

Effects of Heat-Moisture Treatment and Lipids on Gelatinization and Retrogradation of Maize and Potato Starches

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ABSTRACT

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Effects of heat-moisture treatment (HMT) and lipids on the structure and gelatinization of maize and potato starches were studied, and the retrogradation process of 20% HMT starch gels was also investigated. Maize starch was physically modified by HMT or by defatting. Potato starch was physically modified by HMT or by adding monoglycerides. The X-ray pattern of the HMT maize starch was assigned to a combination of A and V patterns, which indicated that HMT formed crystallized amylose complexes and recrystallized amylose in maize starch granules. However, the X-ray pattern of defatted maize starch did not change for HMT, so the lipids originally existing in starch granules were important to the formation

of new crystallites during this treatment. Differential scanning calorimetry (DSC) results suggested that weaker structures in amylopectin crystallites were more susceptible to degradation after HMT, while crystallized amylose complexes developed thermal stability after treatment. The amylose contents increased with increasing degree of HMT, which suggested that the newly created amylose arose from exterior linear chains of amylopectin degraded by the treatment. Investigation of retrogradation process showed that HMT significantly promoted retrogradation of starch gels, especially the initiation of recrystallization.

Starch is one of the most important food hydrocolloids. It is an important source of food energy and has been used for a long time in texture modification and as a water absorption agent, gelling and thickening agent, and fat replacer. When cooked starchy foods such as rice, bread, potatoes, and puddings are stored, hardening of the starch by retrogradation occurs, usually resulting in a decrease in eating quality. With increasing use of processed and simulated foods, great efforts have been made to maintain quality of starch-based products to that just after gelatinization or to control retrogradation of starch in these foods.

Modified starches have become important in processed food because functional properties of modified starches are improved over those of the native starches. Chemically or physically modified starches are often more resistant to retrogradation and are more stable in acid and high temperatures. One physical modification of starches is heat-moisture treatment (HMT) in saturated humidity. HMT starches can be safely used in various food products.

Many researchers have reported on the structural changes and physicochemical properties of starches after HMT since the discovery of HMT starches by Sair and Fetzer (1944). Recent research (Hoover et al 1993; Hoover and Vasanthan 1994; Hoover and Manuel 1996, 1997) has suggested that the extent of starch chain associations within the amorphous regions and the degree of crystalline order are altered during HMT. HMT starches generally have been produced on a laboratory scale but this method might be insufficient for preparing a large amount of the samples. Moreover, some problems such as nonhomogeneous samples with granules partly gelatinized during HMT on a laboratory scale have been also reported. Therefore, the structural changes and physicochemical properties of HMT starches have not been clarified sufficiently and are still the subject of extensive investigation.

We received a large amount of HMT starch from Sanwa Starch Co. (Nara, Japan) that was industrially produced on a large scale. These samples were more suited to further investigation than those produced on a laboratory scale. We previously reported (Kawabata et al 1994) the granule morphology of HMT starch produced on an industrial scale. Microscopic photographs with polarized light showed that after HMT, the polarized cross of starch granules became slightly unclear and we observed a stained trace in the centric hilum of each granule. Also, we observed from scanning electron micro-

scopy (SEM) (Kawabata et al 1994) that the centric hila of the granules were directly damaged by HMT and the treated starches became weaker against enzyme digestion. However, the surface structures surrounding the hilum became crystalline.

Because retrogradation seems to develop more slowly in HMT starches than in native starches, investigation of retrogradation of HMT starch gel state is important for food applications. However, little work has been reported on the retrogradation of HMT starch gels (Takaya et al 2000), in part because a relatively large amount of starch samples is required for the preparation of starch gels.

In the present study, we used various kinds of industrially produced HMT starches and investigated the effects of HMT and lipids on the structure and the physicochemical properties of maize and potato starches compared with previous results from microscopy (Kawabata et al 1994). We also followed the retrogradation process of 20% HMT starch gels by observing the structural changes within the amorphous and crystalline regions.

MATERIAL AND METHODS

Starches

Eight kinds of starch samples were kindly given by Sanwa Starch (Nara, Japan): native maize starch (N-M), HMT maize starch (HMM), defatted maize starch (M-DF), HMT maize starch after defatting (HMM-DF), native potato starch (N-P), HMT potato starch (HMP), potato starch with monoglycerides (stearic acid) (P-F), HMT potato starch after adding monoglycerides (HMP-F).

Preparation of HMT Starch

Each HMT starch sample was industrially produced on a large scale by Sanwa Starch Co. The starch sample (6 kg) was spread uniformly in a large stainless steel vat in a layer \approx 10 cm thick. The vat was placed in the vessel of a retort sterilizer and the vessel was evacuated to a pressure of 60 torr within 5 min. Steam was introduced to the vessel to maintain appropriate pressure for a predetermined time. HMM was heat-moisture treated with saturated humidity for 20 min at 125°C; HMM-DF was prepared by HMT under the same conditions after evacuating. HMP was heat-moisture treated with saturated humidity for 30 min at 110°C; HMP-F was prepared by HMT with saturated humidity for 20 min at 125°C after evacuating. After this treatment, the vessel was evacuated to a pressure of 100 torr for 10 min to remove the moisture, cooled, and finally opened.

Determination of Starch Properties

X-ray diffractograms of starches were obtained with diffractometer (XD-3, Shimadzu Co. Ltd., Japan) with a chart speed of 5mm/min.

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The starch powder was scanned through the 2θ range of $4\text{--}36^\circ$. Diffractograms were obtained using a Cu-K α radiation detector with a nickel filter and scintillation counter operating at 35 kV voltage, 15 mA current, 1-0.3-1 slit systems, 5 sec time constant, 500 cps count range, 0.5°/min scanning rate.

The viscosity of hot starch pastes was determined using a viscoamylograph (model VA-V, Brabender Instruments, South Hackensack, NJ) equipped with 700 cm-g cartridge to study pasting properties at a concentration of 6%. The starch suspensions were stirred at 75 rpm and heated from 30 to 95°C at a scanning rate of 1.5°C/min, kept at this temperature for 30 min, and then cooled down to 30°C at the same scanning rate.

The average initial gelatinization temperature of the starch and the change in translucency of the gelatinized starch with increase in temperature was measured photoelectrically. The 0.1% starch suspensions were heated from 30 to 95°C at a scanning rate of 2.5°C/min. The initial gelatinization temperature was taken at the point where the first increase in transparency begins.

Differential scanning calorimetry (DSC) was performed using (DSC-10, Seiko Electronic, Tokyo, Japan) ≈ 40 mg of 30% starch suspensions sealed hermetically into a silver pan. The scanning temperatures and heating rate were 20–130°C and 1°C/min, respectively. The thermogram was recorded with distilled water as a reference.

Degree of gelatinization of starch was determined by the β -amylase and pullulanase method described by Kainuma et al (1981)

Degree of gelatinization of starch was determined by iodine affinity measured by an automatic amperometric titration method (Sensitive ATR-CU-1, Hiramatsu Kagaku, Japan). Amperometric

titration was performed as described by Fukuba and Kainuma (1977). The degree of gelatinization of starch was determined as: Degree of gelatinization (%) = (amount of iodine absorbed to 100 mg of sample/amount of iodine absorbed to 100 mg of alkaline gelatinized sample) $\times 100$. The amylose content of each sample was calculated as: Amylose content (%) = (amount of iodine absorbed to 100 mg of sample/amount of iodine absorbed to 100 mg of amylose) $\times 100$.

Preparation of Starch Gels

To investigate the retrogradation process of starch gels, 20% gelatinized starch gels were prepared by heating at 100°C for 2 hr and stored at 1°C for 0–168 hr. The starch gels were prepared as described previously (Miyoshi et al 1992, 1993). For each storage time, the sample was dehydrated using ethanol and powdered samples were used for X-ray diffraction, BAB, and iodine affinity.

RESULTS

X-ray Diffraction of Raw Starches

Figure 1 shows X-ray diffraction patterns of various raw starches. The X-ray pattern of N-P is typical of the B pattern of tuber starches, while that of N-M is typical of the A pattern of cereal starch. After HMT, the X-ray diffraction pattern of the potato starch (HMP) was changed from B to A pattern, which is similar to that of maize and other cereal starches. However, the intensities of the major peaks were weaker than those in the A type starch. For HMM, the X-ray pattern for is almost the A pattern, however, the diffraction (4.5Å [$2\theta = 19.5^\circ$]) became much sharper and another specific diffraction feature (6.8Å [$2\theta = 19.5^\circ$]) appeared. These are typical diffraction peaks in the V pattern. Therefore, the X-ray pattern of HMM was assigned to a combination of the A and V patterns, which suggested that HMT caused the formation of crystallized amylose complexes and recrystallization of amylose molecules in maize starch granules. The X-ray pattern of M-DF did not change after treatment (MHC-DF), and they were identical to that of N-M. The X-ray diffraction pattern of the potato starch after addition of monoglycerides (P-F) remained the same as the B pattern. And even after treatment, HMP-F did not change from B to A pattern, although the intensities of the major peaks were significantly weaker compared with those of other starches.

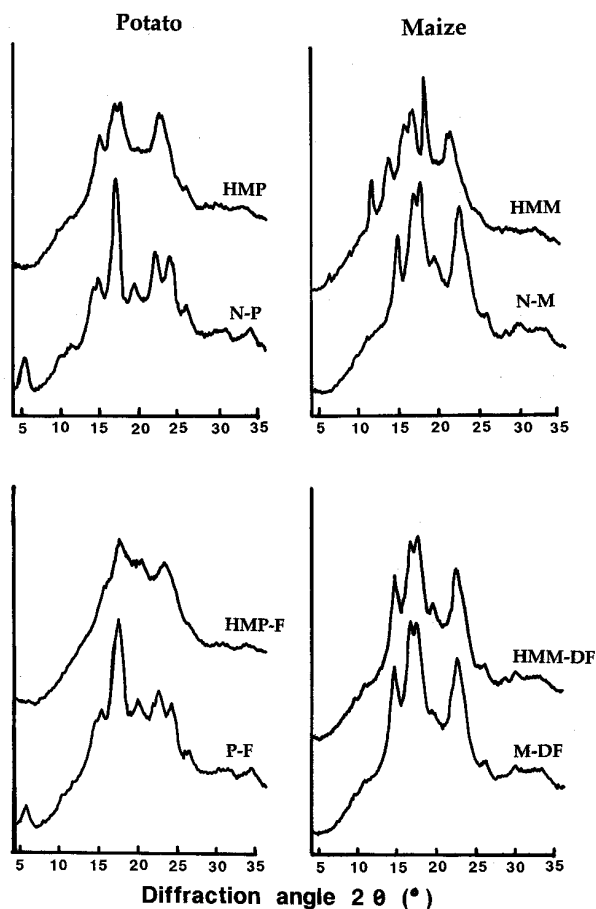


Fig. 1. X-ray diffraction patterns of various raw starches. Native maize starch (N-M), HMT maize starch (HMM), defatted maize starch (M-DF), HMT maize starch after defatting (HMM-DF), native potato starch (N-P), HMT potato starch (HMP), potato starch with monoglycerides (stearic acid) (P-F), HMT potato starch after adding monoglycerides (HMP-F).

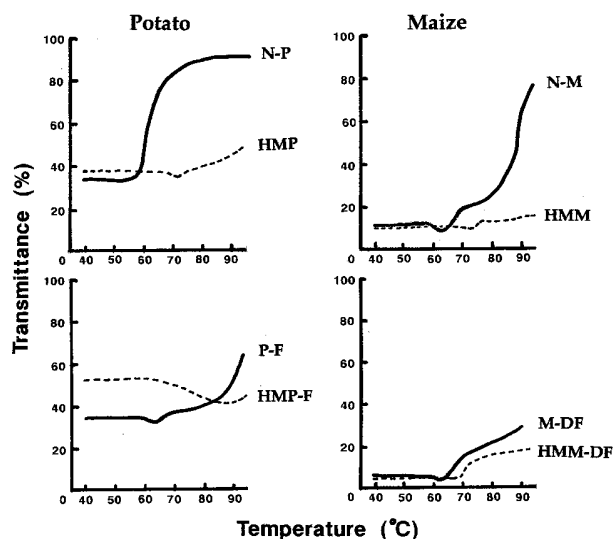


Fig. 2. Gelatinization patterns of 0.1% various starch suspensions. Native maize starch (N-M), HMT maize starch (HMM), defatted maize starch (M-DF), HMT maize starch after defatting (HMM-DF), native potato starch (N-P), HMT potato starch (HMP), potato starch with monoglycerides (stearic acid) (P-F), HMT potato starch after adding monoglycerides (HMP-F).

Gelatinization Properties

Figure 2 shows 0.1% various starch suspensions and the initial gelatinization temperature determined by the first increase in transparency. N-P showed a one-step gelatinization, however, after treatment, HMP changed to a two-step gelatinization. The initial gelatinization shifted to higher temperatures and the increase in transmittance on heating was significantly reduced. P-F showed a two-step gelatinization, however, HMP-F became nonhomogeneous and a clear initial gelatinization temperature could not be detected. N-M and M-DF showed a two-step gelatinization; HMM and HMM-DF showed initial gelatinization shifted to higher temperatures and the increase in transmittance on heating was significantly reduced.

Figure 3 shows the viscosity of various 6% starch suspensions. N-P and N-M showed typical viscosity behaviors. In both HMP and HMM, the initial gelatinization significantly shifted to higher

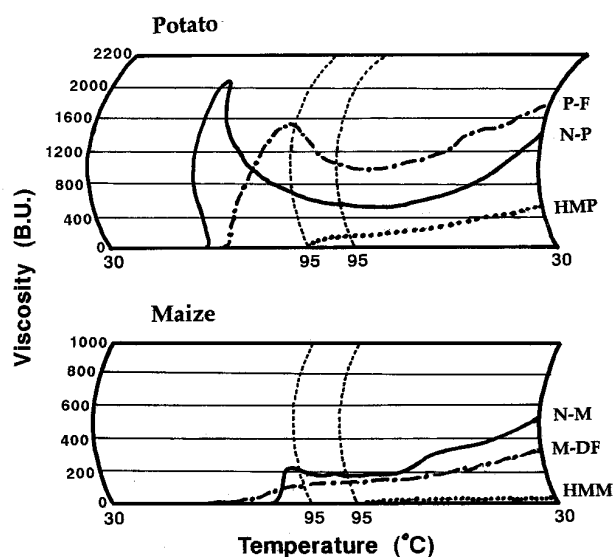


Fig. 3. Brabender viscosity of various 6% starch suspensions. Native maize starch (N-M), HMT maize starch (HMM), defatted maize starch (M-DF), HMT maize starch after defatting (HMM-DF), native potato starch (N-P), HMT potato starch (HMP), potato starch with monoglycerides (stearic acid) (P-F), HMT potato starch after adding monoglycerides (HMP-F).

temperatures, however, the maximum viscosity drastically decreased. For P-F, the initial gelatinization shifted to higher temperatures and the maximum viscosity slightly decreased. For M-DF, the initial gelatinization shifted to lower temperatures compared with that for the native maize starch suspension, however, the two-step gelatinization disappeared after defatting. For HMP-F and HMM-DF, an increase in viscosity was completely hindered (data not detected).

Figure 4 shows DSC curves of various 30% starch suspensions. For N-P, a single endothermic peak was observed at $\approx 62^\circ\text{C}$. For HMP, the main endothermic peak shifted to higher temperatures but this peak became significantly broader and the endothermic enthalpy of main peak significantly decreased compared with N-P. For N-M, the main endothermic peak was observed at $\approx 67^\circ\text{C}$ and other small endothermic peaks corresponding to amylose-lipid complexes were observed at higher temperatures of ≈ 100 and 120°C . For HMM, the endothermic enthalpy of the main peak markedly decreased; the endothermic enthalpy of the other peak at $\approx 120^\circ\text{C}$ significantly increased. For P-F, the main endothermic peak became slightly sharper and the other small peak of the amylose-lipid complex appeared at a higher temperature ($\approx 105^\circ\text{C}$). For HMP-F, the nonhomogeneous endothermic peaks became much broader, and many small peaks were observed, especially at the higher temperatures. For M-DF, the main peak enthalpy significantly decreased and the peak of the amylose-lipid complexes disappeared. For HMM-DF, the endothermic peak shifted to higher temperatures, however, the differences before and after HMT were significantly smaller than those for the other samples.

Retrogradation of Starch Gels

Figures 5 and 6 show the X-ray diffraction pattern of the 20% maize and potato starch gels after storage at 1°C . For any potato starch gel (Fig. 5) just after gelatinization (0 hr), the X-ray diffraction pattern showed the V pattern, which is the typical of gelatinized starches. With developing recrystallization, the X-ray pattern gradually recovered to the B pattern, which is the typical of retrograded starches. The addition of monoglycerides obviously retarded the recrystallization of the potato starch. The HMT significantly promoted recrystallization for potato starch gels with and without monoglycerides. For any maize starch gel (Fig. 6) just after gelatinization (0 hr), the X-ray showed the V pattern. However, the intensities of the peaks for the treated maize starch gels became stronger and typical diffractions (at 4.5 and 6.8\AA) remained much sharper. This indicated that the crystallized amylose com-

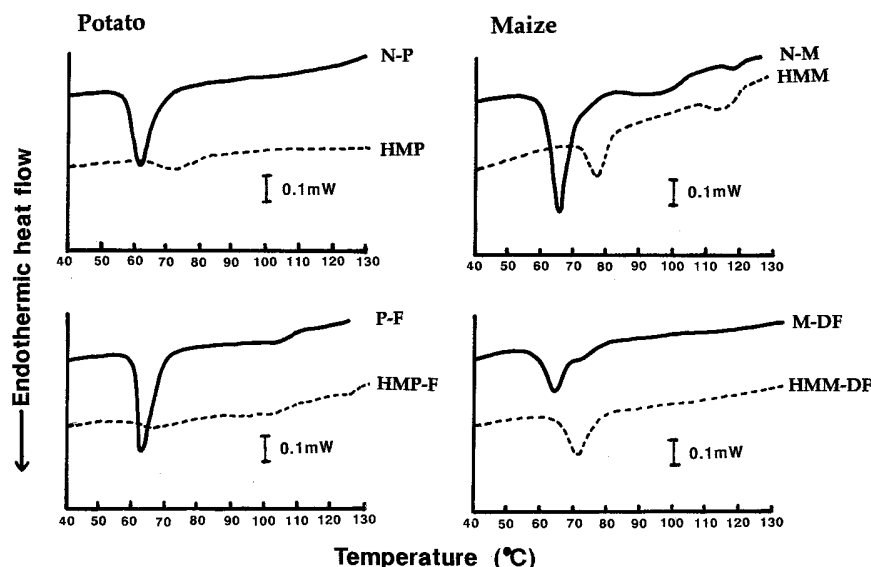


Fig. 4. Differential scanning calorimetry (DSC) curves of various 30% starch suspensions heated at $1^\circ\text{C}/\text{min}$. Native maize starch (N-M), HMT maize starch (HMM), defatted maize starch (M-DF), HMT maize starch after defatting (HMM-DF), native potato starch (N-P), HMT potato starch (HMP), potato starch with monoglycerides (stearic acid) (P-F), HMT potato starch after adding monoglycerides (HMP-F).

plexes formed by HMT (raw) could not be disrupted even after heating at 100°C (0 hr). It has been suggested that the crystallized amylose complexes promote the nucleation and subsequent aggregation of the crystalline chains (Gudmundsson and Eliasson 1990; Gudmundsson 1992). Therefore, these thermally stable crystalline complexes seem to promote recrystallization so that the retrogradation of the treated maize starch gels proceeds rapidly. Defatting obviously retarded recrystallization of maize starch gels, however, HMT significantly promoted recrystallization of native and defatted maize starch gels, especially the initial development of recrystallization.

Figure 7 shows retrogradation of starch gels analyzed with β -amylase and pullulanase (BAP) and iodine affinity. In both methods, just after gelatinization (0 hr), the degree of gelatinization for the native starches was almost perfect (100%). Therefore, native starch granules were almost completely gelatinized on heating to 100°C. However, the degree of gelatinization for the treated starches was \approx 80%, so parts of the starch granules became thermally stable by HMT. The treatment obviously promoted the initial retrogradation

rate (at \leq 24 hr) of the starch gels; however, it did not produce very much further retrogradation. Therefore, the degree of gelatinization for treated starches reached the limiting value of 40% after only 3 hr.

DISCUSSION

Effects of HMT and Lipids on Gelatinization

Hoover and Manuel (1996) have reported that amylose-amylose and amylose-lipid interactions, and crystallite reorientation occurred during HMT, and that these associations involving amylose chains resulted in the formation of new crystallites of different stabilities. In our results, the X-ray diffraction pattern of HMM was assigned to a combination of the A and V patterns (Fig. 1), which supports their suggestion (Hoover and Manuel 1996). Moreover, our results have suggested that the lipids originally existing in starch granules play an important role in the formation of new crystallites during HMT because the X-ray diffraction pattern of M-DF did not change after treatment (Fig. 1). Because the X-ray pattern of HMP-F did not change from B to A, the added monoglycerides seem to exist

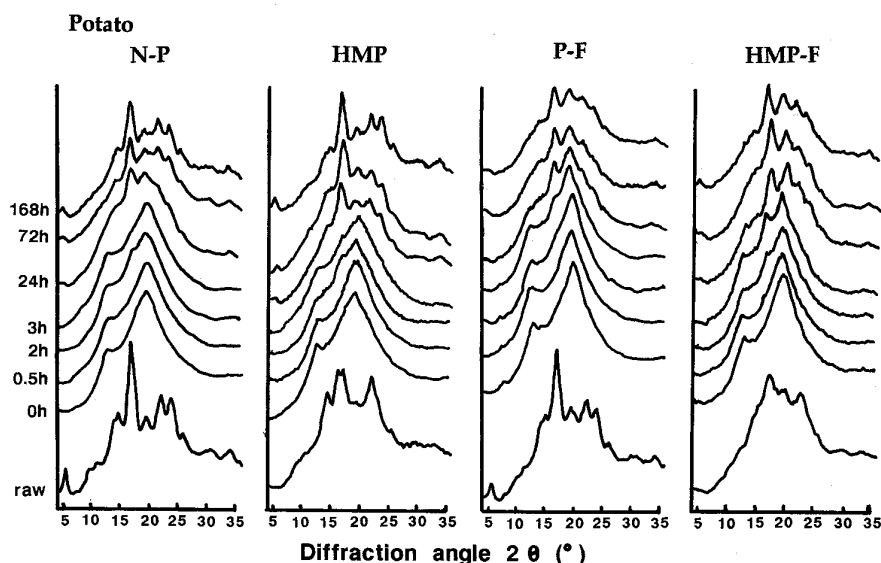


Fig. 5. X-ray diffraction pattern of 20% potato starch gels after storage at 1°C. Native potato starch (N-P), HMT potato starch (HMP), potato starch with monoglycerides (stearic acid) (P-F), HMT potato starch after adding monoglycerides (HMP-F).

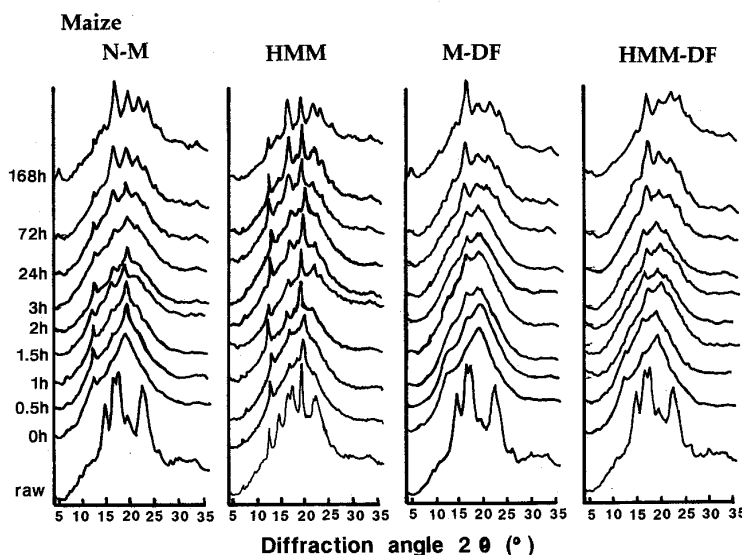


Fig. 6. X-ray diffraction patterns of 20% maize starch gels after storage at 1°C. Native maize starch (N-M), HMT maize starch (HMM), defatted maize starch (M-DF), HMT maize starch after defatting (HMM-DF).

mainly as a free lipids in starch granules and do not contribute much to the formation of amylose-lipid complexes. However, in DSC (Fig. 4), the main endothermic peak for P-F became slightly sharper and a small peak corresponding to amylose-lipid complexes appeared, which indicates that while producing P-F, the free amylose gelatinized easier and complexed partly with the added lipids. In any event, the added lipids increased the thermal stability of potato starch granules during gelatinization because P-F changed to a two-step gelatinization (Fig. 2). The initial gelatinization of P-F shifted to significantly higher temperatures compared with that of N-P (Figs. 2 and 3).

It is well known that starch granules contain a mixture of two polysaccharides, amylose and amylopectin. Amylose is primarily made of linear molecules and forms crystalline complexes of the well known V polymorph with various ligands (Young 1984; Leloup et al 1992). Amylopectin consists of branched macromolecules ($M_r \approx 10^7$) (Manners 1989) and is the main contributor to crystalline order within the granule. The crystalline regions of amylopectin are formed by short branched chains intertwined into double helices (French 1984; Klucinec and Thompson 1999). Using gel permeation chromatography (GPC), Lu et al (1996) reported that HMT leads to the degradation of the amylopectin molecules, so that the amount of large molecules decreased but the amount of smaller molecules increased.

In our DSC results (Fig. 4), the main endothermic enthalpy for any starch decreased after HMT, which indicates that the amylopectin crystallites were degraded by the treatment. The weaker structures in the amylopectin crystallites are apt to be more influenced by the degradation during HMT. Therefore, more thermally stable crystallites in amylopectin molecules remain after treatment, which results in the DSC observation that the main endothermic peak for any starch obviously shifts to higher temperatures after HMT (Fig. 4). Moreover, after HMT, the magnitude of decrease of main peak enthalpy for potato starch was significantly larger than that for maize starch, which partly explains why this treatment more drastically changes the structure and physicochemical properties of tuber starches (potato starch) than those of cereal starches (maize starch) (Stair 1967). Defatting might also degrade the amylopectin crystallites. The main endothermic peak enthalpy of M-DF significantly decreased compared with that of N-M, although the X-ray diffraction pattern of maize starch did not

change as a result of defatting. Moreover, defatting seems to protect starch granules against the effects of HMT. For defatted maize, the differences before and after treatment in DSC curves (Fig. 4) were significantly smaller those for the other samples.

The amylose content of the various starches, calculated by iodine affinity, are shown in Table I. It is clear that for both maize and potato starches, amylose content increased after HMT. Moreover, this value increased with further treatment. Lu et al (1996) reported that the exterior linear chains of amylopectin were degraded by HMT. In our study, the amylose content increased after HMT (Table I). Therefore, it seems plausible that these exterior linear chains of amylopectin, degraded by this treatment, became just like amylose chains and would complex with other amylose chains or lipids. This seems to indicate the formation of new crystallites with different thermal stability within the amorphous regions due to treatment. Endothermic peak enthalpies at higher temperatures corresponding to the amylose-lipid complexes increased after HMT. These DSC results are in good agreement with those obtained by Hoover and Manuel (1996).

From microscopic observations in previous studies (Kawabata 1994), we observed that the maize and potato starch granules were significantly changed by HMT. Micrographs with polarized light the native starch granules of both potato and maize starches showed a distinct polarized cross. However, after HMT, the polarized crosses became slightly unclear and the stained trace was observed in the centric hilum of each granule. In the SEM, HMT did not change the size of the starch granules but significantly changed the shape, thus, the shape of the starch granules became concave after treatment. Moreover, an obvious hole in each granule was observed in SEM of the cross-sections of the starch granules. Therefore, the centric hila of the granules were damaged with HMT and the treated starches became weaker against enzyme digestion. However, the surface structures surrounding the hilum were densely packed after HMT, and thus became crystalline resistant areas. Judging from the present study, these crystalline resistant areas seem to consist of highly crystallized amylose complexes in starch granules and seem to inhibit granule swelling (Tester and Morrison 1990), so treated starch granules became extremely heat-resistant during gelatinization and were not disrupted by heating $\leq 100^\circ\text{C}$. Hoover and Manuel (1996) reported that the viscosity of waxy starches (amylopectin 100%) did not change after HM; however, the viscosity of the

TABLE I
Iodine Affinity and Amylose Content of Starch Samples

| Starch | Iodine Affinity ^a (I ₂ mg/100 mg) | Amylose Content ^b (%) |
|-------------------------------|--|-------------------------------------|
| Native maize | 4.4 | 23.1 |
| Treated maize (125°C, 5min) | 5.1 | 27.0 |
| Treated maize (125°C, 20min) | 5.3 | 27.7 |
| Native potato | 3.9 | 20.4 |
| Treated potato (110°C, 30min) | 4.8 | 25.3 |

^a Amperometric titration as described by Fukuba and Kainuma (1977).

^b Amylose content (%) = (amount of iodine absorbed to 100 mg of sample/ amount of iodine absorbed to 100 mg of amylose) × 100.

TABLE II
Size of Crystallites for Various Starches

| Storage Time (hr) | Native Maize Starch | | Heat-Moisture-Treated Maize Starch | |
|----------------------|------------------------|------|---------------------------------------|-------|
| | 2θ/° | D/Å | 2θ/° | D/Å |
| Raw starch | 19.7 | 73.3 | 19.4 | 201.5 |
| 3 | 19.8 | 57.8 | 20.0 | 149.4 |
| 24 | 19.5 | 89.4 | 19.4 | 160.9 |
| 72 | 19.3 | 89.4 | 19.4 | 201.5 |

^a Size of crystallites calculated from line broadening using Scherrer's equation (Alexander 1969): $D = (0.9 \times \lambda) / (\beta_{1/2} \times \cos \theta)$, where D = a mean dimension, λ = wavelength of X-rays, $\beta_{1/2}$ = half-maximum width, and θ = Bragg angle.

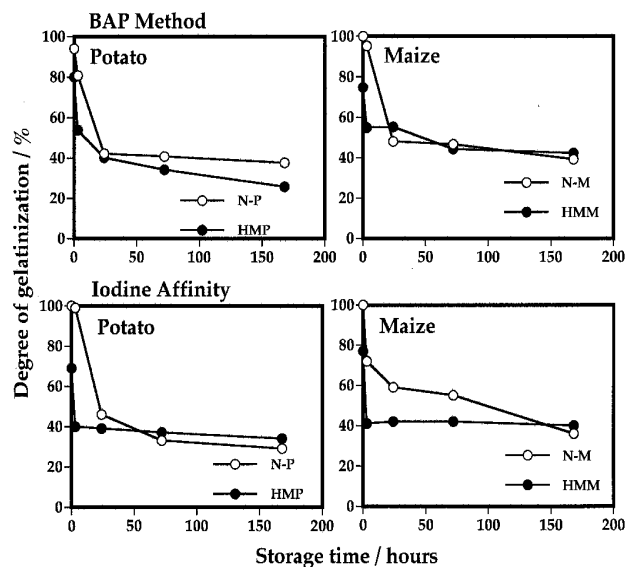


Fig. 7. Retrogradation process of starch gels analyzed by β -amylase and pullulanase (BAP) and iodine affinity. Native maize starch (N-M), HMT maize starch (HMM), native potato starch (N-P), HMT potato starch (HMP). Native untreated starches (○), treated starches (●).

native starches significantly decreased. Therefore, the decrease in viscosity as observed in Figs. 2 and 3, seems to be the result of increased inter- and intramolecular hydrogen bonds due to association of amylose chains and amylose-lipid complexing during HMT.

Effect of HMT on Retrogradation of Starch Gels

Figure 6 shows typical diffractions for HMM at 4.5 Å ($2\theta = 19.5^\circ$) and 6.8 Å ($2\theta = 13.1^\circ$) remained much sharper after heating to 100°C. In the diffraction at 4.5 Å for NM or HMM, the size of crystallites at each storage time was calculated from the line broadening by the use of Scherrer's equation (Alexander 1969): $D = (0.9 \times \lambda) / (\beta_{1/2} \times \cos\theta)$, where D = a mean dimension, λ = wavelength of X-rays, $\beta_{1/2}$ = half-maximum width, and θ = Bragg angle (Table II). The line broadening of N-M at raw corresponds to a crystallite size of 73.3 Å, and this value almost coincided with the results observed by Alexander (1969) and per Muhrbeck (1991). However, the line broadening of HMM at raw corresponds to the crystallite size of 201.5 Å, and this value was $\approx 3\times$ that of NM at raw. Therefore, during HMT, the size of thermally stable crystallites involved amylose complexes developed in maize starch granules. Heating to prepare starch gels at 100°C slightly decreased the size of crystallites for both N-M and HMM but they did not disappear (0 hr). Thus, these maize starch granules with highly crystallized amylose complexes became extremely heat-resistant during gelatinization. Moreover, the degree of heat resistance seems to be proportional to the size of crystallites (comparing physicochemical properties) (Figs. 2 and 3). As described in Table I, the amylose content of starches increased with HMT so that the new created amylose, which arises from exterior linear chains degraded by HMT, seems to contribute to the formation of the heat-resistance area in treated starch granules. These thermally stable crystallites are almost recovered during initial recrystallization of starch gels (Table II), which supports the typical retrogradation of amylose.

Miles et al (1985) and Ring (1987) reported that retrogradation of starch proceeded in two stages. In the first stage, the rigidity and crystallization of the starch gels developed quickly as a result of the amylose gelation. And in the second stage, further crystallites, detected by X-ray diffraction, developed slowly in the amylopectin region. This long-term change was thermoreversible. In our results, the degree of gelatinization analyzed by the iodine affinity method mainly reflected the alteration of the amylose molecules, which also indicates that HMT promotes recrystallization, especially of amylose molecules. As illustrated in Fig. 7, although the degree of gelatinization for HMT starch gels was smaller than that for native starch gels (0 hr), further changes accompanying the retrogradation were significantly smaller in the treated starch gels than in native starch gels. Therefore, these results suggested that the degree of change after gelatinization was smaller in HMT starch gels than in native starch gels, which seems to indicate that HMT starches become more resistant to retrogradation.

In conclusion, we found that HMT influences both the amorphous and crystalline regions of starch granules; thus, this treatment degrades the exterior linear chains of amylopectin and promotes recrystallization and associations mostly involving amylose chains. Therefore, the magnitude of starch chain interactions from HMT is much greater in the amorphous region than in the crystalline region.

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