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Synergistic degradation of konjac glucomannan by alkaline and thermal method

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ABSTRACT

The application of konjac glucomannan (KGM) in the food industry is always limited by its high viscosity. Hereby, low-viscosity KGM was prepared by alkaline-thermal degradation method. This process was demonstrated by the changes of average molecular weight and a kinetic model was developed. The results revealed that high alkalinity and high temperature had a synergetic effect on degradation. The structure of hydrolysates was evaluated by periodate oxidation and their fluidly properties were researched by rheology measurements. The degradation was divided into two regimes. The rate of the first regime (within 1 h) is higher than that of the second one (last 1 h). It is found that alkaline hydrolysis and deacetylation have a synergistic effect on the degradation under high alkalinity (pH 9.2) and low temperature condition (25 °C). Finally, rheology parameters showed alkaline-thermal degradation is a promising way that can be applied in practice to degrade KGM.

1. Introduction

Konjac glucomannan (KGM), a kind of heteropolysaccharide with average viscosity molecular weight ranging from 10^5 to 10^6 (Chua, Baldwin, Hocking, & Chan, 2010; Li & Xie, 2004), is one of the highest viscosity polysaccharides and exhibits a typical shear thinning behavior (Yaseen, Herald, Aramouni, & Alavi, 2005). The viscosity of 1% (w/w) KGM solution could reach 30 000 cps (Takigami, 2000). Due to the unique high viscosity and gelling property, KGM is widely employed as emulsifier and stabilizer in the food, cosmetic and pharmaceutical areas, such as composite materials, biodegradable film and controlled release matrix (Alonso Sande, Teijeiro Osorio, Remuñán López, & Alonso, 2009).

However, the application of KGM as an additive in beverage and liquid transmission during food processing is limited by its high viscosity. It has been reported that KGM oligosaccharides have the potential bioactive benefits as the prebiotic and immunomodulator (Gao, Lou, & Liu, 2010; Jian et al., 2013). Partially hydrolyzed glucomannan polysaccharide could simulate better growth of *Bifidobacterium* and *Lactobacillus* (Al Ghazzewi, Khanna, Tester, & Piggott, 2007). Therefore, lots of studies have focused on exploring efficient methods for degradation of glucomannan such as acid hydrolysis, enzymatic hydrolysis, physical and irradiation degradation, in order to get functional oligosaccharides or other commercial usages (Feng & He, 2008; Gao et al., 2010; Jian et al., 2013; Xu, Sun, Yang, Ding, & Pang, 2007; Yong chun, Qing-ruo, Ren, & Yan, 2005). Although many degradation methods are effective, they still possess several disadvantages. For example, the enzymatic degradation needs rigidly and mildly reactive environment and the enzymes are hardly separated from products, which increase the cost (Chen, Fu, & Ou, 2002). The alkaline degradation has been carried out into various polysaccharides, such as alginate (Haug, Larsen, & Smidsrod, 1967), but rarely studies well accessed on alkaline degradation of KGM.

KGM is composed of a linear chain of β-1,4-linked D-glucose, with side branches through β-1,6-glycosyl units (Chen et al., 2002; Li & Xie, 2004). The acetyl groups along the KGM backbone are located, on average, every 9–19 sugar units at the C-6 position (Nishinari, 2000). Deacetylation which formed by alkaline treatment has been demonstrated to improve the gelling properties of KGM by some researches. Under alkaline condition, deacetylation causes KGM molecular to transform from semi-flexible linear chain (with length of 1054.11 nm) to strong self-crimping elastic microsphere (with diameter of 40–50 nm) (Chen, Li & Li, 2011; Li, Kennedy, Jiang & Xie, 2006; Li, Xia, Wang & Xie, 2005). Therefore, it is necessary to take the effect of deacetylation into

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consideration when the regulation of alkaline degradation was evaluated comprehensively.

Actually, the temperature and molecular conformation also exert a leading role of alkaline degradation (Akbar, Iqbal, Massey, & Masih, 2012; Hansson & Hartler, 1970; Riedo, Scalarone, & Chiantore, 2010). Thermal treatment is a commonly degraded or assissted methods used for modification monosaccharides. For example, thermal treatment of chitosan (Zawadzki & Kaczmarek, 2010) or combined with oxidation degraded starch (Jankovic, 2013).

In the present study, the effects of deacetylation and temperature on alkaline degradation were evaluated. This comprehensive effect of alkaline and thermal treatment was investigated by analyzing oligosaccharides structure and recording the kinetic model of hydrolysis. The rheological properties of hydrolysates were characterized for molecular conformation and entanglement.

2. Materials and methods

2.1. Materials

Konjac glucomannan ($M_w \sim 980\,000$) was supplied by Nongxiang Biotech Co. (Wuhan, China) and used as received without further purification. All other chemicals were analytical reagents which were purchased from Sinopharm Chemical Reagent Co. (Beijing, China).

2.2. Alkaline-thermal degradation of KGM

0.3% (w/w) KGM solution was prepared by suspending KGM powder in distilled water and completely swelling at 25 °C for stirring 2 h. The value of pH with original KGM solution was 5.6. Then the degraded samples were controlled by adjusting pH and temperature. During degradation, 30 mL sample was collected every 30 min for analysis. The pH was adjusted into 7.2, 8.2, 9.2 by 0.1 M NaOH and the temperature was varied from 25 to 80 °C.

2.3. Molecular weight measurement

Viscosity average molecular weight of samples after hydrolysis was measured by an Ubbelodhe viscometer (Liangjing Co., Shanghai, China) at 25 ± 0.1 °C. The relative and specific viscosities (η_r and η_{sp}) were calculated according to

$$\eta_r = \frac{t}{t_0}, \quad \eta_{sp} = \eta_r - 1 \tag{1}$$

where t and t_0 is the flow time for the sample solution and the solvent, respectively. The viscosity-average molecular weight (M_η) was determined using the Mark–Houwink equation:

$$[\eta] = K \cdot [M_\eta]^\alpha \tag{2}$$

where K and α is the Mark–Houwink constants. According to the previous study (Li & Xie, 2004), the values of K and α are 5.96×10^{-2} and 0.73, respectively. The dried hydrolysates were dissolved in 0.2 M NaCl at room temperature. Before measurement, all solutions were purified by filtering through a 0.45 μm Millipore filter. All the measurements were carried out in six replicates.

2.4. Periodate oxidation

Sodium metaperiodate solutions were used at a concentration range of 0.0175–0.14 mM in accordance with the standard curve recommended for periodate oxidation measurement. The solutions of hydrolysate (3 mg/mL) and sodium metaperiodate (0.035 mol/L) were added into the reaction vessel, which was then storaged in the dark place for 7 d (Kristiansen, Potthast, & Christensen, 2010). Subsequently, the absorbance was measured at 223 nm using a UV-1100 spectrophotometer (MAPADA, Shanghai, China). The standard curve was obtained: $y = 0.3965x$ ($R^2 = 0.9974$), where x is represented the consumption of sodium periodate (mol), and y is absorption measured by spectrophotometer.

2.5. Rheological measurements

The rheological measurements were carried out using a controlled stress rheometer (AR2000ex, TA, UK) with parallel plate geometry (40 mm, 1 mm gap). The alkali-thermal degraded products were equilibrated to room temperature for 30 min before measurement. Steady viscosity data were collected at shear rates from 0.01 to 300 s^{-1} at a constant temperature of 25 °C (Gaaloul, Corredig, & Turgeon, 2009). The apparent viscosity versus shear rate data was fit by the power law mode.

Small deformation oscillatory test was performed within the linear viscoelastic range controlled the strain of 0.5% which. Frequency sweep tests were performed at four different temperatures with frequency ranging from 0.1 to 100 rad/s. Temperature sweep tests were carried out at constant frequency (0.1 Hz) with heating from 25 to 90 °C by 1 °C/min and cooling back to 25 °C by 2 °C/min. The samples were covered with a thin layer of paraffin oil to prevent moisture loss. Measurements were carried out in triplicate. G' (storage modulus), G'' (loss modulus), and $\tan\delta$ (G''/G') were recorded respectively (Funami et al., 2009).

2.6. Statistical analysis

All the experiments were performed in triplicates and the results were reported as average value and standard deviation. A least significant difference (LSD) test with a confidence interval of 95% was used to compare the means.

3. Results and discussion

3.1. Molecular changes of KGM during the alkaline-thermal process

M_η can be a good indicator reflecting the rigidity of polymer chains. Hereby, the changes of M_η during the hydrolysis process under various temperature and pH conditions were monitored.

At the natural pH (5.6), M_η decreased slightly. The M_η decreased from 1.587×10^6 to 1.567×10^6, 1.236×10^6 to 1.181×10^6, 1.028×10^6 to 8.71×10^5 and 8.54×10^5 to 5.68×10^5 at 25 °C, 50 °C, 65 °C and 80 °C, respectively (Fig. 1). The data in Fig. 1 indicates that the M_η declined substantially with the pH rising, when the pH 9.2 reached a peak rate. At the same time, it suggests high pH accelerates the process of KGM degradation under the same temperature condition.

Temperature is also considered as one of the important factors affecting M_η during alkaline hydrolysis. At higher temperature, the decreasing trend is more obvious. Taking pH 9.2 as an example, after 2 h degradation, M_η decreased from 1.587×10^6 to 1.51×10^6 at 25 °C, while it decreased from 8.54×10^5 to 3.06×10^5 at 80 °C (Fig. 1). Overall, the decreasing of M_η at low temperature (25 and 50 °C) was much less than that at high temperature (65 and 80 °C). These results are similar to the previous studies about alkaline degradation of alginates (Haug et al., 1967). The alkaline degradation reaction is more pronounced under high alkalinity and high temperature condition. The change of M_η as a function of degradation time at higher temperature (65 and 80 °C) exhibited two stages. The cleavages into hydrolyzed products lead to a rapid decrease of M_η in short times followed by a slower rate. In the first stage, the M_η decreased sharply during the first hour of hydrolysis, which might be because the force of reaction does not rely on oxygen, but