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Effects of High Hydrostatic Pressure on Physicochemical Properties of Waxy Rice Starch

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고압처리 찹쌀전분의 이화학적 특성

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국문요약

찹쌀전분의 고압처리시 pH 3～10 조건에서 고유점도는 1.328～1.426 ㎖/g 범위로 원료전분(1.15 ㎖/g)보다 낮았다. 특히, 고유점도는 산성 및 알칼리성 조건에서 감소하였다. 전분의 호화과정 중 열에너지량을 나타내는 호화엔탈피는 pH 3, 4 및 5 조건에서 고압처리한 찹쌀전분이 각각 13.86, 13.47 및 13.42 J/g으로 원료전분(16.3 J/g)보다 낮은 값을 보였다. 찹쌀전분의 호화온도 및 엔탈피 감소는 고유점도가 낮아지는 현상과 일치하였다.

Key words: high hydrostatic pressure, physicochemical properties, waxy rice starch, intrinsic viscosity, differential scanning calorimetry

INTRODUCTION

Starch is the main constituent of grains, which is generally between 60 and 75% of the weight of the grain and provides 70-80% of the calories consumed by humans worldwide. Due to its unique functional properties, it is widely used in industrial and food applications (Thomas & Atwell 1997; Parker & Ring 2001). However, native starch needs to be modified to develop desirable functional properties, such as solubility, texture, adhesion and heat tolerance (Ronald CD 1998). Starch modification can be accomplished through derivatization (etherification, esterification, cross-linking and grafting of starch), decomposition (acid or enzymatic hydrolysis and oxidation of starch) or physical treatment of starch using heat, pressure and moisture.

Chemical modification involves the introduction of functional groups into the starch molecule, resulting in markedly altered physic-chemical properties (Cha et al. 2007; Choi & Kerr 2003; Kim et al. 1999). Extreme treatments (temperature and pressure) can be used as physical modification techniques that gelatinized the starch (Katleen et al. 2009). Pressurization produces unique properties that are different from those of heat-gelatinization, where heat-treatment destroys starch granules, resulting in a transparent solution, but pressure-treatment swells the granules, while maintaining the granular structure (Hayashi & Hayashida 1989). The potential application of high pressure for food processing and preservation has been investigated with growing interest by various researchers as an alternative to traditional heat treatment procedures (Fonberg-Broczek et al. 2005; Knorr et al. 2006; Hendrickx et al. 1998). This technology has several advantages over heat treatment, including better retention of nutritional and functional ingredients in the processed product. High pressure also makes it possible to produce foods with novel textures (Stolt et al. 2001). High pressure affects only secondary and tertiary bonds, which means only large molecules, cell membranes,

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enzymes etc. are denatured. However, primary or covalent bonds are not affected. This means that low molecular weight quality determining components like vitamins, pigments, flavor substances as well as their precursor, which are highly affected by the traditional thermal processing, remain intact. A pressure of 600 MPa applied to starch granules could deteriorate their structure depending on the water content (Mercier et al. 1968). Meanwhile, a lower pressure 300 MPa applied together with acid and heat was shown to cause fast depolymerization of starch (Kim & Hamdy 1987).

In the case of high pressure application of starch, most previous studies attempted to achieve gelatinization at pressures greater than 300 MPa. Thus, the effect of lower high pressure (100 MPa) on evaluated to expand the potential applications of this technology. The objective of this study was to evaluate the effect of HHP treatment on the rheological properties of WRSs and to evalute the potential of using HHP for obtaining starch-based ingredients with novel texture characteristics.

MATERIALS AND METHODS

1. Waxy Rice Starch

Waxy rice starch (WRS, Indica) was purchased from Bangkok Starch Industrial Co.(Nakornprathom, Thailand). All other chemicals used were of analytical grade.

2. High Hydrostatic Pressure (HHP) Treatment

Fifty g of WRS was suspended in 50 ㎖ of distilled water, and the pH of waxy rice starch was adjusted from 3 to 10 using 0.5 N HCl and 0.5 N NaOH. After pH adjustment, waxy rice starch suspensions were vacuum-packed in polyethylene bags (150×250 ㎜). Packed samples were subjected to the vessel unit of the HHP apparatus (UHP machine TFS-2L, Toyo Koatsu., Hiroshima, Japan). The HHP apparatus consists of cylindrical chamber of 12 ㎝ (diameter) × 20 ㎝ (height), hydrostatic pump, pressure controller and process control system (Fig. 1). The samples were treated at a pressure 100 MPa for 24 hr. The temperature of the vessel unit was thermostatically controlled at 30℃ throughout treatment. The WRS treated under HHP was neutralized and then centrifuged by high speed centrifugation at 3,000×g for 20 min. The starch cake was washed 3 times with distilled water and centrifuged again, and then freeze dried.

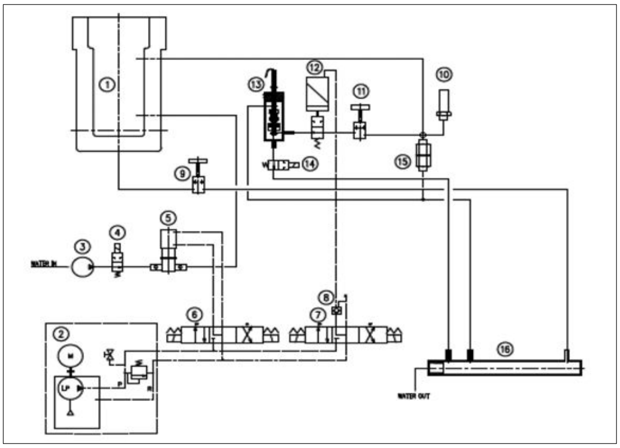


Fig. 1. Schematic diagram of the HHP apparatus. (1) vessel, (2) oil return system, (3) pump, (4) solenoid value, (5) booster pump, (6) solenoid value, (7) solenoid value, (8) pilot check, (9) drain value, (10) safety sensor, (11) relief value, (12) solenoid value, (13) level sensor, (14) solenoid v-alue, (15) safety value, (16) drain pipe.-

3. Intrinsic Viscosity

WRSs were dissolved (0.2-0.28%) in dimethyl sulfoxide (DMSO), held at 100℃ for 4 min, and then filtered through a 0.45 ㎜ Millipore filter. The viscosity of the solutions was measured using a Cannon-Fenske capillary viscometer (size 100; Cannon Instrument Co., State College, PA, USA) at 25℃. Prior to measurement, the solution was placed for 30 min in a 25℃ water bath to equilibrate the temperature. Specific viscosity (η sp) and intrinsic viscosity ($[\eta]$) were determined as follows:

$$\eta_{sp}=(\eta-\eta_s)/\eta_s \quad \text{and} \quad [\eta]=\lim_{c\to 0}\eta_{sp}/C$$

where η is the solution viscosity, η_s is the solvent viscosity, and C is the solution concentration.

4. Differential Scanning Calorimetry (DSC)

The DSC characteristics were measured using a DSC-7 (Perkin-Elmer, Waltham, MA, USA). Starch samples (16 ㎎) were weighed in a large volume stainless steel pan and then distilled water (48 ㎎) was added. The pan was hermetically sealed and heated at a heating rate of 10℃/min and a heating range of 25 to 120℃. An empty pan was used as a reference. The DSC thermogram was analyzed using the Thermal Analysis Pyris Software interfaced with the DSC. The △H and △T values were evaluated from the peak area and the onset point of the endothermic peak of gelatinization at about 60℃, respectively.

RESULTS AND DISCUSSION

1. Intrinsic Viscosity of HHP Treated WRSs

The intrinsic viscosity values of WRSs at different pH values aand HHP treatments are listed in Table 1.

The intrinsic viscosity of HHP treated WRSs ranged from 1.328 to 1.426 mℓ/g and depended on the pH conditions (3 to 10). These value were lower than the intrinsic viscosity of native waxy rice starch (1.15 mℓ/g). The intrinsic viscosities decreased at acidic or alkaline pH. It is well known that hydroxonium ions (H_3O^+) attack glycosidic oxygen atoms and hydrolyse the glycidic linkages during the process of acid thinning. Acid gradually degrades the surface of the starch granule first before entering the inner region.

According to Shon et al. (2005), the rice starch dispersions in a dimethyl sulfoxide (DMSO) solution displayed rheological behaviors similar to those of weak gels. The viscosity of starch pastes changed depending on the pH due to the addition of various sour substances (citric acid, acetic acid, lactic acid, malic acid, tartaric acid and ascorbic acid) to corn starch pastes. The hydrolysis of amylose and a small amount of sour substances caused amylose and amylopectin chains to leach out, which led to an increase in viscosity (Hirashima et al. 2005).

Table 1. Intrinsic viscosity of native and HHP treated waxy rice starches

Starch samples	Intrinsic viscosity (mℓ/g)
Native	1.56 ±0.11[1]
HHP[2] treated at pH 3	1.353±0.14
HHP treated at pH 4	1.426±0.16
HHP treated at pH 5	1.328±0.12
HHP treated at pH 6	1.397±0.13
HHP treated at pH 7	1.408±0.11
HHP treated at pH 8	1.354±0.17
HHP treated at pH 9	1.332±0.15
HHP treated at pH 10	1.357±0.13

[1] All values are mean±S.D. of 3 replicates,

[2] HHP means high hydrostatic pressure.

On the other hand, the intrinsic viscosity of acid thinned starch under high pressure following a combination of acid thinning and high pressure treatment in 1 to 3 passes decreased as much as the viscosity acid thinned the starch for 1 hr or acid starch for 2 hr.

This result shows that the combination of acid thinning and high pressure might be effective for preparing modified starches. According to Stute et al. (1993), most starches display very little swelling and maintain their own granular character such as that observed after heat gelatinization under high pressure treatment. Under high pressure, the pressure acts immediately and independent of the size and the shape of the product, and does not break covalent bonds (Thevelein et al. 1981).

Normally, the intrinsic viscosity is correlated to the molecular weight or size of the material being analyzed. No significant differences were observed between the effect of pressure and pH on WRS (100 MPa and pH 3-10). A pressure of 100 MPa was not sufficient to produce structural changes and therefore, further studies are needed to investigate the disintegration of the granular structure of WRS under the extent pressure-induced condition. Typical type of intrinsic viscosities of WRSs were shown in Fig. 2.

2. DSC Characteristics

The onset temperature and gelatinization enthalpy of native starch and WRSs were listed in Table 2. The onset temperature shifted to lower values in WRSs HHP treated at pH 3 to 5 when compared to that in native starch but increased slightly with an increase in pH from 8 to 10. Gelatinization enthalpy, which

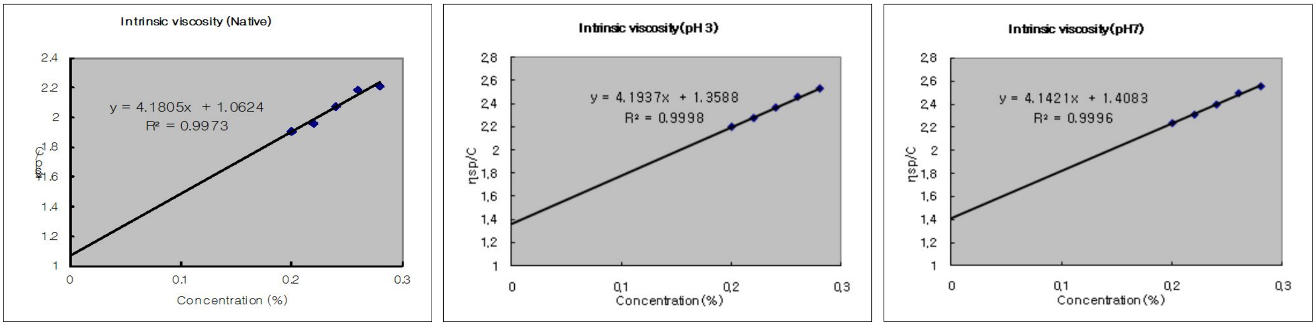


Fig. 2. Intrinsic viscosities of WRS at pH 3, pH 7 and nature WRS.

Table 2. DSC characteristics of native and HHP treated waxy rice starches

Starch samples	DSC characteristics		
	Peak temp. (℃)	Onset (℃)	Enthalpy (J/g)
Native	68.67±0.13[1)]	65.28±0.26	16.31±0.63
HHP[2)] treated at pH 3	77.94±0.21	59.83±0.19	13.86±0.33
HHP treated at pH 4	77.66±0.37	59.72±0.28	13.47±0.86
HHP treated at pH 5	77.87±0.35	59.78±0.16	13.42±0.23
HHP treated at pH 6	78.31±0.11	59.73±0.08	14.73±0.63
HHP treated at pH 7	77.75±0.25	59.86±0.16	14.16±0.53
HHP treated at pH 8	77.69±0.18	59.68±0.11	14.23±0.20
HHP treated at pH 9	77.86±0.44	59.78±0.26	14.24±0.33
HHP treated at pH 10	78.18±0.31	59.95±0.28	14.49±0.85

[1)] All values are mean±S.D. of 3 replicates,

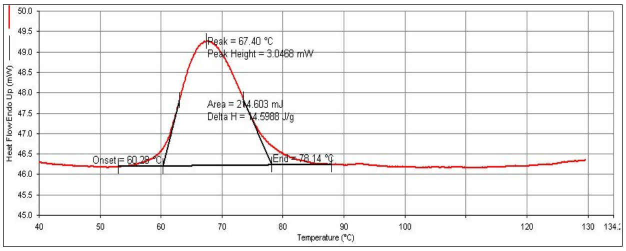
[2)] HHP means high hydrostatic pressure.

represents the amount of thermal energy involved in the gelatinization process, was reduced from 16.3 J/g in native starch to 13.86, 13.47, and 13.42 J/g in WRSs treated at pH 3, 4 and 5, respectively. The onset temperature and gelatinization enthalpy of WRSs under HHP were generally lower than that of native starch (Table 2).

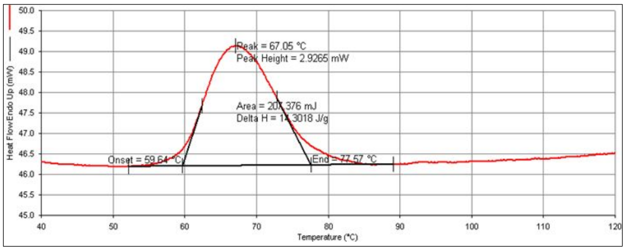
Acid thinning treatment under high pressure was more effective at reducing both the onset temperature and the gelatinization enthalpy of starch. Because of this direct relationship between double helix content and crystallinity, it is thought that leaching of the amorphous region by acid hydrolysis increases starch crystallization and consequently increases both the gelatinization temperature and enthalpy. Enthalpy might be involved in the cleavage of hydrogen bonds and other associative bonding forces among starch molecules, and such bonds must be limited by oxidation and acetylation. This accounts for the reduction of enthalpy following chemical modification (Lawal OS 2004). The decrease in gelatinization temperature and enthalpy are in agreement with the intrinsic viscosity values. Typical DSC thermograms of WRSs were shown in Fig. 3.

CONCLUSION

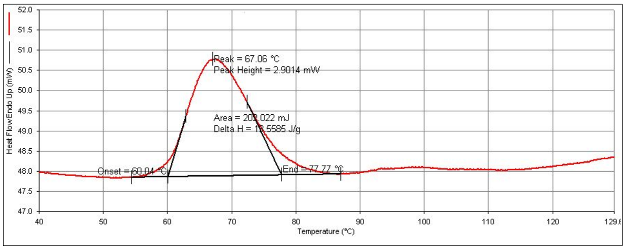
A pressure of 100 MPa was not sufficient to produce structural changes and therefore, further studies are needed to investigate the disintegration of the granular structure of WRS under extent pressure-induced condition. In addition, the result will be applicable for further study of starch modification including microfluidization to assess the value of using physical processing and to develop a fundamental understanding of the relationship between the structure and function of the treated starches.



Native



pH 3



pH 7

Fig. 3. DSC thermograms of native waxy rice starch and waxy rice starches which were HHP treated at 100 MPa for 24 hr.

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