Physicochemical Properties of Normal and Waxy Job's Tears (*Coix lachryma-jobi* L.) Starch

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ABSTRACT

Physicochemical properties of starches from eight coix (*Coix lachryma-jobi* L.) accessions were investigated. There was considerable variation in most measured traits, generally corresponding to the separation into waxy and normal amylose types. The amylose contents of five normal coix ranged from 15.9 to 25.8%, and those of three waxy coix were 0.7–1.1%. Swelling power of waxy coix starches varied between 28.6 and 41.0 g/g, generally higher than waxy maize. Normal coix starches had significantly higher gelatinization peak temperature (T_p) than the normal maize, 71.9–75.5°C. The T_p of waxy coix starches was 71.1–71.4°C, similar to waxy maize. Rapid Visco-Analyser (RVA) pasting profiles of normal coix showed little variation and closely matched the normal maize starch profile. Pasting profiles of waxy coix showed more variation and had lower peak viscosities than waxy maize starch. Waxy coix starches formed very weak gels, while the gel hardness of normal coix starches was 11.4–31.1 g. Amylose content was the main factor controlling differences in starch properties of the coix starches.

Coix lachryma-jobi L., commonly known as coix or Job's Tears, is a relative of maize in the tribe Maydeae widely grown as a grain crop in Asia. It is known as *adlay* in the Philippines, *tie yu mi* in Mandarin Chinese, and *yee mie* in Cantonese. The grain is pear-shaped, ≈5 mm in diameter, and has a hard, shiny dark brown to gray-black hull. It is used in soups and beverages as a flour or whole (dehulled) grain, and is popular in Chinese traditional medicine (Schaaffhausen 1952, Purseglove 1972). Although coix has had food, medical, and forage uses for thousands of years in China, the predominant use is in nutritive medicines. Recently, it has been reported that coix grains may posses antitumor activity (Numata et al 1994) and be effective against viral infection (Hidaka et al 1992). Therefore, coix is now increasingly widely utilized to produce functional foods and drinks because of its perceived nutritional and health value.

Coix grains are high in starch but very little work has been done on the physicochemical properties of its starches. Yang et al (1995) focused only on the starch properties of waxy coix cultivars and found gelatinization temperatures ranging from 63.4 to 76.4°C, and water binding capacity of 103–108%. Ramirez (1996a,b) characterized the extraction and physical properties of a waxy coix starch. The yield of starch from coix grains was 45%, the birefringence loss of starch granules began at 65°C and finished at 75°C, and breakdown during pasting in a Brabender viscoamylograph was substantial. Iodine values indicated that the properties of measured coix starch were similar to those of waxy maize starch. Until now, there has been no systematic report on physicochemical properties of normal coix starches, and the pasting and gel textural properties of starches of a range of waxy coix genotypes have not been investigated. However, these properties are important both for utilizing coix in food industries and exploring new product development with coix.

The major objective of this study was to investigate the thermal, pasting and gel textural properties of starches from a range of waxy and normal coix accessions in China.

MATERIALS AND METHODS

Eight coix accessions originating from China, including four wild accessions, were used (Table I). WH2 and LH were purchased in Wuhan and Hong Kong traditional Chinese medicine stores, respectively, and were used directly. The others were grown in uniform field conditions using normal agronomic practices on the agronomy farm at Huazhong Agricultural University, Wuhan, China, in 1996. Control starches were normal maize starch (Sigma, St. Louis, MO) and waxy maize starch from Starch Australasia Ltd. (Lane Cove, Australia).

Starch Isolation

Coix starch was isolated as described previously for maize (Li et al 1994). Coix grains were steeped with 0.45% $Na_2S_2O_5$ in a water bath at 40°C for 48 hr. Then the germ was removed and the endosperm was ground. The slurry was filtered and the residue was reground and rescreened several times. Extracted starch granules were purified with 0.05*M* NaCl and one-fifth volume toluene. Purified starch granules were washed twice with distilled water and once with acetone. Finally, starch cakes were dried at 40°C.

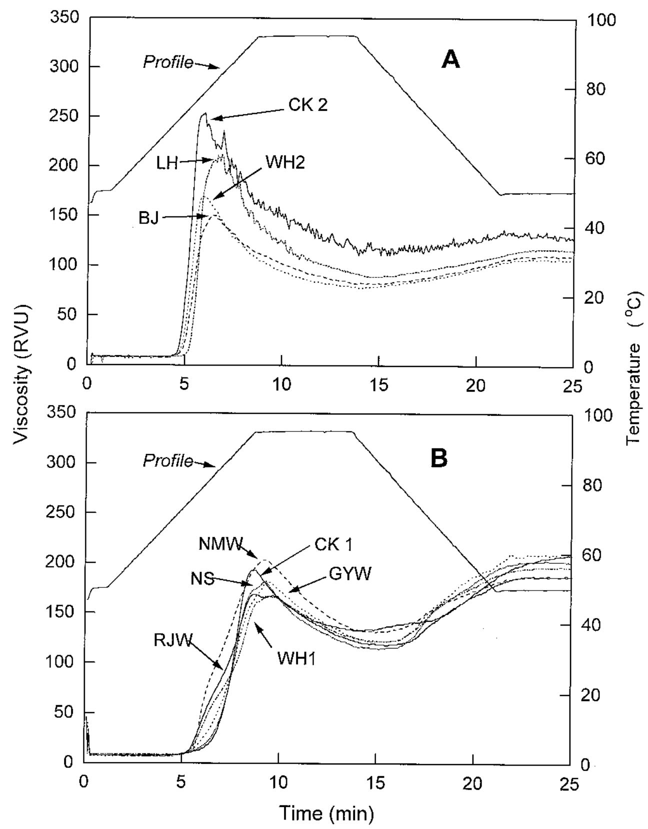

Fig. 1. Rapid Visco-Analyser (RVA) pasting profiles of maize starches with waxy coix (**A**)and normal coix (**B**). (See Table I for sample codes.)

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Amylose Determination

An assay kit (Megazyme International Ireland Ltd., Ireland) was used for determination of amylose content using the concanavalin-A binding method (Gibson et al, 1997).

Swelling Power and Solubility

Swelling power and solubility were determined following Wang et al (1993) with modifications. Starch (0.3 g, dwb) and 15 mL of distilled water were mixed in a centrifuge bottle, placed in a water bath at 85°C for 30 min with continuous stirring, then centrifuged at 2,000 × *g* for 15 min. Clear supernatant was carefully removed into a preweighed dish and dried at 130°C overnight. Swollen starch sediment and dried supernatant were weighed. Swelling power was the ratio of the wet sediment weight to initial sample weight, while solubility was calculated as a percentage of starch dissolved in water.

TABLE I
General and Thermal Properties[a] of Starches from Eight Coix Accessions and Two Maize Checks

Source	Code	Origin	Amylose (%)	SP (g/g)	Solubility (%)	T_p (°C)	T_o (°C)	T_c (°C)	T_r (°C)	ΔH (J/g)
Normal amylose										
Wuhan-1 coix	WH-1	Hubei	25.8	10.3	5.3	72.1	63.9	79.5	15.6	9.2
Guiyang wild coix	GYW	Guizhou	25.4	12.7	8.3	71.9	64.2	78.5	14.3	8.0
Neshi wild coix	NSW	Hubei	22.7	11.8	8.8	74.4	66.9	80.5	13.6	8.6
Rongjiang wild coix	RJW	Guizhou	21.3	12.0	8.3	73.4	64.7	80.8	16.0	8.9
Neimang wild coix	NMW	Neimang	15.9	11.5	4.4	75.5	69.4	82.2	12.8	9.9
Normal maize	CK 1	U.S.	26.4	12.3	4.6	69.1	63.4	76.7	13.6	8.1
Waxy										
Beijing coix	BJ	Beijing	1.1	41.0	1.9	71.4	65.3	80.6	15.3	7.3
Wuhan-2 coix	WH-2	Hubei	0.8	29.1	7.0	71.1	64.1	80.3	16.2	11.1
Lee Hong coix	LH	Hong Kong	0.7	28.6	6.3	71.3	64.7	78.5	13.9	10.9
wx maize	CK 2	Australia	0.6	25.7	2.4	72.1	64.3	81.8	17.5	12.3
LSD[a]			4.8	5.6	2.3	0.8	1.2	1.6	2.0	1.6

[a] T_p = peak temperature; T_o = onset, T_c = completion, and ΔH = enthalpy). Gelatinization range (T_r) was calculated as $T_c - T_o$. SP = swelling power.
[b] Least significant difference ($P < 0.05$) for comparison of means in the same column.

TABLE II
Pasting[a] and Gel Textural Properties of Starches from Eight Coix Accessions and Two Maize Checks

	Pasting Characteristics (RVU)[b]						
Source	PV	HPV	CPV	BD	SB	Hardness (g)	Adhesiveness (g·sec)
Normal amylose							
WH-1	184	122	208	63	87	31	6
GYW	182	113	200	69	87	25	9
NSW	167	120	195	47	75	21	6
RJW	170	119	186	51	67	16	10
NMW	203	130	185	73	55	11	5
CK 1 (maize)	197	134	211	64	77	27	24
Waxy							
BJ	167	77	106	90	29	0.2	21
WH-2	188	85	112	103	28	0.6	22
LH	211	89	115	122	27	1.0	15
CK 2 (maize)	254	109	132	144	23	0.4	15
LSD[c]	3.7	4.0	1.8	5.0	2.7	4.3	9.7

[a] PV = peak viscosity; HPV = hot paste viscosity; CPV = cool paste or final viscosity; BD = breakdown (PV – HPV); SB = setback (HPV – CPV).
[b] Rapid Visco-Analyser units (1 RVU = 10 cp).
[c] Least significant difference ($P < 0.05$) for comparison of means in the same column.

TABLE III
Correlations for Selected Physicochemical Properties of Starches in Eight Coix Accessions

	Property[a]	1	2	3	4	5	6	7	8	9	10	11	12
1	Amylose												
2	PV	–0.33											
3	HPV	0.88*[b]	–0.02										
4	CPV	0.99*	–0.21	0.94*									
5	BD	–0.88*	0.64	–0.78	–0.85*								
6	SB	0.99*	–0.33	0.81*	0.96*	–0.83*							
7	T_p	0.49	–0.02	0.79*	0.59	–0.62	0.38						
8	T_r	–0.14	–0.44	–0.38	–0.24	0.03	–0.11	–0.61					
9	ΔH	–0.41	0.75*	–0.11	–0.31	0.55	–0.43	–0.08	–0.01				
10	Swelling power	–0.28	–0.43	–0.23	0.26	–0.45	0.26	0.42	–0.35	–0.20			
11	Solubility	0.48	–0.13	0.37	0.44	–0.37	0.46	0.15	0.00	0.17	0.43		
12	Hardness	0.96*	–0.29	0.78*	0.94*	–0.78*	0.99*	0.31	–0.06	–0.37	0.23	0.41	
13	Adhesiveness	–0.86*	0.03	–0.95*	–0.92*	0.71	–0.82*	–0.73*	0.55	0.19	–0.33	–0.34	–0.80*

[a] PV = peak viscosity; HPV = hot paste viscosity; CPV = cool paste or final viscosity; BD = breakdown (PV – HPV); SB = setback (HPV – CPV); T_p = peak temperature; T_r = gelatinization range ($T_c - T_o$); ΔH = enthalpy.
[b] * = significance at 5% level.

Differential Scanning Calorimetry

A Mettler DSC20 instrument (Mettler, Naenikon-Uster, Switzerland) was employed for thermal analysis. Based on Li et al (1994) and Wu et al (1995), 2.0 mg of starch was weighed into a preweighed pan and mixed with 4.6 µL of distilled water. Sealed pans were allowed to stand for 90 min to equilibrate. Samples were run from 25 to 125°C at a rate of 10°C/min. Enthalpy (ΔH), gelatinization onset (T_o), gelatinization completion (T_c), and gelatinization peak temperature (T_p) were determined. The gelatinization range (T_r) was calculated as $T_c - T_o$.

Viscoamylography

The pasting properties of the starch samples were measured with a Rapid Visco-Analyser model 3D (RVA) (Newport Scientific Pty. Ltd, Warriewood, Australia). Following McCormick (1993) and Li et al (1997), 2.5 g of starch (dwb) was weighed into an RVA canister, then distilled water was added until a total sample weight of 28 g was reached. The sample was mixed for 30 sec to make a lump-free starch slurry. The time-temperature profile was: holding for 2 min at 50°C, heating to 95°C in 7.5 min, holding for 5 min at 95°C, cooling to 50°C in 7.5 min, and holding for 5 min at 50°C. The peak viscosity (PV), hot paste viscosity (HPV), and cool paste or final viscosity (CPV) were recorded. The breakdown (BD) and setback (SB) were computed as (PV – HPV) and (HPV – CPV), respectively.

Gel Texture

Starch gel texture was determined using a TA-XT2 Texture Analyzer (Stable Micro Systems, Godalming, England) as described by Liu et al (1997). After RVA testing, the starch paste was poured into a mold of 23 × 19 × 11 mm, and kept for 24 hr at 25°C in order to make starch gels. A cylindrical flat-ended probe was used to compress the gel at a speed of 1.0 mm/sec for a distance of 8 mm. Hardness and adhesiveness were computed from the instrument software.

Statistical Analysis

All measurements were performed at least in duplicate. Data were analyzed by a statistical program (SAS Institute, Cary, NC). Least significant differences were computed at $P < 0.05$.

RESULTS AND DISCUSSION

General Properties

The eight coix accessions were divided into two types, normal and waxy (Table I) by amylose content. Normal types had an amylose content of 15.9% (NMW) to 25.8% (WH1), with an average of 22.2%. Only NMW with 15.9% amylose was significantly lower than the normal maize. The waxy types had an amylose content range of 0.7–1.1%, with an average of 0.9%. Of the five normal coix accessions, four were collected wild (noncultivated types) and multiplied in field conditions. In contrast, all the waxy coix accessions were cultivated types. In Hong Kong retail markets, most coix available is waxy, although in other parts of China either type may commonly be found. Retailers generally do not distinguish between the two types. It is reasonable to assume that, as with waxy maize, the waxy coix is a mutant type from normal coix, but this is under further investigation.

All waxy coix starches had high swelling powers in the range of 28.6–41.0 g/g, which was higher than waxy maize at 25.7 g/g (Table I) and consistent with Ramirez (1996a). The swelling powers of normal coix starches were in the range of 10.3–12.7 g/g, not significantly different from the normal maize. There was quite a wide variation among the eight coix accessions in starch solubility (Table I), with most coix accessions showing higher values than the normal and waxy maize controls.

Thermal Properties

The T_p of normal coix starches was significantly higher than normal maize. The T_p of the three waxy coix starches (71.1–71.4°C) was very similar to that of waxy maize (72.1°C) (Table I). There was little difference in T_o and T_c between the waxy coix and waxy maize starches. The starches of normal coix accessions had significantly higher T_o and T_c than normal maize, except for T_o of WH1 and GYW. Generally, the DH of waxy coix starches was lower than that of waxy maize, while the ΔH of normal coix starches was higher than normal maize, except for GYW.

Pasting Properties

The RVA pasting curves of normal coix starches were clearly different from those of waxy coix (Fig. 1A and B). Basically, the curve shapes of both normal and waxy coix starches were similar to normal and waxy maize, respectively, but the numerical values varied significantly. Waxy maize starch had a more jagged curve than the coix samples, although changes in starch concentration in the RVA can make the curve smooth.

The PV values (Table II, Fig. 1) of the normal coix, with the exception of NSW, were slightly lower than those of normal maize, but the waxy coix PV values were substantially lower than waxy maize. The HPV of waxy coix starches were lower than the waxy maize, and normal coix starches had somewhat lower HPV than normal maize, indicating that they would handle differently during processing while giving similar final viscosity. The CPV of normal coix starches was, as expected, nearly twofold higher than that of the waxy starches. The BD and SB of normal coix starches had ranges of 47.0–72.5 RVU and 55.0–87.0 RVU, respectively, and were comparable to the normal maize. The BD of waxy coix starches were up to 54 RVU lower than the waxy maize starch, indicating greater resistance to shear thinning.

Gel Textural Properties

The hardness of gels after one day of storage (Table II) were 11.4–31.1 g for normal and 0.2–1.0 g for waxy coix starches, respectively. Thus, all waxy coix starches formed a very weak gel like the waxy maize starch (0.4 g) consistent with Ring et al (1987) and Wang et al (1992), probably due to the lack of amylose to form the network structure. The gel of NMW had a hardness of only 11.4 g, twofold lower than the normal maize, which may be due to its low amylose content (15.9%). In general, the gels of waxy coix starches had greater adhesiveness than normal coix starches, ranging from 15–22 g·sec and 5–10 g·sec, respectively. There was no significant difference between waxy coix and waxy maize in adhesiveness. However, the adhesiveness of normal coix starches were substantially lower than for normal maize.

Correlation Analysis

Swelling power and solubility were not significantly correlated with any other traits, indicating that, in this material, their use as screening or predictive tests for functional parameters such as gel texture would not be effective (Table III). Amylose content was highly positively correlated with all the pasting parameters except PV (r = 0.88 to 0.99) for CPV because the presence of amylose molecules is related to the reassociation of paste during the cooling. A positive relationship of amylose contents to hardness of gel (r = 0.96) was observed, as expected from amylose retrogradation to produce firmer gels; adhesiveness had a negative relationship (r = –0.86), as expected from the sticky nature of waxy starches. PV was not highly correlated to other pasting parameters or to gel texture (except ΔH), but HPV and CPV were highly correlated (r = 0.93), as were CPV (and other pasting parameters except PV) and hardness (P = 0.94). This supports the conclusion of Bhattacharya et al (1997) that PV is often unreliable as a predictor of end-use related functionality in starch properties, whereas use of CPV may be preferable.

CONCLUSIONS

The differences between coix and maize, and among waxy and normal coix accessions in physicochemical properties of starch offers additional opportunities in producing new products with coix. Coix is a high-yielding cereal grain with well-established uses and considerable potential for development. As a relative of maize with compatible starch properties, it may also have potential in bioengineering of novel starches in maize. For these reasons, further study of its starch is well justified.

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