



# Retardant effect of sodium alginate on the retrogradation properties of normal cornstarch and anti-retrogradation mechanism



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## ABSTRACT

The effect of sodium alginate (AG) on the retrogradation properties of normal cornstarch (NCS) and its anti-retrogradation mechanism were investigated by determining the pasting parameters, gel firmness, gelatinization parameters, retrogradation enthalpy, glass transition temperature, dynamic rheological properties, interaction force, leached amylose content, swelling power, X-ray diffraction patterns and relative crystallinity, respectively. The sodium alginate-normal cornstarch (AG-NCS) blends were treated with different ratio of NCS to AG (ranging from 10:0–9.6: 0.4) and stored at 4 °C and 25 °C for 1d or 3d, respectively. The addition of AG significantly decreased the setback value, which suggested that the short-term retrogradation of NCS was inhibited. AG obviously reduced the retrogradation enthalpy, storage modulus, and relative crystallinity of NCS, which decreased with the increase in the AG concentration. The aforementioned results suggested that addition of AG could retard the retrogradation of NCS, and the retardation effect exhibited positive correlation of AG concentration. The changes in the storage modulus after the addition of NaCl and urea suggested that the hydrogen bonding might be the main force involved in the formation and stability of the AG-NCS blends. The X-ray diffraction patterns showed that the transformation of the A-type to B-type of NCS occurred after gelatinization and retrogradation.

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## 1. Introduction

Cornstarch is one of the most important and abundant materials in nature (Schwartz et al., 2014). It is often used as a thickening, gelling, stabilizing, and binding agent in the food industry (Chen, Tong, Ren, & Zhu, 2014b). However, starch often suffers from some disadvantages, especially the retrogradation during storage that affects the starchy-food quality and shortens shelf life (Tang, Hong, Gu, Zhang, & Cai, 2013). Hydrocolloids can be used to modify the properties of starch-based formulations (such as the increase in viscosity, reduction in retrogradation, and reduction in firmness), which is more economical, convenient, and safe compared to chemical modification methods (Weber, Clerici, Collares-Queiroz, & Chang, 2009). Most studies have focused on the gelatinization and rheological properties of starch-hydrocolloids mixtures. Klein, Pinto, and Vanier (2013)

investigated twenty-one members of five families of hydrocolloids and reported that the addition of all hydrocolloids (other than hydroxypropylmethylcellulose) increased the peak viscosities and made the pastes less solid-like (Kim & BeMiller, 2012). Weber et al. (2009) reported that guar and xanthan gums affected the properties of the normal corn starch paste more significantly compared to the waxy cornstarch paste. Xu et al. (2012) reported that addition of polysaccharides could affect the viscosity of cornstarch dispersions. The effects of crude malva nut gum, konjac glucomannan, corn fiber gum, pullulan, xanthan gum, guar gum, and cellulose gum on the pasting properties, thermal properties, gelatinization behavior, and rheological properties of starch were also investigated in previous studies (Chen et al., 2014b; Kim & Yoo, 2011; Phimolsiripol, Siripatrawan, & Henry, 2011; Qiu et al., 2015; Schwartz et al., 2014; Sim, Aziah, & Cheng, 2011).

Sodium alginate (AG) is a kind of hydrophilic colloids, which is usually used as a food thickener, emulsifier, and stabilizer (Siddhesh & Kevin, 2012). It can also be added to starch and exhibit a marked effect on physicochemical properties of starch. The peak viscosity, final viscosity, and storage modulus ( $G'$ ) of pea starch increased in the presence of AG, whereas the loss tangent ( $\tan\delta$ )

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decreased (Kim & BeMiller, 2012). AG was reported to improve the viscosity and freeze-thaw stability of sweet potato starch (Lee, Baek, Cha, Park, & Lim, 2002). We previously reported the effect of AG and its guluronic acid/mannuronic acid ratio on the physicochemical properties of high-amylose cornstarch (Zhao, Chen, Wang, & Li, 2016).

The addition of hydrocolloids could retard retrogradation of starch. However, most studies have focused on the effect of guar gum, xanthan, spring dextrin, tea polysaccharide, carboxymethyl cellulose, and konjac glucomannan on the retrogradation of starch (Kim & BeMiller, 2012; Tang et al., 2013; Xu et al., 2013; Zhou, Wang, Zhang, Du, & Zhou, 2008). There have been fewer studies on the retardant effect of AG on the retrogradation of starch and the interaction between starch and AG. The storage temperature also affects the retrogradation properties of starch. Hsu (1998) reported that rice starch retrogradation was influenced by the cooling rate, and rapid cooling rate contributed to higher rice starch retrogradation compared to slow cooling rate during storage at 5 °C. Furthermore, some researchers reported that the freezing temperature can effectively retard amylopectin retrogradation after the freezing process during frozen storage for at least 5 months, while amylopectin still retrograded after the freezing process during chill storage at 4 °C (Yu, Ma, & Zheng, 2012). Thus, this study was initiated in order to gain an insight into the role and potential usefulness of AG in affecting retrogradation of cornstarch under different storage temperature by using the methods of rapid visco analysis (RVA), differential scanning calorimetry (DSC), texture analysis, dynamic rheology measurement, and X-ray diffraction analysis. The result can be used to explore the interaction between AG and NCS and clarify the retrogradation mechanism of AG-NCS blends under different temperature. The studies are meaningful in exploring the potential utilization of AG to improve the processing characteristics and storage stability of starchy food.

## 2. Materials and methods

### 2.1. Materials

Native normal cornstarch (NCS, amylose content of 26.2%, moisture content of 6.3%) was purchased from Binzhou Jinhui Corn Co. Ltd., Shandong, China. Sodium alginate (AG, the ratio of mannuronic acid to guluronic acid is about 1.17, moisture content of 12.8%) was gifted by Qingdao Mingyue Haizao Ltd., Shandong, China. All other reagents used were analytical grade.

For the AG-NCS blends in each property experiment, the ratio of NCS to AG was 10: 0, 9.95: 0.05, 9.8: 0.2, 9.6: 0.4 (w/w, dry basis), respectively.

### 2.2. Leached amylose content and swelling power

The swelling power of samples during heating was determined following the method reported by Chen et al. (2014b) with a slight modification. Firstly, suspensions of 2% NCS (dry basis) and AG-NCS blends were prepared in centrifuge tubes with closed screw caps. Then, the samples were heated in a water bath at 95 °C for 30 min. After heating, the samples were cooled to room temperature in 15 min (cooling rate of 4.7 °C/min) and then centrifuged at 16,000 × g for 20 min. The supernatant was separated to determine the leached amylose by the iodine colorimetric reaction, according to the method described by Chen et al. (2014b). The leached amylose was calculated by dividing the amylose content in the supernatant by the original weight of NCS. The precipitate was weighed and then dried to a constant weight at 105 °C. The swelling power was expressed as the ratio of wet weight of the residue to its dry weight. The results are reported as the averages of five trials.

### 2.3. Pasting properties

The total concentration of AG-NCS blends was 9% (w/w, dry basis). AG was first dispersed in distilled water, under magnetic stirring for 30 min. NCS was then poured into the AG solutions and stirred vigorously to avoid the formation of lumps for another 30 min at room temperature (25 °C). According to the method of our previous study (Zhao et al., 2016), the pasting properties of the samples were characterized by using a rapid visco analyzer (RVA, Model 4D, Newport Scientific, Australia). A 2.5-g sample was weighed directly into an aluminum RVA canister. Distilled water was added up to a total of 28 g. In line with the STD1 procedure of RVA, the sample was held at 50 °C for 1 min, heated to 95 °C at the rate of 12 °C/min and held at 95 °C for 2.5 min; it was then cooled to 50 °C at the same rate, and finally held at 50 °C for 2 min. As part of the process, the rotating speed was maintained at 960 rpm for 10 s, and then at 160 rpm. All tests were repeated five times. The pasting parameters including the pasting temperature (PT), and setback value (SB) were also measured and recorded in the present study.

### 2.4. Gel firmness

Warm starch pastes prepared according to the RVA determination method were used for the gel firmness analysis according to the method reported in our previous study (Zhao et al., 2016) with minor modification. The pastes were poured into a cylindrical stainless canister (4 cm inner diameter and 6 cm height). The diameter and height of the sample were 4 cm and 4.5 cm, respectively. The mixed gels were wrapped with plastic film to avoid moisture loss and were held at 4 °C and 25 °C for 1d or 3d to allow gel formation before the analysis. Before the measurement, the samples returned to ambient temperature. Gel firmness analysis was performed with a texture analyzer (TA-XTplus, Stable Micro Systems Ltd., Surrey, England), using a P/0.5 probe (a type of cylinder probe with a 1.27 cm of diameter). The gel was punctured to 25% of its original height at a test speed of 1.0 mm/s. The peak force measured was recorded as the gel firmness value. The results are reported as the averages of five trials.

### 2.5. Differential scanning calorimetry (DSC)

The DSC measurement was determined by a differential scanning calorimeter (DSC-1, Mettler-Toledo International Inc., Switzerland) under nitrogen flow, after being calibrated with indium. The measurement was performed according to the method reported by Zhou et al. (2008). The pan was hermetically sealed and allowed to equilibrate for 12 h before analysis. The heating program increased the sample temperature from 30 to 130 °C at a rate of 5 °C/min, followed by cooling to 30 °C at the same rate. Heating and cooling were performed in an atmosphere of nitrogen gas. The gelatinization and retrogradation properties of the samples were determined from the DSC curves.

The weight ratio of dry NCS to water was maintained at 35% (w/w, dry basis). For dispersion of the AG-NCS blends, a blend of 17.5 g of NCS (35% based on the total sample, w/w, dry basis) was dispersed in a solution containing AG. Then a 30-mg sample was weighed directly into the aluminum pans. The onset temperature ( $T_o$ ), peak temperature ( $T_p$ ), and conclusion temperature ( $T_c$ ) were recorded from the first-run heating DSC curves, as was the gelatinization enthalpy ( $\Delta H$ ). After the first-run heating, the gelatinized samples were cooled to 30 °C in the instrument and stored at 4 °C and 25 °C for 1d or 3d, respectively. The stored samples were reheated to examine the effects of AG on retrogradation. The retrogradation enthalpy of the second heating run was recorded. To determine the glass transition temperature ( $T_{gp}$ ), the samples were

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