Carboxymethylated glucomannan as paper strengthening agent

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A B S T R A C T

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 & Jowsay, 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 α-glucose and β-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 Amorphallus konjac. KGM has a high physiological activity, and it is widely used in food additives, films and drug delivery systems (Bo, Muschin, Kamamoto, 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 Amorphallus 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
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 Yuyang 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 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 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

^{13}C 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 ^{13}C 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 (Mw = 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
the extension of carboxymethylation time, the carbon, hydrogen, and nitrogen content was decreased, while the oxygen content was increased (sodium was not detected in the samples, it will cause to some uncertainty of oxygen content). The results further confirmed that hydroxyl groups in glucomannan had been converted into carboxymethyl groups.

3.3. FTIR spectra

Fig. 1 shows the Fourier transform infrared (FTIR) spectroscopy of glucomannan and carboxymethylated glucomannan. As shown, the absorption peak at 3436 cm\(^{-1}\) is due to \(\text{OH}\) stretching vibration, and the absorption peak at 2925 cm\(^{-1}\) arises from C–H stretching vibration. The absorption at 1631 cm\(^{-1}\) is attributed to the C=O asymmetric stretching vibration in polysaccharides and H\(_2\)O in the sample, and the signal at 1384 cm\(^{-1}\) is originated from C–H vibration. The absorption peak at 1114 cm\(^{-1}\) is ascribed to C–O absorption. After carboxymethylation, the peaks at 1631, 1384 and 1114 cm\(^{-1}\) (signals from carboxymethylated glucomannan) become slightly stronger, implying that the carboxymethylation occurred. In addition, the absorption peaks at 3436 cm\(^{-1}\) became intense, indicating that hydroxyl groups increased in modified glucomannan, which is probably due to hydrolysis of glucomannan during carboxymethylation process.

3.4. NMR spectra

The \(^{13}\text{C}\) NMR spectra of control and carboxymethylated glucomannan were also recorded and are shown in Fig. 2. The resonance signals of C-6 in native glucomannan are detected at 66.0–67.0 ppm (Seung et al., 2009). As can be observed from Fig. 2, it is interesting to note that the signal of the C-6 in carboxymethylated glucomannan is nearly disappeared. Meanwhile, a new signal appeared at 178.0 ppm, which is attributed to the new appeared carboxyl groups in carboxymethylated glucomannan (Yanna et al., 2014; Yi et al., 2014). Therefore, based on the enhanced signal at 178.0 ppm and disappeared signal at 66.0 ppm, it is assumed that the carboxymethylation of glucomannan had been successfully achieved.

3.5. Effect of the dosage of carboxymethylated glucomannan on the paper properties

Table 2 exhibits the effect of dosage of carboxymethylated glucomannan on the paper properties. Compared with the control sample, with the increase of dosage of carboxymethylated

Table 2

<table>
<thead>
<tr>
<th>Dosage of carboxymethylated glucomannan (%)</th>
<th>Density (g/cm(^3))</th>
<th>Tensile index (Nm/g)</th>
<th>Tear index (Nm/g)</th>
<th>Burst index (kPa m(^2)/g)</th>
<th>Folding endurance (double folds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.46</td>
<td>58.7</td>
<td>15.6</td>
<td>5.78</td>
<td>357</td>
</tr>
<tr>
<td>0.3</td>
<td>0.48</td>
<td>67.5</td>
<td>13.6</td>
<td>6.20</td>
<td>435</td>
</tr>
<tr>
<td>0.6</td>
<td>0.49</td>
<td>68.2</td>
<td>12.0</td>
<td>6.30</td>
<td>457</td>
</tr>
<tr>
<td>0.9</td>
<td>0.53</td>
<td>79.0</td>
<td>11.2</td>
<td>7.10</td>
<td>996</td>
</tr>
<tr>
<td>1.2</td>
<td>0.46</td>
<td>66.1</td>
<td>11.5</td>
<td>7.04</td>
<td>586</td>
</tr>
<tr>
<td>1.5</td>
<td>0.45</td>
<td>65.2</td>
<td>12.2</td>
<td>6.57</td>
<td>562</td>
</tr>
</tbody>
</table>

Notes: Carboxymethylation time is 40 min, the samples were prepared with 0.5% Al\(_2\)(SO\(_4\))\(_3\)·18H\(_2\)O on a dry fiber basis. After alum addition the pH was adjusted to 5.
glucomannan, the density, burst index, tensile index, and folding endurance of the paper firstly increased then decreased, and finally reached the maximum value when the dosage was 0.9%, in which the corresponding index increased by 15.2%, 22.8%, 34.6%, 179.0%, respectively. However, the tear index exhibited an opposite trend. This is because that carboxymethylated glucomannan can increase the bonding force between the fibers, which could increase the paper properties (Song & Hubbe, 2014a). An excessive dosage of carboxymethylated glucomannan provides abundant negative surface charges to the system; thus the amount of added aluminum sulfate was insufficient to fully integrate the carboxymethylated glucomannan, and the binding force between carboxymethylated glucomannan and fiber became poor due to the charge repulsion, which will result in the degradation of paper properties.

3.6. Effects of PAE and carboxymethylated glucomannan on the paper properties

Table 3 shows the effects of PAE and carboxymethylated glucomannan on the paper properties. As is shown, after adding 0.6% PAE, with increasing amount of carboxymethylated glucomannan, wet strength of paper was significantly increased. When 0.6% carboxymethylated glucomannan was used, the burst index, dry tensile index, wet tensile index of handsheets were increased by 14.1%, 25.0%, 34.3%, respectively, as compared to the control. By contrast, the folding endurance decreased slightly. All above results indicated that the mixture of PAE and carboxymethylated glucomannan have a better effect on the burst index, dry tensile index, and wet tensile index of paper.

3.7. Effects of carboxymethylation time on the paper properties

When adding 0.6% PAE and 0.6% carboxymethylated glucomannan, the carboxymethylation time of glucomannan also affected the paper properties. As shown in Table 4, when the carboxymethylation time of glucomannan were increased from 25 min to 70 min, the burst index and tear index were slightly changed; however, the dry tensile index and wet tensile index increased significantly. When the carboxymethylation time was 40 min, the dry tensile index was 76.3 Nm/g and the wet tensile index was 13.6 Nm/g. This represents increased by 13.4% and 19.3%, respectively, as compared with the 25 min carboxymethylation. Folding endurance also increased, and the maximum was 786 double folds, increased by 9.3% as compared with the 25 min conditions.

Table 3

<table>
<thead>
<tr>
<th>Dosage of carboxymethylated glucomannan (%)</th>
<th>Density (g/cm²)</th>
<th>Burst index (kPa·m²/g)</th>
<th>Dry tensile index (Nm/g)</th>
<th>Wet tensile index (Nm/g)</th>
<th>Tearing index (Nm/g)</th>
<th>Folding endurance (double folds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.47</td>
<td>6.50</td>
<td>61.5</td>
<td>10.8</td>
<td>11.7</td>
<td>729</td>
</tr>
<tr>
<td>0.2</td>
<td>0.44</td>
<td>6.81</td>
<td>62.3</td>
<td>10.6</td>
<td>11.7</td>
<td>723</td>
</tr>
<tr>
<td>0.4</td>
<td>0.46</td>
<td>7.09</td>
<td>74.2</td>
<td>12.5</td>
<td>10.4</td>
<td>724</td>
</tr>
<tr>
<td>0.6</td>
<td>0.46</td>
<td>7.35</td>
<td>76.9</td>
<td>14.5</td>
<td>10.3</td>
<td>723</td>
</tr>
<tr>
<td>0.8</td>
<td>0.48</td>
<td>7.42</td>
<td>72.2</td>
<td>14.1</td>
<td>9.5</td>
<td>618</td>
</tr>
</tbody>
</table>

Notes: 0.6% of PAE was added into the pulp under stirring, then a certain amount of carboxymethylated glucomannan (Carboxymethylation time is 40 min) was used, the handsheets were prepared after stirring for 10 min.
Table 4
Effect of Carboxymethylated time on paper properties.

<table>
<thead>
<tr>
<th>Carboxymethylated time (min)</th>
<th>Density (g/cm³)</th>
<th>Burst index (kPa m²/g)</th>
<th>Dry tensile index (Nm/g)</th>
<th>Wet tensile index (Nm/g)</th>
<th>Tearing index (Nm/g)</th>
<th>Folding strength (times)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.44</td>
<td>7.49</td>
<td>67.3</td>
<td>11.4</td>
<td>10.7</td>
<td>719</td>
</tr>
<tr>
<td>40</td>
<td>0.46</td>
<td>7.39</td>
<td>76.3</td>
<td>13.6</td>
<td>11.1</td>
<td>786</td>
</tr>
<tr>
<td>55</td>
<td>0.48</td>
<td>7.35</td>
<td>76.9</td>
<td>14.5</td>
<td>10.4</td>
<td>723</td>
</tr>
<tr>
<td>70</td>
<td>0.48</td>
<td>7.35</td>
<td>75.8</td>
<td>14.0</td>
<td>10.2</td>
<td>618</td>
</tr>
</tbody>
</table>

Notes: 0.6% of PAE was added into the pulp under stirring, then 0.6% carboxymethylated glucomannan was used, the handsheets were prepared after stirring for 10 min.

Table 5
Comparison of three paper strengthening agents.

<table>
<thead>
<tr>
<th>Dosage of PAE (%)</th>
<th>Dosage of carboxymethylated glucomannan (%)</th>
<th>Density (g/cm³)</th>
<th>Burst index (kPa m²/g)</th>
<th>Dry tensile index (Nm/g)</th>
<th>Wet tensile index (Nm/g)</th>
<th>Tearing index (Nm/g)</th>
<th>Folding strength (times)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.46</td>
<td>5.78</td>
<td>58.7</td>
<td>–</td>
<td>15.6</td>
<td>357</td>
</tr>
<tr>
<td>0</td>
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<td>0.49</td>
<td>6.30</td>
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<td>76.9</td>
<td>14.5</td>
<td>10.3</td>
<td>723</td>
</tr>
</tbody>
</table>

3.8. Comparison of three paper strengthening agent

Table 5 shows the comparison of three paper strengthening agents. Obviously, the paper properties were significantly increased when the carboxymethylated glucomannan was used as strengthening agent. The properties of paper with 0.6% carboxymethylated glucomannan were similar to paper with 0.6% PAE. However, the mixture of 0.6% PAE and 0.6% carboxymethylated glucomannan could significantly increase paper’s tensile index, burst index and wet tensile index. This is because PAE has positive charge and the fibers have negatively charge, PAE is easy to combine with fiber, then they form a cross-linked structure.
thus improving paper’s dry and wet strength. Then glucomannan becomes clad on the outside of PAE and fiber to form a protective film, which delays the water’s destruction on the combination between PAE and fibers, thus improving wet and dry strength of paper (Awada, Montplaisir, & Daneault, 2014).

3.9. SEM analysis

Fig 3 presents the SEM images of handsheet fracture. As shown, the fibers were untouched when the original paper was broken by tensile force only because the bonds between the fibers were damaged and the fibers were pulled out. However, most fibers of paper enhanced with CMG or CMG and PAE were broken, which indicated that CMG or CMG and PAE could improve the bonding strength between the fibers.

Fig. 3 also displays the SEM cross-section images of handsheets. As shown, the cross-section of original paper was thick, and fiber combination was loose. The cross-section of paper with CMG or CMG and PAE was thin. In short, this indicated that paper strengthening agent could improve the bonding between the fibers.

Fig. 3 gives the SEM surface images of handsheet. As shown, there were more pores in the surface of the original paper than that of the paper treated with CMG or CMG and PAE. This is because that the inter-fiber bonding was increased by paper strengthening agent, which is in agreement with the increased paper density after addition of paper strengthening agent.

4. Conclusions

In conclusion, the present study demonstrated that carboxymethylated glucomannan could improve the paper properties. After adding 0.9% carboxymethylated glucomannan, the density, burst index, tensile index, folding endurance of paper were significantly increased. Polyamide-epichlorohydrin (PAE) could improve the wet strength of paper. When 0.6% PAE and 0.6% carboxymethylated glucomannan were used synergistically, 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 was slightly decreased. In addition, dry tensile index and wet tensile index were increased with increasing the carboxymethylation time of glucomannan. When the carboxymethylation time was 40 min, they were increased by 13.4% and 19.3%, respectively, as compared with that of the 25 min conditions. The results indicated that PAE and carboxymethylated glucomannan had a synergistic effect. SEM analysis showed that paper strengthening agent could increase the combination of fibers in paper.

Acknowledgement

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