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Influence of β-cyclodextrin on the short-term retrogradation of rice starch

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ABSTRACT

The effect of β-cyclodextrin (β-CD) on short-term retrogradation of rice starch was studied. Retrogradation of normal rice starch was reduced more by β-CD than by glycerol monostearate (GMS). β-CD reduced the rate of retrogradation of amylose and normal rice starch but not waxy rice starch. Differential scanning calorimetry (DSC) detected a potential amylose-β-CD complex formation. DSC data were analysed using the Avrami equation. Results showed that β-CD significantly lowered the crystallizing rate (k) and increased the Avrami exponent (n) of amylose recrystallisation ($P < 0.05$). Molecular dynamics (MD) simulation indicated that the stability of the complex was primarily due to non-bonded interactions, such as Van der Waals (Vdw forces), electrostatic force, and hydrogen bonds formed in the presence of β-CD.

1. Introduction

Starch has been incorporated in many ready-meals or precooked chilled foods as an additive or main raw material. As a raw material, the gelatinisation and retrogradation properties of rice starch are important as they affect the sensorial attributes and shelf life of cooked starch gels or starch-containing foods. It has been known that preparation of starch-based products with extended shelf life requires effective retardation of starch retrogradation. Previous studies have reported that the saturated fatty acid, stearic acid, preferentially complexed with amylose and produced a significant decrease in the retrogradation enthalpy compared to that of native starch (Zhou, Robards, Helliwell, & Blanchard, 2007). Food additives, such as non-ionic polysaccharides, food hydrocolloids, and emulsifiers, can interact with starch components and reduce short-term retrogradation (Funami, Kataoka, Omoto, Asai, & Nishinari, 2005a; 2005b). The mechanism of these additives is based on their partial interaction with amylose, which causes an improvement in physical properties of some concentrated starch systems during heating, cooling, and storage (Keetels, Van Vliet, Jurgens, & Walstra, 1996). Furthermore, Vandeputte, Vermeylen, Geeroms, and Delcour (2003) have reported that the rapid recrystallisation of starch relies on the levels of free amylose, the amylose–lipid complex, and also other components.

β-Cyclodextrin (β-CD) is a cyclic and non-reducing oligosaccharide, composed of D-glucose units linked by α-1,4 glycosidic bonds in a donut-shaped ring (Lindner & Saenger, 1982). Its aperture can form inclusion complexes with organic and inorganic molecules in aqueous solution because of its hydrophobic core. Nowadays, β-CD is used to incorporate poorly water soluble ingredients into food, cosmetic and pharmaceutical products. Water-insoluble ingredients interact with β-CD, causing an increase in the stability and apparent water solubility (Loftsson & Duchene, 2007). For example, β-CD has been used for removing cholesterol from cream in the food industry (Shim, Ahm, & Kwak, 2003). Szente and Szejtli (2004) used β-CD to mask or reduce undesired taste, protect against light-induced decompositions and prolong shelf life of food products. Kim and Hill (1984) also found that β-CD significantly increased swelling and solubility of cereal starches. Importantly, β-CD produced an increase in the initial gelatinisation temperature and disrupted amylose–lipid complex formation within the starch granules by complexing with starch lipids (Gunaratne, & Corke, 2007; Kim & Hill, 1984). It is essential to know whether there is a formation or not of an amylose-β-CD complex in the environment of an amylose/β-CD/water mixture, and its potential impact on the short-term retrogradation of rice starch.

The research reported here had two objectives. The first objective was to compare the retardation effect of β-CD and GMS on rice starch retrogradation. GMS is a good anti-retrogradation additive, commonly applied in the food industry. The second objective was to determine the potential amylose-β-CD complex formation

Abbreviations: β-CD, β-cyclodextrin; DSC, differential scanning calorimetry; MD, molecular dynamics; Vdw, Van der Waals; SA, standard amylose; GMS, glycerol monostearate.

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by using DSC and analysing the results using the Avrami model and molecular dynamics (MD) simulation.

2. Materials and methods

2.1. Materials

Waxy rice starch (amylose content 2.1%, proteins content ⩽0.1%, lipids content ⩽0.1%) and normal rice starch (amylose content 29.7%, proteins content ⩽0.2%, lipids content ⩽0.1%) were isolated and purified from various milled fresh grains (Shandong, China) according to previously described protocols (Takeda, Hizukuri, & Juliano, 1986). A rice amylose sample (amylose content 86.3%, proteins content ⩽0.2%, lipids content ⩽0.1%) was purified from the normal rice starch by repeating a butanol-isopentanol (3:1, v/v) sedimentation operation three times. A standard amylose (SA) of rice starch was purchased from Sigma–Aldrich Trading Co., Ltd. (Shanghai, China). β-CD was obtained from Seebio Inc. (Shanghai, China). All other chemicals and reagents were of analytical grade unless otherwise stated.

2.2. Preparation of sample/β-CD and sample/GMS blends

Normal rice starch (1 g) was added to the β-CD solutions, which were prepared by dissolving 0, 5, 10, 15, 20 and 25 mg of β-CD in water (2 ml). The mixtures were gently shaken and heated for 20 min in a vacuum oven at 100 °C and cooled to 25 °C. Waxy rice starch/β-CD and rice amylose sample/β-CD blends were treated in the same manner. GMS solutions, in different concentrations, were prepared by dissolving GMS in ethanol (2 ml) instead of water. The normal rice starch (1 g) was incorporated in the solutions, after which the solvent was evaporated in a vacuum oven at 40 °C. Further water (2 ml) was injected twice into the dry mixture and this blend was heated for 20 min in the vacuum oven at 100 °C and cooled to 25 °C. SA/β-CD mixture was prepared, with the same treatment, by incorporating SA (100 mg) in solutions (0.2 ml) with different β-CD concentrations. These suspensions were gently shaken before the water was evaporated in an oven at 40 °C. SA, treated in the same manner but without β-CD, was provided as a control.

2.3. Degree of retrogradation

The extent of starch retrogradation was measured by an enzymatic method previously described by Tsuge, Hishida, Iwasaki, Watanabe, and Goshima (1990). The degree of starch retrogradation was expressed by the change in gelatinisation.

2.4. DSC measurement

Thermal analysis was performed by using a Pris 1 DSC (Pekin–Elmer, USA) under an ultrahigh-purity nitrogen atmosphere. The equipment was calibrated with indium and tin standards. The prepared samples (β-CD, SA, or SA/β-CD mixtures of 3 mg) and distilled water (6 μl) were together placed in an aluminium pan. The sealed samples were equilibrated for 12 h at 25 °C and then heated from 25 °C to 160 °C at a constant rate of 10 °C/min to detect the transition peak and temperatures. An aluminium pan containing 6 μl of distilled water was used as a reference.

2.5. Isothermal crystallisation

Prepared SA/β-CD samples with distilled water (6 μl) were heated by DSC from 25 °C to 125 °C, kept at 125 °C for 5 min to erase all previous thermal records, and then quenched to the isothermal crystallisation temperature (25 °C) at a nominal rate of 80 °C/min. The resulting samples were stored at 25 °C for 1, 3, 5, 7, 10, and 14 h, and rescanned from 25 °C to 160 °C at a heating rate of 10 °C/min to melt the retrograded amylose crystallites and record the enthalpy change. Data collected were used to perform the Avrami analysis. Empty pans, including 6 μl of distilled water, were used as controls for all measurements.

2.6. Molecular dynamics (MD) modelling

Molecular dynamics simulations of amylose/β-CD interaction in periodic boundary conditions were conducted by the MD model of HYPERCHEM 7.5 software (Hypercube Inc. Waterloo, Canada). In brief, the previously proposed models of the amylose system were composed of 2, 3,. . ., 8 fractions, respectively, each fraction including 14 polymeric glucose units in a rather stiff left-handed helix. The fractions were arranged along a circle (around the *X*-axis), symmetrically, with radius (*R*) of 15 Å, designated by the origin of coordinate (the core of β-CD molecule) to the mass centre per fraction. Fig. 1 shows the view of pre-optimised conformations of two amylose fractions including a β-CD molecule. Fractions were minimised energetically using the AMBER force field by imposing a restraint on a gradient of 0.01 × 4.186 8 kJ/mol Å in the presence and absence of a β-CD molecule. The atom-based cutoff of 12 Å was used for non-bonded interactions, depending on the system. The molecular dynamics simulations were performed directly at 27 °C and a time step of l fs, and the total simulation time was 1 ns. The collected data were analysed to investigate which force interaction had a key role in enhancing the stability of the amylose/β-CD complex.

2.7. Statistical analysis

The data were expressed as means of triplicate determinations. Statistical significance was assessed with one-way analysis of variance (ANOVA) using the ORIGIN 7.5 (OriginLab Inc. USA) for windows programme. Treatment means were considered significantly different at $P < 0.05$.

3. Results and discussion

3.1. Retrogradation behaviour of starch samples

Retrogradation of normal rice starch was reduced when GMS and β-CD were present (Fig. 2). Retrogradation of starch decreased with increased concentration of both GMS and β-CD. At a given concentration, the degree of starch retrogradation was significantly lower with β-CD than with GMS ($P < 0.05$). The difference in retrogradation degree might be attributed to the difference in the percentage of free starch. Richardson, Kidman, Langton, and Hermansson (2004) reported that the decrease in the amount of free starch by an emulsifier was an important factor in altering the retrogradation characteristics of starch. In addition, Keetels et al. (1996) reported that the structures of GMS and β-CD molecules were responsible for the retardation effect of these additives on retrogradation, based on the thermodynamic compatibility of starch/additive. In a starch/GMS system, the hydrophobic part of GMS is thought to be partially inserted into the amylose helix to form an amylose–GMS complex (Biliaderis & Seneviratne, 1990). It has been proposed that β-CD can disrupt the amylose–lipid complex and form a new amylose-β-CD and lipid complex (Gunaratne & Corke, 2007). This formation indicates that starch might preferentially interact with β-CD compared to GMS, which would affect the retrogradation characteristics of starch.

β-CD reduced retrogradation of amylose and normal starch samples but did not affect retrogradation of waxy starch (Fig. 3).

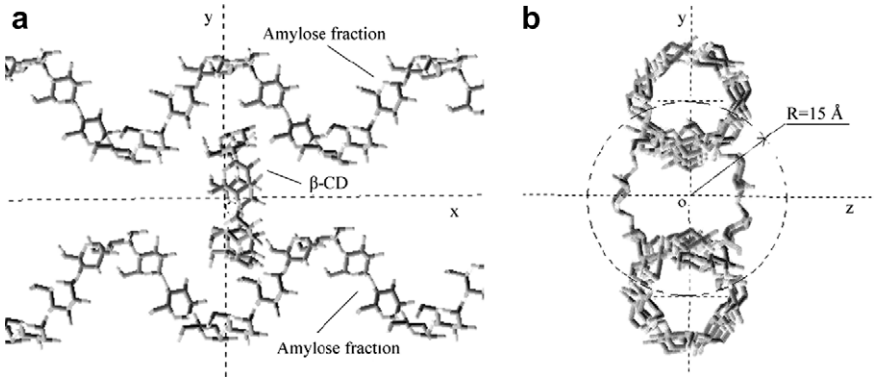

Fig. 1. Views of pre-optimized conformation of two amylose fractions with a β-CD molecule along (a) *z*-axis, (b) *x*-axis.

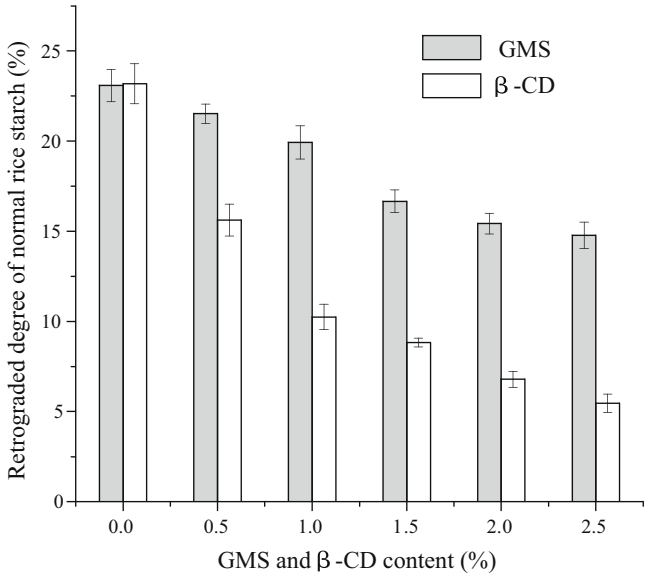

Fig. 2. Inhibition of retrogradation of normal rice starch by GMS and β-CD.

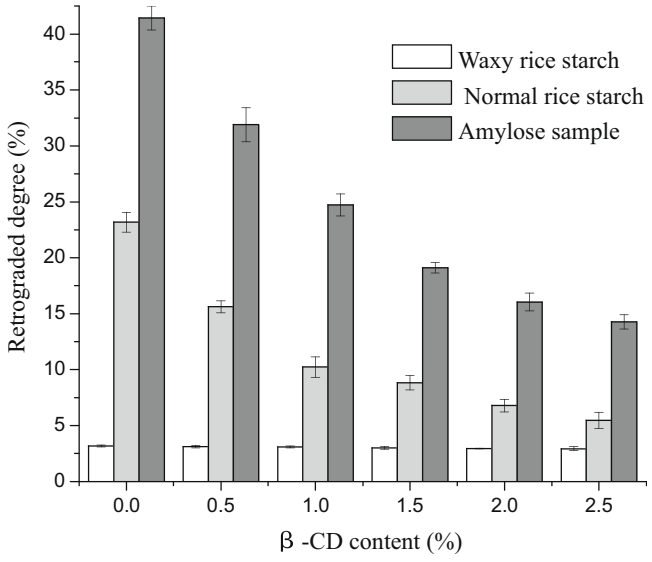

Fig. 3. Inhibition of on retrogradation of amylose, normal rice starch and waxy rice starch by β-CD.

For both amylose and normal starch samples the degree of retrogradation decreased with increased concentration of β-CD. These results indicate that the effect of β-CD, in reducing starch retrogradation, requires the presence of amylose. Is the effect on the amylose aggregation or recrystallisation due to the potential amylose-β-CD complex formation, or not? It should be emphasised that the complex might be formed on the molecular scale when this aggregation involves hundreds or thousands of molecules (Richardson et al., 2004). Previous findings have also reported that β-CD significantly formed a complex with starch and lipid, which was induced by a change of the molecules' electrostatic properties or surface-activity of the surrounding environment (Kim & Hill, 1984). Therefore, the amylose-β-CD complex was possibly produced and this potential complex lowered the rearrangement ability of amylose, causing the decrease in retrogradation degree.

3.2. Thermal properties of samples/β-CD mixtures

Thermoanalysis was used to characterise amylose–lipid complex formation (Eliasson, 1994), and thus it was expected that this technique could also be used to investigate the interaction between amylose and β-CD found in this experiment. As shown in Fig. 4a, β-CD had no endothermic peak detected across a broad temperature (80–160 °C). However, for standard amylose, an endothermic peak was detected at 138.2 °C (Fig. 4b), and probably was derived from the transition of amylose crystallite, which agrees with results of previous studies (Shamai, Bianco-Peled, & Shimoni, 2003). Other findings (Ring et al., 1987) have confirmed that the melting temperature of amylose crystallite was around 140 °C. In general, variation of this melting temperature has been attributed to chain length of amylose, polymeric degree of amylose branching, and the water level included in the starch system (Richardson et al., 2004). For the mixture containing β-CD and amylose, two endotherms were observed. One endothermic peak at 139.7 °C (Tp) was previously assigned to the transition of crystalline amylose. The second broad peak at 113.4 °C (Tp) probably corresponds to the potential amylose-β-CD complex (Fig. 4c). This was partially confirmed by the study of Liang (2001), who reported a Tp at 109.1 °C. Some discrepancy in the Tp might be ascribed to the variation among the types of rice starch, levels of amylose included, and determination methods. On the other hand, the enthalpy change (ΔH) in transition of crystalline amylose significantly decreased ($P < 0.05$) by 14.3% when 5% β-CD was added. This decrease further suggests that free amylose might be apt to interact with β-CD, forming a complex due to the outside hydroxyl groups. This complex could improve the properties of the environment surrounding the starch granule and reduce the enthalpy change of amylose recrystallite transition.

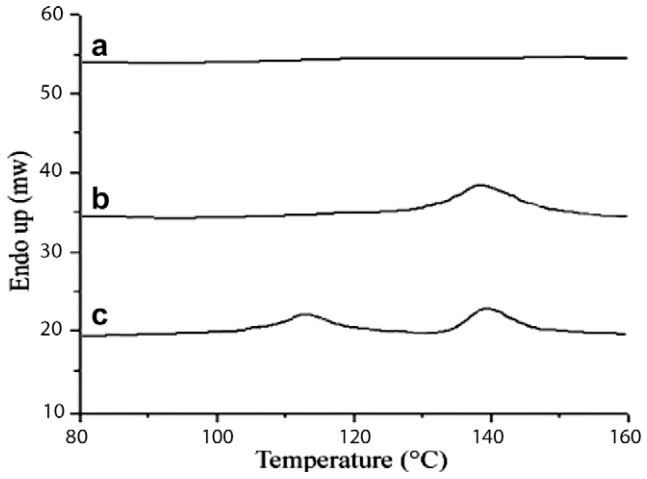

Fig. 4. DSC curves of the gelatinized samples. (a) β-CD, (b) SA and (c) SA with 5% β-CD.

3.3. Isothermal crystallisation kinetics

Avrami's equation, Eq. (1), was used to analyse the isothermal crystallisation calorimetric data obtained by the DSC (Mua & Jackson, 1998; Wang, Wang, Yang, Chen, & Chen, 2004):

$$X(t) = \Delta H_t/\Delta H_\infty = 1 - \exp(-kt^n) \quad (1)$$

where $X(t)$ is the crystalline volume fraction of amylose (%) developed at time t and constant temperature, ΔH_t is enthalpy change (J/g) at time t, ΔH_∞ is limiting enthalpy change (14 h for all samples), n is Avrami exponent determined from the slope of the $\ln[-\ln(1 - \Delta H_f/\Delta H_\infty)]$ versus log$t$ plot, and k is the rate constant evaluated from the intercept of the plot.

As shown in Table 1, recrystallisation kinetics data, obtained at the required temperature, were well suited to the Avrami equation since the r^2 values were close to 1). The value of the rate constant (k) significantly decreased ($P < 0.05$) when β-CD was added. The k values were similar with 1 and 3% β-CD and lowest with 5% β-CD ($P \geqslant 0.05$). The value of the Avrami exponent (n), varied from 0.8407 to 0.9558. This was in accordance with the result from Mua and Jackson (1998), who reported that the n values of some starches with high amylose were lower than 1. The n value was closest to 1 with 5% β-CD. These results suggest that β-CD probably transforms the nucleation type of amylose recrystallisation close to rod-like growth of sporadic nuclei, which occurrs in the condition of $1 \leqslant n \leqslant 2$ (Jouppila, Kansikas, & Roos, 1998; Mua & Jackson, 1998). This transformation probably corresponds to the interaction of amylose and β-CD. The potential amylose-β-CD complex formation might change the environment of amylose disorder and order, resulting in transforming the nucleation mode.

3.4. Interaction of β-CD with amylose fractions

A minimising energy of the final geometry was achieved in the MD runs and yielded a stable conformation in the equilibrium state. It should be noted that the potential energy for the seven chosen simulative systems at a constant temperature provided a reasonable description of the system in a dynamic configurational equilibrium. The interaction energy (ΔE) upon complexation between fractions and the β-CD, calculated for the minimum energy structure, is defined in Eq. (2).

$$\Delta E = E_{complex} - (E_{amylose} + E_{\beta-CD}) \quad (2)$$

where, $E_{complex}$, $E_{amylose}$, and $E_{\beta\text{-}CD}$ represent the minimum energies of the complex, the free amylose and the free β-CD, respectively, in the configuration taken from the optimized complex geometry. The deformation energy (ΔE_{deform}) of fractions is described as follows:

$$\Delta E_{deform} = E_{amylose-bind} - E_{amylose} \quad (3)$$

where, $E_{amylose\text{-}bind}$ represents the single point energy of the amylose fractions in the restricted condition, while $E_{amylose}$ is the energy in a free environment.

The different energies of the amylose-β-CD complex are shown in Table 2. The interaction energies (ΔE) suggest that pure amylose systems are miscible with β-CD. The change in magnitude of the ΔE would be a sign of the driving force towards complexation.

Table 1
Enthalpy change in the transition of the amylose crystallite and Avrami recrystallisation kinetic parameters of samples stored at 25 °C.

Amylose	Enthalpy change[a] (J/g)						Avrami parameters		
	1 h	3 h	5 h	7 h	10 h	14 h	n	k (h^{-n})	r^2
+0.0% β-CD	3.72 ± 0.13	6.03 ± 0.15	7.41 ± 0.21	7.78 ± 0.14	8.01 ± 0.18	8.15 ± 0.17	0.8407 ± 0.0212^{ab}	0.5897 ± 0.0102^{A}	0.9940
+1.0% β-CD	2.85 ± 0.08	4.87 ± 0.21	6.03 ± 0.11	6.32 ± 0.08	6.57 ± 0.29	6.74 ± 0.19	0.8592 ± 0.0187^{B}	0.5370 ± 0.0092^{B}	0.9978
+3.0% β-CD	2.57 ± 0.12	4.42 ± 0.15	5.47 ± 0.23	5.71 ± 0.19	5.93 ± 0.11	6.12 ± 0.14	0.8633 ± 0.0284^{B}	0.5325 ± 0.0131^{B}	0.9980
+5.0% β-CD	2.13 ± 0.06	4.09 ± 0.17	5.07 ± 0.07	5.25 ± 0.12	5.45 ± 0.14	5.69 ± 0.08	0.9558 ± 0.0117^{C}	0.5029 ± 0.0085^{C}	0.9994

[a] Data are expressed as means ± standard deviations of three experiments.
[b] Sample means with different superscripts in the same column are significantly different at $P < 0.05$.

Table 2
Energy parameters[a] of amylose fractions and β-CD interaction (×4.1868 kJ/mol).

Fractions	Single point energy				ΔE	ΔE_{deform}	Bonded interaction	Non-bonded interaction		
	$E_{complex}$	$E_{amylose}$	$E_{\beta\text{-}CD}$	$E_{amylose\text{-}bind}$				ΔE_{vdw}	$\Delta E_{H\text{-}bond}$	$\Delta E_{electrostatic}$
2	332.2 ± 2.5	267.9 ± 1.3	98.8 ± 1.3	276.8 ± 1.7	−34.5 ± 0.4	8.9 ± 0.2	5.2 ± 0.1	−33.5 ± 2.7	−6.5 ± 0.1	−10.9 ± 0.2
3	444.4 ± 4.1	396.8 ± 2.9	98.8 ± 1.3	404.6 ± 2.4	−51.2 ± 1.3	7.8 ± 0.1	5.4 ± 0.1	−46.5 ± 3.0	−7.9 ± 0.2	−11.3 ± 0.1
4	544.6 ± 1.3	500.4 ± 4.1	98.8 ± 1.3	507.5 ± 1.3	−54.6 ± 0.7	7.1 ± 0.1	5.0 ± 0.1	−50.9 ± 1.8	−8.9 ± 0.1	−11.5 ± 0.1
5	679.3 ± 5.2	641.2 ± 3.5	98.8 ± 1.3	647.7 ± 6.4	−60.7 ± 0.8	6.5 ± 0.1	5.3 ± 0.2	−57.9 ± 2.3	−9.7 ± 0.2	−12.9 ± 0.1
6	776.6 ± 3.3	746.8 ± 2.7	98.8 ± 1.3	748.2 ± 3.4	−69.0 ± 1.1	1.4 ± 0.0	4.7 ± 0.1	−71.7 ± 3.1	−14.1 ± 0.2	−13.3 ± 0.2
7	961.6 ± 3.7	930.1 ± 5.6	98.8 ± 1.3	935.8 ± 3.5	−67.3 ± 1.3	5.8 ± 0.2	5.7 ± 0.1	−66.6 ± 1.5	−10.7 ± 0.2	−14.2 ± 0.1
8	1103.3 ± 4.6	1067.4 ± 4.9	98.8 ± 1.3	1072.6 ± 2.7	−62.9 ± 0.6	5.2 ± 0.1	5.2 ± 0.1	−64.4 ± 1.9	−10.9 ± 0.2	−14.6 ± 0.2

[a] Data are expressed as means ± standard deviations of at least three simulations.

The more negative the interaction energy, the more thermodynamically favourable is the complex (Yousef, Zughul, & Badwan, 2007). The systems, as in the case of six fractions (fractions 3–8), exhibited a better compatibility, as ascertained from their interaction energy and their lower deformation energy (Table 2). The microscopic deformation process was governed in principle by the relative rates of microscopic deformation and molecular relaxation, both of which strongly depended on temperature (Farmer, Chapman, Dudis, & Adams, 1993; Ogura & Yamamoto, 1995). In the present adiabatic deformation, the deformation process of amylose was endothermal, as indicated by the positive enthalpy changes and this suggests that the lower ΔE_{deform} was favourable in complex formation. On all accounts, the interaction energy change was attributed to bonded and non-bonded interactions, such as hydrogen bonds, electrostatic forces, and Vdw attraction. The Vdw attraction was the dominant driving force in the amylose-β-CD complex, which is supported by the results of Xie and Soh (2005). The change in non-bonded interaction value was greater in comparison with the deformation energy. This result indicates that the non-bonded interaction played a significant role in the stability of the amylose-β-CD complex, which was essential for amylose deformation prevention. Further, MD simulation showed that the higher energy of hydrogen bonds led to greater stability of the complex. This result agrees with the results of the DSC study, which was partially performed, based on the principle that a greater enthalpy change corresponded to increased hydrogen bond formation during starch retrogradation.

4. Conclusions

This work clarified that the retrogradation characteristics of rice starch were modified by both the β-CD and GMS. The retarding of starch retrogradation by β-CD, on the whole, was greater than that by GMS ($P < 0.05$), and this effect of β-CD was ascribed to its interaction with amylose in starch. The nucleation type of amylose recrystallisation was partially changed, based on the Avrami model. The potential amylose-β-CD complex formation was observed by DSC curves when β-CD was present with amylose. Further, the result of molecular dynamics indicated that non-bonded interactions had an important role in increasing the stability of the complex, based on atoms. There was good agreement between the calculated (molecular dynamics) and observed (DSC) results, suggesting that molecular simulation strategy can provide reliable estimates of stability parameters involved with complex formation.

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References

Biliaderis, C. G., & Seneviratne, H. D. (1990). On the supermolecular structure and metastability of glycerol monostearate-amylose complex. *Carbohydrate Polymers, 13*(2), 185–206.
Eliasson, A. C. (1994). Interactions between starch and lipids studied by DSC. *Thermochimica Acta, 246*(2), 343–356.
Farmer, B. L., Chapman, B. R., Dudis, D. S., & Adams, W. W. (1993). Molecular dynamics of rigid rod polymers. *Polymer, 34*(8), 1588–1601.
Funami, T., Kataoka, Y., Omoto, T., Goto, Y., Asai, I., & Nishinari, K. (2005a). Effects of non-ionic polysaccharides on the gelatinization and retrogradation behavior of wheat starch. *Food Hydrocolloids, 19*, 1–13.
Funami, T., Kataoka, Y., Omoto, T., Goto, Y., Asai, I., & Nishinari, K. (2005b). Food hydrocolloids control the gelatinization and retrogradation behavior of starch. 2b. Functions of guar gums with different molecular weights on the retrogradation behavior of corn starch. *Food Hydrocolloids, 19*, 25–36.
Gunaratne, A., & Corke, H. (2007). Influence of unmodified and modified cycloheptaamylose (β-cyclodextrin) on transition parameters of amylose–lipid complex and functional properties of starch. *Carbohydrate Polymers, 68*, 226–234.
Jouppila, K., Kansikas, J., & Roos, Y. H. (1998). Factors affecting crystallization and crystallization kinetics in amorphous corn starch. *Carbohydrate Polymers, 36*, 143–149.
Keetels, C. J. A. M., Van Vliet, T., Jurgens, A., & Walstra, P. (1996). Effects of lipid surfactants on the structure and mechanics of concentrated starch gels and starch bread. *Journal of Cereal Science, 24*, 33–45.
Kim, H. O., & Hill, D. (1984). Physical characteristics of wheat starch granule gelatinization in the presence of cycloheptaamylose. *Cereal Chemistry, 61*, 432–435.
Liang, X. M. (2001). Effects of lipids, amino acids, and beta-cyclodextrin on gelatinization,pasting, and retrogradation properties of rice starch. *Dissertation Abstracts International*, 63-02, 0603.
Lindner, K., & Saenger, W. (1982). Crystal and molecular structure of cycloheptaamylose dodecahydrate. *Carbohydrate Research, 99*(2), 103–115.
Loftsson, T., & Duchene, D. (2007). Cyclodextrins and their pharmaceutical applications. *International Journal of Pharmaceutics, 329*, 1–11.
Mua, J. P., & Jackson, D. S. (1998). Retrogradation and gel textural attributes of corn starch amylose and amylopectin fractions. *Journal of Cereal Science, 27*, 157–166.
Ogura, I., & Yamamoto, T. (1995). Molecular dynamics simulation of large deformation in an amorphous polymer. *Polymer, 36*(7), 1375–1381.
Richardson, G., Kidman, S., Langton, M., & Hermansson, A. M. (2004). Differences in amylose aggregation and starch gel formation with emulsifiers. *Carbohydrate Polymers, 58*, 7–13.
Ring, S. G., Colonna, P., l'Anson, K. J., Kalichevsky, M. T., Miles, M. J., Morris, V. J., et al. (1987). The gelation and crystallisation of amylopectin. *Carbohydrate Research, 162*, 277–293.
Shamai, K., Bianco-Peled, H., & Shimoni, E. (2003). Polymorphism of resistant starch type III. *Carbohydrate Polymers, 54*, 363–369.
Shim, S. Y., Ahm, J., & Kwak, S. H. (2003). Functional properties of cholesterol-removed whipping cream treated by β-cyclodextrin. *American Dairy Science Association, 86*, 2767–2772.
Szente, L., & Szejtli, J. (2004). Cyclodextrins as food ingredients. *Trends in Food science and Technology, 15*, 137–142.
Takeda, Y., Hizukuri, S., & Juliano, B. O. (1986). Purification and structure of amylose from rice starch. *Carbohydrate Research, 148*(2), 299–308.
Tsuge, H., Hishida, M., Iwasaki, H., Watanabe, S., & Goshima, G. (1990). Enzymatic evaluation for the degree of starch retrogradation in foods and foodstuffs. *Starch/Starke, 42*(6), 213–216.
Vandeputte, G. E., Vermeylen, R., Geeroms, J., & Delcour, J. A. (2003). Rice starches III. Structural aspects provide insight in amylopectin retrogradation properties and gel texture. *Journal of Cereal Science, 38*, 61–68.
Wang, X. L., Wang, Y. Z., Yang, K. K., Chen, D. Q., & Chen, S. C. (2004). Crystallization and morphology of starch-g-poly (1,4-dioxan-2-one) copolymers. *Polymer, 45*, 7961–7968.
Xie, Y. H., & Soh, A. K. (2005). Investigation of non-covalent association of single-walled carbon nanotube with amylose by molecular dynamics simulation. *Materials Letters, 59*, 971–975.
Yousef, F. O., Zughul, M. B., & Badwan, A. A. (2007). The modes of complexation of benzimidazole with aqueous β-cyclodextrin explored by phase solubility, potentiometric titration, 1H-NMR and molecular modeling studies. *Journal of Inclusion Phenomena and Macrocyclic Chemistry, 57*, 519–523.
Zhou, Z. K., Robards, K., Helliwell, S., & Blanchard, C. (2007). Effect of the addition of fatty acids on rice starch properties. *Food Research International, 40*, 209–214.