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Thermal studies on the gelatinisation and retrogradation of heat–moisture treated starch

T. Takaya, C. Sano, K. Nishinari*

Department of Food and Nutrition, Faculty of Human Life Science, Osaka City University, Sumiyoshi, Osaka, Japan

Abstract

The gelatinisation and regelatinisation of heat–moisture treated corn starches with different heating temperatures (120 and 130°C) and corn starch without treatment were studied by differential scanning calorimetry (DSC). The gelatinisation peak in the heating DSC curves shifted to higher temperatures with increasing temperature of heat–moisture treatment. The endothermic enthalpy of the gelatinisation decreased with the severity of heat–moisture treatment whilst those for the disintegration of amylose–lipid complex increased. The retrogradation ratio increased faster for heat–moisture treated corn starch than for corn starch without treatment. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Differential scanning calorimetry; Heat–moisture treatment; Corn starch; Gelatinisation; Retrogradation

1. Introduction

Although heat–moisture treated starch has been used as a texture modifier in the food industry, its gelatinisation and retrogradation are not understood so well.

The degree of crystallinity for wheat and potato starches evaluated from the X-ray diffraction patterns has been shown to decrease with heat–moisture treatment by Lorenz and Kulp (1983). As is well known, tuber starches such as potato starch show the typical B-type X-ray diffraction pattern whereas the typical A-type pattern is observed for cereal starches (Zobel & Stephen, 1995). Potato starch was converted to the intermediate of the typical A-type pattern and the B-type pattern with heat-treatment (Lorenz & Kulp, 1983).

Lorenz and Kulp (1982) have also shown that the swelling power and the viscograph hot plate consistencies decreased whilst the water-binding capacities as well as enzyme susceptibilities increased with heat-moisture treatment for various starches from barley, red millet, triticale, arrowroot and cassava.

Donovan, Lorenz and Kulp (1983) have studied the effect of heat–moisture treatment on thermal properties of wheat and potato starches by differential scanning calorimetry (DSC), and found the broadening of the gelatinisation temperature range and the shift of the gelatinisation endothermic peak to higher temperatures with heat–moisture treatment.

In order to shed some light upon these problems, the change in the regelatinisation behaviour of starch during storage has been observed in the present work.

2. Experimental

2.1. Materials

Heat–moisture treated corn starch HMS-120 (Lot No. 930619) and HMS-130 (Lot No. 930611) and corn starch without treatment (CS, Lot No. 930125) are gifts from Sanwa Starch Co. Ltd. HMS-120 and HMS-130 were prepared by heat–moisture treatment under the condition of saturated humidity for 20 min at 120 and 130°C, respectively, after evacuating to 10 kPa (Kudo, 1993).

2.1.1. Differential scanning calorimetry

Differential scanning calorimetry was performed by a sensitive DSC-8240 from Rigaku Denki Co Ltd (Tokyo) using a silver pan of 70 μl from Seiko Electronics Co Ltd (Tokyo). About 40 mg of a mixture of starch–water was sealed hermetically into a silver pan. Distilled water was used as a reference material. The temperature was raised from the room temperature (25 ± 1°C) to 130°C at 1°C/min for the first run heating. Then, the sample pan was cooled slowly to the room temperature and stored at 5°C

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* Corresponding author. Tel.: + 81-6-6605-2818; fax: + 81-6-6605-3086.

E-mail address: nisinari@life.osaka-cu.ac.jp (K. Nishinari)

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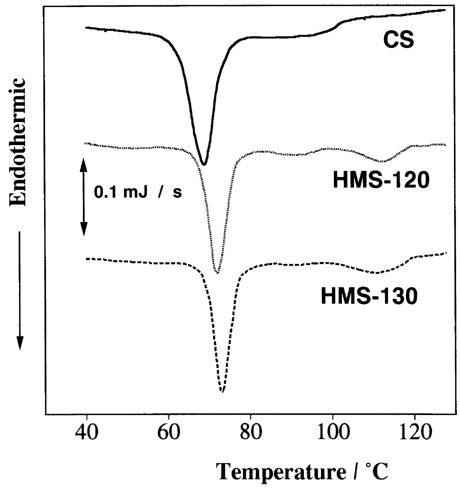

Fig. 1. Heating DSC curves for CS, HMS-120 and HMS-130. Concentration: 20%. Heating rate: 1°C/min.

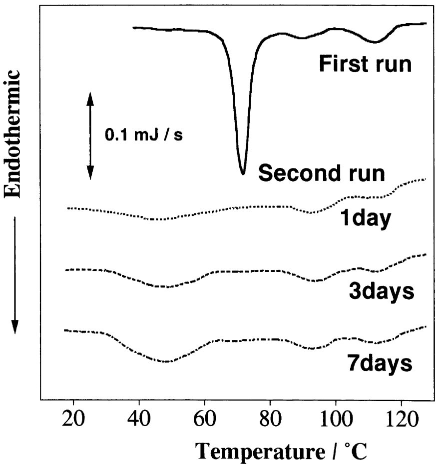

Fig. 3. The first and the second run heating DSC curves for HMS-120. Concentration: 20%. Heating rate: 1°C/min.

for a certain period. The second run heating DSC curve was observed for this sample from 5 to 130°C.

3. Results and discussion

Fig. 1 shows the heating DSC curves for 20% CS, HMS-120 and HMS-130 dispersions. A main endothermic peak accompanying gelatinisation was observed around 67°C, and another endothermic peak was observed around 90°C for CS. The higher temperature endothermic peak is attributed to the disintegration of the amylose–lipid complex (Zobel & Stephen, 1995). In addition to the endothermic peak around 90°C, an endothermic peak around 110°C appeared for both HMS-120 and HMS-130. The gelatinisation peak shifted to higher temperatures with increasing temperature of heat–moisture treatment. This phenomenon has been observed also for wheat and potato starches (Donovan et al., 1983). However, the gelatinisation peak did not broaden for corn starch in contrast to wheat and potato starches as observed by Donovan et al. (1983). The reason why the gelatinisation peak in heating DSC curves for wheat and potato starches broadened by heat moisture treatment has been attributed to the change to a more inhomogeneous structure. Kudo (1993) observed the granule structure of starch, and found that a hollow cavity was formed in heat moisture treated starch. The value of endothermic enthalpy of the gelatinisation decreased with the severity of heat–moisture treatment although the value of endothermic enthalpy of the disintegration of the amylose–lipid complex increased (Kudo, 1993; Zobel & Stephen, 1995).

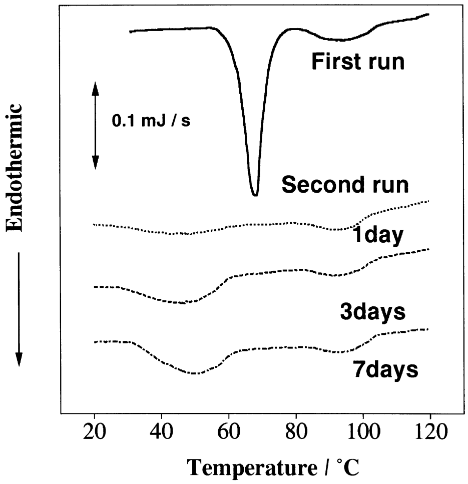

Fig. 2. The first and the second run heating DSC curves for CS. Concentration: 20%. Heating rate: 1°C/min.

Donovan et al. (1983) found the splitting of the gelatinisation peak into two peaks with heat–moisture treatment for both potato and wheat starches, while heat–moisture treated corn starch used in the present work did not show such a splitting. Multiple endothermic peaks in heating DSC curves have been observed in many polymeric materials, and have been attributed to the existence of structures with different thermal stabilities or polymorphism (Wunderlish, 1980). Since the heating rate in Donovan's experiment was 5°C/min, and that in our experiment was 1°C/min, the difference in the heating rate is quite important. Generally, the slower heating rate is more suitable to decompose an endothermic peak into multiple phases, i.e. with higher resolving power. Therefore, this difference should be attributed to the essential difference in granule structures of starches. The reason why the main gelatinisation peak around 67°C was not split into multiple peaks by heat–moisture treatment should be explored in the future. The higher temperature peak originating from the disintegration of the amylose–lipid complex split into two peaks with heat–moisture treatment for corn starch. This experimental finding is different from Donovan's finding for wheat starch.

Fig. 2 shows the second run heating DSC curves of non-treated CS after storage for 1, 3 and 7 days at 5°C together

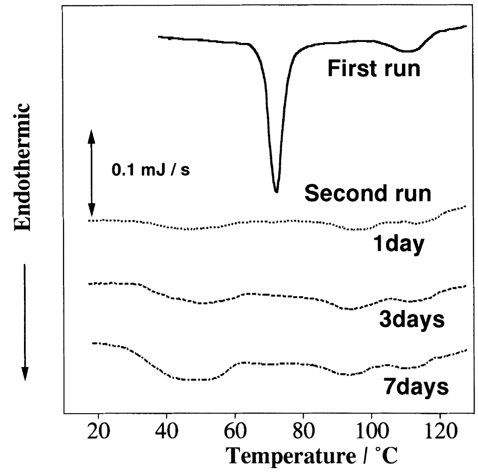

Fig. 4. The first and the second run heating DSC curves for HMS-130. Concentration: 20%. Heating rate: 1°C/min.

with the first run. The regelatinisation peak in the second run heating DSC curves shifted to a lower temperature than the gelatinisation peak in the first run heating DSC curve. It became larger and shifted slightly to a higher temperature with increasing storage time. It is well known that once the starch granules are disintegrated by gelatinisation, the ordered structure cannot be recovered completely even after storage at low temperatures for a long time (Yoshimura, Takaya & Nishinari, 1996). The higher temperature peak around 100°C originating from the disintegration of the amylose–lipid complex did not shift so much. Since amylose gelation plays an important role in the initial stage of retrogradation, and amylose forms a gel much faster than amylopectin (Miles, Morris, Orford & Ring, 1985), the present experimental findings are consistent with previous findings of Miles et al.

Fig. 3 shows the heating DSC curves of HMS-120 after storage for 1, 3 and 7 days at 5°C. The regelatinisation peak shifted to a lower temperature, and it became larger and shifted slightly to a higher temperature with storage time as shown in CS.

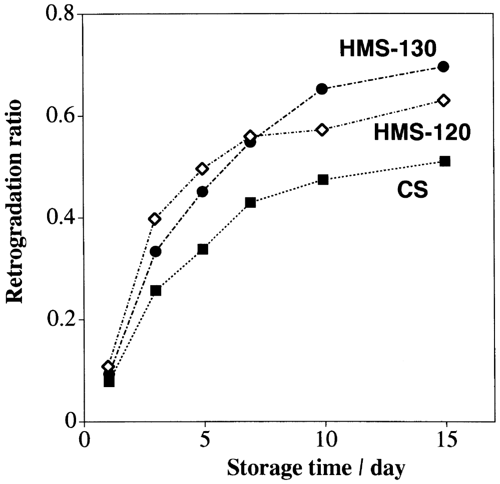

Fig. 5. Retrogradation ratio $\Delta H_2/\Delta H_1$ of CS, HMS-120 and HMS-130 as a function of storage time.

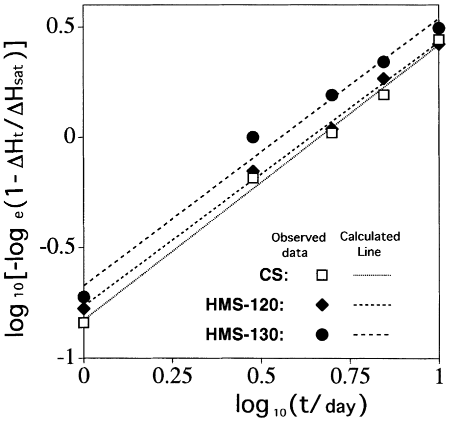

Fig. 6. Avrami's analysis for regelatinisation enthalpy of CS, HMS-120 and HMS-130.

Although only one higher temperature peak originating from the disintegration of the amylose–lipid complex was observed at 110°C for HMS-130 in the first run DSC heating curve, the second run DSC heating curve after storage showed two endothemic peaks at 90 and 110°C (Fig. 4). This should be attributed to the formation of ordered structures with different thermal stabilities in HMS-130 after the first run heating. The detailed mechanism of this phenomenon should be explored in the future.

Fig. 5 shows the retrogradation ratio $\Delta H_2/\Delta H_1$ for CS, HMS-120 and HMS-130 as a function of storage time. The retrogradation ratio was defined as the ratio of the regelatinisation enthalpy ΔH_2 in the second run DSC heating to the gelatinisation enthalpy ΔH_1 in the first run DCS heating (Kohyama & Nishinari, 1991). The increase of retrogradation ratio became faster by heat moisture treatment.

Fig. 6 shows Avrami's analysis for regelatinisation enthalpy of CS, HMS-120 and HMS-130. Avrami's theory has often been employed for kinetic study of the retrogradation of gelatinised starch (Colwell, Axford, Chamberlain & Elton, 1969; McIver, Axford, Colwell & Elton, 1968; Wong & Lelievre, 1982). The regelatinisation enthalpy can be written as follows:

$$\frac{\Delta H_{\mathrm{sat}} - \Delta H_t}{\Delta H_{\mathrm{sat}} - \Delta H_0} = \exp(-kt^n)$$

where ΔH_{sat} the saturated value of regelatinisation enthalpy, ΔH_t is the value of regelatinisation enthalpy at time t, ΔH_0 is the initial value at $t = 0$, and k is the rate constant. When $\log_{10}[-\log_e(1 - \Delta H_t/\Delta H_{\mathrm{sat}})]$ is plotted against $\log t$, the Avrami exponent (n) is obtained from the slope of the straight line, and the rate constant is obtained from the intercept, $\log k$. In the present case, the slope of the straight lines is approximately unity, which indicates instantaneous nucleation followed by rod-like growth of crystals (Cowie, 1991). The value of n did not change by the severity of the heat–moisture treatment, whilst the k value increased with the severity of the heat–moisture treatment.

These thermal results show that the starch gels, especially amylose fraction, retrograde immediately on cooling, and that the heat–moisture treatment promotes the retrogradation of corn starch.

References

Colwell, K. H., Axford, D. W. E., Chamberlain, N., & Elton, G. A. H. (1969). *Journal of Science and Food Agriculture*, *20*, 550–555.

Cowie, J. M. G. (1991). *Polymers: chemistry and physics of modern materials*, 2. Glasgow and London: Blackie.

Donovan, J. W., Lorenz, K., & Kulp, K. (1983). *Cereal Chemistry*, *60*, 381–387.

Kohyama, K., & Nishinari, K. (1991). *Journal of Agriculture and Food Chemistry*, *39*, 1406–1410.

Kudo, K. (1993). *Proceedings of Australia/Japan Symposium on Food Science and Technology 1993* (pp. 205–210).

Lorenz, K., & Kulp, K. (1982). *Starch*, *34*, 50–54.

Lorenz, K., & Kulp, K. (1983). *Starch*, *35*, 123–129.

McIver, R. G., Axford, D. W. E., Colwell, K. H., & Elton, G. A. H. (1968). *Journal of Science and Food Agriculture*, *19*, 560–563.

Miles, M. J., Morris, V. J., Orford, P. D., & Ring, S. G. (1985). *Carbohydrates Research*, *135*, 271–278.

Wong, R. B. K., & Lelievre, J. (1982). *Starch*, *34*, 231–233.

Wunderlish, B. (1980). *Macromolecular physics. Crystal melting*, 3. New York: Academic Press.

Yoshimura, M., Takaya, T., & Nishinari, K. (1996). *Journal of Agriculture and Food Chemistry*, *44*, 2970–2976.

Zobel, H. F., & Stephen, A. M. (1995). Starch: structure, analysis, and application. In A. M. Stephen (Ed.), *Food polysaccharides and their applications* (pp. 19–66). New York: Dekker.