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A quantification method of retrogradation for cooked rice based on a single isolated peak in X-ray diffraction

Atsuko Nagataki [a, d], Haruo Tomita [b, c], Yuki Himeda [a], Toshikazu Takemori [b], Mika Fukuoka [c, *]

[a] Analysis Research Center KRI Inc., 6-19-9, Torishima, Konohana-ku, Osaka 554-0051, Japan
[b] Energy Technology Laboratories, Osaka Gas Co., Ltd., 6-19-9, Torishima, Konohana-ku, Osaka 554-0051, Japan
[c] Tokyo University of Marine Science and Technology, Department of Food Science and Technology, 4-5-7, Konan, Minato-ku, Tokyo 108-8477, Japan
[d] National Institute for Materials Science, 1-1, Namiki, Tsukuba, Ibaraki 305-0044, Japan

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ABSTRACT

We have established a novel quantification method for the evaluation of cooked rice retrogradation by means of X-ray diffraction (XRD). We have focused on the diffraction peak at 5.5° 2θ, which is a single isolated peak apart from the fingerprint region and corresponds to 1.6 nm periodic structure. This signal in the lower angular region is representative of the retrogradation of cooked rice, which formed wide periodic structure with high water content. Our method does not require special pre-treatment of the sample such as drying/rehydration before measurement, complicated mathematical background correction, or peak separation procedures after measurement for evaluation of the crystallinity from the acquired XRD spectra. Furthermore, this method is very sensitive for the small amount of crystal region in the sample, that is, the retrogradation in the short term after cooking, especially for amylose based structure in rice starch. Thus, our proposed method can be applied for the rapid evaluation of short term starch retrogradation, such as one day after cooking for samples having high water content.

Abbreviations

ΔH	calculated enthalpies
DSC	differential scanning calorimetry
Koshi	name of rice Koshihikari
Milky	name of rice Milky Qween
NMR	nuclear magnetic resonance
PES	Polyethersulphone
XRD	X-ray diffraction
Yume	name of rice Yume-Jissyoku

1. Introduction

Many analytical methods, such as differential scanning calorimetry (DSC) (Biliaderis et al., 1980; Donovan, 1979; Kugimiya et al., 1980, Kugimiya and Donovan, 1981; Nakazawa et al., 1984; Wang et al., 2015; Wootton and Bamunuarachchi, 1979), X-ray diffraction (XRD) (Wang et al., 2015), and nuclear magnetic resonance (NMR) (Teo and Seow, 1992; Wang et al., 2015), have been applied to the evaluation of gelatinization and retrogradation of starches, particularly to quantification of the degree of gelatinization and retrogradation. Concerning evaluation of the crystalline structure of starch, XRD is the most commonly used analytical method and X-ray powder diagrams have been recorded for over 90 years (Herzog and Jancke, 1920; Sponsler, 1922). Four types of XRD diagrams have been recognized for native starch, namely A, B, C, and V (Buleon et al., 1997, 1998; Katz and Itallie, 1930; Kreger, 1946, 1951; Zobel, 1988a,b; Zobel et al.,1988), depending on the botanical origin. Most starches give either A or B-type pattern, while C is less frequent and V is very rare. The crystal structure of a typical native cereal starch, such as wheat starch (Lionetto et al., 2005) or rice starch (Wani et al., 2012), shows A-type pattern. However, the crystalline structure of cereal starches formed by aging or retrogradation shows A or B-type pattern, depending on the water content in the system and the storage temperature. In particular, systems with high moisture content stored below room temperature show B-type patterns (Wang et al., 2015).

* Corresponding author.
E-mail address: fukuoka@kaiyodai.ac.jp (M. Fukuoka).

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The crystallinity evaluation method was reported by Wakelin et al. (1959) and hereafter this method is widely applied. According to this method, an acquired diffractogram pattern is subtracted the amorphous halo and is separated into several discrete diffraction peaks originated in crystal part, and then crystallinity value is obtained from the intensity of these separated peaks. This method has also been applied for the evaluation of starch retrogradation. Frost et al. (2009) determined the initial crystallinity and monitored the gelation and retrogradation of high-amylose thermoplastic starch that is used to produce films. However, this method is very complicated, ambiguous, and depending on the fitting procedure.

In this report, we proposed an innovative quantification method for the retrogradation of the cooked rice, by focusing on the low-angle peak at 5.5° of XRD which is a single isolated peak from the crystalline fingerprint. This peak corresponds the recrystallized parts with wide periodic structure of the starch under the water rich system, and generally observed in the XRD pattern of B-type starch, potato starch, maize starch of high amylose content (Buleon et al., 2007; Frost et al., 2009), the extruded resistance starch fraction of gelose (derived from high amylose maize starch) (Amparo et al., 2007) and in most case, retrograded starch presents (Wang et al., 2015). To evaluate the degree of crystallinity and retrogradation, it is common to use crystalline fingerprint region of a higher diffraction angle. An analytical method that uses the low-angle peak utilized herein has not been reported previously. Furthermore, although the XRD method is wildly used for evaluation of crystalline structure of starch, there are no reports that the retrogradation of cooked rice was measured directly using XRD without any treatment. According to our method that is using this low-angle peak of XRD, we can evaluate the retrogradation of starches in edible states containing the high moisture content without any pre-treatment, such as dehydration and drying procedures.

Here, we showed the results for cooked rice of four species having the different amylose/amylopectin ratio. DSC measurement was conducted to verify our novel quantification method. In addition, to confirm the thermal behavior of this recrystallize structure, in situ XRD measurement was applied over a sample temperature range of 30–75 °C.

2. Materials and methods

2.1. Rice samples

Four species having different amylose/amylopectin ratios were examined in this work, as shown in Table 1. Amylopectin content increases in the order: Milky Queen (abbreviated hereafter as Milky), Jasmine, Koshihikari (Koshi), Yume-Jissyoku (Yume). Yume is developed especially for patients with diabetes and has the lowest amylose content on the market. The amylose/amylopectin ratio was measured using a Megazyme kit (Megazyme) produced by Megazyme International.

2.2. Hydrothermal treatment (cooking conditions) of rice

Raw rice (300 g) was washed 3 times by hand and strained adequately in the quite same manner for each sample. Soon after, deionized water (500 g) was added to the washed rice. The rice was soaked for 1 h at room temperature (25 °C) and then heated with a rice cooker (SR-SX101, Panasonic, Japan). The water content of the cooked rice was controlled at 64 ± 1.9 wt%.

2.3. Aging conditions of the cooked rice

The cooked rice was ground to paste under a high humidity atmosphere in a glove box to avoid water evaporation. The paste was molded for XRD measurement and the thickness was adjusted accurately to 1 mm. The molded sample was covered by Mylar 3399N010 (made of polyethersulphone and purchased from Rigaku Corp., Tokyo, Japan) and water evaporation was strictly avoided during measurement and aging. For DSC measurement, the paste was put into a large volume stainless steel capsule (Part No. LVC0319-0218). Then, each prepared paste sample was stored at 5 °C for 1, 3, 4, and 5 days in a refrigerator or at −20 °C for 4 days in a freezer.

2.4. Wide range X-ray diffraction measurement

XRD spectra were acquired on an X-ray diffractometer (SmartLab, Rigaku Corp., Tokyo, Japan) with a scintillation detector. The scan conditions were as follows: X-ray source; Cu-Kα (45 kV,

Table 1
The characteristics of used samples and results of XRD peak area (unit:cps· deg) and DSC measurement.

	Milky- Queen (Milky)	Jasmine	Koshihikari (Koshi)	Yume- Jissyoku (Yume)
Amylose/Amylopectin Ratio	4/96	10/90	13/87	23/77
Starch Content (%)	77.2	74.5	76.4	74.3
Water Content in raw granule (%)	13.1	13.5	14.3	12.3
Others (%)	9.7	12.0	9.3	13.4
	Milky	Jasmine	Koshi	Yume
XRD peak area at 5.5° (Unit:cps·deg)				
As cooked	N.D	N.D	N.D	N.D
Aged				
1 Day at 5 °C	819	923	1194	1621
3 Days at 5 °C	2780	2634	2615	2360
4 Days at 5 °C	2764	2643	2921	2503
5 Days at 5 °C	2918	3126	3138	3545
4 Days at −20 °C	N.D	N.D	N.D	N.D
DSC experiment				
As cooked				
Enthalpy Δ*H* (J/g)	N.D	N.D	N.D	N.D
Aged (4 Days at 5°C)				
Enthalpy Δ*H* (J/g)	5.8	4.3	5.8	3.0
On set Temperature (°C)	35.1	35.0	35.0	37.6
End set Temperature (°C)	61.3	60.1	61.1	59.1
Peak Top Temperature(°C)	52.2	50.9	49.8	50.7