Effect of Polysaccharides on the Gelatinization Properties of Cornstarch Dispersions

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ABSTRACT: Konjac glucomannan (KG, neutral), carboxymethylcellulose (CMC, negatively charged), and chitosan (positively charged) were added to cornstarch dispersions to study the effect of polysaccharide–starch interactions on starch gelatinization properties. Pasting and retrogradation properties were measured with a rheometer and DSC. Swelling properties of the starch granules were determined by solubility index, swelling power, and particle size distribution. Depending on the nature of the different polysaccharides, viscosities of cornstarch dispersions were affected differently. The particle size distributions were not influenced by the addition of any of the polysaccharides. Swelling results showed that the KG and CMC molecules interacted with the released or partly released amylose in the cornstarch dispersions. This was correlated with the short-term retrogradation of the starch pastes being retarded by the additions of KG and CMC. However, the chitosan molecules appeared not to associate with the amylose, so the retrogradation of the chitosan–cornstarch dispersions was not retarded.

KEYWORDS: polysaccharide, cornstarch, pasting, swelling, gelatinization, retrogradation

■ INTRODUCTION

Cornstarch is widely used in processed foods, pharmaceuticals, and textile and paper products among others owing to its unique functional properties, lack of odor, low cost, and availability. In the food industry, starch is used as a stabilizer and thickener of fluid foods, due to its high viscosity, bland flavor, and transparency of the newly prepared starch pastes.[1] However, the shelf life of some starch-based food products may be limited due to retrogradation, the further intramolecular and intermolecular interactions of the starch molecules following gelatinization.[2] Retrogradation of starch causes undesirable changes, such as syneresis and hardening.[3−5] Attempts to prolong the shelf life and to improve the quality of starch-based products by evaluating additives that interact with starch have been reported. The polysaccharides had been widely used in these studies, because their chemical composition allows their carbohydrate units to interact with the carbohydrates in starch systems.[6,7]

Blends of starch with polysaccharides have been used in foods to modify the texture and to control moisture and water mobility.[8−10] Konjac glucomannan (KG), extracted from plant tubers (*Amorphophallus konjac*), is used as a gelling, thickening, and emulsifying agent in food systems.[11,12] KG is composed of mannose and galactose residues in a ratio of 3:2 and provides high water-binding capacity and viscosity with a molecular weight ranging from 1 000 000 to 2 000 000 Da.[13] KG is a neutral polysaccharide that forms viscous solutions in water and gels in aqueous solutions. A mixture of cornstarch and KG (13.50/1.50) accelerated the short-term retrogradation (1−3 days) of cornstarch after gelatinization, whereas the water-holding ability of KG prevented syneresis. KG slowed the long-term retrogradation (14 days) of the cornstarch pastes following gelatinization.[14]

The anionic polysaccharides alginate, carboxymethylcellulose (CMC) and xanthan were effective in reducing syneresis and in retarding retrogradation after freeze–thaw treatments and also increased viscosity by participating in a network with starch.[7,15] The peak viscosity of potato starch was greatly decreased by negatively charged gums such as xanthan, CMC, carageenans, and alginate, because these polysaccharides were thought to adhere to the surface of the granules to stabilize the granules against shear forces.[6] The molecular weight of the neutral galactomannans guar gum, tara gum, and locust bean gum in mixtures with wheat starch had converse effects on the pasting viscosities of wheat starch.[2] Meanwhile, thermodynamic incompatibility between starch and polysaccharide leading to mutual exclusion of each polymer had been reported for the mixtures of amylose and dextran, amylose or waxy rice starch, and galactomannan, potato starch, and xanthan gum.[1,16−20]

Chitosan, the only natural cationic polysaccharide, has gained substantial recognition for its unique functional and biomedical characteristics, such as biocompatibility, biodegradability, and antibacterial and relatively hydrophobic properties.[21] However, most studies focused on its film-forming abilities, and the interactions between this natural cationic polysaccharide and starch paste components have not been well studied. Due to the favorable properties of chitosan, starch-based foods containing chitosan may have desirable functions.

The objectives of this study were to determine the pasting and swelling characteristics during gelatinization as well as the retrogradation properties of cornstarch in the presence of three

different polysaccharides: KG (neutral); CMC (negatively charged); and chitosan (positively charged). This design was necessary to provide better understanding of the differences in the interactions between cornstarch and the chosen polysaccharides.

■ MATERIALS AND METHODS

Materials. Normal cornstarch was obtained from Xingmao Ltd. (Shandong, China). The characteristics of this starch were as follows: moisture, 13.8%; amylose, 23.1%; protein, 0.32%; ash, 0.11%.

KG (M_w = 1 000 000−2 000 000 Da), CMC (M_w = 680 000 Da), and chitosan (M_w = 100 000 Da, degree of deacetylation = 95%) were obtained from Qiangsen Ltd. (Wuhan, China), Aoxing Ltd. (Shandong, China), and Tongda Chemical Ltd. (Yixing, China), respectively.

Pasting Properties. The pasting properties of starch systems were determined in duplicate on a rotational rheometer (AR-G2, T. A. Instruments, New Castle, DE). A stainless steel cone/plate geometry cell with 4° angle and 40 mm in diameter was used. Starch dispersions (8%, w/v) were prepared with degassed water and were continuously stirred before loading between the cone and the bottom plate. The exposed edge of the sample was coated with a thin layer of silicone oil to minimize moisture loss during the measurements. After loading, the starch dispersion was equilibrated at 50 °C for 1 min at 200 s^{-1}. The temperature was raised to 95 °C at the rate of 12 °C/min and held at 95 °C for 2.5 min. The temperature was then decreased to 50 °C at the rate of 12 °C/min and held at 50 °C for 1 min. The shear rate during pasting was maintained at 200 s^{-1}.

Swelling Power, Solubility Index, and Iodine Binding Values. The physical properties of polysaccharide−cornstarch systems, swelling power, and solubility index were determined. A volume of 25 mL of 2% (w/v) cornstarch dispersion was combined with 0.005 g (1%), 0.01 g (2%), 0.015 g (3%), or 0.025 g (5%) of polysaccharide and placed in 50 mL centrifuge tubes. The tubes were sealed and heated in a boiling water bath for 10 min and then immediately cooled in an ice−water bath for 5 min. After centrifuging the samples at 7000g for 15 min, the precipitated paste was separated from the supernatant. The wet and dried weights of the paste were recorded, and the weight of dried supernatant was also recorded (constant weight after drying at 105 °C).

Swelling power was recorded as the ratio of the wet weight of precipitated paste to its dry weight. The solubility index contained two aspects; one was recorded as the percentage of dried supernatant (excluding the polysaccharide) to the dry weight of the cornstarch (amylose in supernatant (ASI)), which was calculated under the assumption that all of the polysaccharides remained in the supernatant.[7] The other one was the total solid in supernatant (TSI), which was recorded as the percentage of total dried supernatant to the dry weight of the cornstarch. TSI was calculated under the assumption that all of the polysaccharides remained in the precipitate.

The amylose content of the soluble supernatant was determined by iodine binding. After the samples had been centrifuged at 7000g for 15 min, the supernatant (1 mL) was diluted with 4 mL of deionized water before 0.1 mL of the mixture was mixed with 2 mL of an aqueous solution of 0.2% KI and 0.65% I$_2$. The absorbance at 690 nm was determined[8] using a spectrophotometer (2802 UV−VIS, UNICO, China). Three replicates were run for each determination.

Particle Sizes in Different Systems. Samples of cornstarch dispersions were removed at various temperatures during heating and pasting on the rheometer. Samples were taken at 50, 60, 70, 80, 90, and 95 °C. The cornstarch dispersions were swiftly transferred into the sample cell of the particle size analyzer (Laser S3500, Microtrac, Montgomeryville, PA). The flow rate of water was set at 60% and run for 30 s. All of the experiments were performed in duplicate.

DSC Assays: Gelatinization and Retrogradation. The thermodynamic properties of the polysaccharide−starch dispersions were determined by DSC (Pyris 1 DSC, Perkin-Elmer, Waltham, MA). All of the samples were accurately weighed (0.01 mg) on Perkin-Elmer DSC pans. Dry weights of the samples were measured by heating to

constant weight in an oven (105 °C). The gelatinization characteristics were determined by a heating program that increased the DSC oven temperature from 30 to 90 °C, at the rate of 10 °C/min. To determine the effects of short-term and long-term storage on retrogradation, samples were rescanned from 25 to 85 °C at 10 °C/min after storage at 4 °C for 1 week and for 1 month. All of the experiments were performed under the flow of nitrogen gas. Results provided by the DSC curves included onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and enthalpy change (ΔH). The retrogradation ratio was calculated by dividing the rescanned enthalpy by the gelatinization enthalpy.[22] Two replicates were run for each determination.

Statistical Analysis. The statistical analysis of the results was conducted by the analysis of variance (ANOVA; SAS Statistic Package; SAS, Cary, NC). Significant differences were defined as $P \leq 0.05$.

■ RESULTS AND DISCUSSION

Effect of Polysaccharides on Pasting Properties of Polysaccharide−Starch Dispersions. Because of the intra- and intermolecular hydrogen bonds among starch molecules, starch granules are insoluble in cold water. However, starch interacts with water when heated, the hydrogen bonds in starch dispersions break and the molecules hydrate and the granules swell, releasing the starch molecules from the granules, and finally intermolecular interactions result in gelatinization. During this process, amylopectin turns from an ordered state into a less ordered state, due to the disruption of the hydrogen bonds by heat energy and hydrogen bond formation with water. Amylose, because of its long linear structure, is able to form multiple hydrogen bonds with other amylose molecules and form gel networks. These changes during heating can be observed from pasting curves or DSC measurements.

The pasting characteristics of polysaccharide−cornstarch mixtures containing 8% of cornstarch and various polysaccharides (as percentage of starch) were measured (Figure 1−3).
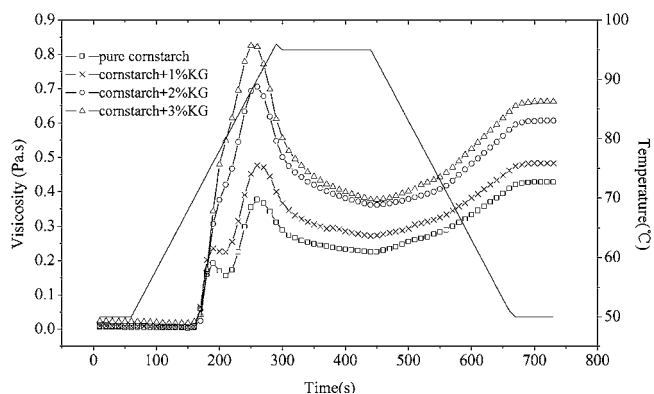

Figure 1. Pasting curves of KG−cornstarch systems. The viscosities of 8% cornstarch and 1, 2, and 3% KG (as percent of cornstarch) were determined using a rotational rheometer. The heating profile is shown as the solid line with the temperature scale at the right.

Initial viscosities of the dispersions before the onset of gelatinization were not increased significantly by the addition of any of the polysaccharides. This suggested that the viscosities contributed by each of the polysaccharides were small with regard to the larger changes in viscosity buildup which were observed during gelatinization of cornstarch dispersions with the polysaccharides. During gelatinization, pure cornstarch dispersion exhibited two peaks, a smaller peak at about 76 °C, which had been reported to be the result of amylose leaching from starch granules,[23] and a larger peak corresponding to the
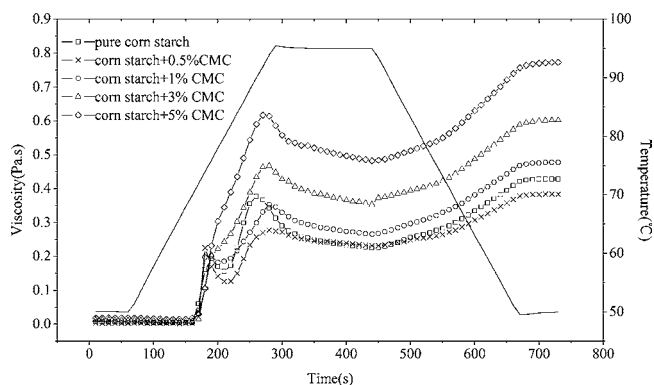
Figure 2. Pasting curves of CMC−cornstarch systems. The viscosities of 8% cornstarch and 0.5, 1, 3, and 5% CMC (as percent of cornstarch) were determined.
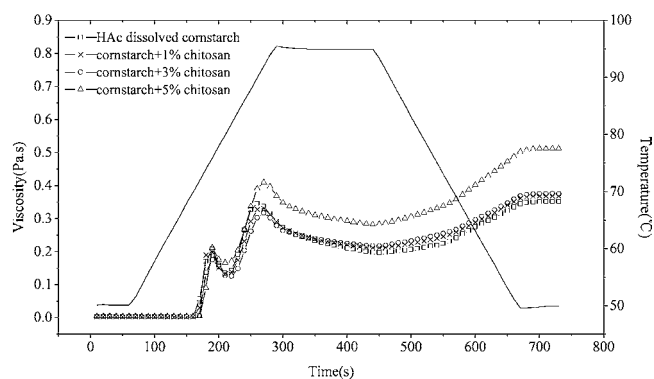

Figure 3. Pasting curves of chitosan−cornstarch systems dispersed in 0.2% acetic acid. The viscosities of 8% cornstarch and 1, 3, and 5% chitosan (as percent of cornstarch) were determined.

peak viscosity of the pasting curve. It is known that the initial pasting step of the starch dispersions occurred in the amorphous regions and subsequently in the crystalline micelle regions, which induced the leaching of the amylose out of the granules. The separation of amylose and amylopectin caused by the weaker interactions in amorphous regions had been associated with the formation of the first peaks in previous studies formed. Shi and BeMiller also observed a small rise in viscosity at 72 °C and a sharper rise at 82 °C in the dispersion of 4% of pure cornstarch using a Brookfield viscometer, but only one major peak was observed by using an RVA.[6]

Increasing KG (1, 2, and 3% relative to starch content) increased peak viscosities, but did not change the peak temperatures (Figure 1). The doubling of the peak viscosities with increasing KG was thought to be due to the increasing concentration of KG interspersed within the starch continuous phase as the granules absorbed water and swelled. No significant pasting temperature (both the onset and peak) differences were observed with the addition of KG, which suggested that water binding by KG was not sufficient to influence the initial leaching of amylose. Khanna and Tester[11] also reported DSC measurements that showed the gelatinization onset and peak temperatures of the normal starches were unaffected by the addition of increasing amounts of KG. With the addition of 2 or 3% of KG, the first pasting peaks of the dispersions became shoulders on the larger second pasting peaks.

When the concentration of KG increased from 1 to 2%, the pasting peak viscosity increased by 45.8%, whereas the final viscosity increased by 27.1%. Peak and final viscosities increased for other dispersions by about 20 and 10%, respectively. The peak viscosity of cornstarch + 3% KG was the highest among the pasting peak viscosities in this investigation. The final pasting viscosities of KG−cornstarch dispersions were lower than their respective peak viscosities.

The characteristics of 1, 3, and 5% of CMC with cornstarch were measured (Figure 2). Because a decrease in pasting peak viscosity upon the addition of 1% of CMC was observed, an additional dispersion was tested with 0.5% of CMC. The onset pasting temperatures of these dispersions were similar to those of the KG−cornstarch dispersions except that the addition of 5% CMC caused a higher onset temperature. The addition of CMC also shifted the peak temperatures 4 °C higher than that of the pure cornstarch. Similar results were reported by Yoshimura et al.[24] when xyloglucan was dispersed with cornstarch. The lower additions of CMC (0.5 and 1%) decreased the peak viscosities of the dispersions relative to pure cornstarch, but higher concentrations of CMC (3 and 5%) increased the cornstarch peak viscosities in a trend that was similar to the additions of KG, although with lower peak viscosity values. The final pasting viscosities of CMC−cornstarch were all higher than their respective peak viscosities, which were opposite to the relationship of the KG−cornstarch pasting viscosities.

The effect of chitosan on the pasting properties of cornstarch was also measured (Figure 3). Because chitosan is soluble only in acidic solutions, these dispersions were prepared with 0.2% acetic acid solution. The additions of 1 and 3% chitosan to cornstarch showed pasting viscosity curves which were similar to that of the pure cornstarch. Cornstarch + 1 and 3% of chitosan dispersions showed slight depressions of the peak viscosities and slightly higher final viscosities as compared to those of the pure cornstarch. The addition of 5% chitosan resulted in an overall increase in viscosity during the pasting process compared to the pure cornstarch. The viscosity effects may be due to the molecular weight of the chitosan, which was about 100 000 Da, much lower than that of CMC (about 680 000 Da), so the effect of viscosity was much less until the concentration of chitosan reached 5%. The pasting onset temperatures of the pure cornstarch and cornstarch + 1% chitosan were 2 °C lower than those with higher levels of chitosan (3 and 5%). However, the peak temperature of pure cornstarch was lower than that of all the other dispersions with chitosan.

From these pasting curves measurements, there were observed effects on the starch pasting curves, which depended on the characteristics of the polysaccharides and their concentration. The interactions between the polysaccharide and starch were thus dependent on the structural compatibility or molecular interactions between starch and polysaccharide.[2] With respect to the increase of the paste viscosity with the addition of the polysaccharides, the cornstarch + 3% KG dispersion gave the highest peak viscosity, whereas the CMC−cornstarch dispersion showed the highest final viscosity at 5%. To investigate the nature of the interactions that related to the viscosity changes, other experiments were conducted.

Effect of Polysaccharides on Swelling Properties of Cornstarch. The changes of the granule swelling properties in the polysaccharide−starch dispersions were measured. Swelling during heating in excess water is a distinctive property of starch

Table 1. Solubility Index, Swelling Power, and Iodine Values of Cornstarch Dispersions with Added Amounts of Polysaccharides[a]

polysaccharide and amount (%) added		amylose in supernatant[b] (%)	total solids in supernatant (%)	swelling power (g/g)	abs (690 nm)
KG	0	2.9 ± 0.1 F	2.9 ± 0.1 J	10.1 ± 0.1 F	0.201 ± 0.001 K
	1	6.2 ± 0.5 D	7.2 ± 0.5 H	11.6 ± 0.2 CD	0.405 ± 0.002 F
	2	6.9 ± 0.1 D	8.9 ± 0.1 FG	11.0 ± 0.0 DE	0.479 ± 0.002 D
	3	10.5 ± 0.4 C	13.5 ± 0.4 C	13.0 ± 0.6 B	0.557 ± 0.001 C
CMC	0.5	4.0 ± 0.1 EF	4.5 ± 0.1 I	10.0 ± 0.6 F	0.217 ± 0.004 J
	1	9.7 ± 0.4 C	10.7 ± 0.4 DE	11.6 ± 0.2 CD	0.465 ± 0.002 E
	3	12.5 ± 0.4 B	15.5 ± 0.4 B	12.8 ± 0.1 B	0.797 ± 0.001 B
	5	15.5 ± 0.3 A	20.5 ± 0.3 A	14.8 ± 0.4 A	0.836 ± 0.003 A
chitosan	0	4.4 ± 0.0 E	4.4 ± 0.0 I	10.6 ± 0.1 EF	0.255 ± 0.002 I
	1	7.3 ± 1.8 D	8.3 ± 1.8 GH	12.0 ± 0.6 C	0.293 ± 0.005 H
	3	6.8 ± 0.4 D	9.8 ± 0.4 EF	13.4 ± 0.4 B	0.317 ± 0.004 G
	5	7.0 ± 0.5 D	12.0 ± 0.5 D	11.9 ± 0.2 C	0.299 ± 0.004 H

[a]Values are the mean ± SD of triplicates. Values in the same column with different letters (A–G) are significantly different ($p \leq 0.05$). [b]Calculated on the basis of the assumption that all of the added polysaccharides remained in the supernatant after centrifugation.

granules due to their source and processing history. Amylose is generally a diluter and depressor of swelling.[25] As a means to determine the leaching of amylose, the swelling properties of all the dispersions were measured. The effect of polysaccharides on solubility index, swelling power, and iodine binding value were determined (Table 1).

Amylose and total solids in the supernatants of the polysaccharide−starch dispersions increased significantly ($P \leq$ 0.05, Table 1) after boiling in water or 0.2% acetic acid solution. The results of iodine binding values (Abs 690 nm) that were used to determine "leached amylose" were consistent with the trend of ASI (amylose in supernatant). From the pasting curves, it was observed that as the concentration of KG increased or when the concentrations of CMC and chitosan were high enough, the first peaks heightened gradually. The phenomenon might be explained by the hypothesis that as amylose leached into the continuous phase, some interactions with the polysaccharides occurred, resulting in the increase of the overall viscosities. Other researchers have found that when cornstarch was heated in water, amylose was mainly found near the starch granules.[26] However, amylose was found throughout the bulk solution when cornstarch was heated in the CMC solution.[6] Amylose was found in the highest concentration in the bulk solution when cornstarch dispersions were heated with CMC, which suggested that CMC molecules may have interacted or associated with leached amylose. Because the CMC molecules are anionic, repulsion effects may have been dominant at low CMC concentrations (0.5 and 1%), causing decreases in viscosities. However, when the concentration was increased to higher levels (3 and 5%), a synergistic effect between amylose and CMC molecules appeared to have played a dominant role and, consequently, caused the viscosity to increase.

Nevertheless, the ASI values among chitosan dispersions with different levels of chitosan did not change significantly ($P \leq$ 0.05), and the initial pasting peaks of these dispersions were similar. In view of the fact that the levels of leached amylose of the chitosan−cornstarch dispersions changed only minimally, chitosan did not promote the leaching of amylose to the same degree as KG and CMC. In other studies, when starch was heated in the presence of various polysaccharides (xanthan,

CMC, guar, etc.), the shape of the starch granules and the solubility as well as the swelling power changed.[8,27]

With increased concentrations of KG, the solubility index, swelling power (SP), and iodine values of cornstarch increased, indicating that more amylose leached from the granules. As more amylose leached out of the granules, more water may have moved into the starch particles, causing the granules to become more swollen and producing higher paste viscosities. Another interpretation could be that higher levels of leached amylose produced higher levels of observed paste viscosities. Likewise, association of leached amylose could also provide a synergist effect on viscosity buildup.

The calculation of the ASI was dependent on the assumption that all of the polysaccharides were in the solution after centrifugation. To justify this assumption, the correlation between ASI and iodine values was analyzed. The R^2 values were 0.918, 0.951, and 0.929 for the KG−, CMC−, and chitosan−cornstarch systems, respectively. When the assumption was that the total solid of the supernatant was amylose (TSI), the R^2 values were 0.932, 0.955, and 0.778. The two methods of R^2 calculation suggested that some of the KG and CMC molecules remained in the precipitate, whereas others were in the supernatant, and the remainder had interacted with the amylose attached to the granules. The poor fit of the chitosan−cornstarch with the precipitate supported the hypothesis that chitosan was mainly in the supernatant. The lack of interaction by chitosan may be due to the lower molecular weight (100 000 Da) and its positive charge.

Particle Sizes in Different Systems. Because the amount of water and the volume of the rheometer cell are fixed, water between the starch granules will be reduced as it is absorbed by the starch granules, and the concentration of the polysaccharide increases. The concentration increases of the polysaccharides may account for the rapid rise in viscosities of the KG− and CMC−cornstarch dispersions. To determine if the increases of the polysaccharide viscosities contributed to the pasting viscosities, the particle size distributions of the cornstarch granules at different temperatures were determined.

Studies of the pasting of starch dispersions have shown an excellent correlation between the sizes of the swelling granules determined by laser light scattering and the viscosities. As

Table 2. Median Diameters (D) in Polysaccharide−Cornstarch Systems during the Pasting Process[a]

sample	D^b					
	50 °C	60 °C	70 °C	80 °C	90 °C	95 °C
cornstarch	15.3 ± 0.1 C	15.3 ± 0.0 E	24.8 ± 0.0 C	34.2 ± 0.0 B	41.8 ± 0.1 B	29.5 ± 2.9 ABC
cornstarch + 2% KG	16.0 ± 0.1 A	15.6 ± 0.1 D	22.3 ± 0.0 F	33.2 ± 0.1 E	41.2 ± 0.1 C	28.9 ± 2.5 BC
cornstarch + 1% CMC	15.2 ± 0.1 C	15.5 ± 0.0 D	22.4 ± 0.0 E	34.1 ± 0.0 BC	41.5 ± 0.1 BC	33.3 ± 2.5 AB
cornstarch + 5% CMC	15.7 ± 0.1 B	16.2 ± 0.0 B	25.0 ± 0.0 B	36.2 ± 0.1 A	43.8 ± 0.4 A	35.8 ± 2.2 A
cornstarch + 1% chitosan	15.4 ± 0.0 C	15.9 ± 0.1 C	26.0 ± 0.0 A	33.8 ± 0.1 D	42.0 ± 0.1 B	24.2 ± 2.4 C
cornstarch + 5% chitosan	16.1 ± 0.1 A	16.4 ± 0.0 A	23.4 ± 0.1 D	34.0 ± 0.0 C	44.1 ± 0.3 A	29.0 ± 2.4 BC

[a]Values are the mean ± SD of duplicates. Values in the same column with different letters (A−F) are significantly different ($p \leq 0.05$). [b]The size at which 50% of particles by volume are smaller and 50% are larger (μm).

shown in Table 2 and Figure 4, when the temperature rose from 50 to 60 °C, median diameters and the distributions of all
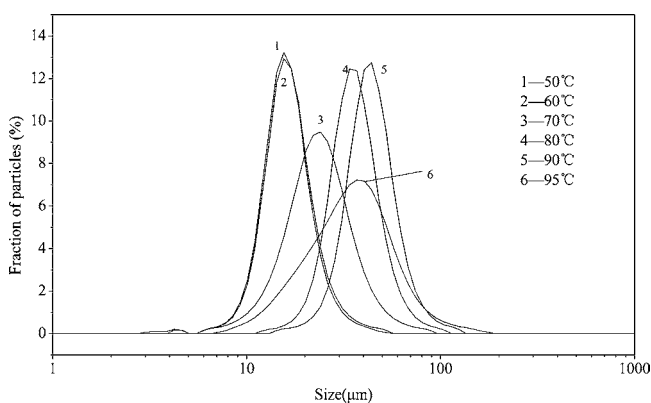
Figure 4. Typical particle size distribution in a cornstarch dispersion at different temperatures.

the systems remained steady. After that, median diameters changed as a result of water absorption. Particle size distributions of the granules at 70 and 95 °C were much broader than those of the others, because most of the particles were in different states; for example, some granules had just started to swell, whereas some others were broken. Moreover, when the temperature was adjusted from 70 to 90 °C, median

diameters of all the systems almost doubled. The narrow distribution of particles at 90 °C indicated that most of the granules were still intact. After a peak hold step of 95 °C, the median diameters of all the systems decreased around 10 μm as a result of the granule rupture. Median diameters of gelatinized granules were at the same level, in accordance with the result of Table 1, and the swelling powers of all the systems were at the same level, because the swelling patterns of all the systems were similar.[28]

The calculated starch granule sizes in KG−cornstarch dispersions at 90 °C and most other temperatures were similar to those of the pure cornstarch (Table 2). Therefore, the contributions to the viscosities of the KG−cornstarch and pure cornstarch dispersions due to the volume fraction of solid should be similar. Because the viscosities of the KG−cornstarch dispersions were much higher, the results of granule sizes supported the hypothesis that the concentration of KG mainly accounted for the increase of the viscosity. For the cornstarch + 1% CMC system, except the median diameters at 70 and 95 °C, others were similar to those of the pure cornstarch, in accordance with the viscosity results (Figure 2). During the whole gelatinization process, the median diameters of cornstarch + 5% CMC were bigger than those of the pure cornstarch. This result suggested that the observed pasting viscosity at 1% of CMC was due to the smaller particle sizes and that the greater solids volume fraction could account for a significant amount of the increase in viscosity at 5%. The high volume fraction also resulted in a more concentrated

Table 3. Effect of Polysaccharides on the Gelatinization of Cornstarch (Moisture > 66%)[a]

polysaccharides and amount (%) added		T_o (°C)	T_p (°C)	T_c (°C)	ΔH_0 (J/g)	R_1 ($\Delta H_1/\Delta H_0$)[b]	R_2 ($\Delta H_2/\Delta H_0$)[c]
KG	0	68.6 ± 0.0 CD	72.7 ± 0.0 BCD	76.9 ± 0.0 AB	12.72 ± 0.15 A	0.29 ± 0.01 BCD	0.45 ± 0.08 AB
	1	68.4 ± 0.2 D	72.1 ± 0.1 D	76.6 ± 0.5 B	11.63 ± 0.23 EF	0.24 ± 0.00 DEF	0.44 ± 0.03 AB
	2	68.6 ± 0.0 CD	72.3 ± 0.1 D	76.5 ± 0.1 B	12.52 ± 0.16 B	0.15 ± 0.00 G	0.31 ± 0.06 C
	3	68.6 ± 0.3 CD	72.3 ± 0.4 D	76.6 ± 0.4 B	12.62 ± 0.15 A	0.23 ± 0.01 EF	0.53 ± 0.06 A
CMC	0.5	68.9 ± 0.3 BCD	73.0 ± 0.1 BCD	77.0 ± 0.4 AB	12.15 ± 0.06 BCD	0.27 ± 0.00 CDE	0.45 ± 0.01 AB
	1	69.0 ± 0.7 BCD	73.1 ± 1.0 BCD	77.4 ± 1.4 AB	12.39 ± 0.03 ABC	0.17 ± 0.04 G	0.30 ± 0.04 C
	3	68.9 ± 0.3 BCD	73.0 ± 0.2 BCD	77.7 ± 0.4 AB	12.00 ± 0.01 CDE	0.18 ± 0.00 GF	0.37 ± 0.04 BC
	5	69.6 ± 0.2 ABC	73.7 ± 0.1 ABC	78.0 ± 0.3 AB	12.59 ± 0.09 AB	0.18 ± 0.02 GF	0.49 ± 0.05 A
chitosan	0	69.2 ± 0.7 ABCD	72.6 ± 0.8 CD	76.8 ± 0.5 AB	11.53 ± 0.04 F	0.34 ± 0.00 AB	0.47 ± 0.00 AB
	1	69.9 ± 1.2 AB	73.9 ± 0.9 AB	78.3 ± 1.2 A	11.89 ± 0.52 DEF	0.34 ± 0.07 AB	0.50 ± 0.03 A
	3	70.2 ± 0.3 A	74.4 ± 0.5 A	78.3 ± 0.5 A	11.55 ± 0.03 EF	0.32 ± 0.02 ABC	0.44 ± 0.02 AB
	5	69.8 ± 0.1 ABC	73.9 ± 0.1 AB	77.7 ± 0.2 AB	11.70 ± 0.17 DEF	0.38 ± 0.00 A	0.48 ± 0.02 AB

[a]Values are the mean ± SD of duplicates. Values in the same column with different letters (A−G) are significantly different ($p \leq 0.05$). [b]R_1 is the ratio of the enthalpy 1 week after gelatinization divided by the initial gelatinization enthalpy. [c]R_2 is the ratio of the enthalpy 1 month after gelatinization divided the initial gelatinization enthalpy.

intergranular concentration that also contributed significantly to the pasting viscosity. The 5% chitosan−cornstarch dispersion also had the same solid volume content as the 5% CMC−-cornstarch dispersion and had an increase in viscosity over pure cornstarch but significantly lower than that of the 5% CMC−cornstarch. The particle size distributions suggested that the difference was due to the difference in viscosities of the two polysaccharides, because of their inherent viscous properties and volume of intergranular space.

Because volume increases as a function of the cube of the radius, doubling of the radius increases volume by 8 times, and tripling of the radius increases the volume by 27 times. If starch in 8% dispersion occupies about 5% of the volume, a 3-fold increase in radius would utilize all of the water of the dispersion. These observations are the basis for the rapid rise in viscosity as the starch granule size increases at the expense of the fluid phase. Some starch−starch interactions can be replaced by polysaccharide−starch interactions with modified properties.

Effect of Polysaccharides on Starch Gelatinization and Retrogradation. Starch granules contain two types of glucose polymers, amylose and amylopectin. Amylopectin, the major component (70−80%) of most normal starches, is highly branched with short chains of 7−20 glucose units (molecular weight $\sim 10^8$).[29] Amylopectin forms the crystalline areas of the starch granule by hydrogen bonding among the branches. The breakdown of the crystalline amylopectin areas requires a characteristic amount of heat that can be measured by DSC. When the moisture content of the dispersion is >60%, starch gelatinization is barely affected by the moisture content.[14]

The DSC results of polysaccharide−cornstarch dispersions are shown in Table 3. Gelatinization temperatures (T_o, T_p, T_c) for the KG−cornstarch dispersions were similar to those of the pure cornstarch dispersion. Khanna and Tester[11] also observed that T_o and T_p of normal starches were minimally affected by the addition of increasing amounts of KG (when the moisture content was relatively high), but T_c shifted to higher values with the increase of the KG content. A similar result was reported by Yoshimura et al.,[14] who suggested that the immobilization of water molecules by KG was the cause of the change in T_c. Zhou et al.[30] reported increases in all of the parameters of gelatinization as the CMC levels increased. They also suggested that the polysaccharide structure may be responsible for the differences in gelatinization. Interactions between the polysaccharide and starch might affect the starch gelatinization by reducing the chain mobility of the starch components.[15] Therefore, if the interaction between polysaccharide solution and starch was stronger than that between water and starch, the gelatinization parameters would increase; otherwise, the parameters would decrease.

Small decreases in short-term retrogradation (R_1) of the cornstarch dispersions with added KG or CMC were observed (Table 3). For the long-term retrogradation (R_2) of the same dispersions, there were decreases observed with smaller additions of KG or CMC followed by increases of R_2 with larger additions of KG or CMC. The addition of chitosan showed no clear trends in the changes of either R_1 or R_2 at different levels of contents.

During the storage of starch pastes, both the amylose and amylopectin molecules rearranged, resulting in an increase of the hardness. The retrogradation might proceed in two different mechanisms: one was the short-term retrogradation, and the other was the long-term retrogradation. Leached

amylose in the aqueous phase was the main cause of the short-term retrogradation, whereas the amylopectin rearranged more slowly and was responsible for the long-term retrogradation. For the KG− and CMC−cornstarch dispersions, short-term retrogradation was retarded, but the long-term retrogradation was retarded with optimum additions of either KG or CMC. The R_1 value of cornstarch + 2% KG was 0.14, which was the lowest of all. Meanwhile, the R_1 values of the CMC−cornstarch systems were about 70% lower than that of pure cornstarch (except cornstarch + 0.5% CMC). Moreover, R_2 values of cornstarch + 2% KG and cornstarch + 1 and 3% CMC were much lower than the others. These results were consistent with the results of previous studies[2,11,15] in which the KG and CMC molecules had been reported to interact with leached amylose only, without influencing the structure of amylopectin.

In the case of chitosan−cornstarch dispersions, neither short-term nor long-term retrogradation was inhibited, suggesting that leached amylose and chitosan molecules were thermodynamically incompatible or, in other words, phase separation might occur in chitosan−cornstarch dispersions. Thermodynamic incompatibility between cornstarch and polysaccharide leading to mutual exclusion had been reported in the mixtures of amylose and amylopectin,[16] amylose and dextran,[20] amylose and galactomannan,[1] and potato starch and xanthan gum.[18] As a result, rearrangement of amylose was not restricted by the addition of chitosan. Conversely, due to the phase separation of chitosan and amylose, the local concentration of amylose became relatively higher, resulting in more short-term retrogradation.

KG and CMC were observed to retard the short-term retrogradation of the cornstarch pastes, due to the interactions between the amylose and the polysaccharide molecules. There was an optimum level of the KG or CMC to suppress retrogradation over time. However, the addition of chitosan retarded neither the short-term nor the long-term retrogradation of the cornstarch pastes, which was consistent with the results of the swelling and pasting properties.

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■ ABBREVIATIONS USED

CMC, carboxymethylcellulose; DSC, differential scanning calorimetry; M_w, molecular weight; UV, ultraviolet; VIS, visible; Abs, absorption.

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