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Pressure Gelatinization of Potato Starch

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ABSTRACT

This article reviews the pressure gelatinization of starch with a special focus on potato starch which is a key food ingredient and an industrial raw material. First of all, the application of high hydrostatic pressure (HHP), as a novel processing parameter, to food processing is briefly overviewed with some historical backgrounds. It has been revealed in the last century that a starch-water mixture can be gelatinized only with HHP: without heating. In the HHP treatment of a starch system, attention should be paid to the ways of compression and difference in the properties between HHP- and heat-gelatinized starches. Physico-chemical changes of various starches after HHP treatment have been studied intensively. However, the behavior of pressure gelatinization has not been studied systematically, since most of the experiments have been carried out at fixed water (or starch) content with only a few treatment pressures. In addition, since potato starch is one of the most pressure-resistant starches, which impose experimental limitations for achievable maximum pressure, pressure gelatinization of potato starch has not been studied sufficiently. Recently, we have treated potato starch-water mixtures of various water (or starch) contents with treatment pressures from 400 to 1,200 MPa, and presented a state diagram of the HHP-treated samples. We expect that the behavior of pressure gelatinization and HHP-induced retrogradation will be understood in more detail with this approach utilizing the state diagram.

Keywords: food processing, high hydrostatic pressure, high pressure, retrogradation, state diagram

Abbreviations: CP/MAS ^{13}C NMR, cross-polarization/magic angle spinning ^{13}C nuclear magnetic resonance; **DSC**, differential scanning calorimetry (-meter); **DTA**, differential thermal analysis; **DTG**, differential thermal gravimetry; **FTIR**, Fourier transform infrared; **HHP**, high hydrostatic pressure; ΔH_{gel}, enthalpy change upon gelatinization measured by DSC; ΔH_{retro}, enthalpy change upon melting of retrograded starch measured by DSC; **RVA**, rapid visco-analyzer; **SEM**, scanning electron microscopy; T_{gel}, onset temperature of gelatinization measured by DSC; **TG**, thermal gravimetry; **UV-Vis**, ultraviolet-visible

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INTRODUCTION

Food processing utilizing high hydrostatic pressure (HHP)

The effect of high hydrostatic pressure (HHP) on biomaterials has been studied, ever since the report on the effect of pressure on the preservation of milk in 1899 (Hite 1899). Nobel Prize Winner, Dr. Bridgeman reported on the coagulation of egg albumen by HHP treatment (Bridgeman 1914). Hite *et al.* (1914) reported on the effect of pressure on microorganisms in the preservation of fruits and vegetables. Since the early reports, however, it was nearly after a century that HHP treatment was first introduced to the food industry. In 1987, Dr. Hayashi (then-associate professor at Kyoto University) had made a suggestion in a Japanese journal to introduce HHP as a novel processing parameter to food processing (Hayashi 1987), and, thereafter, research and development on HHP food processing accelerated in Japan, being supported by the Ministry of Agriculture, Forestry and Fisheries, Japan. In 1990, the first HHP-treated foods (fruit jams) were realized in Japan, and other HHP-treated foods followed in the world. Nowadays, various HHP-treated foods have been put on the market in the world: jams, hams and sausages, instant rice packs, shucked oysters and clams, smoothies (fruit beverages), and so forth (Rovere 2002).

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Invited Review

Fig. 1 Schematic diagram of heat gelatinization of a starch granule (**A**) Starch granule suspended in water: cross section of the granule presents lamellar structure of concentric ellipsoids. (**B**) Heating induces the swelling and disruption of the granule. Molecular motion is accelerated by heating and the lamellar structure is lost by swelling. (**C**) Further heating leads to the complete gelatinization where the granular shape is not observed. (**A**-**C**) Figures re-printed from **Yamamoto K, Fukami K, Kawai K, Koseki S** (2006) (Pressure gelatinization of starch). *Food and Packaging (Shokuhintoyouki)* **47**, 448-456, with kind permission from the Institute of Canning Technology, ©2006.

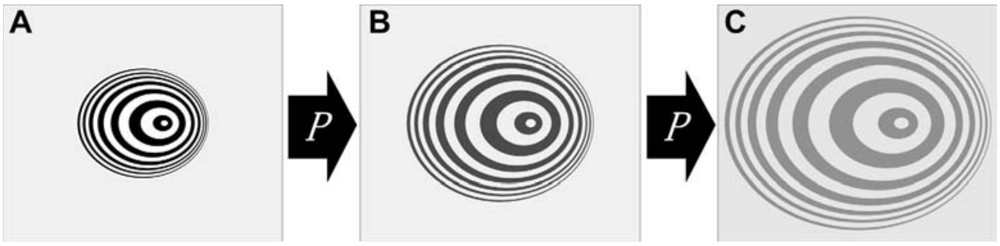

Fig. 2 Schematic diagram of pressure gelatinization of a starch granule as described by Yamamoto *et al.* (2006). (**A**) Starch granule suspended in water. (**B**) The starch granule can be partially gelatinized by HHP with swelling of the granule induced. (**C**) Completely pressure-gelatinized starch granule can retain the granular shape.

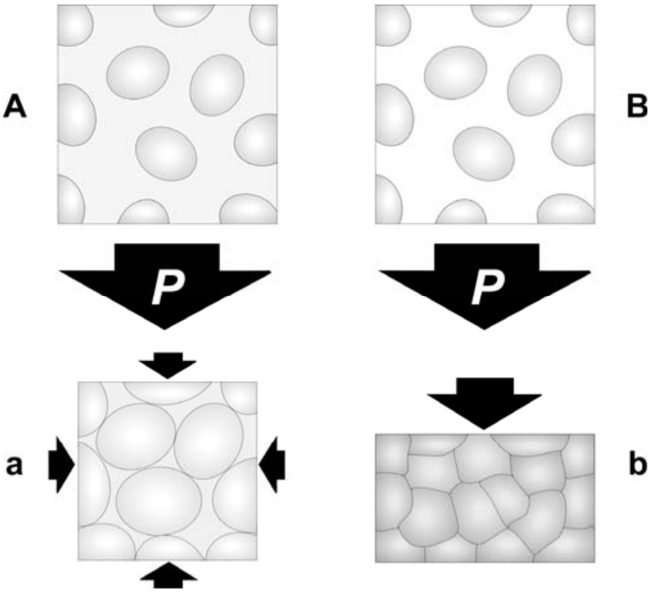

Fig. 3 Isotropic and anisotropic compressions of starch as described by Yamamoto *et al.* (2006). (**A**) to (**a**): Isotropic compression: starch granules suspended in water (pressure medium) can be compressed isotropically and homogeneously via the pressure medium. It can be indicated that water of lower density would permeate the starch granules of higher density and uniformize the density. (**B**) to (**b**): Anisotropic compression: when starch granules in the absence of water are compressed, especially one-dimensionally, the granules are first of all packed due to the high compressibility of air surrounding the granules. Then the pressure is transmitted anisotropically via the loosely-packed granules. Once the granules are tightly packed while the granules are distorted to fill the space among the granules, the pressure is isotropically transmitted via the tightly-packed starch granules as pressure media.

Gelatinization of starch by heat or HHP

Effect of HHP on starch, a key food component, has increasingly studied. HHP can induce gelatinizaion of starch. However, the mechanism of HHP-induced gelatinization is likely to be somehow different from heat-induced one.

When starch is heated in the presence of water, irreversible order-disorder transition occurs and gelatinization of starch is observed. This phenomenon is termed gelatinization or heat gelatinization. During the gelatinization, starch granules absorb water and swell, and concentric ellipsoidal lamellar structure named growth rings and crystalline features are lost (**Fig. 1**). For the gelatinization, water is indispensable and more than 14 water molecules per one glucose molecule are required for a complete gelatinization (Donovan 1979). When gelatinized starch is preserved, for instance in a refrigerator, crystals are newly formed and the starch gel is solidified. This phenomenon is termed retrogradation (Hoover 1995).

On the other hand, when starch-water mixture is treated with HHP, gelatinization of starch is observed. We call this phenomena "pressure gelatinization". In pressure gelatinization, starch granules can swell while maintaining the granular shape and lamellar structure (**Fig. 2**) (Stute *et al.* 1996; Stolt *et al.* 2001).

PRESSURE GELATINIZATION

Anisotropic and isotropic compressions of starch

In the HHP treatment of samples in powder form such as starch granules, special attention should be paid to the manner of compression, either isotropic or anisotropic. In the case where starch granules are suspended in pressure medium such as water in a pouch, external pressure compresses the pouch and the pressure is transmitted isotropically to individual starch granules through the pressure medium (**Fig. 3a**). On the other hand, in the case where starch granules without pressure medium are put in a cylinder and directly and one-dimensionally compressed by a piston, the granules are compressed anisotropically until the granules are distorted and completely packed (**Fig. 3b**).

In the early studies on HHP treatment of starch, there was no viewpoint to utilize HHP actively for the gelatinization: neither the utilization of HHP-treated starch as a novel food ingredient in food industry nor the study of pressure gelatinization behavior in HHP-treated starchy foods. Rather, the objective was to study the effect of pressure on the mechanical damages of starch in the milling process. In the ball milling of starch (Brown and Heron 1879), for instance, anisotropic high pressure impact can be generated when the

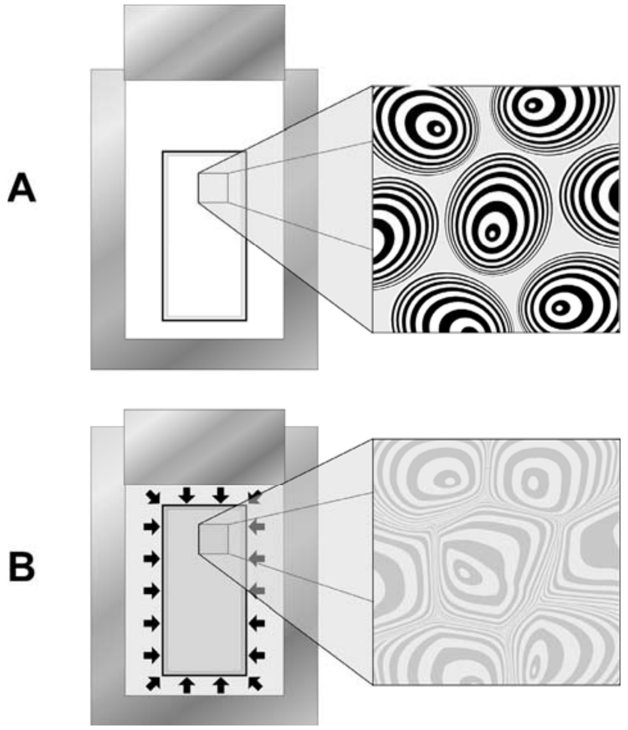

Fig. 4 Pressure gelatinization of starch-water mixture by isotropic compression as described by Yamamoto *et al.* (2006). (**A**) Pouched starch-water mixture. (**B**) Pressure-gelatinized starch granules by isotropic compression via liquid pressure medium retain the lamellar structure while the granules are tightly packed with distortion. At high starch contents (i.e. low water contents), the granules are swollen and packed tightly. At low starch contents (i.e. high water contents), the granules are swollen with the granular shape retained as shown in **Fig. 2**. (**C**), although there are some exceptions.

heavy balls impact starch granules on the surface of the rotating vessel.

One of the oldest descriptions on HHP treatment of starch would be the following German sentence: *Stärke, bei 20000 atm. einem gleitenden Druck ausgesetzt, verliert ihr Röntgenogramm* (Starch exposed to sliding pressure by 20,000 atm loses its X-ray diffractogram) (Meyer *et al.* 1929). Although no detailed experimental procedure including the origin of starch was described in the literature, it is probable that the starch would be subjected to pressure anisotropically under a sliding condition. Mercier *et al.* (1968) compressed several moistened starches anisotropically by using a piston at 588.4 MPa and investigated the microscopic morphology, X-ray diffraction, iodine-binding capacity, water solubility, ethanol solubility, solubilized glucose, and enzymatic degradations by α- and β-amylases. Due to the anisotropic compression, the compressed starch granules under the microscopy appeared flat ellipsoids as observed in milling (Jones 1940). It is a matter of interest that this compression trial aimed to improve starch availability by damaging the starches. After direct compression at 0.8–1.2 GPa, air- or oven-dried starches (Kudła and Tomasik 1992a) and the dry and wet starches in the presence of metal salts (Kudła and Tomasik 1992b) were analyzed by some methods including differential thermal analysis. Liu *et al.* (2008) carried out direct compression of several starches which were analyzed by differential scanning calorimetry (DSC), polarized and scanning electron microscopies, and X-ray diffractometry.

Another way of compression is high pressure extrusion (Kim and Hamdy 1987). Starch colloidal solutions (0.5–2.5% w/v) were extruded via the orifice of a French Pressure Cell while maintaining the high hydraulic pressure at 90, 138, or 276 MPa.

Recently, HHP treatment of starch has been principally carried out in an isotropic way. Since the gelatinization of starch is realized in the presence of water, a starch-water mixture has been adopted in general. The mixture is placed in a pouch and the pouch is further placed in a HHP cylinder filled with pressure medium, which enables isotropic compression (**Fig. 4**).

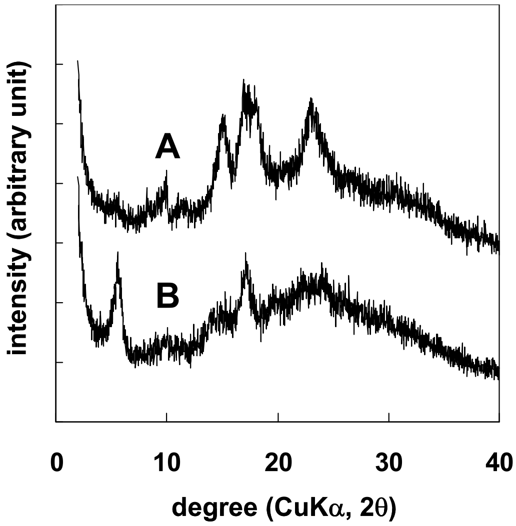

Fig. 5 Typical X-ray diffractograms of A-type (corn) and B-type (potato) starches. (**A**) Native corn starch. (**B**) Native potato starch.

Characteristics of pressure-gelatinized starch

In 1981, a dilute suspension of starch (0.4%) was treated at up to 253.3 MPa for 4 min, and it was reported that the gelatinization temperature was raised by HHP treatment and that the HHP effect reached a plateau over 152 MPa (Thevelein *et al.* 1981). The effect of HHP (200–1,500 MPa) on the gelatinization of wheat and potato starches was investigated by counting the gelatinized granules under a microscope, small angle light scattering, and differential scanning calorimetry; the results were physico-chemically discussed (Muhr and Blanshard 1982). High pressure differential thermal analysis was carried out for further investigation on wheat, potato, and pea starches (Muhr *et al.* 1982).

Since the study on HHP food processing was moved into full swing (Hayashi 1987), pressure gelatinization has been studied intensively. From a viewpoint of application to the food industry, studies on the effect of HHP on starch were deepened afterwards. Amylase digestibility of starch increased after the HHP treatment of starch-water mixture at 100–600 MPa with elevated temperatures (45 and 50°C), and potato starch was more pressure-resistant than wheat and corn starches (Hayashi and Hayashida 1989). This tendency was also observed with potato and wheat starches which were treated with HHP (0.1–650 MPa) at 10°C and digested by α-amylase (Noguchi *et al.* 2003). B-type starches such as potato and lily starches were more resistant to pressure than A-type starches such as corn starch. C-type starches such as sweet potato starch showing mixed X-ray diffractograms of A- and B-type starches had intermediate pressure resistance between A- and B-type starches (Ezaki and Hayashi 1992) (see **Fig. 5** and **Table 1**). The effect of pressure-holding time on gelatinization enthalpy and gel properties was investigated by using barley starch (Stolt *et al.* 2001). Retrogradation was observed immediately after HHP treatment of starch (Hibi *et al.* 1993; Stute *et al.* 1996; Katopo *et al.* 2003). For a fundamental concern, the effects of treatment pressure and pressure-holding (treatment) time on the gelatinization and the retrogradation properties of HHP-treated potato starch were studied, and the holding time did not affect the enthalpy changes upon gelatinization and melting of retrograded starch within the holding times between 1 h and 66 h (Kawai *et al.* 2007b). HHP induced the swelling and gelatinization of starches but retained the granular shapes (Stute *et al.* 1996; Stolt *et al.* 2001).

Table 1 Starch types and varieties.

Type	Starch variety
A	rice (*japonica* var. Koshihikari; *japonica* var. Kinmaze)[a], rice (*indica* var. IR32; *indica* var. IR-36; *indica* var. IR-42)[a], waxy rice (*japonica*)[a], corn[a], waxy corn[a], iris[a], taro[a], wheat(var. Norin No.61)[a], tapioca[a], gladiolus[a], sweet potato (var. Minamiyutaka[b]; var. Koganesengan[a])
B	potato[a], lily[a], tulip[a], lotus[a], canna[a], amylomaize (high amylose corn)[a]
C	kuzu[a], yam[a], sweet potato (var. Norin No.2; var. Hichifuku)[a], water chestnut[c], Japanese horse chestnut[c], lentil bean[d], adzuki(azuki) bean[d]

a, Hizukuri *et al.* (1983); b, Hizukuri (1985); c, Iwaki and Sugimoto (2004); d, Sugimoto and Watsuji (2006)

The effect of HHP on the gelatinization and related changes of starchy foods have also been studied. Watanabe *et al.* (1991) found that the cooking properties of aged rice grains were improved by HHP treatment and that the optimum pressure was 100 MPa. In experiments in which Thai glutinous rice was treated at 0.1–600 MPa, the equilibrium moisture content of rice was greater at a higher pressure (Ahromrit *et al.* 2006), and the gelatinization was facilitated by HHP (Ahromrit *et al.* 2007). Basmati rice flour slurry and extracted rice starch were completely pressure-gelatinized at 650 MPa and 550 MPa, respectively (Ahmed *et al.* 2007). Lille and Autio (2007) evaluated the size and number of ice crystals in high-pressure frozen starch gels using the size and total area of pores in the microscopic image of thawed gel, and they found that the average size and the total area occupied by the pores were clearly reduced by high-pressure freeezing. Kweon *et al.* (2008) indicated that sodium chloride and sucrose have solute-induced barostabilizing (or piezostabilizing) effects on pressure gelatinization.

Properties of HHP-treated starch are different from those of heat-treated starch. Amylose is released from heat-gelatinized starch, but hardly so from HHP-treated one (Douzals *et al.* 1998) or not at all (Stute *et al.* 1996). HHP treatment induced the swelling of starch granules while retaining their granular shapes (Stolt *et al.* 2001). The effect of treatment or holding time of HHP on the gelatinization of barley starch (Stolt *et al.* 2001) and waxy corn starch (Stolt *et al.* 1999) was investigated, and they showed that the rheological properties, the microstructure, the birefringence, and the enthalpy change upon gelatinization were dependent on the holding time and holding pressure. Further studies would be necessary to clarify whether a prolonged HHP treatment could complete the gelatinization of partially gelatinized starch treated with lower pressures. In addition, there is a report discussing the relationship between structure and pasting properties by measuring pasting properties of HHP-treated (690 MPa) various starches having different chemical structures using a RVA (Katopo *et al.* 2003). Swelling and pasting properties of HHP-treated starch were studied and compared among several starches of different botanical origins (Oh *et al.* 2008b).

HHP-gelatinized starch shows increased enzymatic susceptibility (digestibility) as also observed with heat-gelatinized starch (Hayashi and Hayashida 1989). Gomes and Ledward (1998) treated wheat or barley flour suspension with HHP up to 800 MPa, and evaluated the glucose produced by inherent α- and β-amylases during HHP treatment. The degree of gelatinization increased with increasing pressure. However, glucose productivity decreased as HHP was further raised due to the inactivation of the amylases. α-amylase of *Bacillus amyloliquefaciens* (BAA) in a buffer solution with or without a substrate (soluble starch) was treated with HHP up to 400 MPa. The activation volumes for HHP inactivation of the enzyme were evaluated from the rates of hydrolysis as -13.8 ± 2.1 (with substrate) and -28.4 ± 2.2 cm^3/mol (without substrate), respectively (Raabe and Knorr 1996). It was indicated that the pressure resistance of the enzyme could be increased in the presence of the substrate due to binding of the substrate to the enzyme.

Methods of analysis for pressure gelatinization

When starch granules are observed under a polarized microscope, raw starch granules show hilum-centered birefringence, which refracts light in an anisotropic material in two slightly different directions to form two rays and basically corresponds to crystallinity, while gelatinized granules lose the hilum and the birefringence (Zobel 1984). Since the early studies, pressure gelatinization have been evaluated by the loss in birefringence in many reports (Thevelein *et al.* 1981; Muhr and Blanshard 1982; Stute *et al.* 1996; Douzals *et al.* 1998; Stolt *et al.* 2001; Bauer and Knorr 2004, 2005). The number of birefringent granules is counted and the gelatinization degree can be evaluated from the ratio of birefringent to non-birefringent granules. The quantitative performance of judging the degree of gelatinization by birefringence loss was calibrated with DSC results (Douzals *et al.* 2001). Baure and Knorr (2004) showed that there was a good linear relationship between the degree of gelatinization by birefringence loss and that by electrical conductivity.

DSC measurement is widely used for quantitative analysis of pressure gelatinization. Depending on the botanical source of starch, the endothermic peak can be observed at around 60–80°C in the presence of excess water, although the difference in the thermal properties among the starches of different botanical origins has not yet been clarified. The peak area is calculated as enthalpy change upon gelatinization (or simply, gelatinization enthalpy: ΔH_{gel}) which is used as an index of pressure gelatinization. The ΔH_{gel} assumes a maximum value when the starch is intact, and it becomes zero when completely gelatinized. Characteristic temperatures of the peak such as the onset temperature (T_o), the peak top temperature (T_p), and the conclusion temperature (T_c) may vary after HHP treatment (Thevelein *et al.* 1981; Douzals *et al.* 2001; Kawai *et al.* 2007b). By analyzing low moist (moisture content: 10.0–34.0%) barley starch samples using a DSC with pressure chamber (pressurized by nitrogen gas up to 2.5 MPa), it was reported that less moisture level was required for initiation of the gelatinization under the pressurized condition than under atmospheric pressure (Vainionpää *et al.* 1993). Recently, high sensitivity DSC was introduced to analyze waxy wheat, waxy potato, waxy corn, and high amylose corn starches and the mixtures of waxy and high amylose corn starches after HHP treatment (Błaszczak 2007; Błaszczak *et al.* 2007a, 2007b).

Pressure gelatinization can be evaluated by X-ray diffractometry. When pressure-gelatinized, the intensities of the characteristic peaks on a broad halo in the diffractogram of the starch are reduced, indicating the loss of crystallinity. Completely pressure-gelatinized starch shows only an amorphous halo (Hibi *et al.* 1993; Katopo *et al.* 2002; Błaszczak *et al.* 2005b, 2007a). For the quantitative evaluation of pressure gelatinization, a crystallinity index can be used (Hibi *et al.* 1993). Attention should be paid to evaluating pressure gelatinization and retrogradation of B-type starch (Stute *et al.* 1996) such as potato starch, because the B-type diffraction pattern derived from retrogradation in the pressure-gelatinized starch may superimpose on the diffractogram. Therefore, X-ray diffraction should be used for the evaluation of HHP-treated B-type starch in combination with the other methods such as DSC.

Compressibility of HHP-treated starch was calculated versus pressure by measuring volume changes (cross-sectional area of the pressure chamber multiplied by the plunged length of piston) of 16%w/w aqueous suspension of wheat starch (dry matter-basis) and pure water with the pressure varied (Douzals *et al.* 1996). During the compression below 300 MPa, compressibility of the starch suspension was close to that of pure water, while the reduction of the volume was higher for the starch suspension than for pure water at the same pressure over 300 MPa. Pressure gelatinization of wheat starch began above 300 MPa. The compressibility during decompression was higher than that during compression, and starch gels treated with HHP re-

Table 2 Overview of the experimental conditions for pressure gelatinization and other related experiments.

Starch or grain variety	Press	Pressure (MPa)	Temperature (°C)	Time	Starch content	Evaluation	References
n.s.	AN	2027	n.s.	n.s.	n.s.	XRD	Meyer *et al.* 1929
PO, WH, CO	AN	588.4	n.s.	1 min	64 - 99%	LM, XRD, ED, iodine absorption, solubility	Mercier *et al.* 1968
PO	IS	0.1 - 253.3	25	4.5 min	0.4%	BI	Thevelein *et al.* 1981
WH, PO	IS	0.1 - 401	scan: 20 - 130	scan at 15°C/min	33.3% w/w	HP-DTA	Muhr *et al.* 1982
WH, PO	IS	0.1, 200 - 1500	20 -150	>30 min	PO: 12.8, 55.5% w/w WH: 13.3, 57.7, 75.4% w/w	small angle light scattering, DSC	Muhr and Blanshard 1982
Soluble PO	-	89.6 - 275.8	24	-	2.50%	VI, solvent fractionation, dextrose equivalence	Kim and Hamdy 1987
WH, CO, PO	IS	0.1, 392.3, 490.3	25, 45, 50	20 min - 17 h	5% w/w	ED	Hayashi and Hayashida 1989
Aged rice grain	IS	50 - 500	20	10 min	rice grains in water 50% w/v	WU, texturometry	Watanabe *et al.* 1991
CO, WH, RI, PO, MA, LL, SP, TP, MB	IS	0.1 - 600	45	1 h	5%	phase contrast MI, DSC, XRD	Ezaki and Hayashi 1992
PO	AN	800 - 1200	n.s.	1 - 10 min	air- or oven-dried	BI, TG, DTG, DTA, XRD, WU, solubility, reducibility, gelation, iodine reaction, paper elution, infrared, raman	Kudła and Tomasik 1992a
PO	AN	800 - 1200	n.s.	1 and 5 min	2, 5, 10, 15, 18, 20, and 22%	DTA, UV-Vis spectrometry, SEM, compression curve	Kudła and Tomasik 1992b
NCO, WCO, PO, NRI, WRI, defatted NCO, defatted NRI	IS	50 - 500	17 - 23	20 and 60 min	50% w/v	BI, CI, LM, MC, SG, XRD, solubility	Hibi *et al.* 1993
BA	IS	0.1, 1.1, 2.5	scan to 250	10°C/min	66, 70, 78, 90%	DSC with a pressure chamber, LM, BI	Vainionpää *et al.* 1993
WH, PO	IS	0.1 - 600	r.t.	n.s.	0.1 and 16%	MI, DSC, image analysis, volumetric change, compressibility	Douzals *et al.* 1996
WH	IS	100 - 600	n.s.	n.s.	15 - 40% w/w	compressibility, SG	Douzals *et al.* 1996
Soluble PO	IS	100 - 400	25	0 - 120 min	1.5%w/v	ED kinetics	Raabe and Knorr 1996
NCO, WCO, ACO, NRI, WRI, WH, TP, PO, BA, MB, CA, LR, TR, WC, AR, SPE, WPE, BB, KZ, PN, AM, RY, OA, LT, FB	IS	350 - 600	20	15 min	5 and 25% for XRD and BI; 42, 56, and 71% for WH; 8.6% for gel	DSC, XRD, BI, swelling, gel strength	Stute *et al.* 1996
WH	IS	600	25	15 min	5 and 30%	DSC, SI, SG, XRD, iodine titration, compression modulus, drying kinetics	Douzals *et al.* 1998
Flours of WH and BA	IS	100 - 800	r.t.	10 and 20 min	25% w/w	BI, ED, enzyme inactivation, soluble protein	Gomes *et al.* 1998
Ball-milled starches (NCO, WCO, ACO)	IS	709 MPa	r.t.	15 min	5(k?)g starch in 10 ml fatty acid mixture	DSC, XRD, fatty acid content	Yamada *et al*. 1998
WCO	IS	450 -600	30	0 - 120 min	10%	VE, VI	Stolt *et al.* 1999
NCO, WCO, RI, TP, PO, PE	IS	0.1 - about 1000	n.s.	pressure increase at ~ 100 MPa / h	n.s.	LM, FTIR	Rubens *et al.* 1999
WH	IS	0.1 - 600	-25 - 100	15 min	5%	BI, DSC, SI	Douzals *et al.* 2001
BA	IS	400 - 550	30	0 - 75 min	10 and 25% w/w	BI, DSC, LM, VE, VI	Stolt *et al.* 2001
NCO, WCO, ACO, TP, PO, RI	IS	690	r.t.	5 min, 1 h	33% w/v, 50% in water; 50% in ethanol	SEM, XRD, DSC, RVA	Katopo *et al.* 2002
WH, PO	IS	0.1 - 650	10	30 min	5% w/v	ED, DSC, BI, acid hydrolysis	Noguchi *et al*. 2003
WH, TP, PO	IS	300	r.t.	10 and 60 min	0.8% w/w	HP-MI	Bauer *et al.* 2004
WH, TP, PO	IS	0.1 - 700	about 2 - 70	5 min - 4 h	5% w/w	BI	Bauer and Knorr 2005
PO	IS	600	20 ± 2	2 and 3 min	10% w/w	DSC, FTIR, ^{13}C CP/MAS NMR, SEM	Błaszczak *et al.* 2005a
ACO, WCO	IS	650	20 ± 2	0, 3, 6, 9 min	30% w/w	CP/MAS ^{13}C NMR, XRD, HPLC, BI, SEM	Błaszczak *et al.* 2005b
WH	-	0.1 - 100	10 -157 (scan)	0.15°C/min	44 % w/w	scanning transitiometry	Randzio and Orlowska 2005

Table 2 (Cont.)

Starch or grain variety	Press	Pressure (MPa)	Temperature (°C)	Time	Starch content	Evaluation	References
Surimi with PO	IS	400, 650	22	10 min	4 g / 100 g surimi	SEM, water-holding capacity, bulk density	Tabilo-Munizaga and Barbosa-Cánovas 2005
CO, WH, TP, PO, BM	IS	0.1 - 800	n.s.	15 min	5% w/w	BI	Knorr *et al.* 2006
CO	IS	600	r.t.	30 min	5, 10, 15, 20% w/w	DSC, LM, XRD, hydrolysate evaluation	Lee *et al.* 2006
Thai glutinous rice grain	IS	0.1 - 600	20, 50, 60, 70	120 min	14% ± 0.1(initial MC)	MC, diameter, length	Ahromrit *et al.* 2006
Rice flour and its starch	IS	350, 450, 550, 650	max. 24.8-28.5	7.5 and 15 min	16.5, 22.9, and 33% (wet basis flour); 16.5% (starch)	DSC, FTIR, electrophoresis, rheology	Ahmed *et al.* 2007
Thai glutinous rice grain	IS	0.1 - 600	20 - 70	45 - 120 min	20g grains in 100 mL water	DSC, MC	Ahromrit *et al.* 2007
WH, TP	IS	0.1 - 530	29	5 min - 4 h	5% w/w	BI, electrical conductivity	Bauer and Knorr 2004
WCO, ACO, and the mixtures	IS	400 - 650	n.s.	3, 6, 9 min	8, 10, and 30%	^{13}C CP/MAS NMR, FTIR, HPLC, HS-DSC, LM, Pulse ^{1}H-NMR, SI, XRD, VI, solubility, swelling power, odorant binding, turbidity	Błaszczak 2007
WCO, ACO, and the mixtures	IS	650	20 ± 2	9 min	30% w/w	HS-DSC, Pulse ^{1}H-NMR, SEM, SI, XRD	Błaszczak *et al.* 2007a
ACO, WCO, mixtures of the two	IS	650	20 ± 2	9 min	30% w/w	DSC	Błaszczak *et al.* 2007b
WCO, WWH, WPO	IS	650	20 ± 2	9 min	30% w/w	HS-DSC, Pulse ^{1}H-NMR, SEM, SI	Błaszczak *et al.* 2007c
CO	IS	0.1 - 650	30 -75	0 - 35 min	5% w/w	BI, HP-MI, kinetics	Buckow *et al.* 2007
PO	IS	400 - 1200	40	1 h	10 - 70% w/w	DSC	Kawai *et al.* 2007a
PO	IS	600, 800, 1000	40	1, 18, 66 h	10 - 70% w/w	DSC	Kawai *et al.* 2007b
heat-gelatinized WH	IS	150 - 240	freezing from 3°C to -28, -20, and -14°C	< 360 min	20%	MI (pore size), freezing curve	Lille and Autio 2007
NCO, WCO	IS	0.1, 300 - 600	5, 25, 50, 70	15 min	50% w/w	DSC, LM, BI	Kweon *et al.* 2008
NCO, WCO, WH, PO	AN	740-840	22-25	5 min - 2 h	NC1: 86.0 ± 0.1% w/w	DSC, XRD, SEM, BI	Liu *et al.* 2008
	AN	960-1100	22-25	24 h	NC2: 85.8 ± 0.2% w/w		
	IS	1500	25	24 h	WC: 84.9 ± 0.4% w/w		
					W: 85.6 ± 0.2% w/w		
					P: 80.4 ± 0.1% w/w		
NRI, WRI	IS	0.1, 100 - 700	10 - 60	0 - 30 min	10% w/w	BI, SI, VI, leached starch and amylose	Oh *et al.* 2008a
NRI, WRI, NCO, WCO, TP, PO	IS	400, 600	20	30 min	10% w/w	BI, SI, VI	Oh *et al.* 2008b
CO, PO	IS	300, 700	40, 52	5 and 20 min	CO: 20% w/w PO: 30% w/w	SEM, XRD	Szepes *et al.* 2008

n.s., not specified; r.t., room temperature

press: IS, isostatic press; AN, anisotropic press;

starch: NCO, normal corn; WCO, waxy corn; ACO, high amylose corn; WH, wheat; WWH, waxy wheat; NRI, normal rice; WRI, waxy rice; PO, potato; WPO, waxy potato; TP, tapioca; MB, mung bean; LL, lily; CA, canna; MA, marron; BA, barley; LR, lotus root; TR, taro; SPE, smooth; WPE, wrinkled pea; KZ, kozou (kuzu); PN, peanut; AM, amaranth; RY, rye; OA, oat; LT, lentil; FB, faba bean; BB, babassu; AR, arrow root; WC, water chestnut; SP, sweet potato; PE, pea; BM, barley malt

evaluation: BI, birefringence; CI, crystallinity index; ED, enzymatic degradation; HP, high pressure; HS-DSC, high sensitivity DSC; LM, light microscopy; MC, moisture content; MI, microscopy; SI, solubility index; SG, specific gravity; VE, viscoelesticity; VI, viscosity; WU, water uptake; XRD, X-ray diffractometry

mained compressed after the decompression. These results indicated that total volume was reduced by starch melting and that water-starch linkages created under pressure were strong.

NMR analysis of HHP-treated starch has been done using Cross-polarization/magic angle spinning (CP/MAS) ^{13}C NMR which is a powerful tool to analyze the structure of solid organic materials (Błaszczak *et al.* 2005a, 2005b). HHP-treated potato starch presents two resonances (Błaszczak *et al.* 2005a), which are characteristic of amorphous starch (Gidley and Bociek 1985).

Snauwaert and Heremans (1999) monitored *in situ* the pressure gelatinization of potato starch by optical microscopy facilitated with a video camera in a diamond anvil cell (DAC). Once the pressure gelatinization initiated at the initiation pressure, swelling did not stop until the pressure was reduced to below the initiation pressure. From the swelling constant, the activation volume was calculated to be -18 cm^{3}/mol, and elliptical starch granules appeared to have a much lower swelling threshold than spherical ones. Swelling of starch granules in a high pressure cell resistant to 300 MPa was observed under an optical microscope by Bauer *et al.* (2004).

Pressure gelatinization behaviors of rice (Rubens *et al.* 1999; Rubens and Heremans 2000), potato, corn, waxy corn, pea, and tapioca (Rubens *et al.* 1999) starches were studied *in situ* in a DAC by Fourier-transform infrared (FTIR) spectroscopy. The characteristic absorptions observed with amorphous and crystalline features of the above-mentioned starches were specified, and the ratio of specific absorption intensities synergistically changed upon heating or pressurization. In addition, the changes upon heating and pressurization were not synergistic but monotonous in the cases of the aqueous suspensions of amylose, amylopectin, and their mixture (1:1), suggesting the importance of imperfect packings of amylose and amylopectin in starch granules (Rubens and Heremans 2000). The data on the pressure gelatinization by the *in situ* measurements was thermodynamically analyzed as in the case of other biopolymers (Smeller 2002).

As a novel technique, scanning transitiometry of starch-water emulsion is of great interest (Randzio and Orlowska 2005). Thermal and volumetric properties upon gelatinization of wheat starch was studied at a pressure range from 0.1 to 100 MPa and a temperature range from 10 to 157°C (283 to 430 K).

Roles of water in pressure gelatinization

Water is indispensable for both heat gelatinization and pressure gelatinization. In heat gelatinization, 14 molecules of water per one glucose unit are required for a complete hydration upon gelatinization (Donovan 1979). However, a systematic understanding of the effect of water content on pressure gelatinization has not progressed sufficiently. Studies on pressure gelatinization have been carried out under limited conditions of water content.

HHP treatment of starch at low water contents, namely dry or low moist starch, has been carried out by anisotropic compression in many of the reports. Enzymatic digestibilities of potato, wheat, and corn starches at low water contents (2–36%) were measured after piston compression, and the digestibility showed minimums for potato starch at the water content of about 19% and for wheat and corn starches at about 14%, respectively (Mercier *et al.* 1968). Reducibility of air- or oven-dried potato starch of 15.1% water content increased after pelletization by flanger compression, and it was discussed that water might act as a Lewis base and hydrolyze the glucosidic bonds with the help of applied compression energy which was estimated to be in the order of energy of covalent bonds (Kudła and Tomasik 1992a, 1992b). In addition, depolymerization of starch was observed after high pressure extrusion (Kim and Hamdy 1987). On the contrary, several papers reported that the chemical bonds of starch molecules were not influenced by HHP treatment (Hibi *et al.* 1993; Katopo *et al.* 2002).

At high water contents, a few excellent diagrams (gelatinization vs. pressure vs. temperature) were presented with the starch content fixed (Douzals *et al.* 2001; Bauer and Knorr 2005; Knorr *et al.* 2006; Buckow *et al.* 2007). In any case, most of the experiments have been done with the water contents fixed at 70–95% (Muhr *et al.* 1982; Ezaki and Hayashi 1992; Douzals *et al.* 1996, 1998; Stolt *et al.* 1999; Rubens and Heremans 2000; Douzals *et al.* 2001; Stolt *et al.* 2001; Bauer *et al.* 2004; Błaszczak *et al.* 2005a, 2005b; Knorr *et al.* 2006; Buckow *et al.* 2007).

Table 2 provides an overview of the experimental conditions for pressure gelatinization and other related experiments. While most of the experiments were carried out with the water content fixed, Stute *et al.* (1996) have reported that HHP gelatinization required at least a water content of 50% in the DSC measurements of HHP-treated (600 MPa, 20°C, 15 min) samples of the water contents at 42, 56, and 71%. Katopo *et al.* (2002) treated starches (water content: 50% and 67%) of various botanical origins and samples at 690 MPa and ambient temperature for 5 min and concluded that the degree of gelatinization was higher with the samples with 67% water content than those with 50%. However, with the experimental results with limited water contents as found in most of the reports, it will be difficult to discuss the effect of water content on pressure gelatinization. As described above, pressure gelatinization has been studied under limited conditions, especially at a few levels of water content, and, therefore, systematic understanding of pressure gelatinization of various starches has not been achieved.

PRESSURE GELATINIZATION OF POTATO STARCH

Better understanding of pressure gelatinization with potato starch as an example

In terms of pressure gelatinization, potato starch has been reported to be more pressure-resistant than cereal starches such as corn, wheat, and rice (Muhr *et al.* 1982; Ezaki and Hayashi 1992; Stute *et al.* 1996; Katopo *et al.* 2002; Oh *et al.* 2008a, 2008b). It should be noted that pressure gelatinization behavior of potato starch has been less studied than other starches, especially cereal starches, due to the limitation of maximum HHP achieved by laboratory HHP apparatus. Accordingly, the experiments on potato starch were carried out under limited conditions, especially in terms of the pressure range and water content.

Recently, we have treated potato starch-water mixtures at the starch contents of 10–70% w/w (i.e. water contents of 30–90% w/w) with the pressures of 400–1200 MPa (0.4–1.2 GPa) at 40°C for 1 h, and presented a state diagram (Kawai *et al.* 2007a). The pressure gelatinization and pressure-induced retrogradation were evaluated from endothermic peaks by differential scanning calorimetry (DSC) (**Fig. 6**). As can be seen in **Fig. 6**, an endothermic peak, which corresponds to the enthalpy change upon gelatinization (ΔH_{gel}) can be observed at a higher temperature than another which corresponds to the enthalpy change upon melting of retrograded starch (ΔH_{retro}). The value of ΔH_{gel} decreased upon pressure gelatinization, and a higher pressure gelatinization was achieved with the higher treatment pressure and the higher water content (**Fig. 7**). On the other hand, retrogradation was observed with completely or partially pressure-gelatinized starch, and the value of ΔH_{retro} tended to increase with increased starch content (= decreased water content) and with increased treatment pressure (**Fig. 8**). Taking into account that the non-treated potato starch showed $\Delta H_{gel} = 20 \pm 2$ J/g (dry starch basis), the state of the HHP-treated potato starches was classified into 5 categories: complete gelatinization ($\Delta H_{gel} = 0$ J/g), complete gelatinization with retrogradation ($\Delta H_{gel} = 0$ J/g and ΔH_{retro}

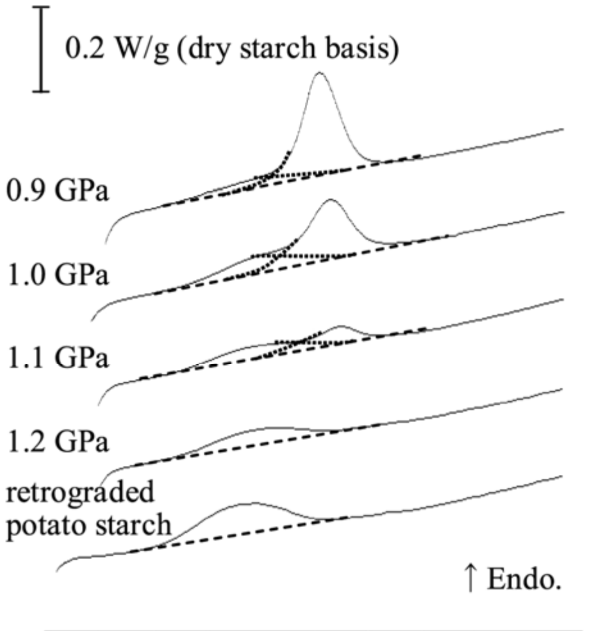

Fig. 6 DSC thermograms of the potato starch-water mixture (water: 50% w/w) treated with HHP (0.9–1.2 GPa) and the retrograded potato starch-water mixture (water: 30% w/w) gelatinized completely with heat and stored at 4°C for 7 days as described by Kawai *et al.* (2007a).

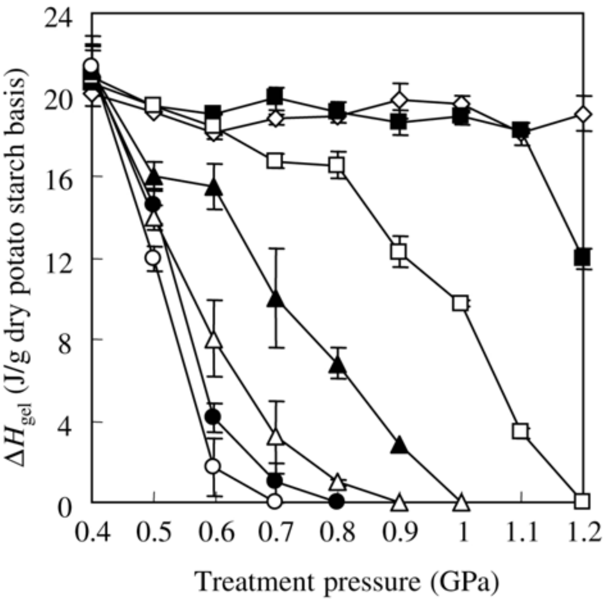

Fig. 7 Dependence of ΔH_{gel} on treatment pressure and starch content of potato starch-water mixture as described by Kawai *et al.* (2007a). Open circle, 10%; closed circle, 20%; open triangle, 30%; closed triangle, 40%; open square, 50%; closed square, 60%; open diamond, 70%.

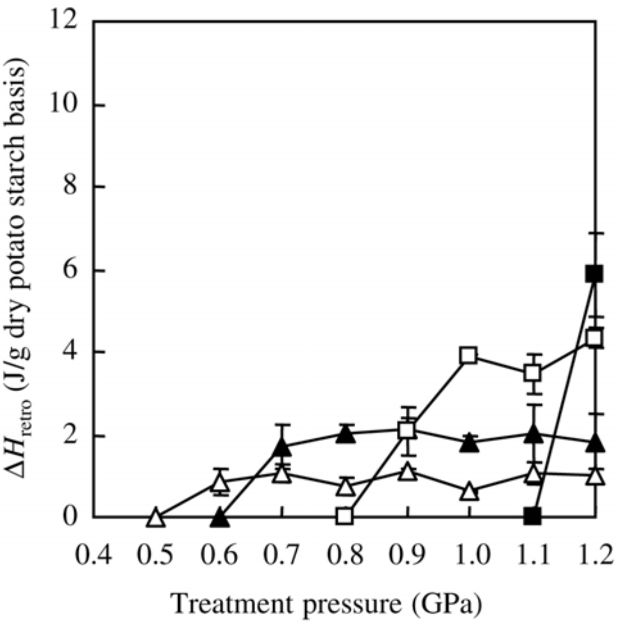

Fig. 8 Dependence of ΔH_{retro} on treatment pressure and starch content of potato starch-water mixture as described by Kawai *et al.* (2007a). Open triangle, 30%; closed triangle, 40%; open square, 50%; closed square, 60%.

> 0 J/g), partial gelatinization ($\Delta H_{gel} < 18$ [= 20 – 2] J/g and $\Delta H_{retro} = 0$ J/g), partial gelatinization with retrogradation ($\Delta H_{gel} < 18$ J/g and $\Delta H_{retro} > 0$ J/g), and thermodynamically no change ($\Delta H_{gel} \geq 18$ J/g and $\Delta H_{retro} = 0$ J/g). The classification was presented as a state diagram (treatment pressure vs. starch content) (**Fig. 9**).

By treating potato starch-water mixtures with HHP, the effects of treatment pressure (600–800 MPa), pressure-holding (treatment) time (1, 18, and 66 h), and starch content (10–70% w/w) on gelatinization and retrogradation properties were investigated (Kawai *et al.* 2007b). The values of ΔH_{gel} and ΔH_{retro}, dependent on the starch content (or water content), were not affected by the holding times (**Fig. 10**), but the onset temperature of gelatinization (T_{gel}) was increased with reduced starch content (or increased water content) and increased holding time (**Fig. 11**).

In utilizing the pressure-gelatinized starch, a recent pub-

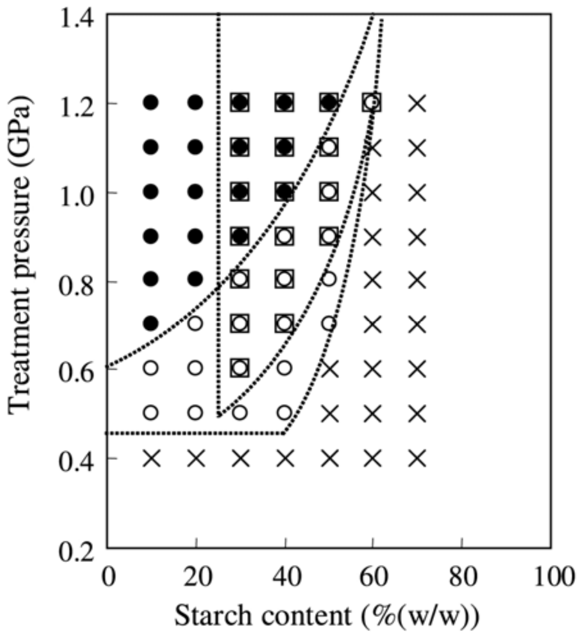

Fig. 9 State diagram (treatment pressure vs. starch content) of HHP-treated potato starch-water mixtures as described by Kawai *et al.* (2007a). Closed circle, complete gelatinization; closed circle in square, complete gelatinization with retrogradation; open circle, partial gelatinization; open circle in square, partial gelatinization with retrogradation; cross, thermodynamically unchanged.

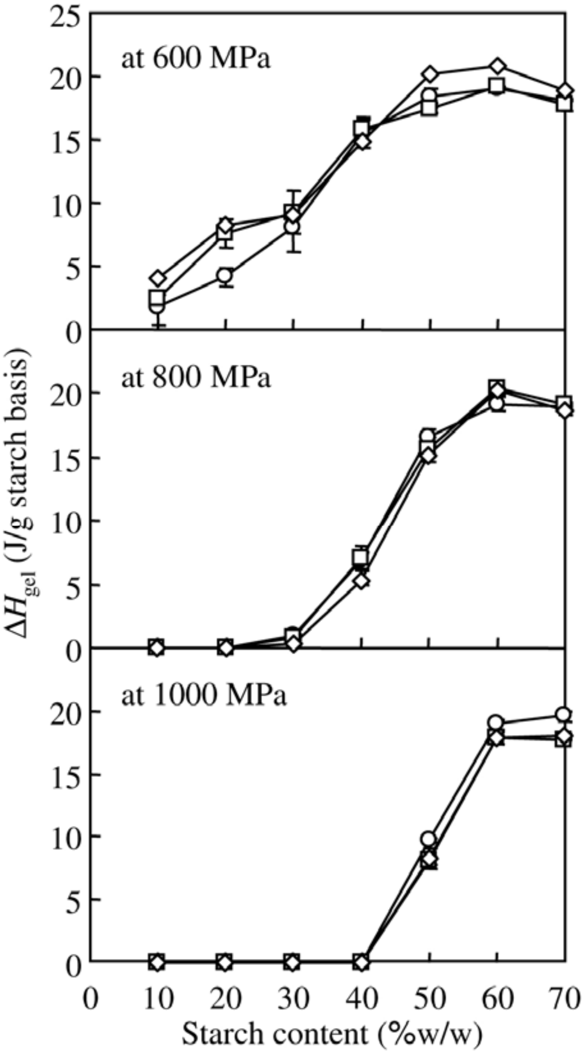

Fig. 10 Dependence of ΔH_{gel} on treatment time (1, 18, and 66 h), treatment pressure, and starch content of potato starch-water mixture as described by Kawai *et al.* (2007b). Circle, 1 h; square, 18 h; diamond, 66 h.

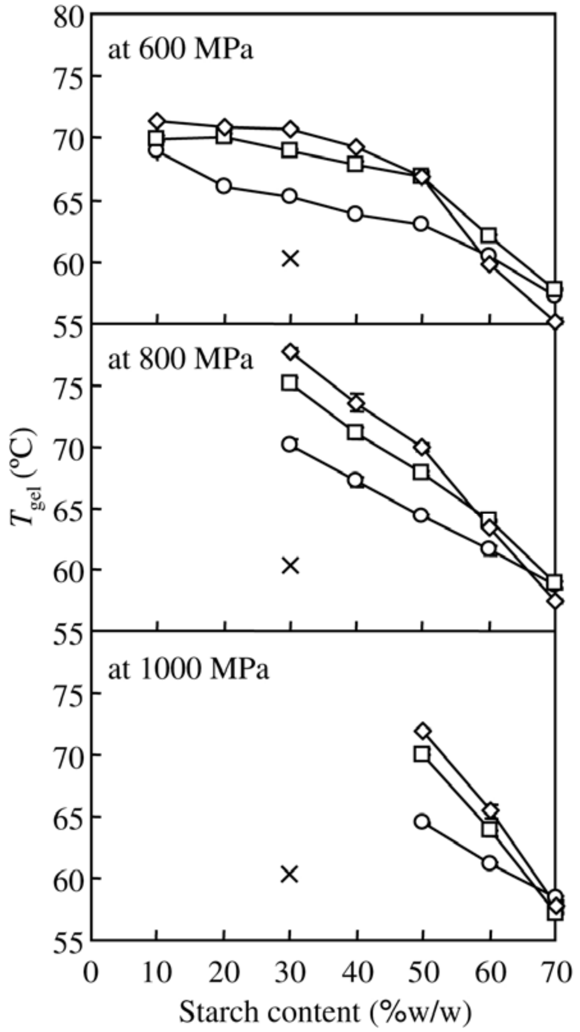

Fig. 11 Dependence of T_{gel} (onset temperature) on treatment time (1, 18, and 66 h), treatment pressure, and starch content of potato starch-water mixture as described by Kawai *et al.* (2007b). Circle, 1 h; square, 18 h; diamond, 66 h. The cross indicates the T_{gel} of native potato starch-water mixture at the starch content of 30% w/w.

lication on starch-based hydrogels will be of interest (Szepes *et al.* 2008). The gels were prepared by using potato starch via isostatic HHP treatment for the aim of drug formulation. The effect of HHP treatment on the binding of odorants to starch was studied by using corn starches (Błaszczak 2007; Błaszczak *et al.* 2007b). Yamada *et al.* (1998) reported some trials to introduce fatty acids to ball-milled starch granules with HHP treatment. However, they focused on ball mill treatment rather than HHP treatment, and the effect of HHP on the fatty acid introduction was not described clearly. The influence of potato starch on HHP-treated surimi gels (400 and 650 MPa, 10 min) was compared with heat-treated ones (90°C, 40 min) (Tabilo-Munizaga and Barbosa-Cánovas 2005). The applied pressures seem to be insufficient for gelatinization, however, the water holding capacity of the HHP-treated surimi gels was higher than heat-treated ones. For further applications of HHP-treated starch, it is expected that the approach depicting state diagrams of HHP-gelatinized starch would promote an understanding of pressure gelatinization and the utilization of HHP-treated starches of various botanical origins.

CONCLUDING REMARKS

Food processing with HHP has been realized since 1990, while studies on the HHP treatment of food components and other biomolecules, including starch, have a longer history. The effect of HHP treatment on the behavior of starch has been studied since the possible first description by Meyer *et al.* (1929), and the experiments have been carried out by anisotropic and isotropic compressions and high pressure extrusion.

It has been revealed that starch in the presence of water can be gelatinized by HHP treatment and that pressure-gelatinized starch shows similar but unique characteristics as compared with heat-gelatinized one. One difference would be that HHP-treated starch granules can be gelatinized while swollen with retained granular shapes. Other properties of pressure-gelatinized starch have been also studied using various starches: thermal and visco-elastic properties, crystalline features (X-ray diffractograms), swelling behavior, amylose release, and enzymatic digestibility. Other than starch itself, starchy foods such as rice were HHP-treated. The effect of additives on pressure gelatinization was investigated from a viewpoint of their solute-induced stabilization. Pressure-gelatinized starch has been recently studied by polarized microscopy (birefringence), DSC, X-ray diffractometry, compressibility, cross-polarization/magic angle spinning (CP/MAS) ^{13}C NMR, and FTIR. The diamond anvil cell is a powerful tool to observe the behavior of pressure gelatinization *in situ*.

Although water is a key factor for pressure gelatinization, the effect of water content has not been intensively studied. However, recently, the effect of water content on pressure gelatinization has been investigated using potato starch with a wide range of water content between 10 and 70% (w/w), and a state diagram (treatment pressure vs. water content) depicting the states of HHP-treated potato starch was presented. The states of HHP-treated potato starch were classified into 5 categories: complete gelatinization, complete gelatinization with retrogradation, partial gelatinization, partial gelatinization with retrogradation, and thermodynamically no change. The state diagram will be of practical use to prepare HHP-treated potato starch with one of 5 different states. State diagrams of potato starch at other temperatures and those for other starches are under preparation in our laboratory.

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