Role of glassy and crystalline transitions in the responses of corn starches to heat and high pressure treatments: Prediction of solute-induced barostability from solute-induced thermostability

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Abstract

The effects of heat and high hydrostatic pressure (HHP) on glassy and crystalline transitions of starches, and the distinctive contributions of amylopectin and amylose, with respect to annealing, gelatinization, pasting, and retrogradation were explored by conducting an experimental design with five factors: type of starch (dent and waxy corn), pressure (atmospheric to 600 MPa), temperature (25–70°C), time (5–60 min), and type of diluent (water, most efficient plasticizer, lowest Tg; salt-water, non-glass-forming solvent; and sucrose-water, glass-forming plasticizer, high Tg). When 50% w/w starch slurries were HHP-treated for 15 min at 25°C, treatment at 300 MPa showed no effects on glassy or crystalline transitions, but treatment at 600 MPa showed significant extents of gelatinization and annealing, and smaller extents of subsequent retrogradation, for both starches. Longer treatment time at 600 MPa showed the role of the glass transition. Elevated treatment temperature at 600 MPa showed the roles of both glassy and crystalline transitions. NaCl (2 M, lyotropic concentration) or sucrose (50% w/w, glass-forming concentration) showed thermostabilizing effects against starch gelatinization at atmospheric pressure and baroprotective effects against starch gelatinization during HHP treatment at 600 MPa, 15 min, 25°C. Both the thermoprotective and baroprotective effects of sucrose were more dramatic than those of salt. In the case of dent and waxy corn starches, solute-induced thermostabilization by both NaCl and sucrose predicted solute-induced barostabilization.

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1. Introduction

Starch granules are partially crystalline, composed of crystalline regions (crystallized branches of amylopectin and crystalline lipid–amylose complexes) and amorphous regions (amorphous backbone and branch points of amylopectin and amorphous amylose). The morphology of starch granules and the structure of starch molecules can be modified irreversibly by heat and pressure treatments. Heat-moisture treatments have been explored with respect to glass and melting transitions of amorphous and crystalline regions of the native starch structure (Eerlingen, Jacobs, Van Win, & Deleour, 1996; Jacobs & Deleour, 1998; Kweon, Haynes, Slade, & Levine, 2000), but responses to HHP treatments have been interpreted previously only on the basis of the crystalline aspects of starch (Hibi, Matsumoto, & Hagiwara, 1993; Katopo, Song, & Jane, 2002; Muhr & Blanshard, 1982).

Among the publications on HHP treatments, numerous researchers reported the effects of pressure only (Blaszcak, Valverde, & Fornal, 2005; Douzals, Perrier-Cornet, Gervais, & Coquille, 1998; Katopo et al., 2002; Stute, Klingler, Boguslawski, Eshtiaghi, & Knorr, 1996), or pressure and temperature combination (Bauer & Knorr, 2005; Rubens & Heremans, 2000) on starches. Stute et al. (1996), using 25% starch suspensions, reported that pressure-induced...
gelatinization is significantly different from heat-induced gelatinization, in that most HHP-gelatinized starches maintain their granular morphology, showing very little swelling, but rapid retrogradation. Douzals et al. (1998) reported the comparison between thermal and pressure gelatinization processes on a 5% wheat starch suspension, for which high pressure at 600 MPa, 25°C, 15 min, generated denser gels than a thermal treatment at 86°C, 15 min. In summary, it is well known that the designed use of combined thermal and HHP processing could enable enhanced food quality (novel textures, as well as retained flavors and nutrients), conformance (reduction in process variation), and safety (preservation).

In order to explore the effects of heat and HHP on glassy and crystalline transitions of starches, and the distinctive contributions of amylopectin and amylose, with respect to annealing, gelatinization, pasting, and retrogradation, an experimental design with dent and waxy corn starches was conducted, using pressure (atmospheric to 600 MPa), temperature (room to 70°C), and time (5–60 min). The type of diluent was also included as a design factor to study the modulation of responses by water (most efficient plasticizer, lowest Tg), salt-water (non-glass-forming solvent), and sucrose-water (glass-forming plasticizer, high Tg).

2. Experimental

2.1. Materials

Dent and waxy corn starches were kindly supplied by Tate and Lyle (A.E. Staley). All other chemicals were of reagent grade.

2.2. High hydrostatic pressure (HHP) treatment

A Multivessel Apparatus Unipress 111 (Warsaw, Poland) (Fig. 1) was used for the HHP treatment. Starch and a diluent (water or 2 M NaCl or 50% w/w sucrose) were mixed in a weight ratio of 1:1. The starch mixture was transferred to a 1 mL pressure vial (UNC cryotube vial, Denmark), and the vial was closed tightly with a cap. Then the vial was placed into the pressure vessel filled with the pressure medium (silicon oil M40.165.10), and the pressure was raised to the target within 1 min. Although the temperature of the pressure vessel increased due to adiabatic heating during pressurization (maximally 10°C at 600 MPa), the pressure vessel returned to the experimental target temperature within 1 min after reaching the target pressure. At the end of the HHP treatment, the sample was depressurized, removed from the pressure vessel, and used for further analyses.

2.3. Differential scanning calorimetry (DSC)

About 40 mg of a starch sample was transferred to a stainless steel DSC sample pan (Perkin–Elmer), and sealed. Each sample was heated in the DSC instrument (DSC-7, Perkin–Elmer, Norwalk, CT) from 30 to 130°C with a 10°C/min heating rate, and an empty pan was used as a reference. Temperature and enthalpy calibrations were performed as described previously (Kweon, Haynes, Slade, & Levine, 2000).

2.4. Microscopic observation of starch granules

Starch samples were suspended in water and observed under normal or polarized light with 400× magnification (Nikon, Japan and Carl Zeiss, Germany, respectively).

3. Results and discussion

3.1. Effect of treatment pressure

DSC thermograms for dent and waxy corn starches after HHP treatment at 25°C showed a significant impact on amylopectin transition peak temperatures with increase in pressure (Figs. 2 and 3, respectively). However, this obser-
vation was not consistent with earlier publications (Douszals, Perrier-Cornet, Coquille, & Gervais, 2001; Muhr & Blanshard, 1982; Muhr, Wetton, & Blanshard, 1982; Stute et al., 1996; Thevelein, Van Assche, Heremans, & Gerlsma, 1981) that did not report an effect on peak transition temperatures, probably because the pressure treatment was conducted on dilute starch suspensions. The HHP treatment at 600 MPa, 15 min, 50% w/w for both starches (Figs. 2 and 3) exhibited a significant annealing and a small extent of retrogradation, much more notable for the dent corn starch (Fig. 2). This retrogradation result was similar to the results of Katopo et al. (2002). They reported that DSC thermograms for pressure-treated (690 MPa, 5 min, 50% and 33% w/w starch suspensions) normal and waxy corn starch samples showed a newly developed peak and stated that the peak “resembled the thermal transition peak of retrograded starch”. Using a lower starch concentration (450–550 MPa, 15 min, 25% w/w starch suspension), Stute et al. (1996) observed an even greater extent of retrogradation. In each case, the greater the amount of amorphous amylopectin generated by the HHP treatment, the greater the extent of retrogradation.

Fig. 4 shows the relationship between the treatment pressure and resulting peak temperature or heat of transition for the dent corn starch. Similar behavior was observed for the waxy corn starch (data not shown). The HHP treatment up to 300 MPa did not have a significant effect on either the peak temperature or the heat of transition. Above 300 MPa, a gradual decrease in the heat of transition was observed, which indicated that gelatinization occurred during the pressure treatment. Finally at 600 MPa, a significant increase in the peak temperature was observed, which indicated that annealing occurred during the pressure treatment. Katopo et al. (2002) observed similar behavior for normal and waxy corn starches, when the starches were not dried between the HHP treatment and the DSC analysis.

DSC and microscopic analyses were used to compare the samples before and after HHP treatment. Starch samples, which were slurries before treatment, gelled due to HHP treatment, except at the lowest treatment pressure, 300 MPa. When the HHP-treated starch granules were observed microscopically under normal light (Fig. 5), the appearance of the sample treated at 300 MPa was not significantly different from that of the native starch (Fig. 5a and b), which was consistent with the absence of changes in the DSC peak temperature and heat of transition of the amylopectin (Fig. 2). In contrast, half of the granules showed swelling and partial loss of integrity due to HHP treatment at 450 MPa (Fig. 5c), and all of the granules showed these effects at 600 MPa (Fig. 5d). Observation under polarized light (Fig. 6) confirmed the results of observation under normal light. Even the HHP-treated starch granules at 600 MPa did not show complete loss of birefringence (Fig. 6d).

Overall, HHP treatment at 25 °C showed a significant impact on amorphous and crystalline transitions of starch and on granule morphology with increasing values of pressure, exhibited as annealing, gelatinization, pasting and subsequent retrogradation (more notable for dent corn starch), even though the treatment was conducted at a temperature below the characteristic value of the glass transition temperature of amylopectin (gelatinization temperature) at atmospheric pressure.

3.2. Effect of treatment temperature

Dent corn starch was HHP-treated at 600 MPa for 15 min at various temperatures (25, 50 and 70 °C). Annealing of amylopectin was exhibited in DSC thermograms (Fig. 7) as a result of HHP treatment at all treatment temperatures. The extent of amylopectin annealing increased with increase in treatment temperature. The peak temperature for annealed amylopectin did not show a significant increase with increase in treatment temperature from 25 to 50 °C, but the melting peak was much narrower after treatment at 50 °C than at 25 °C. In contrast, the peak tem-
Fig. 5. HHP-treated dent corn starch granules observed under normal light with 400× magnification. (a) Native starch; (b) HHP-treated starch at 300 MPa, 15 min, 25 °C; (c) HHP-treated starch at 450 MPa, 15 min, 25 °C; (d) HHP-treated starch at 600 MPa, 15 min, 25 °C.

Fig. 6. HHP-treated dent corn starch granules observed under polarized light with 400× magnification. (a) Native starch; (b) HHP-treated starch at 300 MPa, 15 min at 25 °C; (c) HHP-treated starch at 450 MPa, 15 min at 25 °C; (d) HHP-treated starch at 600 MPa, 15 min at 25 °C.
perature for annealed amylopectin showed a significant increase after treatment at 70 °C with a further decrease in peak width. The peak temperature for amylose–lipid complex melting was almost unchanged by HHP treatment at 25 °C and 50 °C, but annealing was observed even for amylose–lipid crystals after HHP treatment at 70 °C.

Several publications have demonstrated that hydrothermal treatments of starch at atmospheric pressure and moisture contents above 30% w/w in the temperature range between the glass transition temperature and the crystalline melting temperature of amylopectin resulted in annealing (Eerlingen et al., 1996; Jacobs & Delcour, 1998; Kweon et al., 2000). The extent of annealing increased with treatment time. However, the thermograms in Fig. 2 show that treatment for 15 min at elevated pressures resulted in annealing even at 25 °C, which suggests that elevated pressure can induce annealing at a temperature significantly lower than the characteristic glass transition temperature at atmospheric pressure. At atmospheric pressure, structural changes in the crystalline regions of amylopectin can only occur above the glass transition temperature of the amorphous regions. However, at sufficiently high pressures (600 MPa), structural changes in the crystalline regions of amylopectin can occur below the glass transition temperature of the amorphous regions. Douzals et al. (2001) treated wheat starch suspensions (5%) at various pressures (0.1–600 MPa) and temperatures (−20 to 96 °C) for 15 min. The results were reported as a “pressure–temperature gelatinization diagram” which showed that curves of isogelatinization of wheat starch were quite similar to a pressure–temperature diagram for protein denaturation.

3.3. Effect of treatment time

Dent corn starch was HHP-treated at 600 MPa and either lower temperature (25 °C) or higher temperature (70 °C) for various times (5, 15, and 60 min). The DSC thermograms in Figs. 8 and 9 show a dramatic effect of pressurization, but almost no effect of treatment time, on amylopectin annealing. Pressurization caused an immediate change in starch structure, and longer times of HHP treatment resulted in only slight further annealing (increase in peak temperature of annealed amylopectin after treatment at 25 °C or decrease in peak width of annealed amylopectin melting after treatment at 70 °C). Katopo et al. (2002) have also reported that no significant differences in the structure and properties of starches were observed after pressurization for 5 min or 1 h. Regardless of HHP treatment time, the width of annealed amylopectin melting peaks was smaller for the starch samples treated at higher temperature (70 °C) than at lower temperature (25 °C), which demonstrated the larger temperature effect on extent of annealing.

3.4. Effect of solute type in diluent

Dent corn starch suspended in various diluents (water, 2 M NaCl, and 50% w/w sucrose) was HHP-treated at 600 MPa and 25 °C for 15 min. DSC thermograms for untreated starch (Fig. 10, dotted lines) showed that the

4. Conclusions

HHP treatment at 25 °C showed a significant impact on amorphous and crystalline transitions of corn starches with increasing values of pressure, exhibited as annealing, gelatinization, pasting, and subsequent retrogradation (more notable for dent corn starch), even though the treatment was conducted at a temperature below the characteristic value of the glass transition temperature of amylopectin (gelatinization temperature) at atmospheric pressure. At elevated temperatures for HHP treatment, a further effect on annealing was observed. Also, longer times of HHP treatment at the highest pressure (600 MPa) resulted in further annealing at both 25 and 70 °C. At atmospheric pressure, a high (lyotropic) concentration of NaCl or a high (glass-forming) concentration of sucrose showed solute-induced thermostabilizing effects against starch gelatinization, and the extent of thermostabilization was greater with sucrose than with NaCl. Similarly, high concentrations of NaCl or sucrose showed solute-induced baroprotective effects against starch gelatinization during HHP treatment at 25 °C, and the baroprotective effect of sucrose was more dramatic than that of salt. In the case of dent and waxy corn starches, solute-induced thermostabilization by both NaCl and sucrose predicted solute-induced barostabilization. In summary, our results can lead to the suggestion that the designed use of stabilizing solutes with combined thermal and HHP processing could enable enhanced food quality (novel textures, as well as retained flavors and nutrients), conformance (reduction in process variation), and safety (preservation).

