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Glass transition and enthalpy relaxation of cross-linked corn starches

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Abstract

Thermal transition of cross-linked corn starches was characterized by using a differential scanning calorimeter (DSC) in the presence of excess (67%, based on total weight) or limited (15%) water. Normal corn starch (~24% amylose) was cross-linked by reacting with a mixture (99:1) of sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP) in an aqueous alkaline slurry containing sodium sulfate. The amount of the cross-linking agent (STMP/STPP mixture) in the starch slurry (100 g starch, 140 ml water, and 10 g sodium sulfate) was varied (4–12 g), and the level of cross-linking was monitored by the level of incorporated phosphorus, swelling volume, and α-amylase resistance. When analyzed with excess water, the glass transition temperature (T_g', −5.6 and −5.7 °C) of the cross-linked starches was higher than those of native and control starches (−6.6 and −6.5 °C, respectively), and the ice melting enthalpy was also increased by the cross-linking, indicating the increased amount of freezable water. However, in the DSC analysis with limited water, T_g and heat capacity increment (ΔC_p) at T_g decreased by cross-linking. It indicates that the free volume for starch chains was increased by the bulky and ionic phosphate groups. The relaxation enthalpy increased, but the peak temperature of relaxation endotherm decreased as the cross-linking level increased. Retrogradation enthalpy after a week storage at 4 °C was decreased by cross-linking.

Keywords: Cross-linked starch; Glass transition; Enthalpy relaxation

1. Introduction

Cross-linking has been commonly practiced to improve functional properties and paste stability of starch. Recently nutritional benefits of the cross-linked starch as a new source of dietary fiber have also been reported (Woo, 1999; Wurzburg, 1986). For cross-linking, multifunctional reagents are usually used to form intermolecular bridges with hydroxyl groups of starch. The covalently linked network makes cross-linked starch swell less and become more resistant to shear, high temperature and low pH compared to its parent starch (Rutenberg & Solarek, 1984; Wurzburg, 1986).

In the US, the use of cross-linking agents for food starches is regulated by the Code of Federal Regulations, in which monosodium orthophosphate (SOP), sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), and phosphorus oxychloride (CFR, 2001) are allowed. When STMP is used, the phosphorous content in the starch should not exceed 0.04%, but when starch is reacted with a mixture of STMP/STPP, the permitted phosphorus level is ten times higher (0.4%).

Cross-linking alters not only the physical properties but the thermal transition characteristics of starch, and the effect of cross-linking depends on the botanical source of starch and the cross-linking agent. Decrease in retrogradation rate and increase in gelatinization temperature have been observed with cross-linked starches, and these phenomena are related to the reduced mobility of amorphous chains in the starch granule as a result of the intermolecular bridges. However, these studies have focused mainly on the melting behavior of starch crystals, and information on amorphous phase is limited (Morikawa & Nishinari, 2000; Tsai, Li, & Lii, 1997; Yeh & Yeh, 1993; Yook, Pek, & Park, 1993; Zheng, Han, & Bhatty, 1999).

Glass transition and enthalpy relaxation are two major transitions in amorphous polymers. They relate to the changes in quality and physical properties of glassy food products during storage (Blanshard & Lillford, 1993; Hodge, 1994). The glass transition temperature (T_g) is defined as the temperature where the glassy materials are

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softened into a leathery or rubbery state by gaining molecular motions from thermal energy or plasticization (Roos, 1995; Slade & Levine, 1995; Zeleznak & Hoseney, 1987). The enthalpy relaxation is a transition of physically aged amorphous glassy materials which have gradually relaxed toward an equilibrium when stored below its glass transition temperature.

Glass transition of cross-linked starch was recently reported by Chatakanonda, Varaviniti and Chinachoti (2000). They claimed T_g of the starch was not significantly changed by cross-linking or by a cold storage at the moisture content of 67%. However, no study has been reported on the thermal behavior in glassy state of cross-linked starch at limited moisture contents.

In the present study, the effect of cross-linking on thermal transition characteristics, both for crystalline and amorphous phases in starch granule, and the effect of moisture content on the transitions was investigated.

2. Materials and methods

2.1. Starch

Native corn starch was provided by Samyang Genex Company (Seoul, Korea). STMP, STPP and sodium sulfate were purchased from Sigma Chemical Company (St. Louis, MO).

2.2. Preparation of cross-linked starch

Cross-linking was performed according to a modified method of Woo (1999). Corn starch (100 g, dry basis), sodium sulfate (10 g), variable amounts (4, 8, or 12 g) of 99:1 mixture of STMP and STPP were mixed in water (140 ml). The degree of cross-linking increased as the addition of the STMP and STPP mixture increased. The reaction mixture was adjusted to pH 11 by adding 50 ml of 1.0 M NaOH, and then stirred for 3 h at 45 °C. The starch suspension was adjusted to pH 6.5 by adding 1.0 M HCl, and then centrifuged (3000 rpm, 10 min). Extensive washing with distilled water (300 ml × 7) was done to ensure the removal of unreacted inorganic salts. After drying overnight at 40 °C in a convection oven, the cross-linked starch was ground and sieved (100 mesh). Starch similarly treated in the alkali/sodium sulfate solution without STMP nor STPP was used as a control. According to the amounts of STMP/STPP mixture used, the cross-linked corn starch was labeled as CLS4, CLS8, and CLS12, respectively, for 4, 8, and 12% (w/w) of the salt mixture based on starch.

2.3. General methods

Moisture content of the starch samples was determined by the AOAC (1995) method. Phosphorus content was determined by the procedure of Smith and Caruso (1964). The α-amylase resistance of the starch samples (resistant starch content) was determined by the AOAC (1995) method, in which total dietary fiber (991.43) was measured. Swelling volume was determined by the method of Crosbie (1991) with modification. In the method, the sample (5 g) was weighed into a beaker and distilled water (50 ml) was added. The beaker was heated in a boiling water bath with continuous stirring for 30 min. Once cooled, the sample was placed in a measuring cylinder at room temperature overnight. Swelling volume was measured in the measuring cylinder, and calculated by dividing the total volume by the original dry weight of starch sample.

2.4. Thermal analysis

Glass transition temperatures (T_g' and T_g), heat capacity change (ΔC_p) at glass transition temperature, enthalpy relaxation, melting temperature (T_o, T_p, and T_c, respectively, for onset, peak, and conclusion temperatures), and melting enthalpy (ΔH) were determined by using a differential scanning calorimeter (Seiko DSC 6100, Chiba, Japan). Indium and mercury were used for temperature calibration, and sapphire was used for the heat capacity calibration. An empty pan was used as a reference. All measurements were done at least in duplicate. Statistical analysis of the data was performed using Duncan's multiple range tests of an SAS system.

When excess water (67%) was used, ice melting was additionally analyzed. Starch (3.0 ± 0.1 mg) was weighed in an aluminum DSC pan, water added, and then the pan was hermetically sealed. The sealed sample pan was equilibrated at room temperature for 1 h prior to DSC analysis.

The sample pan was heated to 150 °C at a rate of 5 °C/min, rapidly cooled to −40 °C at a rate of 20 °C/min, and then re-heated to 50 °C at a rate of 5 °C/min. In the initial heating up to 150 °C, gelatinization and amylose–lipid complex melting were observed, and during the re-heating, glass transition and ice melting of gelatinized state were analyzed. After the analysis, the pan was stored at 4 °C for 7 days and the recrystallization (retrogradation) and the glass transition temperature (T_g') were measured under the same conditions.

Thermal characteristics of starch with limited water content (15%) were analysed in a thermal cycle different from that with excess water, following the procedure by Lim, Chang, and Chung (2001). The moisture content (15%) of the starch sample was carefully adjusted by equilibrating in a humidity chamber. To improve the resolution and sensitivity, large capacity (70 μl) silver pans were used with large starch sample size (10.0 ± 0.1 mg). Amorphous starch was obtained by heating the DSC sample pan up to 200 °C at a rate of 5 °C/min, followed by immediate cooling to 5 °C at 20 °C/min. The amorphous starch sample was then reheated from 5 to 90 °C at 2 °C/min to measure the glass transition. The sample pan was aged for 5 days at 25 °C for enthalpy relaxation measurement. The aged sample was cooled to

Table 1
Phosphorous content, swelling volume and resistant starch content of native, control and cross-linked corn starches (CLS)

Sample	Phosphorous content (%)	Swelling volume (ml/g)	Resistant starch content (%)
Native	0.019 ± 0.001	Very high	0.36
Control	0.010 ± 0.008	Very high	0.23
CLS4[a]	0.137 ± 0.007	4.23	24.54
CLS8	0.282 ± 0.001	3.44	60.01
CLS12	0.372 ± 0.015	3.26	81.58

[a] Numbers indicate the percent of STMP/STPP mixture (99/1) based on starch weight.

5 °C at 20 °C/min, and then scanned immediately to 90 °C at 2 °C/min (Schmidt & Lammert, 1996). The starch sample used for enthalpy relaxation analysis was rescanned to obtain the DSC thermogram of unaged sample, and the enthalpy of relaxation peak of the aged sample was corrected by subtracting the unaged thermogram.

3. Results and discussion

3.1. Phosphorus content, swelling and enzyme resistance

Reaction of starch with a mixture of STMP/STPP in an alkaline/salt solution resulted in phosphorus incorporation increase with increasing cross-linking (up to 0.37% with CLS12) (Table 1). The decrease in swelling volume and the increase in enzyme resistance indicate that the residual phosphorous formed intermolecular bridges (Janzen, 1969; Woo, 1999; Wurzburg, 1986). The level of incorporated phosphorus was directly proportional ($R^2 = 0.9971$) to the resistant starch content measured by the AOAC method and inversely proportional ($R^2 = -0.9537$) to the swelling volume. Also, the excess cross-linking was confirmed by the absence of the pasting peak in viscographs of the cross-linked starches measured at 10% concentration (data not shown).

3.2. Glass transition in excess water

The glass transition temperature (T_g') of native, control and cross-linked starches in maximally freeze-concentrated solute matrices was in a range between −5 and −7 °C (Table 2). These values were measured with the gelatinized starch samples. Chatakanonda et al. (2000) reported that no significant change in the T_g' of a gelatinized rice starch resulted from cross-linking. In our experiments, the T_g' of corn starch was increased by nearly 1 °C by cross-linking (Table 2).

The T_g' increase on cross-linking has been already reported for synthetic polymers (ten Brinke, Karasz, & Ellis, 1983; Jin, Ellis, & Karasz, 1984). Cross-linking reduces the number of chains thermally activated and the chain mobility, and thus raises the glass transition temperature and diminishes the change in specific heat capacity (ΔC_p). Corn starch, in excess water, displayed the change in glass transition by cross-linking similar to those of synthetic polymers, due to the restricted chain mobility in the freeze-concentrated matrix (Table 2). The T_g' measurement was difficult because ΔC_p at T_g' was decreased by cross-linking (thermograms not shown).

Ice melting was also affected by cross-linking (Table 2). The ice melting enthalpy in the starch paste was increased by cross-linking by upto 18 J/g compared to that of the control. Generally, the ice melting enthalpy reflects the amount of freezable water. As less water is incorporated in a three-dimensional gel matrix, more water becomes freezable. Cross-linking restricted the swelling of the starch granules, and thus, gel formation through interaction between starch chains and water was hindered. Therefore, more water remained freezable, resulting in an increase in

Table 2
Glass transition in the freeze-concentrated phase and ice melting characteristics of native, control and cross-linked corn starches at excess water content (67%)

Samples	Storage time (days)	T_g' (°C)[a]	Ice melting endotherm			
			T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Native	0	−6.6 ± 0.1[b]	−2.3 ± 0.2	0.5 ± 0.4	5.3 ± 0.1	278.3 ± 13.0
	7	−6.2 ± 0.1	−2.5 ± 0.2	0.0 ± 0.2	4.8 ± 0.3	268.7 ± 7.5
Control	0	−6.5 ± 0.3[b]	−2.1 ± 0.2	0.8 ± 0.5	5.6 ± 0.7	282.4 ± 11.9
	7	−5.8 ± 0.1	−2.3 ± 0.4	0.4 ± 0.7	5.2 ± 0.7	271.6 ± 6.8
CLS4	0	−5.7 ± 0.1[a]	−2.4 ± 0.4	0.4 ± 0.3	5.4 ± 0.3	290.6 ± 10.4
	7	−5.2 ± 0.2	−2.3 ± 0.1	0.6 ± 0.1	5.4 ± 0.2	282.0 ± 12.3
CLS8	0	−5.6 ± 0.1[a]	−2.1 ± 0.1	0.8 ± 0.0	5.8 ± 0.3	300.9 ± 6.5
	7	−5.4 ± 0.1	−2.3 ± 0.1	0.6 ± 0.3	5.5 ± 0.1	292.2 ± 0.2
CLS12	0	−5.6 ± 0.1[a]	−2.4 ± 0.1	0.2 ± 0.3	5.2 ± 0.3	296.9 ± 4.6
	7	−5.2 ± 0.0	−2.2 ± 0.0	0.4 ± 0.2	5.1 ± 0.1	284.9 ± 2.1

[a] Values followed by the same letter in the same column are not significantly different ($p < 0.05$).

Table 3
Glass transition and enthalpy relaxation of native, control and cross-linked starches at limited water content (15%)

Sample	Glass transition^{a,b}				Enthalpy relaxation^{a,b}			
	T_1 (°C)	T_g (°C)	T_2 (°C)	ΔC_p (J/deg·g)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Native	50.4 ± 4.9	57.4 ± 4.7^d	65.0 ± 4.7	0.291 ± 0.031	39.2 ± 0.4	44.1 ± 0.7^{a,c}	49.2 ± 0.6	1.479 ± 0.002^{ac}
Control	58.9 ± 2.4	65.5 ± 1.0	72.6 ± 0.6	0.274 ± 0.022	41.1 ± 0.6	45.8 ± 1.0	53.6 ± 0.0	1.135 ± 0.109^d
CLS4	56.8 ± 1.6	63.2 ± 0.3^a	69.5 ± 1.3	0.239 ± 0.020^a	39.8 ± 0.6	45.3 ± 1.0^a	51.4 ± 0.6	1.227 ± 0.101^{cd}
CLS8	53.5 ± 0.6	60.7 ± 0.1^c	69.1 ± 1.2	0.217 ± 0.020^a	40.0 ± 0.2	44.4 ± 1.0^a	50.6 ± 0.3	1.538 ± 0.186^a
CLS12	48.6 ± 1.3	56.5 ± 0.4^d	63.7 ± 0.2	0.193 ± 0.005^c	36.5 ± 0.3	42.5 ± 0.5^c	48.7 ± 0.7	1.789 ± 0.183

[a] Glass transition was determined in unaged state, whereas enthalpy relaxation was determined for sample aged for 5 days at 25 °C.
[b] Values followed by the same letter in the same column are not significantly different ($p < 0.05$).

the ice melting enthalpy. However, the cross-linking did not significantly change the ice melting temperature (Table 2).

Following a week storage at 4 °C, the T_g' of hydrated gelatinized starch increased but the ice melting enthalpy decreased for all the tested samples (Table 2). These changes resulted from starch recrystallization that reduced freezable water, as previously reported (Chung, Lee, & Lim, 2002; Huang, Chang, Chang, & Lii, 1994).

3.3. Glass transition in limited water

When water is limited, glass transition of starch is usually measured after the starch has been transformed to an amorphous state because T_g of native granular starch containing crystals is difficult to measure due to the low heat capacity change at T_g (Chung et al., 2002; Zeleznak & Hoseney, 1987). The glass transition of native cross-linked starch also did not give a clear change in heat capacity in this experiment (data not shown).

The glass transition temperatures (T_g) of the amorphous native and control starches are 57.4 and 65.5 °C, respectively, at 15% moisture content, and T_g of the amorphous cross-linked starches were in the range of 56.5–63.2 °C depending on the cross-linking level (Table 3). The cross-linked starches displayed decreases in T_g, proportional to the amount of cross-linking agent used. DSC thermograms of native, control and CLS12 are shown in Fig. 1.

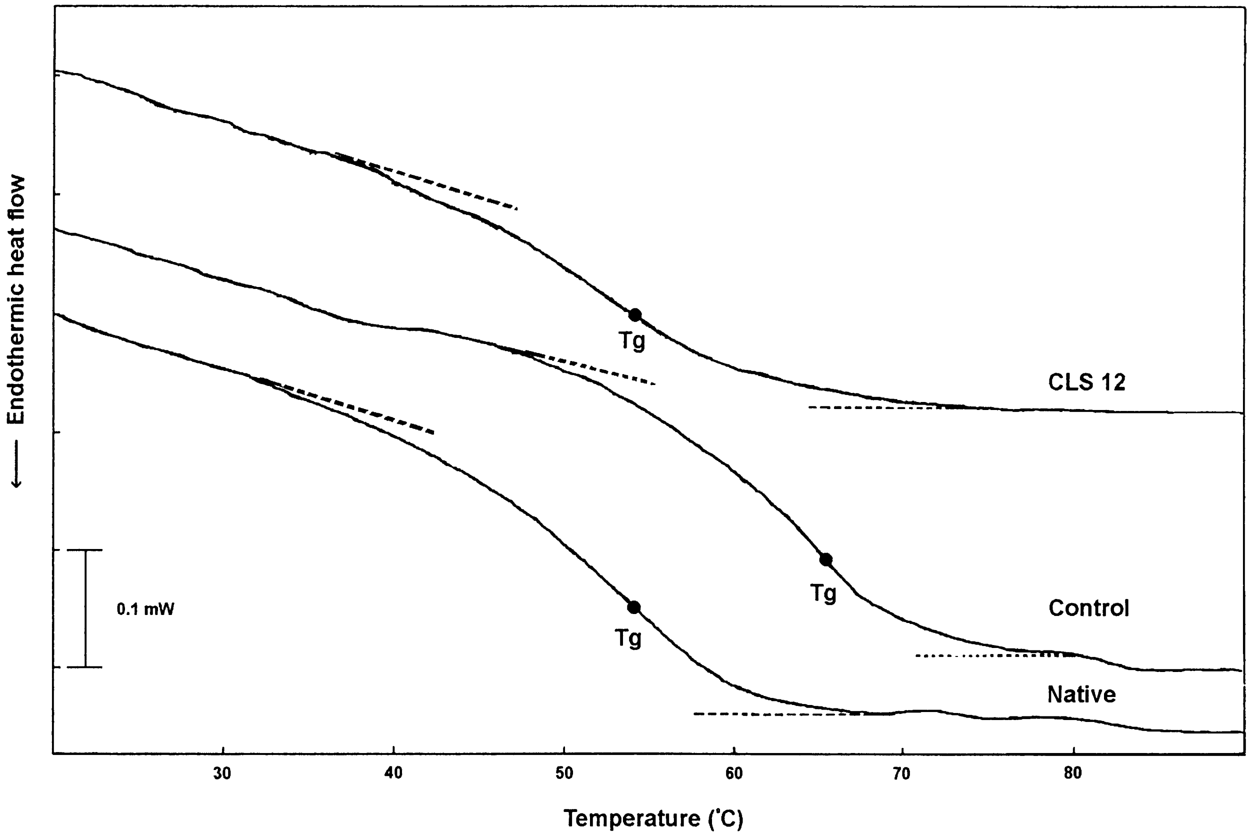

Fig. 1. Glass transition on DSC thermograms of native, control and cross-linked corn starches with limited water (15%).

Alkaline treatment alone (control) resulted in a substantial increase (~8 °C) in T_g. The T_g increase indicates that structural changes in the amorphous phase in starch granules were induced by the alkaline solution. In the alkaline solution, removal of the inherent phosphorous was apparent (~54%, Table 1). Matsunaga and Seib (1997) reported a decrease of the phosphorous content of the starch granule by up to 90% after treatment with alkali/salt. It was because the residual lysophospholipids in the starch granule were washed out. The bulky and charged lysophospholipid might contribute free volume to the adjacent starch chains, and its removal could result in a free volume decrease, causing the T_g increase.

Normally, an increase in cross-linking density reduces the chain mobility and consequently increases the T_g. This effect can be understood in terms of decreasing free volume (Montserrat, 1995). Jin et al. (1984) observed this effect in cross-linked nylon 6 by radiation. Cook, Mehrabi and Edward (1999) and Montserrat (1994) found that the T_g increased with increasing cross-linking density of epoxy resins because of the restriction in molecular mobility imposed by cross-linking. However, the cross-linked starches prepared in this experiment displayed the opposite trend, showing a lower T_g with increasing degree of cross-linking (Table 3). When the starch reacted with mixture of STMP and STPP (99:1), ionic phosphate groups were produced mainly in distarch phosphate. Although these groups cross-linked starch chains, the ionic nature of the bulky phosphate group also provided water affinity and repulsive force for internal plasticization (Armeniaderis & Baer, 1997). Additionally, the cross-linking reagents could produce monoesterified phosphate substituents. Internal plasticization by bulky and ionic monosubstituted phosphate groups contributed to a free volume increase for starch chains, reducing the glass transition temperature.

The heat capacity change (ΔC_p) at T_g was decreased by cross-linking (Table 3), as also reported for synthetic polymers (ten Brinke et al., 1983; Jin et al., 1984). The reduced ΔC_p in this experiment resulted from the reduction in the number of the starch chain units that were thermally activated (ten Brinke et al., 1983).

From the overall glass transition results, it was concluded that the T_g at limited moisture (15% in this experiment) was decreased as the level of cross-linking increased, whereas the T_g' of the freeze-concentrated phase for the excess water (67%) sample was raised. Lim et al. (2001) reported that T_g' in excess water was dependent on the ice forming mechanism, whereas the glass transition temperature (T_g) with limited moisture relied on plastization by residual water. When the starch–water mixture was gelatinized at high moistures (67%), the unfreezable water content in the freeze-concentrated phase was different between the control and cross-linked starches. As already referred in Table 2, the cross-linked starches displayed a higher T_g' values than the control starch. However, at limited moisture content, all the water is used to plasticize the control and cross-linked starches. Therefore, the difference in the behavior of water caused the discrepancy in the effect of crosslinking on the glass transition temperatures (T_g or T_g') between the two different water systems.

3.4. Enthalpy relaxation

When an amorphous starch is cooled below its glass transition temperature (T_g), it usually exists as a non-equilibrium glassy state. When stored in the glassy state, the system gradually changes to a metastable and equilibrium state with the changes in thermodynamic and mechanical properties (Hutchinson, 1995; Struik, 1978). This process is defined as physical aging, which is theoretically reversible by thermal cycling (Struik, 1978). Physical aging is also traditionally referred to as structural relaxation or enthalpy relaxation (Hodge, 1994). Enthalpy relaxation is accompanied by a variety of physical changes, such increases in density and elastic modulus, which determine polymer quality (Hodge, 1995). These property changes may also affect the performance and utilization of the aged polymer.

The enthalpy relaxation peak of the cross-linked starches aged for 5 days at 25 °C appeared in a range of 35–55 °C (Table 3 and Fig. 2). The peak temperatures (T_p) for enthalpy relaxation were 44.1 and 45.8 °C, for native and control starches, respectively. Alkaline treatment caused the peak temperature to rise by about 2 °C, but the enthalpy for the relaxation to decrease by about 0.34 J/g. However, cross-linking slightly decreased the enthalpy relaxation temperatures, whereas the enthalpy value was increased proportionally to the degree of cross-linking. These changes imply that the glassy state in the alkali-treated starch (control) relaxed to a lesser extent than the corresponding native starch. And, with limited water, the cross-linked starches relaxed to a greater extent to the metastable and equilibrium state than the corresponding control starch, due to higher mobility. However, Cook et al. (1999) reported that for epoxy resin cross-linking reduced the relaxation enthalpy due to restriction of the molecular re-adjustment required for densification and aging. The trend in relaxation enthalpy change by cross-linking was similar to the T_g change. The relaxation of the cross-linked starches might be related to the glass transition. The cross-linked structure of the bulky phosphate groups allowed chain segments to move more easily due to free volume as discussed with the T_g result, and the relaxation enthalpy was thus higher than for the control starch.

The difference in relaxation enthalpy among the starch–water mixtures could also be explained as the difference between the glass transition temperature (T_g) and aging temperature (T_a). Montserrat (1994) claimed that the enthalpy for relaxation increased as $T_g - T_a$ decreased. Chung et al. (2002) found the enthalpy increase was positively related to moisture content and claimed that the increased relaxation rate of the glassy state was due to

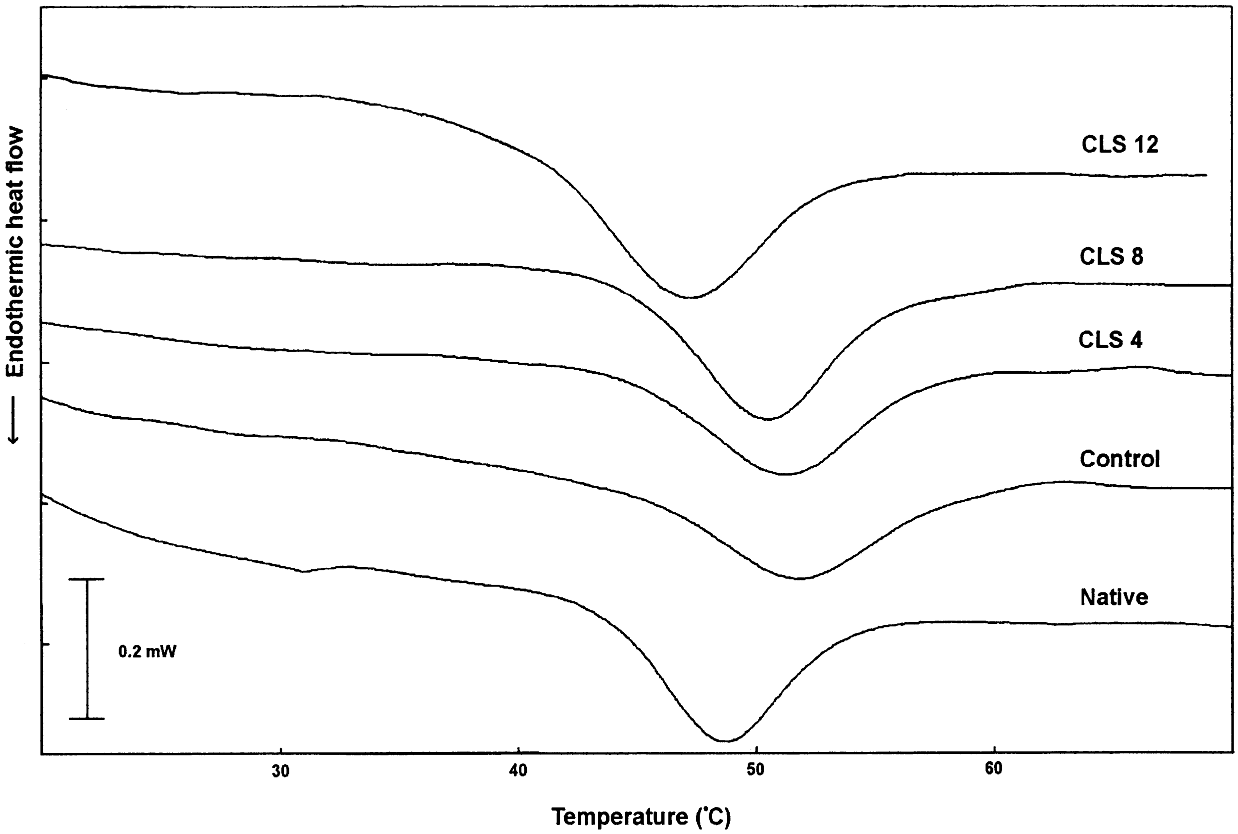

Fig. 2. Enthalpy relaxation on DSC thermograms of native, control and cross-linked corn starches with limited water (15%).

the water-induced free volume increase and thus a decreased $T_g - T_a$. In this study, the T_g of the control starch and cross-linked starch (CLS12) were 65.5 and 56.5 °C, and thus $T_g - T_a$ is 40.5 and 31.5 °C, respectively. Therefore, the lower $T_g - T_a$ for the cross-linked starch resulted in the higher enthalpy for relaxation, in comparison to the control starch.

3.5. Melting and retrogradation of starch

The cross-linked starches showed higher and narrower temperature range for melting than native or control corn starch (Table 4). The onset temperature (T_o) for melting proportionally increased with the degree of cross-linking, but the melting enthalpy of the cross-linked starches was similar to that of the control. However, the melting enthalpy was not significantly changed, although both control and cross-linked starches showed lower ΔH than that of native starch. Woo (1999) reported that cross-linked starch showed higher transition temperatures and lower transition enthalpies than their parent starch, and claimed the increase in gelatinization temperature was caused by the inhibition of cooperative melting of the crystal in the starch granule. Chatakanonda et al. (2000) also reported such increased gelatinization temperature, narrowed the endotherm and decreased the melting enthalpy for cross-linked rice starches.

It was noteworthy that the amylose-lipids complex peak was only apparent in the thermograms of native and control

Table 4
Melting characterization of native and recrystallized states of native, control and cross-linked starches with excess moisture

Sample[a]	Native[b]				Recrystallized[b,c]			
	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Native	63.7 ± 0.3	68.4 ± 0.5^d	75.0 ± 0.8	14.37 ± 1.33^b	36.2 ± 0.4	48.2 ± 0.5^a	61.2 ± 0.4	7.772 ± 0.213^b
Control	63.8 ± 0.5	68.2 ± 0.3^d	74.5 ± 0.3	13.55 ± 0.21^b	36.0 ± 2.0	48.6 ± 0.5^a	61.2 ± 1.2	7.498 ± 1.960^b
CLS4	67.1 ± 0.5	71.0 ± 0.3^c	76.6 ± 0.3	13.63 ± 0.32^b	40.9 ± 0.3	50.1 ± 1.3^a	61.0 ± 1.2	3.125 ± 0.477^a
CLS8	69.0 ± 0.3	73.0 ± 0.0^a	78.6 ± 0.1	13.33 ± 0.27^b	41.3 ± 0.0	51.8 ± 0.1	61.5 ± 2.1	3.090 ± 0.435^a
CLS12	71.1 ± 0.1	74.9 ± 0.0^b	80.0 ± 0.1	13.86 ± 0.60^b	43.7 ± 1.4	53.1 ± 1.6^b	61.9 ± 2.2	2.350 ± 0.080^c

[a] Starch: water ratio was 1:2 (w/w).
[b] Values followed by the same letter in the same column are not significantly different ($p < 0.05$).
[c] Recrystallization was carried out by storing the gelatinized starch sample at 4 °C for 7 days.

starches but not in all the cross-linked starches (data not shown). This result agreed with the observations by Chatakanonda et al. (2000) and Yook et al. (1993). They explained that the cross-linking agent (STMP) or alkali might interfere with the amylose–lipids complex formation, and the more swollen starch granules resulting from alkali treatment allowed the lipids to leach out of the granules. However, in our experiments, the alkali treatment without cross-linking (control) did not affect the amylose–lipids complex formation. Thus, the complex formation was inhibited only by cross-linking.

The melting enthalpy of recrystallized starch was decreased by cross-linking but the melting temperatures (T_o and T_p) for the starch were increased proportionally with the degree of cross-linking, although the conclusion temperature (T_c) for melting did not change. The recrystallization enthalpy decrease by cross-linking has been already reported by several authors (Chatakanonda et al., 2000; Morikawa & Nishinari, 2000). Chatakanonda et al. (2000) claimed that the phosphate groups could induce repulsive force throughout the negative charges, thus retarding the re-association of starch chains in granules. The retrogradation enthalpy decrease could also be explained by the limited mobility of starch chains, which restricted the associations of the amylopectin chains.

4. Conclusions

In excess water condition, increases in ice melting enthalpy and T_g' was observed with the increase of cross-linking in corn starch. Restricted swelling and limited gel network formation by cross-linking was related to the increase in the freezable water in freeze-concentrated starch water mixtures. However, in limited water conditions, adverse effect of cross-linking on T_g of starch were observed. This effect was explained by the free volume increase due to the repulsive forces between phoshate groups in the starch chains. Cross-linked corn starch showed a greater extent of relaxation than the control starch and was also characterized by decreased retrogradation enthalpy and the absence of an amylose-lipids complex peak.

References

Association of Official Analytical Chemists (1995). *Approved methods of the AOAC* (16th ed.). Virginia: AOAC.

Armeniaderis, C. G., & Baer, E. (1997). Transitions and relaxations in polymers. In H. S. Kaufman (Ed.), *Introduction to polymer science and technology*. New York: Wiley.

Blanshard, J. M. V., & Lillford, P. J. (1993). *The glassy state in Foods*. Leicestershire: Nottingham University Press.

ten Brinke, G., Karasz, F., & Ellis, T. S. (1983). Depression of glass transition temperatures of polymer networks by diluents. *Macromolecules*, *16*, 244–249.

CFR (Code of Federal Regulation) (2001). *Food starch modified. In: Food Additives Permitted in Food for Human Consumption, 21/1/172/172.892*, Washington, USA: Government Printing Office.

Chatakanonda, P., Varavinit, S., & Chinachoti, P. (2000). Relationship of gelatinization and recrystallization of cross-linked rice to glass transition temperature. *Cereal Chemistry*, *77*, 315–319.

Chung, H.-J., Lee, E.-J., & Lim, S.-T. (2002). Comparison in glass transition and enthalpy relaxation between native and gelatinized starches. *Carbohydrate Polymers*, *48*, 287–298.

Crosbie, G. B. (1991). The relationship between starch swelling properties, paste viscosity and boiled noodle quality in wheat flours. *Journal of Cereal Science*, *13*, 145–150.

Cook, W. D., Mehrabi, M., & Edward, G. H. (1999). Ageing and yielding in model epoxy thermosets. *Polymer*, *40*, 1209–1218.

Hodge, I. M. (1994). Enthalpy relaxation and recovery in amorphous materials. *Journal of Non-Crystalline Solids*, *169*, 211–266.

Hodge, I. M. (1995). Physical aging polymer glasses. *Science*, *267*, 1945–1947.

Huang, R.-M., Chang, W.-H., Chang, Y.-H., & Lii, C.-Y. (1994). Phase transitions of rice starch and flour gels. *Cereal Chemistry*, *71*, 202–207.

Hutchinson, J. M. (1995). Physical aging of polymers. *Progress in Polymer Science*, *20*, 703–760.

Janzen, G. J. (1969). Digestibility of starches and phosphatized starches by means of pancreatin. *Starch*, *38*, 231–237.

Jin, X., Ellis, T. S., & Karasz, F. E. (1984). The effect of crystallinity and crosslinking on the depression of the glass transition temperature in nylon 6 by water. *Journal of Polymer Science: Polymer Physics Edition*, *22*, 1701–1717.

Lim, S.-T., Chang, E.-H., & Chung, H.-J. (2001). Thermal transition characteristics of heat-moisture treated corn and potato starches. *Carbohydrate Polymers*, *46*, 107–115.

Montserrat, S. (1994). Physical aging studies in epoxy resins. I. Kinetics of the enthalpy relaxation process in a fully cured epoxy resin. *Journal of Polymer Science: Part B: Polymer Physics*, *32*, 509–522.

Montserrat, S. (1995). Effect of crosslinking density on $\Delta C_p(T_g)$ in an epoxy network. *Polymer*, *36*, 435–436.

Morikawa, K., & Nishinari, K. (2000). Rheological and DSC studies of gelatinization of chemically modified starch heated at various temperatures. *Carbohydrate Polymers*, *43*, 241–247.

Matsunaga, N., & Seib, P. (1997). Extraction of wheat starch with aqueous sodium hydroxide. *Cereal Chemistry*, *74*, 851–857.

Rutenberg, M. W., & Solarek, D. (1984). Starch derivatives: production and uses. In R. L. Whistler, J. N. BeMiller, & E. R. Paschall (Eds.), *Starch: chemistry and technology* (pp. 312–366). New York: Academic press.

Roos, Y. H. (1995). *Phase transition in foods*. San Diego: Academic Press.

Schmidt, S. J., & Lammert, A. M. (1996). Physical aging of maltose glasses. *Journal of Food Science*, *61*, 870–875.

Slade, L., & Levine, H. (1995). Glass transition and water-food structure interactions. *Advances in Food and Nutrition Research*, *38*, 103–269.

Smith, R. J., & Caruso, J. (1964). Determination of phosphorous. *Methods in Carbohydrate Chemistry*, *4*, 42–46.

Struik, L. C. E. (1978). *Physical aging in amorphous polymers and other materials*. New York: Elsevier.

Tsai, M. L., Li, C. F., & Lii, C. Y. (1997). Effects of granular structures on the pasting behaviors of starches. *Cereal Chemistry*, *74*, 750–757.

Woo, K.S., (1999). *Cross-linked, RS4 type resistant starch: preparation and properties*. PhD Thesis. Kansas State: University Manhattan, KS.

Wurzburg, O. B. (1986). Cross-linked starches. In O. B. Wurzburg (Ed.), *Modified starches: properties and uses* (pp. 41–53). Florida, USA: CRC press.

Yeh, A. I., & Yeh, S. L. (1993). Some characteristics of hydroxypropylated and cross-linked rice starch. *Cereal Chemistry*, *70*, 596–601.

Yook, C., Pek, U. H., & Park, K. H. (1993). Gelatinization and retrogradation characteristics of hydroxypropylated and cross-linked rices. *Journal of Food Science*, *58*, 405–407.

Zeleznak, K. J., & Hoseney, R. C. (1987). The glass transition in starch. *Cereal Chemistry*, *64*, 121–124.

Zheng, G. H., Han, H. L., & Bhatty, R. S. (1999). Functional properties of cross-linked and hydroxypropylated waxy hull-less barley starches. *Cereal Chemistry*, *76*, 182–188.