



Carbohydrate Polymers 67 (2007) 174-181

# Carbohydrate Polymers

www.elsevier.com/locate/carbpol

# Analysis of genotypic diversity in starch thermal and retrogradation properties in nonwaxy rice

Jinsong Bao <sup>a,b,\*</sup>, Mei Sun <sup>b</sup>, Harold Corke <sup>c</sup>

Institute of Nuclear Agricultural Sciences, College of Agriculture and Biotechnology, Zhejiang University, Hua Jiachi Campus, Hangzhou 310029, PR China
 Department of Zoology, The University of Hong Kong, Hong Kong, PR China

Received 30 October 2005; received in revised form 17 April 2006; accepted 9 May 2006 Available online 30 June 2006

#### Abstract

A total of 236 nonwaxy rice including 56 landraces (landrace set) obtained from the germplasm center and 180 cultivars and breeding lines (breeding line set) obtained from various breeding programs were studied for the genetic diversity of flour thermal and retrogradation properties, focusing on comparison of the differences between the landrace set and breeding line set. Wide diversity was found in all flour physicochemical properties, e.g. peak temperature ( $T_p$ ) ranged from 63.2 to 79.8 °C, width at half peak height ( $\Delta T_{1/2}$ ) of gelatinization ranged from 4.7 to 10.5 °C; enthalpy of gelatinization ( $\Delta H_g$ ) ranged from 5.6 to 11.4 J/g, and retrogradation percentage (R%) ranged from 0.2% to 54.2%. The breeding line set had a larger range of thermal properties and R% than in the landrace set, whereas the range of retrogradation enthalpy was similar between two sets. The mean for all parameters differed between the two sets; mean  $\Delta T_{1/2}$  of the landrace set was smaller than in the breeding line set, whereas other parameters were larger in the landrace set than the breeding line set. Correlation analysis showed that apparent amylose content was positively correlated with  $\Delta H_g$  (r = 0.65, P < 0.001) and R% (r = 0.68, P < 0.001), and negatively correlated with  $\Delta T_{1/2}$  (r = -0.28, P < 0.001). All thermal and retrogradation properties themselves were correlated; the correlation between  $\Delta T_{1/2}$  and all other parameters was negative, whereas all other pairs were positive.

Keywords: Rice flour; Starch; Gelatinization temperature; Thermal property; Retrogradation; Genotype

### 1. Introduction

Differences in starch properties of cereal grains or flours contribute to their applications in different food and industrial uses, and gelatinization (thermal) and retrogradation properties are among the most important physicochemical properties of starch (Bao & Bergman, 2004; Eliasson, 2004; Collado & Corke, 2003; Ji et al., 2003; Patindol & Wang, 2002). The temperature at which starch begins and finishes gelatinization is important because it is related to the cooking time. The heat energy required to completely gelatinize starch in rice is critical to food processor, who must optimize heat input, cooking time, and temperature and, at

the same time, minimize the cost of the entire cooking process. Gelatinization temperature (GT)<sup>1</sup> is an important indicator of cooking and processing quality of both cooked-rice and parboiled rice (Juliano, 1998; Igathinathane, Chattopadhyay, & Pordesimo, 2005; Islam, Shimizu, & Kimura, 2002). It is reported that the cooked high-GT rice is harder in texture on accelerated staling than cooked low-GT rice (Perez, Villareal, Juliano, & Biliaderis, 1993; Villareal, Juliano, & Hizukuri, 1993). Different rice products need unique kinds of rice with diverse

<sup>&</sup>lt;sup>c</sup> Department of Botany, The University of Hong Kong, Hong Kong, PR China

Corresponding author. Tel.: +86 57186971405; fax: +86 571 86971202. *E-mail address:* jsbao@zju.edu.cn (J. Bao).

<sup>&</sup>lt;sup>1</sup> Abbreviations used: AAC, apparent amylose content; DSC, differential scanning calorimetry; GT, gelatinization temperature; LSD, least significant difference; PT, pasting temperature; R%, retrogradation percentage;  $T_{\rm o}$ , onset temperature;  $T_{\rm p}$ , peak temperature;  $T_{\rm c}$ , conclusion temperature;  $\Delta H_{\rm g}$ , enthalpy of gelatinization;  $\Delta H_{\rm r}$ , enthalpy of retrogration;  $\Delta T_{1/2}$ , width at half peak height.

starch properties, e.g. low GT is preferred in manufacturing breakfast cereals, rice breads and beer (Juliano, 1998). In some cases, starch GT correlates negatively with glycemic index and positively with resistant starch, a component of soluble dietary fiber (Juliano, 1999). Thus, diversity in rice starch characteristics are necessary to meet the diverse requirements for specific food processing. To meet these requirements, cereal chemists study what kind of starch properties are needed for a specific food, and breeders seek to explore how to obtain this kind of rice (Bao, Shen, Sun, & Corke, 2006).

Gelatinization temperature of rice grain can be estimated by the degree of disintegration of milled rice in a KOH solution or can be measured by differential scanning calorimetry (DSC). DSC can measure the gelatinization transition temperatures, i.e. onset  $(T_o)$ , peak  $(T_p)$ , conclusion  $(T_c)$  temperatures, enthalpy  $(\Delta H_g)$  of gelatination, and the retrogradation properties (Bao & Bergman, 2004; Singh, Johnson, White, Jane, & Pollak, 2001; Xu, Xie, Kong, & Bao, 2004). Patindol and Wang (2002) studied the physicochemical properties of three nonwaxy longgrain rices and found that although the amylose contents were similar, the different amylopectin structures could affect rice functionality, e.g. gelatinization, retrogradation, and pasting behavior. Sodhi and Singh (2003) found that a rice (PR-113) with amylose content of 7.8% had the highest  $T_{\rm o}$ ,  $T_{\rm p}$ ,  $T_{\rm c}$  and retrogradation percentage in comparison with four other rice with 15.6–18.9% amylose contents. Vandeputte, Vermeylen, Geeroms, and Delcour (2003a) investigated 15 rice with different peak temperature ( $T_p$ from 62.8 to 78.5 °C), and found that absolute and free amylose contents decreased gelatinization temperatures of intermediate and high  $T_p$  rice starches, but lipid-complexed amylose increased  $T_{\rm o}$ ,  $T_{\rm p}$ ,  $T_{\rm c}$  and decreased  $T_{\rm c} - T_{\rm o}$  of all rice starches. Nakamura et al. (2002) measured the thermal properties and amylopectin chain length of starch in 129 rice accessions, finding that the proportion of chains with  $DP \le 10$  to those of  $DP \le 24$  in amylopectin molecules was negatively correlated with the onset temperature of gelatinization.

Starch retrogradation encompasses the changes that occur in gelatinized starch from an initially amorphous to a more ordered state. Many studies concern mechanisms and dynamics of retrogradation of rice starch (e.g. Lai, Lu, & Lii, 2000; Tako & Hizukuri, 2000). Vandeputte, Vermeylen, Geeroms, and Delcour (2003b) studied the structural aspects, i.e. absolute, free and lipid-complexed amylose contents and amylopectin chain length distribution of five waxy and 10 normal rice starches in relation to amylopectin retrogradation behaviour. However, diversity in retrogradation properties of different rice genotypes is little studied. Our previous study showed that high GT starch had higher enthalpy and percentage of retrogradation than low-GT starch among 56 waxy rice accessions (Bao, Sun, & Corke, 2004).

Screening the starch thermal and retrogradation properties in a wider range of genotypes is necessary to search for

interesting extremes and to analyse the relationships among the properties (Ji et al., 2003; Bao et al., 2006; Singh et al., 2001; Nakamura et al., 2002). These kinds of studies will definitely contribute to our understanding how wide the genetic diversity among different genotypes, what the relationships among the physicochemical properties, and how can the variation be explained by the structures of amylose and amylopectin (Bao & Bergman, 2004; Ji et al., 2003; Bao et al., 2006; Vandeputte et al., 2003a, 2003b). Tan and Corke (2002) reported the physicochemical properties of 63 rice varieties and found that  $T_p$  ranged from 65.8 to 83.0 °C. Bao et al. (2004) reported that the  $T_p$ of 56 waxy rice accessions ranged from 66.9 to 79.0 °C. In the present paper, a total of 236 nonwaxy rice genotypes were analyzed for thermal and retrogradation properties of flours. The objectives were to determine the diversity in and relationships among flour thermal and retrogradation properties of nonwaxy rices.

#### 2. Materials and methods

#### 2.1. Plant materials

Flours of 245 rice accessions as in a previous study (Bao et al., 2006) were used, nine of which were identified as waxy rice. Because physicochemical properties of waxy rices were reported before (Bao et al., 2004), only the properties of the 236 nonwaxy rice accessions are reported in this study. Of them, 56 were landraces obtained from the germplasm center (landrace set, those from BP101 to BP300) and 180 were cultivars and breeding lines obtained from various breeding programs (breeding line set). Preparation of the rice materials was the same as previously reported (Bao et al., 2006).

# 2.2. Thermal properties

Thermal properties were analyzed using a DSC 2920 thermal analyser (TA Instruments, Newcastle, DE, USA) equipped with DSC standard and dual sample cells. Rice flour (2.0 mg, dry basis) was weighed into an aluminum pan and 6  $\mu$ L of distilled water was added. The pan was hermetically sealed, equilibrated at room temperature for 1 h, and then heated at a rate of 10 °C/min from 30 to 110 °C. A sealed empty pan was used as a reference. Onset  $(T_o)$ , peak  $(T_p)$ , and conclusion  $(T_c)$  temperature, width at half peak height  $(\Delta T_{1/2})$  and enthalpy  $(\Delta H_g)$  of gelatinization were calculated by Universal Analysis Program, Version 1.9D (TA Instruments, Newcastle, DE, USA). A typical DSC trace is shown Fig. 1.

### 2.3. Retrogradation

The gelatinized samples from DSC were stored at 4 °C for 24 h to increase nucleation, and then at 37 °C for 10 days to increase propagation (Gunaratne & Hoover, 2002). After equilibration at room temperature for 1 hr,

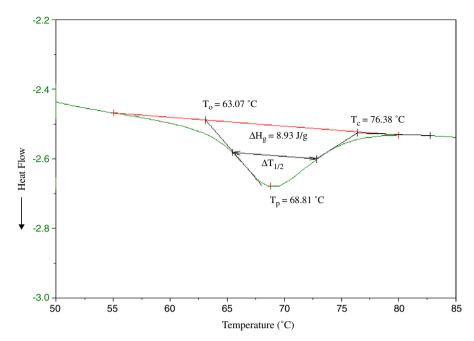


Fig. 1. Typical differential scanning calorimetry (DSC) thermogram of rice flour.  $T_{\rm o}$ , onset temperature;  $T_{\rm p}$ , peak temperature;  $T_{\rm c}$ , conclusion temperature;  $\Delta H_{\rm g}$ , enthalpy of gelatinization;  $\Delta T_{1/2}$ , width at half peak height.

the samples were rescanned from 30 to 110 °C at 10 °C/min to determine the enthalpy ( $\Delta H_{\rm r}$ ) of the retrograded starch. The percentage of retrogradation (R%) was calculated as ( $\Delta H_{\rm r}$ )/( $\Delta H_{\rm g}$ ) × 100.

#### 2.4. Statistical analysis

All properties were measured in duplicate. All the data analyses were performed with the SAS System for Windows version 8 (SAS Institute Inc., Cary, NC, USA). T-test was carried out to determine the significance of differences in mean physicochemical properties between the breeding line set and the landrace set. The least significant difference (LSD) multiple range test was conducted for comparison of mean of individual accessions at P < 0.05. Pair-wise correlations among the physicochemical property parameters were determined on a per accession basis.

## 3. Results

#### 3.1. Thermal properties

Wide diversities in thermal properties were found in the nonwaxy rice (n=236), with a mean of 66.8, 72.4 and 78.8 °C for  $T_{\rm o}$ ,  $T_{\rm p}$  and  $T_{\rm c}$ , respectively (Tables 1 and 2; Figs. 2 and 3). The landrace BP133 had the lowest  $T_{\rm o}$  (56.2 °C),  $T_{\rm p}$  (63.2 °C) and  $T_{\rm c}$  (70.6 °C), the breeding line BP532 had the highest  $T_{\rm o}$  (75.7 °C), and  $T_{\rm p}$  (79.8 °C), but its  $T_{\rm c}$  (84.9 °C) was a little lower than the highest, BP475 (85.1 °C) (Table 2). The landrace set had 2 °C higher mean  $T_{\rm o}$ ,  $T_{\rm p}$  and  $T_{\rm c}$  than the breeding line set (Table 1). From the frequency distribution of the thermal properties, most landrace lines were in the range 69–72 °C for  $T_{\rm o}$ , 74–77 °C for  $T_{\rm p}$  and 79–82 °C for  $T_{\rm c}$ . However, the breeding

line set had more accessions with markedly lower  $T_{\rm o}$ ,  $T_{\rm p}$  and  $T_{\rm c}$  (Fig. 2).

Width at half peak height ( $\Delta T_{1/2}$ ) of all accessions ranged from 4.7 (BP541) to 10.5 °C (BP010) and averaged 6.7 °C (Tables 1 and 2). Although the breeding line set had a greater mean  $\Delta T_{1/2}$  (6.9 °C) than that of the landrace set (6.2 °C) (Table 1), both sets had similar frequency distributions (Fig. 2), indicating that there was similar diversity in both sets.

Enthalpy is one of the most important parameters determine the energy input during gelatinization. Overall mean enthalpy of gelatinization ( $\Delta H_{\rm g}$ ) was 8.0 J/g, ranging from 5.6 J/g (BP461) to 11.4 J/g (BP104) (Tables 1, 2). The breeding line set had more accessions with  $\Delta H_{\rm g}$  ranging from 7.0 to 8.5 J/g than the landrace set, resulting in a mean  $\Delta H_{\rm g}$  of breeding line set (7.9 J/g) lower than that of the landrace set (8.6 J/g) (Fig. 2 and Table 1).

# 3.2. Retrogradation properties

Wide diversity in the enthalpy of retrogradation ( $\Delta H_{\rm r}$ ) was found among all the accessions, ranging from <0.1 to 5.0 J/g (BP114) (Tables 1 and 2; Figs. 2 and 3). It should be noted that many accessions had very small  $\Delta H_{\rm r}$ ; 39 had nearly undetectable  $\Delta H_{\rm r}$  (<0.1 J/g), 63 had  $\Delta H_{\rm r}$  from 0.1 to 1 J/g, most of which were found in the breeding line set (Fig. 2). The mean  $\Delta H_{\rm r}$  of the landrace set was 3.1 J/g, which was twice that of the breeding line set (1.5 J/g), but the ranges were similar between the two sets (Table 1).

The retrogradation percentage (R%) was calculated by dividing  $\Delta H_{\rm r}$  by  $\Delta H_{\rm g}$ . It was not surprising that many accessions (59) had very small R% (<5%) because of very small  $\Delta H_{\rm r}$ . The mean R% of all 236 accessions was 22.8%, ranging from 0.2 (BP540) to 54.2% (BP549) (Tables

Table 1
Means and ranges of physicochemical properties in breeding line set, landrace set and total genotypes

Parameters	Breeding line set $(n = 180)$			Landrace set $(n = 56)$			Total $(n = 236)$		
	$Mean \pm SD$	Min	Max	Mean ± SD	Min	Max	$Mean \pm SD$	Min	Max
T <sub>o</sub> (°C)	$66.2 \pm 5.1$	57.7	75.7	68.7 ± 2.9***	56.2	71.6	$66.8 \pm 4.8$	56.2	75.7
$T_{\rm p}$ (°C)	$71.9 \pm 4.2$	64.1	79.8	$73.8 \pm 2.2^{**}$	63.2	75.3	$72.4 \pm 3.9$	63.2	79.8
$T_{\rm c}$ (°C)	$78.5 \pm 3.5$	70.6	85.1	$79.9 \pm 1.8^{**}$	70.6	81.4	$78.8 \pm 3.3$	70.6	85.1
$\Delta T_{1/2}$ (°C)	$6.9 \pm 1.3$	4.7	10.5	$6.2 \pm 0.9^{***}$	5.2	9.4	$6.7 \pm 1.3$	4.7	10.5
$\Delta H_{\rm g} ({\rm J/g})$	$7.9 \pm 1.0$	5.6	10.7	$8.6 \pm 1.1^{***}$	6.6	11.4	$8.0 \pm 1.1$	5.6	11.4
$\Delta H_{\rm r} ({\rm J/g})$	$1.5 \pm 1.5$	0.0	4.9	$3.1 \pm 1.2^{***}$	0.0	5.0	$1.9 \pm 1.6$	0.0	5.0
R%	$18.7 \pm 18.0$	0.2	54.2	$36.1 \pm 12.7^{***}$	0.5	49.6	$22.8 \pm 18.4$	0.2	54.2

<sup>\*\*</sup> and \*\*\* are significant at  $P \le 0.01$  and  $P \le 0.001$  level for difference between breeding line set and landrace set.

Table 2
Thermal and retrogradation property data for selected rice accessions (mentioned in the text)

Accession	Name	T₀ (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)	$\Delta T_{1/2}$ (°C)	$\Delta H_{\rm g}~({ m J/g})$	$\Delta H_{\rm r}  ({\rm J/g})$	<i>R</i> %
BP010	Zaojing T3	58.4	67.3	75.8	10.5	6.5	0.1	1.9
BP104	Mugu	70.8	74.9	81.2	5.6	11.4	3.9	34.5
BP114	Huanggu	70.6	75.2	81.0	5.7	10.3	5.0	48.0
BP133	Liuyuenuo	56.2	63.2	70.6	8.3	6.9	0.2	3.1
BP461	Gui 99	60.6	66.7	73.7	7.6	5.6	0.1	1.1
BP475	YC9	74.4	79.5	85.1	6.0	9.9	2.2	22.6
BP532	T461	75.7	79.8	84.9	5.0	9.8	1.5	15.7
BP540	NP14	65.1	70.6	77.1	6.8	7.6	0.0	0.2
BP541	99YA162	75.2	78.8	83.9	4.7	10.3	2.3	21.8
BP549	Jianghui 151	70.8	75.8	81.4	5.8	8.1	4.4	54.2
LSD (0.05)	-	0.64	0.56	0.71	0.38	0.95	0.78	7.0

1, 2). The mean R% in the landrace set was 36.1%, twice that of the breeding line set (18.7%) (Table 1). The range in the breeding line set was a little wider than that of the landrace set (Table 1). In breeding line set, there were more accessions in the range R% <10% and 10% to 20% than from landrace set (Fig. 2).

# 3.3. Correlation analysis

The flour thermal and retrogradation parameters of 236 nonwaxy genotypes were used for correlation analysis (Table 3). Apparent amylose content (AAC) is the most important determinant of eating and cooking quality of rice, and pasting temperature (PT) from rapid visco-analyser analysis (Bao et al., 2006) may relate to the gelatinization temperature, so both of them were also included in correlation analysis. AAC did not correlate with  $T_p$ ,  $T_c$ and  $\Delta H_{\rm g}$ , but was slightly correlated with  $T_{\rm o}$  (r = 0.16, P < 0.05) and  $\Delta T_{1/2}$  (r = -0.28, P < 0.001) (Table 3). PT was correlated with all the thermal and retrogradation property parameters with r > 0.58 (P < 0.001). All the thermal and retrogradation properties themselves were significantly correlated at P < 0.001, and only the correlation between  $\Delta T_{1/2}$  and all other parameters was negative, whereas all other pairs were positive (Table 3).

Plotting the AAC,  $T_{\rm p}$  and R% in a three dimension figure, the total rice genotypes could be clearly divided into two subgroups: low  $T_{\rm p}$  subgroup with  $T_{\rm p} < 72$  °C and high  $T_{\rm p}$  subgroup with  $T_{\rm p} > 72$  °C (Fig. 4). It was found that AAC was negatively correlated with  $T_{\rm p}$ , i.e. r = -0.80

(P < 0.001; n = 97) in low the  $T_{\rm p}$  subgroup and r = -0.84 (P < 0.001, n = 139) in the high  $T_{\rm p}$  subgroup, although AAC had no relation with  $T_{\rm p}$  in total genotypes (Table 3).  $T_{\rm p}$  was negatively correlated with R% (r = -0.58 and r = -0.56 for low and high  $T_{\rm p}$  subgroups, respectively) (Fig. 4), but  $T_{\rm p}$  was positively correlated with R% (Table 3) for all genotypes. Only AAC was consistently positively correlated with R% either in two subgroups (r = 0.785 and 0.767 for low and high  $T_{\rm p}$  subgroups, respectively) or in total genotypes (Table 3).

#### 4. Discussion

Genetic diversity in the gelatinization (thermal) properties is important not only for breeders to select breeding lines that harbor unique starch characteristics, but also for food processors to select the raw material with desired properties for food processing. In maize, systematic analysis of the thermal, retrogradation and other physicochemical properties in a diverse germplasm collections was carried out (Ji et al., 2003; Singh et al., 2001), and some exotic lines, e.g. low onset temperature  $(T_o)$  and a wide range of gelatinization temperature, can be identified. In this study, wide genetic diversity of thermal properties among 236 rice accessions is reported. It was found that  $T_{\rm o}$  ranged from 56.2 to 75.7 °C,  $T_{\rm p}$  from 63.2 to 79.8 °C and T<sub>c</sub> from 70.6 to 84.9 °C (Table 1). Among 56 waxy rice, the  $T_{\rm o}$  and  $T_{\rm p}$  ranged from 57.6 to 74.5 °C and from 66.9 to 79.0 °C, respectively (Bao et al., 2004), a range somewhat smaller than in this study, indicating that screening in a

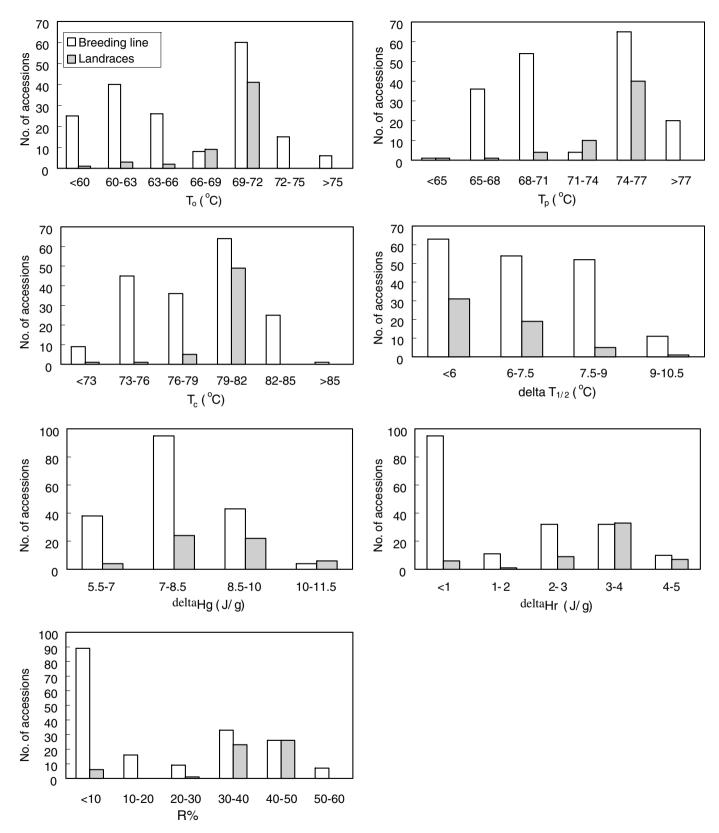


Fig. 2. Frequency distributions for thermal and retrogradation properties for breeding line set (n = 180) and landrace set (n = 56).

large collection may result in some unique starch properties, e.g. lower  $T_{\rm o}$  or  $T_{\rm p}$  and larger ranges (Table 1). Due to different DSC instrumentation and technique in other

studies, the results may not be directly compareable. However, it seemed that the range of thermal properties was a little larger than or similar to those of Tan and Corke

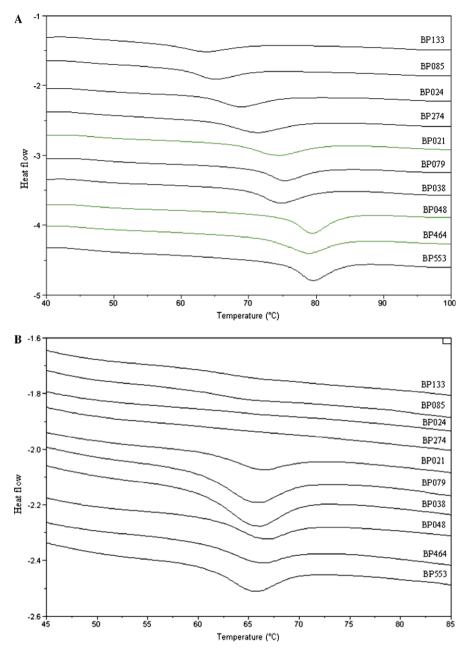


Fig. 3. DSC thermograms for the heating of flour (A) and retrograded gel (B) of some typical rice genotypes.

Table 3 Correlation analysis of flour apparent amylose content, pasting temperature, thermal and retrogradation properties of rice genotypes (n = 236)

	AAC	PT	$T_{\mathrm{o}}$	$T_{\mathrm{p}}$	$T_{ m c}$	$\Delta T_{1/2}$	$\Delta H_{ m g}$	$\Delta H_{ m r}$
$T_{\rm o}$	0.16*	0.95***						
$T_{\rm p}$	0.11	0.96***	0.99***					
$T_{\rm c}$	0.08	0.93***	0.96***	0.98***				
$\Delta T_{1/2}$	-0.28***	$-0.80^{***}$	-0.89***	-0.82***	-0.73***			
$\Delta H_{ m g}$	0.06	0.58***	0.68***	0.65***	0.65***	$-0.61^{***}$		
$\Delta H_{ m r}$	0.65***	0.74***	0.77***	0.74***	0.71***	-0.74***	0.57***	
R%	0.68***	0.73***	0.75***	0.72***	0.70***	$-0.71^{***}$	0.45***	0.98***

<sup>\*</sup> and \*\*\* indicate significant at P < 0.05 and P < 0.001 level, respectively.

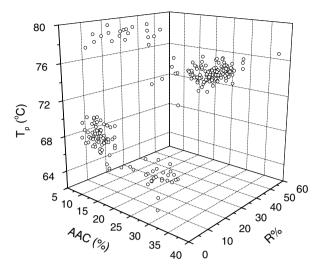


Fig. 4. The relationships among AAC,  $T_p$  and R% (n = 236).

(2002), Nakamura et al. (2002), and Vandeputte et al. (2003a) on rice and those of Singh et al. (2001) and Ji et al. (2003) on maize.

Although AAC was poorly correlated with  $T_o$ , and had no relationship with  $T_p$  and  $T_c$  over all genotypes (Table 2), it was negatively correlated with  $T_p$  when all genotypes were divided into low  $T_p$  (r = -0.80, P < 0.001) and high  $T_p$  subgroups (r = -0.84, P < 0.001) (Fig. 4), indicating that the relationship between AAC and  $T_p$  is genotype dependent. Vandeputte et al. (2003a) found that absolute and free amylose contents had no relation with  $T_{\rm o}$ ,  $T_{\rm p}$ and  $T_c$  of waxy and normal low  $T_p$  rice starches, but was negatively correlated with  $T_{\rm o}$ ,  $T_{\rm p}$  and  $T_{\rm c}$  of normal intermediate and high  $T_p$  starches. Vandeputte et al. (2003a) speculated that gelatinization of low  $T_p$  starches occurred too early in the first swelling step such that amylose could no longer influence the gelatinization temperature.  $\Delta T_{1/2}$ , a measure of gelatinization range, was negatively correlated with AAC and all other thermal and retrogradation properties (Table 2), indicating that higher AAC and higher GT starches give less cooperative melting between the amorphous and crystalline domain during gelatinization. Thus, new starches with low  $T_0$  and large range of gelatinization will be easily found among low AAC and low GT starches (Ji et al., 2003).  $\Delta H_g$  had no correlation with AAC in this study (Table 2), and Varavinit, Shobsngob, Varanyanond, Chinachoti, and Naivikul (2003) and Tan and Corke (2002) also did not observe a correlation between AAC and  $\Delta H_{\rm g}$ . However, some reports indicate that they may be negatively correlated (Vandeputte et al., 2003a; Xu et al., 2004).

Retrogradation describes the process in which a heated starch paste cools to below the melting temperature of starch crystallites, and the extruded amylose and amylopectin reassociate and unite the swollen starch grains in an ordered structure that results in viscosity increase, gel firming, and textural staling of predominantly starch-containing systems (Atwell, Hood, Lineback, Varriano-

Marston, & Zobel, 1998; Bao & Bergman, 2004; Collado & Corke, 2003; Eliasson, 2004). Both  $\Delta H_r$  and R%displayed wide diversity, ranging from not detectable to 5.0 J/g for  $\Delta H_{\rm r}$  and from 0.2% to 54.2% for R%, respectively (Table 1). Because of different measurement systems used, it is difficult to compare with results from other studies, such as Patindol and Wang (2002) and Vandeputte et al. (2003b). The present study showed that  $\Delta H_r$  of rice flour was positively correlated with  $T_{\rm o}$ ,  $T_{\rm p}$ ,  $T_{\rm c}$  and  $\Delta H_{\rm g}$ (Table 2), which is in agreement with the result of Vandeputte et al. (2003b), suggesting that rice starches gelatinizing at higher temperatures retrograde to a larger extent. AAC was consistently positively correlated with  $\Delta H_r$  and R% in the present (Table 2) and previous studies (Xu et al., 2004), but Vandeputte et al. (2003b) found a complex relationship between absolute, free and lipid-complexed amylose contents and  $\Delta H_r$  upon different storage conditions.  $T_p$  was positively correlated with R% for total genotypes (Table 2), but they negatively correlated with R%when all genotypes were divided into low  $(T_p \le 72 \, ^{\circ}\text{C})$ and high  $(T_p > 72 \, ^{\circ}\text{C})$  subgroups (Fig. 4).

There was a significant difference between the breeding set and the landrace set for all thermal and retrogradation properties, reflected in the means, range and frequency distributions (Table 1; Figs. 2 and 3). The differences may be due to the selection of samples; the choice of 56 landrace lines (from BP101 to BP300) was based on their pasting temperatures (PT) (Bao et al., 2006). Almost all landraces with low PT were chosen because most landrace lines are high PT, whereas breeding lines were almost randomly chosen for the measurement of the thermal and retrogradation properties. On the other hand, it is also possible that the wider diversity in breeding lines results from the diverse aims of current breeding efforts, which broadens the genetic diversity used.

In conclusion, wide diversity was present in the physicochemical properties of 236 nonwaxy rices, and this study supports screening in a broad collection of material to find useful and novel starch properties, e.g. lower  $T_{\rm o}$  or  $T_{\rm p}$  and larger ranges. Rice breeders can employ such lines in breeding programs using the genotypes with desirable properties for improvement of grain quality, and thus provide food processors with unique characteristic rice for speciality food processing.

## Acknowledgements

The project was supported in part by grants from National Natural Science Foundation of China (30300227), International Atomic Energy Agency (12847/R0) and the Hong Kong Research Grants Council. The authors thank A. M. McClung at USDA-ARS, Rice Research, US, Liqing Wei at Chinese Academy of Agricultural Sciences, Jiankun Xie at Jiangxi Academy of Agricultural Sciences, Guoqing Tu at China Rice Research Institute, Qinglong Liu and Junmin Wang at Zhejiang Academy of Agricultural Sciences, Wenyue Chen at

Hangzhou Institute of Agricultural Sciences, Xiuru Xu and Honghua Chen at Wenzhou Institute of Agricultural Sciences; and Shengquan Shen at Zhejiang University for kindly supplying the rice materials.

#### References

- Atwell, W. A., Hood, L. F., Lineback, D. K., Varriano-Marston, E., & Zobel, H. F. (1998). The terminology and methodology associated with basic starch phenomena. *Cereal Foods World*, 33, 306–311.
- Bao, J., & Bergman, C. J. (2004). The functionality of rice starch. In A. C. Eliasson (Ed.), Starch in Food: Structure, Function and Applications (pp. 258–294). Cambridge: Woodhead Publishing Ltd..
- Bao, J. S., Shen, S. Q., Sun, M., & Corke, H. (2006). Analysis of genetic diversity in the physicochemical properties of nonwaxy rice flour: apparent amylose content, pasting viscosity and gel texture. Starchl Starke, 58, 259–267.
- Bao, J. S., Sun, M., & Corke, H. (2004). Genetic diversity of starch physiochemical properties in waxy rice (*Oryza sativa L.*). Journal of the Science of Food and Agriculture, 84, 1299–1306.
- Collado, L. S., & Corke, H. (2003). Starch properties and functionalities. In G. Kaletunc & K. J. Breslauer (Eds.), Characterization of Cereals and Flours (pp. 473–506). New York: Marcel Dekker.
- Eliasson, A. C. (2004). Utilization of thermal properties for understanding baking and staling processes. In A. C. Eliasson (Ed.), Starch in food: Structure, Function and Applications (pp. 65–115). Cambridge: Woodhead Publishing Ltd..
- Gunaratne, A., & Hoover, R. (2002). Effect of heat-moisture treatment on the structure and physicochemical properties of tuber and root starches. Carbohydrate Polymer, 49, 425–437.
- Igathinathane, C., Chattopadhyay, P. K., & Pordesimo, L. O. (2005). Combination soaking procedure for rough rice parboiling. *Transactions of ASAE*, 48, 665–671.
- Islam, M. R., Shimizu, N., & Kimura, T. (2002). Effect of processing conditions on thermal properties of parboiled rice. Food Science and Technology Research, 8, 131–136.
- Ji, Y., Wong, K., Hasjim, J., Pollak, L. M., Duvick, S., Jane, J., & White, P. J. (2003). Structure and function of starch from advanced generations of new corn lines. *Carbohydrate Polymer*, 54, 305–319.
- Juliano, B. O. (1998). Varietal impact on rice quality. Cereal Food World, 43, 207–211, 214–216, 218–222.
- Juliano, B. O. (1999). Comparative nutritive value of various staple foods. Food Reviews International, 15, 399–434.

- Lai, V. M. F., Lu, S., & Lii, C. Y. (2000). Molecular characteristics influencing retrogradation kinetics of rice amylopectin. *Cereal Chemistry*, 77, 272–278.
- Nakamura, Y., Sakurai, A., Inaba, Y., Kimura, K., Iwasawa, N., & Nagamine, T. (2002). The fine structure of amylopectin in endosperm from Asian cultivated rice can be largely classified into two classes. Starch, 54, 117–131.
- Patindol, J., & Wang, Y. J. (2002). Fine structures of starches from longgrain rice cultivars with different functionality. *Cereal Chemistry*, 79, 465–469
- Perez, C. M., Villareal, C. P., Juliano, B. O., & Biliaderis, C. G. (1993).
  Amylopectin-staling of cooked nonwaxy milled rices and starch gels.
  Cereal Chemistry, 70, 567–571.
- Singh, S. K., Johnson, L. A., White, P. J., Jane, J. L., & Pollak, L. M. (2001). Thermal properties and paste and gel behaviors of starches recovered from accessions used in the germplasm enhancement of maize project. *Cereal Chemistry*, 78, 315–321.
- Sodhi, N. S., & Singh, N. (2003). Morphological, thermal and rheological properties of starches separated from rice cultivars grown in India. *Food Chemistry*, 80, 99–108.
- Tako, M., & Hizukuri, S. (2000). Retrogradation mechanism of rice starch. Cereal Chemistry, 77, 473–477.
- Tan, Y. F., & Corke, F. (2002). Factor analysis of physicochemical properties of 63 rice varieties. *Journal of the Science of Food and Agriculture*, 82, 745–752.
- Vandeputte, G. E., Vermeylen, R., Geeroms, J., & Delcour, J. A. (2003a). Rice starches. I. Structural aspects provide insight into crystallinity characteristics and gelatinisation behaviour of granular starch. *Journal* of Cereal Science, 38, 43–52.
- Vandeputte, G. E., Vermeylen, R., Geeroms, J., & Delcour, J. A. (2003b).
  Rice starches. III. Structural aspects provide insight in amylopectin retrogradation properties and gel texture. *Journal of Cereal Science*, 38, 61–68.
- Varavinit, S., Shobsngob, S., Varanyanond, W., Chinachoti, P., & Naivikul, O. (2003). Effect of amylose content on gelatinization, retrogradation and pasting properties of flours from different cultivars of Thai rice. Starch/Starke, 55, 410–415.
- Villareal, C. P., Juliano, B. O., & Hizukuri, S. (1993). Varietal differences in amylopectin staling of cooked waxy milled rices. *Cereal Chemistry*, 70, 753–758.
- Xu, L. J., Xie, J. K., Kong, X. L., & Bao, J. S. (2004). Analysis of genotypic and environmental effects on rice starch. 2. thermal and retrogradation properties. *Journal of Agricultural and Food Chemistry*, 52, 6017–6022.