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Retrogradation of corn starch after thermal treatment at different temperatures

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Abstract

Multi-endotherms of the gelatinization of corn starch, such as G, M1, M2, and Z endotherms, have been detected by DSC. The retrogradation of corn starch after initial thermal treatment at different temperatures was studied by DSC; in particular, the effect of thermal treatment before and after each endotherm of gelatinization on retrogradation was determined as a function of annealing time. The effect of thermal treatment at a certain temperature on the residual gelatinization endotherm at a higher temperature is also discussed. It was found that the higher temperature of thermal treatment always removed all the endotherms below that temperature. However, a certain thermal treatment temperature could affect the residual endotherm above this treatment temperature. The time-dependent retrogradation of corn starch is mainly due to G and M1 endotherms. The temperature and enthalpy of the melting of amylose–lipid complexes M2 and nonlipid complex amylose Z were not affected by aging time. The final enthalpy of retrogradation was found to be lower than that of gelatinization.

Keywords: Retrogradation; Gelatinization; Corn starch; DSC; Residual endotherm

1. Introduction

"Retrogradation" has been used to describe the changes that occur in starch after gelatinization, from an initially amorphous state to a more ordered or crystalline state (Atwell, Hood, Lineback, Varriano-Marston, & Zobel, 1988; Bulkin, Kwak, & Dea, 1987; Gudmundsson, 1994; Liu & Thompson, 1998a). These changes are due to the reassociation of starch chains as double helices, and variably ordered semi-crystalline arrays of these helices, as monitored by X-ray diffraction (XRD) or differential scanning calorimetry (DSC), which was used to observe endothermic changes when these structures were lost on heating.

The effects of retrogradation in starch-based products can be desirable or, more usually, undesirable. There is general consensus that starch retrogradation contributes significantly to staling or undesirable firming of bread and other starch-based products (Abd Karim, Norziah, & Seow, 2000; Del Nobile, Martoriello, Mocci, & La Notte, 2003; Liu & Thompson, 1998b). Similarly, the susceptibility of legume starch gels to retrogradation and syneresis makes these types of starches unsuitable for products requiring low-temperature storage. However, retrogradation is sometimes promoted to modify the structural, mechanical or organoleptic properties of certain starch-based products (Morikawa & Nishinari, 2000; Perera & Hoover, 1999; Yoshimura, Takaya, & Nishinari, 1999). Recently, starch-based plastics have attracted more and more attention because of their biodegradability and renewability (Mani & Bhattacharya, 2001; Yu & Christie, 2005). The process of retrogradation significantly affects the mechanical properties of these types of materials.

Starch retrogradation has been widely studied as a function of botanical source (Kalichevsky, Orford, & Ring, 1990; Orford, Ring, Carroll, Miles, & Morris, 1987; Roulet, Maclnnes, Gumy, & Mursch, 1990), the fine structure of

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amylopectin (Kalichevsky et al., 1990; Ward, Hoseney, & Seib, 1994), and the ratio of amylose/amylopectin (Gudmundsson & Eliansson, 1990; Russell, 1987). However, there have only been a few papers dealing with the effects of preheating treatment on retrogradation. Fisher and Thompson (1997) and Liu and Thompson (1998b) studied the effects of thermal treatment on the retrogradation of waxy corn starch. It was shown that the residual gelatinization endotherm peak temperature increased; the endotherm narrowed, and the enthalpy decreased. Samples stored for 7 d at 4 °C showed additional amylopectin retrogradation endotherms. Retrogradation increased dramatically as initial holding temperature was increased from 60 to 70 °C. Kinetics studied by the Avrami equation showed that the initial heating temperature clearly affected the retrogradation process. Waxy corn starch contains only one kind of relatively homogenous microstructure molecule – amylopectin – a highly branched structure of short α-1,4 chains linked by α-1,6 bonds.

Previous studies (Liu, Yu, Xie, & Chen, 2006; Russell, 1987; Yu & Christie, 2001) have shown that the gelatinization process of normal corn starch (a mixture of amylose and amylopectin) is much more complex, and multi-endotherms have been detected. The gelatinization endotherms and enthalpy depend on starch source, water content and the ratio of amylose/amylopectin, and measurement conditions. Up to four endotherms (identified as G, M1, M2, and Z), can be detected by DSC when the water content is about 50%. Endotherms G and M1 are associated with amylopectin disruption, while endotherms M2 and Z are attributed to the melting of amylose–lipid complexes and noncomplex amylose crystalline. The thermal behaviour of corn starch containing about 50% water provides an excellent opportunity to study the mechanisms of both gelatinization and retrogradation, since multiphase transitions are clearly separated in DSC thermograms.

In this study, the retrogradation of corn starch with about 52% water content, after thermal treatment at different initial temperatures, i.e. just above the G, M1, M2, and Z endotherms, respectively; was studied by DSC. In particular, the effects of the thermal treatment before and after each endotherm on the retrogradation was determined as a function of annealing time. The mechanisms of gelatinization and retrogradation are discussed based on the retrogradation behaviour of corn starch after thermal treatment above the temperatures of the G, M1, M2, and Z endotherms. The effects of thermal treatment at a certain temperature on the residual gelatinization endotherms at higher temperature were also studied and discussed.

2. Experimental

2.1. Materials and sample preparation

The corn starch used in this work is commercially available and was supplied by Penford (Australia). The amylose content in the starch used was about 26% (manufacturer's data). An infra-red heating balance (Model DHS-20) was used to measure the moisture contents of samples heated to 110 °C for 20 min. Defatted corn starch was prepared by Soxhlet extraction with methanol, according to the method of Schoch (1945).

Samples were prepared by premixing the starch with additional water in glass vials. The mass of each empty glass vial with its cover was first weighed. Starch was placed into the vial, and the vial was weighed again to calculate the mass of starch. The desired volume of water was added using a syringe, and was mixed well with the starch using a small spatula. The vial was sealed and weighed again to calculate the water content. In order to identify homogeneous samples, the mixed materials were initially equilibrated in the vials for 24 h then transferred to a pan. Sample preparation for DSC have been discussed in our previous paper (Liu et al., 2006; Yu & Christie, 2001). The samples used in this work contained 52% water based on dried starch content. Fig. 1 shows the DSC thermograms of a sample heating at 5 °C/min. It can be seen that four endotherms are clearly identified. Table 1 lists the characteristics of gelatinization of the sample. The temperatures 81, 105, 125, and 155 °C were used to study the effect of thermal treatment, which are just above the temperature of endotherms G, M1, M2, and Z, respectively. After initial thermal treatment to different temperatures, samples were quenched to 5 °C and kept in a refrigerator at 5 °C. After appropriate storage times (0 h, 2 h, 5 h, 10 h, 15 h, 1 d, 3 d, 7 d, 15 d, and 30 d), samples were removed from the refrigerator and DSC measurements were performed again. The second scans were carried out up to 170 °C at the same heating rate (5 °C/min).

2.2. Differential scanning calorimetry

A Perkin–Elmer DSC Diamond-I with an internal coolant (Intercooler 1P) and nitrogen purge gas was used in the experimental work. Melting point and enthalpies of indium were used for temperature and heat capacity calibration. High-pressure stainless steel pans (PE No. B0182901) with gold-plated copper seals (PE No. 042-191758) were used to study the thermal behaviour of test samples with high-moisture content up to 350 °C. The slow heating rate of 5 °C/min

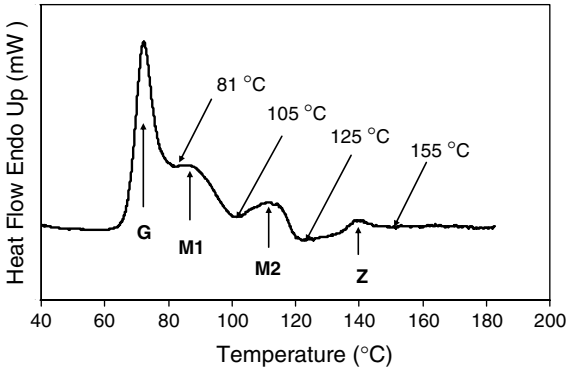

Fig. 1. DSC thermograms of a sample heating at 5 °C/min.

Table 1
Gelatinization characteristics of corn starch with 52% water content detected DSC

Endotherm G					Endotherm M1					Endotherm M2					Endotherm Z				
T_0	T_p	T_c	ΔT (°C)	ΔH (J/g)	T_0	T_p	T_c	ΔT (°C)	ΔH (J/g)	T_0	T_p	T_c	ΔT (°C)	ΔH (J/g)	T_0	T_p	T_c	ΔT (°C)	ΔH (J/g)
68.4	72.2	81.3	13.9	7.54	71.8	86.8	101.8	30	4.92	102.7	114.2	121.4	18.7	1.73	133.8	139.8	148.0	14.2	0.55

±SD, $n = 3$, temperature ±: ~0.5; ΔH ±: ~0.06.

was used to minimize any temperature lag due to the large mass of the steel pans. The enthalpy was calculated based on dry starch. DSC measurements were performed in triplicate, and results are presented as mean values.

3. Results and discussion

Since the retrogradation endotherms are relative to the gelatinization endotherms G, M1, M2, and Z, they are assigned as retrogradation endotherms G_r, $M1_r$, $M2_r$, and Z_r, respectively, in the following discussion. Fig. 2 shows the DSC thermograms of a sample heated to just above the temperatures of the four endotherms detected during gelatinization and after rescanning immediately after heating to 81, 105, 125, and 155 °C. It can be seen that the gelatinization endotherms G, M1, and M2 disappeared after heating to 81, 105, and 125 °C, respectively. The treatment at a higher temperature always remove all endotherms below that temperature, which means that all the ordered structures below the thermal treatment have been destroyed. Two endothermic peaks were detected at 115 and 145 °C during rescanning immediately after preheating to 155 °C. The lower temperature endotherm represents the melting of the amylose–lipid complex, which has been widely reported elsewhere (Liu et al., 2006; Russell, 1987; Yu & Christie, 2001), and is labelled $M2_r$. It is important to note that the melting temperature of amylose–lipid complex M2 during the initial scanning was about 114 °C (see Table 1). However, $M2_r$ only appeared after pretreatment at 155 °C, and did not appear after pretreatment at 125 °C. The endotherm at higher temperature after heating to 155 °C is labelled as Z_r, since it is relative to the gelatinization endotherm Z.

Retrogradation was studied through rescanning samples treated at specific temperatures after being stored in a refrigerator at 5 °C for different periods. Measurements were carried out up to 170 °C at the same heating rate (5 °C/min). Fig. 3 shows the DSC thermograms of a sample after initial heating to 81 °C. It can be seen that there was little change in the endotherm of the sample after storage for 2 h. However, a low-temperature endotherm (T_p at about 59 °C), labelled as G_r, developed after 5 h storage and an appreciable enthalpy was observed. It is important to note that the low-temperature endotherm starts at around 59 and ends up around 55 °C. The enthalpy increased rapidly in the early stage (1 d), and then gradually reached a constant value (Fig. 4). Similar temperature ranges for the endotherms during development suggest the same thermal transition occurred.

It was noted that heat treatment at 81 °C also influenced the residual endotherm M1. Both the temperature and enthalpy of M1 decreased after pretreatment at 81 °C

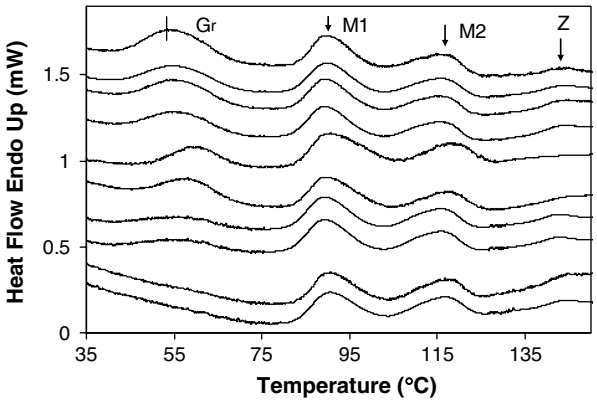

Fig. 3. DSC thermograms of corn starch with 52% water content, heated to final temperature after initial heating to 81 °C and immediate cooling and storage at 5 °C for different periods (from bottom): 0 h, 2 h, 5 h, 10 h, 15 h, 1 d, 3 d, 7 d, 15 d, and 30 d.

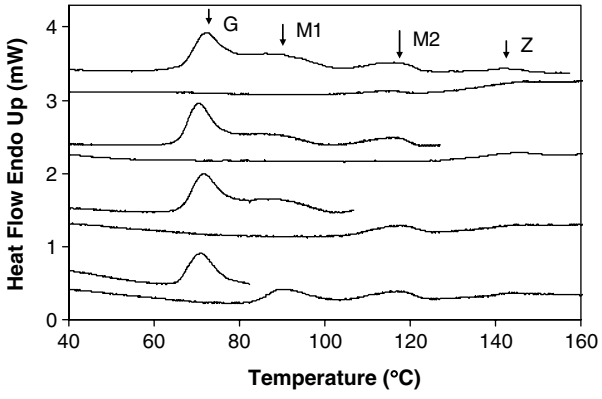

Fig. 2. DSC thermograms of gelatinization and rescanning immediately after initial heating to 81, 105, 125, and 155 °C, respectively.

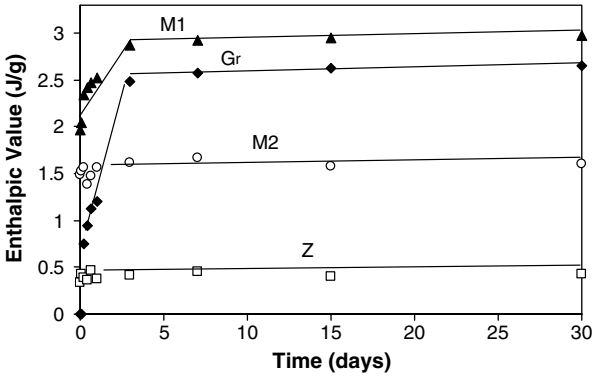

Fig. 4. Retrogradation enthalpy and residual enthalpy after initial heating to 81 °C.

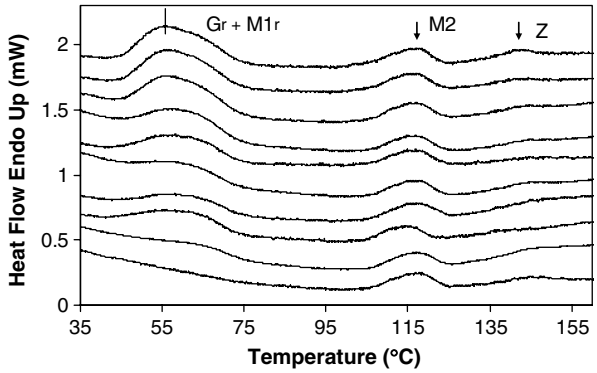

Fig. 5. DSC thermograms of corn starch heated to final temperature after initial heating to 105 °C and immediate cooling and storage at 5 °C for different periods (from bottom): 0 h, 2 h, 5 h, 10 h, 15 h, 1 d, 3 d, 7 d, 15 d, and 30 d.

initially, then the enthalpy increased slightly with time, with a similar trend that of the retrograded endotherm G_r. The final enthalpy of M1 after preheating at 81 °C was lower than that in the first scanning, but no obvious variations were observed in the residual endotherms M2 and Z (see Table 1 and Fig. 4) compared to those of gelatinized starch granules, indicating that the thermal treatment had almost no effect on the endotherms at higher temperatures (>100 °C).

When the starch samples were initially heated to 105 °C, another new endotherm (T_p at about 65 °C), labeled $M1_r$, appeared in the DSC thermogram after 2 h storage (see Fig. 5). Then the main endothermic peak shifted to a lower temperature with increasing time, and overlapped the lower endotherm G_r (after 5 h), which is similar to the one detected for the treatment at 81 °C. This indicates two separate processes, which are related to the two regions of the retrogradation endotherm. The biphasic endotherm gradually became distinct, and the retrograded transition temperature was lower than that for the gelatinization of starch (Tables 1 and 2), indicating that the new order is less stable than the native. Similar thermal transitions have been reported for waxy starches, and are considered to be attributed by amylopectin retrogradation (Eerlingen, Jacobs, & Delcour, 1994; Fisher & Thompson, 1997; White, Abbas, & Johnson, 1989; Yuan, Thompson, & Boyer, 1993). Similar shape, temperature and enthalpy of the residual endotherms M2 and Z for initial heating to 81 and 105 °C indicate that these residual ordered structures are essentially independent from previous heat treatments.

Retrogradation endotherms of amylopectin for samples after preheating to 125 and 155 °C were similar to those initially heated to 105 °C (see Figs. 6 and 7). After storage for 2 h, high-temperature retrogradation endotherms of amylopectin were observed. A bimodal endothermic event became gradually significant with increased storage time. Retrogradation enthalpy increased dramatically within the first 24 h, and then more slowly increased to a limited value after 30 d storage. Retrogradation enthalpies of amylopectin were similar after 15 d storage for all samples initially heated to different temperatures (see Tables 2–4). Since the enthalpy is due to the disassociation of double helices, the endotherm could have been affected by the amount and the molecular characteristics of amylopectin. Although treated at different temperatures, the amount of starch remaining as double helices might be constant, which could explain the near-constant final enthalpic values. However,

Table 2
Characteristics of retrogradation endotherms ($G_r + M1_r$) after initial heating to 105 °C

Storage time	Retrogradation endotherm $G_r + M1_r$				
	T_0 (°C)	T_p (°C)	T_c (°C)	ΔT (°C)	ΔH (J/g)
0 h	–	–	–	–	–
2 h	53.6 ± 0.4	65.8 ± 0.9	73.7 ± 1.1	20.1 ± 1.2	1.11 ± 0.12
5 h	48.9 ± 0.4	63.0 ± 0.6	72.2 ± 0.3	23.2 ± 0.2	2.36 ± 0.09
10 h	48.8 ± 0.8	61.6 ± 0.7	72.9 ± 0.1	24.1 ± 0.9	3.43 ± 0.09
15 h	48.3 ± 0.9	61.3 ± 0.7	72.2 ± 0.4	23.7 ± 0.6	3.61 ± 0.03
1 d	47.3 ± 0.3	57.9 ± 0.4	71.8 ± 0.5	23.9 ± 0.4	4.19 ± 0.10
3 d	48.2 ± 1.1	58.8 ± 0.6	72.6 ± 0.7	24.7 ± 0.5	4.38 ± 0.21
7 d	47.8 ± 0.7	59.1 ± 0.7	72.1 ± 0.9	23.4 ± 0.8	4.85 ± 0.12
15 d	48.2 ± 0.8	58.4 ± 0.6	71.6 ± 0.4	23.3 ± 0.8	5.31 ± 0.11
30 d	48.7 ± 0.5	58.5 ± 0.8	72.4 ± 0.6	23.7 ± 0.6	5.38 ± 0.07

±SD, $n = 3$.

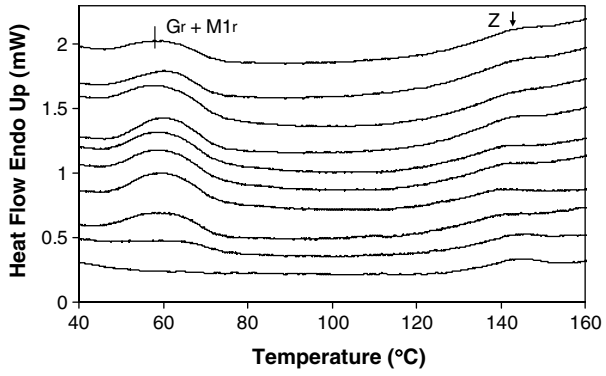

Fig. 6. DSC thermograms of corn starch heated to final temperature after initial heating to 125 °C and immediate cooling and storage at 5 °C for different periods (from bottom): 0 h, 2 h, 5 h, 10 h, 15 h, 1 d, 3 d, 7 d, 15 d, and 30 d.

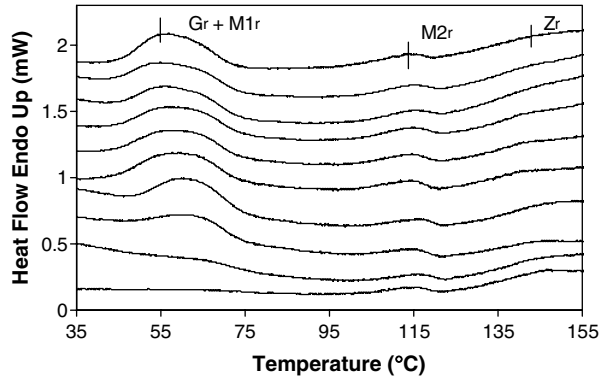

Fig. 7. DSC thermograms of corn starch heated to final temperature after initial heating to 155 °C and immediate cooling and storage at 5 °C for different periods (from bottom): 0 h, 2 h, 5 h, 10 h, 15 h, 1 d, 3 d, 7 d, 15 d, and 30 d.

Table 3
Characteristics of retrogradation endotherms ($G_r + M1_r$) after initial heating to 125 °C

Storage time	Retrogradation endotherm $G_r + M1_r$				
	T_0 (°C)	T_p (°C)	T_c (°C)	ΔT (°C)	ΔH (J/g)
0 h	–	–	–	–	–
2 h	54.5 ± 0.5	65.8 ± 0.2	74.8 ± 1.0	20.5 ± 0.7	1.09 ± 0.07
5 h	48.5 ± 0.5	62.4 ± 0.6	72.6 ± 0.5	24.0 ± 0.2	3.11 ± 0.08
10 h	48.6 ± 0.6	60.4 ± 0.2	72.7 ± 0.6	24.1 ± 1.0	3.45 ± 0.17
15 h	48.8 ± 0.3	59.9 ± 0.7	72.3 ± 0.8	23.5 ± 0.5	3.84 ± 0.11
1 d	48.6 ± 0.9	60.7 ± 0.8	71.9 ± 0.6	23.4 ± 1.2	4.51 ± 0.15
3 d	48.2 ± 0.9	59.7 ± 1.4	71.9 ± 0.8	23.7 ± 0.9	4.97 ± 0.07
7 d	48.5 ± 0.8	58.9 ± 0.9	72.0 ± 0.5	23.8 ± 1.0	5.26 ± 0.14
15 d	48.2 ± 0.8	59.3 ± 0.7	72.0 ± 0.6	23.5 ± 1.0	5.51 ± 0.11
30 d	47.9 ± 0.8	60.1 ± 0.7	71.8 ± 0.8	23.9 ± 0.8	5.56 ± 0.15

±SD, $n = 3$.

the various initial heating temperatures could require different storage times to reach the maximum enthalpies. Fisher and Thompson (1997) considered that higher initial heating temperatures would require longer storage times to reach the maximum enthalpy value. However, in the experimental work reported here, the tendency was not clear (see Fig. 8).

When amylose–lipid complexes are formed, the enclosed lipid molecules contribute to the stability of the amylose helix conformation, preventing the amylose becoming involved in rearrangement (Becker, Hill, & Mitchell, 2001; Gelders, Vanderstukken, Goesaert, & Delcour, 2004). Since the phase transition within an amylose–lipid complex is rapidly reversible, the rescans of the gelatinized corn starch also showed $M2_r$ endotherms in the thermogram of samples initially heated to 155 °C (Figs. 1 and 7). However, it was noted that there was a decrease in the enthalpy for the amylose–lipid complex compared to first heating (see Tables 1 and 4). It is generally believed that the extent of complex formation depends on the amylose content of the starch (Bhatnagar & Hanna, 1994). At temperatures greater than 105 °C, the amylose–lipid complexes inside the starch granules gradually melt. The competitive mechanism between amylose retrogradation and amylose–lipid complex formation could be an explanation for the reduced endotherm $M2_r$ (Gelders et al., 2004), as it decreased the content of dissociative amylose. However, the enthalpic value remained constant, regardless of storage time. The DSC thermograms of samples initially heated to 125 °C show a unique characteristic – the absence of endotherms of amylose–lipid complexes in the second scans. The detailed mechanism of this phenomenon will be explored in the future.

The Z endotherm has been reported previously (Orford et al., 1987; Sievert & Wursch, 1993), but its physical meaning is arguable. Russell (1987) suggested that the Z endotherm might result from annealing of the amylopectin crystallites during heating. Sievert and Holm (1993) considered this endotherm as the melting of nonlipid complex amylose structures. Similarly, Boltz and Thompson (1999) ascribed this transition to melting of amylose crystalline. The Z_r endotherm in this experimental work showed reasonable stability after aging for different periods, which

Table 4
Characteristics of retrogradation endotherms ($G_r + M1_r$, $M2_r$ and Z_r) after initial heating (to 155 °C) with different storage time

Storage time	Endotherm $G_r + M1_r$					Endotherm $M2_r$					Endotherm Z_r				
	T_0 (°C)	T_p (°C)	T_c (°C)	ΔT (°C)	ΔH (J/g)	T_0 (°C)	T_p (°C)	T_c (°C)	ΔT (°C)	ΔH (J/g)	T_0 (°C)	T_p (°C)	T_c (°C)	ΔT (°C)	ΔH (J/g)
0 h	–	–	–	–	–	106.0 ± 0.9	114.9 ± 0.4	121.9 ± 0.6	15.9 ± 0.8	0.56 ± 0.08	135.4 ± 0.5	143.6 ± 0.6	152.6 ± 0.7	19.3 ± 1.0	0.45 ± 0.09
2 h	56.4 ± 0.7	65.4 ± 0.5	74.2 ± 0.3	17.8 ± 0.8	0.96 ± 0.08	106.2 ± 1.4	115.5 ± 0.6	121.3 ± 0.2	16.1 ± 0.9	0.51 ± 0.11	135.2 ± 0.8	144.6 ± 0.9	151.9 ± 0.8	16.2 ± 1.0	0.48 ± 0.093
5 h	48.6 ± 0.8	61.8 ± 0.5	72.4 ± 0.9	23.1 ± 1.0	2.31 ± 0.12	105.1 ± 0.9	115.3 ± 0.6	121.7 ± 0.6	16.5 ± 0.8	0.56 ± 0.03	135.4 ± 1.0	145.3 ± 0.8	152.9 ± 0.9	16.6 ± 0.8	0.52 ± 0.14
10 h	48.9 ± 0.9	61.5 ± 0.7	73.2 ± 0.8	24.2 ± 0.9	3.67 ± 0.09	106.1 ± 0.7	115.0 ± 0.6	121.4 ± 0.5	15.9 ± 1.0	0.52 ± 0.08	135.1 ± 0.5	144.4 ± 1.0	152.1 ± 1.2	16.9 ± 1.1	0.45 ± 0.11
15 h	47.3 ± 0.6	60.1 ± 0.9	73.6 ± 0.8	26.2 ± 0.5	3.98 ± 0.12	105.9 ± 0.6	114.7 ± 0.7	121.9 ± 0.5	16.2 ± 0.3	0.48 ± 0.09	134.4 ± 0.8	144.8 ± 0.4	151.4 ± 0.8	16.3 ± 0.6	0.46 ± 0.08
1 d	46.6 ± 0.9	58.9 ± 0.7	72.7 ± 0.8	26.1 ± 1.2	4.51 ± 0.44	104.7 ± 0.9	115.0 ± 0.9	121.5 ± 0.8	17.1 ± 1.3	0.58 ± 0.07	133.7 ± 0.9	145.0 ± 0.8	151.6 ± 0.7	17.1 ± 0.9	0.54 ± 0.16
3 d	46.4 ± 0.9	58.7 ± 0.8	73.0 ± 0.7	26.6 ± 0.9	5.07 ± 0.11	105.6 ± 0.7	115.4 ± 1.1	122.6 ± 0.2	17.0 ± 0.8	0.61 ± 0.13	134.7 ± 0.6	144.9 ± 0.4	151.3 ± 1.1	16.7 ± 0.6	0.60 ± 0.15
7 d	47.7 ± 1.1	58.4 ± 0.8	73.1 ± 0.7	26.2 ± 1.0	5.27 ± 0.18	105.7 ± 0.8	114.7 ± 0.8	121.5 ± 1.1	16.6 ± 1.0	0.54 ± 0.07	134.8 ± 0.9	143.9 ± 0.8	151.4 ± 1.0	16.9 ± 1.2	0.53 ± 0.11
15 d	47.7 ± 1.2	58.1 ± 0.7	72.9 ± 0.5	25.9 ± 0.8	5.540 ± 0.21	105.1 ± 1.1	115.6 ± 0.7	121.4 ± 0.9	16.5 ± 0.6	0.58 ± 0.09	134.8 ± 0.7	145.0 ± 1.1	151.8 ± 0.8	16.7 ± 1.1	0.6 ± 0.13
30 d	47.8 ± 0.6	58.1 ± 0.6	73.2 ± 0.6	25.4 ± 0.9	5.57 ± 0.12	105.2 ± 0.6	14.5 ± 0.4	121.5 ± 0.5	16.3 ± 0.5	0.56 ± 0.10	134.5 ± 0.3	145.1 ± 0.5	150.6 ± 0.8	16.2 ± 0.7	0.54 ± 0.12

±SD, $n = 3$.

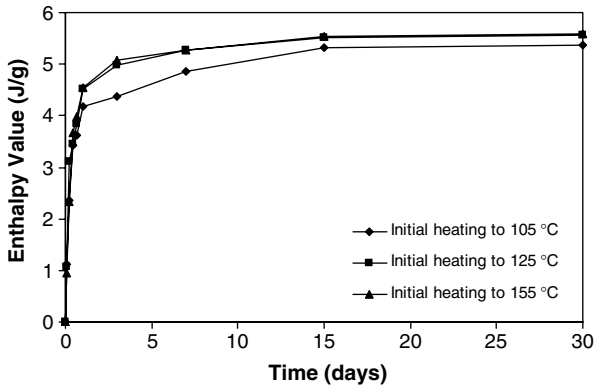

Fig. 8. Retrogradation enthalpy of amylopectin after initial heating to 105, 125, and 155 °C.

supports the theory that the Z endotherm involves amylose melting rather than amylopectin, since retrogradation of highly branched amylopectin is more time dependent. It was also noted that the enthalpy of Z_r was similar to that of Z, but T_p was higher and the temperature range broader, implying that the structures reordered after initial heating. This is consistent with our earlier suggestion. In fact, we have scanned samples at different heating rates and have detected a similar enthalpy for the Z endotherm (unpublished data), which also supports the theory that it is not related to the annealing of amylopectin, otherwise different heating rates should result in differences in the enthalpy.

On the basis of above the results, it can be seen that the time-dependent retrogradation of corn starch is mainly attributed to amylopectin, in particular the gelatinization endotherms G and M1. Cooke and Gidley (1992) presented data from XRD, DSC, and nuclear magnetic resonance measurements, and considered that DSC endothermic enthalpy values primarily reflect loss of double-helical order, rather than loss of crystalline register. Using X-ray data of retrograded waxy corn starch systems, Bulkin et al. (1987) proved that crystals did not begin to develop under 8 h. The initial fast change in amylopectin is not observed by XRD or shear modulus, but by Fourier transform infrared spectroscopy, indicating that a fast conformational change occurs – a coil-to-helix transition in the side chains (Goodfellow & Wilson, 1990). Similarly, Liu and Thompson (1998b) pointed out that the high-temperature peak was due to long-chain double helices that formed rapidly, while the low-temperature region was due to shorter double helices where formation was constrained by the longer helices. Yu and Christie (2005) have proposed a model to explain the effect of orientation on crystallization based on DSC and XRD results. It has been pointed out that the unique microstructures of amylopectin form gel-balls and super-globes after gelatinization. A gel-ball consists mainly of chains from the same sub-main chain, and it remains in a regular pattern and retains a certain "memory". This memory tends to reorganize the disordered chain back to an ordered structure, resulting in retrogradation. All of this could explain the phenomenon that the time-dependent retrogradation of corn starch is mainly attributed to amylopectin.

4. Conclusions

The retrogradation of corn starch with about 52% water content after different initial thermal treatment temperatures just above those of G, M1, M2, and Z endotherms, respectively; was studied by DSC. In particular, the effect of thermal treatment before and after each endotherm on retrogradation was determined as a function of annealing time. The gelatinization endotherms G, M1 and M2 disappeared after heating at 80, 105, and 125 °C, respectively. A higher treatment temperature always removed all the endotherms below that temperature, which indicates that multiphase transition during gelatinization is independent.

A low-temperature endotherm (T_p at about 59 °C), labeled G_r, developed after 5 h storage, and an appreciable enthalpy was observed. The enthalpy increased rapidly in the early stages (up to 1 d), and then gradually increased to a limited value. When the starch samples were initially heated to 105 °C, another new endotherm (T_p at about 65 °C), labeled $M1_r$, appeared in the reheated DSC curve after 2 h storage. Then the main endothermic peak shifted to lower temperatures with increasing time, and overlapped with the lower endotherm G_r (after 5 h). This indicates two separate processes, which are related to the two regions of retrogradation endotherm. The retrograded transition temperature is lower than that for the gelatinization of starch, indicating that the new order is less stable than the native structure.

The time-dependent retrogradation of corn starch is mainly due to the amylopectin endotherms G and M1. Endotherms $M2_r$ and $Z_r$in this experimental work showed reasonable stability after aging for different periods. Both temperature and enthalpy of the $M2_r$ and Z_r were unaffected by aging time. It was also noted the enthalpy of $M2_r$ was smaller than that of M2, indicating that the amount of the new order was less. The enthalpy of Z_r was similar to that of Z, but T_p was higher and the temperature range broader, suggesting that a rearrangement phenomenon occurred.

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References

Abd Karim, A., Norziah, M. H., & Seow, C. C. (2000). Methods for the study of starch retrogradation. *Food Chemistry, 71*(1), 9–36.

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.

Becker, A., Hill, S. E., & Mitchell, J. R. (2001). Relevance of amylose–lipid complexes to the behaviour of thermally processed starches. *Starch – Stärke, 53*(3–4), 121–130.

Bhatnagar, S., & Hanna, M. A. (1994). Amylose–lipid complex formation during single-screw extrusion of various corn starches. *Cereal Chemistry, 71*, 582–587.

Boltz, K. W., & Thompson, D. B. (1999). Initial heating temperature and native lipid affects ordering of amylose during cooling of high-amylose starches. *Cereal Chemistry, 76*(2), 204–212.

Bulkin, B. J., Kwak, Y., & Dea, I. C. M. (1987). Retrogradation kinetics of waxy-corn and potato starches;a rapid, Raman-spectroscopic study. *Carbohydrate Research, 160*, 95–112.

Cooke, D., & Gidley, M. J. (1992). Loss of crystalline and molecular order during starch gelatinization: origin of the enthalpic transition. *Carbohydrate Research, 227*, 103–112.

Del Nobile, M. A., Martoriello, T., Mocci, G., & La Notte, E. (2003). Modeling the starch retrogradation kinetic of durum wheat bread. *Journal of Food Engineering, 59*(2–3), 123–128.

Eerlingen, R. C., Jacobs, H., & Delcour, J. A. (1994). Enzyme-resistant starch: effect of retrogradation of waxy maize starch on enzyme susceptibility. *Cereal Chemistry, 71*, 351–355.

Fisher, D. K., & Thompson, D. B. (1997). Retrogradation of maize starch after thermal treatment within and above the gelatinization temperature range. *Cereal Chemistry, 74*(3), 344–351.

Gelders, G. G., Vanderstukken, T. C., Goesaert, H., & Delcour, J. A. (2004). Amylose–lipid complexation: a new fractionation method. *Carbohydrate Polymers, 56*(4), 447–458.

Goodfellow, B. J., & Wilson, R. H. (1990). A Fourier transform IR study of the gelation of amylose adn amylopectin. *Biopolymers, 30*, 1183–1189.

Gudmundsson, M. (1994). Retrogradation of starch and the role of its components. *Thermochimica Acta, 246*, 329–341.

Gudmundsson, M., & Eliansson, A. –C. (1990). Retrogradation of amylopectin and the effects of amylose and added surfactants/emulsifiers. *Carbohydrate Polymers, 13*, 295–315.

Kalichevsky, M. T., Orford, P. D., & Ring, S. G. (1990). The retrogradation and gelation of amylopectins from various botanical sources. *Carbohydrate Research, 198*, 49–55.

Liu, Q., & Thompson, D. B. (1998a). Effects of moisture content and different gelatinization heating temperatures on retrogradation of waxy-type maize starches. *Carbohydrate Research, 314*(3–4), 221–235.

Liu, Q., & Thompson, D. B. (1998b). Retrogradation of du wx and su2 wx maize starches after different gelatinization heat treatments. *Cereal Chemistry, 75*(6), 868–874.

Liu, H., Yu, L., Xie, F., & Chen, L. (2006). Gelatinization of cornstarch with different amylose/amylopectin content. *Carbohydrate Polymers, 65*(3), 357–363.

Mani, R., & Bhattacharya, M. (2001). Properties of injection moulded blends of starch and modified biodegradable polyesters. *European Polymer Journal, 37*(3), 515–526.

Morikawa, K., & Nishinari, K. (2000). Effects of concentration dependence of retrogradation behaviour of dispersions for native and chemically modified potato starch. *Food Hydrocolloids, 14*(4), 395–401.

Orford, P. D., Ring, S. G., Carroll, V., Miles, M. J., & Morris, V. J. (1987). The effect of concentration and botanical source on the gelatinization and retrogradation of starch. *Journal of the Science of Food and Agriculture, 39*, 169–173.

Perera, C., & Hoover, R. (1999). Influence of hydroxypropylation on retrogradation properties of native, defatted and heat-moisture treated potato starches. *Food Chemistry, 64*(3), 361–375.

Roulet, P., MacInnes, W. M., Gumy, D., & Mursch, P. (1990). Retrogradation kinetics of eight starches. *Starch/Stärke, 42*, 99–101.

Russell, P. (1987). The ageing of gels from starches of different amylose/amylopectin content studied by DSC. *Journal of Cereal Science, 6*, 147–158.

Schoch, T. J. (1945). The fractionation of starch. *Advances in Carbohydrate Chemistry, 1*, 247–277.

Sievert, D., & Holm, J. (1993). Determination of amylose by differential scanning calorimetry. *Starch – Stärke, 45*, 136–139.

Sievert, D., & Wursch, P. (1993). Amylose chain association based on DSC. *Journal of Food Science, 58*, 1332–1335.

Ward, K. E. J., Hoseney, R. C., & Seib, P. A. (1994). Retrogradation of amylopectin from maize and wheat starches. *Cereal Chemistry, 71*, 150–155.

White, P. J., Abbas, I. R., & Johnson, L. A. (1989). Freeze–thaw stability and refrigerated-storage retrogradation of starches. *Starch – Stärke, 41*, 176.

Yoshimura, M., Takaya, T., & Nishinari, K. (1999). Effects of xyloglucan on the gelatinization and retrogradation of corn starch as studied by rheology and differential scanning calorimetry. *Food Hydrocolloids, 13*(2), 101–111.

Yuan, R. C., Thompson, D. B., & Boyer, C. D. (1993). Fine structure of amylopectin in relation to gelatinization and retrogradation behaviour of maize starches from three wx-containing genotypes in two inbred lines. *Cereal Chemistry, 70*, 81–89.

Yu, L., & Christie, G. (2001). Measurement of starch thermal transitions using differential scanning calorimetry. *Carbohydrate Polymers, 46*(2), 179–184.

Yu, L., & Christie, G. (2005). Microstructure and mechanical properties of orientated thermoplastic starches. *Journal of Materials Science, 40*(1), 111–116.