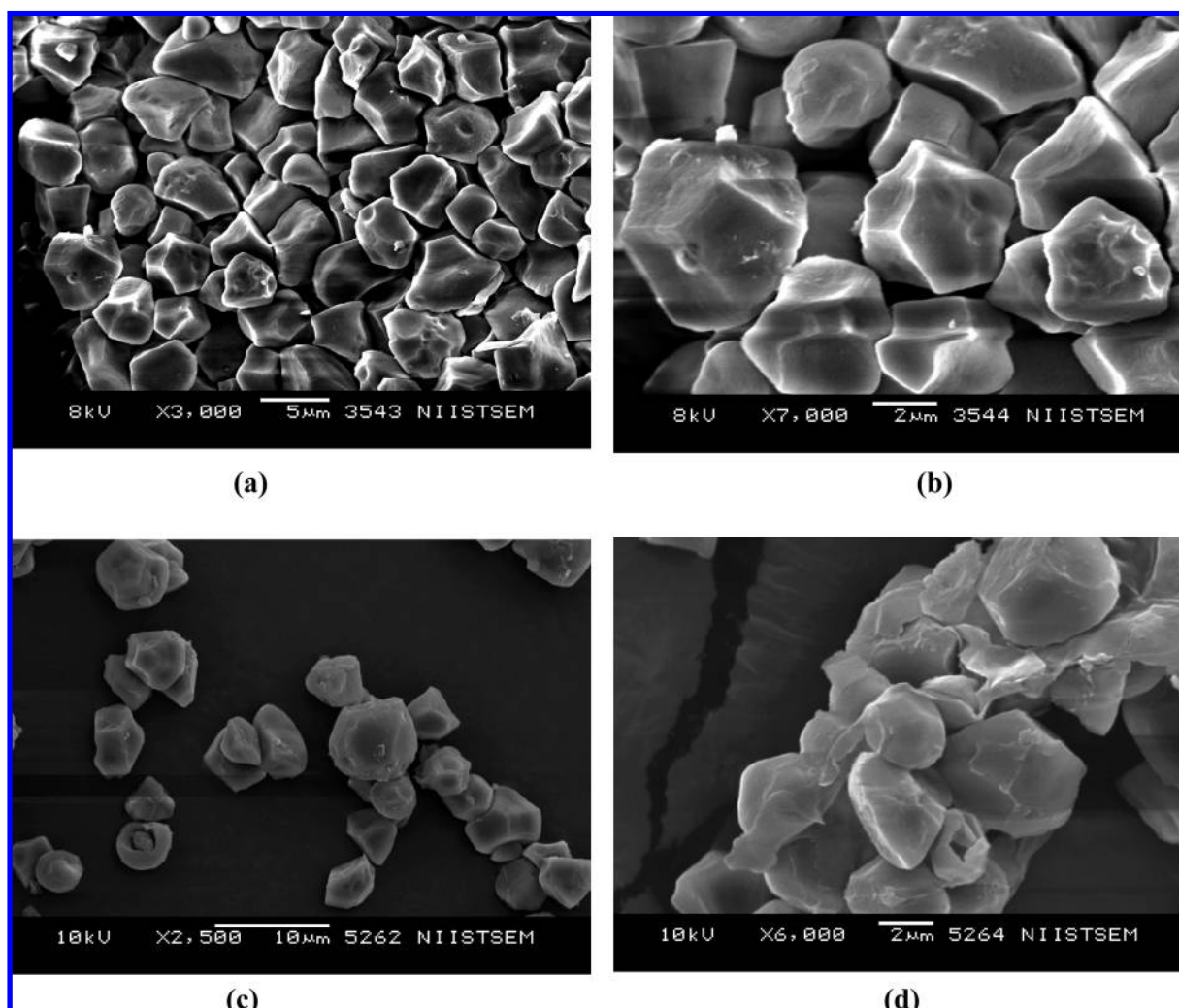


Figure 1. SEM micrograph of Njavara starch and native chamba starch.

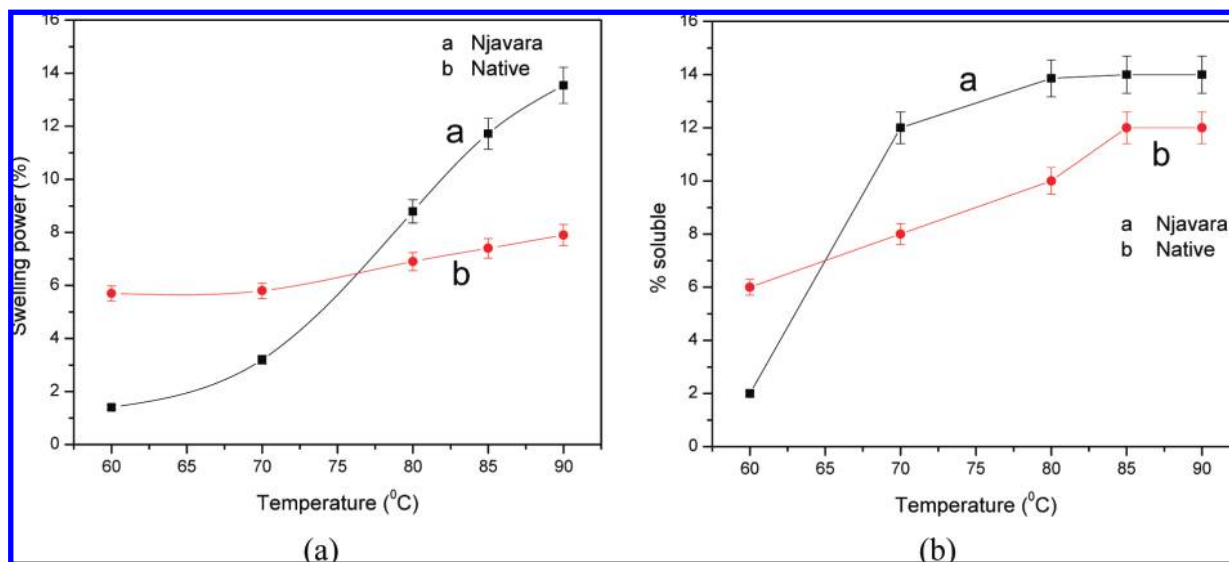


Figure 2. Swelling power and solubility of njavara and native rice starch.

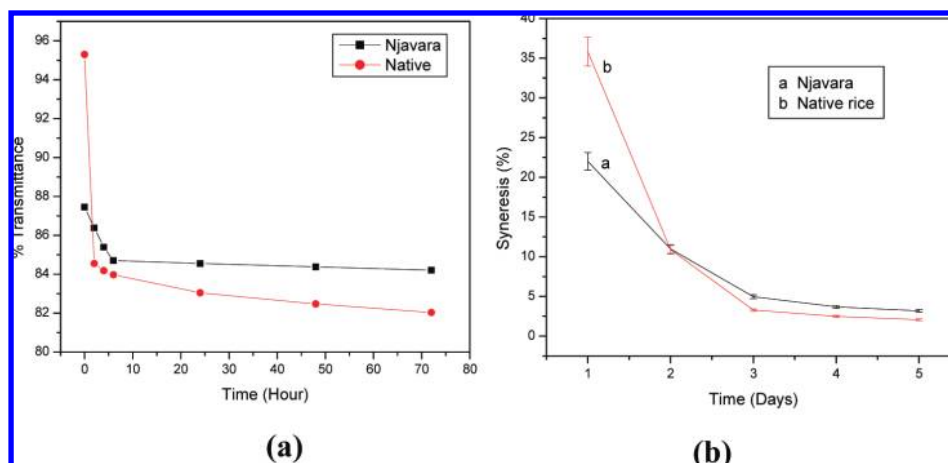


Figure 3. Gel clarity and freeze-thaw stability of njavara and native rice starch.

analysis, the samples were stored in the refrigerator at 4 °C for 7 days for retrogradation studies. These samples were left at room temperature (28 °C) for 2 h before analysis and reheated at the rate of 10 °C/min from 0 to 130 °C. The enthalpies of retrogradation were calculated automatically, and the percent retrogradation was calculated as $\%R = (\text{enthalpy of retrogradation})/(\text{enthalpy of gelatinization}) \times 100$.

Thermogravimetric Analysis. The thermal properties of the starches were measured with a simultaneous DTA-TG apparatus (DTG-60, Shimadzu, Kyoto, Japan) at a heating rate of 20 °C/min in nitrogen atmosphere. The sample weight was varied from 5 to 8 mg and was heated from room temperature (28 °C) to 500 °C.

Pasting Property. Pasting characteristics of the starches were determined with a rapid viscoanalyzer (RVA-4, Newport Scientific, Warriewood, Australia) at a fixed starch concentration of 10% (w/v) and a constant speed 160g using the standard profile. The temperature profile employed was as follows: heating from 50 to 95 °C at 12 °C/min and holding at 95 °C for 2 min. The viscosity profile recorded by the RVA reflects the peak, trough, and final viscosity; pasting temperature; and peak time.

Enzymatic Hydrolysis of Starch. The digestibility of starches was studied using the enzyme α -amylase from *Bacillus amyloliquefaciens*. Starch (25% w/v) was gelatinized in 0.01 M pH 7.0 phosphate buffer in a boiling water bath at 100 °C. The starch gel was then cooled to 80 °C. The gel was incubated at 80 °C for 30 min with 200 units of enzyme and 50 ppm of calcium chloride. After the digestion, the reducing sugar was determined from an aliquot of this sample. DNS was used as the reagent and the absorbance was read at 540 nm using a UV-vis spectrophotometer (Shimadzu, Kyoto, Japan).

Dynamic Rheological Measurement. Rheological measurements were made with an Anton Paar rheometer (TA Instruments Inc., New Castle, DE). A cone and plate measuring geometry was used with a gap width of 0.5 mm.

Temperature Dependence of Starch Sample. Starch samples (approximately 3 mL) were transferred to the rheometer plate and heating was carried out. The temperature was increased from 30 to 90 °C and controlled precisely by a Peltier system attached to the instrument. Moisture loss was prevented by covering the edge of the plate with a thin layer of light paraffin oil. The strain was taken as a constant 0.5% and the frequency as 1 rad/s.

Frequency Dependence. The frequency dependence of the dynamic moduli of starch gels was determined. The storage modulus and loss modulus were determined at 30 °C using a strain-controlled rheometer with cone and plate geometry and 0.5% strain. Frequency was varied from 0.1–100 rad/s. Stress sweep measurements were performed to confirm the data were obtained within the linear viscoelastic strain region.

Texture Studies. Textural properties of 10% starch gels were evaluated on a food texture analyzer (model TADH, Stable Microsystem, Godalming, Surrey, UK). Texture profile analysis (TPA) was performed on the samples in tubes at 25 °C. From the texture profile curve, hardness (HA), cohesiveness (CO), adhesiveness (AD), and springiness (SP) were calculated. In all experiments, gelatinized 10% starch samples were poured in a Petri dish of 50 mm diameter and 10 mm height. After cooling, the texture profile was measured by compressing the gel about 4 mm (40% compression) under a cylindrical probe of diameter 25 mm (P/25) at a test speed of 1 mm/s and a control

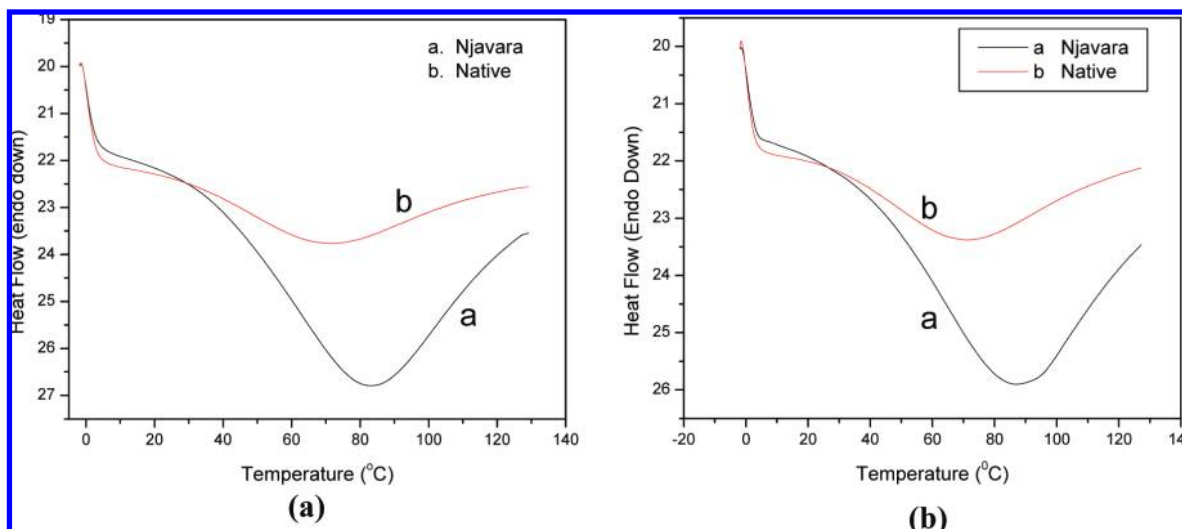


Figure 4. Differential scanning calorimetry of original and retrograded njavara and native rice starch.

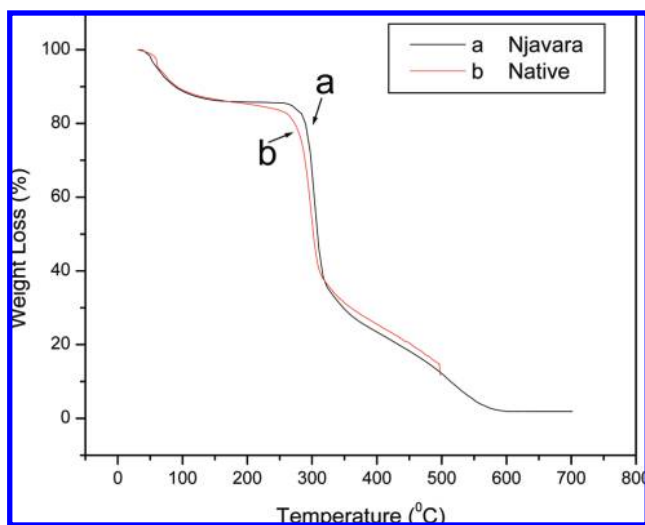


Figure 5. Thermogravimetric analyses of njavara and native rice starch.

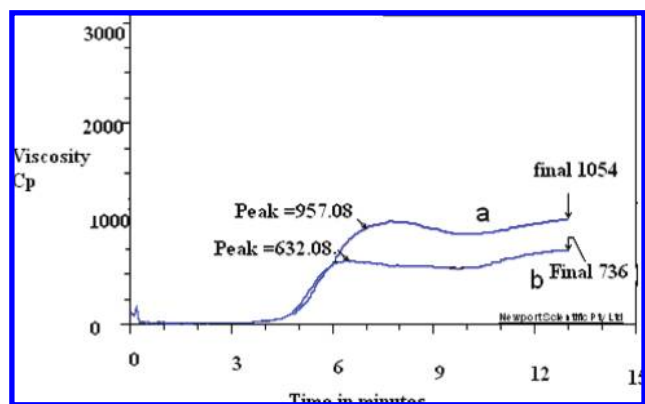


Figure 6. Pasting profiles of njavara and native rice starch.

force of 5 g, using the texture analyzer with accompanying computer software (SAS).

A deformation level between 20% and 50% had been applied on starch gel food systems, because under large deformation, the samples collapsed and invalid parameters were obtained. A crosshead speed (50 mm/min) was chosen, thus avoiding the total destruction of the gel structure in the first compression. This speed was also recommended to get values highly correlating with the sensory responses. Two replicate samples were tested.

XRD Analysis. X-ray diffraction patterns of njavara starch and native rice starch were analyzed using an X-ray diffractometer (XPRT, Philips, Eindhoven, The Netherlands) with nickel-filtered Cu K radiation ($\lambda = 0.154$ nm) at a voltage of 40 kV and current of 30 mA. The degree of crystallinity of samples was quantitatively estimated following the method. A smooth curve that connected peak baselines was plotted on the diffractograms. The area above the smooth curve was taken as the crystalline portion, and the lower area between smooth curve and the linear baseline in the samples was taken as the amorphous section.

The equation of the degree of crystallinity is as follows

$$X_c = A_c / (A_c + A_a)$$

where X_c refers to the degree of crystallinity, A_c refers to the crystallized area on the X-ray diffractogram, and A_a refers to the amorphous area on the X-ray diffractogram.

RESULTS AND DISCUSSION

Morphology of the Starch Granules. The rice starch granules are found to be hexagonal in shape, which is typical of many cereal starches. SEM shows that the njavara starch granule has a diameter in the range of 5–6 μm , whereas chamba rice starch granules were smaller and had a size of 1–2 μm (Figure 1). The variation in starch granule morphology may be due to the biological origin and physiology of the plant and the biochemistry of the amyloplast. This may be also due to the variations in the amylose and amylopectin content and its structure, which in turn play an important role in the control of the starch granule size and shape (10, 11).

Amylose Content. Amylose content in njavara rice starch was found to be $20 \pm 2\%$ and was similar to the native rice varieties, the amylose content of which is in the range of 20–22% (1).

Swelling Power and Solubility. Swelling power and solubility of rice starches at different temperatures were studied. Results are shown in Figure 2. In the case of njavara starch, the swelling power increases steeply over the range of temperatures studied. The pattern shows that njavara starch swelled rapidly at about 76 °C, exceeding the swelling of native rice starch granules, and this starch granule has a comparatively sturdy granule structure. The swelling is due to the breaking of intermolecular hydrogen bonds in the amorphous region of the granule, which allows irreversible and progressive water absorption (8).

In the case of native rice starch, the swelling pattern is less steep and shows a constant increase in swelling power between 60 and 76 °C than njavara. After 76 °C, the swelling power

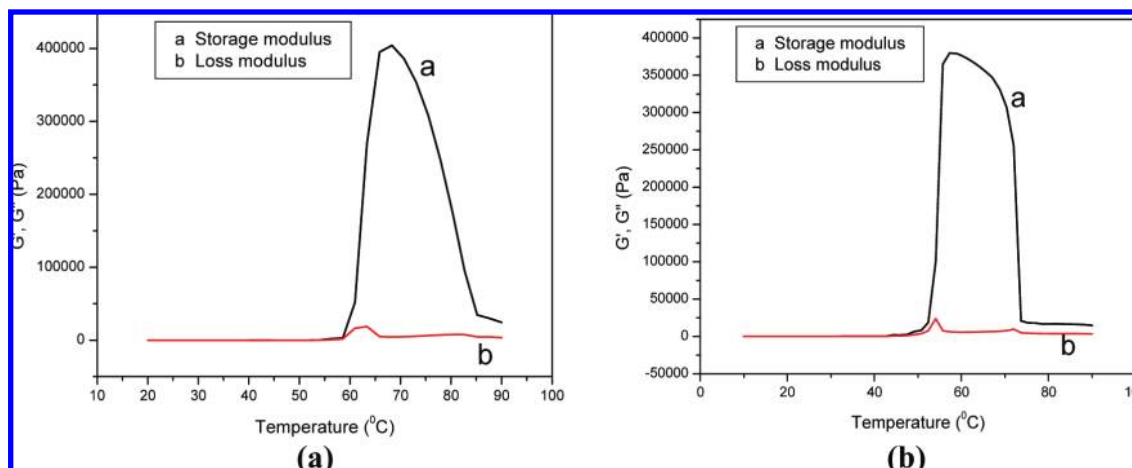


Figure 7. Temperature dependence of (a) njavara and (b) native rice starches.

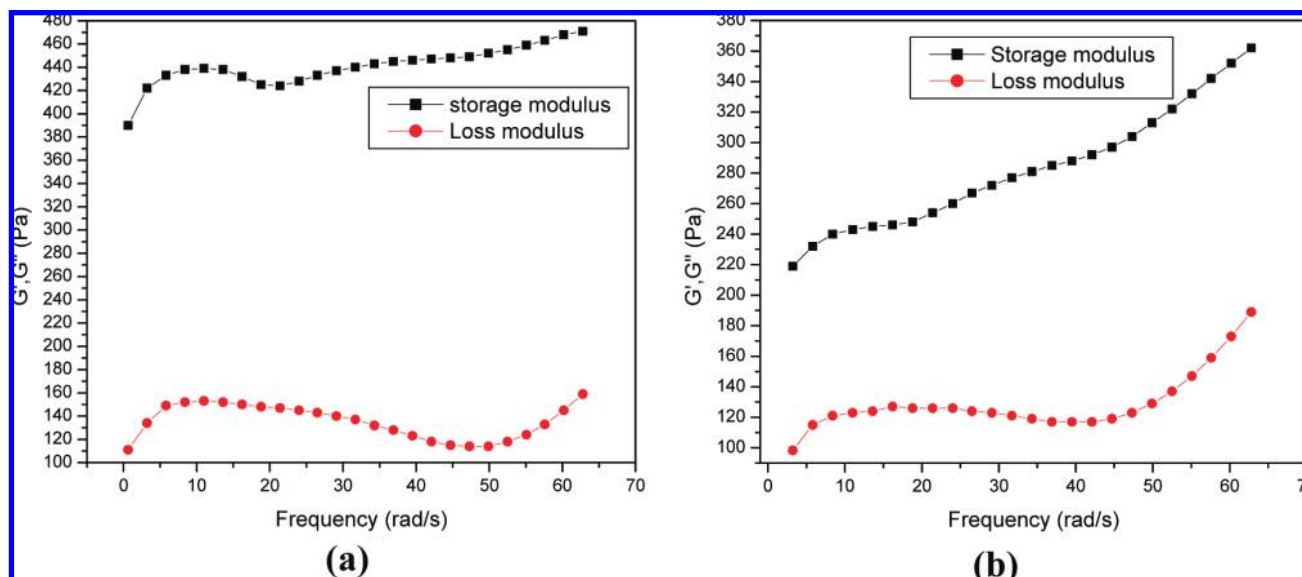


Figure 8. Frequency dependence of (a) njavara and (b) native rice starches.

value is higher for njavara. The low swelling power of njavara starch below 76 °C is mainly due to its higher gelatinization temperature. It is reported that the swelling power is positively correlated to gelatinization temperature, amylopectin chain length, and amylose content (12).

The solubility of njavara starch shows a sudden increase from 60 °C and solubility increases rapidly up to about 68 °C and then slowly between 68 and 78 °C, finally becoming constant. The solubility of native rice starch increases rapidly between 70 and 80 °C. Above 76 °C, it shows a slow increase. The solubility is due to the leaching of amylose chains from the amorphous part of the swollen granules. The swelling power and the percentage soluble are higher in njavara rice at 76 °C; below 76 °C, it shows lower values than native starch. The higher swelling power at a higher temperature makes this starch unique and provides application for panchakarma in ayurveda medical systems.

Starch Gel Clarity. Njavara rice starch gel had a lower transmittance value (87.45%) compared to native rice (95.30%) (Figure 3a), because of the relatively higher granule size of the starch. The percent transmittance of gel decreases with an increase in storage time, due to the retrogradation of starch. In the case of njavara starch gel, the decrease in transmittance was sharp up to 6 h and then it remained almost constant. However, the native rice starch lost its clarity significantly after 2 h. The

degree of transmittance is directly correlated to the water absorption capacity. The njavara rice starch has low water absorption capacity at lower temperatures compared to the native rice starch, and this may be the reason for the lower clarity of starch gel. In njavara, the clarity of the gel is not much affected by the storage time, whereas in the case of native rice starch, the gel becomes opaque after 2 h due to rapid retrogradation. From the studies it was seen that the clarity of gel from njavara starch is more stable than that of rice starch, an advantage in the food industry.

Freeze–Thaw Stability. The freeze–thaw stability of both the starch gels has same pattern as shown in Figure 3b. Njavara starch gel had low syneresis compared to the native rice starch gel, and the percent syneresis is inversely related to the stability of the gel. Starch with high syneresis readily absorbs and eliminates water like a sponge. Njavara rice starch separates less water at the first cycle than the native rice starch. Maximum water was separated in the first cycle and then it was decreased over time. Compared to other starches, rice starch shows low freeze–thaw stability. The low syneresis rate of njavara starch indicates its superior quality for its possible application in the food industry and panchakarma in the ayurveda system of medicine.

Differential Scanning Calorimetry. DSC thermograms of njavara and native rice starches are depicted in Figure 4a. The

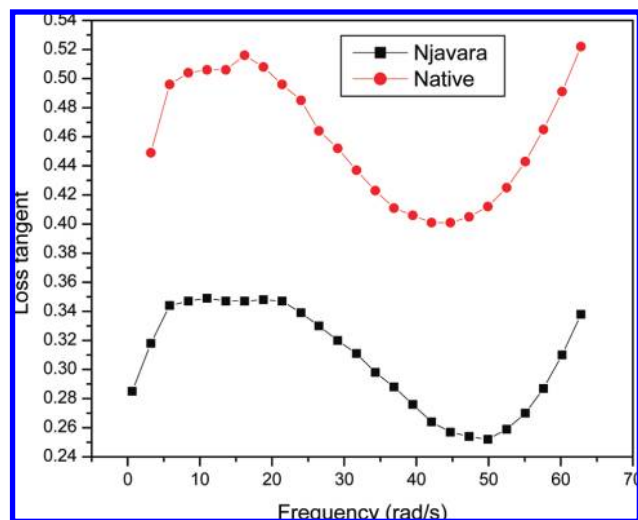


Figure 9. Loss tangent values of njavara and native rice starches.

gelatinization endotherm of native rice starch was broader than that of njavara. The melting temperature range gives an indication of the quality and heterogeneity of the recrystallized amylopectin. Thus, a wide melting range might imply a large amount of crystals of varying stability, whereas a narrow range could suggest crystals of a more homogeneous quality and similar stability (13). Njavara rice had a higher gelatinization temperature (85 °C) than the native starch (70.93 °C). Njavara starch required more energy to gelatinize, since its enthalpy of gelatinization was very high ($\Delta H = 366.17$ J/g). The enthalpy of gelatinization of native rice starch was lower, 61.82 J/g. The difference in gelatinization temperature among the rice starches may be influenced by factors like the granular architecture and molecular structure of amylopectin (14). The rice starch particles have a crystalline region within a starch granule that is composed of small crystallites with different crystal melting temperature that mainly consist of amylopectin (15).

The retrogradation properties of njavara and native rice starches were studied after storage of gelatinized starches at 4 °C for 7 days. The retrogradation peak of njavara starch was shifted in the higher temperature regions. (87.2 °C) and native rice starch shows a similar pattern as in the case of the gelatinization endotherm (70.93 °C) (Figure 4b). The amylopectin and the intermediate materials play a significant role in starch retrogradation during refrigerated storage. Recrystallization of amylopectin branch chains has been reported to occur in a less ordered manner in stored starch gels than in native starches (16). The percentage of retrogradation (%R) was less for njavara starch (85%) as compared to native rice starch (90.56%).

Thermogravimetric Analysis. Njavara and native starch were subjected to thermal degradation. The thermogravimetric plots of njavara starch and native starch are shown in Figure 5. In the case of njavara starch, degradation starts at a temperature of 275 °C, but for native starch, the degradation temperature starts at a lower temperature of 225 °C. This showed that njavara starch is thermally more stable than native rice starch. The temperatures at which there is 5% weight loss of njavara starch and native rice starch were 59.45 and 62.03 °C, respectively. The temperatures corresponding to 10% weight loss of njavara and native rice starch were 85.41 °C (njavara) and 90.3 °C (native rice).

Pasting Property. The pasting profiles of both rice starches are similar and behave as a typical cereal starch. The results are presented in Figure 6. Njavara starch showed a higher

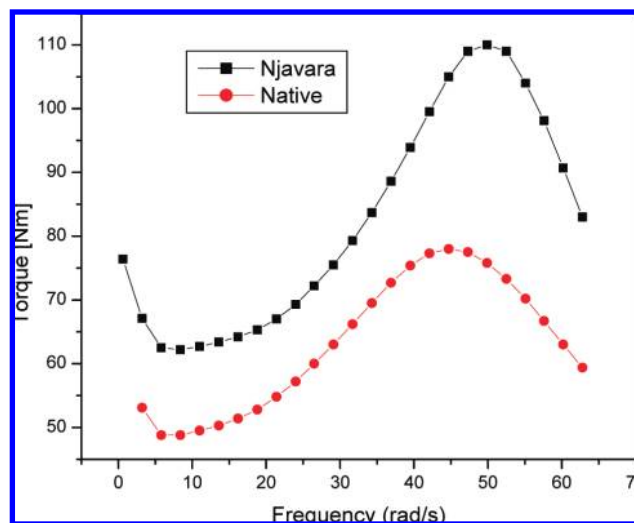


Figure 10. Torque variations with frequency of njavara and native rice starches.

peak viscosity value (957 cP) than native rice (632 cP), mainly due to the bigger granule size, which in turn increases the swelling ratio and viscosity. Pasting properties are reported to be influenced by granule size, amylose/amylopectin ratio, starch molecular characteristics, and the condition of the thermal process employed to induce gelatinization (17). The final viscosity of these starches followed the same pattern (the final viscosity of njavara is 1054 cP and of native chamba rice is 736 cP). Peak viscosity is a measure of the water-holding capacity of the starch in terms of the resistance of swollen granules. The breakdown viscosity is regarded as a measure of the degree of disintegration of granules and shows paste stability. During breakdown, the granules are disrupted and amylose molecule will generally leach out in to the solution. Heating beyond the peak viscosity temperature provides further energy to break down the residual crystalline structure, causing the viscosity to decrease. Njavara starch showed a higher breakdown value (324 cP) than native starch (82 cP). The setback viscosity of njavara (421 cP) is higher due to high peak viscosity and amylose content. The set back is the viscosity increase resulting from the rearrangement of amylose molecules that have leached from the swollen starch granules during cooling and is generally used as a measure of the gelling ability or retrogradation tendency of the starch (18). Njavara starch had higher set back viscosity while the native starch showed the least. The starting gel point temperatures for both njavara and native starch were found to be same (54 °C), but the pasting temperature of njavara rice starch was higher and found to be 84 °C, whereas native rice starch shows pasting temperature at 78 °C. These values are close to the gelatinization temperature obtained by DSC analysis.

Enzyme Digestibility. Njavara and native rice were gelatinized and hydrolyzed using bacterial α -amylase. Both njavara and native starch showed the same rate of hydrolysis: 14% of starch was hydrolyzed at 30 min of incubation. The enzyme digestibility mainly depends upon the interplay of many factors, such as starch source, granule size, and amylose amylopectin ratio, but here the granule size did not affect the hydrolysis rate.

Rheological Properties. Effect of Temperature. The effect on shear modulus of heating a rice starch dispersion at a constant rate of temperature is shown in Figure 7. Both starches shows the same pattern of shear modulus against

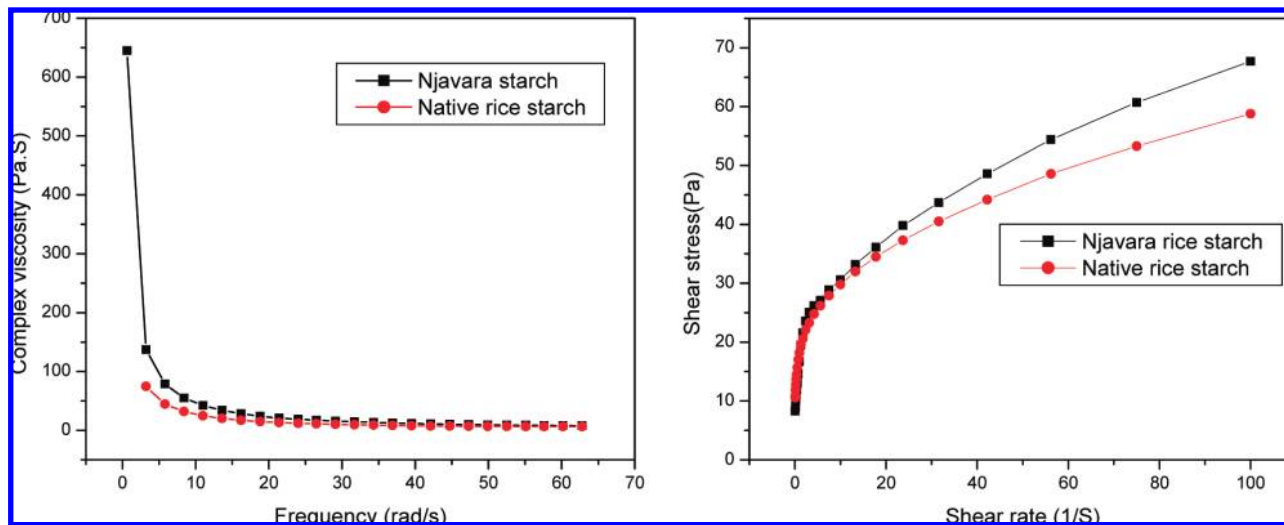


Figure 11. (a) Complex viscosity and (b) non-Newtonian nature of njavara and native rice starches.

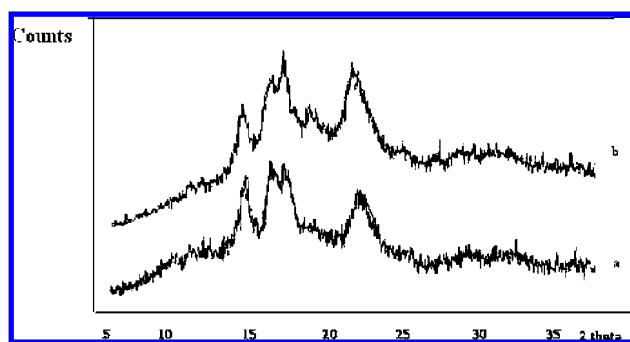


Figure 12. XRD of (a) njavara and (b) native rice starches.

temperature. Up to a certain temperature, both moduli [storage (G') and loss (G'')] were the same; after this, the storage modulus shows a sharp increase, reaches a maximum, and then decreases. The temperature corresponding to higher storage modulus (G'_{max}) is the gelatinization temperature. In njavara and native chamba rice, the gelatinization temperatures are different. Njavara rice gelatinizes at a higher temperature, 68 °C, and gelatinization starts at 59 °C, but in native starch, the gelatinization temperature was found to be 58 °C and gelatinization starts at a lower temperature, 48 °C. The higher value of G' compared to G'' indicates the formation of gel. The significant increase in G' value of rice starch on heating is caused by formation of a three-dimensional gel network developed by leached-out amylose and reinforced by strong interactions among the swollen starch particles (19). Upon further heating beyond G'_{max} , the G' decreased significantly, indicating damage to the gel nature during prolonged heating. The complete loss of the gel nature of njavara starch occurs at higher temperature compared to native rice starch. This indicates the stability of njavara starch gel with temperature. The damage to the structure could be due to the “melting” of the crystalline regions remaining in the swollen starch granule or resulting from the disentanglement of the amylopectin molecules in the swollen particles that softens the particles.

Frequency Dependence. The dynamic rheological properties G' and G'' are presented as a function of frequency in Figure 8. The G' , G'' , and complex modulus (G^*) decreased in the order $G^* > G' > G''$, as commonly observed for normal starch gels. The frequency dependence of G' and G'' gives valuable information about structure. A material that is

frequency-independent over a large time scale range is solidlike; a true gel system is such a material. In contrast, strong frequency dependence suggests a material structure with molecular entanglements that behaves more like a solid at higher frequencies and more like a liquid at lower frequencies. When swollen particles are subjected to shear oscillation at a certain angular frequency and amplitude, G' and G'' are proportional to the dissipated or lost energy during the oscillation process. It can be seen from Figure 8 that with increasing frequency G' and G'' gradually increase. G' is higher than the G'' in the whole frequency range; the elastic behavior of the sample predominates over its viscous behavior and the swollen sample exhibits mechanical rigidity. Both rice varieties show the same pattern of moduli, but the difference between the G' and G'' value is more in njavara starch compared to the native rice. This indicates that the gel rigidity is higher in the case of njavara starch gel. This property is very useful for the application of gels in food industries, adhesives, drug delivery, etc.

The ratio of loss and storage moduli (loss tangent or $\tan \delta$) is a measure of the energy lost compared to energy stored in deformation. The lower \tan value of njavara indicates the formation of a strong gel compared to native rice starch. The results are shown in Figure 9. Torque is the force required to rotate the sample. Figure 10 shows the variation of torque with frequency. Both rices show a similar pattern. Torque increases with frequency to a certain limit, then it decreases. This may be due to the distortion gel structure at higher frequency. Njavara rice required more force to rotate the sample compared to native rice starch.

Complex viscosity or the frequency-dependent viscosity decreases with increase in frequency. Both njavara and native rice starch showed a decrease in viscosity with shear. These results showed that njavara rice behaves as a non-Newtonian fluid with pseudoplastic nature, as in the case other starches. Yield stress is the stress at which a material begins to deform plastically. Above the yield stress, the material acts elastic and will return to its original shape when the applied stress is removed. Once the yield stress point is crossed, the deformation will be permanent and nonreversible. The yield stress of njavara rice starch was found to be 18.384 Pa, but in the case of native rice starch, yield stress was low (13.762 Pa) (Figure 11). This indicates the high gel strength of njavara starch against stress.

All rheological analysis showed that njavara starches have good properties that can be applicable to food industries, medical fields, and adhesives, compared to native rice starch. Its high gel strength, heat capacity, and high gelatinization temperature may be the reason for its wide application in Ayurveda treatments.

Texture Profile Analysis. The hardness (HA), adhesiveness (AD), springiness (SP), cohesiveness, and chewiness of gels from njavara and native rice starches were studied. The textural properties were influenced by starch granule size. The hardness of gelatinized starch gel has related to the amylose matrix and the filling effect of the swollen granules (20). The hardness of njavara starch gel (0.289N) is less than the native rice starch gel (0.391 N). Adhesiveness is a surface characteristic and depends on the combined effect of adhesive and cohesive forces, and also viscosity and viscoelasticity. The negative values for adhesiveness of both rice starches were -0.4041 for njavara and -0.3231 for native rice starch. Springiness or elasticity is a sensitivity of gel rubberiness in the mouth and is a measure of how much the gel structure is broken down by the initial compression. High springiness appears when the gel structure is broken into few large pieces during the first texture profile analyzer compression, whereas low springiness results from the gel breaking into many small pieces. Less springy gels will break down more easily during mastication than a firm and spring gel. Njavara rice starch (6.9368) showed 4 times higher value for springiness compared to native rice starch (1.7849). Chewiness is a quantity to simulate the energy required for masticating a semisolid sample to a steady state before the swallowing process. It is the product of gumminess and springiness. The chewiness of njavara rich gel (1.2923) was three times higher compared to native rice starch (0.4017). Cohesiveness is an index that how well the product withstands a second deformation relative to its behavior under the first deformation. Both of the starch gels did not have much difference in cohesiveness, even though the starch gel of njavara rice showed a slight higher value than native rice. The texture profile analysis showed that njavara starch had good springiness. This may be very useful in food industries.

XRD Analysis. Native starches generally exhibit two main crystalline types, namely, the A-type for cereal starches and the B-type for tuber and amylose-rich starches. The X-ray patterns of A-type starches give the stronger diffraction peaks at around 15° , 17° , 18° , and 23° (21). These four θ values are present in the case of both starches. The XRD pattern of both rice starches are similar. The results are shown in **Figure 12**.

CONCLUSION

The physicochemical properties of njavara starch was studied and compared with properties of native chamba rice starch. The njavara starch has high gelatinization temperature, water absorption capacity, solubility, and swelling power. It degrades at higher temperature, and the enthalpy of gelatinization was very high compared to that of native rice starch. Pasting properties showed that it has higher peak viscosity, break down viscosity, and set back values. These good thermal properties make it useful in products that need to be processed at a high temperature. Because of its high heat-holding capacity, njavara rice is widely and specifically used in ayurveda treatments. Rheological studies gave good results for njavara rice starch. Temperature sweep analysis showed that njavara starch gelatinizes at higher temperature (68°C) compared to native rice starch (58°C). Njavara rice starch

had higher gel strength than native rice starch, and the difference between the G' and G'' values is higher in the case of njavara, indicating the formation of a strong gel. Also the lower tan value and higher torque value of njavara indicate the formation of a strong gel compared to native rice starch. Complex viscosity of both starches decreases with shear rate. Texture profile analysis showed that all the texture properties, like hardness, gumminess, adhesiveness, cohesiveness, and chewiness, are similar in both rice starches, but the springiness of njavara starch gel is 3 times higher than that of native rice starch. The X-ray diffraction pattern showed that both starches are A-type and are similar in nature.

ACKNOWLEDGMENT

Ms. Simi is grateful to Council of Scientific and Industrial Research (CSIR, India) for the financial support as SRF. The authors are grateful to Mr. Shanavas for rheology analysis, Mr. Sajeevan for textural analysis, and Mr. Chandran for SEM analysis.

LITERATURE CITED

- (1) Deepa, G.; Singh, V.; Naidu, K. A. Nutrient composition and physicochemical properties of Indian medicinal rice njavara. *Food Chem.* **2008**, *106*, 165–171.
- (2) Madsen, M. H.; Christensen, D. H. Change in viscosity profile of potato starch during growth. *Starke* **1996**, *48*, 245–249.
- (3) Lii, C. Y.; Tsai, M. L.; Tseng, K. H. Effect of amylose content on the rheological property of rice starch. *Cereal Chem.* **1996**, *73*, 415–420.
- (4) Tsai, M. L.; Li, C. F.; Lii, C. Y. Effects of granular structure on the pasting behavior of starches. *Cereal Chem.* **1997**, *74*, 750–757.
- (5) Ring, S. G. Some studies on starch gelation. *Stärke* **1985**, *37*, 80–83.
- (6) Sowbhagya, C. M.; Bhattacharya, K. R. A simplified colorimetric method for determination of amylose content in rice. *Starke* **1971**, *23*, 53–55.
- (7) Whistler, R. L. *Methods in Carbohydrate Chemistry*; Academic Press: New York, 1964; Vol. IV, pp 106–108.
- (8) Bello-Perez, L. A.; Agama-Acevedo, E.; Sanchez-Hernandez, L.; Paredes-Lopez, O. Isolation and partial characterization of banana starches. *J. Agric. Food Chem.* **1999**, *47*, 854–857.
- (9) Sandhu, K. S.; Singh, N.; Lim, S. T. A comparison of native and acid thinned normal and waxy corn starches: Physicochemical, thermal, morphological and pasting properties. *Lebensm Wiss Technol.* **2007**, *40*, 1527–1536.
- (10) kaur, L.; Singh, J.; Mccarthy, O. J.; Singh, H. Physico-chemical, rheological and structural properties of fractionated potato starches. *J. Food Eng.* **2007**, *82*, 383–394.
- (11) Svegmarm, K.; Hermansson, A. M. Microstructure and rheological properties of composites of potato starch granule and amylose; a comparison of observed and predicted structure. *Food Struct.* **1993**, *12*, 181–193.
- (12) Sasaki, T.; Matsuki, J. Effect of wheat starch structure on swelling power. *Cereal Chem.* **1998**, *75*, 525–529.
- (13) Fredriksson, H.; Silverio, J.; Andersson, R.; Eliasson, A. C.; Aman, P. The influence of amylose and amylopectin characteristics on gelatinization and retrogradation properties of different starches. *Carbohydr. Polym.* **1998**, *35*, 119–134.
- (14) Gunaratne, A.; Hoover, R. Effect of heat–moisture treatment on the structure and physicochemical properties of tuber and root starches. *Carbohydr. Polym.* **2002**, *49*, 425–437.
- (15) Vasanthan, T.; Bhatta, R. S. Physicochemical properties of small and large granule starches of waxy, regular and high amylose barleys. *Cereal Chem.* **1996**, *73*, 199–207.

- (16) Ward, K. E. J.; Hosney, R. C.; Seib, P. A. Retrogradation of amylopectin from maize and wheat starches. *Cereal Chem.* **1994**, *71*, 150–155.
- (17) Zhou, M.; Robard, K.; Glennie-Holmes, M.; Helliwell, S. Structure and pasting properties of oat starch. *Cereal Chem.* **1998**, *75*, 273–281.
- (18) Abd Karim, A.; Norziah, M. H.; Seow, C. C. Methods for the study of starch retrogradation. *Food Chem.* **2000**, *71*, 9–36.
- (19) Biliaderis, C. C.; Maurice, Y. J.; Vose, J. R. Starch gelatinization phenomena studied by differential scanning calorimetry. *J. Food Sci.* **1980**, *59*, 203–212.
- (20) Morris, V. J. Starch gelation and retrogradation. *Trends Food Sci. Technol.* **1990**, *1*, 2–6.
- (21) Buléon, A.; Colonna, P.; Planchot, V.; Ball, S. Starch granules: Structure and biosynthesis. *Int. J. Biol. Macromol.* **1998**, *23*, 85–112.

Received for review August 21, 2008. Revised manuscript received October 14, 2008. Accepted October 17, 2008.

JF802572R