

Retrogradation Kinetics of Rice Flours as Influenced by Cultivar¹

J. Fan² and B. P. Marks^{2,3}

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Retrogradation of gelatinized starch occurs in many starch-based food systems (Fearn and Russell 1982). Retrogradation is considered to be a process in which the molecules of gelatinized starch reassociate to form crystallites. Starch retrogradation and the nature of the formed crystals depend on the starch source, amylose content, storage temperature, and the presence of other food ingredients (Orford et al 1987, Zeleznak and Hosney 1987, Chang and Liu 1991, Ward et al 1994). The extent of retrogradation can significantly influence the texture and quality of starch-containing food products (Fearn and Russell 1982).

Although rice starch and flours have increasingly been used as ingredients and functional modifiers in many foods, limited information is available regarding the retrogradation behaviors of rice materials. In general, grain type and cultivar significantly influence the functional properties of rice and rice flour (Webb 1985, Bean 1986, Juliano 1990). Specifically, Chang and Liu (1991) reported that the retrogradation enthalpy for high-amylose rice starch was higher than that for low-amylose starch or for waxy starch. Recently, Perez et al (1993) also showed varietal differences in hardness after staling of waxy and nonwaxy cooked rices for >4 hr at 2–4°C.

The objectives of this study were to: 1) document the gelatinization and retrogradation behaviors for flours of several rice cultivars studied using differential scanning calorimetry (DSC), and 2) evaluate whether the Avrami model of polymer crystallization (McIver et al 1968) fits the kinetics of starch retrogradation in the gelatinized rice flour systems.

MATERIALS AND METHODS

Four rice cultivars were tested (Kaybonnet, Cypress, Bengal, and Orion); the first two were long-grain cultivars, and the second two were medium-grain cultivars. The Kaybonnet, Cypress, and Bengal were harvested from the University of Arkansas (UofA) Rice Research and Extension Center at Stuttgart, AR, in September 1996, with harvest moisture contents of 19.1, 16.5, and 17.4% (wb), respectively. The Orion was harvested from the UofA Northeast Research and Extension Center at Keiser, AR, in October 1996, with a harvest moisture content of 13.8% (wb). Additionally, rice starch (Sigma Chemical Co., St. Louis, MO) was tested for comparison.

The rough rice was dried under air conditions of 60°C and 16.9% rh for 30 min. in a thin-layer (≈2 cm) laboratory drying chamber, and then transferred to an equilibrium chamber (21°C and 50% rh), where the final moisture content of the rice reached ≈12.5% (wb) after seven to 10 days. The rough rice was subsequently stored in sealed plastic bags at 1°C for three to four months before milling.

After equilibration to room temperature, a rough rice sample (150 g) from each cultivar was dehulled in a McGill sample hulling machine, and the resulting brown rice was milled for 30 sec in a McGill #2 laboratory mill (Seedboro Equipment Co., Chicago, IL) with a 1.5-kg weight positioned at 15 cm on the mill lever arm. The head rice, which is defined as the milled rice kernels three-fourths or more of the original kernel length (USDA 1979), was collected using a rice-sizing device (Seedboro) and then ground to flour in a laboratory cyclone mill equipped with a 0.5-mm screen (Udy Co., Fort Collins, CO). The moisture contents of the flour samples were determined by an air oven method (AOAC 1990). Apparent amylose content was analyzed by the method of Juliano (1971).

Gelatinization and retrogradation of the flour and starch samples were investigated using a differential scanning calorimeter with companion analysis software (Pyris 1, Perkin-Elmer Co., Norwalk, CT). Rice starch or flour (3.5–4.5 mg) was weighed into an aluminum DSC sample pan, and deionized water was added to yield a water-to-flour (dry solid) ratio of 2.5:1. The sealed sample pans were then heated in the calorimeter from 20 to 110°C, with a heating rate of 10°C/min. A pan containing 15 μL of deionized water was used as a reference during the scanning, and the calorimeter was calibrated using indium. To evaluate whether the rice materials were completely gelatinized during the first DSC scan, several samples were rescanned immediately after being cooled to 20°C after the first scan. Over the range of gelatinization temperatures, no endothermic transition was observed in these rescan thermograms, indicating that the rice starch had been fully gelatinized during the first DSC run.

The gelatinized rice sample pans were stored at 4°C for periods of 1, 3, 7, 14, 21, 28, and 35 days. Subsequently, the samples were equilibrated at room temperature for 2 hr, then rescanned in the calorimeter from 20 to 90°C at 10°C/min to measure the retrogradation temperature and enthalpy. The enthalpy (ΔH) which was required to melt starch crystallites was measured from the area of endothermic peaks in the thermograms and expressed on a dry weight basis (J/g). Onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c) of thermal transitions were determined according to Russell (1987). Triplicate measurements were conducted for each sample. Standard deviations among replicate enthalpy and temperature measurements were <0.6 J/g and 0.5°C, respectively. Duncan's multiple range test (SAS Institute, Cary, NC) was applied to test the significance ($\alpha = 0.05$) of differences among means for each parameter.

The Avrami model was employed to describe the kinetics of starch recrystallization in the rice flour gels. The model (McIver et al 1968) can be expressed as:

$$\Theta = \frac{\Delta H_t - \Delta H_i}{\Delta H_t - \Delta H_0} = \exp(-kt^n) \quad (1)$$

where Θ is the fraction of uncrystallized starch at time t , ΔH_0 and ΔH_t are the enthalpy changes at time 0 and time t , respectively, ΔH_i is the limiting enthalpy change, k is the rate constant, and n is the Avrami exponent. ΔH_i was taken to be the enthalpy change

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² Research associate and assistant professor, respectively, University of Arkansas Department of Biological and Agricultural Engineering, 203 Engineering Hall, Fayetteville, AR 72701.

³ Corresponding author: E-mail: bpm1@enr.uark.edu Phone: 501/575-2840. Fax: 501/575-2846.

TABLE I
Temperature and Enthalpy of Gelatinization and Retrogradation and Avrami Parameters for Rice Starch and Flours of Various Cultivars

Cultivar	Apparent Amylose Content ^a	Gelatinization ^b				Retrogradation ^b (4°C, 7 days)				Avrami Parameters ^c		
		ΔH (J/g)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	T_c (°C)	n	k (day ⁻ⁿ)	r^2
Rice starch	28.4	12.0±0.3a	63.2±0.4d	76.4±0.3b	82.8±0.5b	6.7±0.3a	42.3±0.4b	53.4±0.0a	64.5±0.5a	0.63	0.917	0.98
Kaybonnet	25.6	9.3±0.2c	71.1±0.1b	75.8±0.3c	81.8±0.2c	6.6±0.1a	44.4±0.3a	53.4±0.0a	64.5±0.5a	0.76	0.461	0.97
Cypress	20.8	9.9±0.2b	73.8±0.0a	79.0±0.1a	84.8±0.1a	5.5±0.2b	41.3±0.4bc	52.1±0.0b	63.0±0.1b	0.81	0.454	0.94
Bengal	15.6	9.9±0.2b	64.3±0.1c	70.2±0.1d	77.3±0.2d	2.5±0.6c	41.8±0.5b	51.3±0.4c	60.3±0.1c	1.39	0.255	0.95
Orion	15.1	8.1±0.2d	63.2±0.4d	69.6±0.2e	76.0±0.3e	1.8±0.3d	40.3±0.5c	51.9±0.5bc	57.9±0.1d	1.53	0.181	0.93

^a % db.

^b Mean ± standard deviation ($n = 3$); means followed by the same letter are not significantly different according to Duncan's multiple range test ($\alpha = 0.05$).

^c Avrami exponent (n) and rate constant (k) were obtained from linear regression of data shown in Fig. 1 from Eq. 2.

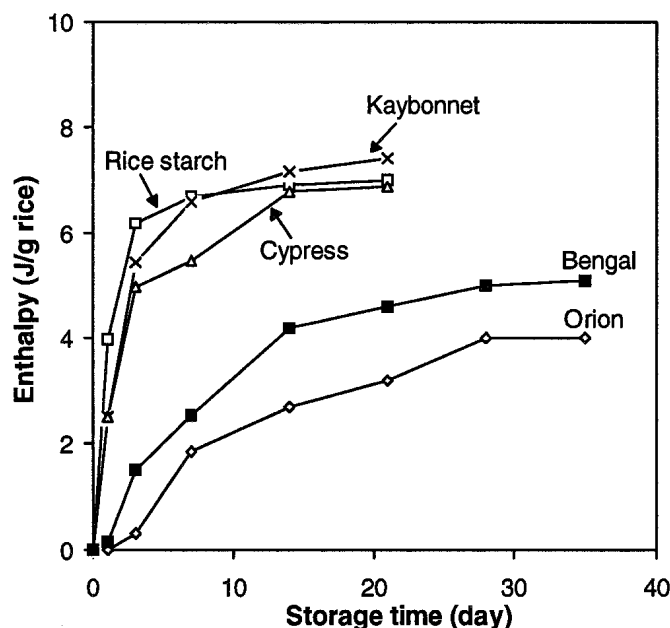


Fig. 1. Retrogradation enthalpy as a function of postcooking storage time for gelatinized rice starch and flours of four different rice cultivars (stored at 4°C).

after aging for 21 days for rice starch, Kaybonnet, and Cypress samples, and after 35 days for Bengal and Orion. ΔH_0 was zero. The rate constants (k) and exponents (n) for the flours and starch were obtained from linear regression of the retrogradation enthalpy data as:

$$\ln\left[\ln\left(\frac{\Delta H_i}{\Delta H_i - \Delta H_0}\right)\right] = \ln k + n \ln t \quad (2)$$

RESULTS AND DISCUSSION

Apparent amylose content of the Kaybonnet and Cypress (long-grain cultivars) were 25.6 and 20.8% (db), respectively, which was much higher than that for the medium-grain cultivars, Bengal and Orion (Table I). Typical U.S. medium-grain rices have a low amylose content in comparison with long-grain varieties (Webb 1985, Linscombe et al 1992).

Of all the rice flours studied (Table I), Cypress (long-grain), and Bengal (medium-grain) had the highest gelatinization enthalpy (9.9 J/g), whereas Orion (medium-grain) exhibited the lowest gelatinization enthalpy (8.1 J/g). As expected, all of the rice flours had significantly ($\alpha = 0.05$) lower gelatinization enthalpies than did the rice starch because of the presence of nonstarch components in the flours. In a DSC study of thermal properties of rice flours, Normand and Marshall (1989) reported that the gelatiniza-

tion enthalpies for cultivars Lemont, Mars, S-201, and Calmochi ranged from 9.5 to 11.2 J/g, which is consistent with our data.

Kaybonnet and Cypress with medium to high amylose content exhibited significantly ($\alpha = 0.05$) higher onset (T_o), peak (T_p), and conclusion (T_c) temperatures of gelatinization than did the medium-grain cultivars (Bengal and Orion). Even though Cypress had a gelatinization enthalpy similar to that of Bengal, the latter had significantly lower gelatinization temperatures (T_o , T_p , and T_c) than did the former. Despite having T_o temperatures similar to that of the rice starch (63.2°C), Bengal and Orion had significantly ($\alpha = 0.05$) lower T_p and T_c temperatures than did the pure starch.

For retrogradation characteristics after seven days at 4°C (Table I), Bengal and Orion had 50–70% lower retrogradation enthalpies than did the long-grain cultivars, Kaybonnet and Cypress. The peak temperatures of retrogradation for Bengal and Orion after seven days of aging were $\approx 51^\circ\text{C}$, which was only 1–2°C lower than those for Kaybonnet and Cypress. Also, Kaybonnet, which had a high amylose content, had retrogradation enthalpy and temperatures similar to those of rice starch, even though their gelatinization enthalpies were markedly different.

The rate of retrogradation was significantly influenced by cultivar (Fig. 1). Bengal and Orion exhibited much slower retrogradation when compared to the long-grain cultivars. Very little retrogradation was observed for the medium-grain samples stored for one day. In contrast, the Kaybonnet, Cypress, and pure starch gels retrograded much more rapidly during the first three days. Furthermore, the pure starch gel underwent somewhat more retrogradation than did Kaybonnet or Cypress during the first week of storage, although they were more similar thereafter.

The major factors influencing rice retrogradation would be starch content, ratio of amylose to amylopectin, and the branch chain length of amylopectin. Although both amylose and amylopectin components are involved in the process of starch retrogradation, the linear fraction, amylose, favors recrystallization in a rapid mode (Orford et al 1987, Chang and Liu 1991). Thus, the lower amylose content of the medium-grain cultivars (Table I) possibly explains the slow retrogradation observed in this study. Normalizing the retrogradation enthalpy in Fig. 1, in terms of amylose mass rather than total dry mass (data not shown), accounted for most of the differences in ΔH_i , but it did not account for the rate differences (i.e., differences in curve shape) among samples. This suggests that, in addition to amylose, other components, such as amylopectin, protein, and fiber, may influence the retrogradation of rice materials.

The Avrami model gave a reasonable description of starch retrogradation in gelatinized rice flour systems, with regression coefficients of 0.93–0.98 (Table I). Kaybonnet and Cypress had similar Avrami exponents (n), with values <1.0, whereas the Avrami exponents (n) for Bengal and Orion were both >1.3. These significant differences in the Avrami exponent values between the long- and medium-grain rices suggest that the mechanism for recrystallization of starch might be different (McIver et al 1968). The Avrami exponent (n) has been reported to be close to unity in Cas-

sava starch (Kim et al 1976) and in wheat starch gels (McIver et al 1968), 0.78–1.26 in acid treated starch (Zhang and Jackson 1992), and 0.75 in baked breads (Fearn and Russell 1982). For the rate constants (k), our results indicate that Kaybonnet and Cypress were very similar, with k values of $\approx 0.46 \text{ day}^{-1}$, which was roughly half the k value for pure starch. The k value for Bengal and Orion was only 0.255 and 0.181 day^{-1} , respectively. In addition, as apparent amylose content of the rice materials decreased, the Avrami exponent (n) for retrogradation increased, while the rate constants (k) decreased.

CONCLUSIONS

Gelatinization and retrogradation of milled rice flour depended on grain type, cultivar, and apparent amylose content. The medium-grain cultivars (Bengal and Orion), with low amylose content, had lower gelatinization temperatures and a lower rate of retrogradation than did the long-grain cultivars (Kaybonnet and Cypress). Cultivar had less effect on retrogradation temperatures than on gelatinization temperatures, but a greater effect on retrogradation enthalpy than on gelatinization enthalpy. The Avrami model gave a good description of the kinetics of retrogradation in rice flour systems. High amylose content rice flours gave a low Avrami exponent but a high rate constant for retrogradation.

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