Effects of preincubation on the gelatinization of cassava and corn starch suspensions containing sodium hydroxide as a main component of corrugating adhesives

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ABSTRACT: Effects of the preincubation temperature and the caustic-ratio, the molar ratio of sodium hydroxide to starch glucose residue, on the gelatinization of cassava starch and corn starch suspensions were studied using differential scanning calorimetry in view of utilization for corrugating adhesives. The gelatinization temperature and enthalpy change of cassava starch suspensions after the preincubation at 30°C decreased as the caustic-ratio increased, similar to those of corn starch ones: The gelatinization starting temperature (T_s) decreased considerably more than the peak temperature and the conclusion temperature (T_c). Although T_s lowered and the width of gelatinization temperature expanded, compared with those of corn starch suspensions, the two starch suspensions with the same half gelatinization transition temperature showed similar gelatinization characteristics of almost the same T_s and T_c. During 1 h-preincubations at 30°C–50°C, the starch granules with T_s that were lowered considerably below each preincubation temperature by sodium hydroxide showed limited gelatinization. The gelatinization transition did not rapidly spread over the whole suspension, but progressed stepwise in response to the increase of the caustic-ratio and the rise of the preincubation temperature. In a prolonged preincubation at a constant temperature, T_s gradually rose at higher caustic-ratios in which stepwise gelatinization commenced. Although the starch gelatinization was irreversible and not in a stable equilibrium state for a long time, we concluded that such stepwise gelatinization progress controlled the practical preparation and use of corrugating adhesives.

Application: This thermodynamic study clearly showed the properties and gelatinization mechanism of starch granules used for corrugating starch adhesives. The essential properties of starch granules for controlling the practical preparation and use of these adhesives were a considerable stepwise reduction of gelatinization temperature, especially the starting temperature in response to the increase of sodium hydroxide and the stepwise gelatinization progress in response to the rise of surrounding temperature.

The recent production of corrugated paperboards has been somewhat saturated in Japan. Globally, however, it is still growing rapidly, especially in the Asian area. Corrugated paperboard is produced by bonding a corrugated medium paper and two flat liner papers for the front and back with the starch adhesives [1-3]. The production mostly consists of the heating and dehydrating processes for the adhesives picked-up: for example, a large and long drier of approximately 15 m length by steam heating is installed for the bonding of a front liner and a single-faced corrugated paperboard. The water evaporated from the adhesive amounts to more than a third of all dehydrated water in the production. Therefore, the adhesives remarkably affect not only the productivity and quality of corrugated paperboard but also the energy consumption. In Japan, corrugating adhesives are usually prepared parallel to the production of corrugated paperboards at the mills, differing from other industrial adhesives, and for this purpose, corn starch has predominantly been used for a long time. Recently, however, cassava starch, an imported cheaper raw material, starts to replace it.

Corrugating adhesives are generally divided into two types; “Stein-Hall (SH)” [1-7] and “No Carrier (NC)” [1,3,6-8]. Both adhesives mainly consist of concentrated suspensions of raw starch, which achieves the lower viscosity of the adhesives for the precise pick up volume and also enables the subsequent rapid dehydration of the gelatinized adhesives. The adhesion is significantly affected by such prompt gelatinization *in situ* of the raw starch granules. Appropriate amounts of sodium hydroxide are added to reduce their gelatinization temperature [3,5-10]. In the preparation of NC- or SH-adhesive, sodium hydroxide is added to the starch suspensions as a solution or as gelatinized starch solution of 40°C–50°C. The finished adhesives are then continuously circulated between a storage tank and a corrugator for several hours until consumed [1], keeping at approximately 40°C, in order to stabilize the viscosity and to allow rapid temperature rise in the following adhesion process. It is considerably important to stabilize the viscosity of adhesives for improving the manufacturing operation, as well as for precisely controlling the pickup volume of adhesives, which remarkably affects the quality of corrugated paperboards. In order to stabilize the preparation of adhesives and the viscosity during use, it is essential to reveal the effects of sodium hydroxide and temperatures of 40°C–50°C on the starch adhesives at various steps, such as the preparation, storage, and use. The calorimetric studies for gelatinization behaviors of cassava starch suspensions containing sodium hydroxide have scarcely been carried out, in spite of the fact that cassava starch is already popular as a main component of corrugating adhesives in Southeast Asia, such as Taiwan, Indonesia, and Thailand.

Here, we investigated the effects of sodium hydroxide and preincubation temperature on the gelatinization of a cassava starch suspension using differential scanning calorimetry (DSC). We also examined the effects of the preincubation time on the gelatinization endotherm of the corn starch suspension in the presence of sodium hydroxide, which have not been explained in detail so far [7-10].

MATERIALS AND METHODS

Preparation of materials and samples

Cassava starch and regular corn starch were provided by Japan Corn Starch Co. Ltd. (Tokyo, Japan) and Oji Cornstarch Co. Ltd. (Tokyo, Japan), respectively. A starch concentration of 25 wt% (as anhydrous), the most general concentration of corrugating adhesives, was used throughout this study. Sodium hydroxide solutions were carefully added to the stirring starch/water suspensions. Adhesives, the suspensions with high starch concentration, were gelatinized by absorbing most of the water containing sodium hydroxide, and the gelatinized pastes consequently contained almost the whole amount of sodium hydroxide. Therefore, the additional amount of sodium hydroxide was expressed as the "caustic-ratio," which was defined as the molar ratio (mol%) of sodium hydroxide to glucose residue (GR:162) in starch. The caustic-ratio showed a good correlation with the gelatinization thermal characteristics similar to the report by Leach [11] and our preceding paper [8]. Caustic-ratios of 0.97 mol%–12.6 mol% were used in this study. The starch suspensions containing sodium hydroxide were gently stirred for a fixed time at the four different preincubation temperatures (30°C, 40°C, 50°C, and 60°C) before use [9].

DSC

DSC measurement was carried out in a heat-flux-type DSC (EXSTAR 6000 DSC-6100, Seiko Instruments Inc.; Tokyo, Japan) scanning from 20°C to the target temperature at a heating rate (HR) of 1.4°C/min. A starch suspension sample (approximately 15 mg) was put into a weighed silver sample cell (15 μL), which was then hermetically sealed. As a reference, a cell containing an equal weight of water only was used. After the measurement, the cells were bored with a pinhole, dried in an oven at 105°C for 5 h, and reweighed. The amount of starch in the sample was determined by the subtraction of the definite weight of sodium hydroxide and an empty cell weight from the whole weight of the dried cell. The gelatinization starting temperature (T_s) and the conclusion temperature (T_c) were the temperatures at the inflection points of the endothermic gelatinization curve, which were determined by differentiation. The peak temperature (T_p) was defined as the temperature at the furthest point from the baseline between T_s and T_c. The gelatinization enthalpy change (ΔH) was obtained by integration of the heat quantity between the baseline and the endothermic curve from T_s to T_c. The DSC apparatus was calibrated using the melting temperature and heat of indium [10].

Swelling starch volume ratio, solute starch weight ratio, and the viscosity of starch suspensions

After preincubations of starch suspensions, approximately 30 mL of the suspension was separated into the supernatant and the two parts of the precipitates, upper and bottom, by centrifugation at 15000 rpm (27720 × g) for 10 min. The upper precipitate was regarded as swollen starch granules [10], and "swelling starch ratio" (vol%) was defined as the volume ratio of the upper precipitate to the whole volume of the suspension, following the previous reports [7-9]. A part of supernatant was titrated to neutralize with 0.02 M sulfuric acid to determine remaining sodium hydroxide. Remaining supernatant was dried at 105°C for 20 h to determine the solute starch weight by subtraction of the weight of sodium hydroxide in the supernatant measured previously from the weight of its dried solid. The ratio of the weight of solute starch to the whole weight of starch was calculated as its anhydrous weight and expressed as "solute starch ratio" (wt%). The viscosity (mPa•s) of starch suspensions was measured at 30°C with a BM-type viscometer (Tokyo Keiki Inc.; Tokyo, Japan).

RESULTS

Effects of caustic-ratio and preincubation temperature on the gelatinization of cassava starch suspensions

1) Preincubation at 30 °C.

The cassava starch suspension containing sodium hydroxide was preincubated at 30°C for 1 h, and the DSC measurement was performed at a heating rate of 1.4°C /min. As shown in **Fig. 1**, the endothermic peak shifted to the slightly higher temperature side at low caustic-ratios (0.97 mol%–1.94 mol%), and then to the lower side, with which the peak shapes became broader, shallower, and more asymmetrical. As a result, T_s, T_p, and T_c slightly rose at low caustic-ratios and subsequently decreased linearly with the caustic-ratio, as shown in

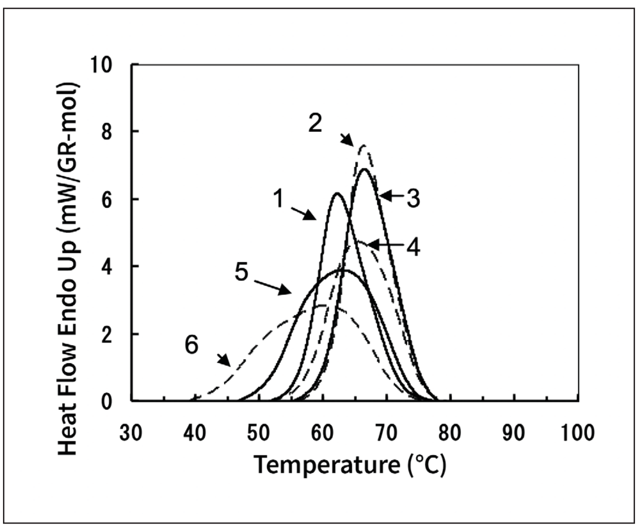
Fig. 2. In particular, a decrease of T_s was larger compared with those of T_p and T_c. Such gelatinization behavior of the cassava starch suspension was similar to that of corn starch suspension observed in our preceding study [9]. If compared at an identical caustic-ratio, however, T_s of the cassava starch suspension was obviously lower than that of the corn starch one, but not so much in T_c, resulting in a wider $T_{s\text{-}c}$ [9]. After the 1 h-preincubation at 30°C, the swelling starch ratio and viscosity of the cassava starch suspension increased at 9.7 mol% (**Figs. 3a** and **3b**).

2) Preincubations at 40°C and 50°C.

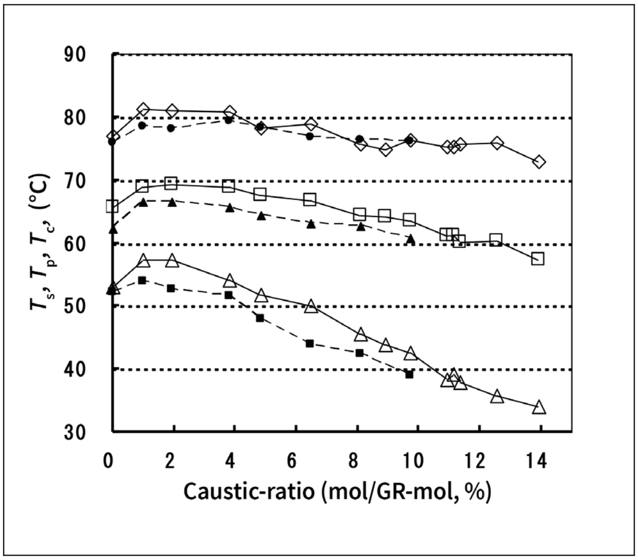
The cassava starch suspension after the preincubation at 40°C for 1 h at caustic-ratios of 0.97 mol%–4.9 mol% showed almost the same decrease of T_s (**Fig. 4**) as that at 30°C. At more than 4.9 mol%, T_s slightly decreased to 43.2°C at 9.7 mol%, which was near the preincubation temperature (40°C) and approximately 3.5°C higher than that at 30°C. However, T_p and T_c almost gradually decreased at 0.97 mol%–9.7 mol%, similar to the preincubation at 30°C. The swelling starch ratio and viscosity increased from 8.1 mol% and then surprisingly at more than 9.7 mol% (Figs. 3a and 3b).

The preincubation for 1h at 50°C decreased T_s up to 3.8 mol% (Fig. 4) similar to that at 30°C. At more than 3.8 mol%, T_s decreased gently to 48.1°C–52.3°C, which was also near the preincubation temperature (50°C) and approximately 4.2°C–6.0°C higher than that at 30°C. On the other hand, T_p and T_c gradually decreased, similar to the preincubations at lower temperatures. Furthermore, the swelling starch ratio and viscosity increased from 6.5 mol% and 4.9 mol%, respectively (Figs. 3a and 3b). The solute starch ratio remained low, even at higher caustic-ratios (Fig. 3c).

In the preincubations for 1 h at both 40°C and 50°C, the swelling starch ratio and viscosity of the cassava starch suspension increased from somewhat lower caustic-ratios compared with those of the corn starch suspension [9]. However, the solute starch ratio of the cassava starch suspension was less than that of the corn one [9]. This may be attributable to the poorly dispersing and dissolving properties of the gelatinized granules of cassava starch under weak agitation, which was in contrast to easy coagulation of the solubilized starch.



1. Effects of the caustic-ratio on differential scanning calorimetry (DSC) curves of the cassava starch suspensions after 1 h of preincubation at 30 °C. Caustic-ratio of curves 1–6 were 0, 0.97, 1.9, 3.8, 6.5, and 9.7 mol%, respectively.

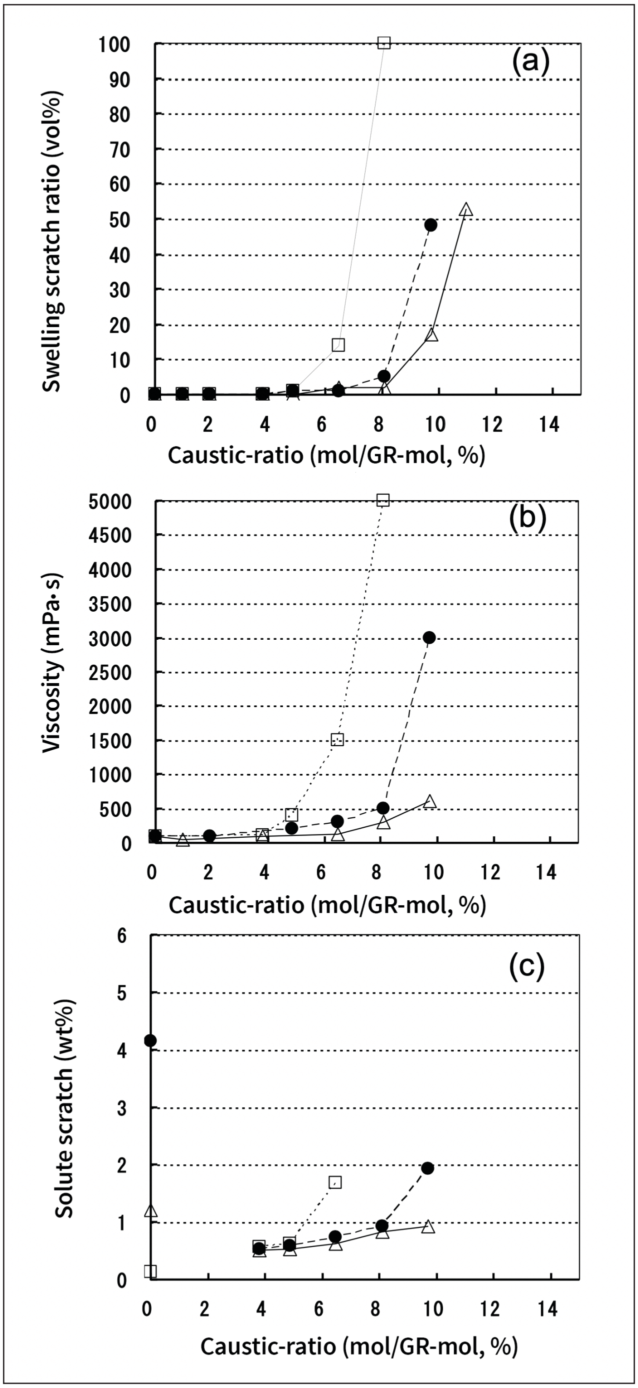


2. Comparison of the gelatinization temperatures of the cassava and the corn starch suspensions at various caustic-ratios after 1 h of preincubation at 30 °C: ■, T_s of cassava starch; △, T_s of corn starch; ▲, T_p of cassava starch; □, T_p of corn starch; ●, T_c of cassava starch; ◇, T_c of corn starch.

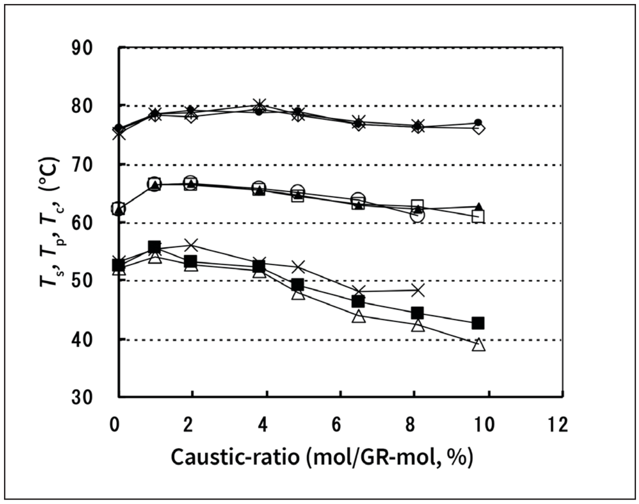
As shown in **Fig. 5**, *ΔH* values of the cassava starch suspensions after the preincubations at 30°C–50°C for 1 h slightly increased at lower caustic-ratios (0.97 mol%–1.94 mol%) and subsequently decreased with the caustic-ratios; there was a further gradual decrease as the preincubation temperature rose (30°C, $Y=-0.054X+2.67$, $R^2=0.683$; 40°C, $Y=-0.078X+2.73$, $R^2=0.889$; 50°C, $Y=-0.081X+2.79$, $R^2=0.824$; Y, *ΔH*; X, caustic-ratio), similar to the *ΔH* values of the corn starch suspensions [9].

Effect of prolonged preincubation on the gelatinization endotherms of corn starch suspensions containing sodium hydroxide

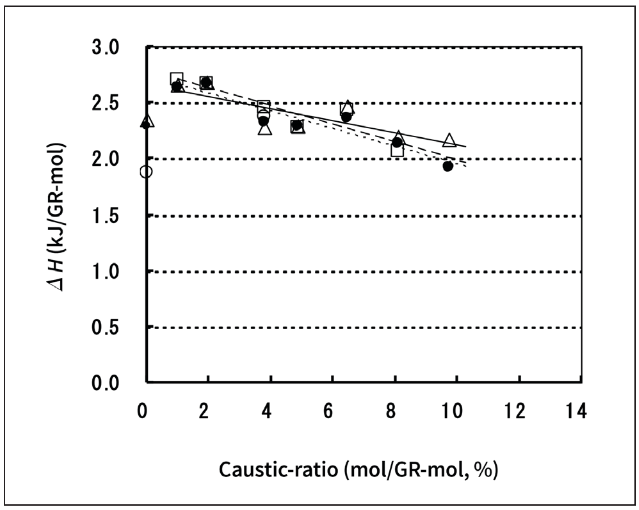
DSC studies were carried out to reveal the effect of preincubation time on the gelatinization endotherm of 25 wt% corn starch suspensions containing sodium hydroxide at four different preincubation temperatures (30°C, 40°C, 50°C, and 60°C). In **Fig. 6** and **Fig. 7**, all approximate lines were expressed in linear formula. Even after the preincubation at 30°C for 10 h, T_s, T_p, and T_c showed no considerable changes compared with those for 1 h in the caustic-ratios up to 10.9 mol%. At more than 11.1 mol%, T_s rose slightly (Fig. 6a), and the swelling starch ratios increased somewhat: The swelling starch ratios at 11.1 mol% and 12.6 mol% increased to 27 vol% and 53 vol% after 3 h of preincubation, and from 21 vol% and



3. Effects of the caustic-ratio on swelling starch ratio, viscosity, and solute starch ratio of the cassava starch suspension after 1 h of preincubation at 30°C–50°C: (a) Swelling starch ratio; (b) viscosity measured at 30°C; (c) solute starch ratio. Preincubation temperatures were: △, 30°C; ●, 40°C; □, 50°C.

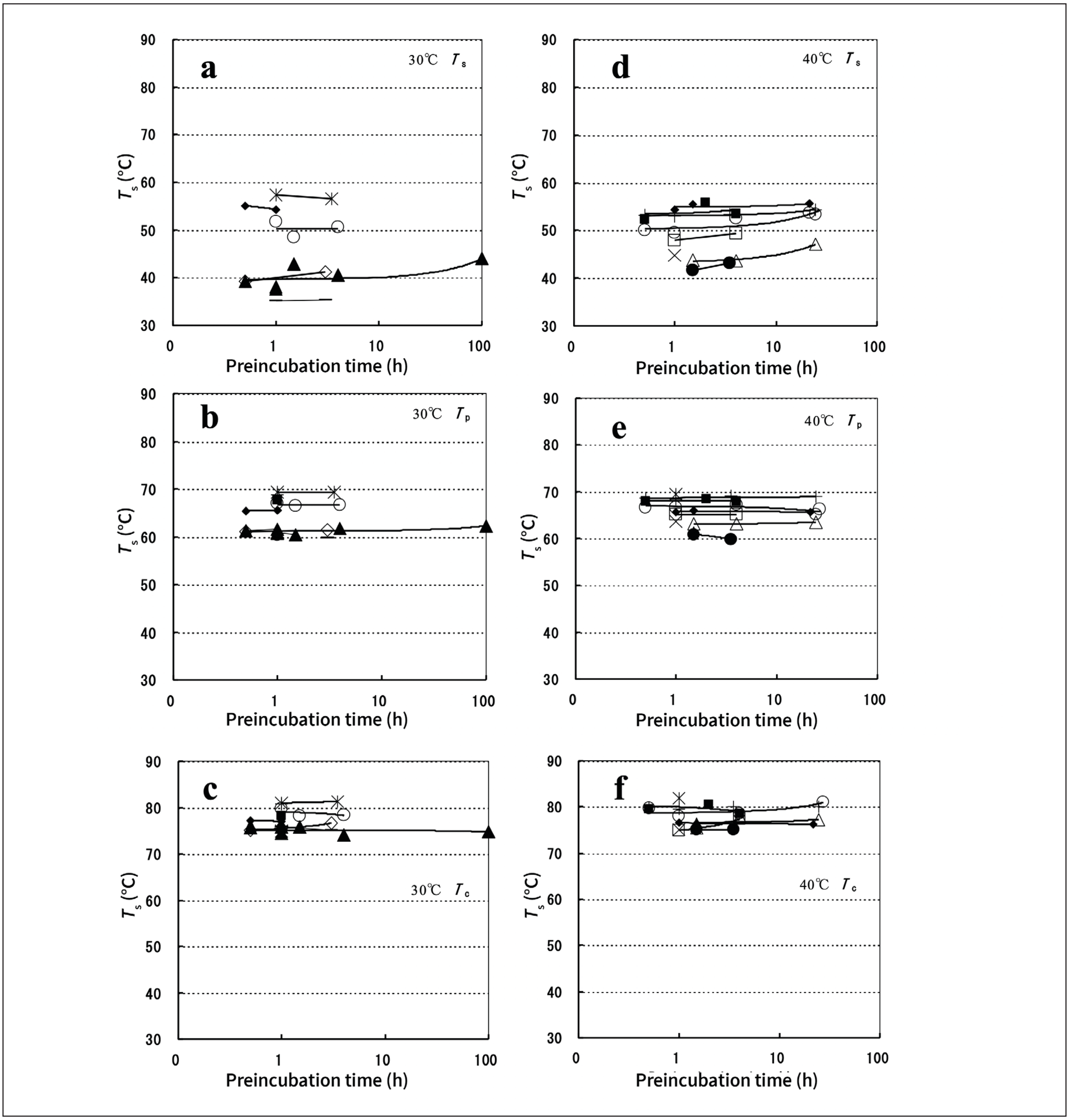


4. Effects of the caustic-ratio on gelatinization temperatures of the cassava starch suspensions after 1 h of preincubation at 30°C–50°C. Preincubation temperatures were: △, T_s at 30°C; ■, T_s at 40 °C; ×, T_s at 50°C; □, T_p at 30°C; ▲, T_p at 40 °C; ○, T_p at 50°C; ◇, T_c at 30°C; ●, T_c at 40°C; ∗, T_c at 50°C.



5. Effects of the caustic-ratio on ΔH of the cassava starch suspensions after preincubation at 30°C–50°C for 1 h. Preincubation temperatures were: △, at 30°C; ●, 40°C; □, 50°C.

45 vol% after 1 h, respectively. After 10 h at 40°C, T_s, T_p, and T_c were practically unchanged up to 8.9 mol% of the caustic-ratios. At more than 9.7 mol%, however, only T_s rose slightly compared with that after preincubation for 1 h; it rose by 3.4°C at 9.7 mol% after 24 h (Figs. 6d, 6e, and 6f). In the preincubation at 50°C, T_s rose by 1.5°C at 6.5 mol% after 3.5 h, by 7.7°C at 6.5 mol% after 24 h, and by 4.2°C at 8.1 mol% after 4 h, compared with each of those after the preincubation for 1 h, respectively, whereas T_p and T_c showed almost no rises after preincubation at both 40°C and 50°C (Figs. 7g, 7h, and 7i). Consequently, in the prolonged preincubation at 40°C and 50°C, gradual rises were observed—particularly for T_s at higher caustic-ratios in which T_s after the 1 h-preincubation declined to almost the same level at respective preincubation temperatures. Therefore, the endothermic peaks became somewhat narrower and deeper compared with those after 1 h of preincubation. The T_s of the corn starch suspension was lower than 60°C after the 1 h-preincubation at 30°C throughout the caustic-ratios tested (Fig. 6a) and consequently rose to

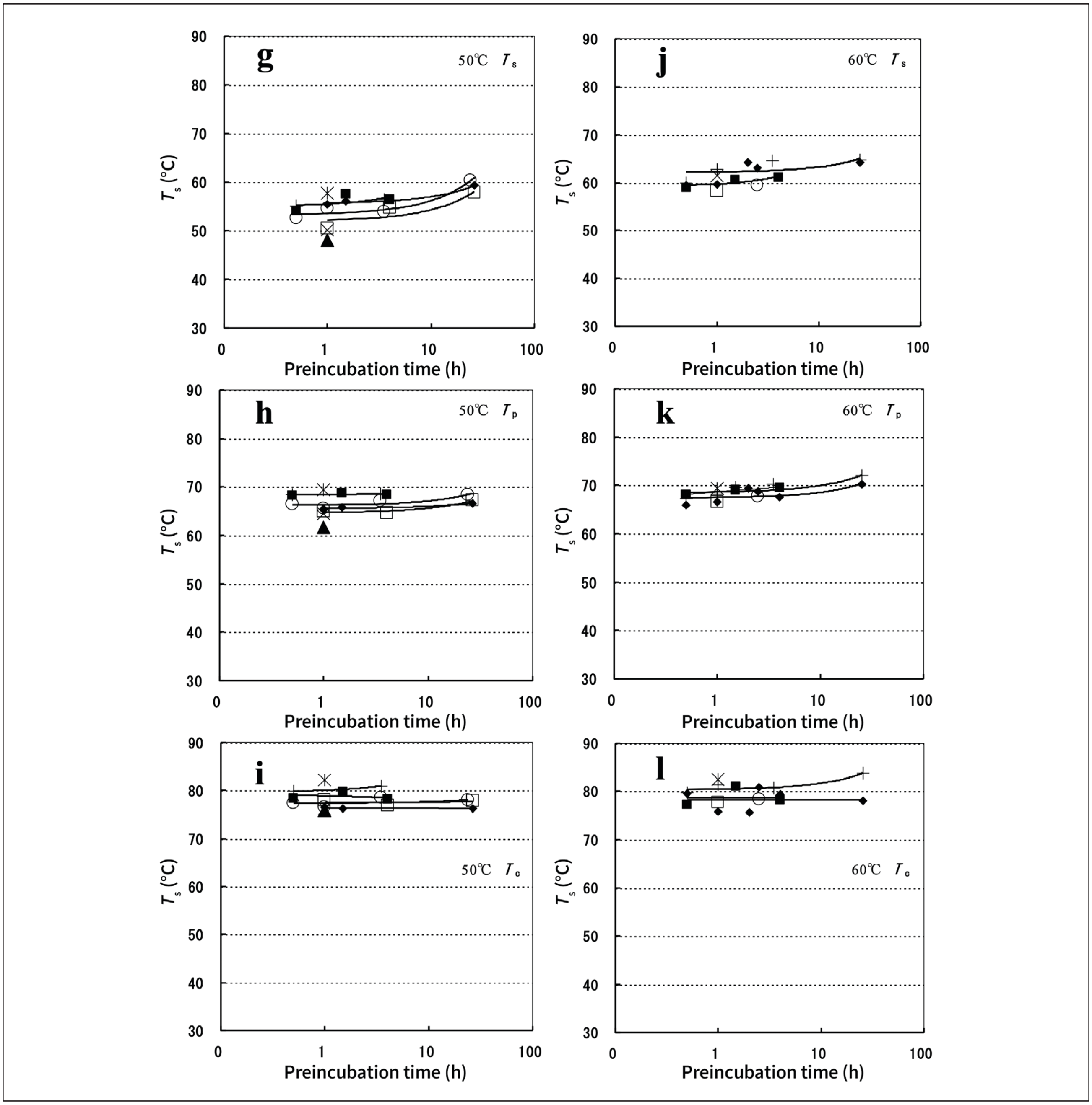


6. Effects of the preincubation time at 30°C and 40°C on gelatinization temperatures of the corn starch suspensions with added sodium hydroxide: a) T_s ***at 30°C; b)*** T_p ***at 30°C; c)*** T_c ***at 30°C; d)*** T_s ***at 40°C; e)*** T_p ***at 40°C; f)*** T_c ***at 40°C. Caustic-ratio (mol%): ◆, 0; ∗, 1.9; +, 3.8; ■, 4.9; ○, 6.5; □, 8.1; ×,8.9; △, 9.7; ▲,10.9; ◇, 11.1; ●, 11.3; –,12.6.***

around 60°C after 1 h of preincubation at 60°C (Fig. 7j). In the prolonged preincubation at 60°C, T_s and T_p rose slightly, even at lower caustic-ratios (0–4.9 mol%) and the endothermic peaks consequently changed more significantly than those after 1 h of preincubation (Figs. 7j, 7k, and 7l). Although ΔH scattered somewhat, it obviously tended to change a little in the prolonged preincubation (30°C–60°C) at the four temperatures (**Fig. 8**).

Comparison of gelatinization behaviors of cassava and corn starch suspensions containing sodium hydroxide.

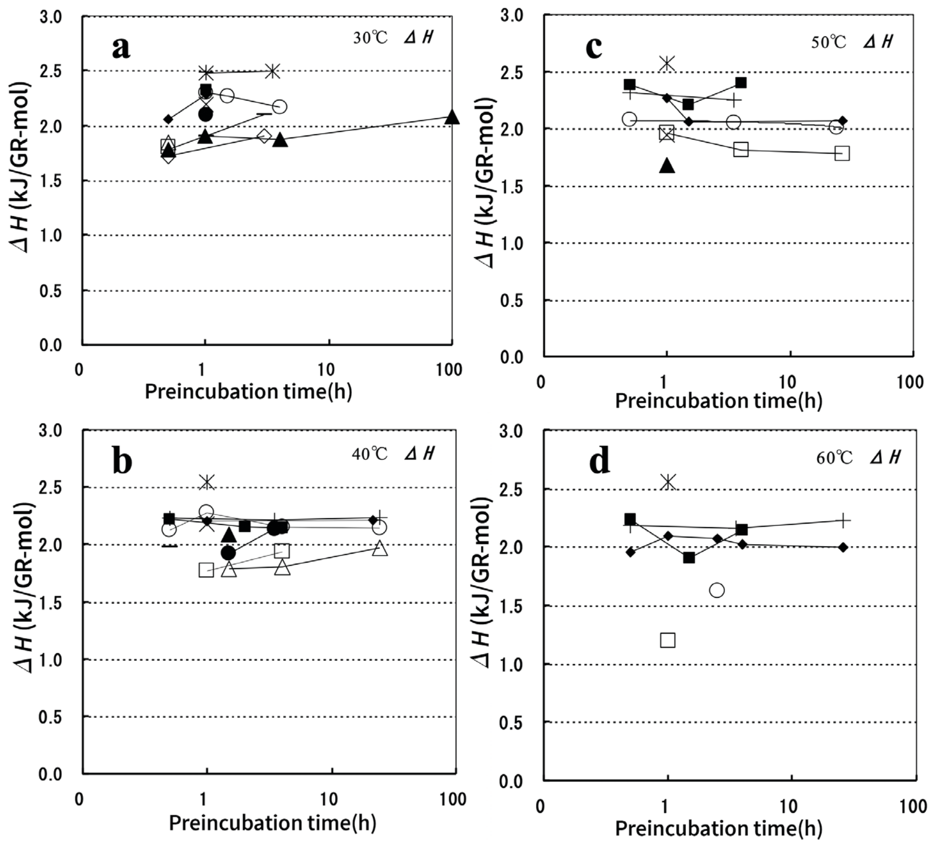
The T_s of the cassava starch suspensions after 1 h of preincubation at 30°C decreased to 50°C and 40°C at caustic-ratios of 4.1 mol% and 9.2 mol%, respectively. On the other hand, T_s of the corn starch suspensions [9] also decreased to 50°C and 40°C at 6.2 mol% and 10.7 mol%, respectively. The swelling



*7. Effects of the preincubation time at 50°C and 60°C on gelatinization temperatures of the corn starch suspensions with added sodium hydroxide: g) T_s at 50°C; h) T_p at 50°C; i) T_c at 50°C; j) T_s at 60°C; k) T_p at 60°C; l) T_c at 60°C. Caustic-ratio (mol%): ◆, 0; *, 1.9; +, 3.8; ■, 4.9; ○, 6.5; □, 8.1; ×, 8.9; △, 9.7; ▲,10.9; ◇, 11.1; ●, 11.3; –,12.6.*

starch ratio and the viscosity of the cassava starch suspensions also increased from slightly lower caustic-ratios after 1 h of preincubation, both at 40°C and 50°C, compared with those of the corn starch suspensions (Figs. 3a and 3b) [9]. To characterize the gelatinization of the two starches of different T_s at a same caustic-ratio, we introduced the temperature corresponding to the half gelatinization transition (T_m), at which ΔH ratio was 50%, as a common gelatinization indicator for the two starches. As shown in **Fig. 9**, when T_s and T_c of the two starch suspensions after the 1 h-preincubation at 30°C were plotted against T_m, T_s and T_c showed the common approximate lines to the two starch ones, respectively (T_s, y=1.70x—60.79 R^2=0.973; T_c, y=0.47x+47.72 R^2= 0.842; y, T_s or T_c; x, T_m).

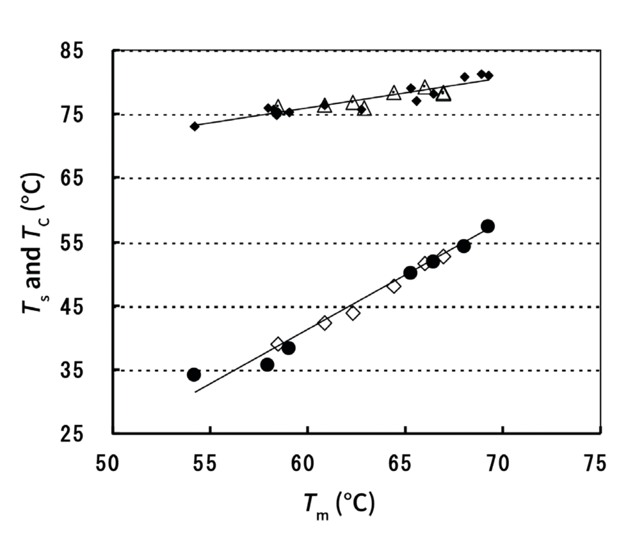
In summary, the cassava starch suspension commenced gelatinization from lower temperature at the same caustic-ratio compared with the corn starch suspension, whereas both starch suspensions, which had almost an equal T_m irrespective of the different caustic-ratio, showed similar gelatinization characteristics of almost the same T_s and T_c.



8. Effects of the preincubation time at 30°C–60°C on ΔH of the corn starch suspensions with added sodium hydroxide. Preincubation temperatures were: a) 30°C; b) 40°C; c) 50°C; d) 60°C. Caustic-ratio (mol%): ◆, 0; ∗, 1.9; +, 3.8; ■, 4.9; ○, 6.5; □, 8.1; ×, 8.9; △, 9.7; ▲,10.9; ◇, 11.1; ●, 11.3; –,12.6.

DISCUSSION

Our previous studies reported the notable effects of sodium hydroxide on the gelatinization of corn starch suspension compared with those of urea: Sodium hydroxide promoted the scission of intermolecular hydrogen bonds in the crystalline region of starch granules to accelerate the gelatinization rate [10], and increased the fluidity of gelatinized starch pastes [5] as well. Conversely, the scission of intermolecular hydrogen bonds by sodium hydroxide occasionally facilitated the realignment of starch molecules [10] and consequently increased the crystallinity of starch granules, which raised the gelatinization temperature at the low caustic-ratios of 0.97 mol%–1.94 mol%. As the caustic-ratio increased, the scission increased and the gelatinization temperature consequently decreased again. We indicated that similar increases in the crystallinity due to realignment of polymer molecules had often been observed for various polymers with the addition of plasticizers and heat treatment [10]. Biliaderis et al. [12] reported that water molecules acted as a plasticizer to promote relaxation of the amorphous region in the starch granules, which induced melting of the crystalline region at lower temperatures. We also indicated that sodium hydroxide acted similar to water molecules to loosen weakly bonding regions and cause gelatinization at low temperatures, lowering T_s significantly to increase $T_{s\text{-}c}$ [10]. This study also indicated that the gelatinization temperatures, especially T_s, of the cassava starch suspensions after the 1 h-preincubations at 30°C, considerably decreased as the caustic-ratio increased, similar to those of corn starch ones [9]. As shown in Figs. 1, 2, and 5: T_s, T_p, T_c, and ΔH also slightly rose at low caustic-ratios of 0.97 mol%–1.94 mol%, and subsequently decreased linearly with the caustic-ratio. It was considered also that these small rises were attributable to the occurrence of realignment of the cassava starch molecules by sodium hydroxide. The cassava starch suspensions commenced the gelatinization at lower caustic-ratio than corn ones after the 1 h-preincubations at 30°C, but both starch suspensions, which were lowered to the same T_m by the different caustic-ratio, showed extremely similar gelatinization characteristics of almost the same T_s and T_c (Figs. 2 and 8). T_s of the cassava starch suspensions after the 1 h-preincubations at higher temperatures of 40°C and 50°C gradually decreased near the respective preincubation temperatures as the caustic-ratio increased, but T_p and T_c simply



9. Relation between T_s and T_c against T_m in the cassava and the corn starch suspensions with added sodium hydroxide: ◇, T_s of cassava; ●, Ts of corn; △, T_c of cassava; ◆, T_c of corn.

decreased and remained almost the same, irrespective of the preincubation temperatures. Simultaneously, the swelling starch ratio and viscosity of the suspension began to increase from the caustic-ratios, in which a gradual decrease of T_s was observed (Figs. 3a, 3b, and 4). The *ΔH* after 1 h-preincubations at 40°C and 50°C gradually decreased as the caustic-ratios increased and as the preincubation temperatures rose compared with that at 30°C (Fig. 5). Such gelatinization behaviors of the cassava starch suspension were extremely similar to those of the corn one [9], although the cassava one commenced the gelatinization from lower caustic-ratio than did the corn one. The gelatinization transitions of both starch suspensions with added sodium hydroxide did not rapidly spread over the whole during the preincubations for 1 h at 30°C–50°C, but progressed stepwise. In both starch suspensions, the starch granules of T_s, which were lowered below the respective preincubation temperatures by sodium hydroxide, had already gelatinized in a limited fashion during the preincubations before the DSC measurement.

The stepwise gelatinization of starch suspensions without sodium hydroxide had been reported by several researchers. Shiotsubo [13,14] showed that the gelatinization degrees of the potato starch suspension reached the respective equilibrium states responding to the incubations at 52.5°C–72.0°C for 30–60 min. Ratnayake et al. [15] measured the gelatinization onset temperature, T_p, T_c, and *ΔH* of corn, wheat, and potato starches in excess water (17 wt%) that had been treated at a fixed temperature (35°C–90°C) for 30 min in a DSC apparatus. They indicated that the gelatinization progressed step by step in response to the elevation of the treatment temperature. On the other hand, Nakazawa et al. [16] measured the gelatinization temperature and the crystalline structure of rice starch after the incubation at the starch concentration of 50% for more than 100 h at various constant temperatures between 40°C and 85°C. They reported rises of T_p, as well as narrowed and deepened DSC spectra, indicating the system did not reach an equilibrium state even after 100 h, whereas *ΔH* became constant within only 5 min. On the other hand, in our investigation, during the prolonged preincubation of the 25 wt% corn starch suspension at a constant temperature between 30°C and 50°C, gradual rises were observed, particularly for T_s at higher caustic-ratios and higher preincubation temperatures than the commencing conditions of the stepwise gelatinization; for example, those of 9.7 mol% at 40°C and 6.5 mol% at 50°C (Figs. 2, 6, and 7). In the prolonged preincubation at 60°C commencing the stepwise gelatinization progress, T_s and T_p gradually rose throughout the caustic-ratios tested, including low 0–4.9 mol% (Figs. 7j, 7k, and 7l). The endothermic peaks became somewhat narrower and deeper at 40°C–50°C and further so at 60°C compared with those after 1 h-incubation, respectively. The *ΔH* values tended to change little in the prolonged preincubations at four temperatures (Fig. 8), which might be similar to the results reported by Nakazawa et al. [16] for the case without sodium hydroxide. The gelatinization transition of starch suspension was irreversible and not in a stable equilibrium state for a long period, which progressed in a stepwise manner in response to the increase of the caustic-ratio and/or to the rise of the temperatures used for the preparation and use of the adhesives [9]. The gelatinization temperature, especially T_s, of the starch granules considerably decreased stepwise in response to the increase of the caustic-ratio, and the granules of the lowered T_s gelatinized stepwise in a limited way in response to the rise of surrounding temperature. In addition, it was also important that the considerable reduction of T_s extended $T_{s\text{-}c}$ [10]. Such extension of $T_{s\text{-}c}$ seemed to give flexibility in the determination of a proper caustic-ratio to facilitate the control of the stepwise gelatinization (i.e., the amounts of the gelatinized starch) in the preparation of the adhesives at 40°C, and consequently enabled make up of adhesives with adequate viscosities [3,6-8]. The corrugating adhesives, especially NC-adhesive, had been prepared exactly on the basis of such stepwise gelatinization and the extension of $T_{s\text{-}c}$ caused by sodium hydroxide. It was suggested also that the adhesives in use and storage were still in the course of stepwise gelatinization, which was started by given conditions of the caustic-ratio and temperature (40°C–50°C) on the preparation [1,7-9]. The excessive progress of the stepwise gelatinization at use and during storage often inappropriately increased the adhesive viscosity, and consequently caused the unstable pickup volume of adhesives and deterioration in quality of corrugated paperboards, such as insufficient adhesion, warp, and washboard [2]. The adhesives should be used and stored at slightly lower temperatures and/or at slightly lower caustic-ratios than those of the preparation. Therefore, we concluded that the essential properties of starch granules to control the practical preparation and use of these adhesives were considerable stepwise reduction of the gelatinization temperature, especially T_s, in response to the increase of caustic-ratio and the stepwise gelatinization progress in response to the rise of surrounding temperature. **TJ**

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We have investigated the influences of sodium hydroxide on starch suspensions or corrugating starch adhesives since 2010, but the characteristics of the starch granules that were utilized in the preparation and use of the adhesives had not been elucidated in detail so far. This is a very important mechanism in the practical preparation and use of the corrugating adhesives, so we chose to study it.

The most difficult aspect of this research was that, to investigate the influences of temperatures and sodium hydroxide on the gelatinization characteristics of the adhesives, we had to preincubate the starch suspensions studied at temperatures of 30°C–60°C before the DSC measurement.

We learned that the essential properties of starch granules for controlling the practical preparation and use of the adhesives were a considerable stepwise reduction of the gelatinization temperature, especially the starting temperature in response to the increase of sodium hydroxide and the stepwise gelatinization progress in response to the rise of surrounding temperature. This stepwise gelatinization was our most interesting finding.

Based on our investigation, we expect to provide major benefits to the corrugated paperboard industry by increasing production speeds, saving heat energy, and stabilizing the quality of corrugated paperboard. Our next step is to summarize the influences of sodium hydroxide on corrugating adhesives revealed by our previous studies.

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