



Effect of a small amount of sodium carbonate on konjac glucomannan-induced changes in wheat starch gel



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ABSTRACT

Wheat starch gels were produced with konjac glucomannan (KGM) and low concentrations of Na₂CO₃ (0.1–0.2 wt% of starch) using a rapid viscosity analyzer (RVA). The gelling properties of wheat starch in varying ratios of KGM and Na₂CO₃ were characterized by differential scanning calorimetry (DSC), rheometry and confocal laser scanning microscopy (CLSM). A small amount of Na₂CO₃ resulted in gels with increased elasticity whereas structural ordering during retrogradation was insignificantly affected. Comparison of CLSM images of composite gels revealed that Na₂CO₃ at 0.2 wt% of starch allowed the formation of fiber-like extensions around scattered swollen granules by KGM and amylose interaction, making swollen granules disperse within the micro phase, which was not typical in CLSM images of gels in the absence of Na₂CO₃. Dynamic storage modulus and dynamic power law exponent were substantially higher than those observed for the same concentration of KGM in the presence of Na₂CO₃, supporting the hypothesis that Na₂CO₃ could promote strong interchain associations between KGM and starch components.

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1. Introduction

Wheat starch granules exist as semi-crystalline particles comprised of a small quantity of lipids, phosphate monoesters and enzymes, 20–30% amylose and 70–80% amylopectin (BeMiller & Whistler, 2009, chaps. 7 and 8). When starch granules are heated in excess water to progressively higher temperatures the granules swell, followed by a release of amylose from the granule structure (BeMiller & Whistler, 2009, chaps. 7 and 8). After swelling to a point, the granules collapse and form a complex colloidal suspension consisting of granule remnants and dissoluble starch components (Koganti, Mitchell, Ibbett, & Foster, 2011). On cooling sufficiently, the rigidity of the gel increases gradually followed by the development of syneresis, which are collectively described as “retrogradation”. Hoover (1995) postulated a two-stage process for starch retrogradation with both amylose and amylopectin involved: the first stage is almost completed within a few hours of storage, which has been ascribed to the conformational ordering

of amylose solubilized within the continuous phase; the subsequent rearrangement and crystallization of amylopectin occur in the second stage, which requires a few days.

The interactions between starch and different hydrocolloids have been extensively studied (BeMiller, 2011; Chaisawang & Supphantharika, 2006; Mali et al., 2003; Sudhakar, Singhal, & Kulkarni, 1995; Viturawong, Achayuthakan, & Supphantharika, 2008; Xu et al., 2012). It is generally accepted that low concentration hydrocolloids can dramatically alter the gelling properties of starch dispersions. Most hydrocolloids including guar gum, locust bean gum and κ-carrageenan could accelerate gelation kinetics, which were rationalized either in terms of thermodynamic incompatibility between amylose and hydrocolloids within a single phase or on the molecular interactions through hydrogen and ionic bonds (Funami et al., 2005; Funami, Nakauma, et al., 2008). There have been a number of previous reports investigating differences in the effects of hydrocolloids on gelling and retrogradation properties of starch, among which the species of the polysaccharides with structural diversity in the respect of ionic charges were emphasized (BeMiller, 2011). A reduction in consistency in either pasted or gelled form with an acceleration of short-term retrogradation was reported in the composite system of gum arabic-wheat starch

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(Funami, Nakauma, et al., 2008; Funami, Noda, Hiroe, Asai, & Ikeda, 2008). Xanthan was effective in depressing swelling power, influencing granule swelling and the polymer leaking (Chaisawang & Supphantharika, 2005), and promoting the association of waxy maize starch (Abdulmola, Hember, Richardson, & Morris, 1996). Galactomannans were found to increase the viscosity of starch (Funami et al., 2005; Sudhakar et al., 1995). The final gel strength of starch gels was never reached by the composite starch–neutral hydrocolloid gels, implying that the hydrocolloid prevented formation of the same number of crosslinks that would occur in a pure starch paste (Chaisawang & Supphantharika, 2005).

Konjac glucomannan (KGM) is a water-soluble, neutral hydrocolloid, extracted from the tubers of the *Amorphaphallus* konjac plants. It is mainly composed of β -1,4-linked D-mannosyl and D-glucosyl residues at a molar ratio around 1.6:1 (Katsuraya et al., 2003; Maeda, Shimahara, & Sugiyama, 1980). The glucomannan backbone possesses between 5% and 10% acetyl substituted residues. Alkali plays an important role in explaining the gelation behavior of KGM by increasing solvation, in addition to facilitating the deacetylation of the chain (Williams et al., 2000). The alkaline concentration exerts a strong influence on the gelation rate of KGM and determines the elastic modulus of gel (Huang, Takahashi, Kobayashi, Kawase, & Nishinari, 2002). When combined with starch, KGM interacts with starch synergistically, which results in a marked increase in the viscosity and further inhibited starch granule association, suggesting that KGM retards rice starch gel retrogradation (Charoenrein, Tahirat, Rengsutthi, & Thongngam, 2011).

In most applications of starch, other components (sugars, salts, alkalis, etc.) are also present and, as a result, affect the gelling and retrogradation behavior of starch. Alkali is essential for the development of desirable product quality characteristics of many traditional starch-based food products. For example, the addition of Na_2CO_3 and NaOH gives the Asian noodle's characteristic yellowness and texture. Na_2CO_3 (1 wt% of starch) could influence the retrogradation properties of both waxy and non-waxy cereal starches of which the effect was less pronounced than that of NaOH at the same addition level (Lai, Karim, Norziah, & Seow, 2004).

Alkali–hydrocolloid combinations have been used in various processed foods based on starch, but the influence of composite alkalis and hydrocolloids on starch retrogradation has not been continuously studied. Obviously, there is need for more fundamental work on structure formation in mixed starch/hydrocolloid/alkali gels. Such studies would provide the basis for predicting and controlling the structure and texture of processed formulated products containing starch.

The present study was designed to gain a further insight into the multiple component system of Na_2CO_3 –KGM–starch. In this study, wheat starch was combined with a KGM– Na_2CO_3 solution to investigate (1) gelling behavior at the very early stage of storage mainly by rheological techniques, and (2) retrogradation behavior during storage mainly by thermal and microscopic techniques.

2. Materials and methods

2.1. Materials

Starch from wheat was purchased from Sigma Chemical Co. (St. Louis, USA). Moisture content was 11.5% and protein content was $\leq 0.3\%$. Amylose and amylopectin were determined using the spectrophotometric method described by Jarvis and Walker (1993). Konjac flour HXZC was kindly supplied by the Huaxianzi Konjac Product Co. (Hubei, China). It was purified by alcohol precipitation before being lyophilized, grounded to a fine powder then sieved. The contents of moisture, ash, crude protein, fat, glucomannan

were 3.7%, 0.8%, 0.6%, 0.1% and 97.8% (dry basis, w/w), respectively. Analytical grade Na_2CO_3 (Beijing Chemical Reagent Co., Beijing, China) was used in the preparation of the Na_2CO_3 solutions without further purification. Fluorescein 5-isothiocyanate (FITC) was purchased from Sigma Chemical Co. (St. Louis, USA).

2.2. Preparation of Na_2CO_3 –KGM starch gels

To create KGM– Na_2CO_3 –starch mixture, the Na_2CO_3 solution was first diluted with distilled water from 0.1 g/mL Na_2CO_3 stock solution; then the required amount of purified konjac powder was slowly dissolved in Na_2CO_3 solution under magnetic stirring, heated to 80 °C for 5 min and cooled to room temperature; last, an appropriate amount of starch was added to the Na_2CO_3 –KGM solutions with an overhead stirrer. Starch dispersions were prepared using RVA Standard 1 profile of the RVA at three concentrations: 4% (w/w) for the CLSM, 8% (w/w) for the rheological analysis, and 20% (w/w) for the DSC. Each sample name was simplified: (1) WS; (2) WS+0.1% Na_2CO_3 ; (3) WS+0.2% Na_2CO_3 ; (4) WS+5% KGM; (5) WS+5% KGM+0.1% Na_2CO_3 ; (6) WS+5% KGM+0.2% Na_2CO_3 ; (7) WS+10% KGM; (8) WS+10% KGM+0.1% Na_2CO_3 ; (9) WS+10% KGM+0.2% Na_2CO_3 , where percentage means weight dividing by that of wheat starch.

2.3. Determination of thermal properties

DSC analysis was conducted to determine the thermal properties of Na_2CO_3 –KGM–starch blends using DSC-60 calorimeter (Shimadzu, Tokyo, Japan). After the first run heating from 20–90 °C at a controlled constant rate of 10 °C/min, the pan was quenched from 90 to 4 °C and stored for 1, 7 or 28 days at 4 °C. After storage, samples were removed and allowed to equilibrate at room temperature for 1 h before being rescanned from 4 to 120 °C at 10 °C/min in the second run. Each sample was run in triplicate. Retrogradation ratio was estimated by dividing the rescanned enthalpy by the gelatinization enthalpy (Temsiripong, Pongsawatmanit, Ikeda, & Nishinari, 2005).

2.4. Determination of rheological properties

Rheological measurements were performed using an AR1500ex rheometer (TA instruments, New Castle, DE, USA) with the 40 mm parallel plate geometry at 25 °C, which was controlled by a water bath connected to the Peltier system in the bottom plate. Fresh pastes obtained from the RVA were stored at 25 °C for 1 h before being loaded to the rheometer plate with a spoon. Prior to each measurement, sample was left for 10 min (gap: 1.000 mm) to recover the structural breakdown on loading. The exposed sample edge was covered with a thin layer of silicon oil in order to prevent moisture evaporation.

Three rheological measurements were performed: (a) steady state shear rate sweep at the shear rate ranging from 0.1 to 100 s^{-1} ; (b) time sweep at a constant frequency (6.283 rad/s) for 30 s followed by stress sweep from 0.1 to 100 Pa to determine linear viscoelastic range (data not shown); (c) frequency sweeps at a constant deformation (0.5% strain) within the linear viscoelastic range. The mechanical spectra were obtained recording the dynamic moduli G' , G'' as a function of frequency. One representative datum was shown because there were no differences in data from triplicate measurements.

2.5. Confocal laser scanning microscopy (CLSM)

The CLSM was used to visualize the distribution pattern of starch granules in KGM– Na_2CO_3 system. Starch pastes (4%, w/w) prepared in aqueous solutions of KGM– Na_2CO_3 using the RVA apparatus

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