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Carbohydrate Polymers 46 (2001) 107–115

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Thermal transition characteristics of heat–moisture treated corn and potato starches

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Received 25 April 2000; revised 13 July 2000; accepted 18 August 2000

Abstract

Normal corn starch containing 25 or 30% moisture and potato starch containing 20 or 25% moisture were heat–moisture treated at 120°C for 1 h and the changes in thermal transition properties of the starches were examined using a differential scanning calorimeter (DSC). Granular crystallinity monitored by the X-ray diffractogram was reduced by the heat–moisture treatment (HMT), especially for potato starch. The $T_g{}'$ of starch measured in frozen state in excess water (starch:water = 1:4) increased by 1–4°C due to the HMT. Under limited moisture conditions (15% based on total weight), however, T_g measured in granular form of starch decreased by 2–6°C. Potato starch had a T_g about 25°C higher than corn starch, regardless of the HMT. At T_g, the change in heat capacity (ΔC_p) of the treated starch was substantially higher than the corresponding native starch. Enthalpy and onset temperature of the relaxation endotherm of the glassy starch was also increased by the HMT. Crystal melting of the heat–moisture treated starches, measured at 80% moisture, appeared to be biphasic on a DSC thermogram, in which the original endotherm became smaller while a new endotherm at higher temperature was observed. However, the total melting enthalpy for starch decreased, indicating a partial loss of crystallinity. The enthalpy associated with melting of the amylose–lipid complex in corn starch was increased by HMT. The degree of retrogradation under DSC was not significantly different between the native and treated starches.

Keywords: Thermal transition; Heat–moisture treatment; Corn and potato starches

1. Introduction

The molecular arrangement in a starch granule can be altered by various physical treatments. Annealing and heat–moisture treatment (HMT) are two common physical means by which the treated starch can acquire modified properties without rupturing the granule. Annealing is generally carried out by heating granular starch with a large quantity of water at a temperature below the starch melting point, whereas HMT is carried out at limited moisture contents but at an elevated temperature (Eliasson & Gudmundsson, 1996). For HMT, pressure is often required to assure sufficient heating, but uniform heat distribution and penetration into the starch is not easy to accomplish. These physical treatments can change certain starch properties using simple and environmentally safe processes.

The physical properties of a heat–moisture treated starch depend on the starch origin and treatment conditions used. Heat–moisture treated starch display an increased paste stability and gelatinization temperature, regardless of origin (Abraham, 1993; Collado & Corke, 1999; Donovan, Lorenz & Kulp, 1983; Hoover & Vasanthan, 1994; Kulp & Lorenz, 1981; Lorenz & Kulp, 1982, 1983; Stute, 1992). Collado and Corke (1999) treated a sweet potato starch, and found that the starch paste became short and shear-stable and the starch gel exhibited marked increases in hardness and adhesiveness.

X-ray diffraction patterns of tuber starches with an initial B-pattern show a transition towards an A-pattern after HMT, whereas cereal starches retain the inherent A-crystal pattern (Kawabata, Takase, Miyoshi, Sawayama, Kimura & Kudo, 1994; Lorenz & Kulp, 1982). Donovan et al. (1983) reported that HMT made the starch melting endotherm on a DSC thermogram biphasic, and claimed that there was new crystal formation or crystalline rearrangement in the treated starch granules.

Hoover and Manuel (1996a,b), Hoover, Swamidas and Vasanthan (1993) and Hoover and Vasanthan (1994) tested various starches of different origins, and claimed that HMT induced changes not only in crystalline regions but also in amorphous regions in starch granules. They found that the amylose content and starch chain length were two significant factors determining the physical properties of the final

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0144-8617/01/$ - see front matter
PII: S0144-8617(00)00287-3

products. It was also reported that amylose–lipid complex formation in cereal starches occurred during the treatment. Kurahashi and Hizukuri (1998) claimed that a small amount of monoglyceride increased the effect of HMT by producing a helical amylose–lipid complex. In addition, the complex formation increased thermal stability in the starch.

Franco, Ciacco and Tavares (1995) found that the enzyme susceptibility of corn starch was increased by HMT at a moisture content higher than 18%, but decreased when heated below 18%. They claimed that the increased enzyme resistance was due to intermolecular interactions between the starch chains.

Although a number of studies have been reported on heat–moisture treated starches, the structural transformation inside the starch granule is still not fully understood. In this study, the HMT effect on the thermal transition characteristics of crystalline and amorphous regions in starch granules was investigated with corn and potato starches, and the granular structural transformation by HMT was described.

2. Materials and methods

2.1. Starches

Normal corn starch and potato starch were provided by Samyang Genex (Seoul, Korea) and Handuk Avebe (Seoul, Korea), respectively.

2.2. Heat–moisture treatment

Water was sprayed onto powdery starch to adjust its moisture content to 20–30%. Corn starch was adjusted to 25 or 30% moisture, whereas potato starch was adjusted to 20 or 25% because potato starch was more susceptible to heat and moisture than corn starch. The starch/water mixtures were extensively mixed with a blender, and then the exact moisture content of the mixtures was measured with an infrared auto-moisture analyzer (Ohaus MB200, Florham Pk, NJ). The moisture-adjusted starch (200 g) was transferred to a pressure-resistant glass bottle (300 ml) and then autoclaved at 120°C for 1 h. After the HMT, the bottle was cooled to room temperature and the starch was dried to approximately 10% moisture content in a convection oven (40°C) overnight.

2.3. X-ray diffraction

The X-ray diffraction pattern of the native and heat–moisture treated starches was measured with a diffractometer (Rigaku Geigerflex G/max II-A, Tokyo, Japan) at 35 kV and 15 mA with Cu–K radiation and Ni filter. The scanning speed and diffraction range of 2θ were 1°/min and 5–50°, respectively.

2.4. Thermal transition analysis

Glass transition temperatures (T_g' and T_g), heat capacity change (ΔC_p), glassy 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).

For the measurement of T_g' and melting characteristics, excess water was added to starch (4:1 weight ratio) in a large capacity (70 μl) silver pan. The sealed sample pan placed in a DSC was quickly chilled with liquid nitrogen to −20°C at a rate of 20°C/min and then heated to 150°C at a rate of 2°C/min. After the melting analysis, the pan was stored at 4°C for 14 days, and then the recrystallization (retrogradation) was measured under the same conditions as the melting analysis.

For the measurement of T_g and glassy enthalpy relaxation (sub-T_g endotherm), starch loaded in an open silver pan was equilibrated in a moisture chamber (>95% RH) until the moisture content reached 15%. The DSC measurement was carried out with sealed pan from 25 to 85°C at a heating rate of 2°C/min. In the first thermogram, the glassy enthalpy relaxation endotherm as well as the glass transition was apparent, but starch melting (gelatinization) did not occur. Right after the initial heating, the same sample was chilled to room temperature and reheated to observe the glass transition only. An accurate measurement of the relaxation endotherm was accomplished by subtracting the reheated thermogram (glass transition) from the initial thermogram. In this way, the amorphous transitions (glassy enthalpy relaxation and glass transition) could be measured in the native state of the starch granule where the crystalline structure remained intact.

The measurements were repeated three times for determination of T_g', T_g and T_m.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of the native and heat–moisture treated corn and potato starches are given in Fig. 1. The treated corn starches (Corn-25-120 and Corn-30-120) retained the typical A-type diffraction pattern of the original starch. At 30% moisture content for the treatment, however, a slight decrease in peak intensity on the diffractogram was found, whereas at 25% no significant change in peak intensity appeared. The heat–moisture treated potato starches (Potato-20-120 and Potato-25-120) also showed decreased peak intensity. It has been reported that excess heat or moisture for HMT results in reduced crystallinity (Takaya, Sano & Nishinari, 2000). Several researchers found that root starches had a transition tendency toward the A-pattern on X-ray diffractogram

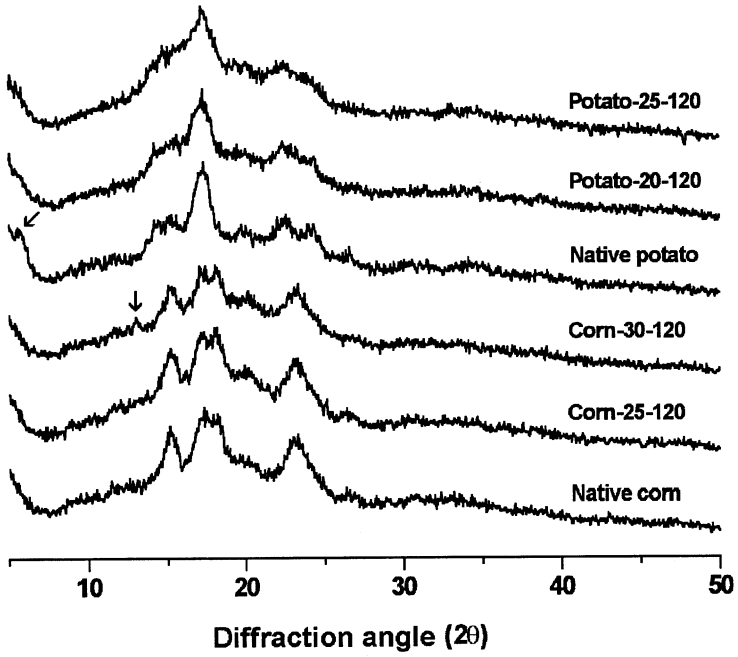

Fig. 1. X-ray diffractograms of native and heat–moisture treated corn and potato starches. The numbers indicate the moisture content (20–30%) and temperature (120°C) for the treatment.

(Kawabata et al., 1994; Lorenz & Kulp, 1982). Under the HMT conditions used here, the small peak at 5° (marked by arrow) for native potato starch indicating the disappearance of typical B-pattern, and the dual peaks at 22–25° merged into a single broad peak. However, due to the reduced peak intensity, identifying the transition was difficult.

Lorenz and Kulp (1982) claimed that amylose chains in cereal starches form complexes with the residual lipids, and this could hinder the amylose rearrangements. Kawabata et al. (1994) also reported evidence for amylose–lipid complex formation in cereal starch from the appearance of a new peak at 13.1° (2θ) on the X-ray diffractogram. The corn starch treated at 30% moisture and 120°C (Corn-30-120) showed a new small peak at approximately 13° (marked by the arrow), which could be indicative of the

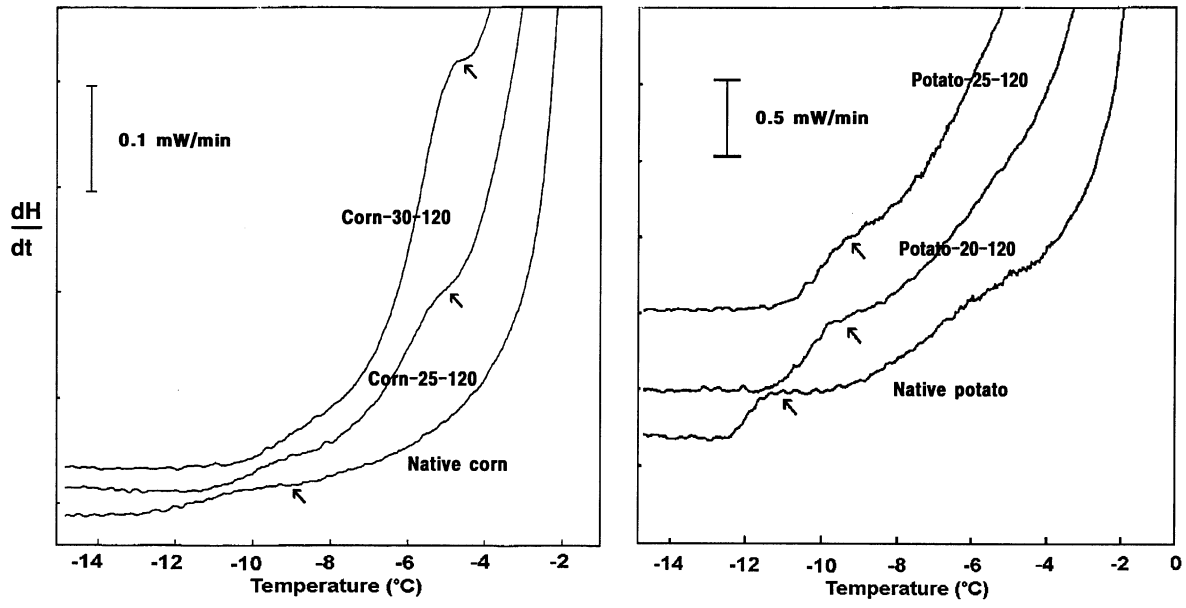

Fig. 2. The first derivative DSC thermograms of native and heat–moisture treated corn and potato starches in the presence of excess water (4× starch) for the analysis of T_g'. The numbers indicate the moisture content (20–30%) and temperature (120°C) for the treatment.

Table 1
Glass transition temperatures and ice melting characteristics of native and heat–moisture treated starches in the presence of excess water (starch: water = 1:4)

Starches	T_g' (°C)	Ice melting			
		T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Native corn	−9.3 ± 0.2	−0.9 ± 0.2	2.0 ± 1.0	4.6 ± 0.4	1235 ± 43
Corn-25-120	−5.1 ± 0.2	−0.9 ± 0.1	1.8 ± 0.5	4.8 ± 0.5	1248 ± 26
Corn-30-120	−5.1 ± 0.2	−0.9 ± 0.1	1.9 ± 0.6	4.8 ± 0.5	1260 ± 32
Native potato	−10.9 ± 0.2	−0.9 ± 0.2	1.5 ± 0.3	4.7 ± 0.4	1224 ± 11
Potato-20-120	−9.5 ± 0.2	−0.9 ± 0.1	1.4 ± 0.2	4.8 ± 0.5	1203 ± 74
Potato-25-120	−9.2 ± 0.2	−0.9 ± 0.1	1.3 ± 0.4	4.7 ± 0.5	1239 ± 59

amylose–lipid complex formation. The complex formation may result in the restriction of starch swelling, and a decrease in paste viscosity and clarity (Craig, Maningat, Seib & Hoseney, 1989; Hoover & Vasanthan, 1994; Hoover et al., 1993).

3.2. Glass transition with excess moisture

The glass transition temperature (T_g') of native corn starch in the frozen state at an excess moisture content (80%) was −9.3°C on the DSC thermogram (Fig. 2, Table 1). The T_g' increased to −5.1°C when the starch was heat–moisture treated either at 25 or 30% of moisture content (Table 1). Native potato starch showed a glass transition at −10.9°C, slightly lower than that of native corn starch (Table 1, Fig. 2). Another minor transition appeared at a higher temperature (approximately −5°C) on the thermogram of native potato starch, but it disappeared during the HMT (Fig. 2). This may imply that the amorphous state of native potato starch is inherently heterogeneous. The major transition of native potato starch (−10.9°C) also shifted to higher temperatures (−9.5 and −9.2°C) during HMT at 20 and 25% moisture contents, respectively, but the T_g' shift was not as significant as that found for corn starch.

There was also a slight change in the ice-melting peak on the DSC thermogram (Fig. 3). The ice-melting process in the treated starches started with a smooth change in heat flow and displayed reduced sharpness compared to that of native starch. However, the onset and end temperatures and enthalpy of melting were essentially the same (Table 1). This difference in the melting shape was more significant for corn starch than for potato starch. The ice-melting endotherm on the DSC thermogram resulted from the water crystals in the starch/water system. The water crystals formed from water molecules had sufficient mobility for intermolecular interactions during rapid cooling in the DSC (20°C/min). The equal enthalpy and melting temperatures between native and treated starches might indicate that there were no significant changes in the quantity of freezable water following HMT. However, from the shape difference of the melting peak, some minor variations between the

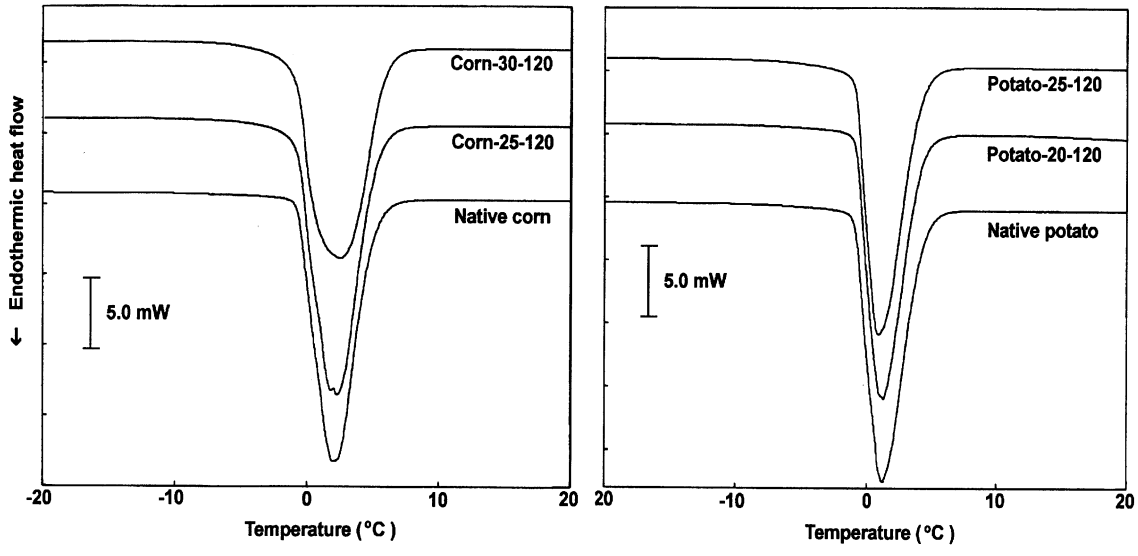

Fig. 3. DSC thermograms for ice melting of water and heat–moisture treated starch mixtures (4:1). The numbers indicate the moisture content (20–30%) and temperature (120°C) for the treatment.

Table 2
Glass transition and enthalpy relaxation of native and heat–moisture treated starches with limited moisture content (15%)

Starches	Glass transition				Enthalpy relaxation			
	T_1[a] (°C)	T_g (°C)	T_2[b] (°C)	ΔC_p (J/deg g)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Native corn	40.5 ± 4.2	52.3 ± 2.9	62.0 ± 2.1	0.018 ± 0.005	34.7 ± 1.6	45.6 ± 2.2	55.9 ± 2.3	0.500 ± 0.095
Corn-25-120	40.2 ± 2.7	47.7 ± 0.8	55.1 ± 2.1	0.058 ± 0.014	40.6 ± 1.2	49.0 ± 0.6	55.4 ± 0.3	0.799 ± 0.071
Corn-30-120	39.5 ± 0.8	46.8 ± 0.6	53.2 ± 1.7	0.082 ± 0.005	38.9 ± 1.1	49.1 ± 1.4	61.5 ± 0.3	1.008 ± 0.142
Native potato	68.2 ± 0.1	77.7 ± 0.3	90.8 ± 1.9	0.007 ± 0.004	37.7 ± 1.3	47.2 ± 0.5	56.7 ± 0.6	0.604 ± 0.072
Potato-20-120	69.9 ± 2.5	76.1 ± 3.3	80.8 ± 2.3	0.020 ± 0.011	38.6 ± 0.8	48.3 ± 0.4	59.6 ± 1.1	0.626 ± 0.032
Potato-25-120	65.7 ± 0.2	73.6 ± 0.8	81.1 ± 1.5	0.046 ± 0.014	39.6 ± 0.3	49.6 ± 0.2	58.5 ± 1.0	0.873 ± 0.043

[a] Onset of glass transition.
[b] End of glass transition.

native and treated starches, at least in the surrounding matrix of the ice crystals, could be proposed.

The glass transition in a frozen starch/water system is governed by its concentrated solute/liquid phase where the residual water remains unfrozen and still has plasticizing activity on starch. The increased T_g' by HMT (Table 1) indicates that the water molecules in the concentrated starch/water phase became less active or less available in providing mobility to the starch chains. Taking into consideration of the identical enthalpies for ice-melting endotherm, a quantitative change in liquid-phase water might not happen. The structural rearrangement in starch granule induced by the HMT resulted in an increase of the thermal stability of the amorphous regions toward the effect of liquid-phase water.

The greater degree of T_g' shift predicted for corn starch compared to potato starch was elusive in our findings. As many researchers have reported (Hoover et al., 1993; Kawabata et al., 1994; Kurahashi & Hizukuri, 1998; Lorenz & Kulp, 1982), the residual lipids in corn starch form inclusion complexes with amylose chains during the HMT, and this may restrict the amylose mobility in the concentrated starch/water phase.

3.3. Glass transitions with limited moisture

The glass transition of a starch when the residual water is limited is usually measured under DSC after the starch has been gelatinized because the transition in the native state does not show a clear change in heat flow or capacity on the thermogram. The T_g measured in a gelatinized state was reported to be similar among starches of different origin (Thiewes & Steeneken, 1997). In the DSC analysis in this study, however, the glass transition was determined in the native state of the starch so that the T_g values represented the transition of the inherent amorphous state of the starch. The measurement was made possible by using large capacity silver pans with a highly sensitive DSC.

When the moisture in the starch was 15%, the T_g of native corn and potato starches appeared at 52.3 and 77.7°C, respectively (Table 2). This T_g difference (25.4°C) between the two starches did not change much during the HMT processes. The T_g difference suggests that there is a distinct difference in the amorphous chain conformation between the two starches.

Considering that potato starch usually starts the melting curve at a lower temperature than corn starch, the substantially higher T_g of potato starch seemed surprising. This may indicate that there is a rare homogeneity in the polymeric arrangement of amorphous and crystalline structures in the native granules of both starches. Likewise, it could be postulated that the amorphous arrangement in a starch is rather specific according to its origin.

Amorphous regions in a starch granule are less defined in structural arrangement compared to the crystalline regions. However, it is well accepted that the amorphous regions in native starch granule consist of the branching regions of the amylopectin and most of the amylose chains (French, 1984; Zobel, 1992). Assuming that the amylopectin molecules are less mobile than the amylose chains due to inter-locking effects from the clusters of short-chain helices, it is probable that the amylose chains play more significant roles in the amorphous phase transition. Several researchers have reported the differences in size, chain length and degree of branching between corn and potato amylose molecules (Hanashiro & Takedo, 1998; Chung, Cho, Chung, Shin, Son & Lim, 1998; Hizukuri, 1996; Takeda, Shirasaka & Hizukuri, 1984). Based on the literature, potato amylose was found to have higher degrees of polymerization and branching than corn amylose. It is not fully understood how these conformational differences influence the glass transition, but the DSC data in this experiment may suggest that potato amorphous structure consisting of the bigger and more branched amylose chains has a higher thermal stability to resist the glass transition compared to corn amorphous structure at a limited moisture content.

As regards the HMT effect, the DSC analysis showed that the HMT used in this study decreased the T_g of both starches. For example, corn starch treated at 30% moisture (Corn-30-120) displayed a T_g of 46.8°C, 5.5°C lower than that of native corn starch. The direction of the T_g change was opposite to that of T_g' (Table 1), and this was not unusual

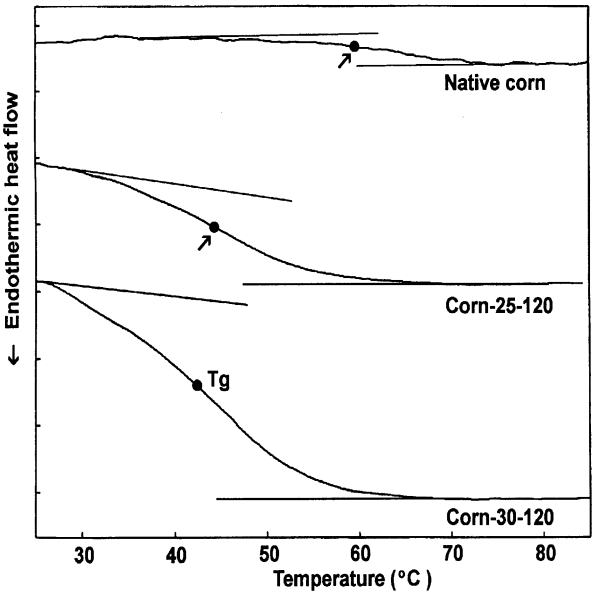

Fig. 4. The glass transition on DSC thermogram of native and heat–moisture treated corn and potato starches in the presence of limited moisture (15%). The numbers indicate the moisture content (20–30%) and temperature (120°C) for the treatment.

because the glass transition in the frozen state (T_g') was dependent on the ice-forming mechanisms whereas the glass transition with limited moisture (T_g) is fully affected by the residual water. The reduced T_g indicates that the amorphous regions in the starch granule transformed to a state where the transition could occur with increased readiness.

Another important change detected on the thermogram was the degree of specific heat change (ΔC_p) at the glass transition. The ΔC_p was increased substantially by HMT, and the temperature range for the transition became narrower (Fig. 4, Table 2). Especially, the T_2 where the glass transition ended was significantly decreased.

The crystalline regions in starch granules were interconnected by the continuous amorphous regions (Billiaderis, Page, Maurice & Juliano, 1986). The presence of crystal micelle thus reduced the freedom of the neighboring amorphous starch chains. Billiaderis et al. (1986) discussed the details of these crystalline effects and claimed the theoretical presence of intercrystalline amorphous parts. This inhibitory effect by the intercrystalline parts on the mobility of amorphous chains caused the T_g of native starch to be higher than the value of the gelatinized starch (Thiewes & Steeneken, 1997).

We suppose that the increased ΔC_p of the heat–moisture treated starches was caused by the transformation of the intercrystalline parts into independent amorphous states during HMT. From this transformation, the amorphous portion in the starch granule could be raised. The reduced or removed cross-linking effect from the intercrystalline parts as well as the raised amorphous portions made the C_p change increase and T_g decrease. The intercrystalline parts are theoretically located on the edge of crystalline micelles exposed to the amorphous regions. It is postulated that the amylose chains form partial helices with the short chains on the edges of the micelles. Because these parts are located in new amorphous regions, it would be expected that the transformation of these parts readily occur on HMT.

3.4. Enthalpy relaxation

Several researchers have pointed out the presence of an endothermic transition in glassy state starch on DSC thermogram normally observed at a temperature range below T_g (Appelquivist, Cooke, Gidley & Lane, 1993; Gidley, Cooke & Ward-Smith, 1993; Kalichevsky, Jaroszkiewicz, Ablett, Blanshard & Lillford, 1992; Shogren, 1992; Yuan & Thompson, 1994). This relaxation phenomenon reflects the approach of a glassy material towards equilibrium. This transition is time- and moisture-dependent (Noel, Ring & Whittman, 1993), but the mode of dependency was quite different from the glass transition, indicating that both transition phenomena occur independently.

The DSC thermograms form the first and second heatings, and the subtracted thermogram for the enthalpy relaxation are given in Fig. 5. The enthalpy relaxation endotherm at 15% of moisture content started at 34.7 and 37.7°C, respectively, for native corn and potato starches (Table 2). The transition continued for ~20° with an endothermic enthalpy of 0.5 or 0.6 J/g. As a result of the HMT, the onset temperature and enthalpy for the relaxation transition were raised by 1–6°C and 0.02–0.5 J/g, respectively. These changes imply that the treated starches required more thermal energy for the relaxation process than the corresponding native starches. The enthalpy relaxation represents the degree of

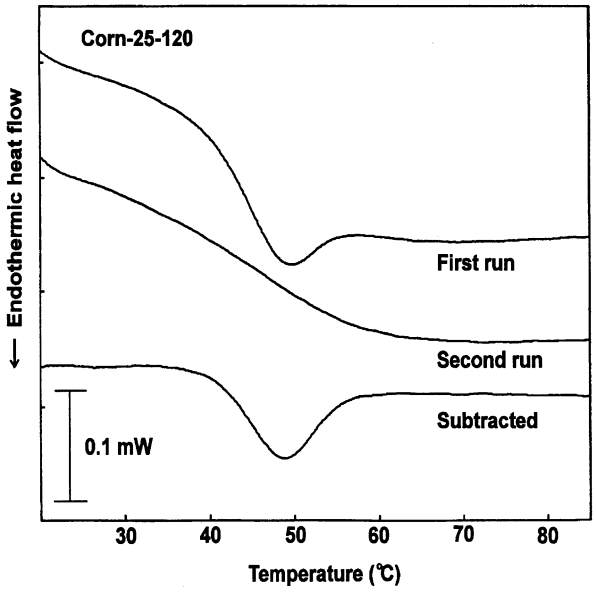

Fig. 5. DSC thermograms from the first and second heatings, and the subtracted thermogram for heat–moisture treated corn starch at 25% and 120°C.

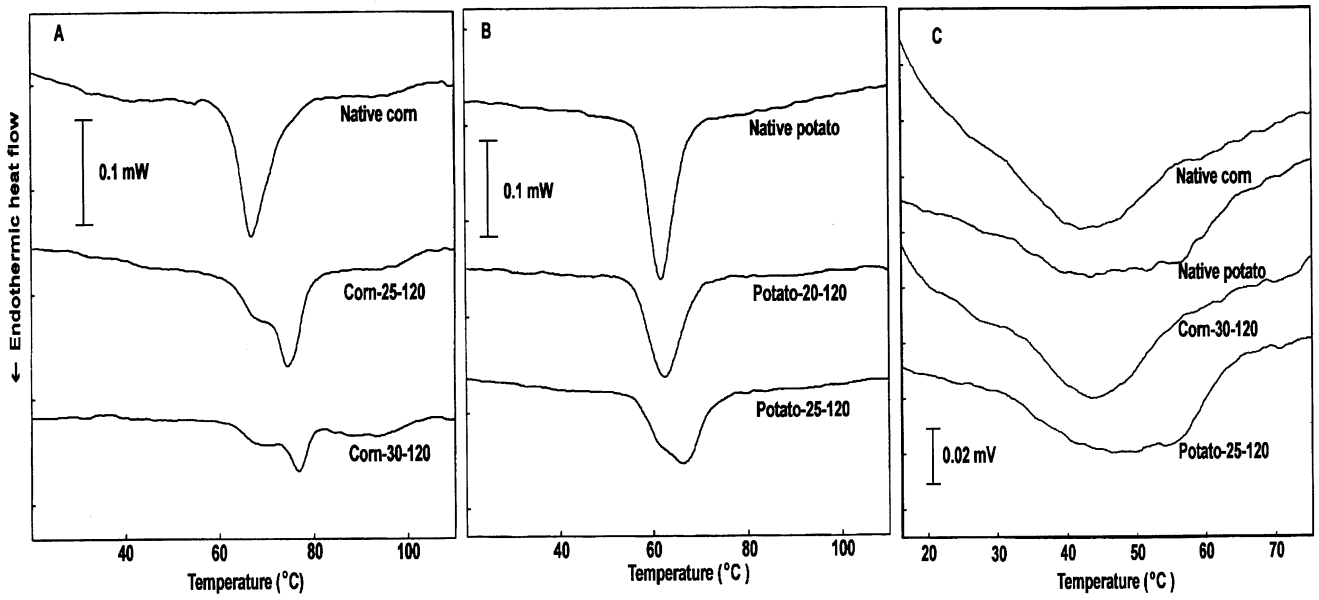

Fig. 6. DSC thermograms for the melting of native and heat–moisture treated corn (A) and potato (B) starches in the presence of excess water (4 × starch), and for the melting of recrystallized corn and potato starches (C). The numbers indicate the moisture content (20–30%) and temperature (120°C) for the treatment.

structural transformation in glassy amorphous state. Therefore, the increased quantity of the amorphous phase, induced by transformation of the intercrystalline and crystalline regions by HMT might cause an increased readiness of the structural transformation, resulting in the higher onset temperature and enthalpy.

As discussed for the glass transition results, the amorphous regions in the treated starch became more independent from the effect of crystals due to the transformation of intercrystalline parts into amorphous regions. The increased freedom or mobility allowed the amorphous chains to more readily interact, and resulted in the raised thermal stability of the glassy state. The changes in glass transition and enthalpy relaxation induced by HMT were highly dependent on the moisture contents used for the treatment. At 25% moisture, both corn and potato starches (Corn-25-120 and Potato-25-120, respectively) exhibited similar degrees of change in T_g and T_p for relaxation, about 4 and 2–3°C, respectively (Table 2). However, at the same moisture content, the ΔC_p for the glass transition was higher for potato starch.

Hoover and coworkers (1981; Hoover & Manuel, 1996a) claimed that amylose content and starch chain length were two significant factors determining the physical properties of the heat–moisture treated products. Not only the complex formation between amylose and lipids, but also the interactions between amylose chains and other starch chains (mainly in amorphous regions), may cause physical changes in the treated starch. The structural difference between corn and potato amylose chains and the presence of lipids in corn starch could result into the different influences by HMT upon the thermal characteristics of the two starches.

3.5. Melting and retrogradation of starch

By HMT, starch melting appeared to be biphasic and the transition temperature range was increased (Fig. 6, Table 3). There was no significant change in T_o, whereas T_p and T_c were substantially increased (Fig. 6). When corn starch was treated at 120°C with 30% moisture, the melting range of the treated starch became 17.7°C, which was 6° greater than that

Table 3
Melting of starch crystals and amylose–lipid complex in native and heat–moisture treated starches in the presence of an excess water (starch: water = 1:4)

Starches	Starch crystals				Amylose–lipid complex			
	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 corn	62.6 ± 0.1	66.9 ± 0.1	75.5 ± 0.3	18.7 ± 0.2	88.5 ± 0.6	96.2 ± 0.3	102.2 ± 0.8	0.717 ± 0.251
Corn-25-120	62.8 ± 0.1	74.2 ± 0.3	79.6 ± 0.5	14.4 ± 0.2	90.1 ± 1.1	96.9 ± 0.1	104.9 ± 3.0	1.088 ± 0.082
Corn-30-120	63.4 ± 0.6	76.7 ± 0.1	80.3 ± 0.6	8.2 ± 2.5	89.9 ± 1.7	95.6 ± 0.1	104.2 ± 0.6	1.392 ± 0.086
Native potato	57.2 ± 0.2	61.8 ± 0.1	67.3 ± 0.3	20.0 ± 0.5	–	–	–	–
Potato-20-120	56.5 ± 0.4	62.1 ± 0.2	69.3 ± 0.2	17.4 ± 0.5	–	–	–	–
Potato-25-120	56.0 ± 0.2	66.2 ± 0.2	71.8 ± 0.4	13.4 ± 0.1	–	–	–	–

of the untreated starch. The melting range increase resulted in reducing the original endothermic peak in native starch while a newly formed high temperature peak appeared.

The melting range increase by HMT has already been reported by several researchers. Hoover and Vasanthan (1994) pointed out that the gelatinization range of a treated potato starch increased by 5–6°C. Donovan et al. (1983) also found broad and biphasic transition with heat–moisture treated wheat and potato starches.

Hoover et al. (1993) and Hoover and Manuel (1994) claimed that HMT allowed the amylose molecules located in the bulk amorphous regions to interact with the branched segments of amylopectin in the crystalline regions. These interactions consequently reduced the mobility of the amylopectin chains and thus increased the transition temperature for melting. According to them, the enthalpy decrease was caused by the reduction of the short-range molecular order (double helices) in the crystalline regions because the long-range order determined by X-ray diffraction did not significantly change or often was slightly increased. However, their theory does not explain the decrease of T_g and increase of ΔC_p observed with the treated starch in this experiment.

We suppose that the increased melting range caused by the generation of a high-temperature endotherm was caused by the annealing of starch crystalline regions during the HMT. As discussed previously, the transformation of the intercrystalline amorphous regions to amorphous phases may provide the short chains in the crystalline structure more freedom. Thus, the crystalline micelles undergo a structural transformation toward an increased thermodynamic stability. This transformation, perhaps by rearrangement of the short amylopectin chains, is facilitated by the heat energy and water provided for the treatment. This reformation in the crystalline regions results in the newly developed high-temperature endotherm. The biphasic endotherm may indicate that this annealing undergoes heterogeneously in the location of the crystalline regions. Also, this may relate to the long-range structural transformation from B- to A-pattern on X-ray diffractogram of the treated potato starch. It should be noted that A-type starches normally melt at higher temperature ranges than B-type starches, which is in agreement with the DSC results in this study.

The thermal energy (ΔH) for melting the crystals in the treated starch was less than that of native starch (Table 3). The enthalpy reduction in the DSC thermogram was substantial even though the crystallinity reduction based on the peak intensity on X-ray diffractogram was relatively small. Therefore, the HMT-induced transformation in this experiment seemed to be more significant for the short-range arrangements than the long-range arrangements. The melting enthalpy on the DSC thermogram can increase or decrease by HMT, according to the treatment conditions (Zobel, 1992). The reduced enthalpy indicates that there was actual starch melting during the treatment. Some imperfect crystals in the native starch granules underwent HMT-induced melting resulting in the decreases in melting enthalpy. This may be attributed to the transformation of the intercrystalline amorphous parts, and thus the crystalline regions could melt more easily, i.e. with lower energy.

It should be noted that there was an increase in the enthalpy for amylose–lipid complex melting in corn starch (Fig. 6, Table 3). This result supports the findings of several researchers which state that amylose tends to form complexes with the residual lipids in cereal starch during HMT. However, it is still not clear how much complex formation occurred during the treatment but the thermogram showed that the total enthalpy for complex melting was higher for the treated starch. Thus, the total complex formation was raised by the HMT.

Although the melting characteristics of heat–moisture treated starch were significantly different from that of the native starch, the retrogradation thermograms were identical (Fig. 6C). This was because starch crystals and amylose–lipid complexes in both native and treated starches had fully melted before storage for recrystallization. Therefore, the differences in chain arrangements or matrix conformation induced by the HMT were completely eliminated by the time recrystallization started.

4. Conclusions

The glass transition temperature measured at a limited moisture (T_g at 15% moisture) of corn or potato starch decreased, but the heat capacity change (ΔC_p) at the T_g was significantly raised by the HMT (20–30% moisture, 120°C for 1 h). Based on the DSC thermal transition data, the HMT may cause the intercrystalline amorphous parts to transform into an independent amorphous state, which would explain why the mutual effects between amorphous and crystalline regions were reduced. This transformation resulted in the reduced melting enthalpy of the starch and decreased T_g but increased ΔC_p. Annealing was facilitated during the treatment resulting in the development of second endotherm at a higher temperature range. DSC thermograms also revealed that there was an increased trend toward amylose–lipid complex formation during the HMT.

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