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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)