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Physicochemical studies of starch from foxtail millet (*Setaria italica* Beauv.)

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Properties of starch granules prepared from 53 varieties of foxtail millet were examined by scanning electron microscopy, amperometric iodine titrimetry and differential scanning calorimetry. The granular size of the starches ranged from 6.8 to 11.8 μm in diameter on average. The wavelength at maximum absorption (λ_{max}) for iodine–starch complexes ranged from 579 to 600 nm and blue values (absorbance at 680 nm, BV) ranged from 0.350 to 0.495 except for two waxy varieties. Amylose contents of non-waxy varieties obtained by amperometric titrimetry ranged from 11.4 to 27.1%. DSC analysis for starch gelatinization indicated that peak temperatures (T_p) of all the samples ranged from 62.5 to 75.1°C, their enthalpy (ΔH) varied from 8.2 to 13.5 J/g, respectively, and that there was a positive relationship between T_p and ΔH. From a correlation matrix of physicochemical parameters of the millet starch, we observed the following: correlations between particle size and four parameters (enzymic degradation of starch granules, amylose content, λ_{max} and BV), between amylose content and two parameters (λ_{max} and BV), and between ΔH and three parameters (amylose content, BV and T_p).

INTRODUCTION

Foxtail millet (Italian millet) has been extensively cultivated in Eurasia as food and forage (Nakao, 1967). In the northern area of China it has been widely used as a nourishing gruel or soup for pregnant and nursing women, and has been applied to food therapy (Li, 1986). In addition to common recipes, the millet grains are often malted and popped for weaning food (Brandtzaeg *et al.*, 1981) and the brewing industry (Briggs *et al.*, 1981). The main components of foxtail millet grain are starch, protein and lipid (Ohara, 1981; Taira *et al.*, 1986; Gu & Li, 1986), but a small amount of free sugar and non-starchy polysaccharides (Malleshi *et al.*, 1986*a*; Kato *et al.*, 1989) are also present.

It has been recognized that there are two phenotypes, waxy (glutinous) and non-waxy, in the starch of the foxtail millet. There are some reports on the amylose content of the millet starch (Taira & Miyahara, 1983; Sakamoto, 1986; Fujita *et al.*, 1989; Inouchi *et al.*, 1993). Lorenz and Hize (1976) and Malleshi *et al.* (1986*a*,*b*) studied physicochemical properties of native and malted starches from finger, pearl and foxtail millet. It has been observed that there is a relationship between gelatinization temperature and enthalpy in 13 varieties of the millet starch measured by differential scanning calorimetry (DSC) (Fujita *et al.*, 1989). In this study, we intend to comprehensively acquire a positive proof of the relationship reported in the previous study, to gain further information on physical and biochemical properties, and to evaluate interrelationships between these parameters.

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MATERIALS AND METHODS

Sample seeds, preparation of starch and determination of their granular size

Fifty-three varieties of foxtail millet have been cultivated in the Millet Research Institute in Hebei, China. Two of the varieties were of the waxy (glutinous) phenotype. Starch granules were prepared by the method of Adkins and Greenwood (1966), and defatted by reflux with 85% methanol, except for those samples for DSC analysis.

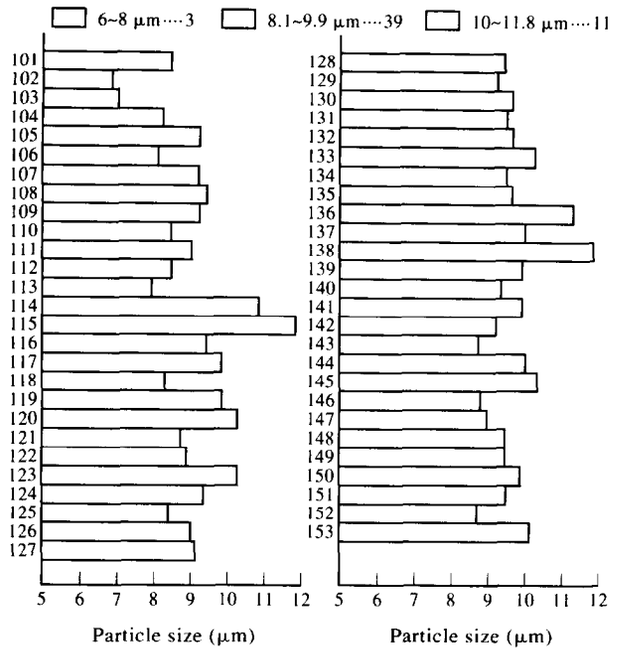

Fig. 1. Particle size on the average of foxtail millet starch.

The average granular sizes of starches were analyzed with a Shimadzu centrifugal particle size analyzer SA-CP2, after dispersing the starch granules in 0.2% of sodium hexametaphosphate (Sugimoto *et al.*, 1984).

Enzymatic digestibility and scanning electron microscopy of starch granules

The determination of per cent degradation of starch granules was calculated from the ratio of hydrolysed soluble saccharide, by hog pancreatic α-amylase, to the original starch weight (Fuwa *et al.*, 1977). The liberated soluble starch was measured by the phenolic–H_2SO_4 method. Native starch granules and residues of granules after enzyme attack were observed using scanning electron microscopy (SEM). The granules were rinsed with water and acetone, and air-dried at room temperature. The specimen, coated with carbon and then gold, was observed on a Hitachi S-500 SEM at 20 kV acceleration potential (Endo *et al.*, 1978).

Spectrophotometry of iodine–starch complexes and iodine affinity

The absorption curves of starch–iodine complexes were measured by a Shimadzu spectrophotometer 160 at 700–500 nm. A solution containing 2 mg of iodine and 20 mg of potassium iodate was added to 1 mg of NaOH-gelatinized and HCl-neutralized starch, and made up to 25 ml. The wavelength at maximum absorption (λ_{max}) and blue value (BV), absorbance at 680 nm, were recorded (Fujimoto *et al.*, 1972). According to the method of Kainuma (1977), amperometric iodine titration of defatted starch was carried out at 1 A and 50 mV.

Differential scanning calorimetry

Five milligrammes of starch was put in an aluminium pan and water was added (net starch:water ratio 1:2). Thermal analysis was performed on a Shimadzu DSC-50 equipped with a data processor. The pan was heated from room temperature up to 100°C under atmospheric conditions at a heating rate of 5°C/min, and then the peak temperature for gelatinization (T_p) and enthalpy (ΔH) were measured. Each data point was the average of six determinations.

Statistical treatment

The methods of least-squares and student's t-distribution were used to generate correlations and significant differences, respectively.

Table 1. Wavelength at maximum absorbtion (λ_{max}) and absorbance at 680 nm (blue value, BV) absorption curves of iodine complexes and apparent amylose contents by amperometric titrimetry of foxtail millet starches

Sample no.	λ_{max} (nm)	Blue value	Amylose % content	Sample no.	λ_{max} (nm)	Blue value	Amylose % content	Sample no.	λ_{max} (nm)	Blue value	Amylose % content
101	594	0.403	22.0	119	595	0.403	22.2	137	599	0.469	27.1
102	528	0.109	1.8	120	597	0.393	22.0	138	597	0.465	26.1
103	594	0.430	22.4	121	599	0.428	25.9	139	598	0.489	24.6
104	530	0.127	2.8	122	597	0.431	21.8	140	597	0.451	26.5
105	592	0.450	23.4	123	599	0.441	26.5	141	594	0.404	21.7
106	591	0.401	22.2	124	600	0.460	27.1	142	592	0.400	20.1
107	595	0.411	22.5	125	598	0.422	26.2	143	595	0.360	21.8
108	579	0.364	17.1	126	599	0.449	26.9	144	596	0.376	21.3
109	585	0.409	19.7	127	593	0.382	21.6	145	594	0.364	22.0
110	582	0.356	21.2	128	598	0.495	26.2	146	596	0.431	22.2
111	579	0.350	15.9	129	594	0.451	20.8	147	595	0.390	21.8
112	580	0.431	16.8	130	599	0.483	27.1	148	595	0.368	21.7
113	580	0.365	11.4	131	596	0.437	24.2	149	596	0.400	22.1
114	596	0.394	22.2	132	598	0.469	26.6	150	595	0.397	21.6
115	595	0.444	23.3	133	598	0.434	26.6	151	594	0.385	21.9
116	592	0.396	21.8	134	599	0.469	27.1	152	593	0.376	21.8
117	594	0.386	21.2	135	599	0.492	26.6	153	597	0.432	25.9
118	593	0.403	21.5	136	599	0.420	26.8				

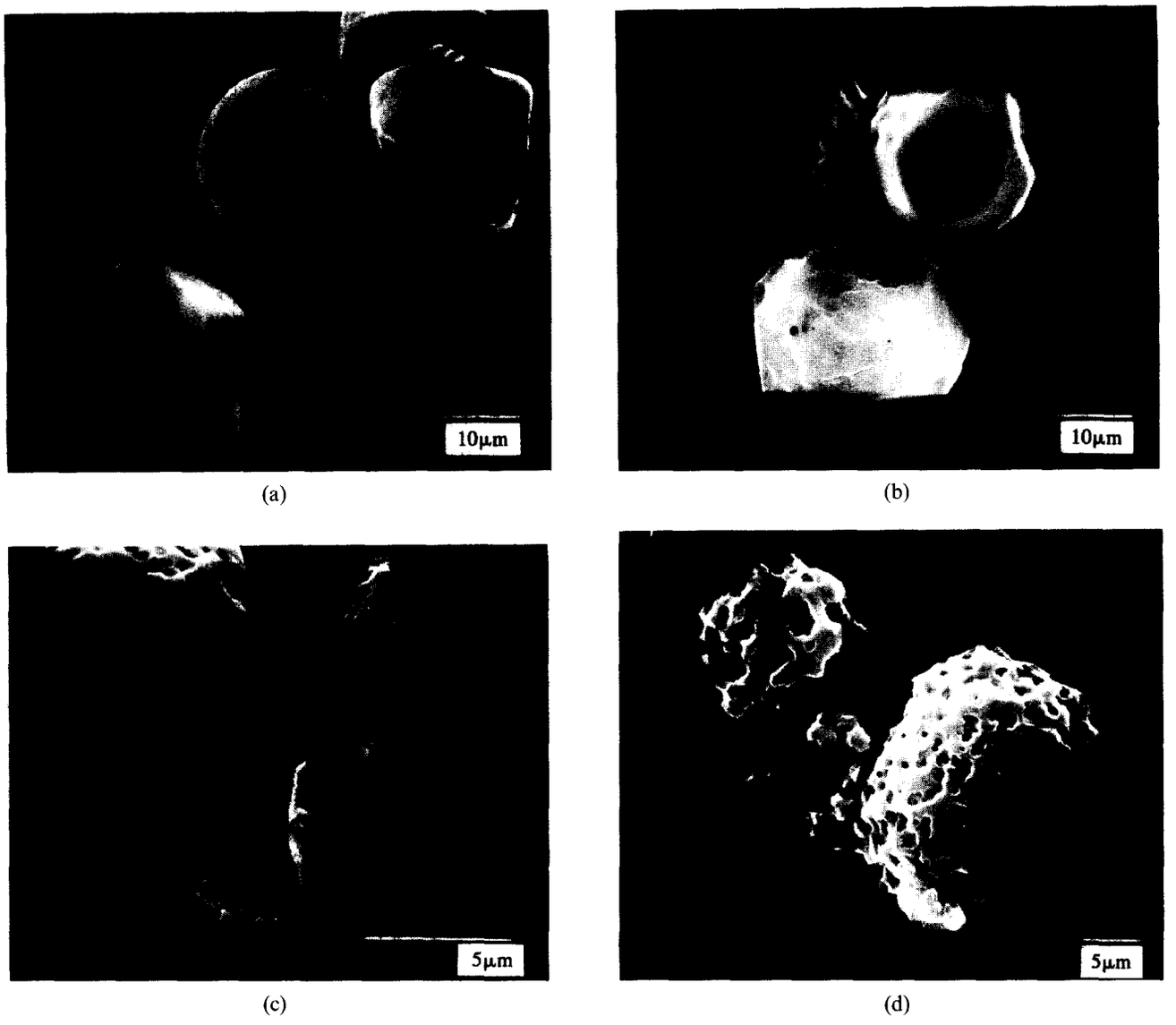

Fig. 2. Scanning electron micrographs of starch granules. (a) Native corn starch, (b) native non-waxy foxtail millet starch, (c) 50% degradation of non-waxy foxtail millet starch and (d) 50% degradation of waxy foxtail millet starch.

RESULTS AND DISCUSSION

Starch granule and its digestibility

The average granule size of 53 millet varieties ranged from 6.8 to 11.8 μm in diameter. Each population showed a normal distribution curve, and the peak granular sizes ranged from 8.1 to 9.9μm, with 39 varieties falling into this range (Fig. 1). The result was similar to that of the previous study which showed that the granular size of foxtail millet starch ranged from 8.0 to 15.0 μm (Ohara, 1981). From SEM observation the starch granules had similar shapes to the maize starch granules (Fig. 2a and b). The digestive process of the millet starch attacked by α-amylase was also similar to that of the non-waxy maize (commercial) used as a reference. After digesting for 3 h, numerous pin holes appeared on the surface and subsequently the step-shaped structures in the inner portion of the non-waxy millet starch granules were observed on SEM (Fig. 2c), which were also observed in maize starch. Digested residues of the waxy millet starch, however had, shapes like sponge tissues (Fig. 2d).

Amylose content

By spectrophotometry of iodine–starch complexes, λ_{max} for the millet starches ranged from 591 to 600 nm except for two waxy varieties, and BV from which the apparent amylose content in starch is often inferred, ranged from 0.350 to 0.495 (Table 1). The BVs for two waxy lines were 0.094 and 0.130, respectively.

By amperometric titrimetry, the apparent amylose contents of non-waxy varieties were widely distributed from 11.4 to 27.1%, among which 46 varieties ranged peaks from 20 to 27.1% and two peaks (22 and 26%, respectively) were observed in the populations of the apparent amylose contents. It was reported by Taira & Miyahara (1983) that amylose contents of 31 varieties varied from 21.9 to 32.8% and were 27.8% on average.

Table 2. Correlation matrix of physicochemical parameters of foxtail millet starches

	1	2	3	4	5	6	7
1. Average particle size	1.000						
2. Enzyme degradation (3 h)	−0.462**	1.000					
3. Amylose content	0.515**	−0.291*	1.000				
4. λ_{max}	0.488**	−0.315*	0.926**	1.000			
5. Blue value	0.435**	−0.278*	0.895**	0.893**	1.000		
6. T_p	0.007	−0.049	0.172	−0.124	−0.145	1.000	
7. ΔH	−0.088	0.151	−0.475**	−0.324*	−0.354**	0.751**	1.000

*Significant at 0.05% level.
**Significant at 0.01% level.
$r(53, 0.01) = 0.350$, $r(53, 0.05) = 0.270$.

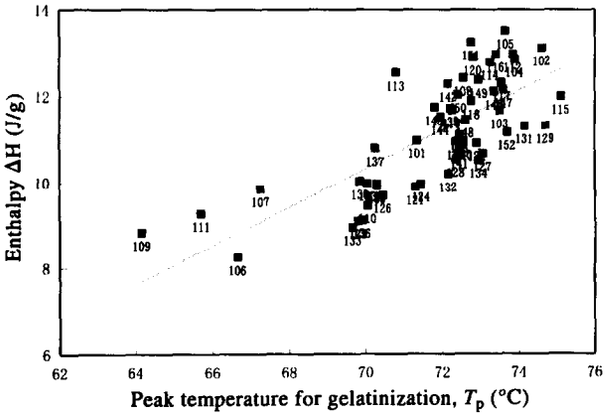

Fig. 3. The relationship between peak temperature and enthalpy for gelatinization (foxtail millet starch).

Sakamoto (1986) reported that amylose contents of 62 non-waxy varieties ranged from 5.0 to 25.1%, having two peaks, 10 and 22%, in the distribution. Amylose contents of two waxy varieties were 1.8 and 2.8%. In the previous study we have shown that fraction-I, that is the amylose fraction, by gel filtration of isoamylase-debranched starches, was 1.3 and 2.7%, respectively (Fujita *et al.*, 1989).

Differential scanning calorimetry

DSC data indicate that T_p of all the samples ranged from 62.5 to 75.1°C, and their gelatinization enthalpy varied from 8.2 to 13.5 J/g, respectively (Fig. 3). The statistical treatment showed that T_p and enthalpy values for all samples were strongly correlated at 0.755 of the coefficient of correlation (r), while r was 0.740 after excluding two waxy-type millets from the calculation. We previously observed a relationship between T_p and enthalpy in barley, proso-millet and rice starches(Fujita *et al.*, 1993). These correlations, however, do not always hold good for all gramineous crops. T_p and enthalpy values of starches from gramineous crops having waxy phenotypes are more widely distributed than non-waxy (Fujita *et al.*, 1993).

Correlation between these parameters

Table 2 shows a correlation matrix of several physico-chemical parameters of millet starch. We could observe correlations in the table as follows: between particle size and four parameters (enzymic degradation, amylose content, λ_{max} and BV) at the 0.01% level of significance, between amylose content and two parameters (λ_{max} and BV) at 0.01% level of significance, and between enthalpy and three parameters (amylose content, BV and T_p) at the 0.01% level of significance. There is a relationship between particle size and gelatinization temperature in potato starches which were air-classified into smaller, medium and larger groups (Fujita *et al.*, 1983) because the distribution of particle sizes of potato starch varies more widely than that of a gramineous endosperm starch. The correlation between the amylose content and BV have often been applied to estimate the amylose content. Our intention is to compare these parameters with rheological results, especially viscosity and elasticity.

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