Annealing of Long-Term Stored Rice Grains Improves Gelatinization Properties

Aijiro Yamamoto[1,2] and Kiyoka Shirakawa[3]

Cereal Chem. 76(5):646–649

ABSTRACT

We found new characteristics of annealing (or warm water treatment) in this rheological study. Japonica rice grains from long-term storage at an ambient temperature for 10–24 years showed gelatinization properties analogous to that of indica rice but recovered properties similar to that of newly harvested rice after annealing at 55°C for 24 hr. Annealing significantly augmented the enthalpy from differential scanning calorimetry of raw and treated rice. This treatment also strengthened peak heights of the A pattern of rice in the X-ray diffraction intensity diagram. Annealing of long-term stored rice grains showed reverse effects to that of newly havested rice and purified starches. This effect of annealing on long-term stored rice might be useful for industrial purposes.

We previously examined the effects of prolonged steeping in hot or warm water on the physicochemical properties of rice grains to explain the gelatinization process at 50–75°C and the mechanism of production of abnormally cooked rice (Yamamoto 1995). Then we conducted X-ray diffraction pattern analysis and amylography on the japonica and indica rice grains and clarified the optimum crystallization conditions of annealing (Yamamoto et al 1996). In our preliminary study, we found by amylography that annealing of rice stored for 24 years recovered gelatinization characteristics similar to those of newly harvested rice (Yamamoto et al 1997).

In this study, we examined the gelatinization properties of newly harvested and long-term stored japonica rice grains with a Rapid ViscoAnalyser (RVA) (Newport Scientific, Narrabeen, Australia) and discovered interesting characteristics of annealed long-term stored rice grains. We also examined the calorimetric enthalpy by differential scanning calorimetry (DSC) and the X-ray diffraction intensity diagrams of raw and annealed long-term stored rice.

MATERIALS AND METHODS

The long-term stored rice grains used in this experiment were Koshihikari (a typical japonica cultivar grown in Niigata Prefecture in 1972), Sasanishiki (another japonica cultivar grown in Miyagi Prefecture in 1977), Yukihikari (a japonica cultivar with a slightly higher amylose content [21.6%] grown in Hokkaido in 1986). All rice specimens had been polished and packed in laminated film bags of 25-µm nylon and 50-µm polyethylene with CO_2 by the CO_2 exchange method (CEM) described by Mitsuda et al (1972) and stored at ambient temperature.

Newly harvested rice grains (Koshihikari, Sasanishiki, and Yukihikari) from the same cultivar and originating from the same prefectures were harvested in 1996. The amylose contents were 17–18% for Koshihikari, 18–18.5% for Sasanishiki, and 20–21% for Yukihikari. Indica rice used in this study for comparison with the RVA profile of the long-term stored japonica rice was a high-amylose rice imported from Thailand in 1994. The cultivar was unknown but its amylose content was 32%. Rice grains were stored at 5°C in a polyethylene bag until use.

Preparation of Rice Specimens

Raw and treated rice specimens were prepared for DSC measurements as reported previously (Yamamoto 1995). Raw polished rice flour was prepared by grinding rice grains with a centrifugal mill and screening through a 60-mesh sieve. Annealed rice was prepared by steeping 200 g of polished rice in 1L of water at 55°C in a water bath for 24 hr. Hot-water-treated rice was prepared by steeping 200 g of polished rice in 300 mL of water at 75°C in an automatic electric cooker (Sharp KS-05T2, 0.54L) for 8, 12, and 18 hr. Cooked rice was prepared by cooking 200 g of rice grains in 300 mL of water using an automatic electric cooker (National SR-3060, 0.6L) for 20 min at up to 100°C. All rice specimens were homogenized in a Waring blender and rapidly dehydrated with ethanol and ether as described by Mitsuda et al (1983) to prevent further change to the degree of gelatinization.

Analytical Methods

We collected data using a DSC 4207 scanning microcalorimeter (CSC Co. Ltd.) at a scan rate of 1.0K/min after adding ≈200 mg of distilled water to a weighed amount of rice flour (≈50 mg) in the DSC cell and letting the mixture stand for 1 hr at 25°C. We evaluated the calorimetric enthalpy (ΔH) by integrating the DSC curves according to the method of Takahashi and Sturtevant (1981).

Based on the analytical method used in the cooperative test by Toyoshima et al (1997), we determined the gelatinization characteristics of rice specimens with an RVA by suspending 3 g of the rice flour in 25 mL of distilled water in an aluminum vessel. The time program was maintenance for 1 min at 50°C, heating for 4 min from 50°C to 93°C, maintenance for 7 min at 93°C, cooling for 4 min from 93°C to 50°C, and maintenance for 4 min at 50°C. The gelatinization characteristics were the same as those obtained by amylography, including the gelatinization temperature, maximum viscosity, minimum viscosity, breakdown, final viscosity at 50°C, consistency, and breakdown-consistency ratio. We calculated the means and standard deviations after three repeated experiments and determined the probability of difference between samples with the t-test.

X-ray diffraction pattern was observed for rice specimens and used to determine the state of crystalline structure of starch. Rice flour used in X-ray diffraction pattern analysis was prepared by grinding rice grains with a centrifugal mill and mortar screening through a 200-mesh sieve. An X-ray diffractometer (RAD-RVC, Rigaku Denki Co. Ltd., Japan) was used. Operating conditions were target Cu (monochromator) excited at 40 kV, 100 mA; slit DS 1, RS 0.3, SS 1 mm; scanning speed 5°/min; step/sampling 0.02°. Peaks in the X-ray diffraction pattern were named according to Hizukuri and Nikuni (1957).

RESULTS AND DISCUSSION

Changes in Gelatinization Characteristics

During the storage experiments on nonglutinous polished japonica and indica rice, we found that indica rice (Thailand high-amylose rice) showed complete loss of breakdown and high consistency by amylography after storage at 40°C for 12 months (Yamamoto et al 1997). We also reported that breakdown of japonica rice stored at an ambient temperature for 24 years was as low

[1] Professor, Division of Food and Nutritional Science, Graduate School of Nutrition, Koshien University l0-1, Momijigaoka, Takarazuka 665-0006, Japan.

[2] Corresponding author. E-mail: yamamoto@koshien.ac.jp Phone: 0797-87-5111. Fax: 0797-87-5666.

[3] Student of master course, Division of Food and Nutritional Science, Graduate School of Nutrition, Koshien University, l0-1, Momijigaoka, Takarazuka 665-0006, Japan.

Publication no. C-1999-0727-02R.

as one-eleventh of the consistency, but annealing showed amylographic findings similar to those obtained from newly harvested rice, which showed high breakdown and almost equal values of breakdown and consistency.

Therefore, we further examined these phenomena in detail with long-term stored rice grains of other japonica cultivars. Figure 1 shows RVA curves typical of newly harvested and long-term stored japonica rice (Koshihikari from 1996 and 1972). The curve of 72-Koshihikari is analogous to that of Thailand high-amylose rice that shows low breakdown, high consistency, and low breakdown-consistency ratio. Figure 2 shows RVA curves of raw japonica rice, stored rice at 37°C for 12 months, and annealed rice after storage. As a result of storage, the gelatinization temperature and maximum viscosity slightly increased, and consistency markedly increased, while breakdown markedly decreased. Therefore, breakdown-consistency ratio decreased to 0.4, while that of raw rice was 1.8. Annealing, however, produced a RVA curve similar to that of raw rice. That is, the gelatinization temperature, final viscosity, and consistency decreased, while maximum viscosity, breakdown, and peak time increased as a result of annealing. Breakdown-consistency ratio increased from 0.4 to 1.1. Table I shows the gelatinization characteristics of newly harvested and long-term stored rice from three cultivars. Two other long-term stored rice grains (Sasanishiki from 1977 and Yukihikari from 1986) also showed low breakdown and high consistency in comparison with newly harvested rice grains from the same cultivar. These long-term stored rice grains also recovered RVA curves similar to those of newly harvested rice by annealing at 55°C for 24 hr. Degrees of change in long-term stored rice grains were higher than those in newly harvested rice grains. For example, the breakdown of annealed long-term stored rice was 3.5 to 3.8 times higher than that of the raw rice, while that of newly harvested rice was only 0.8-1.1. The gelatinization temperature of long-term stored rice grains decreased as a result of annealing, while that of newly harvested rice grains slightly increased. These results indicated that even 12 months storage of rice at 37°C might cause marked changes in the gelatinization characteristics. Unpublished data from storage experiments of japonica rice at –35, 5, 15, and 37°C showed that maximum viscosity and breakdown increased up to three months and then decreased at 37°C but continued to increase after 12 months at 15°C. For rice stored for 10–24 years at an ambient temperature (<30°C), the changes might have occurred within a few years and remained stable thereafter. Extremely mild storage conditions might cause the same changes, but more slowly. The product of the

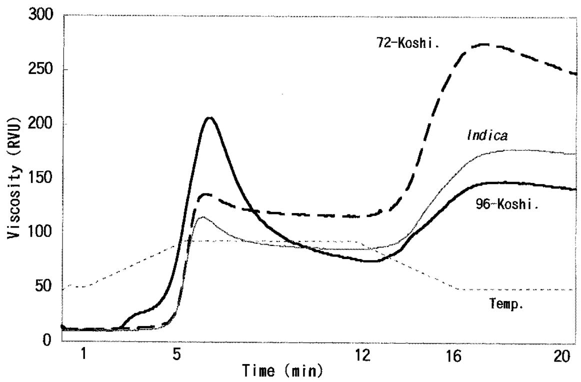

Fig. 1. Rapid ViscoAnalyser curves of newly harvested and long-term stored japonica and indica rice.

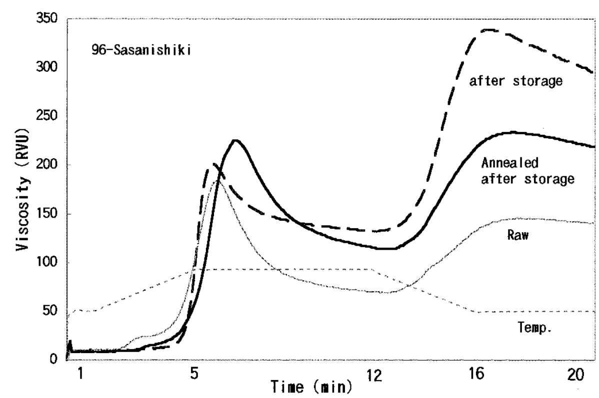

Fig. 2. Rapid ViscoAnalyser curves of raw japonica rice, rice stored for 12 months, and rice annealed after storage.

TABLE I
Changes in Gelatinization Characteristics of Newly Harvested and Long-Term Stored Rice With or Without Annealing[a]

Rice[c]	Maximum Viscosity	Breakdown	Minimum Viscosity	Final Viscosity	Consistency	Ratio[b]	Gelatinization Temperature (°C)
Long-term stored rice[c]							
72-Koshihikari							
Raw	156 (25.1)	31 (17.1)	124 (8.5)	275 (14.3)	150 (6.4)	0.21 (0.12)	81.7 (3.2)
Annealed	244** (1.5)	110** (1.7)	134 (2.5)	235** (2.0)	101** (0.6)	1.09** (0.02)	76.8 (3.3)
77-Sasanishiki							
Raw	142 (2.7)	23 (0.6)	119 (2.1)	249 (5.0)	130 (3.0)	0.17 (0.01)	83.3 (0.5)
Annealed	252** (4.6)	88** (15.0)	164** (10.4)	28 (22.5)2	118 (12.2)	0.76** (0.20)	75.9 (6.5)
86-Yukihikari							
Raw	151 (2.0)	43 (1.0)	108 (1.0)	224 (2.3)	116 (1.5)	0.37 (0.01)	82.8 (1.3)
Annealed	300** (1.5)	156** (1.0)	144** (1.2)	251** (1.5)	108** (2.1)	1.45** (0.02)	68.9** (0.7)
Newly harvested rice[d]							
96-Koshihikari							
Raw	198 (13.9)	122 (14.5)	76 (1.2)	139 (5.3)	63 (4.6)	1.96 (0.36)	62.3 (1.3)
Annealed	241** (3.5)	134 (1.7)	107** (1.7)	180 (0.6)	73* (1.5)	1.85 (0.06)	68.8** (0.5)
96-Sasanishiki							
Raw	185 (1.0)	116 (1.2)	69 (0.6)	131 (0.6)	61 (0.6)	1.89 (0.00)	60.5 (1.2)
Annealed	205** (5.0)	98** (2.1)	107** (3.0)	184 (5.0)	77** (2.0)	1.89 (0.00)	67.1** (0.4)
96-Yukihikari							
Raw	178 (2.5)	111 (2.5)	67 (0.0)	119 (0.0)	52 (0.0)	2.14 (0.05)	61.3 (1.2)
Annealed	187 (6.7)	86** (2.5)	101** (4.6)	181 (7.2)	80** (2.7)	1.07** (0.02)	66.4* (2.5)

[a] Measured in Rapid ViscoAnalyser units (RVU) unless otherwise indicated. Mean values for three replicates ± standard deviation (in parentheses). * = $P < 0.05$, ** = $P < 0.01$.
[b] Breakdown-consistency ratio.
[c] Harvested in 1972, 1977, and 1986.
[d] Harvested in 1996.

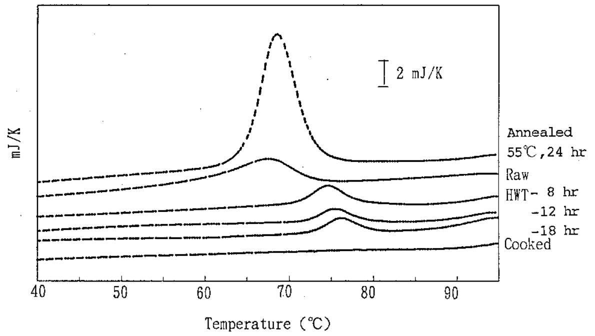

Fig. 3. Differential scanning calorimetry patterns of raw and hot-water-treated rice.

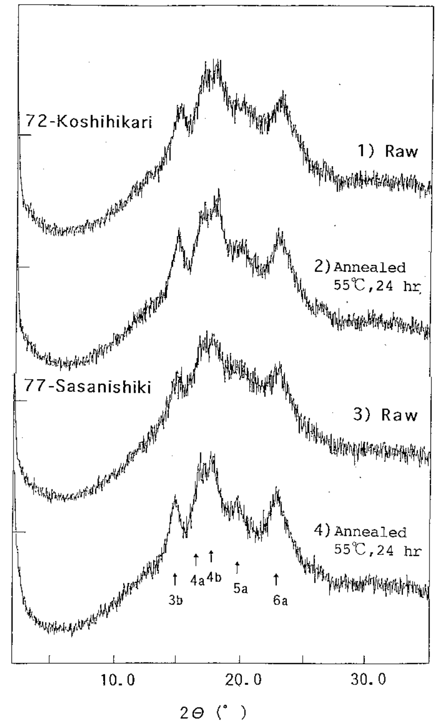

Fig. 4. X-ray diffraction intensity diagrams of raw and annealed long-term stored rice flours.

storage period and temperature may be correlated with the degree of changes in gelatinization characteristics of stored rice. We propose that gelatinization characteristics of rice grains change not only according to their amylose content but also according to their post-harvest time-temperature history.

Gough and Pybus (1971) reported both an increased gelatinization temperature and a narrower gelatinization temperature range as a result of annealing. Jacobs et al (1995) also obtained RVA curves of native and annealed starches for potato, pea, wheat, and rice, and reported that viscosity development was only slightly increased for rice starch and annealing increased the viscosity during the cooling phase for all starches. Our results on long-term stored rice, however, showed new effects of annealing such as decreased gelatinization temperature, final viscosity and consistency, and increased maximum viscosity, breakdown, peak time, and breakdown-consistency ratio. These changes might have occurred due to several factors such as contribution of a starch granule-associated protein (Hamaker et al 1991) or changes in cell wall components (Shibuya and Iwasaki 1982) in addition to the changes in the rice starch itself. Considering the different effects of annealing on newly harvested and long-term stored rice with regards to gelatinization characteristics, we hypothesized that annealing leads to optimum or native crystalline conditions of starches similar to those just after the grain-filling period.

DSC Patterns of Raw and Treated Rice

Figure 3 shows the DSC patterns of raw and treated rice. Cooked rice showed no peak because it received the highest heat treatment in an automatic electric cooker. Hot-water-treated rice for 8, 12, and 18 hr showed smaller peaks in the higher temperature region. The endothermic heat decreased to 42–12% that of raw rice in inverse proportion to heating time. Peak temperatures (T_p) also shifted to higher regions in inverse proportion to heating time, indicating that the starch granules remained in an ungelatinized state even after hot water treatment at 75°C for 18 hr. Annealed rice, however, showed ≈2.7-fold higher enthalpy than raw rice. This increased gelatinization enthalpy after annealing was coincident with the data reported by other investigators (Jacobs et al 1995). These results clearly distinguished between annealing and hot water treatment and were in accordance with the estimation of the gelatinization degree of rice specimens reported previously (Yamamoto 1995).

Changes in X-ray Diffraction Intensity Diagrams

Figure 4 shows the X-ray diffraction intensity diagrams of raw and annealed long-term stored rice. Annealing strengthened the peak heights of the A pattern of long-term stored rice in the X-ray diffraction intensity diagram. These findings confirmed that rearrangement of the crystalline structure of the rice starch could occur during annealing. Changes in intensity for Sasanishiki rice were larger than those for Koshihikari rice, indicating that the effect of annealing may depend on the cultivar and storage period.

CONCLUSIONS

We confirmed that annealing of long-term stored rice stored for 10–24 years recovered gelatinization characteristics similar to those of newly harvested rice as measured by RVA in addition to amylographic findings reported in our preliminary study (Yamamoto et al 1997). Based on the results of the DSC measurements, we confirmed that annealing increased gelatinization enthalpy. We also concluded that the hot-water-treated rice was clearly different from annealed rice. The former is probably partly gelatinized starch and the latter ungelatinized starch with a firm crystalline structure. The X-ray diffraction intensity diagram of annealed rice showed that annealing strengthened peak heights of the A pattern of rice.

Our results on long-term stored rice showed new effects of annealing. This effect of annealing on long-term stored rice grains might be useful for industrial use of such rice.

ACKNOWLEDGMENTS

This study was supported partly by the Nutrition and Food Science Fund of the Japanese Society of Nutrition and Food Science. We thank S. Kitamura of Kyoto Prefectural University, K. Takahashi, and H. Hukada of the University of Osaka Prefecture for their advice and assistance with the DSC measurements.

LITERATURE CITED

Gough, B. M., and Pybus, J. N. 1971. Effect on the gelatinization temperature of wheat starch granules of prolonged treatment with water at 50°C. Staerke 23:210-212.

Hamaker, B. R., Griffin, V. K., and Moldenhauer, K. A. K. 1991. Potential influence of a starch granule-associated protein on cooked rice stickiness. J. Food Sci. 56:1327-1346.

Hizukuri, S., and Nikuni, Z. 1957. X-ray diffractometric studies on starches. J. Agric. Chem. Soc. Jpn. 31:371-374.

Jacobs, H., Eerlingen, R. C., Clauwaert, W., and Delcour, J. A. 1995. Influence of annealing on the pasting properties of starches from varying botanical sources. Cereal Chem. 72:480-487.

Mitsuda, H., Kawai, F., and Yamamoto, A. 1972. Underwater and underground storage of cereal grains. Food Technol. 26:50-56.

Mitsuda, H., Kawai, F., Yamamoto, A., and Ueno, S. 1983. Capsule-packed freezing of cooked rice and glutinous rice cakes. J. Food Sci. 48:1139-1144.

Shibuya, N., and Iwasaki, T. 1982. Effect of the enzymatic removal of endosperm cell wall on the gelatinization properties of aged and unaged rice flours. Starch/Staerke 34:300-305.

Takahashi, K., and Sturtevant, J. M. 1981. Thermal denaturation of streptomyces subtilisin inhibitor, subtilisin bpn, and the inhibitor-subtilisin complex. Biochemistry 20:6185-6190.

Toyoshima, H., Okadome, H., Ohtsubo, K., Suto, M., Horisue, N., Inatsu, O., Narizuka, A., Aizaki, M., Okawa, T., Inouchi, N., and Fuwa, H. 1997. Cooperative test on the small-scale rapid method for the gelatinization properties test of rice flours with a Rapid ViscoAnalyser (RVA). Nippon Shokuhin Kagaku Kogaku Kaishi 44:579-584.

Yamamoto, A. 1995. Physicochemical properties of rice steeped in hot or warm water. J. Food Sci. 60:1307-1312.

Yamamoto, A., Sako, E., Yokotani, I., Hase, M., and Kobayashi, M. 1996. Optimum conditions of warm water treatment of japonica and indica rice. Bull. Koshien Univ. 24(A):81-86.

Yamamoto, A., Tuzuki, K., Hase, M., Yokotani, I., and Kobayashi, M. 1997. Changes in gelatinization characteristics of non-glutinous polished rice of the japonica and indica varieties during storage—Effect of defatting and warm water treatments. Bull. Koshien Univ. 25(A):33-39.

[Received September 3, 1998. Accepted June 17, 1999.]