Chapter 20
Pressure Gelatinization of Starch

Kazutaka Yamamoto and Roman Buckow

Abstract Starch, which is conventionally processed by heat, is a key food component and an industrial raw material. High hydrostatic pressure (HHP) can induce gelatinization of starch without heating. Spontaneous retrogradation can be observed immediately after HHP-induced gelatinization, depending on the starch content and temperature. In HHP treatment of starch systems, it should be differentiated whether it is anisotropic or isotropic compression, each of which results in different properties of the obtained starches. Physicochemical changes of various starches due to thermal or HHP treatment have been studied intensively by various methods, and the behavior of starch gelatinization under combinations of heat and HHP has been systematically revealed in recent years. In this paper, trends in the study of HHP-treated starch are reviewed from the viewpoints of fundamental and application approaches.

Keywords Starch • Gelatinization • Retrogradation • High hydrostatic pressure • High pressure • 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

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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

20.1 Introduction

20.1.1 *Starch and Gelatinization*

Starch is a granular storage material found in terrestrial plants abundantly and universally, and it is also important for humans as a key food component (Zobel 1984). When heated in the presence of water, the intermolecular bonds of starch molecules are broken down, allowing hydrogen bonding sites (hydroxyl hydrogen and oxygen) to bind with water. Disruption of this structure is usually referred to as heat gelatinization or, simply and conventionally, gelatinization, which is essential in all kinds of industrial and culinary utilization of starch. It is characterized by a loss in crystallinity and birefringence, solubilization of amylose, and irreversible swelling of the granules (Waigh et al. 2000). Thus, starch is utilized as a texture modifier in the food industry and as an adhesive agent in other industries.

Starch is primarily composed of amylose and amylopectin, which are homoglycans comprised only of α-D-glucose. Amylose is an α-1,4-linked linear glucose polymer, and amylopectin is an α-1,6-branched tuft of α-1,4-linked linear glucose oligomers (branched chains) and/or polymers. The chemical structures of amylose and amylopectin depend on the botanical origin of starch and other environmental factors during plant growth. Starch granules appear in different shapes depending on its botanical origin. In general, each of starch granules has a porous core called "hilum," which is the ignition point of growth rings, i.e., alternate concentric ellipsoidal lamellar structure. It is speculated that some pores exist on the granular surface, and these pores are connected to the hilum through channels. The crystalline layers of the granule consist of ordered regions composed of double helices formed by the short chains of amylopectin, most of which are further ordered into crystalline structures known as crystalline lamellae. Amorphous regions of the semicrystalline layers and amorphous layers are composed of amylose and non-ordered amylopectin branches (Waigh et al. 1997). Glucose monomers in amylopectin are oriented radially in the starch granule, with the nonreducing ends of the chains toward the granule surface. As the radius increases, so does the number of branches required to fill the space, with the consequent formation of concentric regions of alternating amorphous and crystalline structure.

Physicochemical properties of starch are strongly affected by the length and number of amylose molecules and/or amylopectin branched chains. Starch with deficiency of amylose may form sticky gels, being referred to as waxy starch. It is currently understood that two branched chains of amylopectin form a double strand, and the double strands further form tufts comprising microcrystalline domains. Wide-angle X-ray diffractometry classifies these diffraction patterns into three categories. Type A is often observed in cereal starch such as maize, wheat, and rice (Hizukuri et al. 1983; Parker and Ring 2001). Type B is typical for high-amylose (>50 %) cereal starches and for tuber starches such as potato, lily, tulip, lotus, and canna (Hizukuri et al. 1983; Parker and Ring 2001). Type C represents intermediate superimposed patterns of types A and B and can be found in tropical plants and legume starches such as peas and beans (Sugimoto and Watsuji 2006) and chestnuts (Iwaki and Sugimoto 2004). Diffraction patterns have not yet been revealed based on currently available information on the chemical structure of amylopectin, although information on these patterns has been intensively accumulated (Hizukuri 1985; Jane et al. 2003; Seetharaman and Bertoft 2013). Although some models have been suggested, there is no conclusive three-dimensional structure model for starch granules (Pérez et al. 2009).

20.1.2 Pressure-Induced Gelatinization

The effect of HPP on starch gelatinization has recently been studied intensively. Although the mechanism of HPP-induced gelatinization is likely to be different from heat gelatinization, both temperature and pressure are, as in the case of protein denaturation, crucial parameters when changes in starch structures are intended to be brought about in food processing (Knorr et al. 2006).

Starch can change into gel or paste irreversibly due to order–disorder transition when heated in the presence of water. During heat gelatinization, starch granules absorb water and swell, and the growth rings and crystalline features are lost (Fig. 20.1). For a complete hydration and gelatinization of (potato) starch, more
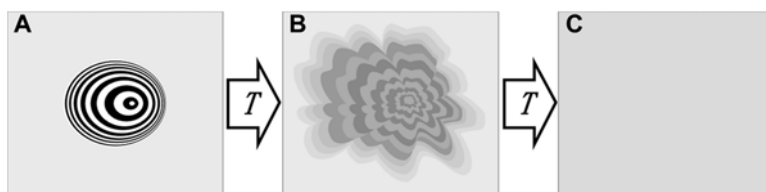

Fig. 20.1 Schematic diagram of heat gelatinization of a starch granule. (**a**) Starch granule suspended in water: cross section of the granule presents lamellar structure of concentric ellipsoids. (**b**) Heating induces swelling and disruption of the granule. Molecular motion is accelerated by heating and lamellar structure is lost by swelling. (**c**) Further heating leads to complete gelatinization where the granular shape is not observed. (**a–c**) Figures reprinted from Yamamoto, K.; Fukami, K.; Kawai, K.; and Koseki, S. 2006. Pressure gelatinization of starch. *Food and Packaging* (*Shokuhin to Youki*) 47: 448–456, with copyright permission of the Institute of Canning Technology, ©2006
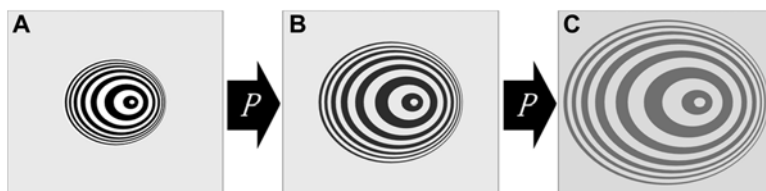
Fig. 20.2 Schematic diagram of pressure gelatinization of a starch granule as described by Yamamoto et al. (2006). (**a**) Starch granule suspended in water. (**b**) Starch granule can be partially gelatinized by HHP with swelling of the granule induced. (**c**) Completely pressure-gelatinized starch granule can retain granular shape

than 14 water molecules per one glucose unit are required (Donovan 1979). When gelatinized starch is stored, for instance, in a refrigerator, new starch crystals are formed and its texture becomes stiff. This hardening phenomenon is referred to as retrogradation (Hoover 1995). Heat-gelatinized starch shows increased enzymatic susceptibility and, thus, high degradability by amylases, while retrograded heat-gelatinized starch becomes resistant to amylase digestion.

On the other hand, starch gel or paste can be obtained when a mixture of starch and water is treated with HHP. This phenomenon is referred to as pressure gelatinization. In pressure gelatinization, starch granules can swell while often maintaining their granular shape and lamellar structure (Fig. 20.2) (Stute et al. 1996; Stolt et al. 2001; Fukami et al. 2010). Knorr et al. (2006) suggested that under pressure the disintegration of the macromolecule is incomplete, since the pressure stabilization of hydrogen bonds favors the helix conformation (Fig. 20.3). Crystalline conversion from A to B isomorph under pressure has also been reported (Katopo et al. 2002).

20.1.3 *Anisotropic Versus Isotropic Compressions of Starch*

In HHP treatment of relatively dry starch samples in powder form, special attention should be paid to the mode of compression, either isotropic or anisotropic. In the case where starch granules are suspended in a liquid pressure medium such as water in a pouch, external pressure compresses the pouch and pressure is transmitted isotropically to individual starch granules through the medium (Fig. 20.4a). On the other hand, in the case where starch granules without a 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. 20.4b).

Fig. 20.4 (continued) 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 packed due to the high compressibility of air surrounding the granules. Pressure is then transmitted anisotropically via loosely packed granules. Once the granules are tightly packed while the granules are distorted to fill the space among the granules, pressure is isotropically transmitted via tightly packed starch granules as pressure media
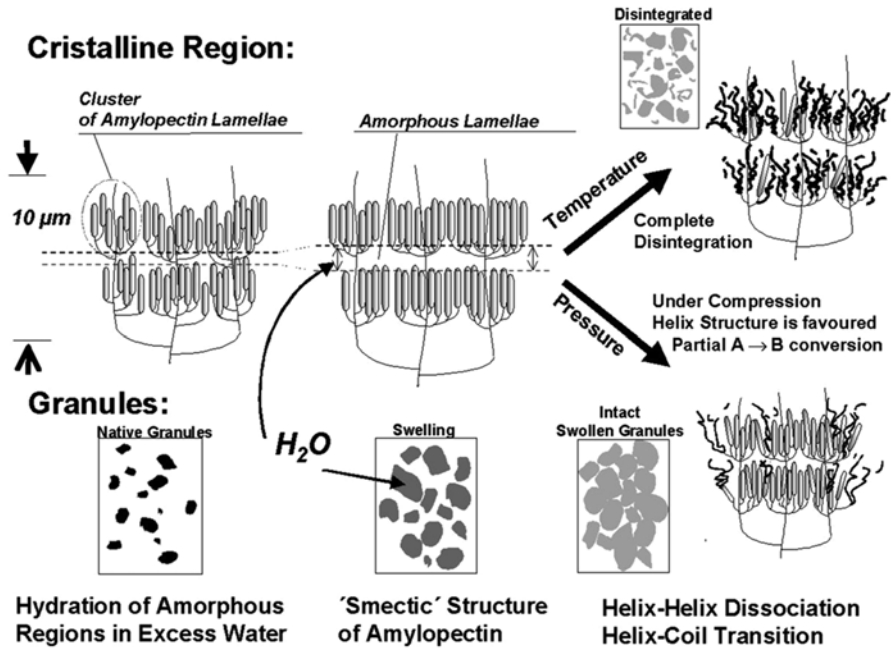
Fig. 20.3 Scheme of starch gelatinization under pressure or at high temperature in excess water. Figure reprinted from Knorr et al. (2006)
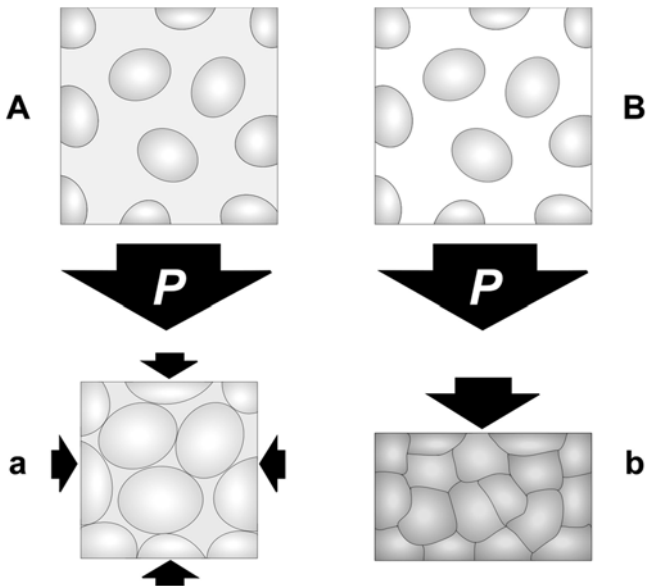

Fig. 20.4 Isotropic and anisotropic compressions of starch as described by Yamamoto et al. (2006). (**A**) to (**a**) Isotropic compression: starch granules suspended in water (pressure medium) can be compressed isotropically and homogeneously via the pressure medium. It can be indicated that

In early studies on HHP treatment of starch, there was no viewpoint to utilize HHP actively for 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 was the focus of such studies. In fact, the objective in these early studies was to study the effect of pressure on the mechanical damages of starch in the milling process. For instance, in ball milling of starch, anisotropic high pressure can be generated when heavy balls impact the starch granules on the inner surface of the rotating vessel (Brown and Heron 1879).

One of the oldest descriptions of HHP treatment of starch could be the following: *Stärke, bei 20,000 atm. einem gleitenden Druck ausgesetzt, verliert ihr Röntgenogramm* (Starch exposed to a sliding pressure of 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 this literature, it is probable that the starch was subjected to pressure anisotropically under a sliding condition. Mercier et al. (1968) compressed several moistened starches anisotropically at 588.4 MPa by using a piston 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 anisotropic compression, compressed starch granules under a microscope appeared as flat ellipsoids which were observed in milling as well (Jones 1940). It is a matter of interest that this compression trial aimed to improve starch availability by damaging native starches. After direct compression at 0.8–1.2 GPa, air- or oven-dried starches (Kudta and Tomasik 1992), and dry and wet starches in the presence of metal salts (Kudla and Tomasik 1992) were analyzed by methods including differential thermal analysis. Liu et al. (2008) carried out direct compression on several starches (approximately 14 % moisture) at up to 1500 MPa for 24 h. Differential scanning calorimetry (DSC) and scanning electron microscopy indicated that gelatinization temperature and enthalpy change were slightly lowered and starch granule shape and surface appearance were changed after the high pressure treatment. However, X-ray diffraction patterns and birefringence of HHP starches were not changed.

Another method of compression is high pressure extrusion (Kim and Hamdy 1987). Starch colloidal solutions (0.5–2.5 % w/v) were extruded via an orifice of a French pressure cell while maintaining high hydraulic pressure at 90, 138, or 276 MPa. A combination of high pressure homogenization (22.0 MPa, 67.5 °C for 11 min) and spray drying results in a starch product that is similar in terms of morphology but less enzymatically digestible than that produced by a combination of heat gelatinization (5 % w/w starch–water suspension, gelatinized at 121 °C for 20 min) and spray drying (Le Thanh-Blicharz et al. 2012).

Recently, HHP treatment of starch has principally been carried out in isotropic ways. In many cases, starch gelatinization is studied in the presence of water, and a starch–water mixture is transferred into a pouch which is placed in an HHP cylinder filled with pressure medium enabling isotropic compression (Fig. 20.5).
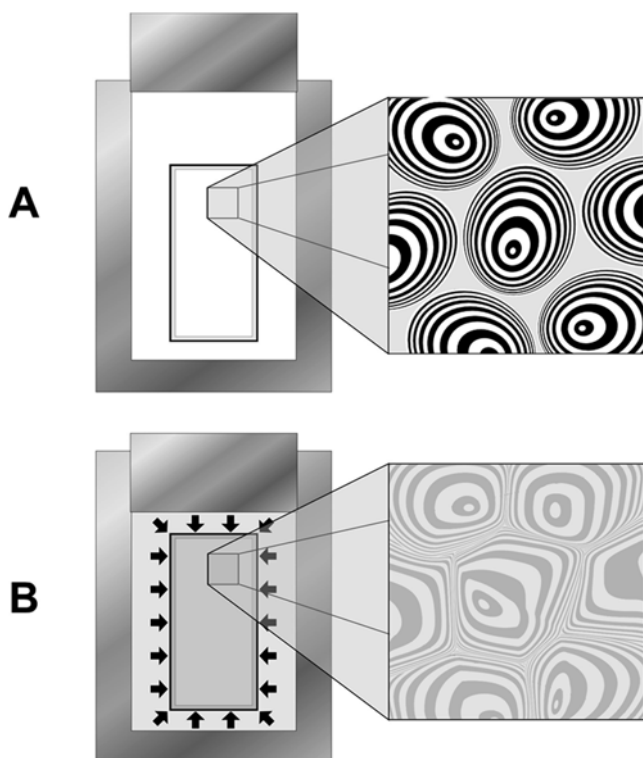
Fig. 20.5 Pressure gelatinization of a starch–water mixture by isotropic compression as described by Yamamoto et al. (2006). (**a**) Pouched starch–water mixture. (**b**) Pressure-gelatinized starch granules by isotropic compression via liquid pressure medium retain lamellar structure while the granules are tightly packed with distortion. At high starch content (i.e., low water content), granules are swollen and packed tightly. At low starch content (i.e., high water content), granules are swollen with granular shape retained, as shown in Fig. 20.2c, although there are some exceptions

20.1.4 Characteristics of Pressure-Gelatinized Starch

Early studies reported an increase in the gelatinization temperature of a dilute suspension of potato starch (0.4 %) after HHP treatment at up to 253.3 MPa for 4 min (Thevelein et al. 1981). In contrast, Muhr and Blanshard (1982) reported that HHP treatment (200–1500 MPa) decreased gelatinization temperature. High pressure differential thermal analysis was carried out for further investigation on wheat, potato, and pea starches, indicating that starch gelatinization temperature first increases by a few degrees and decreases when pressure exceeds 150–250 MPa (Muhr et al. 1982).

Since HHP was suggested as a means of food processing in Japan (Hayashi 1987), pressure gelatinization has been studied intensively. It was reported that potato starch was more pressure resistant than wheat and maize starches (Hayashi and Hayashida 1989). Thereafter, pressure resistance was discussed in terms of starch crystalline types (Ezaki and Hayashi 1992): B-type starches such as potato and lily starches were more resistant to pressure than A-type starches such as maize starch, while C-type starches such as sweet potato starch had intermediate pressure resistance between A- and B-type starches. The effect of pressure holding time on gelatinization enthalpy change and gel properties was investigated 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. 2002). Hu et al. (2011) compared the retrogradation behaviors between pressure- and heat-gelatinized rice starches, demonstrating that the retrogradation rate of pressure-gelatinized rice starch was slower than that of heat-gelatinized starch. Other studies indicated that pressure holding times between 1 and 66 h did not affect enthalpy changes upon pressure gelatinization and melting of retrograded potato starch (Kawai et al. 2007a). HHP treatment induced swelling and gelatinization of starches but retained the granular shapes (Stute et al. 1996; Stolt et al. 2001).

Properties of HHP-treated starch are different from those of heat-treated starch. Amylose is released from heat-gelatinized starch but little from HHP-treated starch (Douzals et al. 1998; Oh et al. 2008b) or not at all (Stute et al. 1996). HHP treatment induces the swelling of starch granules while retaining their granular shapes (Stolt et al. 2001; Fukami et al. 2010). HHP treatment of barley starch and waxy maize starch showed that rheological properties, microstructure, birefringence, and enthalpy change upon gelatinization were dependent on holding time and holding pressure (Stolt et al. 1999, 2001; Buckow et al. 2007). However, further studies are necessary to clarify whether prolonged HHP treatment could complete the gelatinization of partially gelatinized starch treated at lower pressures. In addition, one report discussing the relationship between structure and pasting properties of HHP-treated (690 MPa) various starches having different chemical structures has been presented (Katopo et al. 2002).

20.1.5   Methods of Analysis for Pressure Gelatinization

When starch granules are observed under polarized light, 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). This method has been found to be suitable to detect very low degrees of pressure gelatinization and has been used by several authors (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 total (birefringent and non-birefringent) granules. The quantitative performance of judging the degree of gelatinization by birefringence loss was calibrated with differential scanning calorimetry (DSC) results, indicating that the method often slightly overestimates the gelatinized fraction in comparison with DSC measurements (Douzals et al. 2001). On the other hand, Bauer and Knorr (2004) showed that there was a good linear relationship between degree of gelatinization by birefringence loss and that by electrical conductivity.

DSC measurement is widely used for quantitative analysis of the degree of gelatinization. Depending on the botanical source of starch, an endothermic peak can be observed at around 60–80 °C in the presence of excess water, although the difference in thermal properties among 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. 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. 2007a).

Analysis of moist (10.0–34.0 %) barley starch samples by DSC under pressure (pressurized by nitrogen gas up to 2.5 MPa) showed that less water is required for initiation of gelatinization under the pressurized condition than under atmospheric pressure (Vainionpää et al. 1993). Recently, high sensitivity DSC was introduced to analyze dilute suspensions (0.5 %) of waxy wheat, waxy potato, waxy maize, and high amylose maize starches and mixtures of waxy and high-amylose maize starches after HHP treatment (Blaszczak 2007; Blaszczak et al. 2007a, b).

Pressure gelatinization can also 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 loss of crystallinity. Completely pressure-gelatinized starch shows only an amorphous halo (Hibi et al. 1993; Katopo et al. 2002; Blaszczak et al. 2005b). For a quantitative evaluation of pressure gelatinization, a crystallinity index can be used (Hibi et al. 1993). However, attention should be paid to evaluating pressure gelatinization and retrogradation of B-type starch (Stute et al. 1996), since the diffraction pattern of B-type crystallinity can be superimposed by that of retrograded starch in the pressure gelatinization. Therefore, X-ray diffraction should be used for evaluation of HHP-treated B-type starch in combination with other methods such as DSC.

Compressibility of HHP-treated starch was calculated by measuring volume changes (cross-sectional area of the pressure chamber multiplied by the plunged length of the piston) of 16 % w/w (dry matter basis) aqueous suspension of wheat starch and pure water under varying pressure conditions (Douzals et al. 1996a, b). During compression below 300 MPa, compressibility of starch suspension was close to that of pure water, while reduction of volume was higher for starch suspension at higher pressures due to starch gelatinization. Interestingly, compressibility

of starch suspension was higher during decompression than during compression, and starch gels treated with HHP remained compressed after decompression. These results indicated that total volume was reduced due to starch melting and that water binding to starch under pressure is strong.

NMR analysis of HHP-treated starch has been performed using cross-polarization/magic angle spinning (CP/MAS) ^{13}C NMR which is a powerful tool to analyze the structure of solid organic materials (Blaszczak et al. 2005a, b). HHP-treated potato starch presents two resonances (Blaszczak et al. 2005b), which are characteristic to 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 pressure gelatinization was initiated under 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 pressure than spherical ones. Swelling of wheat starch granules under HHPs of up to 300 MPa was also observed under an optical microscope by Bauer et al. (2004). Similarly, Buckow et al. (2007) observed in situ maize starch gelatinization in aqueous solution (5 % w/w) in a high pressure cell at HHPs of up to 650 MPa (Fig. 20.6).
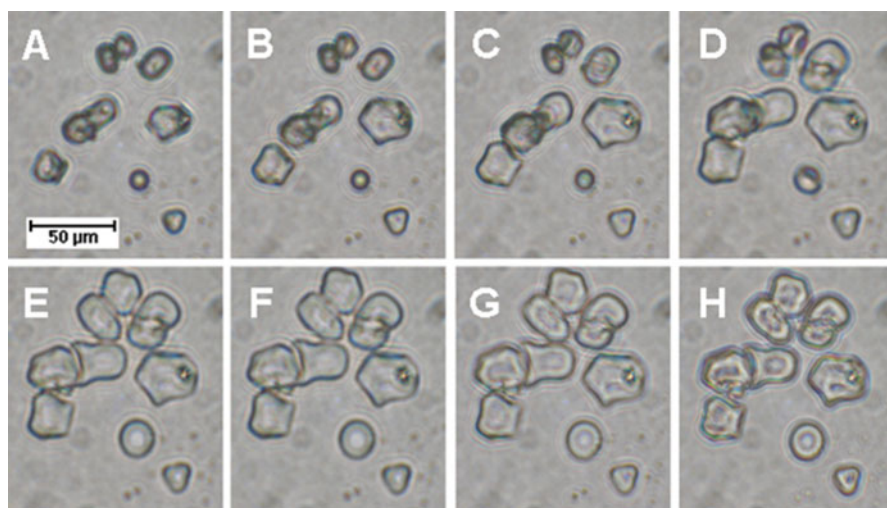

Fig. 20.6 In situ observation of maize starch granule gelatinization in aqueous solution (5 % w/w) at 30 °C and 0.1 MPa. (**a**) Pressure increases up to 650 MPa (**b**), after 1 min at 650 MPa (**c**), after 2 min at 650 MPa (**d**), after 5 min at 650 MPa (**e**), after 10 min at 650 MPa (**f**), after 20 min at 650 MPa (**g**), and after pressurization at 650 MPa for 20 min and pressure release to ambient pressure (**h**). Figure reprinted from Buckow et al. (2007)

Pressure gelatinization behaviors of rice, potato, maize, waxy maize, pea, and tapioca starches were studied in situ in a DAC by Fourier transform infrared (FTIR) spectroscopy (Rubens et al. 1999; Rubens and Heremans 2000). 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 were studied at a pressure range from 0.1 to 100 MPa and a temperature range from 10 to 157 °C (283 to 430 K).

20.1.6 Pressure Gelatinization and Enzymatic Digestibility

Amylase digestibility of starch increased after HHP treatments of starch–water mixture at 100–600 MPa and elevated temperatures (45 and 50 °C) (Hayashi and Hayashida 1989). This tendency was also observed with potato and wheat starches which were HHP-treated (0.1–650 MPa) at 10 °C and digested by α-amylase (Noguchi et al. 2003). HHP-gelatinized starch shows increased enzymatic susceptibility (digestibility) similar to heat-gelatinized starch (Hayashi and Hayashida 1989). Gomes et al. (1998) pressure-treated wheat or barley flour suspension at up to 800 MPa and evaluated the level of 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. *Bacillus amyloliquefaciens* alpha-amylase (BAA) in a buffer solution with or without a substrate (soluble starch) was treated with HHPs of 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. Furthermore, a retarded enzymatic hydrolysis of starch by BAA under pressures of up to 400 MPa at 25 °C was detected, indicating a reversible inhibition of the reaction but irreversible inactivation of the enzyme. Similarly, enhanced maize starch hydrolysis by glucoamylase from *Aspergillus niger* was found with increasing HHP (Buckow 2006), but pressures of up to 300 MPa can induce changes in product composition accompanying the hydrolysis of maltooligosaccharides by porcine

pancreatic α-amylase (Matsumoto et al. 1997; Baks et al. 2008b). However, applying HHPs of up to 600 MPa at elevated temperatures (e.g., 60–80 °C) can significantly increase enzyme activity and starch digestibility (Heinz et al. 2005).

20.1.7 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 complete hydration upon gelatinization (Donovan 1979). However, a systematic understanding of the effect of water content on pressure gelatinization has not yet progressed sufficiently, as most studies on pressure gelatinization have been carried out under limited conditions in terms of water content.

HHP treatment of starch with low water content, i.e., dry or low moist starch, has been carried out by anisotropic compression in many reports. Enzymatic digestibility of potato, wheat, and maize starches at low water content (2–36 %) was measured after piston compression, and digestibility showed minimums for potato starch at a water content of about 19 % and for wheat and maize starches at about 14 %, respectively (Mercier et al. 1968). Reducibility of air- or oven-dried potato starch at a water content of 15.1 % increased after pelletization by plunger compression (Kudla and Tomasik 1992, 1992). The authors suggested 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. In addition, depolymerization of starch was observed after high pressure extrusion (Kim and Hamdy 1987). On the contrary, several papers have reported that the chemical bonds of starch molecules were not influenced by HHP treatment (Hibi et al. 1993; Katopo et al. 2002).

At higher water content (≥70 %), a few phase transition diagrams (gelatinization vs. pressure vs. temperature) have been presented (Douzals et al. 2001; Knorr et al. 2006; Buckow et al. 2007, 2009) and an example of complete gelatinization of barley malt, wheat, tapioca, normal maize, and potato starch slurries (5 % w/w) after 15-min processing at isothermal/isobaric conditions can be seen in Fig. 20.7.

Pressure gelatinization and other related experiments were often carried out at a fixed water content. However, some studies have investigated pressure gelatinization of starch at several water contents (Yamamoto et al. 2009). Stute et al. (1996) reported that HHP gelatinization requires at least a water content of 50 % as evaluated in the DSC measurements of HHP-treated (600 MPa, 20 °C, 15 min) starch samples at water contents of 42 %, 56 %, and 71 %. Katopo et al. (2002) treated starches of various botanical origins at water contents of 50 % and 67 % at 690 MPa and room temperature for 5 min and concluded that the degree of gelatinization was higher in starches at 67 % than in those at only 50 %. As indicated above, pressure gelatinization has been studied at limited water contents, and, therefore, a systematic understanding on the role of water in pressure gelatinization of various starches is not yet possible.
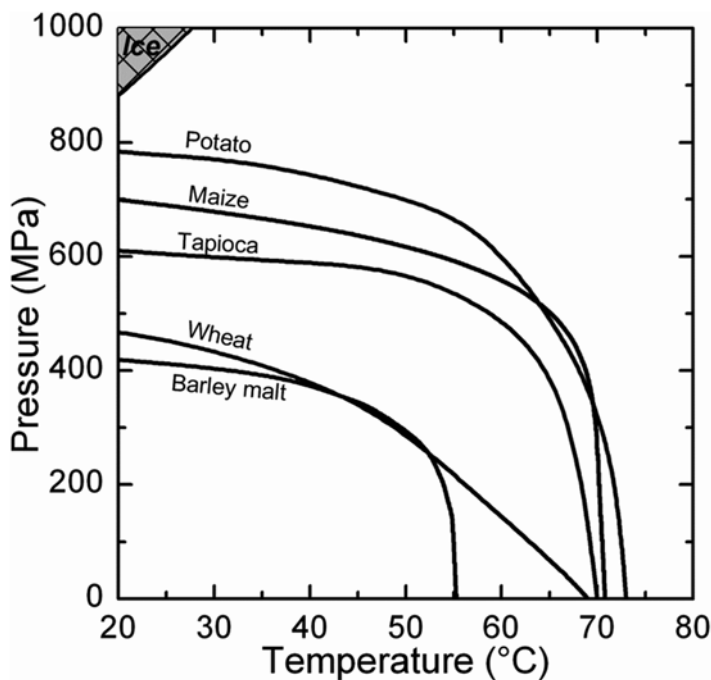
Fig. 20.7 Phase diagram for complete gelatinization of barley malt, wheat, tapioca, normal maize, and potato starch slurries (5 % w/w) after 15-min processing at isothermal/isobaric conditions. Isolines were taken from Knorr et al. (2006)

20.1.8 Effect of Water Content on Pressure Gelatinization

Potato starch has been reported to be more pressure resistant than cereal starches such as maize, wheat, and rice starches (Muhr et al. 1982; Ezaki and Hayashi 1992; Katopo et al. 2002; Oh et al. 2008a, b).

Kawai et al. (2007b) treated potato starch–water mixtures at water contents of 30–90 % w/w with pressures of 400–1200 MPa at 40 °C for 1 h andpresented a state diagram. Pressure gelatinization and pressure-induced retrogradation were evaluated from endothermic peaks by differential scanning calorimetry (DSC). As shown in Fig. 20.8, an endothermic peak, which corresponds to the enthalpy change upon gelatinization (ΔH_{gel}), can be observed at approximately 75 °C, whereas another peak at approximately 58 °C corresponds to the enthalpy change upon melting of retrograded starch (ΔH_{retro}). The value of ΔH_{gel} decreased upon pressure gelatinization, and increased gelatinization was achieved with increasing pressure in starches with higher water content (Fig. 20.9). On the other hand, retrogradation was observed with completely or partially pressure-gelatinized starch, and the value of ΔH_{retro} tended to increase with decreased water content of the starch samples and with increased treatment pressure (Fig. 20.10). Taking into account that the non-treated potato starch
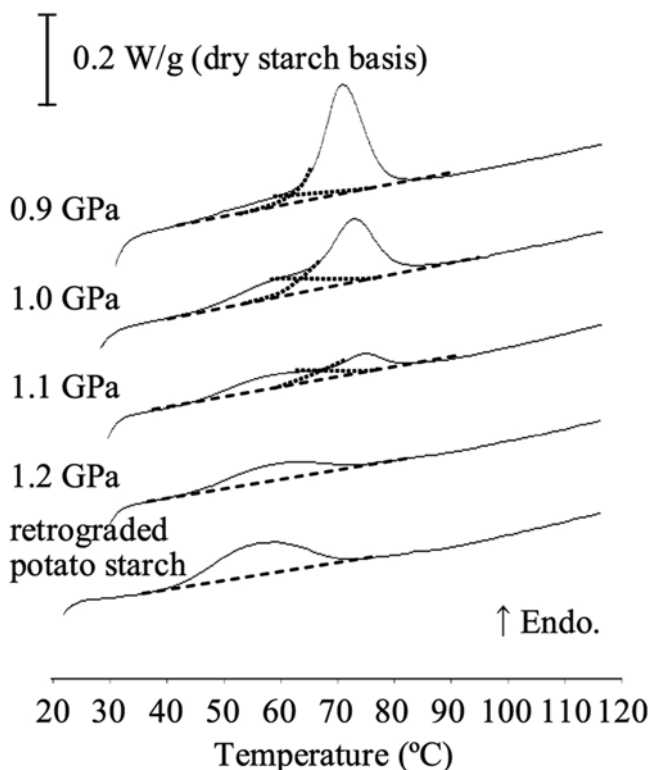
Fig. 20.8 DSC thermograms of the potato starch–water mixture (water: 50 % w/w) treated with HHP (0.9–1.2 GPa) and the retrograded potato starch–water mixture (water: 30 % w/w) gelatinized completely with heat and stored at 4 °C for 7 days, as described by Kawai et al. (2007a)

showed $H_{gel} = 20 \pm 2$ J/g (dry starch basis), the state of the HHP-treated potato starches was classified into five categories: complete gelatinization ($\Delta H_{gel} = 0$ J/g), complete gelatinization with retrogradation ($\Delta H_{gel} = 0$ J/g and $\Delta H_{retro} > 0$ 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. 20.11). Data for depicting the state diagrams were physicochemically analyzed using mathematical models and were compared with those of wheat starch–water mixtures (5–80 % w/w) published by Baks et al. (2008a). Thereafter, the state diagram of potato starch–water mixtures at water contents of 30–90 % w/w and pressures of 400–1000 MPa (Fig. 20.12) was extended in terms of treatment temperature (20–70 °C) (Kawai et al. 2012). With increased temperature and/or water content, the pressure required for complete gelatinization decreased. Retrogradation was observed at starch contents ranging from 20 % to
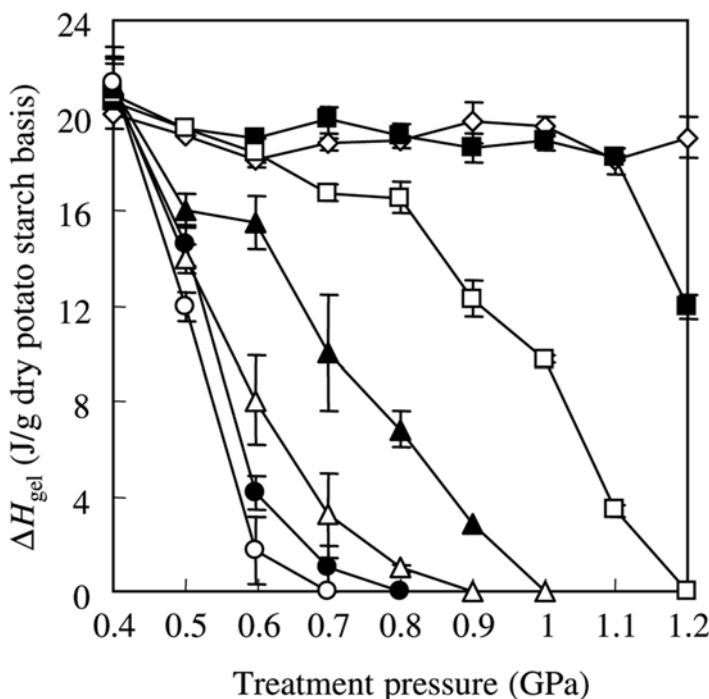
Fig. 20.9 Dependence of ΔH_{gel} on treatment pressure and starch content of potato starch–water mixture, as described by Kawai et al. (2007a). *Open circle*, 10 %; *closed circle*, 20 %; *open triangle*, 30 %; *closed triangle*, 40 %; *open square*, 50 %; *closed square*, 60 %; *open diamond*, 70 %

70%w/w, which is wider than the reported general range of 30–60 % w/w observed after heat gelatinization at ambient pressure (Hoover 1995). At a water content of 80 %, retrogradation was observed at relatively low temperatures of 20 °C and 30 °C, while at a water content of 30 %, retrogradation only occurred at relatively high temperatures of 60 °C (only at 1000 MPa) and 70 °C (at 400–1000 MPa).

20.1.9 Effect of Treatment Time on Pressure Gelatinization

Only a few reports have examined pressure gelatinization of starch as a function of pressure holding time (Stolt et al. 2001; Buckow et al. 2007; Kawai et al. 2007a). Kawai et al. (2007a) reported on the effect of treatment time (1, 18, and 66 h) on gelatinization and retrogradation of potato starch–water mixtures (water content: 30–90 % w/w) treated at 600–1000 MPa. The values of ΔH_{gel} and ΔH_{retro} were dependent on the water content and were not affected by treatment time in the tested range (Fig. 20.13). However, the onset temperature of gelatinization (T_{gel})
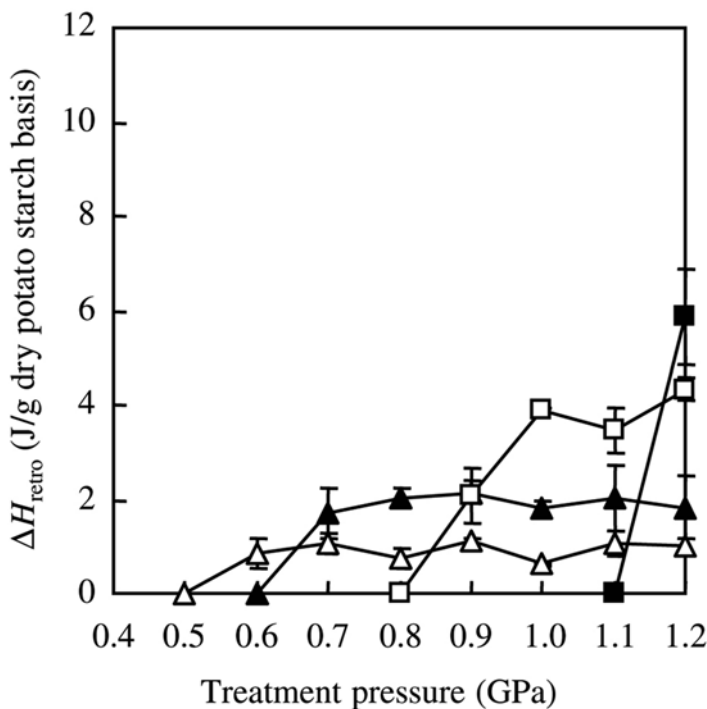
Fig. 20.10 Dependence of ΔH_{retro} on treatment pressure and starch content of potato starch–water mixture, as described by Kawai et al. (2007a). *Open triangle*, 30 %; *closed triangle*, 40 %; *open square*, 50 %; *closed square*, 60 %

increased with increased water content and treatment time (Fig. 20.14). Although long-time HHP treatment is impractical from the viewpoint of running cost in the food and starch industries, it is of fundamental importance to understand gelatinization and retrogradation properties of HHP-treated starch, especially from the viewpoint of annealing.

20.1.10 Effect of Amylose on Pressure Gelatinization

Amylose is considered to play an important role in pressure gelatinization. Fukami et al. (2010) pointed out that amylose maintains the granular structure of HHP-treated (600 MPa and 40 °C for 1 h) normal and waxy maize starches. When completely gelatinized (as confirmed by DSC and birefringence), the granules of waxy maize starch lost their granular structure, while those of normal maize starch maintained their granular shape although they were swollen (Fig. 20.15). Buckow et al. (2009) also demonstrated that temperature and pressure stabilities of high amylose maize starches are significantly higher than those of waxy and normal starches. Blaszczak et al. (2007c) subjected waxy maize, amylopectin wheat, and
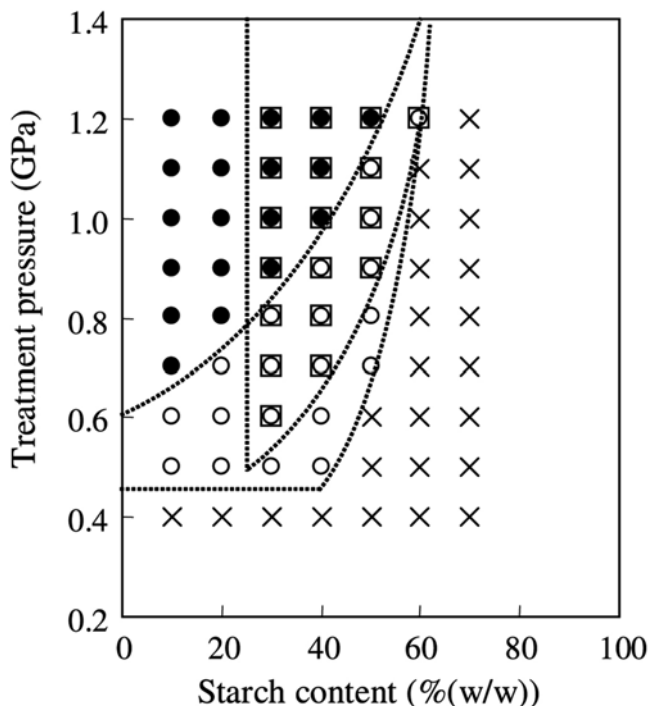
Fig. 20.11 State diagram (treatment pressure vs. starch content) of HHP-treated potato starch–water mixtures, as described by Kawai et al. (2007a). *Closed circle*, complete gelatinization; *closed circle in square*, complete gelatinization with retrogradation; *open circle*, partial gelatinization; *open circle in square*, partial gelatinization with retrogradation; *cross*, thermodynamically unchanged

amylopectin potato starches in excess water to 650 MPa for 9 min and measured the relaxation time constants of the starch gels. Two different relaxations were observed, indicating different mobility of water molecules due to differences in the structure of the waxy or amylopectin starch gels.

20.1.11 Toward Practical Applications of Pressure-Gelatinized Starches

For utilization of pressure-gelatinized starch, a recent publication on starch-based hydrogels is of interest (Szepes et al. 2008). Gels were prepared using potato starch via HHP treatment with the aim of drug formulation. The effect of HHP treatment on the binding of odorants to starch was studied by using maize starches (Blaszczak 2007; Blaszczak et al. 2007c). Yamada et al. (1998) reported on some trials introducing 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 clearly described.
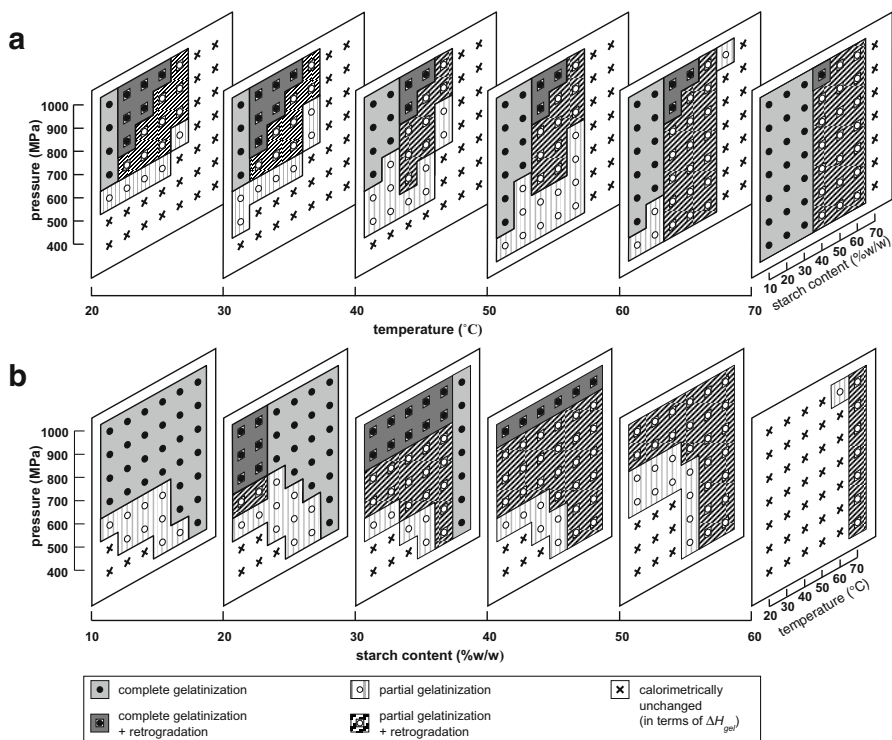
Fig. 20.12 State diagrams of potato starch–water mixtures (10–60 % w/w) HHP treated (400–1000 MPa) in a temperature range between 20 and 70 °C, as described by Kawai et al. (2012). (**a**) Diagrams (treatment pressure vs. starch content) are arranged along the axis of treatment temperature; (**b**) diagrams were replotted (treatment pressure vs. treatment temperature) and arranged along the axis of starch content. *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

HHP treatment has been applied to study its effect on food or its model system. The influence of potato starch on HHP-treated surimi gels (400 and 650 MPa, 10 min) was compared with heat-treated gels (90 °C, 40 min) (Tabilo-Munizaga and Barbosa-Cánovas 2005). The applied pressures seem to be insufficient for gelatinization, although the water holding capacity of the HHP-treated surimi gels was higher than for heat-treated gels. Huttner et al. (2009) evaluated impacts of HHP on oat batters, and Barcenas et al. (2010) reported microbial, physical, and structural changes in HHP-treated wheat dough. Vallons and Arendt (2010) studied HHP-induced rheological changes of wheat flour–water suspensions. Ten-min treatment of starch-gluten suspension at 400 or 600 MPa led to starch gelatinization and formation of protein network, which promoted strengthening of the flour structure. However, gelatinization of starch due to HHP treatment was the main cause of the enhanced viscoelastic properties.
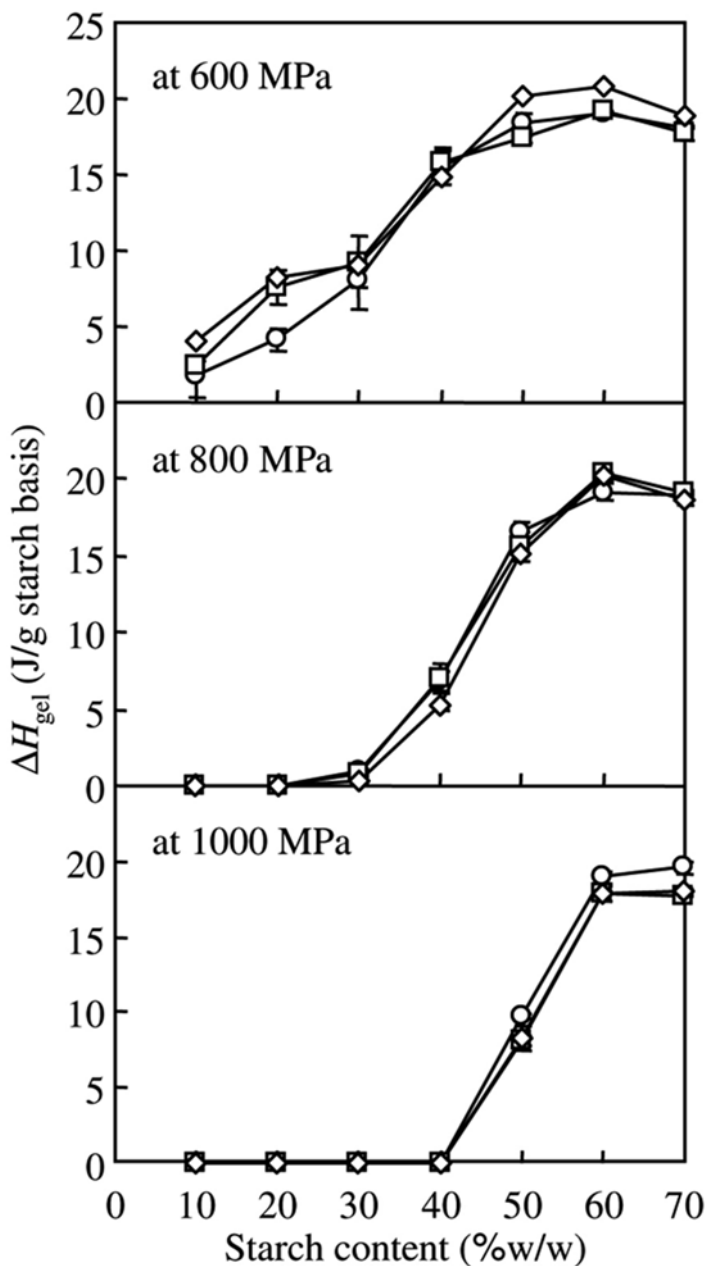
Fig. 20.13 Dependence of ΔH_{gel} on treatment time (1, 18, and 66 h), treatment pressure, and starch content of potato starch–water mixture, as described by Kawai et al. (2007b). *Circle*, 1 h; *square*, 18 h; *diamond*, 66 h
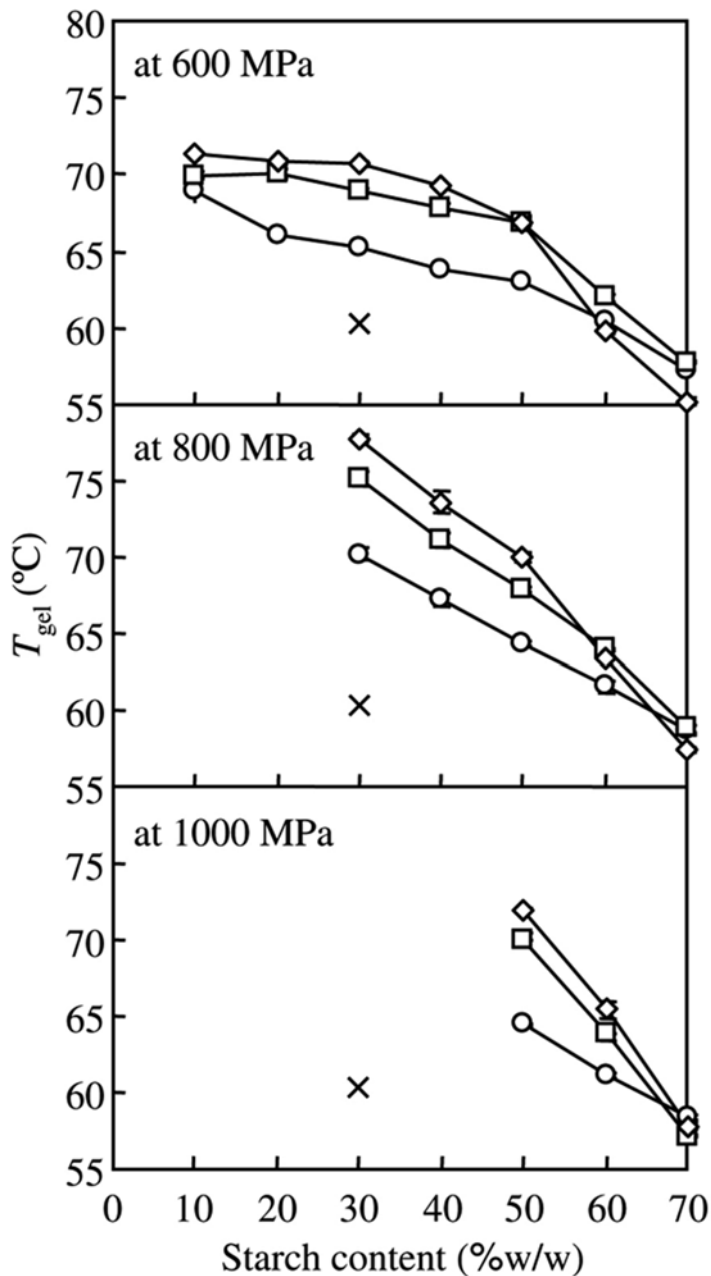
Fig. 20.14 Dependence of T_{gel} (onset temperature) on treatment time (1, 18, and 66 h), treatment pressure, and starch content of potato starch–water mixture, as described by Kawai et al. (2007b). *Circle*, 1 h; *square*, 18 h; *diamond*, 66 h. The *cross* indicates the T_{gel} of native potato starch–water mixture at the starch content of 30 % w/w
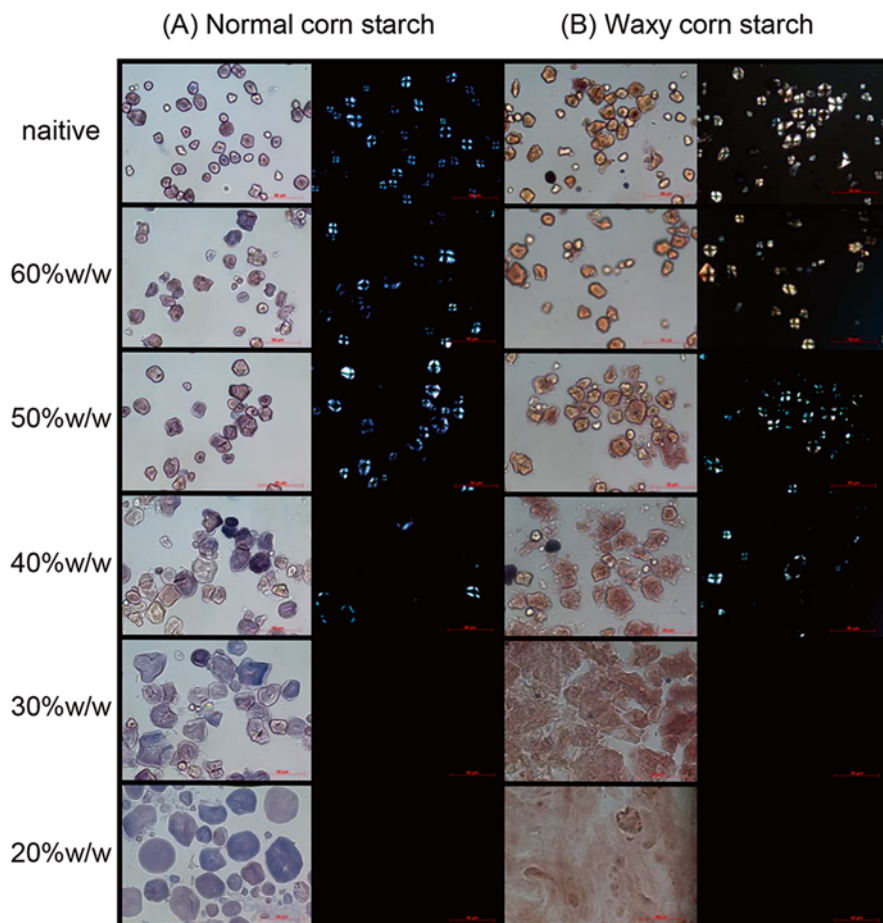
Fig. 20.15 Micrographs of (**a**) normal and (**b**) waxy maize starches treated at 600 MPa and 40 °C for 1 h at a range of starch contents, as described by Fukami et al. (2010). *Left*, bright-field micros-copy; *right*, polarized microscopy; bar, 50 μm

Watanabe et al. (1991) found that the cooking properties of aged rice grains were improved by HHP treatment and that optimum pressure was 100 MPa in treatments at 20 °C for 10 min. Increasing pressure during HHP treatment at 0.1–600 MPa and 20–70 °C for up to 2 h facilitated gelatinization and improved water uptake and moisture equilibrium of Thai glutinous rice during soaking (Ahromrit et al. 2006, 2007). Basmati rice flour slurry and extracted rice starch were completely HHP-gelatinized after 15 min at 650 MPa and 550 MPa (approximately at room tempera-ture), respectively (Ahmed et al. 2007). Lille and Autio (2007) evaluated the size and number of ice crystals in HHP-frozen starch gels using size and total area of pores in microscopic images of thawed gel. This study showed that average size and total area occupied by the pores were clearly reduced by HHP freezing. Kweon

et al. (2008) indicated that sodium chloride and sucrose have solute-induced barostablizing (or piezostabilizing) effects on HHP gelatinization (600 MPa at 25 °C for 15 min) of maize starch. Application of HHP to chemical conversion of starch into chemically engineered starches has been reported recently. For example, HHP can enhance the decrease of thermally generated radicals (Blaszczak et al. 2008), acid hydrolysis (Lee et al. 2006; Choi et al. 2009b), cross-linking (Hwang et al. 2009; Kim et al. 2012a, b), phosphorylation (Blaszczak et al. 2010, 2011), acetylation (Choi et al. 2009a; Kim et al. 2010), and hydroxypropylation (Kim et al. 2011) of maize and potato starches. Blaszczak et al. (2011) reported a decrease in thermally generated radicals in phosphorylation of maize starches with various amylose content after HHP treatment. HHP-assisted chemical conversion of starch has been reviewed by Kim et al. (2012b).

For industrial applications of HHP-treated starch, it is necessary to predict and control the process condition of gelatinization and retrogradation while demonstrating possible ways of commercialization of HHP-treated starches. An approach depicting state diagrams of HHP-gelatinized starches of various botanical origins would promote prediction and control of the process. New applications of HHP treatment to chemical modifications and other industrial process may be of great interest. It is also expected that analysis of HHP-treated starch through various and novel approaches will contribute to better understanding of starch granular structures.

20.2   Conclusions

The effect of HHP treatment on the behavior of starch has been studied since the (possibly) first description by Meyer et al. (1929), and 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. Functional and rheological properties of HHP-treated starches such as viscosity, pasting properties, retrogradation, and enzymatic digestibility often differ from the properties of heat-gelatinized starches. One difference is that regular (non-waxy) starch granules can be swollen and gelatinized by HHP but still retain their granular shapes. These phenomena may be affected by amylose content. Nonetheless, new insights into the mechanics of HHP-induced starch hydration and gelatinization could be achieved through in situ studies with diamond anvil cells, which permit the use of infrared and Raman spectroscopies, X-ray diffraction, and optical microscopy techniques.

Systematic studies on different types of starches at a wide range of pressures, temperatures, times, and water content are still rare. Investigations of microstructural changes of different starches during HHP treatment would be of interest in order to gain a better understanding of the interplay of amylose and amylopectin. Similarly, a comparison of crystallinity and molecular order within granules of HHP-treated and heat-treated starches can provide new information on the underlying mechanisms of starch granule swelling under different physical conditions.

A detailed study on the effect of water content on pressure gelatinization of potato starch showed that the state diagram (treatment pressure vs. water content) can classify the state of HHP-treated starch into five categories: complete gelatinization into five categories: complete gelatinization, complete gelatinization with retrogradation, partial gelatinization, partial gelatinization with retrogradation, and thermodynamically no change. Such state diagrams can be of practical use and, thus, remain important to the food industry for preparing HHP-treated starches and foods with defined properties.

Sugars and salts are common co-solutes in starchy foods, and thus the effects of such additives on pressure gelatinization have been investigated from the viewpoint of their solute-induced stabilization. However, further studies on the influence of saccharides, fibers, fats, and proteins, for example, on gelatinization under pressure may be needed to make this process of practical interest in the food industry. Recent studies also suggest that HHP treatment can enhance flour properties post-milling by structure modification of proteins and partial swelling of the starch granules.

Finally, HHP can also achieve targeted gelatinization degrees in starch, possibly resulting in a product with defined enzymatic digestibility and glycemic response. HHP-treated starch also gives unique retrogradation patterns, which can be attractive in terms of food functionality as nondigestible starch and/or fat replacers in low-energy formulations.

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