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Structure-viscosity relationships for starches from different rice varieties during heating

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Abstract

The effects of starch particle size and leached amylose on the viscosity of rice starch dispersions and changes of short-range structure and amylose content in starch granules of different rice varieties during heating were investigated. It was found that starch granule swelling increased rice starch dispersion viscosity during heating. The viscosities of the starch dispersions during heating were principally dependent on granular volume fraction and independent of starch variety. A distinct correlation between the amount of leached amylose and swelling of starch granules was also found. High initial amylose concentrations in starch granules reduced swelling during heating, thereby reducing rice dispersion viscosities. Fourier-transform IR spectroscopy indicated that the loss of short-range order was significant when the temperature reached the pasting onset temperature. The short-range order of waxy and medium grain rice starches was higher than that of long grain rice starches before gelatinization. The loss of order of waxy and medium grain rice starches was greater than that of long grain rice starches during heating, which was due to the presence of amylose, restraining the swelling and disruption of starch granules during heating.
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Keywords: Rice starch; Viscosity; Particle size; Amylose; Short-range order

1. Introduction

Starch is widely used in the formulation of food products and has many industrial applications. The cooking procedures for many foods and their cooked characteristics are related to starch gelatinization and pasting (Kar, Jacquier, Moran, Lyng, & Mckenna, 2005; Yeh & Li, 1996). Gelatinization describes several changes in the starch granule, which include losing crystallinity, absorbing water, swelling, and leaching of some components (e.g. amylose). Consequently, substantial rheological changes of starch dispersions occur during heating (Ellis & Ring, 1985; Tsai, Li, & Lii, 1997). Pasting encompasses the changes that occur after gelatinization upon further heating and these include further swelling of granules, leaching of molecular components from the granules, and eventual disruption of granules, especially with the application of shear forces (Tester & Morrison, 1990a, 1990b).

Starch granules swell when heated in excess water and their volume fraction and morphology play important roles in the rheological behaviour of starch dispersions; the alterations during gelatinization and pasting also reflect various aspects of conformational structure in starch granule (Bagley & Christiansen, 1982; Da Silva, Oliveira, & Rao, 1997; Evans & Haisman, 1979; Sandhu & Singh, 2007). Olkku and Rha (1978) pointed out that the swelling of starch granules resulted in an increase in starch solubility, paste consistency and paste clarity. Noosuk, Hill, Pradipasena, and Mitchell (2003) studied the structure-viscosity relationship for Thai rice starches. They reported that waxy rice starches had a higher swelling volume, resulting in a higher

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viscosity, than had other rice classes. Yeh and Li (1996) determined the changes in size distribution of rice starch granules, using a polarized light microscope in combination with a hot stage and an image analysis system. It was reported that the size of starch granules increased slightly as the temperature was raised from 35 to 55 °C, and increased rapidly at 65 °C. Recently, Kar et al. (2005) compared the gelatinization properties of native nonwaxy, surface-defatted nonwaxy, internal-defatted nonwaxy and waxy rice starch. A two-step phenomenon was seen in the granule diameter of native nonwaxy starch with increasing cooking temperature. From 55 to 65 °C, a relatively small increase in granule diameter from 6 to 10 μm was observed, and a significant increase occurred at 90 °C. Upon further heating, above 90 °C, the granules reached an average diameter of 16 μm.

Although amylose leaching is a factor influencing the functional properties of heated rice starch, little work has been reported on the effect of amylose leaching on the pasting viscosity. More detailed information about the relationship between the changes in amylose and amylopectin in starch granules during heating and the functional property of rice starch paste is still needed.

This paper relates the viscosity of rice starch dispersion to the starch granule structure and the molecular components during heating. The effects of starch particle size and leached amylose on the viscosity of rice starch dispersions during heating were investigated. Changes of short-range structure and amylose content in starch granules of waxy, medium and long grain rice varieties were studied.

2. Materials and methods

2.1. Materials

Waxy (Calmochi 101), medium (M202 and Koshi), and long (Cocodrie and L205) grain rice samples were grown and milled by the California Cooperative Rice Research Foundation, Biggs, CA. Protease N "Amano" (activity 150,000 units/g, optimum pH 7.5) provided by Amano Pharmaceutical Co. Ltd. (Nagoya, Japan), was used to isolate the rice starches granules.

2.2. Isolation of rice starch

Milled rice (50 g) was soaked in 150 ml of deionized water for 18 h. The rice and water were then blended in a Waring blender for 3 min. The initial pH of the solution was adjusted to 8.5 and Protease N (100 units/ml) was added. The protease hydrolysis was conducted at 50 °C for 4 h with constant stirring. After the hydrolysis, the slurry was centrifuged at 10,000*g* for 10 min. The supernatant and the surface brown layer of the starch were removed and the lower white starch layer was washed with deionized water, followed by centrifugation. The washed starch was freeze-dried, passed through a 200 mesh sieve and stored until analyzed.

2.3. Chemical composition of isolated starches

The moisture content of isolated starches was analyzed using AACC method 44–40 (2000). Nitrogen was measured by the Kjeldahl procedure, according to AACC Approved Method 46–13 (2000), and protein content of isolated starches was calculated by multiplying nitrogen contents by 5.95. Lipid content was determined according to AOAC methods (1995). Amylose content of rice starches was analyzed with an amylose/amylopectin assay kit (Megazyme International Ireland Ltd., Bray, Co. Wicklow, Ireland), based on the concanavalin A method (Yun & Matheson, 1990).

2.4. Pasting properties

The pasting properties of the isolated rice starches and flour were determined in triplicate on a rotational rheometer (Rheolyst AR 1000, TA instrument, New Castle, DE, USA). A cone and plate geometry was used. The cone was made from a polysulfone plastic with 4° angle and 60 mm in diameter. Starch dispersions of 1%, 3%, 6%, 8% or 8.8% (w/v) were prepared. The starch dispersions were prepared with degassed water. The starch was dispersed in the water with stirring for 5 min under vacuum before loading between the cone and the bottom plate. The following programme was used for the pasting of the starch slurries. After loading starch dispersion between the cone and plate, it was equilibrated to 50 °C for 1 min at 200 s^{-1}. The temperature was raised to 95 °C at the rate of 12 °C/min, holding at 95 °C for 2 min 30 s. The temperature was then decreased to 50 °C at the same rate, and finally held at 50 °C for 1 min. The shear rate during the pasting was maintained at 200 s^{-1}.

2.5. Particle size distribution

Aqueous starch suspensions of 1%, 3%, 6% or 8% (w/v) were loaded between the cone and plate of the rheometer. The dispersions were equilibrated to 50 °C and maintained for 1 min. To measure the change in the size of the starch granules upon heating, samples were heated to a pre-defined temperature (i.e. either 70, 75, 80, 85, 90 or 95 °C) at the rate of 12 °C/min. When the pre-defined temperature was reached, the sample was immediately cooled to 50 °C, removed from the rheometer, and allowed to cool to room temperature within 10 min in order to avoid the retrogradation of the amylose. The cooled dispersion was analyzed in triplicate for particle size distribution with laser diffraction in triplicate with a Microtrac S3500 (Microtrac Inc., North Largo, FL, USA).

2.6. Measurement of amylose content during heating

The starch dispersions (3%, w/v) were prepared and treated on the rheometer in the same fashion as for the particle size measurements described above. After cooling to

50 °C on the rheometer, the sample was removed and centrifuged at 10,000*g* for 10 min. The supernatant (leached amylose) and the precipitate (pasted granules) were collected separately for analysis. Amylose contents in the supernatant and the precipitate were analyzed in triplicate with an amylose/amylopectin assay kit, based on the concanavalin A method (Megazyme International Ireland Ltd., Bray, Co. Wicklow, Ireland).

2.7. Determination of the viscosity of amylose

The viscosities of amylose from M202 and Cocodrie dispersions were measured in duplicate on the AR1000 rotational rheometer. The amylose was prepared using the rheometer as described above. The amylose dispersion (M202 or Cocodrie, 6% w/v) was loaded onto the plate of the rotational rheometer, equilibrated to 50 °C and maintained for 1 min. Temperature was raised from 50 to 85 °C at the rate of 12 °C/min. The starch sample on the plate of the rheometer was then collected. After centrifugation, the supernatant (leached amylose dispersion) was collected and loaded between the plate and the 4 degree-angled cone on the rheometer to measure the viscosity of leached amylose. The gap was set at 0.1 mm and the shear rate was maintained at 200 s^{-1}.

2.8. Fourier-transform IR spectroscopy

Absorbance spectra were recorded on a spectrometer (Thermo Necolet Co., Waltham, USA) equipped with a deuterated triglycine sulphate (DTGS) detector using the Digilab attenuated total reflectance (ART) accessory. Starch dispersions (6%) were prepared using the rheometer, as described in 2.4 for particle size distributions. Each spectrum, obtained at a resolution of 4 cm^{-1}, was an average of 64 scans, recorded against an empty cell as background, and was subtracted from the spectrum of water. Spectra were baseline-corrected at 1200 and 800 cm^{-1} by drawing a straight line. All spectra were deconvoluted. The ratio of absorbance height at the wave number 1047 cm^{-1} to the height at 1022 cm^{-1} was obtained for the deconvoluted spectra.

2.9. Statistical analysis

The averages and Duncan-*t*-test were performed by SPSS 13.0 for windows software (SPSS Institute Inc., Cary, NC, USA).

3. Results and discussion

3.1. Chemical composition of isolated starches

The chemical composition of isolated starches is presented in Table 1. Moisture content of isolated starches was around 10.8%. Lipid and protein contents were less than 0.53% and 0.7%, respectively. These levels indicated a successful isolation of starch using the protease N treatments. In our previous study, the protein contents of native rice flour from these rice varieties ranged from 5.2% to 7.2%, with lipid contents from 0.5% to 0.9%. The lipid and protein contents showed no significant differences from the isolated starches of different varieties ($p < 0.05$). The amylose contents of the isolated waxy and nonwaxy rice starches varied from 0.8% to 20.8%.

3.2. Pasting properties

The pasting of the rice starches was conducted on a rotational rheometer with cone and plate fixtures. This produce was adapted for three reasons. Firstly, the use of a cone and plate provided for a constant shear rate throughout the sample. Secondly, with a plastic upper fixture and temperature control of ±0.1 °C of the bottom plate, the dispersion was subjected to an even temperature throughout the sample. Thirdly, with the Pelitier temperature control system and large surface area exposure of the sample to the heating plate, the temperature could be changed more quickly relative to other configurations used for pasting experiments.

The pasting onset and peak temperature correlated positively with amylose content, and the breakdown viscosity was negatively correlated with the amylose content (Tables 2 and 1). This is consistent with previous reports (El-Khayat, Samaan, & Brennan, 2003; Varavinit, Shobsngob, Varanyanond, Chinachoti, & Naivikul, 2003). The waxy starch exhibited the highest peak viscosity and lowest setback among the rice starches. Waxy starches consist mainly of amylopectin, and thus the granules are easily swollen. With small amounts of amylose present in the waxy starch, setback viscosity, which reflects gel network formation, was generally low. Setback viscosity was found to be correlated positively with amylose content, except in Cocodrie. The low setback viscosity of Cocodrie was attributed to its low peak, trough and final viscosities (setback is defined as subtracting the viscosity at the trough from the final viscosity). The low peak viscosity of Cocodrie was probably due to the nature of the variety.

3.3. Viscosities of starch dispersions and leached amylose

It has been reported that concentration, temperature, volume fraction of the swollen granules, the deformability of the granules, and the degree of molecular entanglement affect the viscosity of starch pastes during pasting (Doublier, 1990; Noosuk et al., 2003). Viscosities of M202 (medium grain) and Cocodrie (long grain) starch dispersions were measured at different concentrations during heating (Table 3). At the lowest concentration (1%), the dispersion viscosities showed no significant changes with increasing temperature. For 3% dispersions, the viscosity started to increase at temperatures above 85 °C. When the concentration was increased to 6%, the viscosity of both M202 and Cocodrie starch dispersions increased significantly over

Table 1
The chemical compositions of isolated starches

Rice starch varieties	Moisture (%)	Lipid (%)	Protein (%)	Amylose content (%)
Calmochi101	10.8 ± 0.05	0.53 ± 0.08	0.64 ± 0.02	0.80 ± 0.06
M202	10.8 ± 0.06	0.49 ± 0.09	0.61 ± 0.03	13.4 ± 0.3
Koshi	10.8 ± 0.05	0.46 ± 0.05	0.62 ± 0.03	14.4 ± 0.2
L205	10.9 ± 0.04	0.52 ± 0.06	0.70 ± 0.05	17.6 ± 0.4
Cocodrie	10.6 ± 0.03	0.51 ± 0.06	0.65 ± 0.02	20.8 ± 0.4

Each of the chemical compositions of isolated starches is expressed on dry basis and analyzed in triplicate.

Table 2
Amylose content and pasting property of the starches

Rice starch varieties	Onset Temp (°C)	Peak Temp (°C)	Peak Visco (Pa s)	Trough Visco (Pa s)	Final Visco (Pa s)	Break down (Pa s)	Setback (Pa s)
Calmochi101	65.4 ± 0.2^{a}	73.1 ± 0.3^{a}	0.86 ± 0.03^{e}	0.52 ± 0.04^{c}	0.80 ± 0.04^{b}	0.34 ± 0.04^{c}	0.27 ± 0.04^{a}
M202	66.5 ± 0.3^{b}	92.8 ± 0.2^{b}	0.55 ± 0.02^{b}	0.30 ± 0.02^{a}	0.67 ± 0.03^{a}	0.26 ± 0.03^{b}	0.37 ± 0.04^{b}
Koshi	66.6 ± 0.3^{b}	93.7 ± 0.3^{bc}	0.62 ± 0.03^{c}	0.37 ± 0.02^{b}	0.90 ± 0.04^{c}	0.25 ± 0.03^{b}	0.53 ± 0.05^{c}
L205	68.5 ± 0.4^{c}	93.9 ± 0.3^{c}	0.72 ± 0.04^{d}	0.48 ± 0.03^{c}	1.09 ± 0.05^{d}	0.25 ± 0.04^{b}	0.61 ± 0.05^{c}
Cocodrie	72.8 ± 0.3^{d}	94.1 ± 0.3^{c}	0.48 ± 0.03^{a}	0.30 ± 0.02^{a}	0.60 ± 0.04^{a}	0.18 ± 0.03^{a}	0.30 ± 0.04^{ab}

Pasting properties of the starches were measured in duplicate at 8.8% concentration.
Mean values in the same column with different letters are significantly different ($P < 0.05$).

Table 3
Viscosities of starch granule and amylose dispersions from M202 and Cocodrie rice starches at different concentrations and temperatures

Temp (°C)	Viscosity ($\times 10^{-3}$ Pa s)									
	M202					Cocodrie				
	1%	3%	6%	8%	Amylose	1%	3%	6%	8%	Amylose
70	3.99 ± 0.03^{b}	3.43 ± 0.03^{a}	5.12 ± 0.02^{a}	6.18 ± 0.03^{a}	3.86 ± 0.02^{a}	2.98 ± 0.02^{a}	3.08 ± 0.01^{a}	4.15 ± 0.02^{a}	4.98 ± 0.02^{a}	3.65 ± 0.03^{a}
75	3.94 ± 0.03^{b}	3.39 ± 0.01^{a}	6.52 ± 0.02^{b}	15.2 ± 0.55^{b}	3.83 ± 0.04^{a}	3.32 ± 0.03^{b}	4.02 ± 0.03^{b}	4.58 ± 0.01^{b}	9.18 ± 0.78^{b}	3.61 ± 0.04^{a}
80	3.88 ± 0.02^{b}	3.38 ± 0.03^{a}	7.32 ± 0.03^{c}	21.2 ± 0.45^{c}	3.92 ± 0.04^{a}	3.02 ± 0.02^{a}	3.96 ± 0.03^{b}	6.09 ± 0.03^{c}	14.2 ± 0.82^{c}	3.68 ± 0.02^{a}
85	3.92 ± 0.04^{b}	3.63 ± 0.03^{b}	14.3 ± 0.30^{d}	52.1 ± 0.88^{d}	3.95 ± 0.03^{a}	2.99 ± 0.03^{a}	3.98 ± 0.02^{b}	9.29 ± 0.04^{d}	34.2 ± 0.86^{d}	3.65 ± 0.04^{a}
90	3.47 ± 0.04^{a}	4.88 ± 0.03^{c}	79.8 ± 1.2^{e}	218 ± 2.2^{e}	3.89 ± 0.04^{a}	3.02 ± 0.03^{a}	4.18 ± 0.02^{c}	60.8 ± 0.81^{e}	165 ± 2.5^{e}	3.75 ± 0.05^{a}
95	3.89 ± 0.03^{b}	21.2 ± 0.44^{d}	221 ± 2.0^{f}	390 ± 2.8^{f}	3.85 ± 0.03^{a}	3.36 ± 0.03^{b}	9.56 ± 0.04^{d}	122 ± 0.95^{f}	345 ± 2.2^{f}	3.72 ± 0.03^{a}

The amylose was prepared by aqueous leaching using a rotational rheometer. The amylose solution was the supernatant from 6% M202 or Cocodrie starch dispersion at 85 °C after centrifugation.
Mean values in the same column with different letters are significantly different ($P < 0.05$).

the temperature range 70–95 °C. Greater increases of viscosity were observed for the 8% dispersions. Steeneken (1989) has reported that, in a dilute regime, the viscosity is governed by the volume fraction of swollen granules. At low concentration, the volume fraction of granules was very low, resulting in a low viscosity during heating. Okechukwu and Rao (1995) have reported that, at low concentration, the granules were sufficiently far apart and did not affect viscosity substantially. As concentration increased, the inter-granular interactions became greater, due to swelling, and this caused a significant increase in dispersion viscosity.

Before studying the effect of particle size on dispersion viscosity, the viscosities of amylose dispersions were measured. Amylose (M202 and Cocodrie) was first isolated by leaching from starch granule dispersions (6%). For leaching, the starch dispersions were heated to 85 °C on the rheometer with the pasting temperature programme. The dispersions were immediately cooled to 50 °C and centrifuged. The viscosities of the supernatants were then measured as a function of temperature (Table 3). There were no significant changes of the viscosity of the amylose dispersons, for both M202 and Cocodrie, as the temperature was increased from 70 to 95 °C. However, the viscosities of 6% M202 or Cocodrie starch dispersions increased significantly over the same temperature range (Table 3). This suggested that the effect of dispersed amylose on the viscosity of the continuous phase was significantly smaller than in the swelling of the granules during heating. However, this did not discount the possibility of interactions of the leached amylose and swollen granules, which would have had an effect on dispersion viscosity.

3.4. Particle size distributions

The particle size and volume fraction of native starch granules were measured (Table 4). All native starch samples displayed bi-modal size distributions, with the first

Table 4
Peak particle size and volume fraction of starch granules in dispersions before heating

Rice starch varieties	First mode		Second mode	
	Peak particle size (μm)	Volume fraction (%)	Peak particle size (μm)	Volume fraction (%)
Calmochi101	1.23 ± 0.02^{a}	23.3 ± 0.3^{b}	4.85 ± 0.03^{c}	76.7 ± 0.3^{a}
M202	1.22 ± 0.03^{a}	21.4 ± 0.2^{a}	4.78 ± 0.04^{c}	78.6 ± 0.2^{b}
Koshi	1.25 ± 0.04^{a}	21.7 ± 0.3^{a}	4.88 ± 0.03^{c}	78.3 ± 0.3^{b}
L205	1.18 ± 0.03^{a}	20.6 ± 0.4^{a}	4.56 ± 0.04^{b}	79.4 ± 0.4^{b}
Cocodrie	1.19 ± 0.02^{a}	20.4 ± 0.2^{a}	4.39 ± 0.03^{a}	79.6 ± 0.2^{b}

Mean values in the same column with different letters are significantly different ($P < 0.05$).

peak value ranging from 1.18 to 1.25 μm and that the second peak ranging from 4.39 to 4.88 μm.

The shape of the size distributions changed from bimodal to single peaked distributions when the temperature was increased to 60 °C. The volume mean particle diameter of different starches was measured at different pasting temperatures (Fig. 1). Starches from medium grain showed similar mean particle diameters during heating. From 60 to 70 °C, particle diameter increased significantly from 4.8 to 8 μm. The pasting onset temperatures of M202 and Koshi starches were 66.5 and 66.6 °C, respectively. Therefore, the granules started to swell slightly before the pasting onset temperature, but a rapid increase of particle size began at the pasting onset temperature. The rate of swelling slowed around 5 °C above the pasting onset temperature (75 °C). At 85 °C, a second stage with a rapid rate of swelling was observed.

A similar trend was observed for the starches isolated from the long grain rice varieties, L205 and Cocodrie. When the pasting onset temperatures (68.5 °C for L205 and 72.8 °C for Cocodrie) were reached, a significant increase in particle diameter was observed. There was a slower rate of granular swelling from 75 to 85 °C, and the swelling increased at a greater rate at temperatures above 85 °C.

The mean volume particle diameter of waxy starch increased from 5 μm at 60 °C and reached 12 μm at 70 °C (Fig. 1). Upon further heating, above 70 °C (peak temperature), the particle size displayed bi-model size distributions, with the first mode involving about 10% of the granules with a mean diameter of 9 μm and the second mode about 90% of the granules with a mean diameter of 190 μm. Sandhya Rani and Bhattacharya (1989) have reported that low amylase-containing starch granules were less rigid, swelling freely when heated.

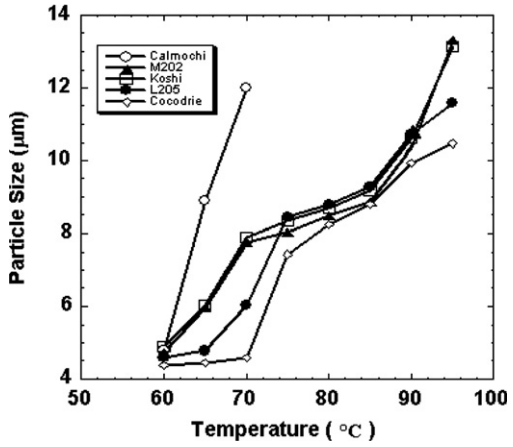

Fig. 1. Volume mean particle diameter of different starches at different temperatures (concentration: 3%).

Since both granule concentration and size affect the viscosities of starch dispersions, the particle size distributions at different concentrations were measured (Table 5). No significant differences of particle size were found among the different concentrations when heated to the same temperature. This suggested that the granule concentration did not affect the swollen granule size, though it did affect the viscosity during heating.

3.5. Relationship between viscosity and particle size during heating

In order to address the relationship between the granule size and the viscosity of the starch dispersions during heating, data from Tables 3 and 6 were combined to investigate relationship between dispersion viscosity and granule volume fraction. In order to relate viscosity to the volume fraction of swollen granules, the different rates of granular swelling for each starch variety had to be taken into account. With measurements of the diameter of the granules (Table 6) and the dispersion viscosities (Table 3) of M202 and Cocodrie during heating, an attempt to relate the dispersion viscosity to volume fraction was made.

The viscosity of hard sphere dispersions can be expressed as:

$$\eta = \eta_0(1 + 2.5\Phi)$$

for dispersions of low volume fractions (less that 0.10) (Einstein, 1906). For higher volume fractions, more complex equations have been proposed, such as:

$$\eta = \eta_0(1 + 2.5\Phi + 6.2\Phi^2 + c\Phi^3 + \ldots)$$

where Φ is the volume fraction of the dispersed spheres, and η_0 is the viscosity of the continuous phase (Batchelor, 1977). The latter equation shows a rapid increase in viscosity rather than the constant linear change predicted by the first equation as the volume fraction increases above 0.10. However, in either case, the viscosity solely depends on the volume fraction of the dispersed particles. To test the

Table 5
Volume mean particle diameter (μm) of M202 at different concentrations and temperatures

Concentration	Volume mean granule diameter (μm)					
	70 °C	75 °C	80 °C	85 °C	90 °C	95 °C
1% M202	7.79 ± 0.01	8.05 ± 0.02	8.52 ± 0.02	8.87 ± 0.03	10.76 ± 0.02	13.38 ± 0.04
3% M202	7.75 ± 0.02	8.04 ± 0.03	8.48 ± 0.03	8.86 ± 0.02	10.73 ± 0.01	13.32 ± 0.03
6% M202	7.79 ± 0.03	8.03 ± 0.02	8.46 ± 0.01	8.84 ± 0.02	10.71 ± 0.02	13.35 ± 0.04
8% M202	7.74 ± 0.04	8.02 ± 0.04	8.46 ± 0.03	8.85 ± 0.03	10.66 ± 0.02	13.31 ± 0.05

All the mean values in the same column are not significantly different ($P < 0.05$).

Table 6
Volume mean granule diameter (μm) of starches at different temperatures

Rice starch varieties	Volume mean granule diameter (μm)					
	70 °C	75 °C	80 °C	85 °C	90 °C	95 °C
M202	7.75 ± 0.03	8.04 ± 0.04	8.48 ± 0.05	8.86 ± 0.03	10.73 ± 0.04	13.32 ± 0.05
Cocodrie	4.59 ± 0.02	7.43 ± 0.04	8.24 ± 0.04	8.60 ± 0.04	9.94 ± 0.05	10.82 ± 0.06

Granule size of M202 and Cocodrie starches at different temperatures was analyzed in 1%, 3%, 6% and 8% starch dispersions, respectively. Since there were no significant differences of starch granule size at different concentrations, the average values shown are from means at each concentration of duplicate measurements.

hypothesis that the viscosity of the starch dispersion depends principally on the volume fraction of the swollen starch granules during heating, the viscosity of M202 and Cocodrie were plotted versus granular volume fraction. For both M202 and Cocodrie starches, 95 °C was after the peak temperature (Table 2) and the granules may have been distorted, thus generating erroneous results. The temperature range of the data we used was from 70 to 90 °C in Tables 3 and 6. In order to calculate the volume fractions of the particles at different concentrations and particle sizes, it was necessary to estimate the number of particles present and the volumes of each. Several assumptions were applied to both starches. The granules were mono-disperse and spherical. Their densities were the same throughout their swelling during the heating. When the viscosities of the M202 and Cocodrie dispersions were plotted together as a function of volume fraction (Fig. 2), their viscosities appeared to follow the same dependence on volume fraction. This would suggest that the viscosities of the starch dispersions during heating were principally dependent on granular volume fraction.

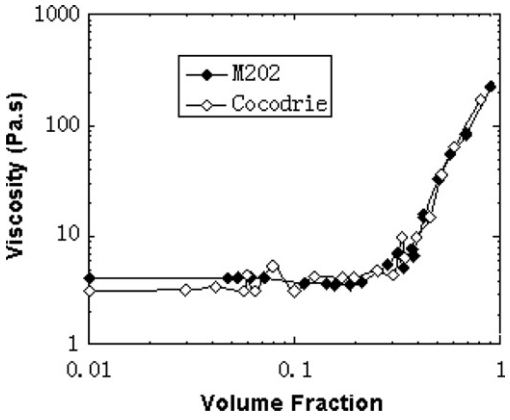

Fig. 2. The relationship of the viscosities of two rice starch dispersions to the volume fraction of the starch granules during heating. The data points are composite of data from Tables 2 and 5.

3.6. Changes of amylose content

It has been reported that the swelling behaviour of cereal starch is primarily a function of its amylopectin content, and amylose acts as both a diluent and an inhibitor of swelling (Lii, Tsai, & Tseng, 1996; Patindol & Wang, 2003). The amylose content remained in the starch granules at different temperatures after leaching was measured (Fig. 3). From 60 to 70 °C the amylose of two medium grain rice starches (M202 and Koshi) had began to leach out. The amylose of the two long grain starches did not start to leach until 70 °C. This correlated with the higher pasting onset temperatures of the long grain rice varieties. The apparent rate of amylose leaching was relatively constant over a wide temperature range (65–90 °C). The two medium and two long grains had slower leaching rates until about 85 °C, when the rate increased considerably. When comparing the loss of amylose to granule size during heating (Fig. 4), it was observed that a significant degree of swelling occurred before the leaching of amylose. This would suggest that granular swelling was necessary before amylose leaching occurred. Continued swelling was retarded in rice granules with a high level of amlyose (long grain varieties) as compared to the short and medium grain. It has been postulated that amylose molecules within the granules are entangled with the amylopectin structure (Tsai et al., 1997). This entanglement retards the swelling of the granules during heating. With increasing temperature, the degree of molecular entanglement decreases, resulting in granular swelling, followed by amylose leaching and continued granular swelling. Amylose thus plays

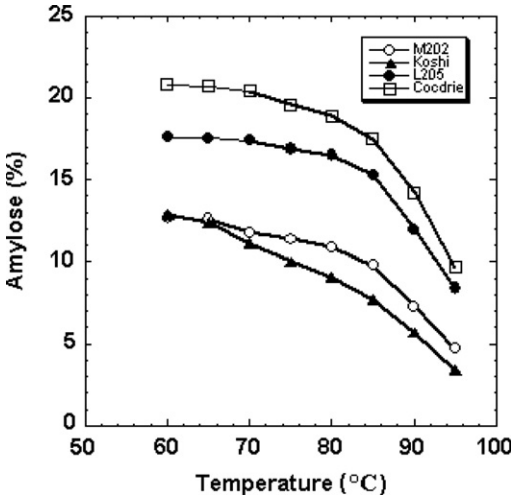

Fig. 3. Amylose content remaining in the starch granules at different temperatures after aqueous leaching.

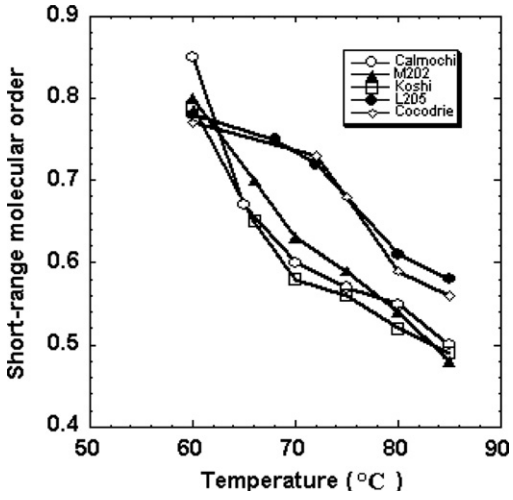

Fig. 5. Short-range molecular order (the ratio of absorbance at wave number 1047 cm^{-1} to 1022 cm^{-1}) from FTIR of different starches during heating.

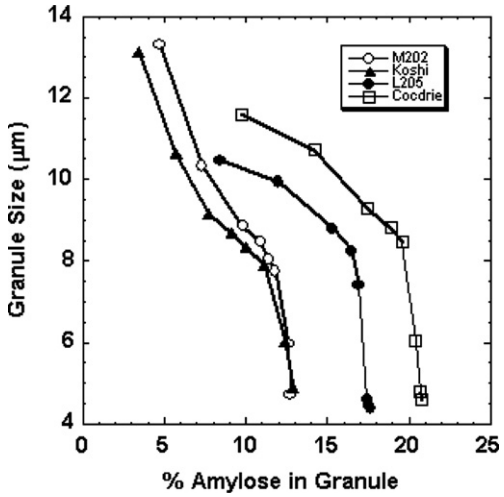

Fig. 4. Relationship between the loss of amylose and granule size during heating.

an indirect role in affecting rice dispersion viscosity during heating by reducing granular swelling.

3.7. Changes of short-range molecular order

The IR spectrum of starch has been shown to be sensitive to changes in structure on a molecular level (short-range order). It has been reported that the IR adsorption band at 1047 cm^{-1} is sensitive to the amount of ordered or crystalline starch and the band at 1022 cm^{-1} is characteristic of amorphous starch. The ratio of the heights of these bands expresses the amount of ordered starch relative to amorphous starch (Karim, Norziah, & Seow, 2000; Kirill, 2002; van Soest, Tournois, de Wit, & Vliegenthart, 1995). The changes in short-range molecular order of the different starches during heating were measured (Fig. 5). Short-range order correlated positively with amylopectin content at 60 °C (before gelatinization). This was consistent with a previous report (Noosuk et al., 2003). The short chains of amylopectin are thought to be arranged in crystallites responsible for the crystallinity of the native starch granule. The short-range order of waxy and medium grain rice starches decreased rapidly when temperature increased from 60 to 70 °C, which indicated that the loss of order was significant as soon as the temperature reached the pasting onset temperature. At temperatures above 70 °C, a relatively small decrease of short-range order was observed. In the case of long grain rice starch (Cocodrie and L205), significant decreases of short-range order were observed from 70 to 80 °C. This was due to the higher pasting onset temperature of long grain rice starch. There was also a relatively small decrease of short-range order at temperatures above 80 °C. It was noticed that the short-range order of long grain rice starches was higher than that of waxy and medium grain rice starches after gelatinization, and the loss of order of waxy and medium grain rice starches was greater than that of long grain rice starches during heating. This again was probably due to the presence of amylose. The amylose could restrain the swelling and disruption of starch granules, resulting in a greater loss of short-range order of waxy and medium grain starches than of long grain starches.

4. Conclusion

The increasing viscosity of rice starch dispersions during pasting was attributed to the swelling of the starch granules. The presence of amylose in the starch granules acted to retard the granular swelling of the normal rice varieties as compared to the waxy varieties. The removal of amylose from the granules by leaching resulted in greater swelling of the starch granules. Fourier-transform IR spectroscopy indicated that the loss of short-range order was significant when the temperature reached the onset pasting temperature. The short-range order of waxy and medium grain rice

starches was higher than that of long grain rice starches before gelatinization. The loss of order of long grain rice starches was smaller than that of waxy and medium grain rice starches during heating, due to the presence of amylose.

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