Carbohydrate Polymers 116 (2015) 182–188

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

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

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ARTICLE INFO

Article history:
Received 14 November 2013
Received in revised form 26 February 2014
Accepted 28 February 2014
Available online 12 March 2014

Keywords:
Konjac glucomannan
Na_2CO_3
Starch gel
Phase separation
Retrogradation

ABSTRACT

Wheat starch gels were produced with konjac glucomannan (KGM) and low concentrations of Na_2CO_3 (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 Na_2CO_3 were characterized by differential scanning calorimetry (DSC), rheometry and confocal laser scanning microscopy (CLSM). A small amount of Na_2CO_3 resulted in gels with increased elasticity whereas structural ordering during retrogradation was insignificantly affected. Comparison of CLSM images of composite gels revealed that Na_2CO_3 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 Na_2CO_3. Dynamic storage modulus and dynamic power law exponent were substantially higher than those observed for the same concentration of KGM in the presence of Na_2CO_3, supporting the hypothesis that Na_2CO_3 could promote strong interchain associations between KGM and starch components.

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 & Suphantharika, 2006; Mali et al., 2003; Sudhakar, Singhal, & Kulkarni, 1995; Viturawong, Achayuthakan, & Suphantharika, 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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http://dx.doi.org/10.1016/j.carbpol.2014.02.087
0144-8617/

(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 & Suphantharika, 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 & Suphantharika, 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, Tatirat, 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 ≤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

Table 1
Thermal properties of wheat starch (WS) in the presence of konjac glucomannan (KGM) or Na_2CO_3 obtained from the differential scanning calorimetry (DSC) thermograms.[a]

Treatments	Thermal properties		
	R_1 ($\Delta H_1/\Delta H_g$)[b]	R_2 ($\Delta H_2/\Delta H_g$)[c]	R_3 ($\Delta H_3/\Delta H_g$)[d]
WS	0.32 ± 0.016 b	0.61 ± 0.009 a	0.76 ± 0.008 b
WS + 0.1% Na_2CO_3	0.33 ± 0.013 ab	0.63 ± 0.031 a	0.73 ± 0.017 bc
WS + 0.2% Na_2CO_3	0.35 ± 0.011 a	0.55 ± 0.006 b	0.75 ± 0.012 b
WS + 5% KGM	0.31 ± 0.010 bc	0.53 ± 0.019 bc	0.71 ± 0.009 c
WS + 5% KGM + 0.1% Na_2CO_3	0.29 ± 0.013 c	0.56 ± 0.022 bc	0.79 ± 0.017 a
WS + 5% KGM + 0.2% Na_2CO_3	0.30 ± 0.016 bc	0.35 ± 0.010 e	0.75 ± 0.006 b
WS + 10% KGM	0.28 ± 0.028 bcd	0.56 ± 0.020 bc	0.78 ± 0.018 ab
WS + 10% KGM + 0.1% Na_2CO_3	0.26 ± 0.022 d	0.53 ± 0.010 c	0.65 ± 0.021 d
WS + 10% KGM + 0.2% Na_2CO_3	0.23 ± 0.019 d	0.45 ± 0.006 d	0.68 ± 0.026 cd

[a] Results are presented as mean values ± standard deviation in triplicate. Values in the same column with different letters (a–d) indicate significantly different ($p \leq 0.05$) between each parameter tested.
[b] R_1 is the ratio of the rescanned enthalpy after 1-day storage at 4 °C divided by the gelatinization enthalpy.
[c] R_2 is the ratio of the rescanned enthalpy after 3-day storage at 4 °C divided the gelatinization enthalpy.
[d] R_3 is the ratio of the rescanned enthalpy after 14-day storage at 4 °C divided the gelatinization enthalpy.

as described above were observed upon storage for 48 h. Stock solution of fluorescein 5-isothiocyanate (FITC) was prepared by dissolving the 0.2 g FITC in 100 mL distilled water. Starch suspensions (100 μL) were stained by mixing with 20 μL FITC stock solution. Samples were stored for 24 h at room temperature before analysis, to avoid staining gradients as a result of diffusion. An aliquot of the stained sample was deposited onto a glass slide and observed within 15 min. A Leica TCS SP5 confocal scanning laser microscope (CLSM) equipped with an inverted microscope was used in single photon mode with an Ar laser. The following Leica objective lenses were used: 10 × 0.4 IMM/dry/HC PL APO. The excitation wavelength was 488 nm and the emission maxima were within 500–525 nm. Digital image files were acquired in 512 × 512 pixel resolution.

2.6. Statistical analysis

The results were statistically analyzed using SPSS (SPSS Inc., Chicago, USA). Analysis of variance (ANOVA) was used to determine significant differences between the results and Duncan's test was used to separate the mean with a significance level of 0.05.

3. Results and discussion

3.1. DSC

The DSC has been used extensively to monitor retrogradation of starch gels (Prokopowich & Biliaderis, 1995). During storage of starch pastes, the development of the retrogradation endotherm (40–60 °C) has been considered to reflect reordering of starch components (Ring et al., 1987). The influence of KGM and Na_2CO_3 on the retrogradation behaviors of wheat starch gel (20%, w/w) is shown in Table 1. Small decreases in the ratio of the rescanned enthalpy after 1-day storage at 4 °C divided by the gelatinization enthalpy (R_1) of the KGM–starch suspensions were observed, which could be interpreted on the basis of stabilization of water. Diffusion-controlled chain aggregation processes are important determinants of the network structure (BeMiller & Whistler, 2009, chaps. 7 and 8). It is possible that the mobility of the linear amylose chain in the water–starch–KGM system was retarded, thereby decreasing the initial formation of crosslinks significantly.

R_2, the ratio of the rescanned enthalpy after 3-day storage at 4 °C divided the gelatinization enthalpy, could be ascribed to the short-term retrogradation of starch, which might involve mainly conformational ordering (double helices) of amylose and the short-range ordering of amylopectin side chains (Yoshimura, Takaya, & Nishinari, 1996). After starch pastes were stored for 3 days, Na_2CO_3 took the dominating role on affecting the kinetics of ΔH_2 (the rescanned enthalpy after 3-day storage) development to determine the retrogradation ratio (Table 1). According to our previous study, the amount of leached amylose decreased following the order: WS-WS + KGM-WS + KGM + Na_2CO_3 (calculated on the basis of starch amount), which was consistent with the R_2 values. The initial rate of amylose aggregation and crystallization development was related to the amount of amylose solubilized (Biliaderis & Zawistowski, 1990), which can readily explain the inhibition of short-term retrogradation.

KGM was described to be extremely effective at retarding long-term starch retrogradation (Khanna & Tester, 2006). However, there was no tendency observed about the changes of R_3 (the ratio of the rescanned enthalpy after 14-day storage at 4 °C divided the gelatinization enthalpy) with additions of KGM or Na_2CO_3. Solutes which fit well into the hydrogen-bonded network structure of water have a stabilizing effect on the polymer chains, thus retarding retrogradation (Kulp, Ponte, & D'Appolonia, 1981). The reverse might be true for incompatible solutes, like KGM, which greatly disturb the "normal" water structure, forming strong hydration layers around them, promoting chain ordering and crystallization of amylopectin.

3.2. Rheological study of Na_2CO_3–KGM–starch pastes

3.2.1. Steady shear measurements

The effects of various concentrations of KGM and Na_2CO_3 on steady flow curves of the model starch pastes are shown in Fig. 1. Steady rheological characteristics of samples were described by fitting the shear rate and shear stress of the experimental data in the Oswald-de Waele model:

$$\tau = K\dot{\gamma}^n$$

where τ is shear stress (Pa), $\dot{\gamma}$ is shear rate (s^{-1}), K is the consistency coefficient (Pa s^n), and n is flow behavior index (dimensionless).

The linear regression results are presented as K and n values and shown in Table 2. The apparent viscosities of all samples decreased depending on the shear forces applied, indicating that they were non-Newtonian, which had been ascribed to typical behavior of many polysaccharides in water dispersion. The apparent viscosity was increased with the increase of both KGM and Na_2CO_3 concentration, indicated by consistency coefficient K, where a higher K value implies a higher viscosity. The flow behavior index (n) was in the range of 0.17–0.24 ($n < 1$) signifying that all the samples were pseudoplastic, irrespective of the blends composition. The value of n remains virtually constant across the samples with no KGM. However, pseudoplastic behavior of the mixtures was dependent of Na_2CO_3 concentrations in 5% KGM and 10% KGM–starch samples.

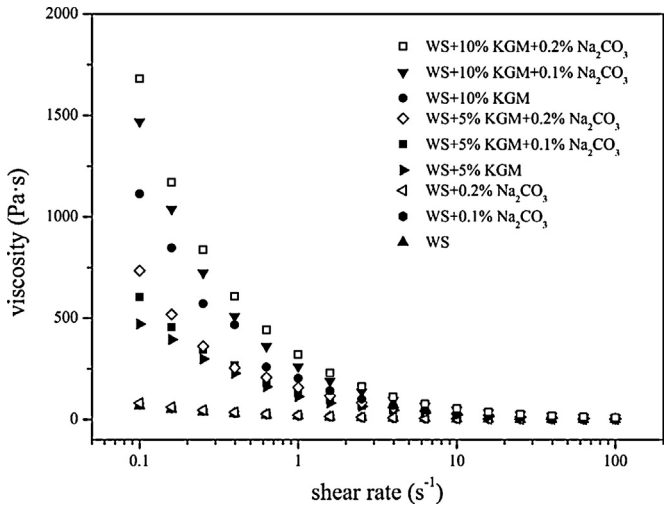

Fig. 1. Apparent viscosity of Na_2CO_3–KGM–starch mixtures at 25 °C. Each datum is the representative one from triplicate measurements. WS: wheat starch; KGM: konjac glucomannan.

KGM consists of a glucomannan backbone with 5–10% acetyl substituted residues, inhibiting the formation of intramolecular hydrogen bonding in dilute solutions (Zhou et al., 2013, 2014). This keeps the molecule in an extended form, which can readily interact with amylose molecules, which in turn, increases the degree of pseudoplasticity. Starch pastes are composites, in which swollen amylopectin-enriched granules are embedded in an interpenetrating matrix of entangled amylose molecules leached. Thus, the description of the rheological properties of such a complex system has to take into account contributions from both the particulate and the solubilized material. As investigated in our previous results (unpublished), comparatively more low-swelling starches and small amount of leached amylose were resultant upon heating in the presence of KGM and Na_2CO_3, implying that, in addition to amylose and starch granules, other factors contribute to the mechanical properties of such composite networks. A continuous network contributed by both KGM and amyloses with the assistance of Na_2CO_3 might be retained within the peripheral layers of the swollen granules to yield a higher viscosity, resulting in a more closely packed network of granules. Such a layer with certain rigidity might interfere with the dynamic network of junction zones created by the amylose and KGM chains entanglement. Even at higher shear rate, it was enabled to inhibit junction zones oscillating simultaneously, apparently decreasing the extent of shear-thinning reflected on n value.

Table 2
Steady shear rheological properties of wheat starch pastes at 25 °C.

Treatments	K^a (Pa s^n)	n^b	$R^{2\,c}$
WS	17.50 ± 0.82	0.23 ± 0.01	0.998
WS + 0.1% Na_2CO_3	19.25 ± 0.7	0.23 ± 0.01	0.989
WS + 0.2% Na_2CO_3	21.17 ± 1.99	0.23 ± 0.01	0.977
WS + 5% KGM	122.96 ± 5.97	0.22 ± 0.01	0.962
WS + 5% KGM + 0.1% Na_2CO_3	132.51 ± 2.73	0.24 ± 0.01	0.969
WS + 5% KGM + 0.2% Na_2CO_3	156.71 ± 4.99	0.24 ± 0.01	0.996
WS + 10% KGM	202.20 ± 5.35	0.16 ± 0.01	0.974
WS + 10% KGM + 0.1% Na_2CO_3	274.34 ± 8.48	0.23 ± 0.01	0.959
WS + 10% KGM + 0.2% Na_2CO_3	310.61 ± 5.81	0.24 ± 0.01	0.991

[a] K is the consistency coefficient (Pa s^n).
[b] n is flow behavior index (dimensionless).
[c] R^2 is correlation coefficient (dimensionless).

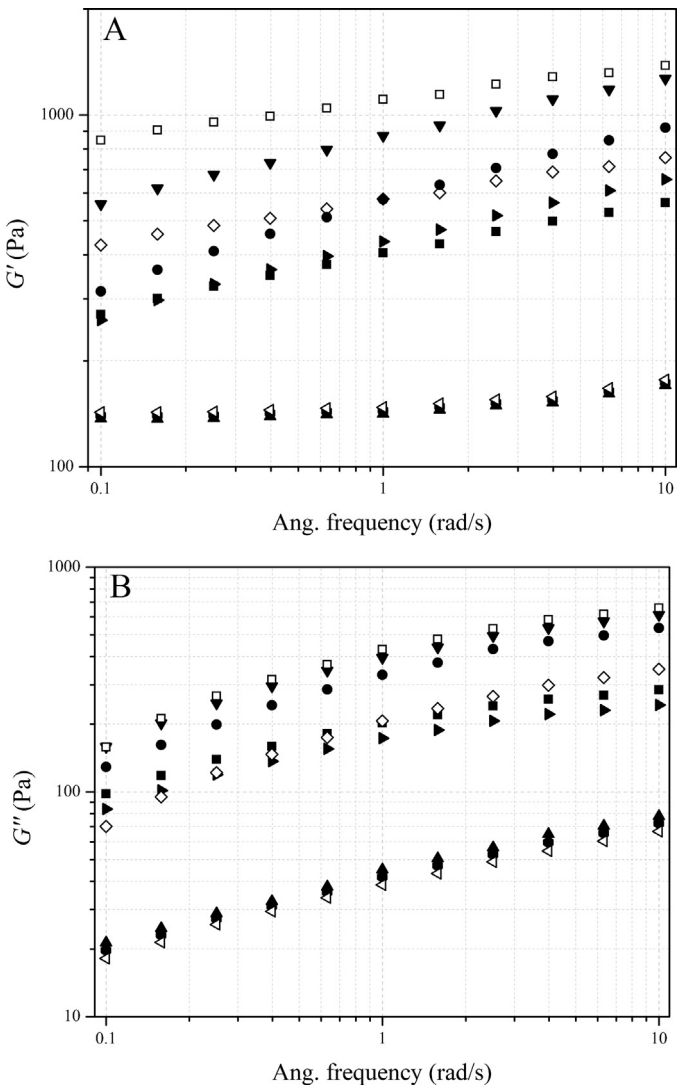

Fig. 2. Mechanical spectrum for Na_2CO_3–KGM–starch mixtures of WS (▲), WS + 0.1% Na_2CO_3 (⬢), WS + 0.2% Na_2CO_3 (◁), WS + 5%KGM (►), WS + 5% KGM + 0.1% Na_2CO_3 (■), WS + 5% KGM + 0.2% Na_2CO_3 (◇), WS + 10% KGM (●), WS + 10% KGM + 0.1% Na_2CO_3 (▼), WS + 10% KGM + 0.2% Na_2CO_3 (□): (A) the storage modulus (G'); (B) the loss modulus (G''). Each datum is the representative one from triplicate measurements. WS: wheat starch; KGM: konjac glucomannan.

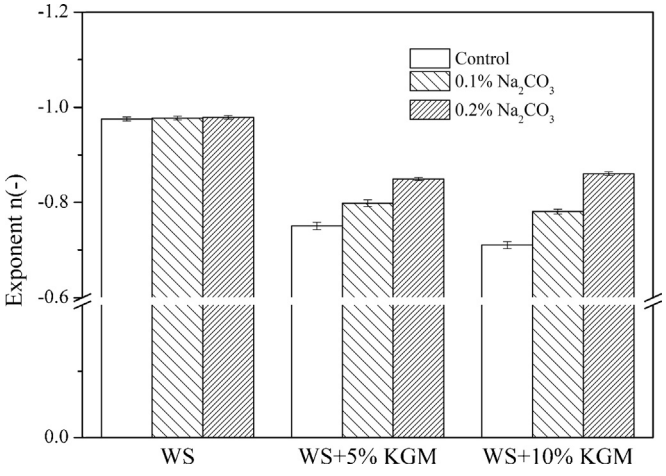

Fig. 3. Dynamic power law exponent n determined by relationship between dynamic complex viscosity η^* and frequency ω of Na_2CO_3–KGM–starch composite system. Results are presented as mean values ± standard deviation in triplicate.

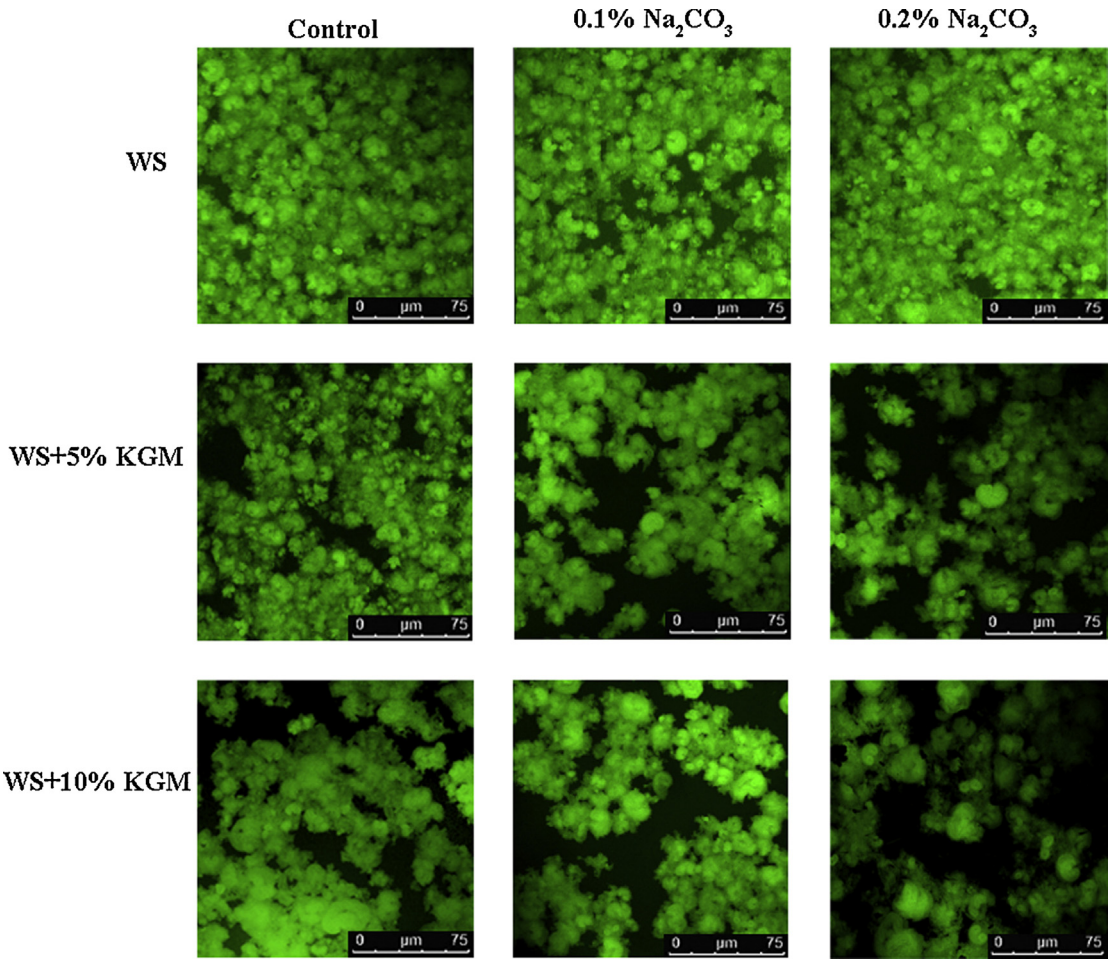

Fig. 4. CLSM images of the Na_2CO_3–KGM–starch composite systems. WS: wheat starch; KGM: konjac glucomannan.

3.2.2. Frequency sweep

The dynamic shear storage modulus (G') is a measure of the energy recovered per cycle of deformation and can be taken as an indicator of the solid or elastic character of the material. The loss modulus (G'') is an estimate of the energy dissipated as heat per cycle of deformation, serving as an indicator of the viscous properties of the material. For a gel network structure with non-permanent crosslinks, as most of the polysaccharide gels are, strong interchain associations contribute to G', whereas weak and rapidly relaxing bonds contribute only to G'' (BeMiller & Whistler, 2009, chaps. 7 and 8).

Mechanical spectra with changes in G', G'' for each starch dispersion at 25 °C are presented in Fig. 2. Dynamic rheological characteristics of samples were determined by fitting the dynamic complex viscosity and frequency of the experimental data to the power law equation (Funami, Nakauma, et al., 2008; Funami, Noda, Hiroe, Asai, & Ikeda, 2008):

$$\eta^* = K'\omega^{n'}$$

where η^* is defined by $\{(G'^2 + G''^2)^{1/2}\}/i\omega$ (Pa s), K' is constant representing the dynamic consistency index, ω is angular frequency (rad/s) and n' is dynamic power low factor (Keogh & O'Kennedy, 1998).

When n' is equal to -1, the system is perfectly elastic and η^* decreases with ω increasing. When n' is equal to 0, on the other hand, the system is completely viscous, and η^* remains constant regardless of ω.

As is observed from Fig. 2, the magnitudes of G' and G'' increased and G' was higher than G'' in the range of the frequency measured with a small frequency dependency in all samples. The separation between G' and G'' is as large as an order of magnitude in KGM free samples, similar to conventional biopolymer gels. In the presence of KGM, frequency-dependence of both moduli is greater, indicating "weak gel" character reported in numerous previous publications on the rheology of hydrocolloids–starch gels (BeMiller, 2011). Dynamic power law exponent n (Fig. 3) of the composite system was increased in the presence KGM, representing depressed gel-like characters of the system in accordance with Fig. 2. It has been suggested that gelation of amylose (concentration < 10%) involves rapid formation of double helical structures from an amorphous sol upon cooling, which act as junction zones among polymer chains (Goodfellow & Wilson, 1990). These coil-to-helix transitions are intermolecular processes which lead to the establishment of a three-dimensional hydrated gel network. KGM might cause the steric hindrance to prevent amylose gelation, which may relate to molecular associations between KGM and amylose. However, thermodynamic incompatibility of KGM and starch components might be of more importance to the microstructure and viscoelastic properties of starch gels, as noted by Funami et al. (2005). When phase separation occurs, the effective concentration of polymers in their respective micro phases is raised to cause viscosity properties enhancement.

Interestingly, the variation of G' with frequency for the KGM–starch mixtures with different Na_2CO_3 concentrations was significant. The spectrum obtained for 5% and 10% KGM has the form

characteristic of a "weak gel", but the G' moduli are substantially higher than those observed for the same concentration of KGM in the presence of Na_2CO_3, indicating additional intermolecular association. Moreover, polymer compositions of the continuous and dispersed phases may have a profound influence on the mechanical properties of the composite system. Actually, Na_2CO_3 did affect the amylose concentration and even contributed to more low-swelling starch granules. KGM–amylose interactions (chain entanglements) in the peripheral layers of the swollen granules might be facilitated as transitional sites, and thereby, predominantly viscous behavior exhibited in KGM–starch samples was altered in the presence of Na_2CO_3.

3.3. CLSM

CLSM images of starch gels with or without KGM and Na_2CO_3 are shown in Fig. 4. Starch granules were swollen and amylose diffused outside the granules, forming a continuous and glutinous network around the surface of the swollen granules in all the samples. Na_2CO_3–KGM samples presented granules larger in size with more apparent cloud-like surroundings. However, there is no significant difference induced by Na_2CO_3 in granular size in the absence of KGM, which is in good accordance with what was observed in the rheological measurements, where both G' and G'' modulus were significantly increased by KGM and Na_2CO_3 and unaffected with only Na_2CO_3 included.

For fluorescein isothiocyanate (FITC), affinity is largely equivalent to hydrophobicity, i.e. the FITC accumulates in hydrophobic regions. Consequently, structural elements will be highlighted in a way which is dominated by the kinetics and thermodynamics of the probe molecules in the polymer matrix (Tromp, van de Velde, van Riel, & Paques, 2001), rather than stand out from undyed components, so that KGM cannot be distinguished from starch components. However, the majority of each polysaccharide seemed to be outside rather than to penetrate the starch granules, since the fiber-like extensions of starch granules were frequently presented on the images in the presence of both KGM and Na_2CO_3 of the larger concentrations. The subsequent further phase separation induced by Na_2CO_3 lead to concentrated remnants of starch granules within the KGM-rich region. The discontinuous and non-uniform layer of KGM existed around the surface of the granules, making the swollen starch granules scattered in the matrix.

In 0.2% Na_2CO_3 samples, swollen granules are not able to coalesce and form "aggregated" structures as evident in only KGM–starch systems. According to electrical double layer theory, an electrical double layer of cations surrounding the starch exists which excludes the anions (Oosten, 1983). The Na_2CO_3 at the given concentrations here might cause a sharp decrease in intensity of the electrical double layer, whereby the penetration of KGM is facilitated and hence repulsion of other starch granules can occur insusceptibly in these systems, giving rise to the sharply altered G' while not changing G''.

4. Conclusion

The present work attempts to clarify the effect of Na_2CO_3 on konjac glucomannan (KGM)-induced changes in wheat starch gel properties, which are important for predicting and controlling the structure and texture of processed formulated starch-based products. A small amount of Na_2CO_3 (0.1–0.2% of starch concentration) affects diffusion-controlled chain aggregation of KGM–starch systems, but does not significantly affect conformational ordering of amylose and amylopectin in short-term and long-term retrogradation. The strong interchain associations occur on mixing with 0.2% Na_2CO_3 in the presence of KGM, leading to fiber-like extensions and a discontinuous network formed around swollen granules. It is concluded that the KGM–starch mixtures show normal phase separation, but Na_2CO_3 prevents them from concentrating into two phases, and that the minimum potential energy favorable interactions are instead maximized by decreasing intensity of the electrical double layer. In general, the effects of Na_2CO_3 addition on the rheological properties of starch gels were more pronounced with increasing concentrations of Na_2CO_3 and these effects depended on the amount of KGM added.

Acknowledgements

This work was supported by the grants from the National Science Foundation of China (31371717) and National Key-technologies R&D Project (2012BAD37B05) during the 12th 5-year Plan of the People's Republic of China. The authors gratefully acknowledge Dr. Huiyuan Guo and Ms. Fang Wang (College of Food Science and Nutritional Engineering, China Agricultural University) for the help of rheological analysis.

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