Physicochemical Properties and Gelatinization Kinetics of Covered Barley Starch

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겉보리 전분의 이화학적 특성및 호화기작

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Abstract

Physicochemical properties and gelatinization kinetics of *Ol* barley starch were studied. The granule size was 13-28 μ and the granule shape was oval or circular. Also, *Ol* barley starch had amylose content of 32%. Swelling power and solubility reached to the maximum values of 7.22 and 2.28% at the gelatinization temperature of 90°C. The pasting temperature of starch was slightly higher than those of powder and defatted powder. Most of the increase in light penetration was accomplished from the gelatinization temperature of 80°C to 90°C. The gelatinization reaction of *Ol* barley starch occurred in 2 stages. The activation energy of 1st stage gelatinization reaction was 23.84 *kcal/mole*, whereas activation energies of 2nd stage gelatinization reaction were 33.38 and 72.82 *kcal/mole* around 80°C.

Introduction

Barley is one of staple raw materials in Korea. In recent year, demands for processed barley products such as barley flake have been increasing continuously. Therefore, the elucidation of barley starch chracteristics is essential for making processed barley products which have good palatability, nutritive value, and rheological characteristics.

Up to now, researches on barley have been concentrated on compositional analyses,[1-3] energy requirements on cooking,[4] optimum conditions for making bread and roasted barley,[5,6] hydration processes,[7] and rheological characteristics.[8,9]

In this research, physicochemical characteristics and gelatinization kinetics of covered barley starch were determined to present basic informations for processing covered barley.

Materials and Methods

Starch preparation. 1 *kg* of *Ol* barley grain was steeped with 6ℓ of 0.01 *M* acetate buffer (pH 6.5) at 5°C for 24 hrs. After steeping, *Ol* barley grain was grinded in a blender. The resulted slurry was repititively screen-ed through 120 and 325 mesh standard sieves to obtain purified starch suspension. After centrifugation at 6000 x *g* for 30 mins, the supernatant was decanted and the brown, upper layer of sludge scraped off. The starch was resuspended in distilled water and centrifuged, and the sludge was again removed. White starch layer was air-dried, and passed through 60 mesh sieve.

Preparation of barley powder and defatted barley powder. *Ol* barley grain was milled through 3 staged mill (Brabender Co.) to obtain 60 meshed barley powder. The resulted barley powder was defatted with 4 parts of n-hexane for 2 hrs and washed with the same solvent 3 times (defatted barley powder).

Determination of physicochemical characteristics. Proximate compositions were determined routinely. Blue value and amylose content were analyzed as reported previously.[10] The microscopic examination of starch granule was made at 600 x using Nikon photomicroscope (type 107).[11] Swelling power and solubility were determined by the method of Leach *et al.*.[12] The light penetration of dilute starch suspension was recorded by the increase of transmittance.[13] Pasting properties were chased by Brabender amylograph.

Gelatinization extent. Gelatinization extent was determined according to the previous reports.[14-16] After

gelatinization of 1% starch solution according to time (2-120 mins) and temperature (60-95°C) in rapid amylograph accessory, 5 ml of gelatinized starch suspension was picked up and centrifuged at 3000 x g for 30 mins. 1 ml of supernatant and 0.1 ml of iodine solution (including 4% KI and 1% I₂) were pipetted into 50 ml volumetric flask. After filling-up to the mark, absorbance at 600 nm (X) was determined. Alkali gelatinization of starch was done by mixing 0.5 g of starch, 47.5 ml of distilled water, and 2.5 ml of 10 N KOH and reacting for 5 mins. After centrifugation, the supernatant was treated as described above and the absorbance at 600 nm (X$_e$) was also determined.

$$\text{Gelatinization extent} \atop \text{(G.E.)} = \frac{X}{X_e}$$

where,

X: gelatinization parameter at time t

X$_e$: gelatinization parameter at the end point

Results and Discussion

Physicochemical properties of *Ol* barley starch are presented in Table 1. Amylose content of 32.0% in *Ol* barley starch was slightly higher than 31.7-31.8%, reported in naked barley starch.[9] Blue value was conspicuously high, compared with 0.30-0.37 of rice starch.[17] The granule size was 13-28 μ and the granule shape was oval or circular.[18] *Ol* barley starch showed some striae in microscopic examination. Photomicrographs of *Ol* barley starch about 600 x are shown in Fig. 1.

Table 2 shows swelling power and solubility of *Ol* barley starch. Swelling powers at 60, 70, 80, and 90°C

Table 1. Physicochemical properties of *Ol* barley starch

Moisture (%)	7.82
Ash (%)	0.21
Protein (%)	0.49
Fat (%)	0.26
Amylose content (%)ᵃ	32.0
Blue value•	0.72
Granule size (μ)	13-28
Granule shape	Oval, circular

ᵃ dry basis

were 4.17, 6.06, 6.95 and 7.22, respectively. Although solubility also increased according to the increase in gelatinization temperature, the trend in increase was relatively small, compared with that of swelling power. Swelling power and solubility at 90°C were lower than those of naked barley starch.[19] From this result, it is inferred that cover barley starch has much stronger micelle structure than naked barley starch and the resulting strong binding force within starch granule inhibits the swelling of *Ol* barley starch.[20]

Amylographic characteristics of *Ol* barley starch were compared with those of *Ol* barley powder and defatted *Ol* barley powder (Table 3). Although gelatinization profiles of the mixed powder of barley and wheat were studied by some researchers,[5,21] the report on comparison of pasting properties in starch with corresponding powder and defatted powder has not been found. As described in Table 3, the pasting temperature was lowered in the order of starch, defatted powder, and powder. The
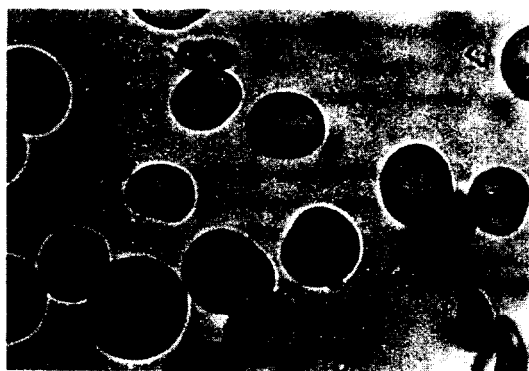
Fig. 1. Photomicrographs of *Ol* barley starch under oridnary light (about 600 x). a: starch granule without staining, b: starch granule stained with 0.3% I₂-KI solution

**Table 2. Swelling power and solubility of *Ol* barley starch**

Temperature (°C)	Swelling power*	Solubility* (%)
60	4.17	1.25
70	6.06	1.14
80	6.95	1.63
90	7.22	2.28

* dry basis

maximum viscosity of 6% *Ol* barley starch was 140 B.U., however, was decreased to 70 and 45 B.U. in case of powder and defatted powder.

The change of light penetration according to the gelatinization temperature in 0.1% dilute *Ol* barley starch suspension is depicted in Fig. 2. It is reported that the dilute starch suspension becomes clear and transparent when gleatinization temperature rises.[22,23] In this experiment, transmittance of gelatinized starch suspension decreased until 75°C, whereas increased abruptly from 80°C. Most of the increase in light penetration was accomplished until 90°C. The initial decrease in light penetration was more conspicuous than the case of millet starch.[19] Mok *et al.*[24] previously reported that the swelling of naked barley starch granule preceded the gelatinization between 55 and 60°C. So, the initial decrease in light penetration seems to be related with the swelling of starch granule.

Gelatinization kinetics of starches have been reported by some researchers.[25,26] Fig. 3 shows changes in gelatinization extents according to gelatinization condition. Most of the increase in gelatinization extent occurred during the initial phase of gelatinization reaction. Over 85°C, the decrease in gelatinization extent was found. This phenomenon displays the decomposition of starch
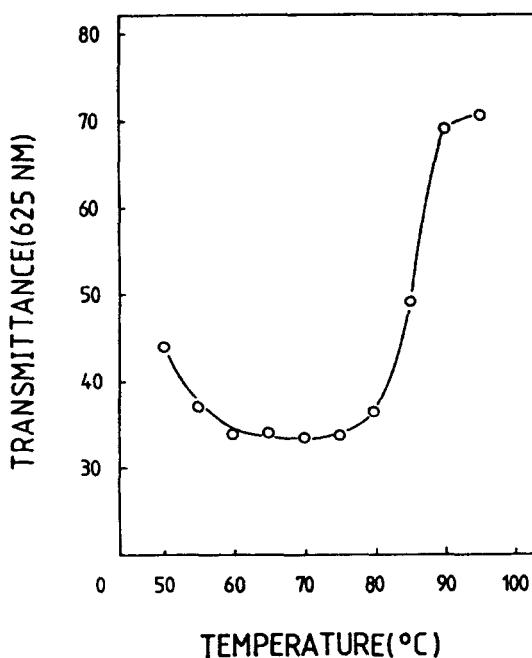
Fig. 2. The effect of gelatinization temperature on the light penetration of 0.1% *Ol* barley starch suspension

granule at this gelatinization condition.

Udani *et al.* suggested the following 1st order kinetic equation for the gelatinization reaction of starch.[27]

$$\frac{dx}{dt} = k(1-x) \quad \text{...(1)}$$

where,

x: gelatinization extent

k: reaction rate coefficient

Equation (1) is transformed to equation (2)

$$\ln 1/1-x = kt \quad \text{...(2)}$$

The relationship between gelatinization time (t) and ln 1/1 − x is depicted in Fig. 4. Fig. 4 clearly shows that the gelatinization reaction of *Ol* barley starch occurs in

Table 3. Pasting properties of *Ol* barley starch, *Ol* barley powder, and defatted *Ol* barley powder

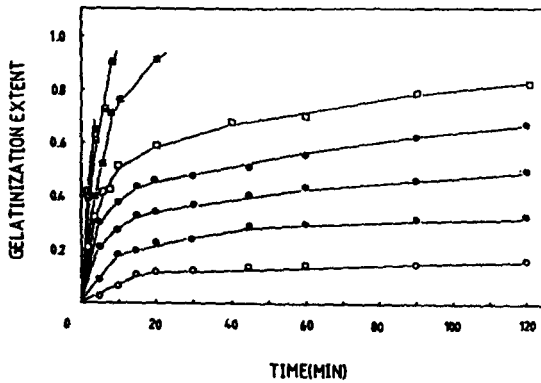| Type	Concn.* (%)	Pasting temp. (°C)	Maximum viscosity (B.U.)	Temp. at max. viscosity (°C)	Viscosity at 95°C (B.U.)	Viscosity at 95°C after 15 min (B.U.)
Starch	6	87.9	140	95.0	140	140
Powder	6	82.5	70	94.2	70	70
Defatted powder	6	84.0	45	95.0	45	42

* dry basis

Fig. 3. Effects of gelatinization condition on gelatinization extents of 1% Ol barley starch suspension. Gelatinization temperature;
○——○ : 60°C, ●———● : 65°C, ◒———◒ : 70°C,
◑———◑ : 75°C, □———□ : 80°C, ■———■ : 85°C,
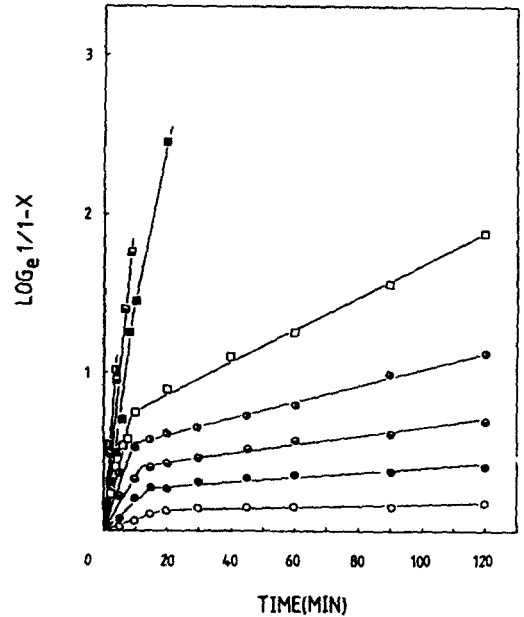▣———▣ : 90°C, ◩———◩ : 95°C.

Fig. 4. The semilog plot of gelatinization time versus $\ln 1/1 - x$. Gelatinization temperature;
○——○ : 60°C, ●———● : 65°C, ◒———◒ : 70°C,
◑———◑ : 75°C, □———□ : 80°C, ■———■ : 85°C,
▣———▣ : 90°C, ◩———◩ : 95°C.

2 stages.[28] Marchant and Blanshard proposed the knots (representing the crystallites and junction zone) and ties(representing the entangled chains in amorphous region) mechanism of starch gelatinization.[29] Accoridng to it, there are two ways to gelatinize the starch granule by a rapid process of cutting the knots or by a slow process of disentangling the ties. If sufficient energies are provided, there is no need for the slow process of disentangling the ties. In this experiment, there only occurred the fast 1st stage gelatinization reaction over 90°C. However, under 85°C, some cut (1st stage gelatinization reaction) and disentanglement (2nd stage gelatinization reaction) occurred concomitantly.

　Table 4 displays gelatinization rate coefficients deduced from Fig. 4. Gelatinization rate coefficients in 1st stage

gelatinization reaction were higher than those of 2nd stage gelatinization reaction. This means that it takes a much longer time to obtain the complete gelatinization under 85°C. Over 90°C, gelatinization rate coefficients of 1st and 2nd stage gelatinization reactions match well. The result of Table 4 was redrawn following Arrhenius equation (Fig. 5). Rate coefficients of 2nd stage gelatinization reaction were plotted as 2 different straight lines around 80°C.

　From the slope of Fig. 5, the activation energy of gelatinization reaction in Ol barley starch was determined (Table 5). The activation energy of 1st stage gelatinization reaction was 23.84 $kcal/mole$, whereas activation energies of 2nd stage gelatinization reaction were 33.38 and 72.82 $kcal/mole$ around 80°C. According to Satter-

Table 4. Gelatinization rate coefficients of Ol barley starch solution

Temperature (°C)	Rate coefficient (min⁻¹)	
	1st stage	2nd stage
60	0.0073	5.0×10^{-4}
65	0.0188	1.5×10^{-3}
70	0.0347	2.9×10^{-3}
75	0.0585	5.1×10^{-3}
80	0.0855	0.0103
85	0.1460	0.0965
90	0.2040	0.2040
95	0.2720	0.2720

Table 5. Activation energy of Ol barley starch solution

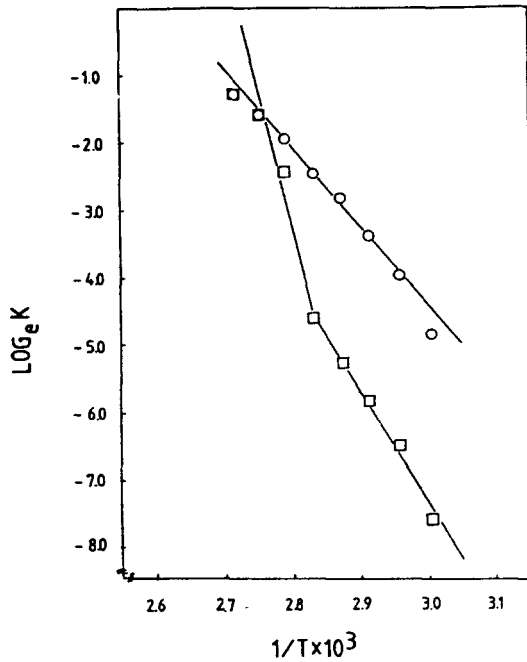| E_a ($kcal/mole$)	
1st stage	2nd stage
23.04	33.38(below 80°C)
	72.82(above 80°C)

Fig. 5. Arrhenius plot of gelatinization rate coefficients
O———O : 1st stage gelatinization reaction,
□———□ : 2nd stage gelatinization reaction.

field,[30] the activation energy observed in diffusion-limited reaction is about one half of the activation energy observed in the case of reaction only. Cooking of rice and barley are typical examples of this heterogenous catalytic reaction. And in these instances, activation energies of cooking decrease by one half as the cooking temperature increases over a certain point where diffusion of water is limiting factor.[15,26,31] In the case of starch suspension, however, values of equivalent activation energy on the gelatinization of starch are not smaller than values of under 10kcal/mole for general diffusion phenomena. Thus, it can be concluded that the diffusion rate of water in starch granule is negligible, and the gelatinization rate is limited by the chemical reaction rate of starch components with water and/or the physical transforming rate such as the melting of starch crystalline regions.[25,32] As shown in Table 4, rate coefficients of 2nd stage gelatinization reaction were increased more conspicuous above 80°C than below 80°C. This fact means that the slow process of starch gelatinization occurs very fast above 80°C than below 80°C, causing more stiff line above 80°C in Arrhenius plot. This results in higher activation energy above 80°C in 2nd stage gelatinization reaction.The activation energy of gelatinization reaction in O1 barley starch was very high, compared with 14.0 *kcal/mole* in rice starch[25] and smilar to that of naked barley starch.[28]

요 약

울보리 전분의 물리화학적 특성 및 호화기작을 구명하였다.

울보리 전분의 크기는 13—28μ였으며, 전분의 모양은 난형이나 원형이었다. 호화온도의 상승에 따라 팽윤도와 용해도는 증가하여 90°C에서 최대치인 7.22와 2.28%에 이르렀다. 울보리 전분에 있어서의 광투과성의 증대는 80°C와 90°C 사이에서 완료되었다. 울보리 전분의 호화반응은 2단계로 나타났으며, 1단계 호화반응의 활성화 에너지는 23.84 *kcal／mole*, 2단계 호화반응의 활성화에너지는 80°C 이하에서는 33.48*kcal／mole*, 그 이상에서는 72.82 *kcal／mole*이었다.

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