



Carboxymethylated glucomannan as paper strengthening agent



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ABSTRACT

Strength additives play an important role in allowing the papermaking industry to achieve its objectives. In this study, a new kind of paper strengthening agent based on glucomannan was developed by treating it with sodium chloroacetate under alkaline conditions, and the effects on paper properties were evaluated. Results indicated that carboxymethylated glucomannan could significantly improve the paper properties. Compared to the untreated paper, the density, burst index, tensile index, and folding endurance were increased by 15.2%, 22.8%, 34.6%, 179.0%, respectively, when 0.9% carboxymethylated glucomannan was used. Polyamide-epichlorohydrin (PAE) was used to improve the wet strength of the paper. When 0.6% PAE and 0.6% carboxymethylated glucomannan were used, the burst index, dry tensile index, wet tensile index of paper were increased by 14.1%, 25%, 34.3%, respectively, as compared to that of the control, while the folding endurance decreased slightly. In addition, dry tensile index and wet tensile index were increased with increasing the carboxymethylation time of glucomannan. The results demonstrated that PAE and carboxymethylated glucomannan displayed a synergistic effect. SEM analysis illustrated that paper strengthening agent could increase the combination of fibers in paper.

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1. Introduction

With increasing demand for paper and reducing availability of traditional raw materials for paper, a lot of straw and recycled paper are currently being used in paper making, which results in the degradation of paper properties. To solve this problem, paper strengthening agents have been developed (Clark, 1978; Helle, 1963; Hubbe, 2006). At present, the most widely used paper strengthening agents are polyacrylamides, polysaccharides, starch and fibers (Bai, Hu, & Xu, 2012; Lee, Lee, Youn, & Xiang, 2010; Oksanen, Buchert, & Viikari, 1997; Sehaqui, Zhou, & Berglund, 2013; Suurnäkki, Oksanen, Kettunen, & Buchert, 2003; Vega et al., 2013; Wang, Song, & Qian, 2012). Natural polysaccharides cannot be used directly due to their poor solubility in water. Some chemically modifications are often needed (Fatehi, Qian, Kititerakun, Rirksomboon, & Xiao, 2009; Howard & Jowsey, 1989; Ren, Peng, & Sun, 2009; Song & Hubbe, 2014a, 2014b; Sun, Fang, Tomkinson, & Jones, 1999). Among various modification methods, carboxymethylation is an excellent method of polysaccharide modification, which aims to change hydroxyl group of a polysaccharide into carboxymethyl form to increase polysaccharide's solubility in water (Chen, Wan, Dong, & Ma, 2013; Song & Hubbe, 2014a, 2014b).

Konjac Glucomannan (KGM) is a non-ionic water-soluble polysaccharide polymer. It is composed of D-glucose and D-mannose (molecular ratio 1:1.6) by β -(1–4) bond polymerization. About 3280 sugar residues in the main chain have a branched chain, in which there are several to several tens of sugar residues. It is linked by β -(1–3) at position C-3 of the sugar residue in the main chain, with an acetyl ester bond approximately every 19 saccharide residues (Sun, Wu, Zhan, & Huang, 1998). KGM's molecular weight is 200,000–2,000,000 Daltons. The maximum viscosity of industrial production is 20,000 MPa s, which is one of the highest viscosity gels in water-soluble edible plants. The content of Konjac Glucomannan is about 50% in *Amorphallu Konjac*. KGM has a high physiological activity, and it is widely used in food additives, films and drug delivery systems (Bo, Muschin, Kanamoto, Nakashima, & Yoshida, 2013; Cheng, Ding, Hua, & Zhao, 2014; Liu et al., 2013; Zhang, Chen, & Yang, 2014).

A benefit of using glucomannan as a starting material for this work is its high content in *Amorphophallus konjac*, which is widely available. Konjac flour can be obtained after removing starch, alkaloids, and other impurities from the konjac tuber, and refining into white particles. Though a detailed cost of glucomannan is not calculated in this work, the authors wanted to find out whether carboxymethylation of glucomannan could improve the paper strength as other dry-strength agent.

In the present study, konjac glucomannan was used to develop paper strengthening agent by reacting with sodium chloroacetate

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under alkaline conditions for 25, 40, 55, 70 min, respectively, and their effects on the paper properties are comprehensively evaluated.

2. Experiment

2.1. Materials

Amorphophallus konjac flour was obtained from Henan Zhongxin Chemical Company, and aspen kraft pulp was provided by Hunan Yueyang Paper Group. The pulping conditions were sulfidity 21.8%, active alkali 15.2%, maximum temperature 168 °C, heating up time 1.8–2 h, yield 45%, and beating degree 40° SR.

2.2. Preparation of carboxymethylated glucomannan

7.17 g glucomannan (dry basis), 120 mL 80% ethanol (v/v) and 0.64 g of sodium hydroxide were added into a 250 mL three-necked flask, which was equipped with an impeller stirring apparatus and a reflux condensation device. The mixture were stirred at room temperature for 20 min, 4.75 g of sodium chloroacetate and 0.96 g of sodium hydroxide were put into the flask, and then the temperature rose to 65 °C. The carboxymethylation reaction conditions were held for 25, 40, 55, 70 min, respectively. After the reaction, diluted acetic acid was used to neutralize the pH to 7, and then the mixture was filtered by filter paper. The solids were washed with 50 mL 65% (v/v) ethanol and four times with 50 mL 100% ethanol, then the sample was dried at room temperature for further use.

2.3. Polyamide-epichlorohydrin (PAE) preparation

41.0 g diethylenetriamine, 7.5 g H₂O, and 0.5 g *p*-toluenesulfonic acid were put into a three-necked flask, which was equipped with an impeller stirring apparatus and a steam flow device. 55.0 g of adipic acid was added into the flask after stirring, and the temperature of the mixture was automatically raised to 125 °C. The water was distilled off, and the mixture was heated to 150–160 °C and reacted for 3 h. When the distilled liquid was about 17.5 g, the heating was stopped, the temperature was decreased to less than 100 °C, and 80 g of water was put into the flask and stirred it to uniformity. Then 200 g water was added into the flask. 40 g of epichlorohydrin was added under stirring, with the temperature controlled at 70 °C. The reaction was carried out for 1–2 h, during which time the viscosity increased to 30–150 MPa s. The pH was adjusted to 3.0–5.0 with acetic acid, giving the PAE sample.

2.4. The degree of substitution

The degree of substitution (DS) was determined by acidimetric titration (Ren et al., 2009).

2.5. Carboxyl content

Carboxyl content was determined by the conduction metric titration technique (Katz, Beatson, & Scallan, 1984).

2.6. Pulping and papermaking

Standard kraft pulp handsheets (1.88 g o.d.) were prepared and tested in accordance with the China GB standard methods.

2.7. Infrared spectroscopic analysis

A certain amount of solid KBr and the carboxymethylated glucomannan sample were oven-dried and ground into powder, and then the powder was pressed into a tablet for FTIR analysis. The

absorbance between 4000 cm⁻¹ and 400 cm⁻¹ was obtained with a Spectrum-100D instrument from Perkin Elmer (USA).

2.8. NMR spectra analysis

¹³C NMR spectra were recorded on a Bruker spectrometer at 100.6 MHz. The sample (20 mg) was dissolved in 0.5 mL of D₂O (99.8% D). The ¹³C NMR spectra were recorded at 25 °C (298 K) after 30,000 scans. A 30 pulse flipping angle, a 9.2 μs pulse width, a 1.89 s delay time, and a 1.36 s AQ between scans were used.

2.9. Elemental analysis

The carbon, hydrogen, and nitrogen contents were analyzed by using an Aria EL III instrument. Oxygen content was obtained from the total elements, excluding carbon, hydrogen, and nitrogen.

2.10. Molecular weight

Molecular weight was determined by the gel permeation chromatography by using the Agilent PL aquagel–OH mix column (300 mm × 7.5 mm, Polymer Laboratories, Ltd.) at a flow rate of 0.5 mL min⁻¹ and a column temperature of 30 °C. Data were calibrated with pullulan polysaccharide standards (M_w = 738, 12,200, 100,000, and 1,600,000 Daltons, Polymer Laboratories, Ltd). The glucomannan was dissolved in 0.02 M NaCl in 0.005 M sodium phosphate buffer at pH 7.5 as the eluent.

2.11. Scanning electron microscopy (SEM)

The morphology of samples was analyzed by using a S-3000N SEM device after gold sputtering. The images of handsheet surface, fracture surfaces by tensile force and cut section of paper were collected.

3. Results and discussion

3.1. The solubility of carboxymethylated glucomannan

The particles appearance of raw glucomannan was white and fine due to grinding in the mill. However, the particles of carboxymethylated glucomannan were significantly larger and yellow due to the aggregation of small particles and oxidation in the course of filtration and drying process. The solubility of raw glucomannan in distilled water at room temperature was very low, as only a small parts of particles were dissolved, and most parts of particles were deposited at the bottom of the flask. However, the solubility of glucomannan was obviously increased after the carboxymethylation, and most particles were dissolved in distilled water at room temperature. This observed result indicated that carboxymethylation could significantly improve the glucomannan's solubility.

3.2. Effects of carboxymethylation time on the substitution degree

The effects of carboxymethylation time on the substitution degree were also investigated. As shown in Table 1, it was found that the substitution degree increased with increasing of carboxymethylation time, indicating that hydroxyl groups were gradually converted into carboxymethyl form during the carboxymethylation process. Meanwhile, the molecular weight of glucomannan decreased after carboxymethylation treatment. However, the decrease of the molecular weight was not evident when the carboxymethylation time was increased from 40 min to 70 min.

Table 1 also depicts the elemental contents of original glucomannan and carboxymethylated glucomannan. As expected, with

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