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Effect of temperature on gelatinization and retrogradation in high hydrostatic pressure treatment of potato starch–water mixtures

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ABSTRACT

The effect of temperature (20–70 °C) on the gelatinization and retrogradation of potato starch–water mixtures (10–70%, w/w) treated with high hydrostatic pressure (HHP) (400–1000 MPa) was investigated. Gelatinization enthalpy change (ΔH_{gel}) and re-gelatinization enthalpy change of retrograded crystalline part ($\Delta H_{\mathrm{retro}}$) of the HHP-treated starch were evaluated using differential scanning calorimetry. The value of ΔH_{gel} of 10–20% (w/w) mixtures decreased with increased pressure and temperature, while ΔH_{gel} of 30–50% (w/w) mixtures decreased to certain values with increased pressure and the values depended on treatment temperature. With higher temperature and pressure conditions, ΔH_{gel} of 10–40% (w/w) mixtures reached zero, but ΔH_{gel} of 50–70% (w/w) mixtures did not. Retrogradation was observed with HHP-treated 20–60% (w/w) mixtures and the value of $\Delta H_{\mathrm{retro}}$ depended on the starch content, pressure, and temperature. The value of $\Delta H_{\mathrm{retro}}$ trended to increase with increase in starch content. In addition, retrogradation was promoted by HHP treatment at low temperature. Gelatinizaiton and retrogradation behaviors of HHP-treated (400–1000 MPa) potato starch–water mixtures (10–70%, w/w) at 20–70 °C were summerized in a series of state diagrams.

1. Introduction

Gelatinization, which has been conventionally achieved by heating starch in the present of excess water, is an important process, since gelatinized starch has been widely used as a major food ingredient in food industry and as industrial materials such as biodegradable polymers and starch glue. It is recognized that heat gelatinization involves multi-steps; the amorphous region in a starch granule is destabilized by water absorption and swelling, while the crystalline region in the granule (mainly amylopectin crystallites) melts simultaneously with progressively increasing hydration (Jacobs & Delcour, 1998; Jacobs, Mischenko, Koch, Eerlingen, Delcour & Reynaers, 1998; Tester & Debon, 2000). In the case of starch systems with limited water content at temperatures higher than the gelatinization temperature, starch gelatinizes partially, and thus amylopectin crystallites remained partially unmolten in starch granule. Melting temperature of amylopectin crystallites increases with decrease in water content (Cruz-Orea, Pitsi, Jamée, & Thoen, 2002; Tester & Debon, 2000).

When gelatinized starch is held under a certain condition, the molten and hydrated amylopectin molecules re-wind and recrystallize gradually. The recrystallization phenomenon of the unwound amylopectin molecules is recognized as "retrogradation". While retrogradation has been usually treated as a typical quality loss of gelatinized starchy foods, it is of interest in recent years to utilize retrograded starch as resistant starch (Bauer, Wiehle, & Knorr, 2005; Chung, Lim, & Lim, 2006; Escarpa, González, Mañas, García-Diz, & Saura-Calixto, 1996). Retrogradation is promoted generally at low temperatures above the freezing temperature of water (Colwell, Axford, Chamberlain, & Elton, 1969; Hoover, 1995), and the degree of retrogradation increases with increased starch content in the range between 30 and 60% (w/w) (Miles, Morris, Orford, & Ring, 1985; Orford, Ring, Carroll, Miles, & Morris, 1987).

Gelatinization of starch is achieved also by high hydrostatic pressure (HHP) (Yamamoto, Kawai, Fukami, & Koseki, 2009). There is considerable interest in the use of HHP treatment for physical modification of starch, since HHP-gelatinized starch shows different properties from heat-gelatinized one, as reported by Knorr, Heinz, and Buckow (2006) and Fukami, Kawai, Hatta, Taniguchi, and Yamamoto (2010). Many efforts have been devoted to understand the various properties of HHP-gelatinized starch in terms of treatment pressure and temperature. At a constant treatment temperature, aqueous suspension of most starches (e.g., corn, waxy corn, rice, wheat, and pie) gelatinizes partially at a treatment

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pressure of above 300 MPa and completely at a treatment pressure of up to 600 MPa (Bauer, Hartmann, Sommer, & Knorr, 2004; Bauer & Knorr, 2005; Błaszczak, Fornal, Valverde, & Garrido, 2005; Douzals, Marechal, Coquille, & Gervais, 1996; Douzals, Perrier-Cornet, Gervais, & Coquille, 1998; Douzals, Perrier-Cornet, Coquille, & Gervais, 2001; Muhr & Blanshard, 1982; Rubens & Heremans, 2000; Stolt, Oinonen, & Autio, 2001; Stute, Klingler, Boguslawski, Eshtiaghi, & Knorr, 1996). Potato starch, however, is more pressure resistant than other starches (Bauer et al., 2004; Błaszczak, Fornal et al., 2005; Błaszczak, Valverde, & Fornal, 2005; Douzals et al., 1996; Hibi, Matsumoto, & Hagiwara, 1993; Katopo, Song, & Jane, 2002; Muhr & Blanshard, 1982; Muhr, Wetton, & Blanshard, 1982; Selmi, Marion, Perrier Cornet, Douzals, & Gervais, 2000; Stute et al., 1996), and it requires treatment pressure higher than 600 MPa for completing the gelatinization (Kawai, Fukami, & Yamamoto, 2007a). For example, gelatinization pressure, treatment pressure required for complete gelatinization, was suggested to be 800 MPa for 12.8% potato starch–water mixture (Muhr & Blanshard, 1982). Degree of gelatinization of 5% (w/w) tapioca, potato, corn, and wheat starch suspensions increased with increased treatment temperature in the range between 25 °C and their heat gelatinization temperatures (Bauer & Knorr, 2005; Buckow, Heinz, & Knorr, 2007; Douzals et al., 2001). In contrast, there was little effect of holding temperature on the pressure gelatinization behavior of 10 mg/ml (approximately 1%, w/w) rice starch suspension in the temperature range between −5 °C and 45 °C (Rubens & Heremans, 2000). However, little is known on the effect of starch content on pressure gelatinization of starch–water mixtures.

Retrogradation can be induced only by treating starch–water mixture with HHP, although the mechanism remains unclear (Hibi et al., 1993; Katopo et al., 2002; Kawai et al., 2007a; Kawai, Fukami & Yamamoto, 2007b; Stute et al., 1996). In general, retrogradation of heat-gelatinized starch requires day-long storage (e.g., 1–7 d) at low temperature (e.g., 4 °C). However, HHP-induced retrogradation is observed immediately after HHP treatment, namely, without day-long storage at low temperature.

The effect of starch content on the gelatinization and retrogradation of potato starch–water mixtures (10–70%, w/w) was investigated by treating with HHP at a constant temperature of 40 °C (Kawai et al., 2007a). With higher starch content, higher pressure was required for the gelatinization, and a pressure between 700 and 1200 MPa was required for complete gelatinization. In addition, retrogradation was observed with HHP-treated 30–60% mixtures, and the degree of retrogradation increased with increases in the degree of gelatinization and starch content. However, the effect of treatment temperature on the gelatinization and retrogradation was not investigated in the study. It is reasonable to presume that the properties of HHP-treated potato starch–water mixtures would be affected by treatment temperature, since heat activates molecular motions in general and it induces starch gelatinization and suppresses retrogradation. Furthermore, since the range of starch content required for HHP-induced retrogradation of potato starch–water mixtures (Kawai et al., 2007a) was comparable to that for retrogradation of heat-gelatinized starch (Colwell et al., 1969; Hoover, 1995; Miles et al., 1985; Orford et al., 1987), it can be expected that the retrogradation of HHP-treated starch–water mixtures would also be promoted at decreased treatment temperature above the freezing temperature of water.

The purpose of this study was to investigate the effect of treatment temperature (20–70 °C) on the gelatinization and retrogradation properties of HHP-treated (400–1000 MPa) potato starch–water mixtures (10–70%, w/w). The results are also compared with those obtained by the treatment with HHP of 400–1200 MPa at 40 °C in our previous study (Kawai et al., 2007a).

2. Materials and methods

2.1. Preparation of potato starch–water mixtures

Potato starch was purchased from Hokuren, Japan. The initial moisture content was gravimetrically determined to be 19.7% (w/w) by drying at 105 °C for 12 h. The starch (50–200 mg) and distilled water were put into a polymer pouch (7 cm × 2 cm), and then heat-sealed to prepare 10–70% (w/w) starch-water mixtures. Hereafter, starch content of the sample mixture in percent weight per weight is expressed simply as percent (%), if not indicated otherwise. For preparing 60 and 70% mixtures, the mixtures in the pouch were stirred with a spatula before the heat sealing, and then the pouched mixtures were preserved at ambient temperature for a few days in order to minimize its inhomogeneity of water (Kawai et al., 2007a). For preparing 10–40% mixtures, 2% (w/w) heat-gelatinized waxy corn starch was used instead of water in order to prevent the sedimentation of potato starch during pressure treatment (Kawai et al., 2007a; Stolt et al., 2001). In our preliminary experiment, it was confirmed visually that phase separation between gelatinized starch and bulk water due to the sedimentation of potato starch during HHP treatment was prevented by using the heat-gelatinized waxy corn starch as a thickener. Although the thickener might reduce the impact of HHP treatment on gelatinization and retrogradation because of its elevated viscosity as pointed out by Bauer and Knorr (2005), it was essential to prevent the sedimentation and to obtain homogeneous HHP-gelatinized samples in the experimental system in this study. The pouches containing 10–40% mixtures were shaken manually and transferred into a HHP-generating system.

For comparison, heat-gelatinized starch–water mixtures and their retrograded samples were prepared. Heat-gelatinized samples were prepared by heating the above-mentioned mixtures for 1 h at each treatment temperature. The heat-gelatinized mixtures were subsequently stored for 7 d at 4 °C to prepare the retrograded samples. The samples were applied to DSC analysis as well as HHP-treated samples.

2.2. High hydrostatic pressure treatment

The sample was treated by a HHP-generating system (HPS-1400: Syn Corporation Ltd., Japan). Castor oil and ethanol mixture (volume ratio of 1:1) was used as a pressure medium. The overall temperature of pressure vessel was kept at 20–70 °C by circulating heat medium using a temperature controller. The temperature inside the HHP vessel (2 cm ϕ × 6.5 cm) was not monitored during the build-up (come-up) and release (come-down) of pressure due to the limitations of the HHP system used. Pouched sample was put into the HHP vessel containing the pressure medium. In the cases of HHP treatment at 50–70 °C, the sample was kept in the vessel for 15 min to achieve the temperature equilibrium. Pressure was built up at approximately 100 MPa/min and held at 400–1000 MPa for 1 h. Since 1 h was sufficient for complete gelatinization (Kawai et al., 2007b), treatment time was fixed at 1 h in this study. The treatment pressure was kept within the variation of ±5% by an automatic pressure control system built in the machine. Pressure was released at approximately 100 MPa/min. The HHP-treated sample was taken out of the pressure chamber, placed at ambient temperature, and applied to calorimetric analysis within 1–3 h.

2.3. Differential scanning calorimetry

Gelatinization and retrogradation of HHP-treated mixtures were investigated by using a differential scanning calorimeter (Diamond DSC: Perkin-Elmer Co., Ltd., USA). Empty stainless steal pan was used as a reference, and the temperature and heat flow were calibrated using indium and distilled water. Sample (10–30 mg) was put into the steal pan, and then the starch content was adjusted below 30% (w/w) by adding distilled water to complete heat-induced melting of starch crystals in the next thermal analysis. Measurement by differential scanning calorimetry (DSC) was performed at 10 °C/min (Donovan, 1979) in the temperature range from 10 to 120 °C. DSC thermogram was analyzed by using Thermal Analysis Pyris Software interfaced with the DSC. The values of enthalpy change for heat gelatinization (ΔH_{gel}) and that for re-gelatinization of retrograded starch ($\Delta H_{\mathrm{retro}}$) were evaluated from the peak areas of the endothermic peaks at about 60 °C and at about 40 °C, respectively. In the case that the endothermic peaks of the heat gelatinization and re-gelatinization of retrograded starch overlapped, both ΔH_{gel} and $\Delta H_{\mathrm{retro}}$ were evaluated by deconvolution of the overlapped curve into two endothermic peaks with the analytical software (Kawai et al., 2007a). All the DSC measurements were carried out in duplicate, and the values of ΔH_{gel} and $\Delta H_{\mathrm{retro}}$ in figures are presented as mean and range.

3. Results

3.1. Gelatinization of potato starch–water mixtures

The effects of treatment pressure (400–1000 MPa) and temperature (20–70 °C) on ΔH_{gel} value of HHP-treated 10–70% mixtures are shown in Fig. 1. For comparison, the ΔH_{gel} values at 40 °C reported in our previous study (Kawai et al., 2007a) are plotted with open squares. The ΔH_{gel} value varied in the range of ±2 J/g and decreased with increased pressure and temperature and with decreased starch content.

The mixtures of 10 and 20% showed decrease in ΔH_{gel} with increases in pressure and temperature. The ΔH_{gel} value of 10% mixture reached 0 J/g when the mixture was treated at 700 MPa and 20–40 °C, at 600 MPa and 50 °C, at 500 MPa and 60 °C, and at all the tested pressures at 70 °C. The ΔH_{gel} value of 20% mixture reached 0 J/g when the mixture was treated at 800 MPa and 20–40 °C, at 700 MPa and 50 °C, at 600 MPa and 60 °C, and at all the tested pressures at 70 °C. The mixture of 30% showed decrease in ΔH_{gel} with increases in pressure and temperature. The mixture gave $\Delta H_{\mathrm{gel}} = 0$ J/g at 900 MPa at 20–60 °C and at all the tested pressures at 70 °C. The mixture of 40% gave $\Delta H_{\mathrm{gel}} = 0$ J/g at 1000 MPa irrespective of temperature, and there was little effect of temperature on the ΔH_{gel} at pressures above 600 MPa. At 70 °C the ΔH_{gel} value was below 1 J/g below 1000 MPa irrespective of pressure. As for 50–70% mixtures, complete gelatinization was not achieved. When treated at 20–50 °C, the ΔH_{gel} was not markedly affected by temperature. At 60 and 70 °C, the ΔH_{gel} values below 1000 MPa were almost independent of temperature, being about 12 and 6 J/g, respectively, and the ΔH_{gel} values at 1000 MPa decreased slightly from those values. The ΔH_{gel} values of 60% mixture treated at 400–1000 MPa and 20–60 °C were almost constant at about 20 J/g. When treated at 70 °C, ΔH_{gel} values were about 13 J/g and no remarkable effect of temperature was observed. In the case of 70% mixture, ΔH_{gel} values did not decrease markedly under all the conditions of HHP treatment.

3.2. Retrogradation of potato starch–water mixtures

Retrogradation of HHP-treated mixtures was observed with 20–60% mixtures but not with 10% and 70% mixtures as an enthalpy change upon re-gelatinization of retrograded starch ($\Delta H_{\mathrm{retro}}$). The values of $\Delta H_{\mathrm{retro}}$ of the mixtures were plotted against treatment pressure as shown in Fig. 2. Although the deviation of each $\Delta H_{\mathrm{retro}}$ value was relatively large as compared with that of ΔH_{gel} value in Fig. 1, there were increasing trends in the dependence of $\Delta H_{\mathrm{retro}}$ value on the starch content, pressure, and temperature. With 20 and 60% mixtures retrogradation was observed under more limited ranges than 30–50% mixtures: at 700–1000 MPa at 20–30 °C and at 0.1–1000 MPa at 70 °C, respectively. The other mixtures showed the following trends. In the temperature range between 20 and 50 °C, the higher the starch content was, at the higher treatment pressure retrogradation was observed, and the maximal value of $\Delta H_{\mathrm{retro}}$ increased with increased starch content. At a temperature of 60 or 70 °C, retrogradation was observed at 0.1–1000 MPa, and both pressure and starch content did not affect the $\Delta H_{\mathrm{retro}}$ values markedly.

As reported by Kawai et al. (2007a), retrogradation was observed in the cases where starch–water mixtures were gelatinized partially or completely. In order to clearly present the relationship between gelatinization and retrogradation, $\Delta H_{\mathrm{retro}}$ was plotted against ΔH_{gel} at each holding temperature as shown in Fig. 3. It was confirmed that $\Delta H_{\mathrm{retro}}$ was observed when ΔH_{gel} was below 16 J/g at each temperature. In the temperature range between 20 and 60 °C, it was found that the $\Delta H_{\mathrm{retro}}$ values increased with increase in starch content. In addition, the $\Delta H_{\mathrm{retro}}$ values trended to increase with decreased treatment temperature.

3.3. State diagrams at temperatures 20–70 °C

Gelatinization and retrogradation of HHP-treated potato starch–water mixtures were evaluated by DSC as seen in Figs. 1–3. However, it is not very easy at a glance of the figures to understand the overview of the gelatinization and retrogradation behaviors. Therefore, the data was summarized in state diagrams (Fig. 4). For comparison, the relevant data at 40 °C (Fig. 5 in Kawai et al., 2007a) was incorporated in the figures. To facilitate the understanding of the effects of temperature and starch content on the pressure-induced behaviors, the data in Figs. 1 and 2 were summarized in state diagrams. From the change in ΔH_{gel} and $\Delta H_{\mathrm{retro}}$ values, the physically modified states of HHP-treated potato starch–water mixtures were classified into five states: cross (×), calorimetrically unchanged state ($\Delta H_{\mathrm{gel}} \geq 18$ J/g (dry potato starch basis) and $\Delta H_{\mathrm{retro}} = 0$ J/g); open circle (○), partially gelatinized state ($\Delta H_{\mathrm{gel}} < 18$ J/g and $\Delta H_{\mathrm{retro}} = 0$ J/g); closed circle (●), completely gelatinized state ($\Delta H_{\mathrm{gel}} = 0$ J/g and $\Delta H_{\mathrm{retro}} = 0$ J/g), open circle embedded into square (◙), partially gelatinized and retrograded state ($\Delta H_{\mathrm{gel}} < 18$ J/g and $\Delta H_{\mathrm{retro}} > 0$ J/g); closed circle embedded into square (▣), completely gelatinized and retrograded state ($\Delta H_{\mathrm{gel}} = 0$ J/g and $\Delta H_{\mathrm{retro}} > 0$ J/g). According to the classification, state diagrams (pressure vs. starch content) were arranged along the temperature axis (Fig. 4A) and their replotted state diagrams (pressure vs. temperature) were arranged along the starch content axis (Fig. 4B). From the figures, it is clearly understood that gelatinization was promoted with increased treatment temperature (Fig. 4A) and/or reduced starch content (Fig. 4B).

4. Discussion

4.1. Gelatinization of HHP-treated potato starch–water mixtures

The gelatinization behavior of HHP-treated potato starch–water mixtures was dependent highly on the starch content, pressure, and temperature as seen in Figs. 1 and 2.

At the starch contents of 10–30%, gelatinization of starch suspension was sensitively affected by the pressure and temperature; the ΔH_{gel} of 10–30% mixtures decreased with increases in the pressure and temperature. The results were in agreement with those in previous studies on dilute starch suspensions such as 5% (w/w) wheat starch suspension (Douzals et al., 2001), 5% (w/w) tapioca,

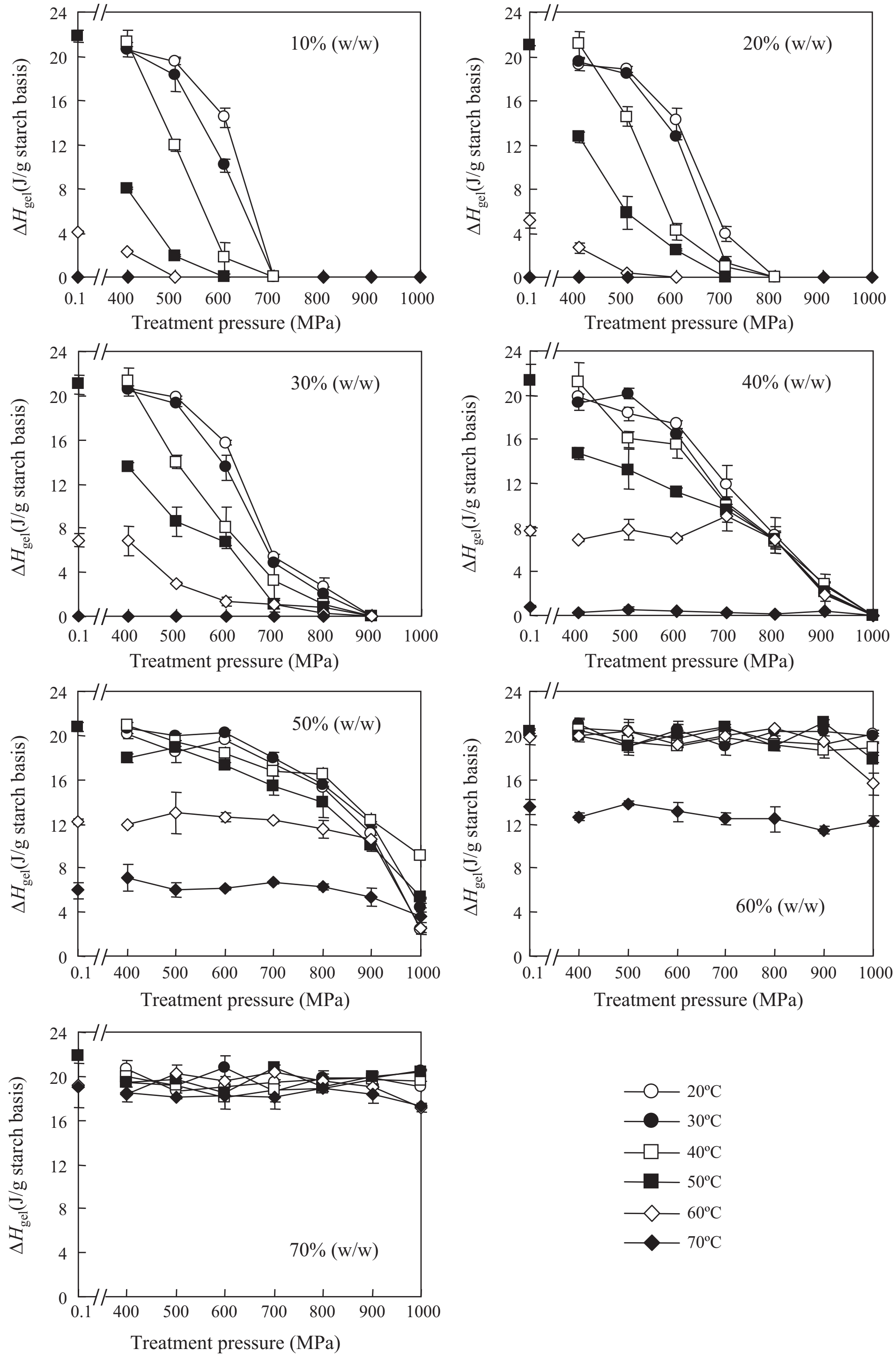

Fig. 1. Effect of HHP treatment on ΔH_{gel} value of 10–70% (w/w) mixtures in the temperature range between 20 and 70 °C: open circle, 20 °C; closed circle, 30 °C; open square, 40 °C; closed square, 50 °C; open diamond, 60 °C; closed diamond, 70 °C.

potato, and wheat starch suspensions (Bauer & Knorr, 2005), and 5% (w/w) corn starch suspension (Buckow et al., 2007). At the starch content of 40% and higher, the dependence of ΔH_{gel} on pressure and temperature was gradually lost as starch content increased. In addition, gelatinization pressure increased with increased starch content irrespective of tested temperatures: 700 MPa (at a starch content of 10%), 800 MPa (20%), 900 MPa (30%), and 1000 MPa (40%). The dependence of gelatinization pressure on starch content at tested temperatures in this study was in agreement with that in the report on HHP-treated potato starch–water mixtures at 40 °C (Kawai et al., 2007a).

No complete gelatinization was achieved with the starch content of 50% and higher. For 50% mixture at 60 and 70 °C, the ΔH_{gel} values were almost independent of pressure, respectively. No remarkable effect of pressure on the ΔH_{gel} values were observed with 60 and 70% mixtures.

For heat gelatinization of starch suspension with excess water, it is known that amylopectin crystallites melt with progressively

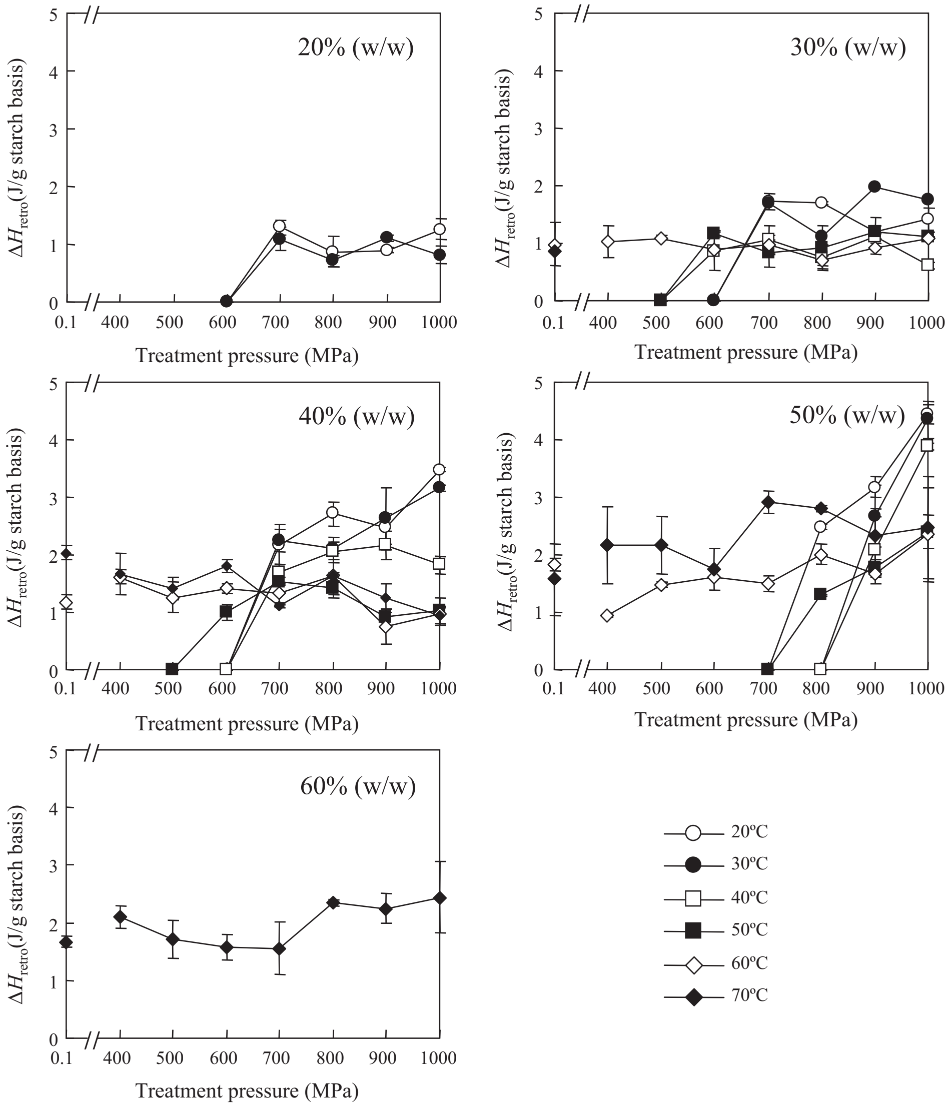

Fig. 2. Effect of HHP treatment on ΔH_{retro} value of 20–60% (w/w) mixtures in the temperature range between 20 and 70 °C: open circle, 20 °C; closed circle, 30 °C; open square, 40 °C; closed square, 50 °C; open diamond, 60 °C; closed diamond, 70 °C.

increasing hydration (Jacobs & Delcour, 1998; Jacobs et al., 1998; Tester & Debon, 2000). On the other hand, starch with limited amount of water gelatinizes partially and then amylopectin crystallites melt at higher temperature than the gelatinization temperature (Tester & Debon, 2000; Cruz-Orea et al., 2002). In this study, complete gelatinization was not achieved with 50–70% mixtures, even though temperature and pressure were raised to 70 °C and 1000 MPa, respectively. According to the report by Kawai et al. (2007a), potato starch–water mixtures at a starch content of 50% was completely gelatinized with higher HHP (1200 MPa) at 40 °C, but 60% mixture did not completely gelatinize under the same condition. Therefore, it can be concluded that potato starch–water mixture requires at least 50% of water for its complete gelatinization under pressures up to 1200 MPa. It was reported that 14 water molecules per one building block (anhydroglucose unit) were required for full hydration (complete gelatinization) of potato starch (Donovan, 1979). The molar ratio (14:1) corresponds to weight percent ratio (water/starch) of 61:39, or taking into account the effective digit of the reported molar ratio, the ratio will be 6:4, denoting that 0–40% starch–water mixtures can be completely gelatinizated in terms of the composition. Based on the composition and the results in this study, it was indicated that the amount of water in HHP-treated 50–70% mixtures was insufficient for complete gelatinization and that a part or all of amylopectin crystallites in the mixtures would remain unmolten due to insufficient hydration. Since ΔH_{gel} of 10–30% mixtures was highly affected by pressure and temperature, it is suggested that pressure and temperature may affect melting of amylopectin crystallites with sufficient hydration more sensitively than that with insufficient hydration. In order to understand more in detail the effects of pressure and temperature on melting of amylopectin crystallites in the presence of sufficient or insufficient hydration, further study will be necessary. For instance, *in situ* real-time measurement of volumetric change of starch–water mixtures under HHP may contribute to analyze the hydration.

4.2. Retrogradation of HHP-treated potato starch–water mixtures

It has been reported that retrogradation is observed immediately after HHP treatment (Hibi et al., 1993; Katopo et al., 2002; Stute et al., 1996), although the mechanism remains unclear due to lack of systematic approach to understand HHP-induced retrogradation. As one of possible interpretations, Stute et al. (1996) suggested that the retrogradation might have occurred “already

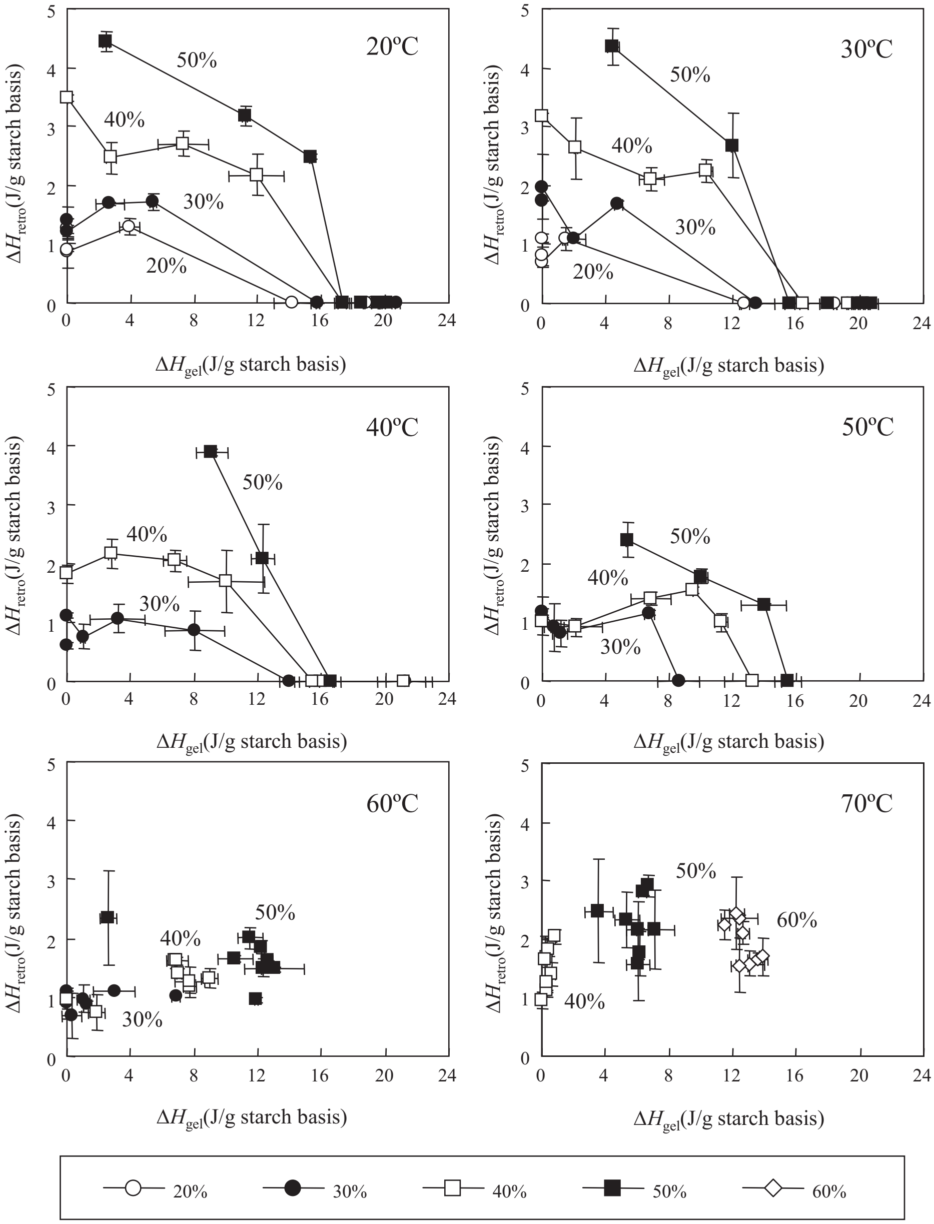

Fig. 3. Relationship between ΔH_{retro} and ΔH_{gel} for 20–60% (w/w) mixtures HHP-treated in the temperature range between 20 and 70 °C. The symbol indicates the starch content of the mixtures: open circle, 20%; closed circle 30%; open square, 40%; closed square, 50%; open diamond, 60%.

within" (during) or "immediately after" HHP treatment. However, there is little experimental evidence to support the suggestion. If retrogradation occurs during pressure holding, it is expected that ΔH_{retro} value would increase with prolonged pressure holding time. In our previous study (Kawai et al., 2007b), the effect of holding time (1–66 h) on ΔH_{reto} value of potato starch–water mixtures HHP-treated at 40 °C was investigated, and no correlation was found between the holding time and the ΔH_{retro} values. This result suggested that the retrogradation progressed "immediately after" rather than "during" pressure holding.

Based on viscoelastic measurements of starch gels which were freshly prepared and quenched to room temperature (20 °C), Orford et al. (1987) suggested that retrogradation of maize starch is dominated by amylose gelation for the first few hours with smaller changes in shear modulus of the gel and subsequently by amylopectin crystallization which requires long term resulting in larger shear modulus. In this study, HHP-treated samples were applied to DSC measurement within 1–3 h. Furthermore, other publications indicate that HHP-induced gelatinization occurred immediately after HHP treatments (Hibi et al., 1993; Katopo et al., 2002; Stute et al., 1996). Therefore, HHP-induced retrogradation in general may principally be induced by amylose gelation.

As seen in Fig. 3, retrogradation was observed when ΔH_{gel} was below 16 J/g. This indicates that a certain degree of gelatinization is required for retrogradation to occur. At fixed ΔH_{gel} value, ΔH_{retro} values showed trend to increase with increase in starch content (Fig. 3). This trend is in agreement with that of heat-gelatinized starch in some reports where retrogradation was promoted at starch contents between 30 and 60% and the degree of retrogradation increased with increase in starch content (Miles et al., 1985; Orford et al., 1987).

As shown in Fig. 2, 30–60% mixtures treated at 0.1 MPa and 60 or 70 °C were retrograded as well as those treated with HHP,

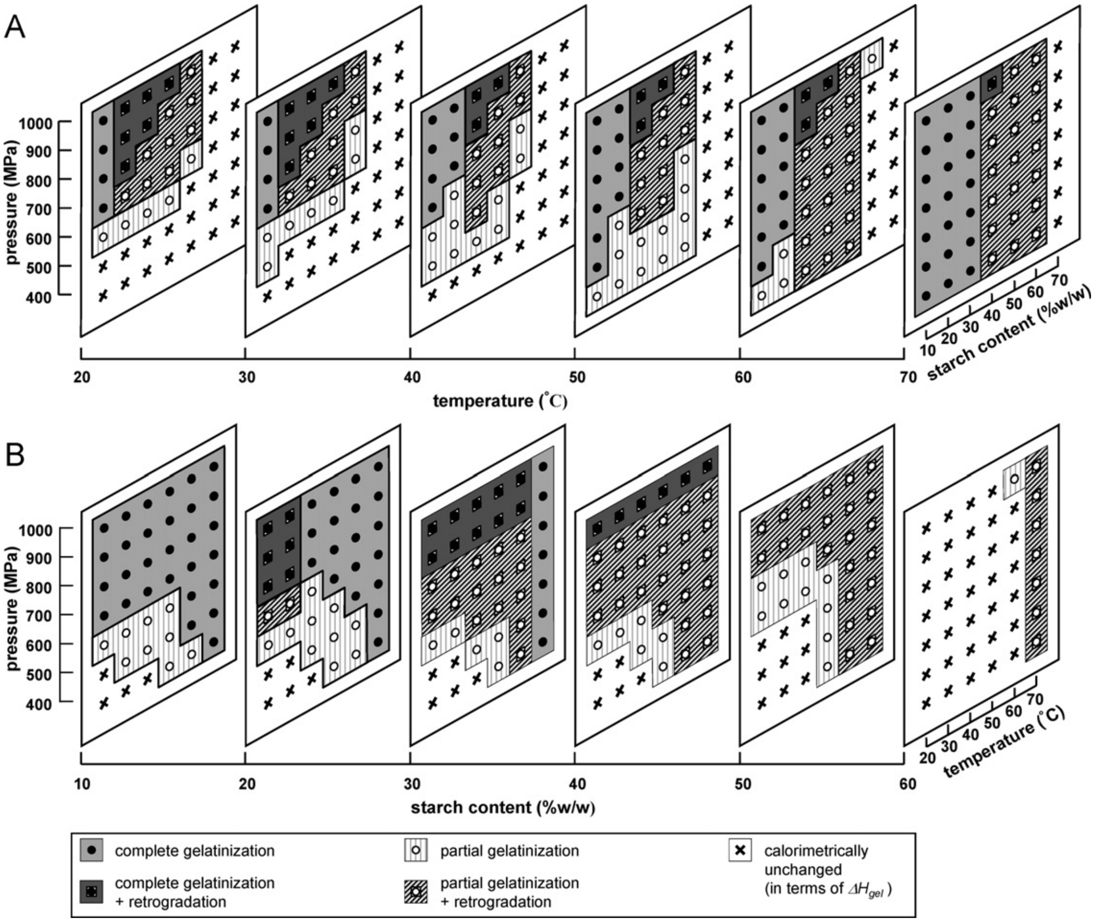

Fig. 4. State diagrams of potato starch–water mixtures (10–60%, w/w) which were HHP-treated (400–1000 MPa) in the temperature range between 20 and 70 °C. (A) Diagrams (treatment pressure vs. starch content) are arranged along the treatment temperature; (B) the diagrams were replotted (treatment pressure vs. treatment temperature) and arranged along the starch content. From the change in ΔH_{gel} and $\Delta H_{\mathrm{retro}}$ values, the physically modified states of HHP-treated potato starch–water mixtures were classified into five states: cross, calorimetrically unchanged state ($\Delta H_{\mathrm{gel}} \geq 18$ J/g (dry potato starch basis) and $\Delta H_{\mathrm{retro}} = 0$ J/g); open circle, partially gelatinized state ($\Delta H_{\mathrm{gel}} < 18$ J/g and $\Delta H_{\mathrm{retro}} = 0$ J/g); closed circle, completely gelatinized state ($\Delta H_{\mathrm{gel}} = 0$ J/g and $\Delta H_{\mathrm{retro}} = 0$ J/g), open circle embedded into square, partially gelatinized and retrograded state ($\Delta H_{\mathrm{gel}} < 18$ J/g and $\Delta H_{\mathrm{retro}} > 0$ J/g); closed circle embedded into square, completely gelatinized and retrograded state ($\Delta H_{\mathrm{gel}} = 0$ J/g and $\Delta H_{\mathrm{retro}} > 0$ J/g).

and simultaneous application of HHP and heat (60 or 70 °C) only slightly changed the value of $\Delta H_{\mathrm{retro}}$. This indicates that there is little difference in the progress of retrogradation between HHP-gelatinized mixtures and heat-gelatinized ones when treatment temperature is set at 60 or 70 °C. On the other hand, there was a trend that $\Delta H_{\mathrm{retro}}$ of 20–50% mixtures treated at 20–50 °C increased with decreased treatment temperature (Fig. 3). This trend observed with the HHP-treated starch mixtures is also in agreement with that of heat-gelatinized starch (Colwell et al., 1969; Hoover, 1995): retrogradation is promoted generally at low temperatures above its freezing temperature. At 0.1 MPa potato starch gelatinized at temperature above 60 °C; this temperature is not favorable for the progress of retrogradation. However, HHP treatment can gelatinize starch even at low temperatures, and adiabatic expansion during the decompression process may decrease the sample temperature. Taking account of the phenomena, it is concluded that HHP treatment at temperatures below 50 °C will promote the progress of retrogradation. Although retrogradation is understood to be a typical quality loss of starchy foods, it is of interest in recent years to utilize retrograded starch as resistant starch (Bauer et al., 2005; Chung et al., 2006; Escarpa et al., 1996). It is expected that HHP treatment at temperatures lower than 50 °C would be useful for the production of HHP-gelatinized and/or HHP-retrograded starch as physically modified starch.

4.3. State diagrams at temperatures 20–70 °C

In this study, state diagrams of HHP-treated (400–1000 MPa) potato starch–water mixtures with wide ranges of starch content (10–70%, w/w) and treatment temperature (20–70 °C) were presented. There have been only a limited number of reports on state diagram of HHP-treated starch. A two-dimensional pressure-temperature phase transition diagram was presented by Douzals et al. (2001) for 5% (w/w) wheat starch–water suspension. Knorr et al. (2006) also presented two-dimensional pressure (0.1–800 MPa) and -temperature (0–80 °C) diagrams for HHP-treated water suspensions (5%, w/w) of various starches (potato, maize, tapioca, wheat, and barley malt). In addition, Buckow et al. (2007) reported a two-dimensional pressure-temperature diagram (0.1-700 MPa, 0-70 °C) for HHP-treated maize starch–water suspension (5%, w/w) to describe different gelatinization degrees (10, 50, 90, and 100%). Bauer and Knorr (2005) presented a three-dimensional diagram (pressure, 0.1–500 MPa; temperature, 0–70 °C) depicting a relationship among pressure, temperature, and degree of gelatinization of wheat starch–water suspension (5%, w/w) treated for 15 min. As described above, the reported diagrams were drawn by using the data for dilute (5%, w/w) starch–water suspension. Kawai et al. (2007a) presented a state diagram at 40 °C of potato starch–water mixtures in a wider range of starch content (10–70%, w/w). In this study, the state diagram was extended in terms of treatment temperature and a series of state diagrams at 20–70 °C was depicted. By referring to the set of state diagrams, process conditions for HHP-induced gelatinization and retrogradation will easily be determined at least for potato starch–water mixtures. For other starches, such state diagrams as in this study should be depicted for optimizing process conditions of their HHP-treated products.

In this study, treatment time was set at 1 h to achieve plateau levels of gelatinizaiton and it may not be realistic in food processing. However, the state diagrams provide required process conditions for processing HHP-treated starches, and those regions where partial gelatinization was observed in state diagrams indicate less gelatinization in shorter treatment time. The conditions corresponding to no gelatinization region must anyway give no gelatinization in shorter treatment time than 1 h.

5. Conclusion

Gelatinization and retrogradation of potato starch–water mixtures treated with HHP were investigated in the temperature range between 20 and 70 °C by DSC analysis. Increased treatment temperature and/or reduced starch content promoted pressure gelatinization. Retrogradation induced by HHP treatment of starch–water mixture may be an alternative to conventional production of resistant starch which passively utilizes retrogradation. Further study under various pressure and temperature conditions will be necessary for a better understanding of the mechanisms of HHP-induced gelatinization and retrogradation. Potato starch is more resistant to pressure than other starches, and, in general, gelatinization and retrogradation properties of starch–water mixture depend on the botanical sources of starch. Therefore, studies on HHP treatment of the other starches will contribute to deepen the understanding of the mechanisms of HHP-induced gelatinization and retrogradation.

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