Effects of the Noncyclic Cyanamides on the Retrogradation of Waxy Corn Starch

Kazuo Ogawa,*,# Kenji Aso, Shin Ono,*
Toshiaki Yoshimura, Seichi Rengakuji,
Yuuko Nakamura, Isao Yamazaki,†
Satoru Murotani, and Choichiro Shimasaki

Department of System Engineering of Materials and Life Science, Faculty of Engineering, Toyama University,
3190 Gofuku, Toyama 930-8555

†Yayoikagaku Kogyo Co., Ltd., 70 Honryo, Fukuoka-machi, Toyama 939-0135

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The suppressive effects of noncyclic cyanamides (guanidine hydrochloride, urea, and thiourea) on the retrogradation of waxy corn starch (WCS) gel were examined using differential scanning calorimetry and X-ray powder diffraction. We demonstrated that thiourea, guanidine hydrochloride, and urea effectively suppressed the retrogradation of the WCS gel in this order.

To search for compounds that suppress the retrogradation of starch, we studied the retrogradation process of waxy corn starch (WCS) using differential scanning calorimetry (DSC), X-ray diffraction, FT-IR, and solid-state NMR.[1,2] Moreover, the effect of guanidine hydrochloride (Gu-HCl) on the retrogradation of WCS was examined; consequently, Gu-HCl was suggested to suppress retrogradation due to a hydrogen bond-forming ability.[2,3] On the other hand, we also examined the effects of noncyclic cyanamides on the gelatinization of WCS, and have reported that Gu-HCl, urea, and thiourea could promote the gelatinization of WCS.[4] Such noncyclic cyanamides having hydrogen bond-forming ability should cause a disruption of the hydrogen bonds among the O–H groups of WCS molecules in the crystal state, resulting in the promotion of gelatinization. These results have suggested that intra- and intermolecular hydrogen-bond formations in the WCS gel should be involved in the gelatinization and retrogradation processes. In this work, the effects of noncyclic cyanamides on the retrogradation of the WCS gel were studied using DSC and X-ray powder diffraction. The urea, Gu-HCl, and thiourea were used as noncyclic cyanamides.

Results and Discussion

We measured the re-gelatinization enthalpy changes for WCS gels with and without urea, Gu-HCl, and thiourea as a function of the storage time at −2 °C (Fig. 1). In this experiment, each content of the noncyclic cyanamides was expressed in a molar quantity per 1 mg of WCS. The re-gelatinization enthalpy for WCS gel without the noncyclic cyanamides increased with increasing the storage time, indicating the progress of the retrogradation of WCS during 30-day storage.

On the contrary, the increasing rates of the re-gelatinization enthalpy values decreased upon the addition of urea, Gu-HCl, and thiourea, compared with that for WCS gel without the noncyclic cyanamides. The endothermic peak corresponding to the re-gelatinization of the WCS gel appeared when thiourea (0.5×10^{-5} mol mg^{-1} of WCS) was added, but the re-gelatinization endothermic peak of the WCS gel containing thiourea (1.0×10^{-5} and 1.5×10^{-5} mol mg^{-1} of WCS) was not observed during 120-day storage (Fig. 1C). A similar suppressive effect on the retrogradation of WCS was observed in the cases of urea and Gu-HCl (Figs. 1A and 1B). However, the suppressive effects of urea and Gu-HCl were weaker than that of thiourea under the same conditions. For example, the re-gelatinization enthalpy values for WCS gels containing Gu-HCl and urea (1.5×10^{-5} mol mg^{-1} of WCS) during storage for 120 d were 0.35 and 1.2 J g^{-1}, respectively, while the WCS gel containing the same amount of thiourea gave no endothermic peak, even during storage

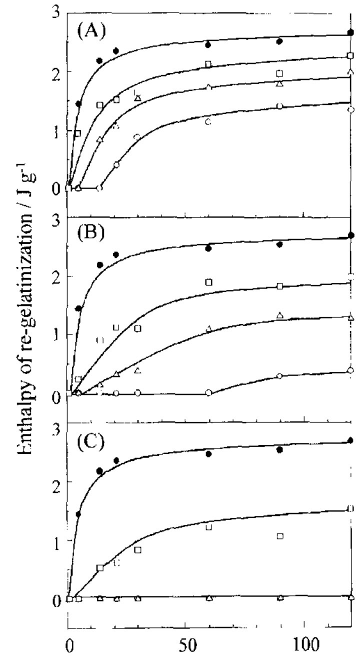

Fig. 1. Changes in the re-gelatinization enthalpy for 20% WCS gels containing (A) urea, (B) Gu-HCl, and (C) thiourea as a function of storage time. The contents of the noncyclic cyanamides were 0 (●), 0.5×10^{-5} (□), 1.0×10^{-5} (△), 1.5×10^{-5} (○) mol mg^{-1} of WCS.

Present address: Department of Materials Science, Yonago National College of Technology, 4448 Hikona-cho, Yonago 683-8502, Japan.

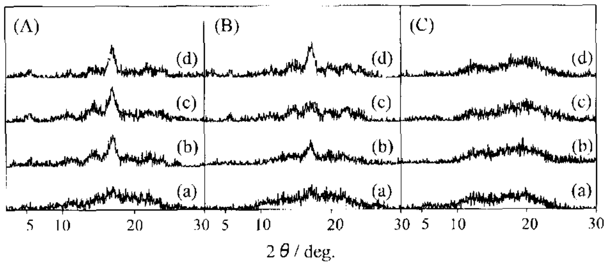

Fig. 2. X-Ray diffractograms for 20% WCS gel to, which (A) urea, (B) Gu-HCl, and (C) thiourea 1.0×10^{-5} mol mg^{-1} of WCS was added, obtained (a) immediately after the gelatinization, and that stored for (b) 30 d, (c) 60 d, and (d) 120 d.

Table 1. Comparison of Relative Energies for Hydrogen Bonds formed by Urea and Thiourea

Hydrogen bond	Relative energy[a)]/kJ mol^{-1}
Urea (C=O)–Water (O–H)	13.68
Urea (C=O)–Methanol (O–H)	13.37
Thiourea (C=S)–Water (O–H)	13.07
Thiourea (C=S)–Methanol (O–H)	12.61

a) Relative energies were calculated at the ab initio level and within the frame of DFT at the Becke3LYP/6-311++G (3df, 2pd) level with the Gaussian 94 program.

for 120 d. All of these results demonstrate that the retrogradation of WCS is effectively suppressed by the addition of thiourea, Gu-HCl, and urea in this order.

A gelatinized starch in the amorphous state is found to partly transform to a B-form structure upon storage at low temperature.[5,6] Therefore, to examine the effect of the noncyclic cyanamides on WCS retrogradation, we also compared the X-ray diffraction patterns for WCS gels with and without urea, Gu-HCl, and thiourea during storage at −2 °C. For WCS gels containing urea and Gu-HCl, the X-ray diffraction patterns corresponding to the B-form structure were seen after storage for 30 d (Figs. 2A and 2B). On the other hand, such a B-form pattern was not observed for WCS gel containing thiourea during 120-day storage (Fig. 2C). Moreover, the appearance of the B-form pattern was suppressed with increasing the content of the noncyclic cyanamides. For example, a disappearance of the B-form pattern was observed for WCS gel containing Gu-HCl during 120-day storage (1.5×10^{-5} mol mg^{-1} of WCS), but not for WCS gel containing urea at the same content (data not shown). As a result of all the X-ray diffraction data, it was also demonstrated that noncyclic cyanamides (thiourea, Gu-HCl, and urea) effectively suppress the retrogradation of WCS in this order, based on the above DSC data.

The suppressive effect of noncyclic cyanamides on the retrogradation of WCS should be related to their hydrogen bond-forming abilities. To estimate the difference in the hydrogen bond-forming abilities between urea and thiourea, the relative energies for their hydrogen bonds formed with H_2O and methanol were calculated as model systems using GAUSSIAN 94, as shown in Table 1. The relative energies for thiourea–H_2O and thiourea–methanol are slightly smaller than those for urea–H_2O and urea–methanol. However, these data (12.61—13.68 kJ mol^{-1}) indicate that both urea and thiourea can form stable hydrogen bonds with the hydroxy groups in the WCS gel, and that there is no significant difference in the hydrogen bond-forming ability.

The retrogradation of starch means re-crystallization resulting from the dehydration of water molecules hydrogen-bonded to gelatinized starch. This phenomenon should be involved in the properties of water to form a hydrogen-bonded network structure. Although there is no substantial difference in the hydrogen bond-forming ability between thiourea and urea, as described above, the molecular size of thiourea is larger than that of urea due to the difference between sulfur and oxygen atoms. Therefore, the existence of thiourea might more effectively change the structure and properties of water than urea, consequently resulting in a suppression of the dehydration from WCS. In addition, thiourea might also protect the WCS molecule chains from the close contact required for re-crystallization. Similar effects of thiourea were also observed for the gelatinization of WCS, i.e., thiourea more effectively promoted the gelatinization of WCS than urea.[4] Thus, thiourea should affect the gelatinization of WCS in a similar way for retrogradation.

Experimental

DSC measurements were carried out using a Rigakudenki DSC 8230B, and the temperature profile for all samples sealed in aluminum pans was from 30 to 100 °C at a heating rate of 5 °C min^{-1}. Water sealed in the same pan was used as a reference.

X-Ray diffraction analyses were performed with a Rigakudenki MJ200HS9 powder X-ray diffractometer operating at 40 kV and 20 mA with Cu $K\alpha$ radiation. The diffractograms were recorded from 2° to 30° (diffraction angle, 2θ) at a scanning rate of 2° min^{-1}.

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