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Retrograding characteristics of high hydrostatic pressure processed corn and wheat starch

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Special Chapter dedicated to the memory of dr. Michel Ollivon

Abstract High hydrostatic pressure (HHP) has been investigated as an alternative to thermal processing for food preservation. HHP has been known to affect high molecular weight polymers causing phase change. Starch is gelatinized at a pressure on the order of 600–700 MPa, at 25 °C. Gelatinized starch recrystallizes during storage affecting the texture and shelf life of food products. The effect of HHP processing on the crystallization of starches from different botanical origins during storage at 4 and 23 °C was investigated. Crystallization kinetics of HHP treated wheat and corn starch gels were compared using DSC. The effect of crystallization on structure was evaluated in terms of storage modulus. The rate of retrogradation depended on the storage temperature (23 °C and 4 °C) and the botanical origin of the starch. The least crystallization was observed in HHP treated wheat starch stored at 23 °C. The storage modulus increased with crystallization of starch.

Keywords Retrogradation · High pressure processing · Corn starch · Wheat starch · Kinetics of crystallization · DSC

Introduction

Starches are utilized in many food products to increase viscosity or to form gels. Starch granules suspended in water swell with heat and the viscosity of the suspension increases depending on starch concentration. Thermal processing changes the physico-chemical properties of starch such as increased water solubility and development of viscoelastic behavior [1–3]. Starches from different biological origins show different physical and chemical properties including gelatinization temperature (52–66 °C for wheat and 62–67 °C for corn) and viscosity after heat treatment [4].

High hydrostatic pressure (HHP) has been shown to affect high molecular weight polymers causing denaturation of proteins [5, 6] and gelatinization of starch [7–9]. Douzals et al. [8] found that wheat starch granules swelled as a result of HHP treatment. Studies on 16% (w/w) wheat starch showed that starch gelatinization by pressure as evaluated by differential scanning calorimetry (DSC) starts at 300 MPa and starch is completely gelatinized at 600–700 MPa, at 25 °C [7–11].

Gelatinized starch recrystallizes during storage, affecting the texture, appearance and shelf life of food products. This phenomenon is known as retrogradation. Retrogradation contributes to quality defects in foods such as loss of viscosity and phase separation. Jouppila et al. [12] reported that water content, storage temperature, and the difference between the storage temperature and the glass transition temperature were important factors in retrogradation of thermally treated corn starch. The Avrami equation [13] was shown to describe starch crystallization behavior based on x-ray diffraction [12] and DSC data [14]. Douzals et al. [8] reported that crystallization of HHP gelatinized wheat starch (30% dry matter) during storage reached to a constant value after 6 days, with the extent of retrogradation higher for starch gelatinized by heat than for starch gelatinized by pressure at 600 MPa. However, Stolt et al. [15] reported that retrogradation of heat (90 °C, 30 min) and pressure (550 MPa, 30 °C, 10 min) treated 25% (w/w)

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barley starch stored at 4 °C were similar and continued to increase after 7 days of storage. The results suggest that retrogradation depends on the botanical source of the starch, storage temperature, and starch concentration. It should also be noted that starches from different botanical origins have different compositions, specifically different amylose to amylopectin ratios. Therefore, in order to decide the suitability of a particular starch for a specific application, it is imperative to explore the impact of HHP processing on retrogradation characteristics of starches from different botanical origins.

An understanding of the effect of high pressure on properties of starch based food systems under conditions relevant to food storage are necessary to predict storage stability of such systems so that HHP processing protocols can be optimized for successful development of HHP processed commercial food products. Knowledge of the retrogradation properties of starch as a function of formulation and high pressure processing conditions is essential for optimization of processing conditions so as to improve the physical stability of HHP processed food products.

The purpose of this study was to evaluate the retrogradation characteristics of HHP processed corn and wheat starch stored at 4 °C (refrigeration) and at 23 °C (ambient) using a differential scanning calorimeter (DSC) in order to determine crystallization kinetic parameters. The storage modulus (G′) was also characterized for HHP processed corn and wheat starch systems as a function of storage time to determine the effect of starch crystallization on the development of rheological properties.

Materials and methods

Materials

Wheat starch (Sigma, St. Louis, MO) and corn starch (Sigma, St. Louis, MO) were used to prepare starch suspensions. Corn or wheat starch was suspended in distilled water at a concentration of 15% (w/w) starch. Bakeshure 250 (Bachem, Slate Hill, NY), which includes sorbic acid was added at a concentration of 0.1% to the starch suspensions to eliminate mold growth during storage.

High pressure processing of starch suspensions

50 mL of the starch suspension was placed inside a sterile polyethylene bag (Fisher Scientific, Canada) and vacuum sealed. The bags were then placed in a hydrostatic high pressure unit (Quintas AFP-6, ABB Autoclave Systems, Columbus, OH). The pressure transmitting medium fluid in the pressure unit contained 50% propylene glycol (Houghton-Safe 620-TY, Houghton Int., Valley Forge, PA) and 50% distilled water. The high pressure processing was performed at 600 MPa and 25 °C for 15 min.

DSC study

The degree of gelatinization by pressure and crystallization of HHP treated starch as a function of storage time were determined using DSC (model 2090, TA Instruments, New Castle, DE). Samples of HHP treated starch (50–55 mg) were placed in a high volume stainless steel crucible and DSC curves were recorded from 1 °C to 100 °C at a heating rate of 5 °C min^{-1}. Each DSC curve was analyzed to calculate the onset and peak temperatures and the enthalpy of the endothermic transition corresponding to the melting of starch crystals. Enthalpy values are reported as J g^{-1} based on the grams of dry starch, except in Figs. 1 and 2 they are based on the grams of wet starch.

Analysis of DSC data

The enthalpy data as a function of time were used to evaluate the crystallization kinetics of the HHP treated starch. The fraction of crystalline material, α, at time t, during crystallization is described by the Avrami equation [13] and is also expressed in terms of the melting enthalpy of starch crystals (Eq. 1),

$$\alpha = 1 - \exp(-kt^n) = \frac{\Delta H_t - \Delta H_i}{\Delta H_f - \Delta H_i} \tag{1}$$

where k is the rate constant, n is the Avrami exponent, ΔH_i is the enthalpy measured immediately following the pressure treatment, ΔH_f, and ΔH_t are the enthalpy of starch crystal melting after maximal crystallization and after storage for time t, respectively. Equation 1 was rearranged and fitted to enthalpy data to determine crystallization kinetic parameters for HHP treated starch,

$$\Delta H_t = \Delta H_i + [(\Delta H_f - \Delta H_i)(1 - e^{-kt^n})] \tag{2}$$

The half-life ($t_{1/2}$) of crystallization was also calculated for the corn and wheat starch using the following equation derived by setting the fractional crystallization to 0.5 and solving for t.

$$t_{1/2} = \left(-\frac{\ln(0.5)}{k}\right)^{\frac{1}{n}} \tag{3}$$

Rheological properties

The rheological properties of the pressure treated corn and wheat starch were studied as a function of time at storage temperatures of 23 °C and 4 °C using a controlled stress rheometer (AR 1000-N, TA Instruments, DE). Dynamic measurements were performed in order to evaluate viscoelastic behavior of HHP treated wheat and corn starch pastes. A 6 cm diameter acrylic cone geometry with 4° angle was used to perform dynamic rheological tests. Stress sweep experiments at 1 Hz were carried out to determine the linear viscoelastic region. Then frequency sweep tests were performed from 0.1 to 50 Hz in the linear viscoelastic range. Data obtained from frequency sweep tests were used to determine the G′. Plots of G′ (Pa) at 1 Hz versus time were used to compare the textural characteristics of pressure treated starch systems as a function of storage time and temperature.

Results and discussion

The effect of HHP processing on the crystallization of starches from different botanical origins as a function of time at 4 and 23 °C storage temperatures was investigated. Crystallization characteristics of HHP treated starch gels were evaluated using DSC to compare their crystallization kinetics.

Effect of pressure treatment on gelatinization of starch

DSC curves of 15% (w/w) corn and wheat starch suspensions show that the two starches have different thermal gelatinization characteristics (Fig. 1). The gelatinization temperature of corn starch is higher than that of wheat starch as evaluated in terms of the onset (66 °C vs. 58 °C) and peak temperatures (70 °C vs. 64 °C) of the gelatinization endotherm. In addition, corn starch required a larger thermal energy for gelatinization per gram of dry starch (16.1 J g^{-1} vs. 11.2 J g^{-1}). Our findings are in agreement with the results reported in the literature [4]. Thermally induced gelatinization required higher temperatures and exhibited larger enthalpy change for corn starch than wheat starch suggesting a more stable crystalline structure for corn starch.

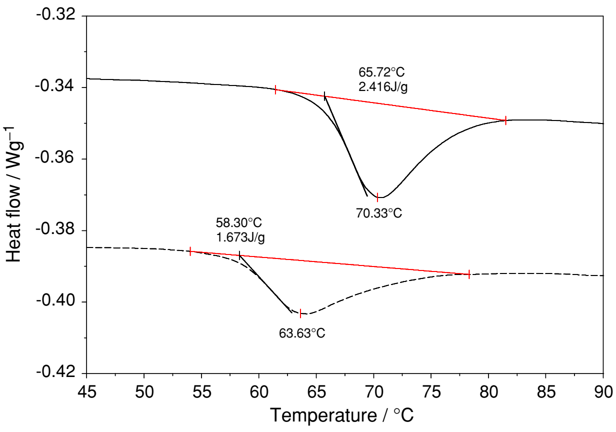

Fig. 1 DSC curves of 15% (w/w) native corn and wheat starch suspensions. Corn starch (——) and wheat starch (- - -)

Immediately after HHP treatment, the DSC curve of 15% (w/w) starch pastes displayed no endotherms indicating that both wheat and corn starches were completely gelatinized by pressure treatment at 600 MPa and 25 °C for 15 min. Based on the results reported in the literature, it is established that starch can be partially or completely gelatinized by adjusting pressure at constant temperature and treatment time [7, 8, 11, 16, 17]. The pressures necessary for complete gelatinization of starches were reported to be higher for B-type starches than A- and C- type starches [7]. For corn and wheat starches, which are A-type starches, the observations of this study were consistent with earlier reports that these starches can be completely gelatinized by 600 MPa pressure treatment at 25 °C [8]. Incomplete gelatinization after high pressure treatment at 600 MPa reported [18] for corn starch suspensions at 50% w/w concentration can be attributed to the presence of a limited amount of water for starch gelatinization. Complete gelatinization manifested as a single gelatinization endotherm in a DSC curve is only observed when water is present above 60% w/w. Therefore, gelatinization by pressure can be considered starch concentration dependent as well as pressure, temperature and treatment time dependent.

Analysis of HHP treated starch crystallization during storage by DSC

HHP treated corn and wheat starches were stored at 4 and 23 °C. Starch samples were removed periodically and DSC curves were recorded. Figure 2 shows the melting endotherms of starch crystals formed during storage for corn and wheat starches after a storage time of 31 days at 4 °C. The DSC curves indicate that the crystallization characteristics of corn and wheat starches are different. The enthalpies, onset and peak temperatures of HHP treated corn and wheat starch melting are 6.4 and 4.9 J g^{-1}, 42.3

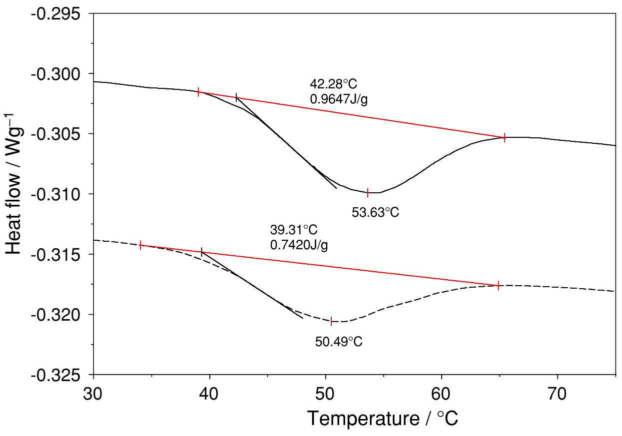

Fig. 2 DSC curves of pressure treated corn and wheat starch after 31 days of storage at 4 °C. Corn starch (——) and wheat starch (- - -)

and 39.3 °C, and 53.6 and 50.5 °C respectively. For starch pastes stored at 23 °C, the peak melting temperature of 61 °C observed for corn starch is in agreement with the 60.7 °C peak temperature reported for 15% dent corn starch gel stored for 34 days at 23 °C [19]. Similar to the gelatinization properties, the thermal stability of corn starch crystals formed during storage was higher than that of wheat starch indicating a more stable crystal structure for corn starch. The higher thermal energy requirement for melting of corn starch crystals in comparison with melting of wheat starch crystals may be attributed to one or more of a combination of the following reasons: increased enthalpy because of increased transition temperature of melting event (due to temperature dependence of specific heat), a larger amount of crystalline starch formed in the corn starch paste, and/or a larger enthalpy of melting per unit mass of crystals formed in corn starch paste suggesting better ordered corn starch crystallites.

Storage temperature affects the thermal stability and enthalpy of crystal melting for starch of a given botanical origin. However, the melting temperature of each starch did not vary with time under each storage temperature indicating annealing of crystals is not apparent during 60 days of storage. The average peak temperatures (calculated over 60 days of storage) of the melting transition for crystallites formed at 4 °C are 53 ± 3.2 °C for wheat starch and 55 ± 2.8 °C for corn starch and for crystallites formed at 23 °C are 61 ± 1.1 °C for wheat starch and 62 ± 1.0 °C for corn starch. The results indicate a higher thermal stability for starch crystallites formed during incubation at higher storage temperature. A similar finding of lower melting temperature for crystallites formed during incubation at low storage temperature was reported for corn starch by Joupilla and Roos [14] and attributed to less perfect crystal formation due to a smaller temperature difference between the storage temperature and the glass transition temperature.

The melting enthalpy of wheat and corn starch crystals formed during storage increases as a function of time suggesting an increasing extent of crystallization up to a constant value. The ultimate value of melting enthalpy depends on the starch botanical origin and the storage temperature (Fig. 3a, b). Equation 2 was fitted to the enthalpy data to evaluate the kinetic parameters of crystallization of HHP treated starch. Figure 3a and b show the fitted curves for corn and wheat starch stored at 4 and 23 °C as well as the experimental data. The resultant parameters for the Avrami equation and the final melting enthalpy of starch crystals are summarized in Table 1. The final thermal energy for melting of starch crystals formed during storage reached 2.2 J g^{-1} and 0.9 J g^{-1}, for corn and wheat starch stored at 23 °C and was 7.8 J g^{-1} and 5.3 J g^{-1} for corn and wheat starch stored at 4 °C suggesting a varying extent of crystallization for starches stored at 4 and 23 °C although the initial starch concentrations were identical. Comparison of the final melting enthalpy of starch crystals to gelatinization enthalpy for each starch shows that the extent of starch recrystallization after HHP treatment during storage of 60 days at 4 °C is approximately 47 (wheat) and 48 (corn) percent of the initial starch crystals, while storage at 23 °C resulted in only 14 (corn) and 8 (wheat) percent recrystallized starch. The recrystallization of starch has been attributed to amylose within the starch granules [2, 8]. However, Fennema [1] states that both amylose and amylopectin are involved in crystallization of starch, amylose crystallizing at a faster rate than amylopectin. Because the amylose/amylopectin ratios are similar for both starches, the difference in extent of crystallization can not be attributed to

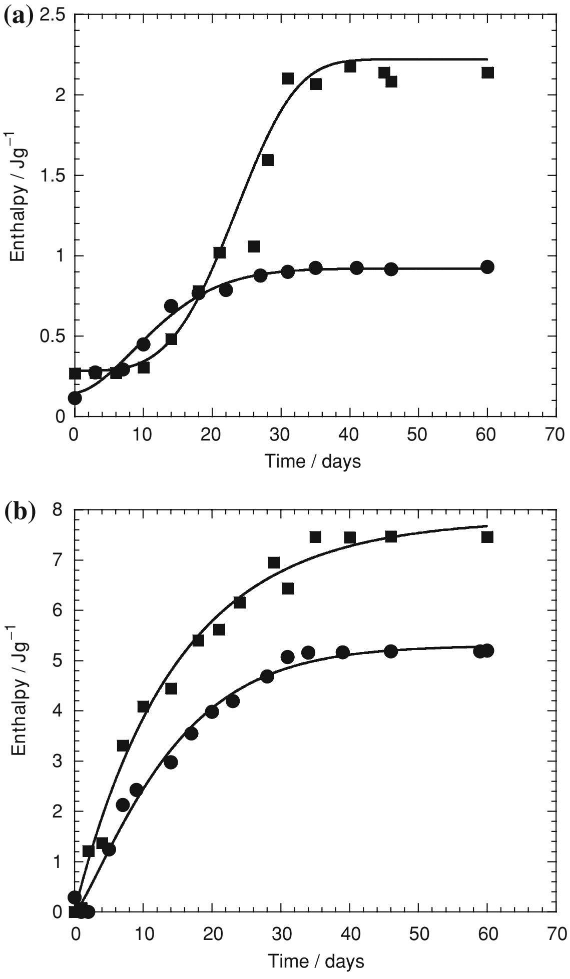

Fig. 3 **a** Melting enthalpy of pressure treated corn and wheat starch crystals formed as a function of storage time at 23 °C. corn starch (■) and wheat starch (●). Solid lines are fitted curves using Eq. 2. **b** Melting enthalpy of pressure treated corn and wheat starch crystals formed as a function of storage time at 4 °C. Corn starch (■) and wheat starch (●).Solid lines are fitted curves using Eq. 2

Table 1 Avrami equation parameters for corn and wheat starch stored at 23 °C and 4°C

Starch	Storage temperature (°C)	ΔH_f/J g^{-1}	ΔH_i/J g^{-1}	k/days^{-n}	n	$t_{1/2}$ (days)
Corn	23	0.33	0.04	0.00004	3.0	23.8
	4	1.17	0.00	0.07000	1.0	10.0
Wheat	23	0.14	0.02	0.0100	1.7	11.3
	4	0.79	0.00	0.0400	1.2	10.4

amylose/amylopectin ratio only. Furthermore, the structures of amylose and amylopectin molecules and the presence of other molecules such as granule associated proteins were proposed by Han et al. [20] to affect the viscoelastic properties of starch pastes.

The effect of storage temperature on the overall crystallization rate, which is influenced by both nucleation and crystal growth rates, is described by a bell shaped curve. Starch gels that are stored between the glass transition and melting temperatures exhibit crystallization with the overall rate of crystallization decreasing as the storage temperature approaches either the glass transition or melting temperature [21]. The maximum rate of crystallization is expected to be at a temperature corresponding to the midpoint of the temperature range between the glass transition and melting temperatures. The glass transition temperature for the starch-water system (15% w/w) used in the present study was calculated to be −126.5 °C using the Couchman–Karasz equation [22]. The melting temperature of native starch crystals in the present study measured by DSC was 70 °C for corn starch and 64 °C for wheat starch. The temperatures at which the rate of crystallization for corn and wheat starch are expected to be maximum are approximately −28 °C and −31 °C respectively. These temperatures are closer to 4 °C storage temperature than 23 °C storage temperature for both starches. The observed larger melting enthalpy and higher rate constant of crystallization for starches stored at 4 °C in comparison with starches stored at 23 °C shown in Table 1 are in agreement with expectation.

The Avrami exponent (n) were observed to depend on the starch type and the storage temperature (Table 1). The Avrami equation exponent describes nucleation and growth mechanisms. A value of one, suggesting instantaneous nucleation and rod-like growth, describes the crystallization behavior of corn ($n = 1$) and wheat starch ($n = 1.2$) at 4 °C. A value of 2, indicates either two dimensional growth with instantaneous nucleation or one dimensional, rod-like growth with a heterogeneous random nucleation. The Avrami exponent originally was assumed to be only integer valued. Fractional values were later attributed to a complex crystallization mechanism comprising one and two dimensional growth with instantaneous nucleation. The shapes of the curves in Fig. 3a and b indicate that crystallization of starch starts immediately following processing for all conditions tested except for corn starch stored at 23 °C. Both the presence of a lag time (~6 days) in the starch crystallization curve and an n value of 3 for corn starch stored at 23 °C may be attributed to random nucleation followed by two dimensional growth. Moo-Yeol et al. [23] report a value of 1 for the Avrami exponent for crystallization of rice starch stored at an initial temperature of 4 °C followed by various time–temperature combinations. It appears that low temperature storage results in instantaneous nucleation as supported by our studies on corn and wheat starch as well as for crystallization of rice starch reported by Moo-Yeol et al. [23].

It is imperative to note that the thermal stability and enthalpy data obtained from DSC studies and Avrami equation parameters provide complementary and confirmatory information to explain the crystallization mechanism in HHP processed starch pastes. At the lower storage temperature, an instantaneous nucleation and one dimensional growth results in formation of numerous initial nuclei from which a number of one dimensional crystallites form. On the other hand, at higher storage temperature random nucleation may promote annealing of crystals leading to two dimensional growth and perfection of crystals which manifests itself as the higher thermal stability of melting transitions observed in DSC curves of starch pastes stored at 23 °C in comparison with the lower thermal stabilities observed for crystallites formed at 4 °C. It is also known that crystal growth stops when neighboring chains are impinged upon. It is expected that a larger number of one dimensional crystals fit into a given volume relative to the number of two or three dimensional crystals. Therefore, a larger enthalpy of crystallization is observed for starch pastes stored at 4 °C due to the larger amount of rod-like crystalline starch (e.g. $n = 1$) grown before the crystallization stops in comparison to the amount of two or three dimensional crystal growth (e.g. $n = 2$ or $n = 3$) for starches stored at 23 °C. Consequently, the larger final melting enthalpy, lower thermal stability, and Avrami exponent value of 1 confirm the probability of a larger amount but less stable crystal formation for starches stored at 4 °C.

A significantly shorter half-life values for recrystallization is observed for wheat starch relative to corn starch at 23 °C, while similar half-life values are observed for both corn and wheat starch at 4 °C (Table 1). Based on the half-life comparison, the starch crystallization rate is expected to be slowest for corn starch stored at 23 °C. When designing a starch-containing food system, in addition to the rate of crystallization, the ultimate amount of crystalline starch present in the system should also be considered because its presence affects texture and phase separation due to syneresis. Therefore, considering the lower maximal amount of starch crystallized during storage, it appears that the most stable system would be obtained with wheat starch stored at 23 °C.

Rheological properties of HHP treated starch during storage

A stress sweep at 1 Hz frequency was performed to determine the linear viscoelastic region for all HHP processed starch samples as a function of time during storage. A frequency sweep was performed at a constant stress value, which was determined from the stress sweep test. Typically, the frequency sweep test was conducted at 1 Pa stress with a corresponding value of ~1% strain level. Storage modulus values above which the linear viscoelastic region was not maintained in a frequency sweep test were not included in analysis of data.

The storage modulus was calculated at 1 Hz for HHP treated corn and wheat starch. Figure 4 shows the storage modulus development and the corresponding melting enthalpy of starch crystals formed during storage at 23 °C. The G′ values for HHP treated corn and wheat starch increase during storage. For wheat starch, G′ increases for 10 days and then stays approximately constant similar to the behavior observed for the melting enthalpy change during storage. A relatively higher G′ is observed for corn starch than for wheat starch confirming the higher extent of crystallization during storage revealed by DSC. Furthermore, corn starch exhibits a more complex crystallization behavior observable as G′ a rapid increase in G′ followed by a short plateau region and a second increase (Fig. 4). The initial rapid rise of G′ is reported in the literature as crystallization of amylose, it being the fast component of the retrogradation process, followed by slow amylopectin crystallization [1, 19, 24]. In Figure 4, the plateau region and the second increasing region coincide in both the DSC and the rheological studies (as monitored in terms of the time dependence of melting enthalpy and storage modulus) while the initial amylose crystallization is only observed by rheology studies. After 25 days storage, G′ values decrease drastically for the HHP treated corn starch stored at 23 °C (data not shown in Fig. 4). A similar low G′ values were observed for both HHP treated corn and wheat starch stored at 4 °C after 1 day and 3 days of storage, respectively. The enthalpy of starch melting is approximately 1.6 J g^{-1} at the time corresponding to the observed decrease in storage modulus. It could be speculated that for 15% starch concentration samples, once a critical starch crystal concentration is reached, significant syneresis and phase separation occurs causing G′ to decrease.

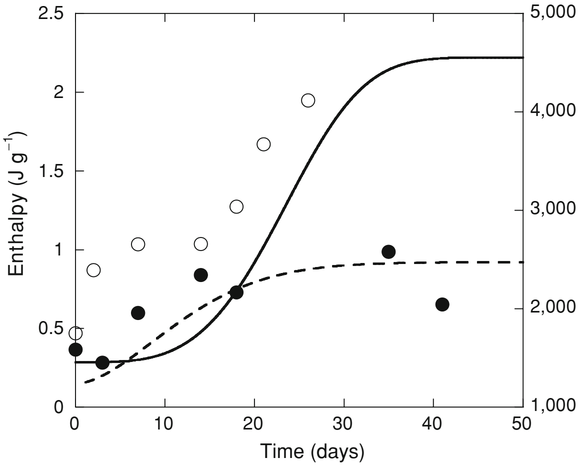

Fig. 4 Storage Modulus (G′) at 1 Hz, corn (○), wheat (●) and melting enthalpy, corn (——), wheat (- - -) as a function of time for starch pastes stored at 23 °C

Conclusions

Rheological and thermal properties can be used to characterize crystallization behavior of high pressure processing treated starch paste during storage thereby providing means to evaluate the stability of starch pastes as a function of storage conditions. DSC results show that the amount of crystallization in starch increases, while the dynamic rheological experiments reveal a concomitant increase of G′ as a function of storage time.

The calorimetric and rheological analysis of HHP processed starches show that retrogradation depends on the storage temperature and botanical origin of the starch. HHP processed wheat starch stored at 23 °C for 60 days exhibited the least amount of crystallization while the crystallization rate was the lowest for the HHP processed corn starch stored at 23 °C. The results also reveal a stronger dependence of thermal stability of formed crystals on storage temperature than on the botanical origin of the starch. The fitted Avrami equation parameters are consistent with a crystallization mechanism featuring instantaneous nucleation and one dimensional crystal growth at lower incubation temperature, while at higher incubation temperature random nucleation and two dimensional growth are indicated. This proposed mechanism of crystal growth provides a basis for understanding the DSC-derived observations of higher thermal stability of crystals formed at high incubation temperature and for larger melting enthalpy of crystals formed at low incubation temperature.

The results of DSC and rheological studies provide complementary information and underscore the importance of development of an understanding of the behavior of biopolymer systems under conditions relevant to food storage to predict storage stability of such systems. Studies on the retrogradation properties of starch in the presence of common food ingredients are also essential for optimization of processing conditions so as to improve the physical stability and textural characteristics of HHP processed food products.

References

1. Fennema OR. Food chemistry, 3rd edn. NY: Marcel Dekker Inc.; 1996.
2. Rao AM. Rheology of fluid and semisolid foods. Gaithersburg, Maryland: Aspen Publishers; 1999.
3. Jobling S. Improving starch for food and industrial applications. Curr Opin Plant Biol. 2004;7:210–8.
4. Roos YH. Phase transitions in food. San Diego, California: Academic Press; 1995.
5. Messens W, Van Camp J, Huyghebaret A. The use of high pressure to modify the functionality of food proteins. Trends Food Sci Technol. 1997;8:107–12.
6. Famelart MH, Chapron L, Piot M, Brule G, Durier C. High pressure-induced gel formation of milk and whey concentrates. J Food Eng. 1998;36:149–64.
7. Stute R, Heilbronn KRW, Boguslawski S, Eshtiaghi MN, Knorr D. Effects of high pressures treatment on starches. Starch/Starke. 1996;48:399–408.
8. Douzals JP, Cornet JMP, Gervais P, Coquille JC. High-pressure gelatinization of wheat starch and properties of pressure-induced gels. J Agric Food Chem. 1998;46:4824–9.
9. Zuo C, Ma C, Zhang S. Effects of high hydrostatic on gelatinization of corn starch. In: Volume 4 proceedings of the international conference on agricultural engineering (ICAE), Beijing, China 1999, p. 91–3.
10. Rubens P, Heremans K. Pressure-temperature gelatinization phase diagram of starch: an in situ fourier transformation infrared study. Biopolymers. 2000;54:524–30.
11. Lowe K, Kaletunç G. Calorimetric analysis of starch gelatinization by high pressure processing. In: Kaletunç G, editor. Calorimetry in food processing: analysis and design of food systems. Wiley-Blackwell; 2009. p. 341–9.
12. Jouppila K, Kansikas J, Roos YH. Factors affecting crystallization and crystallization kinetics in amorphous corn starch. Carbohydr Polym. 1998;36:143–9.
13. Avrami M. Kinetics of phase change. I. General theory. J Chem Phys. 1939;7:1103–12.
14. Jouppila K, Roos YH. The physical state of amorphous corn starch and its impact on crystallization. Carbohydr Polym. 1997;32:95–104.
15. Stolt M, Oinonen S, Autio K. Effect of high pressure on the physical properties of barley starch. Innov Food Sci Emerg Technol. 2000;1:167–75.
16. Douzals JP, Marechal PA, Coquille JC, Gervais P. Microscopic study of starch gelatinization under high hydrostatic pressure. J Agric Food Chem. 1996;44:1403–8.
17. Bauer BA, Knorr D. The impact of pressure, temperature and treatment time on starches: pressure-induced starch gelatinization as pressure time temperature indicator for high hydrostatic pressure processing. J Food Eng. 2005;68:329–34.
18. Kweon M, Slade L, Levine H. 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. Carbohydr Polym. 2008;72:293–9.
19. Lewen KS, Paeschke T, Reid J, Molitor P, Schmidt SJ. Analysis of the retrogradation of low starch concentration gels using differential scanning calorimetry, rheology, and nuclear magnetic resonance spectroscopy. J Agric Food Chem. 2003;51:2348–58.
20. Han X, Campanella OH, Guan H, Keeling PL, Hamaker BR. Influence of maize starch granule-associated protein on the rheological properties of starch pastes. Part II. Dynamic measurements of viscoelastic properties of starch pastes. Carbohydr Polym. 2002;49:323–30.
21. Levine H, Slade L. A food polymer science approach to structure-property relationships in aqueous food systems: non-equilibrium behavior of carbohydrate water systems. In: Levine H, Slade L, editors. Water relationships in foods: advances in the 1980s and trends for the 1990s. New York: Plenum Press; 1991. p. 29–103.
22. Couchman PR, Karasz FW. A classical thermodynamic discussion of the effect of composition on glass-transition temperatures. Macromolecules. 1978;11:117–9.
23. Baik MY, Kim KJ, Cheon KO, Ha Y, Kin WS. Recrystallization kinetics and glass transition of rice starch gel system. J Agric Food Chem. 1997;45:4242–8.
24. Biliaderis CG, Zawitowski J. Viscoelastic behavior of aging starch gels: effect of concentration, temperature, and starch hydrolysates on network properties. Cereal Chem. 1990;67:240–6.