Carbohydrate Polymers 117 (2015) 1–10

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Preparation and characterization of a novel pH-response dietary fiber: Chitosan-coated konjac glucomannan

Xiaoguo Zhao[a,b,c], Jing Li[a,b], Weiping Jin[a,b], Xiaopeng Geng[a,b], Wei Xu[a,b], Ting Ye[a,b], Jieqiong Lei[a,b], Bin Li[a,b,*], Ling Wang[a,b,*]

[a] Key Laboratory of Environment Correlative Dietology (Huazhong Agricultural University), Ministry of Education, Wuhan, China
[b] College of Food Science and Technology, Huazhong Agricultural University, Wuhan 430070, China
[c] College of Food Science and Nutritional Engineering, China Agricultural University, Beijing 100083, China

ARTICLE INFO

Article history:
Received 3 August 2013
Received in revised form 30 August 2014
Accepted 10 September 2014
Available online 23 September 2014

Keywords:
Konjac glucomannan
Chitosan
pH-response
Rheological properties
Swelling behavior

Chemical compounds studied in this article:
Hydrochloric acid (PubChem CID: 313)
Ethanol (PubChem CID: 702)
Sodium carbonate (PubChem CID: 10340)

ABSTRACT

The purpose of this study was to prepare a kind of novel pH-response dietary fiber from chitosan-coated konjac glucomannan (KGM) powders (KGM/Chitosan or K/C powders) by a physical grind method. The K/C powders were selectively soluble in aqueous solutions of different pH. Meanwhile, the coated chitosan could largely decrease the viscosity of KGM in neutral condition, which is the main limitation for KGM application in food industry. Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), swelling ability and rheological measurements were utilized to characterize the performance of K/C powders. K/C powders exhibited much higher viscosity and swelling ability in acidic condition than in neutral condition. Therefore, this study will extend the application of KGM in food industry and in other pH-specific applications as well.

1. Introduction

Konjac glucomannan (KGM), composed of β-1,4 linked mannose and glucose units (Li, Ji, Xia, & Li, 2012; Takahashi et al., 1984), is a water-soluble and high molecular weight polysaccharide from the tubers of the *Amorphophallus konjac* plant (Fang & Wu, 2004). Due to its special chemical structure and composition, KGM has notable physiological activities (Alonso-Sande, Teijeiro-Osorio, Remuñán-López, & Alonso, 2009). For example, it has been demonstrated to be effective in losing weight, blood cholesterol reduction and immune function improvement (Chua, Baldwin, Hocking, & Chan, 2010). Besides, serving as a valuable 'functional foods additive' or prebiotic carbohydrate, KGM could selectively stimulate the gut-friendly bacteria (Chen, Fan, Chen, & Chan, 2005; Venter, Vorster, & Nest, 1990).

Due to its remarkable properties both physiologically and technologically, KGM has presented great potential in application as functional food additive, thickener and stabilizer (Gläser, Wenk, & Scheeder, 2004; Tye, 1991; Zhang et al., 2001) in many fields, such as food industry, bio-pharmaceutical industry and human health. It has been used to produce many kinds of bionic and healthy foods with low calories which are popular internationally, such as solid beverages, noodles, tofu, jelly and snacks (Chua et al., 2010). In addition, its use as food additive and dietary supplement has been authorized in Europe and classified as Generally Recognized as Safe (GRAS) by the Food and Drug Administration (FDA) (Jiménez-Colmenero et al., 2012). In traditional Chinese medicine, it is available in capsule form to treat asthma, cough, hernia, breast pain, burns as well as haematological and skin disorders (Chua et al., 2010). In view of its great commercial value, it is worth developing more functional products based on KGM.

However, the apparent viscosity of 1% (w/w) KGM is about 30,000 cps (Tatirat & Charoenrein, 2011), which exhibits the highest viscosity among polysaccharides (Vuksan et al., 2001). The deficiencies of KGM viscosity and low mobility of its solutions have markedly limited its applications. For example, the properties make it inconvenient for people to consume or be added into liquid

* Corresponding authors at: Huazhong Agricultural University, College of Food Science and Technology, Wuhan 430070, Hubei, China. Tel.: +86 27 63730040; fax: +86 27 87282966.
E-mail addresses: libinfood@mail.hzau.edu.cn (B. Li), wangling@mail.hzau.edu.cn (L. Wang).

http://dx.doi.org/10.1016/j.carbpol.2014.09.038
0144-8617/

food matrix (Pan et al., 2012). Indeed, the native KGM has been banned for confectionery applications in many countries because of a real risk of choking due to excess swelling (in the throat) (EFSA, 2005). The common techniques being used to decrease the KGM viscosity are acid, alkaline, enzyme and irradiation hydrolyses (Alonso-Sande et al., 2009; Jacon, Rao, Cooley, & Walter, 1993; Zhang, Xie, & Gan, 2005). However, the structures of KGM would be destroyed and the molecular weight decreased by using the above methods, resulting in the decline of dietary fiber functions. Further, the preparation processes are complicated, time-consuming and high-cost. To achieve the desired product of KGM with low viscosity while maintaining its native structures, pH-response dietary fibers based on chitosan and KGM have been researched (Li et al., 2011).

Chitosan is a functional biopolymer and linear polysaccharide obtained from deacetylation of chitin which is found in abundance in nature (Cao et al., 2010; Gaidhane, Rahatgaonkar, Tiwari, & Chorghade, 2010; Mourya, Inamdar, & Tiwari, 2010; Tiwari et al., 2011). Nowadays, chitosan has aroused great concerns for its commercial applications in the biomedical, food, and chemical industries (Li et al., 2007; Nguyen & Lee, 2012; Shukla & Tiwari, 2011; Shukla, Deshpande, Shukla, & Tiwari, 2012). The biological activities of chitosan have been researched by many scientists, such as antimicrobial property (Shen, Wu, Chen, & Zhao, 2010; Xia, Liu, Zhang, & Chen, 2011), hypocholesterolemic effects (Kim & Rajapakse, 2005; Liao, Shieh, Chang, & Chien, 2007), immunity-enhancing and antitumor effects (Han et al., 2008; Lee, Kim, Lee, & Jon, 2009), drug delivery (Alonso & Sánchez, 2010; Bhattarai, Gunn, & Zhang, 2010) and accelerating Calcium and Ferrum absorption (Bravo-Osuna, Millotti, Vauthier, & Ponchel, 2007; Jeon & Kim, 2000; Jung, Moon, & Kim, 2006). Besides, chitosan exhibits selectively dissolution in acidic medium, which makes it suitable to be a pH dependent material. Severed as a safe polysaccharide, chitosan was technically and physiologically used as coating materials on other polysaccharides (Kim, Park, Kim, & Cho, 2003).

In recent years, the intelligent or responsive materials have aroused great attention due to their response properties in special situations (Tiwari, 2010; Tiwari & Kobayashi, 2013; Tiwari, Mishra, Kobayashi, & Turner, 2012a; Tiwari, Ramalingam, Kobayashi, & Turner, 2012b; Tiwari & Syvajarvi, 2014; Tiwari & Tiwari, 2013a,b). In a patent, it has been reported that chitosan-coated KGM powders (K/C powders) prepared by a chemical method could decrease its high viscosity and resolve the problem of forming flocks in hot water (Li et al., 2011). Meanwhile, the K/C powders have the pH-response property. The pH-dependent powders exhibited higher viscosity and swelling ability in acidic medium (pH < 6.0) than neutral condition (pH 7.0) due to the dissolution of coated chitosan and the exposure to water of inner KGM. However, during the preparation process in the patent, if the purity of konjac powders or KGM was not high enough, the incorporation of alkali which could react with polyphenols in konjac material would cause the generation of dark substances. Further, the preparation process was complicated and time-consuming. In this paper, a physical, green, high-efficiency and low-cost method was provided to prepare the K/C powders. The powders also broadened KGM applications in food and other pH-specific systems.

2. Materials and methods

2.1. Materials

Konjac glucomannan (KGM) with 92% degree of purity was bought from Shiyan Huaxianzi Konjac Productions Co., Ltd. (Shiyan, China). Chitosan with 90% degree of deacetylation and average molecular weight of 8.0×10^5 was purchased from Zhejiang Golden-shell Biochemical Co., Ltd. (Taizhou, China). Hydrochloric acid, ethanol and sodium carbonate were of analytical grade reagents (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and were used without further purification.

2.2. Preparation of chitosan solutions

Six kinds of chitosan solutions with varied concentrations were prepared. 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 g of chitosan were, respectively, added in 30 mL of 10% (v/v) ethanol containing 0.6 g of concentrated hydrochloric acid (36.4%, w/w) under slow stirring at room temperature till complete dissolution.

2.3. Preparation of K/C powders

Based on preliminary experiments, the solid-liquid ratio of 1:1.5 (w/w) was selected in this study. 15 g of chitosan solutions with varied concentrations mixed with 10 g of powdered KGM were grinded in the mortars for 10 min, respectively. The resulting mixture was washed and neutralized by 40% (v/v) ethanol containing sodium carbonate (0.16 g/500 mL), and following by 40% (v/v) ethanol. Then it was vacuum-dried at 80 °C for 2 h. Finally, the obtained powders were grinded in the mortars, filtered with 100 M sieve. The resulting K/C powders with different chitosan content were named as K/C-1, K/C-2, K/C-3, K/C-4, K/C-5, K/C-6, respectively.

2.4. Fourier-transform infrared (FTIR) spectroscopy

The dried K/C powders were mixed with potassium bromide and made into pellets. Then the IR spectra were recorded with a Nicolet (USA) Nexus 470 FTIR spectrometer from 400 to 4000 cm^{-1} with 32 scans and resolution of 4 cm^{-1}. Stage control, data collection, and processing were performed using OMNIC 8.0 (Thermo-Nicolet, Madison, WI).

2.5. Scanning electron microscopy (SEM)

The surface and microstructure of KGM, K/C-1 and K/C-5 powders were investigated using a scanning electron microscope (JSM-6390/LV, Japan) with an accelerating potential of 5.0 kV and magnifications of 1000 and 1500. The powders deposited on a metal stub were made electrically conductive by coating with a thin layer of gold (approximately 300 Å) in a vacuum for 30 s. Then the surface and microstructure would be observed by the SEM.

2.6. X-ray photoelectron spectroscopy (XPS)

The surface elements of K/C-5 powders were examined by XPS. In this study, the instrument of VG Multilab2000 from Great Britain was employed and spectra were analyzed using the Avantage 4.54 software.

2.7. Apparent viscosity measurements

Apparent viscosity measurements of all samples were investigated using a NDJ-8S rotation viscometer (Shanghai Jingmi Equipment and Instrument Co. Ltd, China). KGM and K/C powders, respectively, added in neutral distilled water and acidic distilled water (pH 2.0) at 60 °C, were made into 1% (w/w) solutions. The solutions were maintained at 60 °C in water baths and all viscosities were measured in triplicate every 10 min using a No. 4 rotator at 12 rpm.

2.8. Rheological characterization

In this study, a strain/stress controlled rheometer (AR500, TA, UK) was used for the assessment of steady shear rheological properties and the measurement of dynamic viscoelasticity with frequency sweep mold adopted.

2.8.1. Steady shear rheological measurements

Sample preparation: The powders of KGM, K/C-1, K/C-3, K/C-5 were incorporated in both neutral and acidic distilled water to be made into 1% (w/w) solutions and then continuously stirred for 2 h to achieve homogeneity and full-swelling at constant room temperature, respectively. All the solutions were placed for 4 h before measurements.

Steady shear rheological measurements: Steady shear measurements were performed in shear rate range of 0.01–300 s^{-1} at constant temperature (25 °C). The flow curves were recorded.

2.8.2. Dynamic viscoelasticity measurements

Sample preparation: The powders of KGM, K/C-1, K/C-3, K/C-5 were incorporated in both neutral and acidic distilled water to be made into 1% (w/w) solutions and then continuously stirred for 30 min to achieve homogeneity at constant room temperature, respectively.

Dynamic viscoelasticity measurements: Dynamic frequency sweep measurements from 0.1 Hz to 100 Hz were performed using the parallel-plate geometry (50 mm diameter) with a 1.5 mm gap at a constant strain of 1.0%. In the measurements, the edges of all samples were covered with silicon oil to avoid water evaporation. The measurements were made at 25 °C.

2.9. Morphology characterization

The powders of K/C-1, K/C-3, K/C-5 were used for measurements with KGM considered as control. To demonstrate the pH-response property of K/C powders, two stages were adopted. In the first stage, the powders were added into boiled neutral water to be made into 1% (w/w) solutions with slow stirring. In the second stage, 0.1 mL of diluted hydrochloric acid (10%, w/w) was put into the solutions with slow stirring for 2 min, respectively. The photos in both the first and second stages were taken.

3. Results and discussion

3.1. Fourier-transform infrared (FTIR) spectroscopy

The FTIR spectra of K/C-1, K/C-3, K/C-5, KGM and chitosan are shown in Fig. 1. There were no significant differences among the samples of K/C-1, K/C-3, K/C-5, indicating that the content of coated chitosan had no effect on the structure of the K/C powders. In addition, the peak of chitosan at 1598 cm^{-1} is corresponded to —NH_2 or —NH angular deformation (de Britto, de Moura, Aouada, Mattoso, & Assis, 2012), which do not exist in KGM and K/C-1, K/C-3, K/C-5. However, the peak of K/C-1, K/C-3 and K/C-5 at 1577 cm^{-1} do not exist in KGM and chitosan, which is corresponded to N—H bending vibrations of —NH_3^+ (Lawrie et al., 2007). The phenomenon was attributed to the protonation of chitosan during the production process in which chitosan was dissolved in HCl and the coated blends were washed using ethanol containing sodium carbonate. Therefore, it was evident from FTIR that chitosan was coated on KGM only by physical interaction, and no new groups or bonds were generated during preparation. Further, the similar effects of K/C-2, K/C-4 and K/C-6 could be predicted from the above results.

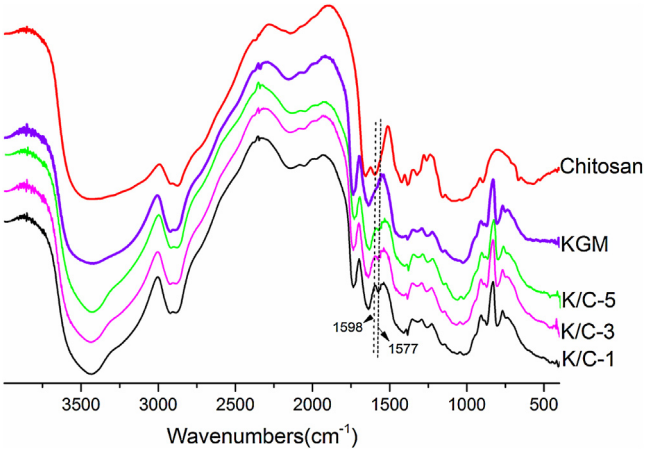

Fig. 1. FTIR spectra of chitosan, KGM, K/C-1, K/C-3 and K/C-5 powders.

3.2. Scanning electron microscopy (SEM)

SEM has been used for the evaluation of chitosan-coated powders when trying to correlate the properties of powders with the same morphological structure (de Souza et al., 2009). Fig. 2 shows the morphological structure and surface images of KGM, K/C-1 and K/C-5 powders, respectively. K/C-1 and K/C-5 powders possess a rougher and much more irregular surface, while KGM powders present a smoother and more regular surface (Tatirat & Charoenrein, 2011). The reason might be attributed to the preparation process of the coated powders. When the mixture of KGM and chitosan solution was grinded in the mortar, it was difficult to keep the resulting K/C powders coated with chitosan evenly. Meanwhile, higher chitosan content in K/C-5 would cause rougher and much more irregular surface than K/C-1. The coated chitosan layer in K/C-5 was also thicker than that in K/C-1. The results indicated that the K/C powder which was prepared using more chitosan presented more irregular and thicker surface.

3.3. Surface atomic composition of K/C powders

Based on the fact that chitosan is composed of C, O, H and N elements while KGM is composed of C, O, H elements, XPS was utilized to analyze the surface atomic composition of K/C powders. The existence of element N can prove whether the chitosan has been coated on the KGM. Fig. 3 shows the surface atomic composition of K/C-5. The binding energy of 399.05 eV is corresponding to element N. Further, the chemical compositions calculated from the XPS spectrum of the K/C-5 sample are C (66.16%), N (6.13%), O (27.71%). The data demonstrated that chitosan was successfully coated on the surface of the KGM powders. Conclusions could be inferred that the existence of N in the other five samples would also be detected and the chemical composition ratios would be different among them.

3.4. Apparent viscosity properties

Apparent viscosity is usually used to illustrate the molecules interaction between KGM chains and water, which reflects the dissolving degree of KGM to some extent (Liang et al., 2011). Fig. 4 presents the stirring time-independence of apparent viscosities when the control KGM and all of K/C powders were dissolved under neutral and acidic conditions. Fig. 4A shows that at the same stirring time point of K/C powders exhibited significantly lower viscosities than the control KGM, and K/C-1 powders represented significantly higher viscosity than the other K/C powders ($P \leq 0.05$). Meanwhile, there was a tendency that the viscosities

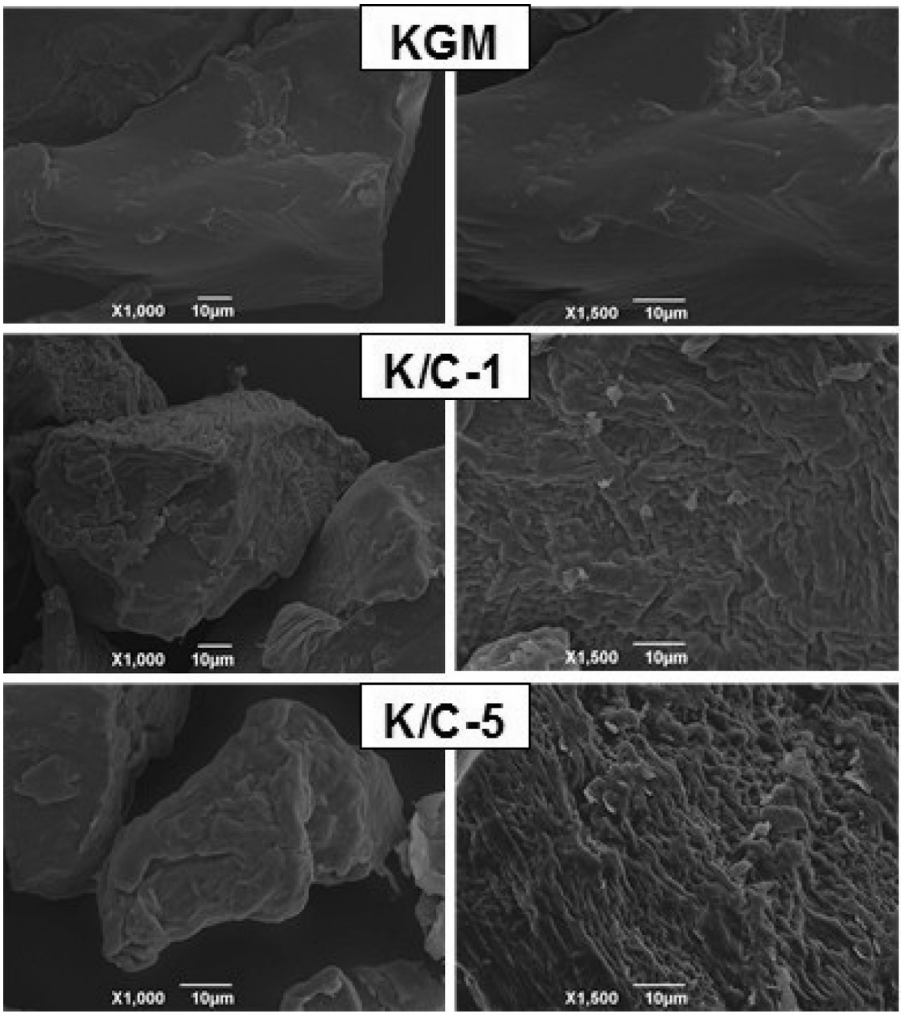

Fig. 2. Scanning electron micrographs with magnification (left) 1000× and (right) 1500× of KGM, K/C-1 and K/C-5 powders.

increased with the longer stirring time and decreased with the coated-chitosan content for the majority of the samples. On one hand, KGM is a neutral hydrophilic polysaccharide which can be easily dissolved in water to form solution with high viscosity (Zhang et al., 2001). However, the coated chitosan which is insoluble in neutral aqueous solution prevented inner KGM from contacting with water molecules or interaction between KGM and chitosan molecules. On the other hand, it was difficult to make sure that the coated chitosan on the surface of KGM was uniform during preparation. But to some extent, higher chitosan content might contribute to form more uniform chitosan coatings on the surface of KGM, which was helpful to decrease the exposure of KGM into water molecules. It can be deduced that KGM solutions with lower viscosities could be prepared by coating chitosan. With the stirring time increasing, the KGM molecules exposed to water were forming much more extended conformation and the tighter hydrogen bond binding of konjac glucomannan and entanglements formed, which contributed to increasing viscosities.

Fig. 4B demonstrates that the viscosities of K/C powders under acidic condition (pH 2.0) were much higher than those under neutral condition. The viscosities reached the maximum within 10 min and decreased with stirring time increasing, while the stirring time within 50 min had little effect on the viscosity of the control KGM. This may be explained that the coated chitosan could be dissolved in acidic aqueous solution and the inner KGM became available to aqueous solution. Then KGM molecule chains expanded and interacted with water molecules by hydrogen bonding, which caused the entanglements formed among molecules, leading to high viscosity. With increasing stirring time, the shear force broke the hydrogen bonds between KGM and water molecules, and the tolerance of mechanical destruction decreased, both of which resulted in decreasing viscosity of K/C powders.

3.5. Rheological characterization

3.5.1. Steady shear rheological measurements

Fig. 5A and B shows the shear behavior of KGM, K/C-1, K/C-3, K/C-5 solutions at 25 °C under neutral and acidic conditions. The shear behavior largely depends on the pH condition. The viscosities of K/C powders at low pH were much higher than those at high pH, while the changing of pH value had little effect on the viscosity of KGM. At low pH, the higher viscosities came from the dissolution of coated chitosan, the inter-molecular and intra-molecular entanglements between KGM and chitosan, and the hydrogen bonding between polysaccharides and water. Whereas, chitosan could not be easily dissolved at high pH (pH > 6.0), which decreased the interaction among KGM, chitosan and water.

Under neutral condition, all the samples had a clearly shear thinning behavior at high shear rates after a first Newtonian region at low shear rates (Fig. 5A). This result is consistent with previous study about KGM (Jacon et al., 1993) and other polysaccharides such as galactomannans, chitosan or gellan (Hwang & Shin, 2000;

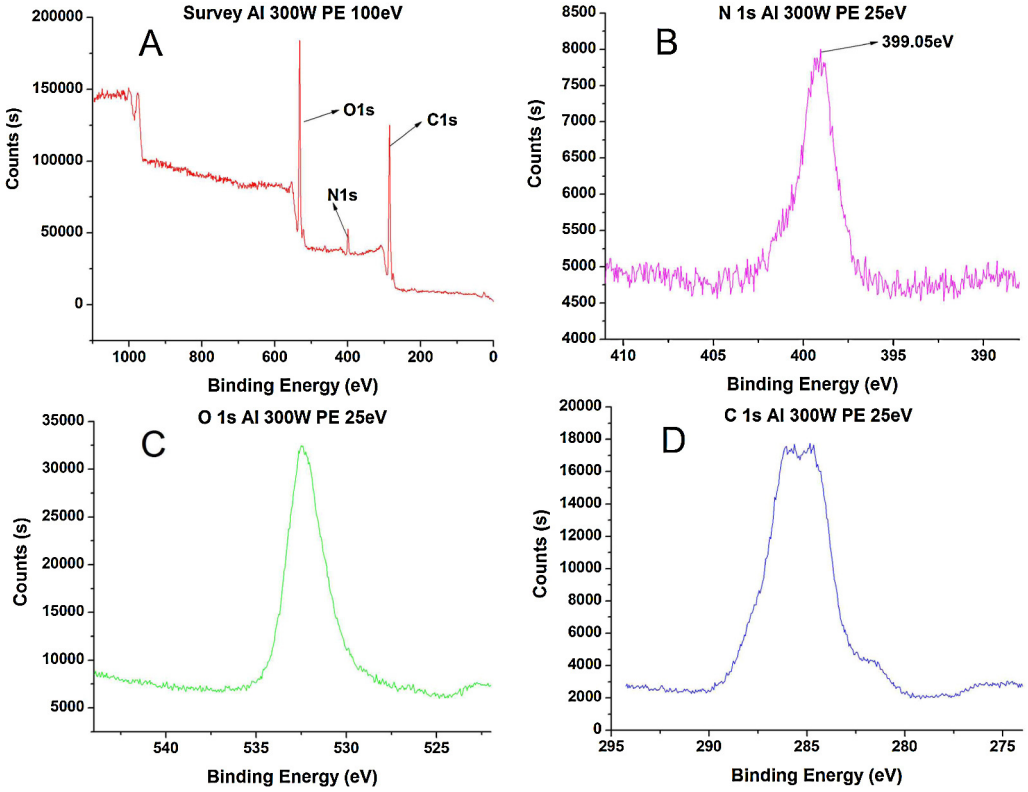

Fig. 3. XPS survey scan spectra of K/C-5 powders (A) and magnifications of N1s (B), O1s (C), C1s (D) narrow scans with the curve fit for K/C-5 sample.

Miyoshi & Nishinari, 1999; Oblonšek, Šostar-Turk, & Lapasin, 2003). At low shear rates, the rate of disruption of inter-molecular and intra-molecular entanglements induced by the shear force was balanced by the formation of new ones, so no net change in the entanglements occurred and a constant zero-shear viscosity (η_0) could be maintained. While at high shear rates, with the shear rate increasing, the disruption of entanglements predominated over the formation of new ones and the molecules align tended to the direction of flow and thus the apparent viscosity decreased. It was found that the increasing chitosan content in K/C powders decreased their viscosities. This is attributed to the more uniform distribution of chitosan on KGM at higher chitosan content during K/C powders preparation by grind method. Oppositely, lower chitosan content leaded to more KGM exposed in water and increased the solution viscosity. It can easily be seen from Fig. 5B that viscosity of K/C powders under acidic condition was much higher than that under neutral condition. That is because the coated chitosan could be dissolved in acidic aqueous solution, and then KGM molecules were exposed. A clearly shear thinning behavior at high shear rates after a first Newtonian region at low shear rates was also found under acidic condition for all the samples, the same as those under neutral condition. However, the higher coated-chitosan content increased the viscosities of K/C powders solutions at low shear rates, and the viscosities of all the samples became close to zero at high shear rates. At the low shear rates, both the dissolution of chitosan and the inter-molecular and intra-molecular interactions between KGM and chitosan contributed to high viscosity. While at the high shear rates, the disruption rate of entanglements overcame the formation rate of the new ones, and the inter-molecular and intra-molecular interactions weakened (Alvarez-Manceñido et al., 2006).

The shear thinning behavior of polysaccharide solutions can be described by many equations (Lapasin & Pricl, 1995). Cross model is the best fit to describe accurately the flow properties of the samples solutions in both neutral aqueous solutions and acidic aqueous solutions. Cross model may be defined in the equation:

$$\eta_a = \frac{\eta_\infty + (\eta_0 - \eta_\infty)}{\left[1 + (\tau r)^m\right]}$$

where η_a is the apparent viscosity (Pa s) measured at the shear rate(1/s), η_0 is the zero-shear rate viscosity (Pa s), η_∞ is the in finite shear rate viscosity (Pa s), τ and r are time constants, and m is dimensionless exponent which dictates the degree of shear thinning. Values of m tending to zero describe more Newtonian liquids and the most shear thinning liquids have a value of m tending to unity.

Table 1 presents the parameters derived from Cross model for KGM and three kinds of K/C powders in neutral and acidic aqueous solutions, respectively. The results in the tables were in agreement

Table 1
Magnitudes of the Cross model parameters for steady simple shearing, obtained for KGM, K/C-1, K/C-3 and K/C-5 powders dissolved in neutral (a) and acidic (pH 2.0) (b) aqueous solutions.

Samples	η_0 (Pa s)	τ (s)	m	S.E.[a]
(a)				
KGM	84.34	0.8286	0.8568	5.019
K/C-1	53.71	0.7087	0.8108	3.675
K/C-3	23.03	0.4669	0.7971	4.257
K/C-5	6.355	0.2258	0.7775	15.44
(b)				
KGM	94.63	1.005	0.8424	6.324
K/C-1	122.7	1.404	0.8261	8.72
K/C-3	121.5	1.492	0.8201	8.614
K/C-5	149.4	1.887	0.8125	8.339

[a] S.E. $= \left(\left[\left(\sum_{i=1}^{i=n} (x_{\text{exp}.i} - x_{\text{cal}.i})^2 \right) / (n-2) \right] / \text{range}\,(x_{\text{exp}}) \right) \times 1000 \times$ mean (S.D.).

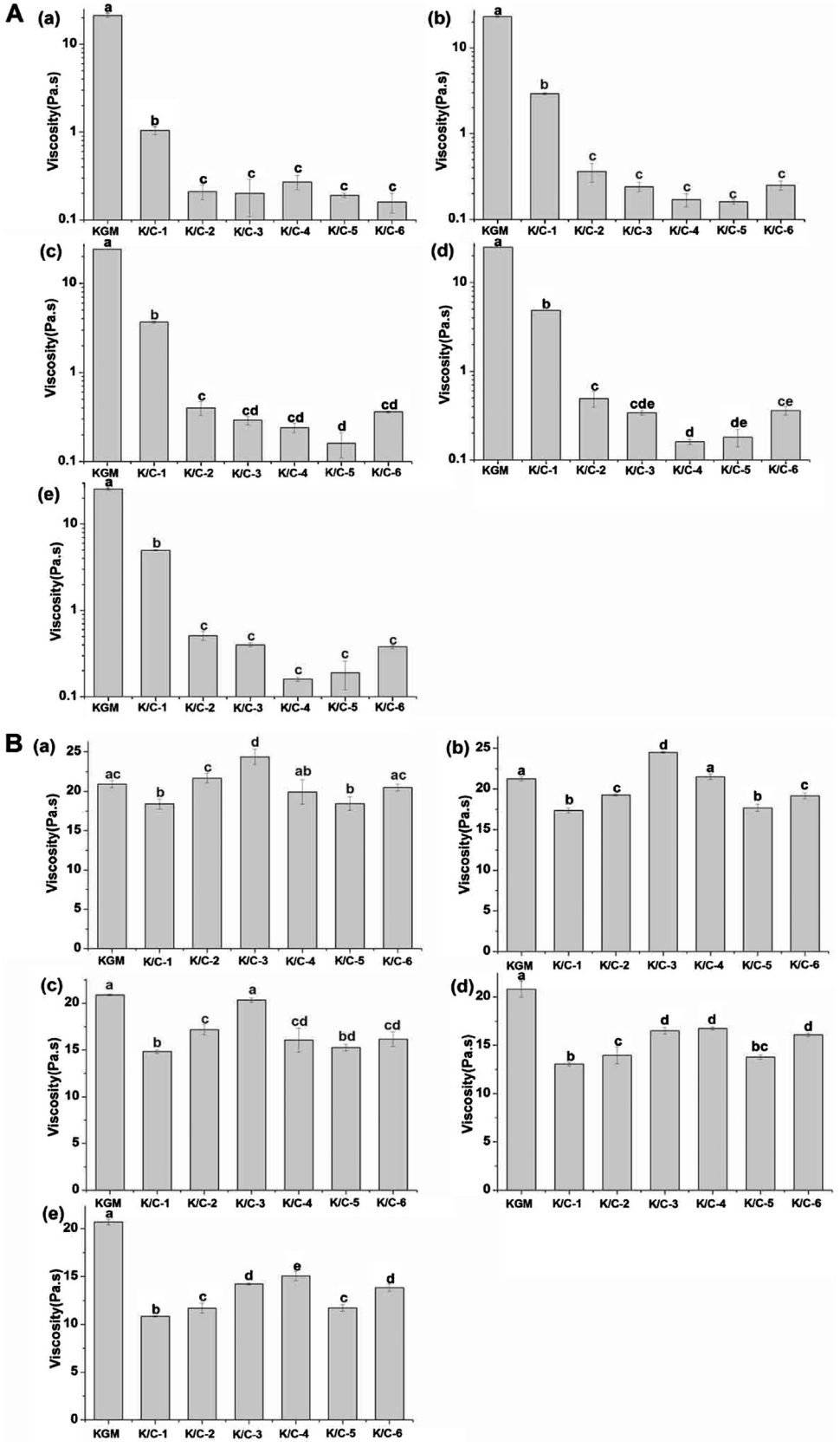

Fig. 4. The apparent viscosities with stirring time increasing of 1% (w/w) KGM and six samples dissolved in neutral aqueous solution (A) and acidic aqueous solution (pH 2.0) (B). Parts (a)–(e) represent the stirring time for 10, 20, 30, 40 and 50 min, respectively. Bars/mean values with different letters are significantly different ($P < 0.05$).

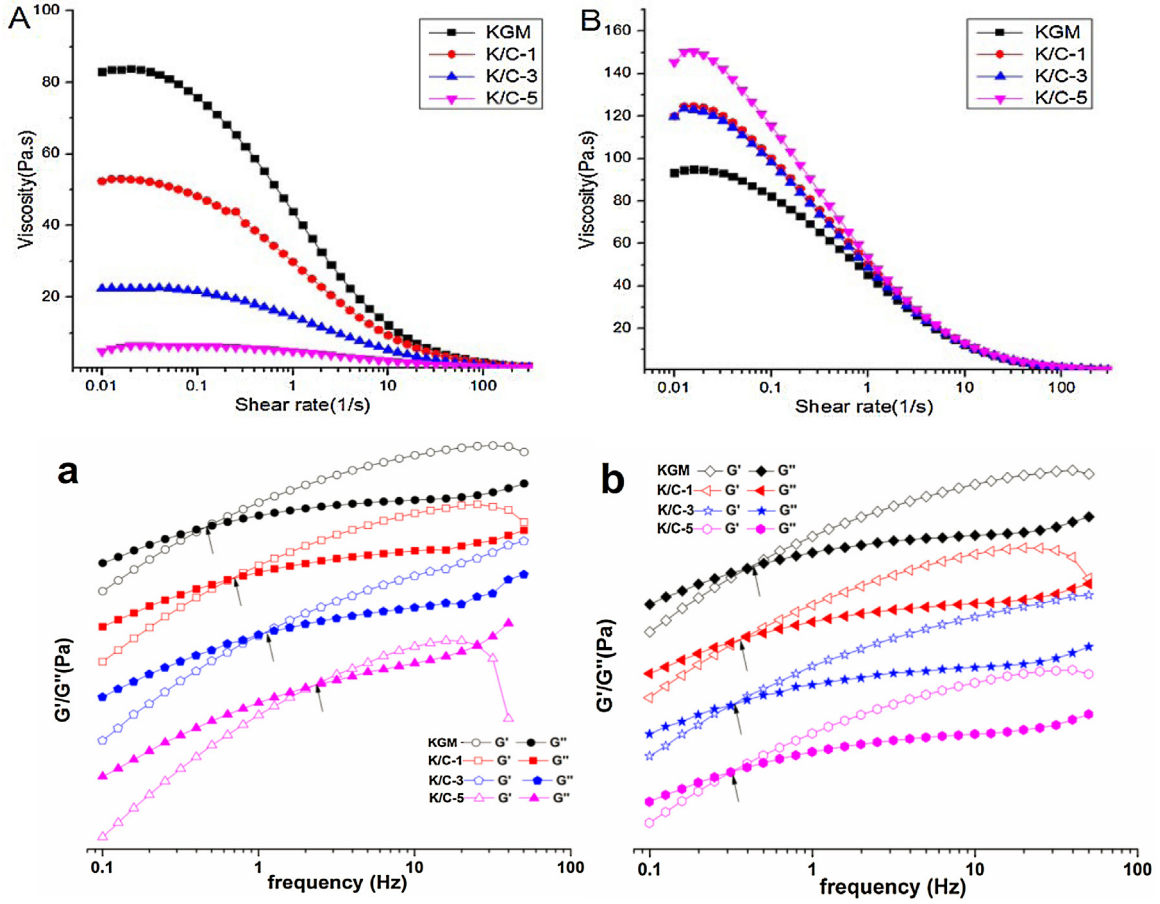

Fig. 5. Steady shear flow curves ((A) and (B)) and frequency sweeps ((a) and (b)) for the solutions of 1% (w/w) KGM, K/C-1, K/C-3 and K/C-5 powders dissolved in neutral aqueous solution ((A) and (a)) and acidic aqueous solution (pH 2.0) ((B) and (b)).

with Fig. 5A and B. Under neutral condition (Table 1a), values of η_0 and m decreased with the coated-chitosan content increasing, indicating that shear-thinning behavior decreased and Newtonian behavior increased. However, under acidic condition (Table 1b), the values of η_0 increased with the coated-chitosan content increasing, indicating that shear-thinning behavior increased and Newtonian behavior decreased. The phenomenon may be illustrated by the above explanation for Fig. 5A and B.

3.5.2. *Dynamic viscoelasticity properties*

Fig. 5a and b depicts the dynamic viscoelasticity properties of KGM, K/C-1, K/C-3, K/C-5 solutions under neutral and acidic conditions. The rheological spectra present a linear viscoelastic range to determine the frequency dependence of the storage (G') and loss modulus (G''). For all the samples, both G' and G'' increased with higher frequency. At lower frequency, all the solutions exhibited liquid-like behavior ($G'' > G'$), because there was sufficient time for substantial disentanglement within the period of oscillation. While at higher frequency, all the solutions exhibited solid-like behavior ($G'' < G'$), due to less disentanglement. The obtained results are consistent with the previous study (Alvarez-Manceñido et al., 2006).

Fig. 5a and b also shows the influence of coated chitosan content on the "cross-over frequency" (where $G'' = G'$). Under neutral condition (Fig. 5a), the "cross-over frequency" shifted to higher frequency values with increasing coated-chitosan content, which meant K/C powders solution containing higher chitosan content had more liquid-like or sol-like properties. The opposite phenomenon was found under acidic condition (Fig. 5b). It demonstrated that the rheological behavior of the K/C powders solution coated with more chitosan was more solid-like under acidic condition. It can be concluded that both chitosan content and pH had synergism effect on the rheological behavior of K/C powders, as the dissolved chitosan coated on KGM affected the formation and disruption of intermolecular and intra-molecular entanglements between chitosan and KGM.

3.6. *Morphology characterization*

The influence of pH on swelling behaviors of the control KGM, K/C-1, K/C-3 and K/C-5 powders are presented in Figs. 6 and 7. All the solutions were prepared by dispersing weighed powders into boiled water to form 1% (w/w) solutions. And then the pH was adjusted. The swelling ability of all the samples was investigated by visually observation. The pictures were taken at 5 min after sample preparation. Under neutral condition (Fig. 6), the swelling ability of K/C powders decreased with increasing coated-chitosan content. However, there was not obvious difference between different samples under acidic condition (Fig. 7), due to the partial dissolution of chitosan at low pH. For the other samples, the trends could be inferred, which was similar with K/C-1, K/C-3 and K/C-5 powders. Thus, in the neutral condition, K/C powders could decrease KGM viscosities and the viscosity of K/C powder coated with more chitosan was lower.

From the above results, it was demonstrated that the physical preparation method of the K/C powders was feasible. Compared to the previous research (Li et al., 2011), the current method had

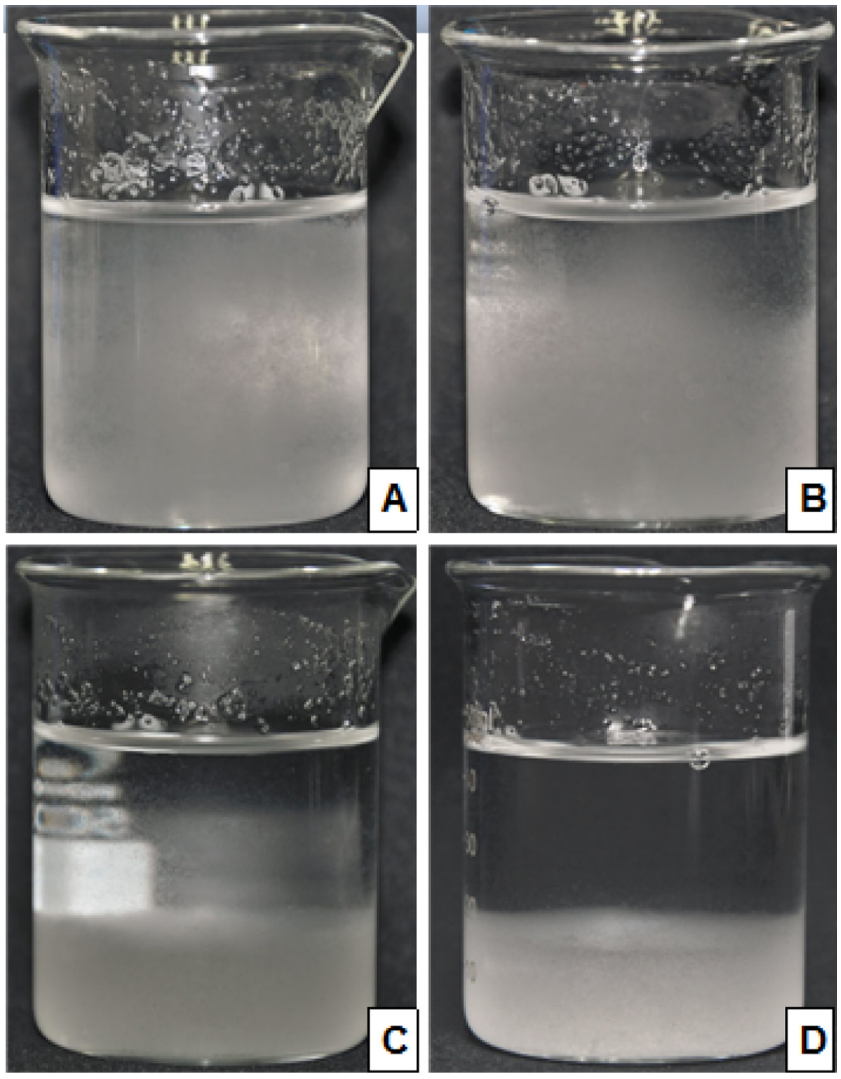

Fig. 6. Swelling behaviors of KGM (A), K/C-1 (B), K/C-3 (C) and K/C-5 (D) powders dissolved in neutral aqueous solutions.

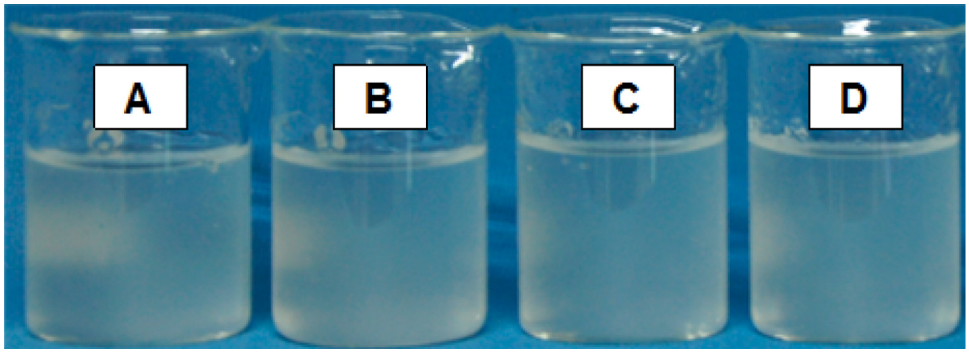

Fig. 7. Swelling behaviors of KGM (A), K/C-1 (B), K/C-3 (C) and K/C-5 (D) powders dissolved in acidic aqueous solutions.

some advantages. First, it was a physical blending method without using much alkaline agent to harden the K/C powders, which is time-consuming. Second, the total process was conducted under acidic or neutral condition, which could avoid the reaction between polyphenols and alkali, protecting the color of powders. Third, the present method did not need heating, which could reduce the energy consumption. Thus, the current method was simple, time-saving and economical.

4. Conclusion

A novel pH-response dietary fiber (K/C powders), selectively soluble in acidic aqueous solution, was fabricated using a green physical grind method. FTIR and XPS results showed that chitosan could be successfully coated on the surface of KGM. Compared with control KGM, the coated KGM powders had a rougher and much more irregular surface. Rheological studies demonstrated that the

viscosity of KGM under neutral condition could be decreased by incorporation of chitosan. Meanwhile, the rheological and swelling behaviors of K/C powders were pH-dependent. First, the results would be useful to extend the application of KGM in food industry without the high viscosity limitation under neutral condition. Second, it could be as a promising healthy fiber to control the obesity due to its pH-responsibility.

Acknowledgment

The research has been financially supported by the National Natural Science Foundation of China (No. 31371841). The authors kindly acknowledge the financial support.

References

Alonso-Sande, M., Teijeiro-Osorio, D., Remuñán-López, C., & Alonso, M. (2009). Glucomannan, a promising polysaccharide for biopharmaceutical purposes. *European Journal of Pharmaceutics and Biopharmaceutics*, *72*(2), 453–462.

Alonso, M. J., & Sánchez, A. (2010). The potential of chitosan in ocular drug delivery. *Journal of Pharmacy and Pharmacology*, *55*(11), 1451–1463.

Alvarez-Manceñido, F., Braeckmans, K., De Smedt, S. C., Demeester, J., Landin, M., & Martínez-Pacheco, R. (2006). Characterization of diffusion of macromolecules in konjac glucomannan solutions and gels by fluorescence recovery after photobleaching technique. *International Journal of Pharmaceutics*, *316*(1), 37–46.

Bhattarai, N., Gunn, J., & Zhang, M. (2010). Chitosan-based hydrogels for controlled, localized drug delivery. *Advanced Drug Delivery Reviews*, *62*(1), 83–99.

Bravo-Osuna, I., Millotti, G., Vauthier, C., & Ponchel, G. (2007). In vitro evaluation of calcium binding capacity of chitosan and thiolated chitosan poly (isobutyl cyanoacrylate) core–shell nanoparticles. *International Journal of Pharmaceutics*, *338*(1), 284–290.

Cao, S., Mishra, R., Pilla, S., Tripathi, S., Pandey, M. K., Shah, G., et al. (2010). Novel chitosan/gold-MPA nanocomposite for sequence-specific oligonucleotide detection. *Carbohydrate Polymers*, *82*(1), 189–194.

Chen, H.-L., Fan, Y.-H., Chen, M.-E., & Chan, Y. (2005). Unhydrolyzed and hydrolyzed konjac glucomannans modulated cecal and fecal microflora in Balb/c mice. *Nutrition*, *21*(10), 1059–1064.

Chua, M., Baldwin, T. C., Hocking, T. J., & Chan, K. (2010). Traditional uses and potential health benefits of *Amorphophallus konjac* K. Koch ex NE Br. *Journal of Ethnopharmacology*, *128*(2), 268–278.

de Britto, D., de Moura, M. R., Aouada, F. A., Mattoso, L. H. C., & Assis, O. B. G. (2012). *N,N,N*-trimethyl chitosan nanoparticles as a vitamin carrier system. *Food Hydrocolloids*, *27*(2), 487–493.

de Souza, J. R. R., de Carvalho, J. I. X., Trevisan, M. T. S., de Paula, R., Ricardo, N. M. P. S., & Feitosa, J. (2009). Chitosan-coated pectin beads: Characterization and *in vitro* release of mangiferin. *Food Hydrocolloids*, *23*(8), 2278–2286.

EFSA. (2005). Opinion of the scientific panel on food additives, flavourings, processing aids and materials in contact with food (AFC) on a request from the commission related to butylbenzylphthalate (BBzP) for use in food contact materials. *EFSA Journal*, *241*, 1–14.

Fang, W., & Wu, P. (2004). Variations of konjac glucomannan (KGM) from *Amorphophallus konjac* and its refined powder in China. *Food Hydrocolloids*, *18*(1), 167–170.

Gaidhane, M. K., Rahatgaonkar, A. M., Tiwari, A., & Chorghade, M. S. (2010). Ion sequestration, solvent extraction and antimicrobial behavior of quinoline functionalized chitosan. *Journal of Inorganic and Organometallic Polymers and Materials*, *21*(1), 118–127.

Gläser, K. R., Wenk, C., & Scheeder, M. R. L. (2004). Evaluation of pork backfat firmness and lard consistency using several different physicochemical methods. *Journal of the Science of Food and Agriculture*, *84*(8), 853–862.

Han, H. D., Song, C. K., Park, Y. S., Noh, K. H., Kim, J. H., Hwang, T., et al. (2008). A chitosan hydrogel-based cancer drug delivery system exhibits synergistic antitumor effects by combining with a vaccinia viral vaccine. *International Journal of Pharmaceutics*, *350*(1), 27–34.

Hwang, J. K., & Shin, H. H. (2000). Rheological properties of chitosan solutions. *Korea-Australia Rheology Journal*, *12*(3–4), 175–179.

Jacon, S., Rao, M., Cooley, H., & Walter, R. (1993). The isolation and characterization of a water extract of konjac flour gum. *Carbohydrate Polymers*, *20*(1), 35–41.

Jeon, Y. J., & Kim, S. K. (2000). Production of chitooligosaccharides using an ultrafiltration membrane reactor and their antibacterial activity. *Carbohydrate Polymers*, *41*(2), 133–141.

Jiménez-Colmenero, F., Cofrades, S., Herrero, A., Fernández-Martín, F., Rodríguez-Salas, L., & Ruiz-Capillas, C. (2012). Konjac gel fat analogue for use in meat products: Comparison with pork fats. *Food Hydrocolloids*, *26*(1), 63–72.

Jung, W. K., Moon, S. H., & Kim, S. K. (2006). Effect of chitooligosaccharides on calcium bioavailability and bone strength in ovariectomized rats. *Life Sciences*, *78*(9), 970–976.

Kim, S. K., & Rajapakse, N. (2005). Enzymatic production and biological activities of chitosan oligosaccharides (COS): A review. *Carbohydrate Polymers*, *62*(4), 357–368.

Kim, T. H., Park, Y. H., Kim, K. J., & Cho, C. S. (2003). Release of albumin from chitosan-coated pectin beads in vitro. *International Journal of Pharmaceutics*, *250*(2), 371–383.

Lapasin, R., & Pricl, S. (1995). *Rheology of industrial polysaccharides: Theory and applications*. London: Blackie Academic & Professional.

Lawrie, G., Keen, I., Drew, B., Chandler-Temple, A., Rintoul, L., Fredericks, P., et al. (2007). Interactions between alginate and chitosan biopolymers characterized using FTIR and XPS. *Biomacromolecules*, *8*(8), 2533–2541.

Lee, E., Kim, H., Lee, I. H., & Jon, S. (2009). In vivo antitumor effects of chitosan-conjugated docetaxel after oral administration. *Journal of Controlled Release*, *140*(2), 79–85.

Li, J., Ji, J., Xia, J., & Li, B. (2012). Preparation of konjac glucomannan-based superabsorbent polymers by frontal polymerization. *Carbohydrate Polymers*, *87*(1), 757–763.

Li, Y., Chen, X. G., Liu, N., Liu, C. S., Liu, C. G., Meng, X. H., et al. (2007). Physicochemical characterization and antibacterial property of chitosan acetates. *Carbohydrate Polymers*, *67*(2), 227–232.

Li, Y. X., Liu, M., Luo, L. X., Luo, T. R., Xiao, X., Xu, C., et al. (2011). Chitosan inwrapped konjak composition, preparation process and application thereof. In *CN 101775162 B (in Chinese)*. Faming Zhuanli Shenqing Gongkai Shuoming-shu. ⟨http://worldwide.espacenet.com/publicationDetails/biblio?CC=CN&NR=101775162B&KC=B&FT=D⟩.

Liang, S., Li, B., Ding, Y., Xu, B., Chen, J., Zhu, B., et al. (2011). Comparative investigation of the molecular interactions in konjac gum/hydrocolloid blends: Concentration addition method (CAM) *versus* viscosity addition method (VAM). *Carbohydrate Polymers*, *83*(3), 1062–1067.

Liao, F. H., Shieh, M. J., Chang, N. C., & Chien, Y. W. (2007). Chitosan supplementation lowers serum lipids and maintains normal calcium, magnesium, and iron status in hyperlipidemic patients. *Nutrition Research*, *27*(3), 146–151.

Miyoshi, E., & Nishinari, K. (1999). Non-Newtonian flow behaviour of gellan gum aqueous solutions. *Colloid & Polymer Science*, *277*(8), 727–734.

Mourya, V. K., Inamdar, N. N., & Tiwari, A. (2010). Carboxymethyl chitosan and its applications. *Advanced Materials Letters*, *1*(1), 11–33.

Nguyen, T.-H., & Lee, B.-T. (2012). The effect of cross-linking on the microstructure, mechanical properties and biocompatibility of electrospun polycaprolactone–gelatin/PLGA–gelatin/PLGA–chitosan hybrid composite. *Science and Technology of Advanced Materials*, *13*(3), 035002.

Oblonšek, M., Šostar-Turk, S., & Lapasin, R. (2003). Rheological studies of concentrated guar gum. *Rheologica Acta*, *42*(6), 491–499.

Pan, T., Peng, S., Xu, Z., Xiong, B., Wen, C., Yao, M., et al. (2012). Synergetic degradation of konjac glucomannan by γ-ray irradiation and hydrogen peroxide. *Carbohydrate Polymers*, *93*, 761–767.

Shen, X. L., Wu, J. M., Chen, Y., & Zhao, G. (2010). Antimicrobial and physical properties of sweet potato starch films incorporated with potassium sorbate or chitosan. *Food Hydrocolloids*, *24*(4), 285–290.

Shukla, S., & Tiwari, A. (2011). Synthesis of chemical responsive chitosan-grafted-polyaniline bio-composite. *Advanced Materials Research*, *306*, 82–86.

Shukla, S. K., Deshpande, S. R., Shukla, S. K., & Tiwari, A. (2012). Fabrication of a tunable glucose biosensor based on zinc oxide/chitosan-graft-poly(vinyl alcohol) core–shell nanocomposite. *Talanta*, *99*, 283–287.

Takahashi, R., Kusakabe, I., Kusama, S., Sakurai, Y., Murakami, K., Maekawa, A., et al. (1984). Structures of glucomanno-oligosaccharides from the hydrolytic products of konjac glucomannan produced by a β-mannanase from *Streptomyces* sp. *Agricultural and Biological Chemistry*, *48*(12), 2943–2950.

Tatirat, O., & Charoenrein, S. (2011). Physicochemical properties of konjac glucomannan extracted from konjac flour by a simple centrifugation process. *LWT—Food Science and Technology*, *44*(10), 2059–2063.

Tiwari, A. (2010). *Polysaccharides: Development, properties and applications*. New York: Nova Science Publishers.

Tiwari, A., & Kobayashi, H. (2013). *Responsive material methods and applications*. New Jersey: John Wiley & Sons.

Tiwari, A., Mishra, A. K., Kobayashi, H., & Turner, A. P. (2012). *Intelligent nanomaterials*. New Jersey: John Wiley & Sons.

Tiwari, A., Ramalingam, M., Kobayashi, H., & Turner, A. P. (2012). *Biomedical materials and diagnostic devices*. New Jersey: John Wiley & Sons.

Tiwari, A., & Syvajarvi, M. (2014). Advanced materials for agriculture. In *Food and environmental safety*. New Jersey: John Wiley & Sons.

Tiwari, A., Terada, D., Sharma, P. K., Parashar, V., Yoshikawa, C., Pandey, A. C., et al. (2011). An ultra sensitive saccharides detection assay using carboxyl functionalized chitosan containing Gd_2O_3: Eu^{3+} nanoparticles probe. *Analytical Methods*, *3*(1), 217–226.

Tiwari, A., & Tiwari, A. (2013a). *Bioengineered nanomaterials*. Florida: CRC Press.

Tiwari, A., & Tiwari, A. (2013b). Nanomaterials in drug delivery. In *Imaging and tissue engineering*. New Jersey: John Wiley & Sons.

Tye, R. J. (1991). Konjac flour: Properties and applications. *Food Technology*, *45*(3), 82–92.

Venter, C. S., Vorster, H. H., & Nest, D. (1990). Comparison between physiological effects of konjac-glucomannan and propionate in baboons fed Western diets. *Journal of Nutrition*, *120*(9), 1046–1053.

Vuksan, V., Sievenpiper, J. L., Xu, Z., Wong, E. Y., Jenkins, A. L., Beljan-Zdravkovic, U., et al. (2001). Konjac-Mannan and American ginsing: Emerging alternative therapies for type 2 diabetes mellitus. *Journal of the American College of Nutrition*, *20*(Suppl 5), 370S–380S.

Xia, W., Liu, P., Zhang, J., & Chen, J. (2011). Biological activities of chitosan and chitooligosaccharides. *Food Hydrocolloids*, *25*(2), 170–179.

Zhang, H., Yoshimura, M., Nishinari, K., Williams, M., Foster, T., & Norton, I. (2001). Gelation behaviour of konjac glucomannan with different molecular weights. *Biopolymers*, *59*(1), 38–50.

Zhang, Y.-q., Xie, B.-j., & Gan, X. (2005). Advance in the applications of konjac glucomannan and its derivatives. *Carbohydrate Polymers*, *60*(1), 27–31.