



## Starch gelatinization under pressure studied by high pressure DSC

Hongsheng Liu<sup>a,b,c</sup>, Long Yu<sup>b,a,\*</sup>, Katherine Dean<sup>b</sup>, George Simon<sup>c</sup>, Eustathios Petinakis<sup>b</sup>, Ling Chen<sup>a</sup>

<sup>a</sup> Centre for Polymers from Renewable Resources, ERCPS, SCUT, Guangzhou, China

<sup>b</sup> CSIRO, Materials Science and Engineering, Gate 4, Normanby Road, Clayton South, Melbourne, Australia

<sup>c</sup> Department of Materials Engineering, Monash University, Melbourne 3169, Australia

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### ABSTRACT

The gelatinization process of waxy corn starch under different pressures up to 10.0 MPa was investigated using a high pressure DSC. Compressed air and carbon dioxide were used as pressure resources. Effect of pressure and annealing under pressure on gelatinization of waxy corn starch was systematically studied, in particular on the gelatinization temperature and enthalpy. The results show that the peak temperature of gelatinization was increased slightly initially then remained stable with increasing pressure. The gelatinization enthalpy was decreased under pressure processing. Annealing the starch under pressure condition, just below its gelatinization temperature, increased gelatinization temperature but kept gelatinized enthalpy constant. Morphologies of starch granules treated under pressure were studied using an optical microscope and SEM. There is no discernable difference of starch granules treated with and without pressure, which indicates the pressures are not high enough to destroy crystalline structure. The intensity of the pressure acts as a key factor to influence the gelatinization of starch rather than the nature of the gas. Effect of pressure on the multi-endotherm detected by DSC for starch with intermediate water is used to study the mechanisms. The effect of pressure can be explained by the enhancement of water diffusion in the amorphous range.

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### 1. Introduction

When starches were heated in an aqueous medium in an atmospheric environment, the conventional gelatinization (temperature-induced gelatinization) occurred. The heat-induced gelatinization has been extensively investigated and well-accepted as indicating the destruction of the crystalline structure in starch granular (Atwell, Hood, Lineback, Varriano-Marston, & Zobel, 1988; Lelievre, 1974). Starch gelatinization is an irreversible process and includes granular swelling, native crystalline melting, loss of birefringence and starch solubilization (Sullivan & Johnson, 1964). Previous researchers (Blaszcak et al., 2007; Rubens & Heremans, 2000) reported that high pressure (up to 650 MPa) treatment could also cause an irreversible distortion of the crystalline region in starch granules prior to a reversible hydration of the amorphous phase, which in turn leads to the destruction of the granular structure.

High pressure processing has been widely applied in the food industry from early in 1980s (Bauer & Knorr, 2005; Knorr, Heinz, & Buckow, 2006; Lopez-Fandino, 2006) for its unique advantages (Stute, Klingler, Boguslawski, Eshtiaghi, & Knorr, 1996): (1) it only affects secondary and tertiary bonds rather than primary bonds;

(2) it acts immediately and is independent of the size and the shape of product. The mechanism of the pressure-gelatinization is significantly different from heat-gelatinization (Stolt, Oinonen, & Autio, 2001; Stute et al., 1996). Compared to traditional temperature-gelatinization starch, some starch samples after high pressure treatment did not show any extensive swelling and kept granular character, which resulted in a weaker gel (Douzals, Perrier Cornet, Gervais, & Coquille, 1998; Stolt et al., 2001; Stute et al., 1996). In addition, there was only a lower quantity of amylose (Buckow, Heinz, & Knorr, 2007; Douzals et al., 1998), sometimes even no amylose (Stute et al., 1996), released during pressure-induced gelatinization processes. Furthermore, the extrusion processing also involves pressure up to 10 MPa in an extruder barrel that has been rarely considered previously.

The presence of water is vital for pressure-gelatinization as well as for temperature-gelatinization. A certain minimum amount of water, specific to different starches, is essential for the onset of gelatinization. Vainionpaa, Forssell, and Virtanen (1993) stated that, below this water level, pressure treatment advanced the rupture of the granular structure which lead to melting or plastification of starch rather than proper gelatinization. Blaszcak et al. (2007), Blaszcak, Fornal, Valverde, and Garrido (2005a) considered the degree of the crystalline structure melting under high pressure was related to the amylose/amylopectin ratio. Under the same pressure condition, the waxy cornstarch showed an amorphous character while the degree of crystallinity of amylo maize

\* Corresponding author. Address: CSIRO, Materials Science and Engineering, Gate 4, Normanby Road, Clayton South, Melbourne, Australia. Tel.: +61 3 9545 2777; fax: +61 3 9544 1128.

E-mail address: [long.yu@csiro.au](mailto:long.yu@csiro.au) (L. Yu).

(about 70% amylose content) was significantly decreased along with the treatment time. Similarly Stolt et al. (2001) pointed out the stabilizing effect of amylose during pressure-gelatinization. Moreover, A- and C-type starches are reported more sensitive to pressure treatment compared with B-type starch (Muhr & Blanshard, 1982; Rubens & Heremans, 2000; Stute et al., 1996).

There are numerous papers dealing with the effect of high pressure on starch gelatinization. Some researchers (Blaszcak, Valverde, & Fornal, 2005b; Buckow et al., 2007) observed a decrease in gelatinization temperature and an increase in disordering conformations for potato starch treated at 600 MPa pressure. Microscope observation for some waxy maize starch granules after treating at 500 MPa for 20 and 60 min, discovered disappearance of birefringence (Hibi, Matsumoto, & Hagiwara, 1993). Similarly a scanning electrical microscopy (SEM) study confirmed the changes of surface characteristic of pressurized granules and indicated significant alteration in the internal structure (Blaszcak et al., 2005b; Stolt et al., 2001; Stute et al., 1996). X-ray diffraction pattern showed the transformation from A-type crystalline to B-type after pressure treatment (Hibi et al., 1993; Katopo, Song, & Jane, 2002). Furthermore, Stute et al. (1996) reported that, for 5% waxy maize starch suspensions, a complete gelatinization occurred during pressure treatment at 600 MPa and 20 °C.

However, all these results were mainly limited to ex situ observations where samples were monitored before and after the pressurization step. Few papers dealt with an online study of the pressure effect on starch gelatinization. A sealed high pressure stainless pan can provide pressure from steam during heating (Liu, Yu, Chen, & Li, 2007; Liu, Yu, Xie, & Chen, 2006). But the steam pressure is quite low when the temperature in the system is lower than that of the boiling temperature of water. Recently a high pressure microscope was used and discovered swelling of starch granules during pressurization (Bauer, Hartmann, Sommer, & Knorr, 2004; Rubens, Snauwaert, Heremans, & Stute, 1999) under 300 MPa. Vainionpää et al. (1993) have studied the gelatinization of barley starch with lower moisture content (<35%) under compressed nitrogen gas (up to 2.5 MPa) using a DSC pressure chamber. It was found the pressure decreased the gelatinization enthalpy. In this work, the gelatinization of waxy corn starch was studied by combination of temperature and high pressure using a high pressure differential scanning calorimetry (HP-DSC). HP-DSC presents a method of observing the thermal behaviors of gelatinization in situ and simultaneously records both the effect of heat and pressure. The pressure varied from 0.1 up to 10 MPa using compressed air and carbon dioxide. Effect of pressure and annealing under the pressure on the gelatinization of waxy corn starch were investigated, in particular gelatinization temperature and enthalpy. Morphological variations of starch granules treated under different pressures were studied by microscope and SEM. The technique of online measurement by DSC will be used to study kinetics of gelatinization under pressure.

## 2. Experimental work

### 2.1. Materials and sample preparation

A commercially available waxy corn starch from Penfold (Australia) was used in the experimental work. In order to study the mechanism, waxy corn starch containing mainly amylopectin (99%) was used in the experimental work to avoid the confusion of amylose/amylopectin. The material contains about 13.2% moisture and the water contents in all samples are based on the dry-based starch.

A starch suspension was prepared in a 40 µl DSC aluminum pan. Starch (about 5 mg) was weighed in the pan, and then distilled water was injected by a micro-syringe. The ratio of starch/water is approximately 1:3 and 1:1 (W/W), respectively. The pan was

sealed using a cover with a hole. Instrument recommendation suggests pans need no cover in pressure runs. However, the loss of water has been detected, whilst still allowing the pan contents to be pressurized. The cover can efficiently provide evaporation of moisture under pressure. The mass of the samples kept stable after DSC running (water loss between 0.5% and 2.0%).

Food grade compressed air (99.9%) and carbon dioxide (99.9%) were used as pressure resource.

### 2.2. High pressure differential scanning calorimetry (HP-DSC)

A Mettler Toledo high pressure DSC 827e with a pressure chamber was used in the present experimental work. The equipment allows pressurization from 0.1 to 10 MPa and a special internal coolant ensured the stable temperature during pressure process. Melting point and enthalpies of indium were used for temperature and heat capacity calibration.

The defined pressure was created by introducing compressed air or carbon dioxide into the measuring chamber through controlling the pressure gauge. On reaching the desired pressure condition, the DSC heating program was immediately started at a heating rate 15 °C/min from 25 to 110 °C. After scanning, the pressure was released and the mass of sample and pan was reweighed to calculate water loss. The enthalpy of gelatinization was calculated on the dry mass of the starch. DSC measurements were performed in triplicate, and results are presented as the mean.

### 2.3. Light microscopy

Starch suspension was treated under 5.0 MPa for 5 h at room temperature (about 23 °C) in the DSC pressure chamber. Then one drop of the slurry samples was dispersed by distilled water and observed using a microscope (Olympus BH-2, Japan) equipped with a polarized filter. Samples were examined with normal and polarized light. In this work, the magnification was 500× (50 × 10).

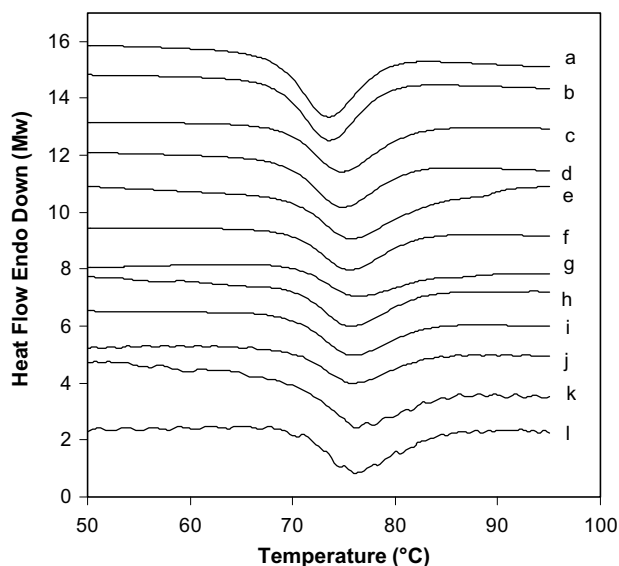
### 2.4. Scanning electron microscopy (SEM)

The microstructure of starch granules and their surfaces after pressure treatment was examined with SEM. The air-dried starch powders were stuck on a specimen holder using a silver plate, and then coated with gold in a vacuum evaporator. The obtained specimens were viewed in a FEI Quanta 200 scanning electron microscope at the accelerating voltage of 10 kV.

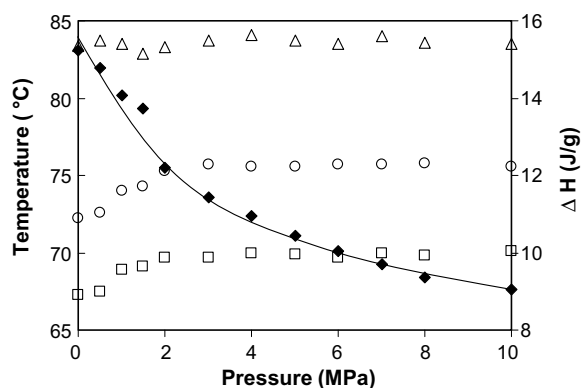
## 3. Results and discussions

Fig. 1 shows the gelatinization endotherms of waxy starch with excess water (about 75%) detected by HP-DSC under various pressures of compressed air. It is observed that the gelatinization peak was shifted to higher temperature, becoming broad and weak, with increasing pressure. The effect of pressure on the onset ( $T_o$ ), peak ( $T_p$ ) and conclusion ( $T_c$ ) temperatures, as well as gelatinization enthalpy ( $\Delta H$ ) is provided in Fig. 2. It is seen that,  $T_o$  and  $T_p$  increased about 2.5 and 3 °C, respectively, in the pressure range 0.1–3.0 Mpa, and no further change was observed with increasing pressure up to 10 MPa. However it is noted that,  $T_c$  was little influenced by pressure and remained constant at about 84 °C. The gelatinization enthalpy decreased with increasing pressure, but the decrease rate was not linear. The enthalpic values initially fell sharply and changed slightly with further increased pressure. These results indicate that some weaker starch structure was damaged but the near-perfect part was not altered during pressurization.

Similar results, increasing gelatinization temperature and decreasing gelatinization enthalpy, have been observed for the gelatinization behaviors under pressure provided by carbon diox-



**Fig. 1.** Gelatinization endotherms of waxy starch detected by a high pressure DSC under different compressed air (MPa): (a) 0.1; (b) 0.5; (c) 1.0; (d) 1.5; (e) 2.0; (f) 3.0; (g) 4.0; (h) 5.0; (i) 6.0; (j) 7.0; (k) 8.0; (l) 10.0.

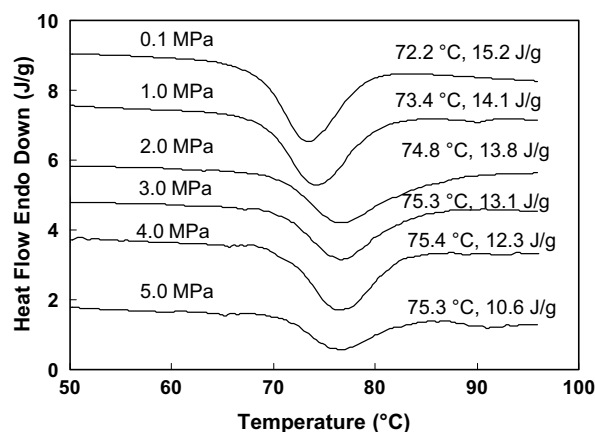


**Fig. 2.** Plot of the effect of pressure on gelatinization temperatures (□, ○, △ represented the  $T_o$ ,  $T_p$  and  $T_c$  of gelatinization, respectively) and gelatinization enthalpy (◆).

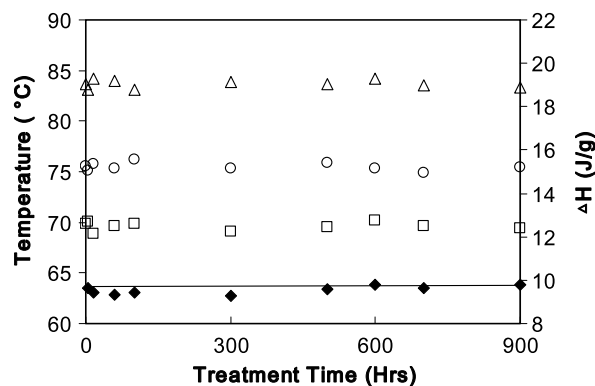
ide (Fig. 3). The intensity of the pressure seemed to act as key factor to influence the starch gelatinization rather than the nature of the pressuring gas. Both compressed gases damaged and diminished the weaker structure of starches, which resulted in the higher gelatinization temperature.

Effect of pressurization time under a certain pressure (5 MPa) at room temperature (about 23 °C) on the gelatinization is presented in Fig. 4. It is observed that processing time has little influence on the gelatinization behaviors. No discernable changes of gelatinization temperature and enthalpy were observed for samples with prolonging pressurized time. It indicated the pressurization treatment affected the starch structure as soon as the desired pressure was reached. The weaker structure was destroyed significantly while the stable part displayed little change with increasing treating time.

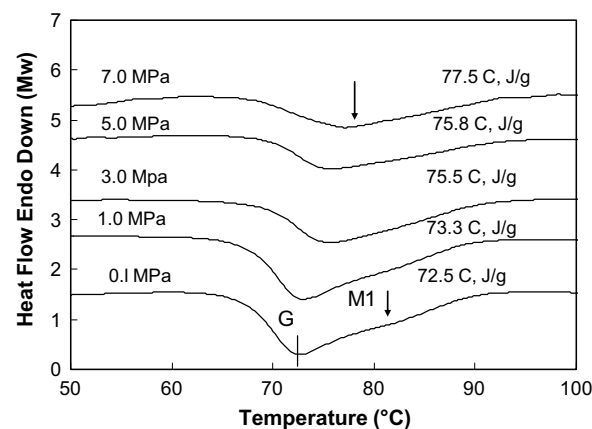
There are two endotherms, denoted as G and M1 (Liu et al., 2006; Russell, 1987; Shogren, 1992), that have been observed for waxy starch with intermediate water content. They are related to double helices of amylopectin (Cooke & Gidley, 1992; Liu & Thompson, 1998; Liu et al., 2007; Ring & Colonna, 1987). Fig. 5 shows the effect of pressure on these endotherms for the sample



**Fig. 3.** Gelatinization endotherms of waxy corn starch in excess water detected by a high pressure DSC under different compressed carbon dioxide (MPa): (a) 0.0 (under atmosphere condition); (b) 1.0; (c) 2.0; (d) 3.0; (e) 4.0; (f) 5.0.



**Fig. 4.** Effect of pressure treatment (5.0 MPa) at room temperature (23 °C) for different time on the gelatinization temperatures (□, ○, △ represented the  $T_o$ ,  $T_p$  and  $T_c$ , respectively) and gelatinization enthalpy (◆).



**Fig. 5.** Gelatinization endotherms of waxy corn starch with intermediate water content (about 50%) under atmosphere and 5.0 MPa pressure condition.

with about 50% water. It is observed that the sample exhibited bimodal endothermic transitions under atmospheric condition. The new endotherm (M1) appeared as a shoulder of endotherm G. It is interesting to note that the endotherm G became weaker and the onset temperature moved to higher temperature with increased pressure. As the air pressure reaches 5.0 MPa, due to the loss of the low temperature part of the endotherm G, the bimodal

peak turned into a broad peak and the overlapped tail was difficult to observe. This phenomenon suggested that some part of the structure related to endotherm G was damaged during pressurization, and the remaining part contributed to the broad peak together with the part of endotherm M1. However, there was no change for endotherm M1 during the pressurization process. The result is similar to our previous investigation on starch annealing (Liu et al., 2006). Both experimental works suggested that the weaker starch structure which is related to the endotherm G was damaged more, whereas the endotherm M1 kept stable under the experimental conditions.

It is generally believed that heat-gelatinization is a phase transition of granules from an ordered state to a disordered one during heating in excess water. It involves melting of ordered regions, both on the crystallite and on the level of double-helical order. The degradation of granules occurs in a somewhat different manner, but gelatinization could be initiated at a lower temperature as heating starch suspensions subjected to a pressure higher than 200 MPa (Douzals et al., 1998; Stolt et al., 2001; Stute et al., 1996). Pressurization treatment distorts the crystalline region in starch granules prior to a reversible hydration of the amorphous phase, which results in the destruction of the granular structure (Blaszcak et al., 2007; Rubens & Heremans, 2000). Moreover, water reactivity is also increased during pressurization (Vainionpää et al., 1993). It is expected that pressure will enhance the process of water diffusion into starch granules, especially into the amorphous phase. The diffusion leads to break the crystal structure further. Therefore, gelatinization could start at the room temperature, zero or even subzero temperatures if pressure is high enough (Muhr & Blanshard, 1982; Stolt, Stoforos, Taoukis, & Autio, 1999; Stute et al., 1996; Thevelein, Van Assche, Heremans, & Gerlisma, 1981). In present experimental work the pressure was only in the range of 0.1–10 MPa. The decreased DSC enthalpy under pressure supports the theory that some order structure has been destroyed, but the relatively low increase in pressure seems to only affect samples to a certain level.

Although the gelatinization enthalpy corresponds to the overall crystallinity of amylopectin, loss of double-helical order is considered to be responsible for the enthalpic transition in the DSC thermograms (Altay & Gunasekaran, 2006; Cooke & Gidley, 1992; Liu et al., 2006; Liu & Thompson, 1998; Waigh, Gidley, Komanshek, & Donald, 2000). Moreover, two types of phase transition were suggested in starch granules: helix–helix dissociation and helix–coil transition (Waigh, Donald, Heidelbach, Riekel, & Gidley, 1999; Waigh et al., 2000). The relatively lower pressures in the present experimental work only dissociated the helices side by side, but were not high enough to damage the double helices to coil state. The destruction of inter-helix interactions under pressurization condition results in decreasing gelatinization enthalpy. However the remaining double helices are stabilized even at higher pressure, since the nature of the consistent helices (their length, cohesive energy, etc.) was not changed (Waigh et al., 2000). That explained why the  $T_o$  and  $T_p$  were increased while the  $T_c$  remained constant for pressurized samples in DSC thermograms.

Fig. 6 shows the DSC thermograms of the sample annealed at just below its gelatinization temperature (60 °C) under atmospheric and 5 MPa pressure (air) conditions for different times. The observable increase in gelatinization temperatures was accompanied by a narrowing of gelatinization temperature interval independent of pressure. The comparison of the effect of annealing on the gelatinization temperature and enthalpy is provided in Fig. 7. It is observed that, though samples under different conditions had different  $T_o$  and  $T_p$  of gelatinization, they had similar increasing trend with increasing annealing time. The  $T_c$  of gelatinization remained stable, with no effect of pressure. Moreover, there was no discernable change of enthalpy during annealing process.

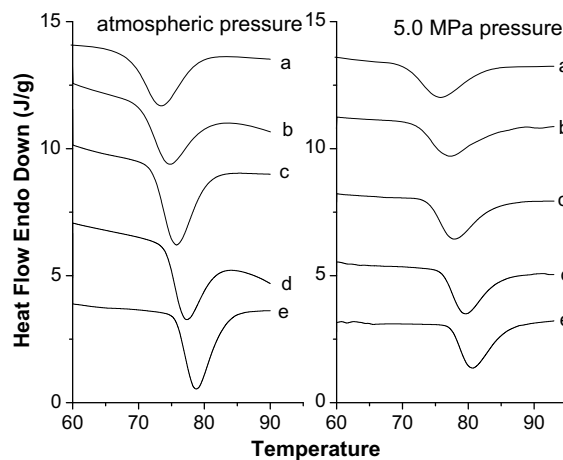


Fig. 6. Gelatinization endotherms of waxy corn starch after annealing at 60 °C under atmosphere (left) and 5 MPa (right) pressure for different times (min): (a) 0; (b) 10; (c) 60; (c) 300; (d) 600, respectively.

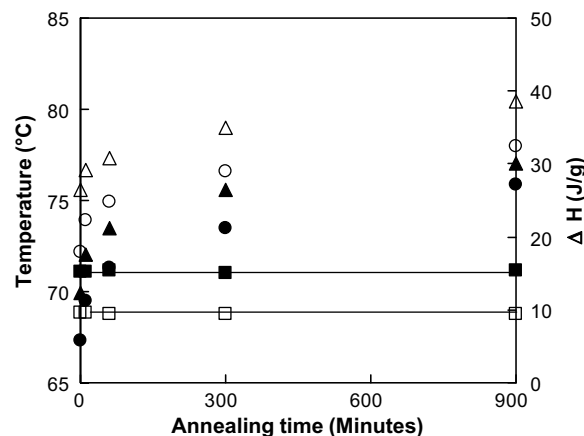
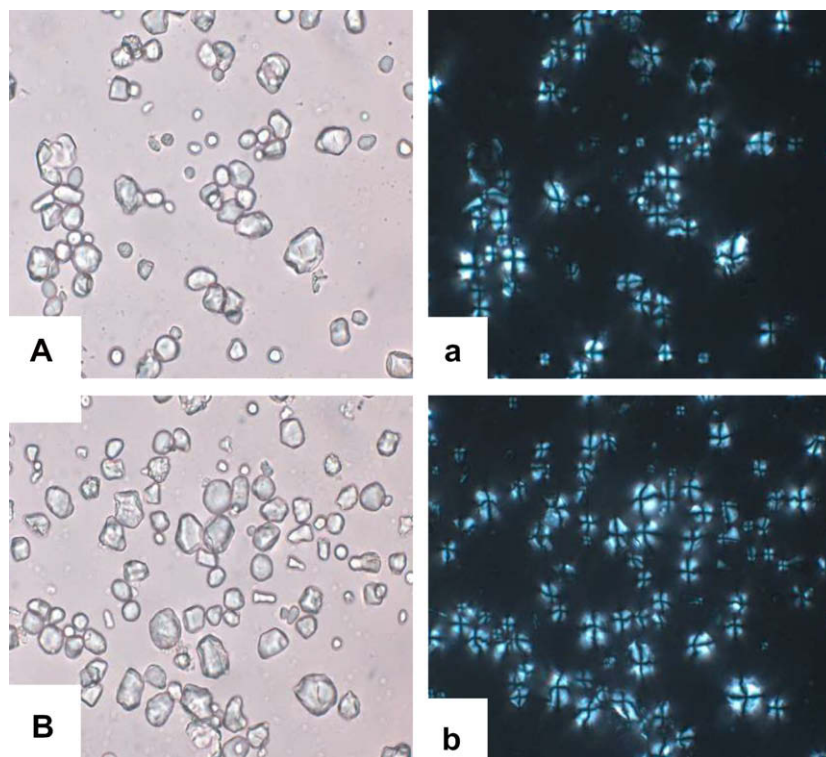


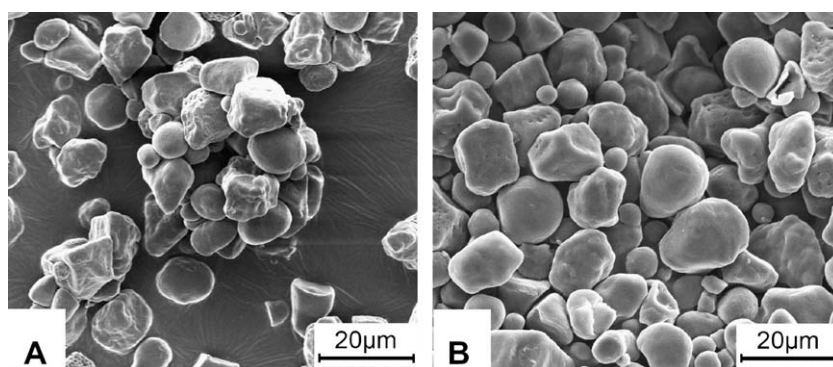
Fig. 7. Effect of annealing time at 60 °C on gelatinization behaviors under atmosphere ("●" and "▲" represent  $T_o$  and  $T_p$ , respectively, "■" represent gelatinization enthalpy) and 5.0 MPa pressure ("○" and "△" represent  $T_o$  and  $T_p$ , respectively, "□" represent gelatinization enthalpy) condition.

Starch annealing is defined as a physical reorganization of starch granules in water at a temperature above the glass transition but below the gelatinization temperature (Jacobs et al., 1998; Knutson, 1990; Krueger, Knutson, Inglett, & Walker, 1987a; Larsson & Eliasson, 1991; Tester, Debon, & Karkalas, 1998). It implied the physical treatment only modified the physicochemical properties of starch without destroying the granule structure. Annealing increases the starch gelatinization temperature and narrows the temperature range (Gough & Pybus, 1971; Hoover & Vasanathan, 1994; Tester, Debon, & Somerville, 2000; Tester et al., 1998; Yost & Hosney, 1986). The unchanged enthalpy for waxy starch under atmosphere pressure has been discussed by previous researchers (Krueger, Walker, Knutson, & Inglett, 1987b; Larsson & Eliasson, 1991; Tester et al., 2000). However, to the best of our knowledge, there is no paper reporting about the effect of annealing under a certain pressure. From the present work, it is seen that gelatinization enthalpy remained stable during the annealing process no matter with or without pressure. The pressurization had little extra influence for the annealing effect. The recognizable increasing  $T_o$ ,  $T_p$  and the decreasing enthalpy, for the samples annealed with pressure, were due to dislocation of the amylopectin helices next to each other as the pressurization was built up. The natures of the double helices were not altered by annealing below their unwinding transition.





**Fig. 8.** Morphologies of waxy starch under normal and polarized light: native (A and a) and treated (B and b) starch granules under 5.0 MPa pressure for 5 h.



**Fig. 9.** Scanning electron micrographs of native and pressurized waxy starch: native (A) and treated (B) starch granules under 5.0 MPa pressure for 5 h.

Fig. 8 shows the micrographs of native and pressure treated starch samples under normal and under polarized light. All samples exhibit typical granule shape (A and B) and birefringence under polarized light (a and b). It is seen that there is no observable difference for the samples with and without pressure treatment (5 MPa). That indicates the pressure may enhance the diffusion of water into the amorphous phase but is not high enough to destroy crystalline structure. Fig. 9 shows the granules observed by SEM. There are no discernable changes of size but the surface of the treated samples has become smoother. The smooth surface can also be explained by the water diffusion and granule swelling. These microscopic observations correspond with the DSC results.

#### 4. Conclusion

Effect of pressure and annealing under pressure on the gelatinization of waxy corn starch were systematically studied using a high pressure DSC, in particular the gelatinization temperature

and enthalpy. The intensity of the pressure significantly influenced the gelatinization of starch rather than the type of gas. The gelatinization temperature was increased while enthalpy was decreased under pressure for the loss of weaker inter-helix structure. However the endotherm M1, which is attributed to double helices structure, remained stable. Annealing the starch just below its gelatinization temperature under atmosphere and high pressure increased the gelatinization temperature but the gelatinization enthalpy remained constant. The effect of pressure on gelatinization can be explained by the water diffusion. Morphological variations of starch granules treated under pressure were studied by microscope and SEM, and no observable changes were detected under present experimental condition.

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## References

- Altay, F., & Gunasekaran, S. (2006). Influence of drying temperature, water content, and heating rate on gelatinization of corn starches. *Journal of Agricultural and Food Chemistry*, 54(12), 4235–4245.
- Atwell, W. A., Hood, L. F., Lineback, D. R., Varriano-Marston, E., & Zobel, H. F. (1988). The terminology and methodology associated with basic starch phenomena. *Cereal Foods World*, 33, 306–311.
- Bauer, B. A., Hartmann, M., Sommer, K., & Knorr, D. (2004). Optical in situ analysis of starch granules under high pressure with a high pressure cell. *Innovative Food Science & Emerging Technologies*, 5(3), 293–298.
- Bauer, B. A., & Knorr, D. (2005). The impact of pressure, temperature and treatment time on starches: Pressure-induced starch gelatinisation as pressure time temperature indicator for high hydrostatic pressure processing. *Journal of Food Engineering*, 68(3), 329–334.
- Blaszczak, W., Fornal, J., Kiseleva, V. I., Yuryev, V. P., Sergeev, A. I., & Sadowska, J. (2007). Effect of high pressure on thermal, structural and osmotic properties of waxy maize and Hylon VII starch blends. *Carbohydrate Polymers*, 68(3), 387–396.
- Blaszczak, W., Fornal, J., Valverde, S., & Garrido, L. (2005a). Pressure-induced changes in the structure of corn starches with different amylose content. *Carbohydrate Polymers*, 61(2), 132–140.
- Blaszczak, W., Valverde, S., & Fornal, J. (2005b). Effect of high pressure on the structure of potato starch. *Carbohydrate Polymers*, 59(3), 377–383.
- Buckow, R., Heinz, V., & Knorr, D. (2007). High pressure phase transition kinetics of maize starch. *Journal of Food Engineering*, 81(2), 469–475.
- Cooke, D., & Gidley, M. J. (1992). Loss of crystalline and molecular order during starch gelatinisation: Origin of the enthalpic transition. *Carbohydrate Research*, 227, 103–112.
- Douzals, J. P., Perrier Cornet, J. M., Gervais, P., & Coquille, J. C. (1998). High-Pressure gelatinization of wheat starch and properties of pressure-Induced gels. *Journal of Agricultural and Food Chemistry*, 46(12), 4824–4829.
- Gough, B. M., & Pybus, J. N. (1971). Effect on the gelatinization temperature of wheat starch granules of prolonged treatment with water at 50 °C. *Starch-Stärke*, 23(6), 210–212.
- Hibi, Y., Matsumoto, T., & Hagiwara, S. (1993). Effect of high pressure on the crystalline structure of various starch granules. *Cereal Chemistry*, 70(1), 671–676.
- Hoover, R., & Vasanathan, T. (1994). The effect of annealing on the physicochemical properties of wheat, oat, potato and lentil starches. *Journal of Food Biochemistry*, 17, 303–325.
- Jacobs, H., Mischenko, N., Koch, M. H. J., Eerlingen, R. C., Delcour, J. A., & Reynaers, H. (1998). Evaluation of the impact of annealing on gelatinisation at intermediate water content of wheat and potato starches: A differential scanning calorimetry and small angle X-ray scattering study. *Carbohydrate Research*, 306(1–2), 1–10.
- Katopo, H., Song, Y., & Jane, J.-I. (2002). Effect and mechanism of ultrahigh hydrostatic pressure on the structure and properties of starches. *Carbohydrate Polymers*, 47(3), 233–244.
- Knorr, D., Heinz, V., & Buckow, R. (2006). High pressure application for food biopolymers. *Biochimica et Biophysica Acta (BBA)–Proteins & Proteomics*, 1764(3), 619–631.
- Knutson, C. A. (1990). Annealing of maize starches at elevated temperatures. *Cereal Chemistry*, 67(4), 376–384.
- Krueger, B. R., Knutson, C. A., Inglett, G. E., & Walker, C. E. (1987a). A differential scanning calorimetry study on the effect of annealing on gelatinization behaviour of corn starch. *Journal of Food Science*, 52(3), 715–718.
- Krueger, B. R., Walker, C. E., Knutson, C. A., & Inglett, G. E. (1987b). Differential scanning calorimetry of raw and annealed starch isolated from normal and mutant maize genotypes. *Cereal Chemistry*, 64(3), 187–190.
- Larsson, I., & Eliasson, A.-C. (1991). Annealing of starch at an intermediate water content. *Starch-Stärke*, 43, 227–231.
- Lelievre, J. (1974). Starch gelatinization. *Journal of Applied Polymer Science*, 18(1), 293–296.
- Liu, H., Yu, L., Chen, L., & Li, L. (2007). Retrogradation of corn starch after thermal treatment at different temperatures. *Carbohydrate Polymers*, 69(4), 756–762.
- Liu, H., Yu, L., Xie, F., & Chen, L. (2006). Gelatinization of cornstarch with different amylose/amylopectin content. *Carbohydrate Polymers*, 65(3), 357–363.
- Liu, Q., & Thompson, D. B. (1998). Effects of moisture content and different gelatinization heating temperatures on retrogradation of waxy-type maize starches. *Carbohydrate Research*, 314(3–4), 221–235.
- Lopez-Fandino, R. (2006). High pressure-induced changes in milk proteins and possible application in dairy technology. *International Dairy Journal*, 16, 1119–1131.
- Muhr, A. H., & Blanshard, J. M. V. (1982). Effect of hydrostatic pressure on starch gelatinisation. *Carbohydrate Polymers*, 2(1), 61–74.
- Ring, S. G., & Colonna, P. (1987). The gelation and crystallization of amylopectin. *Carbohydrate Research*, 162, 277–293.
- Rubens, P., & Heremans, K. (2000). Pressure-temperature gelatinization phase diagram of starch: An in situ Fourier transform infrared study. *Biopolymers*, 54(7), 524–530.
- Rubens, P., Snauwaert, J., Heremans, K., & Stute, R. (1999). In situ observation of pressure-induced gelation of starches studied with FTIR in the diamond anvil cell. *Carbohydrate Polymers*, 39(3), 231–235.
- Russell, P. L. (1987). Gelatinisation of starches of different amylose/amylopectin content. A study by differential scanning calorimetry. *Journal of Cereal Science*, 6(2), 133–145.
- Shogren, R. L. (1992). Effect of moisture content on the melting and subsequent physical aging of cornstarch. *Carbohydrate Polymers*, 19, 83–90.
- Stolt, M., Oinonen, S., & Autio, K. (2001). Effect of high pressure on the physical properties of barley starch. *Innovative Food Science & Emerging Technologies*, 1(3), 167–175.
- Stolt, M., Stoforos, N. G., Taoukis, P. S., & Autio, K. (1999). Evaluation and modelling of rheological properties of high pressure treated waxy maize starch dispersions. *Journal of Food Engineering*, 40(4), 293–298.
- Stute, R., Klingler, R. W., Boguslawski, S., Eshtiaghi, M. N., & Knorr, D. (1996). Effects of high pressures treatment on starches. *Starch-Stärke*, 48(11–12), 399–408.
- Sullivan, J. W., & Johnson, J. A. (1964). Measurement of starch gelatinization by enzyme susceptibility. *Cereal Chemistry*, 41, 73–77.
- Tester, R. F., Debon, S. J. J., & Karkalas, J. (1998). Annealing of wheat starch. *Journal of Cereal Science*, 28(3), 259–272.
- Tester, R. F., Debon, S. J. J., & Somerville, M. D. (2000). Annealing of maize starch. *Carbohydrate Polymers*, 42(3), 287–299.
- Thevelein, J. M., Van Assche, J. A., Heremans, K., & Gerlisma, S. Y. (1981). Gelatinisation temperature of starch, as influenced by high pressure. *Carbohydrate Research*, 93(2), 304–307.
- Vainionpää, J., Forsell, P., & Virtanen, T. (1993). High-pressure gelatinization of barley starch at low moisture levels and elevated temperature. *Starch-Stärke*, 45(1), 19–24.
- Waigh, T. A., Donald, A. M., Heidebach, F., Riekel, C., & Gidley, M. J. (1999). Analysis of the native structure of starch granules with small angle X-ray microfocus scattering. *Biopolymers*, 49(1), 91–105.
- Waigh, T. A., Gidley, M. J., Komanshek, B. U., & Donald, A. M. (2000). The phase transformations in starch during gelatinisation: A liquid crystalline approach. *Carbohydrate Research*, 328(2), 165–176.
- Yost, D. A., & Hoseney, R. C. (1986). Annealing and glass transition of starch. *Starch-Stärke*, 38(9), 289–292.