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THERMAL TRANSITION CHARACTERISTICS AND GEL PROPERTIES OF HEAT-MOISTURE TREATED CORN AND POTATO STARCHES

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 characteristics and gel properties of the starches were examined. Granular crystallinity on X-ray diffractogram, especially for potato starch, was reduced by the heat-moisture treatment (HMT). At a limited moisture content (15% based on total weight), T_g measured in granular form of starch decreased by 2-6°C. At T_g, the change in heat capacity (ΔC_p) of the treated starch was substantially higher than of the corresponding native starch. Crystal melting of the heat-moisture treated starches, measured at 80% moisture, appeared to be biphasic on a DSC thermogram, in that the original endotherm became smaller while a new endotherm at higher temperature was enlarged by the HMT. However, the total melting enthalpy for starch decreased, indicating a partial loss of crystallinity. The degree of retrogradation under DSC was not significantly different between the native and treated starches. The HMT starches formed the gel with more opaqueness and brittleness. The gel stability from freeze-thawing treatment was slightly increased with corn starch, but decreased with potato by the HMT. Overall results on the paste viscosity and gel properties indicated that the HMT provided physical cross-linking effects on starch.

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 overall granular shape. Annealing is generally carried out in the granular form of the starch with a large quantity of water at a temperature below the starch melting

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point, whereas HMT is done with limited moisture content but at an elevated temperature [1].

The physical properties of a heat-moisture treated starch depend on the starch origin and treatment conditions used. Heat-moisture treated starch displays an increased paste stability and gelatinization temperature, regardless of its origin [2-8]. Collado and Corke [8] 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.

On X-ray diffraction patterns, root starches having a B-pattern showed a transition toward an A-pattern by HMT, whereas cereal starches remained in the inherent A-crystal pattern [3, 9]. Donovan et al. [6] 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 coworkers [10-12] tested various starches of different origins, and claimed that HMT induced the 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 important factors determining the physical properties of the final products.

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 changes in physical properties of starch gel such as textural properties and freeze-thaw stability were also examined.

Materials and methods

Materials

Normal corn starch and potato starch were provided by Samyang Genex (Seoul, Korea) and Handuk Avebe (Seoul, Korea), respectively. 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 moisture-adjusted starch (200 g) in a pressure-resistant glass bottle (300 ml) was autoclaved at 120°C for 1 h. After cooling to room temperature, the starch was dried to approximately 10% moisture content in convection oven (40°C) overnight.

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.

Thermal transition analysis

Glass transition temperature (T_g), heat capacity change (ΔC_p), melting temperature (T_o, T_p, and T_c), and melting enthalpy (ΔH) were determined by using a differential scanning calorimeter (Seiko DSC 6100, Chiba, Japan). For the measurement of T_g, 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 from 25 to 85°C at a heating rate of 2°C/min. Right after the initial heating, the sample was reheated to observe the glass transition only.

Pasting viscosity

Pasting viscosity profile was measured with a Rapid Viscoanalyzer (Newport Scientific, Warrenwater, Australia). Starch content in the aqueous dispersion was 7% (w/v) and the starch dispersion was heated from 25 to 95°C at a rate of 3.5°C /min, held for 10 min at 95°C, and then cooled to 50°C at 3.5 °C.

Gel preparation and texture analysis

Starch dispersion in water (10% w/v) was pasted in a boiling water-bath for 15 min while mechanically stirring. The paste was carefully poured into Petri-dish (50 mm diameter, 10 mm height) and stored with cover in a refrigerator (4°C) for 24 h. The gel was carefully removed from the petri-dish and tested by Texture Analyzer (TA-XT2, Stable Microsystems, Surrey, UK) with a cylinder plunger (12.8 mm diameter). The compression on the gel was done up to 60% of the height at a constant probe speed of 1.2 mm/sec, and initial modulus (surface firmness), fracture strain, and fracture strength (gel hardness) were measured.

Freeze-thaw stability

The starch gel was also frozen by storing at –20°C for 24 h and thawed at 25°C for 4 h. The gel was vacuum-filtered with an aspirator for 20 min. During the filtration, a weigh (600 g) was loaded on the gel to facilitate water release. The syneresis was calculated as the weight percent of the released water to the original water in the gel.

Results and discussion

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 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 also showed decreased peak intensity. It has been reported that excess heat or moisture for HMT results in reduced crystallinity [13]. Several researchers found that root starches had a transition tendency toward the A-pattern on X-ray diffractogram [3,9]. Under the HMT conditions used here, the small peak at 5° (marked by arrow) for native potato starch indicating the typical B-pattern disappeared, and the dual peaks at 22-25° seemed mixed together. However, due to the reduced peak intensity, identifying the transition was difficult.

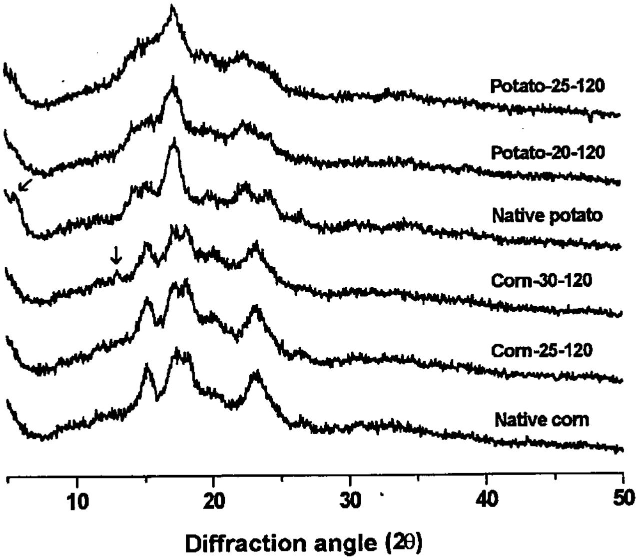

Fig. 1. X-ray diffractograms of native and heat-moisture treated corn and potato starches. The numbers indicate moisture content (20-30%) and temperature (120°C) for the treatment.

Kawabata et al. [9] also reported the amylose-lipid complex formation in cereal starch by pointing out a new peak presence at 13.1° (2θ) on X-ray diffractogram. The corn starch treated at 30% moisture showed a new small peak at approximately 13° (marked by arrow), which could be indicative of the amylose-lipid complex formation. The complex formation may result in the restriction of starch swelling, and a decrease in paste viscosity and clarity [10].

Glass transitions with limited moisture

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. 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 1). This T_g difference (25.4°C) between the two starches remained not much changed during the HMT processes. The T_g difference suggests that there is a distinct difference in the amorphous chain conformation between the two starches. Several researchers have reported the differences in size, chain length and degree of branching between corn and potato amylose molecules [14-16]. Based on the literature, potato amylose was found to have higher degrees of polymerization and branching than corn amylose. Therefore, 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.

Table 1

Glass transition and crystal melting of heat-moisture treated starches.

Starches	Glass transition				Starch crystal			
	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 corn	40.5±4.2	52.3±2.9	62.0±2.1	0.018±0.005	62.6±0.1	66.9±0.1	75.5±0.3	18.7±0.2
Corn-25-120	40.2±2.7	47.7±0.8	55.1±2.1	0.058±0.014	62.8±0.1	74.2±0.3	79.6±0.5	14.4±0.2
Corn-30-120	39.5±0.8	46.8±0.6	53.2±1.7	0.082±0.005	63.4±0.6	76.7±0.1	80.3±0.6	8.2±2.5
Native potato	68.2±0.1	77.7±0.3	90.8±1.9	0.007±0.004	57.2±0.2	61.8±0.1	67.3±0.3	20.0±0.5
Potato-20-120	69.9±2.5	76.1±3.3	80.8±2.3	0.020±0.011	56.5±0.4	62.1±0.2	69.3±0.2	17.4±0.5
Potato-25-120	65.7±0.2	73.6±0.8	81.1±1.5	0.046±0.014	56.0±0.2	66.2±0.2	71.8±0.4	13.4±0.1

* onset of glass transition

** end of glass transition

As regards the HMT effect, the HMT decreased the T_g of both starches. For example, corn starch treated at 30% moisture displayed its T_g at 46.8°C, 5.5°C lower than that of native corn starch. Another important change detected on the thermogram was the degree of specific heat capacity 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. 2, Table 1). 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 [17]. The crystal micelle presence thus reduced the freedom of the neighboring amorphous starch chains. Billiaderis et al. [17] 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 [18].

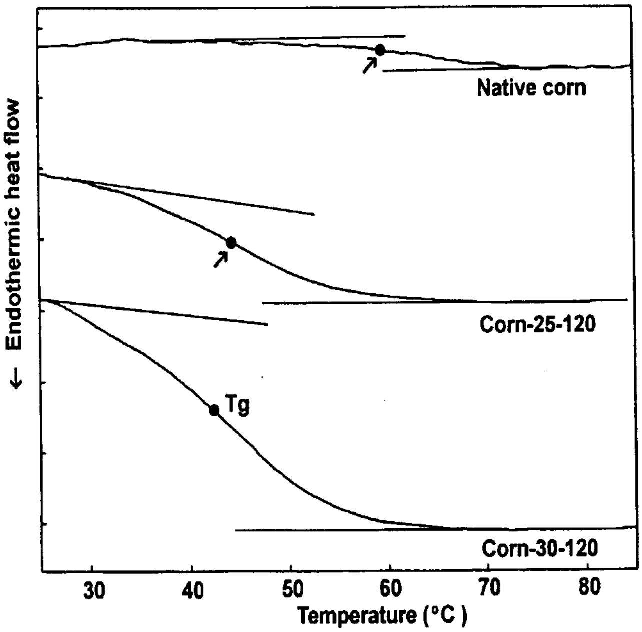

Fig. 2. The glass transition on DSC thermogram of native and heat-moisture treated corn and potato starches in the presence of limited moisture (15%). The numbers indicate moisture content (20-30%) and temperature (120°C) for the treatment.

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 by the intercrystalline parts as well as the raised amorphous portions made the ΔC_p change increase and T_g decrease.

Melting and retrogradation of starch

By the HMT in this experiment, starch melting appeared to be biphasic and the transition temperature range was raised (Fig. 3, Table 1). There was no significant change in T_o, whereas T_p and T_c were substantially increased on the endotherm

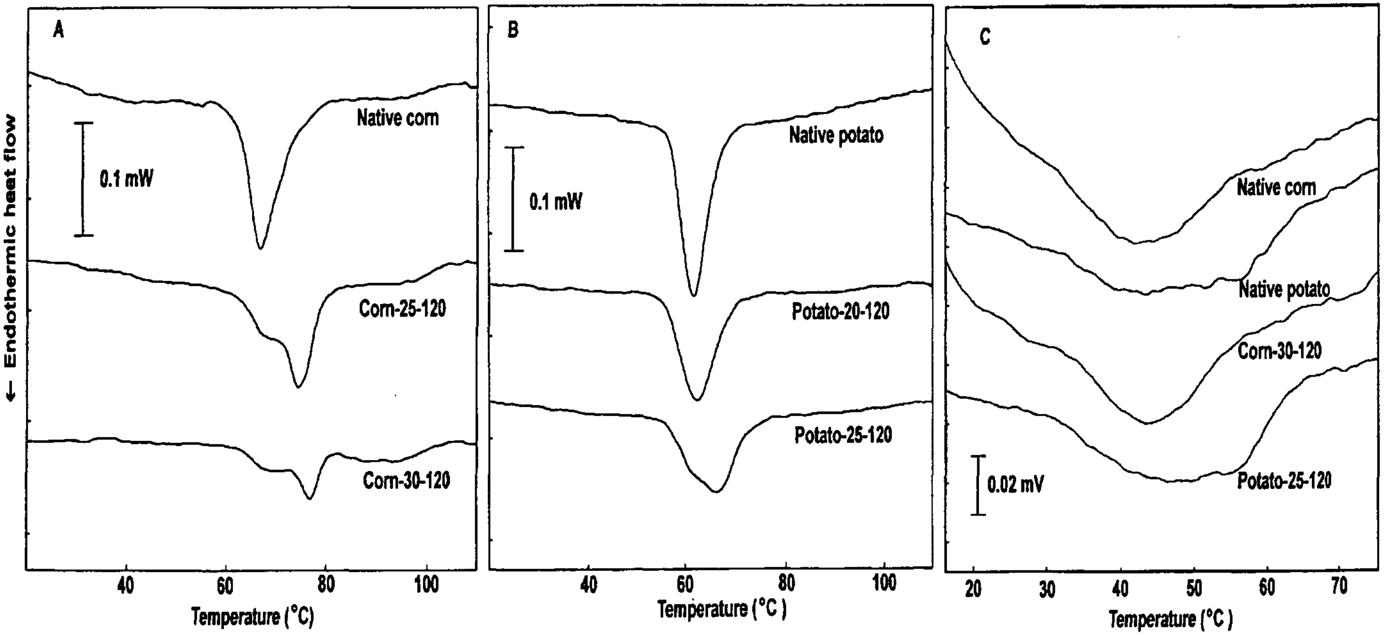

Fig. 3. DSC thermograms for the melting of native and heat-moisture treated corn (A) and potato (B) starches in the presence of excess water (4 x starch), and for the melting of recrystallized corn and potato starches (C). The numbers indicate moisture content (20-30%) and temperature (120°C) for the treatment.

(Fig. 3). The melting range increase resulted from the trend toward a smaller original endothermic peak in native starch while a newly formed high temperature peak appeared and became enlarged by the HMT. The melting range increase on thermogram by HMT has already been reported by several researchers. Donovan et al. [6] also found broad and biphasic transition with heat-moisture treated wheat and potato starches.

As discussed in the data of amorphous transitions, 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 increased thermodynamic stability. This reformation in crystalline regions results in the newly-developed high temperature endotherm. The biphasic endotherm may indicate that this annealing undergoes heterogeneity, presumably in the location of the crystalline regions.

The thermal energy (ΔH) for melting the crystals in the treated starch was less than that of native starch (Table 1). The enthalpy reduction on 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 in the short-range arrangements than in the long-range arrangements. 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.

Although the melting characteristics of heat-moisture treated starch were significantly different from that of the native starch, the retrogradation thermograms were identical (Fig. 3c).

Pasting viscosity

The pasting viscosity profile of potato and corn starches was significantly changed by the HMT (Fig. 4). As expected from the results in thermal transition and X-ray diffraction, the HMT at a higher moisture content caused more changes on the pasting profile. The HMT inhibited the swelling of starch granules, and pasting temperature increased and peak viscosity decreased, but the treated starch had improved stability during hot shearing.

The overall results in this experiment agreed with the initial findings by Kulp and Lorenz [2]. Hoover and Manuel [11] reported that the viscosity decrease by the heat-moisture treatments was caused by the interactions among the amylose chains and between amylose and residual lipids. The interactions induced by amylose chains might be concentrated in the amorphous regions under the treatment conditions where the moisture was not enough and the granular shape was unchanged. The amylose chain interactions in the amorphous regions formed the matrix having an increased rigidity of the starch granules. Karahshi and Hizukuri [19] claimed that a small amount of monoglyceride increased the effect of HMT by producing a helical amylose-lipid complex. And the complex formation increased thermal stability to starch. The DSC data showing the raised melting range support this (Fig. 3, Table 1)

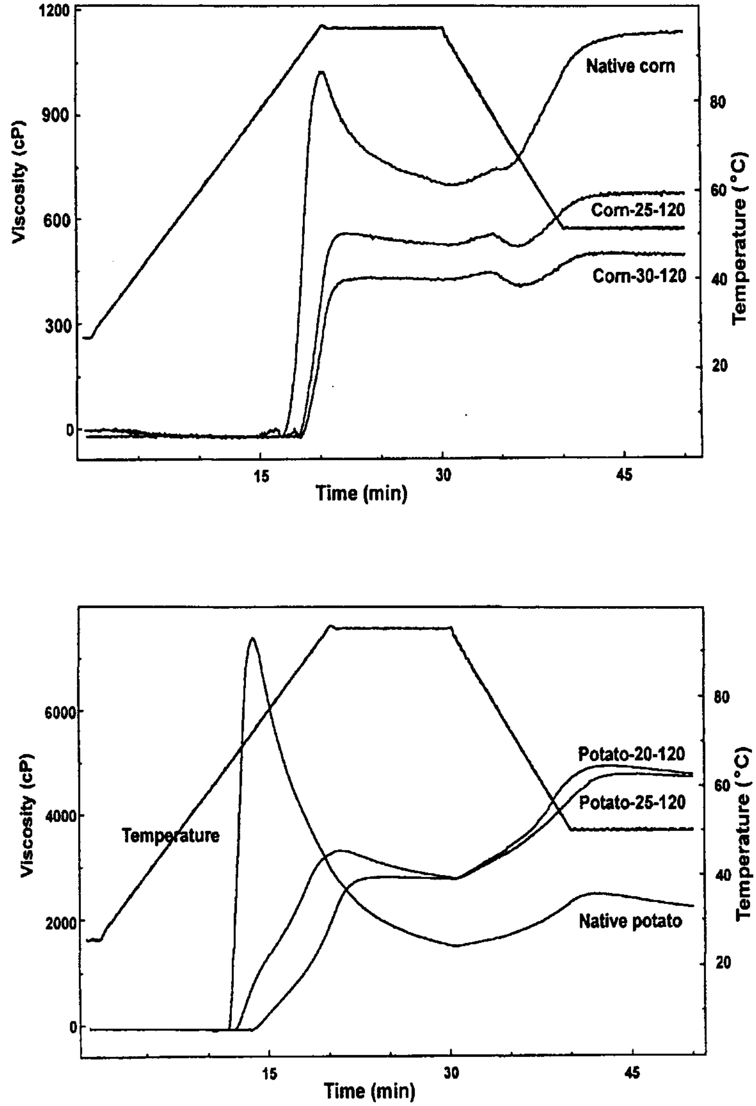

Fig. 4. Pasting viscograms of native and heat-moisture treated corn and potato starches. The numbers indicate moisture content (20–30%) and temperature (120°C) for the treatment.

Because potato starch was almost free of lipids, the interactions between amylose and lipids were not expected to occur. The absence of lipids might allow more amylose chains to form single helices or to interact each other, and this could be one reason for the greater changes in pasting profile of potato starch.

Gel texture

The textural properties of the gels of native and heat-moisture treated starches are given in Table 2. Both corn and potato starch gels showed reduced strain for gel fracture. Fracture strength, however, increased with the treated corn starch gels, whereas it decreased with potato starch gels. Native potato starch gel was very soft but not fractured up to the maximum strain used (60%). By the HMT, the potato starch gels also became brittle, resulting in the lower values for fracture strain (29 or 39%).

Initial modulus which represented the surface hardness increased by the HMT. Native corn and potato starches showed the initial moduli of 15.2 and $14.3\cdot10^7$ dyne/m^2, respectively. And these increased up to more than $27\cdot10^7$ dyne/m^2 by the HMT (Table 2). Therefore the HMT made the starch gel firmer but more brittle.

Table 2

Textural properties and syneresis by repeated freeze-thawing of native and heat-moisture treated starch gels.

Starches	Starch crystals			Syneresis	
	Fracture strain (%)	Fracture strength (g$_f$)	Initial modulus (× 10^7 dyne/m^2)	1 cycle (%)	3 cycle (%)
Native corn	41.7^a	243.2^b	15.2^b	25.7^a	58.1^b
Corn-25-120	33.4^b	325.3^a	35.1^a	13.8^b	44.1^a
Corn-30-120	31.1^b	324.3^a	33.0^a	7.6^b	55.2^a
Native potato	NF	305.1^a	14.3^b	26.6^{ab}	45.0^a
Potato-20-120	38.6^b	251.5^a	27.7^a	19.6^b	51.1^a
Potato-25-120	28.9^b	218.4^a	29.6^a	50.0^a	67.6^a

Hoover and Vasanthan [10] also found the increased rigidity of starch gel by the HMT, and claimed that it was caused by the increased amount of amylose leaching by the treatment. The pastes and gels of the treated starches in this experiment appeared more opaque than those of the native starch. The opaqueness of starch pastes or gels may be caused by incomplete dispersion of starch granules, reassociation of the starch chains, and complexation of amylose with lipids. The restricted granular swelling as shown in the pasting curves and the amylose-induced interaction with other starch chains or lipids were attributed to the increased opaqueness.

Freeze-thaw stability

The syneresis of the starch gels while the freeze-thawing cycle was repeated are given in Table 2. With the first freeze-thawing, heat-moisture treated starch gels showed the reduced syneresis (13.8 and 7.6%, respectively at 25 and 30% moisture), compared to the value of native corn gel (25.7%). With three cycles of freeze-thawing, the gels of the heat-moisture treated corn starches remained still having better stability against the treatment than the native starch gel although the difference in syneresis was minor.

The intermolecular associations among the amylose chains that helped the gel formation for the heat-moisture treated starch affected the syneresis of the gel system. As shown in corn starch, the matrix formation between amylose chains in the amorphous regions and the restrict starch swelling as shown in pasting curves could raise the water stability in the gel matrix. But for potato starch these changes in the starch caused the opposite effect.

The pasting (Fig. 4) and gel characteristics (Table 2) showed that the HMT used in this experiment showed the physical changes which were commonly determined with chemically cross-linked starches. With minor cross-linking, the paste and gel stability of starch can be improved. But with excess level of cross-linking made the starch granules more intact and less swelling, and so gave the adverse effects. Therefore the HMT can be effectively used as the substitute of chemical cross-linking which is widely used for shear and acid stabilization of the potato or substituted starches.

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 by the development of second endotherm at a higher temperature range than the original endotherm of native starch. The structural change by the HMT improved the paste and gel stability.

REFERENCES

[1] Eliasson A.-C., Gudmundsson M.: Carbohydrates in Foods. Marcel Dekker, New York, 1996, pp. 431.
[2] Kulp K., Lorenz K.: Cereal Chem., **58**, 1981, 46.
[3] Lorenz, K., Kulp K.: Starch/Staerke, **34**, 1982,76.
[4] Lorenz K., Kulp K.:. Starch/Staerke, **35**, 1983, 123.
[5] Abraham T.E.: Starch/Staerke, **45**, 1993, 131.
[6] Donovan J. W., Lorenz, K., Kulp, K.: Cereal Chem., 60, 1983, 381.
[7] Hoover R., Vasanthan, T., Senanayake, N. J., Martin, A.: Carbohydr. Res., **261**, 1994, 13.
[8] Collado L.S., Corke H.: Food Chem., **65**, 1999, 339.
[9] Kawabata A., Takase N., Miyoshi E., Sawayama S., Kimura T., Kudo K.: Starch/Staerke, **46**, 1994, 463.
[10] Hoover R., Vasanthan T.: Carbohydr., Res., **252**, 1994, 33.
[11] Hoover R., Manuel H.: Food Res. Int., **29**, 1996, 731.
[12] Hoover R., Manuel H.: J. Cereal Sci., **23**, 1996, 153.
[13] Takaya T., Sano C., Nishinari K.: Carbohydr. Polym., **41**, 2000, 97.
[14] Takeda Y., Shirasaka K., Hizukuri S.: Carbohydr. Re., **132**, 1984, 83.
[15] Hizukuri S.: Carbohydrates in Foods. Marcel Dekker, New York, 1996, pp. 347.
[16] Chung H., Cho S., Chung J., Shin T., Son H., Lim S.-T.: Food Sci. Biotechnol., **7**, 1998, 269.
[17] Billiaderis C.G., Page C.M., Maurice T.J., Juliano B.O.: J. Agri. Food Chem., **34**, 1986, 6.
[18] Thiewes H.J., Steeneken P.A.M.: Carbohydr. Polym., **32**, 1997, 123.
[19] Kurahashi Y., Kurahashi Y., Hizukuri S.: AACC Annual Meeting. Minneapolis, 1998, pp. 293.

TERMICZNE I KLEIKUJĄCE WŁAŚCIWOŚCI SKROBI OBRABIANEJ HYDROTERMALNIE

Streszczenie

Zwykłą skrobię kukurydzianą i skrobię ziemniaczaną obrabiano hydrotermalnie (HMT) (20–30% wilgoci, w 120°C, przez 1 godzinę, w zatopionej rurze szklanej), a następnie badano zmiany w temperaturze przejść fazowych i kleikowaniu. Obserwowana w widmie rentgenowskim krystaliczność skrobi ziemniaczanej obniżała się. W wyniku HMT T_g przy stosunku skrobia : woda jak 1 : 4 podnosiła się o 1–4°C. Jednakże przy ograniczonej wilgotności T_g spadało o 2–6°C. Skrobia ziemniaczana miała T_g o ok. 25°C wyższą niż skrobia kukurydziana bez względu na zastosowaną HMT. Zmiany pojemności cieplnej (OCp) w T_g, skrobi poddanych HMT były o wiele wyższe niż dla skrobi natywnych. Entalpia i temperatura początku przemiany także wzrastały dzięki HMT. Jak pokazały wykresy DSC topnienie krystalitów skrobi po HMT przy stosunku skrobia : woda = 1 : 4 było dwufazowe. Skrobia kukurydziana pokazała niewielki wzrost entalpii topnienia dla kompleksu amylazowo-lipidowego. HMT wywoływała wieksza opalescencję żelu, który stawał się bardziej kruchy. Po HMT nieco wzrastała odporność żelu ze skrobi kukurydzianej na zamrażanie i rozmrażanie, natomiast żel ze skrobi ziemniaczanej zachowywał się odwrotnie. Dane o kleikowaniu wskazują, że HMT wywoływała takie zmiany, jak fizyczne sieciowanie.