

# Effects of Konjac-Glucomannan on the Gelatinization and Retrogradation of Corn Starch As Determined by Rheology and Differential Scanning Calorimetry

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Effects of konjac-glucomannan (KM) on retrogradation and gelatinization of corn starch (CS) were studied as a function of mixing ratio and of storage time by measuring force-deformation curves, dynamic viscoelasticity, and differential scanning calorimetry (DSC). Total polysaccharide concentration for the rheological experiments was 15 wt % and CS/KM ratios were 15/0, 14.25/0.75, 13.50/1.50, and 12.75/2.25. A mixed gel with a CS/KM ratio of 13.50/1.50 showed a larger breaking strain and Young's modulus than a gel of CS plus water (15/0) stored for 1 day. Mixed gels of CS and KM stored for 14 days showed a smaller breaking stress than a gel of CS plus water. The DSC endothermic peak accompanying the gelatinization shifted slightly to higher temperatures with increasing KM concentration. A CS–KM–water mixture (total polysaccharide concentration, 33 wt %) retrograded faster than CS plus water during short storage. Enthalpies of CS–KM–water mixtures stored for 14 days were smaller than that of CS plus water. From the rheological and DSC changes it is suggested that KM promoted CS retrogradation during short-term storage and then retarded it slightly during longer storage times.

**Keywords:** *Corn starch (CS); konjac-glucomannan (KM); gelatinization; retrogradation; rheology; differential scanning calorimetry (DSC)*

## INTRODUCTION

Starch and hydrocolloid mixtures are often used to modify and control the texture of food products. The rheological properties of starch and hydrocolloid mixtures have been reported. It is well known that the addition of hydrocolloids (e.g., locust bean gum, guar gum, xanthan gum, etc.) increases the viscosity of starch (Christianson et al., 1981; Sajjan and Rao, 1987; Tye, 1988; Alloncle et al., 1989; Alloncle and Doublier, 1991; Annable et al., 1994; Yousria and William, 1994) and influences the retrogradation rate (Kim and D'Appolonia, 1977; Gudmundsson et al., 1991; Kohyama and Nishinari, 1992). The gelatinization and retrogradation of starches are important properties in food processing and cooking.

It is well known that starch is composed of amylose and amylopectin. The retrogradation of starch proceeds in two crystallization stages. In the first stage, the rigidity and crystallinity of starch gels develop quickly by amylose gelation. In the second stage, the crystallinity develops slowly by amylopectin (Miles et al., 1985). Roulet et al. (1988) reported that the rheological measurements of starch–water systems can be a good index of starch retrogradation at the macromolecular network level. Differential scanning calorimetry (DSC) has been used to investigate the gelatinization and retrogradation of starch (Donovan, 1979; Wada et al., 1979; Shiotsubo and Takahashi, 1984; Biliaderis et al., 1986; Roulet et al., 1988; Gudmundsson et al., 1991; Biliaderis, 1991; Inouchi et al., 1991; Kohyama and Nishinari, 1992; Shiotsubo, 1992).

Konjac-glucomannan (KM) is the main component of the tuber of *Amorphophallus konjac* C. Koch and forms a thermally stable gel (Konnyaku) upon addition of an alkaline coagulant. KM shows an interaction with other hydrocolloids; for examples, carrageenan (Cairns et al., 1988, 1991; Nishinari et al., 1992; Williams et al., 1992, 1993; Kohyama et al., 1993, 1996), and xanthan gum (Brownsey et al., 1988; Shatwell et al., 1991; Williams et al., 1991a,b; Nishinari et al., 1992).

Since ancient times in Japan there have been dessert jellies that are made of starch, such as kuzumochi and kuzukiri, and they are still made today. We tried to emulate these desserts by using corn starch and KM. However, KM plus water does not form a gel but forms a viscous solution. We expected that the addition of a small amount of KM to corn starch might be useful to control the texture and extend the shelf life of these desserts.

In this study we investigated the physical properties of corn starch and KM mixtures by determining force-deformation curves and dynamic viscoelasticity, and by differential scanning calorimetry (DSC).

## MATERIALS AND METHODS

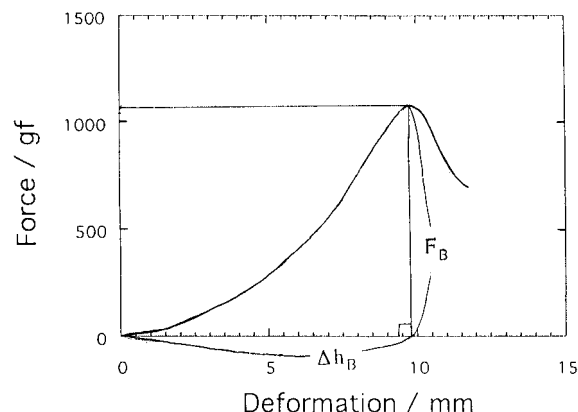
**Materials.** Corn starch (CS) was a gift from Sanwa Cornstarch Company Ltd. (Nara, Japan). Konjac-glucomannan (KM) was a gift from Ogino Company Ltd. (Gunma, Japan). The moisture content of the KM was 7.90%. The moisture and protein contents of the CS were 12.5 and 0.28%, respectively. The amylose content of the CS was 25%.

**Preparation of Gels.** Powders of CS or CS and KM mixture were dispersed in distilled water in a separatory flask by a motorized stirrer with a Teflon mixing blade (Shintosh Science Ltd., Tokyo, Japan, HEIDON 3000H) at 200 rpm for 2 h at room temperature. Then the dispersion was heated in

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**Figure 1.** Typical force-deformation curve for a cylindrical gel of CS and KM (13.50/1.50; total polysaccharide concentration, 15 wt %). Breaking stress,  $\sigma_B$ , was estimated by the force at which a gel was broken,  $F_B$ , divided by an initial cross section of a gel,  $S$ , in a force-deformation curve. Breaking strain,  $\epsilon_B$ , was estimated by the deformation,  $\Delta h_B$ , divided by the initial height of the sample,  $h$ , in a force-deformation curve. Young's modulus,  $E$ , was estimated from an initial slope of force-deformation curve.  $\sigma$  is defined as  $F/S$ ,  $\epsilon$  is defined as  $\Delta h/h$ , and  $E = \sigma/\epsilon$  at small  $\epsilon$ .

an oil bath to 95 °C and held at 95–98 °C for 30 min. The mixture was stirred continuously at 400 rpm. Boiling distilled water was added to the hot mixture, and the total polysaccharide content was adjusted to 15 wt %. The concentration used in the present report is based on the weight of the powders of CS (moisture content, 12.5%), and KM (moisture content, 7.9%). The hot mixture was poured into cylindrical teflon molds (20 mm diameter and 20 or 30 mm height) and held at room temperature (25 °C) for 1 h and then at 5 °C. Gels were stored at 5 °C for 14 days in silicon oil to prevent water evaporation.

**Compression Tests.** Compression tests of gels were carried out with a Rheoner RE-3305 (Yamaden Company Ltd., Tokyo, Japan) with a 2-kg load cell and a crosshead speed of 30 mm/min. The diameter of the plunger was 40 mm. A typical force-deformation curve is shown in Figure 1. The measurement was repeated >16 times, and the mean value and standard deviation were determined.

**Dynamic Viscoelasticity.** The storage Young's modulus  $E'$  and the loss Young's modulus  $E''$  were determined by the observation of longitudinal vibrations of CS and KM gels molded into cylinders (20 mm diameter and 30 mm height) as a function of storage time. Temperature dependence of  $E'$  for 15 wt % mixed gels stored at 5 °C for 1 day were also measured. The stress produced in the specimen is detected by a strain gauge, then amplified and introduced to a computing circuit. With this circuit, the stress is divided into the

**Table 1. Compression Behaviors of a Gel of CS plus Water and Mixed Gels of CS and KM after 1 Day of Storage<sup>a</sup>**

CS/KM	breaking strain (m/m)	breaking stress ( $10^4 \text{ N}\cdot\text{m}^{-2}$ )	Young's modulus ( $10^4 \text{ N}\cdot\text{m}^{-2}$ )
15.0/0.0	$0.430 \pm 0.025$	$2.98 \pm 0.61$	$1.45 \pm 0.09$
14.25/0.75	$0.460 \pm 0.019$	$3.20 \pm 0.36$	$1.55 \pm 0.18$
13.50/1.50	$0.482 \pm 0.017$	$3.61 \pm 0.31$	$1.64 \pm 0.14$
12.75/2.25	$0.468 \pm 0.013$	$3.21 \pm 0.54$	$1.83 \pm 0.10$

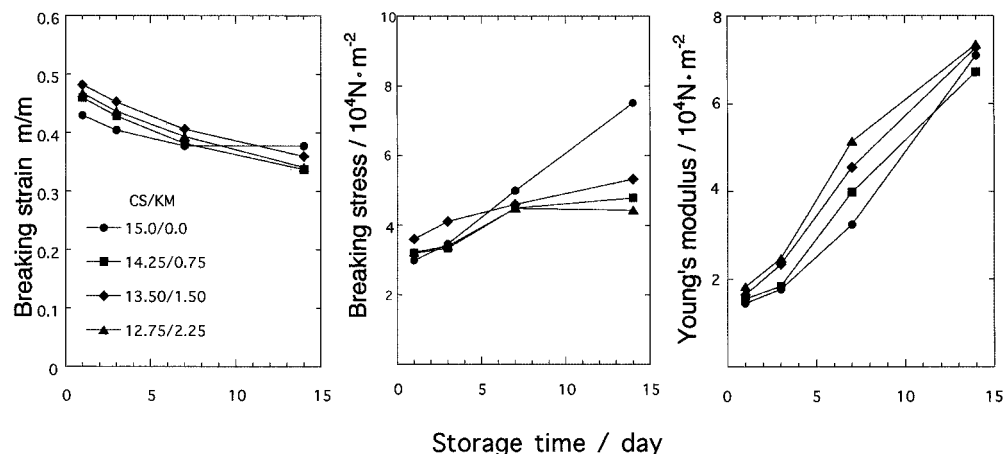
<sup>a</sup> The values are means and standard deviations for > 16 trials.

component in phase with the applied strain (real part) and the component with leading phase  $\pi/2$  to the applied strain (imaginary part). These values are proportional to  $E'$  and  $E''$  and are indicated in digital display. The apparatus used was a Rheograph gel (Toyo Seiki Seisakusho Ltd., Tokyo, Japan) set at a frequency of 3Hz and an amplitude of 100  $\mu\text{m}$ . The temperature was controlled in a silicon oil bath. Details of the measurement procedures were described previously (Nishinari et al., 1980).

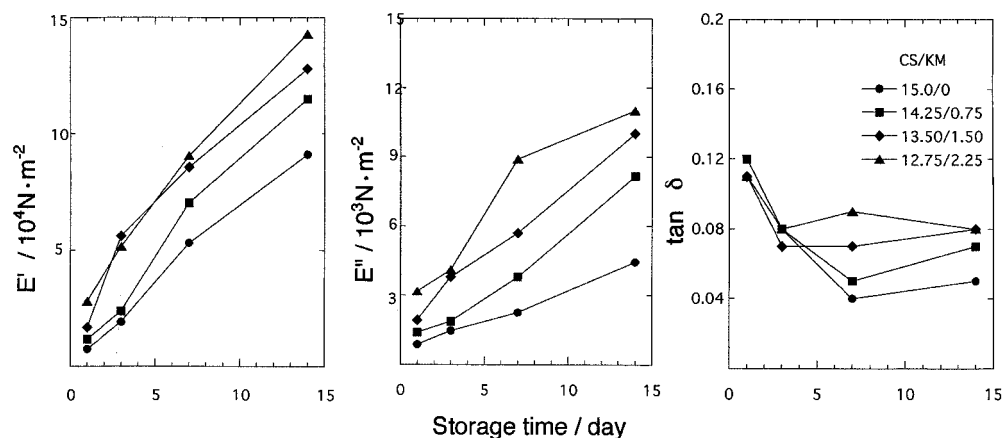
**Differential Scanning Calorimetry.** (DSC) measurements were made with a DSC apparatus PTC10D (Rigaku Company Ltd., Tokyo, Japan). We could not use the same total polysaccharide concentration of 15 wt % in rheological data for DSC measurements because the sensitivity of the instrument was not high enough. The peak area for the second run DSC curve was too small to be detected. Each 20 mg of powdered mixture and 40 mg of water were directly weighed into a 70- $\mu\text{L}$  silver pan. Total polysaccharide concentration was adjusted to 33 wt %. A pan containing an equal amount of water was used as a reference. The temperature was raised from room temperature to 130 °C at 1.0 °C/min. After the first run heating, the pan was quenched from 130 to 5 °C and stored for 14 days at 5 °C. The temperature was raised again from 5 to 130 °C at 1 °C/min in the second run. Heating DSC curves of KM plus water (10 wt %) and CS plus water (16.5–60.0 wt %) were also observed.

## RESULTS AND DISCUSSION

The changes in compression test behavior for a gel of CS plus water (15.0/0) and mixed gels of CS and KM (total polysaccharide concentration 15 wt %) as a function of storage time at 5 °C are shown in Figure 2. The mean value and standard deviation of compression behaviors for CS plus water (15.0/0) and mixed gels of CS and KM after 1 day of storage are shown in Table 1. Mixed CS/KM gels with mixing ratios of 13.50/1.50 showed larger breaking strain and Young's modulus than those of CS plus water (15/0) after 1 day of storage.



**Figure 2.** Compression behaviors of a gel of CS plus water (15.0/0) and mixed gels of CS and KM as a function of storage time. The total polysaccharide concentration was 15 wt %, the measurement temperature was 10 °C, the storage temperature was 5 °C, and the crosshead speed was 30 mm/min. CS/KM mixing ratio: (●) 15.0/0; (■) 14.25/0.75; (◆) 13.50/1.50; (▲) 12.75/2.25.



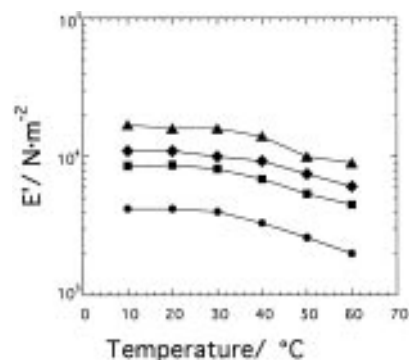
**Figure 3.** Storage and loss Young's moduli  $E'$  and  $E''$  of a gel of CS plus water (15.0/0) and mixed gels of CS and KM as a function of storage time. The total polysaccharide concentration was 15 wt %, the measurement temperature was 10 °C, the storage temperature was 5 °C, and the frequency was 3 Hz. CS/KM mixing ratio: (●) 15.0/0; (■) 14.25/0.75; (◆) 13.50/1.50; (▲) 12.75/2.25.

Although breaking stress for mixed gels of 13.50/1.50 seemed to be slightly larger than that for a gel of CS plus water (15.0/0), the difference was not significant. The Young's modulus for mixed gels of CS and KM increased with increasing KM concentration after 1, 3, and 7 days of storage. Breaking stress and Young's modulus increased, but breaking strain decreased with storage time. The breaking stress for mixed gels of CS and KM increased slowly with storage time compared with a gel of CS plus water. Apparently the KM slowed the retrogradation rate of the CS. Molecules of KM entangle with CS and prevent structure ordering, and hence retard the retrogradation. KM prevents the syneresis of CS (as will be reported in a subsequent paper; Yoshimura et al., 1996); thus it is not the exuded water that retards the retrogradation by lowering the CS concentration.

The storage and loss Young's moduli  $E'$  and  $E''$ , and the mechanical loss tangent  $\tan \delta$  ( $=E''/E'$ ) for gels as a function of storage time are shown in Figure 3. The storage and loss Young's moduli for mixed gels of CS and KM increased with increasing KM concentration. The storage and loss Young's moduli  $E'$  and  $E''$  increased with storage time. The values of  $\tan \delta$  for mixed gels of CS and KM initially decreased and then leveled off with storage time. The values of  $\tan \delta$  for 15 wt % mixed gels of CS and KM were smaller at 3 days of storage; however, they became larger than that of a gel of CS plus water after 7 days of storage, indicating that KM promoted retrogradation of CS during short storage times and then prevented it during longer storage times.

The temperature dependence of the storage Young's modulus  $E'$  for a gel of CS plus water (15.0/0) and mixed gels of CS and KM stored at 5 °C for 1 day is shown in Figure 4. Young's modulus  $E'$  increased with increasing KM content at temperatures between 10 and 60 °C and decreased monotonically with increasing temperature, indicating that the network structure of gels was weakened by heating. This observation suggests that main molecular forces that stabilize the network are secondary bonds, such as hydrogen bonds (Nishinari et al., 1985).

The DSC curves of CS plus water are shown in Figure 5. Concentrations of CS were 16.5–33.0 wt % in Figure 5A and 40–60 wt % (except for CS powders alone without added water) in Figure 5B. Gelatinization enthalpies ( $\Delta H_1$ ) were estimated from the area of the main endothermic peak ( $M_1$ ) per milligram of starch.

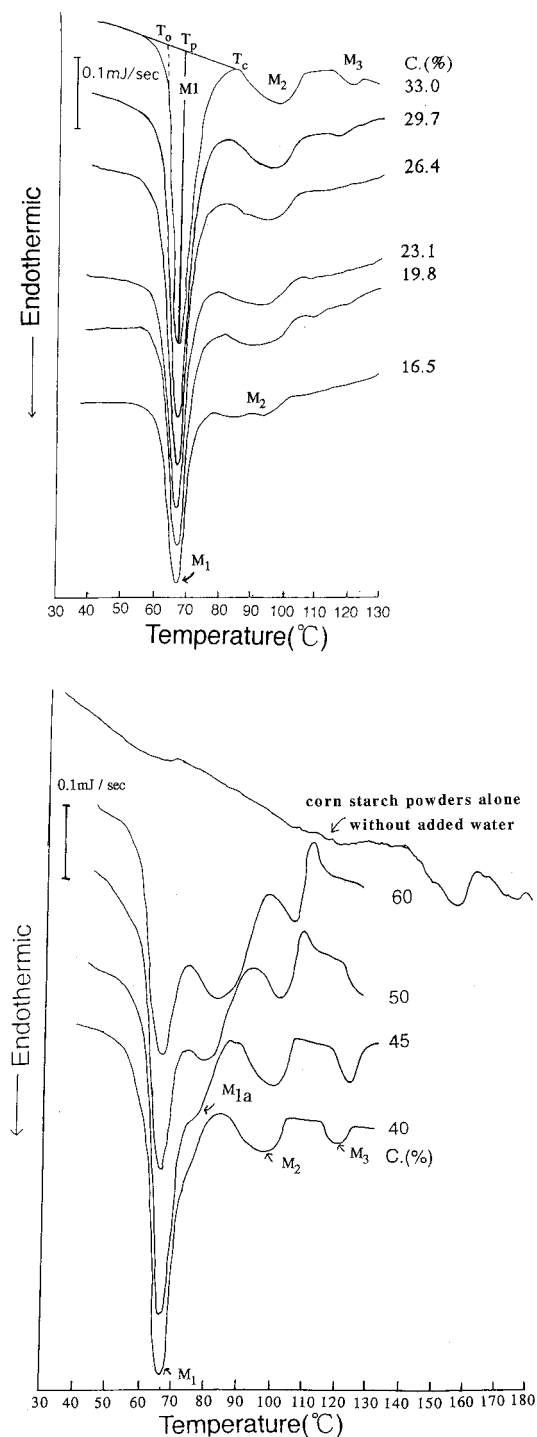


**Figure 4.** Temperature dependence of  $E'$  for a gel of CS plus water (15.0/0) and mixed gels of CS and KM stored at 5 °C for 1 day. The total polysaccharide concentration was 15 wt %, the measurement temperature was 10 °C, the storage temperature was 5 °C, and the frequency was 3 Hz. CS/KM mixing ratio: (●) 15.0/0; (■) 14.25/0.75; (◆) 13.50/1.50; (▲) 12.75/2.25.

The onset temperature ( $T_0$ ), the peak temperature ( $T_p$ ), and the conclusion temperature ( $T_c$ ) were determined (Figure 5A). CS plus water (16.5–26.4 wt % in Figure 5A) showed a large endothermic peak ( $M_1$ ) at 66–67 °C and a small endothermic peak ( $M_2$ ) at 92–95 °C. CS plus water (29.7, 33.0 wt % in Figure 5A) and 40, 45 wt % in Figure 5B) showed a large endothermic peak ( $M_1$ ) at 66–67 °C and two small endothermic peaks ( $M_2$ ,  $M_3$ ) at 92–95 °C and  $\sim 120$  °C, respectively. The  $T_0$  was almost the same value, and  $T_c$  shifted to lower temperatures with decreasing CS concentration (16.5–33.0 wt %), as shown in Table 2. The value of the peak height divided by the half-width of the main endothermic peak ( $M_1$ ) became smaller with decreasing CS concentration (i.e., the peak became broader). Gelatinization enthalpies ( $\Delta H_1$ ) of CS plus water were independent of the starch concentration (Table 2).

A similar tendency was found for potato starch by Shiotsubo and Takahashi (1984). They reported that  $T_0$  and  $T_p$  were independent of the potato starch concentration, whereas  $T_c$  shifted to lower temperatures with decreasing concentration over the range of starch concentration 1–50%. Gelatinization enthalpies were almost independent of the starch concentration at <40% (Shiotsubo and Takahashi, 1984). A similar tendency was also found for rice starch at lower concentrations (<50 wt %) (Biliaderis et al., 1986).

Shiotsubo (1992) reported that  $T_p$  and  $\Delta H$  of 17 wt % CS (amylose content, 24%) determined by DSC were



**Figure 5.** Heating DSC curves of CS plus water at (A, top) 16.5–33.0 wt % and (B, bottom) 40–60 wt %. (C, concentration of corn starch; heating rate, 1 °C/min).

66.2 °C and 11.4 mJ/mg starch, respectively, when the DSC heating rate was 0.2 °C/min. Inouchi et al. (1991) reported a  $T_p$  value for 33% CS (amylose content, 24%) of 66 °C when the DSC heating rate was 2 °C/min. These results correspond well with our DSC results that  $T_p$  and  $\Delta H$  of 33 wt % CS were 66.3 °C and 11.5 mJ/mg starch, respectively. In CS containing >60 wt % water (CS concentration, <40 wt %), a single symmetrical endotherm ( $M_1$ ) was observed (Figure 5A, B). However, in CS containing <55 wt % water (CS concentration, >45 wt %), an endothermic peak had a shoulder ( $M_{1a}$ ) or a second peak. A similar phenomenon was also observed in the report on rice starch by Biliaderis (1991). The endothermic peak temperature of ~66–67

°C was independent of the CS concentration (16.5–60 wt %, Figure 5A,B). The height of the main endothermic peak ( $M_1$ ) steeply increased with increasing CS concentration (16.5–40 wt %). However, in CS containing <55 wt % water (CS concentration, >45 wt %), the height of the main endothermic peak ( $M_1$ ) steeply decreased with increasing CS concentration (45–60 wt %) and the second peak area increased and the second peak temperature shifted to higher temperatures. Powders of CS alone (without added water, moisture content of 12.5%) showed a small endothermic peak at ~150 °C.

Heating DSC curves of CS plus water (10/0), CS–KM–water mixtures (9.5/0.5–5.0/5.0), and KM plus water (10 wt %) are shown in Figure 6. KM plus water (the lowest curve) did not show any exothermic and endothermic peak at the temperature range studied. This result is similar to the experimental observation that KM plus water (0.6 and 1.2 wt %) did not give rise to an enthalpy change (Williams, 1991; Williams et al., 1992). CS plus water and the CS–KM–water mixture showed one large endothermic peak ( $M_1$ ) at 66–71 °C and two small peaks at 97–100 °C ( $M_2$ ) and at 117–120 °C ( $M_3$ ). The endothermic peak ( $M_1$ ) for CS plus water became slightly broader with decreasing CS concentration, as shown in Figure 5A. The main endothermic peak ( $M_1$ ) for CS–KM–water mixture also became broader with decreasing CS concentration (Figure 6). The conclusion temperature ( $T_c$ ) shifted to higher temperatures with increasing KM concentration. The values of gelatinization enthalpies per 1 mg of starch ( $\Delta H_1$ ) of CS–KM–water mixtures estimated from a main endothermic peak ( $M_1$ ) were similar to that of CS plus water, as shown in Table 3. The endothermic peak temperature ( $T_p$ ) accompanying the gelatinization shifted slightly to higher temperatures with increasing KM concentration (Figure 6 and Table 3). The reason why the peak temperature shifted to higher temperatures by the addition of KM may be attributed to one or both of the following two possibilities: (1) the increase of the effective concentration of CS by the immobilization of water molecules by KM, or (2) the interaction of CS with KM leading to a more stable structure. The endothermic peak temperature  $T_p$  was independent of the CS concentration (16.5–60 wt %; Figure 5A,B), so the first possibility can be excluded. However, for CS plus water and for the CS–KM–water mixture, the experimental findings that the gelatinization enthalpy ( $\Delta H_1$ ) (Tables 2 and 3) was independent of the CS/KM mixing ratios should exclude the second possibility. It is difficult to know why the gelatinization enthalpy did not depend on the mixing ratio, but the gelatinization peak shifted to higher temperatures with increasing content of KM. This shift should be explored in the future.

The reheating DSC curves of CS plus water (16.5–33.0%) stored for 14 days at 5 °C are shown in Figure 7. Regelatinization enthalpies per milligram of starch ( $\Delta H_2$ ), estimated from the area of peak ( $M_1$ ) of CS plus water stored for 14 days, decreased with decreasing CS concentration (Table 2).

The reheating DSC curves of CS plus water (10/0) and CS–KM–water mixtures (9.5/0.5–5.0/5.0) stored for 14 days at 5 °C are shown in Figure 8. Regelatinization enthalpies ( $\Delta H_2$ ) of CS–KM–water mixtures stored for 14 days were slightly smaller than that of CS plus water (Tables 2 and 3).

**Table 2. Gelatinization Temperature and Enthalpy and Retrogradation Ratio for CS plus Water<sup>a</sup>**

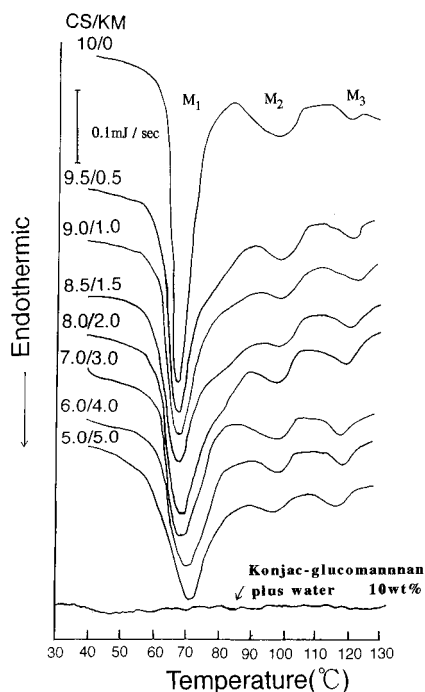
starch content (%)	first run				stored for 14 days at 5 °C				retrogradation ratio $\Delta H_2/\Delta H_1$
	$T_{o1}$ (°C)	$T_{p1}$ (°C)	$T_{c1}$ (°C)	$\Delta H_1$ (mJ/mg of starch)	$T_{o2}$ (°C)	$T_{p2}$ (°C)	$T_{c2}$ (°C)	$\Delta H_2$ (mJ/mg of starch)	
33.00	60.1	66.3	81.4	11.5	30.1	45.6	64.4	7.2	0.63
29.70	60.9	66.7	81.5	11.7	29.5	44.8	62.1	7.5	0.64
26.40	60.8	66.9	81.2	11.8	29.8	44.2	61.2	6.8	0.58
23.10	60.9	66.9	80.4	10.9	30.2	45.4	62.1	6.6	0.60
19.80	60.6	67.0	79.5	11.4	30.0	45.4	62.0	6.3	0.55
16.50	60.7	67.1	78.7	11.0	29.5	44.0	59.0	6.3	0.57

<sup>a</sup>  $T_o$ , onset temperature;  $T_p$ , peak temperature;  $T_c$ , conclusion temperature;  $\Delta H$ , gelatinization enthalpy.

**Table 3. Gelatinization Temperature and Enthalpy and Retrogradation Ratio for CS and KM Mixed Gels<sup>a</sup>**

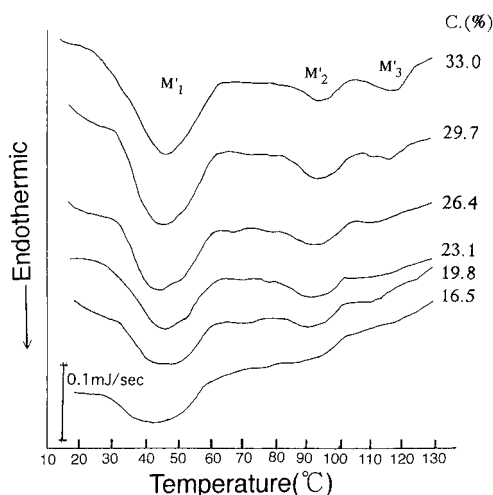
CS/KM mixing ratio	starch content (%)	first run				stored for 14 days at 5 °C				retrogradation ratio $\Delta H_2/\Delta H_1$
		$T_{o1}$ (°C)	$T_{p1}$ (°C)	$T_{c1}$ (°C)	$\Delta H_1$ (mJ/mg of starch)	$T_{o2}$ (°C)	$T_{p2}$ (°C)	$T_{c2}$ (°C)	$\Delta H_2$ (mJ/mg of starch)	
10/0	33.00	60.1	66.3	81.4	11.5	30.1	45.6	64.4	7.2	0.63
9.5/0.5	31.35	60.1	67.4	90.7	11.5	30.4	44.8	66.8	7.0	0.61
9.0/1.0	29.70	60.2	67.6	91.2	11.3	30.6	44.9	66.9	6.8	0.60
8.5/1.5	28.05	60.3	67.9	92.0	11.3	30.9	45.9	64.8	6.8	0.60
8.0/2.0	26.40	61.1	69.0	89.0	11.4	29.6	46.1	65.0	6.7	0.59
7.0/3.0	23.10	61.2	69.3	90.0	11.0	31.6	48.5	65.5	6.5	0.59
6.0/4.0	19.80	61.5	70.6	90.1	11.0	31.9	47.9	65.8	5.8	0.53
5.0/5.0	16.50	61.9	73.6	91.8	11.2	31.6	48.5	65.5	5.8	0.52

<sup>a</sup>  $T_o$ , onset temperature;  $T_p$ , peak temperature;  $T_c$ , conclusion temperature;  $\Delta H$ , gelatinization enthalpy.



**Figure 6.** Heating DSC curves of CS plus water (10/0) and CS-KM-water mixtures. The total polysaccharide concentration was 33 wt % for all curves except the lowest curve for KM plus water (heating rate, 1 °C/min).

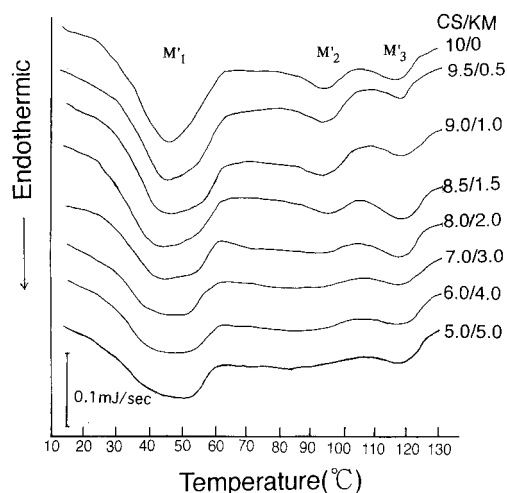
The reheating DSC curves of CS and KM mixed gels after storage for 1 and 14 days at 5 °C (with mixing ratios 10/0, 8.5/1.5, and 5.0/5.0), together with the reheating curves observed immediately after heating to 130 °C and then quenched are shown in Figure 9. The peak at ~115 °C was attributed to disorganization of amylose-lipid complexes (Donovan, 1979; Biliaderis, 1991) because it was reversible on immediate reheating at 0 day. The peak at ~95 °C also reappeared after storing for 1 day. This peak may also be attributed to disorganization of amylose-lipid complexes. The peak at ~45 °C reappeared more slowly than the peaks at ~95 and ~115 °C. The lower temperature (~45 °C) endothermic peak is attributed to the regelatinization



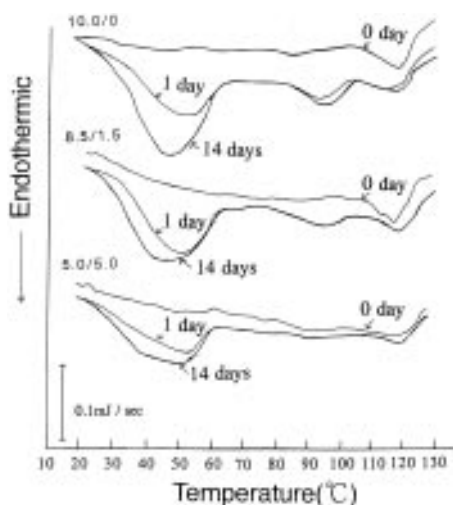
**Figure 7.** Reheating DSC curves for CS plus water after heating to 130 °C and storing for 14 days at 5 °C (C, concentration of corn starch; heating rate, 1 °C/min).

that reflects heat-moisture-induced order-to-disorder phenomena of starch crystallites, which mainly consist of amylopectin (Donovan, 1979).

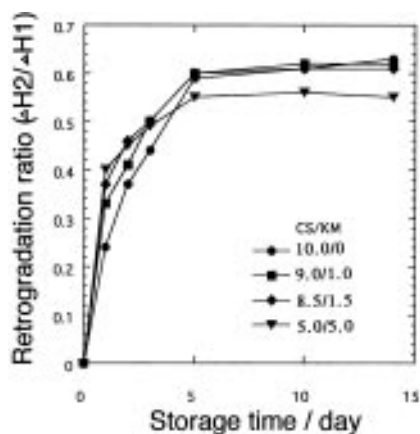
The retrogradation ratio, shown in Figure 10, was estimated by a regelatinization enthalpy ( $\Delta H_2$ ) divided by a gelatinization enthalpy ( $\Delta H_1$ ) (Kohyama and Nishinari, 1991) as a function of storage time. The retrogradation ratio increased with increasing KM concentration at 1 and 3 days of storage; however, at 14 days of storage, the retrogradation ratio for CS plus water was larger than that of CS-KM-water mixtures with mixing ratio 5.0/5.0. This result is consistent with the previous rheological conclusion that KM promoted starch retrogradation during short storage but retarded it during longer storage times. We used a total polysaccharide concentration of 15 wt % to obtain rheological data and 33 wt % to obtain DSC data, so we would presume that the thermal properties and rheological properties of mixed gels could not be compared directly. The retrogradation of 33 wt % CS might proceed faster than that of 15 wt % CS. However, the DSC results are useful for understanding rheological behavior.



**Figure 8.** Reheating DSC curves for CS plus water (10/0) and a CS-KM-water mixture after heating to 120 °C storing for 14 days at 5 °C (total polysaccharide concentration, 33 wt %; heating rate, 1 °C/min).



**Figure 9.** Reheating DSC curves for CS plus water (10/0) and CS-KM-water mixtures (8.5/1.5, 5.0/5.0). The total polysaccharide concentration was 33 wt % and the heating rate was 1 °C/min.



**Figure 10.** Retrogradation ratio as a function of storage time.

We examined the effects of KM on syneresis of CS and found that the water-holding capacity of KM prevented the syneresis (Yoshimura et al., 1996). The effective concentration of CS might be increased by the addition of KM. Thus, retrogradation might be promoted by KM, which absorbed water in the mixed gel during short storage times. Gel strength, Young's

modulus (Figure 2), and storage and loss Young's moduli (Figure 3) after 1 day of storage were increased by the addition of KM. These results might be caused by the same mechanism. However, the breaking stress for mixed gels of CS and KM increased slowly with storage time compared with a gel of CS plus water, and enthalpies of CS-KM-water mixtures stored for 14 days were slightly smaller than that of CS plus water. These observations suggest that KM slowed the retrogradation rate of starch during longer storage times. KM might interact with the amylose and amylopectin in CS and prevent reorganization of amylopectin molecules.

In conclusion, changes in the rheological and DSC results of CS-KM-water mixtures with storage time suggest that retrogradation of CS was promoted by KM during short storage times, but slowed during longer storage times. The basic studies presented here should be useful to control the texture and extend the shelf life of dessert jellies such as kuzukiri, kuzumochi, and uirou during long storage times.

#### LITERATURE CITED

- Alloncle, M.; Lefebvre, J.; Llamas, G.; Doublier, J. L. A rheological characterization of cereal starch-galactomannan mixtures. *Cereal Chem.* **1989**, *66*, 90-93.
- Alloncle, M.; Doublier, J. L. Viscoelastic properties of maize starch/hydrocolloid pastes and gels. *Food Hydrocolloids* **1991**, *5*, 455-467.
- Annable, P.; Fittton, M. G.; Harris, B.; Phillips, G. O.; Williams, P. A. Phase behavior and rheology of mixed polymer systems containing starch. *Food Hydrocolloids* **1994**, *8*, 351-359.
- Biliaderis, C. G.; Page, C. M.; Maurice, T. J.; Juliano, B. O. Thermal characterization of rice starches: a polymeric approach to phase transitions of granular starch. *J. Agric. Food Chem.* **1986**, *34*, 6-14.
- Biliaderis, C. G. Thermal analysis of food carbohydrates. In *Thermal Analysis of Foods*; Harwalkar, V. R., C.-Y. Ma., Eds.; Elsevier Applied Science: London, 1990; pp 168-220.
- Brownsey, G. J.; Cairns, P.; Miles, M. J.; Morris, V. J. Evidence for intermolecular binding between xanthan and konjac glucomannan. *Carbohydr. Res.* **1988**, *176*, 329-334.
- Cairns, P.; Miles, M. J.; Morris, V. J. X-ray diffraction studies on konjac mannan-kappa carrageenan mixed gels. *Carbohydr. Polym.* **1988**, *8*, 99-104.
- Cairns, P.; Atkins, E. D. T.; Miles, M. J.; Morris, V. J. Molecular transforms of kappa carrageenan and furcellaran from mixed gel systems. *Int. J. Biol. Macromol.* **1991**, *13*, 65-68.
- Christianson, D. D.; Hodge, J. E.; Osborne, D.; Detroy, R. W. Gelatinization of wheat starch as modified by xanthan gum, guar gum and cellulose gum. *Cereal Chem.* **1981**, *58*, 513-517.
- Donovan, J. W. Phase transition of the starch-water systems. *Biopolymers* **1979**, *18*, 263-275.
- Gudmundsson, M.; Eliasson, A. C. L.; Bengtsson, S.; Aman, P. U. The effects of water soluble arabinosylxylan on gelatinization and retrogradation of starch. *Starch* **1991**, *43*, 5-10.
- Inouchi, N.; Glover, D. V.; Sugimoto, Y.; Fuwa, H. DSC characteristics of gelatinization of starches of single-, double-, and triple-mutants and their normal counterpart in the inbred Oh43 maize (*Zea mays* L.) background. *Starch* **1991**, *43*, 468-472.
- Kim, S. K.; D'Appolonia, B. L. Effect of pentosans on the retrogradation of wheat starch gels. *Cereal Chem.* **1977**, *54*, 150-160.
- Kohyama, K.; Nishinari, K. Effect of soluble sugars on gelatinization and retrogradation of sweet potato starch. *J. Agric. Food Chem.* **1991**, *39*, 1406-1410.
- Kohyama, K.; Nishinari, K. Cellulose derivatives effects on gelatinization and retrogradation of sweet potato starch. *J. Food Sci.* **1992**, *57*, 128-131, 137.
- Kohyama, K.; Iida, H.; Nishinari, K. A mixed system composed of different molecular weights konjac glucomannan and

- kappa carrageenan: large deformation and dynamic viscoelastic study. *Food Hydrocolloids* **1993**, *7*, 213–226.
- Kohyama, K.; Sano, Y.; Nishinari, K. A mixed system composed of different molecular weights konjac glucomannan and  $\kappa$ -carrageenan, II. Molecular weight dependence of viscoelasticity and thermal properties. *Food Hydrocolloids* **1996**, *10*, 229–238.
- Miles, M. J.; Morris, V. J.; Orford, P. D.; Ring, S. G. The roles of amylose and amylopectin in the gelation and retrogradation of starch. *Carbohydr. Res.* **1985**, *135*, 271–28.
- Nishinari, K.; Horiuchi, H.; Ishida, K.; Ikeda, K.; Date, M.; Fukada, E. A new apparatus for rapid and easy measurement of dynamic viscoelasticity for gel-like foods. *Nippon Shokuhin Kogyo Gakkaishi* **1980**, *27*, 15–21 (in Japanese with English summary and figure captions).
- Nishinari, K.; Koide, S.; Ogino, K. On the temperature dependence of elasticity of thermo-reversible gels. *J. Phys. (Fr.)* **1985**, *46*, 793–797.
- Nishinari, K.; Williams, P. A.; Phillips, G. O. Review of the physico-chemical characteristics and properties of konjac mannan. *Food Hydrocolloids* **1992**, *6*, 199–222.
- Roulet, Ph.; MacInnes, W. M.; Wursch, P.; Sanchez, R. M.; Raemy, A. A comparative study of the retrogradation kinetics of gelatinized wheat starch in gel and powder form using X-rays, differential scanning calorimetry and dynamic mechanical analysis. *Food Hydrocolloids* **1988**, *2*, 381–396.
- Sajjan, S. U.; Rao, M. R. R. Effect of hydrocolloids on the rheological properties of wheat starch. *Carbohydr. Polym.* **1987**, *7*, 395–402.
- Shatwell, K. P.; Sutherland, I. W.; Ross-Murphy, S. B.; Dea, I. C. M. Influence of the acetyl substituent on the interaction of xanthan with plant polysaccharides xanthan-konjac mannan systems. *Carbohydr. Polym.* **1991**, *14*, 131–147.
- Shiotsubo, T.; Takahashi, K. Differential thermal analysis of potato starch gelatinization. *Agric. Biol. Chem.* **1984**, *48*, 9–17.
- Shiotsubo, T. Differential scanning calorimetry of gelatinization of starches of roots, cereals and beans. *Osaka Joshi-Gakuen Junior College* **1992**, *36*, 7–12.
- Tye, R. J. The rheology of starch/carrageenan systems. *Food Hydrocoll.* **1988**, *2*, 259–263.
- Wada, K.; Takahashi, K.; Shirai, K.; Kawamura, A. Differential thermal analysis (DTA) applied to examining gelatinization of starches in food. *J. Food Sci.* **1979**, *44*, 1366–1368, 1372.
- Williams, P. A.; Day, D. H.; Langdon, M. J.; Phillips, G. O.; Nishinari, K. Synergistic interaction of xanthan gum with glucomannans and galactomannans. *Food Hydrocolloids* **1991**, *4*, 489–493.
- Williams, P. A.; Clegg, S. M.; Day, D. H.; Phillips, G. O.; Nishinari, K. Mixed gels formed with konjac mannan and xanthan gum. In *Food Polymers Gels and Colloids*; Dickinson, E., Ed.; RSC Publication: London, 1991; pp 339–348.
- William, P. A.; Clegg, S. M.; Langdon, M. J.; Nishinari, K.; Phillips, G. O. Studies on the synergistic interaction of konjac mannan and locust bean gum with kappa carrageenan. In *Gums & Stabilisers for the Food Industry 6*; Phillips, G. O., Wedlock, D. J., Williams, P. A., Eds.; Oxford University: Oxford, New York, Tokyo, 1992; pp 209–216.
- Williams, P. A.; Clegg, S. M.; Langdon, M. J.; Nishinari, K.; Piculell, L. Investigation of the gelation mechanism in  $\kappa$ -carrageenan/konjac mannan mixtures using differential scanning calorimetry and electron spin resonance spectroscopy. *Macromolecules* **1993**, *26*, 5441–5446.
- Yoshimura, M.; Takaya, T.; Nishinari, K. *J. Agric. Food Chem.* **1996**, submitted for publication.
- Yousria, A. B.; Williams, M. B. Rapid visco-analyzer (RVA) pasting profiles of wheat, corn, waxy corn, tapioca and amaranth starches in the presence of konjac flour, gellan, guar, xanthan and locust bean gums. *Starch* **1994**, *46*, 134–141.

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