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Correlation of morphological changes of rice starch granules with rheological properties during heating in excess water

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Abstract : Morphological changes of starch granules from 12 different varieties of rice were examined by scanning electron microscopy during heating at 2.5% (w/v) concentration. Rice starch granules proceeded through a similar pattern of progressive morphological changes during heating, regardless of variety. Rice starch granules began to swell radially in the initial stage of gelatinization and then undergo radial contraction and random tangential expansion to form complex structures in the latter stage of gelatinization temperature range. At higher temperatures, starch granules softened and melted into thin flat discs, and then stretched into thin filaments to form three-dimensional networks. These progressive morphological changes were reflected in the changes of swelling power, solubility and amylograph viscosity of starch. During the transition of melting or softening, swelling power, solubility and amylograph viscosity increased rapidly. The time of loss of granular structure of starch depended on gelatinization temperature range. The ratio of amylose to amylopectin was largely responsible for the rate of melting or softening and the fineness of a three-dimensional filamentous network above the gelatinization temperature range. Therefore, both the gelatinization temperature range and amylose content of starch affect the rate of cooking, and amylose content of starch affects the final texture of cooked starch paste(Received December 12, 1991, accepted December 30, 1991).

A major use of processed starch is to give body or thickness to foods where starch is used in relatively low concentrations. Paste viscosity, fluidity and other physical properties of starch paste are of major importance in establishing proper food texture and quality. How the crystalline-amorphous phase transitions and the resultant granule morphology changes that occur during gelatinization affect the development of viscosity and other rheological properties of starch is of particular interest. Aside from swelling of starch granules during gelatinization, the viscosity of the medium also increases. Both the molecular and granular structures contribute to the increase in viscosity.[1]

From the comparative ultrastructural-viscosity studies, Miller et al[2] Allen et al[3] and Hoover and Hadziyev[4] agreed that the exudate (primarily unbranched amylose chains) forms a network that entangles the individual granules, thereby increasing viscosity except in extremely concentrated starch suspension.

Morphological changes of starch granules during gelatinization have been investigated with different kinds of starches. Bear and Samsa[5] indicated that swelling of potato starch granule is tangential rather than isotropic or radial. A radial contraction during swelling cannot be ruled out. From the present knowledge of starch granule structure, it seems likely that the tangential swelling is due to the hydration and lateral expansion of amylopectin

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crystallites. The amylopectin molecule as a whole cannot expand radially, that is, along its molecular axis. Radially oriented amylose molecules, whether in the crystallites or in the amorphous phase, also restrict swelling along their molecular axis.[6]

From the study of lenticular wheat starch granules, Bowler et al[7] concluded that swelling of wheat starch is a two-stage process, which occurs primarily in the plane of the two major axes only. The process involves radial expansion to form a flattened disc followed by tangential expansion to produce a complex puckered granule. Christianson et al[8] investigated the swelling pattern of the corn starch granules, basically spherical with some granules having faceted sides. Corn starch granules begin to swell radially, then undergo radial contraction and random tangential expansion. They form complex geometrical structures between the range of 67～70℃ unlike the more uniform single-dimensional tangential swelling of lenticular wheat starch. At higher temperatures, when starch begins to solubilize, corn starch granules lose their distinct ridges and appear to melt into thin flat discs.

There have been few investigations on the morphological changes of rice starch which is similar to corn starch in shape and much smaller in size.

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 rices.[9] 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.[10]

Gelatinization temperature range

The gelatinization temperature 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 Waston.[11]

Rheological properties

Swelling power and solubility were measured by the method described by Schoch.[12] The viscosity pattern of a 7% (db, w/v) starch suspension was determined using the Visco/amylo/Graph (C.W, Brabender Instruments Inc., NJ) as described by Tipples.[13]

Scanning electron microscopy (SEM)

For observation of rice starch granules with a scanning electron microscope (JSM-35, Jeol Ltd., Japan), several drops were removed from a 2.5% (as-is basis, w/v) starch suspension heated up to one of the various temperatures used for swelling power measurement. The drops were frozen quickly by immersion in melting trichlorodifluoromethane (Freon 113, TED Pella Inc., CA) in liquid nitrogen (m.p. −195.8℃) to avoid the insulation effect of nitrogen bubbles. Each frozen sample was freeze-dried and dried granules were sprinkled sparsely on the specimen stub covered with metal tape.

Results and Discussion

SEM studies were carried out on the uncooked starch suspension and on the starch suspensions heated (65～95℃ at 5℃ intervals) at low concentration (2.5%, w/v) for 30 minutes with minimum stirring. All the samples showed similar patterns of morphological changes of starch granules during heating, regardless of variety. The variations were when and to what extent the starch granules deform, which may depend on gelatinization temperature of starch and the ratio of amylose to amylopectin of starch. Therefore, only the representative micrographs and relative data(Table 1) will be shown here. The progressive morphological changes occurred in swelling of rice starch granules within the range of gelatinization temperature and in exudate entanglement with swollen granules at higher temperatures.

At 65℃, very little swelling of starch granules occurred when compared to uncooked starch granules, even though starch granules absorb water about 2 times of their weight (Swelling Power (SP) =2.94, Fig. 1). It appears that most of the water infiltrated into starch granules at 65℃ might be restricted in the central region of the granule, according to the views of Allen et al.[3] At 70℃, the sizes of the granules increased and started to produce thick ridges at the surface as more water was absorbed (SP=5.25). Rice starch granules began to swell radially below their gelatinization temperature, and then underwent radial contraction and random tangential expansion to form complex structures within the gelatinization temperature range. Sterling[14] postulated that the molecular organization of radially elongated molecules of both the branched and unbranched components is responsible for radial contraction and tangential expansion during gelatinization.

These ridges became thinner and more numerous and then started to collapse as further heating and hydration weaken the granule structure at 75℃, where all the granules lost their birefringent characteristics. At 80℃, the granules appeared to go through a transition of melting or softening, which is even more evident at 85℃ (Fig. 2). During this transition, the swelling power and solubility has been forced to increase rapidly because of loss of granular structure. As temperature was raised to 90℃, the melted granules stretched into threads by tangential expansion and fused together to form a three-dimensional network. At 95℃, they produced thinner filaments and relatively homogeneous matrix structure, which can hold water inside. Therefore, swelling power at 95℃ seems to depend on the water holding capacity of matrix structure as

Table 1. Amylose content and gelatinization temperature (GT) range of rice starches from different varieties[a)]

Variety	Amylose %, db	GT range[b)] ℃	BEPT ℃
Labelle	20.5	59.3~75.8	75.8
S-6	19.7	55.0~64.7	64.7
Brazos	15.2	58.0~68.0	68.0
Lebonnet	23.2	60.5~74.7	74.7
Century Patna 231	10.4	65.2~78.8	78.8

[a)]Mean value of three replicates.
[b)]2% birefringence loss-98% birefringence loss (BEPT).

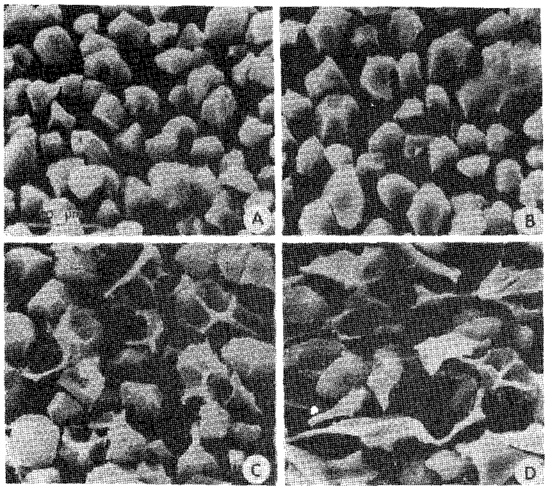

Fig. 1. Uncooked rice starch granules (A), and starch granules cooked in a 2.5% (w/v) suspension of Labelle for 30 min at 65°C (B), 70°C (C), 75°C (D).

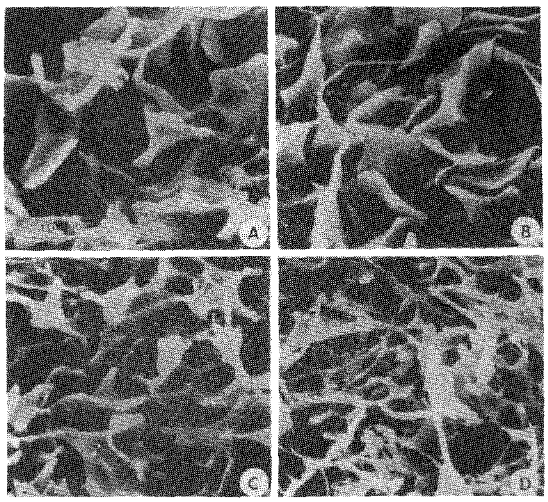

Fig. 2. Starch granules in a 2.5% (w/v) suspension of Labelle for 30 min at 80°C (A), 85°C (B), 90°C (C) and 95°C (D).

well as the water binding capacity of starch molecules by hydrogen bonding. These morphological changes differ from those observed in the lenticular granules of wheat starch[7] and are similar to those in the corn starch granules.[8] This may indicate that granule shape reflects the molecular organization of amylose and amylopectin chains within the granule.

To show the variations in morphological changes among varieties which are related to the differences in swelling power, solubility and amylograph viscosities, representative SEMs of starches with different amylose content and gelatinization temperature

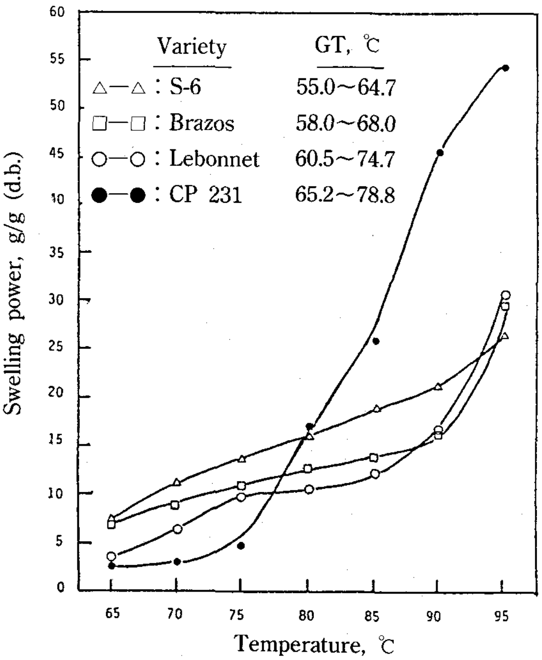

Fig. 3. Swelling patterns of starches from different varieties of rice (2.5% (w/v), 30 min).

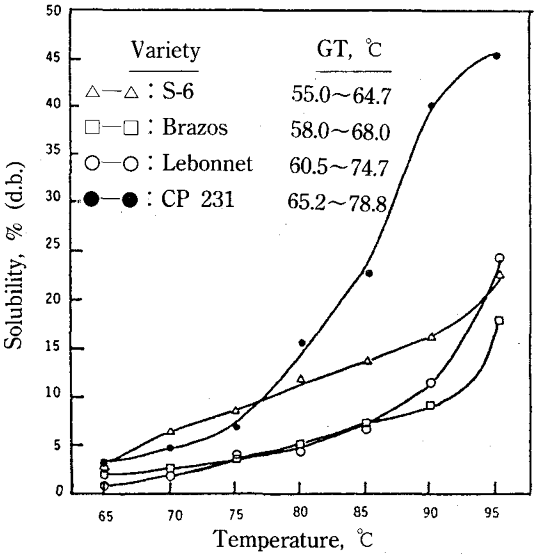

Fig. 4. Solubility patterns of starches from different varieties of rice (2.5% (w/v), 30 min).

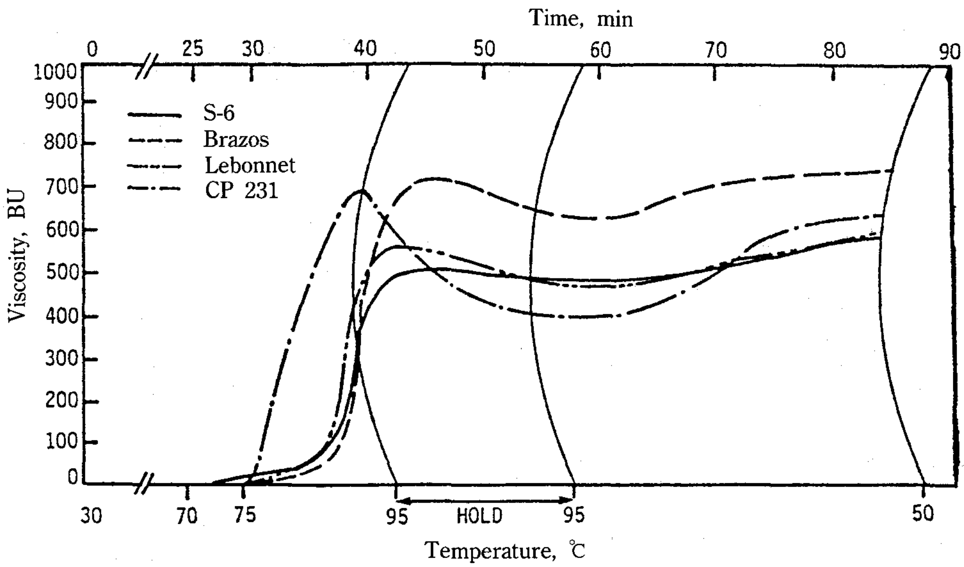

Fig. 5. Amylograph viscosity pattern of starches from different varieties of rice (7% (w/v), db).

ranges are presented (Table 1 and Fig. 6~9). At 65℃, starch granules of S-6 and Brazos with low gelatinization temperature have already swelled and started to collapse, whereas those of Lebonnet and Century Patna 231 showed little swelling and still maintained their characteristic granular shape (Fig. 6). Susceptibility of the granule to change as a result of heat and moisture treatment is dependent on the degree of crystallinity of starch granule. Especially, Century Patna 231 showed some extragranular material solubilized from starch granules without any swelling of starch granules themselves. This observation is well correlated with the higher solubility value compared to swelling power of Century Patna 231 at this temperature (Fig. 3 and 4).

As the temperature increased to 75℃ (Fig. 7), S-

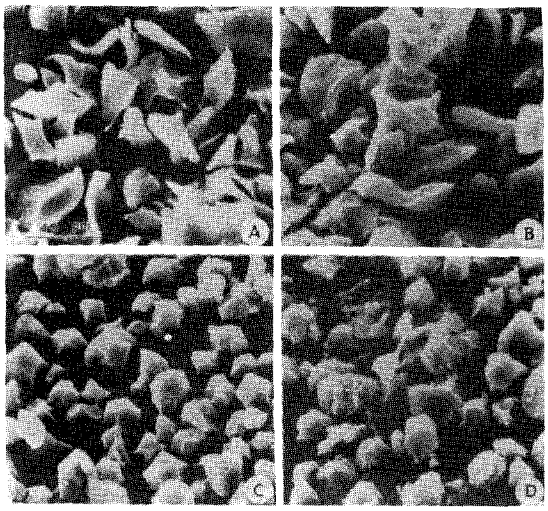

Fig. 6. Starch granules cooked at 65°C for 30 min in a 2.5% (w/v) suspension of S-6 (A), Brazos (B), Lebonnet (C) and Century Patna 231 (D).

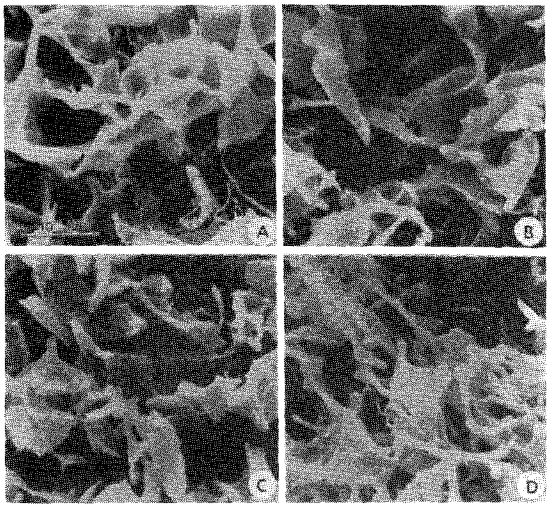

Fig. 8. Starch granules cooked at 85°C for 30 min in a 2.5% (w/v) suspension of S-6 (A), Brazos (B), Lebonnet (C) and Century Patna 231 (D).

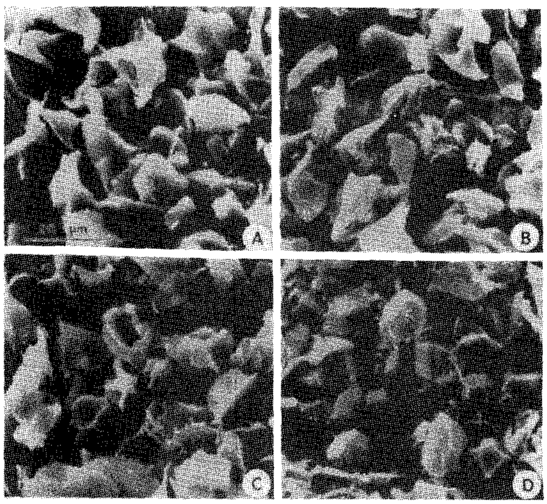

Fig. 7. Starch granules cooked at 75°C for 30 min in a 2.5% (w/v) suspension of S-6 (A), Brazos (B), Lebonnet (C) and Century Patna 231 (D).

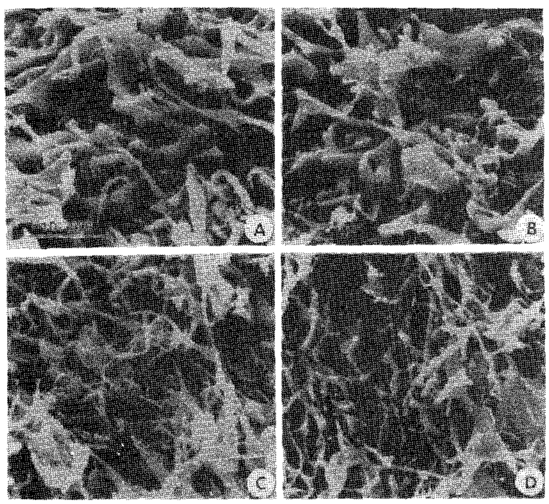

Fig. 9. Starch granules cooked at 95°C for 30 min in a 2.5% (w/v) suspension of S-6 (A), Brazos (B), Lebonnet (C) and Century Patna 231 (D).

6 and Brazos granules underwent progressive changes in their configuration. By this temperature, however, Lebonnet granules had lost nearly all their original shape, which agreed with the loss of their birefringences. In the case of Century Patna 231, about half of the granules still maintained their shape and showed little swelling, but the rest underwent some melting. This observation confirmed that 75℃ is about the midpoint of the gelatinization temperature range of Century Patna 231. This abrupt change in the structure of Century Patna 231 granules is related to the rapid increase of amylograph viscosity(Fig. 5) after all the starch granules swell to collapse. Once starch granules start to lose their original shape and collapse, the rate seems to be affected primarily by amylose content (Fig. 8). At 85℃, Century Patna 231 granules, with low amylose content, melted faster and produced thinner filaments more quickly than any others. This correlates well with their rapid increase in swelling power (Fig. 3), solubility (Fig. 4), and amylograph peak viscosity (Fig. 5). At 95℃, a thinner and more extensive filamentous network structure was developed with increased hydrothermal stress (Fig. 9). The more fragile and lacy appearance of Century Patna 231 at 95℃ explains why, with the shearing force of the amylograph, the swollen granules were broken down more rapidly than those of the other varieties, causing a greater decrease in viscosity (Fig. 5).

The amylograph viscosity curves have been explained by the morphological changes that occurred during heating. Schoch[15] proposed the theory that viscosity developed as a result of the swollen granules restricting the flow of the suspension. However, this does not take into account the extensive extragranular starch network which was observed in SEM studies.[2,3,16] Miller et al[2] demonstrated the extent of this extragranular network at low starch concentrations and postulated that it was responsible for viscosity development in low starch concentrations. However, Allen et al[3] indicated that neither of the latter two theories was sufficient to explain the situation in higher starch concentrations. They postulated that the development of viscosity was a result of the interaction of the swollen granules and the extragranular network, since the final image at peak viscosity does not show any identifiable granules. This study supports the result of Allen et al.[3]

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가열 조리시 쌀 전분 입자들의 형태학적 변화와 리올로지 특성과의 관계

이영은 · 엘리자베스 엠 오스만*(한국과학기술원 자연과학연구소, *미국 일리노이 주립대학 식품영양학과)

초록 : 12품종의 쌀로 부터 분리 정제한 전분의 2.5% (w/v) 현탁액을 각각 65℃에서 95℃까지 5℃ 간격으로 30분간 가열 조리한 후, 전분 입자들의 형태학적 변화를 주사현미경으로 관찰하였다. 품종에 관계없이 쌀 전분 입자들은 온도가 증가함에 따라 점진적인 형태학적 변화를 보여주었다. 이들 형태학적 변화는 전분의 팽윤도, 용해도 및 아밀로그라프점성 특성등과 밀접한 연관성을 보였다. 전분 입자로 부터 가용성 물질이 용출되는 것과 팽윤된 전분 입자가 그 자체의 독특한 형태를 잃고 서로 망상구조로 연결되면서 이들 리올로지 특성들의 급격한 증가를 가져왔다. 초기 팽윤 단계에서 전분 입자들의 독특한 구조손실 시기는 각각의 호화 온도에 영향을 받았다. 호화 온도 이상의 높은 온도에서 전분 입자들이 삼차원적 망상구조를 형성하는 정도는 아밀로오스 함량이 감소할 수록 망상구조가 더 세밀해지며, 증가하는 경향을 보였다.