

Oxidized Konjac Glucomannan as a Paper Strength Agent

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A paper strength agent is an important type of chemical additive used in the papermaking industry. In this work some new paper strengthening agent samples were obtained by treating konjac glucomannan with hydrogen peroxide under acidic conditions, and their effects on paper properties were studied. Results showed that oxidized konjac glucomannan (OKG) can improve the paper properties effectively. When 1% oxidized glucomannan (oxidation 60 min, 35 °C) was added, the burst index, tensile index, and folding endurance were increased by 7.0%, 16.9%, and 102.3%, respectively, compared to the control. With increasing of oxidation time, the paper strength increased first and then decreased, reaching the maximum in 60 min. In addition, OKG can improve the properties of recycled paper more significantly. When the pH of paper making system was 7, the tensile index, burst index, and folding endurance of the recycled paper were increased by 22.2%, 19.9%, 59.9%, respectively, compared to the control. SEM analysis showed that paper strengthening agent resulted in a more contiguous junction between the fibers in paper.

Keywords: Oxidation; Glucomannan; Paper properties; Paper strengthening agent

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INTRODUCTION

With an increase in demand for paper quality and the shortage of wood materials, a great deal of straw and recycled fibers are being used in the papermaking industry, and this has resulted in the degradation of paper properties. To solve this problem, a promising method is to use paper strengthening agents (Helle 1963; Clark 1978; Hubbe 2006). At present, the most widely used paper strengthening agents are polyacrylamides, polysaccharides such as starch, and fibers (Howard and Jowsey 1989; Oksanen *et al.* 1997; Fatehi *et al.* 2009; Ren *et al.* 2009; Lee *et al.* 2010; Bai *et al.* 2012; Ashori *et al.* 2013). Some natural polysaccharides cannot be used directly due to their poor solubility in water. Chemical modifications are often needed (Khorasani *et al.* 2013; Sehaqui *et al.* 2013; Vega *et al.* 2013; Song and Hubbe 2014a,b). Oxidation is a promising means for polysaccharide modification, which aims to change hydroxyl groups of a polysaccharide into their corresponding aldehyde, ketone group, or carboxyl forms so as to increase the polysaccharide's solubility in water (Seung *et al.* 2009; Song and Hubbe 2014c).

Konjac, which is a plant widely found in China, is well known for its edible root. It is an Araceae herbaceous perennial plant, has a very wide range in use, and raw konjacs have a little poison. There are about 100 species of konjac in the world, and China has more than 30 species. After nearly 10 years of research, the production of konjac purified powder has been achieved, and its major usage has been in the food industry. Research has

indicated multiple potential applications for konjac, such as treating lipid hypoglycemic cancer. Amorphophallus konjac contains 50% of glucomannan, a high molecular weight of nonionic glucomannan mainly composed of mannan and glucose connected by beta 1,4 glycosidic linkages [mole ratio 1.6:(1 to 4)]. There is a small amount of beta 1,3 linkages in the structure, and the main chain is composed of glucomannan. On average every 9 to 19 monosaccharide units there is an acetyl group, which helps to dissolve glucomannan. Glucomannan's molecular weight is 200,000 to 2,000,000; thus it can be regarded as a high molecular compound. It exhibits good water absorption, and its volume can expand 80 to 100 times after absorbing water. Thus, it is easy to digest and absorb after eating (Vipul and Stephen 1997). Glucomannan can adsorb cholesterol and bile acid; thus it can have a certain effect on lowering blood pressure and cardiovascular disease. Konjac contains soluble dietary fiber, which is very effective in curbing the rise in blood sugar after meals, and it also can reduce the burden on the pancreas islet; for this reason konjac purified powder and its products are the ideal hypoglycemic food for diabetic patients (Zhang 2014). In this paper, konjac glucomannan was used to produce a paper strengthening agent by its reaction with hydrogen peroxide under acidic conditions for 45, 60, 75, and 90 min, respectively, and their effects on the paper properties were evaluated.

EXPERIMENTAL

Materials

Amorphophallus konjac flour (98% of konjac glucomannan) 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 g/L, maximum temperature 168 °C, heating up time 1.8 to 2 h, yield 45%, and beating degree 40 ° SR.

Methods

Preparation of oxidized konjac glucomannan

The oxidizing agent of this experiment was hydrogen peroxide. Batches were prepared with 5.6 g of konjac glucomannan (dry basis), and 145 mL of water. A certain amount of 30% hydrogen peroxide (V/V) relative to the konjac glucomannan and 0.045 g of FeSO₄ were added into a 500 mL conical flask. The concentration of hydrogen peroxide was 0.4%, 0.6%, 0.8%, or 1.0% in the reaction liquid, and the reactions' temperature was 30 °C, 35 °C, 40 °C, or 45 °C. The oxidized reaction timing was 45, 60, 75, or 90 min, respectively. The pH value of the whole process of reaction was about 5, controlled with sodium hydroxide solution and dilute hydrochloric acid solution. After the reaction, the samples were washed with 50 mL 100% ethanol four times. Then the samples were dried at room temperature.

Pulping and papermaking

In accordance with the China GB standard methods, 1.88 g (o.d.) kraft pulp handsheets were made, and the properties were tested. Handsheets having a mass of 1.88 g were immersed in water at room temperature for a night, then were disintegrated into pulp and made into paper again without any further chemical addition, and the properties were tested.

Infrared spectroscopic analysis

A certain amount of solid KBr and the oxidized konjac 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 PerkinElmer (USA).

Elemental analysis

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

Scanning electron microscopy (SEM)

The samples were analyzed using the S-3000N type of SEM after gold sputtering. The images of handsheet surface, fracture section by tensile force and cut section of paper were obtained.

RESULTS AND DISCUSSION**Elemental Analysis**

Table 1 depicts the elemental contents of original konjac glucomannan and oxidized konjac glucomannan. As is shown, with increasing of the concentration of hydrogen peroxide, the carbon and oxygen contents remained almost unchanged, and the nitrogen content decreased, while the hydrogen content increased. This possibly indicated that polysaccharide molecules chain was broken and that new hydroxyl groups were generated in the oxidation process.

Table 1. Elemental Analysis of Original Konjac Glucomannan and Oxidized Konjac Glucomannan

	N (%)	C (%)	H (%)	O (%)
Original konjac glucomannan	1.25	38.99	5.58	54.18
Oxidized konjac glucomannan (60 min, H ₂ O ₂ concentration 0.4%)	1.00	38.79	6.26	53.95
Oxidized konjac glucomannan (60 min, H ₂ O ₂ concentration 0.8%)	0.97	38.85	6.33	53.85

Notes: The standard deviation is <5%

FT-IR Spectra

The FT-IR spectra of original konjac glucomannan and oxidized konjac glucomannan are illustrated in Fig. 1. As can be seen, they exhibited almost similar spectroscopic patterns, implying the small amount of structural change. An intense peak at 3445 cm^{-1} originated from the -OH stretching vibrations, and the peak at 1632 cm^{-1} corresponds to the C=O stretching vibrations. Compared with original konjac glucomannan, the OKG's peak value of about 1632 cm^{-1} to 3445 cm^{-1} had diminished; this indicated that new hydroxyl groups had been generated. The band at 1735 cm^{-1} is assigned to ester (COOR), whereas the absorption peak at 1725 cm^{-1} and 1715 cm^{-1} are attributed to aldehydes and ketones. The weak peak at 1713 cm^{-1} is ascribed to carboxyl groups (Kemp 1975). Based on the results it could be concluded that the oxidation was weak.

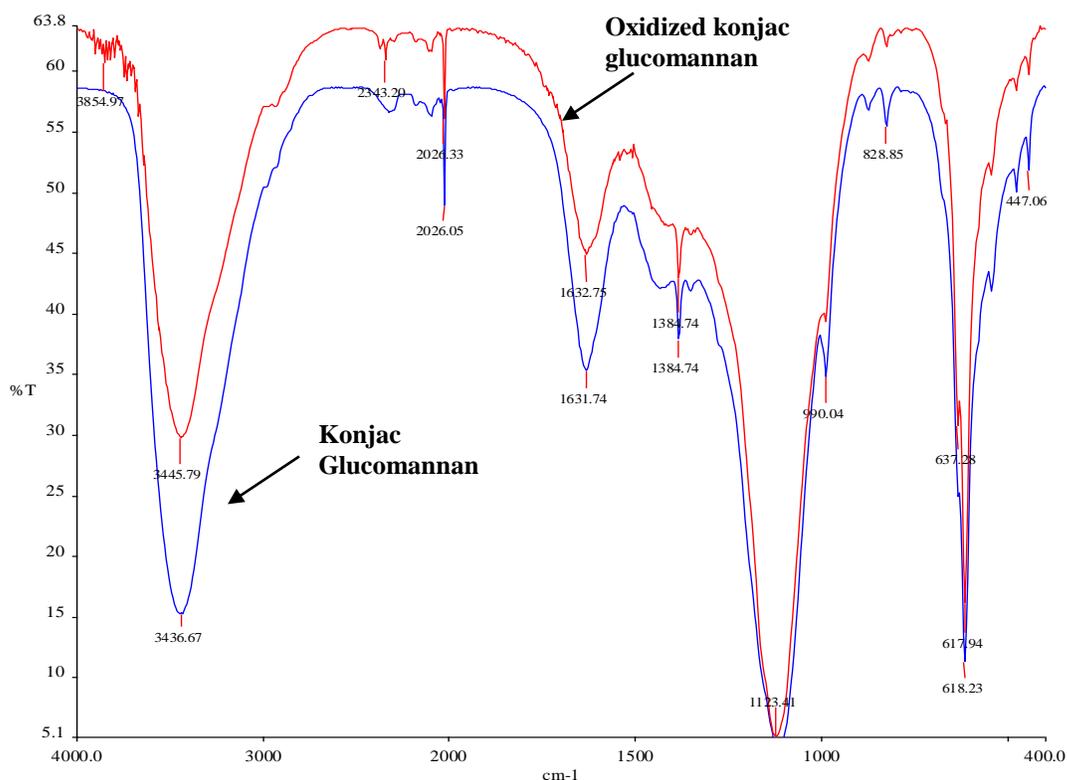


Fig. 1. FTIR spectra of the original konjac glucomannan (blue) and oxidized konjac glucomannan (red)

Effects of Concentration of Hydrogen Peroxide on Paper Properties

Table 2 exhibits the effect of concentration of hydrogen peroxide on paper properties. As is shown, with increasing of concentration of hydrogen peroxide, the density and tear index did not change obviously. The tensile index, burst index, and folding endurance of the paper first increased and then either remained about the same or decreased. When the dosage was 0.8 %, the tensile index, burst index, and folding endurance of the paper increased by 6.0%, 8.8%, 51.3%, respectively, compared with the control.

Table 2. Effects of Concentration of Hydrogen Peroxide on Paper Properties

H ₂ O ₂ concentration (%)	Density (g/cm ³)	Tensile index (N·m/g)	Tear index (N·m/g)	Burst index (KPa·m ² /g)	Folding endurance (double folds)
Control	0.60	98.72	22.62	7.28	335
0.4	0.58	99.51	22.00	7.43	436
0.6	0.59	103.71	21.71	7.53	453
0.8	0.57	104.63	21.10	7.92	507
1.0	0.59	104.22	21.62	7.85	489

Note: Oxidation time is 60 minutes at 40 °C, the samples were prepared with 1% OKG and 0.5% Al₂(SO₄)₃·18H₂O on a dry fiber basis. After alum addition the pH was adjusted to 5. The standard deviation is <5%

Effect of OKG's Oxidation Time on Paper Properties

Table 3 presents the effects of OKG's oxidation time on the paper properties. As is shown, with an increase in oxidized time, the change of density and tear index of the paper were not changed obviously. The tensile index and burst index of the paper increased but did not change significantly. However, the folding endurance of the paper was enhanced obviously, first increasing, then decreasing, and finally reaching a maximum value when the time was 60 min. At that point the folding endurance of the paper was increased by 51.3% compared with the control.

Table 3. Effects of OKG's Oxidation Time on Paper Properties

Oxidation time (min)	Density (g/cm ³)	Tensile index (N·m/g)	Tear index (N·m/g)	Burst index (KPa·m ² /g)	Folding endurance (double folds)
0	0.60	98.72	22.62	7.28	335
45	0.60	104.30	21.71	7.68	407
60	0.57	104.62	21.11	7.92	507
75	0.56	103.00	22.30	7.58	398
90	0.59	102.71	22.31	7.44	371

Note: Oxidation temperature is 40 °C, concentration of hydrogen peroxide is 0.8%. The handsheets were prepared with 1% OKG and 0.5% Al₂(SO₄)₃·18H₂O on a dry fiber basis. After alum addition the pH was adjusted to 5. The standard deviation is < 5%

Effects of OKG's Oxidation Temperature on Paper Properties

Table 4 lists the effects of OKG's oxidation temperature on the paper properties. As is shown, compared with the control sample, with increasing of reaction temperature, the density and tear index did not change obviously. The tensile index, burst index, and folding endurance of the paper firstly increased then decreased. The best oxidation temperature was 35 °C, at which the tensile index, burst index, and folding endurance of the paper were increased by 7.0%, 16.9%, and 102.3%, respectively compared with the control sample.

Table 4. Effects of OKG's Oxidation Temperature on Paper Properties

Reaction temperature (°C)	Density (g/cm ⁻³)	Tensile index (N·m/g)	Tear index (N·m/g)	Burst index (KPa·m ² /g)	Folding endurance (double folds)
Control	0.60	98.70	22.62	7.28	335
30	0.58	105.41	21.41	8.19	423
35	0.60	105.62	21.93	8.51	698
40	0.57	104.61	21.10	7.92	507
45	0.61	101.50	21.52	8.41	613

Note: Oxidation time is 60 min; concentration of hydrogen peroxide is 0.8%. The handsheets were prepared with 1% OKG and 0.5% Al₂(SO₄)₃·18H₂O on a dry fiber basis. After alum addition the pH was adjusted to 5.

With increasing of concentration of hydrogen peroxide, oxidation time, or oxidation temperature, the oxidation reaction was stronger. Hence, more aldehydes,

ketones, and carboxyl groups would be produced, leading to improved paper properties. However, at the same time, the polysaccharide molecular chains were broken. Taking everything into account, the best conditions for preparation of OKG can be judged from Tables 2, 3, and 4.

Effects of the pH of Papermaking on Paper Properties

Table 5 shows the effects of the pH of papermaking on paper properties. As is shown, with an increase of pH, compared with the control sample, the density and tear index did not change obviously. The tensile index, burst index, and folding endurance of the paper first increased then decreased. A pH value of 5 appeared to give the best combination of results. This is attributed to the Al^{3+} , which is the dominant form in solution at pH of 4 and 5. Al^{3+} is a highly cationic ion that can tie any dissociated anion charge such as carboxyl groups or aldehyde group to form stable complexes, these stable complexes can contact with the surfaces of fines and fibers, which will improve bond strength between the fibers.

Table 5. Effects of $Al_2(SO_4)_3$ Dosage on Paper Properties

pH	Density (g/cm ³)	Tensile index (N·m/g)	Tear index (N·m/g)	Burst index (KPa·m ² /g)	Folding endurance (double folds)
The control	0.60	98.72	22.61	7.28	335
5	0.57	104.60	21.11	7.92	507
6	0.60	103.93	22.00	7.72	472
7	0.60	101.72	21.81	7.68	463
8	0.61	100.60	23.00	7.51	451

Note: OKG's oxidation time is 60 min, oxidation temperature is 40 °C, concentration of hydrogen peroxide is 0.8%. The samples were prepared with 1% OKG and 0.5% $Al_2(SO_4)_3 \cdot 18H_2O$ on a dry fiber basis. After alum addition the pH was adjusted to 5,6,7,8. The standard deviation was < 5%.

Effects of OKG on Properties of Recycled Paper

Table 6 presents the effects of OKG on properties of recycled paper. Compared with the control, OKG was found to improve the properties of recycled paper significantly.

Table 6. Effects of OKG on Properties of Recycled Paper

pH	Density (g/cm ³)	Tensile index (N·m/g)	Tear index (N·m/g)	Burst index (KPa·m ² /g)	Folding endurance (double folds)
The control	0.55	55.4	28.1	5.22	277
5	0.56	65.0	29.1	5.76	391
6	0.52	65.6	29.3	6.01	396
7	0.55	67.7	29.6	6.26	443
8	0.54	65.5	27.0	6.10	438

Note: OKG's oxidation time is 60 min, oxidation temperature is 40 °C, concentration of hydrogen peroxide is 0.8%. The samples were prepared with 1% OKG and 0.5% $Al_2(SO_4)_3 \cdot 18H_2O$ on a dry fiber basis. After alum addition the pH was adjusted to 5,6,7,8. The standard deviation is < 5%

When the pH of papermaking was 7, the tensile index, burst index, and folding endurance of the paper were increased by 22.20%, 19.92%, and 59.93%, compared to the control paper. These findings indicated that OKG remaining in the secondary fibers from the first cycles of papermaking can also improve the bond strength between fibers.

SEM Analysis

Figure 2 gives SEM images of handsheets. As is shown in images a and b of Fig. 2, there were more pores in the surface of the original paper than that of the paper with OKG. This is consistent with the idea that the inter-fiber bonding was increased by the paper strengthening agent, which curtailed the pores between fibers.

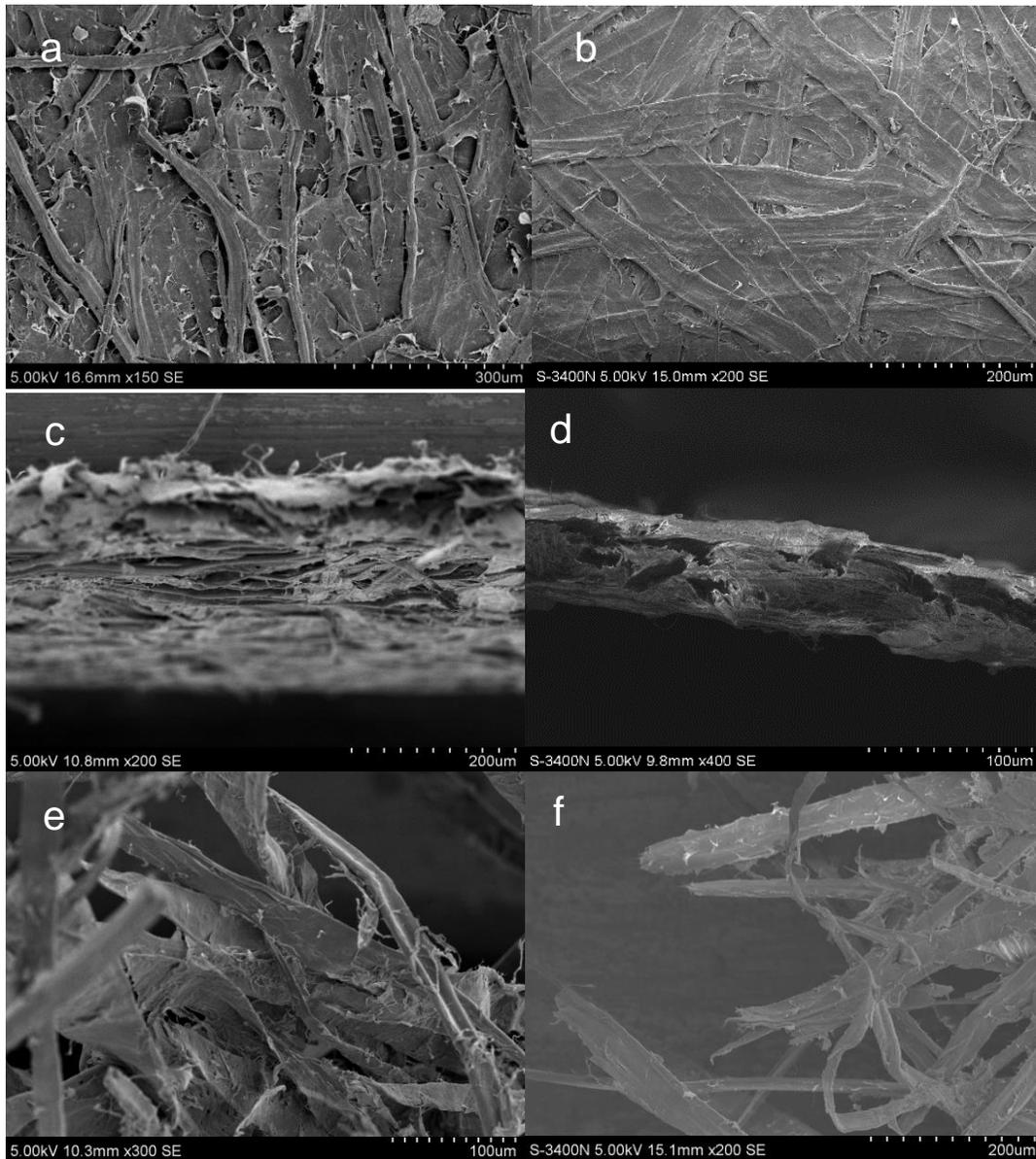


Fig. 2. SEM images of handsheet (Image a, b are surface images, a: original, b: with OKG. Image c,d are section images, c: original, d: with OKG. Image e, f are fracture images, e: original, f: with OKG)

Image c and d of Fig. 2 show that the cross-section of original paper was thick, the fiber combination was loose, whereas the cross-section of paper with OKG was thinner. The fibers were unbroken when the original paper was broken by tensile force. Because only the bonds between the fibers were broken, the fibers were pulled out, as shown in images e and f. However, most fibers of paper prepared with OKG were broken. This also indicates that paper strengthening agent could improve the bonding between the fibers.

CONCLUSIONS

1. Oxidized glucomannan was able to improve the paper properties. Also the reaction conditions of glucomannan affected paper properties evidently. The best oxidation conditions were as follows: Oxidation time 60 min; concentration of hydrogen peroxide 0.8%; and oxidation temperature 35 °C.
2. When 1% oxidized glucomannan was used, tensile index, burst index, and folding endurance of the paper were increased by 7.0%, 16.9%, and 102.2%, respectively compared with the control.
3. Oxidized glucomannan also improved properties of recycled paper. When pH of the first time papermaking was 7, the tensile index, burst index, and folding endurance of the recycled paper were increased by 22.20%, 19.92%, and 59.93% compared to the control paper.
4. SEM analysis showed that oxidized glucomannan could increase the inter-fiber bonding in paper.

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