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

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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

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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.