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Carboxymethyl modification of konjac glucomannan affects water binding properties

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ABSTRACT

The water binding properties of konjac glucomannan (KGM) and carboxymethyl konjac glucomannan (CMKGM) are important for their application in food, pharmaceutical, and chemical engineering fields. The equilibrium moisture content of CMKGM was lower than that of KGM at the relative humidity in the range 30–95% at 25 °C. The water absorption and solubility of CMKGM in water solution were lower than that of KGM at 25 °C. Carboxymethyl modification of KGM reduces the water adsorption, absorption, and solubility. Both carboxymethylation and deacetylation could confer hydrophobicity for CMKGM. These data provide the basis for expanding CMKGM application.

1. Introduction

Konjac glucomannan (KGM) is a high molecular weight, water-soluble, and non-ionic natural polysaccharide derived from roots and tubers of *Amorphophallus konjac* K. Koch (Chua et al., 2012; Williams et al., 2000).

KGM is a linear polysaccharide, consisting of β-D-glucose and β-D-mannose residues in a molar ratio of 1: 1.6 linked by β-1,4-glycosidic bonds, the acetyl groups along the KGM backbone are located, on average, every 9–19 sugar units at the C-6 position (Katsuraya et al., 2003).

KGM are widely used in food, pharmaceuticals, and chemical engineering due to their specific physical and chemical properties (Alonso-Sande, Teijeiro-Osorio, Remuñán-López, & Alonso, 2009). However, some potential applications of KGM are limited by its high water absorption index, as high as 100 g water/g sample (Koroskenyi & McCarthy, 2001). To reduce hydration of KGM in aqueous solution, chemical modification of KGM through acetylation has been done, and acetylated konjac glucomannan exhibits lower water absorption comparing to KGM (Enomoto-Rogers, Ohmomo, & Iwata, 2013; Huang, Takahashi, Kobayashi, Kawase, & Nishinari, 2002; Koroskenyi & McCarthy, 2001).

Carboxymethyl konjac glucomannan (CMKGM) is the carboxymethyl modification of KGM. CMKGM and CMKGM derivatives have proven to be a promising new biodegradable material for the preparation of biodegradable films (Tang, Du, Zheng, & Fan, 2003; Wang et al., 2014), a biomaterial in the drug delivery systems (Du et al., 2005; Ha et al., 2011), for enzyme encapsulation (Li et al., 2011), and adsorption of heavy metal ions from aqueous solution (Niu, Wu, Wang, Li, & Wang, 2007). When these biomaterials are exposed to water solution, interactions between CMKGM-based materials and water will influence the properties of materials, e.g., moisture resistance of film, controlled release of drug, and enzyme activity. CMKGM (degree of carboxymethylation = 0.29) and soy protein isolate blend films were reported in our previous work (Wang et al., 2014), the results showed that the water adsorption of the CMKGM/SPI films progressively decreased with increasing CMKGM level, and the surface wettability of the blended films was improved with increasing CMKGM content, but the author did not give explanation for moisture resistant of films. CMKGM, as one of film components, its water binding properties inevitably influence moisture sorption of films. Hence, CMKGM-water binding properties are fundamental information for understanding material function and application.

Abbreviations: KGM, konjac glucomannan; CMKGM, carboxymethyl konjac glucomannan; DS, degree of substitution; DD, degree of deacetylation; RH, relative humiditym; DVS, dynamic vapor sorption; XRD, X-ray diffraction; SEM, scanning electron microscopy; AFM, atomic force microscopy.

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Therefore, the objective of this work was to evaluate the water binding properties of CMKGM. Moisture adsorption isotherms, water absorption and solubility in water solution of KGM and CMKGM were determined. Mechanism of carboxymethyl modification of KGM reducing the water binding was proposed.

2. Materials and methods

2.1. Purification of native konjac glucomannan

The native konjac glucomannan was a gift from Wuhan Li Cheng Industry Co. Ltd. (Wuhan, China) and further purified by the method of Chua et al. (2012). Briefly, KGM (1.00 g) was stirred in 50% (v/v) ethanol (100 mL) for 90 min at room temperature, followed by centrifugation (5000×*g*, 30 min, 25 °C) to remove the aqueous ethanol. Centrifugal sediment was added to deionized water (200 mL) and stirred for 3 h at room temperature, followed by KGM precipitation with absolute ethyl alcohol (800 mL), centrifugation, dehydration, and oven drying. The purified KGM was referred to as KGM-0.

The glucomannan content of KGM-0 was determined using 3, 5-DNS colorimetric assay according to the methods of Agricultural Standard of People's Republic of China (Chinese, 2010). The total starch content in KGM-0 was quantified using the total starch assay kit (Megazyme, Bray, Ireland) according to the manufacturer's instructions. The total nitrogen in KGM-0 was determined by Kjeldahl method (AOAC, 2000a: method 979.09) using a protein analyzer (K9860 Kjeltec Analyzer, Hanon Instruments, China), and recalculated into proteins by multiplying it by a factor of 6.25. Moisture and ash in KGM-0 were determined using AOAC methods (AOAC, 2000b: method 945.38).

2.2. Preparation of carboxymethyl konjac glucomannan (CMKGM)

Carboxymethyl konjac glucomannan (CMKGM) was prepared by the method of Zhou et al. (2006) with minor modifications. Briefly, one gram KGM-0 was added to 200 mL deionized water with stirring at 200 rpm for 2 h. Then sodium acetate dissolved in 40 mL 70% (v/v) ethanol was added. After 1 h, 0.6 g monochloroacetic acid dissolved in 25 mL 70% (v/v) ethanol was added. After a few hours of chemical reaction, the product was precipitated with 80% (v/v) aqueous ethanol, then washed with 50% (v/v) aqueous ethanol until there was no residual chloridion in the filtrate, filtered off and dried. CMKGM samples with different substitution degrees were obtained with the change of the reaction temperature (50, 60, and 70 °C), the dosage of sodium acetate (2 and 4 g), and the reaction time (1, 2, and 3 h). The degree of substitution (DS) of carboxymethylated KGM samples was determined by the potentiometric titration according to a previous report (El-Sherbiny, 2009). The carboxymethylated KGM samples with different DS were referred to CMKGM-1, CMKGM-2, and CMKGM-3, respectively.

The weight percent of acetyl-substituted residues in the KGM backbone was determined by a published method (Chua et al., 2012; Chen, Zong, & Li, 2006), with minor modifications. Briefly, the solutions of Ca. 0.4 mol L^{-1} KOH and 0.2 mol L^{-1} HCl were prepared. Potassium hydrogen phthalate (PHP) (1.000 g) was dissolved in de-ionized water and titrated with KOH solution using phenolphthalein indicator. The titration volume was recorded as V_a (mL) and the mass of PHP was recorded as m_{PHP} (g). HCl solution (10.00 mL) was titrated with KOH solution using phenolphthalein indicator and the titration volume was recorded as V_b (mL). The sample (m_s = 1.000 g) was stirred in de-ionized water (250 mL) for 3 h at room temperature. The solution was titrated with Ca. 0.1 mol L^{-1} KOH using phenolphthalein indicator to a permanent pink color (pre-neutralization). KOH solution (10.00 mL) was then added and the mixture stirred for 3 h at room temperature. The excess alkali was back titrated with HCl and the titre recorded V_c (mL). The solution was stood for 2 h, and then any additional alkali, which may have leached from the sample, was titrated if pink color of the solution appeared again. A blank (to which no sample had been added) was titrated in parallel and the titre recorded V_d (mL). The content of acetyl groups in the samples was calculated by evaluation of Eq. (1),

$$\text{Acetyl content}(\%) = \frac{430\ m_{PHP}V_b(V_d - V_c)}{204.23\ V_a m_s} \quad (1)$$

2.3. Determination of particle size, molecular weight, and apparent viscosity of KGM and CMKGM

The KGM and CMKGM samples were ground with mortar and pestle, and then passed through a 0.15 mm sieve (Cole-Parmer). The powder was suspended in 95% (v/v) ethanol, and then particle size and specific surface area of the powder were measured using BT-9300H Laser Particle Size Analyzer (Dandong Bettersize Instruments, Dandong, China) at 25 °C.

Molecular weight was measured by size exclusion chromatography (Shodex SB 805HQ, Showa Denko America, New York, NY) coupled on-line to a MALS system with the detector Dawn Heleos II and Optilab rEx (Wyatt Technology Corporation, Santa Barbara, CA). The samples were dissolved in 0.1 mol L^{-1} NaCl solutions and filtered with 0.45 μm pore size filter (Millipore). The concentration of samples was from 0.1 to 0.5 mg mL^{-1}. The injected volume was 200 μL. The flow rate was 0.40 mL min^{-1}. The columns temperature was maintained at 25 °C. The data obtained with MALS detectors were analyzed using ASTRA software (version 4.90.07 for Windows, Wyatt Technology Corporation, Santa Barbara, CA).

Stock solution of samples (1%, w/w) was prepared by adding sample (0.5 g) to de-ionized water (49.5 g), the mixture was stirred for 12 h at 25 °C. The apparent viscosity was performed using a rotational viscosity meter (NDJ-8S, Shanghai Hengping Scientific Instrument, Shanghai, China) at 25 °C. The viscosities of KGM-0 and CMKGM 1–3 were measured with a No. 3 rotator set at 30 rpm and a No. 1 rotator set at 12 rpm, respectively.

2.4. Dynamic vapor adsorption of KGM and CMKGM

The water sorption isotherms of KGM-0 and CMKGM samples 1–3 were determined using a DVS Intrinsic apparatus (Surface Measurement Systems, London, UK). The sample (Ca. 6 mg) was placed in a sample pan and exposed to a relative humidity (RH) range from 0 to 95% (RH = 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 95%, respectively). Mass equilibrium at each humidity stage was reached by measuring the percentage rate of change in mass with time (dm/dt). Once the dm/dt was below a predetermined threshold value (dm/dt = 0.002%/min) over a 10 min period and equilibrium was achieved at each humidity stage. All measurements were performed at 25 °C. Experimental data points were collected and plotted as an isotherm using Microsoft Excel 2010 together DVS Standard Analysis Suite Version 6.3.

Only one measurement was carried out for each sample in the current study. Because DVS method has high data reproducibility and can provide accurate isotherms at any desired relative humidity (0–95%) with short measurement time at different preset isotherm temperatures, the highly reproducibility of the data using this DVS technique is generated (Hill, Norton, & Newman, 2009), and the water adsorption isotherms of KGM-0 gave high reproducibility in this study (data not shown).