



Enzymatic and cold alkaline pretreatments of sugarcane bagasse pulp to produce cellulose nanofibrils using a mechanical method

Shuangxi Nie^{a,b,*}, Chenyuan Zhang^a, Qi Zhang^a, Kun Zhang^a, Yuehua Zhang^a, Peng Tao^a, Shuangfei Wang^{a,b,*}

^a College of Light Industry and Food Engineering, Guangxi University, Nanning 530004, China

^b Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control, Nanning 530004, China



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ABSTRACT

Lignocellulosic biomass is the most abundant renewable resource on the earth. With the development of related fields, the high value utilization of lignocellulosic biomass has gradually become a new avenue for research. In this study, unbleached bagasse pulp was pretreated with xylanase and cold alkali to partially remove hemicellulose and convert to some cellulose I into cellulose II. Cellulose nanofibrils (CNF) were then obtained through ultra-micro grinding and high-pressure homogenization. The prepared CNF were characterized by TEM, Zeta potential, ATR-FTIR and XRD, and a thermogravimetric analyzer was used to analyze the thermal stability of CNF. The results show that xylanase pretreatment can improve the dispersion of fibers during mechanical treatment and can enhance the crystallinity of CNF. With an increase in alkali concentrations, the proportion of cellulose II structures increased, while cellulose crystallinity levels decreased due to the folding of cellulose chains. Under the common influence of crystallinity and crystal structures, the thermal stability of the CNF prepared after cold alkali pretreatment underwent an increasing trend. This shows that the influence of crystal structures on the thermal stability of CNF gradually plays a dominant role as alkali concentrations increase.

1. Introduction

With the continuous development of human society, demands for energy, materials and other resources are increasing (He et al., 2016; Nie et al., 2016). The large-scale use of traditional fossil energy had serious environmental ramifications, rendering research on renewable resources particularly important (Fan et al., 2017; Nie et al., 2014; Yao et al., 2017). Cellulose is the most abundant natural polymer compound found on earth; it is highly biocompatible and biodegradable, and it can be biosynthesized (Lin et al., 2018). With the rapid development of materials science, research on cellulose-based materials has gradually become a major topic of research (Song et al., 2016). The application of nanotechnology has greatly extended the application of cellulose-based materials. Products composed of cellulose nanofibrils (CNF) products are characterized by their strength, low density, and low coefficient of thermal expansion due to their high aspect ratio and mesh-like entangled structure (Fukuzumi et al., 2010), which offers application potential in the field of high-performance products.

Various changes in CNF observed under heated conditions directly affect the thermal stability of nanocellulose-based materials. The

thermal stability of CNF refers to their ability to maintain their own performance at high temperatures. This trait can be evaluated by the change in temperature observed at breakage or under heated conditions, and thermal transition temperature or decomposition temperatures are often used to characterize the thermal stability of CNF (Lavoine et al., 2016). A traditional wood fiber begins to degrade at roughly 230 °C. Cellulose is the most thermally stable component of wood fibers (Gardner et al., 2008; Goring, 1963). According to the “Broido-Shafizadeh” cellulose pyrolysis model proposed by Bradbury et al. (Bradbury et al., 1979), the pyrolysis process undergone by cellulose can be divided into two stages. The first stage occurs at 150–300 °C. At 150 °C, the cellulose glycosidic bond begins to break down, and the degree of polymerization decreases to about roughly 200. When temperatures further increase to roughly 300 °C, cellulose enters the second stage of pyrolysis. The severe depolymerization of cellulose results in the formation of intermediate cellulose, which is mainly composed of dehydrated sugar, and this is transferred into tar by evaporation or aerosol. With an increase in temperature, dehydration, dehydrogenation, deoxygenation, decarboxylation and other reactions occur in cellulose molecules to generate thermally degraded small

* Corresponding authors at: College of Light Industry and Food Engineering, Guangxi University, Nanning 530004, China.

E-mail addresses: nieshuangxi@gxu.edu.cn (S. Nie), wangsf@gxu.edu.cn (S. Wang).

molecule products (Orfão et al., 1999; Zhu et al., 2012).

In plant fibers, hemicellulose and lignin act as fillers and binders that wrap multiple cellulose molecular chains together to form fiber bundles (Li et al., 2018a; Nie et al., 2015; Yao et al., 2015). Therefore, in the preparation of CNF, the pretreatment of cellulose tends to be hindered by the presence of hemicellulose (Pei et al., 2016). Penttila et al. (Penttila et al., 2013) used xylanase to treat bleached birch pulp and then used cellulase to pretreat fibers. Their XRD results show that the presence of loosely structured xylan limits contact between cellulose and cellulose and the hydrolysis of amorphous regions of cellulose. Li et al. (Li et al., 2013) used low-concentration sodium hydroxide to treat bleached kraft pulp to remove most hemicellulose in the examined pulp, and they used mechanical methods to prepare cellulose nanofibrils. The experimental results show that after removing most hemicellulose content, the crystallinity of fibers is significantly increased, and their thermal stability is slightly greater than that of fibrils. The CNF and PVA were composited into films, and the removal of hemicellulose proved beneficial from the enhancement of mechanical properties of the studied composites.

The lignin molecule contains a large amount of chromophoric and color-helping groups, affording the material it produces a high degree of absorbance (Li et al., 2018b). Nguyen et al. found that the initial pyrolysis temperature of lignin is roughly 220–250 °C. At this temperature, lignin molecules begin to undergo polycondensation accompanied by the cleavage of branches (Nguyen et al., 2007). As this temperature is lower than the initial pyrolysis temperature (roughly 260 °C) of cellulose, it is generally believed that the presence of lignin reduces the overall thermal stability of the fiber. Furthermore, lignin reduces the porosity of plant cell walls, which in turn reduces the accessibility of chemicals to the internal structure of plant cells (Lee et al., 2010). To ensure the thermal stability and modification effects of nanocellulose-based materials, most researchers prefer to use bleached pulp in the preparation of nanocellulose, and pulp is purified through the use of chemical methods to further remove lignin and hemicellulose from the raw material. Regarding the above conclusions, Nair & Yan propose a different view. They prepared CNF by mechanical methods designed for fiber raw materials with different lignin content levels and analyzed them by thermogravimetry. Their analysis results show that high lignin content levels (21% w/w) in fibers are superior to low lignin contents levels (5% w/w) in terms of thermal stability. This is the case because during mechanical grinding, lignin is wrapped onto the surfaces of fibers, which can limit the generation of hydrogen bonds between fibers such that they do not form sheet-like connections, reducing size of the heated area and thereby increasing its thermal stability (Nair and Yan, 2015).

In this study, unbleached bagasse pulp was used as a raw material, and raw materials were pretreated by combining xylanase with cold alkali. Then, CNF were prepared by ultra-micro grinding and high-pressure homogenization. The enzyme-alkali combined pretreatment changed the chemical composition of the lignocellulosic biomass and the crystal structure of the cellulose, thereby improving the thermal stability of the nanocellulose-based material. We thus provide theoretical support for the high-value utilization of lignocellulosic biomass.

2. Materials and methods

2.1. Raw materials and chemicals

Unbleached bagasse pulp was obtained from Guangxi Guitang (China) Co., Ltd. and was pulped using the caustic soda method. The alkali content level was measured at 17.5%, the liquid ratio was measured at 1:3.5, the heating time was set to 45 min, and the maximum cooking temperature was set to 165 °C (which was maintained for 110 min). The unbleached pulp used had a Kappa number of 18.12 and a viscosity value of 1173.67 mg/L. Xylanase (X2753, enzyme activity 2980 IU/g) was purchased from Sigma-Aldrich (Germany), sodium

hydroxide was purchased from Aladdin (Shanghai, China), and citric acid was purchased from Tianjin Guangfu Technology Development Co., Ltd. (Tianjing, China). All chemicals used were of analytical grade.

2.2. Sample preparation

2.2.1. Xylanase pretreatment

We placed 200 g (bone dry) of bagasse unbleached pulp in a polyethylene bag. The controls, 30 IU/g xylanase treated samples, xylanase + 1%NaOH treated samples, xylanase + 3%NaOH treated samples and xylanase + 5%NaOH treated samples were labeled 1# to 5#, respectively. Citric acid-sodium hydrogen phosphate buffer was added to each sample. The samples were thoroughly mixed to adjust the pH of the pulp to 6. We added 30 IU/g xylanase to 2#–5# samples as well as buffer to adjust the consistency to 8%. The samples are kneaded and thoroughly combined with xylanase. All of the samples were stored in a constant temperature water bath at 50 °C for 2 h, and the pulp in the bag was agitated once every 15 min to allow the pulp to fully react with the xylanase. After 2 h, the polyethylene bag was removed from the water bath, and the xylanase was inactivated at 100 °C for 20 min. Deionized water was then used to rinse the pulp to be pH neutral. The pulp was placed in a 4 °C environment for 12 h to balance moisture levels.

2.2.2. Cold alkali pretreatment

After measuring moisture levels in the enzymatically pretreated pulp, 200 g (bone dry) was weighed into a 15 L polyethylene plastic bucket. We prepared 1 L of 100 g/L, 300 g/L, and 500 g/L NaOH solution and then added them to the 3#, 4#, and 5# sample barrels, respectively. The polyethylene bucket was shaken to mix the pulp with the alkali, and the pulp concentration was adjusted to 2% with deionized water. The sample was completely frozen at -20 °C and then thawed at room temperature. The pulp was rinsed with deionized water until it was deemed neutral, and it was then placed in a 4 °C environment for 12 h to balance moisture levels.

2.2.3. Preparation of CNF

The pretreated pulp was diluted to 2% (w/w) with deionized water and ground with an ultra-micro mill (MKZA 10-15JIV, Japan) at a disc rotation speed of 1500 rpm, with a disc gap of -100 μm, and with 10 rounds of grinding. After grinding, the sample concentration was adjusted to 0.8% using deionized water, and homogenization was performed using a high-pressure homogenizer (M-110EH-30, Netherlands). A large-aperture (200 μm) high pressure homogenization chamber was used with a pressure level of 350 bar, and the number of sample passes was set to 5. Then, a small-bore (87 μm) high-pressure homogenization chamber was used with a pressure level of 1500 bar, and the number of sample passes was set to 15. After high-pressure homogenization, the sample is subjected to freeze-drying to obtain a finished CNF powder for subsequent analysis (Nie et al., 2018).

2.2.4. CNF film preparation

The CNF film was prepared using the following method. 119.22 g of 0.2% (w/w) concentration CNF was placed in a 500 mL beaker, to which we added 450 mL of deionized water. The sample was then mixed by stirring. The sample was vacuum filtered with a 0.22 μm polytetrafluoroethylene film. The filter and wet CNF sample were both transferred to a sheet former (HAAGE Sheet Former BB, Germany) to form a film, and then the dry CNF film was peeled off.

2.3. Analysis methods

2.3.1. Transmission electron microscope (TEM)

The CNF sample was diluted to 0.008% and sonicated for 20 min under ultrasound. Samples were stained with 1% uranyl acetate and were observed by transmission electron microscopy (HT7700, Japan).

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