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Factors Affecting Gelatinization Temperature of Rice Starch

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Abstract

Factors affecting gelatinization temperature of rice starches from different varieties were investigated. Birefringence end-point temperature(BEPT), amylose content, granule size distribution and degree of crystallinity of rice starches showed the significant varietal differences at α =0.01. Susceptibility of the granule to gelatinization was dependent mainly on the degree of crystallinity, as indicated by the significant positive correlation between BEPT and the relative crystallinity(r=0.67, $p<0.01$). However, granule size distribution did not affect the GT(gelatinization temperature) range, nor did amylose content of rice starch, which was confirmed by the correlation coefficients and the scanning electron microscopy(SEM). SEM also confirmed that there is no relationship between the size and the shape and the amylose content of the rice starch.

Key words : gelatinization temperature, amylose content, granule size, degree of crystallinity

INTRODUCTION

Gelatinization temperature is one of the most important starch characteristics. Although gelatinization temperature seems to have little relation to the palatability characteristics of table rice[1], it may have some influence on the cooking quality of rice (i.e., cooking time), and on the processing quality of rice. Beachell and Stansel[2] noted that varieties suitable for parboiling and canning and for quick-cooking processing have an intermediate gelatinization temperature ; varieties with low gelatinization temperature, regardless of their amylose content and setback viscosity, are considered unsuitable. Low-gelatinization temperature rices are preferred by brewers and cereal manufacturers using diastatic digestion in their process. A low gelatinization temperature allows complete liquefaction of starch before thermal inactivation of the enzyme can occur[3].

Also, gelatinization temperature seems to have some relation to the palatability characteristics of products made from waxy rice, such as rice cakes made in Japan and in the Philippines[4]. Therefore, it is interesting to understand which factors affect the gelatinization temperature of starch.

Gelatinization of starch is a hydrothermal process. Therefore, the conditions during gelatinization and the physicochemical properties of starch itself may affect the extent and temperature of gelatinization. If standard conditions for gelatinization during cooking are fixed, the extent and temperature of gelatinization of starch will be governed by varietal differences in physicochemical properties of starches, such as granule size, degree of crystallinity, and amylose content. Because of contradictory and/or insufficient evidence on the effect of granule size, degree of crystallinity and amylose content on gelatinization characteristics, these factors require further investigation.

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MATERIALS AND METHODS

Materials

Rice starches were isolated by alkali extraction of protein using cold 0.2% sodium hydroxide solution to minimize the starch damage from twelve varieties of nonwaxy rices[5]. All the varieties except Kokuho Rose were obtained from the National Rice Research Laboratory, Beaumont, TX. Kokuho Rose was obtained from the local store, Ames, IA.

Amylose content

Amylose content of rice starch was measured by the potentiometric iodine titration method described by Schoch[6].

Gelatinization temperature range

The gelatinization temperature (GT) range was determined by the percent loss of birefringence (2%~98%) under a polarizing microscope (Leitz Wetzlar, Germany) equipped with a hot-stage using the method described by Watson[7]. The 98% loss-point was taken as the birefringence end point temperature (BEPT).

Degree of crystallinity

X-ray diffraction data were collected on rice starches. Cu-K radiation (λ = 0.154nm, 50 KV, 14MA) was generated by a Picker 2 Theta-Theta diffractionmeter (Picker X-ray Co., OH) with a Ni beta filter. The scan was made from a diffraction angle (2θ) of 4° ~ 36°, using a time constant of 2 second, scanning angular velocity of 0.05°.

The relative crystallinity of starch was measured on the basis of the theory of Hermans and Weidinger[8]. The background (primarily due to the amorphous fraction) was estimated by connecting each point of minimum intensity far apart by a smooth curve, but when any points of minimum intensity were adjacent to each other, some of the points were not joined by a smooth curve (Fig. 1).

The ratio of the area of the crystalline fraction (Ac) to that of total (Ac + Aa) was calculated to offset the differences in the amount of sample used and served as the measure of degree of crystallinity. Relative crystallinity was indicated as the ratio of the degree of crystallinity of the sample to that of Bellemont which has the highest degree of crystallinity.

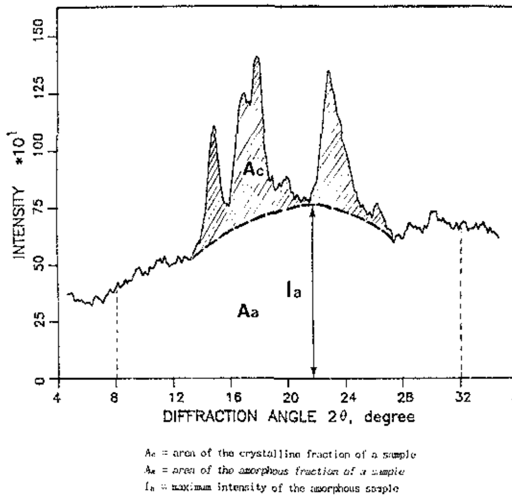

Fig. 1. Determination of degree of crystallinity.

Granule size distribution

The size and shape of starch granule was observed by scanning electron microscope (JSM-35, Jeol Ltd., Japan). From the micrograph, circumference of each starch granule was measured and then converted automatically into the area using a graphic tablet connected to an Apple IIe computer. The diameter of each starch granule was calculated from the area by assuming that each starch granule is basically a circle.

RESULTS AND DISCUSSION

Correlation of BEPT with the granule size

BEPT ranged from 64.7 to 78.8℃ and varied significantly among studied varieties (α =0.01, Table 1).

Gelatinization of the starch usually occurs over a 10℃ temperature range, indicating the heterogeneity of granules in a sample. S-6 showed the narrowest GT range, 9.7℃, and Kokuho Rose the widest, 18.5℃.

The diameter of starch granules ranged from 1.99 to 9.65 μm with an average of 4.85μm (n=1387). The granular starch samples showed the significant varietal differences in their mean sizes (r=0.01, Table 1). The granule size distributions were close to normal distributions ; values from large group of granules are concentrated near the total mean

Table 1. Factors affecting gelatinization temperature of rice starch[a]

Variety	BEPT °C	GT range °C	Amylose %, db	Mean granule[b] size, μm	Granule size range, μm	Relative crystallinity
S-6	64.7	55.0~64.7	19.7	5.03	2.44~8.20	0.81
Pecos	67.3	55.7~67.3	23.0	4.85	3.05~7.53	0.92
Brazos	68.0	58.0~68.0	15.2	4.57	2.42~7.28	0.86
Early Colusa	68.8	56.2~68.8	12.8	4.74	2.99~9.24	0.83
Vista	71.2	59.7~71.2	11.2	5.69	3.03~9.65	0.84
Kokuho Rose	73.5	55.0~73.5	18.2	5.02	2.29~8.69	0.87
Lemont	74.0	61.2~74.0	14.1	4.80	2.34~7.18	0.95
Lebonnet	74.7	60.5~74.7	23.2	4.66	2.51~7.53	0.87
Newrex	74.8	61.5~74.8	27.8	4.49	2.32~7.27	0.85
Bellemont	75.1	58.5~75.1	21.2	4.46	1.99~6.55	1.00
Labelle	75.8	59.3~75.8	20.5	4.95	2.24~7.87	0.97
Century Patna 231	78.8	65.2~78.8	10.4	4.94	2.23~8.49	1.00

a : Mean value of three replicates
b : n=102~140

value of 4.85μm (Fig. 2).

Therefore, comparison of the mean granule size with BEPT is justified.

Mean granule sizes and BEPTs of the samples, however, were not correlated (r=-0.14), nor were their gelatinization temperature ranges measured by the loss of birefringence correlated with their granule size ranges (Table 1). The granule size distribution (Fig. 2) and SEM (Fig. 3) confirmed no

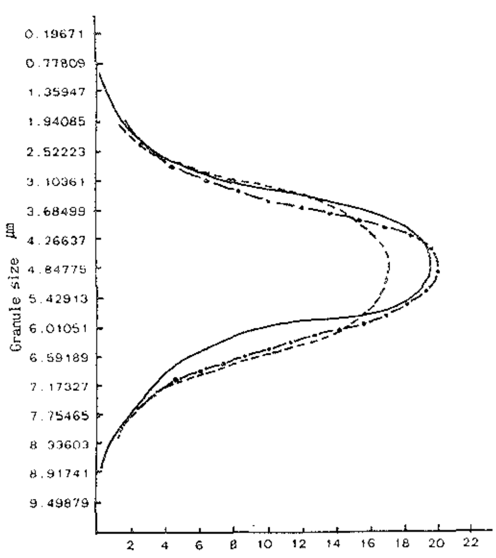

Fig. 2. Granule size distribution of total(—, n=1387) Century Patna 231(---, n=114, the highest BEPT=78.8°C), S-6(- · -, n=130, the lowest BEPT=64.7°C) rice starches.

correlation between granule size and gelatinization temperature.

From microscopic observation, Banks and Greenwood[9] suggested that, in any one population, the larger granules appear to be the most susceptible to gelatinization and vice versa. Similar observations were reported by other investigators[10~12].

On the contrary, differential scanning calorimetry study by Wirakartakusumah[13] showed that larger rice starch granules in one sample were more resistant to gelatinization. Merca and Juliano[4] also reported that samples with high gelatinization temperature had a larger mean granule sizes than those with low gelatinization temperature among waxy and intermediate-amylose rices.

Another group of investigators[15~18] reported no significant effect of granule size on the gelatinization temperature. Goering et al.[16] observed that it appeared as if the large granules were first to lose polarization crosses followed by the medium size granules and finally the small granules, because with the former, loss of contrast was very evident and in many cases it appeared that the granule was swelling and expanding in size. By careful observation at high magnification, however, both large and small granules are seen to lose polarization crosses simultaneously.

The granule size of wheat starches varies from 2μm to approximately 35μm, and its distribution shows a bimodal population of the granules with approximately the same number of granules in each size (small spherical and large lenticular). Unlike wheat

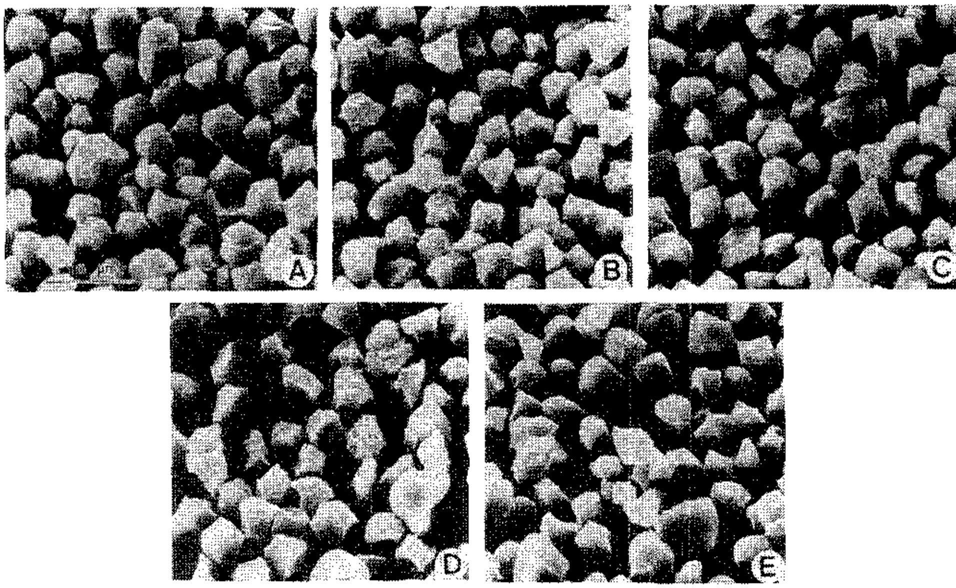

Fig. 3. Sizes and shapes of rice starch granules of Vista (A, the largest mean granule size=5.69μm), Bellemont (B, the smallest mean granule size=4.46μm), Newrex(C, the highest amylose content=27.8%), Century Patna 231(D, the lowest amylose content=10.4%, the highest BEPT=78.8°C), S−6, the lowest BEPT=64.7°C.

starch, the range of granule size in rice starch is narrow (2~10μm) and the distribution is close to the normal distribution. Even though there might be a difference in the susceptibility to gelatinization due to the granule size, varietal difference in granule size may be considered relatively minor compared to the other factors affecting varietal difference in gelatinization temperature of rice starch.

Correlation of BEPT with amylose content

Amylose content ranged from 10.4 to 27.8% (dry basis) and showed the significant varietal difference (α =0.01, Table 1). In a single type of starch, amylose content varies widely, especially in rice : from less than 2% in waxy to 7~33% among nonwaxy varieties.

BEPT was not affected by the amylose content at all (r=0.00). It has been known that BEPT and amylose content are independent properties of starch and are affected by environmental factors, mostly the ambient temperature during grain development[19]. Although the intermediate BEPT type (70~74℃) is rare in waxy (<2% amylose) and low-amylose rices (7~20%), whereas the high BEPT type (74.5~79℃) is rare for intermediate (20~25%) and high-amylose (25~33%) rices, whether this limited occurrence of the gelatinization temperature type and the amylose type of rices is due to genetic coincidence is still unknown at this time.

There have been several observations about the relationship between size and shape and amylose content. According to Greenwood[20], the granule size and shape dependent on the apparent amylose content of the parent starch. This behavior was exemplified by maize starch where the typical angular granule of normal maize (25% amylose) becomes more rounded as the amylose content of 70% is reached, and very bizarre sausage-like granules appear. However, Hood[21] indicated that granule shape and size were not well correlated with amylose content because tapioca, corn, wheat and potato starches all have 15~25% amylose but have and very different granule morphologies. Even though waxy corn and normal corn, waxy rice and nonwaxy rice have very different amylose contents, it is impossible to distinguish between them by their granule size and shape. In Fig.3, Newrex (27.8%) and Century Patna 231 (10.4%), which are very different in amylose content, do not show any difference in their granule size and shape. At the inception of growth in the plant cell, all granules have the same shape. Characteristic shapes develop as the granule grows by apposition at its surface.

Correlation of BEPT with degree of crystallinity

The x-ray diffraction patterns from twelve different varieties of rice starch exhibited the A-type characteristic of most cereal starches[22]. The principal indices of the pattern were at diffraction angles (2θ) of 15.3°(s), 17.1°(s), 18.2°(s), 20.3°(m), 23.5°(s), and 27.0°(w+). These peaks corresponded to interplanar Angstrom spacings of 5.78, 5.17, 4.86, 4.37, 3.78, and 3.30, respectively (Fig. 4).

Because the crystallities in starch granules are very small(100~150 Å), estimates of the degree of crystallinity cannot be rigorously or unambiguously assigned. The theory of x-ray diffraction indicates that very small or imperfect crystals give broadened diffractions. At the border of a crystallite, there is a zone in which the crystallinity changes from a high degree of perfection to a totally disordered structure characteristic of a liquid or amorphous arrangement[23].

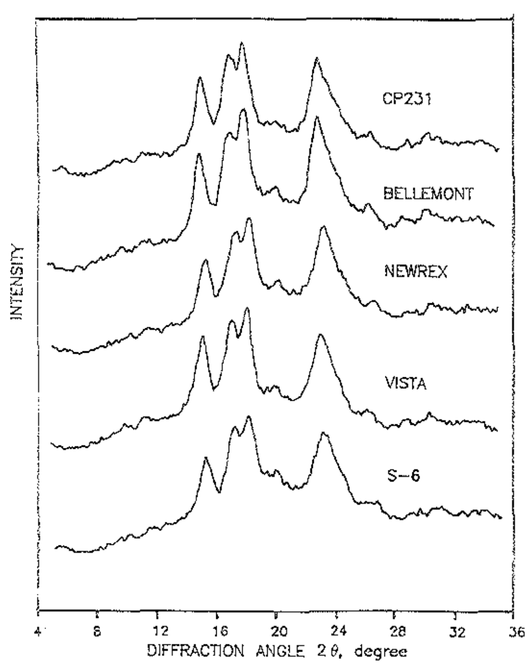

Fig. 4. Representative X-ray diffraction patterns of rice starches.

Crystallinity of starch was significantly correlated with BEPT ($r=0.67$, $p<0.01$). Similar observations were made by Reyes et al.[15], Lugay and Juliano[24], and Juliano et al.[25] Studies with Lintnerized starch supported this relationship between crystallinity of starch and BEPT[26-28]. Lintnerized starch had sharper x-ray diffraction peaks than native starch. BEPT values of starch were shown to be negatively correlated with the amounts of dry substance lost during Lintnerization (Lintnerization loss), regardless of amylose contents. This correlation between crystallinity of starch and BEPT is not surprising theoretically since the starch granule is generally considered as a semicrystalline polymer which contains both crystalline and amorphous regions. The BEPT is thus a measure of the degree of orderliness of the granule organization by the loss of birefringent characteristics of starch granules. The micellar structure of the molecules in the starch granule seems to be the main factor determining the varietal differences in BEPT.

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쌀 전분의 호화온도에 영향을 주는 요인들

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요 약

품종을 달리한 쌀 전분에서 호화온도에 영향을 주는 인자들을 조사하였다. 품종에 따라 호화온도, 아밀로오스 함량, 전분입자의 크기 분포도 및 결정화도는 모두 유의적인 차이를 보여주었다(α=0.01). 전분의 호화온도는 전분입자의 결정화도와 높은 양의 상관관계를 보여주었다($r=0.67$, $p<0.01$). 그러나 전분입자의 크기분포도와 아밀로오스 함량은 쌀 전분의 호화온도에 전혀 영향을 주지 못했으며, 이는 상관관계 계수와 주사 전자현미경에 의한 관찰에 의해 확인되었다. 또한 쌀 전분입자의 성상 및 크기와 아밀로오스 함량과는 아무런 관계가 없음이 주사 현미경 관찰에 의해 확인되었다.