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Short communication

Preparation and characterization of konjac glucomannan microcrystals through acid hydrolysis

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ABSTRACT

Konjac glucomannan (KGM) was treated by a facile acid hydrolysis to fabricate KGM microcrystals. At the first day of hydrolysis, KGM microcrystals were formed. With the extension of hydrolysis time, the particle size of KGM microcrystals decreased from 45 μm to 15 μm. In addition, compared with native KGM, the morphological, physicochemical, crystalline, and thermal properties of KGM microcrystals changed significantly. SEM images showed the irregular shapes and rough surfaces of KGM microcrystals as well as the smooth surface of native KGM. FTIR measurements revealed the cleavage of carbonyl groups in KGM microcrystals. XRD curves clearly presented the crystalline structure of KGM microcrystals, and the relative crystallinity increased to approximately 50%. DSC analysis showed that microcrystals had a better thermal stability than native KGM, which could be preferably used as reinforcement in the biocompatible material at high temperature.

1. Introduction

Among natural polysaccharides, konjac glucomannan (KGM) is an inexpensive, naturally renewable, and biodegradable polysaccharide. KGM is a neutral polysaccharide derived from the tuber of *Amorphophallus konjac* and native to Southeast Asia. It is composed of β-(1,4)-linked D-mannose and D-glucose residues in a molar ratio of 1.6:1 (Cescutti, Campa, Delben, & Rizzo, 2002; Q. Xu et al., 2013). Acetyl groups attached to the saccharide units are scattered randomly along the molecule, with an occurrence of approximately 1 per 19 sugar residues at C-6 positions (Katsuraya et al., 2003; Wei, Xu, Jin, & Tian, 2014). KGM is water-soluble giving highly viscous and pseudoplastic solutions. Owing to the unique structure and properties, KGM has been widely used in food and functional applications, such as fat analogue (Jimenez-Colmenero, Cofrades, Herrero, Solas, & Ruiz-Capillas, 2013; J. Li, Wang, Jin, Zhou, & Li, 2014), film-forming (Du, Yang, Ye, & Li, 2013; Leuangsukrerk, Phupoksakul, Tananuwong, Borompichaichartkul, & Janjarasskul, 2014) and controlled release (Guo, Yang, Cui, Lin, & Qu, 2013; Wang, Liu, Shuai, Cui, & Nie, 2014).

In recent years, the preparation and application of polysaccharide crystals have been attracting more interests. Most researches focused on cellulose, chitin and starch (Lin, Huang, & Dufresne, 2012). These polysaccharide crystals could be prepared in the following ways: acid, alkali or enzymatic hydrolysis, regeneration, and mechanical treatment. An enzymatic pretreatment of starch could reduce the acid hydrolysis duration. With a 2 h pretreatment of waxy maize starch, the extent of acid hydrolysis currently reached in 24 and 120 h (5 days) were reached in only 6 and 45 h, respectively (D. LeCorre, Vahanian, Dufresne, & Bras, 2012). As for recrystallization, a supercritical ammonia was used to help the conversion of cellulose I to cellulose III_I (Wada, Nishiyama, & Langan, 2006). As mentioned to physical treatment, ultrasonication could induce cellulose folding, surface erosion, and external fibrillation, together with the shorter average length of nanocrystalline cellulose (96 nm) than that prepared without ultrasonication (150 nm) (W. Li, Wang, & Liu, 2011). Besides, the morphologies of polysaccharide crystal were relative to origins. The crystal shapes of cellulose, chitin and starch were rod-like, whiskers, and platelet-like, respectively (Kargarzadeh et al., 2012; Ifuku et al., 2009; Le Corre, Bras, & Dufresne, 2010).

Recently, intensive exploration on polysaccharide crystals mainly focused originally on their use as a reinforcing nanophase in nanocomposites. Biobased cellulose nanocrystals and cellulose nanofibrils showed strong reinforcing effects on poly(ethylene oxide) (PEO) nanofiber mats (X. Z. Xu et al., 2014). Potato starch nanocrystals were found to serve as an effective reinforcing agent for natural rubber. The tensile strength and modulus of the composites were found to improve tremendously with increasing nanocrystal content. This dramatic increase observed can be attributed to the formation of starch nanocrystal network (Rajisha, Maria, Pothan, Ahmad, & Thomas, 2014). More diverse potential applications of polysaccharide crystals were exploited, such as biomedical materials, biomimetic optical materials, bio-inspired mechanically adaptive materials, permselective nanostructured membranes, template for synthesizing inorganic nanoparticles, polymer electrolytes, emulsion stabilizer and decontamination of organic pollutants (Lin et al., 2012).

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However, reports on the crystal of konjac have not been abundant. Early in 1982 Chanzy found that regardless of recrystallization temperature, mannan II persistently existed in KGM gel (Chanzy, Grosrenaud, Joseleau, Dube, & Marchessault, 1982). Generally, the recrystallization behavior of glucomannans depended on three factors: the temperature of crystallization, the polarity of the crystallization medium, and the chain length of the polysaccharide. High-molecular-weight, low temperature of crystallization, or a polar crystallization medium favored the mannan II polymorph, whereas low-molecular weight, high temperature of crystallization, and a crystallization medium of low polarity yielded the mannan I polymorph. Afterwards, Gidley applied ^{13}C NMR spectroscopy to compare molecular structures within powders, hydrates and gels of KGM (Gidley, McArthur, & Underwood, 1991). In the state of dry powder, the spectra showed the broad signals with only limited resolution. KGM belonged to non-crystalline polysaccharide, and amorphous conformations might be responsible for the breadth of signals. Upon hydration, the spectra owned narrower resonances and increased resolution. It suggested that hydration leads to the adoption of quite well-defined molecular conformations. However, gels of deacetylated KGM showed similar spectra with the hydrate, suggestive of a lack of major conformational differences between solid-like and solution-like segments. Some authors further pointed out that the structure of KGM crystallized in the mannan II polymorphic form, in an orthorhombic unit-cell with a = 9.01 Å, b = 16.73 Å, c (fiber axis) = 10.40 Å, and a probable space group *I222*. The backbone conformation of the chain was a two-fold helix (Yui, Ogawa, & Sarko, 1992).

In this paper, we used a facile method of acid hydrolysis to prepare KGM microcrystals. The structure, crystallinity and thermal stability of KGM crystals obtained at time intervals were characterized in detail. Meanwhile, the morphology was also presented. This investigation provided a theoretical foundation for understanding the structural changes that occurred during the preparation of KGM crystal and facilitated more functional applications.

2. Materials and methods

2.1. Materials

Native KGM was kindly provided by Qiang Sheng Co. Ltd. (Hubei, China). Sulfuric acid (96–98%) and sodium azide were purchased from Sigma-Aldrich. Distilled water was used all along the process.

2.2. Preparation of KGM microcrystals

The preparation of KGM crystal was according to the literature (Wei et al., 2014). KGM (2% wt/wt) was dispersed in previously prepared diluted sulfuric acid (2.8 M). The suspension was kept at 40 °C while shaken at 150 rpm. At time intervals, the suspension was taken out and washed by successive centrifugation in distilled water until the pH of supernatant was constant. Sodium azide was added to the suspension before storage at 4 °C to avoid microbial growth. The hydrolysis yields were calculated as the dry weight of non-solubilized particles as a percentage of initial KGM's dry weight. Measurements were carried out three times for error analysis.

$$\text{Yields}(\%) = \text{weight of KGM at a given time(g)}/\text{weight of initial native KGM(g)}$$

2.3. Light scattering

Particle size measurements were performed at 25 °C with a Mastersizer APA2000 (Malvern, England). The particle diameter was controlled by light scattering. For each measurement, a given volume of the KGM microparticle suspension was injected in 1000 mL distilled water at the concentration of 1%–5%. Measurements were carried out three times for error analysis.

2.4. Fourier transform infrared spectroscopy (FTIR)

Native KGM and KGM microcrystals were grinded together with potassium bromide (weight ratio 1:100) and pressed into disks for scanning with a Nexus 470 spectrometer (Nicolet, USA). Samples were scanned at 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

2.5. X-ray diffraction (XRD)

XRD patterns were obtained for the samples with a D/Max-IIIA diffractometer (Rigaku, Japan) using Ni-filtered Cu Kα radiation (λ = 1.54 Å) at 40 kV and 20 mA. The diffraction angle ranged from 5° to 45° with a step-scan of 0.02° and count time of 2.0 s per step.

Sample crystallinity was determined by plotting the peak baseline on the diffractogram and calculating the area using the software (Jade 5.0). The area above and under the curve corresponded to crystalline domains and amorphous regions, respectively. The ratio of upper area to total area was taken as relative crystallinity: Crystallinity percentage (%) = area under the peaks / total curve area × 100.

2.6. Differential scanning calorimetry (DSC)

The thermal stabilities of samples were done with DSC 204-F1 (Netzsch, Germany) filled with a manual liquid nitrogen cooling system. The amount of sample for each measurement was between 2 and 3 mg. All measurements were heated from 25 °C to 450 °C with a heating rate of 10 °C/min under a nitrogen atmosphere. The flow capacity of nitrogen was 30 mL/min. Two replicates were analyzed for each sample.

2.7. Scanning electron microscopy (SEM)

SEM was performed using a JEOL JSM 6390/LV (Akishima, Japan) at accelerating voltage (10 kV). Native KGM and KGM microcrystals were spread onto the copper grids and coated with gold for observation.

3. Results and discussion

3.1. Acid hydrolysis

Native KGM granule consisted of amorphous and crystalline regions, and the hydrolysis of KGM contained a "peeling process" of amorphous parts from microparticles. The kinetics of the mass yield and particle size were presented in Fig. 1. After one day of hydrolysis, the yield decreased from 100% to 45% and the corresponding particle size dropped from 150 μm to 45 μm. (The particle size of initial KGM granule was obtained by SEM). This fast hydrolysis step presumably was due to the

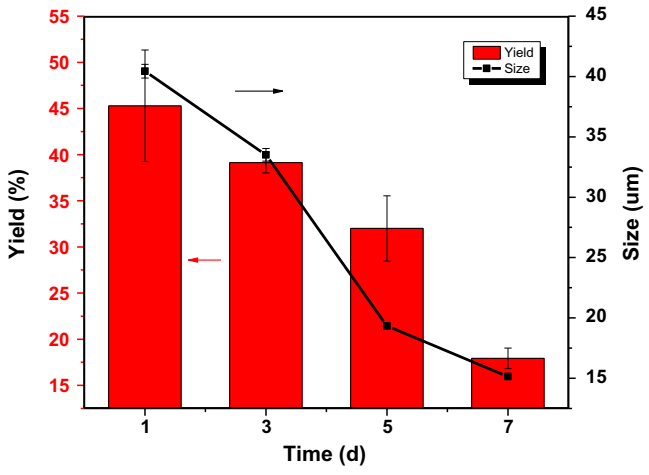

Fig. 1. Kinetics of the mass yield and particle size of KGM by acid hydrolysis.