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Nanocrystalline cellulose from aspen kraft pulp and its application in deinked pulp

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ABSTRACT

Nanocrystalline cellulose (NCC) isolated from bleached aspen kraft pulp was characterized, and its application as pulp strengthening additive and retention aid was investigated. Results showed that NCC with high crystallinity of more than 80% can be obtained using 64 wt% sulfuric acid. The structure of nanocrystalline cellulose is parallelepiped rod-like, and their cross-sectional dimension is in the nanometer range with a high aspect ratio. The formation of microparticle retention systems during the application of NCC together with cationic polyacrylamide and cationic starch in deinked pulp was able to further improve pulp retention and strength properties without negative influence on the drainage.

1. Introduction

Under the current situation of the exhausting non-renewable resources such as coal, oil and natural gas, many efforts have been directed at extending the utilization of renewable resources for new energy and new materials [1,2]. Cellulose, natural polymer from the cell wall of green plants with the formula of $(C_6H_{10}O_5)_n$, is the most abundant renewable resources on earth [3,4]. It exists not only in various plants, but also in some organisms such as bacteria and animals. The unique chemical and physical properties of cellulose make it being a biomass resource for many decades, and will still be an indispensable raw material for papermaking, food, and additives in optical and pharmaceutical industries [5].

Cellulose molecular chains are biosynthesized and self-assembled into microfibrils, which are composed of orderly crystalline domains and disordered amorphous domains. Cellulose keeps the supramolecular structures and the fiber morphology by hydrogen bonding within molecular area and van der Waals force between cellulose chains [6]. The amorphous domains are susceptible to acid attack because cellulose chains in these regions are randomly oriented and with a lower density. Nanocrystalline cellulose (NCC) extracted from natural fibers by acid is in the size of nano-scale, which demonstrates not only the features of nanoparticles, but also unique strength and optical properties. It was reported that the rod-like cellulose particles acquired from different sources through acid hydrolysis are basically with a diameter from 5 to 20 nm, and a length from 100 nm to several micrometers [7,8]. Recent researches showed that NCC had wide application prospects in nanocomposite field [6,9–11], while its application in pulp and paper has seldom been reported.

In the pulp and paper industry, many efforts have recently been made to increase the utilization of recycled pulp in producing paper and paperboard products in order to protect the environment, save energy and lower production cost [12,13]. However, with the increase of the ratio of recycled pulp, the strength and quality of paper and paperboard decreases. Paper strengthening agents can give the required dry strength to paper and paperboard even when they are made with a large amount of recycled pulp. Drainage and retention are also very important parameters for the deinked pulp in the papermaking process, because they limit the production efficiency of a paper machine [14]. As the paper and paperboard industry continues to increase the speed and output of paper machines, the demands on retention and drainage aids are increasing greatly. Increased water system closure and increased water temperatures are also altering the environment within which the retention and drainage aid has to function, requiring an alternative approach in many cases.

The importance of "green" characteristics such as biodegradability, biocompatibility and favorable CO_2 balance grows with the

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awareness of consumers and engineers [15,16]. To meet the environmental requirements, so as to make the pulp and papermaking industry sustainable, it is desirable to develop bio-based papermaking chemicals [17]. Approaches of effective utilization of renewable lignocellulosic resources to produce chemicals and materials are attracting the interest of scientific and industrial committee all over the world. By applying mechanical, chemical, physical or biological methods, cellulosic fibers can be disintegrated into cellulose substructures with micro- or nano-size dimensions, which have the advantages of bio-based materials such as being lightweight, bio-degradable, bio-compatible, and renewable. However, these methods tend to be energy-demanding and/or chemical-demanding. A common method of obtaining cellulose nano-fibers involves conventional refining procedures, in which large quantities of energy are required [18]. Acid hydrolysis is the main process used to produce nanocrystalline cellulose, in which H_2SO_4, HCl or H_3PO_4 are usually used [19]. When sulfuric acid is used as hydrolyzing agent, it interacts with the surface hydroxyl groups of cellulose to yield charged surface sulfate groups, which can promote the dispersibilty of nano whiskers in water [7].

It was reported that the nano fibrillation cellulose (NFC) can be used for improving the physical properties of papers and cellulosic films [20]. Henriksson et al. [2] and Zimmermann et al. [21] reported that microfibrillated cellulose (MFC) could be formed into sheets with high strength properties. Similar results for enhancing paper strength are obtained when MFC was added into the pulp suspension [21,22]. In papermaking process, it is important that the papermakers are able to effectively retain mineral fillers and fiber fines while simultaneously improving dewatering rate [23]. NCC provides a very high water retention capacity due to their large surface area and high aspect ratio. However, the strong water retention property may deteriorate the drainage rate of the pulp.

In this study, NCC was isolated from bleached aspen kraft pulp by acid hydrolysis, and characterized by particle charge detector, X-ray diffraction, and atomic force microscopy, respectively. Then, NCC was used as an additive in the deinked pulp, and the retention of fines and improvement of paper strength were evaluated and discussed. In addition, its influence on the drainage rate of the pulp when applied together with cationic polyacrylamide and cationic starch was also investigated.

2. Experimental

2.1. Materials

Bleached aspen kraft pulp was provided by Yinxing Paper Co., Ltd. (Jinan, China). Old newsprint deinked pulp, CPAM with molecular weight 1–4 million and CS were provided by Huatai Group (Dongying, China). Sulfuric acid (95–98%) for hydrolysis, and poly-dimethyldiallylammoniumchloride (PDADMAC) standards for titration were all analytically pure.

2.2. Preparation of NCC

The preparation of NCC was conducted according to the literature [24]. The bleached aspen kraft pulp was ground with a Wiley mill, and the fraction passing through a 20-mesh screen was collected for the hydrolysis step. 20 g (o.d.) of the milled pulp was hydrolyzed by using 64 wt% sulfuric acid at different temperatures, acid-to-pulp ratios and reaction times. Immediately following the hydrolysis, the suspensions were diluted (10 times volume of the acid solution used) to terminate the reaction, and settled overnight. The clear top layer was decanted off and the remaining white cloudy layer was centrifuged. The clear top layer after centrifugation was decanted off, and deionized water was added and mixed with the thick white suspension and then centrifuged again. Such a procedure was repeated 2–3 times. The resulting precipitate was transferred to a cellulose dialysis membrane which have a molecular weight cut off of 12,000–14,000 and dialyzed against deionized water for several days until the pH value became constant. The suspension were sonicated for 7 min at 60% output control, while cooling in an ice bath to avoid overheating. Five samples were investigated in this work, and their corresponding hydrolysis conditions were as follows: NCC1, with hydrolysis time of 25 min, 45 °C and acid-to-pulp ratio of 8.5 mg/l; NCC 2, 30 min, 45 °C, and 8.5 mg/l; NCC 3, 30 min, 55 °C and 8.5 mg/l; NCC 4, 30 min, 45 °C and 9.5 mg/l; NCC 5, 30 min, 45 °C and 10.5 mg/l.

2.3. Characterization

Surface charge density of NCC samples was determined with a streaming current detector (PCD03PH, Mutek Company, Germany). PDADMAC was used as the standard titration reagent. The surface charge density was calculated based on the formula below according to the literature [25],

$$Ep = \frac{V \times C}{\text{wt}} \tag{1}$$

where C, V are the concentration and consumption volume of the standard PDADMAC solution, respectively, and wt is the weight of the NCC sample.

X-ray powder diffraction analyses were performed with a Bruker D8 Advance powder X-ray diffractometer (Bruker AXS, Germany) equipped with a CuXa X-ray tube. Crystallinity degree was calculated from X-ray diffraction curves by the ratio of the crystalline area to the total area.

The dimensions and surface morphology of the samples were studied using an AFM (SPM9600, Shimadzu, Japan) in tapping mode in air. A drop of sample was air dried overnight on a clean mica surface at ambient conditions. Images from 5 different places on the samples were scanned. The scan rate is 1 Hz.

2.4. Physical properties testing of handsheets

The NCC samples were blended with old newsprint deinked pulp at varied ratios. Handsheets with a basis weight of 60 ± 2 g/m^2 were prepared according to TAPPI standard method T205. The breaking length and tear index were evaluated in accordance with TAPPI standard procedures T494 om-1 and T414, respectively.

2.5. Retention ratio and drainage rate measurement

A Britt Dynamic Drainage Jar (a 100-mesh screen) was used for determining retention and drainage of pulp suspensions. 500 ml of pulp furnish containing deinked fibers, NCC samples and 20% of precipitated calcium carbonate (on o. d. fibers) was employed in the test.

In the monocomponent retention test, various dosages of NCC were added into the furnish under the agitation speed of 750 rpm. 30 s later, the filtrate was collected and the time for the first 100 ml of filtrate was recorded to calculate the drainage rate according to the formula as follow,

$$\text{Drainage rate (ml/s)} = \frac{100}{\text{time}} \tag{2}$$

Light transmittance was measured at the wavelength of 500 nm using a Hitachi UV 4100 spectrophotometer (Hitachi, Japan). The concentration of filtrate was calculated according to the curve of light transmittance against filtrate concentration, and the first pass