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Preparation and characterization of heterogeneous deacetylated konjac glucomannan

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ABSTRACT

Deacetylated konjac glucomannan (Da-KGM) powder was prepared in heterogeneous system. Kinetics of heterogeneous deacetylation was investigated to predict the optimum reaction conditions. The results indicated that: heterogeneous deacetylation was influenced by the kind and amount of alkali, ethanol concentration, temperature and reaction time. Meanwhile, it followed first-order kinetics and the apparent activation energy was 15.59 kJ/mol. The properties of Da-KGM were studied by Fourier-transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC) and X-ray diffraction (XRD), which proved that there was no significant difference of primary structure, thermal properties and crystal properties among Da-KGMs. The solubility was also analyzed and evaluated. As deacetylation degree (DD) increased, the solubility of KGM showed exponential decrease. In addition, lower temperature was more effective to promote the dissolution of Da-KGM.

1. Introduction

KGM is extracted from the tubers of *Amorphophallus konjac* C. Koch (Nishinari, Williams, & Phillips, 1992) and regarded as a kind of dietary fiber, which has significant health functions. It has been widely used in food industry because of its good swelling, gelling and other features. This natural material can be used for the preparation of composite materials, edible film, coating/packaging film, biodegradable film, and controlled release matrix. KGM is a water-soluble polysaccharide, composed of β-(1 → 4) linked D-mannose and D-glucose in a molar ratio of 1.6:1 (Kato, 1969) or 1.4:1 (Dey & Dixon, 1985), with about 1 in 19 units being acetylated (Corp., 1993; Katsuraya et al., 2003). It is widely accepted that the presence of acetyl-substituted residues confers water-solubility to the KGM in aqueous solution (Koroskenyi & McCarthy, 2001). In addition, Da-KGM may be used as adsorbent in many fields. Carboxylic acid functionalized Da-KGM was synthesized with copolymerization of methyl acrylate and methyl methacrylate by free radical graft, which showed a fast adsorption rate and high removal efficiency of Pb^{2+} and Cu^{2+} from aqueous solution (Liu, Luo, Lin, Liang, & Chen, 2009). Furthermore, it was observed that Da-KGM can be utilized as a low-cost and readily available biosorbent for removal of tannin from aqueous solutions (Liu, Luo, & Lin, 2010).

Plenty of studies have been carried out to treat KGM with alkali for deacetylation (Bin & Bi-jun, 2003; Cheng, Abd Karim, Norziah, & Seow, 2002). The deacetylated KGM can form a heat-stable gel (Perols, Piffaut, Scher, Ramet, & Poncelet, 1997). The gelation of KGM was studied by rheological measurements with low-amplitude oscillation experiments in the presence of different salts (e.g. NaSCN, NaCl, Na_2SO_4), and compared with those of methylcellulose, gelatin, acrylamide and pectin (Case, Kropp, Hamann, & Schwartz, 1992). It was suggested that the gelation kinetics of KGM samples was governed by deacetylation rate (Gao & Nishinari, 2004a). After that, a new study showed that a faster gelation rate and a more elastic modulus were facilitated by increasing the deacetylation degree (DD). The hydrophobic interaction and hydrogen bonding were both presented in KGM gelation, and hydrophobic interactions strengthen while hydrogen bonding weaken with increasing DD (Du, Li, Chen, & Li, 2012).

So far, the deacetylation of KGM has been performed in homogeneous systems (mostly in water) by alkali treatment. However, KGM solution of large concentration cannot be carried out with this method due to its high viscosity as well as the complicated procedures. To sum up, these disadvantages have severely limited the

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applications of homogeneous deacetylation. Recent attention to solid-phase reaction by the mechanochemical (MC) treatment has been increased due to the growing economical and eco-logical requirements (Pan, He, & Wang, 2008). However, considering the rate of solid-phase reaction was very slow theoretically, the increasing DD might be caused by ethanol washing during the later step instead of the removal of acetyl group. As a result, the common disadvantages of these two methods made it hard to obtain Da-KGM with accurate deacetylation degree (DD). There were many reports on heterogeneous deacetylation of chitin since the early 1930s (Bin & Bi-jun, 2003; Cheng et al., 2002; Nishinari et al., 1992). The studies of Aiba et al. suggested that chitosan obtained by heterogeneous deacetylation had a block-type distribution of acetyl group along the polymer chain (Aiba, 1991; Kurita, Sannan, & Iwakura, 1977). Some other researchers comparatively studied the heterogeneous deacetylation of α- and β-chitins from shrimp, squid pens and shells in a multistep process, which allowed them to obtain chitosan with high molecular weight and high DD (Jiang & Xu, 2006; Kurita, Ishii, Tomita, Nishimura, & Shimoda, 1994; Lamarque, Viton & Domard, 2004). However, the heterogeneous deacetylation of KGM has not been reported as yet. In this paper, Da-KGM was obtained in a heterogeneous system on the basis of heterogeneous deacetylation of chitin. This method was proposed to obtain Da-KGM with precise and controllable DD, which would provide the ideal material for the research of the gelation mechanism and determining the role of acetyl group in gelation. Moreover, heterogeneous deacetylation was excellent for mass production. In addition, kinetic profile was investigated to predict the optimum reaction conditions. The physical properties of Da-KGM were studied by FT-IR, DSC and XRD. The solubility was also analyzed and evaluated.

2. Material and methods

2.1. Material

The raw KGM was purchased from Hubei Jianshi, Nongtai Industrial Co., Ltd. The absolute value of degree of acetyl-substituted residues in neat-KGM was 0.053. All chemicals were purchased from Sinopharm Chemical Reagent Company. They were all of A.R. grade and used without further purification.

2.2. Heterogeneous deacetylation

2.2.1. Effect of influence factors on deacetylation reaction

Thirty grams (30.00 g) of purified KGM powder and 200 ml of a certain concentration of ethanol solution was mixed in a 250 ml conical flask. The mixed suspension was swelled in a constant thermostat oscillator at a certain temperature for 30 min (150 rpm). Subsequently, the suspension with alkali solution was reacted for a certain period. After deacetylation, each sample was washed three times with aqueous ethanol (50%, 75%, and 95%) to remove excess alkali and finally washed with absolute ethanol. The excess of ethanol was evaporated in a fume cupboard followed by vacuum drying for 6 h at 40 °C and the powdered Da-KGM was obtained.

2.2.2. Preparation of KGM with different deacetylation degree

Thirty grams (30.00 g) of purified KGM powder and 200 ml of 50% (v/v) ethanol was mixed in a 250-ml conical flask. The mixed suspension was swelled in a constant thermostat oscillator at 40 °C for 30 min (150 rpm). Subsequently, the suspension with Na_2CO_3 solution was reacted at 40 °C for 24 h. After deacetylation, each sample was washed three times with aqueous ethanol (50%, 75%, and 95%) to remove excess alkali and finally washed with absolute ethanol. The excess of ethanol was evaporated in a fume cupboard followed by vacuum drying for 6 h at 40 °C and the powdered Da-KGM was obtained. KGM with different DD was obtained by changing the volume of Na_2CO_3, which were coded as Da0, Da1, Da2, Da3, Da4, Da5, Da6 and the corresponding molar ratio of Na_2CO_3 to acetyl group was 0.5:8, 1:8, 2:8, 3:8, 4:8 and 8:8, respectively.

2.2.3. Determination of deacetylation degree

Deacetylation degree (DD) is defined as the ratio of content of acetyl groups been removed and total acetyl groups in KGM. This method was based on the Eberstadt method including saponification and successive titration (Chen, Zong, & Li, 2006; Tanghe, Genung, & Mench, 1963). Five grams (5 g) of the KGM powder with 50 ml of 75% ethanol was mixed in a 250-ml conical flask. The mixed suspension was then heated to 50 °C in constant water bath for 30 min before cooling down to room temperature. 5 ml of KOH (0.5 mol/L) was added into the suspension for saponification in a digital water bath oscillator for 48 h. The excess of alkali was back titrated with 0.1 mol/L hydrochloric acid with phenolphthalein as an indicator. The titration process for each sample was repeated three times and the repeated results were calculated to obtain the average value. DD was calculated by Eq. (1):

$$\mathrm{DD}\ (\%) = \frac{(V_2 - V_1) \times (1 - \omega_0)}{(V_0 - V_1) \times (1 - \omega_1)} \times 100\% \quad (1)$$

Where V_0 is the average value of the volume of hydrochloric acid consumed for the blank in liters, V_1 is the average value of the volume of hydrochloric acid consumed for the sample in liters, V_2 is the average value of the volume of hydrochloric acid consumed for the KGM powder in liters, ω_0 is water content of KGM powder, ω_1 is water content of deacetylated KGM.

2.2.4. Kinetics of heterogeneous deacetylation of KGM

Deacetylation of KGM is actually a hydrolytic reaction of ester, namely, a typical nucleophilic substitution reaction. Assuming that the deacetylation of KGM is a pseudo first order reaction of which the reaction rate is only concerned with the content of acetyl group, the dynamical equation could be expressed as Eq. (2) and Eq. (3):

$$-\ln(1 - \mathrm{DD}) = kt \quad (2)$$

$$\ln k = -E_a/RT + B \quad (3)$$

where k is reaction rate constant, t is reaction time, T is reaction temperature (absolute temperature), E_a is activation energy, R is gas constant.

2.3. Characterization

2.3.1. FT-IR analysis

Fourier transform infrared (FT-IR) measurements of KGM samples were carried out at a FT-IR spectrometer (Nexus 470, Nicolet, USA) at a resolution of 4 cm^{-1} in the range 400–4000 cm^{-1}. KGM samples were prepared as KBr discs and were scanned against an air background (Du et al., 2012).

2.3.2. DSC analysis

The thermal analyses of the KGM samples were carried out with a model DSC 204 F1 (Netzsch, Germany). Temperature and enthalpy of the instrument were calibrated by pure indium (99.99%). 2.0 ± 0.1 mg of the samples in an aluminum crucible with a reference sample of an empty crucible were analyzed in a dried N_2 gas atmosphere at a heating rate of 10 °C min^{-1} in a temperature