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TEMPO-mediated oxidation of oat β-D-glucan and its influences on paper properties

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ABSTRACT

An enhanced bonding agent for papermaking was prepared by selective oxidation of a hemicellulose-rich byproduct of oat processing, which will be identified here by its primary component, β-D-glucan. The β-D-glucan was treated sequentially with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and sodium hypochlorite, or alternatively just with sodium hydroxide. When added to a slurry of unbleached softwood kraft fibers, in combination with an optimal dosage of aluminum sulfate, the oxidized β-D-glucan yielded greater increases in tensile strength and folding endurance in comparison to untreated β-D-glucan. NaOH treatment also improved dry-strength performance of the β-D-glucan, except for folding endurance. The improvements were attributed to increased charge density of the treated polyelectrolytes, leading to better distribution and retention on fibers prior to sheet formation. Modified β-D-glucan also enhanced the strength of recycled sheets when the treated paper was repulped and formed into recycled paper with no further chemical addition.

1. Introduction

Bonding between cellulosic fibers is known to play a critical role in meeting the strength requirements of paper products (Page, 1969). Though the strength of paper also depends on the strength of the component fibers, the inter-fiber bonds frequently can be considered as the "weak link" in a paper structure (Helle, 1963; Howard & Jowsey, 1989). Kraft pulp fibers suffer a reduction in their bonding ability when they are recycled (Weise & Paulapuro, 1996; Hubbe, Venditti, & Rojas, 2007). Further demands are placed on paper's inter-fiber bonding ability due to increasing levels of mineral fillers (Shen, Song, Qian, & Liu, 2009), and also a gradual trend toward reduction in the mass per unit area of various paper and paperboard products (Nahrath, 2004; Kerman, Wirth, & Welt, 2009; Li, Dai, Wan, & Zhu, 2012).

It is well known that paper's inter-fiber bonding strength can be increased by addition of certain water-soluble polyelectrolytes such as cationic starch or acrylamide copolymers; these products are added as solutions to the fibrous slurry before formation of the sheet (Hubbe, 2006). It has been shown that related beneficial effects can be achieved by the addition of hemicellulose products as dry-strength agents (Denis, Rubens, & Marcos, 2003; Suurnäkki, Oksanen, Kettunen, & Buchert, 2003; Bai, Hu, & Xu, 2012). Hemicelluloses serve as a natural bonding agent when they are a component in ordinary kraft pulp fibers. Thus, it has been shown that excessive removal of hemicellulose, as in the case of overly aggressive "pre-extraction" treatments, can lead to paper that exhibits relatively low inter-fiber bond strength (Oksanen, Buchert, & Viikari, 1997; Al-Dajani & Tschirner, 2008; Yoon & Van Heiningen, 2008).

Another approach that can be used to enhance the strength of paper is chemical modification. It has been shown, for example, that the dry strength properties of paper can be enhanced by TEMPO-mediated oxidation of bleached hardwood kraft fibers (Song & Law, 2010). The treatment was found to benefit not only the strength of paper made from never-dried fibers, but it also had a beneficial effect on recycled paper made from the same fibers. Best results were obtained when the oxidation of the fiber surfaces was carried out before the initial drying of the fibers.

The present work concerns the possible usage of a bonding agent prepared from a hemicellulose-rich byproduct of oat processing, a β-D-glucan product. The authors surmised that a more effective dry-strength additive could be prepared from a commercially available β-D-glucan-rich product by subjecting it to TEMPO-mediated oxidation (Isogai & Kato, 1998). In other words, the natural polysaccharide product was subjected to a form of oxidation that mainly affects the C6 position on the accessible glucopyranose units of the polysaccharide, leaving the polyelectrolyte chains and other —OH groups largely unaffected. The increased anionic charge of the treated β-D-glucan product was intended to allow the material to be dissolved more readily in water, which is one criterion for selection of promising candidate materials to be evaluated as dry-strength agents (Hubbe, 2006). The additional negatively charged

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carboxylate groups also provide more handles by which the polyelectrolytes later can be retained during the papermaking process (Linke, 1968). The described approach was used for the first time as a strengthening system for papermaking.

2. Experiment

2.1. Materials

Oat β-D-glucan was obtained from the Biovelop Company, Kimstad, Sweden. The molecular weight of the β-D-glucan was 1,300,000 Da. The compositional data were as follows: 32–35% of dietary fiber (soluble β-D-glucan), 34–37% of total dietary fiber, 54–56% of carbohydrate (maltodextrin), 2.5–3.5% of protein, 3–4% of ash, and 0.5–1% of fat. Kraft pulp of loblolly pine was prepared under the following laboratory conditions: liquor ratio 1:4.5, alkali dosage 19%, sulfidity 25%, and an H-Factor of 180. The yield of the pulp was 50%. After refining to 400 ml (Canadian standard freeness), the fibers above 48 mesh were collected.

2.2. TEMPO-mediated oxidization

5 g of oat β-D-glucan and 200 ml of distilled water were combined in a 500-ml flask equipped with an impeller stirring apparatus. The flask was then put in a water bath at 21 °C with 0.0248 g of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and 0.031 moles of sodium bromide. Then 1.149 ml of sodium hypochlorite solution (5.65–6.00% concentration, w/v) was added to the flask, still with stirring. The pH was adjusted to 10.5 with 0.5 M sodium hydroxide solution, after which the timer was started. 5 min later, another 1.149 ml of sodium hypochlorite solution was added in the flask. The pH was adjusted to 10.5. Reaction times of 20 min, 30 min, 40 min, and 60 min were compared. The reaction was stopped by addition of 5 ml ethanol, whereupon the pH was adjusted to 7 with 4 M HCl. The oxidized β-D-glucan was precipitated by the addition of 400 ml ethanol, followed by centrifugation. The solid was broken up with a glass rod, rinsed with acetone (5 times) and ethanol (1 time), and finally dried in air. In this manner four samples of oxidized β-D-glucan were obtained.

2.3. Sodium hydroxide treatment

5 g of oat β-D-glucan and 200 ml distilled water were combined in a 500-ml flask equipped with an impeller stirrer. The flask was then put in a water bath at 21 °C. The pH was adjusted to 10.5 with 0.5 M sodium hydroxide solution, and then the timing was started. The reaction time was 30 min. When the time was finished, the reaction was stopped by addition of 5 ml of ethanol, whereupon the pH was adjusted to 7 with 4 M HCl. The β-D-glucan was precipitated by the addition of 400 ml of ethanol, followed by centrifugation and mashing with a glass stirring rod in the presence of acetone (5 times) and ethanol (1 time); then it was dried in air. In this manner sodium hydroxide treated samples of β-D-glucan were obtained.

2.4. Papermaking and physical properties of handsheets

Standard handsheets were prepared (1.2 g o.d.) and tested in accordance with the TAPPI standard methods. Chemical additives (as solutions) to the papermaking furnish were as follows, based on the dry mass of fibers: 0.5% of $Al_2(SO_4)_3{\cdot}18H_2O$, pH adjusted as specified, then 0.05% of cationic polyacrylamide retention aid (dry basis). A portion of the handsheets were dried under different conditions: gentle dryness means dried at room temperature; ordinary dryness means dried in an oven at 105 °C for 30 min; and severe dryness means dried in oven at 150 °C for 60 min. The handsheets were immersed in water at room temperature for 24 h, then disintegrated. Without further addition of chemicals the pulp samples were formed again into recycled handsheets, following TAPPI methods.

2.5. Fourier transform infrared (FTIR) analysis

The oxidized and alkali-treated β-D-glucan samples were ground into powder form, then mixed with KBr powder to obtain a sample suitable for FTIR analysis. The absorbance between 4000 cm^{-1} and 400 cm^{-1} was studied, using a Spectrum-100D instrument from PerkinElmer (USA).

2.6. Scanning electron microscopy (SEM)

An S-3000N SEM device (Hitachi Ltd., Japan) was used for observation of handsheet surfaces and fracture surfaces. A sputtering procedure was used to coat the surfaces with gold to dissipate electrical charge.

2.7. Elemental analysis

Elemental analysis was carried out using a Flash EA1112 instrument. The carbon, hydrogen, and nitrogen contents were tested. Oxygen content was obtained from the total elements, excluding carbon, hydrogen, and nitrogen.

2.8. Viscosity

The viscosity of oxidized β-D-glucan was tested with a capillary viscometer of the ubbelohde type. The temperature was controlled at 25 °C.

2.9. Molecular weight test

Molecular weight was determined by gel permeation chromatography, using an Agilent PL aquagel–OH mix column (300 × 7.5 mm, Polymer Laboratories Ltd.) at a flow rate of 0.5 ml/min 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 Da, Polymer Laboratories Ltd.). The β-D-glucan was dissolved in 0.02 M NaCl in 0.005 M sodium phosphate buffer at pH 7.5 as the eluent.

3. Results and discussion

3.1. Molecular weight of oxidized β-D-glucan

The viscosity data for the oxidized oat β-D-glucan are presented in Table 1. As shown, the viscosity values were decreased by 8.7%, 42.4%, and 64.4%, respectively, compared with the original β-D-glucan after thermal treatment, oxidation treatment (30 min), and alkali treatment. The decreases in viscosity values for oxidized oat β-D-glucan increased with increasing time of oxidation. These results indicate that the conditions of thermal treatment, oxidation, and alkali treatment were sufficient to cause degradation of β-D-glucan, which would lead to the reduction of viscosity.

Table 1 also shows the molecular weight data for oxidized β-D-glucan. The molecular weight of oat β-D-glucan decreased after oxidation treatment. With increasing time of oxidation, the decrease of the molecular weight was greater.

3.2. FTIR analysis

FTIR spectra of oat β-D-glucan are presented in Fig. 1. As shown, the top (blue) curve corresponds to the NaOH-treated sample, the middle (red) curve to the untreated sample, and the bottom (green)

Table 1
Viscosity and elemental analysis of oxidized oat β-D-glucan.

Treat	Original	Oxidized 20 min	Oxidized 30 min	Oxidized 40 min	Oxidized 50 min	Oxidized 60 min	NaOH treat 30 min
Viscosity (cst)	11.28	–	7.28	–	–	6.50	4.01
Viscosity (cst)[a]	10.29	–	5.72	–	–	5.18	3.77
Molecular weight (Da)	1.3×10^7	5.79×10^5	–	–	5.62×10^5	–	–
N (%)	0.83	0.46	–	0.48	–	0.45	–
C (%)	43.12	41.84	–	41.36	–	40.95	–
H (%)	6.53	6.30	–	6.22	–	6.12	–
O (%)	49.52	51.40	–	51.94	–	52.48	–

[a] *Note*: The samples were dried at 105 °C for 30 min.

curve to the TEMPO-oxidized sample. The main features of all three curves were consistent with polysaccharide materials (Kemp, 1975). Main absorbance maxima can be assigned as follows: The 3429 cm^{-1} peak can be attributed to hydroxyl group stretching, the 2925 cm^{-1} peak corresponds to methylene group stretching, and the 1633 cm^{-1} peak corresponds to carbonyl (C=O) groups. The peak at 1380 cm^{-1} is attributable to C—H vibrations. That at 1157 cm^{-1} is due to C—O—C vibrations, and that at 1047 cm^{-1} can be ascribed to C—O—H vibrations.

Fig. 2 provides an expanded view of the carbonyl region of the FTIR spectra. The peak appearing at about 1745 cm^{-1} of the as-received oat β-D-glucan is tentatively ascribed to the presence of ester groups. For comparison, earlier studies involving acetylation of other hemicellulose samples yielded increased absorbances at 1752 cm^{-1} (Xu et al., 2010; Sun, Fang, Tomkinson, & Jones, 1999). An earlier study of β-D-glucan showed a small peak at about 1745 cm^{-1}, in agreement with the present findings (Ahmad, Anjum, Zahoor, Nawaz, & Ahmed, 2010). The fact that the corresponding peak in Fig. 2 was reduced to a shoulder or mostly eliminated upon TEMPO-mediated oxidation or alkali treatment of β-D-glucan may be due to saponification of ester groups (such as acetate groups). The overall reaction can be shown as follows:

$$R\text{–}OCOCH_3 + NaOH \rightarrow R\text{–}OH + CH_3COO^- + Na^+$$

This explanation, based on saponification, is strengthened by the fact that Fig. 2 shows corresponding shifts in absorbances within the range of 1630–1660 cm^{-1}. The assignment of 1630 cm^{-1} to the carboxylic acid form of β-D-glucan was established by Johannson, Tuomainen, Ylinen, Ekholm, and Virkki (2004). It is evident in Fig. 2 that both treatments of β-D-glucan made the peak at 1630 cm^{-1} become more prominent relative to that at 1660 cm^{-1}.

The main features of the FTIR results were confirmed by analysis of peak heights and peak areas. Results are shown in the Supplementary Data (Table S1). Though the results based on integrated areas of absorbance bands may be preferred on theoretical grounds (Randriamahefa, Renard, Guerin, & Langlois, 2003; McClure, 1987), the peak height analysis is simpler and less prone to errors due to baseline uncertainties and the overlap of absorption regions. Unfortunately, it was not possible with the software employed

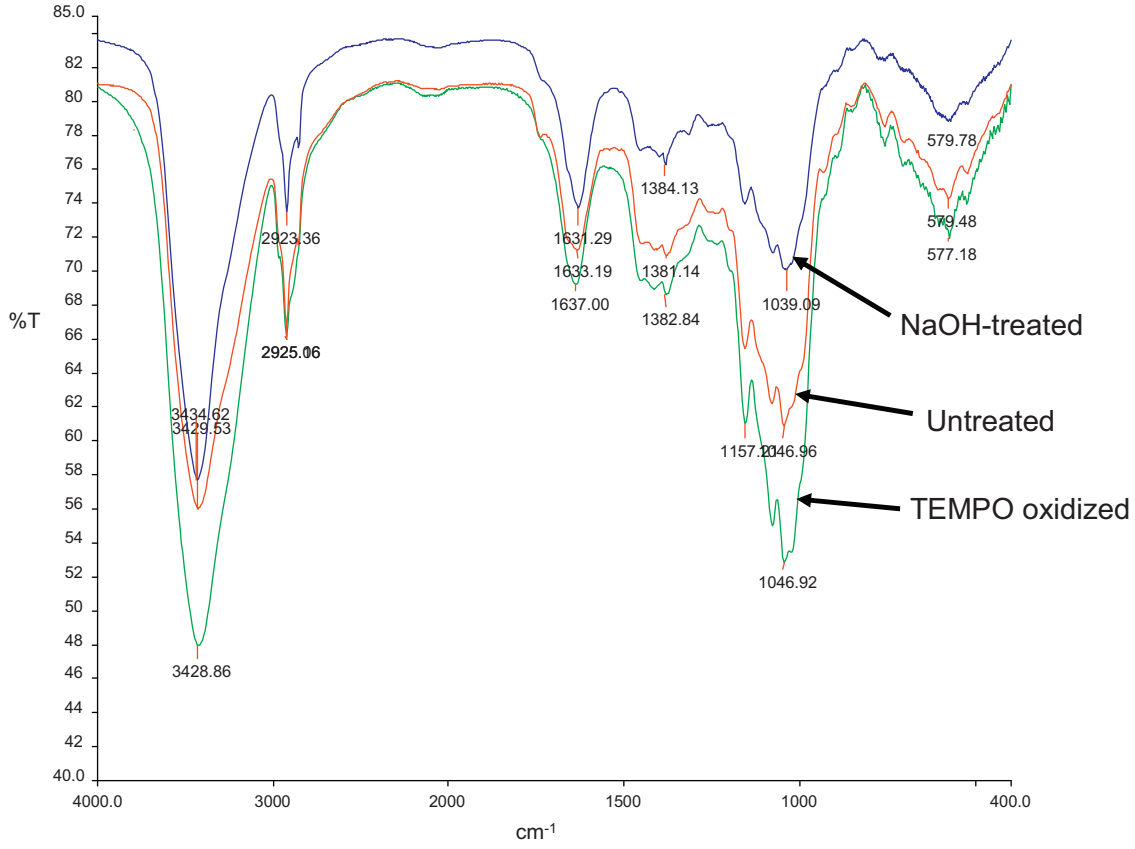

Fig. 1. FTIR spectrogram of alkali-treated oat β-D-glucan (blue), untreated β-D-glucan (red), and oxidized β-D-glucan (green). (For interpretation of the references to color in text, the reader is referred to the web version of this article.)

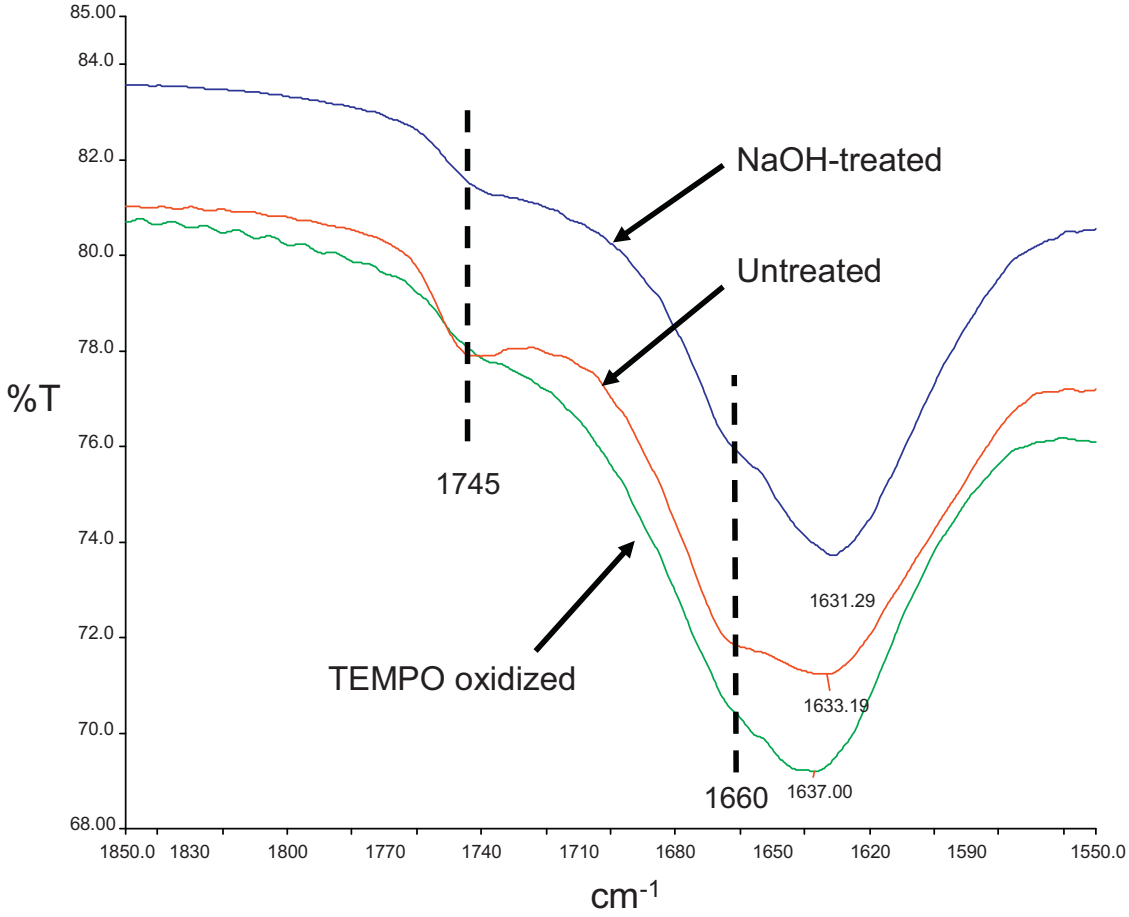

Fig. 2. Carbonyl region of FTIR spectrogram of alkali-treated oat β-D-glucan (blue), untreated β-D-glucan (red), and oxidized β-D-glucan (green). (For interpretation of the references to color in text, the reader is referred to the web version of this article.)

(Spectrum-100D) to resolve more than one peak in each of the key wavenumber regions of 1730–1745 cm^{-1} and 1630–1660 cm^{-1}.

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.08.070.

3.3. Elemental analysis of oxidized oat β-D-glucan

Table 1 gives the results of elemental analysis of oxidized oat β-D-glucan. As shown in Table 1, nitrogen, carbon, hydrogen, and oxygen were detected in the oat β-D-glucan. The nitrogen can be attributed to the protein, which is 2.5–3.5% in the oat β-D-glucan. In the course of oxidation treatment the nitrogen content was progressively decreased; this was attributed to loss of protein during the oxidation process. With increasing time of oxidation the oxygen content was slowly increased. This indicates that some hydroxyls had been converted into carboxyls. At same time, the proportional amounts of carbon and hydrogen decreased accordingly.

3.4. Physical properties of handsheets

As shown in Table 2, compared with the control, the tensile index, burst index, and folding endurance of handsheets prepared with oxidized β-D-glucan were increased significantly. The tear index showed a divergent trend with increasing bonding, as has been reported by others (Scott, 1996). With the increase of oxidization time, the tensile index, burst index and folding endurance of handsheets first increased, then they decreased. The effect of increasing oxidization time was attributed to a gradual increase of carboxyl content. The presence of an effective dry-strength agent can be expected to increase the amount of hydrogen bonding between the fibers within bonded areas (Clark, 1978; Nissan, Byrd, Batten, & Ogden, 1985). Tensile index and folding endurance

Table 2
Oxidation time of oat β-D-glucan vs. handsheets properties.

Oxidation time (min)	Density (g/m^3)	Tear index ($mN\ m^2/g$)	Burst index ($kPa\ m^2/g$)	Tensile index (Nm/g)	Folding endurance (double folds)
Control	0.518	5.73	4.25	52.79	456
0 min	0.553	3.81	5.91	68.17	899
20 min	0.531	3.69	5.92	68.75	902
30 min	0.540	3.63	6.52	71.81	1028
40 min	0.543	4.18	6.19	71.09	1017
50 min	0.534	4.19	5.88	71.08	953
60 min	0.529	4.21	5.86	71.64	948

Note: Control sample is kraft pulp handsheet. 1% oxidized β-D-glucan is added in the other samples.

Table 3
Effects of dosage of aluminum sulfate on handsheet properties.

Aluminum sulfate (%)	Oxidized time (min)	Tensile index (Nm/g)	Tear index (mN m^2/g)	Burst index (kPa m^2/g)	Folding endurance (double folds)
	0	68.57	3.73	5.80	884
0.2	20	70.81	4.68	5.80	889
	30	73.41	4.85	6.12	998
	0	68.17	3.81	5.91	899
0.5	20	68.75	3.69	5.92	902
	30	71.81	3.63	6.52	1028
1	20	68.81	4.98	5.83	875

Note: 1% oxidized β-D-glucan is added in the samples. The aluminum sulfate dosage was based on the mass of $Al_2(SO_4)_3 \cdot 18H_2O$ on a dry fiber basis. After alum addition the pH was adjusted to 5% and 0.05% cationic polyacrylamide retention aid was added. Zero oxidation time means the original oat β-D-glucan.

Table 4
Dosage of oxidized β-D-glucan or alkali treatment vs. properties of handsheets.

Sample	Dosage of β-D-glucan (%)	Density (g/m^3)	Tear index (mN m^2/g)	Burst index (kPa m^2/g)	Tensile index (Nm/g)	Folding Endurance (double folds)
Control [a]	0	0.518	5.73	4.25	52.79	456
Oxidized 0 min	1.0	0.553	3.81	5.91	68.17	899
Oxidized 30 min	0.5	0.540	3.93	5.97	68.48	983
Oxidized 30 min	1.0	0.540	3.63	6.52	71.81	1028
Oxidized 30 min	1.5	0.542	3.42	6.94	79.11	1374
Oxidized 40 min	1.0	0.543	4.18	6.19	71.09	1017
NaOH treat 30 min	1.0	0.535	3.77	6.84	81.68	865

[a] *Notes*: The control sample was prepared with no chemical additives; the other samples were prepared with 0.5% $Al_2(SO_4)_3 \cdot 18H_2O$ on a dry fiber basis. After alum addition the pH was adjusted to 5 and 0.05% cationic polyacrylamide retention aid was added.

increased by 36.0% and 125.4%, respectively, when the oxidation time was 30 min.

3.5. Effects of dosage of aluminum sulfate on handsheet properties

The effects of dosage of aluminum sulfate on properties of paper sheets are presented in Table 3. As shown, the tensile index, burst index, and folding endurance of handsheets changed with the increasing of dosage of aluminum sulfate. When the dosage of aluminum sulfate was 0.5%, the handsheets exhibited the most favorable properties in terms of tensile, burst, and folding endurance. The reason is that Al^{3+} is a highly cationic additive that ties negatively charged polyelectrolytes such as β-D-glucan onto the surfaces of fines and fibers, which will improve the strength of paper sheets. But when the dosage of aluminum sulfate exceeded 0.5%, the physical properties of handsheets became worse, probably because of an overdose of cationic charge, which would result in repulsive forces among the materials in suspension.

3.6. Effects of dosage of oxidized β-D-glucan on handsheet properties

As shown in Table 4, with increasing dosage of oxidized β-D-glucan, the tensile index, burst index, and folding endurance of handsheets increased markedly, while the tear index again showed a divergent trend. The increase in sheet density relative to the control sample provides further demonstration of increased inter-fiber bonding due to the oxidation treatment. Tensile index, burst index and folding endurance of handsheets increased by 49.9%, 63.3%, and 201.3%, respectively, compared with the control, when the dosage of oxidized β-D-glucan was 1.5%.

Table 5
Oxidation or alkali treatments of β-D-glucan vs. properties of recycled paper.

Sample	Density (g/m^3)	Tear index (mN m^2/g)	Burst index (kPa m^2/g)	Tensile index (Nm/g)	Folding Endurance (double folds)
Gentle dryness					
Control	0.473	5.87	3.73	45.21	59
Oxidized 0 min	0.528	4.82	4.08	53.46	407
Oxidized 30 min	0.508	4.47	4.73	59.36	578
Oxidized 40 min	0.517	4.21	4.73	57.48	502
NaOH treat	0.522	4.73	4.66	51.81	344
Ordinary dryness					
Control	0.506	5.35	3.35	37.54	56
Oxidized 0 min	0.465	5.82	3.48	44.58	97
Oxidized 30 min	0.495	4.98	4.51	53.58	353
Oxidized 40 min	0.506	5.07	4.48	49.83	334
NaOH treat	0.525	5.92	4.34	47.97	135
Severe dryness					
Control	0.444	4.18	3.15	26.41	6
Oxidized 0 min	0.401	4.91	3.29	26.84	12
Oxidized 30 min	0.456	6.20	4.26	39.81	110
Oxidized 40 min	0.465	5.33	4.30	33.92	32
NaOH treat	0.465	4.76	4.20	33.39	19

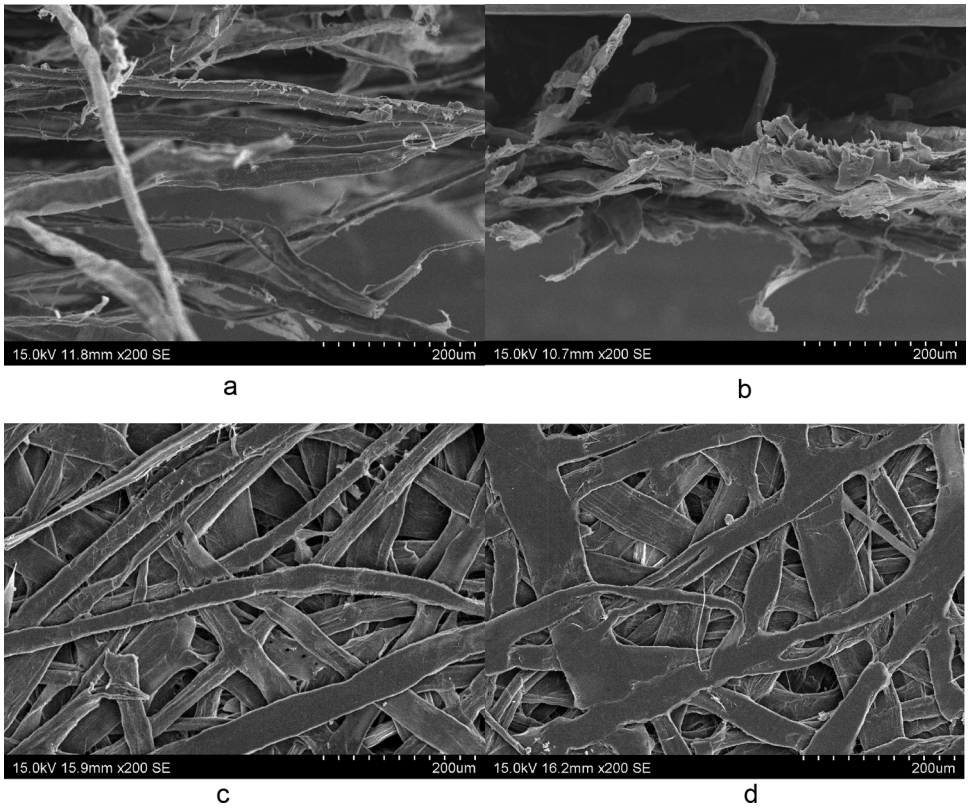

Fig. 3. SEM fracture images and surface images of a paper sample: (a) control, (b) with oxidized β-D-glucan, (c) control and (d) with oxidized β-D-glucan.

3.7. *Influence of hydrolysis of β-D-glucan*

Table 4 also compares effects of TEMPO-mediated oxidation and alkali treatment with untreated β-D-glucan in terms of paper strength properties. As shown, when the β-D-glucan was treated at pH 10.5 for 30 min, the tensile index, burst index, and folding endurance of handsheets all increased obviously, while tear index showed a divergent trend. However the folding endurance of handsheets was lower than that achieved by oxidation for 30 min. This indicates that hydrolysis of β-D-glucan can lead to an increase of handsheets strength properties related to bonding. These results for alkali treatment are again consistent with saponification of ester groups, thus creating carboxyl groups and rendering the material more soluble, more ready to interact with aluminum sulfate, and more effective as a bonding agent.

3.8. *Properties of recycled paper*

The effects of treated β-D-glucan on physical properties of recycled paper are presented in Table 5. Paper sheets dried under the different conditions, after the specified treatments with β-D-glucan products, was repulped and formed into recycled sheets with no further addition of chemicals. Compared to the recycled paper without β-D-glucan, the tensile index, burst index, and folding endurance of recycled paper increased significantly even after severe drying. The tensile index, burst index, and folding endurance, respectively, increased by 31.3%, 26.8%, and 880% relative to the control after the gentle dryness when 1% oxidized β-D-glucan (oxidized 30 min) was used. The tensile index, burst index, and folding endurance, respectively, increased by 42.7%, 34.6% and 530% after ordinary drying. However, they were increased by 50.7%, 35.2% and 1700% relative to the control after severe drying. It is thus clear that the fibers that had been treated with oxidized β-D-glucan also can be more effective for the production of recycled paper even after severe drying.

3.9. *Electron microscopy*

SEM images of a handsheet samples without and with oxidized β-D-glucan, are presented in Fig. 3a and b, respectively. The images show the fractured edge of paper samples following tensile strength testing. As is shown in Fig. 3a, the majority of fibers were intact, while most of fibers in Fig. 3b were fractured during the tensile test. Such breakage of fibers can be taken as an indication of increased bonding within the paper.

SEM surface images of a paper sample without and with oxidized β-D-glucan are presented in Fig. 3c and d, respectively. As shown, there was more pore space between the fibers in Fig. 3c compared to Fig. 3d. These results can be attributed to the role of oxidized β-D-glucan in increasing bonding force among fibers.

4. Conclusions

The following main conclusions may be drawn from this study:

1. Oxidized β-D-glucan prepared by TEMPO-mediated oxidation was effective in improving paper physical properties. Tensile index and folding endurance were increased by 36.0% and 125.4%, respectively, when the oxidized time was 30 min. Oxidation was confirmed by FTIR and elemental analyses.
2. The dosage of oxidized β-D-glucan played the most important role in papermaking. Tensile index, burst index, and folding endurance of handsheets increased by 49.9% 63.3%, and 201.3%, respectively, compared with the control, when the dosage of oxidized β-D-glucan was 1.5%.
3. Oxidized β-D-glucan provided increased strength when the used fibers were repulped and formed into recycled sheets, despite

the fact that there was no further addition of dry-strength additive. The tensile index, burst index, and folding endurance, respectively, increased by 50.7%, 35.2%, and 1700% relative to the control (which was dried in the same way) after the severe drying when 1% oxidized β-D-glucan (oxidized 30 min) was used in preparing the original sheets.

4. SEM micrographs showed that fibers were integrated more closely as a benefit of the presence of oxidized β-D-glucan.
5. Alkaline pretreatment of the β-D-glucan resulted in saponification of ester groups. Such pretreatment resulted in improved performance as a dry-strength additive, though not in the case of folding endurance of the paper.

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